The anaerobic biodegradation of emerging organic contaminants by horizontal subsurface flow constructed wetlands

H. Ilyas, I. Masih and E. D. van Hullebusch

ABSTRACT

The horizontal subsurface flow constructed wetland (HFCW) is widely studied for the treatment of wastewater containing emerging organic contaminants (EOCs): pharmaceuticals, personal care products, and steroidal hormones. This study evaluates the performance of HFCW for the removal of these types of EOCs based on the data collected from peer-reviewed journal publications. In HFCW, anaerobic biodegradation is an important removal mechanism of EOCs besides their removal by the filter media (through sedimentation, adsorption, and precipitation) and plant uptake. The average removal efficiency of 18 selected EOCs ranged from 39% to 98%. The moderate to higher removal efficiency of 12 out of 18 selected EOCs in HFCW indicates the suitability of this type of constructed wetland (CW) for the treatment of wastewater containing these EOCs. The reasonably good removal (>50% in most of the cases) of these EOCs in HFCW might be due to the occurrence of anaerobic biodegradation as one of their major removal mechanisms in CWs. Although the effluent concentration of EOCs was substantially decreased after the treatment, the environmental risk posed by them was not fully reduced in most of the cases. For instance, estimated risk quotient of 11 out of 18 examined EOCs was extremely high for the effluent of HFCW.

Key words | anaerobic biodegradation, emerging organic contaminants, horizontal subsurface flow constructed wetland, removal efficiency, removal mechanism, wastewater

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HIGHLIGHTS

- HFCW is widely studied for the treatment of wastewater containing EOCs.
- In HFCW, anaerobic biodegradation is an important removal mechanism of EOCs.
- The average removal efficiency of 18 selected EOCs was in the range of 39% to 98%.
- HFCWs play a considerable role in reducing the ecological risk posed by EOCs.

INTRODUCTION

Emerging organic contaminants (EOCs) such as pharmaceuticals (PhCs), personal care products (PCPs), and steroidal hormones (SHs) are discharged to water resources and environment through various sources such as domestic wastewater (from excretion, bathing, shaving, spraying, swimming, etc.), industrial wastewater (from product manufacturing discharges), landfill leachate (from improper disposal of used, defective or expired items), and effluent discharge from wastewater treatment plants (WWTPs) (Caliman & Gavrilescu 2009; Luo *et al.* 2014; Barbosa *et al.* 2016; Yi *et al.* 2017; Gogoi *et al.* 2018; Tran *et al.* 2018, 2019; Yin *et al.* 2019). Although EOCs are often found in very low concentrations (e.g., ng L^{-1} to μg L^{-1}) in water bodies, they can still pose negative impacts on human health as well as aquatic and terrestrial life, if these are

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discharged continuously through various sources including WWTPs (Caliman & Gavrilescu 2009; Qiang *et al.* 2013; Carvalho *et al.* 2014; Vymazal *et al.* 2015; Gorito *et al.* 2017; Vystavna *et al.* 2017; Tran *et al.* 2018). It has been indicated that higher concentration of PCPs and SHs compared with their potential no effect concentration could pose severe risk to human health, since many of the PCPs and SHs are considered as prospective endocrine disruptors (e.g., Caliman & Gavrilescu 2009; Töre *et al.* 2012; Gogoi *et al.* 2018).

Constructed wetlands (CWs) are environmentally friendly, low cost, and nature-based treatment technologies that have been extensively investigated for wastewater treatment containing EOCs such as PhCs, PCPs, and SHs (e.g., Töre *et al.* 2012; Verlicchi & Zambello 2014; Zhang *et al.* 2014; Verlicchi *et al.* 2015; Gorito *et al.* 2017; Vo *et al.* 2018; Ilyas *et al.* 2020; Ilyas & van Hullebusch 2020a, 2020b, 2020c). The investigated CWs are free water surface CW (FWSCW), horizontal subsurface flow CW (HFCW), vertical subsurface flow CW (VFCW), and hybrid CW (HCW). The available evidence in the literature and physicochemical properties of EOCs indicate that specific processes are involved in the removal of a certain type of EOC in CWs (Ilyas & van Hullebusch 2020a, 2020b, 2020c), and these complex physical, chemical, and biological processes may occur simultaneously, including photodegradation, volatilization, adsorption/sorption, plant uptake and accumulation, as well as biodegradation (aerobic and anaerobic), mainly depending on the design of the CWs (e.g., Zhang *et al.* 2014; Gorito *et al.* 2017). In all types of CWs, the pollutant removal mechanisms are different, which govern treatment process and resulting performance of CWs. Due to the variation in the dominant removal mechanisms of different types of EOCs, their removal efficiency varies in different types of CWs (Ilyas & van Hullebusch 2020a, 2020b, 2020c).

In HFCW, wastewater stays below the surface of the media and flows horizontally through the bed until it reaches the outlet (e.g., Kadlec & Wallace 2009). The oxygen transfer in HFCW occurs through convection and diffusion from the air to surface water with the estimated oxygen transfer rates in the range of 0.3–3.2 g O_2 m^{-2} d^{-1} (Kadlec & Wallace 2009; Tyroller *et al.* 2010). Therefore, due to limited oxygen availability in this type of CW, anaerobic biodegradation is an important removal mechanism of EOCs besides their removal by the filter media (through sedimentation, adsorption, and precipitation) and plant uptake (Figure 1). For example, anaerobic biodegradation was reported as a possible removal mechanism for acetaminophen, diclofenac, naproxen, ofloxacin, sulfadiazine,

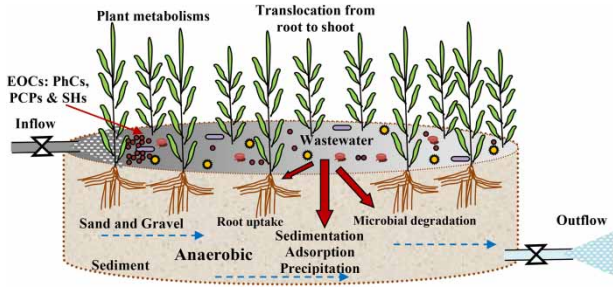


Figure 1 | Horizontal subsurface flow constructed wetland (HFCW) and associated removal mechanisms of emerging organic contaminants (EOCs).
Note: Adapted from Ilyas & van Hullebusch (2020a).

sulfamethoxazole, and 17ß-estradiol in HFCW (Ilyas & van Hullebusch 2020a, 2020b, 2020c). The anaerobic biodegradation process is a multi-step process, which occurs in CWs in the absence of oxygen. This process is governed by either facultative or obligate anaerobic heterotrophic bacteria (e.g., strictly anaerobic sulfate-reducing bacteria and methane-forming bacteria). In this process, high molecular weight carbohydrates degrade into low molecular weight organic compounds, generally in the form of dissolved organic carbon, which is eventually available to microbes (e.g., Valiela 1984; Vymazal 2005). On the other hand, aerobic biodegradation occurs in CWs if sufficient supply of oxygen is available. This process is governed by aerobic heterotrophic bacteria, ammonifying bacteria, and nitrifying bacteria (e.g., Cooper *et al.* 1996; Vymazal 2005). Considering that anaerobic biodegradation of organic compounds is slower than the aerobic biodegradation (Cooper *et al.* 1996), longer hydraulic retention time (HRT) of CWs is needed to achieve the same removal efficiency (Auvinen *et al.* 2017). Nevertheless, at high organic loadings, anaerobic biodegradation predominates due to the limitation of oxygen (Cooper *et al.* 1996). More details on aerobic and anaerobic biodegradation processes in CWs can be found in the literature, for instance, in the studies by Cooper *et al.* (1996) and Vymazal (2005).

Although the performance of HFCW for the removal of EOCs (PhCs, PCPs, and SHs) has been investigated by the individual studies, a comprehensive statistical analysis is missing, for instance, a meta-analysis of existing studies to ascertain the performance of HFCW for the removal of these types of EOCs. Furthermore, most of the studies examined only a limited number of EOCs (PhCs and/or PCPs and/or SHs) (Supplementary materials 1: Tables S1–S3). The environmental risk posed by PhCs and/or PCPs and attenuation in risk after the treatment of wastewater by HFCW was considered by few studies such as in Chen

et al. (2016a), Matamoros et al. (2017), and Vymazal et al. (2017).

Therefore, the focus of this study is to fill the above-mentioned research gaps. In this study, the treatment performance of HFCW for the removal of several categories of PhCs, PCPs, and SHs was investigated based on the available scientific evidence published in peer reviewed journals. The main objectives of this study are: (1) to conduct a comprehensive assessment of EOCs, which are on the European Union (EU) watch list and classified under high environmental risk category in wastewater, and their removal by HFCW; (2) to critically evaluate and summarize the available evidence on major EOCs removal mechanisms in HFCW; (3) to examine the impact of physicochemical properties of EOCs on their removal mechanisms; and (4) to assess the environmental risk posed by EOCs, and contribution of HFCW in their risk reduction.

METHODOLOGY

This research is based on the secondary data and a critical review of the published literature. The research papers, review papers, and books were searched from various sources, such as Scopus, Google Scholar, and individual journal websites, related to the performance of HFCW for the removal of selected types of EOCs (PhCs, PCPs, and SHs). The snowball sampling method yielded over 50 journal articles, which were further screened and used for the purpose of this research. The screening was carried out to check the quality of published data. Only peer-reviewed journal papers were selected for this research, which helped to ensure the reliability of given data. The selected studies have used generally accepted and reliable analytical methods such as solid phase extraction-gas chromatography-tandem mass spectrometry (SPE-GC-MS/MS); SPE-(ultra) high performance liquid chromatography-diode array detector (SPE-(U)HPLC-DAD); liquid-liquid phase extraction-GC-micro electron capture detector (LLPE-GC-μECD); LLPE-(U)HPLC-MS/MS; and SPE-rapid resolution liquid chromatography-MS/MS (SPE-RRLC-MS/MS). Instrumental detection and quantification limits described as limit of detection (LOD) and limit of quantification (LOQ) were in the range of 0.00003–2.6 $\mu g\ L^{-1}$ and 0.00006–10 $\mu g\ L^{-1}$, respectively. The samples were analyzed soon after the collection, as the storage time was less than one or two days in most of the cases. The selected studies contained the required information on most of the key parameters such as concentration of EOCs in influent and effluent waters, removal efficiency, chemical oxygen demand (COD), biochemical oxygen demand (BOD), hydraulic loading rate (HLR), and HRT.

In this way, a global database was compiled containing information of 117 HFCWs (with several PhCs: 93; PCPs: 19; and SHs: 24) that were reported in 35 peer reviewed journal publications (that examined PhCs: 30; PCPs: seven; and SHs: five) with case studies from 12 countries (PhCs: 10; PCPs: six; and SHs: five) for the removal of PhCs, PCPs, and SHs (Supplementary materials 1: Tables S1–S3). In the present study, the treatment performance of HFCW was evaluated for the removal of 18 selected EOCs (PhCs: 12; PCPs: one; and SHs: five), including six out of 18 EOCs that are on the EU watch list as per EU decision 2015/495 and EU decision 2018/840 (clarithromycin, diclofenac, erythromycin, 17ß-estradiol, 17α-ethinylestradiol, and estrone) (EU 2015, 2018; Barbosa et al. 2016; Gorito et al. 2017; Loos et al. 2018) and those classified under high environmental risk category (Ilyas et al. 2020; Ilyas & van Hullebusch 2020b, 2020c).

The removal mechanisms were identified for the selected EOCs as presented in the published case studies. Most of the studies only attributed removal to certain mechanisms (e.g., biodegradation, adsorption/sorption, plant uptake, and photodegradation) (Table 1). The relative contribution of mechanisms to removal was only quantified in a few experimental studies (see information in Ilyas et al. 2020; Ilyas & van Hullebusch 2020b, 2020c). Therefore, the analysis of removal mechanisms was based on a critical oversight of both qualitative and quantitative information. The information on the physicochemical properties (molecular formula/structure/weight, water solubility, octanol-water partition coefficient (Log Kow), octanol-water distribution coefficient (Log Dow), soil organic carbon sorption coefficient (Log Koc), Henry's law constant, and dissociation constant (pKa), cationic or anionic nature (charge) of 18 selected EOCs was gathered from various sources (e.g., Quantitative Structure Activity Relationship (QSAR) Toolbox (version 4.3.1), journal papers, reports, and websites) (Table 2). The available evidence regarding the role of these properties in the removal of EOCs in CWs was comprehensively and critically analyzed. The linkages between physicochemical properties and removal mechanisms were delineated from this analysis.

Additionally, environmental risk assessment of 18 selected EOCs in HFCW was carried out by estimating risk quotient (RQ) (a ratio between the predicted or measured environmental concentration (PEC or MEC), and the worst-case predicted no effect concentration

Table 1 | Removal mechanisms of 18 selected EOCs in different types of CWs

EOCs	Possible removal mechanism	References	Dominant removal mechanism*
PhCs			
Acetaminophen	Biodegradation (aerobic)	Ávila *et al.* (2013, 2015); Koottatep *et al.* (2017); Li *et al.* (2017); Vystavna *et al.* (2017)	Biodegradation (aerobic)**
	Biodegradation (anaerobic)	Chen *et al.* (2016a)	
	Photodegradation	Ávila *et al.* (2015); Li *et al.* (2017)	
	Adsorption	Ávila *et al.* (2015); Koottatep *et al.* (2017)	
	Sorption	Chen *et al.* (2016a)	
	Plant uptake	Li *et al.* (2017)	
Clarithromycin	Biodegradation	Hijosa-Valsero *et al.* (2011a); Berglund *et al.* (2014)	Photodegradation; Sorption
	Sorption	Hijosa-Valsero *et al.* (2011a); Berglund *et al.* (2014)	
	Photodegradation	Hijosa-Valsero *et al.* (2011a); Berglund *et al.* (2014)	
Diclofenac	Biodegradation (anaerobic)	Ávila *et al.* (2010, 2014b); Hijosa-Valsero *et al.* (2010a); Chen *et al.* (2016a); Kahl *et al.* (2017); He *et al.* (2018); Zhang *et al.* (2018a); Nivala *et al.* (2019)	Photodegradation; Biodegradation (aerobic)**
	Biodegradation (aerobic)	Hijosa-Valsero *et al.* (2010a, 2010b, 2011b); Ávila *et al.* (2013, 2014b); Kahl *et al.* (2017)	
	Photodegradation	Matamoros *et al.* (2008a); Matamoros & Salvadó (2012); Ávila *et al.* (2014a, 2015); Rühmland *et al.* (2015); Chen *et al.* (2016a); Francini *et al.* (2018); Zhang *et al.* (2018a)	
	Plant uptake	Hijosa-Valsero *et al.* (2010b); Zhang *et al.* (2011, 2012a)	
Erythromycin	Biodegradation (aerobic)	Rühmland *et al.* (2015); Chen *et al.* (2016b)	Biodegradation (aerobic); Adsorption
	Adsorption	Chen *et al.* (2016b)	
	Plant uptake	Hijosa-Valsero *et al.* (2011a)	
Gemfibrozil	Biodegradation (aerobic)	Conkle *et al.* (2008); Yi *et al.* (2017); Zhang *et al.* (2018a)	Biodegradation (aerobic)
Ibuprofen	Biodegradation (aerobic)	Matamoros *et al.* (2007, 2008b); Hijosa-Valsero *et al.* (2010b, 2011c); Ávila *et al.* (2010, 2013, 2014a, 2014b, 2015); Matamoros & Salvadó (2012); Li *et al.* (2014); Zhu & Chen (2014); Chen *et al.* (2016a); Vymazal *et al.* (2017); Březinova *et al.* (2018); Zhang *et al.* (2018a); Nivala *et al.* (2019)	Biodegradation (aerobic)
	Sorption	Dordio *et al.* (2010)	
	Adsorption	Auvinen *et al.* (2017)	
	Photodegradation	Reyes-Contreras *et al.* (2012); Zhang *et al.* (2014)	
	Plant uptake	Hijosa-Valsero *et al.* (2010b); Li *et al.* (2016a, 2016b)	
Naproxen	Biodegradation (aerobic)	Matamoros *et al.* (2007, 2009); Hijosa-Valsero *et al.* (2010b); Matamoros & Salvadó (2012); Zhang *et al.* (2012b); Chen *et al.* (2016a); He *et al.* (2018); Zhang *et al.* (2018a); Nivala *et al.* (2019)	Biodegradation (aerobic)**; Photodegradation
	Biodegradation (anaerobic)	Matamoros *et al.* (2009); Ávila *et al.* (2010); Li *et al.* (2014); He *et al.* (2018); Nivala *et al.* (2019)	
	Photodegradation	Matamoros *et al.* (2008a); Reyes-Contreras *et al.* (2012); Hijosa-Valsero *et al.* (2016); Zhang *et al.* (2018a)	
	Plant uptake	Hijosa-Valsero *et al.* (2010b); Zhang *et al.* (2013); He *et al.* (2018)	
Ofloxacin	Adsorption	Chen *et al.* (2016b)	Biodegradation (anaerobic)**; Adsorption
	Biodegradation	Chen *et al.* (2016b); Yan *et al.* (2016)	

(*continued*)

Table 1 | continued

EOCs	Possible removal mechanism	References	Dominant removal mechanism*
Salicylic acid	Biodegradation	Hijosa-Valsero *et al.* (2010b, 2011b); Reyes-Contreras *et al.* (2012); Zhang *et al.* (2012c)	Biodegradation (aerobic)**
	Plant uptake	Hijosa-Valsero *et al.* (2016)	
Sulfadiazine	Biodegradation	Xian *et al.* (2010)	Biodegradation (anaerobic)**
	Fermentation	Dan *et al.* (2013)	
Sulfamethazine	Adsorption	Liu *et al.* (2014); Chen *et al.* (2016b); Choi *et al.* (2016)	Biodegradation (aerobic)**; Plant uptake
	Biodegradation	Xian *et al.* (2010); Liu *et al.* (2014); Chen *et al.* (2016b); Choi *et al.* (2016)	
	Fermentation	Dan *et al.* (2013)	
	Plant uptake	Xian *et al.* (2010)	
Sulfamethoxazole	Adsorption	Choi *et al.* (2016); Liang *et al.* (2018)	Biodegradation (aerobic; anaerobic)**
	Sorption	Zhu & Chen (2014)	
	Biodegradation (aerobic)	Conkle *et al.* (2008); Choi *et al.* (2016); Sgroi *et al.* (2018); Button *et al.* (2019)	
	Biodegradation (anaerobic)	Hijosa-Valsero *et al.* (2011a), Dan *et al.* (2013); Rühmland *et al.* (2015); Liang *et al.* (2018); Sgroi *et al.* (2018)	
	Photodegradation	Hijosa-Valsero *et al.* (2011a)	
	Plant uptake	Xian *et al.* (2010); Hijosa-Valsero *et al.* (2011a)	
PCPs			
Triclosan	Adsorption	Carranza-Diaz *et al.* (2014); Chen *et al.* (2016a); Liu *et al.* (2016); Xie *et al.* (2018); Button *et al.* (2019); Wang *et al.* (2019)	Adsorption; Biodegradation (aerobic); Photodegradation
	Sorption	Ávila *et al.* (2014a); Vystavna *et al.* (2017)	
	Biodegradation (aerobic)	Ávila *et al.* (2014a 2014b, 2015); Zhang *et al.* (2014); Zhao *et al.* (2015); Chen *et al.* (2016a); Liu *et al.* (2016); Li *et al.* (2017); Vymazal *et al.* (2017); Xie *et al.* (2018); Button *et al.* (2019); Chen *et al.* (2019); Wang *et al.* (2019)	
	Biodegradation (anaerobic)	Park *et al.* (2009); Vystavna *et al.* (2017)	
	Photodegradation	Matamoros & Salvadó (2012); Zhang *et al.* (2014); Ávila *et al.* (2014a, 2015); Matamoros *et al.* (2016); Li *et al.* (2017); Vymazal *et al.* (2017); Vystavna *et al.* (2017); Francini *et al.* (2018); Chen *et al.* (2019)	
	Plant uptake	Zhang *et al.* (2014); Liu *et al.* (2016); Dai *et al.* (2017); Li *et al.* (2017); Vymazal *et al.* (2017); Francini *et al.* (2018); Xie *et al.* (2018)	
SHs			
17ß-estradiol	Biodegradation (aerobic)	Song *et al.* (2009); Sharif *et al.* (2014)	Biodegradation (anaerobic); Sorption onto organic surfaces; Biotransformation
	Biodegradation (anaerobic)	Song *et al.* (2009); Herrera-Melián *et al.* (2018)	
	Sorption onto organic surfaces	Sharif *et al.* (2014); Herrera-Melián *et al.* (2018)	
	Biotransformation	Gray & Sedlak (2005); Cai *et al.* (2012); Qiang *et al.* (2013); Chen *et al.* (2014); Vymazal *et al.* (2015); Herrera-Melián *et al.* (2018)	
	Photodegradation	Sharif *et al.* (2014)	
	Plant uptake	Song *et al.* (2009)	

(*continued*)

Table 1 | continued

EOCs	Possible removal mechanism	References	Dominant removal mechanism*
17α-ethinylestradiol	Biodegradation (aerobic)	Gray & Sedlak (2005); Song *et al.* (2009); Kumar *et al.* (2011); Nuel *et al.* (2018); Campos *et al.* (2019)	Sorption onto organic surfaces; Biodegradation (aerobic)
	Sorption onto organic surfaces	Song *et al.* (2009); Ávila *et al.* (2014a); Vymazal *et al.* (2015); Herrera-Melián *et al.* (2018))	
	Photodegradation	Ávila *et al.* (2014a); Campos *et al.* (2019)	
	Plant uptake	Song *et al.* (2009); Nuel *et al.* (2018)	
Estriol	Biodegradation (aerobic)	Kumar *et al.* (2011); Herrera-Melián *et al.* (2018)	Sorption onto organic surfaces; Biodegradation (aerobic)
	Sorption onto organic surfaces	Chen *et al.* (2014); Herrera-Melián *et al.* (2018); Nuel *et al.* (2018)	
	Plant uptake	NA	
Estrone	Biodegradation (aerobic)	Song *et al.* (2009); Chen *et al.* (2014); Dai *et al.* (2017); Hakk *et al.* (2018); Herrera-Melián *et al.* (2018)	Plant uptake; Sorption onto organic surfaces; Biodegradation (aerobic)
	Biodegradation (anaerobic)	Song *et al.* (2009)	
	Biotransformation	Chen *et al.* (2014); Hakk *et al.* (2018)	
	Sorption onto organic surfaces	Song *et al.* (2009); Hakk *et al.* (2018); Herrera-Melián *et al.* (2018)	
	Plant uptake	Song *et al.* (2009); Hakk *et al.* (2018)	
Testosterone	Biodegradation (aerobic)	Sharif *et al.* (2014); Herrera-Melián *et al.* (2018); Chen *et al.* (2019)	Biodegradation (aerobic); Photodegradation; Sorption onto organic surfaces
	Sorption onto organic surfaces	Sharif *et al.* (2014)	
	Photodegradation	Sharif *et al.* (2014)	
	Plant uptake	NA	

Note: Authors' own insight based on physicochemical properties, removal mechanisms, and limited evidence in the literature (*); Authors' own insight based on physicochemical properties and removal mechanisms (**). Adapted from Ilyas & van Hullebusch (2020a, 2020b, 2020c).

(PNEC)) (Hernando *et al.* 2006). The MEC was based on average EOC concentration of influent and effluent of HFCW. Following on the recommendations by Hernando *et al.* (2006) and several applications (Gros *et al.* 2010; Verlicchi *et al.* 2012; Kosma *et al.* 2014; Zhu & Chen 2014; Chen *et al.* 2016a; Auvinen *et al.* 2017; Matamoros *et al.* 2017; Vymazal *et al.* 2017), the risk was categorized into four levels: high risk (RQ > 1.0), medium risk ($0.1 \leq RQ \leq 1.0$), low risk ($0.01 \leq RQ \leq 0.1$), and no risk (RQ < 0.01) (Table 3).

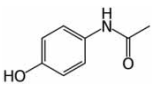
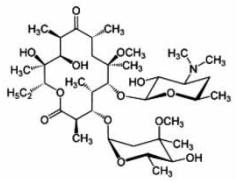
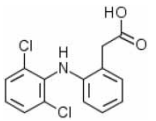
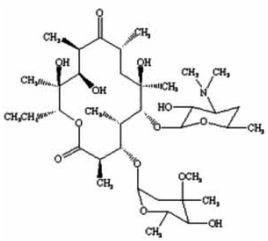
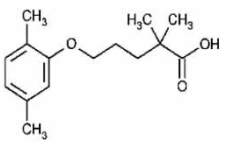
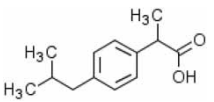
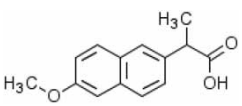
Firstly, a comprehensive analysis of the investigated EOCs was carried out based on the studied literature and the mechanisms responsible for their removal were identified. Secondly, statistical analysis was conducted to estimate mean and standard deviation of the selected studied variables (Supplementary materials 2 and 3: Tables S4 and S5). In addition to mean and standard deviation of influent and effluent RQs, the effluent RQs were estimated based on extremes (minimum and maximum values), median and various other percentiles. The resulting statistics are given in Supplementary materials 4: Table S6.

RESULTS AND DISCUSSION

Removal of EOCs by HFCW

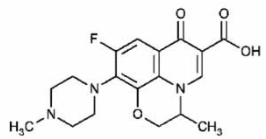
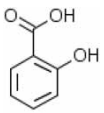
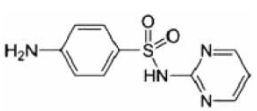
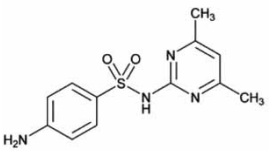
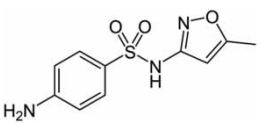
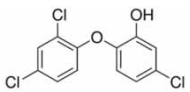
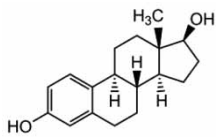
The results show reasonably good removal efficiency for most of the EOCs, as 12 out of 18 selected EOCs indicated removal efficiency above 50% on average (Figure 2). The estimated statistics (mean and standard deviation of influent and effluent concentrations, removal rate, and removal efficiency of 18 selected EOCs are given in Supplementary materials 2: Table S4. Ofloxacin indicated the highest removal efficiency ($98 \pm 4\%$), while diclofenac depicted the lowest removal efficiency ($39 \pm 24\%$). However, in general, the performance of the HFCW systems could be considered reasonably good in most of the cases, which showed the removal efficiency above 50%, such as in the case of testosterone (90%), estrone (83%), 17ß-estradiol (79%), salicylic acid (79%), acetaminophen (70%), naproxen (63%), erythromycin (61%), gemfibrozil (58%), triclosan (56%), ibuprofen (53%), and 17α-ethinylestradiol (52%). The moderate to higher removal efficiency of some of the

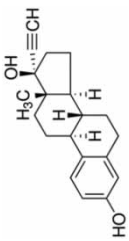
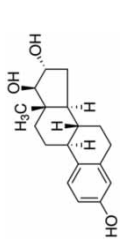
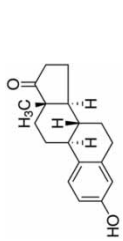
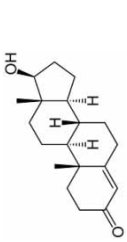
Table 2 | Physicochemical properties of 18 selected EOCs

Type of EOCs/MW (g mol^{-1})	Molecular formula	Molecular structure	WS at 25 °C (mg L^{-1})	Log Kow	Log Koc	Log Dow	HC (atm m^3 mol^{-1})	pKa/charge at pH 7	Reference
PhCs									
Acetaminophen 151.17	$C_8H_9NO_2$		3.04×10^4	0.46	–	0.90	6.42×10^{-13}	9.38/neutral	(1); Verlicchi *et al.* (2012, 2013); Chen *et al.* (2016a); Petrie *et al.* (2018)
Clarithromycin 747.97	$C_{38}H_{69}NO_{13}$		0.342	3.16	2.174	2.31	1.73×10^{-29}	8.99/positive	(1); Verlicchi *et al.* (2012, 2013); Chen *et al.* (2016a); Petrie *et al.* (2018)
Diclofenac 296.15	$C_{14}H_{11}Cl_2NO_2$		4.52	4.51	2.921	0.96	4.73×10^{-12}	4.15/negative	(1); Hijosa-Valsero *et al.* (2010b); Zhang *et al.* (2012a, 2012b, 2018a); Verlicchi *et al.* (2012, 2013); He *et al.* (2018); Petrie *et al.* (2018)
Erythromycin 733.93	$C_{37}H_{67}NO_{13}$		0.517	3.06	2.754	–	5.42×10^{-29}	8.9/positive	(1); Verlicchi *et al.* (2012, 2013); Chen *et al.* (2016a); Yi *et al.* (2017)
Gemfibrozil 250.33	$C_{15}H_{22}O_3$		4.964	4.77	2.636	–	1.2×10^{-8}	4.8/negative	(1); (2); Verlicchi *et al.* (2013); Yi *et al.* (2017); Zhang *et al.* (2018a); Wang *et al.* (2019)
Ibuprofen 206.29	$C_{13}H_{18}O_2$		41.05	3.97	2.596	1.25	1.52×10^{-7}	4.91/negative	(1); Hijosa-Valsero *et al.* (2010b); Verlicchi *et al.* (2012, 2013); He *et al.* (2018); Park *et al.* (2018); Petrie *et al.* (2018); Zhang *et al.* (2018a); Wang *et al.* (2019)
Naproxen 230.27	$C_{14}H_{14}O_3$		144.9	3.18	2.543	0.30	3.39×10^{-10}	4.15/negative	(1); Verlicchi *et al.* (2012, 2013); Hijosa-Valsero *et al.* (2016); He *et al.* (2018); Petrie *et al.* (2018); Zhang *et al.* (2018a)

(*continued*)

Table 2 | continued

Type of EOCs/MW (g mol^{-1})	Molecular formula	Molecular structure	WS at 25 °C (mg L^{-1})	Log Kow	Log Koc	Log Dow	HC (atm m^3 mol^{-1})	pKa/charge at pH 7	Reference
Ofloxacin 361.37	$C_{18}H_{20}FN_3O_4$		2.83×10^4	−0.39	1.086	–	–	5.97/neutral; negative	(1); (2); Verlicchi *et al.* (2012, 2013)
Salicylic acid 138.12	$C_7H_6O_3$		3.80×10^3	2.26	1.379	1.79	1.42×10^{-8}	2.97/negative	(1); Verlicchi *et al.* (2012, 2013); Hijosa-Valsero *et al.* (2011b, 2016)
Sulfadiazine 250.28	$C_{10}H_{10}N_4O_2S$		2.81×10^4	−0.09	1.871	−0.23 to −1.5	–	pK1 = 6.4; pK2 = 2.1/ neutral; negative	(1); Verlicchi *et al.* (2012, 2013); Dan *et al.* (2013)
Sulfamethazine 278.33	$C_{12}H_{14}N_4O_2S$		1.12×10^4	0.89	2.282	0.79–0.16	3.05×10^{-13}	pK1 = 7.6; pK2 = 2.3/ neutral; negative	(1); Verlicchi *et al.* (2012, 2013); Dan *et al.* (2013); Chen *et al.* (2016a)
Sulfamethoxazole 253.28	$C_{10}H_{11}N_3O_3S$		3.94×10^3	0.89	2.412	−0.03	9.56×10^{-13}	pK1 = 5.7; pK2 = 1.8/ neutral; negative	(1); Verlicchi *et al.* (2012, 2013); Chen *et al.* (2016a); Petrie *et al.* (2018)
PCPs									
Triclosan 289.55	$C_{12}H_7Cl_3O_2$		10	5.34	4.26	4.76	2.13×10^{-8}	7.9/neutral; negative	(1); (2); Park *et al.* (2009); Verlicchi *et al.* (2012, 2015); Zhang *et al.* (2014); Zhu & Chen (2014); Carranza-Diaz *et al.* (2014); Dai *et al.* (2017); Li *et al.* (2017); Vystavna *et al.* (2017); Petrie *et al.* (2018); Wang *et al.* (2019)
SHs									
17ß-estradiol 272.38	$C_{18}H_{24}O_2$		82	4.01	2.90	3.74	3.64×10^{-11}	10.33; 0.88/ neutral	(1); (2); (3); (4); Song *et al.* (2009); Liu *et al.* (2012); Verlicchi *et al.* (2012); Sharif *et al.* (2014); Vymazal *et al.* (2015); Wang & Wang (2016); Dai *et al.* (2017); Petrie *et al.* (2018)

17α-ethinylestradiol 296.40	$C_{20}H_{24}O_2$		116	3.67	2.70	3.90	7.94×10^{-12}	10.33; −1.7/ neutral	(1); (2); (3); (4); Song *et al.* (2009); Liu *et al.* (2012); Verlicchi *et al.* (2012); Vymazal *et al.* (2015); Dai *et al.* (2017); Petrie *et al.* (2018); Huang *et al.* (2019)
Estriol 288.38	$C_{18}H_{24}O_3$		441	2.45	3.50	–	1.33×10^{-12}	10.33; −3.2/ neutral	(1); (2); (3); (4); Verlicchi *et al.* (2012); Vymazal *et al.* (2015); Wang & Wang (2016); Hakk *et al.* (2018)
Estrone 270.37	$C_{18}H_{22}O_2$		147	3.43	3.02	4.31	3.80×10^{-10}	10.33; −5.4/ neutral	(1); (2); (3); (4); Song *et al.* (2009); Liu *et al.* (2012); Verlicchi *et al.* (2012); Vymazal *et al.* (2015); Dai *et al.* (2017); Vystavna *et al.* (2017); Hakk *et al.* (2018); Petrie *et al.* (2018)
Testosterone 288.42	$C_{19}H_{28}O_2$		68	3.32	2.55	–	3.53×10^{-9}	18.52; −0.88 /neutral	(1); (2); (3); (4); Liu *et al.* (2012); Sharif *et al.* (2014); Vymazal *et al.* (2015); Wang & Wang (2016)

Note: Molecular weight (MW); Water solubility (WS); Octanol-water partition coefficient (Log Kow); Octanol-water distribution coefficient (Log Dow); Soil organic carbon sorption coefficient (Log Koc); Henry's law constant (HC); Dissociation constant (pKa); Chemical structures are taken from website: https://images.google.com/; QSAR Toolbox 4.3.1 (1); https://www.ncbi.nlm.nih.gov/pccompound (2); https://www.drugfuture.com/chemdata/ (3); https://www.drugbank.ca/drugs (4).

selected EOCs such as acetaminophen, naproxen, ofloxacin, and 17ß-estradiol in HFCW indicates the suitability of HFCWs for the treatment of wastewater containing these EOCs.

In addition to that, the removal efficiency of 18 selected EOCs was analyzed when HFCWs were used for primary, secondary, and tertiary treatment levels (Supplementary materials 3: Table S5). However, the results indicate no clear pattern of high or low performance in the case of primary, secondary or tertiary treatment (Figure 3). For instance, in some cases, higher removal efficiencies are achieved when HFCWs are used as tertiary treatment compared to primary treatment and vice versa. Therefore, it is challenging to establish the level of treatment for improved performance and risk attenuation by HFCW.

Removal mechanisms of EOCs in HFCW

The moderate to higher removal efficiency of 12 out of 18 selected EOCs in HFCW might be due to the reason that anaerobic biodegradation is one of their major removal mechanisms in CWs (Figure 2 and Table 1). However, the low to moderate removal efficiency of diclofenac, sulfamethoxazole, triclosan, naproxen, and acetaminophen in HFCW also indicates the role of their physicochemical properties as well as the environmental conditions in this type of CW in the removal mechanisms. The removal mechanisms of selected EOCs (ofloxacin, diclofenac, sulfamethoxazole, triclosan, and 17ß-estradiol) are discussed in this section. Detailed discussion on the removal mechanisms of other EOCs can be found in Ilyas & van Hullebusch (2020a, 2020c).

Ofloxacin

In the case of ofloxacin (removal efficiency: 98 ± 4%) (Figure 2 and Table S4), its moderate molecular weight (361.37 g mol^{-1}) and anionic form under neutral conditions (pH = 7) (Table 2) favor its adsorption to the substrate media. This can be seen by its complete removal (100%) in HFCW, 24% of which was removed by adsorption onto zeolite (Chen *et al.* 2016b). It is highly water soluble (28.3 g L^{-1} at 25 °C) and anionic or neutral at pH = 7, but due to less lipophilic characteristics (Log Kow = -0.39) (Table 2), the lower ability to partition into lipophilic cell structure hinders its removal by plant uptake in CWs. This can be seen by its low uptake by the plant (*Callitriche palustris*) (13 µg kg^{-1}) (Nuel *et al.* 2018) and low concentration in the plant leaves (*Cyperus alternifolius*) (7.4 ± 0.1 µg kg^{-1}) (Yan *et al.* 2016).

Table 3 | Risk assessment of 18 selected EOCs based on influent and effluent concentration in HFCW

EOCs	PNEC (μg L^{-1})	(MEC) Influent conc. (μg L^{-1})	(MEC) Effluent conc. (μg L^{-1})	Influent RQ	Effluent RQ	Risk rank* Influent/Effluent	References for PNEC values
PhCs							
Acetaminophen	1.0	2.9	0.1	**2.9**	0.1	High/Medium	Verlicchi *et al.* (2012)
Clarithromycin	0.07	0.4	0.2	**5.8**	**2.8**	High/High	Verlicchi *et al.* (2012)
Diclofenac	9.7	24	12	**2.4**	**1.2**	High/High	Verlicchi *et al.* (2012)
Erythromycin	0.02	9.6	3.7	**481**	**186**	High/High	Verlicchi *et al.* (2012)
Gemfibrozil	0.9	50	23	**56**	**26**	High/High	Verlicchi *et al.* (2012)
Ibuprofen	1.65	33	14	**20**	**8.8**	High/High	Verlicchi *et al.* (2012)
Naproxen	2.62	27	6.9	**10**	**2.6**	High/High	Verlicchi *et al.* (2012)
Ofloxacin	0.016	0.04	0.005	**2.5**	0.3	High/Medium	Verlicchi *et al.* (2012)
Salicylic acid	1.28	16	2.3	**12**	**1.8**	High/High	Verlicchi *et al.* (2012)
Sulfadiazine	0.135	0.07	0.04	0.5	0.3	Medium/Medium	Verlicchi *et al.* (2012)
Sulfamethazine	4.0	1.5	0.7	0.4	0.2	Medium/Medium	Gros *et al.* (2010)
Sulfamethoxazole	0.027	0.5	0.2	**18**	**5.7**	High/High	Verlicchi *et al.* (2012)
PCPs							
Triclosan	0.13	9.8	1.4	**75**	**11**	High/High	Kosma *et al.* (2014); Zhu & Chen (2014)
SHs							
17α-ethinylestradiol	0.0001	50	21	**501,064**	**211,218**	High/High	Young *et al.* (2002); Caldwell *et al.* (2012); Laurenson *et al.* (2014)
17β-estradiol	0.002	0.008	0.001	**4.1**	0.5	High/Medium	Caldwell *et al.* (2012)
Estriol	0.06	0.01	0.007	0.2	0.1	Medium/Medium	Caldwell *et al.* (2012)
Estrone	0.006	17	1.9	**2797**	**313**	High/High	Caldwell *et al.* (2012)
Testosterone	0.1	0.007	0.0005	0.1	0.01	Medium/Low	Liu *et al.* (2015); Chen *et al.* (2019)

Note: Predicted no effect concentration (PNEC); Measured environmental concentration (MEC); PNEC values are taken from the referred studies; Bold values indicate a high risk category; Risk rank is based on our results (*). Risk is categorized into four levels: high risk (RQ > 1.0), medium risk (0.1 ≤ RQ ≤ 1.0), low risk (0.01 ≤ RQ ≤ 0.1), and no risk (RQ < 0.01).

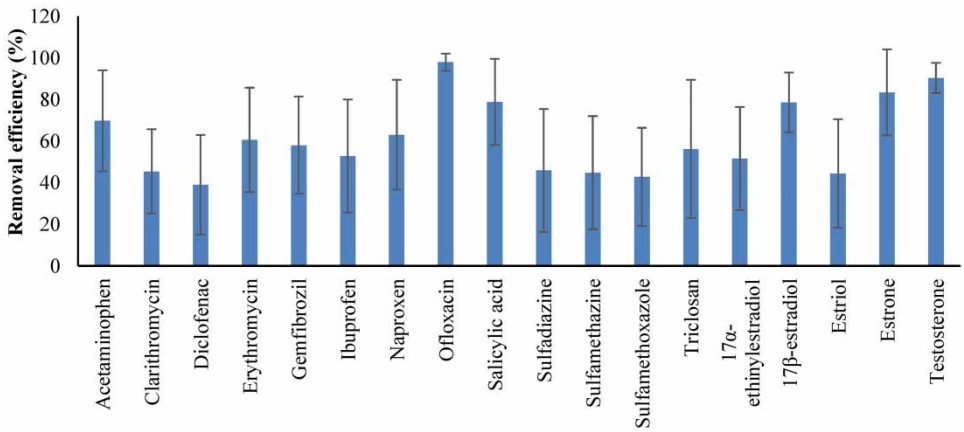


Figure 2 | The observed removal efficiency (mean and standard deviation) of 18 selected EOCs in HFCW.

Nevertheless, the higher removal efficiency by planted HFCW and VFCW (Ilyas *et al.* 2020) indicates the indirect effects of plants' presence such as enhancement in biodegradation. This is obvious by the major contribution of biodegradation pathways (67%) to its total removal efficiency (100%) in HFCW (Chen *et al.* 2016b). Therefore, based on physicochemical properties, removal mechanisms, and evidence from the literature, the anaerobic biodegradation and

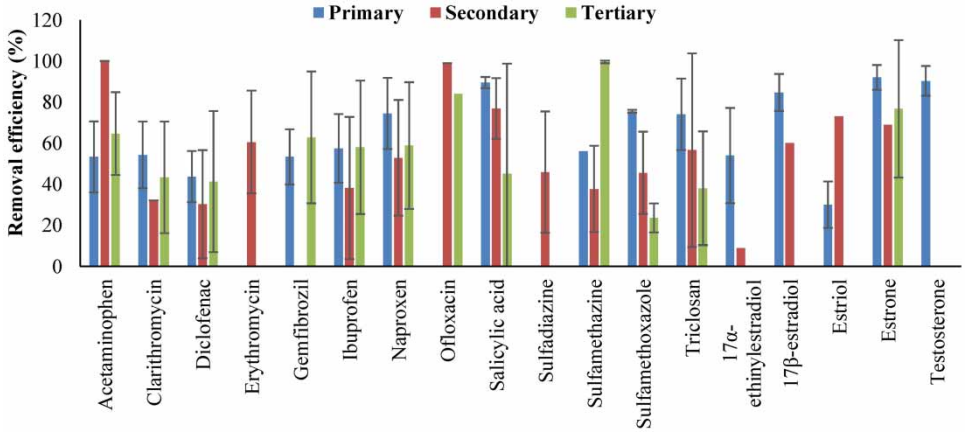


Figure 3 | The observed removal efficiency (mean and standard deviation) of 18 selected EOCs in HFCW used for primary, secondary, and tertiary treatment.

adsorption are considered its dominant removal mechanisms in CWs (Table 1). Its high removal efficiency in HFCW might be due to the reason that these removal mechanisms also play a dominant role in the performance of HFCW.

17ß-estradiol

The dominant **role** of anaerobic biodegradation is also evident by the moderate to high removal efficiency of 17ß-estradiol in HFCW (79 ± 14%) (Figure 2 and Table S4). Its low water solubility (82 mg L^{-1} at 25 °C), high hydrophobicity and distribution coefficient (Log Kow = 4.01; Log Dow = 3.74) with moderate molecular weight (272.38 g mol^{-1}) (Table 2) suggest that the adsorption onto soil particles can be considered as one of its removal pathways in CWs. It can also be removed by sorption onto organic surfaces due to its high organic carbon sorption capacity (Log Koc = 2.90) (Table 2). Sharif *et al.* (2014) observed its sorption (17 ± 2%) onto the wetland plants (*Scirpus validus*) in a batch sorption experiment. This can be exemplified by its better removal in palm mulch (organic substrate media) based VFCW (31 ± 96%) compared with its negative removal in gravel-based VFCW (−53 ± 33%) (Herrera-Melián *et al.* 2018). Next to adsorption and sorption, its removal by photodegradation was achieved in photolysis experiments (12 ± 1%) and by biodegradation (34 ± 4%) in microcosm experiments (Sharif *et al.* 2014). Some studies ascribed its removal to anaerobic biodegradation in CWs, and in river water and anaerobic sediments (Jürgens *et al.* 2002), which is evident by its better removal efficiency in HFCW-anaerobic (30 ± 28%) compared with VFCW-aerobic (20 ± 14%) (Herrera-Melián *et al.* 2018). Furthermore, Czajka & Londry (2006) reported the chemical transformation of 17ß-estradiol to estrone in the lake water and sediment under anaerobic conditions (e.g., methanogenic, sulfate, iron, and nitrate-reducing conditions). This might be the reason that several studies considered that its biotransformation into estrone can be one of its major removal mechanisms in CWs (Table 1). Thus, based on physicochemical properties, removal mechanisms, and evidence from the literature, the anaerobic biodegradation, sorption onto organic surfaces, and biotransformation are considered its dominant removal mechanisms in CWs (Table 1). Among these removal mechanisms, anaerobic biodegradation plays a dominant role in the performance of HFCW, which might be the reason for its moderate to high removal efficiency in HFCW.

Diclofenac

In the case of diclofenac (removal efficiency: 39 ± 24%) (Figure 2 and Table S4), it is suggested that the presence of chlorine in its structure makes it highly recalcitrant to biodegradation (Kimura *et al.* 2005). It is a hydrophobic compound (Log Kow = 4.51) with moderate molecular weight (296.15 g mol^{-1}) and anionic in nature under neutral conditions (pH = 7) (Table 2), which suggests the removal by adsorption onto soil particles following complex formation with metal ions, but its low distribution coefficient (Log Dow = 0.96) (Table 2) might restrict this removal pathway. However, its removal by adsorption has not been tested in adsorption experiments as well as it is not reported in CWs. Nevertheless, its low removal efficiency by plant uptake in hydroponic microcosm (4.4 ± 2.7%) explains that it is not a possible removal pathway (Zhang *et al.* 2012a, 2013). This was confirmed by Zhang *et al.* (2012a); they calculated the bioaccumulation factor (BAF) and reported that its BAF in the shoots was less than half

(0.17–0.51) compared with BAF in the roots (0.40–1.36). This can be attributed to both its high hydrophobicity and relatively low water solubility (4.52 mg L^{-1} at 25 °C) (Table 2). It has been suggested that organic compounds with Log Kow > 3.5 have a high potential for retention in the plant roots (Dietz & Schnoor 2001). Therefore, the difference in the removal efficiency of planted and unplanted HFCW (50 ± 24% and 32 ± 16%, respectively) (Hijosa-Valsero *et al.* 2010b; Zhang *et al.* 2011, 2012c, 2018a; Carranza-Diaz *et al.* 2014; He *et al.* 2018) might be due to indirect positive effects of plants' presence such as degradation by enzymatic exudates as well as an increase of the amount of oxygen released by the plant roots in the rhizosphere which can support high microbial activity (biodegradation). However, in hydroponic microcosms it has been revealed that the contribution of biodegradation to its removal efficiency was low (3.0%) (Zhang *et al.* 2013). Its high removal efficiency by photodegradation was achieved in hydroponic microcosm (79 ± 2%) (Zhang *et al.* 2012a, 2013) and it was confirmed in unplanted HCW system with a free water surface (FWS) on top of the horizontal flow filter (HFF) which provides the most appropriate environment for photodegradation (Reyes-Contreras *et al.* 2012). Its higher removal efficiency in the unplanted HCW (29%) compared with the planted HCW (1.7%) during summer was attributed to photodegradation (Reyes-Contreras *et al.* 2012). Therefore, based on physicochemical properties, removal mechanisms, and evidence from the literature, photodegradation and aerobic biodegradation are considered its dominant removal mechanisms in CWs (Table 1). Its low removal efficiency in HFCW might be due to the limitation of photodegradation and aerobic biodegradation in HFCW.

In addition to physicochemical properties of diclofenac, the environmental conditions in HFCW also play a considerable role in its removal mechanisms. For instance, some studies suggested that high oxidation-reduction potential (ORP) in CWs could promote its removal by aerobic biodegradation. In contrast, it has also been suggested that its removal efficiency could be enhanced under anaerobic conditions (biodegradation). Several studies indicated the need of integrated design of HCW that should display features of different types of CWs. For instance, the required aerobic and anaerobic environments to achieve efficient removal of EOCs necessitate combining VFCW with HFCW (e.g., Kahl *et al.* 2017; Nivala *et al.* 2019) to achieve reductive and oxidative processes in CWs (e.g., Vymazal 2005). For instance, Nivala *et al.* (2019) reported that the removal efficiency of diclofenac in HCW, VFCW, and HFCW was 77, 53, and 25%, respectively.

Sulfamethoxazole

The removal efficiency of sulfamethoxazole was low in HFCW (43 ± 24%) (Figure 2 and Table S4). Adsorption to the substrate cannot be considered its removal mechanism due to its high water solubility (3.94 g L^{-1} at 25 °C) and high hydrophilicity (Log Kow = 0.89), although its molecular weight is moderate (253.28 g mol^{-1}) (Table 2). Additionally, due to its neutral or anionic form under neutral conditions (pH = 7) (Table 2), its binding to biomass is likely to be minimal, although it has moderate sorption capacity (Log Koc = 2.41) (Dan *et al.* 2013). This can be seen by non-significant difference in its removal efficiency between hydroponic system and FWSCW (planted and gravel bed) (38% and 35%, respectively) (Hijosa-Valsero *et al.* 2011a). Similarly, Zhu & Chen (2014) reported its slight sorption to the sludge (19–43 μg kg^{-1}) in HCW. Its high water solubility, hydrophilic character, and neutral form (Table 2) suggest its uptake by the plants in CWs. This is made explicit by its better removal in the planted compared with the unplanted FWSCW (92% and 73%, respectively) (Xian *et al.* 2010), and the planted compared with unplanted HFCW (71 and 46%, respectively) (Hijosa-Valsero *et al.* 2011a). However, in the planted and unplanted VFCW, its complete removal (100%) was achieved (Button *et al.* 2019) and in the planted and unplanted HCW its removal was 58% and 61%, respectively (Hijosa-Valsero *et al.* 2011a), which indicates that in planted CWs direct uptake by the plants is minimal due to its low Log Kow, but the plants also support biodegradation (Choi *et al.* 2016; Liang *et al.* 2018). This is evident by the major contribution of biodegradation pathways (68%) to its total removal of 71% in hydroponic system (Choi *et al.* 2016). In unplanted CWs, the removal may be because the substrates provide a surface area suitable for the growth of microorganisms and the formation of biofilm for biodegradation (Dan *et al.* 2013; Choi *et al.* 2016). This is obvious by its higher removal in biotic system (73%) compared with abiotic system (67%) during a soil adsorption experiment under biotic and abiotic conditions (Choi *et al.* 2016). Furthermore, Choi *et al.* (2016) observed 23% of its removal by photodegradation in a photolysis experiment. Therefore, a slight increase in the removal efficiency by the unplanted HCW (FWS on top of HFF) compared with the planted HCW indicates that photodegradation might contribute to its removal (Hijosa-Valsero *et al.* 2011a). Hence, based on physicochemical properties, removal mechanisms, and evidence from the literature, biodegradation (aerobic and anaerobic) is considered its dominant removal mechanism in CWs

(Table 1). Its low removal efficiency in HFCW might be due to the limitation of aerobic biodegradation in HFCW.

Triclosan

The removal efficiency of triclosan was low to moderate in HFCW (56 ± 33%) (Figure 2 and Table S4). Its very low water solubility (10 mg L^{-1} at 25 °C), high hydrophobicity (Log Kow = 5.34; Log Dow = 4.76) with moderate molecular weight (289.55 g mol^{-1}), and neutral or anionic nature under neutral conditions (pH = 7) with pKa value of 7.9 (Table 2), suggest its removal by adsorption onto soil particles following complex formation with metal ions such as calcium ion (Ca^{2+}), magnesium ion (Mg^{2+}), ferric ion (Fe^{3+}), or aluminum ion (Al^{3+}) (Berglund *et al.* 2014). This can be explained by its better removal efficiency in winter (45%) compared with summer (35%) (Matamoros *et al.* 2016), because the abiotic processes like adsorption are exothermic processes and favored by low temperature (in winter) (Reyes-Contreras *et al.* 2012). Its high organic carbon sorption capacity (Log Koc = 4.26) (Table 2) also favors its removal by sorption. This is made explicit by its sorption (19%) to the vessel of hydroponic microcosm (Matamoros *et al.* 2012). The dominance of adsorption/sorption processes in its removal is further supported by the almost similar removal efficiency in the planted and unplanted CWs (54 ± 65% and 51 ± 69%, respectively) (Carranza-Diaz *et al.* 2014; Button *et al.* 2019) as well as lower contribution of plants (11%) in hydroponic system (*Spirodela polyrhiza*) compared with the control without plants (95 and 84%, respectively) (Li *et al.* 2017). Its translocation factor was zero or below 1.0 from roots to the shoots of the plant, which indicates rhizofiltration as one of the sources of remediation (Wang *et al.* 2019). Similarly, Petrie *et al.* (2018) did not observe its uptake by any of the studied plants. However, the presence of plants enhances microbial activity (biodegradation), which might be responsible for its removal (Ávila *et al.* 2014b; Zhao *et al.* 2015; Chen *et al.* 2016a; Li *et al.* 2017). This can be seen by the high contribution (up to 84%) of this process to its removal efficiency in the case of hydroponic microcosms (Li *et al.* 2017). In addition to that, its high removal efficiency by photodegradation was achieved in hydroponic microcosm (69 ± 16%) (Matamoros *et al.* 2012; Li *et al.* 2017). This can be explained by its higher removal efficiency in FWSCW (97 ± 2%) (Ilyas & van Hullebusch 2020b), which suggests that photodegradation might be a considerable removal pathway (Matamoros & Salvadó 2012; Zhang *et al.* 2014; Ávila *et al.* 2015; Matamoros *et al.* 2016; Vymazal *et al.* 2017). Therefore, based on physicochemical properties, removal mechanisms, and evidence from the literature, adsorption, aerobic biodegradation, and photodegradation are considered its dominant removal mechanisms in CWs (Table 1). Its low to moderate removal efficiency in HFCW might be due to the limitation of aerobic biodegradation and photodegradation in HFCW.

Environmental risk assessment for the selected EOCs

Ecological risk was assessed for EOCs based on their PNEC estimates. In the literature, the PNECs are reported based on experimental and modeling studies related to several organisms such as fish, *Daphnia magna*, algae, invertebrates, and bacteria in the case of PhCs (e.g., Verlicchi *et al.* 2012), *Daphnia magna* in the case of PCPs (Zhu & Chen 2014; Matamoros *et al.* 2016), and fish, crustaceans, algae, and invertebrates in the case of SHs (e.g., Liu *et al.* 2015; Zhang *et al.* 2018b; Chen *et al.* 2019; Luo *et al.* 2019). Considering the approach of these studies, the lowest estimate of PNEC is used to calculate RQ. For instance, PNEC estimates for erythromycin were available from the studies by Sanderson *et al.* (2003) cited in Verlicchi *et al.* (2012) for fish (61–900 μg L^{-1}), *Daphnia* (7.8 μg L^{-1}), algae (0.02–4.3 μg L^{-1}), and invertebrates (15 μg L^{-1}). In this case, the lowest value of 0.02 μg L^{-1} was used as the PNEC to estimate the RQ of erythromycin. Similarly, PNEC estimates for estrone were available for fish (0.006 μg L^{-1}), crustaceans (0.410 μg L^{-1}), and invertebrates (0.604 μg L^{-1}) from Luo *et al.* (2019). In this case, the lowest value of 0.006 μg L^{-1} was adopted as the PNEC to estimate the RQ of estrone. Although PNEC values of selected EOCs show large variation in water, these were below 0.5 μg L^{-1} in most of the cases, which indicates the high toxicities of these compounds in the aqueous phase (Zhu & Chen 2014) (Table 3). Therefore, the stringent approach of using lowest PNEC value is considered, as it is safest from the ecological protection point of view.

Then, RQ was calculated using the lowest PNEC value and the MEC of influent and effluent of EOCs. These calculations were performed for the 18 selected EOCs based on all the available data points (Table 3). The mean RQ were estimated from this analysis, and are discussed in detail in this section. Since mean could be biased towards high values, median and various other percentiles were also estimated. The RQ was also estimated based on extremes (minimum and maximum values). The resulting statistics are given in Supplementary materials 4: Table S6. The mean RQ estimates are given by Figure 4 and Table 3.

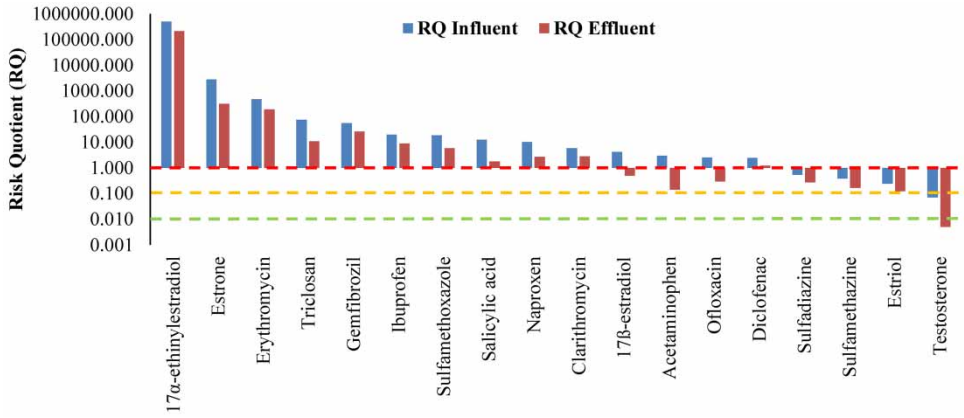


Figure 4 | Risk quotient (RQ) of the 18 selected EOCs based on the influent and effluent concentration in HFCW.
Note: Risk is categorized into four levels: high risk (RQ > 1.0; above red line), medium risk (0.1 ≤ RQ ≤ 1.0; between red and orange line), low risk (0.01 ≤ RQ ≤ 0.1; between orange and green line), and no risk (RQ < 0.01; below green line).

Based on effluent RQ assessment, 11 out of 18 selected EOCs could be grouped under high risk category. Among the 12 selected PhCs, clarithromycin, diclofenac, erythromycin, gemfibrozil, ibuprofen, naproxen, salicylic acid, and sulfamethoxazole could be classified under high risk category (Figure 4 and Table 3), whereas, acetaminophen, ofloxacin, sulfadiazine, and sulfamethazine could be grouped to medium risk category. Triclosan is assessed as high risk PCP, despite considerable risk reduction after the treatment (Figure 4 and Table 3). Among the five selected SHs, 17α-ethinylestradiol and estrone could be classified under high risk category (Figure 4 and Table 3). 17ß-estradiol and estriol could be grouped to medium risk category and testosterone could be classified under low risk category.

Similar to our findings, Vymazal *et al.* (2017) reported ibuprofen and clarithromycin under the high risk category. However, Chen *et al.* (2016a) reported that ibuprofen had a high to medium risk, and diclofenac had a medium risk. The study by Matamoros *et al.* (2017) indicated that ibuprofen had a medium risk in the effluent. Matamoros *et al.* (2017) also reported triclosan under the high risk category. The differences in risk estimates and categories could be attributed to the varying nature of design and operational conditions of the CWs. For example, influent concentrations in the wastewater under consideration is an important factor in determining the environmental risk before and after the treatment. As notable from Supplementary materials 1 (Tables S1–S3), the influent concentrations vary across different studies for domestic wastewater as well as other wastewater types under consideration. Additionally, influent concentrations in synthetic wastewater are higher than those reported for domestic wastewater. To further check the sensitivity of wastewater type on risk assessment, we also estimated RQ based on studies with only domestic wastewater excluding synthetic and other wastewater types; the risk category is the same for most of the EOCs, although RQ values are lower in most of the cases. The risk categorization based on only domestic wastewater studies indicated eight of the 11 high risk EOCs (clarithromycin, erythromycin, ibuprofen, salicylic acid, sulfamethoxazole, triclosan, 17α-ethinylestradiol, and estrone) based on effluent RQ of HFCW under high risk; whereas as three EOCs (diclofenac, naproxen, and gemfibrozil) were classified under the medium risk category. Therefore, these differences influence the risk calculations for individual studies as well as combined assessment. Nevertheless, the results reveal that the estimated RQs based on effluent concentrations are significantly lower than those based on influent values (Figure 4 and Table 3), thus, indicating effective role of HFCW in reducing the ecological risk posed by EOCs.

Based on our study with data from several countries, we see the need of including several PhCs, PCP, and SHs (e.g., those emerged under the high risk category) in regulatory monitoring, water quality standard formulation and control purposes. For instance, the EU watch list of four PhCs (azithromycin, clarithromycin, erythromycin, and diclofenac) and three SHs (17α-ethinylestradiol, 17ß-estradiol, and estrone) (EU 2015, 2018; Barbosa *et al.* 2016; Gorito *et al.* 2017; Loos *et al.* 2018) could be enhanced by considering these EOCs.

CONCLUSIONS

In this paper, the removal of 18 selected EOCs (PhCs: 12; PCPs: one; and SHs: five), including six out of 18 EOCs

that are on the EU watch list have been investigated by HFCW. The environmental risk posed by these EOCs and the attenuation in risk after the treatment with HFCW were estimated. Additionally, the impact of physicochemical properties of these EOCs on their removal mechanisms was comprehensively analyzed. The following specific conclusions are drawn from this research.

1. In HFCW, anaerobic biodegradation is an important removal mechanism of EOCs besides their removal by the filter media (through sedimentation, adsorption, and precipitation) and plant uptake.
2. In HFCW, the average removal efficiency of 18 selected EOCs, which are on the EU watch list and classified under high environmental risk category was in the range of 39% to 98%.
3. The moderate to higher removal efficiency of some of the selected EOCs such as acetaminophen, naproxen, ofloxacin, and 17ß-estradiol in HFCW indicates the suitability of this type of CW for the treatment of wastewater containing these EOCs.
4. HFCW contributed considerably in reducing the environmental risks posed by 18 selected EOCs. Although the risk is not fully abolished by HFCW, it is significantly reduced in most of the cases. Our analysis of global data classified 11 out of 18 selected EOCs (clarithromycin, diclofenac, erythromycin, gemfibrozil, ibuprofen, naproxen, salicylic acid, sulfamethoxazole, triclosan, 17α-ethinylestradiol, and estrone) under the high risk category, whereas, acetaminophen, ofloxacin, sulfadiazine, sulfamethazine, 17ß-estradiol, and estriol were grouped under the medium risk category. These high to medium risk EOCs are recommended to consider for regulatory monitoring, control and water quality standard formulation purposes.
5. Although HFCW(s) (either alone or in combination) are widely studied for the treatment of wastewater containing EOCs (PhCs, PCPs, and SHs), due to the limitation of the occurrence of aerobic environment and photodegradation, this type of CWs could be redesigned and replaced with integrated systems by combining VFCW, HFCW, and FWSCW when multiple types of EOCs needs to be treated.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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