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Removal of Pharmaceuticals and Personal Care Products (PPCPs) from Urban Wastewater in a Pilot Vertical Flow Constructed Wetland and a Sand Filter

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Removal efficiencies and elimination kinetics of 13 pharmaceuticals and personal care products (PPCPs) and BOD_5, TSS, and ammonium were evaluated in a pilot vertical subsurface-flow constructed wetland (VFCW) and compared with those obtained by a sand filter. On the basis of the observed removals, the PPCPs studied were grouped in relation to their removal efficiency into (i) PPCPs very efficiently removed, that is, >95% removal in one of the systems (caffeine, salicylic acid, methyl dihydrojasmonate, CA-ibuprofen, hydrocinnamic acid, oxybenzone, ibuprofen, OH-ibuprofen); (ii) PPCPs moderately removed, with removals between 70 and 90% in the two systems (naproxen, diclofenac, galaxolide, and tonalide); and finally (iii) PPCPs poorly removed, with elimination rates of <30% (carbamazepine). At design hydraulic loading rate (HLR) the planted VFCW and the nonplanted SF exhibited similar PPCP removal efficiencies, but the VFCW was less sensitive to removal decline in overloading conditions (up to 2 times the design HLR). Moreover, under a clogging simulation, the HLR and the presence of vegetation were some of the key aspects affecting the PPCPs, BOD_5, and ammonium removal from domestic wastewater. The VFCW evaluated was more efficient in terms of removal efficiency and loading rate for most of the PPCPs studied in comparison to constructed wetlands of other configurations (i.e., horizontal subsurface flow) and SF (nonplanted). The shorter hydraulic residence time (a few hours) in VFCW compared to that in other CW configurations ranging from days to weeks makes VFCWs a very appropriate wastewater treatment option in space-limited areas.

Introduction

Pharmaceuticals and personal care products (PPCPs) have been continuously discharged into the aquatic environment for more than a century without any restrictions (*1*, *2*). PPCPs have been detected in effluents from a variety of wastewater treatment plants (WWTPs) in concentrations from parts per trillion to low parts per billion (*3*, *4*). Some compounds such as ibuprofen and salicylic acid are generally removed with high efficiencies in conventional WWTPs, but others, such as carbamazepine and clofibric acid, are not efficiently removed (*1*). Tertiary treatments such as ozonolysis and advanced oxidation techniques have been evaluated (*5*) and found to increase PPCP removal, but the additional treatment also increases the costs. Consequently, variable concentrations of these compounds are detected in surface, ground, and coastal waters receiving treated sewage effluents (*6*), and recent studies on the environmental risk assessment of PPCPs in Denmark have shown that their concentrations could exceed the predicted noneffect concentration (PNEC) (*7*).

Constructed wetlands (CW) are land-based wastewater treatment systems that consist of shallow ponds, beds, or trenches that contain floating or emergent, rooted wetland vegetation (*8*). The removal of PPCP in lagoons, free water surface CWs (FWSCWs), and horizontal subsurface-flow CWs (HFCWs) has been studied (*9*–*11*). A main limitation of these CWs is the large surface area generally required, which limits their application to the sanitation of small populations (<2000 inhabitants) or tertiary treatments. Vertical-flow constructed wetlands (VFCWs) are more efficient because they operate under aerobic conditions and require smaller surface area (*12*). The hydraulic residence time (HRT) in VFCWs is a few hours (*13*) instead of days as is typical for HFCWs. VFCWs thus have the potential to be used for larger populations because they are more area efficient. In this study, we present for the first time data on the elimination of PPCPs from urban wastewater in aerobic VFCWs. Moreover, a comparison between a planted VFCW and an unplanted system (a sand filter, SF) was carried out to evaluate the influence of vegetation on PPCP removal. Finally, the VFCW and SF were flooded with wastewater to simulate clogging and its effect on the treatment performance. A flooded system or clogged system will have a reduced oxygen supply. The microbial processes in the bed might then be oxygen limited and result in a rapid failure of the treatment performance as well as a reduction of the PPCP removal (*9*). Compounds selected in this study included a variety of chemical classes that originate from human use (i.e., analgesics, lipid regulators, antiepileptic drugs, sunscreens, and fragrances).

Materials and Methods

Chemicals. GC grade (Suprasolv) hexane, methanol, ethyl acetate, acetone, and dichloromethane were obtained from Merck (Darmstadt, Germany). Analytical grade acetic acid and hydrochloric acid were obtained from Panreac (Barcelona, Spain). Hydrocinnamic acid, oxybenzone, carbamazepine, ibuprofen, caffeine, methyl dihydrojasmonate, galaxolide, tonalide, ketoprofen, salicylic acid, diclofenac, 2,2′-dinitrophenyl, and dihydrocarbamazepine were purchased from Sigma-Aldrich (Steinheim, Germany). 2,4,5-Trichlorophenoxypropionic acid (2,4,5-TPA) was obtained from Reidel-de-Haen (Seelze, Germany). Trimethylsulfonium hydroxide (TMSH) was purchased from Fluka (Buchs, Switzerland), and 0.45 μm glass fiber filters of 47 mm were purchased from Millipore (Bedford, MA).

Pilot Plant. The study took place at an experimental pilot plant located in the vicinity of Århus, Denmark (*14*). The plant was constructed during the spring of 2001 within the grounds of a municipal WWTP of a 30000 population equivalent (PE) town. The pilot plant consists of a prefabricated 2 m^3 three-chamber polyethylene sedimentation tank, a 5 m^2 VFCW, and a 10 m^2 SF bed. The two beds are constructed in a HDPE-lined metal container divided into

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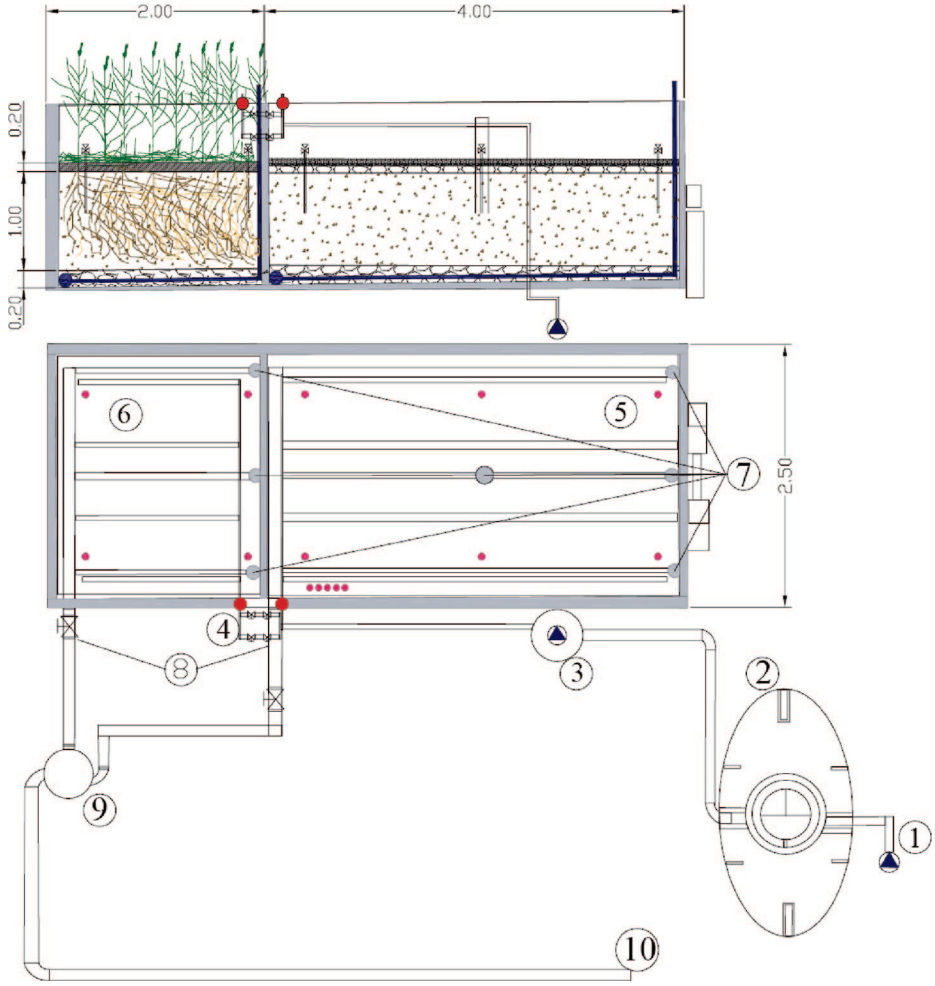

FIGURE 1. Layout of the experimental pilot plant: (1) inlet pumping well; (2) sedimentation tank; (3) pumping well; (4) flow control manifold control; (5) biological sand filter (SF); (6) vertical flow constructed wetland (VFCW); (7) aeration pipes; (8) effluent from VFCW and SF; (9) sampling well; (10) final effluent.

two sections. Each bed is filled with two layers of different diameter gravel. The bottom layer of 0.20 m depth contains coarse gravel (8–16 mm) and houses the drainage system. On top of this layer lies a 0.8 m deep gravel section of 0–4 mm (D_{10} = 0.55 mm and D_{60} = 3.1 mm). The wastewater distribution system is placed on top of this gravel layer and consists of four 40 mm perforated polyethylene pipes in each bed. The VFCW has a dense vegetation of *Phragmites australis*, and the SF is covered by a perforated plastic liner (0.2 m of 16–32 mm gravel to simulate conditions in buried sand filters). The *Phragmites* vegetation was 5 years old; hence, the plants were well developed and the roots penetrated to the bottom of the gravel filter at the time of the study. The pilot plant is fed with raw urban wastewater taken from a well located just before the WWTP influent. Raw wastewater is pumped by a timer-controlled pump into the sedimentation tank. From there, the water drains to a level-controlled pumping well from which the water is distributed through pressure pipes onto the surface of the two systems. The distribution of loading between the two systems was controlled and monitored by flow meters. After percolating vertically through the gravel filters (unsaturated flow), the effluent is collected in drainage pipes located in the bottom of the system and led by gravity to the outlets. Valved 4 mm diameter stainless steel piezometers were installed in the beds (four in the VFCW and six in the SF) for the collection of gas samples from the unsaturated filters.

Experimental Design and Sampling Strategy. Four different hydraulic loading rates (HLRs) were applied onto the systems to evaluate the dependency of treatment performance on loading rate (13, 30, 70, and 160 mm day^{-1}). The loading rates were controlled by increasing the frequency of pumping of settled wastewater from the inlet well. The systems were operated at a specific loading rate for 2 weeks, and inlet and outlet samples were collected daily during the last 3 days of the loading period when performance of the systems had stabilized under the particular loading rate. The inlet and outlet samples were collected in 1 L glass amber bottles and kept refrigerated during transportation to the laboratory, where they were stored at 4 °C until analysis (within 2 days). The samples were analyzed for general parameters and PPCPs as described below. Gas samples from the piezometers were taken by 50 mL glass syringes and analyzed for CO_2, O_2, and CH_4 by gas chromatography (GC) the same day. When the four loading rates had been tested, the outlet levels from the two beds were raised to the bed surface to saturate the beds completely with water and to simulate the effects of clogging. The performance of the water-saturated systems was measured at a HLR of 70 mm day^{-1}. The experiments were carried out during June and July 2006 when the vegetation was well developed.

Analytical Methodology. *Wastewater Analysis.* Conventional wastewater parameters including TSS, BOD_5, and NH_4^+ were analyzed following standard methods (*15*). The pH was measured in influent wastewater by a conventional pH-electrode, and dissolved oxygen (DO) and temperature were measured with an OxyGard DO meter. The composition of the gas samples (CO_2, O_2, and CH_4) was analyzed by a gas

TABLE 1. Average (±1 SD) Influent and Effluent Water Quality of the Vertical Flow Constructed Wetland (VFCW) and the Sand Filter (SF) at Different Hydraulic Loading Rates (HLR)[a]

HLR	system	DO (mg L^{-1})	pH	BOD_5 (mg L^{-1})	TSS (mg L^{-1})	NH_4-N (mg L^{-1})
13 mm day^{-1}	inlet	0.5 ± 0.2	7.3 ± 0.1	217 ± 15	60 ± 16	41.3 ± 1.3
	VFCW	8.4 ± 0.4	8.2 ± 0.1	5.7 ± 3.2 (97)	2.8 ± 0.3 (80)	0.1 ± 0.1 (99)
	SF	5.1 ± 0.9	7.9 ± 0.4	4.0 ± 3.5 (98)	2.8 ± 0.1 (62)	0.1 ± 0.1 (99)
30 mm day^{-1}	inlet	0.3 ± 0.1	7.2 ± 0.1	213 ± 6	59 ± 7	46.2 ± 2.3
	VFCW	9.2 ± 0.4	8.2 ± 0.1	1.0 ± 0.1 (99)	0.7 ± 0.3 (99)	0.1 ± 0.1 (99)
	SF	8.9 ± 0.5	8.0 ± 0.2	1.0 ± 0.1 (99)	2.4 ± 1.6 (96)	0.1 ± 0.1 (99)
70 mm day^{-1}	inlet	0.3 ± 0.1	7.2 ± 0.1	247 ± 3	84 ± 6	45.1 ± 0.5
	VFCW	9.0 ± 0.5	8.1 ± 0.1	0.7 ± 0.6 (99)	1.7 ± 1.2 (98)	0.1 ± 0.1 (99)
	SF	5.9 ± 0.5	7.6 ± 0.1	1.7 ± 0.6 (99)	1.3 ± 0.5 (98)	0.9 ± 0.6 (98)
160 mm day^{-1}	inlet	0.1 ± 0.1	7.3 ± 0.1	227 ± 21	79 ± 10	45.5 ± 2.0
	VFCW	7.5 ± 0.3	7.7 ± 0.1	3.0 ± 0.1 (98)	2.1 ± 0.3 (97)	0.1 ± 0.1 (99)
	SF	2.3 ± 0.9	7.2 ± 0.1	12.3 ± 3.2 (95)	4.6 ± 1.9 (94)	14.9 ± 1.2 (67)
70 mm day^{-1} (water saturated)	inlet	0.1 ± 0.1	6.7 ± 0.1	230 ± 18	97 ± 8	59.3 ± 3.1
	VFCW	4.8 ± 1.0	7.2 ± 0.1	10.7 ± 1.5	15.1 ± 5.1 (84)	8.1 ± 0.8 (86)
	SF	1.2 ± 0.26	7.1 ± 0.2	17.7 ± 2.1	21.3 ± 0.8 (78)	14.0 ± 4.7 (76)

[a] Values in parentheses are the removal percentages.

chromatograph equipped with a thermal conductivity detector (Shimadzu GC-8A, Kyoto, Japan) as described by Brix (*16*). The concentrations of PPCPs in wastewater samples were analyzed after the samples had been filtered and processed as reported by Matamoros et al. (*9*). Briefly, a sample volume of 500 mL was spiked with 1 μg of a surrogate standard mix (i.e., fenoprop for the acidic compounds, 2,2′-dinitrophenyl for musk, and dihydrocarbamazepine for neutral compounds). The spiked sample was percolated through a polymeric solid-phase extraction cartridge (100 mg Strata X) from Phenomenex (Torrance, CA). Activated cartridges were eluted with 10 mL of hexane/ethyl acetate (1:1). The extract was evaporated to ca. 20 μL under a gentle nitrogen stream, and 186 ng of triphenylamine was added as internal standard. Then the vial was reconstituted to 300 μL with ethyl acetate.

Methylation of the carboxylic acid group was performed online in a hot GC injector by adding 10 μL of TMSH (0.25 mol L^{-1} in methanol) to a 50 μL sample before injection. Derivatized samples were injected onto a TRACE GC-MS (Thermo-Finnigan, Dreieich, Germany) in the electron impact mode (70 eV ionization energy) fitted with a 30 m × 0.25 mm i.d. × 0.25 μm DB-5 column (J&W Scientific, Folsom, CA). Temperature program and quantification details are described elsewhere (*9*). In addition, for sunscreen compounds the following diagnostic ions were monitored for time-scheduled acquisition for target analyte quantification (in bold) and identification: oxybenzone **227**/151/105; hydrocinnamic acid **104/**164/91.

The LOD and LOQ of the analytical procedure were determined (using Milli-Q water) from the mean background noise plus 3 or 10 times the standard deviation of the background noise, respectively. LOD and LOQ were 8 and 25 ng L^{-1}, respectively, for hydrocinnamic acid, 98 and 364 ng L^{-1}, respectively, for oxybenzone, and 22 and 67 ng L^{-1}, respectively, for carbamazepine. Filters were processed and analyzed as reported elsewhere with LOD and LOQ between 0.1 and 229 ng L^{-1} and between 0.44 and 0.770 ng L^{-1}, respectively (*10*). The blank values of analytical procedure for water and filters remained always below the quantification limit (LOQ).

Statistical Analysis. SPSS v13 package (Chicago, IL) was used for statistical data analysis. The removal comparison between planted and nonplanted systems was analyzed by using the Mann–Whitney test for two independent samples (nonparametric statistics).

TABLE 2. Content of Oxygen, Carbon Dioxide, and Methane (Average ± 1 SD) in the Interstitial Gases in the Vertical Flow Constructed Wetland (VFCW) and the Sand Filter (SF) at Different Hydraulic Loading Rates (HLR)

HLR	system	O_2 (vol %)	CO_2 (vol %)	CH_4 (vol %)
13 mm day^{-1}	VFCW	20 ± 05	0.5 ± 0.5	nd[a]
	SF	20 ± 0.5	0.3 ± 0.1	nd
30 mm day^{-1}	VFCW	19 ± 0.3	0.4 ± 0.1	nd
	SF	19 ± 0.3	0.6 ± 0.1	nd
70 mm day^{-1}	VFCW	19 ± 0.6	1.4 ± 0.4	nd
	SF	18 ± 1.1	1.6 ± 0.8	nd
160 mm day^{-1}	VFCW	18 ± 0.9	2.5 ± 0.7	0.02 ± 0.01
	SF	13 ± 3.9	5.3 ± 3.3	0.03 ± 0.01
70 mm day^{-1} (water saturated)	VFCW	ns[b]	ns	ns
	SF	ns	ns	ns

[a] Not detected. [b] Not sampled.

Results and Discussion

General Parameters. The surface organic loading rate varied between 3 and 37 g of BOD_5 m^{-2} day^{-1} during the experimental period. Table 1 shows TSS, BOD_5, and NH_4^+ concentrations, measured at each HLR checked, and shows efficient removal of all the parameters studied. The high BOD_5 and ammonium removal is consistent with the prevailing oxic conditions of the filters, suggesting that aerobic pathways are predominant to remove organic matter, as generally reported for VFCWs and unsaturated SFs (*12*). Moreover, the gas composition measured in each system confirmed the occurrence of high O_2 levels and the release of CO_2 as a result of organic matter mineralization (Table 2). As expected, an increase in the HLR led to a slight decrease in TSS, NH_4^+, and BOD_5 removal, particularly in the SF. The reduced removal occurred concurrently with a decrease in O_2 and an increase in CO_2. Also, at the highest HLR, methane production was detected in the SF and VFCW, indicating methanogenic processes in anaerobic microsites of the filters (*17*). The better BOD_5 and NH_4^+ removal in the VFCW compared to the SF is probably due to the positive plant influence. The presence of plants may increase oxygen transfer into the system, and roots of the plants may stimulate Biofilm development (*18*). Flooding of the systems at a 70 mm day^{-1} loading rate resulted in lower O_2 levels in the effluent water and lower BOD_5 and NH_4^+ removals. The effects of flooding were more severe for SF than for the VFCW probably due, again, to the positive plant influence (*18*).

TABLE 3. Minimum, Maximum (in Parentheses), and Average Concentrations of PPCPs in the Wastewater Influent for All Loading Rates and the Removal Efficiencies (Percent) Observed in the Vertical Flow Constructed Wetland (VFCW) and the Sand Filter (SF) at a Hydraulic Loading Rate of 70 mm Day^{-1} and Working with either Unsaturated Water Flow or Saturated Flow[a]

		unsaturated flow		saturated flow			
	influent[b,c] (μg L^{-1})	VFCW (% rem)	SF (% rem)	VFCW (% rem)	SF (% rem)	HFCW (*9*) (% rem)	WWTP (% rem)
Pharmaceuticals							
salicylic acid	(45.7–72.3) 53.9	98 ± 1	98 ± 1	85 ± 7	77 ± 7	96	99 (*3*)
ibuprofen	(8.3–17.2) 11.7	99 ± 1	90 ± 3*[d]	55 ± 1	49 ± 1*	71	60–70 (*33*)/ 90 (*1*)
OH-ibuprofen	(12.4 – 16.9) 3.7	99 ± 1	86 ± 3*	51 ± 1	47 ± 2*	62	95 (*34*)
CA-ibuprofen	(8.7–12.4) 10.6	99 ± 1	95 ± 3*	71 ± 6	68 ± 8	87	95 (*34*)
naproxen	(0.96–2.15) 1.57	89 ± 5	80 ± 5	62 ± 3	66 ± 7	85	40–55 (*33*)/66 (*1*)
diclofenac	(0.48–1.28) 0.82	73 ± 3	76 ± 7	53 ± 2	39 ± 22	15	9–75 (*1*)/17 (*23*)
carbamazepine	(1.24–2.9) 2.06	26 ± 14	11 ± 7	20 ± 4	8 ± 15	16 (*35*)	8 (*23*)/7 (*1*)
caffeine	(35.2–64.0) 48.4	99 ± 1	98 ± 1	82 ± 1	75 ± 6*	97	99 (*23*)
Personal Care Products							
methyl-dihydrojasmonate	(18.8–31.8) 22.8	99 ± 1	98 ± 1*	78 ± 4	76 ± 8	99	98 (*21*)
hydrocinnamic acid	(11.2–17.6) 15.4	99 ± 1	99 ± 1	82 ± 3	69 ± 11	na[e]	na
oxybenzone	(8.58–22.1) 14.8	97 ± 1	95 ± 2	88 ± 3	64 ± 24	na	68–99 (*36*)
galaxolide	(3.05–12.4) 5.62	90 ± 1	92 ± 1	88 ± 2	88 ± 2	86	70–85 (*33*)/89 (*21*)
tonalide	(0.66–1.83) 0.99	82 ± 1	82 ± 1	75 ± 2	73 ± 4	88	75–90 (*33*)/88 (*21*)
HRT (h)		4–6	4–6	137	126	114	12–24

[a] Removals obtained in horizontal flow constructed wetlands (HFCW) and conventional wastewater treatment plants (WWTP) are listed for comparison. [b] $n = 15$. [c] Particulate and dissolved wastewater. [d] Statistically significant differences at a significance level of 0.05 (VFCW vs SF). [e] Not available.

PPCP Removal at Design HLR. PPCP levels detected in the influent (Table 3) are consistent with the levels found in other raw wastewaters from the EU and Denmark (*19, 20*). The set of PPCP was selected on the basis of their concentration and a high detection frequency. Analgesics, fragrances, and sunscreen products are major compounds in urban wastewater. Nevertheless, high PPCP variability in inlet concentration was observed between campaigns. When HLR increased, then HRT in the sedimentation tank decreased, which led to an increase in PPCP concentration in sedimentation tank outlet (i.e., the influent to SF and VFCW). This suggests that some removal took place in the sedimentation tank at low HLR. Contaminant removal was calculated by analyzing both dissolved and particulate phases from the influent and effluent. Whereas the major portion of PPCP occurred in the dissolved phase (*9*), galaxolide and tonalide were strongly bound to the particulate phase due their high hydrophobicity (log $K_{ow} = 5.7$–5.9) (*21*).

PPCP removal was higher for the most abundant compounds, which is in agreement with their high biodegradation reported elsewhere (*9*). Although an apparent difference in PPCP removal efficiency between the planted VFCW and the SF was observed at the design HLR of 70 mm day^{-1}, a statistically significant difference was observed for only some of them (Table 3). On the basis of the observed removals, the PPCPs studied can be grouped in relation to their removal efficiency into (i) PPCPs very efficiently removed, that is, >95% removal in one of the systems (caffeine, salicylic acid, methyl dihydrojasmonate, CA-ibuprofen, hydrocinnamic acid, oxybenzone, ibuprofen, OH-ibuprofen); (ii) PPCPs moderately removed, with removals between 70 and 90% in the two systems (naproxen, diclofenac, galaxolide, and tonalide); and finally (iii) PPCPs poorly removed, with elimination rates of <30% (carbamazepine). A similar difference in removals has been observed in treated wastewater irrigated on arable land. In this case, compounds were sorbed or transformed while percolating through the topsoil layer, and only some of them (i.e., carbamazepine) were detected in the lysimeter wells (*22*).

Comparing the obtained PPCP removal in the VFCW with the removals obtained in conventional WWTPs and HFCW, VFCWs appear to be more efficient for some PPCPs. Even diclofenac, a compound that has been extensively reported as recalcitrant in a variety of wastewater treatment technologies (*23, 24*), showed a removal efficiency of ca. 73% in the VFCW studied. Some of the highly efficiently removed compounds (i.e., salicylic acid, caffeine, methyl dihydrojasmonate, and oxybenzone) as well as the compounds that can be eliminated by sorption onto the organic matter (i.e., galaxolide and tonalide) (*9*) and carbamazepine, which have a low removal efficiency, seem to behave very similarly in the two systems studied. The better PPCP removal observed in the VFCW and the SF compared to HFCWs is probably caused by the fact that aerobic processes predominate in VFCWs and SFs, whereas HFCW are usually oxygen deficient because of the water-saturated conditions. This is consistent with previously reported removals of PPCPs in aerated microcosms (*25, 26*). Therefore, the two main removal mechanisms postulated in this study are biodegradation and sorption onto the substrate. Whereas sorption of galaxolide and tonalide onto the organic matter retained in the substrate is supported by their high log K_{ow} values, plant uptake is not considered to be significant, at least for negatively charged compounds (*27*) or highly hydrophobic ones (galaxolide and tonalide) (*28*). Further research is needed to ascertain the role of plant uptake for other neutral compounds (i.e., caffeine, methyl dihydrojasmonate, and oxybenzone).

Effect of HLR on PPCP Removal. To compare the PPCP removal of the VFCW with that of the SF and the relationship to HLR, the total mass removal of each compound was plotted against its total mass loading rate (Figure 2). It is seen from the plots that (i) salicylic and hydrocinnamic acids in both systems are not affected by the mass loading rate and are nearly completely removed in both systems; (ii) oxybenzone, caffeine, methyl dihidrojasmonate, ibuprofen, OH-ibuprofen, and CA-ibuprofen are nearly completely removed in the VFCW at all loading rates but in the SF the removal decreased at the highest loading rate; (iii) galaxolide and tonalide are removed at similar rates <95% in both systems; (iv) naproxen is removed more efficiently in the VFCW compared to the SF, particularly at the highest loading rate; and (v) carbamazepine and diclofenac are poorly removed in both types of

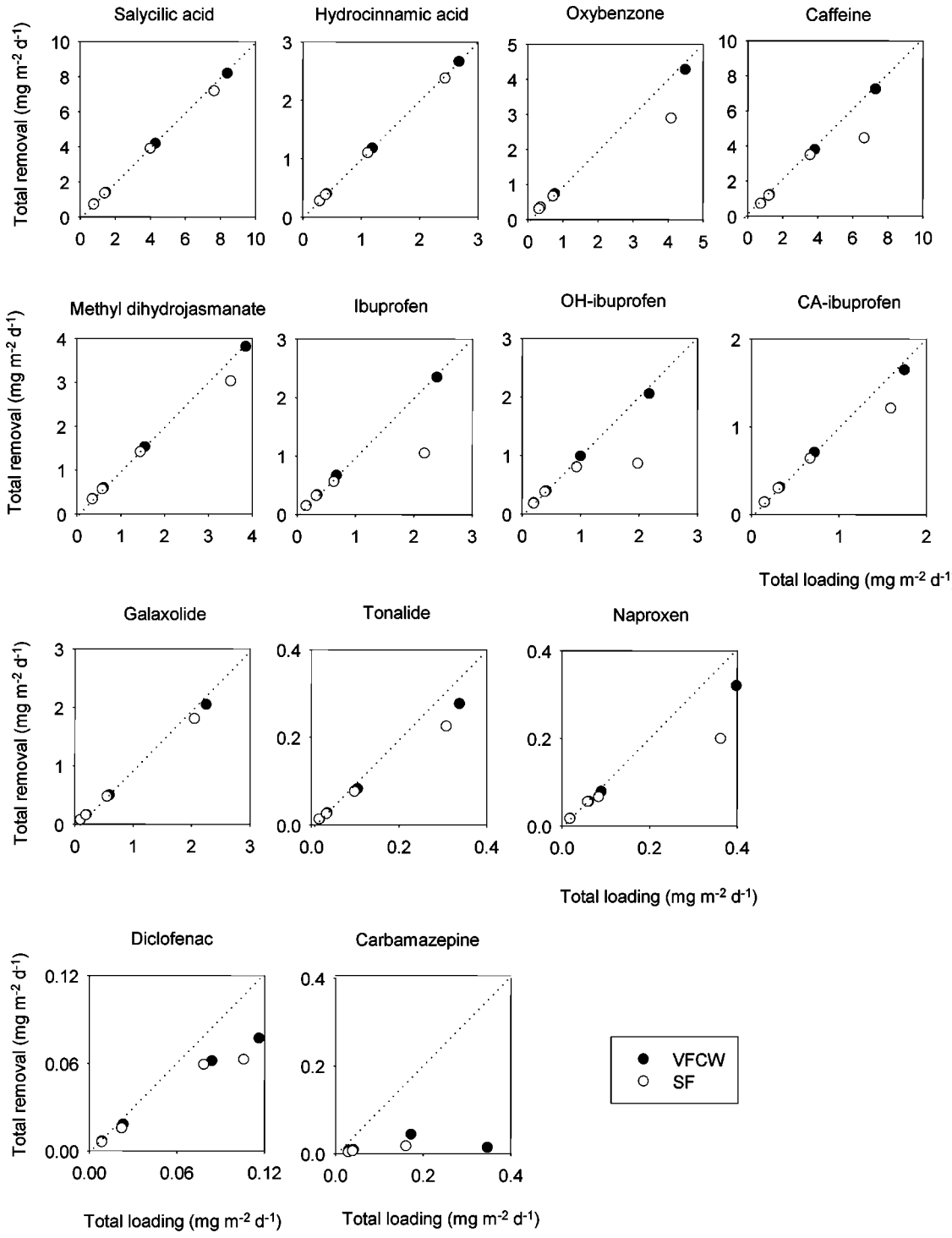

FIGURE 2. PPCP average mass removal rate in the vertical flow constructed wetland (VFCW) and the sand filter (SF) against their mass loading rates. Discontinuous line represents 100% removal.

systems. Overall, the VFCW generally removed PPCP more efficiently than the SF, probably due to a more oxygenated bed. Compounds such as carbamazepine and diclofenac do not follow this general rule due to their remarkable recalcitrance in comparison to other PPCPs (*23*). Galaxolide and tonalide also behave differently due to the fact that their removal is mainly attributable to the interaction and sorption onto the organic matter present in the system (*9*). Salicylic and hydrocinnamic acid were nearly completely removed in both systems, and therefore any effect of the plants could not be observed in the present study.

Effects of Flooding. Clogging of constructed wetland and sand filters affects many treatment processes and generally will lead to a decreased removal efficiency of many constituents of wastewaters (*29*). To simulate the clogging effect, both systems were filled with wastewater at the design HLR (70 mm day^{-1}) and their performances compared. As shown in Table 3, PPCP removals decreased as a consequence of flooding for all of the PPCPs studied, except for carbamazepine, and the fragrances galaxolide and tonalide [because their removal is closely related to sorption onto organic matter (*21*)]. Nevertheless, statistically significant differences were

TABLE 4. Area-Based First-Order Removal Rate Constants and Mass Loading Rates in the Vertical Flow Constructed Wetland (VFCW) and the Sand Filter at a Hydraulic Loading Rate of 70 mm Day^{-1}[a]

	VFCW		SF		HFCW (*9*)	
	loading (mg m^{-2} day^{-1})	k_{A1} (m day^{-1})	k_{A1} (m day^{-1})	ratio	loading (mg m^{-2} day^{-1})	k_{A1} (m day^{-1})
General Parameters						
BOD_5	16.9[b]	0.43	0.34	1.22 ± 0.31	6.75[b]	0.06
TSS	6.11[b]	0.28	0.29	1.23 ± 0.25		
NH_4^+	3.30[b]	0.56	0.27	2.83 ± 2.91	1.47[b]	0.04
Pharmaceuticals						
salicylic acid	4.14	0.29	0.27	1.12 ± 0.22		na[c]
ibuprofen	0.65	0.40	0.16	2.78 ± 2.64	0.71	0.05
OH-ibuprofen	0.96	0.37	0.14	2.65 ± 2.13	0.77	0.04
CA-ibuprofen	0.65	0.31	0.21	1.37 ± 0.63	1.12	0.11
naproxen	0.08	0.16	0.11	1.50 ± 0.57	0.06	0.08
diclofenac	0.08	0.10	0.10	1.22 ± 0.15	0.07	<0.01
carbamazepine	0.17	0.02	0.01	1.39 ± 0.61		na
caffeine	3.67	0.37	0.29	1.90 ± 2.03	0.23	0.11
Personal Care Products						
methyl-dihydrojasmonate	1.49	0.34	0.28	1.47 ± 0.74	0.61	0.19
hydrocinnamic acid	1.15	0.41	0.44	1.00 ± 0.44		na
oxybenzone	0.72	0.26	0.21	1.48 ± 0.85		na
galaxolide	0.59	0.14	0.14	1.05 ± 0.13	0.32	0.05
tonalide	0.11	0.11	0.11	1.15 ± 0.19	0.20	0.06

[a] Average ratio values ± 1 SD. Literature data for horizontal flow constructed wetlands (HFCW) are listed for comparison. [b] In g m^{-2} day^{-1}. [c] Not available.

observed only for ibuprofen, OH-ibuprofen, and caffeine. This could be attributable to the relatively small sample size per each HLR ($n = 3$) evaluated. The PPCPs that were most efficiently removed in the systems were less affected by flooding. The planted bed (VFCW) generally performed better than the SF when flooded. In the VFCW oxygen levels were less affected than in the SF, indicating that aerobic processes were more predominant in that system. The contribution of aerobic pathways decreases (e.g., a decline in ammonium removal), and anaerobic pathways (denitrification, sulfate reduction, and methanogenesis) start to occur (*30*). Hence, the aerobic processes seem to be more efficient in the elimination of most of the PPCPs evaluated than anaerobic processes.

Correlation between General Parameters and PPCP Removal. CO_2, O_2, DO pH, BOD_5, TSS, and NH_4^+ were correlated with the PPCP removal using the complete data set from the VFCW and the SF study. Significant positive correlations were observed between removal of all PPCPs and the general wastewater parameters (Table 1 of the Supporting Information), which shows that under conditions where BOD_5, TSS, and NH_4^+ are efficiently removed, PPCPs will most likely also be removed. PPCP removal correlated positively with O_2 gas in the filter and negatively with CO_2 gas, indicating the importance of aerobic processes. Due to the high hydrophobicity of galaxolide and tonalide and their tendency to absorb into organic matter particles, positive correlations between the removal of these compounds and the total content of TSS were expected. However, these correlations were not observed, probably because the TSS breakthrough point was not reached at any time in this study. Therefore, low correlations were observed between PPCP removal and TSS. The two PPCP compounds that showed the lowest removals in this study (carbamazepine and diclofenac) presented the lowest correlation coefficients. The recalcitrance of these two compounds has been extensively reported (*23, 26*).

Removal Kinetics. The area-based first-order removal rate constants (k_{A1}), using the equation described by Kadlec and Knight (*31*), were calculated using the average inflow and outflow concentrations at the different loading rates Figure 1 of the Supporting Information shows the estimated area-based rate constants for all PPCPs plotted against loading rate. As can be inferred from these plots, the rate constants are dependent on the mass loading rates. Table 4 compares the rate constants estimated at design HLR of 70 mm day^{-1} with rate constants observed in a HFCW at HLR of 36 mm day^{-1}. It can be seen that VFCWs are more efficient in terms of both BOD_5, TSS, and NH_4^+ removal and PPCP removal.

The ratios between the average rate constants for the PPCP removal in the two systems were calculated by using eq 1 to compare the performance of the two systems:

$$\text{ratio} = \frac{\sum_{n=1}^{n=i}\left(\frac{k_{A1,\text{VFCW}}}{k_{A1,\text{SF}}}\right)}{n} \quad (1)$$

where n is the number of HLR checked and k_{A1} is the rate constant obtained at each loading rate and type of system, respectively. The high variability of this ratio is attributable to the wide range of HLR evaluated.

It can be seen from Table 4 that high ratio values (>2) corresponded to compounds that showed different behaviors between VFCW and SF and low ratio values were observed for compounds that were not affected by the type of system. In this regard, it become evident that NH_4^+ removal is highly affected by the oxygen occurrence, probably due to the requirements of the nitrification processes. Similarly, the removal of ibuprofen and OH-ibuprofen is highly oxygen dependent (*25*). On the other hand, BOD_5 and TSS removals were only slightly affected, as were PPCP compounds that were only slightly affected by HLR and flooding (i.e., hydroccinnamic and salycilic acid, galaxolide and tonalide, diclofenac and carbamazepine). Finally, the removal of caffeine, CA-ibuprofen, oxybenzone, methyl dihydrojamonate, and naproxen was almost independent of the system evaluated. Accordingly, bed aeration is a key aspect to promote the removal of most of the PPCPs analyzed. Moreover, the contribution of the rhizosphere biofilm and

root exudates to the degradation of some chemical compounds is unknown (*32*).

In summary, this study clearly documents that VFCWs achieve a better performance compared to HFCW and only slightly better when it is compared with SF and conventional WWTPs for most of the PPCPs studied. Nevertheless, the use of VFCW could be a feasible technology to remove most PPCPs from domestic wastewater from small populations, allowing the design of more compact systems.

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Supporting Information Available

Pearson correlation coefficients and area-based removal rate constants. This information is available free of charge via the Internet at http://pubs.acs.org.

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