Removal of Personal Care Products in Constructed Wetlands

Paola Verlicchi, Elena Zambello, and Mustafa Al Aukidy

Abstract This chapter is an overview of the occurrence of common personal care products in the influent and effluent of different types of constructed wetlands fed with domestic wastewaters, acting as primary, secondary, or tertiary steps and the corresponding removal efficiency achieved by these treatments. The reviewed personal care products belong to eight different classes: 3 antioxidants, 2 antiseptics, 1 deodorant, 1 insect repellant, 1 plasticizer, 3 sunscreen products, 5 synthetic musks, and 16 surfactants (seven anionic and nine nonionic).

Data are collated from 35 peer review papers, referring to investigations carried out in Europe (66%), America (28%), and Asia (6%). Of the 87 treatment lines reviewed, the most common constructed wetland type was the horizontal subsurface flow (49%) followed by the surface flow (38%) and, in a few cases, the vertical subsurface flow. Removal was mainly influenced by redox potential, temperature, hydraulic retention time, and influent concentration of the compound.

The highest values of removal were found for fragrances in secondary systems and fragrances and triclosan in polishing systems.

Due to the different and simultaneous removal mechanisms occurring within these systems and their buffer capacity, they might represent a reliable and feasible treatment which is able to control and reduce the spread of personal care products in the aquatic environment.

Keywords Constructed wetlands, Occurrence, Personal care products, Removal efficiencies, Removal mechanisms

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Contents

1 Introduction

Every day we use products for our personal care and hygiene, in particular cosmetics (skin care products, hair sprays, and sunscreens), toiletries (bath additives, soaps, hair tonics, shampoos, oral hygiene products), and fragrances (perfumes, aftershaves). These products, commonly called personal care products (PCPs), contain synthetic organic chemicals with a specific function, the *ingredients*. They may be antimicrobial disinfectants (triclosan, triclocarban), preservatives (methylparaben, ethylparaben, butylparaben), or sunscreen agents (oxybenzone, avobenzone). In addition, some of them may contain synthetic surfactants (generally anionic and nonionic compounds). These are substances widely used in the formulation of many commercial PCPs not only for their wetting, cleaning, foaming, and emollient properties but also as they can create dispersed systems (suspension or emulsion), modify the cosmetic rheological properties, prolong the durability of the product, and control the release of active ingredients [1] which greatly improves the quality of the substance.

PCPs are used in the range of several thousand tons per year: parabens are used in more than 22,000 cosmetic products [2], approximately 350 tons of triclosan are produced annually in Europe [3], and in 1998, 1,473 tons of galaxolide, 343 tons of tonalide, and 18 tons of celestolide were consumed in Europe [4].

These products are disposed of or discharged into the environment on a continuous basis via municipal/industrial sewage facilities and also directly by untreated discharges [5–7]. This means that their exposure potential may reach critical level for the environment, even for those compounds that might have a low persistence.

In recent years, increasing attention has been paid to the occurrence of some of them in aquatic environments, also due to the finding that some PCPs can induce known or suspected undesirable effects on humans and ecosystems (included endocrine disruptions) [8].

Limits of concentrations have been set for surfactants with regard to wastewater treatment plant discharges into surface water bodies or for the direct reuse of treated effluents. However, limits do not exist for many other PCPs occurring in wastewaters.

Environmental quality standards have also been set for some micropollutants in surface water bodies within the European Union [9].

In the European Union, USA, and other countries, a debate is open regarding the compilation of lists including *priority compounds* requiring monitoring in the aquatic environment [9–12]. However, due to the lack of information on toxicity and environmental impacts, a large number of contaminants, especially organic compounds, are not included in these lists. The number of compounds which could become priorities is therefore likely to grow.

Recent studies have remarked that due to the wide spectrum of characteristics of emerging contaminants, including PCPs, it is quite difficult to find a treatment able to remove most of them at a high percentage.

Recent studies [13, 14] pointed out that different groups of micropollutants can be removed at a medium-high extent only in those treatment trains where different removal mechanisms may occur. Multi-barrier treatment systems are necessary. As highlighted in Verlicchi et al. [15], constructed wetlands (CWs) are systems where oxic-anoxic-anaerobic environments may coexist, especially in subsurface flow beds or in sequence of different kinds of CW types. In surface flow systems, solar radiation may also contribute to the removal of micropollutants.

Increasing attention is being paid to the investigation of the occurrence and removal of common PCPs from wastewater but only a few studies deal with CWs. This chapter provides an overview of these issues, focusing on the different types of CWs acting as primary, secondary, or tertiary steps. Influent and effluent concentrations for 32 PCPs, belonging to eight different classes, were collected and discussed, along with their corresponding removal efficiencies achieved in the investigated types of CWs. The chapter concludes with an analysis of the influence of the main design parameters and operational and environmental conditions on the removal of the reviewed compounds.

2 Chapter Framework

This chapter is based on data collected from 35 peer reviewed papers published between 2001 and 2014, referring to 32 PCPs. All compounds are listed in Table 1, grouped according to their class. For each of them, chemical formula, CAS number and molecular structure are reported together with the references of the investigations included in the review dealing with it. A focus on surfactant classes is available in Table 2 where the nine most common ones are reported. Table 3 reports the schematics to which the investigated wetlands refer (i.e., if they act as a primary, secondary, or tertiary step) and Table 4 shows the CW types included.

The study continues with an analysis of the occurrence of the PCPs in the influent and effluent of CW acting as a primary, secondary, and tertiary step and a discussion of their removal achieved in the three steps distinguishing between the CW types (Figs. 1, 2, 3, 4, 5, 6, 7, 8, and 9). The characteristics and performance of restoration wetlands are then discussed, and finally data referring to occurrence (Figs. 10 and 11) and removal (Fig. 12) in hybrid systems complete the analysis of the different reviewed configurations. The final part of the chapter discusses how CW type, design parameters, and operational and environmental conditions influence the removal of investigated compounds on the basis of the collected literature data.

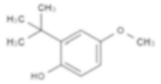
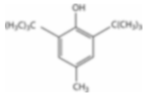
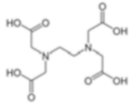
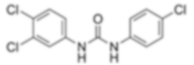
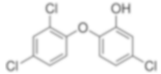
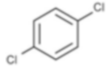
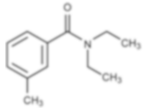
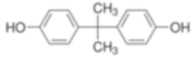
3 Personal Care Products in the Environment and Compounds Included in the Study

The chapter refers to 32 PCPs belonging to eight different classes: 3 antioxidants, 2 antiseptics, 1 deodorant, 1 insect repellant, 1 plasticizer, 3 sunscreen products, 5 synthetic musks, and 16 surfactants (seven anionic and nine nonionic ones).

Reviewed compounds are reported in Table 1 and classes of surfactants in Table 2. Their molecular structure is particularly complex due to the presence of aromatic and/or condensed rings, carboxylic and ketonic groups, double or triple bonds, and, in the case of surfactants, long hydrocarbon chains.

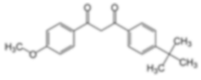
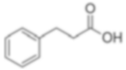
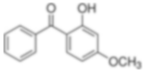
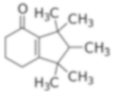
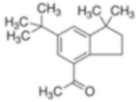
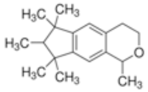
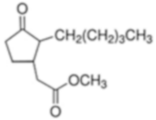
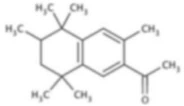
In Italy, NP and *p*-dichlorobenzene have been included among the substances to be monitored in the surface water [54]; in Switzerland, EDTA, NP, triclosan, DEET, and bisphenol A are included in the list of *relevant micropollutants in wastewater,* and they could be considered "target compounds" for which Swiss WWTPs, with a high environmental impact, should guarantee desired removal efficiencies [55]. At a European level, NP is included in the list of priority substances [9], requiring monitoring in water, and in the USA, BHA is included in the contaminant candidate List 3 U.S.EPA 2009 [10].

Table 1 List of reviewed PCPs, grouped according to their class with the corresponding references

	Class	Compound	Molecular structure	n. papers	References
1	Antioxidant	Butylated hydroxyanisole (BHA) $C_{11}H_{16}O_2$ 25013-16-5		1	[16]
2	Antioxidant	Butylated hydroxytoluene (BHT) $C_{15}H_{24}O$ 128-37-0		1	[16]
3	Antioxidant	Ethylenediaminetetraacetic acid (EDTA) $C_{10}H_{16}N_2O_8$ 60-00-4		1	[17]
4	Antiseptic	Triclocarban $C_{13}H_9C_{13}N_2O$ 101-20-2		3	[18–20]
5	Antiseptic	Triclosan $C_{12}H_7Cl_3O_2$ 3380-34-5		14	[16–29]
6	Deodorant	1,4-Dichlorobenzene (*p*-DCB) $C_6H_4Cl_2$ 106-46-7		1	[17]
7	Insect repellent	Diethyl-3-methylbenzoyl-amide (DEET) $C_{12}H_{17}NO$ 134-62-3		1	[20]
8	Plasticizer	4,4′-(Propane-2,2-diyl)diphenol (bisphenol A) $C_{15}H_{16}O_2$ 80-05-7		4	[17, 26, 31, 33]

(continued)

Table 1 (continued)

	Class	Compound	Molecular structure	n. papers	References
9	Sunscreen product	Avobenzone (Parsol) $C_{20}H_{22}O_3$ 70356-09-1		1	[33]
10	Sunscreen product	Hydrocinnamic acid $C_9H_{10}O_2$ 501-52-0		3	[25, 34, 35]
11	Sunscreen product	Oxybenzone $C_{14}H_{12}O_3$ 131-57-7		6	[24, 25, 27, 32, 34, 35]
12	Synthetic musk	Cashmeran $C_{14}H_{22}O$ 33704-61-9		1	[24]
13	Synthetic musk	Celestolide $C_{17}H_{24}O$ 13171-00-1		4	[24–27]
14	Synthetic musk	Galaxolide (HHCB) $C_{18}H_{26}O$ 1222-05-5		15	[16, 23–27, 33, 34, 36–42]
15	Synthetic musk	Methyl dihydrojasmonate (MDHJ) $C_{13}H_{22}O_3$ 24851-98-7		13	[16, 24–27, 33–37, 39, 42, 43]
16	Synthetic musk	Tonalide (AHTN) $C_{18}H_{26}O$ 1506-02-1		16	[16, 23–27, 31, 32, 34, 36–42]

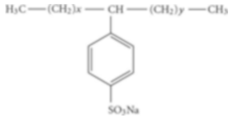
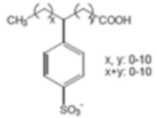
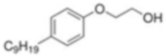
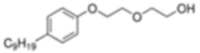
17–20	Anionic surfactants	Linear alkylbenzene sulfonate (LAS)		2	[44, 45]
		$NaSO_3C_{10}H_{13}(CH_2)_{x+y}$			
		LAS C10	$x+y=7$		
		1322-98-1			
		LAS C11	$x+y=8$		
		27636-75-5			
		LAS C12	$x+y=9$		
		25155-30-0			
		LAS C13	$x+y=10$		
		26248-24-8			
21–23	Anionic surfactants	Sulfophenyl carboxylate		1	[44]
		SPC			
		$C_9H_9SO_5Na(CH_2)_{x+y}$			
		SPC-C9,	$x+y=6$		
		SPC-C10,	$x+y=7$		
		SPC-C11	$x+y=8$		
24	Nonionic surfactant	Nonylphenol (NP)		2	[46, 47]
		25154-52-3			
		$C_{15}H_{24}O$			
25–26	Nonionic surfactants	Nonylphenol-mono-ethoxylate (NP1EO)		2	[46, 47]
		Nonylphenol diethoxylate (NP2EO)			

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Table 1 (continued)

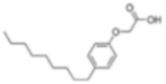
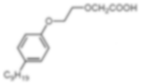
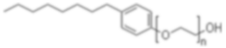
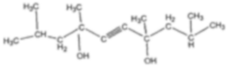
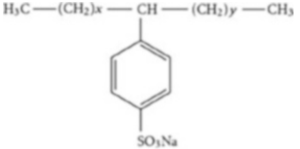
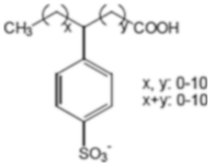
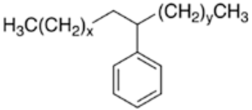
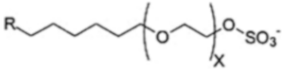
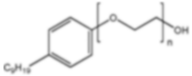
	Class	Compound	Molecular structure	n. papers	References
27–28	Nonionic surfactants	Nonylphenol-mono-ethoxycarboxylic acid (NP1EC)		1	[17]
		$C_{17}H_{26}O_3$			
		3115-49-9			
		Nonylphenol-di-ethoxycarboxylic acid (NP2EC)			
		$C_{19}H_{30}O_4$			
		106807-78-7			
29	Nonionic surfactant	4-Tert-octylphenol (OP)		1	[17]
		$C_{14}H_{22}O$			
		140-66-9			
30–31	Nonionic surfactants	4-Tert-octylphenolmono ethoxylate (OP1EO)		1	[17]
		$C_{16}H_{26}O_2$	$n = 1$		
		4-Tert-octylphenol-diethoxylate (OP2EO)	$n = 2$		
		$C_{18}H_{30}O_3$			
32	Nonionic surfactant	Surfynol 104		1	[33]
		$C_{14}H_{26}O_2$			
		8043-35-4			

Table 2 Classes of surfactants included in the chapter and corresponding references

	Type	Class	Molecular structure	n. papers	References
A	Anionic surfactants	Methylene blue active substances (MBAS)		3	[45, 48, 49]
B	Anionic surfactants	Linear alkylbenzene sulfonate (LAS) $NaSO_3C_9H_{11}(CH_2)_{x+y}$		3	[44, 45, 50]
C	Anionic surfactants	Sulfophenyl carboxylate (SPC)		1	[44]
D	Anionic surfactants	Linear alkyl benzene (LAB) $C_6H_5CHR_1R_2$ where $R_1 = C_nH_{2n+1}$, $R_2 = C_mH_{2m+1}$ $m \geq 0$, $n \geq 1$ (typically 10–16)		1	[33]
E	Anionic surfactants	Alkyl ethoxy sulfates (AES)		1	[50]
		$CH_3(CH_2)_y(O\ CH_2CH_2)_xOSO_3X$	$x = 0–12$ $y = 12–13$ X most often being Na		
F	Nonionic surfactants	NP(1–3)EO, NP(4–9)EO		2	[46, 47]
			Mixture of NPnEO With $n = 1–3$ With $n = 4–9$		

(continued)

Table 2 (continued)

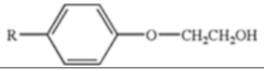
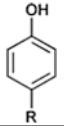
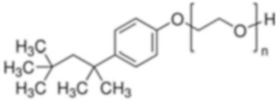
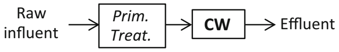
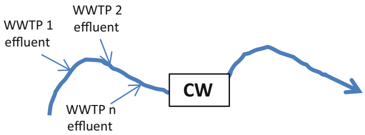
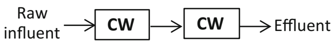
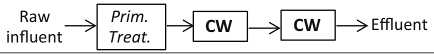
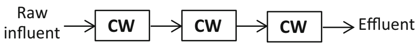
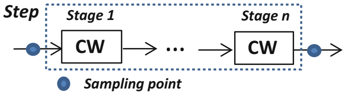
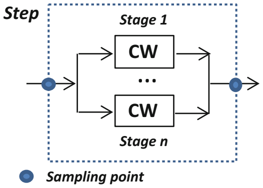
	Type	Class	Molecular structure	n. papers	References
G	Nonionic surfactants	4-Alkylphenol monoetoxylated (APE) $C_9H_{16}(CH_2)_nO_2$		1	[33]
H	Nonionic surfactants	Alkylphenols (AP) $C_7H_7O(CH_2)_n$		1	[33]
I	Nonionic surfactants	Triton X 100 (4-octylphenol polyethoxylate $C_{14}H_{22}O(CH_2\ CH_2O)_n$		3	[45, 51, 52]

Table 3 Schematics of wastewater treatments including CWs in different configurations, with the corresponding references

CW acting as	Schematic	References
Primary step		[22, 23, 45, 46, 49, 51]
Secondary step		[31, 34–37, 39, 42, 44, 48]
Tertiary step		[16, 17, 19, 20, 24, 25, 27–30, 38, 40, 41]
Restoration wetland		[26, 33]
		[18]
Hybrid system		[21, 32, 43, 47, 48, 50]
		[43]
		[16, 17, 20, 21, 24, 25, 27, 28, 31, 37, 43, 47, 49]
Multistage step		[32, 43]

4 Classifications of Constructed Wetlands and Types Included in the Chapter

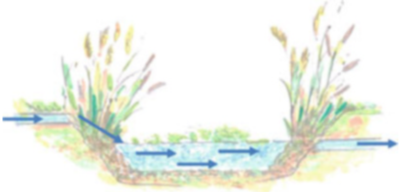
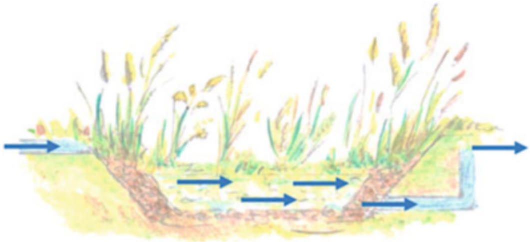
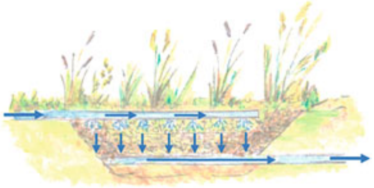
The CWs have been classified according to the treatment step and the main flow direction.

Depending on the treatment level, they have been divided into primary, secondary, or tertiary steps (Table 3). In cases where they were fed by a river whose water flow is primarily made up of a wastewater treatment plant effluent or even untreated wastewater, the system was called *restoration wetland*. If the treatment system includes two or three steps relying on CWs, it is called *hybrid plant*.

Finally, a step may also include more than one stage, either of the same type (monotypic) or of different types (polytypic), thus resulting in a *multistage system*.

Referring to the flow direction, CWs are classified in surface flow systems (SF) and horizontal and vertical subsurface flow beds, H-SSF and V-SSF,

Table 4 Classification of constructed wetlands and corresponding references

CW Type	Schematic	References
Surface flow (SF):		
Classic schematic (A)		[16]^{3}, [17]^{3}, [18]$^{1+2}$, [19]^{3}, [21]$^{2+3}$, [22]^{1}, [23]^{1}, [24]^{3}, [25]^{3}, [26]^{a}, [27]^{3}, [28]^{3}, [29]^{3}, [30]^{3}, [33]^{a,1}, [36]^{2}, [38]^{3}, [40]^{3}, [41]^{1}, [42]^{2}, [43]^{1}, [43]$^{1+2+3;2+3}$, [47]$^{2+3}$, [48]$^{2+3}$, [50]$^{2+3}$
Modified schematic (B)		
Horizontal subsurface flow (H-SSF)		[16]^{3}, [21]$^{2+3}$, [31]^{2}, [32]$^{2+3}$, [35]^{2}, [36]^{2}, [37]^{2}, [39]^{2}, [42]^{2}, [43]$^{2+3}$, [44]^{2}, [46]^{1}, [47]$^{2+3}$, [48]^{2}, [50]$^{2+3}$
Vertical subsurface flow (V-SSF)		[21]$^{2+3}$, [35]^{2}, [41]^{3}, [44]^{2}, [47]$^{2+3}$, [49]^{1}

The numbers (1,2,3) reported as apex for each reference refer to the treatment steps of the investigated plants while the letter "a" means restoration wetland

respectively (Table 4). In SF basins, the majority of flow occurs through a water column overlying a benthic substrate, whereas the flow in H-SSF and V-SSF beds is through a porous medium (generally gravel) and classified as either horizontal, if the feed is from one side of the bed to the other part, or vertical, if the feed is spread over the surface of the bed, crossing it from the top to the bottom. Additionally, in H-SSF beds the feed is continuous, while in V-SSF beds it is intermittent. Surface flow systems investigated also include a modified system, Hijosa-Valsero et al. [36], where the effluent leaves the system after a passage through a stratum of

Fig. 1 Occurrence of investigated PCPs in the influent of CWs acting as a primary step. Data from: [18, 33, 43, 46]

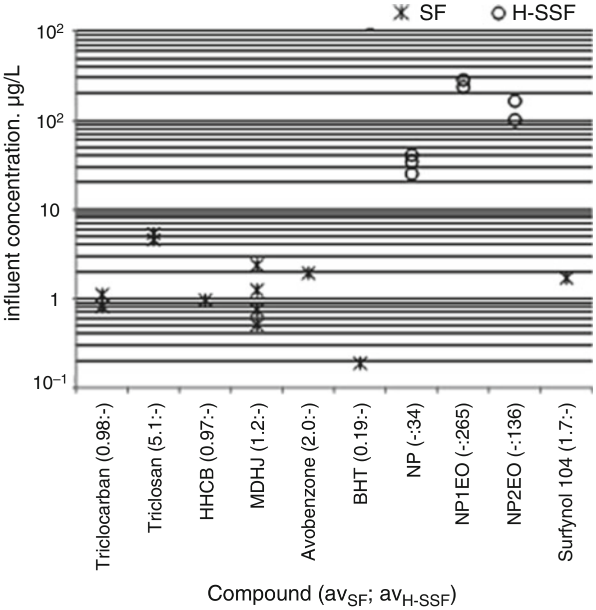
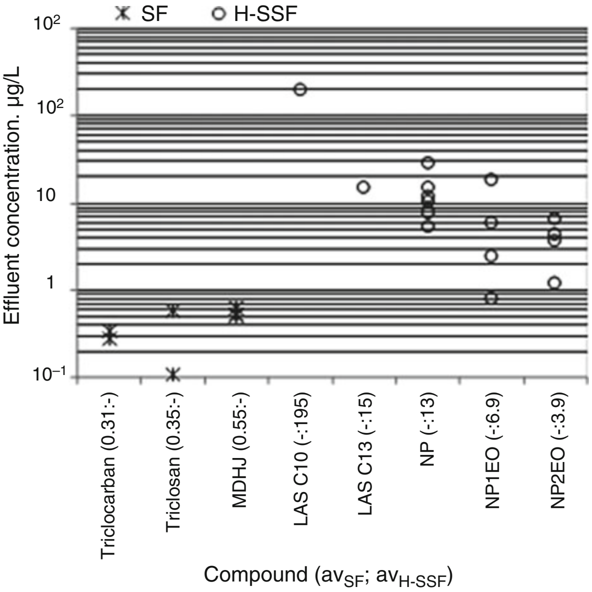


Fig. 2 Occurrence of investigated PCPs in the effluent of CWs acting as a primary step. Data from: [18, 22, 43, 46, 51]



materials at the bottom of the bed, resulting in a combination of surface and subsurface flow systems (Table 4).

In addition, there are two systems which are considered *nonconventional*. They are a pilot system fed by the secondary effluent of Empuriabrava WWTP, Spain,

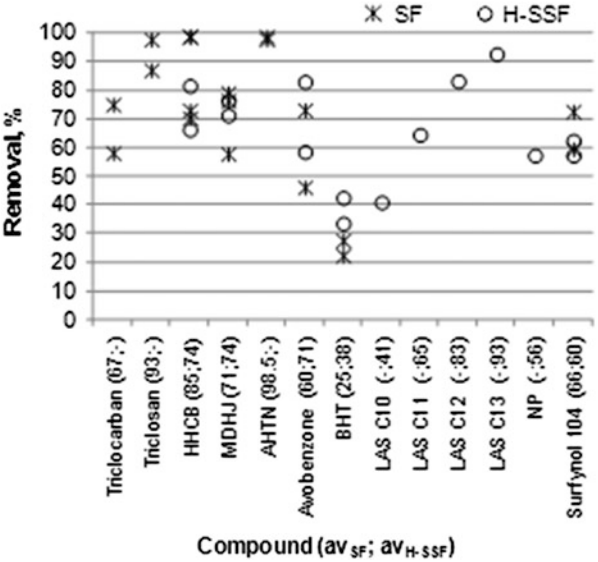


Fig. 3 Removal efficiencies observed in primary CWs for selected PCPs. Data from: [18, 23, 33, 43, 45, 46]

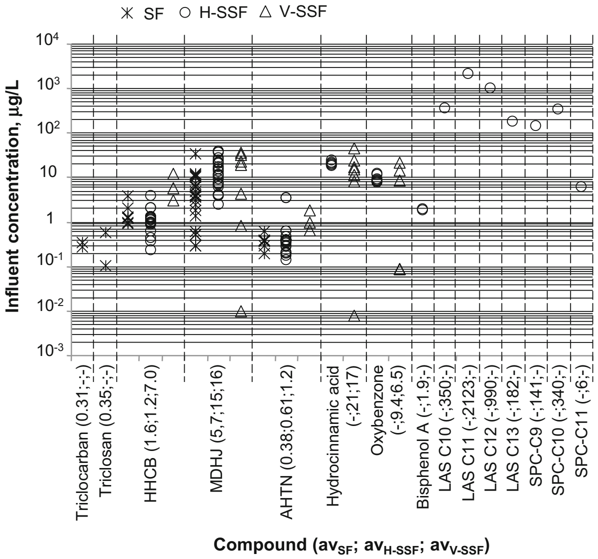


Fig. 4 Occurrence of investigated PCPs in the influent of CW acting as a secondary step. Data from: [18, 32, 34–37, 39, 42–44]

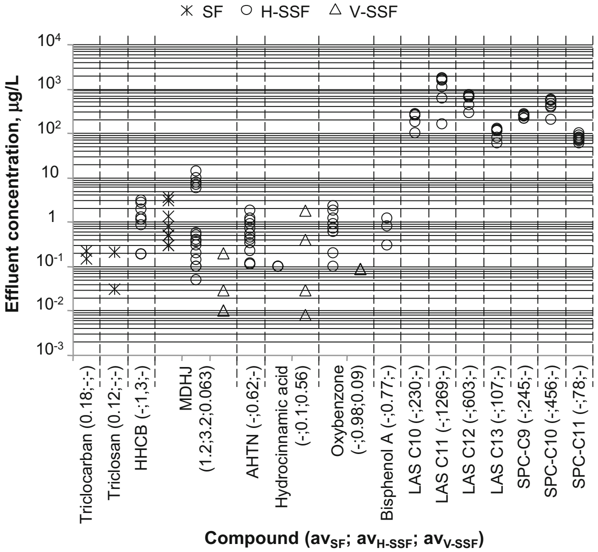


Fig. 5 Occurrence of investigated PCPs in the effluent of CW acting as a secondary step. Data from: [18, 32, 35, 37, 43, 44]

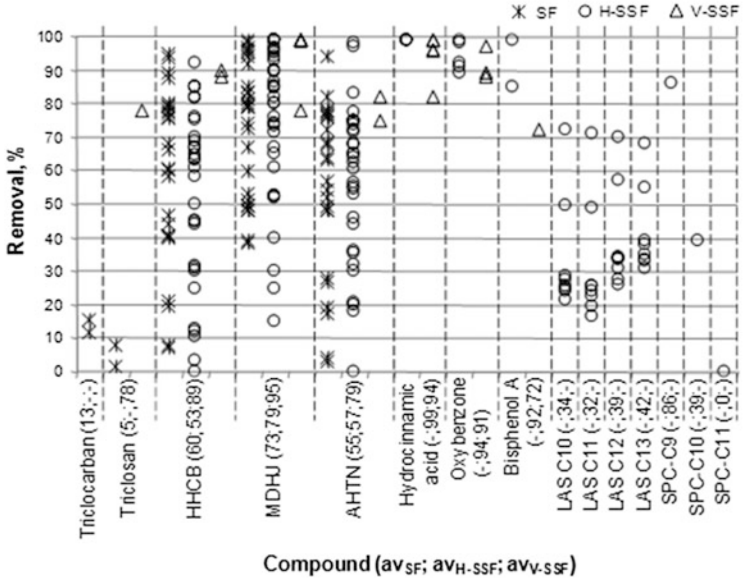


Fig. 6 Removal efficiencies for the investigated PCPs in different types of CWs acting as a secondary step. Data from: [18, 21, 31, 34–37, 39, 42–44]

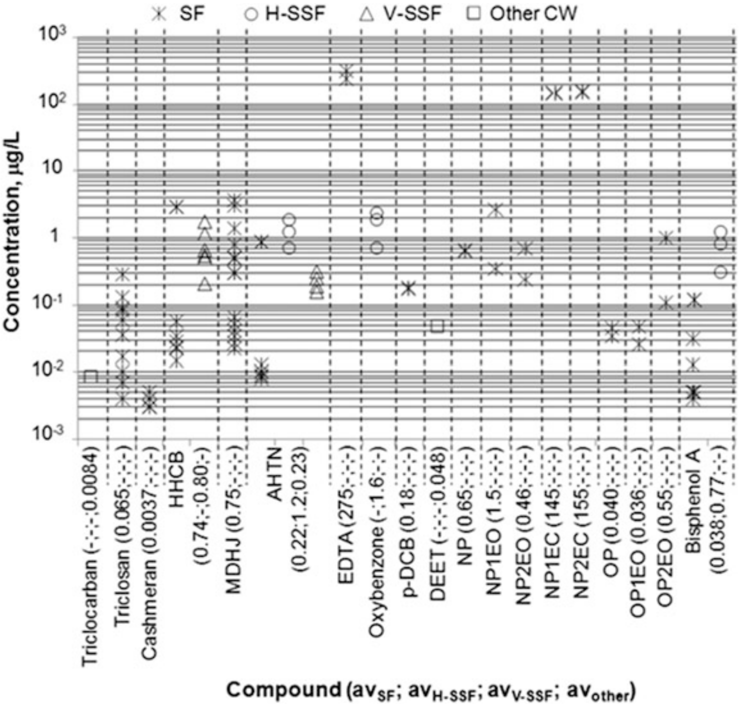


Fig. 7 PCP concentrations in the influent of CWs acting as a polishing step. Data from: [17, 26, 29, 30, 32, 38, 41, 43, 53]

which is operated in parallel with the full-scale reclamation plant consisting of surface flow basins [27] and a sequence of SF and H-SSF cells [20].

4.1 Main Features of the Investigated Plants

The chapter is based on investigations of PCP occurrence and removal in CWs carried out in Europe (64%: Spain, Denmark, England, and Czech Republic), America (28%: USA, Canada, and Mexico), and Asia (8%: Korea and China).

In the 35 peer reviewed papers, 87 treatment lines were investigated. They mainly include H-SSF beds (49%) and SF basins (38%) and in a few cases V-SSF systems (10%). The types of CW are not well specified in only 3% of the plants. Of the 87 treatment lines, 54 refer to pilot plants and 30 to full-scale plants, while the remaining 3 refer to full-scale plants followed by a pilot plant. Moreover, 12 treatment lines refer to hybrid systems.

In nine lines the investigated CW acted as a primary step, in 42 as a secondary step, in 15 as a tertiary one, and in nine to restoration wetlands.

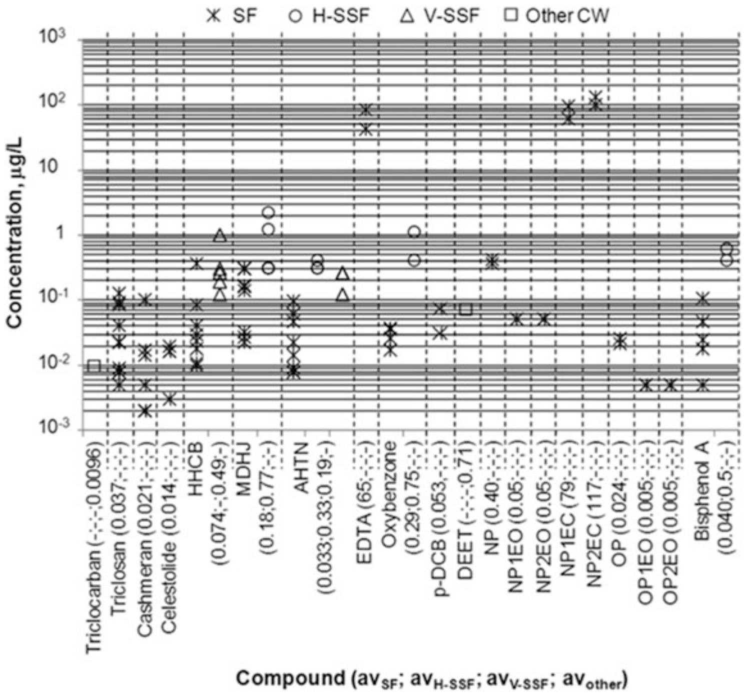


Fig. 8 PCP concentrations in the effluent of CWs acting as a polishing step. Data from: [17, 20, 26, 27, 29, 38, 41–43]

The feeding was always a real domestic wastewater, with a few cases where domestic wastewater was injected with selected PCPs at the desired concentration [21, 31, 32, 46] and one more where the influent contained a consistent percentage of industrial wastewater [33]. Two studies [49, 50] investigated occurrence and removal from grey water. All the treatment trains investigated were outdoor with the sole exception of the one investigated by Belmont et al. [47]. In nearly all studies, analyses were processed on grab samples of water.

5 Occurrence and Removal in the Different Treatments Steps

Figures 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 report concentrations observed in the influent and effluent of CWs acting as primary, secondary, and tertiary steps and in the case of hybrid systems. They also report removal efficiencies for the investigated compounds in the systems under study. In the *X*-axis of each graph, the numbers in brackets after the PCP name correspond to the average values of the collected data for each of the CW types considered.

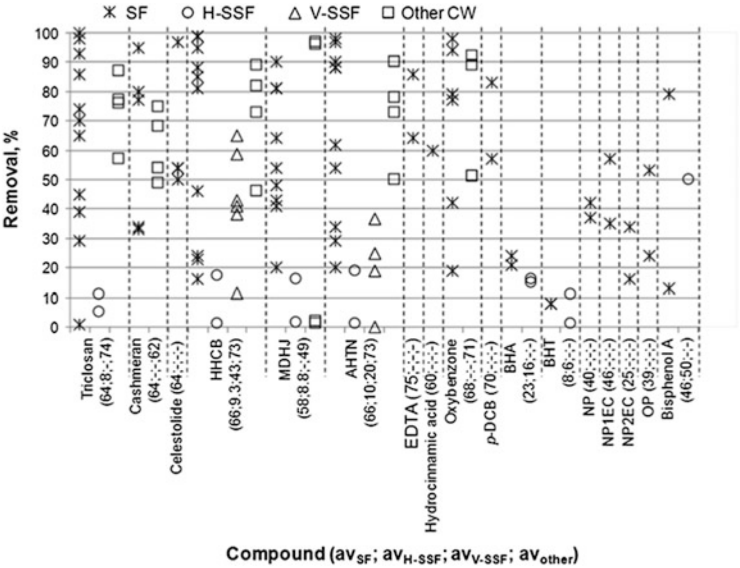


Fig. 9 Removal efficiencies for PCPs in different types of CWs acting as a polishing step. Data from: [16, 17, 24, 25, 27, 28, 30, 40, 41, 43]

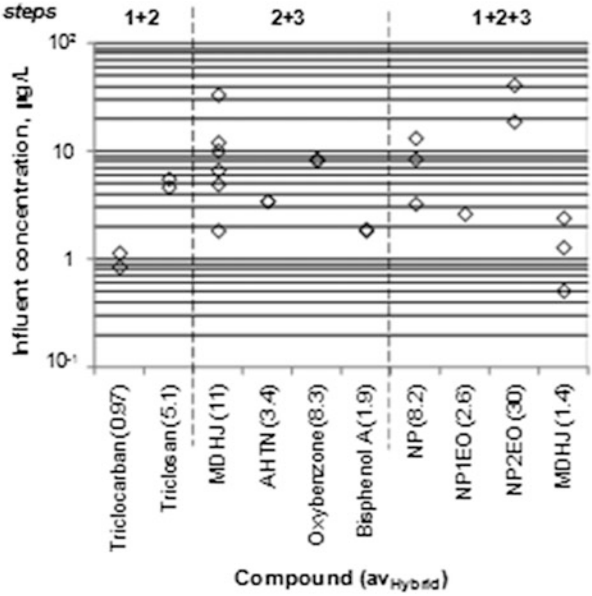


Fig. 10 Occurrence of investigated PCPs in the influent of hybrid CWs. Data from: [18, 42, 43, 47, 50]

Fig. 11 Occurrence of investigated PCPs in the effluent of hybrid CWs. Data from: [18, 42, 43, 47, 50]

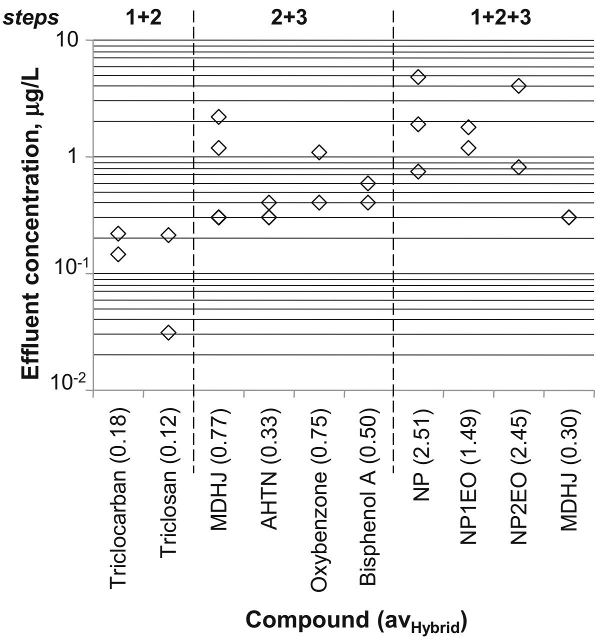
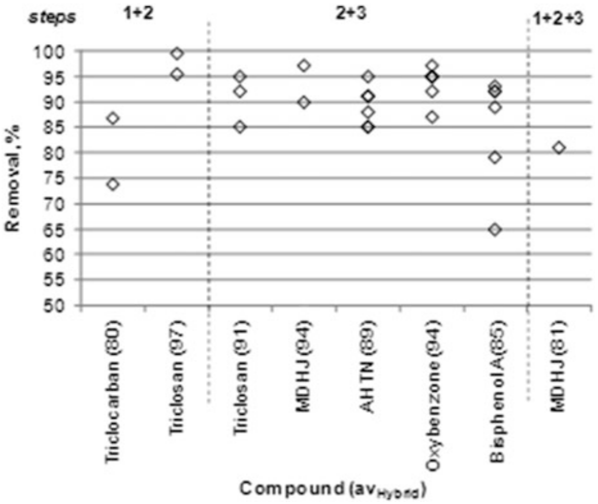


Fig. 12 PCP Removal in hybrid CWs. Data from: [18, 21, 32, 43]



Finally, ranges of concentration data for *groups* or *mixtures* of surfactants (MBAS, LAS, LAB, Triton X100; see Table 2) in the influent and effluent of some plants were reported in the discussion.

5.1 Primary Step: Occurrence and Removal of Selected PCPs

Only a few investigations reported PCP concentrations in the influent and effluent of CWs acting as a primary step. These are reported in Figs. 1 and 2, which show ten PCPs in the influent and eight in the effluent. The feeding was always only domestic wastewaters, with the exception of Navarro et al. [33] where the influent was a river receiving both untreated domestic as well as industrial wastewaters (see also Sect. 5.4).

Belmont and Metcalfe [46] and Sima and Holcová [51] investigated subsurface flow beds. All the other studies examined SF basins, which greatly differed for influent flow rate, geometry and size, configuration, and environmental and operational conditions. Hydraulic retention time (HRT) varied between 0.4 days [43] and 5 days [33].

The highest influent concentrations were found for the common nonionic surfactants NP1EO (289 μg/L), NP2EO (168 μg/L), and NP (41.5 μg/L), followed by triclosan (5.44 μg/L). The highest concentrations in the effluent were found for LAS C10 (195 μg/L), NP (28 μg/L), NP1EO (18 μg/L), and LAS C13 (15 μg/L). The same compounds exhibited the highest average values.

Referring to NP, NP1EO, and NP2EO, the effluent concentration is always lower than the corresponding influent one, but for NP the reduction is the smallest. This is due to the fact that NP1EO and NP2EO may transform into NP during anaerobic degradation throughout the system.

Classes of surfactants were found at very high concentrations both in the influent and effluent of primary CWs: MBAS (methylene blue active substances) 1,390–17,100 μg/L in the influent and 340–4,560 μg/L in the effluent [49], NP(1–3)EO 441 μg/L in the influent and 13 μg/L in the effluent [46], and Triton X100 978 μg/L in the influent and 99 μg/L in the effluent [45, 51]. These data point out that surfactants are present in a wide spectrum of substances commonly used in households, not only PCPs.

Removal – Figure 3 shows the observed removal efficiencies for selected PCPs in SF basins as well as H-SSF beds. In SF systems, high removals were observed for galaxolide and tonalide (both 99%, [23] and triclosan (98%, [18]), while these were very poor for BHT (less than 30%).

In H-SSF beds, the removal efficiencies for the reviewed compounds were in general lower than in SF systems and the best performances were found for LAS C13 (92.9%) and LAS C12 and avobenzone (both at 83%).

For the five substances investigated in both systems, higher average removals were observed in SF basins for HHCB and Surfynol 104, while avobenzone, BHT, and MDHJ were removed well in H-SSF beds. APE, AP, and LAB were removed to a greater extent in H-SSF beds than in SF systems [33], suggesting that removal was mainly due to sorption mechanisms. Moreover, APEs exhibited higher removal than APs, around 75 and 50%, respectively, which is correlated to the fact that APs may form during the biodegradation of APEs [33].

In H-SSF beds, nonionic surfactants were removed to a greater extent than anionic ones [45] and also more quickly [56].

Studies of the occurrence and degradation of LAS and SPC in CWs remarked that homologues with an alkyl chain shorter than C10 were rarely detected, as the alkyl chain is first preferably oxidized to carboxylic acid and then it is degraded [56].

5.2 Secondary Step: Occurrence and Removal of Selected PCPs

Figures 4 and 5 show concentrations in the influent and effluent of CWs acting as a secondary step and Fig. 6 shows the observed removal efficiencies for the reviewed 15 PCPs.

Synthetic musks were the most investigated in the influent, followed by sunscreen products, while in the effluent the most studied were surfactants followed by synthetic musks.

The highest influent concentrations were detected for the surfactants LAS C11 (2,123 μg/L), LAS C12 (990 μg/L), LAS C10 (350 μg/L), and SPC C10 (340 μg/L) [44]. It is worth noting that all the investigated surfactants were found at concentrations greater than 100 μg/L (with the only exception of SPC C11). The other PCPs were found below 45 μg/L (the highest values were due to hydrocinnamic acid [35] followed by the musk MDHJ (39 μg/L [39].

Regarding the effluent, the highest concentrations were detected for the same surfactants mentioned for the influent: LAS C11 (1,774 μg/L), LAS C12 (731 μg/L), SPC C10 (570 μg/L), and LAS C10 (264 μg/L) [44]. All the remaining investigated compounds exhibited concentrations at least one order of magnitude below.

A rapid glance at Figs. 4 and 5 shows that for each LAS compound, average effluent concentration is lower than the corresponding influent one, while this does not occur for SPCs as they were formed during the biodegradation of LAS in the system, and their formation was faster than their removal as pointed out in the work by Huang et al. [44]. For all the other compounds, a reduction of the average concentration was found from inlet to outlet of each type of CW.

Only for MDHJ is it possible to compare performance of the three kinds of CW on the basis of the measured concentrations. The lowest effluent concentrations were found in V-SSF systems leading to the supposition that the aerobic conditions of the bed favor its biodegradation [35].

Referring to oxybenzone and hydrocinnamic acid, similar performances were observed in H-SSF and V-SSF beds [34].

As remarked for primary CWs, much higher concentrations were found for classes of surfactants in the influent/effluent of secondary CWs: MBAS were detected around 15,000/2,500 μg/L [48], LAS around 3,600/2,900 μg/L, and

SPCs around 500/900 µg/L [44]. It is worth noting that only SPCs exhibited an increment in the concentrations due to the biodegradation of LAS, resulting in a formation of PCPs as discussed above.

Removals – Regarding collected removal efficiencies (Fig. 6), the most investigated compounds were the three fragrances in the SF and H-SSF basins. They exhibited a wide range of variability of removal values. This is also due to the fact that these studies were carried out with the aim of analyzing the influence which different factors have on PCP removal. These factors include design parameters [36], hydraulic loading rates (HLRs) [34, 35], operational conditions [21, 37], and environmental conditions [36, 42]. In addition, the investigated plants might have different ages and different sizes (lab, pilot, or full scale), they may be planted or unplanted, and they may also be affected by clogging, leading to a reduction in the HRT. These factors may greatly influence the removal of PCPs within the system, as discussed in Sect. 6.

All the investigated compounds were removed up to 95% with the only exceptions of the antiseptics triclosan and triclocarban and the surfactants.

In SF CWs, the best removals were achieved for the three fragrances. This occurred in the modified SF type reported in Table 4 [36], where the passage of the water through the filling media before discharge into the environment allowed the (lipophilic) pollutants to sorb onto filling materials.

In H-SSF beds, the highest average removals were found for hydrocinnamic acid (99%), oxybenzone (94%), and bisphenol A (92%) and also for fragrances, while surfactants generally exhibited lower removal levels.

In V-SSF beds the best performances were observed for MHDJ (95%), HHCB (89%), and AHTN (79%), suggesting that the intermittent feeding and the aerobic environment are beneficial to the removal of these micropollutants.

Figure 6 does not include negative removal values. These were rarely found, were limited to fragrances and SPCs, and were due to the internal generation of some compounds following the biodegradation of others (SPCs as intermediates of biodegradation of LAS or longer SPCs, Huang et al. [44]), release phenomena of selected compounds (HHTN and AHTN), and clogging conditions, resulting in HRT reduction and malfunctions including the release of compounds that could not be removed from the bed due to lack of time (i.e., MDHJ) [42]. Peculiar situations were reported in literature. Huang et al. [44], for example, found that in warm periods, suspended solids containing LAS retained within the bed quickly decomposed, resulting in a much higher quantity of SPCs generated compared to cold periods. In contrast, Reyes-Contreras et al. [42] found release phenomena for the three fragrances in winter in H-SSF beds but not in summer, perhaps due to an inhibition of the biological activity at low temperatures and a release of the biofilm within the system where fragrance molecules could be present.

5.3 Tertiary Step: Occurrence and Removal of Selected PCPs

Figures 7 and 8 refer to the concentrations of PCPs detected in the influent and effluent of CWs acting as a tertiary step, while Fig. 9 shows the removal efficiencies reported by the different authors in the polishing CWs. Nineteen PCPs were monitored in the influent and twenty compounds in the effluent (the same as the influent plus the fragrance celestolide), and removal values are available for seventeen compounds.

SF systems were the most studied CW type, followed by H-SSF beds. Different authors analyzed multistage polishing systems (see also Table 3). The investigated systems consisted of series of SF basins, with the exception of those studied by Reyes-Contreras et al. [16] and Hijosa-Valsero et al. [43], which were sequences of SF and H-SSF CWs. In addition, the multistage polishing plant investigated by Zhu and Chen [20] included 30 cells between SF and H-SSF types; this plant was classified as a nonconventional CW in Figs. 7, 8, and 9.

The highest influent concentration was detected for EDTA (310 μg/L [17]). This surprisingly high value is in accordance with those found in literature in the effluent of secondary WWTPs as reported by Kase et al. [55]. The second highest concentrations were for NP2EC with 160 μg/L and NP1EC with 150 μg/L. All the other PCPs exhibited influent concentrations of two orders of magnitude lower, the highest values being for MDHJ (3.7 μg/L) and galaxolide (2.9 μg/L).

The highest average influent concentrations were found for EDTA (275 μg/L), NP2EC (155 μg/L), NP1EC (145 μg/L), oxybenzone (1.6 μg/L), NP1EO (1.5 μg/L), and AHTN (1.23 μg/L). For the remaining investigated compounds, average values were always less than 1 μg/L.

Referring to CW effluent, the highest effluent concentrations were found for NP2EC (135 μg/L), NP1EC (97.5 μg/L), and EDTA (87 μg/L) [17], followed by MDHJ (2.2 μg/L) [43].

A comparison between Figs. 7 and 8 highlights that a general decrement in the concentrations occurs from influent to effluent.

Referring to cashmeran, average influent concentration is lower than that of the effluent, but an analysis of the investigations dealing with it reveals that some of the reviewed studies only provided effluent values and removal efficiencies, and in all of them a removal was always observed, as reported in Fig. 9, and no release occurred.

Only DEET exhibited a slight increase in the passage through the polishing system investigated by Zhu and Chen [20], but there is still little available data and it is not possible to conclude that a release would occur.

The only PCP investigated in surface and subsurface flow systems is AHTN – for this all three CW types showed a removal ability.

Removals – In SF systems, the highest values were found for triclosan (99.99%, [28]) and HHCB (99%, [24, 25]), AHTN and oxybenzone (both 98% [25]), celestolide (97% [25]), and cashmeran (95% [24]). All refer to two-stage systems. The high attenuation of EDTA (on average 75%) should be due to photolytic reactions as the compound is quite resistant to biodegradation and has a low affinity for sorption [17]. Finally, very low removals are observed for NPs and NPnECs [17].

Modest removal values were observed in the V-SSF beds. Based on data reported by Reif et al. [41], they ranged between 65% (HHCB) and 0% (AHTN). The removals found in H-SSF beds are even poorer: Reyes-Contreras et al. [16] always found them to be less than 20% for triclosan, HHCB, MDHJ, AHTN, BHA, and BHT.

An interesting investigation was carried out by Sacco et al. [52] into the removal of the mixture of nonionic surfactants Triton X-100 dosed at 30 and 300 mg/L in the pilot H-SSF bed. Their mixture contained up to 13 EO groups in different percentages. They found that in the first 40 cm of the bed, OP and its monoethoxylate (EO = 1) had the biggest increment. The decrease (sometimes also the disappearance) in certain octylphenol ethoxylate (OPEO) oligomers seems to be correlated to increases in others (characterized by a shorter EO chain), and the biodegradation rate of those oligomers with a number of EO greater than 3 is higher than those observed for compounds with shorter chains.

Promising results were observed in the (nonconventional) biologically based filtration water reclamation plant investigated by Matamoros et al. [27] for oxybenzone, AHTN, HHCB, triclosan, and cashmeran, especially in summer time. MDHJ exhibited very high removal in summer (>96%), while in winter the removal was nearly absent.

In the multistage (SF + H-SSF) systems by Reyes-Contreras et al. [16], a consistent increment in the removal efficiencies of MDHJ, triclosan, AHTN, HHCB, and BHT was observed during the summer season with respect to the winter one (about 2–8 times higher).

The results obtained by Matamoros et al. [25] are quite interesting. They compared the removal for a group of PCPs in a tertiary pond and in a conventional tertiary treatment by UV radiation and chlorine disinfection. They found that solar radiation can degrade parental compounds in their intermediates both in the UV reactor and the pond. In most cases these reaction products are more toxic than the parental ones. However, in pond systems other mechanisms including biodegradation, sorption onto solids and sediments, and plant uptake may reduce their concentration.

5.4 Restoration Wetlands

Two restoration wetlands were included in this study. The first one, described in Matamoros et al. [26], is located in Denmark and is fed by two rivers – Aarhus (watershed 120 km^2) and Lyngbygaards (watershed 132 km^2) – which are impacted by urban sewage and agricultural runoff. The wetland is interconnected to a lake whose effluent discharges into the sea. The lake is used for recreational purposes and near it there are some of the city's water supply wells. The wetland was created in 2003 to reduce the nutrient concentrations discharged into the lake and then into the sea and to preserve the downstream water environment conditions. It covers an area of 100 ha and consists of a surface flow basin with an average water depth of 0.5 m and a maximum depth of 2 m, an HRT ranging between 3 and 20 days, on average 7 days. Based on a mass balance between influent and effluent streams to the wetland, a consistent reduction was found in the effluent concentration (mitigation effect passing through the wetland) for most of the investigated PCPs (for triclosan, cashmeran, MDHJ, HHCB, AHTN, and bisphenol A, it was >40%). In winter, due to the low sunlight exposure and cold temperatures, bio- and photodegradation processes were limited. It is important to highlight that in the wetland outlet, the concentrations of all the investigated PCPs kept quite constant, although the influent values exhibited a wide variability confirming wetland buffer capacity.

The second restoration wetland is a pilot plant fed with the water of the Sordo River (in southeastern Mexico) which receives untreated urban sewage and industrial wastewaters [33]. The CWs consist of 8 cells: four are SF type (substrate upland soils, 0.4 m deep, free water surface flow column, 10 cm high) and four are H-SSF type (filled with 0.4 m of volcanic gravel, water flow 10 cm below the surface). Each of them has an HRT of 5 days. A high attenuation was found for galaxolide, MDHJ, parasol, and APE.

5.5 *Hybrid Systems: Occurrence and Removal of Selected PCPs*

Nine compounds were monitored in the influent (Fig. 10) and effluent (Fig. 11) of different types of hybrid systems, and data on observed removal efficiencies were provided for six of them (Fig. 12).

The most adopted CW type in the hybrid systems was SF basins, followed by H-SSF beds, and the most investigated sequences included SF + H-SSF systems [43, 50] and only H-SSF ones [32]. All three types were investigated in the hybrid systems by Avila et al. [21] and Belmont et al. [47].

A rapid glance at Figs. 10 and 11 highlights that for each substance a reduction was observed. The same was observed for classes of surfactants in the hybrid systems (steps 2 + 3) investigated by Conte et al. [48] and Jokerst et al. [50]. The first found that MBAS decreased from 3,200 and 16,000 μg/L in the influent to 2,000–2,500 μg/L in the effluent and the second that AES decreased from 50–16,500 μg/L in the influent to 15–50 μg/L in the effluent.

Avila et al. [21] investigated a hybrid system (V-SSF as secondary step and H-SSF + SF as tertiary step) fed by municipal wastewater where PCPs were injected at the desired concentrations. Their investigation also analyzed the operational characteristics inside the tank, in particular redox potential which resulted in the range 110 + 128 mV in the V-SSF bed, in the range from −59 to −115 mV in the H-SSF bed, and between 156 and 171 mV in the SF basin.

Their investigation pointed out that the first stage, a V-SSF bed, was responsible for most of the removal of the selected PCPs, and the following polishing treatment contributed to the removal but to a smaller extent. In particular the effect of the SF stage on the removal of these compounds was quite negligible.

The highest removal efficiencies were found for triclosan in series of aerated lagoons (on average 97%, [18]) and in a hybrid-polytypic system (V-SSF acting as a secondary step followed by H-SSF + SF as a tertiary step); average removal 91%, Avila et al. [21], for MDHJ (97%) in the sequence SF + H-SSF beds [43], and for oxybenzone (97%) in the sequence of H-SSF beds by Reyes-Contreras et al. [42].

For triclosan, photodegradation greatly contributes to its removal followed by biodegradation, while for MDHJ photolysis is less important than biodecomposition. This fact is confirmed by the lower removal (81%) found by the same authors for MDHJ in a series of ponds (steps 1 + 2 + 3). Oxybenzone, instead, is mainly removed by biodegradation and then by sorption.

Many investigations confirmed that most of the removal of PCPs occurs in the first step. The comparison provided by Avila et al. [21] of the contributions in the accumulated average removal efficiencies achieved in each unit of the hybrid system for AHTN, oxybenzone, triclosan, and bisphenol A is quite interesting.

Referring to bisphenol A, the main removal mechanism is biodegradation and the lowest removal efficiencies (about 65%) were observed at the lowest redox values (anaerobic conditions in H-SSF beds by Avila et al. [32]).

6 Discussion of the Influence of the Main Design Parameters and Operational Conditions of PCP Removal Efficiencies

As already mentioned, for many reviewed compounds, the removal achieved in CWs exhibited a wide range of variability. In fact, in many cases the studies investigated the influence of some operational conditions (mainly HLR and temperature) and all the removal values observed were reported. As a consequence, the lowest values do not necessarily mean that these systems are not appropriate. In addition, removals are correlated to the influent concentrations. As will be discussed later, higher concentrations generally correspond to higher removal efficiencies.

The following paragraphs analyze the influence of the main design parameters as well as the operational and environmental conditions on the removal of the selected compounds.

6.1 Variation in the Influent Concentrations of PCPs

Higher influent concentrations often correspond to higher removal efficiencies, as reported by some authors (among them [24, 27, 40]). Variations in the influent could be attributed to a different consumption of the compound, infiltration in the sewage network by seawater [27] or groundwater, a malfunction in the upstream treatments (if CW acts as a secondary or a tertiary step) [24], or in the treatment itself.

Reyes-Contreras et al. [16] found a seasonal variation in the concentrations of the two fragrances: AHTN and HHCB occurred at concentrations three times higher in summer than in winter (tonalide: 1.5 μg/L against 0.44 μg/L and galaxolide 1.2 μg/L against 0.45 μg/L), and their removals were more than twice higher in summer than in winter.

6.2 Primary Treatment

The influence of two primary treatments – a septic tank and an anaerobic hydrolysis upflow sludge bed (HUSB) – on the removal of PCPs in the following H-SSF bed was compared by Hijosa-Valsero et al. [37]. The former produces an effluent of more constant quality during the year and therefore the effluent of a CW fed by a septic tank is slightly better than the effluent produced by a CW fed by a HUSB system.

Surfactants were removed at a consistent fraction in pretreatments. MBAS, for instance, was removed up to 20% in screens, horizontal sand traps, and sedimentation basins [51, 56].

6.3 HLR and HRT

A variation in the influent flow rate may be caused by a different wastewater flow, rainwater, snow melting, and seawater and groundwater infiltration. The main and most frequent disturbance is an increment of the HLR resulting in a shortening of HRT, with respect to the corresponding design values. Prolonged rain events (together with cleanup or reconstruction of the wetlands) may lead to a pulsed, albeit delayed release of the accumulated PCPs due to desorption.

Many studies agree with the fact that whatever the CW step, the higher the HRT, the higher the removal efficiencies achieved by the system for the investigated PCPs in wastewater (i.e., [40]).

Avila et al. [21] investigated ability in removing a selected group of PCPs (AHTN, oxybenzone, triclosan, and bisphenol A) at the three different HLRs (0.06, 0.13, and 0.18 m/day) in their treatment line, consisting of a V-SSF bed, followed by an H-SSF bed and an SF basin as a polishing step. They found that the removal of triclosan decreased with the increase of HLR, while no clear patterns were found for AHTN, bisphenol A, and oxybenzone. The same increment of HLR applied to the H-SSF bed only affected the removal of AHTN that decreased, while for bisphenol A, oxybenzone, and triclosan, no correlation was found between HLR and observed removal.

In V-SSF beds an increment in the HLR (13–70 mm/day) did not result in a decrement of the removal of MDHJ, hydrocinnamic acid, oxybenzone, HHCB, and AHTN [34], while in SF basins, it resulted in a decrement in the removal efficiencies for oxybenzone and MDHJ [34] and in H-SSF beds for anionic [53] and nonionic surfactants [51].

6.4 Aging of the CW

The age of the CW may influence the removal of PCPs. In SF basins, biomass growth causes shading of the upper water layer resulting in a reduction of photodegradation processes. Moreover, clogging, matrix saturation, and hydraulic conductivity losses may be detrimental for removal mechanisms in (H- and V-) SSF beds, as found by Matamoros et al. [39] for MDHJ, HHCB, and AHTN. An H-SSF bed could work closer to as a SF basin if surface and volume clogging phenomena occur. In fact they may lead to a flooding of the bed, with a higher oxygen transfer from the air and a lower HRT, as remarked by Matamoros et al. [35] and Reyes-Contreras et al. [42]. Removal efficiencies are then affected by these phenomena and organic matter could be mainly removed by aerobic reactions.

6.5 Biomass Acclimatization

Some long experimental investigations on surfactant removal in H-SSF beds highlighted that microbial flora requires a period of time to adapt itself to the type of pollutant load. Sacco et al. [52] reported that in their pilot, H-SSF bed removal of Triton X 100 changed along the 12-month period of observation. A development of new bacteria strains appeared and others increased during the dosage of the mixture, suggesting that these bacteria were adapting to the presence of these surfactants and/or they used them as a source of nourishment.

6.6 Redox Conditions

The three types of CW differ not only in the main flow direction but also in their operational conditions. Avila et al. [21] reported the values of redox potential measured in the three types of systems, confirming aerobic conditions in V-SSF beds and SF basins and anaerobic conditions in H-SSF beds. Hijosa-Valsero et al. [37] analyzed the seasonality variation of redox potential in H-SSF beds, and they found that in summer time redox may increase up to positive values, promoting the development of different microbial communities.

Redox potential within a system may vary during the life of the wetland, due to its aging and clogging phenomena and changes in the influent quality. It mostly influences the removal of PCPs as well as surfactants. Avila et al. [32], Navarro et al. [33], and Conkle et al. [57] remarked that higher redox values promote PCP removal with the exceptions of BHT and AP.

Huang et al. [44] and Sima et al. [45] agreed that anionic and nonionic surfactants can be degraded in a wide range of redox values. Referring to LAS, more oxidized conditions improve their removal, and in deeper SSF beds where the environment is characterized by sulfate-reducing methanogenic conditions, low LAS removals were observed [44].

In addition, redox conditions can also influence the degradation of PCPs bioaccumulated in sediments or gravel of a wetland. This influence was investigated by Conkle et al. [57] who found that DEET is appreciably degraded under aerobic sediments, while in anaerobic conditions this does not occur.

6.7 Removal Processes Along the System

Most of the removal occurs in the first meters of the system for many of the investigated compounds. The fragrances AHTN and HHCB mainly accumulated in the first section of the H-SSF bed investigated by Matamoros and Bayona [39] and a large fraction of nonionic surfactants (about 80%) and anionic ones (about 50%) degrade in the first meter of the H-SSF beds investigated by Sima and Holcová [51] and Sima et al. [53], respectively. The same profile was confirmed by the investigation of Zarate et al. [19] into the accumulation of triclosan and triclocarban on the sediments of a polishing SF basin.

Avila et al. [31] and Hijosa-Valsero et al. [37] investigated the removal of AHTN, HHCB, MDHJ, and bisphenol A in secondary multistage CWs consisting of two H-SSF beds in series.

They found that for AHTN, HHCB, and bisphenol A, most removal occurred in the first stage and near the inlet zone, probably due to the detention of most of the particulate matter with which all these compounds are associated. A different removal pattern was found for MDHJ as its main removal mechanism is biodegradation favored at high temperature.

6.8 H-SSF Bed Depth

Shallow H-SSF beds (0.3 m water depth) were found to be more efficient than deeper ones (0.5 m) in the removal of LAS due to differently oxidized conditions occurring on the two kinds of wetlands [44]. In the first, in fact, denitrification, sulfate reduction and methanogenesis occurred simultaneously, while in the second, the prevailing reactions were sulfate reduction and methanogenesis and denitrification is insignificant.

The effect of the depth of V-SSF beds on the removal of anionic surfactants was investigated by Kadewa et al. [49]. They found that in an *acclimatized* and vegetated 0.7 m-deep V-SSF bed, anionic surfactant removal was in the range of 76–85%, while in a cascade of three still-ripening and unplanted 0.2 m V-SSF beds, it was less, between 37 and 74%. These findings could be attributed to a more developed microbial community in the ripe higher V-SSF bed which could guarantee a complete biodegradation of the different surfactants, while in the cascade of shallow V-SSF beds, the more oxidized conditions promoted the alkyl chain shortening of the surfactants, but not their complete degradation.

Sima et al. [53] found that the removal of anionic surfactants in an H-SSF bed was faster in the upper 10 cm. At lower depths, anaerobic degradation of LAS occurs where sulfates were shown to be reduced. On the contrary, studies of nonionic surfactants showed that they can be effectively degraded at both depths, independent of aerobic or anaerobic conditions [51].

6.9 Filling Material in SSF Beds

Lower effluent concentrations were detected for LAS and SPCs in beds filled with finer gravel ($D_{60} = 3.5$ mm, $C_u = 1.7$) than in those containing coarse gravel ($D_{60} = 10$ mm, $C_u = 1.6$) [44].

6.10 Seasonality and Effect of Temperature

A seasonal variation was found for the removal efficiency of many compounds, but not for their occurrence. As a rule of thumb, removal efficiencies for dissolved-phase compounds are greatly influenced by temperature as biodegradation is their main removal mechanism, while depletion referring to compounds associated with particulate matter does not exhibit such a pronounced temperature variation since their removals are mainly due to physical mechanisms (sedimentation and adsorption).

For compounds such as MDHJ and oxybenzone, whose main removal mechanism is biodegradation, low temperatures directly reduce the physiological activities of the microorganisms themselves, resulting in a slowing down of the degradation reactions that may occur [27, 42].

In H-SSF beds, summer removals were generally found to be very high (often greater than 80%) for HHCB, AHTN, and MDHJ, with a few exceptions related to unplanted H-SSF beds, where HHCB and AHTN were not removed at all, while MDHJ had variable removal efficiencies. The first two fragrances present a similar removal pattern as they have a great sorption potential due to their lipophilic properties, while MDHJ is mainly removed by biodegradation. The seasonality variation found in the removal of the investigated hydrophobic compounds can be explained by the release of these compounds in winter and accumulation in summer, when biofilm and plants are more active [37].

In SF basins, HHCB and AHTN exhibited the same (high) removal efficiencies in both seasons at around 85–90% [40].

For photodegradable compounds such as triclosan and cashmeran, lower values in their removal observed in SF basins in winter could also be due to lower levels of sunlight exposure [27].

6.11 Vegetation

Vegetation can insulate wetland surfaces and thus contribute to maintaining microbial activity; roots provide a surface for the development of microbial colonies and contribute to the creation of aerobic microenvironments within the bed, thus favoring biodegradation. Moreover, vegetation can contribute to the removal of micropollutants by plant uptake.

Higher removal levels of anionic surfactants were observed in planted and acclimatized V-SSF beds with respect to unplanted and non-acclimatized ones [49]. In SF basins covered by *Lemna minor*, the removal efficiencies of the photodegradable triclosan were found to be lower than in control unplanted SF wetlands [24].

Young CWs are more efficient when they are planted. When CWs get older, the efficiency of planted and unplanted systems is similar as many disturbing factors may occur (clogging, shading) causing a performance decrease in the planted CWs.

Reinhold et al. [58] found in their flask scale plants that duckweed can contribute to removing triclosan, while it is not efficient with respect to DEET. Zarate et al. [19] investigated bioconcentration patterns of triclosan and triclocarban among three different macrophytes (*Typha latifolia*, *Pontederia cordata*, *Sagittaria graminea*) and their concentrations in different sites of the investigated surface flow basin. They found that concentrations of the two analytes were higher in roots rather than in shoots and tended to decrease from the inflow to the outflow.

To complete this brief discussion, attempts to correlate observed removal efficiencies of the different PCPs with their LogK_{ow}, LogD_{ow}, and pK_a were carried by different authors (among them [28, 30]) but unfortunately no significant correlations were found.

Referring to surfactants, Sima and Holcová [51] found similar removal efficiencies for BOD_5 and nonionic surfactants.

7 Conclusions

It is well known that CWs, if well designed, exhibit a good ability in removing common conventional pollutants. Their potential in removing emerging organic contaminants is, however, still under discussion. This chapter focuses on the ability of CWs in removing common PCPs, substances frequently used worldwide and with increasing levels of consumption. They are quite complex molecules, with different chemical and physical properties and are, in many cases, quite persistent to biodegradation.

On the basis of the collated data, in general a removal was observed for each reviewed compound with very few exceptions, mainly referring to groups of surfactants, such as SPCs, as their formation due to LAS degradation is faster than their removal.

The highest removal levels were found for the fragrances in all three treatment steps. These compounds were the most studied, while for many others there is still little data, and further investigations of their removal in the different types of CWs are necessary.

The coexistence of different microenvironments within each type of CW which guarantee different redox conditions and the simultaneous occurrence of biological, physical, and chemical removal mechanisms make CWs a potentially adequate system for the removal of PCPs, with limited operational costs.

The main weaknesses are the wide footprint of these systems – resulting in high investment costs – and the extremely long time required to reactivate the processes within them in the case of malfunctions which are mainly due to clogging phenomena and an influent which accidentally becomes highly polluted. These weaknesses lead to long rest periods (in the first case) or expensive maintenance interventions (in the second).

However, CWs, due to their buffer capacity, could represent a barrier to reducing the spread of these types of PCPs into the aquatic environment.

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