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Longitudinal Removal of Bisphenol-A and Nonylphenols from Pretreated Domestic Wastewater by Tropical Horizontal Sub-SurfaceConstructed Wetlands

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Abstract: Bisphenol A (BPA) and nonylphenols (NPs), with a high potential to cause endocrine disruption, have been identified at levels of nanograms per liter and even micrograms per liter in effluents from wastewater treatment plants. Constructed wetlands (CWs) are a cost-effective wastewater treatment alternative due to the low operational cost, reduced energy consumption, and lower sludge production, and have shown promising performance for treating these compounds. A CW pilot study was undertaken todetermine its potential to remove BPA and NP from municipal wastewater. Three CWs were used: the first CW was planted with *Heliconia* sp., a second CW was planted with *Phragmites* sp., and the third CW was an unplanted control. The removal efficiency of the *Heliconia*-CW was 73 ± 19% for BPA and 63 ± 20% for NP, which was more efficient than the *Phragmites*-CW (BPA 70 ± 28% and NP 52 ± 23%) and the unplanted-CW (BPA 62 ± 33% and NP 25 ± 37%). The higher capacity of the *Heliconia*-CW for BPA and NP removal suggests that a native plant from the tropics can contribute to a better performance of CW for removing these compounds.

Keywords: municipal wastewater; constructed wetlands; Bisphenol A; nonylphenol; biodegradation; tropical environment

1. Introduction

Exposure to trace concentrations of certain synthetic and natural chemicals compounds, e.g., pharmaceuticals and personal care products (PPCPs), may induce negative environmental and health effects. The United States Geological Survey found 13 compounds related to organic wastewater contaminants in samples from the water supplies that ranged from 0.0120 to 0.480 $\mu g \cdot L^{-1}$, and concentrations of pharmaceutical and personal care compounds ranged from 0.0037 to 0.0576 $\mu g \cdot L^{-1}$ [1]. The main source of these compounds in the water cycle is their discharge by sewage systems. Several synthetic compounds with a high potential to cause endocrine disruption at

low concentrations (e.g., micrograms per liter, $\mu g \cdot L^{-1}$, or even nanograms per liter, $ng \cdot L^{-1}$) have been identified to be present in the effluents of wastewater treatment plants (WWTPs) [2,3]. Furthermore, due to their chemical and recalcitrant characteristics, some of these PPCP compounds pass through conventional wastewater treatment processes without undergoing any transformation, resulting in their direct discharge to the receiving waters [4,5].

Compounds such as Bisphenol A (BPA) are widely used in industrial processes as a primary raw material in the manufacturing of many products such as plastics for engineering applications (e.g., epoxy resins and polycarbonate plastics), electronic devices, food cans, bottles, and dental sealants [6]. There is evidence that relates BPA appearance directly to adverse reproductive and carcinogenic effects in mice with a dose of 25 $ng \cdot kg^{-1}$ per day and 1 $\mu g \cdot kg^{-1}$ per day, respectively [7]. Nonylphenols (NPs) are used in the manufacturing of anionic detergents, lubricants, agrochemicals, tanneries, and lubricant oil additives. The main source of NP in municipal wastewater is due to the intermediate degradation products of soaps and detergents. NPs are found to be endocrine disruptive compounds (EDCs), and have effects in the reproductive system of some mammals, including the reduction in testis and ovaries weight, and the appearance of an irregular estrous cycle [8].

Different treatment systems for the reduction of EDCs from wastewater are being evaluated, such as membrane bioreactors, activated sludge systems, ozonation, photocatalysis, and sequencing batch reactors. Most of these processes require a high economic investment with high environmental costs related to their operation and maintenance which makes their implementation difficult in developing countries. Some studies focus on sustainable wastewater treatment by decreasing electricity consumption and mitigating its greenhouse gas footprint [9]. In this sense, constructed wetlands (CWs) are natural wastewater treatment systems that offer cost-effective treatment for small to medium-sized systems [10]. Recently, the removal of pharmaceuticals in horizontal and vertical subsurface flow constructed wetlandswas evaluated [9] with removal efficiencies for ibuprofen of 51–54% in winter and 85–96% in summer and for carbamazepine of 24–36% in winter and 48% in summer.

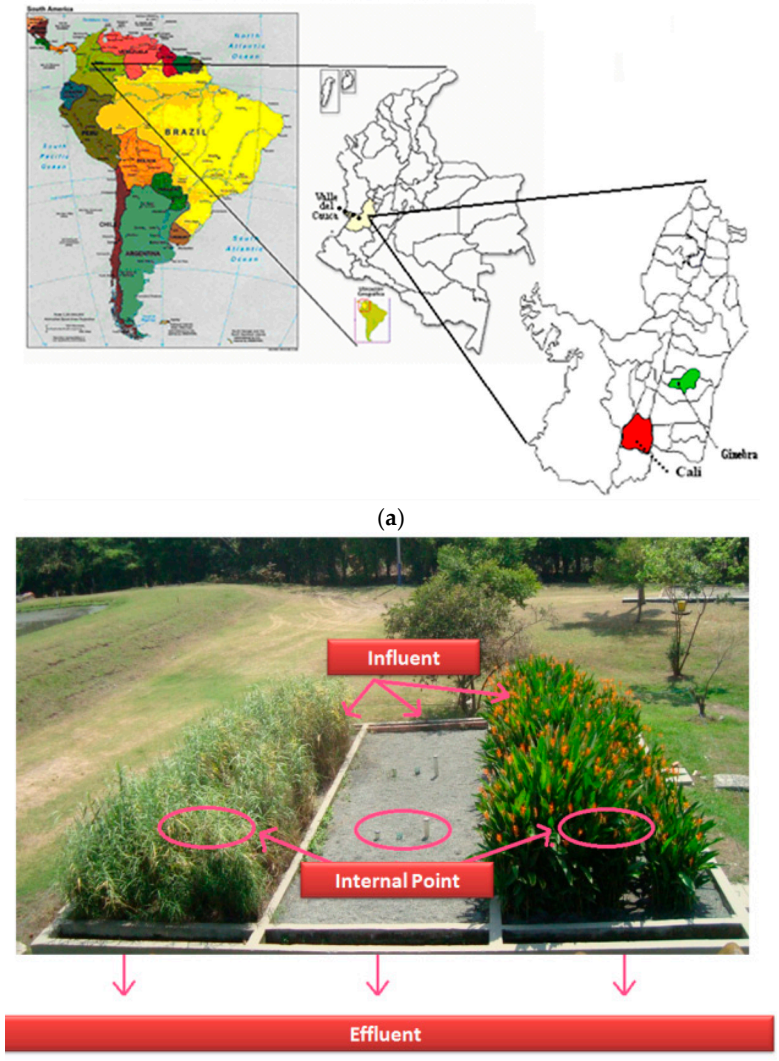
The behavior of EDC removal in CW wastewater treatment systems is not fully understood. Data display a high variation in removal efficiency, ranging from 20% to 99%, depending on the chemical compound characteristics, plant type, flow conditions (regime), and geographic location [11]. Particularly under tropical climate conditions, some research has observedthat CW are capable of removing phenolic compounds in a range from 60% to 77% [12]. However, more research is required to understand the potential of CWs in the removal of EDCs, specifically regarding the effect of variables such as plant type and hydraulic retention time. Pilot-scale research is essential to enable extrapolation to full-scale CW design for effective removal of EDCs.

2. Materials and Methods

2.1. Location and Description of Horizontal Sub-Surface Constructed Wetlands (HSSF-CWs)

This research was performed at a test site (3°43′50″ N and 76°16′20″ O) located approximately 1.1 km away from the urban area of Ginebra, Colombia, a small city of Valle del Cauca, located approximately 50 km northwest of Cali (Figure 1a). The test site is a research and technology transfer station of the domestic wastewater treatment and reuse research center of the Universidad del Valle (Cali, Colombia).

The study was carried out in a module consisting of three pilot scale horizontal subsurface flow constructed wetlands (HSSF-CWs), as shown in Figure 1b. The influent to the CWs comes from the effluent of an anaerobic pond as primary treatment of the domestic wastewater of the city. Each CW was designed to treat a flow of 3.5 $m^3 \cdot day^{-1}$ with an effective volume of 6.35 m^3 ($9 \times 3 \times 0.6$ m and 40% porosity). This design corresponded to a nominal hydraulic retention time of 1.8 days, a nominal surface loading rate of 0.13 $m \cdot day^{-1}$. One CW was planted with *Heliconias* sp. (a native flowering and marketable plant) and a second CW was planted with *Phragmites* sp. (a native perennial wetland grass). The third CW (in between the other two CWs) was a control without plants.



(**a**)

(**b**)

Figure 1. (**a**) Location of the pilot scale; (**b**) pilot scale horizontal subsurface flow constructed wetlands used in this study.

The EDC removal efficiency throughout each HSSF-CW was measured and two sampling points were provided to quantify the longitudinal concentration changes in BPA and NP concentration. The first was an internal sampling point, located at six meters from the inlet, which represents two-thirds of the length of the CW. These points were labeled H1 for *Heliconias*-CW, P1 for *Phragmites*-CW and C1 for control-CW. The other sample point was located at the outlet and was labeled H2, P2, and C2 respectively. The main response variable was the removal efficiency of BPA and NP. One sample was collected once per week over a seven-week periodat each sampling point, including the beginning of the first week (i.e., eight samples were collected at each sample point). Unfortunately, the third effluent *Phragmites* sample was broken in shipping, and the entire fourth set of samples was lost in shipping.

2.2. Endocrine Disruptive Compounds

Bisphenol A was spiked into the wastewater to ensure detection, whereas NP was detected at higher concentrations naturally in the wastewater samples and did not required an external injection. For BPA spiking, a feeding system was built to supplement the anaerobic pond effluent with an average mass loading of 2.08 mg·day^{-1} BPA (i.e., a daily average concentration of 0.59 µg·L^{-1} BPA in the

influent to the CW units). The feeding system consisted of a 50 L storage tank with piping to the CWs. From the BPA stock solution (200 mg·L^{-1}, prepared with analytical grade (>98%) BPA from Sigma-Aldrich (St. Louis, MO, USA) and stored at 4 °C), a 25 mg·L^{-1} solution was prepared separately using distilled water. Every day, at the same time, the storage tank was filled with 50 L of anaerobic pond effluent and 83 mL of 25 mg·L^{-1} BPA, (after completing the research, it was observed that spiking the influent with BPA was unnecessary).

Samples from the CWs were collected in 100 mL pre-cleaned amber bottles, labeled and stored in a dark room at <4 °C until shipment to the University of Texas (UTEP), El Paso, USA. To minimize the effect of microbiological degradation, each sample was centrifuged and filtered through 0.45 and 0.12 µm cellulose membrane filter before the shipping to UTEP. The shipping time was between 1.5 and 2 days. Upon arrival, the samples were kept in a refrigerator at 4 °C until chemical analysis.

To determine the EDC concentrations, samples were analyzed at UTEP using stir bar sorptive extraction (SBSE) with in-line thermal-desorption and gas chromatography/mass spectrometry (TDU-GC–MS). Briefly, (i) twenty milliliters of the filteredsample were transferred to a 20-mL screw cap vial, (ii) sodium carbonate (200 mg) was added to adjust the pHto 11.5, and (iii) acetic acid anhydride (200 µL) was added as the derivatization reagent. A pre-conditioned stir bar (three hours at 300 °C in a flow of nitrogen) was placed in each vial, and the samples were stirred at 1000 rpm for four hours. After the extraction, the stir bar (Gerstel, Linthicum, MD, USA) was removed with forceps, rinsed with purified water, and dried with lint-free tissue paper. The stir bar was thermally desorbed in a thermal desorption (TDU) system at the sample introduction inlet of a GC-MS system (Agilent, Santa Clara, CA, USA).

2.3. Influent Concentration of HSSF-CW

Table 1 shows the physical and chemical composition of the influent supplied to the HSSF-CW units, including the EDC concentrations. The influent composition varied throughout the study period due to variations in the background concentrations present in the domestic wastewater.

Table 1. Composition of the influent supplied to the horizontal subsurface flow constructed wetlands (HSSF-CWs).

Statistical Results	Parameters					
	BPA (µg·L^{-1})	**NPs (µg·L^{-1})**	**DOC * (mg·L^{-1})**	**COD * (mg·L^{-1})**	**COD$_f$ * (mg·L^{-1})**	**TSS * (mg·L^{-1})**
$\hat{y}$	8.80	1671	17.6	252	134	63.7
σ	6.40	838	4.23	48.6	28.8	26.2
C.V.	0.73	0.50	0.24	0.19	0.21	0.41

Notes: DOC: Dissolved Organic Carbon; COD: Chemical Oxygen demand; COD$_f$: Filtered COD; TSS: Total Suspended Solids; $\hat{y}$: mean value; σ: standard deviation; and C.V.: Coefficient of variation. * These parameters were measured in accordance with the Standard methods 21th Ed.

Of the three locations sampled in the CWs, the influent had the lowest redox potential (ORP) value (−420 ± 189 mV), which was understandable given that the influent was from an anaerobic pond. Likewise, the influent dissolved oxygen (DO) concentration was low (<0.15 ± 0.3 mg·L^{-1}). The unplanted (control) CW had higher ORP and DO (−253 mV and 0.6 mg·L^{-1}, respectively) than the influent, but the effluents of the planted CWs (*Phragmites* and *Heliconia*) had the highest average ORP values (−158 and −127 mV, respectively) and DO concentrations (0.9 and 0.8 mg·L^{-1}, respectively). The higher ORP and DO in the planted CWs is likely due to oxygen translocation by plants through its roots system [13].

2.4. Statistical Analysis

Data were recorded and analyzedwith Microsoft Excel, and Minitab 15 software was used for the Friedman Two-Way Analysis of Variance by Ranks combined with a non-parametric post hoc analysis (Wilcoxon signed-rank test).

3. Results and Discussion

3.1. Longitudinal Removal of BPA in HSSF-CWs

Figure 2 shows the influent and effluent BPA concentrations for the (a) *Heliconia*-CW, (b) unplanted (control), and (c) *Phragmites*-CW, as well as the longitudinal removal efficiencies for each (parts (d), (e), and (f), respectively). A significant reduction in the BPA concentrations was observed at the internal sampling points H1, C1 and P1—each at two-thirds of the horizontal length of the CW—compared to the influent (Figure 2). This implies that BPA was transformed, sorbed, or consumed in the first two-thirds of each CW. From this point until the effluent discharge point, the BPA concentrations were fairly consistent, and decreased only marginally. The differences in the partial and total BPA removal for the internal sample point and effluent were established by a Wilcoxon signed rank test in each CW and displayed significant differences for the *Heliconia*-CW and unplanted-CW. Regarding the *Phragmites*-CW, the final third of the CW did not contribute to the improvement of the total BPA removal.

From the literature, the main removal mechanism of BPA in a CW is sorption [14–16], due to a higher octanol–water partition coefficient of the hydrophobic BPA molecule (log K_{ow} is 3.4), as well as a large surface area in the CW, which enhances sorption onto the biofilm, suspended solids, support media, and rhizosphere [17]. The sorption capacity of a compound can be better expressed in terms of the organic carbon partition coefficient (K_{oc} or K_d) related to the quantity of the sorbed compound in the solid phase with respect to the concentration in the aqueous phase [18]. This is important because BPA has two hydroxyphenyl groups, which tend to promote sorption in soils (or support media) and sediments [19]. The research of this manuscript did not include BPA measurements on the sediments or support media, but based on other research of BPA partitioning in wastewater sediment [20], a log K_d ($L \cdot kg^{-1}$) value of 4.37 was calculated for BPA at the average concentration reported in Table 1. If the log $K_d < 2.47$, sorption can be neglected, while for values higher than 4.0, sorption onto the solid phase is one of the major removal processes [18,20]. The calculated log K_d value of BPA suggests that it is likely that sorption of BPA was one of the significant removal processes in each of the three CW types investigated.

Sorption onto the support media or onto the biofilm and sediments on the media implies a longer EDC residence time for BPA in the CW. This may favor bioremediation by increasing exposure to plant uptake or microbial degradation. Indeed, phytoremediation can also be an important removal pathway, where the EDC may possibly be degraded by phytostimulation or rhizodegradation, phytodegradation, phythoextraction, sequestration or volatilization [13,21]. In some cases, the plants growing in the CW may play a significant role in the direct uptake of many organic pollutants from wastewater. For instance, the presence of *Phragmites australis* in a CW improved the removal efficiency of BPA compared to an unplanted CW [12,22,23]. In a study by Dodgen et al. [24], the plant uptake of BPA, 4-NP, diclofenac (DCL), and naproxen (NPX) during the hydroponic cultivation of *Lactuca sativa* (lettuce) and *Brassica oleracea* (collard) was investigated, and EDC accumulation was observed in both plant species with a trend in descending order of BPA > NP > DCL > NPX [24].

The Friedman Test indicates significant differences (p-value: 0.03) for the removal of BPA (Figure 2) at the intermediate sampling point (H1, C1, and P1). The post hoc test revealedthat P1 obtained the highestaverage removal efficiency (64.3%) compared with C1 (55.2%) and H1 (61.4%). Also, significant differences (p-value: 0.015) were observed for the average effluent BPA removal (H2, C2, and P2), and the post hoc test showed that the *Heliconia*-CW had the highest average BPA removal efficiency (73.3%) compared withthe unplanted-CW (62.2%) and *Phragmites*-CW (70.2%), as shown in Table 2.

Both planted CWs had greater average effluent removal efficiencies than the unplanted control, and both planted CWs had greater effluent removal efficiencies than the unplanted-CW for all but one of the sampling events; thus, it is assumed that plant vegetation had a role in BPA removal. The specific removal mechanism by the plants was not investigated.

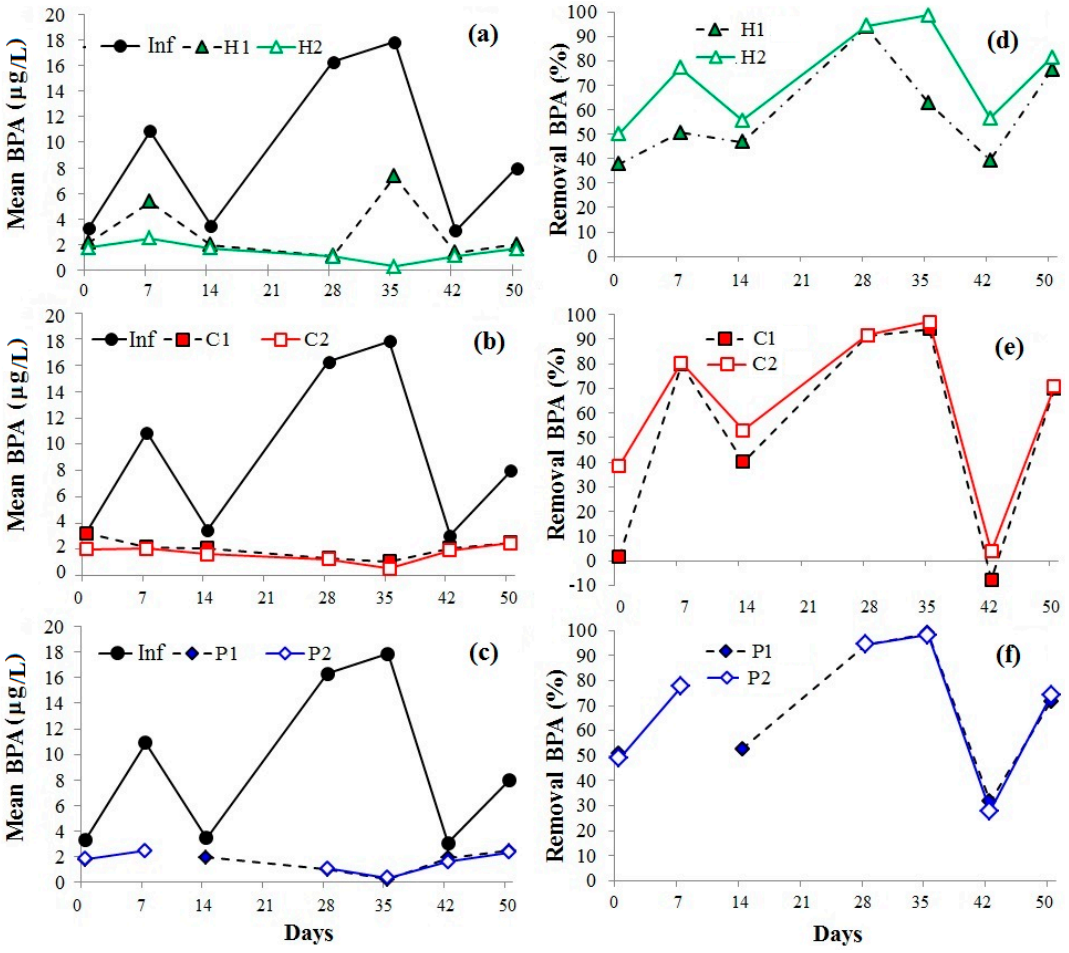


Figure 2. Longitudinal BPA concentrations in CWs of (**a**) *Heliconia* (H); (**b**) unplanted control (C), and (**c**) *Phragmites* (P), for influent (Inf), two-thirds internal (1), and effluent (2) sample points.Removal efficiency of BPA in (**d**) *Heliconia*; (**e**) unplanted control; and (**f**) *Phragmites*.

Table 2. Average effluent BPA removal for *Heliconia*-CW, unplanted-CW and *Phragmites*-CW.

Removal Efficiencies (%)	BPA		
	Heliconia	***Unplanted***	***Phragmites***
$\hat{y}$	73.3%	62.2%	70.2%
Maximum	98.6%	97.1%	98.3%
Minimum	50.0%	3.7%	27.9%
σ	19.6%	33.1%	27.1%
C.V.	0.27	0.53	0.39
n *	7	7	6

* The third *Phragmites* sample was broken in shipping. Notes: $\hat{y}$: mean value; σ: standard deviation; C.V.: coefficient of variation; and n number of samples.

3.2. Longitudinal Removal of NP in HSSF-CWs

The average total NP concentration in the influent was (1671 ± 838) µg·L^{-1}. A reduction of the NP concentration was observed at the internal sampling point (two-thirds of the length)

of each wetland (H1, P1, and C1), with average concentrations of (724 ± 453), (1150 ± 499) and (1041 ± 446) $\mu g \cdot L^{-1}$, respectively. The lowest final effluent concentrations were obtained for the *Heliconia*-CW (629 ± 318 $\mu g \cdot L^{-1}$) and *Phragmites*-CW (736 ± 284 $\mu g \cdot L^{-1}$), showing more NP removal in the final third of the CWs. The NP removal efficiencies were less than those of BPA. A Wilcoxon signed rank test was used to establish significance of differences between the internal sampling point and effluent concentrations in each CW. Although the plantedCWs had a higher average NP removal efficiency in the effluent than the internal sample point, these results are not statistically different.

The unplanted-CW displayed a different behavior, showing an increment of the NP concentration in the effluent (1103 ± 538 $\mu g \cdot L^{-1}$) compared with its internal point. NP desorption was observed in the final third of the CW, despite NPs having high K_{ow} values (log K_{ow} 3.80 to 4.77). This negative removal efficiency in CW was also reported in other research [18] for seven different PPCPs, attributed to an initial retention and sorption, but subsequent release during passage of the wastewater through the medium of the CW.

The *Heliconia*-CW showed the highest average effluent NP removal efficiency of 62.8 ± 20.1%, while the *Phragmites*-CW and unplanted-CW had a removal efficiency of 25.3 ± 37.1% and 52.1 ± 23.2%, respectively (Table 3). These results confirm a statistically significant difference between planted and unplanted CWs with *p*-values of 0.042 for the internal sample point and 0.03 for the effluent. The posthoc test corroborated this conclusion, confirming that the *Heliconia*-CW showed a higher NP removal efficiency than the *Phragmites*-CW and the unplanted-CW.

Table 3. Average effluent NP removal for *Heliconia*-CW, unplanted-CW, and *Phragmites*-CW.

Removal Efficiencies (%)	NP		
	Heliconia	***Unplanted***	***Phragmites***
$\hat{y}$	62.8%	25.3%	52.1%
Maximum	90.0%	83.7%	80.2%
Minimum	28.0%	−12.3%	20.4%
σ	20.1%	37.1%	23.2%
C.V.	0.32	1.46	0.4
n *	7	7	6

* The third *Phragmites*-CW sample was broken in shipping. Notes: $\hat{y}$: mean value; σ: standard deviation; C.V.: coefficient of variation; and n number of samples.

3.3. EDC Removal Rate Against Mass Loading Rates

The total mass removed of each EDC compound was plotted against its total inlet mass loading rate (Figure 3). The removal rate of BPA in the *Heliconia*-CW, unplanted-CW and *Phragmites*-CW increased as the mass loading rate increased as well. BPA removal efficiency in all three CW types investigated was not sensitive to the mass loading rate and was almost completely removed in all CWs investigated (Figure 3a). However, NP removal decreased at a high mass loading rate. Moreover, NP was poorly removed in the unplanted-CW both at low and high mass loading rates (Figure 3b).

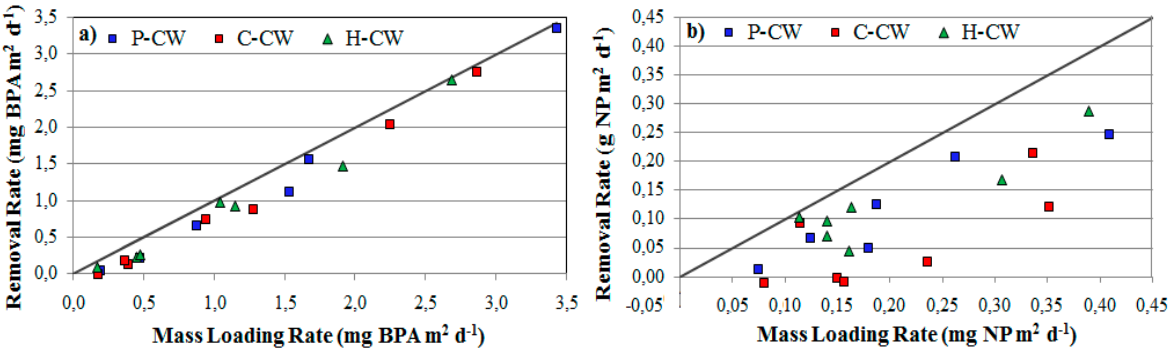


Figure 3. Endocrine disruptive compound(EDC) removal rate for H-CW, C-CW, and P-CW against their mass loading rates (**a**) BPA and (**b**) NP. Continuous line represents 100% removal.

3.4. Overall Performance of Each HSSF-CW in EDC Removal

Four scenarios (quadrants) were identified (Figure 4) according to the weekly effluent removal efficiencies of BPA and NP. Zone I is the worst scenario in which both compounds were removed with less than 50% efficiency. In Zone II, BPA removal was greater than 50%, but NP was less than 50%. Zone III shows a BPA removal efficiency less than 50% and NP greater than 50%. Finally, in Zone IV, both compounds were removed with efficiencies greater than 50%. The best CW removal efficiencies were observed for the *Heliconia*-CW, in which six of seven (85%) of the data points are in zone IV, compared with the unplanted-CW with more than five of seven (71%) of the data points in zone II. Overall, the BPA and NP removal efficiencies were in the following descending order: *Heliconia*-CW > *Phragmites*-CW > unplanted-CW. This performance is likely due to sorption in the HSSF-CW onto support media. Also, the rhizosphere of planted CWs likely generates benefits such as increasing DO concentrations and releasing organic exudates that serve as nutrient sources for the growth of microorganisms [25].

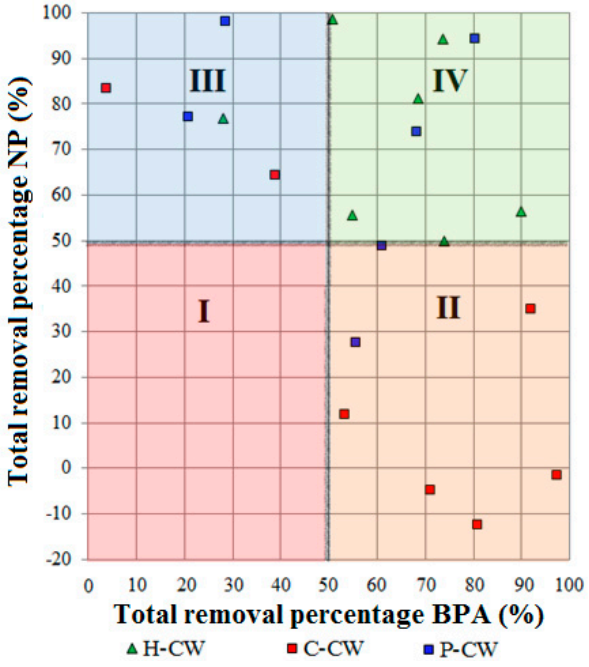


Figure 4. Quadrant chart for NP removal efficiency versus BPA removal efficiency for the *Heliconia*-CW (H), *Phragmites*-CW (P) and unplanted-CW (C).

This study showed that BPA and NP can beeffectively removed by planted HSSF CW under tropical conditions, with removal being more efficient withthe native and marketable plant *Heliconia* sp. in the CW.

4. Conclusions

The *Heliconia*-CW removed BPA (73%) and NP (62%) more efficiently than the *Phragmites*-CW (70% and 52%, respectively) and unplanted-CW (62% and 25%). The *Heliconia*-CW showed an improvement in BPA removal in the last third of the length of the wetland (p-value: 0.015). In contrast, the last third section of the *Phragmites*-CW and unplanted-CW did not contribute to additional BPA removal. Desorption of NP in the unplanted-CW was observed in the last third of the lengthof the CW, suggesting that a sorption–desorption equilibrium can be reached. This situation was not found for *Phragmites* sp. and *Heliconias* sp., corroborating that plants had a positive influence in the CW.

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Author Contributions: Andrés Toro-Vélez, Miguel Peña-Varón, Hector García-Hernández and Carlos Madera-Parra conceived and designed the experiments; Andrés Toro-Vélez performed the experiments; Andrés Toro-Vélez, analyzed the data; Wen Yee Lee and Shane Walker contributed reagents/materials/analysis tools; Andrés Toro-Vélez, Piet Lens and Shane Walker wrote the paper.

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