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Removal of selected organic micropollutants in planted and unplanted pilot-scale horizontal flow constructed wetlands under conditions of high organic load

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ABSTRACT

The aim of this study was to investigate the removal of eleven selected organic micropollutants (OMPs) occurring in municipal wastewater in a 1–100 $\mu g L^{-1}$ concentration range during the treatment in two (planted and unplanted) pilot-scale horizontal subsurface flow constructed wetlands in order to elucidate (i) the role of plants on the mass removal and (ii) to understand the removal behavior of the micropollutants at different sampling locations along the flow path. The research was conducted in Langenreichenbach (Saxony), Germany, over a period of one year. The high organic load was chosen for both constructed wetlands (CWs) to study the removal of OMPs, because it is often occurring in the "real" world, but seldom investigated as a research objective.

The concentration of the OMPs in the treated inflow wastewater varied more strongly (by a factor of 10) than the total organic and nitrogen loads (by a factor of 4). A wide range of removal efficiencies were found. Higher removals were observed in the pilot-scale CW planted with *Phragmites australis* than in the unplanted one. The stimulant caffeine was the investigated OMP which showed the highest removal with an average efficiency of 66%. The average removal efficiency of the other OMPs was below 30%. The plants in the CWs supported not only the removal of the fragrances galaxolide and tonalide but also the removal of the pharmaceuticals carbamazepine, diclofenac, ibuprofen, ketoprofen and naproxen, even under the conditions of high organic load. The endocrine disruptors bisphenol A and nonylphenol, and the antibacterial triclosan showed on average the lowest removal efficiencies. Under the studied operating conditions of high load, a positive correlation between the internal removal behavior of naproxen and diclofenac and concentration of sulfide was found.

1. Introduction

Over the last decades, bioactive organic trace compounds, also termed organic micropollutants (OMPs), such as pharmaceutical residues and endocrine disrupting compounds, have increasingly emerged in the environment (Schwarzenbach et al., 2006; Luo et al., 2014). Due to their low concentration and persistency, their removal using conventional sewage treatment technologies such as activated sludge processes is often incomplete (Joss et al., 2008; Anderson et al., 2013) and traces of bioactive substances pass through the treatment plants and enter the receiving water systems with unknown consequences for ecosystems. Recently, researchers have focused their interest on the efficiency of alternative wastewater treatment technologies such as constructed wetlands (CWs) to remove these trace compounds (Zhang et al., 2011; Ávila et al., 2014). The efficiency of CWs is influenced by a variety of different processes including (i) aerobic and anaerobic microbial transformation/degradation, (ii) adsorption of pollutants to soil, microorganisms and plant roots, (iii) plant uptake and further metabolism of the pollutants and (iv) physical

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filtration (Kadlec and Wallace, 2009; Verlicchi and Zambello, 2014).

The ability of CWs to degrade OMPs has already been demonstrated in previous investigations (Matamoros and Bayona, 2006; Hijosa-Valsero et al., 2010; Ávila et al., 2013).

In most studies, the removal of OMPs by CWs is given by comparing the inflow (influent) and outflow (effluent) concentrations of the contaminants (Matamoros et al., 2009; Hijosa-Valsero et al., 2011). However, in the case of water loss by evapotranspiration, the concentrations of OMPs should be correlated to both the water in- and outflow rates so that the resulting mass loads of OMPs can be compared (Bojcevska and Tonderski, 2007). Furthermore, as compared to an intermittently loaded vertical down-flow CW, an horizontal flow CW (HFCW) increase the amount of aerobic/anaerobic interfaces (White et al., 2006) and redox processes occurring at rhizosphere and CW system scale (Imfeld et al., 2009) which could result in a better removal of some OMPs (Hijosa-Valsero et al., 2010; Zhang et al., 2012; Reyes-Contreras et al., 2012; Ávila et al., 2013). The removal of individual OMPs is dependent on the subsurface environmental conditions (e.g. redox conditions and water temperature) in a constructed wetland (Imfeld et al., 2009). Thus, ibuprofen, a frequently used analgesic, was more efficiently removed by shallow (0.3 m water depth) horizontal flow CWs than in 0.5 m water depth system in terms of their in- and outflow concentration (Matamoros et al., 2005). However, detailed studies on the removal of OMPs within HFCWs, such as at different depths and along the flow paths in the wetland beds, have been rare (Matamoros and Bayona, 2006; Ranieri et al., 2011) and therefore the understanding of the internal degradation mechanisms is limited.

In addition, the operational performance of HFCWs is more sensitive toward seasonal variations as shown for the elimination of selected analgesics (Hijosa-Valsero et al., 2010). While naproxen and diclofenac were removed more efficiently during the summer time, the removal of ketoprofen was found to be more successful during the winter season (Reyes-Contreras et al., 2012). As reported previously, Mediterranean and tropical conditions promote higher elimination efficiencies in terms of OMPs due to enhanced biological activity in warmer climates (Hijosa-Valsero et al., 2011; Zhang et al., 2011). In contrast, comparable data about HFCWs operated under temperate climate conditions are less available (Matamoros et al., 2009).

Due to the generally low concentrations of OMPs in municipal wastewater, the microbes are theoretically unable to use them as a substrate, and co-metabolism would therefore be the preferred degradation pathway (Onesios et al., 2009; Tran et al., 2013). Furthermore, the low concentration of OMPs in sewage is a challenge for chemical analysis. Consequently, for laboratory and pilot-scale studies, continuous injection experiments have been conducted (Matamoros et al., 2005; Zhang et al., 2011), allowing the investigation of the OMPs even under steady-state conditions (Ávila et al., 2013). Nonetheless, in these experiments, the inflow concentrations were often far higher than actual concentrations measured in real municipal wastewater.

The aim of this study was to investigate the removal of 11 selected OMPs present in municipal wastewater during the treatment in pilot-scale CWs under conditions of high organic load. A planted (*Phragmites australis*) CW was investigated in parallel to an unplanted one. Both pilot-scale CWs had the same dimensions and were fed with the same municipal wastewater using the same loading regime. Special focus was directed to the effect of the spatial (depth and distance from the inflow) influences during three different time periods along a one-year study.

2. Materials and methods

2.1. Experimental site

The investigations were carried out at the experimental site in Langenreichenbach, Germany, that has already been described in detail by Nivala et al. (2013). A schematic description is given in Fig. 1. The pilot-scale CWs investigated included one unplanted horizontal flow constructed wetland (H50) and one planted horizontal flow constructed wetland planted with *Phragmites australis* (H50p). The systems each measure 4.7 m long, 1.2 m wide and have a saturated water depth of 50 cm. The systems were dosed with the same pre-treated municipal wastewater at a rate of 5 L every 30 min, leading to an average inflow rate of 0.18 $m^3\ d^{-1}$. The studied CWs with a surface area of 5.64 m^2 per bed had to treat a hydraulic load of 36 ± 4 mm d^{-1} with a nominal hydraulic retention time of approximately 5.5 days (Nivala et al., 2013). The size of the granular medium of the pilot-scale CW was predominantly medium gravel (8–16 mm), but coarse gravel (16–32 mm) was used for the influent and effluent zones.

2.2. Sampling procedure

Over a twelve month period (from August 2011 to August 2012), 20 sampling events were performed. In each sampling campaign, grab samples were taken at the influent and the effluent of both H50 and H50p. This approach allowed the inflow-outflow performance to be studied in terms of mass removal in the pilot-scale CWs. Moreover, pore water samples were taken within the beds during each sampling event. The sampling locations were spatially defined as the fractional distance within the bed. The internal behavior of the selected OMPs in the H50 and the H50p systems was studied in three different time periods (see Table 1). Every period lasted two months and considered the different physiological conditions of the plants. During Period I, internal concentration profiles were measured at a 0.13 m bed depth and at four selected sampling locations along the flow path. The depth of 0.13 m was chosen because it can be assumed as the zone of highest root density (Imfeld et al., 2009). During Periods II and III, two internal sampling locations along the flow path at two different depths (0.13 m and 0.4 m) were studied. For correlation analysis selected data from the twelve months period were considered. The inflow samples were collected before dosing into the wetland beds (Nivala et al., 2013); because of special construction design where air contact could not be excluded, the outflow samples were taken within the wetland beds from the outflow collection pipe at the bottom of the wetlands. Internal samples were taken using steel lances and peristaltic pumps. A graphic description of the internal sampling locations in the beds is shown in Fig. 1.

2.3. Selection and analysis of target OMPs and wastewater parameters

For the selection of the target substances, general criteria such as persistency, production volumes and occurrence in the environment were considered. Thus, the neuroleptic pharmaceutical carbamazepine, known as very persistent and nearly ubiquitously occurring in aquatic systems (Tixier et al., 2003) was included, as well as analgesics, including ibuprofen, diclofenac, ketoprofen and naproxen based on their use in human therapy worldwide (Ternes and Joss, 2006). Frequently, these semi-polar compounds have been classified as potential environmental pollutants, as their reduction by conventional wastewater treatment has often been inefficient (Cirja et al., 2008). In addition, triclosan, a highly persistent antiseptic (Ying et al., 2007), was chosen. Additionally,