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Ibuprofen and iohexol removal in saturated constructed wetland mesocosms

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ABSTRACT

The removal of pharmaceuticals by constructed wetlands (CWs) has been gaining more interest in the last decade. However, it is still unclear which are the key factors influencing the removal process. The aim of the present study is to investigate the removal efficiency of ibuprofen (IBU) and iohexol (IOH) by saturated CW mesocosms, depending on type of mesocosm (planted with *Typha latifolia, Phragmites australis*, *Iris pseudacorus*, *Juncus effusus*, *Berula erecta* or unplanted control), season (summer and winter), hydraulic loading rate (HLR) (0.7, 1.8, 3.4, 6.9 and 13.8 cm d^{-1}) and initial spiking concentration (10 and 100 $\mu g\,L^{-1}$). The results show that the presence of IBU and IOH had no influence on the monitored water parameters, while the type of mesocosm (different plant species and unplanted control) and season were the main factors explaining the differences observed in pH, dissolved oxygen (DO), oxygen saturation (SAT), total nitrogen (TN), ammonium (NH_4-N) and phosphate (PO_4-P). IBU was more efficiently removed (>80%) by mesocosms planted with *J. effusus* and *B. erecta* under low HLR and low initial spiking concentration in summer. For IOH, higher removal efficiency (>80%) was achieved by *B. erecta*-planted mesocosms under low HLR and high initial spiking concentration. Data on IBU removal from mesocosms could be fitted by the first-order kinetic model, with removal rate constants ranging from 0.2 to 4.0 d^{-1}. For IOH, however, different kinetic models were applied but none could sufficiently describe the removal rate. Regression analysis on IBU demonstrated that 64% of the variation in removal efficiency could be explained by temperature, NH_4-N and DO. In contrast, IOH removal correlation with any of the variables studied only accounted for 10.6% of the removal variation observed.

1. Introduction

Pharmaceuticals are extensively used to prevent and alleviate the effects of disease and illness in humans and animals. As pharmaceuticals are not completely metabolised in the body, large amounts of pharmaceuticals and their metabolites have been introduced into the aquatic environment through sewage, which carries the excreta of individuals who have used these chemicals and agricultural runoff comprising livestock manure. The insufficient removal of pharmaceuticals by conventional wastewater treatment plants (WWTPs) (Jelić et al., 2012) have made sewage and agricultural runoff the main source of these compounds to the environment. Consequently, concentration levels of pharmaceuticals at the scale of ng L^{-1}–$\mu g\,L^{-1}$ have been detected in different water bodies around the globe (Nikolaou et al., 2007). These concentration levels of pharmaceuticals have been reported by recent environmental risk assessments to possibly exceed the predicted no-effect concentration, resulting in adverse effects on fish and algae growth (Hernando et al., 2006). Hence, pharmaceuticals have become public concerns because of their potential adverse effect on biota and presence in drinking-water sources. Therefore, removal of pharmaceuticals from contaminated water has become the target of many organisations, such as the EU Water directives (Kunz et al., 2015) and the National Natural Science Foundation of China (National Natural Science Foundation of China, 2014).

Constructed wetlands (CWs), as a robust and low-cost technology for treating wastewater, have been proven to be efficient in also removing pharmaceuticals (Verlicchi and Zambello, 2014). Published research about removal of pharmaceuticals by CWs can

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be found for several scales of systems (microcosm, mesocosm, pilot and full-scale systems), covering a range from primary, secondary or tertiary treatment steps, as well as for hybrid systems, either working with artificial or real wastewater (Verlicchi and Zambello, 2014). Despite the extensive list of publications dealing with the removal of pharmaceuticals by CWs, as shown by the comprehensive reviews available, questions still exist on the role of filling media, plant species, wastewater type, system design and environmental parameters on the removal of pharmaceuticals by CWs (Li et al., 2014; Verlicchi et al., 2013).

A key issue in improving the removal of pharmaceuticals by CWs is to develop an understanding of their kinetics. CW practitioners widely use the P-K-C* kinetic model for CW sizing (Kadlec and Wallace, 2008). Regarding pharmaceuticals, however, the more commonly used model is the first-order kinetic model (Matamoros and Bayona, 2006). However, zero-order and second-order kinetic models have also been used in CWs (Mitchell and McNevin, 2001; Pérez et al., 2014). Studies on pharmaceutical degradation kinetics in CWs are scarce, and previous research has mainly focused on the effects of single factors, such as plant species, season etc., while the potential synergy between factors has been neglected.

In the present study, ibuprofen (IBU) and iohexol (IOH) were selected as model compounds. IBU is a non-steroidal anti-inflammatory drug frequently used by humans and is known to be easily biodegradable and widely studied, allowing for better comparison of results. IOH is not a pharmaceutical with a therapeutic effect, but a diagnostic iodinated contrast agent used in high doses in hospitals. It is excreted from the body by urine in a non-metabolized form. The aim of the present study is to assess the effects of plant species, season, HLR, and the concentration of IBU and IOH on the removal efficiency and removal kinetics of these compounds in saturated CW mesocosms.

2. Materials and methods

2.1. Reagents and materials

Commercial products of IBU and IOH were purchased from a local pharmacy for the artificial influent preparation. The exact concentrations of IBU and IOH in the commercial products were analysed prior to the experiment. All the reagents and materials used for the analytical work are described in the Supplementary material. Characteristics of IBU and IOH are shown in Table S1.

2.2. Experimental setup

The experimental setup was established outdoors at an experimental field station close to Aarhus, Denmark, under a glass roof providing protection against rain and snow. Similarly sized plants from the five species *Typha latifolia* L., *Phragmites australis* (Cav.) Trin. ex Steud., *Iris pseudacorus* L., *Berula erecta* (Huds.) Coville and *Juncus effusus* L. were selected (fresh biomass 120 ± 10 g) and planted in the mesocosms after being rinsed carefully. Each mesocosm, a 6 L pot, was filled with substrate in the following order: coarse gravel (1900 g) at the bottom, followed by quartz sand (5700 g, particle size 0.5–1 mm with average porosity of 37%) and coarse gravel (1700 g) on top to avoid light exposure. A geotextile was placed in between the bottom coarse gravel and the sand layer to maintain the draining system. The surface area of each mesocosm was 0.36 m^2. The mesocosms simulated water-saturated CWs conditions, where the water flowed from the top surface through the substrate to the bottom collection device. Water drip of the mesocosms upper outlet by hydrostatics (Fig. S1). Eighteen mesocosms (5 plant species and 1 unplanted control, in triplicate), together with a 350 L influent water storage tank and an Ø 16 mm PE pipe fitted with 0.5 L h^{-1} pressure-compensated drippers for each mesocosm constituted a working line in the experiment (Fig. 1). Three working lines were used: one spiked with IBU, one spiked with IOH, and one without pharmaceuticals was set up as a control line. The artificial influent was prepared with tap water, "Pioner Grøn" N: P: K nutrients (total-N, 19.3 mg L^{-1}; NO_3-N11.9; NH_4-N, 7.4; P, 2.0 mg L^{-1}; Mg, 3.0 mg L^{-1}; K, 15.4 mg L^{-1}; and S, 3.9 mg L^{-1}) (Brøste Group, Denmark) and acetic acid (12 mg L^{-1} TOC). The whole system was acclimatized for one month before the start of the experimental period. The HLR was adjusted by a timer-controlled pump at five different levels (0.7, 1.7, 3.4, 6.9 and 13.8 cm d^{-1}). Two spiking concentrations for IBU and IOH were used: 10 μg L^{-1} and 100 μg L^{-1}.The experiment was performed covering two seasons, summer and winter, between July 2014 and March 2015.

2.3. Sampling strategy

For each HLR tested, a stabilization period of three complete hydraulic cycles was followed, after which performance was assumed to be representative for the particular HLR. The influent volume of each mesocosm was calculated from the measured total volume consumed in the input tank per sampling time. The effluent volume of each mesocosm was measured by sample weight. For each working line, approximately 1 L of water was sampled from the influent (storage tank, n = 3) and effluent of each mesocosm (n = 1). For each water sample, 500 mL was transferred to an amber bottle for IBU or IOH analysis, and 40 mL was transferred to a poly ethylene bottle for analysis of total organic carbon (TOC), total nitrogen (TN), ammonium (NH_4-N), nitrate (NO_3-N), and phosphate (PO_4-P). The remaining amount was used for the *in-situ* measurements of pH, water temperature, dissolved oxygen (DO), oxygen saturation (SAT), and electrical conductivity (EC). The samples were stored in portable refrigerators until arrival at the lab, where samples were acidified to pH2 using hydrochloric acid and kept at 5 °C until analysis.

Air temperature and relative air humidity (RH) were registered every 30 min throughout the experimental period. Furthermore, leaf chlorophyll content (n = 3) was measured randomly for each planted mesocosm in summer. In winter, all plants wilted except for *J. effusus*.

The plant aerial tissue (100 g FW from each planted mesocosm) was collected for IBU and IOH analysis at the end of the summer and winter; only *J. effusus* material was collected in winter. Roots were not sampled to avoid mesocosm destruction. Each mesocosm's substrate was sampled at the end of the summer and winter periods using a syringe to collect 10-cm cores with Ø 0.5 cm (10 g FW) for pharmaceutical analysis. Substrate collection was a compromise between collecting acceptably representative samples while simultaneously avoiding the destruction of the mesocosms. The plant aerial tissue (n = 1) and the substrate samples (n = 1) from each mesocosm were freeze-dried and stored at −8 °C until analysis of IBU and IOH, which took place within 1 month.

2.4. Analytical methodology

Detailed information on the measurement of environmental variables, and the IBU and IOH analyses are found in the Supplementary material. Briefly, the environmental variables were monitored continuously with loggers and the water quality measured using standard methods. The IBU and IOH were analysed by a high performance liquid chromatography (HPLC) system equipped with a diode array detector (DAD) (Ultimate 3000, Thermo Scientific, Denmark). For water samples, prior to the HPLC analysis, solid phase extraction (SPE) was conducted as