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

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...
discharged continuously through various sources including WWTPs (Caliman & Gavrilescu 2009; Qiang et al. 2015; 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; Gogoï 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 flow (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 O₂ 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, 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-EC); 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 0.00005–2.6 μg L⁻¹ and 0.00006–10 μg 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, 17β-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); Výstavna et al. (2017) | Biodegradation (aerobic)**   |
|            | Biodegradation (anaerobic)   | Chen et al. (2016a)                                                                            |                             |
|            | Photodegradation             | Ávila et al. (2013); 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, 2014a); 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 (anaerobic)** |
|            | 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); Brezinova 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)** |
|            | Biodegradation               | Chen et al. (2016b); Yan et al. (2016)                                                        | Adsorption                 |

(continued)
| EOCs                      | Possible removal mechanism | References                                                                 | Dominant removal mechanism* |
|--------------------------|----------------------------|--------------------------------------------------------------------------|-----------------------------|
| Sulfamethoxazole         | Adsorption                 | Choi et al. (2016); Liang et al. (2018)                                   | Biodegradation (aerobic)    |
|                          | Sorption                   | Zhu & Chen (2014); Conkle et al. (2008); Choi et al. (2016); Sgroi et al. (2018); Button et al. (2019) | Biodegradation (aerobic; anaerobic) |
|                          | Biodegradation (aerobic)   | Hijosa-Valsero et al. (2011a), Dan et al. (2015); Rühmländ et al. (2015); Liang et al. (2018); Sgroi et al. (2018) | Biodegradation (anaerobic)** |
|                          | Biodegradation (anaerobic) |                                                                         |                             |
|                          | Photodegradation            | Hijosa-Valsero et al. (2011a)                                            |                             |
|                          | Plant uptake                | Xian et al. (2010); Hijosa-Valsero et al. (2011a)                         |                             |
| PCPs                     | Triclosan                  | Adsorption; Biodegradation (aerobic); Photodegradation                    |                             |
|                          | Sorption                   | 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) |                             |
|                          | Biodegradation (aerobic)    | Ávila et al. (2014a); Vystavna et al. (2017)                              |                             |
|                          | Biodegradation (anaerobic)  | 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); Dí et al. (2017); Li et al. (2017); Vymazal et al. (2017); Francini et al. (2018); Xie et al. (2018) |                             |
| SHs                      | 17β-estradiol               | Song et al. (2009); Sharif et al. (2014)                                  | Biodegradation (anaerobic); Sorption onto organic surfaces; Biotransformation |
|                          | Biodegradation (aerobic)    | Song et al. (2009); Herrera-Melián et al. (2018)                         |                             |
|                          | Biodegradation (anaerobic)  |                                                                         |                             |
|                          | 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)
(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 ≤ RQ ≤ 1.0), low risk (0.01 ≤ RQ ≤ 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 ± 4%), while diclofenac depicted the lowest removal efficiency (39 ± 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%), 17β-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 (atm m³ mol⁻¹) | HC (atm m³ mol⁻¹) | pKa/charge at pH 7 | Reference |
|---------------------------|-------------------|---------------------|----------------------|---------|---------|-------------------------|-----------------|----------------|-----------|
| **PhCs**                  |                   |                     |                      |         |         |                         |                 |                |           |
| Acetaminophen 151.17      | C₈H₉NO₂           | ![image](image1.png) | 3.04 × 10⁴           | 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     | C₃₈H₆₉NO₁₃       | ![image](image2.png) | 0.342                | 3.16    | 2.174   | 2.31                    | 1.73 × 10⁻²⁰    | 8.99/positive   | (1); Verlicchi et al. (2012, 2013); Chen et al. (2016a); Petrie et al. (2018) |
| Diclofenac 296.15         | C₁₄H₁₁Cl₂NO₂     | ![image](image3.png) | 4.52                 | 4.51    | 2.921   | 0.96                    | 4.73 × 10⁻¹²    | 4.15/negative   | (1); Hijosa-Valsero et al. (2016b); Zhang et al. (2022a, 2023b, 2018a); Verlicchi et al. (2012, 2013); He et al. (2018); Petrie et al. (2018) |
| Erythromycin 733.93       | C₃₇H₆₇NO₁₃       | ![image](image4.png) | 0.517                | 3.06    | 2.754   | –                       | 5.42 × 10⁻²⁰    | 8.9/positive    | (1); Verlicchi et al. (2012, 2013); Chen et al. (2016a); Yi et al. (2017) |
| Gemfibrozil 250.33        | C₁₃H₂₂O₃         | ![image](image5.png) | 4.964                | 4.77    | 2.636   | –                       | 1.2 × 10⁻⁸      | 4.8/negative    | (1); (2); Verlicchi et al. (2015); Yi et al. (2017); Zhang et al. (2018a); Wang et al. (2019) |
| Ibuprofen 206.29          | C₁₃H₁₈O₂         | ![image](image6.png) | 41.05                | 3.97    | 2.596   | 1.25                    | 1.52 × 10⁻⁷     | 4.91/negative   | (1); Hijosa-Valsero et al. (2016b); 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           | C₁₄H₁₄O₃         | ![image](image7.png) | 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. (2016b); He et al. (2018); Petrie et al. (2018); Zhang et al. (2018a) |

(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 m³ mol⁻¹) | pKa/charge at pH 7 | Reference |
|--------------------------|-------------------|---------------------|---------------------|---------|---------|---------|----------------|------------------|----------|
| Ofloxacin 561.37         | C₁₈H₂₀FN₅O₄       | ![Ofloxacin structure](image) | 2.83 × 10⁴         | −0.39   | 1.086   | −       | 5.97/neutral; negative | (1); (2); VERLICCHI ET AL. (2012, 2013) |
| Salicylic acid 138.12    | C₇H₆O₃            | ![Salicylic acid structure](image) | 5.80 × 10³         | 2.26    | 1.379   | 1.42 × 10⁻⁸ | 2.97/negative | (1); VERLICCHI ET AL. (2012, 2013); HIJOSA-VALSERO ET AL. (2016) |
| Sulfadiazine 250.28      | C₁₀H₁₀N₄O₂S       | ![Sulfadiazine structure](image) | 2.81 × 10⁴         | −0.09   | 1.871   | −       | pK1 = 6.4; pK2 = 2.1/neutral; negative | (1); VERLICCHI ET AL. (2012, 2013); DAN ET AL. (2015) |
| Sulfamethazine 278.33    | C₁₂H₁₄N₄O₂S       | ![Sulfamethazine structure](image) | 1.12 × 10⁴         | 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  | C₁₀H₁₃N₃O₃S       | ![Sulfamethoxazole structure](image) | 3.94 × 10³         | 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         | C₁₂H₁₂Cl₃O₂       | ![Triclosan structure](image) | 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, 2013); 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 & WANG (2019) |
| SHs                      |                   |                     |                    |         |         |         |                  |                  |          |
| 17ß-estradiol 272.38     | C₁₃H₂₄O₂          | ![17ß-estradiol structure](image) | 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) |
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).
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

### 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) |
| Ofloxacine | 0.016 | 0.04 | 0.005 | 2.5 | 0.5 | High/Medium | Verlicchi et al. (2012) |
| Salicylic acid | 1.28 | 16 | 2.5 | 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 | 3.0 | 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](image-url) | The observed removal efficiency (mean and standard deviation) of 18 selected EOCs in HFCW.
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 \(K_{ow}\) = 4.01; Log \(D_{ow}\) = 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 \(K_{oc}\) = 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 (51 ± 96%) compared with its negative removal in gravel-based VFCW (−53 ± 35%) (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 \(K_{ow}\) = 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 \(D_{ow}\) = 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 \(K_{ow}\) > 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. 2022a, 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 \(K_{ow}\) = 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.
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 = 5.54; 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 (Ca²⁺), magnesium ion (Mg²⁺), ferric ion (Fe³⁺), or aluminum ion (Al³⁺) (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-Díaz 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. 2013; Zhang et al. 2018b; Chen et al. 2015; 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. (2005) 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 estroestrogen 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 estroestrogen. 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.
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). 17β-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, 17β-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 water 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.

REFERENCES

Ávila, C., Matamoros, V., Reyes-Contreras, C., Piña, B., Casado, M., Mita, L., Rivetti, C., Barata, C., García, J. & Bayona, J. M. 2014a Attenuation of emerging contaminants in a hybrid constructed wetland system under different hydraulic loading rates and their associated toxicological effects in wastewater. Science of the Total Environment 470–471, 1272–1280.

Ávila, C., Nivala, J., Olsson, L., Kassa, K., Headley, T., Mueller, R. A., Bayona, J. M. & García, J. 2014b Emerging organic contaminant removal in a horizontal subsurface flow constructed wetlands: influence of media size, loading frequency and use of active aeration. Science of the Total Environment 494–495, 211–217.

Ávila, C., Bayona, J. M., Martín, I., Salas, J. J. & García, J. 2015 Emerging organic contaminant removal in a full-scale hybrid constructed wetland system for wastewater treatment and reuse. Ecological Engineering 80, 108–116.

Barbosa, M. O., Moreira, N. F. F., Ribeiro, A. R., Pereira, M. F. R. & Silva, A. M. T. 2016 Occurrence and removal of organic micropollutants: an overview of the watch list of EU Decision 2015/495. Water Research 94, 257–279.

Berglund, B., Khan, G. A., Weisner, S. E. B., Ehde, P. M., Fick, J. & Lindgren, P. E. 2014 Efficient removal of antibiotics in surface-flow constructed wetlands, with no observed impact on antibiotic resistance genes. Science of the Total Environment 476–477, 29–37.

Brezinova, T. D., Vymazal, J., Koželuh, M. & Kule, L. 2018 Occurrence and removal of ibuprofen and its metabolites in full-scale constructed wetlands treating municipal wastewater. Ecological Engineering 120, 1–5.

Button, M., Cosway, K., Sui, J. & Weber, K. 2019 Impacts and fate of triclosan and sulfamethoxazole in intensified re-circulating vertical flow constructed wetlands. Science of the Total Environment 649, 1017–1028.

Bai, K., Elliot, C. T., Phillips, D. H., Scippio, M.-L., Muller, M. & Connolly, L. 2012 Treatment of estrogens and androgens in dairy wastewater by a constructed wetland system. Water Research 46, 2333–2345.

Caldwell, D. J., Mastrogroco, F., Anderson, P. D., Länge, R. & Sumpter, J. P. 2011 Predicted-no-effect concentrations for the steroid estrogens estrone, 17β-estradiol, estriol, and...
17α-ethinylestradiol. *Environmental Toxicology and Chemistry* **31**, 1396–1406.

Caliman, F. A. & Gavrilas, M. 2009 Pharmaceuticals, personal care products and endocrine disrupting agents in the environment-A review. *Clean* **37** (4–5), 277–303.

Campos, J. M., Queiroz, S. C. N. & Roston, D. M. 2019 Removal of the endocrine disruptors ethinyl estradiol, bisphenol A, and levonorgestrel by subsurface constructed wetlands. *Science of the Total Environment* **693** (135514), 1–8.

Carvalho, P. N., Basto, M. C. P., Almeida, C. M. R. & Brix, H. 2013 Removal of selected organic micropollutants in planted and unplanted pilot-scale horizontal flow constructed wetlands under conditions of high organic load. *Ecological Engineering* **71**, 234–245.

Chen, Y., Ji, E.-Y., Chang, H.-R. & Sheu, S.-C. 2016 Occurrence, removal and environmental risk assessment of pharmaceuticals and personal care products in rural wastewater treatment wetlands. *Science of the Total Environment* **566–567**, 1660–1669.

Chen, J., Wei, X.-D., Liu, Y.-S., Ying, G.-G., Liu, S.-S., He, L.-Y., Su, H.-C., Hu, L.-X., Chen, F.-R. & Yang, Y.-Q. 2016b Removal of antibiotics and antibiotic resistance genes from domestic sewage by constructed wetlands: optimization of wetland substrates and hydraulic loading. *Science of the Total Environment* **565**, 240–248.

Choi, Y.-J., Kim, L.-H. & Zoh, K.-D. 2016 Removal characteristics and mechanism of antibiotics using constructed wetlands. *Ecological Engineering* **91**, 85–92.

Conkle, J., White, J. R. & Metcalfe, C. D. 2008 Reduction of pharmaceutically active compounds by a lagoon wetland wastewater treatment system in Southeast Louisiana. *Chemosphere* **73** (11), 1741–1748.

Cooper, P. F., Job, G. D., Green, M. B. & Shutes, R. B. E. 1996 Reed Beds and Constructed Wetlands for Wastewater Treatment. WRc Publications, Medmenham, Marlow, UK.

Czajka, C. P. & Londry, K. L. 2006 Anaerobic biotransformation of estrogens. *Science of the Total Environment* **367**, 932–941.

Dai, Y., Tao, R., Tai, Y., Tam, N. F., Dan, A. & Yang, Y. 2017 Application of a full-scale newly developed stacked constructed wetland and an assembled bio-filter for reducing phenolic endocrine disrupting chemicals from secondary effluent. *Ecological Engineering* **99**, 496–503.

Dan, A., Yang, Y., Dai, Y.-n., Chen, C.-x., Wang, S.-y. & Tao, R. 2015 Removal and factors influencing removal of sulfonamides and trimethoprim from domestic sewage in constructed wetlands. *Bioresource Technology* **146**, 363–370.

Dietz, A. C. & Schnoor, J. L. 2001 Advances in phytoremediation. *Environmental Health Perspectives* **109**, 163–168.

Dordio, A. V., Carvalho, A. J. P., Teixeira, D. M., Dias, C. B. & Pinto, A. P. 2010 Removal of pharmaceuticals in microcosm constructed wetlands using *Typha spp.* and LECA. *Bioresource Technology* **101**, 886–892.

European Union (EU) 2015 Commission Implementing Decision (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council (OJ L 348, 24.12.2008, p. 84).

European Union (EU) 2018 Commission Implementing Decision (EU) 2018/840 of 5 June 2018 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council (OJ L 348, 24.12.2008, p. 84), and repealing Commission Implementing Decision (EU) 2015/495.

Francini, A., Mariotti, L., Gregorio, S. D., Sebastiani, L. & Andreucci, A. 2018 Removal of micro-pollutants from urban wastewater by constructed wetlands with *Phragmites australis* and *Salix matsudana*. *Environmental Science and Pollution Research* **25** (36), 36474–36484.

Gogoi, A., Mazumder, P., Tyagi, V. K., Chaminda, G. G. T., An, A. K. & Kumar, M. 2018 Occurrence and fate of emerging contaminants in water environment: a review. *Groundwater for Sustainable Development* **6**, 169–180.

Górrito, A. M., Ribeiro, A. R., Almeida, C. M. R. & Silva, A. M. T. 2017 A review on the application of constructed wetlands for the removal of priority substances and contaminants of emerging concern listed in recently launched EU legislation. *Environmental Pollution* **227**, 428–443.

Gray, J. L. & Sedlak, D. L. 2005 The fate of estrogenic hormones in an engineered treatment wetland with dense macrophytes. *Water Environment Research* **77**, 24–31.

Gros, M., Petrovic, M., Ginebreda, A. & Barceló, D. 2010 Removal of pharmaceuticals during wastewater treatment and environmental risk assessment using hazard indexes. *Environment International* **36**, 15–26.

Hakk, H., Sikora, L. & Casey, F. X. M. 2018 Fate of estrone in laboratory-scale constructed wetlands. *Ecological Engineering* **111**, 60–68.

He, Y., Sutton, N. B., Lei, Y., Rijnaarts, H. H. M. & Langenhoff, A. A. M. 2018 Fate and distribution of pharmaceutically active compounds in mesocosm constructed wetlands. *Journal of Hazardous Materials* **357**, 198–206.

Hernando, M. D., Mezcuza, M., Fernández-Alba, A. R. & Barceló, D. 2006 Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. *Talanta* **69** (2), 334–342.

Herrera-Melián, J. A., Guedes-Alonso, R., Borrego-Fabelo, A., Santana-Rodríguez, J. J. & Sosa-Ferrera, Z. 2018 Study on the removal of hormones from domestic wastewaters with lab-scale constructed wetlands with different substrates and flow directions. *Environmental Science and Pollution Research* **25** (21), 20374–20384.
Hijosa-Valsero, M., Matamoros, V., Martin-Villacorta, J., Becares, E. & Bayona, J. M. 200a Assessment of full-scale natural systems for the removal of PPCPs from wastewater in small communities. Water Research 44, 1429–1439.

Hijosa-Valsero, M., Matamoros, V., Sidrach-Cardona, R., Martin-Villacorta, J., Bécares, E. & Bayona, J. M. 200b Comprehensive assessment of the design configuration of constructed wetlands for the removal of pharmaceuticals and personal care products from urban wastewaters. Water Research 44, 3669–3678.

Hijosa-Valsero, M., Fink, G., Schlüsener, M. P., Sidrach-Cardona, R., Martín-Villacorta, J., Ternes, T. & Bécares, E. 200a Removal of antibiotics from urban wastewater by constructed wetland optimization. Chemosphere 83, 713–719.

Hijosa-Valsero, M., Matamoros, V., Pedescoll, A., Martín-Villacorta, J., Bécares, E., García, J. & Bayona, J. M. 201c Evaluation of primary treatment and loading regimes in the removal of pharmaceuticals and personal care products from urban wastewaters by subsurface-flow constructed wetlands. International Journal of Environmental Analytical Chemistry 91 (7–8), 652–653.

Hijosa-Valsero, M., Sidrach-Cardona, R., Martín-Villacorta, J., Valsero-Blanco, M. C., Bayona, J. M. & Bécares, E. 201c Statistical modelling of organic matter and emerging pollutants removal in constructed wetlands. Bioresource Technology 102, 4981–4988.

Hijosa-Valsero, M., Reyes-Contreras, C., Domínguez, C., Bécares, E. & Bayona, J. M. 2016 Behaviour of pharmaceuticals and personal care products in constructed wetland compartments: influent, effluent, pore water, substrate and plant roots. Chemosphere 145, 508–517.

Huang, Y., Guo, J., Yan, P., Gong, H. & Fang, F. 2019 Sorption-desorption behavior of sulfamethoxazole, carbamazepine, bisphenol A and 17α-ethinylestradiol in sewage sludge. Journal of Hazardous Materials 368, 739–745.

Ilyas, H. & van Hullebusch, E. D. 200a Performance comparison of different types of constructed wetlands for the removal of pharmaceuticals and their transformation products: a review. Environmental Science and Pollution Research 27 (13), 14342–14364.

Ilyas, H. & van Hullebusch, E. D. 200b Performance comparison of different constructed wetlands designs for the removal of personal care products. International Journal of Environmental Research and Public Health 17 (9), 5091. 1-26.

Ilyas, H. & van Hullebusch, E. D. 200c A review on the occurrence, fate, and removal of steroidal hormones during treatment with different types of constructed wetlands. Journal of Environmental Chemical Engineering 8 (3), 103793.

Ilyas, H., Masih, I. & van Hullebusch, E. D. 2020 Pharmaceuticals removal by constructed wetlands: a critical evaluation and meta-analysis on performance, risk reduction and role of physicochemical properties on removal mechanisms. Journal of Water and Health 18 (3), 253–291.

Jürgens, M. D., Holthaus, K. I. E., Johnson, A. C., Smith, J. J. L., Hetheridge, M. & Williams, R. J. 2002 The potential for estradiol and ethinylestradiol degradation in English rivers. Environmental Toxicology and Chemistry 21, 480–488.

Kadlec, R. H. & Wallace, S. D. 2009 Treatment Wetlands, Second Edition. CRC Press, Boca Raton, FL, USA.

Kahl, S., Nivala, J., Afferden, M. V., Müller, R. A. & Recentmsa, T. 2017 Effect of design and operational conditions on the performance of subsurface flow treatment wetlands: emerging organic contaminants as indicators. Water Research 125, 490–500.

Kimura, K., Hara, H. & Watanabe, Y. 2005 Removal of pharmaceutical compounds by submerged membrane bioreactors (MBRs). Desalination 178, 135–140.

Koottatep, T., Phong, V. H. N., Chapagain, S. K., Panuvatvanich, A., Polprasert, C. & Ahn, K.-H. 2017 Potential of laterite soil coupling fenton reaction in Acetaminophen (ACT) removal in constructed wetlands. Water, Air, and Soil Pollution 228, 283.

Kosma, C. I., Lambropoulou, D. A. & Albanis, T. A. 2014 Investigation of PPCPs in wastewater treatment plants in Greece: occurrence, removal and environmental risk assessment. Science of the Total Environment 466–467, 421–438.

Kumar, A. K., Chiranjeevi, P., Mohanakrishna, G. & Mohan, S. V. 2011 Natural attenuation of endocrine-disrupting estrogens in an ecologically engineered treatment system (EETS) designed with floating, submerged and emergent macrophytes. Ecological Engineering 37, 1555–1562.

Laurenson, J. P., Bloom, R. A., Page, S. & Sadrieh, N. 2014 Ethynl estradiol and other human pharmaceutical estrogens in the aquatic environment: a review of recent risk assessment data. The AAPS Journal 16 (2), 299–310.

Li, Y., Zhu, G., Ng, W. J. & Tan, S. K. 2014 A review on removing pharmaceutical contaminants from wastewater by constructed wetlands: design, performance and mechanism. Science of the Total Environment 468–469, 908–932.

Li, Y., Wu, B., Zhu, G., Liu, Y., Ng, W. J., Appan, A. & Tan, S. K. 2016 High-throughput pyrosequencing analysis of bacteria relevant to cometabolic and metabolic degradation of ibuprofen in horizontal subsurface flow constructed wetlands. Science of the Total Environment 562, 604–613.

Li, Y., Zhang, J., Zhu, G., Liu, Y., Wu, B., Ng, W. J., Appan, A. & Tan, S. K. 2016a Phytoextraction, phytotransformation and rhizodegradation of ibuprofen associated with Typha angustifolia in a horizontal subsurface flow constructed wetland. Water Research 102, 294–304.

Li, J., Zhou, Q. & Campos, L. C. 2017 Removal of selected emerging PPCP compounds using greater duckweed (Spirodela polyrhiza) based lab-scale free water constructed wetland. Water Research 126, 252–261.

Liang, Y., Zhu, H., Bañuelos, G., Shutes, B., Yan, B. & Cheng, X. 2018 Removal of sulfamethoxazole from salt-laden wastewater in constructed wetlands affected by plant species, salinity levels and co-existing contaminants. Chemical Engineering Journal 341, 462–470.

Liu, S., Ying, G.-G., Zhao, J.-L., Zhou, L.-J., Yang, B., Chen, Z.-F. & Lai, H.-J. 2012 Occurrence and fate of androgens, estrogens, glucocorticoids and progestagens in two different types of...
municipal wastewater treatment plants. *Journal of Environmental Monitoring* **14**, 482–491.
Liu, L., Liu, Y.-h., Wang, Z., Liu, C.-x., Huang, X. & Zhu, G.-f. 2014 Behavior of tetracycline and sulfamethazine with corresponding resistance genes from swine wastewater in pilot-scale constructed wetlands. *Journal of Hazardous Materials* **278**, 304–310.
Liu, S., Chen, H., Zhou, G.-j., Liu, S.-S., Yue, W.-Z., Yu, S., Sun, K.-F., Cheng, H., Ying, G.-G. & Xu, X.-R. 2015 Occurrence, source analysis and risk assessment of androgens, glucocorticoids and progestagens in the Hailing Bay region, South China Sea. *Science of the Total Environment* **536**, 99–107.
Liu, J., Wang, J., Zhao, C., Hay, A. G., Xie, H. & Zhan, J. 2016 Triclosan removal in wetlands constructed with different aquatic plants. *Applied Microbiology and Biotechnology* **100** (3), 1459–1467.
Loos, R., Marinov, D., Sanseverino, I., Napierska, D. & Lettieri, T. 2018 Review of the 1st Watch List Under the Water Framework Directive and Recommendations for the 2nd Watch List. EUR 29175 EN, Publications Office of the European Union, Luxembourg.
Luo, Y., Guo, W., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J., Liang, S. & Wang, X. C. 2014 A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Science of the Total Environment* **475–476**, 619–641.
Luo, Z., Tu, Y., Li, H., Qiu, B., Liu, Y. & Yang, Z. 2019 Endocrine-disrupting compounds in the Xiangjiang River of China: spatio-temporal distribution, source apportionment, and risk assessment. *Ecotoxicology and Environmental Safety* **167**, 476–484.
Matamoros, V. & Salvadó, V. 2012 Evaluation of the seasonal performance of a water reclamation pond-constructed wetland system for removing emerging contaminants. *Chemosphere* **86** (2), 111–117.
Matamoros, V., Arias, C., Brix, H. & Bayona, J. M. 2007 Removal of pharmaceuticals and personal care products (PPCPs) from urban wastewater in a pilot vertical flow constructed wetland and a sand filter. *Environmental Science and Technology* **41**, 8171–8177.
Matamoros, V., García, J. & Bayona, J. M. 2008a Organic micropollutant removal in a full-scale surface flow constructed wetland fed with secondary effluent. *Water Research* **42** (3), 653–660.
Matamoros, V., Caselles-Osorio, A., García, J. & Bayona, J. M. 2008b Behaviour of pharmaceutical products and biodegradation intermediates in horizontal subsurface flow constructed wetland. A microcosm experiment. *Science of the Total Environment* **394**, 171–176.
Matamoros, V., Hijosa, M. & Bayona, J. M. 2009 Assessment of the pharmaceutical active compounds removal in wastewater treatment systems at enantiomeric level. Ibuprofen and naproxen. *Chemosphere* **75**, 200–205.
Matamoros, V., Nguyen, L. X., Arias, C. A., Salvadó, V. & Brix, H. 2012 Evaluation of aquatic plants for removing polar microcontaminants: a microcosm experiment. *Chemosphere* **88** (10), 1257–1264.
Matamoros, V., Rodríguez, Y. & Albàigés, J. 2016 A comparative assessment of intensive and extensive wastewater treatment technologies for removing emerging contaminants in small communities. *Water Research* **88**, 777–785.
Matamoros, V., Rodríguez, Y. & Bayona, J. M. 2017 Mitigation of emerging contaminants by full-scale horizontal flow constructed wetlands fed with secondary treated wastewater. *Ecological Engineering* **99**, 222–227.
Nivala, J., Kahl, S., Boog, J., Afferden, M., Reemtsma, T. & Müller, R. A. 2019 Dynamics of emerging organic contaminant removal in conventional and intensified subsurface flow treatment wetlands. *Science of the Total Environment* **649**, 1144–1156.
Nuel, M., Laurent, J., Bois, P., Heintz, D. & Wanko, A. 2018 Seasonal and ageing effect on the behaviour of 86 drugs in a full-scale surface treatment wetland: removal efficiencies and distribution in plants and sediments. *Science of the Total Environment* **615**, 1099–1109.
Park, N., Vanderford, B. J., Snyder, S. A., Sarp, S., Kim, S. D. & Cho, J. 2009 Effective controls of micropollutants included in wastewater effluent using constructed wetlands under anoxic condition. *Ecological Engineering* **35**, 418–423.
Park, J., Cho, K. H., Lee, E., Lee, S. & Cho, J. 2018 Sorption of pharmaceuticals to soil organic matter in a constructed wetland by electrostatic interaction. *Science of the Total Environment* **635**, 1345–1350.
Petrie, B., Rood, S., Smith, B. D., Proctor, K., Youdan, J., Barden, R. & Kasprzyk-Hordern, B. 2018 Biotic phase micropollutant distribution in horizontal sub-surface flow constructed wetlands. *Science of the Total Environment* **630**, 648–657.
Qiang, Z., Dong, H., Zhu, B., Qu, J. & Nie, Y. 2013 A comparison of various rural wastewater treatment processes for the removal of endocrine-disrupting chemicals (EDCs). *Chemosphere* **92**, 986–992.
Reyes-Contreras, C., Hijosa-Valsero, M., Sidrach-Cardona, R., Bayona, J. M. & Bécares, E. 2012 Temporal evolution in PPCP removal from urban wastewater by constructed wetlands of different configuration: a medium-term study. *Chemosphere* **88**, 161–167.
Rühmland, S., Wick, A., Ternes, T. A. & Barjenbruch, M. 2015 Fate of pharmaceuticals in a subsurface flow constructed wetland and two ponds. *Ecological Engineering* **80**, 125–139.
Sanderson, H., Johnson, D. J., Wilson, C. J., Brain, R. A. & Solomon, K. R. 2005 Probabilistic hazard assessment of environmentally occurring pharmaceuticals toxicity to fish, daphnids and algae by ECOSAR screening. *Toxicology Letters* **144** (3), 383–395.
Sgroi, M., Pelissari, C., Roccaro, P., Segerino, P. H., García, J., Vagliasindi, F. G. A. & Ávila, C. 2018 Removal of organic carbon, nitrogen, emerging contaminants and fluorescing organic matter in different constructed wetland configurations. *Chemical Engineering Journal* **332**, 619–627.
Sharif, F., Westerhoff, P. & Herckes, P. 2014 Impact of hydraulic and carbon loading rates of constructed wetlands on...
contaminants of emerging concern (CECs) removal. Environmental Pollution 185, 107–115.

Song, H. L., Nakano, K., Taniguchi, T., Nomura, M. & Nishimura, O. 2009 Estrogen removal from treated municipal effluent in small-scale constructed wetland with different depth. Bioresource Technology 100 (12), 2945–2951.

Töre, G. Y., Merić, S., Lofrano, G. & Feo, G. D. 2012 Removal of Trace Pollutants from Wastewater in Constructed Wetlands. In: Emerging Compounds Removal From Wastewater, Natural and Solar Based Treatment (G. Lofrano, ed.). Springer Dordrecht, Heidelberg, New York, London, pp. 39–58. doi:10.1007/978-94-007-3916-1.

Tran, N. H., Reinhard, M. & Gin, K. Y.-H. 2018 Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions—a review. Water Research 133, 182–207.

Tran, N. H., Reinhard, M., Khan, E., Huiting, C., Nguyen, V. T. L., Y., Goh, S. G., Nguyen, Q. B., Saedi, N. & Gin, K. Y.-H. 2019 Emerging contaminants in wastewater, stormwater runoff, and surface water: application as chemical markers for diffuse sources. Science of the Total Environment 676, 252–267.

Tyroller, L., Rousseau, D., Santa, S. & García, J. 2010 Application of the gas tracer method for measuring oxygen transfer rates in subsurface flow constructed wetlands. Water Research 44, 4217–4225.

Valiela, I. 1984 Marine Ecological Processes. Springer-Verlag, New York, NY, USA.

Verlicchi, P. & Zambello, E. 2014 How efficient are constructed wetlands in removing pharmaceuticals from untreated and treated urban wastewaters? A review. Science of the Total Environment 470–471, 1281–1306.

Verlicchi, P., Al Aukidy, M. & Zambello, E. 2012 Occurrence of pharmaceutical compounds in urban wastewater: removal, mass load and environmental risk after a secondary treatment—a review. Science of the Total Environment 429, 123–155.

Verlicchi, P., Galletti, A., Petrovic, M., Barceló, D., Al Aukidy, M. & Zambello, E. 2013 Removal of selected pharmaceuticals from domestic wastewater in an activated sludge system followed by a horizontal subsurface flow bed-analysis of their respective contributions. Science of the Total Environment 454–455, 411–425.

Verlicchi, P., Zambello, E. & Aukidy, M. A. 2015 Removal of personal care products in constructed wetlands. In: Personal Care Products in the Aquatic Environment; The Handbook of Environmental Chemistry, Vol. 36 (M. S. Díaz-Cruz & D. Barceló, eds). Springer, Cham, Switzerland, pp. 319–354.

Vo, H.-N.-P., Bui, X.-T., Nguyen, T.-M.-H., Kootatap, T. & Bandypadhyay, A. 2018 Insights of the removal mechanisms of pharmaceutical and personal care products in constructed wetlands. Current Pollution Reports 4 (2), 93–103.

Vymazal, J. 2005 Horizontal subsurface flow and Hybrid constructed wetlands systems for wastewater treatment. Ecological Engineering 25, 478–490.

Vymazal, J., Březinová, T. & Koželuh, M. 2015 Occurrence and removal of estrogens, progesterone and testosterone in three constructed wetlands treating municipal sewage in the Czech Republic. Science of the Total Environment 536, 625–631.

Vymazal, J., Březinová, T. D., Koželuh, M. & Kule, L. 2017 Occurrence and removal of pharmaceuticals in four full-scale constructed wetlands in the Czech Republic – the first year of monitoring. Ecological Engineering 98, 354–364.

Vystavna, Y., Frikova, Z., Marchand, L., Vergeles, Y. & Stolberg, F. 2017 Removal efficiency of pharmaceuticals in a full scale constructed wetland in East Ukraine. Ecological Engineering 108, 50–58.

Wang, J. & Wang, S. 2016 Removal of pharmaceuticals and personal care products (PPCPs) from wastewater: a review. Journal of Environmental Management 182, 620–640.

Wang, Y., Yin, T., Kelly, B. C. & Gin, K. Y.-H. 2019 Bioaccumulation behaviour of pharmaceuticals and personal care products in a constructed wetland. Chemosphere 222, 275–285.

Xian, Q., Hu, L., Chen, H., Chang, Z. & Zou, H. 2010 Removal of nutrients and veterinary antibiotics from swine wastewater by a constructed macrophyte floating bed system. Journal of Environmental Management 91, 2657–2661.

Xie, H., Yang, Y., Liu, J., Kang, Y., Zhang, J., Hu, Z. & Liang, S. 2018 Enhanced triclosan and nutrient removal performance in vertical up-flow constructed wetlands with manganese oxides. Water Research 143, 457–466.

Yan, Q., Feng, G., Gao, X., Sun, C., Guo, J.-S. & Zhu, Z. 2016 Removal of pharmaceutically active compounds (PhACs) and toxicological response of Cyperus alternifolius exposed to PhACs in microcosm constructed wetlands. Journal of Hazardous Materials 301, 566–575.

Yi, X., Tran, N. H., Yin, T., He, Y. & Gin, K. Y.-H. 2017 Removal of selected PPCPs, EDCs, and antibiotic resistance genes in landfill leachate by a full-scale constructed wetlands system. Water Research 121, 46–60.

Yin, T., Tran, N. H., Huiting, C., He, Y. & Gin, K. Y.-H. 2019 Biotransformation of polyfluoroalkyl substances by microbial consortia from constructed wetlands under aerobic and anoxic conditions. Chemosphere 233, 101–109.

Young, W. F., Whitehouse, P., Johnson, I. & Sorokin, N. 2002 Proposed Predicted-no-Effect Concentrations (PNECs) for Natural and Synthetic Steroid Oestrogens in Surface Water. Environment Agency R&D Technical report P2-T04/1. England and Wales Environment Agency, Bristol, UK, pp. 93–95.

Zhang, D. Q., Tan, S. K., Gersberg, R. M., Sadreddini, S., Zhu, J. & Tuan, N. A. 2011 Removal of pharmaceutical compounds in tropical constructed wetlands. Ecological Engineering 37, 460–464.

Zhang, D. Q., Hua, T., Gersberg, R. M., Zhu, J., Ng, W. J. & Tan, S. K. 2012a Fate of diclofenac in wetland mesocosms planted with Scirpus validus. Ecological Engineering 49, 59–64.

Zhang, D. Q., Gersberg, R. M., Zhu, J., Hua, T., Jinadasa, K. B. S. N. & Tan, S. K. 2012b Batch versus continuous feeding strategies for pharmaceutical removal by subsurface flow constructed wetland. Environmental Pollution 167, 124–131.

Zhang, D. Q., Gersberg, R. M., Hua, T., Zhu, J., Tuan, N. A. & Tan, S. K. 2012c Pharmaceutical removal in tropical subsurface
flow constructed wetlands at varying hydraulic loading rates. *Chemosphere* **87**, 273–277.

Zhang, D. Q., Gersberg, R. M., Hua, T., Zhu, J. F., Goyal, M. K., Ng, W. J. & Tan, S. K. 2015 Fate of pharmaceutical compounds in hydroponic mesocosms planted with *Scirpus validus*. *Environmental Pollution** **181**, 98–106.

Zhang, D., Gersberg, R. M., Ng, W. J. & Tan, S. K. 2014 Removal of pharmaceuticals and personal care products in aquatic plant-based systems: a review. *Environmental Pollution** **184**, 620–639.

Zhang, X., Jing, R., Feng, X., Dai, Y., Tao, R., Vymazal, J., Cai, N. & Yang, Y. 2018a Removal of acidic pharmaceuticals by small-scale constructed wetlands using different design configurations. *Science of the Total Environment** **639**, 640–647.

Zhang, J.-N., Ying, G.-G., Yang, Y.-Y., Liu, W.-R., Liu, S.-S., Chen, J., Liu, Y.-S., Zhao, J.-L. & Qian-Qian Zhang, Q.-Q. 2018b Occurrence, fate and risk assessment of androgens in ten wastewater treatment plants and receiving rivers of South China. *Chemosphere** **201**, 644–654.

Zhao, C., Xie, H., Xu, J., Xu, X., Zhang, J., Hu, Z., Liu, C., Liang, S., Wang, Q. & Wang, J. 2015 Bacterial community variation and microbial mechanism of triclosan (TCS) removal by constructed wetlands with different types of plants. *Science of the Total Environment** **505**, 633–639.

Zhu, S. & Chen, H. 2014 The fate and risk of selected pharmaceutical and personal care products in wastewater treatment plants and a pilot-scale multistage constructed wetland system. *Environmental Science and Pollution Research** **21** (2), 1466–1479.

First received 5 February 2021; accepted in revised form 26 April 2021. Available online 7 May 2021