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Removal of Emerging Pollutants in Horizontal Subsurface Flow and Vertical Flow Pilot-Scale Constructed Wetlands

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Abstract: We assessed constructed wetland (CW) performance in the removal of six emerging pollutants (EPs) from university campus wastewater. The EPs considered were: diethyl phthalate (DEP), di-isobutyl phthalate (DIBP), di-n-octyl phthalate (DNOP), bis(2-ehtylxexyl) phthalate (DEHP), tris(1-chloro-2-propyl) phosphate (TCPP) and caffeine (CAF). Six pilot-scale CWs, i.e., three horizontal subsurface flow (HSF) and three vertical flow (VF), with different design configurations were used: two types of plants and one unplanted for both the HSF and the VF, two hydraulic retention times (HRT) for the HSF, and two wastewater feeding strategies for the VF units. The results showed that the median removals in the three HSF-CWs ranged between 84.3 and 99.9%, 79.0 and 95.7%, 91.4 and 99.7%, 72.2 and 81.0%, 99.1 and 99.6%, and 99.3 and 99.6% for DEP, DIBP, DNOP, DEHP, TCPP, and CAF, respectively. In the three VF-CWs, the median removal efficiencies range was 98.6–99.4%, 63.6–98.0%, 96.6–97.8%, 73.6–94.5%, 99.3–99.5% and 94.4–96.3% for DEP, DIBP, DNOP, DEHP, TCPP and CAF, respectively. The study indicates that biodegradation and adsorption onto substrate were the most prevalent removal routes of the target EPs in CWs.

Keywords: horizontal subsurface flow constructed wetlands; vertical flow constructed wetlands; phthalate esters; flame retardant (TCPP); caffeine

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1. Introduction

The western modern lifestyle imposes great pressure on environmental compartments, which constitute the receivers of a great list of chemical compounds, known as emerging pollutants (EPs). Many of these substances are included in the EU Water Framework Directive priority list of 33 substances [1]; some of them are regulated [2,3], while others still remain unregulated.

The current study focused on three groups of EPs: phthalate esters (i.e., diethyl phthalate, DEP; di-isobutyl phthalate, DIBP; di-n-octyl phthalate, DNOP; bis(2-ehtylxexyl) phthalate, DEHP), a flame retardant (tris(1-chloro-2-propyl) phosphate, TCPP) and a stimulant (caffeine, CAF), due to their high production volume, widespread use and frequent residual presence in environmental compartments [4–7].

Phthalate esters (PEs) are vastly used in industrial, agricultural and domestic applications. They are mainly used as plasticizers in order to improve the durability, elasticity

and flexibility of polymeric products [8–10]. PEs can also be applied in many consumer products, such as polyvinyl chloride (PVC) flooring, building materials, cosmetics, home furnishing, vinyl toys, food packaging and medicinal products [6,9]. These substances exhibit high environmental concern due to their production rates and ecotoxicological potential. Annually, more than 8×10^6 tons of phthalates are produced worldwide [8]. Certain PEs are currently regulated by the European Union [10] and DEHP is identified as a priority hazardous substance according to the EU Water Framework directive [1], and its use in cosmetics, medical devices and children's items (i.e., toys, care items) has been banned [3,9]. DEHP is the most widely used PE, characterized by low solubility and high sorption capacity to the solid phase, and as a result, it is the PE most often detected in the environment [9,11]. On the whole, due to their widespread application, PEs have frequently been detected in air, water, sediments, soil and food [4,10,12,13].

Since some brominated flame retardants (BFRs) have been banned, phosphorus flame retardants (PFRs) (i.e., inorganic, organic, halogen containing BFRs) have been proposed as alternatives [7,14]. Organophosphorus flame retardants (OPFRs) are categorized as emerging contaminants due to their extensive use in various applications (e.g., in plastics, textiles and building materials) and their eventual presence in environmental matrices [7,15–17]. Their high environmental persistence and adverse effects on aquatic ecosystem and human health are well documented [14,16,18]. Among OPFRs, tris(1-chloro-2-propyl) phosphate (TCPP) attracts interest for several reasons: TCPP's high persistence in the environment, high release from finished products and TCPP heavy production and wide applications [7]. Therefore, TCPP constitutes an EU high production volume chemical listed in the EC fourth priority list [2,19] and is currently regulated [20]. According to previous studies, TCPP has been detected in wastewater effluents, surface and coastal waters, groundwater and drinking water [21–27].

Caffeine is a purine alkaloid and is normally found in drinks, such as coffee, tea and cocoa, but also constitutes a component of several prescription and non-prescription drugs [5,28]. It represents the most used tracer compound for wastewater pollution and has been frequently detected in WWTP effluents and final recipients [29–31]. One should bear in mind that, from a daily average consumption of caffeine of 131 mg/d, only 3.9 mg is excreted unchanged in the urine, while 127.1 mg is metabolized [5].

Conventional wastewater treatment facilities are not designed to remove these emerging pollutants; thus, they can be partially removed or not removed at all, and therefore end up in final recipients [12,13,17,26,30,32–35]. Due to the widespread presence and persistence of these pollutants, several advanced treatment technologies have been applied, such as advanced oxidation technologies (Fenton or photocatalytic oxidation), ozonation or UV radiation. [17,36]. However, their application at the large-scale level is often cost-prohibitive [6]. Nowadays, constructed wetlands (CWs) provide a very popular and attractive alternative solution to the wastewater treatment technology, since the construction, operation and maintenance costs are very low [37–40]. CWs are used in treating various wastewaters, such as municipal [41–44], agricultural [45,46] and industrial wastewaters [47]. Over the last two decades, CWs have been used in the removal of several EPs [48–50]. However, although CWs have been found to be a successful technology for removing a number of EPs, including caffeine [28,29,31,51], there are fewer studies regarding PEs and TCPP [52–57]. The current study intends to focus on the fact that these compounds are often discharged into water bodies (coastal, surface and groundwater) as residual concentrations [32,49]. In addition, the investigation of the influence of several factors, including plant presence and type, seasonal variation, long term performance and hydraulic loading rate (HLR), is absent. Finally, there are no studies that compare and evaluate the simultaneous operation of two different types of CWs (VF and HSF) under the same climatic conditions. The current study will try to cover these gaps.

2. Materials and Methods

2.1. Wastewater Treatment System Facility Description and Wastewater Quality Monitoring

In the present study, three horizontal subsurface flow (HSF), with code names HSF-R, HSF-C and HSF-Z, and three vertical flow (VF), with code names VF-R, VF-C and VF-Z, pilot-scale units were used. The units operated in the open space of the Laboratory of Ecological Engineering and Technology, Department of Environmental Engineering (location 41°08′47″ N, 24°55′09″ E). The HSF-CW and VF-CW units were constructed in 2003 and 2007, respectively, and are considered mature CWs as they have operated continuously since then for the conduction of several experiments [58–63].

Each HSF-CW unit was a rectangular tank 3 m long, 0.75 wide and 1 m deep (Figure 1a), filled with medium gravel (D_{50} = 15.0 mm, range 4–25 mm) as a substrate at a thickness of 45 cm. The plant type in the first unit was reed (*Phragmites australis*; HSF-R unit), in the second was cattail (*Typha latifolia*; HSF-C unit), and the third was used as a control and was kept unplanted (HSF-Z unit). In the HSF units, two hydraulic residence times (HRTs) of 14 and 20 days were applied with hydraulic loading rates ranging from 15.8 to 28.6 L/day. A full description of the HSF units is given by Akratos and Tsihrintzis [58].

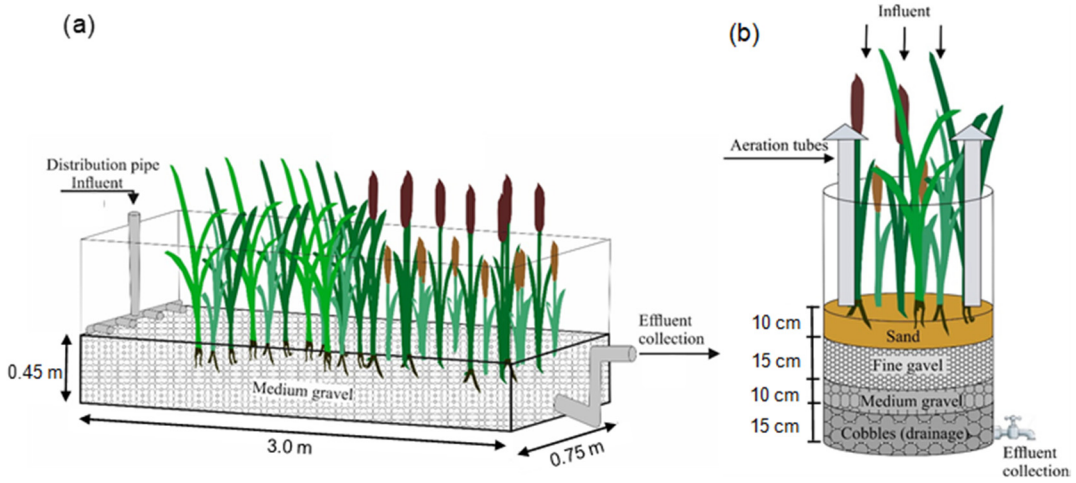


Figure 1. Experimental constructed wetlands: (**a**) horizontal subsurface flow constructed wetland; (**b**) vertical flow constructed wetland.

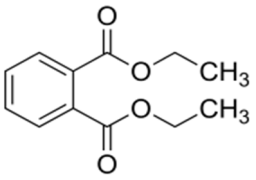
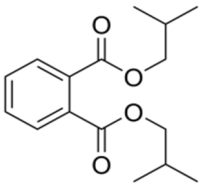
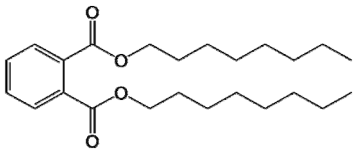
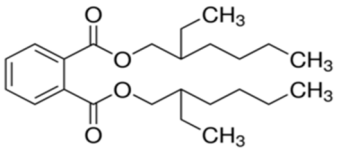
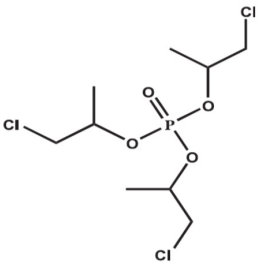
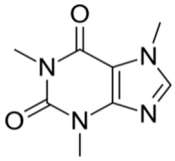
The VF-CWs pilot-scale units were cylindrical plastic tanks with a diameter of 0.82 m and a height of 1.5 m. The porous media thickness was 50.0 cm and was placed in the following four layers (Figure 1b): (a) a drainage layer of cobbles, 15 cm thick (D50 = 90 mm), placed at the bottom; (b) a 10 cm thick layer of medium gravel (D50 = 24.4 mm); (c) a 15 cm thick layer of fine gravel (D50 = 6 mm); and finally, (d) a 10 cm thick top layer of sand (D50 = 0.5 mm). The drainage layer also contained aeration tubes, which were plastic pipes (50 mm in diameter) perforated only within the cobble drainage layer (Figure 1b). The first unit was planted with *Phragmites australis* (VF-R unit), the second with *Typha latifolia* (VF-C unit), and the third one was used as control unit (unplanted; VF-Z unit). A full description of the HSF units is given by Stefanakis and Tsihrintzis [59]. Two feeding strategies were applied as follows: in the first (strategy A), the loading (wet) and the resting (dry) period were two and four days, respectively, and in the second (strategy B), the wet and dry periods were two and six days, respectively; the respective hydraulic loading rates (HLR) were 0.209 m/d (strategy A) and 0.283 m/d (strategy B).

During the experimental period (about two years), all CW units (both HSF and VF) were supplied with municipal wastewater that originated from Democritus University Campus [62,63]. The influent wastewater was entered to the CW units every 8 h each day, while influent and effluent samples were collected in all seasons from each unit once every 15 days.

2.2. Chemicals and LC–MS Analysis

For LC–MS analysis, methanol, H_2O and isopropanol suitable for LC–MS applications from Fisher Scientific were used. Ammonium formate for mass spectrometry $\geq$ 99.0% was supplied by Sigma Aldrich (Steinheim, Germany). Di-2-ethylhexyl-phthalate (DEHP) with a purity of 99.9% was supplied by Supelco. The other phthalates (di-ethyl phthalate, di-isobutyl phthalate, di-n-octyl phthalate) were obtained from Dr. Ehrenstorfer (Germany). Analytical standards of TCPP (mixtures of isomers) and caffeine (> 99%) were purchased from Sigma Aldrich (Steinheim, Germany). Table 1 lists the physicochemical characteristics and chemical structure of the study compounds [64].

Table 1. Physicochemical properties of substances under investigation [64].

Substance	Formula	Chemical Structure	Molecular Weight (g/mol)	Water Solubility (mg/L)	$LogK_{ow}$
Phthalate Esters (PAEs)					
Diethyl phthalate (DEP)	$C_{12}H_{14}O_4$		222.24	1100	2.47
Di-isobutyl phthalate (DIBP)	$C_{16}H_{22}O_4$		278.35	6.2	4.45
Di-n-octyl phthalate (DNOP)	$C_{24}H_{38}O_4$		390.56	0.022	8.06
Bis(2-ethylhexyl) phthalate (DEHP)	$C_{24}H_{38}O_4$		390.56	0.27	7.50
Flame retardant					
Tris (1-chloro-2-propyl) phosphate (TCPP)	$C_9H_{18}Cl_3O_4P$		327.56	1600	2.59
Tracer (Stimulant)					
Caffeine (CAF)	$C_8H_{10}N_4O_2$		194.19	22 (g/L)	−0.07

The micropollutant extraction from wastewaters and effluents as well as the LC–MS–TOF analysis followed previously published methods and protocols [65]. High resolution accurate mass data, retention time, the adopted mode of ionization, and the limits of detection (LODs) and quantification (LOQs) of the compounds studied are given in Table 2.

Table 2. High resolution accurate mass data (exact mass, mass error Δ (ppm), retention time) and limits of detection (LOD) and quantification (LOQ) for target compounds using LC–MS/TOF.

Compound	Ionization Mode	Measured m/z	Δ (ppm)	Rt (min)	LOD (ng/L)	LOQ (ng/L)
Diethyl phthalate (DEP)	positive	223.0961	1.9	8.9	1.2	4.0
Di-isobutyl phthalate (DIBP)	positive	279.1597	−2.3	11.1	2.5	8.3
Di-n-octyl phthalate (DNOP)	positive	391.2833	2.5	12.3	1.8	6.0
Bis(2-ethylhexyl) phthalate (DEHP)	positive	391.2837	1.5	13.8	2.8	9.3
Tris (1-chloro-2-propyl) phosphate (TCPP)	positive	327.0071	3.1	9.7	1	3.3
Caffeine (CAF)	positive	195.0880	−1.9	5.6	3	10.0

Rt: Retention time; LOD: Limit of detection; LOQ: Limit of quantification

2.3. Statistical Analyses

In the statistical analyses, which were conducted using the SPSS 25.0 statistical package software, the measured values of EPs below LOQ or LOD were set at half of LOQ or LOD. The non-parametric Kruskal–Wallis (KW) test and Mann–Whitney (MW) U-test were used, because the majority of the data failed to meet the assumption of normality and/or homogeneity. Differences in removal capacity among the three HSF-CW units and among the three VF-CW units were determined using the KW test. Where the KW test showed significant differences between units, the MW U-test was used to evaluate pairwise comparisons.

3. Results and Discussion

3.1. Physicochemical Parameters in CWs

Box-plots of the physicochemical parameters of the influent and effluents of the HSF and VF-CW units are presented in Figure 2. The mean wastewater temperature (T) at the inlet of the six pilot-scale units was 20.0 °C, while at the outlet it ranged between 17.9 and 21.4 °C. The wastewater temperature range was between a minimum of 4.7 °C and a maximum of 28.8 °C (Figure 2a) and followed the seasonal variation, depending greatly on air temperature. The dissolved oxygen (DO) concentration in the six CWs also followed the seasonal variation, as it depends on the temperature with the highest values measured during the low temperature winter season. The mean DO concentrations in the effluent were greater than those in the influent in all CW units (Figure 2b). Higher mean DO concentrations were observed in the planted CWs (i.e., HSF-R, HSF-C, VF-R, VF-C) compared to the unplanted CWs (i.e., HSF-Z, VF-Z), indicating oxygen transfer to the rhizosphere by the plants. The mean pH values in the six pilot-scale units were in the alkaline range (Figure 2c), not greatly varying during the monitoring period, ranging between 7.0 and 7.9. The highest mean pH values were measured in the unplanted units (i.e., HSF-Z, VF-Z) compared to the planted ones, which showed lower values, as also observed by Kadlec and Wallace [66].

The mean electrical conductivity (EC) value of wastewater was 1299 μS/cm; mean values at the outlet of the six pilot-scale CWs ranged between 1087 and 1691 μS/cm. Higher effluent EC values were observed in the planted units compared to the unplanted units, something that is attributed to condensation due to evapotranspiration (Figure 2d). As also reported by Gikas et al. [67], higher EC values were observed in the planted CW units with *Phragmites australis* (i.e., HSF-R and VF-R) compared to those planted with cattails, which may be attributed to the action of the plant root system in releasing ions in the substrate and/or increased evapotranspiration losses.

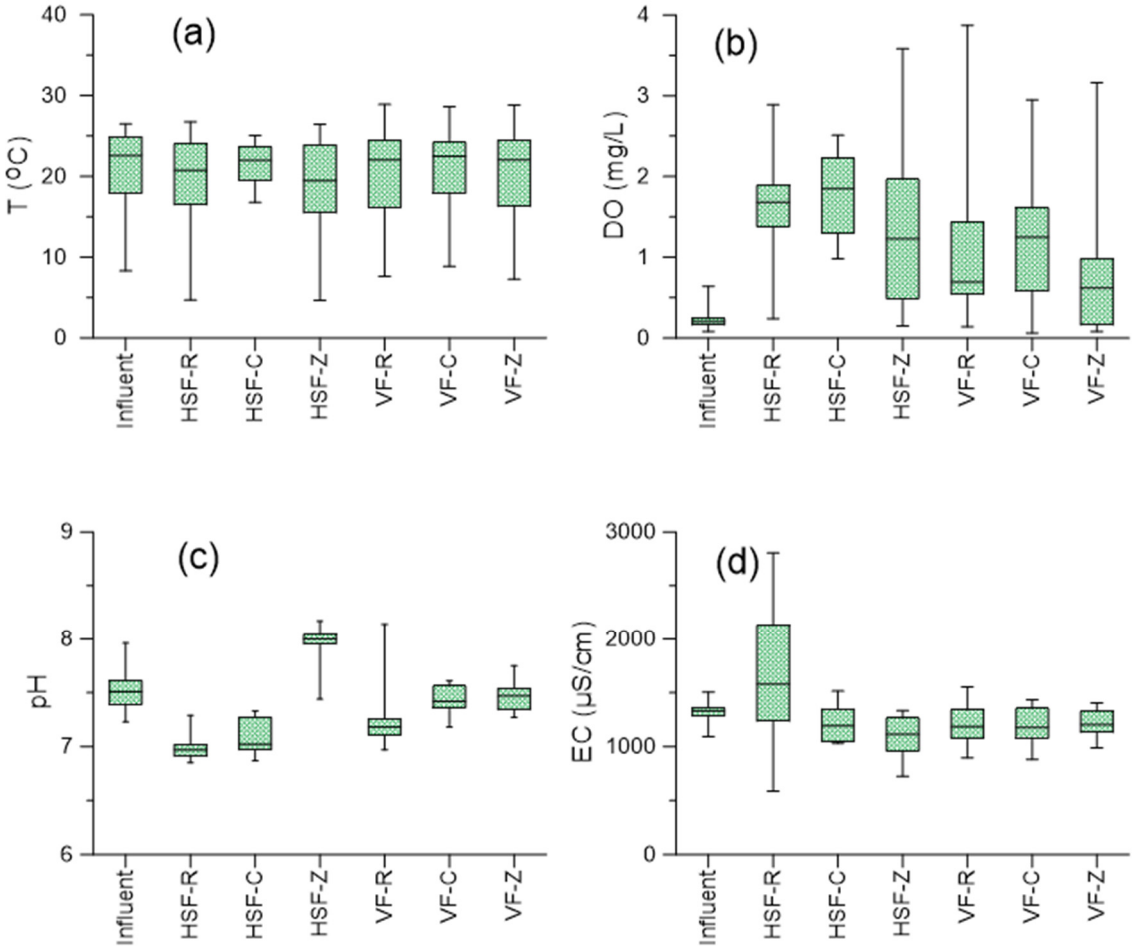


Figure 2. Box-whisker plots of the physicochemical parameters of the influent and effluents in the HSF and VF-CW units: (**a**) temperature; (**b**) dissolved oxygen; (**c**) pH; (**d**) electrical conductivity. The whiskers at the end of each box indicate the minimum and maximum values. The box is defined by the lower and upper quartiles, and the line inside the box denotes the median value.

3.2. Performance Statistics of HSF-CW Pilot-Scale Units

Table 3 summarizes the mean, standard deviation (SD) and the min and max of influent and effluent EP concentrations in each pilot-scale CW. Figure 3a presents the removal efficiencies of each HSF-CW unit, and Figure 4 presents the time series of the EP concentrations in the influent and effluent of the HSF-CW units during the study period. The DEP influent concentrations ranged from 0.066 to 3.044 µg/L (Table 3). The effluent mean concentration values for the HSF-R, HSF-C and HSF-Z units were 0.119, 0.004 and 0.076 µg/L, respectively.

Table 3. Statistical parameters of influent and effluent concentrations.

		HSF-CW				VF-CW			
	Parameter	**Influent**	**Effluent**			**Influent**	**Effluent**		
			HSF-R	**HSF-C**	**HSF-Z**		**VF-R**	**VF-C**	**VF-Z**
DEP (µg/L)	Mean	1.086	0.119	0.004	0.076	1.085	0.058	0.025	0.012
	SD	1.106	0.176	0.005	0.132	1.074	0.119	0.067	0.021
	min	0.066	BQL(10)	BQL(6)	BQL(5)	0.091	BQL(11)	BQL(11)	BQL(14)
	max	3.044	0.544	0.016	0.624	3.044	0.486	0.263	0.085
	n	21	21	7	21	20	20	15	20

Table 3. *Cont.*

		HSF-CW				VF-CW			
	Parameter	Influent	Effluent			Influent	Effluent		
			HSF-R	HSF-C	HSF-Z		VF-R	VF-C	VF-Z
DIBP (µg/L)	Mean	1.121	0.299	0.288	0.147	0.710	0.289	0.048	0.106
	SD	0.809	0.440	0.680	0.326	0.786	0.425	0.017	0.396
	min	0.024	0.016	0.026	0.018	0.040	0.024	BQL(1)	BQL(12)
	max	2.564	1.431	1.831	1.486	2.141	1.236	0.074	1.788
	n	21	21	7	21	20	20	15	20
DNOP (µg/L)	Mean	0.425	0.051	0.017	0.024	0.412	0.045	0.016	0.015
	SD	0.255	0.072	0.015	0.047	0.309	0.078	0.019	0.016
	min	0.043	BDL(5)	BDL(2)	BDL(13)	0.024	BDL(10)	BDL(7)	BDL(10)
	max	0.958	0.261	0.045	0.185	1.434	0.323	0.065	0.043
	n	21	21	7	21	20	20	15	20
DEHP (µg/L)	Mean	1.597	0.663	0.461	0.643	1.334	0.431	0.060	0.181
	SD	1.173	0.705	0.562	0.460	0.981	0.493	0.022	0.328
	min	0.154	0.053	0.037	0.028	0.246	0.069	0.015	0.015
	max	4.126	2.041	1.326	1.789	4.126	1.985	0.088	1.256
	n	21	21	7	21	20	20	15	20
TCPP (µg/L)	Mean	0.115	0.005	0.001	0.001	0.103	0.001	0.001	0.001
	SD	0.095	0.009	0.000	0.000	0.085	0.003	0.000	0.000
	min	0.015	BDL(17)	BDL(7)	BDL(21)	0.015	BDL(19)	BDL(15)	BDL(20)
	max	0.302	0.034	BDL(7)	BDL(21)	0.302	0.014	BDL(15)	BDL(20)
	n	21	21	7	21	20	20	15	20
CAF (µg/L)	Mean	1.372	0.042	0.010	0.076	1.319	0.014	0.011	0.006
	SD	1.896	0.128	0.006	0.149	1.911	0.010	0.008	0.002
	min	BQL(6)	BQL(14)	BQL(4)	BQL(7)	BQL(5)	BQL(10)	BQL(9)	BQL(18)
	max	6.805	0.597	0.018	0.570	6.975	0.032	0.026	0.011
	n	21	21	7	21	20	20	15	20

BDL = below detection limit: DNOP < 1.8 ng/L, TCPP < 1.0 ng/L
BQL = below quantification limit: DEP < 4.0 ng/L, CAF < 10.0 ng/L
Values in parenthesis indicate the number of samples that were either BDL or BQL

The DEP effluent concentrations were below the LOQ at frequencies of 48%, 86% and 24% for units HSF-R, HSF-C and HSF-Z, respectively (Table 3; Figure 4a), while the respective mean removal efficiencies were 92.4%, 96.9% and 75.0% (Figure 3a). The statistical analysis (Table 4) indicated statistically significant differences in percent removal between the pilot-scale units ($p < 0.05$). The MW U-test showed that the DEP removal in the HSF-C unit was statistically significantly higher than that of the HSF-Z (unplanted) unit (Table 4; $p < 0.05$). The planted HSF unit presented higher removal efficacy than the unplanted unit, and it seems that the cattail contributes to the removal of DEP more than the reed. According to Verlicchi and Zambello [68], cattails have been found in some studies to be more effective in EP removal, while other studies found reeds to be more effective. Zheng et al. [69] reported 19.2% DEP removal in a full-scale HSF-CW, which is lower than that of the present study.

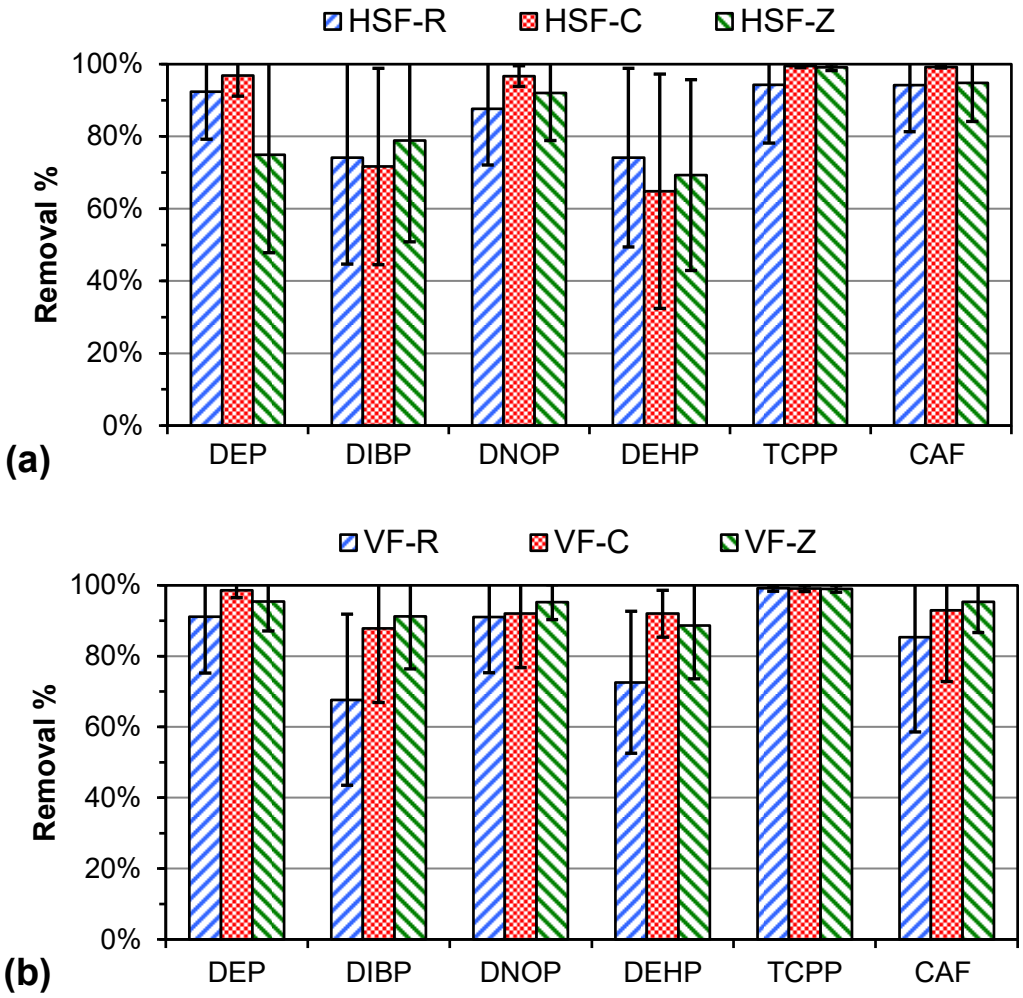


Figure 3. Mean removal values and standard deviation of EPs at pilot-scale units: (**a**) HSF-CW, (**b**) VF-CW.

The DIBP influent mean value for the HSF-CW units was 1.121 µg/L and the effluent mean values for the HSF-R, HSF-C and HSF-Z units were 0.299, 0.288 and 0.147 µg/L, respectively. Lower effluent concentrations of DIBP were observed in most cases compared to influent values (Figure 4b). The mean removal efficiencies of DIBP were 74.1%, 71.7% and 78.9% for the HSF-R, HSF-C and HSF-Z units (Figure 3a), respectively, and there were no statistically significant differences ($p > 0.05$) in percent removal between the HSF-CW units (Table 4).

Zheng et al. [69] reported 19.4% DIBP removal in a full-scale HSF-CW, which is lower than that of the present study, and the main removal mechanism was the adsorption on the substrate. On the other hand, Reyes-Contreras et al. [48] reported percent removals of about 30%, 20% and 50% in winter (February 2008) and 15%, 25% and 25% in summer (June–July 2009) for DEP, DIBP and DEHP, respectively, in an HSF-CW unit with 75 m^2 surface in plan-view and HRT of 2.3 days.

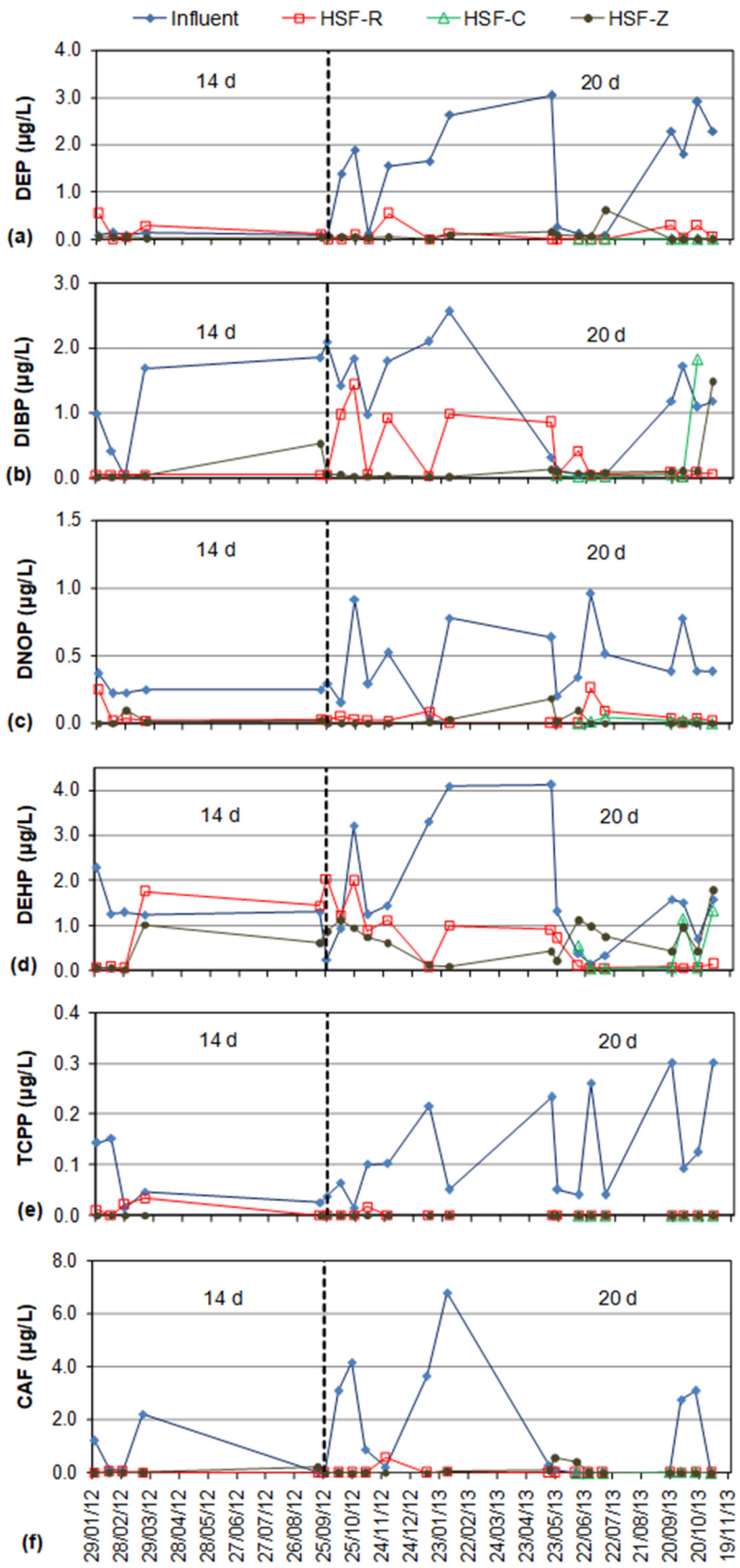


Figure 4. Time series of influent and effluent concentration values in each HSF-CW unit (HRT indicated) for all pollutants: (**a**) DEP; (**b**) DIBP; (**c**) DNOP; (**d**) DEHP; (**e**) TCPP; (**f**) CAF.

Table 4. Kruskal–Wallis and Mann–Whitney U-test results of removal EPs at CW units.

HSF Pilot-Scale Units					VF Pilot-Scale Units				
EPs	**Kruskal–Wallis Test**		**Mann–Whitney U-Test**		**EPs**	**Kruskal–Wallis Test**		**Mann–Whitney U-Test**	
	Test Statistic	***p***	**Compared CWs**	***p***		**Test Statistic**	***p***	**Compared CWs**	***p***
DEP	6.470	0.039	HSF-R, HSF-C	0.679	DEP	4.160	0.125		
			HSF-R, HSF-Z	0.328	DIBP	9.149	0.010	VF-R, VF-C	0.294
			HSF-C, HSF-Z	0.048				VF-R, VF-Z	0.008
DIBP	1.335	0.513						VF-C, VF-Z	0.905
DNOP	3.428	0.180			DNOP	0.146	0.930		
DEHP	0.380	0.827			DEHP	13.112	0.001	VF-R, VF-C	0.010
TCPP	1.675	0.433						VF-R, VF-Z	0.003
CAF	0.168	0.919						VF-C, VF-Z	0.971
					TCPP	0.072	0.965		
					CAF	1.627	0.443		

DNOP effluent concentrations were below LOD at frequencies 24%, 29% and 62% for HSF-R, HSF-C and HSF-Z units, respectively (Table 3; Figure 4c). They were also lower than influent values throughout the experimental period for all HSF-CW units. The influent mean concentration value for the HSF-CWs was 0.425 μg/L, and the effluent mean concentration values for the HSF-R, HSF-C and HSF-Z units were 0.051, 0.017 and 0.024 μg/L, respectively, while the respective removal capacities were 96.7%, 92.0% and 87.6% (Figure 3a). The statistical analysis (Table 4) indicated no statistically significant differences ($p > 0.05$) in the DNOP removal rates among the HSF-CWs.

The DEHP concentrations at the outlet were lower than the influent values for unit HSF-C, while the HSF-R and HSF-Z units showed relatively high outflow values, often exceeding those of the inflow at frequencies 23% and 40%, respectively (Figure 4d). This resulted in low mean removal efficiencies for DEHP, which were 74.1%, 64.8% and 69.3% for the units HSF-R, HSF-C and HSF-Z (Figure 3a), respectively. Table 4 shows no statistically significant differences ($p > 0.05$) in percent removal between the HSF-CW units. The removal of DEHP in the present study was found to be higher than the removals reported in previous studies, e.g., 48.6% DEHP removal in a full-scale HSF-CW [69]. Moreover, Xiaoyan et al. [6] reported removal of 31–45% and 21–34% for DNOP and DEHP, respectively, in pilot-scale HSF-CW units—values lower than in the present study. Several studies conducted in activated sludge wastewater treatment plants (WWTP) reported that 74–81% of DEHP was eliminated due to microbial degradation [27]. However, several studies reported that DEHP is a persistent compound with a low biodegradation rate [70]. Finally, the accumulation of DEHP in the shoots of plant species like *Typha* was reported by Diepenheim et al. [71].

Regarding TCPP and CAF, the influent concentrations were higher than the effluent values throughout the experimental period for all HSF-CWs. The TCPP concentration was below LOD at frequencies higher than 81% (Table 3; Figure 4e), and the CAF concentration was below LOQ at frequencies 67%, 57% and 33% for the HSF-R, HSF-C and HSF-Z units, respectively (Table 3; Figure 4f). The mean removal efficiencies of TCPP were 94.3%, 99.4% and 99.1%, and of CAF 94.2%, 99.1% and 94.8% for the HSF-R, HSF-C and HSF-Z units, respectively (Figure 3a). Table 4 (KW test) shows no statistically significant differences in percent removal ($p > 0.05$) between the HSF-CW units for both TCPP and CAF. The results of laboratory degradation experiments conducted by Regnery and Püttmann [15] showed that TCPP is resistant to degradation by sunlight. In addition, according to Iqbal et al. [72], TCPP has low biodegradability, which makes it more abundant in river water. On the other hand, Reemtsma et al. [18] reported that TCPP sorption on activated sludge was the major removal process in a WWTP. Furthermore, according to Qin et al. [73], the absorption and

accumulation of TCPP by hydrophytes contributes to TCPP removal in CWs. In addition, Brunsch et al. [74] reported that biodegradation, sorption on substrate and/or plant uptake likely occurs in CWs. Consequently, biodegradation, adsorption on the substrate and plant uptake are the main mechanisms of TCPP removal in CWs. The mean removal efficiencies of CAF were high (94.2–99.1%) in the HSF-CWs of the present study and are in agreement with previous studies, which showed that CAF is an easily removable EP. Chen et al. [31] reported CAF removal of 93–99% in full-scale HSF-CWs, and other studies also reported high removal efficiencies of CAF (65–98%) in HSF-CWs [29,49].

According to the experimental setup, the HSF-R and HSF-Z units operated at HRTs of 14 and 20 days, while the HSF-C unit only operated at an HRT of 20 days (Figure 4). The mean removal efficiencies in HSF-CW units for HRTs of 14 and 20 days are presented in Table 5. The MW U-test (Table 6) indicated a statistically significant difference ($p < 0.05$) between the HRT of 14 days and 20 days only for DEHP and CAF in the HSF-R unit, and for DNOP in the HSF-Z unit. The $LogK_{ow}$ of DNOP and DEHP are 8.06 and 7.50, respectively (Table 1), and are characterized as hydrophobic compounds. Other studies have reported that mainly for hydrophobic organic compounds there is positive correlation between HRT and the removal efficiency [68,75]. Zhang et al. [56] reported a linear correlation between CAF removal and HRT. The results of the present study indicate that an HRT of 14 days may be adequate for target compound removal.

Table 5. Removal efficiencies (%) observed in the constructed wetlands.

EPs	HSF Pilot-Scale Units						VF Pilot-Scale Units						
	Overall Removal	HRT 14d		HRT 20d			Overall Removal	Feeding Strategy A			Feeding Strategy B		
		HSF-R	HSF-Z	HSF-R	HSF-C	HSF-Z		VF-R	VF-C	VF-Z	VF-R	VF-C	VF-Z
DEP	85.4	88.1	67.1	94.1	96.9	80.2	94.6	91.9	98.8	92.6	90.0	98.5	99.5
DIBP	76.7	90.9	87.5	63.4	71.7	75.8	81.8	63.7	80.8	86.3	74.3	93.6	96.8
DNOP	90.9	82.5	87.6	90.4	96.7	94.8	92.9	88.3	87.2	94.4	94.7	96.3	96.5
DEHP	70.7	92.1	79.1	66.6	64.8	60.7	84.0	75.1	93.8	85.7	68.7	90.4	93.3
TCPP	98.2	94.7	98.8	97.9	99.4	99.2	99.0	99.1	99.0	98.9	99.1	99.1	99.1
CAF	95.2	86.4	93.5	99.2	99.1	95.6	91.2	76.5	86.3	92.6	99.2	98.7	99.3

Table 6. Mann–Whitney U-test results of comparison for HRT and feeding strategy.

HSF Pilot-Scale Units			VF Pilot-Scale Units		
HRT Comparison: 14d and 20d			Feeding Strategy Comparison: A and B		
EPs	CW Unit	*p*	EPs	CW Unit	*p*
DEP	HSF-R	0.882	DEP	VF-R	0.642
	HSF-Z	0.162		VF-C	0.459
DIBP	HSF-R	0.052		VF-Z	0.012
	HSF-Z	0.183	DIBP	VF-R	0.386
DNOP	HSF-R	0.361		VF-C	0.855
	HSF-Z	0.040		VF-Z	0.500
DEHP	HSF-R	0.020	DNOP	VF-R	0.115
	HSF-Z	0.083		VF-C	0.082
TCPP	HSF-R	0.201		VF-Z	0.374
	HSF-Z	0.289	DEHP	VF-R	0.751
CAF	HSF-R	0.027		VF-C	0.634
	HSF-Z	0.276		VF-Z	0.751
			TCPP	VF-R	0.454
				VF-C	0.379
				VF-Z	0.331
			CAF	VF-R	0.076
				VF-C	0.516
				VF-Z	0.119

3.3. Performance Statistics of VF-CW Pilot-Scale Units

The removal efficiencies of the VF-CW units are presented in Figure 3b, and the temporal variation of the EP concentrations in the influent and effluent of VF-CW units throughout the study period is presented in Figure 5. In the VF-CW units, the DEP influent concentration ranged from 0.091 to 3.044 μg/L (Table 3), and for all VF units and the whole monitoring period, the effluent concentrations were lower than the influent values (Figure 5a). The DEP effluent concentrations were below LOD at frequencies 55%, 73% and 70% for units VF-R, VF-C and VF-Z, respectively (Table 3). The DEP effluent mean concentration values for the VF-R, VF-C and VF-Z units were 0.058, 0.025 and 0.012, respectively, while the respective mean removals were 91.1%, 98.6% and 95.4% (Figure 3b). There were no statistically significant differences ($p > 0.05$) in percent removals between the VF pilot-scale units (Table 4).

Similar to the HSF-CW units, the VF-C unit demonstrated better overall performance than the VF-R unit, likely due to the more vigorous root system of cattails, something that may lead to increased uptake of DEP. The results also indicate higher removal of DEP in VF-CWs than HSF-CWs. Xiaoyan et al. [6] also reported similar results, where the VF-CWs achieved higher removal (58–83%) than the HSF-CW units (44–51%), which was attributed to the fact that aerobic biodegradation is considered a major removal process for PEs in constructed wetlands.

DIBP effluent concentrations, in most cases, were lower than the influent values for all VF-CW units (Figure 5b). These were below LOQ at frequencies 7% and 60% for units VF-C and VF-Z, respectively (Table 3). The influent mean value for the VF-CW units was 0.710 μg/L, and the effluent mean values for the VF-R, VF-C and VF-Z units were 0.289, 0.048 and 0.106 μg/L, respectively (Table 3), while the respective mean removal rates of DIBP were 67.7%, 87.8% and 91.2% (Figure 3b). The VF-R unit presented the worst performance, while the overall performance of VF-C and VF-Z units was satisfactory. The statistical analysis (Table 4) indicated statistically significant differences ($p < 0.05$) in percent removals of DIBP between the VF pilot-scale units. The performance of the VF-R unit was statistically lower ($p < 0.05$) than that of the unplanted unit VF-Z (Table 4; MW U-test). These results indicate that DIBP removal by plant uptake in the CW units is negligible, which is in agreement with Li et al. [76], who studied the dibutyl phthalate removal in VF-CW and pointed out negligible plant uptake, photodegradation, volatilization and adsorption on porous media of DIBP, while biodegradation is the primary process for its removal. In VF-CWs, plant uptake photodegradation and volatilization can be considered negligible, and therefore, biodegradation is likely to be the main mechanism in removing DIBP.

As in the case of HSF units, the DNOP effluent concentrations of VF-CW units were lower than influent values for all VF-CW pilot-scale units, and they were also below the LOD at frequencies 50%, 47% and 50% for VF-R, VF-C and VF-Z units, respectively (Table 3; Figure 5c). The influent mean concentration value for the VF-CW units was 0.412 μg/L, and the effluent mean concentration values for the VF-R, VF-C and VF-Z units were 0.045, 0.016 and 0.015 μg/L, respectively, while the respective mean DNOP removal rates were 91.0%, 92.0% and 95.2% (Figure 3b). No statistically significant differences ($p > 0.05$) in percent removals between the VF-CW units were found (Table 4). In most cases, DEHP effluent concentrations were lower than the influent values for all VF-CW units (Figure 5d). The influent mean concentration value for the VF-CW units was 1.334 μg/L, and the effluent mean concentration values were 0.431, 0.060 and 0.181 μg/L for VF-R, VF-C and VF-Z units, respectively, while the respective mean DEHP removal rates were 76.2%, 92.0% and 88.6% (Figure 3b). Statistical analysis (Table 4) indicated statistically significant differences ($p < 0.001$) in percent removal between the VF-CWs. The DEHP removal efficiency in VF-R was statistically significantly lower than those of VF-C ($p < 0.05$) and VF-Z ($p < 0.05$), and there was no other statistically significant difference (Table 4; MW U-test). The removals of DNOP and DEHP in the present study were found to be higher than the values reported by Xiaoyan et al. [6], where the removals of DNOP and DEHP in pilot-scale VF-CWs were 42–45% and 45–49%, respectively, using a non-selective detection (GC-FID).

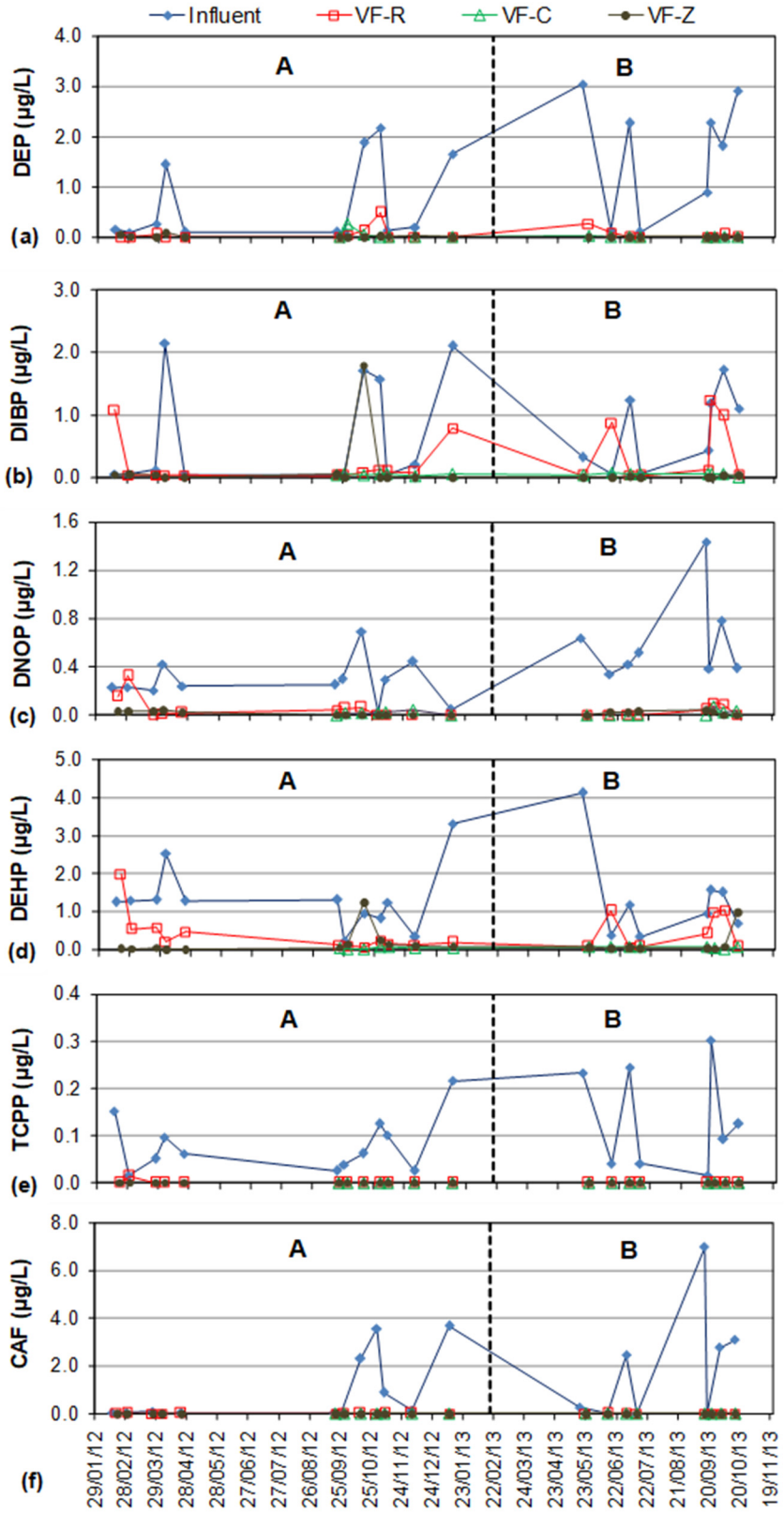


Figure 5. Time series of influent and effluent concentration values in each VF-CW unit for: (**a**) DEP; (**b**) DIBP; (**c**) DNOP; (**d**) DEHP; (**e**) TCPP; (**f**) CAF. Feeding strategies (A: 0.209 m/d and B: 0.283 m/d) are also indicated.

Regarding TCPP and CAF, the influent concentrations were higher than the effluent values throughout the experimental period for all VF-CW units; they were below the LOD at frequencies higher than 95% for TCPP (Table 3; Figure 5e), and for CAF, they were below the LOQ at frequencies 50%, 60% and 90% for VF-R, VF-C and VF-Z units, respectively (Table 3). The mean removal rates of TCPP were 99.1%, 99.0% and 99.0%, and of CAF 85.3%, 92.9% and 95.3%, for VF-R, VF-C and VF-Z pilot-scale CWs, respectively (Figure 3b). Table 4 (KW test) indicates there were no statistically significant differences in percent removal ($p > 0.05$) between the VF-CW units for both TCPP and CAF. The results show that VF-CWs can remove caffeine at high rates. Similar results with removal efficiencies of 99% and 82–99% were reported by Matamoros et al. [77,78].

The mean removal capacities in VF-CW units for both feeding strategies A and B are presented in Table 5. Regarding the mean removal of DEP and DEHP in the VF-R and VF-C units, the removal efficiency was greater for the lower HLR (strategy A). These results agree with the study by Li et al. [76], who found that DIBP removal was higher at a HLR of 0.11 m/d than that of 0.33 m/d. However, statistically significant differences (Table 6; MW U-test: $p < 0.05$) in the removal capacity between the two feeding strategies (i.e., A and B) were only found for DEP in the VF-Z unit. Therefore, the feeding strategy of the VF-CWs in the present study does not affect the removal of the studied EPs. Matamoros et al. [78] investigated the removal efficiencies of CAF in a VF-CW system at different HLRs (0.013, 0.030, 0.070 and 0.160 m/d) and also found that CAF removal was slightly affected by the loading rate. However, Xiaoyan et al. [6] reported that HLRs play an important role in PE removal in pilot-scale VF-CWs, and PE removal efficiency decreases as the HLR increases.

3.4. CW Configuration Comparison and Possible Treatment Mechanisms

The mitigation/elimination and average overall removal of PEs (i.e., DEP, DIBP, DNOP and DEHP) is lower in HSF-CW units than that of VF-CW units (Table 5), indicating that the more oxidizing environment of VF-CWs favors the PEs' microbial degradation [66,79]. In VF-CWs, the presence of the aeration tubes and intermittent feeding allowing for a resting period enhance the transfer of oxygen to the media, boosting PE removal. Xiaoyan et al. [6] reported that VF-CWs showed better performance than HSF-CWs for DEP, DIBP, DNOP and DEHP. Previous studies showed that microorganisms play a major role in PE degradation under aerobic and anaerobic conditions [6,76,80]. Furthermore, the length of the alkyl side chains and the alkyl branch chains, as well as the molecular weight, affects the biodegradability of the PEs [13]. PEs with lower molecular weight and short alkyl chains are more easily degraded than PEs with higher molecular weight and long alkyl chains. Thus, the DEP reduction was higher than that of DEHP in the VF pilot-scale units.

Additionally, these compounds can be removed in the CW environment by various mechanisms, such as plant uptake, sedimentation and/or adsorption on porous media. Compounds with $LogK_{ow}$ values ranging from 3.0 to 4.0 are more easily transported and accumulated in plant tissues with optimum root uptake and translocation to shoots for $LogK_{ow}$ values 1 to 3 [81]. Therefore, high phytoaccumulation of DEP is expected because of its $LogK_{ow}$ value of 2.47 (Table 1). The results showed that the removal of DEP in the planted HSF-CWs was higher than that in the unplanted unit, and the removal in HSF-C unit (planted with cattail) was statistically significantly higher than that of the unplanted HSF-Z CW (Table 4; Figure 3a). Table 4 also shows that, for the remaining PEs studied, no significantly different removals between the planted and unplanted units were observed. This means that the contribution of plants to the removal of these compounds is negligible. On the other hand, many studies have reported that as $LogK_{ow}$ increases, there is a greater tendency for PEs to adsorb on substate or accumulate in plants [6,13,69,80]. DIBP, DNOP and DEHP have low water solubility and $LogK_{ow} > 4$, and, therefore, high adsorption of them on substrate is expected. Specifically, DEHP plant uptake by *Typha* species was reported by Diepenheim et al. [71]. TCPP and CAF are not affected by direct photodegradation [15,28]. TCPP has a low octanol-water coefficient ($LogK_{ow} = 2.59$) and low biodegradability. According to Zhang et al. [56], plant uptake plays the dominant

role in CAF elimination, due to its high polarity and water solubility (Table 1), while biodegradation only plays a minor role.

4. Conclusions

Three HSF and three VF pilot-scale CWs with different configurations were shown to be a reliable and efficient technology for emerging pollutant (EP) removal from domestic wastewater originating in a university campus. HSF-CW units showed relatively low removal capabilities for DIBP and DEHP, with an overall average removal of 76.7% and 70.7%, respectively. The highest phthalate ester (PE) removal was seen in the VF-CWs (81.8–94.6%), although in HSF-CWs, PE removal efficiency (70.7–90.9%) was quite satisfying. The results of the present study indicate that for HSF-CW units, an HRT of 14 days may be adequate for target compound removal, and the loading rate of the VF-CWs does not play an important role in the removal of the EPs studied. Biodegradation under aerobic and/or anaerobic conditions and adsorption on the substrate are the main removal mechanisms of the target EPs, while the presence of plants has little impact on their removal in CWs. This research highlights the overall efficacy of HSF and VF-CWs in EP removal, and indicates that CWs may be a useful technology in removing EPs from municipal wastewaters.

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