Ecological Engineering 80 (2015) 125–139

Contents lists available at ScienceDirect

Ecological Engineering

journal homepage: www.elsevier.com/locate/ecoleng

Fate of pharmaceuticals in a subsurface flow constructed wetland and two ponds

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ARTICLE INFO

Article history:
Received 17 March 2014
Received in revised form 23 January 2015
Accepted 23 January 2015
Available online 24 February 2015

Keywords:
Subsurface flow constructed wetland
Pond
Pharmaceutical
Photodegradation
Biodegradation
Redox condition

ABSTRACT

Removal and fate of 18 pharmaceuticals of different compound classes and 11 human metabolites were investigated in a subsurface flow constructed wetland (SSF), a pond and a pond with floating plants. Equal in surface area and flow rate, they functioned as the advanced treatment stage following conventional biological wastewater treatment in a municipal wastewater treatment plant equipped for nutrient removal. The influent and the effluents of the three treatment wetlands were measured in two studies during summer and one study during winter. The influence of the treatment design and the inherent environmental conditions (redox potential and irradiation) on the range of compounds removed as well as on the removal efficiency was investigated. This field-site study was accompanied by an in situ degradation experiment to assess the influence of photodegradation and biodegradation on the overall removal of pharmaceuticals.

In total, 13 compounds (diclofenac, 3-hydroxycarbamazepine (3-OH-CBZ), venlafaxine (VLX), *O*-desmethylvenlafaxine (*O*-DM-VLX), tramadol (TMD), trimethoprim, erythromycin, clarithromycin, metoprolol, atenolol, bezafibrate, acyclovir and codeine) were consistently removed in quantities more than 70% in at least one of the treatment systems during summer. In the open water pond, photodegradation was found to be an important process for the removal of diclofenac, *O*-desmethyltramadol (*O*-DM-TMD), *O*-DM-VLX as well as 2-hydroxycarbamazepine (2-OH-CBZ) and 3-OH-CBZ. In contrast to the field-site study, no removal of target compounds by biodegradation was observed in the in situ degradation experiments without sediment additions except for metoprolol. This suggests that biodegradation of most substances is improved by the presence of microbially active surfaces such as those provided by the sediment in the pond and, to a higher extent, by the filter passage in the SSF.

Low redox conditions (absence of nitrate) within the SSF and the pond with floating plants in summer were favourable for the anaerobic degradation of some compounds that are aerobically quite persistent, such as sulfamethoxazole (SMX) and diatrizoate. During winter, the increase of redox conditions (presence of oxygen) in the SSF consistently led to an enhanced removal of aerobically degradable compounds such as iopromide. In contrast, the removal of the target pharmaceuticals in the open water pond was generally lower during winter. This could be attributed to a decrease of photodegradation and biodegradation due to the lower global radiation and microbial activity, respectively.

Based on the conclusion drawn from the influence of constructed wetland design and season on the compound specific removal, a hybrid constructed wetland is suggested. The combination of an inundated SSF followed by a shallow open water pond would steadily remove a wide range of aerobically degradable pharmaceuticals throughout the year. Additionally during summer, the open water pond would allow for photodegradation and the SSF for partial degradation of anaerobically degradable pharmaceuticals.

Abbreviations: 2-OH-CBZ, 2-hydroxycarbamazepine; 3-OH-CBZ, 3-hydroxycarbamazepine; BDOC, biodegradable dissolved organic carbon; CBZ, carbamazepine; CW, constructed wetland; DHDH-CBZ, 10,11-dihydro-10,11-dihydroxycarbamazepine; DHH-CBZ, 10,11-dihydro-10-hydroxycarbamazepine; DOC, dissolved organic carbon; ESI, electrospray ionization; HRT, hydraulic retention time; LOQ, limit of quantification; *N*-DM-TMD, *N*-desmethyltramadol; *N*-DM-VLX, *N*-desmethylvenlafaxine; *N*,*O*-DDM-TMD, *N*,*O*-didesmethyltramadol; *N*,*O*-DDM-VLX, *N*,*O*-didesmethylvenlafaxine; $^1O_2$, singlet oxygen; $^{\bullet}CO_3$, carbonate radicals; *O*-DM-TMD, *O*-desmethyltramadol; *O*-DM-VLX, *O*-desmethylvenlafaxine; SF, surface flow constructed wetland; SMX, sulfamethoxazole; sMRM, scheduled multiple reaction monitoring; SRT, sludge retention time; SF, surface flow constructed wetland; SSF, subsurface flow constructed wetland; TMD, tramadol; TP, transformation product; VLX, venlafaxine.

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http://dx.doi.org/10.1016/j.ecoleng.2015.01.036
0925-8574/

1. Introduction

The widespread occurrence of pharmaceuticals in the aquatic environment has raised concerns regarding their potential to endanger non-target species by negatively affecting their metabolisms and behaviour. For example, the antimicrobial sulfamethoxazole (SMX) is able to alter the composition of microbial communities and hinder their nitrate reduction capacity at concentrations as low as 1.3 μg/L (Underwood et al., 2011). Quite recently, Bisesi et al. (2014) reported that the antidepressant venlafaxine (VLX) can influence the predatory behaviour of bass.

Municipal wastewater treatment plants act as point sources for human pharmaceuticals and their metabolites. Therefore, a well-directed post-treatment is needed to preserve the aquatic ecosystems and the drinking water resources from the influence of pharmaceuticals (Ternes et al., 2004). Constructed wetlands (CWs) and ponds provide various options for the removal of pharmaceuticals by photodegradation, biodegradation and sorption (Wicke 2013). Zhang et al. (2014) showed in their review of 18CWs that this treatment process can significantly reduce the load of different micropollutants. Hence, CWs might be a valuable alternative as a post-treatment compared to physical–chemical treatment by ozone or activated carbon. This is especially true if space is not a limiting factor and the habitat value of wetlands is considered. A range of compounds can either be degraded by direct photolysis due to absorption of photons (e.g. diclofenac, Matamoros et al., 2012) or by indirect photolysis due to the interaction with reactive species produced by solar radiation (e.g. carbamazepine (CBZ) and SMX Jasper and Sedlak, 2013). These species include photosensitisers for which nitrate and coloured DOC (dissolved organic carbon) are the main precursors (Zepp et al., 1987). The rate of indirect photolysis is especially strongly influenced by several environmental parameters such as DOC and nitrate concentration as well as pH (Laurentiis et al., 2012). Ryan et al. (2011) showed that the matrix of treated wastewater can even lead to an enhanced photodegradation compared to surface waters.

The range and amount of compounds being biodegraded also depends on environmental parameters such as redox conditions, temperature, biodegradable dissolved organic carbon (BDOC) concentration as well as the composition and activity of the microbial communities. While in general oxic conditions seem to facilitate the removal of many pharmaceuticals (Zhang et al., 2014), recent studies revealed the potential of anaerobic conditions for the removal of some compounds such as SMX (Mohatt et al., 2011), which is quite persistent under aerobic conditions. However, studies linking an enhanced removal of certain pharmaceuticals to anaerobic conditions are scarce so far (Zhang et al., 2014).

Due to the influence of environmental parameters on bio- and photodegradation, the specific configuration of CWs can have a significant effect on the removal of certain compounds. For example, Hijosa-Valsero et al. (2011) confirmed in an experiment with CW mesocosms that design characteristics such as flow-type, presence of plants as well as the plant species have an influence on the removal of antibiotics.

While open water surface CWs are favourable for an enhanced removal of photosensitive compounds (Zhang et al., 2014), other systems providing a high contact time with microbially active surfaces such as plants, roots or sediment might be beneficial for removal by biodegradation processes (Hijosa-Valsero et al., 2011). The inundated vertical subsurface flow CW applied here provides a passage through sand that is comparable to a filtration through the saturated zone of the soil and is characterised by a sequence of different redox conditions. Hence, aerobic, anoxic as well as strictly anaerobic degradation processes can occur and might broaden the range of compounds being biodegraded. However, in contrast to existing studies dealing with surface flow CWs (SFs) or ponds (e.g. Matamoros et al., 2008; Park et al., 2009) information about the potential of SSFs for micropollutant removal is less abundant.

A change of seasons brings along a shift in several environmental conditions. Summer, with its high global radiation and high temperatures, has been described as the most efficient season for the removal of micropollutants (Hijosa-Valsero et al., 2011; Hijosa-Valsero et al., 2011). Thus, the performance during winter is crucial for the applicability of CWs as a year-round technology for pharmaceutical removal.

The objective of the current study was to provide new information on the potential of an SSF as well as two pond systems (a pond with and one without floating plants) on the removal of a broad range of pharmaceuticals and their metabolites at different seasons. The main focus was set on (i) assessing the contribution of photodegradation on the overall removal, (ii) linking the compound removal to seasonal variations of redox conditions and global solar radiation and (iii) deriving treatment options for an optimised removal of the targeted pharmaceuticals.

2. Material and methods

2.1. Layout of constructed wetland and ponds

The CW and the ponds were built and planted in 2004 and 2005. They are fed with the same effluent from a large conventional wastewater treatment plant with denitrification and nitrification (hydraulic retention time (HRT) ~35 h, sludge retention time (SRT) ~25 d) on the outskirts of Berlin in Germany.

The hydraulic loading was 50 mm/d corresponding to 220 m^3/d treated wastewater. The following treatment plants were examined:

- Subsurface flow constructed wetland (SSF): sandy subsurface flow CW; 1320 m^2; water level normally above filter bed providing vertical flow, estimated actual HRT = 11 d, *Phragmites australis* covered 50% in 2013 and 20% in 2012; *Lemna* covered the rest of the area in 2013; floating algae provided 60% coverage in 2012.
- Pond with floating plants: floating aquatic macrophyte system, *Iris pseudacorus*,*Scirpus* sp. and *Carex* sp., *Lemna* and floating algae; 70% of the surface covered; 1520 m^2, depth = ca. 1.2 m, estimated actual HRT = 5.5 d.
- Pond, 1550 m^2, two groundsills at the bottom, depth = ca. 1.1 m, estimated actual HRT = 4 d.

2.2. Set-up and sampling for in situ degradation experiment

Test tubes made of quartz glass (volume 32 mL) were filled with pond water from the influent zone and sealed with a silicone plug. They were positioned horizontally on a rack in the pond. There was a separate rack for each tested depth. These racks were located side by side to avoid shade. The uppermost tubes were located just below the surface. The other tubes were positioned at water depths of 10, 20 and 40 cm. The tubes of the dark control were wrapped up in aluminium foil and located at a depth of 10 cm. Autoclaved tubes were used as sterile control and were fixed directly below the surface. All test tubes were inserted on 26 September 2013 and taken out after 3 h, 8.6 h, 24 h, 48 h, 72 h and 6 d for sampling. For each sampling time an individual tube was used. The samples were kept frozen until analysis (see Section 2.5). Oxygen concentration and pH were measured using separate PE bottles for each of the respective depths. The water temperature was 12 ± 1 °C and the local daily mean for the air temperature was 8.6 ± 1 °C. Sunshine lasted 1.6 h on the first day and 9 ± 1 h on the subsequent days. The global radiation was determined with a pyranometer (SP-110,