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Behaviour of pharmaceuticals and personal care products in constructed wetland compartments: Influent, effluent, pore water, substrate and plant roots

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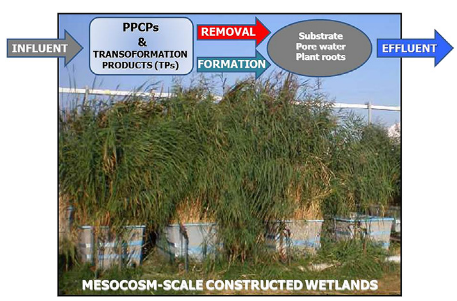
HIGHLIGHTS

- PPCPs were detected in influent, pore water, effluent and plant tissues.
- Ketoprofen undergoes photo-degradation and pH-dependent degradation.
- *De novo* PPCP transformation products formation suggest *in situ* biodegradation.
- Increase in the internal LAB isomers supports biodegradation in the gravel bed.
- Macrophytes can take up PPCPs through their roots.

GRAPHICAL ABSTRACT



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ABSTRACT

Seven mesocosm-scale constructed wetlands (CWs) with different design configurations, dealing with primary-treated urban wastewater, were assessed for the concentration, distribution and fate of ten pharmaceutical and personal care products (PPCPs) [ibuprofen, ketoprofen, naproxen, diclofenac, salicylic acid, caffeine, carbamazepine, methyl dihydrojasmonate, galaxolide and tonalide] and eight of their transformation products (TPs). Apart from influent and effluent, various CW compartments were

Abbreviations: 1-OH-IBU, 1-Hydroxy-ibuprofen; 2-OH-IBU, 2-Hydroxy-ibuprofen; 3-EBP, 3-Ethylbenzophenone; 4-OH-DCF, 4-Hydroxy diclofenac; CAF, Caffeine; CAR, Carbamazepine; COOH-IBU, Carboxy-ibuprofen; CW, Constructed wetland; DCF, Diclofenac; DES-NAP, *O*-desmethyl naproxen; DH-CAR, 10,11–Dihydrocarbamazepine; DH-KET, Dihydro-ketoprofen; DNB, 2,2′-Dinitrobiphenyl; FEN, Fenoprop; FM, Floating macrophytes; FW, Free-water layer; GAL, Galaxolide; IBU, Ibuprofen; IBU-AMD, Ibuprofen-amide; KET, Ketoprofen; LABs, Linear alkylbenzenes; LOD, Limit of detection; LOQ, Limit of quantification; MDHJ, Methyl dihydrojasmonate; NAP, Naproxen; PPCPs, Pharmaceuticals and personal care products; SAL, Salicylic acid; SF, Surface flow; SSF, Subsurface flow; TON, Tonalide; TON-D3, Tonalide-D3; TPhA, Triphenylamine; TPs, Transformation products.

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analysed, namely, substrate, plant roots and pore water. PPCP content in pore water depended on the specific CW configuration. Macrophytes can take up PPCPs through their roots. Ibuprofen, salicylic acid, caffeine, methyl dihydrojasmonate, galaxolide and tonalide were present on the root surface with a predominance of galaxolide and caffeine in all the planted systems. Naproxen, ibuprofen, salicylic acid, methyl dihydrojasmonate, galaxolide and tonalide were uptaken by the roots. In order to better understand the removal processes, biomass measurement and biodegradability studies through the characterization of internal-external isomeric linear alkylbenzenes present on the gravel bed were performed. Three TPs namely, ibuprofen-amide, 3-ethylbenzophenone and 4-hydroxy-diclofenac were identified for the first time in wetland pore water and effluent water, which suggests *de novo* formation (they were not present in the influent). Conversely, *O*-desmethyl-naproxen was degraded through the wetland passage since it was detected in the influent but not in the subsequent treatment stages. Biodegradation pathways are therefore suggested for most of the studied PPCPs in the assessed CWs.

1. Introduction

Urban wastewaters contain a large variety of pharmaceuticals and personal care products (PPCPs) coming from domestic sewage, hospital sewage and several human activities (Kaplan, 2013; Jones et al., 2005). Most pharmaceuticals are not completely metabolized after human intake; as a result, their metabolites and some parent compounds are excreted and find their way into sewerage systems.

Constructed wetlands (CWs) are low-cost wastewater treatment options, which are able to remove or attenuate a variety of waterborne contaminants including PPCPs (Conkle et al., 2008; Zhang et al., 2014). However, due to the large surface area per inhabitant needed to reach the target water quality parameters (Kadlec and Wallace, 2008), their implementation is only feasible in small urban communities or as tertiary treatments dealing with a small, diverted fraction of conventional WWTP effluents.

The mechanisms involved in pollutant removal in CWs can be classified into biotic processes (e.g. microbiological degradation, biofilm, root and plant uptake) and physico-chemical processes (evaporation, photodegradation, oxidation, hydrolysis, retention or root sorption into the gravel bed). Nevertheless, CWs are highly complex systems presenting several environments and microenvironments (Imfeld et al., 2009), where different physical-chemical conditions can reign, influencing the various abovementioned removal processes (Wieβner et al., 2005; Hijosa-Valsero et al., 2011). These different environments inside the system depend on the specific CW design, namely, pore water, upper layer exposed to the sunlight, plants, biofilm on the substrate, and roots' biofilm. Therefore, due to this complexity, removal mechanisms in CWs are not fully understood yet.

The most common approach to assess the CW removal efficiency consists of a comparison between the concentration or mass of a pollutant in the influent and the effluent (Kadlec and Wallace, 2008). The fact that the mass of a pollutant in the effluent is lower than in the influent does not imply that the compound has been eliminated in the CW. Although it is true that some pollutants may have been degraded, transformed or even mineralised in the CW, and their remains are expelled with the effluent; many others may have been retained as original compounds or as transformation products (TPs) in the wetland compartments (physical retention on the substrate or organic matter, adsorption onto biofilm or roots, incorporation to microbial biomass or to vegetal tissues, permanence in pore water). Several attempts to elucidate the fate of emerging pollutants in CWs, by analysing substrate media or sediments, vegetal tissues, and influent and effluent water samples have been performed (Moore et al., 2000, 2001, 2002; Matamoros and Bayona, 2006; Dordio et al., 2011; Reyes-Contreras et al., 2011; Zarate et al., 2012; Zhang et al., 2014).

It is a well-known fact that PPCP TPs can be found in wastewater treatment systems; however, the conditions under which these TPs are formed are not clear yet. In order to get further insight into the phenomena involved in the PPCPs removal through CWs and to find out how the design parameters of each system component can affect this process, seven mesocosm-scale CWs were studied. These systems differed among them in flow configuration, and absence or presence of vegetation or substrate. These different configurations allow the evaluation of biogeochemical conditions on elimination pathways. Accordingly, this study included the determination of emerging pollutants in the influent, effluent, pore water, gravel bed and macrophyte vegetal tissues (roots). Furthermore, eight TPs were also considered in order to get a further insight into the processes involved into the removal of PPCPs. Finally, the possible relationship between PPCPs removal and the amount of vegetal biomass was evaluated.

2. Material and methods

2.1. Chemicals and materials

All standards were analytical-grade. Reagent details are provided in the Supplementary Material (SM).

2.2. Description of the wastewater treatment systems

Seven mesocosm-scale CWs were set up in the open air in the facilities of the León WWTP, in the northwest of Spain (807 m a.s.l.). Some climatic values of the site during the system operational period are provided in Fig. SM-1. All CWs consisted of a fiberglass container (80 cm wide, 130 cm long, 50 cm high) with a surface area of approximately 1 m^2. CWs differed in their design parameters, which are summarized in Fig. 1. In May 2007, seedlings were collected in nearby wet areas and planted in wetlands CW1, CW2, CW3, CW5 and CW6 with a density of 50 plants m^{-2}. Wetlands CW1, CW2 and CW3 were planted with *Typha angustifolia*. Wetlands CW5 and CW6 were planted with *Phragmites australis*. Two months later, vegetation coverage reached 100% in all these CWs. Wetlands CW4 and CW7 were left unplanted as controls. The aerial part of the plants was harvested in October 2008 and October 2009. However, the living roots remained inside the beds and the plants grew again during the subsequent warm periods. Actual CWs HRTs measured at the end of the experimental period (October 2010) were 37.4, 29.6, 37.8, 54, 37.4, 71.1 and 41.8 h, respectively (Pedescoll et al., 2013).

León WWTP consists of a primary treatment (screening, sand removal, fat removal and primary clarifier) followed by a secondary treatment (plug-flow activated sludge with nitrification/