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Impact of hydraulic and carbon loading rates of constructed wetlands on contaminants of emerging concern (CECs) removal

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ABSTRACT

Constructed wetlands remove trace organic contaminants via synergistic processes involving plant biomass that include hydrolysis, volatilization, sorption, biodegradation, and photolysis. Wetland design conditions, such as hydraulic loading rates (HLRs) and carbon loading rates (CLRs), influence these processes. Contaminant of emerging concern (CEC) removal by wetland plants was investigated at varying HLRs and CLRs. Rate constants and parameters obtained from batch-scale studies were used in a mechanistic model to *evaluate the effect of these two loading rates on* CEC removal. CLR significantly influenced CEC removal when wetlands were operated at HLR >5 cm/d. High values of CLR increased removal of estradiol and carbamazepine but lowered that of testosterone and atrazine. Without increasing the cumulative HLR, operating two wetlands in series with varying CLRs could be a way to improve CEC removal.

1. Introduction

Contaminants of emerging concern (CECs) are discharged into the environment from sources including wastewater treatment plant (WWTP) effluent, agricultural runoff, over land flow from animal feedlots, storm water outfall, and recreational activity. Constructed wetlands can be operated at or near many of these pollution sources to protect the receiving water bodies from pathogens and traditional bulk pollutants (e.g., biological oxygen demand (BOD), nitrate (NO_3^-)). However, constructed wetlands may also facilitate CEC removal, which is becoming more important as concerns about CECs reaching aquatic environments grow.

CECs are a broad category of contaminants that includes pharmaceuticals and personal care products (PPCPs), endocrine-disrupting contaminants (EDCs), perfluorinated compounds, and engineered nanomaterials. CEC removal was not investigated in constructed wetlands until recently. Many studies have shown that wetlands can remove similar levels of PPCPs and EDCs as do conventional wastewater treatment systems (Reed et al., 1995; Matamoros et al., 2005, 2006, 2008a,b; 2009; Huang et al., 2004, 2005; Gray and Sedlak, 2005; Conkle et al., 2008; Park et al., 2009; Hijosa-Valsero et al., 2010; Zhang et al., 2012). Although these studies identified wetland as a potential treatment system for CECs, few investigated how design parameters of constructed wetlands especially loading rates (e.g. hydraulic and carbon loading rates) affect CEC removal.

Contaminant removal in wetlands occurs by natural attenuation, which involves multiple removal mechanisms e.g. sorption, biodegradation, and photolysis supported by plants and soils/sediments (Kadlec and Wallace, 2009). Wetland plants maintain aquatic habitats and perform critical functions in contaminant removal. For example, plants provide surface area on which contaminant sorption can occur. Bacteria can attach to and grow on plant surfaces (Kadlec and Wallace, 2009). Plant uptake has been also implicated as a potential removal mechanism for PPCPs (Reinhold et al., 2010; Matamoros et al., 2012). Exudates from plant decomposition and biofilms on plant surfaces can support contaminant removal (Matamoros et al., 2012). Microbial activities supported by the exudates of vegetated wetlands cause removal of polar contaminants that are not amenable to uptake or sorption processes (Matamoros et al., 2008a, 2012). In contrast, dissolved organic carbon (DOC) leached from decaying plants, can reduce the actual intensity of light and lower the contribution of contaminant photolysis (Jasper and Sedlak, 2013). Although DOC is a photosensitizer that generates radical oxidant species including singlet oxygen ($^1O_2$) and OH radicals (OH•) (Lin and Reinhard, 2005), it also inhibits photo-induced reactions by self-reacting with the radical species (Wenk et al., 2011).

The design parameters of wetlands can influence contaminant removal. Hydraulic loading rate (HLR), which refers to flow rate per

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unit area, is a parameter commonly used to determine the size of a constructed wetland. Constructed wetlands are often operated at low HLR, which results in long hydraulic retention times (HRTs) and thus requires that the wetland be larger. HLR affects bulk pollutants including ammonia (NH_4–N), nitrate (NO_3^-), and chemical oxygen demand (COD) (Trang et al., 2010). Carbon loading rate (CLR) or plant productivity is another parameter that is not directly linked with the size but influences contaminant removal processes supported by wetland plants (Ingersoll and Baker, 1998). In this study, sorption, biodegradation, and photolysis of selected CECs were investigated in the presence of wetland plants (Table 1). Wastewater effluent contains plethora of organic CECs but goal of this study was to select as few compounds as possible with different physico-chemical properties because variation in the properties determined the relative strength for undergoing certain attenuation mechanisms. Dried wetland plants (*Scripus* spp.) were added into continuous-flow type lab-scale microcosms to mimic the areas where growing plants senesce over time and facilitate pollutant removal. Batch-scale studies were conducted using the plant materials to study the different removal mechanisms. To understand the effect of HLR and CLR on CEC removal, a fate-transport model was developed in AQUASIM, a software used to simulate aquatic systems. The removal mechanisms were incorporated into the model with the help of rate expressions that were parameterized with partitioning coefficients and rate constants obtained from batch-scale studies. Model predictions were used to investigate how varying HLR and plant addition rates affect removal of different types of CECs

2. Material and methods

2.1. Materials

17β-estradiol (E2), testosterone, atrazine, carbamazepine, and sodium azide (NaN_3) were obtained from Sigma–Aldrich, St. Louis, MO, USA. Potassium bromide was obtained from ICN Biomedicals Inc., Ohio, USA. HPLC-grade acetonitrile and formic acid were obtained from Fisher Scientific, New Hampshire, USA. The water used for analytical purposes was nanopure water with 18.3 Ω conductivity (Milipore Inc., Billerica, MA). Isotope-labeled compounds (99% purity)-Estradiol-[$^{13}C_6$], Testosterone-[d_5], Atrazine-[d_5] and Carbamazepine-[d_{10}] were purchased from Cambridge Isotope Laboratories, Inc (Tewksbury, MA, USA).

2.2. Lab-sale microcosms

The microcosms used in this study were acrylic tanks (20 cm × 25 cm × 13 cm) with internal baffles to reduce short circuiting (Fig. S1) and represent areas of free water surface wetlands with floating and submerged vegetation. Similar microcosms were previously used to study removal of bulk and trace level contaminants (Ingersoll and Baer, 1998; Pinney and Westerhoff, 2000; Sharif et al., 2013). The influent water was activated carbon filtered dechlorinated filtered tap water (Tempe, AZ) to provide trace level metal ions essential for bacterial growth. Nutrient constituents (0.2 mM K_2HPO_4, 1 mM NH_4Cl) were added to simulate WWTP effluent (Pinney and Westerhoff, 2000). The water (pH 7.3 ± 0.2) was pumped through a Monistat cassette peristaltic pump at different flow rates. Air-dried bulrushes (*Scirpus validus*) collected from the Tres Rios wetlands, AZ, were chopped (~2 inch) and added into the microcosms. Plant addition rates were based on the productivity of emerging macrophytes in the Sonoran deserts of Arizona; 6000 g DW (dry weight) m^2/yr were considered a reasonable estimate, which translated into an addition of 3 g of plants per week (Ingersoll and Baker, 1998). Microcosms were operated at an HLR of 3.4 cm/d and 5.6 cm/d respectively to obtain effluent water with different DOC levels.

Table 1
Physico-chemical properties of selected organic CECs.[a]

CECs (class)	Molecular weight MW (g/mole)	pK_a	Log K_{OW}
17 β-estradiol (E2) (steroid hormones)	272.4	10.4	4.02
Testosterone (steroid hormones)	288.4	–	3.32
Atrazine (pesticides)	215.7	1.7	2.61
Carbamazepine (pharmaceuticals)	236.3	13.9	2.45

[a] Source: EPI Suite™ (U.S. EPA).

2.3. Sorption experiments

Sorption experiments were conducted using the method described elsewhere (Sharif et al., 2013). Air-dried wetland plant materials were autoclaved for 15 min at 1500 PSI prior to conduct the experiments to minimize microbial activity. The ratio of plant materials to volume of water was 100 mg: 10 mL and 300 mg: 10 mL. The measured amount of plants was placed in 40 mL amber vials with Teflon-lined screw caps and hydrated in microcosm influent water. pH was adjusted to 7 using sodium hydroxide (NaOH) prior to the addition of the target CECs with initial concentrations ranging 0.1 μM–1 μM. Controls were prepared by spiking the contaminants in background water with no plant materials to find out if other types of abiotic loss (e.g. hydrolysis) was occurring. The vials were then covered with aluminum foils to avoid photolysis and equilibrated for 3 days at 150 rpm at room temperature. Samples were equilibrated based on the sorption kinetics and after equilibration supernatants were taken, filtered with GF/F filters (0.7 micron) and kept at 4 °C until analysis. The amount of a CEC sorbed by the plant material, q (μmole/g) was calculated from the difference between the initial, C_0 (μM) and final C_e (μM) concentrations.

2.4. Biodegradation experiments

Batch experiments were conducted in 100 mL volume serum bottles (prepared in triplicates) containing decaying plant biomass and effluent water from microcosms. The ratio of the mass of decaying plant biomass to volume of water was 1 g: 100 mL and 3 g: 100 mL. The amount of plant biomass represents bulk weight, not actual dry weight. 1 mM ammonia (NH_3–N) was added as nutrient in these experiments. Target CECs were spiked to obtain an initial concentration of 1 μM, samples were taken periodically and filtered. Contributions from abiotic processes (sorption or hydrolysis) were estimated using controls that were prepared using the same plant biomass but autoclaved prior to addition into the serum bottles. The serum bottles were covered with aluminum foil to prevent photolysis and kept at room temperature (25 °C). To further stop microbial activity, samples were spiked with NaN_3 to a concentration of 100 mg/L. Biodegradation experiments were conducted in aerobic conditions and at room temperature, but no stirring or external addition of O_2 was provided.

2.5. Photolysis experiments

Batch photolysis experiments were conducted with simulated sunlight irradiation system equipped with a temperature controlled water bath maintained at 25 °C. The schematics of the apparatus are shown in Fig. S2. Light was provided by a 300-W xenon arc lamp (Spectraphysics Oriel, 91160A). The output of the arc lamp was filtered through a standardized air mass 1.5 filter (AM