High-rate algal pond for removal of pharmaceutical compounds from urban domestic wastewater under tropical conditions. Case study: Santiago de Cali, Colombia

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ABSTRACT

This study evaluated the capacity of a pilot-scale high-rate algal pond (HRAP) to remove pharmaceutical compounds (PCs) from domestic wastewater in the city of Santiago de Cali, Colombia. The compounds analyzed included antiepileptics, hypolipidemic drugs, tranquilizers and analgesics, and anti-inflammatory drugs. The HRAP operated under a continuous water flow of 0.2 $m^3 d^{-1}$ and a 3-day hydraulic retention time (HRT). Removal efficiencies were high (>70%) for fenofibric acid, ibuprofen, and paracetamol; medium (30–70%) for gabapentin, lamotrigine, fenofibrate, gemfibrozil, diclofenac, ketoprofen, naproxen, and pentoxifylline; and low (<30%) for carbamazepine and its metabolite 10,11-Dihidro-10,11-dihidroxicarbamazepine (CBZ-Diol). The findings herein are similar to other studies, but were obtained with a shorter HRT. These results show that tropical environmental conditions favor photodegradation and contribute to the development of microalgae and the biodegradation process. Twenty microalgae species were identified, with the phylum *Chlorophyta* as the most abundant, particularly due to its natural introduction. The removal of the PCs also reflected a percentage reduction (>50%) in the ecological hazard posed by most of the compounds, although it is important to note that the hazard from gemfibrozil and ibuprofen remained high even after treatment, indicating the need for complementary treatment.

Key words | *Chlorophyta*, Colombia, domestic wastewater, high-rate algal pond, pharmaceutical compounds, tropical conditions

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HIGHLIGHTS

- The removal efficiency of pharmaceutical compounds under conditions of the American tropic was evaluated.
- Removal efficiencies obtained were similar to other studies but with a 3-day HRT.
- The results suggest that removal mechanisms could have been biodegradation and photodegradation.
- The microalgal diversity was determined, phylum *Chlorophyta* being the most abundant.
- The ecological hazard was reduced by more than 50%.

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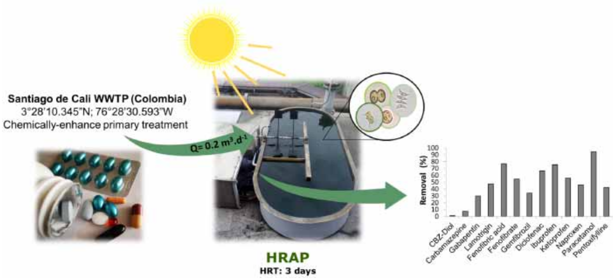
GRAPHICAL ABSTRACT



INTRODUCTION

Pharmaceutical compounds (PCs) are substances that are used to prevent, cure, or alleviate diseases and treat their sequelae. Since they have been designed to withstand inactivation before their therapeutic effect is released, they can retain their chemical structure for as long as they remain in the organism (Fent et al. 2006). As a result, they can be released into the environment in concentrations of μgL^{-1} and ngL^{-1}, thereby becoming microcontaminants. Their persistent nature and/or continuous introduction into the environment, along with low removal efficiencies by conventional wastewater treatment (Zhou et al. 2012), facilitate their entrance into water bodies and their contact with aquatic biota.

Studies in Colombia have reported the presence of PCs in wastewater, surface water, and drinking water in the cities of Bogota, Medellin, Cali, Florencia, and Tumaco (Bedoya-Ríos et al. 2018; Botero-Coy et al. 2018; Madera-Parra et al. 2018). A study conducted in Cali showed that the wastewater contains paracetamol, naproxen, ibuprofen, diclofenac, gemfibrozil, fenofibric acid, gabapentin, carbamazepine, and CBZ-Diol, in average concentrations between 75 and 4,900 ngL^{-1} (Madera-Parra et al. 2018). The presence of these compounds is associated with cultural trends in self-medication, given easy access to over-the-counter medications, widespread advertising, and delays in obtaining medical care.

A high-rate algal pond (HRAP) consists of a shallow raceway reactor where microalgae and bacteria are grown in symbiosis, with mechanical mixing of the mixed liquor to increase biomass production and improve removal of pollutants (Passos et al. 2014; Solimeno & García 2017). The different biotic and abiotic processes that come together in an HRAP contribute to reducing microcontaminants through mechanisms such as biodegradation, photodegradation, and sorption (Matamoros et al. 2015; Xiong et al. 2018). Biodegradation and photodegradation are transformation processes that involve the action of microalgae, bacteria, and sunlight, in which complex molecules transform into simpler ones. Sorption refers to absorption and adsorption in the microalgae and/or sediments. These mechanisms transfer the compound from the liquid matrix to the solid fraction in the HRAP, although since the process is not selective, the capture of target contaminants could be impeded by other contaminants that may occupy the adsorption surface (Xiong et al. 2018; Sutherland & Ralph 2019).

Based on this context, the present study was aimed at evaluating the capacity of a pilot-scale HRAP to remove PCs present in domestic wastewater under American tropical conditions, by analyzing the effects of environmental conditions and algal diversity on possible removal mechanisms. The Hazard Quotient (HQ) method was also applied in order to measure the ecological hazard from the contaminants before and after the HRAP.

METHODS

Location of the pilot plant

The experimental unit was operated with the effluent of the Santiago de Cali wastewater treatment plant, at geographic coordinates 3°28′10.345″N–76°28′30.593″W. This plant is operated using chemically-enhanced primary treatment with coagulation, flocculation, and sedimentation processes, with ferric chloride as a coagulant and the polymer FLOPAM AN 945 as an adjuvant.

The HRAP was designed with a volume of 0.6 m^3, a surface area of 2 m^2, a width of 1.0 m, a length of 2.2 m, a depth of 0.3 m, a continuous water flow of 0.2 m^3d^{-1}, and a 3-day HRT. A paddle wheel was installed at the entrance, with a velocity of 5 RPM. Figure S1 (supplementary material) shows the reactor's dimensions.

Sample collection and handling

The bioreactor was operated in two phases, according to the bimodal precipitation pattern characteristic of the region. The first phase was between February and June (it was mostly influenced by the wet season) and the second phase was between June and August (dry season). The start-up period was 30 days in both phases (February–March for the former and June–July for the latter). No samples were taken during the start-up periods, only *in situ* parameters were measured. The microalga *Parachlorella kessleri* was only inoculated in the first phase. During the second phase the HRAP was colonized by natural introduction.

PCs and the chemical oxygen demand (COD) were determined by conducting 16 compound samplings (12 samplings in the first phase and 4 samplings in the second phase), in which one sample was collected weekly (every Wednesday) from the influent and effluent of the bioreactor. The samplings were taken at 12-hour periods, taking aliquots every hour through 7–19 hours. The samples were collected in amber-colored glass containers, which were refrigerated at 4 °C until the chemical analysis.

The COD was determined in accordance with ASTM D1252-00. The effluent COD was filtered (fCOD) using 1.5-μm fiberglass filters to remove the organic load of microalgae. For the determination of PCs, the samples collected were submitted to double filtration using 1.5-μm fiberglass filters and 0.45-μm cellulous membranes. They were then packed in previously-refrigerated stainless steel flasks and shipped to the Karlsruhe Technologiezentrum Wasser-TZW laboratory (Germany) for chemical analysis.

In situ parameters were also measured, including pH, dissolved oxygen (DO), temperature, and oxido-reduction potential (ORP, electrode Ag/AgCl with reference Thermo Scientific 9179BNMD) at the influent, middle, and effluent of the pond, and photosynthetically active radiation (PAR) and chlorophyll-a in the middle of the pond. These measurements were taken three days per week over 12-hour periods with records taken every hour.

Analytical procedure

The determination of PCs began with acidification of 20 mL of the sample to a pH of 3 by adding hydrochloric acid. Solid-phase extraction was then performed with 60 mg of Strata × (Phenomenex) and elution was conducted with 4 ml of acetone and 1.5 mL of methanol. The solvent was then evaporated until dry. The dry residual was reconstituted with 20 μL of a 50:50 (v:v) mixture of methanol and acetone and 180 μL of distilled water. A 60-μL aliquot was then injected into the HPLC/MS-MS system, which consisted of a 1,260 Infinity liquid chromatography (Agilent Technologies) that was coupled to an API 5500 mass spectrometer (AB Sciex) with an Electrospray interface. Chromatographic separation was performed in a 100 mm × 2.1 mm Zorbax Eclipse XDB-C18 analytical column (Agilent Technologies) using a 5-mM aqueous ammonium formate solution (eluent A) and a 2-mM ammonium formate solution, with a 1:2 mixture (v:v) of methanol and acetonitrile (eluent B) as elution solvents. The elution gradient began with 70% of eluent A, which was adjusted to 100% of eluent B at minute 3 and held constant until minute 7, and adjusted again to 70% of eluent A from minute 7 to 8. The second gradient program began after 5 minutes of equilibrium. The eluent flow rate was 0.2 $mLmin^{-1}$ and the temperature in the column oven was set to 30 °C. Detection was performed in negative or positive mode depending on the properties of the analyte.

Identification of algal diversity

The biological samples were collected weekly (every Wednesday) from the middle of the pond in 250-mL amber containers. The algae diversity was identified during four periods: period I (February–March), period II (April–May), period III (June), and period IV (July–August). The first three periods corresponded to the first phase of operations. Period IV corresponded to a second phase with a second bioreactor start-up (without inoculum) in order to facilitate the natural introduction of local algal species, due to an herbivory problem that required suspending the first phase.

The cellular density of the algae species was determined by cell count with a Neubauer chamber and an inverted microscope (Nikon Eclipse T5100), based on the formula proposed by Wetzel & Likens (2000).

The individuals were identified to the highest level possible based on a literature search and review in AlgaeBase, Wehr & Scheath (2003) keys and taxonomic descriptions, and Bicudo & Menezes (2006). Microalgae diversity was calculated using the Shannon diversity index (H') and Simpson's dominance index (1-D), with Past 3.21 software (2001).

Estimation of ecological hazard

The ecological hazard was estimated with the deterministic HQ method (Hazard Quotient), which is the ratio of the field-measured environmental concentration (MEC) to the predicted no-effect concentration (PNEC). This corresponds to the highest concentration at which there are no adverse effects on an indicator organism (European Commission 2003).

$$HQ = MEC/PNEC \quad (1)$$

The available aquatic toxicity information was used to determine PNEC by applying Assessment Factors (AF) based on available long-term NOEC (no observed effects concentration) toxicity information or short-term EC50 data on fish, daphnias, and algae (European Commission 2003), according to the following equation:

$$PNEC = \text{Most sensitive toxicity datum}/AF \quad (2)$$

HQ was interpreted as follows: no hazard when HQ<0.1, insignificant hazard but potential adverse effects should be considered when between 0.1 and 1.0, medium hazard with moderate effects when between 1.0 and 10, and high hazard when HQ>10.

Statistical methods

The significant differences of the results of *in situ* parameters in the influent, middle of the pond, and the effluent were determined during the time of sampling. Linear models with different covariance structures were used (homogeneous and heterogeneous variances). The best model was selected through the penalized likelihood methods Akaike information criterion (AIC) and Bayesian information criterion (BIC). Correlation indicators between *in situ* parameters and PCs were analyzed with the Pearson or Spearman correlation coefficient, according to the Shapiro Wilk normality test.

The statistical analysis was carried out through the freeware program R version 3.5.0 for the determination of statistical differences and significant correlations at a level of significance of 5%.

RESULTS AND DISCUSSION

In situ parameters

Table 1 presents the minimum, maximum and average results of the *in situ* parameters and the COD measured in the HRAP. The results of daily monitoring for each parameter are presented in the supplementary material (Figure S2 to Figure S9).

The results of the *in situ* parameters show that the environmental conditions were ideal for good development of microalgae, especially in the afternoon (between 3pm and 7pm) when more photosynthetic activity was registered, as measured by chlorophyll-a (Figure S7), with values as high as 1.36 μgmL^{-1}. Values between 1.1 and 4.0 μgmL^{-1} have been reported for algae systems with substrates such as domestic wastewater (Arashiro *et al.* 2019; Galès *et al.* 2019). The values in the present study were low because of unstable algae populations due to variations in the influent contaminant load (Figure S9).

Table 1 | Results of the parameters measured at the influent, middle, and effluent of the HRAP

	Influent			Middle			Effluent		
Parameter	**Min**	**Max**	**Average**	**Min**	**Max**	**Average**	**Min**	**Max**	**Average**
pH	5.75	7.36	6.94 ± 0.16	6.02	11.53	8.99 ± 0.97	6.95	11.13	8.97 ± 0.93
Conductivity (μScm^{-1})	187	740	617.33 ± 70.75	310	653	483.22 ± 64.99	355	656	495.62 ± 64.82
Temperature (°C)	13.6	36.2	26.89 ± 2.26	21.6	31.8	25.91 ± 2.5	21.6	31.7	25.95 ± 2.45
ORP (mV)	−350.6	−49.3	− 158.57 ± 39.54	−343.6	−14.9	−117.7 ± 35.92	−343.1	−10.1	− 122.44 ± 35.92
DO (mgL^{-1})	0	2.2	0.53 ± 0.32	0.17	36.3	9.51 ± 5.82	0.15	29.67	9.63 ± 6
Chlorophyll A (μg mL^{-1})	NM	NM	NM	0	1.36	0.78 ± 0.31	NM	NM	NM
PAR (μmol m^{-2} s^{-1})	NM	NM	NM	0	2,380.33	874.85 ± 593.09	NM	NM	NM
COD (mgL^{-1})	89.18	275.3	162.38 ± 50.17	NM	NM	NM	24.32[a]	98.36[a]	55.91 ± 28.69[a]

NM, Not measured.
[a]fCOD.

An increase in pH and DO (Figure S2 and Figure S6) was found in the pond, with average values of 8.99 units and 9.51 mgL^{-1}, respectively. This was due to the photosynthetic activity through which CO_2 and HCO_3 are consumed, resulting in a basic medium with high pH values, greater DO production (Park & Craggs 2010; Craggs et al. 2011). The ORP values (Figure S5) remained negative in all monitoring, showing a reducing environment characteristic of wastewater with high concentrations of organic pollutants (Mahapatra et al. 2013). The ORP had a slight increase in the middle and effluent of the HRAP due to the increased DO levels. The negative ORP values could be associated with the high levels of pH (Mahapatra et al. 2013), the dynamic of all micro-organisms to different depths and light/dark cycles with a change of aerobic to anaerobic conditions (See Figure S10), for example, presence of denitrifying or reducing-sulfate bacteria, in addition to organic exudates of these micro-organisms, and reduction of Fe^{+3} ions (Dušek et al. 2008).

COD reduction was also observed (Figure S9) with an average removal efficiency of 65.49% and an average fCOD of 55.91 mgL^{-1} in the effluent. The average conductivity (Figure S2) was associated with the removal of nutrients such as nitrogen and phosphorus. Although this study did not measure those nutrients, this technology is known for its high potential for removing them (García et al. 2006; Gentili & Fick 2017).

Temperature is an important parameter for the physiochemical processes in the pond. This stayed within a range of 21.6–31.8 °C, which is favorable to algae production. Midday was a critical period when temperatures were highest, in the middle of the pond (Figure S4), which increases the risk of photorespiration and the consequent decrease in productivity (Park et al. 2011).

PAR refers to the amount of energy that organisms can use for photosynthesis. The average PAR value was 874.85 $\mu mol \cdot m^{-2}s^{-1}$, with a maximum of 2,380.33 $\mu mol \cdot m^{-2}s^{-1}$ registered at 12:00 noon (Figure S8). High solar radiation values can cause photoinhibition, thereby affecting the photosynthetic activity of the microalgae, which can become saturated at a value of 200 $\mu mol \cdot m^{-2}s^{-1}$ (Masojídek et al. 2003). Nevertheless, other mechanisms that remove micro-contaminants can also be stimulated, such as direct photolysis.

Removal efficiency of pharmaceutical compounds

Table 2 presents the minimum, maximum, and average concentrations and removal efficiency values of the PCs. Fenofibric acid, ibuprofen, and paracetamol had high average efficiencies (>70%). Medium average efficiencies (30–70%) were obtained for gabapentin, lamotrigine, fenofibrate, gemfibrozil, diclofenac, ketoprofen, naproxen, and pentoxifylline, and low efficiencies (<30%) were found for carbamazepine and CBZ-Diol.

Carbamazepine and CBZ-Diol are frequently found in wastewater (Fenet et al. 2012; Madera-Parra et al. 2018). In an HRAP, Matamoros et al. (2015) obtained higher carbamazepine removal efficiencies than those reported herein; specifically, 46 and 62% with an HRT of 4 and 8 days, respectively. Meanwhile, de Wilt et al. (2016) reported efficiencies <30% with an HRT between 0 and 31 days and Villar-Navarro et al. (2018) reported efficiencies <50% with an HRT of 3 and 9 days. Other antiepileptics that were detected by the present study were gabapentin and lamotrigine, with a medium removal efficiency. Gabapentin is frequently detected in wastewater (Chen et al. 2016; Madera-Parra et al. 2018), while the lamotrigine had a low occurrence in the wastewater studied, having exceeded the limit of quantification (LOQ) in only two samples.

Analgesics/anti-inflammatory drugs are one group of compounds that have been widely studied and detected in wastewater. In this regard, the present study obtained medium removal efficiencies for diclofenac, ketoprofen, and naproxen, which is similar to findings by other investigations (de Wilt et al. 2016; Hom-Diaz et al. 2017; Villar-Navarro et al. 2018) but much lower than the efficiencies reported by Matamoros et al. (2015), which were over 80%. Other authors have reported higher removal efficiencies for ibuprofen and paracetamol, as much as 100% (Matamoros et al. 2015; de Wilt et al. 2016; Hom-Diaz et al. 2017; Villar-Navarro et al. 2018).

With regard to the hypolipidemic group, studies have reported the presence of fenofibric acid and gemfibrozil in wastewater (Madera-Parra et al. 2018). In the present study, fenofibrate exceeded the LOQ in only two samples (with a removal efficiency of 54.5%), since it is more common to find fenofibric acid, which is a byproduct of the metabolization of fenofibrate in the organism. The average removal efficiency of fenofibric acid in the HRAP was 77.1%. The removal efficiency of gemfibrozil varied widely over the study period, from 0 to 84.3%.

With regard to the tranquilizer group, pentoxifylline was the only one detected, which was found in two samples. This compound was not detected by Madera-Parra et al. (2018) and its presence in wastewater has been reported much less than other PCs. The present study found removal efficiencies of 30.0 and 54.5%.

In general, the present study obtained removal efficiencies that are very similar to those reported by other

Table 2 | Concentrations and removal efficiency of pharmaceutical compounds with HRAP

Therapeutic group	PCs	Influent concentration (μgL^{-1})	Effluent concentration (μgL^{-1})	Removal efficiency
Antiepileptics	CBZ-Diol	0.45–1.30 (0.98 ± 0.20)	0.81–1.50 (1.10 ± 0.20)	0.0–10.0 (1.2 ± 3.26)
	Carbamazepine	0.10–0.35 (0.17 ± 0.07)	0.11–0.23 (0.16 ± 0.03)	0.0–48.6 (7.7 ± 15.06)
	Gabapentin	0.25–0.93 (0.55 ± 0.18)	0.11–0.66 (0.38 ± 0.15)	0.0–86.3 (30.1 ± 23.82)
	Lamotrigine	0.10[a]	0.052–0.053 (0.053 ± 0.001)	47.0–48.0 (47.5 ± 0.71)
	Primidone	< 0.10	< 0.05	–
Hypolipidemic drugs	Clofibric acid	< 0.10	< 0.05	–
	Fenofibric acid	0.16–0.32 (0.23 ± 0.05)	0.05[a]	68.8–84.4 (77.1 ± 4.61)
	Bezafibrate	< 0.10	< 0.05	–
	Etofibrate	< 0.10	< 0.05	–
	Fenofibrate	0.11	0.05[a]	54.5
	Gemfibrozil	1.10–2.60 (1.99 ± 1.99)	0.22–2.40 (1.33 ± 0.68)	0.0–84.3 (34.2 ± 31.03)
Analgesics and anti-inflammatory drugs	Diclofenac	0.13–0.47 (0.29 ± 0.09)	0.05[a]–0.18 (0.09 ± 0.03)	42.3–89.4 (66.6 ± 11.94)
	Fenoprofen	< 0.10	< 0.05	–
	Ibuprofen	1.40–4.60 (3.18 ± 0.93)	0.05[a]–2.10 (0.75 ± 0.61)	17.6–98.6 (75.7 ± 21.18)
	Indomethacin	< 0.10	< 0.05	–
	Ketoprofen	0.11–0.12 (0.11 ± 0.01)	0.05[a]	54.5–58.3 (55.8 ± 2.19)
	Naproxen	3.20–8.10 (5.91 ± 1.39)	1.30–4.20 (3.03 ± 0.83)	15.6–83.1 (46.3 ± 16.75)
	Paracetamol	0.21–120 (24.78 ± 41.97)	0.05[a]	76.2–100.0 (94.4 ± 8.88)
Tranquilizers	Diazepam	< 0.10	< 0.05	–
	Oxazepam	< 0.10	< 0.05	–
	Pentoxifylline	0.10–0.11 (0.11 ± 0.01)	0.05[a]–0.07 (0.06 ± 0.01)	30.0–54.5 (42.3 ± 17.36)

[a]The value of the limit of quantification (LOQ) was assumed to estimate the removal efficiency.

authors (Matamoros *et al.* 2015; de Wilt *et al.* 2016; Hom-Diaz *et al.* 2017; Villar-Navarro *et al.* 2018), but with a shorter HRT, which can indicate that the conditions in the American tropics may have a positive effect on the performance of the HRAP. According to Luo *et al.* (2014), the efficiency of removing organic contaminants depends on the operations of the treatment system and environmental conditions. Previous studies have reported that summer conditions improve the removal of PCs (Matamoros *et al.* 2015; Villar-Navarro *et al.* 2018; Tolboom *et al.* 2019), during which temperature and solar radiation is greater, and therefore, there is more microalgae activity. In addition, Norvill *et al.* (2016) have suggested that biodegradation rates of PCs can increase as a result of changes in pH and DO, conditions that are characteristic of the American tropics.

Villar-Navarro *et al.* (2018) obtained higher removal efficiencies with an increase of solar radiation of 20 $MJm^{-2}d^{-1}$ (1,058 $\mu mol\ m^{-2}s^{-1}$), especially for anti-inflammatory analgesics. This value is very similar to the average solar radiation measured in the present study. In addition, Matamoros *et al.* (2015) found that an increase in average daily solar radiation from 74 Wm^{-2} to 282 Wm^{-2} improved removal of diclofenac and ketoprofen.

Effects of environmental conditions on PC removal efficiencies

Table 3 presents the correlation analysis between PCs most frequently observed in this study and the *in situ* parameters such as temperature, PAR, pH, DO and ORP. No strong

Table 3 | Correlations between PC removal efficiencies and *in situ* parameters

	Temperature (°C)	PAR (μmol m^{-2} s^{-1})	pH	DO (mgL^{-1})	ORP (mV)
PAR (μmol m^{-2} s^{-1})	− 0.49				
pH	**0.72**	− **0.77**			
DO (mgL^{-1})	**0.86**	− **0.71**	0.90		
ORP (mV)	0.16	− 0.26	− 0.32	− 0.25	
CBZ-Diol	− 0.65	**0.65**	− 0.41	− 0.41	− **0.65**
Carbamazepine	**0.64**	− 0.46	− 0.09	− 0.15	− 0.06
Gabapentin	− 0.19	0.37	0.09	− 0.04	− **0.55**
Fenofibric acid	− **0.53**	0.49	− **0.84**	− **0.74**	**0.63**
Gemfibrozil	− 0.03	− **0.58**	**0.63**	**0.58**	− 0.21
Diclofenac	0.09	0.20	0.29	0.30	− **0.63**
Ibuprofen	**0.54**	− **0.94**	**0.73**	**0.75**	0.03
Naproxen	0.31	− **0.90**	0.34	0.35	− 0.18
Paracetamol	− 0.14	− 0.14	− 0.43	− 0.43	**0.54**

Figures in bold indicate a high positive correlation (>0.5).

correlations were observed; however, this analysis suggests positive correlations between CBZ-Diol and PAR; carbamazepine and temperature; fenofibric acid and ORP; gemfibrozil with pH and DO; ibuprofen with temperature, pH, and DO; and paracetamol and ORP. Nonetheless, it is important to note that more specific studies are required.

Previous studies had reported that CBZ-Diol and carbamazepine have a highly hydrophilic and recalcitrant nature, they are very stable and resistant to mechanisms such as biodegradation and photodegradation (Matamoros *et al.* 2015; Villar-Navarro *et al.* 2018). They also have a low potential for sorption (de Wilt *et al.* 2016; Villar-Navarro *et al.* 2018). Nevertheless, the results of the correlation may indicate that the main removal mechanism of CBZ-Diol was direct photodegradation, possibly, facilitated by the paddle wheel movement that allowed its frequent exposure to sunlight (Norvill *et al.* 2016). The correlation between carbamazepine and temperature is not conclusive for predicting the removal mechanisms, but these may be associated with anaerobic biodegradation through the hydrolysis of the amide group of carbamazepine (Schwarzenbach *et al.* 2016), especially in the evenings when the anaerobic conditions prevailed.

According to earlier studies, the main removal mechanism of ibuprofen is the biodegradability (Koumaki *et al.* 2017; Sutherland & Ralph 2019). In the present study, the positive correlation between ibuprofen with temperature, pH, and DO support aerobic biodegradation as its main removal mechanism, which is associated with enantioselective degradation (Matamoros *et al.* 2009, 2016).

Some studies have reported that the biodegradability of gemfibrozil is low (Grenni *et al.* 2013; Fabbri *et al.* 2017), but a slight positive correlation with the pH and DO may relate its removal in the HRAP with aerobic biodegradation. Grenni *et al.* (2018) found that the co-presence of naproxen had a negative influence over gemfibrozil biodegradation because the bacterial community presumably found naproxen easier to degrade than gemfibrozil and neglected the latter. In this regard, the variation of gemfibrozil removal efficiency in the HRAP may be related to competition with other compounds with better biodegradability; for example, paracetamol and ibuprofen.

Paracetamol and fenofibric acid had a slight positive correlation with ORP. This could be related to multiple biotic and abiotic processes due to the HRAP being a dynamic ecosystem. Paracetamol has been considered as biodegradable and photodegradable (Sutherland & Ralph 2019), while fenofibric acid is known for its rapid photodegradation (Cermola *et al.* 2005; Mathon *et al.* 2019). The correlation with ORP could be associated with an indirect photodegradation caused by the reduction of Fe^{+3} through photosensitizers such as chromophoric dissolved organic matter (CDOM) and the complexation of carboxylic acids (degradation products of the organics excreted by algae) with iron. This reaction promotes the hydroxyl radical production, which is highly oxidizing (Norvill *et al.* 2016).

Other compounds showed negative correlations or lower than 0.5, possibly by the few data available. According to previous studies, the removal of gabapentin is associated with aerobic biodegradation (Chen *et al.* 2016; Henning *et al.*

2018) and it can also be susceptible to photodegradation (Herrmann *et al.* 2015). Lamotrigine has been found to be hydrophilic, persistent (Bollmann *et al.* 2016), and weakly affected by direct photolysis (Keen *et al.* 2014). Diclofenac is a hydrophobic compound that can have an affinity to the solid fraction in the HRAP (sediments and microalgae). Nevertheless, previous studies have indicated that this compound is mostly affected by photodegradation, and to a lesser degree by biodegradation, just like ketoprofen and naproxen (Baena-Nogueras *et al.* 2017; Koumaki *et al.* 2017; Villar-Navarro *et al.* 2018; Mathon *et al.* 2019). Pentoxifylline is highly hydrophilic and biodegradable (Maeng *et al.* 2011).

Microalgal diversity

A total of 20 microalgal morphospecies were identified, which belonged to six phyla, eight classes, and 11 families. Similar morphospecies were found by Sardi-Saavedra *et al.* (2016) in an HRAP for bioremediation landfill leachate evaluated in a nearby area to the present study. Table 4 presents the total cellular density for each one of the species found in the phyla *Chlorophyta*, *Euglenophyta*, *Bacillariophyta*, *Cryptophyta*, *Charophyta*, and *Cyanobacteria*.

Similar to what was reported by Matamoros *et al.* (2015), the phylum *Chlorophyta* had the greatest species abundance and richness, although the species that were most abundant varied over the evaluation period. Figure 1 shows the microalgae diversity throughout the four periods. *Parachlorella kessleri*, which was used as an inoculum, was dominant during the start-up period (period I), with a cellular density of 5.61E + 07 cell mL^{-1}. Its density then decreased over time due to the natural colonization of *Chlorophyceae* class, especially *Desmodesmus serratus* and other species such as *Scenedesmus denticulatus* Lagerheim, *Scenedesmus dimorphus* (Turpin) Kützing, *Scenedesmus acuminatus* (Lagerheim) Chodat, *Scenedesmus protuberans* F.E.Fritsch & M.F.Rich, *Scenedesmus praetervisus* Chodat, and *Scenedesmus javanensis* Chodat.

Figure 2 presents the variation in total cellular density over the four periods. The total cellular density was greater during period I due to inoculation. It then decreased considerably during the later periods as a result of the natural introduction of other species, an increased contaminant load in the influent, and the arrival of rotifers, copepods, and insect larvae belonging to the Trichoptera genus. The latter resulted in herbivory, which markedly decreased the cellular density of *Desmodesmus serratus* and *Scenedesmus denticulus*, the dominant species in the system at that time. The decrease in the algal density required a second start-up of the bioreactor (without inoculate) and subsequent operation in period IV.

The Shannon diversity index (H′) and Simpson's dominance index (1-D) indicated low diversity during the first phase of the reactor's operations (between 0

Table 4 | Total cellular density of the phyla identified in the HRAP

Phylum	Classes	Families	Species	N (Cell mL^{-1})
Chlorophyta	Trebouxiophyceae	Chlorellaceae	*Parachlorella kessleri*	5.72E + 07
	Chlorophyceae	Scenedesmaceae	*Desmodesmus serratus*	4.80E + 06
	Chlorophyceae	Scenedesmaceae	*Scenedesmus denticulatus*	1.13E + 06
	Chlorophyceae	Scenedesmaceae	*Scenedesmus dimorphus*	4.00E + 05
	Chlorophyceae	Scenedesmaceae	*Scenedesmus acuminatus*	1.30E + 05
	Chlorophyceae	Scenedesmaceae	*Scenedesmus protuberans*	4.00E + 04
	Chlorophyceae	Scenedesmaceae	*Scenedesmus javanensis*	1.00E + 04
	Chlorophyceae	Scenedesmaceae	*Scenedesmus apiculatus*	2.00E + 04
	Chlorophyceae	Scenedesmaceae	*Scenedesmus Praetervisus*	6.00E + 04
	Undetermined	Undetermined	*"Rombocistis"*	2.83E + 06
	Zygnemophyceae	Closteriaceae	*Closterium sp*	1.00E + 04
	Chlorophyceae	Radiococcaceae	*Radiococcus nimbatus*	7.00E + 04
Euglenozoa	Euglenophyceae	Phacaceae	*Phacus sp*	5.00E + 04
	Euglenophyceae	Euglenaceae	*Euglena sp. 1*	5.00E + 04
	Euglenophyceae	Euglenaceae	*Euglena sp. 2*	1.00E + 04
Bacillariophyta	Bacillariophyceae	Cymbellaceae	*Encyonopsis sp*	2.00E + 04
	Bacillariophyceae	Pinnulariaceae	*Pinnularia sp.*	2.00E + 04
Cryptophyta	Crytophyceae	Cryptomonadaceae	*Criptomonas sp.*	1.00E + 04
Charophyta	Conjugatophyceae	Desmidiaceae	*Cosmarium sp.*	8.00E + 04
Cyanobacteria	Cyanophyceae	Phormidiaceae	*Phormidium sp*	1.00E + 04

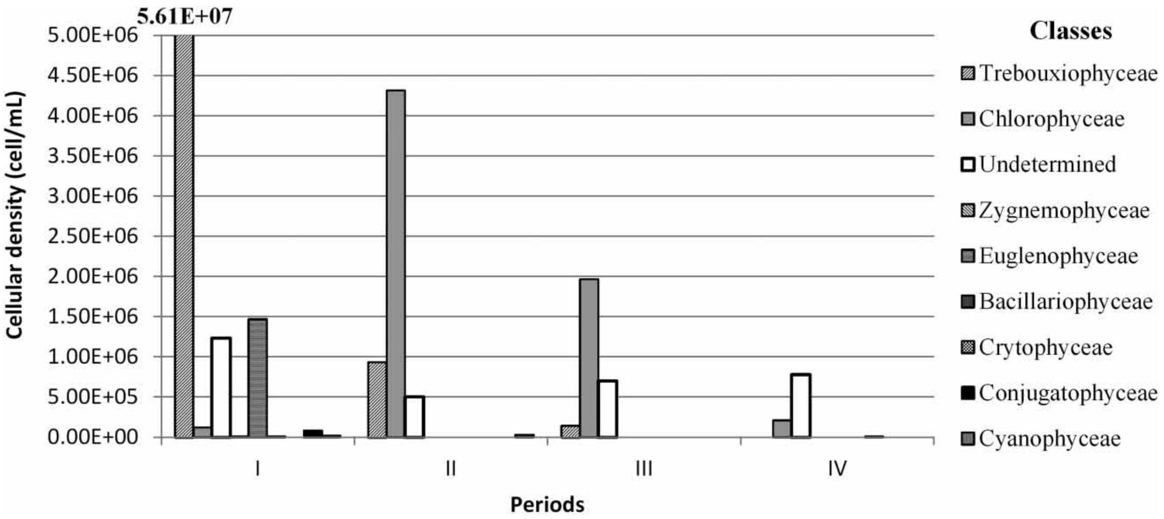


Figure 1 | Microalgae diversity in the HRAP by operation periods.

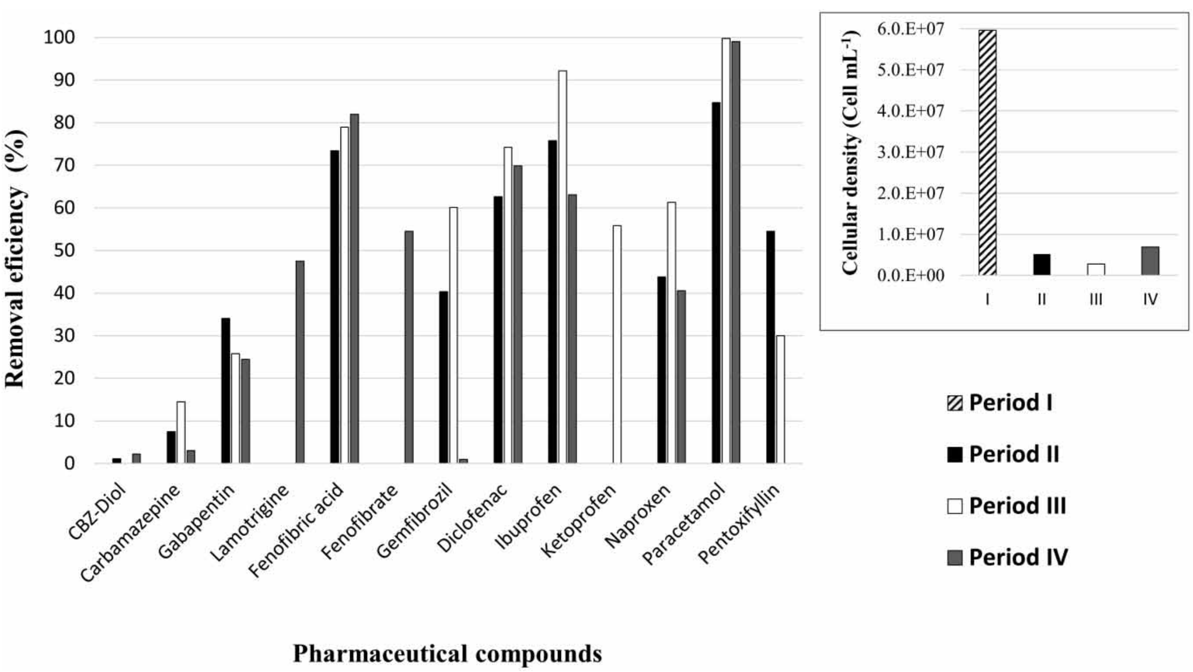


Figure 2 | Average removal efficiency by period of operations and cellular density in the HRAP.

and 2). Diversity and abundance were lowest during period I ($H' = 0.1366$; $1\text{-}D = 0.0556$), they increased during period II ($H' = 1.383$; $D = 0.6242$), and remained constant during periods III and IV ($H' = 1.32$; $1\text{-}D = 0.625$).

Removal efficiencies could be attributed to changes in the algal density over different periods of operation (II, III, and IV), rather than seasonal variation (dry or wet season), as American tropics have the characteristic of keeping low variations of environmental conditions during the year. Figure 1 shows the changes in the average removal efficiencies of the compounds over the different operating periods (II, III, and IV). In exploratory terms, the removal efficiencies of gabapentin and pentoxifylline decreased as the algal density decreased, which may have been associated

Table 5 | Estimation of the HQ in the HRAP

PCs	Influent		Effluent		Reduction (%)
Carbamazepine	0.07	No hazard	0.06	No hazard	6.30
Gabapentin	0.01	No hazard	4E-03	No hazard	30.8
Fenofibric acid	0.03	No hazard	0.01	No hazard	77.9
Gemfibrozil	52.30	High	35.12	High	32.9
Diclofenac	2.93	Medium	0.92	Insignificant	68.7
Ibuprofen	318.13	High	74.91	High	76.5
Ketoprofen	0.01	No hazard	0.01	No hazard	55.9
Naproxen	17.92	High	9.19	Medium	48.7
Paracetamol	0.22	Insignificant	4E-04	No hazard	99.8

with limitations in the biodegradation mechanism. During period III, average removal efficiencies increased for fenofibric acid, gemfibrozil, diclofenac, ibuprofen, naproxen, and paracetamol, which may be related with an increase in direct photolysis due to a reduction in the algal biomass.

Estimation of ecological hazard

The PNEC and the HQ coefficients were determined for the compounds with the greatest occurrence in the wastewater studied (Table 5), based on the ecotoxicity data reported in the literature (Table S1). The findings indicated that gemfibrozil, ibuprofen, and naproxen had a high potential ecological hazard before the HRAP, followed by diclofenac with a medium hazard, and paracetamol with an insignificant hazard. At the effluent of the HRAP, the hazard from diclofenac and paracetamol decreased, while it remained high for gemfibrozil and ibuprofen, suggesting the need to evaluate a complementary treatment that can increase the removal efficiencies of those compounds. Nevertheless, there was a percentage reduction in the HQ value for most of the compounds, indicating a decrease in the hazard to the aquatic biota in the receptor source.

A high HQ for ibuprofen and gemfibrozil suggests a possible alteration of the aquatic biota. Studies of Japanese *Medaka* fish have reported that ibuprofen affects reproduction, including vitellogenin induction in male fish and delayed hatching at concentrations of 0.1 μgL^{-1} (Flippin *et al.* 2007; Mezzelani *et al.* 2018). Nephrotoxicity and an immunosuppressant effect in *Rhamdia quelen* have also been found, at concentrations of 0.1 and 1.0 μgL^{-1}, respectively (Mathias *et al.* 2018). Gemfibrozil is considered to pose a high risk to aquatic biota (Verlicchi *et al.* 2012), with genotoxicity effects in fish at concentrations of 0.38 μgL^{-1} (Rocco *et al.* 2012).

CONCLUSIONS

At a preliminary level, this study confirmed the presence of PCs in wastewater in the city of Cali (Colombia). It also found high average removal efficiencies (>70%) in the HRAP for fenofibric acid, ibuprofen, and paracetamol. The present study obtained efficiencies that were very similar to other investigations, while using a short HRT. This was related with conditions in the American tropics that may favor removal mechanisms such as biodegradation and photodegradation.

Parachlorella kessleri and *Desmodesmus serratus* microalgae species belonging to the phylum *Chlorophyta* were the dominant species in the HRAP. A reduction in algal density played a role in decreasing removal efficiency, especially for compounds such as gabapentin and pentoxifylline. Meanwhile, efficiency increased for fenofibric acid, gemfibrozil, diclofenac, ibuprofen, naproxen, and paracetamol, possibly due to an increase in direct photolysis as a result of a reduction in algal biomass.

A decrease in concentration after treatment reflected a percentage decrease (>50%) in the ecological hazard of most of the PCs. Nevertheless, gemfibrozil and ibuprofen continued to pose a high hazard, demonstrating the need to implement complementary treatment.

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DATA AVAILABILITY STATEMENT

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

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