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# Removal and transformations of diclofenac and sulfamethoxazole in a two-stage constructed wetland system

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ABSTRACT

The aim of this study was to evaluate the removal of sulfamethoxazole (SMX) and diclofenac (DCF) in a mesocosm two-stage constructed wetland system consisting of a subsurface-flow bed (first stage; CW-1) and a surface-flow system (second stage; CW-2) with an emphasis on the effect of artificial aeration as a potential performance intensification option. Furthermore, the additional aim was to identify the transformation products of DCF and SMX along the flow path of the treatment system. This two-stage system was fed for 442 days with an artificial municipal wastewater containing DCF and SMX at a concentration of 2 mg/L each. The removal of SMX in the CW-1 was found to be significantly higher under non-aerated conditions (> 77%) as compared to aerated conditions (26%), but the aeration of the CW-2 was insignificant for the SMX removal. In contrast, the removal of DCF was not affected by aeration in the CW-1 (removal efficiency of approximately 50%), but was significantly positively influenced by the combined effect of plants and aeration in the CW-2. The overall removal of SMX and DCF in the two-stage system was 95.8% and 77.6%, respectively. The transformation products of SMX and DCF detected in the studied system indicated the potential contribution of both oxic and anoxic transformation pathways, potentially including also abiotic reaction between SMX and Fe(II) leading to the cleavage of the isoxazole ring in this compound. Some of the transformation products found in the CW-1 were not further detected in the CW-2. Based on the literature data the antimicrobial activity and potential activity of the identified transformation products cannot be ruled out. Giant miscanthus growing in the CW-1 was unaffected by the high concentrations of DCF and SMX in contrast to the emergent macrophytes (on the floating island) or the free-floating plants present in the CW-2, which failed to adapt to the presence of the pharmaceuticals. As a result, the CW-2 was colonized by an unidentified species of a water moss and algae.

## 1. Introduction

The treatment of domestic wastewater in decentralized areas is essential to prevent the pollution of the aquatic environment by the nutrient compounds (Wu et al., 2015, 2011) and alleviate the input of other contaminants as for example the broad group of emerging organic compounds (EOCs). The elimination (or at least partial removal) of nutrient compounds can be achieved by various on-site solutions based on biological processes such as constructed wetlands (CWs), drain-field systems, lagoons, aerobic biological treatment units, and membrane bioreactors (Wu et al., 2011) but the solutions for the efficient EOCs removal such as advanced oxidation processes have been scarcely applied in decentralized areas (Chong et al., 2012). The biological treatment methods are not designed for the elimination of EOCs, however, they were found to be capable of decreasing the load of these contaminants with diverse elimination efficiencies for specific compounds (Garcia-Rodríguez et al., 2014; Luo et al., 2014), thus they can serve as a viable treatment option in decentralized areas. For example, CWs were able to efficiently eliminate such EOCs as acetaminophen or atenolol (Li et al., 2014) but on the other hand, the removal of some persistent compounds as fluconazole (Rühmland et al., 2015) or ampicillin was found to be negligible (Li et al., 2014). Some of the EOCs

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that have been widely studied in terms of their occurrence and elimination in CWs on a full- and experimental-scale are, for instance, diclofenac (DCF) and sulfamethoxazole (SMX). The reason for this wide interest is the common usage of those pharmaceutical compounds and the resulting presence in the wastewater and the aquatic environment. DCF belongs to the group of non-steroidal anti-inflammatory drugs and is often recognized as the most popular pain killer (Lonappan et al., 2016). Vymazal et al. (2017), based on the results from four CWs treating sewage in rural locations, indicated that DCF was detected in all of the influent samples taken in the course of seven measuring campaigns performed over a 1-year period. DCF is excreted from human body in urine (65%) and as bile conjugates in faeces (35%) (Benzon et al., 2011). The metabolites in the urine are mostly present in hydroxylated form with the unchanged form of the drug constituting 6% of the metabolites, but some metabolites (glucuronide conjugates) can be deconjugated or back-transformed thus apparently increasing the amount of the parent compound in the waste streams (Zhang et al., 2008). The amount of DCF metabolites in faeces is still unknown (Zhang et al., 2008). The oral daily dosage of DCF is 75–150 mg (Zhang et al., 2008), however, this drug can be also applied dermally and in fact this source was identified as the main one for the occurrence of its residues in municipal sewage (Heberer and Feldmann, 2005). The maximum concentration of DCF in the municipal wastewater was 94.2 μg/L (Luo et al., 2014), but the peak concentrations in household effluents can be probably much higher (even as high as milligrams-per-liter level), which may as well apply to many other EOCs of household relevance.

SMX is a low adsorptive, polar sulfonamide antibiotic which is commonly administered and thus frequently detected in aqueous and terrestrial environments (Müller et al., 2013; Mohatt et al., 2011). SMX enters wastewater mainly via human excretion as unmodified SMX (13–15%) or as its human transformation products (TPs) N-acetyl-SMX (43–55%) or N-SMX-glucuronide (10–13%) (Müller et al., 2013). The maximum literature concentration of SMX in untreated wastewater were reported to be up to microgram-per-liter levels (Larcher and Yargeau, 2012), but importantly the concentration of SMX metabolites can be as high as the parent compound (e.g. 1.6 μg/L of N-acetyl-SMX) (Göbel et al., 2007). Taking into account the deconjugation observed for some SMX metabolites negative removal efficiencies may be observed in biological wastewater treatment systems (Göbel et al., 2007). The daily dose of SMX is usually in the range 800–1600 mg for both hospital or home administration (Drugs.com, 2018), thus it can be assumed that peak concentrations of SMX and its metabolites may reach milligram-per-liter level on a single-household scale.

The removal efficiencies of DCF and SMX in CWs (including surface and subsurface flow systems) are within a wide range from negative to almost complete removal (Li et al., 2014; Miksch et al., 2016). It can be, however, inferred that SMX removal is enhanced in the systems with submerged filtering beds providing anoxic conditions, and that DCF removal was especially high in well aerated systems (such as vertical-flow CWs) and systems with open water surface enabling effective sunlight exposure (preferably without extensive plant cover). These contradictory conditions that are needed for the simultaneous removal of SMX and DCF can be achieved in systems offering temporally alternating conditions (e.g. intermittently aerated CWs or fill-and-drain CWs) or spatially zoned conditions (e.g. various hybrid systems). Indeed, the studies dedicated to hybrid CWs proved that apart from higher nutrient removal (Vymazal, 2005; Sochacki and Miksch, 2016) those systems enhance also the overall removal of EOCs (Rühmland et al., 2015; Matamoros et al., 2012; Kahl et al., 2017; Ávila et al., 2014, 2017; Conkle et al., 2008; Vymazal, 2013). One of the possible configurations of hybrid CW-based system for decentralized wastewater treatment is a combination of a vertical-flow CW bed with a polishing/permeable surface-flow system (sometimes termed as a ‘pond’). This hybrid system is a frequently used solution for decentralized treatment in Poland (Jucherski et al., 2017; Myszograj and Bydałek, 2016) but also in other countries (Vymazal, 2013; Belmont et al., 2004).

The removal of SMX and DCF can be highly variable and the underlying mechanism for CWs has not been fully elucidated (Miksch et al., 2016; Kahl et al., 2017). The application of diverse conditions as those offered by hybrid treatment systems tends to enhance the removal of EOCs, however this aspect is still understudied. Moreover, the fate of EOCs along the flow path of hybrid CWs has been rarely reported. This is especially important for the EOCs that may undergo transformation into more toxic compounds and also for metabolites that can be re-transformed to the parent compound.

Thus, the aim of this study was to evaluate the removal of DCF and SMX in a two-stage system consisting of a subsurface-flow CW and a surface-flow CW with an emphasis on the effect of a forced aeration. Furthermore, the additional aim was to identify the TPs of DCF and SMX along the flow path of the treatment system.

## 2. Materials and methods

### 2.1. Experimental system and timeline of the experiment

The experimental system was a mesocosm hybrid CW comprising two sequential treatment stages: subsurface-flow CW bed (as the first stage of the system; CW-1) and a surface-flow CW (as the second stage of the treatment, CW-2) fed with the effluent from the CW-1. The experimental system has already been described by Sochacki and Miksch (2016), therefore only major construction features will be recalled here. The CW-1 was set up in a plastic cylindrical tank (diameter 60 cm, height 90 cm), which was filled up to 80 cm with mineral media (15 cm of 4–8 mm gravel at the bottom, and 65 cm of 0.5–1.0 mm quartz sand) (Fig. S1, Supporting information (SI)). The CW-1 tank had four orifices (diametrically opposite) on the side wall directly above the bottom. Three orifices were interconnected with a plastic pipe that extended up to the upper brim of the barrel, which was used as a passive aeration or forced (active) aeration when it was connected with an air pump through plastic tubing. The fourth orifice was used as an outflow of the treated wastewater. The construction details of the CW-1 system are depicted in Fig. S1-2, (SI). No specific air distribution system, as e.g. perforated pipes, was used inside the CW-1 assuming that the bottom layer of gravel would distribute evenly the air sucked or pumped into the system. The forced aeration of the system was carried out using an air pump HIBLOW-HP-60 manufactured by Techno Takatsuki (Japan) with a maximum airflow 60 L/min. The same pump was used to aerate the CW-2 (through EPDM-HD200 disc diffuser (effective diameter 184 mm) manufactured by Jäger Gummi und Kunststoff GmbH Germany) on the bottom of the tank. The CW-1 and CW-2 were intermittently aerated in a 4 h on/2 h off mode until day 56, next the aeration of the CW-1 was discontinued, and the CW-2 was aerated in a continuous mode until day 142, and from day 143 until the end of the experiment the CW-2 was not aerated (see Table 1 for aeration timeline). The tank of the CW-2 was constructed using steel frame and glass panes (length 150 cm, width 100 cm, water depth 50 cm). Taking into account dimensions of the system and the water depth the water volume in the system was 750 L. The CW-2 contained a 5-cm layer of sediment layer composed mostly of ceramsite gravel. The sampling and draining of excessive wastewater was performed by tubing attached to an outlet stub at the bottom side of the wall of the system. The construction details of the CW-2 tank are presented in Fig. S3 (SI).

The experimental system was operated under indoor conditions with artificial lighting system comprising one 600 W high-pressure sodium lamp (HPS) and one metal-halide lamp (600 W). The lighting system was purchased from Flora and Fauna Sp. z o.o. (Poland). The light/dark conditions were 16/8 h throughout the experiment.

The vegetation of the CW-1 was a monoculture of giant miscanthus (*Miscanthus* × *giganteus*) which was planted 356 days before the present experiment. The stem density was approximated as at least 1000 stems/$m^2$, which is typical of very dense macrophyte stands. It should be also