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Removal of the pesticide tebuconazole in constructed wetlands: Design comparison, influencing factors and modelling☆

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ABSTRACT

Constructed wetlands (CWs) are a promising technology to treat pesticide contaminated water, but its implementation is impeded by lack of data to optimize designs and operating factors. Unsaturated and saturated CW designs were used to compare the removal of triazole pesticide, tebuconazole, in unplanted mesocosms and mesocosms planted with five different plant species: *Typha latifolia*, *Phragmites australis*, *Iris pseudacorus*, *Juncus effusus* and *Berula erecta*. Tebuconazole removal efficiencies were significantly higher in unsaturated CWs than saturated CWs, showing for the first time the potential of unsaturated CWs to treat tebuconazole contaminated water. An artificial neural network model was demonstrated to provide more accurate predictions of tebuconazole removal than the traditional linear regression model. Also, tebuconazole removal could be fitted an area-based first order kinetics model in both CW designs. The removal rate constants were consistently higher in unsaturated CWs (range of 2.6–10.9 cm d^{-1}) than in saturated CWs (range of 1.7–7.9 cm d^{-1}) and higher in planted CWs (range of 3.1–10.9 cm d^{-1}) than in unplanted CWs (range of 1.7–2.6 cm d^{-1}) for both designs. The low levels of sorption of tebuconazole to the substrate (0.7–2.1%) and plant phytoaccumulation (2.5–12.1%) indicate that the major removal pathways were biodegradation and metabolization inside the plants after plant uptake. The main factors influencing tebuconazole removal in the studied systems were system design, hydraulic loading rate and plant presence. Moreover, tebuconazole removal was positively correlated to dissolved oxygen and all nutrients removal.

1. Introduction

Tebuconazole is a triazole pesticide that is widely used in agriculture for crop protection due to its broad spectrum of antifungal activities (Shikuku et al., 2014) and included as an active ingredient in wood preservatives (Miyauchi et al., 2005). Concentration levels of tebuconazole (Table S1) ranging from ng L^{-1} to μg L^{-1} have been found in both rural and urban water bodies (Bollmann et al., 2014; Casas and Bester, 2015; Shikuku et al., 2014). However, tebuconazole is reported to be toxic to aquatic life and human health at μg L^{-1} level (EFSA, 2014). In the last few decades, the occurrence of pesticides, including tebuconazole, in the aquatic environment has become a worldwide issue of increasing environmental concern. Thus, due to its wide-spread use and detection as well as its potentially harmful effects, tebuconazole was selected as the model pesticide in this study.

Constructed wetlands (CWs) have become widely used to treat pesticide contaminated wastewater as an economical, robust and sustainable technology (Vymazal and Březinová, 2015). Previous research on removal of pesticides in CWs has been conducted mostly in saturated systems, such as free water surface CWs or horizontal subsurface flow CWs, while unsaturated systems, such as vertical flow CWs, have been less studied. Vegetated and non-vegetated saturated surface flow CWs have been reported to result in removal of 45%–90% of the tebuconazole at an inflow

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concentration of 0.1–10 μg L^{-1} in agricultural landscapes in Europe (Passeport et al., 2013; Tournebize et al., 2013). Unsaturated CWs have usually better removal efficiency of the typical wastewater constituents BOD and ammonium, due to better oxygen transfer capability in their wetland beds (Wu et al., 2014). However, there are no results of direct comparisons in pesticide removal efficiencies among different types of CWs. Thus, the most effective CW type to treat pesticides has not yet been determined. Unsaturated CWs have different hydrological characteristics including water flow pathway and hydraulic retention time compared with saturated CWs. These features suggest possibly different contaminant removal efficiencies and mechanisms (Gregoire et al., 2009; Kadlec and Wallace, 2008; Vymazal, 2007). Thus, comparisons of pesticide removal performance, kinetics and mechanisms in different CW designs are necessary to provide better information for future applications.

To date, the factors influencing removal of the pesticide tebuconazole in different CWs have been rarely investigated. For instance, one popularly used pesticide, chlorpyrifos, has been reported that the removal efficiency and removal rate constant were negatively affected by increased influent concentrations from 100 μg L^{-1} to 500 μg L^{-1} to 1 mg L^{-1} levels through phytoremediation (Prasertsup and Ariyakanon, 2011). These concentrations are high, especially if considering that typical concentrations in urban storm water are usually below 100 μg L^{-1} (Bollmann et al., 2014; Casas and Bester, 2015). Thus, the effect of the influent concentration of pesticide on removal under real environmental levels is unknown. Different hydraulic loading rates (HLRs) affect pollutant/microbial contact time and reaction rates, which has an effect on pollutants, such as BOD, nitrogen and some pharmaceuticals, biodegradation (Lin et al., 2008; Zhang et al., 2017). Despite this, the effect of HLR on pesticide removal in CWs has not received much attention, even though removal kinetics models, such as the zero or first order kinetics models, are calculated based on pollutant removal under different HLRs. Thus, we lack the information on pesticide removal efficiencies under different HLRs that is needed to be able to determine pesticide removal kinetics. It is expected that different plant species may influence pesticide removal in CWs differently due to their different root structure, root exudate release, compound uptake ability and associated different microbial communities. Lv et al. (2016c) observed that tebuconazole removal in saturated CW mesocosms was influenced by the identity of the plant species, while plant uptake and substrate sorption made limited contributions towards tebuconazole removal. However, whether these factors also influence tebuconazole removal in unsaturated CW is unknown. Understanding the factors influencing removal of the pesticide tebuconazole in different CW designs would undoubtedly improve the design and operation of CWs for the treatment of not only tebuconazole but also other triazole pesticides.

Reliable numerical models can be used to increase the understanding of pollutant removal processes occurring in CWs and to improve existing design criteria of CWs (Langergraber, 2007). Linear regression has been the most widely used model in CWs for predictions of pollutant removal (Rousseau et al., 2004). However, linear regression provides rather crude approximations of the complex assortment of nonlinear relationships present in environmental systems (May and Sivakumar, 2009). Artificial neural network (ANN) modelling is a technique inspired by biological neuron processing, which addresses an interconnected structure of processing elements. ANN is widely used in solving complex and nonlinear problems (Schmidhuber, 2015). In recent years, ANN has been successfully applied to predict the removal abilities of organic matter (COD and BOD_5) (Akratos et al., 2008), TSS (Naz et al., 2009), different phosphorous species (ortho-P and TP) (Akratos et al., 2009) and nitrogen (NH_4^+-N and TN) (Guo et al., 2014; Kotti et al., 2016) in various types of CWs. However, no study has been conducted on ANN model-based simulation for pesticides or other emerging organic contaminants.

Consequently, the main objectives of the present study were the following: (1) to compare the removal efficiency, kinetics and mechanism of tebuconazole removal in both unsaturated and saturated CWs with different plant species; (2) to investigate the main influencing factors (system design, HLR, initial concentration and plant species) of tebuconazole removal in both types of CW designs; and (3) to compare ANN with traditional linear regression models in order to explore a simple and robust methodology suitable for predicting tebuconazole removal in CWs.

2. Materials and methods

2.1. Mesocosm-scale CWs and experimental conditions

Each mesocosm-scale CW was made of a black plastic container with both a height and diameter of 20 cm. Each container was filled with a 4 cm layer of gravel (Ø 0.8–1.2 cm) on the bottom, a geotextile, a 10 cm layer of sand (Ø 0.05–0.1 cm with average porosity of 37%) and finally a 4 cm layer of gravel. All mesocosm-scale CWs were intermittently pulse fed by water artificially spiked with tebuconazole from the surface. The outlet height was set at 3 cm for unsaturated CWs (Fig. 1a) and 15 cm for saturated CWs (Fig. 1b). The system was setup and used for a previous experiment along summer 2014 and winter 2015 by Lv et al. (2016c). Both unsaturated and saturated CWs consisted of an influent tank and triplicates of six planting types: unplanted and planted with *Juncus effusus* (*Juncus*), *Typha latifolia* (*Typha*), *Berula erecta* (*Berula*), *Phragmites australis* (*Phragmites*) and *Iris pseudacorus* (*Iris*). In total, 36 mesocosm-scale CWs were constructed, 18 for the unsaturated and 18 for the saturated design. Artificially spiked tebuconazole water was prepared in 300 L doses and constantly mixed by a submerged centrifugal pump placed at the bottom of the influent tank. New influent was prepared every 2–5 days, and the influent load was controlled by a timer and pump. Two concentrations of tebuconazole (10 and 100 μg L^{-1}) and four hydraulic loading rates (1.7, 3.4, 6.9 and 13.8 cm d^{-1}) were used. The corresponding hydraulic retention time (HRT) for the saturated CWs were 2, 1, 0.5 and 0.25 days, respectively. The wastewater was prepared with "Pioner Grøn" (Brøste Group, Denmark) N:P:K full strength nutrient solution added to tap water (supplementary material). An additional carbon source for basic microbial community survival using acetic acid was used to simulate a 20 mg L^{-1} TOC load. The experiment lasted from July to August 2015 (57 days) after a two-month stabilization period. The air temperature ranged from 15 to 25 °C and the relative air humidity from 51 to 78% (Fig. 1c).

2.2. Sampling and analysis

Before each sampling, the mesocosms were allowed to stabilize for three complete hydraulic cycles (calculated by the saturated mesocosms), after which the effluent quality was assumed to be representative. The triplicates samples of the influent were collected directly from the influent tank using a 1 L amber flask. Similar 1 L amber flasks were connected to the CW effluent flow valve and left *in-situ* for 2–10 h, in order to collect a minimum of 800 mL of composite water samples. In total, eight sampling campaigns were conducted. For each campaign, a total of 42 samples were collected: the influent (3) plus effluent samples (3 × 6) for each design (x2). The volume of each effluent was noted to calculate water loss by evapotranspiration (Equation S1, supplementary materials). Dissolved oxygen (DO), pH, temperature and electrical