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Removal and environmental risk assessment of contaminants of emerging concern from irrigation waters in a semi-closed microalgae photobioreactor

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ABSTRACT

The present study evaluated the efficiency of a semi-closed, tubular, horizontal photobioreactor (PBR) to treat a mixture of irrigation and rural drainage water, focusing in the removal of different contaminants of emerging concern (CECs), and evaluating the environmental impact of the resulting effluent. Target CECs included pharmaceuticals, personal care products and flame retardants. Of the 13 compounds evaluated, 11 were detected in the feed water entering the PBR, and diclofenac (DCF) (1107 ng L^{-1}) and N,N-diethyl-toluamide (DEET) (699 ng L^{-1}) were those present at the greatest concentrations. The best removal efficiencies were achieved for the pharmaceuticals diazepam (94%), lorazepam (LZP) (83%) and oxazepam (OXA) (71%), and also for ibuprofen (IBU) (70%). For the rest of the CECs evaluated, attenuation was similar to that obtained after conventional wastewater treatment, ranging from basically no elimination (carbamazepine (CBZ) and tris-(2-chloroethyl) phosphate (TCEP)) to medium efficiencies (DCF and tributyl phosphate (TBP) (50%)). Environmental risk assessment based on hazard quotients (HQs) resulted in HQ values < 0.1 (no risk associated) for most of the compounds and most of the trophic levels considered. Values between 1 and 10 (moderate risk) were obtained for tonalide (AHTN) (fish) and CBZ (invertebrates). The most sensitive trophic level was green algae, whereas fish and aquatic plants were the most resilient. Our results suggest that microalgae-based treatments could become a green, cost-effective alternative to conventional wastewater treatment regarding the efficient elimination of these contaminants.

1. Introduction

Agricultural activities and animal feeding operations (without regulated slurry or manure pits) are becoming more intensive in order to satisfy the also increasing food demand, leading to a constant raise in the use of veterinary pharmaceuticals in cattle farming activities, and inorganic fertilizers and/or synthetic pesticides in agriculture (Oerke, 2006; Popp et al., 2013). This results in relevant amounts of diffuse pollution affecting both surface and groundwater systems (Dolliver and Gupta, 2008; García-Galán et al., 2010; Sabourin et al., 2009). Furthermore, crops irrigation with reclaimed wastewater has become a common practice in countries under a significant water scarcity (such as those in the Mediterranean area). Wastewater effluents are considered as one of the main entrance pathways for a broad variety of organic micropollutants into the aquatic environment, as these are not fully removed even after tertiary and/or advanced treatments such as UV radiation, membrane bioreactors (MBR), reverse osmosis (RO) or nanofiltration (NF) (Biel-Maeso et al., 2018; Mamo et al., 2018; Racar et al., 2020). In consequence, this practice can only contribute to increase the environmental occurrence of the so-called contaminants of emerging concern (CECs), which include compounds such as pharmaceuticals and personal care products (PPCPs), fundamental in our daily routine, but also high production volume chemicals such as plasticizers, preservatives or flame retardants, which are frequently used in industrial processes (Krzeminski et al., 2017; Loos et al., 2009; van Wezel et al., 2018). Currently, there is no European legislation regarding reclaimed water quality and CECs. Spain is the European country with the highest volume of wastewater reuse, and this practice is regulated by

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the RD1620/2007, describing the water quality required depending on its final use. Nevertheless, CECs are not included. Last of all, the application of cattle manure or biosolids from urban wastewater treatment plants (WWTPs) as organic amendment should not be neglected, as these may still contain residues of non-polar CECs (Langdon et al., 2010; Sabourin et al., 2009). Overall, depending on the polarity of these pollutants, irrigation or storm events can lead to the translocation of these CECs from the crop fields (Ccanccapa et al., 2016; Langdon et al., 2010; Postigo et al., 2016). Drainage channels (and also open irrigation channels) can receive a large amount of this rural run-off; these channels usually discharge into rivers, as their diversion into main collectors towards WWTPs is usually unfeasible. Thus, these pollutants eventually spread in aquatic ecosystems and may indirectly affect a huge variety of non-target species, endangering the natural equilibrium of river and streams (García-Galan et al., 2017; Proia et al., 2013). For instance, bioaccumulation of anti-inflammatories such as diclofenac (DCF) and ibuprofen (IBU) has been observed in larvae of caddisflies and leeches at concentrations up to 183 ng g^{-1} (Huerta et al., 2015), and the bioaccumulation of the anxiolytic oxazepam (OXA) in the freshwater shrimp *Gammarus fossarum* was also recently demonstrated (Maria Jesus García-Galan et al., 2017). Furthermore, the corroborated spread of antibiotic resistance genes and the endrocrine disruption caused by the plasticizer bisphenol A and other synthetic hormones in certain fish species are amongst the most critical environmental issues to tackle nowadays (Cacace et al., 2019; Huerta et al., 2016).

Nature-based, low-cost treatment systems, such as constructed wetlands (CWs) or microalgae-based treatments, are gradually becoming a feasible and more appropriate alternative to conventional WWTPs for small populations in rural areas. These alternative technologies are being intensively investigated and, so far, promising results regarding CECs removal have been observed, performing both as secondary and tertiary treatments (Ávila et al., 2014; García-Galán et al., 2018; Matamoros et al., 2015; Vassalle et al., 2020a). Specifically, microalgae-based treatments have received a renewed consideration due to their high efficiency removing nutrients and organic matter within a more sustainable operation than conventional wastewater treatments. Microalgae biomass grows fixating CO_2 and assimilating the nutrients (mostly nitrogen (N) and phosphorus (P)) present in the influent wastewater. Oxygen is generated through photosynthesis and used up by heterotrophic aerobic bacteria to degrade the organic matter present in the water (including CECs). Microalgae systems have the dual capacity of treating wastewater efficiently and producing microalgae biomass which, after an appropriate harvesting/separation technique from the aqueous phase, can be further profited to produce bioenergy (biogas) (Zhu, 2015) or other added-value products such as pigments, biofertilizers or even bioplastics (Arashiro et al., 2020; Khan et al., 2019; Rueda et al., 2020). In consequence, if this biomass is managed properly, the waste generated during microalgae treatment is considerably reduced, as well as the operation and maintenance (O&M) costs when compared to conventional systems, as external aeration is no required due to photosynthesis.

There are two basic types of microalgae treatment systems, open and closed reactors. Open systems or high rate algal ponds (HRAPs) are the most frequently used systems, mainly due to their lower O&M costs, but cultures are more exposed to external contamination, and the different growth and environmental parameters (temperature, sunlight) can hardly be regulated (Park and Craggs, 2010). Closed systems are

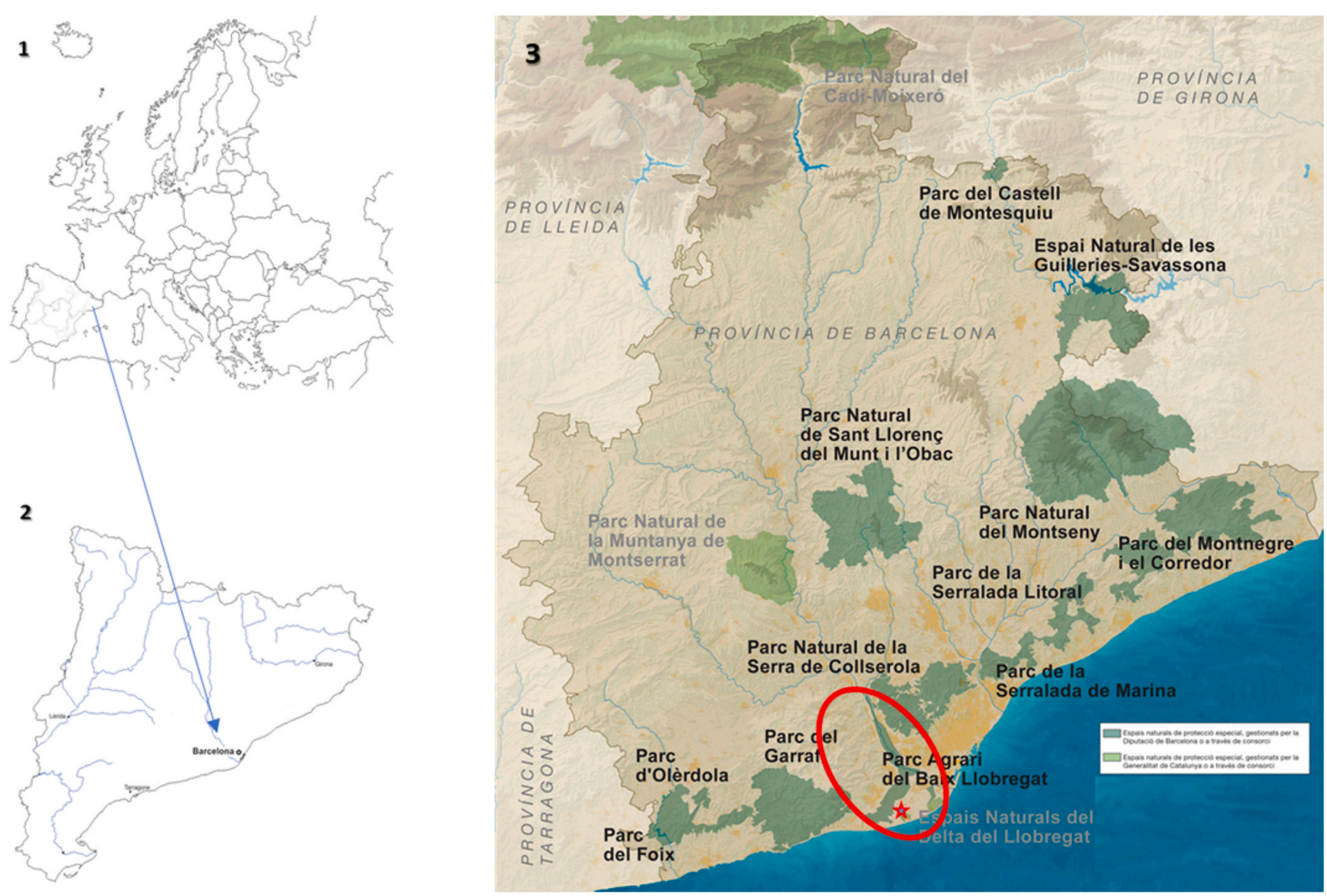

Fig. 1. Location of the province of Barcelona (1), the Llobregat River (2), and the Baix Llobregat Agricultural Park (3) (highlighted in red). Agròpolis (UPC experimental campus) approximated location is pointed by the red star. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

presented as horizontal tubular photobioreactors (PBRs), as vertical cylinders (column PBRs) or flat plate PBRs (consisting of flat, thin panels). They are mostly used for commercial production of microalgae biomass (growing single, pure cultures), as the biomass yields are typically higher, microalgae cultures are more protected against external contamination and control of the operation parameters is better. Yet, the costs of O&M are higher (higher energy requirements for mixing), dissolved oxygen (DO) may accumulate within the tubes to toxic levels and biofouling may also appear in their inner walls. Recently, an innovative design of a hybrid or semi-closed PBR (combining the advantages and avoiding the limitations of both open and closed systems) has been tested, evaluating its efficiency in wastewater bioremediation and biomass yield (Díez-Montero et al., 2020) and also in the removal of different antibiotics, sunscreens, plasticizers and pesticides (García-Galán et al., 2020b, 2018; Vassalle et al., 2020b), with favorable outcomes. To the author's knowledge, the use of closed or semi-closed PBRs is not frequent, as HRAPs are predominant in wastewater treatment systems.

The present study aims to investigate the capacity of a semi-closed, horizontal tubular PBR, acting as a tertiary treatment and operating at full-scale, to remove 13 different CECs from irrigation water, including 6 pharmaceuticals, 4 personal care products, 2 flame retardants and one surfactant. The different removal pathways within the PBR have been discussed, and the potential ecotoxicity of the PBR effluent has been evaluated, estimating the risk quotients associated to the CECs and ensuring a safe reclaimed wastewater reuse in irrigation or final discharge in receiving, natural water bodies.

2. MATERIALS and methods

2.1. Description and operation of the semi-closed tubular horizontal PBR

An innovative, new prototype of a semi-closed tubular horizontal PBR was conceived, deployed and validated within the framework of the H2020 EU project INCOVER "Innovative Eco-technologies for Resource Recovery from Wastewater" (http://incover-project.eu/GA 689242). Three PBRs were the core of a more complex pilot plant at demonstrative scale, which main objective was to use agricultural drainage water and domestic wastewater as a valuable resource to produce different added-value products. The plant was located in the Agròpolis experimental campus of the Universitat Politècnica de Catalunya-BarcelonaTech (UPC), next to the agricultural area of the Llobregat Delta that belongs to the Baix Llobregat Agrarian Park (Fig. 1). The park comprises 2900 Ha of fruit and vegetable crops located in the alluvial plains of the Llobregat Delta and the lower valley of the Llobregat River (Montasell i Dorda and Callau i Berenguer, 2008).

A detailed description of the PBRs, the start-up of the plant and the main outcomes regarding wastewater treatment can be found elsewhere (García et al., 2018; Uggetti et al., 2018). Briefly, each PBR consisted of two open tanks of polypropylene connected by 16 horizontal tubes (Fig. 2). The useful volume of each PBR was 11.7 m^3. Paddlewheels were installed in the middle of each open tank to promote and favor the homogeneous distribution and mixing of the liquor and also the release of the excess DO accumulated along the closed tubes. They also contributed to create a water level difference (0.2 m) between both tanks, which made the mixed liquor flow by gravity from one tank to the opposite one (Fig. 2). The PBRs operated under a hydraulic residence time (HRT) regime of 5 d (feeding of 2.3 $m^3\ d^{-1}$ approximately). Online sensors of pH (Hach Lange Spain S.L.), DO (Neurtek, Spain) and temperature (Campbell Scientific Inc., USA) were installed in one of the two open tanks of the PBR.

2.2. Sampling strategy

The three PBRs were fed daily with water from an open channel near the facilities, which carried both reclaimed wastewater from an urban WWTP nearby and agricultural run-off from the surrounding agricultural land (from now on, irrigation water). The WWTP serves 375,000 PE and has been designed to treat 64,000 $m^3\ d^{-1}$. Wastewater treatment consisted of a primary physicochemical treatment, followed by MBR and disinfection by means of UV and chloration. Biosolids are not applied in the crop fields of this area. The water collected from the channel was mixed with domestic wastewater from a septic tank (7:1, v:v), in order to provide more nutrients for biomass growth. This feed water was mixed in a homogenization tank with constant stirring, right before the feeding operation (it was filled up anew every day). Sampling was carried out during two consecutive weeks during summer (July), three days per week and always at the same time, 10 a.m. Feed water of the PBR (PBR influent) and effluent mixed liquor were taken in one of the PBRs ($n = 12$ samples). For physicochemical characterization of the samples, these were taken in PVC bottles and directly analyzed in the laboratory. For CECs analyses, samples were collected in amber glass bottles and immediately filtered through 0.45 μm PVDF membrane filters (Millipore, USA) and frozen upon arrival to the laboratory (amber glass bottles).

2.3. Analytical methodologies

2.3.1. Samples characterization

Both influent and effluent samples were analyzed on the following wastewater quality parameters: DO and temperature (EcoScan DO 6, ThermoFisher Scientific, USA) and pH (Crison 506, Spain) which were also measured on-site; turbidity (Hanna HI 93703, USA); total suspended solids (TSS), volatile suspended solids (VSS), alkalinity, chemical oxygen demand (COD) following Standard Methods (APHA-AWWA-WEF, 2012); NH_4^+-N according to Solórzano method (Solórzano, 1969). The ions NO_2^--N, NO_3^--N and PO_4^{3-}–P were measured by ion chromatography (ICS-1000, Dionex Corporation, USA). Total carbon (TC), total phosphorus (TP) and total nitrogen (TN) were measured by a TOC analyzer (multi N/C 2100S, Analytik Jena, Germany). All the analyses were done in triplicate and results are given as average values. Mixed liquor samples were examined under an optic microscope (Motic, China) for qualitative evaluation of microalgae populations, employing taxonomic books and databases for their identification.

2.3.2. CECs analysis

Thirteen target compounds were selected based on their occurrence in WWTP effluents and surface water bodies (Couto et al., 2019; Loos et al., 2013; Margenat et al., 2017; Serra-Roig et al., 2016). These

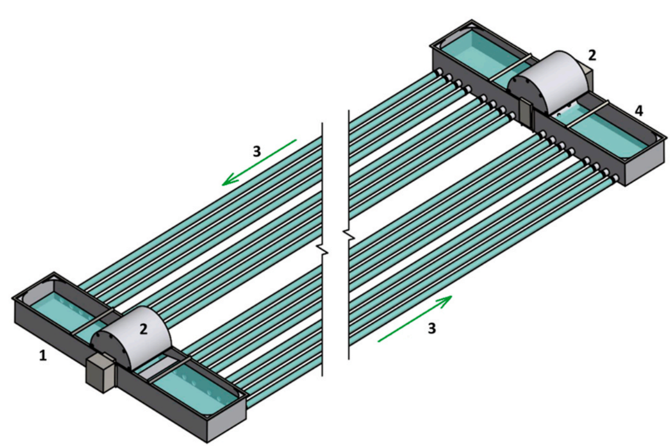

Fig. 2. Scheme of the semi-closed tubular closed photobioreactor used in this study. 1:inflow from the homogenization tank; 2: paddle wheel; 3: direction of the flow within the tubes; 4: outflow to the storage tanks. samples were taken in the inlet (1) and 4 (effluent).

included 6 pharmaceuticals (diazepam (DZP), carbamazepine (CBZ), DCF, IBU, lorazepam (LZP) and OXA), 2 organophosphate flame retardants (tributyl phosphate (TBPh) and tri-(2-chloroethyl) phosphate (TCEP)), 3 fragrances (galaxolide (HHCB), tonalide (AHTN) and methyl dihydrojasmonate (MDHJ), 1 insect repellent (N,N-diethyl-toluamide (DEET)) and 1 surfactant (2,4,7,9-tetramethyl-5-decyne-4,7-diol, also known as Surfynol-104 (TMDD)). Further information on their physico-chemical characteristic are given in Table S1 of Supplementary Material. Analytical standards for all the compounds were purchased from Sigma–Aldrich (Steinheim, Germany), including the deuterated compounds atrazine-d_5, mecoprop-d_3, tonalide-d_3 and dihydroCBZ. Trimethylsulfonium hydroxide (TMSH) was obtained from Fluka (Buchs, Switzerland). Strata-X polymeric cartridges (200 mg) were purchased from Phenomenex (Torrance, CA, USA). The 1–2 μm glass fiber filters (∅ 47 mm) and 0.45 μm PVDF membrane filters were obtained from Whatman (Maidstone, UK) and (Millipore, USA), respectively.

2.3.2.1. GC-MS-MS analysis. For the determination of the different target analytes, samples were analyzed by gas chromatography coupled to mass spectrometry (GC-MS/MS), adapting the methodology by Matamoros and Bayona (2006). For both influent and effluent water samples, 100 mL were preconcentrated using a previously activated polymeric solid-phase extraction cartridge (200 mg Strata X, Phenomenex, US). Further information on pretreatment and GC-MS/MS methodology validation and application is given elsewhere (Margenat et al., 2017; Matamoros and Bayona, 2006).

2.4. Environmental risk assessment

In order to evaluate the potential ecotoxicological risk of those CECs still present in the PBR effluent, hazard quotients (HQ) have been estimated as indicated in equation (1).

[1]:

$$HQ = \frac{MEC}{PNEC} \tag{1}$$

where MEC is the measured environmental concentration, and PNEC is the predicted-no effect concentration. When PNEC data are not available, alternative PNECs can be derived by dividing the toxicity endpoint values found in the literature (EC_{50} or LC_{50}) by an uncertainty factor of up to 1000 (Sanderson et al., 2004). HQ values < 0.1 mean that no adverse effects are expected. When $0.1<HQ<1$, the risk is low but it should not be neglected; when $1<HQ<10$, a moderate risk is implied, and $HQ > 10$ meanS a relevant ecological hazard (EMEA, 2006).

Eventually, for the purpose of evaluating the overall ecotoxicity risk of the PBR effluent, cumulative HQs were calculated for each trophic level considered, adding all HQs calculated for each individual CEC detected in the effluent.

3. Results

3.1. Water quality parameters

On-line measurements of temperature, DO and pH are given in the Supplementary Material (Figure S1). The photosynthetic activity of microalgae caused daily variations of DO and pH, characteristic of these systems, with DO ranging from 8 to 14 mg L-1 and pH from 8 to 10.5. The mixed liquor temperature increased during daylight, reaching values up to 41 °C, due to the high solar radiation and ambient temperature. At night, the mixed liquor was cooled, decreasing to approximately 24 °C.

Data on the performance of the PBR were already published elsewhere (Vassalle et al., 2020b), and are included in the Supplementary Material (Table S2). Briefly, the average biomass productivity in the PBR

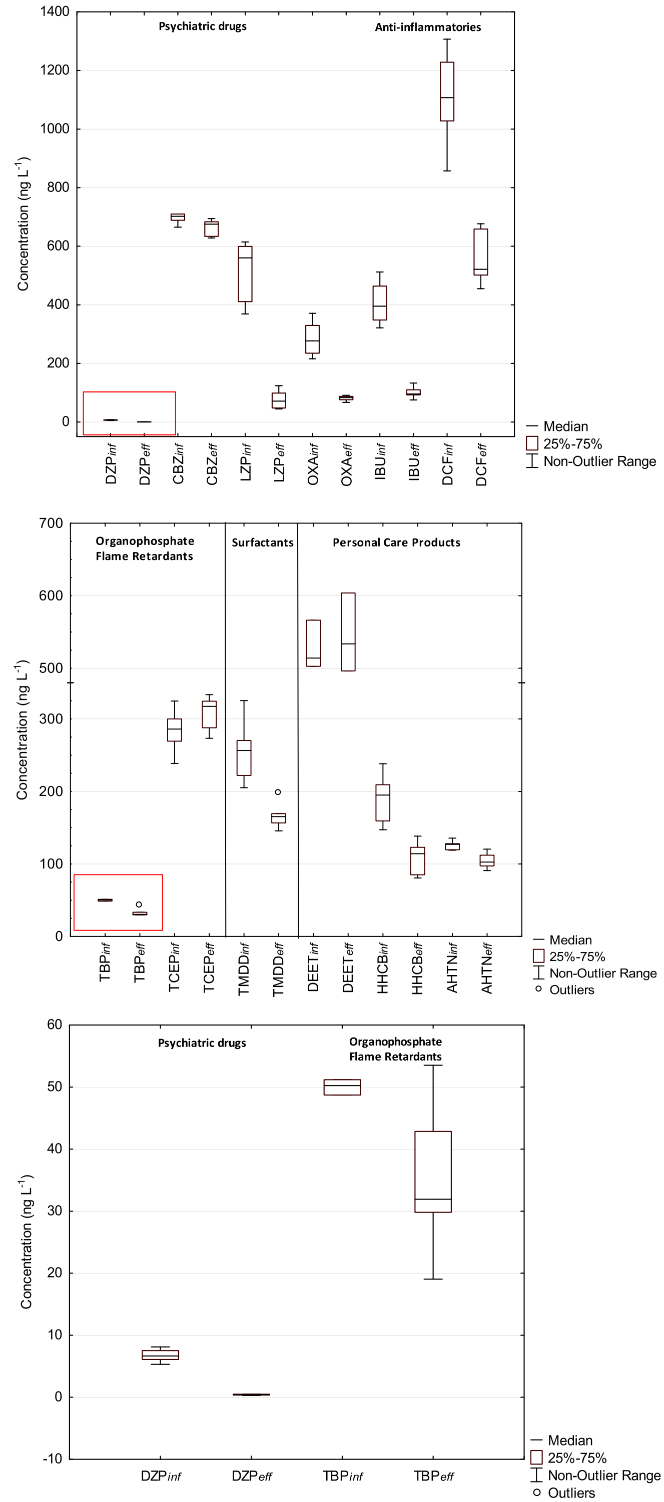

Fig. 3. Box plots of the concentrations of pharmaceuticals and fragrances (A) and other contaminants of emerging concern (B) in rural run-off (influent) and effluent samples of the PBR. Marked compounds have been zoomed in graph C'.

was low (6.9 ± 0.7 g VSS m^{-2} d^{-1}) due probably to the low concentration of total inorganic nitrogen (TIN), $N–NH_4^+$ and phosphate ($P-PO_4^{3-}$) in the PBR feed water. Average VSS concentration in the PBR effluent (mixed liquor) was 215 mg L^{-1}, corresponding to a 74% of the TSS, which is in accordance with the values generally observed in microalgae-based systems (García-Galán et al., 2018; Gutiérrez et al., 2016). The registered pH values > 8 promoted precipitation of inorganic salts of different nature, leading to an increase of the VSS/TSS ratio.

COD concentration increased a 16% during PBR treatment, which is generally linked to the release of a fraction of the carbon fixed during photosynthesis as dissolved organic carbon (DOC) by microalgae (Arbib et al., 2013; García-Galán et al., 2018; García et al., 2006).

3.2. Occurrence of contaminants of emerging concern in the irrigation water

3.2.1. Pharmaceuticals

The six targeted pharmaceuticals, 4 psychiatric drugs and 2 non-steroidal anti-inflammatory drugs (NSAIDs), were detected in the PBR feed water all the sampling days (Fig. 3A). CBZ was the most abundant psychiatric drug (660–830 ng L^{-1}), followed by LZP, OXA and DZP. The concentration of CBZ was in agreement with that found in previous studies on the same site (García-Galán et al., 2018) and in the Baix Llobregat area (Margenat et al., 2017). The ubiquity of this anticonvulsant in the aquatic environment has been frequently demonstrated, being currently considered as one of the most reliable anthropogenic pollution tracers given its resilience to biodegradation during conventional wastewater treatment (WWT), and also to photodegradation (Guo and Krasner, 2009; Hai et al., 2018). Its presence in agricultural run-off waters has also been reported by Pedersen et al. (2005), who detected CBZ in agricultural run-off from crop fields irrigated with effluent wastewater in California, at levels between 320 and 440 ng L^{-1}. Lower concentrations were reported in rural run-off in Mexico (1–35 ng L^{-1}) (Moeder et al., 2017) and also by Tran et al. (2019) in both urban and agricultural run-off. LZP was present at average concentration of 511 ng L^{-1}, slightly higher than levels previously detected in irrigation water in the same area by Margenat et al. (2017) and in the Llobregat river by Proia et al. (2013), probably due to the mixing of the irrigation water with the septic tank wastewater. DZP was detected at much lower levels (5.3–8.1 ng L^{-1}), similar to those reported by Proia et al. (2013). OXA was detected at concentrations between 216 ng L^{-1} and 371 ng L^{-1}. This psychiatric drug is also the final degradation product of DZP and LZP aforementioned, which are amongst the most highly consumed anti-depressants worldwide (Kosjek et al., 2012). It has been detected at similar levels other irrigation channels near our study site, also fed with reclaimed wastewater (178 ng L^{-1}), but also in irrigation channels fed with surface water (25–36 ng L^{-1}) and groundwater (<2 ng L^{-1}) (Margenat et al., 2017). It was also present in surface water influenced by agricultural run-off in the UK (White et al., 2019), and frequently detected in WWTP effluents all over Europe (81 out of the 90 effluent samples analyzed in 18 countries) at average concentration of 162 ng L^{-1} (Loos et al., 2013). Regarding the NSAIDs evaluated, DCF was present at levels in the range 860–1306.8 ng L^{-1}, higher than concentrations reported in a previous campaign on the same site (García-Galán et al., 2018) (similarly to LZP, it is probably due to the mix with the water from the septic tank, which could have had residual DCF). and also higher than those found in rural run-off in Mexico or Singapore (Moeder et al., 2017; Tran et al., 2019). IBU was also detected at concentrations in the range 321–512 ng L^{-1}, data which is in agreement with that detected in the aforementioned work by Moeder et al. (2017). Similar levels were detected by White et al. (2019) in surface waters receiving rural run-off in the UK.

3.2.2. Personal care products

Two of the three fragrances investigated, HHCB and AHTN, were detected at average concentrations of 191 ng L^{-1} and 127 ng L^{-1}, similar levels to those detected in a previous sampling campaign in the same location (García-Galán et al., 2018). Their presence in surface waters is frequent and usually attributed to wastewater effluent discharges and not to agricultural run-off (Blum et al., 2018; Celeiro et al., 2019; Corada-Fernández et al., 2017; Gómez et al., 2012). The insect repellent DEET was present at concentrations ranging from 502 to 698 ng L^{-1}, higher than those found by Margenat et al. (2017) in other irrigation channels nearby. This high levels were due to the marked seasonal variability associated to this compound, as its usage is much higher during summer and mosquitoes proliferation (Merel et al., 2015). Despite it is clearly a compound of domestic application and, therefore, from wastewater origin (Gago-ferrero et al., 2017; Launay et al., 2016), its environmental ubiquity has been demonstrated in several studies, including stormwater run-off, surface waters and groundwaters (Brausch and Rand, 2011; Burant et al., 2018; Rehrl et al., 2020), and also in agricultural run-off and at similar levels than those observed in this study (Tran et al., 2019).

3.2.3. Organophosphate flame retardants and surfactants

The organophosphate flame retardants TBP and TCEP were present at average values of 34.8 ng L^{-1} and 284 ng L^{-1} respectively (Fig. 3B), levels slightly higher than those detected in other irrigation channels (Margenat et al., 2017). These compounds have been detected in basically all the environmental compartments due to their broad range of applications (pesticides solvents, detergents antifoaming, additives, etc.) and their extensive use in industrial activities, as well as the progressive disuse of polybrominated flame retardants (Yang et al., 2017). Different authors have also found both TBP and TCEP in stormwater run-off at similar or higher concentration ranges, and also in precipitation water (rain and snow) (Burant et al., 2018; Regnery and Püttmann, 2010). These authors stated that, when used as additives, these compounds do not bind to the matrix and so they can be released to the environment by volatilization and dissolution. Precipitation wash-off and dry deposition, together with WWTPs effluents discharges, are their main entry pathways. The surfactant and anti-foaming TMDD, known with the commercial name of Surfynol 104®, was present at concentrations ranging from 205 ng L^{-1} to 325 ng L^{-1}. TMDD is used in the industry to reduce the surface tension of coatings, adhesives, paints and printing inks, but it is also used in pesticide formulations and in

Table 1
Maximum, median and average concentrations (±SDV) detected for the different CECs evaluated, and removal efficiency (R%) after PBR treatment.

FAMILY	NAME	Maximum (ng L^{-1})	Median (ng L^{-1})	Average (ng L^{-1})	Removal (R%)
PHARMACEUTICALS	**Carbamazepine (CBZ)**	833	702	717 ± 59	11 ± 8
	Diclofenac (DCF)	1307	1107	1106 ± 111	52 ± 6
	Ibuprofen (IBU)	512	395	406 ± 138	70 ± 12
	Lorazepam (LZP)	615	560	511 ± 113	83 ± 6
	Oxazepam (OXA)	371	277	284 ± 60	71 ± 7
	Diazepam (DZP)	8	7	7 ± 1	94 ± 5
PERSONAL CARE PRODUCTS	**Galaxolide (HHCB)**	238	195	191 ± 27	45 ± 14
	Tonalide (AHTN)	136	127	126 ± 6	20 ± 5
	N,N-diethyl-m-toluamide (DEET)	1328	574	699 ± 90	- 4 ± 12
ORGANOPHOSPHATE FLAME RETARDANTS	**Tributyl phosphate (TBP)**	81	50	54 ± 4	43 ± 7
	Tris(2-chloroethyl) phosphate (TCEP)	325	286	284 ± 29	- 4 ± 5
SURFACTANTS	**Surfinol 104 (TMDD)**	325	256	256 ± 42	33 ± 7

toilet and kitchen paper in the domestic context (Guedez and Püttmann, 2014). It has been detected in surface waters impacted by WWTPs effluents, in concentrations ranging from 16 to 240 ng L^{-1} (Blum et al., 2018), and up to the μg L^{-1} level in rivers impacted by industrial activities (Guedez and Püttmann, 2014).

3.3. Removal of CECs during PBR treatment

3.3.1. Pharmaceuticals

The pharmaceuticals entering the PBR have been classified according to their removal efficiency (RE%): efficiently removed (>70%) namely IBU, DZP, LZP and OXA; moderately removed (35–50%), namely DCF, and poorly removed (<25%), namely CBZ (Table 1).

The good removal of DZP (94% ± 5) is significant, as it is usually inefficiently removed during conventional WWTs. Indeed, many studies have reported RE% ranging from negative eliminations to barely a 18% (García-Galán et al., 2016; Mamo et al., 2018; Rodriguez-Mozaz et al., 2015), although also better removals have been observed (30–60%) (Gros et al., 2012; Mira et al., 2019). West and Rowland (2012) studied direct and indirect photodegradation of DZP (also OXA) and concluded that the presence of humic substances increased its photodegradation rate; in the case of our PBR, both the humic acids present in the open channel and the carbon exudates from the microalgae within the reactor could have enhanced the photodegradation of this drug. On the contrary, the aforementioned authors also observed that humic substances seemed to slow down the photodegradation of OXA. This drug is highly resilient to both aerobic and anaerobic biodegradation and also to photodegradation (Kosjek et al., 2012; Calisto et al., 2011; Loos et al., 2013), and some authors have indicated that it is likely to persist in water for decades (Klaminder et al. (2015). Considering its high log K_{ow} (3.3), adsorption onto the microalgae biomass seems to be the main removal pathway within the PBR, despite its recalcitrance during conventional WWTs. In a previous study by Gojkovic et al. (2019), removals in the range 2–27% were obtained in a laboratory-scale flat panel PBR, using different microalgae species. In that study, OXA was indeed detected in the biomass (37% maximum). To the author's knowledge, there are no previous studies on the elimination of OXA in full scale microalgae systems. Last of all, it should be regarded that both DZP and OXA (and other benzodiazepines) can persist in soils long enough after irrigation to be uptaken by different crops, as demonstrated by Carter et al. (2018) with radish and silverbeet. The excellent removals obtained in the present study highlight the feasibility of microalgae-based treatment to remove these drugs before water reclamation.

Regarding LZP (83% ± 5 removal), given its low solubility and high log K_{ow}, it seems that microalgae uptake is the most likely removal pathway, although photodegradation cannot be neglected either (Calisto et al., 2011). Lower removals (30–57%) were obtained by Hom-Diaz et al. (2017) in a smallers cale closed PBR operating as secondary treatment, with a similar TSS concentration than the PBR in this work, but with higher HRT (8–12 h). LZP is also incompletely removed during conventional WWTs (<50%) (Dolar et al., 2012; Mira et al., 2019).

For IBU (RE% of 70% ± 12), the results obtained in the present study agree with those obtained in removals in HRAPs operating as secondary treatments (García-Galán et al., 2020a; Villar-Navarro et al., 2018). These authors attributed its removal mostly to aerobic biodegradation, as adsorption onto biomass was very low. Indeed, despite its high log Kow (3.97), IBU is charged negatively at the pH of the PBR ($pK_a = 5.3$), being repelled by the negative charge of the microalgae cell walls (Matamoros et al., 2016). Ding et al. (2017) obtained lower removals for IBU (20%–60%) in laboratory batch experiments with the fresh-water diatom Navicula sp. The higher initial concentrations (1–50 mg L-1) could be responsible of these lower eliminations due to toxicity events against the diatom. In a different study, IBU removal in the presence of microalgae was attributed to indirect photodegradation rather than to sorption, due to the presence of dissolved organic matter acting as a photocatalyst of the reaction (de Wilt et al., 2016).

CBZ was poorly removed (11% ± 8). Different studies have also reported low removals in HRAPs operating as secondary treatments, ranging from no removal (García-Galán et al., 2020a) to eliminations in the range of 9–23% with HRT of 6 d (Villar-Navarro et al., 2018). Matamoros et al. (2015) obtained removals of 46% (4 d of HRT) and 62% (8 d HRT) also during the warm season, highlighting that even under the best conditions for microalgae-based treatment efficiency (summer campaigns), CBZ is highly stable towards photodegradation and aerobic biodegradation. Díaz-Garduño et al. (2017) obtained similar results in laboratory scale experiments (RE% in the range 0–23%); removals in the range of 10–30% have been obtained with different species of green algae (Chlorella sp., Scenedesmus sp., Coelastrum astroideum and Chlamydomonas mexicana (de Wilt et al., 2016; Gojkovic et al., 2019; Matamoros et al., 2016; Xiong et al., 2016). These authors reached the conclusion that bioadsorption and/or bioaccumulation were negligible, being biodegradation the main elimination mechanism. On the contrary, García-Galán et al. (2020a) observed concentrations of CBZ in the biomass equivalent to the 39% of the initial concentration in the influent, but yet it was not eliminated in the system, but still present in the effluent and at higher than those in the influent. These results indicated a clear bioaccumulation in the biomass of this drug. Some authors also point out that glucuronide moieties of CBZ have never been included in monitoring studies (due to the lack of commercial standards), and demonstrated the presence and cleavage of these metabolites during conventional wastewater treatments (Vieno et al., 2007). Bahlmann et al. (2014) even suggested a concentration increase of CBZ of nearly 100% during wastewater treatment due to this cleavage.

DCF was removed by a 52% ± 6 on average. These results agree with those obtained in previous studies in HRAPs acting as secondary treatment, with removals of 55% (Vassalle et al., 2020a), 39–74% (Villar-Navarro et al., 2018) and 51–55% (García-Galán et al., 2020a). The latter pointed out that bioadsorption/bioaccumulation played a relevant role in its removal from the aqueous phase (log Kow = 4.5), given the high concentrations detected in the biomass (267.9 ng g-1), whereas biodegradation was low. On the other hand, de Wilt et al. (2016) attributed the removal of DCF in different types of wastewater (40–60%) to phototransformation, as they observed its elimination in laboratory batches without microalgae inoculum. Photodegradation of DCF in surface waters has been previously reported (Kunkel and Radke, 2012; Zhang et al., 2008). In HRAPs, Matamoros et al. (2015) observed that the removal of this drug was considerably higher during the warm/summer season (82–92%) compared to the cold season (21–29%). Other factors such as the transparency of the plastic material of the tubes in the PBR (Harris et al., 2013) may also reduce the light penetration and the photodegradation rates of photosensitive compounds, compared to those observed in open systems.

3.3.2. Personal care products

The fragrances HHCB and AHTN were only partially removed, with average RE% of 45% and 20%, respectively. These results are lower than those obtained in a previous campaign in the same location (García-Galán et al., 2018), and also to those obtained in open systems operating as secondary treatments (51% ± 12 for HHCB and 46% ± 7 for AHTN) (Matamoros et al., 2015). Laboratory scale assays also yielded higher removals (near 100%) after 7–10 d (Díaz-Garduño et al., 2017; Matamoros et al., 2016). Both compounds have high log K_{ow} (>5) and log K_{oc} (>3.7) and a very low biodegradability, being biomass adsorption the most probable removal pathway. Regarding DEET, an average negative removal was obtained for DEET. Díaz-Garduño et al. (2017) obtained removal efficiencies for DEET ranging from negative values (n = 2) to 55% (n = 1) in laboratory scale batch reactors.

3.3.3. Organophosphate flame retardants and surfactants

TBP was removed by a 43% ± 7, whereas TCEP concentrations in the effluent of the PBR were similar than those of the influent. This is

Table 2
Average PBR effluent concentrations (ng L^{-1}) (used as measured environmental concentrations, MEC), ecotoxicity endpoints used for the different trophic levels considered (mg L^{-1}) and hazard quotients (HQ) estimated.

		Average MEC (ng L^{-1})	TOXICITY ENDPOINTS (mg L^{-1})				HQ (effluent)			
			Green algae	Invertebrate	Crustaceans (*Daphnia magna*)	Fish	Green algae	Invertebrate	Crustaceans	Fish
PHARMACEUTICALS	**Diazepam (DZP)**	0.38 ± 0.07	–	47.3[5]*	4.3[6]	0.3[9]*	–	8.2E-06	9.2E-05	1.4E-03
	Carbamazepine (CBZ)	665.1 ± 27.5	74[2]	0.4[5]	13.8[6]	54.2[9]	8.9E-03	**1.8**	4.8E-02	1.2E-02
	Ibuprofen (IBU)	101.4 ± 68.6	315[2]	–	>45[6]	0.7[7]*	3.2E-04	–	2.2E-03	1.5E-01
	Diclofenac (DCF)	555.9 ± 90.4	72[2]	–	28.1[6]	71[10]*	7.7E-03	–	1.9E-02	7.8E-03
PERSONAL CARE PRODUCTS	**Galaxolide (HHCB)**	109.2 ± 22.8	0.7[1]	0.3[4]*	2.7[6]	3.6[9]*	1.5E-01	3.8E-01	4.1E-02	7.8E-01
	Tonalide (AHTN)	101.1 ± 8.5	0.5[1]	0.5[4]*	0.2[6]	0.1[7]*	2.2E-01	2.2E-01	4.1E-01	**1.01**
	N,N-diethyl-toluamide (DEET)	544.6 ± 54.6	–	–	1[6]	71.2[8]*	–	7.8E-02	5.4E-01	7.6E-03
ORGANOPHOSPHATE FLAME RETARDANTS	**Tributyl phosphate (TBP)**	28.2 ± 6.3	1.1[2]	12.5[5]	35[6]	1.3[7]*	2.6E-02	2.2E-03	8.1E-04	2.8E-02
	Tris-(2-chloroethyl) phosphate (TCEP)	308.9 ± 23.5	51[2]	–	330[6]	3.7[9]*	6.1E-03	–	9.4E-04	8.2E-02
SURFACTANTS	**2,4,7,9-Tetramethyl-5-decyne-4,7-diol (TMDD)**	167.2 ± 20			91[6]	36			2.2E-03	5.5E-03

1- Pseudokirchneriella subcapicata; 2-Desmodesmus subspicatus; 3: Tetrahymena pyriformis: 4:Chironomus riparius; 5: Brachionus calyciflorus: 6- Daphnia magna 7: Pimephales promelas. 8: Oncorhynchus mykiss. 9: Danio rerio. 10- Cyprinus carpio
*: LC_{50} values (the other toxicity endpoints are EC_{50} values).
Values for TMDD are taken from Guedez and Puttman (2014).
Green algae and crustaceans endpoint values for TCEP are taken from Cristale et al., (2013).

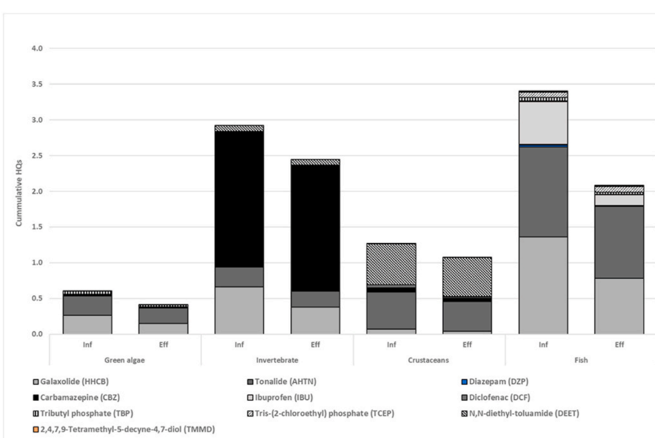

Fig. 4. Cumulative HQs for each of the thropic levels considered in the feed water of the PBR (first column) and effluent (second column). For all the compounds, HQs were available for at least 3 of the 4 trophic levels considered, with the exception of TMDD (only crustaceans and fish).

probably due to the plastic components of the PBR system, which may release TCEP to the aqueous phase during treatment, as already suggested by (Rodil et al., 2012, 2009) in conventional WWTPs facilities. In a previous sampling campaign in the same location, TCEP was removed only in a 20% (García-Galán et al., 2018). In open systems acting as secondary treatments, Matamoros et al. (2015) obtained RE% in the range 15–39% for TCEP and 24–82% for TBP under HRT of 4 d, reaching better results with longer HRTs (8 d). High Henry constant for TBP (K_H of 0.3 atm m^3 mol^{-1}) may be indicative of volatilization events and its partial removal in HRAPs, and also in the open tanks of the semi-closed PBR. Indeed, aerated batch reactors at laboratory scale confirmed the recalcitrance of TCEP, which was removed <20% after 10 d, whereas that TBP was more efficiently removed (Matamoros et al., 2016). TCEP is a highly hydrophilic compound (log $k_{ow} = 1.44$) so it is not likely to be adsorbed onto the biomass either, contrary to TBP (log $k_{ow} = 4$). Furthermore, TCEP is a highly stable molecule, not prone to biodegradation, which, together with its high solubility, makes it a highly mobile and persistent pollutant once discharged into environmental waters (Blum et al., 2018; Reemtsma et al., 2008; Rodil et al., 2012). Last of all, the surfactant TMDD was removed by a 33% in the PBR, and considering its low solubility and high log K_{ow}, adsorption onto biomass seems a feasible removal pathway within the system. Conventional WWT is generally quite inefficient in removing this surfactant, with barely no elimination (Blum et al., 2018, 2017; Guedez and Püttmann, 2014).

3.4. Environmental risk assessment

As indicated in section 2.5, hazard quotients (HQs) were calculated for those CECs not fully removed during PBR treatment, following equation [1]. To estimate the PNEC, toxicity data for different standard test species covering different trophic levels were obtained from the ECOTOX database of the Environmental Protection Agency (EPA). Chronic exposure indicators (NOEC) would be preferable in the case of CECs, as non-target species are exposed to low concentrations of these contaminants during long periods of time, so unexpected long-term effects could eventually appear. However, as chronic toxicity data are frequently unavailable, PNECs were calculated using EC_{50} and LC_{50} as indicators of acute toxicity (regarding immobilization and mortality, respectively). These values were divided by an uncertainty factor (1000) to become more representative values of the real situation under environmental conditions (longer periods of exposure) (Sanderson et al., 2004; Valcárcel et al., 2011). HQs were estimated for green algae, invertebrates, crustaceans and fish (standard test species, see Table 2). In order to establish a worst case scenario, when different toxicity endpoints were available for a given compound, the lowest toxicity value was used (Table S3 in Supplementary Material). Given their homogeneity, the average measured concentrations in the PBR effluent for each CEC were used. HQ values are shown in Table 2. Calculations were subjected to the availability of the toxicity data; in consequence, risk evaluation for LZP and OXA could not be done. However, both drugs have a similar low solubility and high log K_{ow}-K_{oc} values that indicate a high tendency to adsorb onto biomass and bioaccumulate, as demonstrated in previous studies (García-Galan et al., 2017; Lagesson et al., 2016). Amongst the different CECs still present in the PBR effluent, HQ values between 1 and 10 were obtained only for AHTN (fish) and CBZ (invertebrates), implying a moderate hazard in the receiving water body. HQ values between 0.1 and 1 (low risk) were obtained for the fragrances AHTN and HHCB in most cases, for IBU against fish and for DEET against crustaceans. Nevertheless, the majority of the compounds yielded HQs <0.1, meaning that no environmental risk would be derived from their discharge on the PBR effluent. Given the results obtained, and considering the cumulative HQs in the effluent, the sensitivity of the different trophic levels would be as follows: invertebrates > fish > crustaceans > green algae (Fig. 4). Despite the overall good removal efficiency of the PBR for the different CECs studied, the decrease of the derived ecotoxicity risk was only moderate, with a 38% reduction for fish, 15% for invertebrates, 16% for crustaceans and only a 3% for green algae. The low removals of CBZ or AHTN would lead to a higher impact against different species, which are mostly unaffected by the presence of the other CECs. Indeed, different authors have reported a moderate to high environmental risk derived from the CBZ presence in European surface waters (Palma et al., 2020; Zhou et al., 2019), and Díaz-Garduño et al. (2017) obtained HQ>1 for AHTN and green algae after microalgae treatment. In the prioritization study for pharmaceuticals performed by Zhou et al. (2019) in different European countries, DCF, IBU and CBZ posed the highest risk to aquatic ecosystems. However, the levels obtained after microalgae treatment in the present study yielded HQ<0.1 for all of them (except for CBZ against invertebrates). It should be considered that PBR effluent concentrations will be subjected to further dilution once discharged in the receiving water bodies. Therefore, the estimated risk derived from exposure would be considerably lower. On the contrary, the number of CECs potentially present in the water analyzed is much higher than the 15 compounds considered in the present study. Furthermore, it should be taken into account that conventional risk assessment of CECs is usually based on this concentration addition for estimating the mixture toxicity (European Comission, 2009), ignoring toxicity derived from synergies, additive effects or antagonistic effects (Baek et al., 2019). Likewise, addition of HQs of pharmaceuticals with similar modes of action (i.e. psychiatric drugs or anti-inflammatories) could result in the overestimation of adverse effects. Mixture toxicity is out of the scope of the present study, but it is actually a hot topic within the scientific community, which is currently devoting a huge effort to discern and evaluate more realistic toxicity scenarios.

4. Conclusions

The capacity of a semi-closed, tubular horizontal PBR to remove 13 contaminants of emerging concern (CECs) detected in water from an agricultural irrigation channel was evaluated. Removal efficiencies ranged from efficiently removed (>70%) for IBU, DZP, LZP and OXA; moderately removed (35–70%), for DCF, HHCB, TBP and TMDD; and poorly removed (<35%) for AHTN, CBZ, TCEP and DEET. Nevertheless, for most of the compounds their removal were comparable to those obtained in conventional WWTPs. On the other hand, very good elimination efficiencies were obtained for the benzodiazepines OXA (highly recalcitrant) and DZP, which are generally barely removed in conventional treatment systems. An environmental toxicity evaluation has been performed to fathom out the impact of the PBR effluent in the receiving water body. Despite most of the compounds have an HQ <0.1, implying no risks associated, the cumulative assessment highlighted a low to moderate risk (1<HQ<3.5) for the different trophic levels except for green algae. The PBR treatment reduced the environmental risk between a 3% (green algae) and 38% (fish). Overall, the good treatment efficiency of the PBR, together with the related low O&M costs and sustainability, makes this treatment approach a feasible alternative to conventional treatment. Removal data from large scale systems operating under real conditions is still scarce, especially in closed or semi-closed systems, as studies under laboratory controlled conditions are predominant. On the other hand, research usually does not consider the adsorbed concentration of the target CECs in the biomass, which would contribute to discern the main removal mechanisms in these systems. Therefore, future research should focus on the role of biomass adsorption in the elimination of these (and other) CECs, contributing to establish complete mass balances in microalgae systems. Thus, biomass analysis should be performed to obtain actual adsorbed concentrations on it. Furthermore, other potentially influencing parameters, such as temperature, pH or the presence of other living organisms or substances such as protozoa and/or heavy metals, should not be neglected in future studies.

Credit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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