Emerging organic contaminant removal in a full-scale hybrid constructed wetland system for treatment and reclamation of wastewater in small communities of warm climate regions

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Abstract

A full-scale hybrid constructed wetland (CW) system based on three-stages of different wetland configurations showed to be a very robust ecotechnology for wastewater treatment and reuse in small communities. It consisted of a 317-m2 vertical subsurface flow (VF), a 229-m2 horizontal subsurface flow (HF), and a 240-m2 free water surface (FWS) CWs operating in series. An excellent overall treatment performance was exhibited on the elimination of conventional water quality parameters (99% average removal efficiency for TSS, BOD5 and NH4-N), and its final effluent proved to comply with existing guidelines for its reclamation in various reuse applications. The removal of studied emerging contaminants, which included various pharmaceuticals, personal care products and endocrine disruptors, was also very high (average 90 ± 11%), being compound dependent. The high rates were achieved due to the differing existing physico-chemical conditions occurring at different CW configurations, which would allow for the combination and synergy of various abiotic/biotic removal mechanisms to occur (e.g. biodegradation, sorption, volatilization, hydrolysis, photodegradation). While aerobic metabolic pathways and solids retention are enhanced in the VF bed, other removal mechanisms such as anaerobic biodegradation and sorption would predominate in the HF bed. At last, photodegradation through direct sunlight exposure, and less importantly, sorption onto organic matter, seem to take an active part in organic contaminant removal in the FWS wetland.

Keywords: endocrine disruptor; pharmaceuticals; photodegradation; decentralized wastewater treatment; treatment wetland.

1. Introduction

The occurrence of emerging organic contaminants (EOCs), such as pharmaceutical and personal care products (PPCPs), pesticides or antiseptics in poorly treated wastewater and eventually in other watercourses constitutes nowadays an increasing concern worldwide due to their possible toxicological effects to the environment and living organisms (Daughton, 2005; Cunningham et al., 2006; Kümmerer et al., 2009). Constructed wetlands (CWs) are natural wastewater treatment systems that emphasize the processes happening in natural wetlands so as to improve their treatment capacity (Kadlec and Wallace, 2009). They constitute an alternative cost-effective technology to conventional wastewater treatment plants (WWTPs), especially in the context of small communities with less than 2000 people equivalent (Puigagut et al., 2007). Various types of constructed wetlands have been combined in order to achieve higher treatment efficiency, especially for nitrogen. These hybrid systems are normally comprised of vertical subsurface flow (VF) and horizontal subsurface flow (HF) beds arranged in many possible manners, including recirculation from one stage to another. While in HF wetlands nitrification is not achieved due to a lack of oxygen, in VF aerobic conditions prevail, which provide good conditions for nitrification, but little to negligible denitrification occurs in these systems. Thenceforward, the strengths and weaknesses of each type of system can balance each other out and it in consequence it is possible to obtain an effluent low in total nitrogen concentrations, as well as other pollutants (Cooper, 1999; Vymazal, 2007; Masi and Martinuzzi, 2007).

Since EOCs are often poorly removed in conventional WWTPs (Heberer, 2002), advanced water reclamation technologies have been studied (e.g. advanced oxidation, photo-fenton, ozonitzation) (Klavarioti et al., 2009; Rosal et al., 2010). However, these

often require a high level of energy consumption and O&M cost, and thus are very unlikely to be implemented in the context of wastewater treatment of small communities. To this regard, several studies have shown a great capacity for EOC removal of constructed wetland systems at full-scale for domestic wastewater treatment of small communities in warm climates. These were conducted at systems consisting of a single wetland configuration at a time, including VF, HF (Matamoros et al., 2009) and FWS (Matamoros et al., 2008b; Llorens et al, 2009). However, studies which evaluate the contribution to EOC removal of different wetland types within a hybrid system through potential synergies in treatment processes are scarce, and include other treatment units (e.g. WWTP, ponds) as a treatment step prior to CWs (Hijosa-Valsero et al., 2010a; Matamoros and Salvadó, 2012). Evaluating the physicochemical properties and behavior of emerging contaminants in different constructed wetland units remain, thus, a future challenge to be developed so as to help in refining CW design and operation modes, which in turn may increase CW acceptance and implementation as a cost-effective and operational alternative to conventional wastewater treatment technologies in decentralized areas (Imfeld et al., 2009).

In the context of a collaborative project between the Universitat Politècnica de Catalunya (Barcelona) and the Foundation Centre for New Water Technologies (Seville), aiming at the treatment of wastewater up to quality standards appropriate for reuse through the sole use of CWs, an experimental mesoscale hybrid constructed wetland system aiming at combining different CW configurations (VF, HF and free water surface) showed an excellent performance, both in terms of water quality parameters but also on EOC removal (Ávila et al., 2013a,b). Parallely, a comprehensive approach implemented at full-scale with the same wetland configuration in a Mediterranean climate area of south Spain (Seville) proved to be a highly efficient

97 ecotechnology for an integrated sanitation of small communities in warm climates,
98 holding very low O&M requirements (Ávila et al., 2013d). The treatment technology,
99 which received combined sewer effluent, exhibited a great performance on solids,
100 organic matter and total nitrogen removal, and showed to be very resilient to water flow
101 fluctuations when evaluated during stormy periods and first-flush events. The final
102 effluent of this proved to be of sufficient quality for its further reuse in various
103 applications (i.e. silviculture and irrigation of forests and other green areas non
104 accessible to the public. etc.).

105 However, the disposal into the aquatic environment of emerging contaminants
106 due to incomplete wastewater treatment has been of great concern for more than a
107 decade (Kolpin et al., 2002; Cunningham et al., 2006). Additionally, in recent times
108 there is a clear need to include irrigation as an additional exposure route for chemicals
109 in terrestrial ecosystems. As an example, recent research is being done to explore
110 whether these contaminants can transfer to crop plants irrigated with reclaimed water
111 (Matamoros et al., 2012b; Calderón-Preciado et al., 2013). Although concentrations are
112 low, questions have been raised about the potential impacts of these substances in the
113 environment and animal and public health after long-term exposure (Matamoros et al.,
114 2012b).

115 In this scenario, the aim of this study was to evaluate the treatment performance
116 of a full-scale hybrid CW system located in a Mediterranean climate on the elimination
117 of various EOCs from a combined sewer effluent. The selected compounds consisted of
118 various commonly used pharmaceuticals and personal care products (PPCPs), as well as
119 a high-production chemical widely used in epoxy resins lining food and beverage
120 containers. These were: three non-steroidal anti-inflammatory drugs (ibuprofen –IB-,
121 diclofenac –DCF-, acetaminophen –ACE-), three personal care products (tonalide –

AHTN-, oxybenzone –OXY-, triclosan –TCS-) and two endocrine disrupting compounds (bisphenol A –BPA- and ethynilestradiol –EE2-).

2. Materials and methods

2.1. Pilot-plant description

The hybrid treatment system was part of a larger pilot-scale treatment plant (41,000-m^2 experimental plant of the Foundation Centre for New Water Technologies, CENTA) that received the wastewater from 2500 PE from the municipality of Carrión de los Céspedes (Seville) together with the runoff collected in a combined sewer system. Pretreatment chambers are common to all technologies in the plant and its effluent is diverted towards each of them. After pretreatment (i.e. screener (2 sieves, 3 cm and 3 mm wide), degreaser/desander), the effluent is conveyed towards a pumping chamber, from which the water is distributed through submersible pumps to the different treatment technologies. The constructed wetland system started operation in 2005, though the treatment line as it is now began to operate in July 2009. In particular, a hybrid system consisting of a combination of various CW configurations was set in order to balance out the strengths and weaknesses of each type of system. The treatment line consisted of an Imhoff tank followed by a vertical subsurface flow CW (VF), a horizontal subsurface flow constructed wetland (HF) and a free-water surface CW (FWS) connected in series (Fig. 1).

The VF wetland had a surface area of 317 m^2 and received an average organic loading rate (OLR) of about 9 g BOD_5 m^{-2} d^{-1} and a hydraulic loading rate (HLR) of 0.044 m d^{-1}. It was fed intermittently at about 20 pulses d^{-1} to an average inflow of 14 m^3 d^{-1}. The bed consisted of a top layer of 0.05 m of sand (1-2 mm), followed by a 0.6 m layer of gravel (4-12 mm) and an underlying 0.15 m stone layer (25-40 mm). Feeding

147 of the VF was done through five lengthwise pipes (diameter = 125 mm) perforated with
148 1 cm diameter holes every 1.8 m distance. Five draining pipes were installed lengthwise
149 at the bottom of the wetland within the 15 cm-thick gravel layer. Every draining pipe
150 had three 1m-tall chimneys so as to provide oxygen transfer into the wetland bed.

151 The HF unit had a surface area of 229 m^2 and consisted of a gravel bed of 0.4 m
152 depth (4-12 mm), with an inlet and outlet zone of stones (40-80 mm) to facilitate the
153 flow. Feeding of the bed was done through a 63 mm diameter polyethylene pipe
154 perforated with 1 cm holes every 1 m distance. The outlet of the wetland was done by
155 means of two 125 mm-diameter draining pipes located at the bottom of the stone layer
156 and connected to a flexible pipe, which held the water level 5 cm below the top of the
157 gravel. Both the VF and the HF were planted with *Phragmites australis*. Vegetation was
158 very well developed at the time of the study.

159 Finally, the FWS had a surface area of 240 m^2 and a water depth ranging 10-50
160 cm. A mixture of *Typha* spp., *Scirpus* spp., *Iris pseudacorus*, *Carex flacca*, *Cyperus*
161 *rutundus* and *Juncus* spp. were planted on a 0.2 m gravel bed. Since the treatment
162 system had been working for several years, it was mature and the vegetation was well
163 developed in all units. The final effluent of the treatment line was collected in an open-
164 air water tank with a capacity of 20 m^3 so as to store the treated water for its further
165 reuse. Further details on the system can be found in Ávila et al. (2013d).

166

167 ***2.2. Sampling procedure***

168 Sampling was performed twice a week for five consecutive weeks (n = 8) during
169 May and June 2011. Effluent 24-h composite samples of the influent, Imhoff tank, VF,
170 HF and FWS were taken by autosamplers (about 500 mL every 1 h). Grab samples from
171 the water tank were also taken so as to measure the final quality of the stored water.

172 Samples for the evaluation of EOCs were transported to the laboratory in 250 mL amber
173 glass bottles and kept refrigerated at 4ºC until analysis. The sample holding time was
174 less than 24 h. Conventional water quality parameters and studied EOCs were analyzed
175 as described in Section 2.4. Moreover, it should be noted that no rainfall events were
176 recorded two weeks before or during the sampling period.
177
178 ***2.3. Chemicals***
179 Gas chromatography (GC) grade (Suprasolv) hexane, methanol, ethyl acetate
180 and acetone were obtained from Merck (Darmstadt, Germany) and analytical-grade
181 hydrogen chloride was supplied by Panreac (Barcelona, Spain). ENR, SMZ, DC, ETM,
182 LIN, IB, ACE, DCF, AHTN, OXB, BPA, TCS, EE2 and 2,2′-dinitrophenyl were
183 obtained from Sigma-Aldrich (Steinheim, Germany). 2,4,5-trichlorophenoxypropionic
184 acid (2,4,5-TPA) was from Reidel-de-Haen (Seelze, Germany). Trimethylsulfonium
185 hydroxide (TMSH) was supplied by Fluka (Buchs, Switzerland). Strata-X polymeric
186 SPE cartridges (200 mg) were purchased from Phenomenex (Torrance, CA, USA) and
187 the 0.7 µm glass fiber filters of ø = 47 mm were obtained from Whatman (Maidstone,
188 UK).
189 ***2.4. Analytical methods***
190 Onsite measurements of DO, pH and turbidity were taken using a Hach HQ 30d
191 oxymeter, a Hach SensIon i30 pH-meter and a Hach 2100Q turbidity meter,
192 respectively. Water temperature and EC were also measured in situ by using a Hach
193 SensIon i30 thermometer and conductivity meter. Conventional wastewater quality
194 parameters, including TSS and COD were determined by using Standard Methods
195 (APHA, 2001). BOD_5 was measured by using a WTW® OxiTop® BOD Measuring
196 System. TN, TP, NH_4-N, NO_x-N and PO_4-P were determined by using a Bran Luebbe

197 AutoAnalyzer 3. Isolation and enumeration of *E. coli* was made using a Chromogenic
198 Membrane Filtration technique (APHA, 2001).

199 Determination of EOCs in water samples was carried out after samples had been
200 filtered and processed as previously described by Matamoros et al. (2005). The linearity
201 range was from 0.01 to 3 mg L^{-1}. The correlation coefficients (R^2) of the calibration
202 curves were always higher than 0.99. The limit of detection (LOD) and limit of
203 quantification (LOQ) were compound dependent in the range from 0.009 to 0.08 µg L^{-1}
204 and 0.02 to 0.27 µg L^{-1}, respectively.

205

206 **3. Results and discussion**

207 ***3.1. General water quality parameters***

208 Table 1 shows concentrations of the studied water quality parameters along the
209 hybrid CW system. Temperatures were fairly high at the time of the study (24 ± 2 ºC),
210 as expected for the hot summers of the Mediterranean climate of Seville. Indeed, EC
211 values showed to increase as water passed through the FWS and the water tank, which
212 could be explained by the high evapotranspiration taking place at their free water
213 columns.

214 Average overall removal efficiencies achieved in the treatment system up to the
215 water tank were unquestionably high for most water quality parameters (99% TSS, 89%
216 COD, 99% BOD_5, 98% NH_4-N). These results are in conformity with those obtained by
217 Ávila et al. (2013d) in this treatment plant, after a 1.5-year monitoring period under dry
218 and wet weather conditions, including an intensive sampling campaign during a first-
219 flush event. Solids entrapment and organic matter removal was very high within the VF
220 wetland (90 and 91% for TSS and BOD_5, respectively). Those values remained low
221 along the treatment system. The elimination of NH_4-N was also fairly high within the

222 VF (67%), where the high values for TN removal (65%) together with the low
223 concentrations of NO_x-N suggest once again both nitrification and denitrification
224 processes to take place within this wetland type, due to the coexistence of aerobic and
225 anoxic microsites within the wetland bed (Cooper et al, 1996; Ávila et al., 2013c).
226 Further denitrification occurred within the HF and FWS wetlands, up to an overall TN
227 removal of 94%. This removal rate is much higher than most values reported by full-
228 scale hybrid CWs of similar configuration at warm climates, such as the one by Masi
229 and Martinuzzi (2007) at a system consisting of a 160-m^2 HF followed by a 180-m^2 VF,
230 which treated the wastewater from a medium scale tourist facility in Italy (60% TN
231 removal). To this regard, Ayaz et al. (2012) performed some experiments at a pilot-
232 system in Turkey consisting of a HF (18 m^2) and a VF (14 m^2) in series, and found how
233 recirculation from the VF to the HF enhanced the treatment efficacy, especially in terms
234 of nitrogen removal (up to 79% TN removal). Overall removal efficiencies of TP and
235 PO_4-P were 47 and 16%, respectively.

236 The hybrid treatment system proved to have a great disinfection capacity,
237 exhibiting overall *E.coli* reductions of about 5 log-units, which is in conformity with
238 previous long-term microbiological pathogen evaluations in this system (Ávila et al.,
239 2013d). Final effluent concentrations complied with Spanish regulation limits for some
240 water reuse applications. The function made by the HF and FWS wetlands proved
241 crucial to achieve a water quality appropriate for its reclamation.

242

243 ***3.2. Emerging organic contaminants***

244 *3.2.1. Ocurrence and overall treatment performance*

245 Background concentrations of studied EOCs in influent wastewater ranged 13.5-
246 24.5 µg L^{-1} for IB, 0.4-1.9 µg L^{-1} for DCF, <LOD-8.5 µg L^{-1} for ACE, 0.4-0.9 µg L^{-1} for

247 AHTN, 0.1-0.2 µg L^{-1} for TCS and 1.4-5.7 µg L^{-1} for BPA (Table 2). Those were in the
248 range previously reported in raw wastewater by other authors (Matamoros et al., 2007;
249 Miège et al., 2009; Hijosa-Valsero et al., 2010b; Ávila et al., 2013c). The sunscreen
250 agent OXY and the synthetic estrogen EE2 were not detected at any of the sampling
251 days. The analgesic paracetamol (ACE) was detected in 50% of the influent samples
252 and its concentrations varied significantly. The rest of compounds were detected at
253 every sample of influent wastewater.

254 The hybrid constructed wetland system (up to the effluent of the FWS unit)
255 performed remarkably well also in the removal of EOCs, achieving very high overall
256 removal efficiencies for the majority of the studied compounds (average of 90 ± 11%).
257 These rates are in agreement with those reported by Ávila et al. (2013b) at an injection
258 experiment conducted at a meso-scale experimental hybrid CW system consisting of the
259 same wetland configurations, and with those found by Hijosa-Valsero et al. (2010a) at
260 three-full scale hybrid CW systems consisting of different combinations of waste
261 stabilization ponds and FWS and HF CWs in series. Moreover, Matamoros and Salvadó
262 (2012) observed very high removal efficiencies (around 90%) for most studied
263 compounds (e.g. IB, DCF, AHTN, TCS) at a full-scale reclamation pond-FWS wetland
264 system in Girona, Spain, treating secondary effluent from a conventional WWTP.
265 However, influent concentrations were much lower than this study.

266 Final effluent concentrations of target EOCs were extremely low, being below
267 the limit of detection for various contaminants (i.e. ACE, BPA). The rest were in the ng
268 L^{-1} order (20-100), which is in accordance with average concentrations of four receiving
269 water bodies in Denmark (Matamoros et al., 2009). These were also in the range of
270 those obtained in advanced treatment technologies applied at full-scale, such as
271 ozonation or membrane filtration (Snyder et al., 2007; Rosal et al., 2010).

The high removal efficiencies can be explained by differing existing physico-chemical conditions at different CW configurations, which would allow for the combination and synergy of various physicochemical and biological removal mechanisms to occur (e.g. biodegradation, sorption, volatilization, hydrolysis, and photodegradation) and thus achieve improved treatment efficiency of most pollutants (Imfeld et al., 2009). In this sense, while aerobic metabolic pathways and solids retention are enhanced in VF wetlands, other removal mechanisms such as anaerobic biodegradation and sorption would predominate in HF beds. At last, the FWS wetland would be responsible for potential photodegradation of compounds, and less importantly through adsorption onto organic matter and plant material (Matamoros and Salvadó, 2012).

3.2.2. VF performance

Fig. 2 shows average removal efficiencies of selected emerging contaminants accumulated at each stage of the hybrid constructed wetland system. The VF bed showed variable removal of emerging contaminants, being compound dependent. It performed best for ACE (>99%), IB (78%) and TCS (63%), while lower removal efficiencies were achieved for AHTN (56%), BPA (48%) and DCF (44%).

Comentari [CA1]: OJO: esta % es la adquirida desde el raw WW hasta el efluente del VF. En algunos casos está inflada, (mirar tabla 2) ya que se está teniendo en cuenta también lo eliminado dentro del tanque imhoff (que para algunas sustancias puede no ser despreciable!). Qué hago? Las recalculo y hago el grafico incluyendo el imhoff tank?? O lo dejo como está porque total, puede obviarse…?

In particular, ACE was completely removed within the VF bed (>99%). This analgesic has shown to be readily biodegraded (Yamamoto et al., 2009; Ranieri et al., 2011) to concentrations below the limit of detection in all types of wetlands, including HF (Ávila et al., 2013c), VF (Ávila et al., 2013b) and hybrid treatment wetlands (Conkle et al., 2008; Ávila et al., 2013b), as well as conventional WWTPs (Miège et al., 2009). Average elimination rates achieved for IB (78%) did not fluctuate much during the sampling campaign and are in agreement with the attributed aerobic biodegradation

297 of this compound, being oxidizing conditions provided by the unsaturated operation, as
298 well as intermittent feeding, of the VF bed of key importance for an enhanced
299 degradation (Zwiener and Frimmel, 2003; Matamoros et al., 2008a). To this regard,
300 Matamoros et al. (2007) showed how removal rates for IB were higher for unsaturated
301 (99 ± 1%) than for saturated (55 ± 1) VF wetlands (5 m^2) at an experimental pilot plant
302 in Denmark. Similar results were obtained by Ávila et al. (2013c) at an injection
303 experiment at HF CW system comparing permanently saturated operation vs. operation
304 on cycles of saturation/unsaturation (63 and 85%, respectively). What is more, Ávila et
305 al. (2013b) reported an average of 55% of IB elimination at two alternating VF beds (3
306 m^2) at an experimental hybrid system in Spain, and treatment performance in terms of
307 IB removal seemed to be negatively correlated to hydraulic loading rates. In that
308 particular case, higher HLRs would translate into a higher number of feeding pulses and
309 shorter resting times, resulting in a decrease of oxygen diffusion into the system and
310 hence a lower treatment performance (Torrens et al., 2009). Nevertheless, this
311 compounds seems to be quite easily biodegraded, and is well attenuated also in
312 conventional WWTPs (Lishman et al., 2006; Miège et al., 2009). The prevailing aerobic
313 conditions of the VF bed seemed to be especially important for the elimination of TCS
314 (63%). These results are in agreement with those by Ávila et al. (2013b) in a VF bed
315 ($3m^2$), who reported an average removal of 78% and observed how the operation under
316 higher HLRs decreased treatment performance (from 85 to 71%). Although sorption
317 onto the substrate could constitute a relevant removal mechanism for TCS given its
318 hydrophobic characteristics (log K_{ow} = 4.7), a negligible removal took place within the
319 HF bed (Fig. 2). While other substances, like AHTN, show a great reduction within the
320 HF presumably due to sorption processes, results for TCS would exhibit little sorption
321 capacity. The behavior of TCS within the three different wetland configurations indicate

aerobic biodegradation as the major removal mechanism involved in the elimination of this compound (Singer et al., 2002; Ying et al., 2007).

Conversely, the removal of DCF within the VF wetland was lower (44%) and more variable. Although DCF has been reported to be recalcitrant in activated sludge WWTPs (Heberer, 2002a; Miège et al., 2009), variable (from negligible to very high) removal efficiencies of this substance have been reported at CW systems (Matamoros and Bayona, 2006; Matamoros et al., 2009). Well-replicated experimental mesoscale studies carried out in HF wetlands have demonstrated that higher redox conditions enhance the removal of this compound, among other EOCs (Hijosa-Valsero et al., 2010b; Ávila et al., 2013b,c). In this way, Matamoros et al. (2007) reported a better elimination in an unsaturated VF bed (73%) if compared to a saturated VF (53%). Zhang et al. (2012) found significantly better performance of experimental mesoscale HF beds operating in pulses than those continuously fed. What is more, Ávila et al. (2013b) recently found how DCF was efficiently removed within the first stage (VF) of the experimental hybrid CW system (around 65%), but conversely no removal of DCF occurred at the following HF bed, where degenerated oxygen conditions prevailed. Nevertheless, very high (99%) removal rates were found by Ávila et al. (2010) during a continuous injection experiment in summer in an experimental HF CW system operating under anaerobic conditions (E_h = -123 mV; DO <LOD). The similarly high removal efficiencies achieved in the current study in the HF bed (24%) if compared to the VF (44%) suggest that various alternative mechanisms may determine the elimination of this compound, and to that respect, anaerobic biodegradation through dehalogenation could constitute a predominant degradation pathway of DCF when anaerobic conditions prevail (Park et al., 2009; Hijosa-Valsero et al., 2010a; Ávila et al., 2010). Average removal rate of the musk fragrance AHTN in the VF wetland was lower

(55%), than that found by Matamoros et al. (2007) in unsaturated and saturated VF wetlands (82 and 75%, respectively), and Ávila et al. (2013b) (average of 69%), which found a dependence of this substance on the applied HLR, suggesting that decreased entrapment of hydrophobic compounds onto particulate matter occurred due to reduced contact time at higher HLRs. The removal of this compound occurs mainly through sorption on the particulate matter, given its high hydrophobicity (Matamoros et al., 2007). Moreover, the elimination of the endocrine disruptor BPA was one of the lowest among all compounds (48%). Removal rates for this compound were found to vary a lot (from 0 to 100%). A much higher removal (72%) was found by Ávila et al. (2013b). The degradation of this substance could be owed to multiple mechanisms which seem to vary significantly in time, including association to the particulate matter (Wintgens et al, 2004), and biodegradation (Ávila et al., 2010).

The superior treatment performance of the VF over the other treatment units could be owed to energetically favourable aerobic microbial reactions, as well as hydrolysis reactions, taking place within this wetland type and provided by its design and operation strategy. Although low average redox potentials (-124 ± 9 mV) and dissolved oxygen concentrations (2.0 ± 1.7 mg O_2 L^{-1}) were observed in the bulk water at the effluent of the VF wetland, this wetland type is characterized by holding a great oxygen transfer capacity due to the unsaturated conditions of the bed, with passive aeration, as well as to the intermittent feeding operation. Oxygen transfer is achieved by means of diluted oxygen present in wastewater, convection while intermittent loading, and diffusion processes occurring between doses (Torrens et al., 2009). In fact, significantly higher enzymatic activities and microbial biomass have been found in the upper layer of the sand filter of VF wetlands, where there is more substrate and nutrient availability, indicating favorable redox conditions for aerobic metabolism, including

carbon, nitrogen and other pollutants' degradation (Zhou et al., 2005; Tietz et al., 2007; Imfeld et al., 2009). However, the synergic nitrification-denitrification activity observed in the VF bed within this study (Section 3.1) suggest the co-existence of both aerobic and anaerobic microenvironments within this wetland bed, which would allow both processes to take place. Similarly, this finding indicates that although aerobic biodegradation and sorption onto organic matter may be the major removal mechanisms contributing to EOCs reduction in VF wetlands, alternative processes based on anaerobic metabolism could simultaneously be occurring at anoxic microsites or micropores within the wetland bed (i.e. in lower layers) (Cooper et al., 1996; Ávila et al., 2010), which contribute to its elimination. Finally, it is worth noting that the large removal rates achieved at this wetland in comparison to the other wetland units are also influenced by the fact that this bed was the first stage of the system, where the major part of the removal would occur (Hijosa Valsero et al. 2010a; Ávila et al., 2013b).

3.2.3. HF performance

Target emerging organic contaminants within the HF bed as a second stage of the hybrid CW system exhibited removal efficiencies, which were best for DCF (24%), AHTN (23%) and BPA (19%) and IB (19%) (Fig. 2). Note that these were not individual efficiencies in respect to the influent of the HF, but the further proportion of elimination in respect to the previous treatment unit (% accum.). The purpose was to ease the comparison of the efficiency of removal within this bed in respect to the other two units. The remaining IB was considerably reduced up to average effluent concentrations of 0.5 ± 0.3 µg L^{-1}. The fragrance AHTN, due to its high hydrophobicity, was moderately removed, presumably by sorption onto the particulate material of the gravel matrix (Carballa et al., 2005; Matamoros and Bayona, 2006). Removal of TCS

was extremely poor within this wetland bed (3%), as compared to the VF bed (63%). Similarly low removal efficiencies (<10%) were obtained at the HF bed of the mesoscale hybrid CW system studied by Ávila et al. (2013b). Although TCS has been detected in plant and sediments of a HF CW and its concentration generally decreased from inflow to outflow (Zarate et al., 2012), sorption and plant uptake do not appear to constitute principal mechanism of TCS removal in constructed wetlands. Otherwise, higher degradation rates would have been expected at the HF beds (Singer et al., 2002). The degradation of BPA was only moderate (19%), especially if compared to the reduction rates achieved at the VF (48%) and particularly FWS (33%) wetlands. This would be explained by the occurrence of less energetically-favorable metabolic processes occurring at lower redox conditions, which would result in lower degradation kinetics and hence lower elimination rates (Ávila et al., 2013c).

In general, HF wetlands have exhibited lower treatment capacity on the removal of EOCs than VF beds, which could be attributed to the dependence of their transformation processes on a high redox status of the system (Matamoros et al., 2009; Ávila et al., 2013b). However, the treatment performance of HF wetlands has been found to be significantly enhanced in respect to the removal of EOCs (including IB, DCF, or BPA) at experiments at micro, meso and pilot-scale by optimized operation strategies resulting in high redox potentials, such as operating these wetlands in cycles of feed and rest, providing a shallow depth of the water table, or a using a primary treatment based on a conventional settler rather than anaerobic treatments (Matamoros et al., 2005; Song et al., 2009; Ávila et al., 2013c).

3.2.4. FWS performance

421 The FWS wetland performed especially well for BPA (33%), followed by DCF
422 (20%). The removal of BPA within this wetland was fairly high if compared to the HF
423 unit, which could be explained by enhanced biodegradation of this substance under
424 higher redox and dissolved oxygen conditions within the water column of the FWS (Liu
425 et al., 2009; Ávila et al., 2013c). Sorption onto particulate matter (Stevens-Garmon et
426 al., 2011) and photodegradation (Matamoros et al., 2012a) could further contribute to
427 BPA removal in FWS wetlands. Moreover, the reduction of DCF was in accordance
428 with elimination rates reported by Llorens et al. (2009) at a full-scale FWS wetland
429 receiving secondary effluent. The reduction of DCF was also significantly high (20%
430 accum.) at a mesoscale FWS (Ávila et al., 2013b). These results support
431 photodegradation as a principal removal mechanism involved in DCF reduction in water
432 bodies (Buser et al., 1998; Andreozzi et al., 2003; Matamoros and Salvadó, 2012a,
433 2013; Ávila et al., 2013b), together with less predominant mechanisms (i.e.
434 aerobic/anaerobic biodegradation, plant uptake) (Ávila et al., 2010). Removal of
435 remaining IB took place in this wetland (3%), presumably due to biodegradation since
436 low photodegradation rates are expected for this compound (Yamamoto et al., 2009;
437 Szabó et al., 2011). Although the removal of TCS was negligible (around 4%), some
438 more reduction within the water reuse tank seemed to occur, indicating that
439 photooxidation processes may constitute a small contribution to its removal (Mezcua et
440 al., 2004; Ávila et al., 2013b; Matamoros and Salvadó, 2012, 2013). Additionally, the
441 further reduction of AHTN concentrations within this wetland bed was significant
442 (11%), accumulating an overall removal efficiency of 90%. Although the reduction of
443 AHTN concentrations in the FWS could be attributed to sorption onto particulate matter
444 and sediment, further reduction was achieved at the water reuse tank, suggesting
445 photodegradation through sunlight exposure as one of the principal mechanisms of

AHTN's removal within this type of wetland configuration. Similarly high removal efficiencies were obtained at other FWS wetlands operating as a tertiary treatment step (Matamoros et al., 2008b; Llorens et al., 2009; Matamoros and Salvadó, 2012; Ávila et al., 2013b).

4. Conclusions

A hybrid CW system at full-scale consisting of a combination of CW configurations, which included a vertical flow (VF) CW, a horizontal subsurface flow (HF) CW, and a free water surface (FWS) CWs operating in series, showed to be a very robust ecotechnology for wastewater treatment and reuse in small communities. Excellent overall treatment performance was exhibited on the elimination of conventional water quality parameters (99% average removal efficiency for TSS, BOD_5 and NH_4-N), and its final effluent proved to comply with existing guidelines for its reclamation in various reuse applications. The elimination of emerging organic contaminants, which included various pharmaceuticals, personal care products and endocrine disruptors, was also very high (90 ± 11%).

Most organic matter contaminant removal, as well as the major part of EOC removal took place in the first stage of the treatment system (VF), where aerobic conditions are expected to prevail. The intermittent feeding and unsaturation of the bed constitute key practices in that approach. However, significant denitrification was also found to occur within this wetland bed, suggesting that although aerobic degradation and sorption onto organic matter might constitute the major removal mechanisms contributing to EOCs removal in VFs, alternative processes based on anaerobic microbial metabolism could simultaneously be occurring at anoxic microsites or micropores within the bed, possibly at lower layers. Conversely, a lower removal

efficiency was found for the HF bed, where mostly anaerobic degradation and sorption onto the gravel matrix are expected to occur. Finally, photodegradation through direct sunlight exposure and sorption to organic matter seem to take an active part in EOC elimination in FWS wetlands.

The combination of different wetland configurations has shown to optimize a number of important treatment processes, achieving an excellent overall EOC reduction, as well as removal of conventional water quality parameters. This has been possible thanks to the occurrence of complementary abiotic/biotic removal pathways taking place under differing physico-chemical conditions existing at wetlands of different configuration.

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669 **Tables**

670 Table 1. Mean concentrations, standard deviations and overall removal efficiency of water quality parameters along the hybrid CW system and
671 the water reuse tank (n=8). Individual removal efficiencies (%) are shown in parentheses.

	Influent	Imhoff tank	VF	HF	FWS	Water reuse tank	Overall removal efficiency (%)
Temperature (°C)	24 ± 2	24 ± 2	23 ± 2	22 ± 2	20 ± 2	21 ± 2	n.a.
DO (mg L^{-1})	0.2 ± 0.0	0.2 ± 0.0	2.0 ± 1.7	4.2 ± 0.4	2.7 ± 0.3	3.8 ± 0.6	n.a.
E_h (mV)	-138 ± 8	-198 ± 31	-124 ± 9	-61 ±44	-71 ±61	+10 ± 63	-
pH	7.8 ± 0.1	7.5 ± 0.5	7.4 ± 0.4	7.5 ± 0.4	7.8 ± 0.1	7.8 ± 0.2	n.a.
EC (mS cm^{-1})	1.5 ± 0.1	1.5 ± 0.08	1.5 ± 0.05	1.5 ± 0.03	1.7 ± 0.09	1.8 ± 0.09	n.a.
Turbidity (NTU)	228 ± 33	108 ± 30	22 ± 18	28 ± 13	8 ± 3	4 ± 2	98
TSS (mg L^{-1})	212 ± 59	114 ± 33 (46%)	11 ± 4 (90%)	13 ± 4 (-18%)	6 ± 2 (54%)	3 ± 1 (50%)	98
COD (mg L^{-1})	405 ± 106	258 ± 42 (36%)	44 ± 14 (83%)	29 ± 7 (34%)	47 ± 8 (-62%)	43 ± 8 (8%)	89
BOD_5 (mg L^{-1})	320 ± 57	125 ± 7 (61%)	11 ± 8 (91%)	7 ± 2 (36%)	6 ± 2 (14%)	4 ± 3 (33%)	99
NH_4-N (mg L^{-1})	25.5 ± 5.4	24.2 ± 6.6 (5%)	8.0 ± 2.2 (67%)	2.5 ± 1.8 (69%)	0.7 ± 0.11 (72%)	0.6 ± 0.1 (14%)	98
NO_x-N (mg L^{-1})	0.3 ± 0.3	0.2 ± 0.2	0.8 ± 0.9	0.5 ± 0.2	0.2 ± 0.2	0.1 ± 0.1	n.a.
TN (mg L^{-1})	40.1 ± 8.8	38.5 ± 6.1 (4%)	13.3 ± 3.6 (65%)	3.6 ± 1.4 (73%)	2.4 ± 0.6 (33%)	2.2 ± 0.5 (8%)	94
TP (mg L^{-1})	5.9 ± 1.2	5.9 ± 1.6 (0%)	5.3 ± 1.8 (10%)	4.2 ± 2.0 (21%)	3.1 ± 0.4 (26%)	3.1 ± 0.6 (0%)	47
PO_4-P (mg L^{-1})	3.2 ± 0.7	3.2 ± 0.6 (0%)	2.9 ± 0.4 (9%)	2.2 ± 0.9 (24%)	2.7 ± 0.3 (-23%)	2.7 ± 0.7 (0%)	16
E. coli (CFU/100 mL)	$1 \cdot 10^7$	$5 \cdot 10^6$	$9 \cdot 10^5$	$3 \cdot 10^3$	<40	<40	99.999

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679 Table 2. Mean values and standard deviations of studied EOCs along the hybrid CW system and the activated sludge system (n=8).

	Influent	Imhoff tank	VF	HF	FWS	Water tank	Overall removal efficiency (%)
Analgesic-antiinflammatory drugs							
Ibuprofen (µg L^{-1})	18.66 ± 3.89	14.78 ± 1.53	4.01 ± 1.54	0.52 ± 0.34	0.03 ± 0.02	0.03 ± 0.03	>99
Diclofenac (µg L^{-1})	0.90 ± 0.62	0.66 ± 0.22	0.50 ± 0.18	0.28 ± 0.12	0.10 ± 0.04	0.10 ± 0.03	89
Acetaminophen (µg L^{-1})	2.64 ± 3.30	3.32 ± 2.98	<LOD	<LOD	<LOD	<LOD	99
Personal Care Products							
Tonalide (µg L^{-1})	0.54 ± 0.22	0.33 ± 0.11	0.24 ± 0.07	0.11 ± 0.03	0.05 ± 0.02	0.02 ± 0.00	90
Oxybenzone (µg L^{-1})	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-
Triclosan (µg L^{-1})	0.15 ± 0.03	0.12 ± 0.03	0.05 ± 0.01	0.05 ± 0.01	0.04 ± 0.01	0.03 ± 0.00	79
Endocrine disrupting compounds							
Bisphenol A (µg L^{-1})	4.06 ± 1.19	3.90 ± 1.59	2.12 ± 1.33	1.35 ± 0.52	<LOD	<LOD	>99
Ethynil-estradiol (µg L^{-1})	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-

Figures

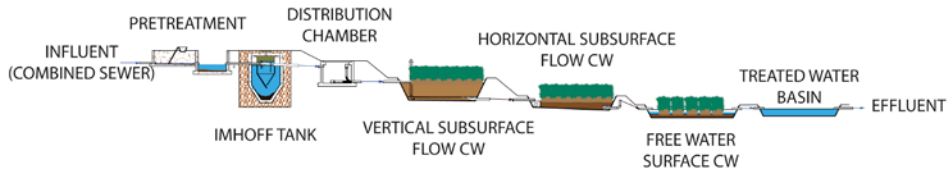

Figure 1. Layout of the hybrid constructed wetland system.

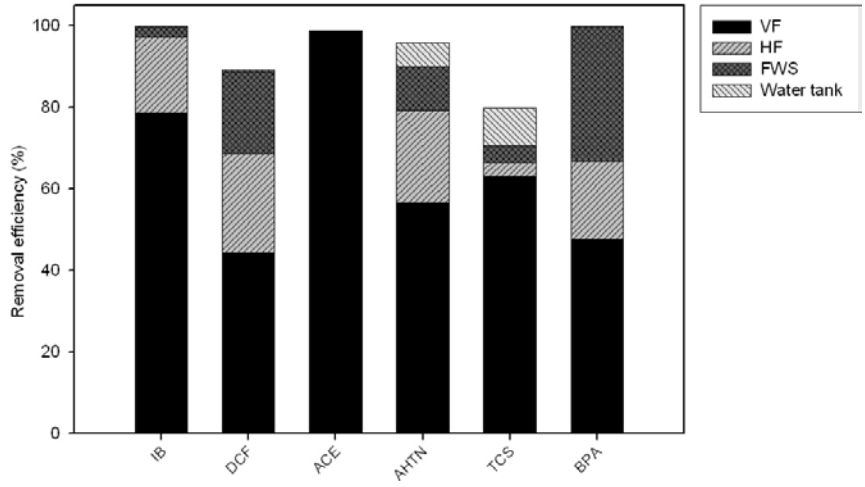

Figure 2. Accummulated removal efficiencies for the selected emerging contaminants at the different units of the treatment system.