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COMPORTAMENT DE CONTAMINANTS ORGÀNICS EN AIGUAMOLLS CONSTRUÏTS
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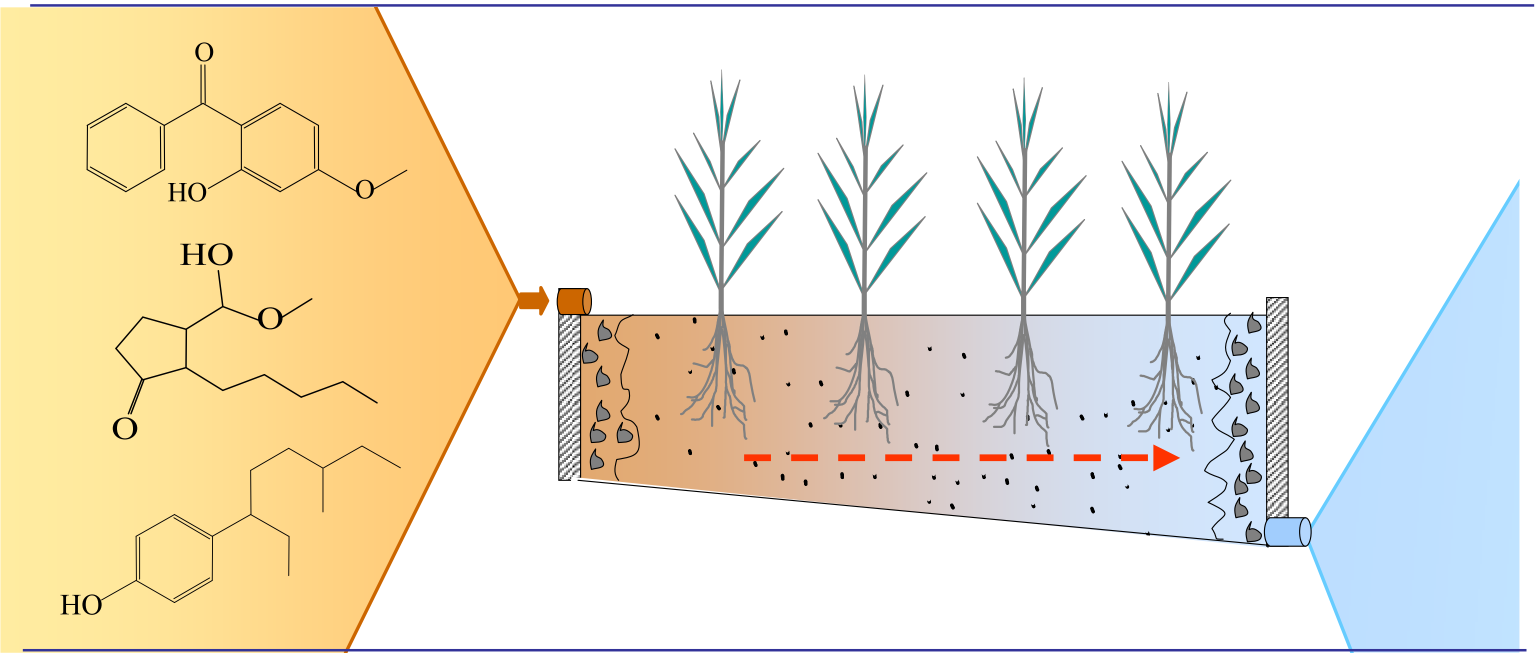

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Annex I:

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Behavior of Emerging Pollutants in Constructed Wetlands

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Abstract Constructed wetlands (CWs) constitute a cost-effective wastewater treatment alternative for small communities due to the low operational cost, reduced energy consumption, and reduced sewage sludge production. Although much information is available about conventional water quality parameters in CWs, few data exist regarding emerging pollutants. In this chapter, following a short introduction on the different wetland configurations, the removal efficiency for anti-inflammatory drugs, lipid regulators, anti-epileptic agents, fragrance materials, surfactants, and estrogens in different wetland systems is discussed. Among the parameters affecting wetland performance, it is shown that removal efficiency of a variety of emerging pollutants is dependent on the oxygen availability and sorption interactions. For that reason the vertical flow constructed wetlands exhibited the best performance in terms of hydraulic residence time and removal efficiency.

Keywords Constructed wetlands · Hydraulic loading rate · PPCPs · Removal efficiency · NSAID · Estrogens · Anionic surfactants

Abbreviations

APE	Alkylphenol ethoxylates
APEC	Alkylphenol polyethoxycarboxylate
CAPEC	Carboxylic acid alkylphenol ethoxylate
CW	Constructed wetland
BOD_5	Biological oxygen demand
FM	Fragrance material
HFCW	Horizontal flow constructed wetland

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HRT	Hydraulic residence time
HLR	Hydraulic loading rate
MLR	Mass loading rate
NP	Nonylphenol
NPEO	Nonylphenol ethoxylate
NSAID	Non-steroidal anti-inflammatory drug
PE	Person equivalent
PPCPs	Pharmaceuticals and personal care products
SFCW	Surface flow constructed wetland
SSFCW	Subsurface flow constructed wetland
TSS	Total suspended solids
VFCW	Vertical flow constructed wetland
WWTP	Wastewater treatment plant

1
Introduction

Constructed wetlands (CWs) are land-based wastewater treatment systems that consist of shallow ponds, beds, or trenches that contain floating or emergent-rooted wetland vegetation [1]. CWs have been used in order to treat domestic wastewater from rural areas all over the world since they were firstly applied in Germany in the 1960s [2]. The potential of CWs for the removal of contaminants occurring in urban wastewater has attracted increasing interest over the past decade, with a view to treating wastewaters from small populations to comply with environmental regulations such as the European Union Directive 91/271 and the US EPA Clean Water Act. Other wetland applications are the attenuation of agricultural contamination runoff to surface waters [3, 4], combined sewer overflows [5], urban storm water [6], industrial effluents [7–9], landfill leachates [10], and sludge consolidation [11].

In addition, such treatment systems are well suited to treat wastewater from isolated populations because they do not require external energy, there is no need for highly qualified personnel, the production of sewage sludge is low, and because of the low operational and maintenance costs.

Nevertheless, available information on the removal performance of these systems is limited to common contamination parameters, such as total suspended solids (TSS), biological oxygen demand (BOD_5), nutrients, bacteria, metals, herbicides, and pesticides [2–4, 12]. Nonetheless, limited information is available related to emerging pollutants, so that will be reviewed hereafter.

This chapter will focus on the use of CWs for urban wastewater treatment according to different wetland configurations, and their performance is discussed under diverse operational conditions. Following the experience gathered in different case studies, a positive correlation has been found between the dissolved oxygen concentration in the CW effluent and the removal of emerging pollutants. Moreover, the CW performance for the emerging pollutant selected will be compared with conventional wastewater treatment plants (WWTPs).

2

Types of Constructed Wetlands

The two principal classes of CWs designed for treating wastewater are the surface and subsurface flow systems [13, 14], depending on whether or not the wastewater is flowing on the wetland surface.

Surface flow constructed wetlands (SFCWs) consist of shallow basins or channels with planted wetland vegetation where water flows over a compacted low permeability clay liner at relatively shallow depths. These wetlands are typically used to polish effluents from secondary treatment processes and require large surface areas associated with long retention times (i.e., several weeks) (Fig. 1a).

Subsurface flow constructed wetlands (SSFCWs) involve shallow basins or channels with planted vegetation overlying a liner where the wastewater is treated as it flows through the gravel media and around the roots and rhizomes of planted vegetation. Attending to the water flow direction, SSFCWs can be classified as horizontal flow constructed wetlands (HFCW) (Fig. 1b) or vertical flow constructed wetlands (VFCW) (Fig. 1c). If the plant is properly designed, wastewater flows by gravity, so no external energy is needed.

According to the oxygen availability, the biodegradation of organic matter in CW occurs through different pathways. In this regard, whereas in the HFCW the organic matter removal is mostly by anaerobic pathways (i.e., denitrification, sulfate reduction, and methanogenesis), in VFCW the aerobic environment prevails. These different environments, according to the CW configuration, are of primary interest in order to eliminate the emerging pollutants from wastewater because of their high oxygen dependence [15, 16]. Hence, these wetlands are typically used to treat primary effluents (following a sedimentation step) to reach typical secondary treatment standards.

In addition, a few European countries have incorporated willow systems [17] to treat wastewater. The main feature of these treatment systems is the absence of effluent (zero-discharge of water). It is accomplished by water evapotranspiration and removal of the organic matter by biodegradation, plant uptake, or/and mineralization.

Different types of plants are used in CWs depending on their configuration. In SFCW, the vegetation can be emerged or submerged and fixed or free-floating. In case of SSFCWs, the common reed (*Phagmitis autralis*) and narrowleaf cattail (*Typha angustifolia*) are the most widely used since they are resistant under a variety of environmental conditions and facilitate air transport by the stem. Accordingly, a localized oxic environment in the rhi-

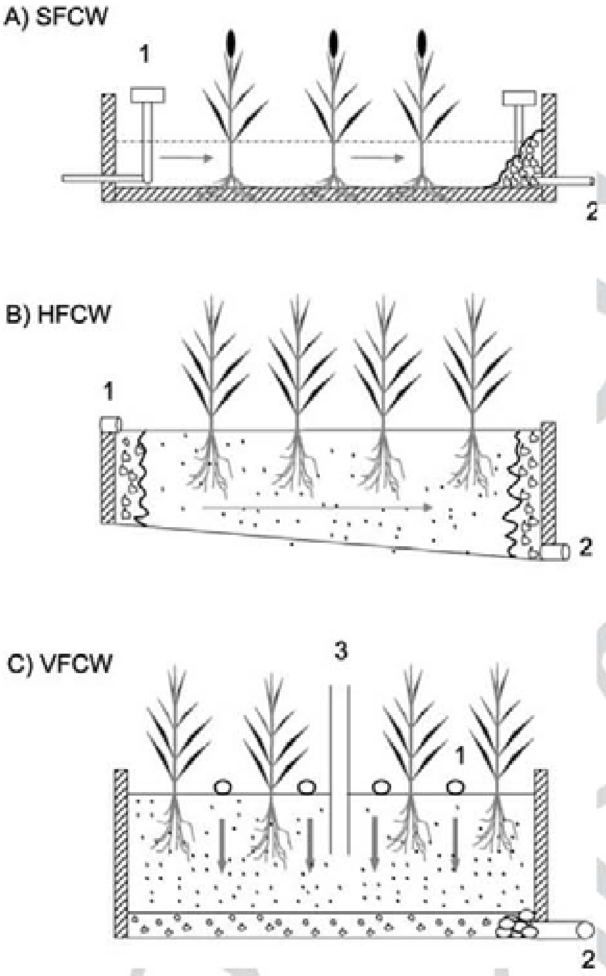


Fig. 1 Longitudinal section of constructed wetlands with three different configurations: **a** SFCW, **b** HFCW, and **c** VFCW. *Arrows* indicate the water flow direction; *1* inflow; *2* outflow; *3* aeration tip

zosphere is generated, which facilitates the biodegradation of contaminants in such oxic zones.

The main difference between CWs and trickling filters or sand filters, extensively used in wastewater treatment, is the presence of vegetation. The role of plants in CWs is multiple, from biological to physical aspects (i.e., biofilm support, plant uptake, rhizosphere oxygenation, and enhanced filtration) [18].

One of the problems associated with SSFCWs is clogging. It is characterized by a gradual loss in the hydraulic conductivity according to the operational time. It is associated with the accumulation of settled solids in the wetland inlet. Accordingly, clogging induces several processes, which lead to a reduction in the infiltration capacity at the substrate surface. The lower infiltration rate causes a reduced oxygen supply and as a consequence leads to

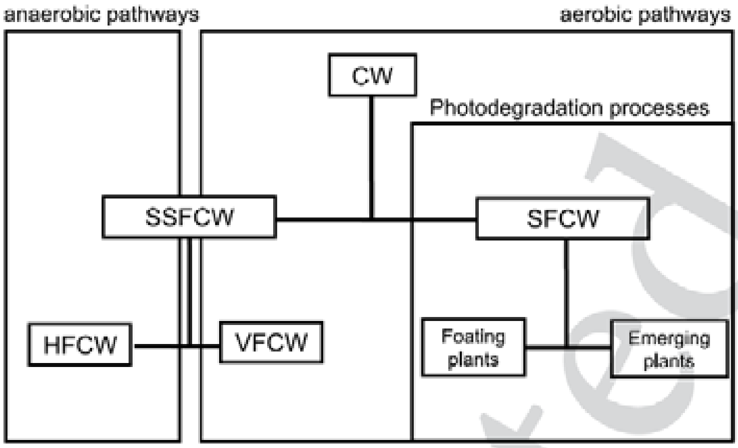


Fig. 2 Types of CWs according to the water flow. Main removal pathways for organic matter in each system

a rapid failure of the treatment performance [19]. Causes of substrate clogging include accumulation of suspended solids, large biofilm development, chemical precipitation and deposition in the pores, growth of plant-rhizomes and roots, generation of gas, and compaction of the clogging layer [20].

The removal of pollutants from wastewater is related to a variety of physical, chemical, and biological processes, which depend on the wetland configuration (Fig. 2). The main removal processes of organic contaminants are due to the physical interactions with organic matter, biodegradation, microbial and plant uptake, volatilization, and photodegradation. Obviously, the latter removal process only takes place in surface flow beds where water is directly exposed to sunlight.

Although the use of CWs for wastewater has been postulated as a feasible technology, their high area requirements, ca. 3.2 m^2 $person^{-1}$ equivalent (PE) in VFCW [21] and 5 m^2 PE^{-1} in HFCW [22] have limited their use to small communities with less than 2000 inhabitants. Nevertheless, CWs possess several others functions in addition to improve water quality. In fact, they can also function as landscape restoration, natural habitats, recreational areas, hydrological buffers, or as a reservoir. So, this technology is of increasing interest all over the world. In Europe alone, more than 5000 SSFCWs systems are in operation [13].

3
Behavior of Emerging Contaminants in CWs

In the following sections, the behavior of the different PPCP categories are reviewed according to the different CW configurations and their performance compared with conventional WWTPs.

3.1
Non-steroidal Anti-inflammatory Drugs (NSAIDs)

NSAIDs are the pharmaceuticals with the highest widespread human use. They and their metabolites exhibit a high frequency of detection in influent and effluent from urban WWTPs [23]. Consequently, they can occur at high concentrations, exceeding in some cases the predicted no-effect concentration (PNEC) [24, 25]. Hence, their occurrence attracted the attention of the scientific community and legislators. As shown in Fig. 3, these compounds are negatively charged at environmental pH (nearly 8) due their low pK_a (between 3 and 4), consequently their sorption into sludge was found to be negligible [26]. Then, their removal in CWs as well as in WWTPs is mainly attributable to biodegradation [19, 27].

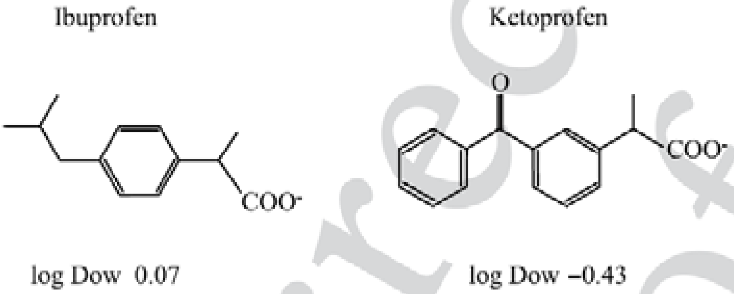


Fig. 3 Chemical structures of some NSAIDs. Ionized forms are shown. log D_{ow} calculated at pH 8 [64, 73]

Table 1 summarizes the removal efficiencies of some analgesic drugs evaluated in different CWs case studies and compares them to those reported for WWTPs. As shown, CWs could be a suitable alternative for elimination of these compounds from wastewater or for improving the quality of WWTP effluents. VFCW and SFCW appear to be the CW configurations that allows the highest NSAIDs removal, even higher than conventional WWTP. Nevertheless, when hydraulic residence times (HRTs) were taken into account, VFCW appears to be the most efficient system. Indeed, NSAID removal in the SFCW with low HRT (48–96 h) is lower than in the others (Matamoros et al., unpublished results). Following these case studies, factors affecting NSAID removal in CW are listed and discussed (i.e., oxygen, photodegradation, water depth, loading rates, clogging and plant occurrence).

As reported earlier for biofilm reactors [28], oxygen is a key factor affecting the removal of some NSAIDs. Therefore, the removal in VFCW is more efficient because different pathways are involved. In vertical beds with unsaturated flow, aerobic biodegradation pathways prevail whereas in saturated HFCWs anaerobic biodegradation is predominant (Matamoros et al., unpublished results).

Table 1 Removal efficiency (%) of NSAIDs in CWs and comparison with WWTPs

	HFCW a	b	VFCW	SFCW c	d		WWTP	Refs.
Salicylic acid	96	87	98	–		–	99	[26]
Ibuprofen	71	34	99	96	95	47	60–70 90	[67] [23]
OH-ibuprofen	62	26	99	–		33	95	[68]
CA-ibuprofen	87	49	99	–		–	95	[68]
Naproxen	85	24	89	92	52	–	40–55 66	[67] [23]
Diclofenac	15	6	73	96	73	–	24 17	[69] [70]
Ketoprofen	38	n.r.	–	99	97	–	48–69	[23]
HRT (h)	114	155	6		720	48–96	12–24	

HFCW case study was carried out in Spain on primary effluent at different water depths: *a* 0.3 m; *b* 0.5 m [19]
VFCW case study was carried out in Denmark on primary effluent
SFCW case studies were carried out in Spain on secondary effluent in different seasons: *c* warm season (high sun light); *d* cold season (low sun radiation) [31], and thirdly in the EUU in river effluent [40]
WWTP measurements were made in raw wastewater
n.r. no removal

Additionally, water depth has been noted as an important design parameter for HFCWs. When a normally designed bed (0.5 m water depth) was compared with a shallower bed (0.3 m) a difference in the removal of NSAIDs was shown (Table 1). These differences were attributable to a less negative redox potential of the shallower bed compared to the deeper one [29]. Therefore, whereas in the deep bed the anaerobic pathways are predominant, in the shallow one they coexist with some aerobic pathways (i.e., nitrification). Consequently, the redox status seems to be a key factor for NSAID removal.

The mass loading rate (MLR), defined as the mass of pollutant treated for each bed surface area, is an important operational parameter in CWs. The MLR is optimized by using kinetic constants through two different approaches. Whereas in HFCW this was accomplished by increasing the surface treatment area, in VFCW kinetics were calculated by increasing the hydraulic loading rate (Fig. 4). The elimination of emerging pollutants, as well as general parameters (i.e., BOD_5, TSS), usually follows first-order kinetics, showing a concentration dependence [30]. In this regard, NSAID removal through

SSF fitted first-order kinetics, with values of 0.04–0.19 and 0.11–0.40 m d^{-1} for HFCW and VFCW, respectively. The fact that these values agree with the BOD_5 elimination rates reported by SSF (0.06–1.00 m d^{-1}) [30] might suggest that the NSAID removal pathway is comparable to the elimination of the unspecific organic matter. Therefore, the high kinetic values obtained in VFCW yield similar elimination in VFCW to elimination in HFCW using a low surface area or high mass loading rate.

Figure 4 summarizes the three main behaviors observed in HFCW: the highly efficiently removed compounds, when a low surface area is needed to obtain a high removal (i.e., carboxy-ibuprofen and salicylic acid); the moderately removed compounds, when their removal progresses by increasing the surface area (i.e., naproxen, ibuprofen, and OH-ibuprofen), and finally the recalcitrant compounds (i.e., diclofenac and ketoprofen), for which their removal is independent of the surface area. Nevertheless, small differences in their performance were noted when hydraulic loading was increased in VFCW, showing similar high removal for all compounds with the exception of diclofenac.

Another important parameter that affects NSAIDs removal in VFCW and in HFCW is clogging. In addition to decreasing the HRT, clogging in VFCW

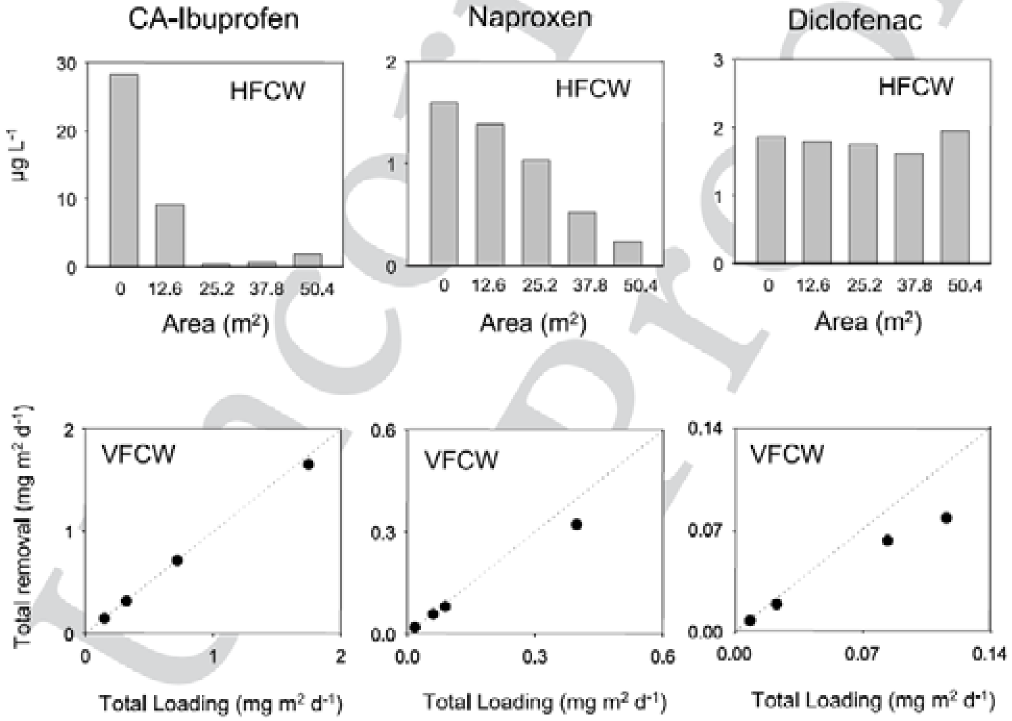


Fig. 4 PPCP behavior through the HFCW and VFCW according to the surface area and loading rates, respectively. *Discontinuous line* represents 100% removal. Reprinted with permission from [19]. © (2006), American Chemical Society

seems to directly affect the removal pathway. It produces a decrease in the contribution of the aerobic pathways (i.e., decline on ammonium removal) and replaces it by anaerobic pathways (denitrification, sulfate reduction, and methanogenesis). Therefore, aerobic pathways seem to be more efficient for the elimination of most of the NSAIDs evaluated than the anaerobic pathways.

The role of plants on NSAIDs removal was evaluated in an intercomparison study between two vertical beds (VFCW vs. sand filter) (Matamoros et al., unpublished results). Plant enhanced the removal of ibuprofen and OH-ibuprofen, attributable to the oxygen availability [28]. On the other hand, salicylic acid and diclofenac were only slightly affected by vegetation, similarly to BOD_5 and TSS. Finally, removal efficiency of CA-ibuprofen and naproxen showed a moderate plant effect.

Furthermore, photodegradation has been shown to be a key factor in SFCW. Indeed, the high diclofenac and ketoprofen (i.e., 99%) removal obtained in SFCW treatment of a WWTP effluent [31] was ascribed to their high photodegradation rates [32, 33]. Moreover, whereas a seasonal difference in diclofenac and ketoprofen removal attributable to sunlight has been observed in SFCW (Table 1) as well as in other open systems [32, 34], no differences were observed for the rest of the analgesics. This could be attributable to a fast biodegradation rate instead of the transformation of the compound by photodegradation. In fact, ibuprofen is considered to be a compound recalcitrant to photodegradation [33].

To summarize, NSAID removal in VFCW and SFCW apparently is better than in conventional WWTP, and is similar to emerging wastewater treatment technologies like membrane bioreactors [35]. Indeed, as shown previously in membrane reactors [36], we found that the removal efficiencies of drug residues in HFCW were dependent on their molecular structure [19] (e.g., extended aromatic structures as in ketoprofen and diclofenac).

3.2
Lipid Regulator Drugs and Anti-epileptic Agents

Carbamazepine is an important drug used in the treatment of epilepsy, as well as for other psychotherapy applications. On the other hand, clofibric acid is the active metabolite in a series of widely used blood lipid regulators (Fig. 5). Studies in Europe and North America have shown that these two compounds are two of more frequently detected pharmaceuticals in WWTP effluents, in surface and groundwater and even in sea water [23, 37].

Generally, the low removal of carbamazepine and clofibric acid observed in CWs agrees with the high recalcitrance described for these compounds in conventional WWTP as well as in MBR. Accordingly, removal has not been observed for both compounds in HFCWs [38] but it was fair for carbamazepine in VFCW (ca. 25%) and moderate for carbamazepine, clofibric

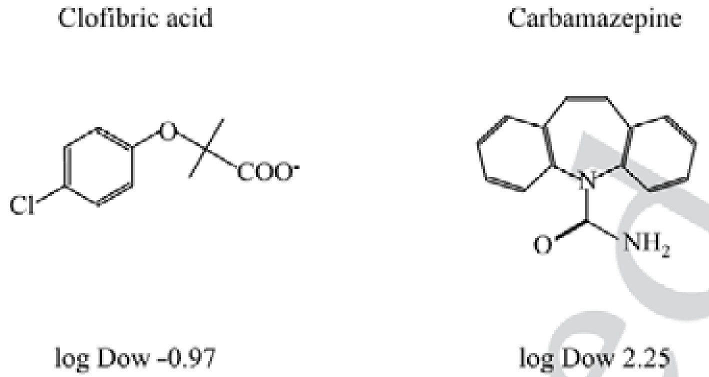


Fig. 5 Chemical structures. Ionized forms are shown. log D_{ow} calculated at pH 8 [64, 73]

acid, and gemfibrozil in SFCW (ca. 30–60%) [39, 40]. The higher removal of clofibric acid and carbamazepine in SFCW is attributable to their high HRT (i.e., 720 h) that allows interactions with the different wetland compartments (organic matter, biofilm, biota, and plants) and the completeness of removal processes.

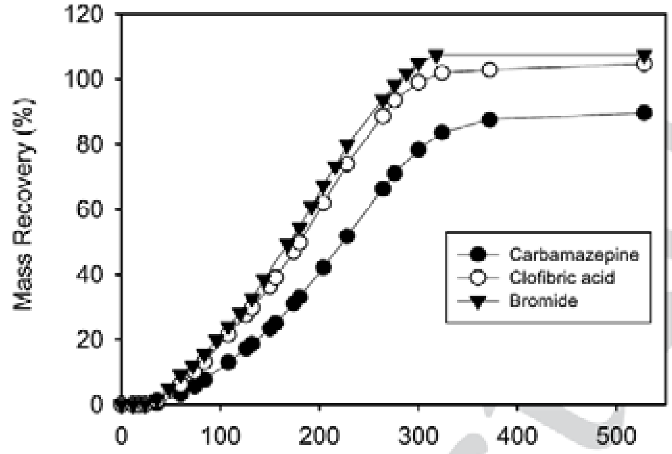
We suggested that the transport of these compounds along CWs [31] is similar to that in groundwater and packed sediment columns [41–43]. Therefore, in a singular study where carbamazepine and clofibric acid were continuously injected into a HFCW together with bromide as tracer (Fig. 6), their retention was shown to be dependent on their hydrophobicity. Hence, whereas clofibric acid behaved similarly to bromide due its low hydrophobicity (Fig. 5), carbamazepine was retarded by interaction with the gravel bed. Consequently, a carbamazepine load on the gravel bed was observed.

No plant or clogging effect was found on the removal of these compounds on account of their high recalcitrance. Nevertheless, in vertical beds, the presence of plants led to a moderate carbamazepine attenuation (i.e., 26 vs. 11%) perhaps attributable to some sorption or/and degradation associated with roots.

3.3
Fragrances

Fragrances are compounds used frequently in washing powder, fabric softeners, shampoos, and other consumer products. They are semi-volatile compounds with a wide range of water solubilities (10^3–10^{-1} mg L^{-1}). For example, whereas, galaxolide and tonalide are strongly bound to suspended solids due their high hydrophobicity ($\log K_{ow} = 5.7–5.9$), methyl dihydrojasmonate and benzyl acetate occurred in the dissolved phase [44] (Fig. 7). Simonich et al. investigated the fate of fragrances in WWTP and reported a mean removal of 87% during wastewater treatment. Since residues of fragrances are discharged via WWTP, these compounds occur at high concentra-

a) shallow bed wetland (0.3 m)



b) deeper bed wetland (0.5 m)

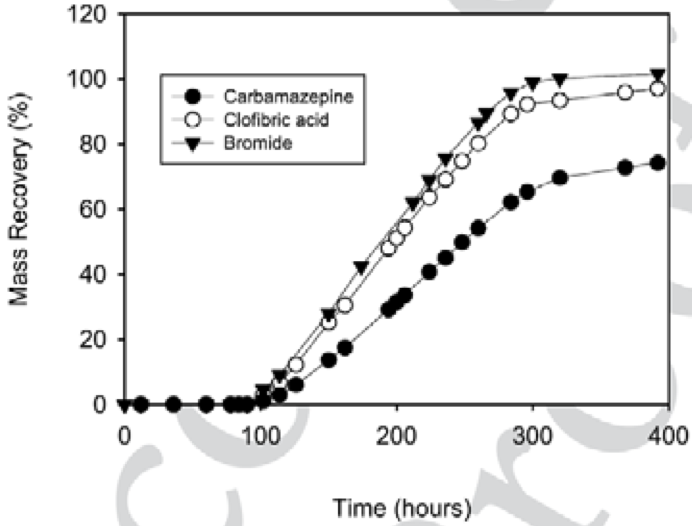


Fig. 6 Cumulative percent mass recovery for carbamazepine and clofibric acid in a continuous injection experiment for two HFCWs (**a** shallow system and **b** depth system) and comparison with bromide as a tracer. Reprinted with permission from [39]. © (2005), American Chemical Society

tions in sewage sludge but have also been detected in the surface waters from continental to marine waters and exposed biota.

Because removals achieved in HFCW, VFCW, and in SFCW are always higher than 80% [19, 31], the use of CWs for fragrance removal is a suitable technology close to WWTP. Fragrance behavior along CWs was studied according to the HFCW surface area (Fig. 8). The high removal observed in the first section was in concordance with the high organic matter accumulation in this part of the wetland. The moderate concentrations of polycyclic

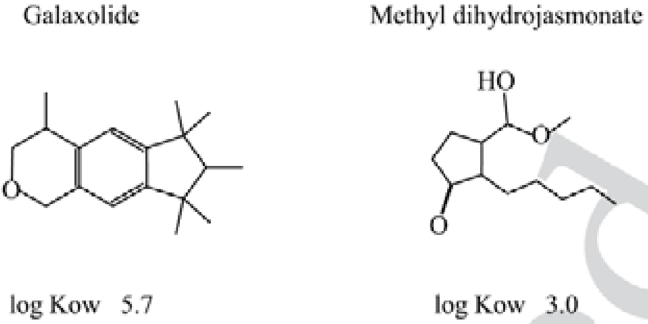


Fig. 7 Chemical structures and physicochemical properties of two fragrances [64]

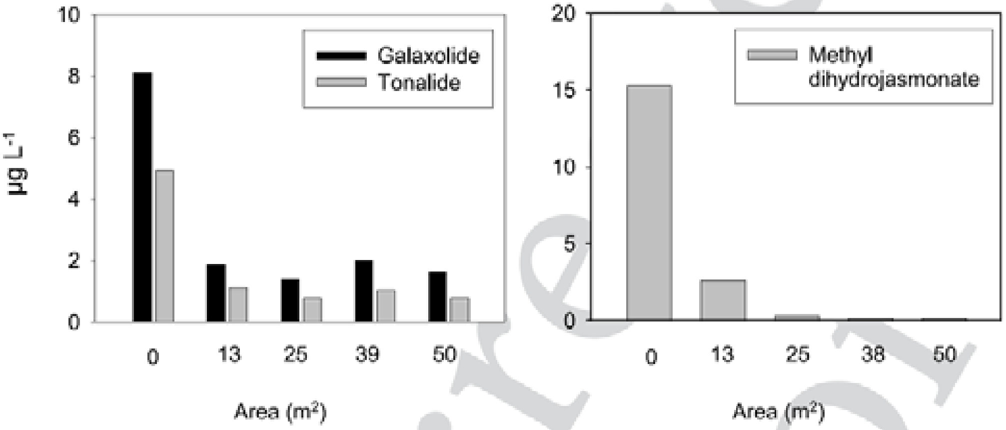


Fig. 8 Fragrance behavior through HFCW, according surface area. Reprinted with permission from [19]. © (2006), American Chemical Society

musks (i.e., galaxolide and tonalide) in the gravel bed (up to 824 $\mu g\,kg^{-1}$), in contrast to the low concentrations of methyl dihydrojasmonate, suggest their recalcitrance to biodegradation as compared to the high biodegradability of methyl dihydrojasmonate. Therefore, whereas sorption onto organic matter retained in the first part of CW was the predominant removal mechanism of the polycyclic musks, biodegradation appears to be prevalent for methyl dihydrojasmonate, a less hydrophobic compound.

Current knowledge suggests that the plant contribution to polycyclic musk elimination is negligible. As expected from its high hydrophobicity, its sorption is primarily dependent on the presence organic matter in the gravel bed.

3.4
Estrogens

The natural estrogens (e.g., estrone, estriol, 17α-estradiol and 17β-estradiol), and the synthetic 17α-ethynyl estradiol are considered to be the most potent endocrine disruptors. The estrogen hormone concentrations in the effluent of a conventional WWTP typically range from a few nanograms per liter to several micrograms [45]. These hormones have an impact on the reproductive development in some fish, even at concentrations as low as a few nanograms per liter [46, 47] (Fig. 9).

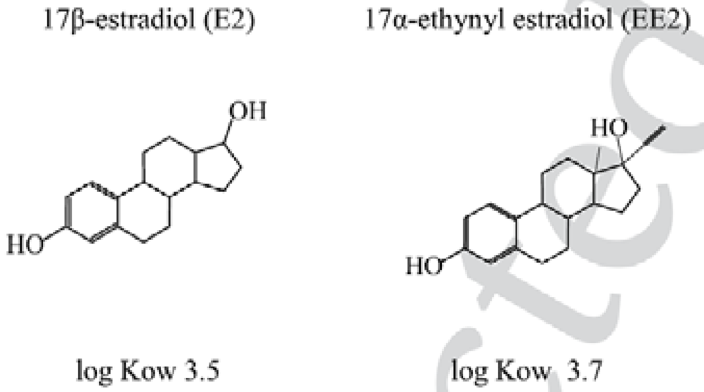


Fig. 9 Chemical structures and physicochemical properties of some estrogens [64]

Table 2 summarizes the estrogen removal efficiency, reported as estrogen removal or as a decrease in estrogenic activity, depending on the analytical procedure used. Masi et al. [48] reported a high estrogen removal (i.e., > 90%) in CWs composed of a first stage HFCW and a second stage VFCW (the so-called hybrid system). These authors pointed out that adsorption onto suspended particulate matter was considerable due to its high hydrophobicity (Fig. 9). On the other hand, although SFCW could reach similar removals to those obtained in a hybrid system, SFCWs require retention times of months instead of days. Moreover, large differences in estrogen removal were observed when SSFCWs with HRTs of days and months were compared, attributable to the high interaction of estrogens with organic matter.

Therefore, CWs can reach similar performances to those reported for WWTP, at least for VFCW and HFCW. The literature concluded that conven-

Table 2 Removal efficiency (%) of estrogens in CW and its comparison with WWTP

	SFCW [49]	SFCW [71]	HFCW-VFCW [48]	WWTP [72]
E2	36	–	–	85–99
EE2	41	–	–	71–78
Estrogens	–	83–93[a]	> 90[b]	60–99[b]
HRT (days)	3.5	22–55	3	0.5–1

[a] Referred to estrogenic activity
[b] Overall average estrogens removal

tional WWTP is efficient for the removal of E2 (85–99%) but that estrone removal is relatively poor (25–80%) due the metabolism of E2 to estrone [45].

The mobility of estrogens in CWs was evaluated by a discrete injection of E2, EE2 (Fig. 9), and lithium chloride as tracer in a pilot SFCW [49]. The results show that concentration profiles of hormone and lithium differ significantly.

The literature seems to indicate that removal mechanism for these compounds in CWs are mainly associated with sorption by organic matter and biofilm interaction, similar to that reported for sewage sludge in WWTP [45] with subsequent biodegradation. Estrogen removal could be improved by an increase in the HRT since it might increase the interaction time, as reported for activated sludge systems [50]. Because the major elimination pathway is by sorption, subsurface flow is considered to give the best elimination performance, as compared to HFCW or VFCW.

3.5
Surfactants

About 3–4 million t year^{-1} of synthetic surfactants are produced in Western Europe, Japan, and the USA and are intentionally released in large amounts into the aquatic environment [51, 52]. Although the behavior of the most relevant classes of surfactants (namely non-ionic and anionic) has been investigated in CWs, only the non-ionic ones will be reported here.

Alkylphenol ethoxylates (APEO), namely nonyl (NPEO) and to a lesser extent octylethoxylates (OPEO), are surfactants of major environmental concern due to the estrogenic properties of their degradation intermediates, nonylphenol (NP) and octylphenol (OP) (Fig. 10) [53]. Their behaviors in CWs have been evaluated at scales from the microcosmic to pilot plant.

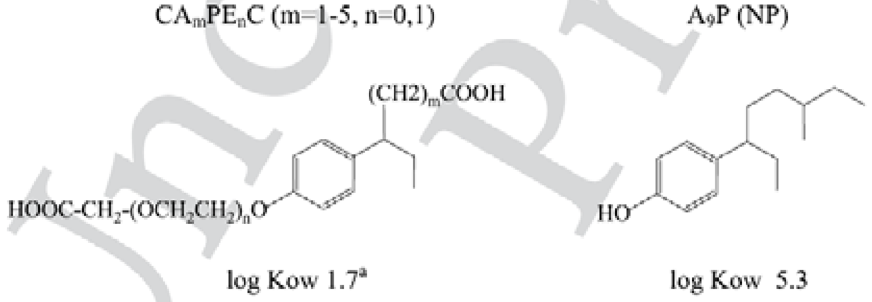


Fig. 10 Chemical structure and physicochemical properties of some non-ionic surfactants [64]; $^a m = n = 1$

Belmont and Metcalfe [54]observed high removal rates of NPEO (96.6%) in planted and unplanted microcosmic scale HFCW (HRT = 1–2 days). However, the presence of plants did not significantly contribute to the removal of the selected contaminants and it was suggested that adsorption to the substrate was the removal mechanism since the shorter alkyl-chain NPEOs are relatively hydrophobic. Moreover, the removal of ethoxylated (1–3 ethoxy groups) nonylphenols was higher (96–98%) than nonylphenols without ethoxy groups (54–57%). This was attributed to the conversion of ethoxylated derivatives to nonylphenol, as reported previously in conventional WWTPs [55].

In a subsequent study, Belmont et al. [56] evaluated CWs for the removal of NP and NPEOs from a polluted domestic wastewater. The CWs consisted of three sedimentation terraces, stabilization pond, and then a hybrid system (HFCW–VFCW) with a HRT of 2.3 days. The NPEO removal was higher than 75%, nevertheless, most of the reduction occurred in the sedimentation terraces and in the stabilization pond. The rest of the system contributed only marginally to the total removal rate. These results showed again that sorption to sediments and solids is a major removal pathway for these compounds from the aqueous phase [57].

In other study, the elimination of APs, APEOs, AP polyethoxycarboxylates (APECs), and carboxylated APECs (CAPECs) by a SFCW, in order to reduce river pollution, resulted in a partial removal of these compounds. In fact, whereas AP and APEOs were removed at an average of 75%, only 8% of the APECs and CAPECs were eliminated. Thus, it appears that SFCW treatment is fairly effective at removing neutral compounds but it does not correctly eliminate the acidic biodegradation intermediates due their low hydrophobicity.

3.6
Other Emerging Compounds

Caffeine and triclosan are employed worldwide as a stimulant and antibacterial agent, respectively [58–61]. Although both compounds have been detected in several aquatic compartments (i.e., wastewater, surface water, groundwater, and sea water) [62], caffeine shows a higher frequency of detection. Consequently, it has been used as a tracer of anthropogenic pollution in several studies [63].

High removal of caffeine in subsurface flow constructed wetlands has been reported in VFCW as well as in HFCW (94–99%). These results are comparable to the ones in WWTPs [19] (also, Matamoros et al. unpublished results). In this regard, caffeine is presented as an easily biodegradable compound, according with its high biodegradation index provided by the EPI suite software [64].

Matamoros and Bayona [19] reported that water depth is an important design factor for the removal of caffeine in HFCW, as mentioned before for BOD_5 [29], LAS [65], and NSAIDs (see Sect. 3.1). Furthermore, the negative clogging effect on caffeine removal was also reported in VFCW as well as in HFCW.

Waltman and colleagues [66] studied the elimination of triclosan in a SFCW that received the effluent of treated wastewater from an activated sludge. They achieved moderate removals (i.e., 50%) instead of the high removals obtained in WWTP (i.e., 97–99%). As reported above for NSAIDs (see Sect. 3.1), the elimination of emerging pollutants often follows first-order kinetics. Therefore, removal efficiency is concentration dependent: whereas high inlet concentrations are conductive to high removals, low inlet concentrations lead to a low removal.

4

Concluding Remarks

The elimination of NSAIDs, lipid regulator drugs, anti-epileptic agents, fragrances, surfactants, estrogens, caffeine, and triclosan by CWs could constitute a feasible alternative to WWTP in small communities. However, until now most of the information has been related to small plants or pilot scale studies.

Different factors affecting removal of emerging pollutants have been found relevant, of which oxygen concentration was shown to be one of the most important because of the best performance of aerobic pathways. Hence, VFCW has been postulated as the best option for a wide variety of compounds. Water depth in HFCW was observed to be an important design parameter for the removal of compounds that were better removed by aerobic pathways (i.e., ibuprofen). Loading rate was another important design parameter that needs to be optimized. Whereas some compounds require high surface area or low hydraulic loading rate (e.g., naproxen) for their elimination, the removal of others can be achieved using less surface area (i.e., methyl dihydrojasmonate, CA-ibuprofen). On the other hand, bed clogging produces a negative impact on pollutant removal, except for those that were removed by interaction with organic matter (i.e., galaxolide and tonalide) and those that were not eliminated at all (i.e., clofibric acid). Another important factor is sorption into organic matter (roots and biofilm), which was shown to be important for compounds with high or moderate hydrophobicity (musk, estrogens, and some alkyl phenol derivates). Finally, photodegradation, which only occurs in SFCW, is observed to be compound-dependent, allowing the possibility of increasing the removal of compounds that were low or not biodegradable at all in other systems (i.e., diclofenac and ketoprofen).

In summary, VFCWs are postulated as the best option for achieving high removals with low HRTs, a few hours instead of the days or weeks typically used for other CWs. Nevertheless, the performance, in terms of effluent quality, is believed to be better for some emerging pollutants (estrogens and AP), as shown in hybrid designs (combination in series of different CW configurations). Therefore, the possibilities of using CWs rather than high-cost technologies (i.e., MBR, ultrafiltration, and ozonation) to remove emerging pollutants from contaminated waters are opened to discussion.

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Annex II:

Article: **Els aiguamolls construïts: una tecnologia sostenible per l'eliminació de fàrmacs i productes d'higiene personal d'aigües residuals domèstiques**.
Societat Catalana de Química. Acceptat

Els aiguamolls construïts: una tecnologia sostenible per l’eliminació de fàrmacs i productes d’higiene personal d’aigües residuals domèstiques

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Resum

Aquest treball dóna una perspectiva general de la problemàtica dels fàrmacs i productes d’higiene personal en el medi aquàtic, així com a l’ús d’aiguamolls construïts per tal de eliminar-los de les aigües residuals. Així doncs, s’analitzen diferents tipus d’aiguamolls, tot buscant els més eficients a l’hora d’eliminar aquests compostos. Després de l’experiència assolida en diferents estudis duts a terme a Catalunya i Dinamarca, s’observa una relació positiva entre l’eliminació de contaminants i la concentració d’oxigen dissolt a l’aigua residual, arribant a la conclusió que els sistemes de flux vertical (aerobis) són els més eficients. A més, es posa de manifest la importància dels macròfits (*Phragmites sp.*) per tal d’eliminar aquests compostos, degut a l’augment de la transferència d’oxigen i la proliferació de biofilm en els rizomes. Finalment, es presenta l’estat d’implantació d’aiguamolls construïts a Catalunya.

Abstract

This work is focused on the use of constructed wetlands (CWs) for domestic wastewater treatment, paying attention on pharmaceuticals and personal care products (PPCPs) removal. PPCPs and CWs are described and their performance discussed in terms of PPCP removal. Following different case studies carried out in Catalonia and Denmark, a positive relation between the dissolved oxygen concentration in the CW effluent and the PPCP removal was obtained. Moreover the enhancement of PPCP removal due to oxygen transfer and biofilm proliferation in the

CWs planted with macrophytes (*Phragmites* sp) was described. Finally, the experience about the use of CWs for wastewater treatment of small communities in Catalonia is presented.

Aiguamolls construïts

La construcció d'aiguamolls artificials per al tractament d'aigües residuals es basa en l'aprofitament de l'elevada productivitat dels sistemes naturals en quant al reciclatge de carboni, tot dissenyant-los per fer-los fins i tot més eficients que els naturals.

D'entre totes les definicions que hom pot trobar a la literatura sobre els aiguamolls construïts, caldria esmentar la feta per Cole(1) degut a la seva funcionalitat: "Els aiguamolls construïts són sistemes de tractament d'aigües residuals que consisteixen en llacunes poc profundes, llits o basses que contenen vegetació emergent, arrelada o flotant"

L'ús d'aiguamolls construïts per al tractament d'aigües residuals té els seus inicis a l'Institut Max Planck d'Alemanya prop de la dècada dels 60 de la centúria anterior amb els estudis duts a terme per Seidel i Kickuth (1976). A partir d'aquesta primera aproximació John i Bob Kadlec van estendre als anys 70' la seva investigació als Estats Units(2). A partir d'ençà, aquesta tecnologia s'ha anat estenent arreu del planeta. En l'actualitat existeixen de l'ordre de milers d'instal·lacions en funcionament.

Pel que fa a la Unió Europea, els aiguamolls construïts són molt adients de cara al compliment de la directiva Europea 91/271, la qual va establir que tots els estats membres haurien d'haver garantit la depuració de les aigües residuals urbanes de totes les poblacions de menys de 2000 habitants per abans del desembre del 2005.

Així, doncs, aquests sistemes han sorgit com una alternativa a les estacions depuradores d'aigües residuals (EDARs) convencionals.

Classificació

Els aiguamolls construïts es poden classificar segons l'esquema que es mostra a la figura 1. En primer lloc es poden diferenciar dos grans grups tenint en compte el tipus de flux de l'aigua: aiguamolls de flux superficial (*surface flow*, SF), on hi ha contacte directe de la làmina d'aigua amb l'atmosfera, i aiguamolls de flux subsuperficial (*subsuperficial flow*, SSF), on l'aigua circula per sota de la superfície i no hi ha contacte directe d'aquesta amb l'atmosfera. Dintre d'aquest últim grup s'hi poden trobar sistemes de flux horitzontal (*horitzontal flow*, HF) i sistemes de flux vertical *(vertical flow*, VF). Finalment, i com a un últim grup, apareixen els sistemes plantats amb salzes (*willow systems*, WS) desenvolupats els últims anys al nord d'Europa. Cal destacar la manca d'efluent d'aquests últims sistemes.

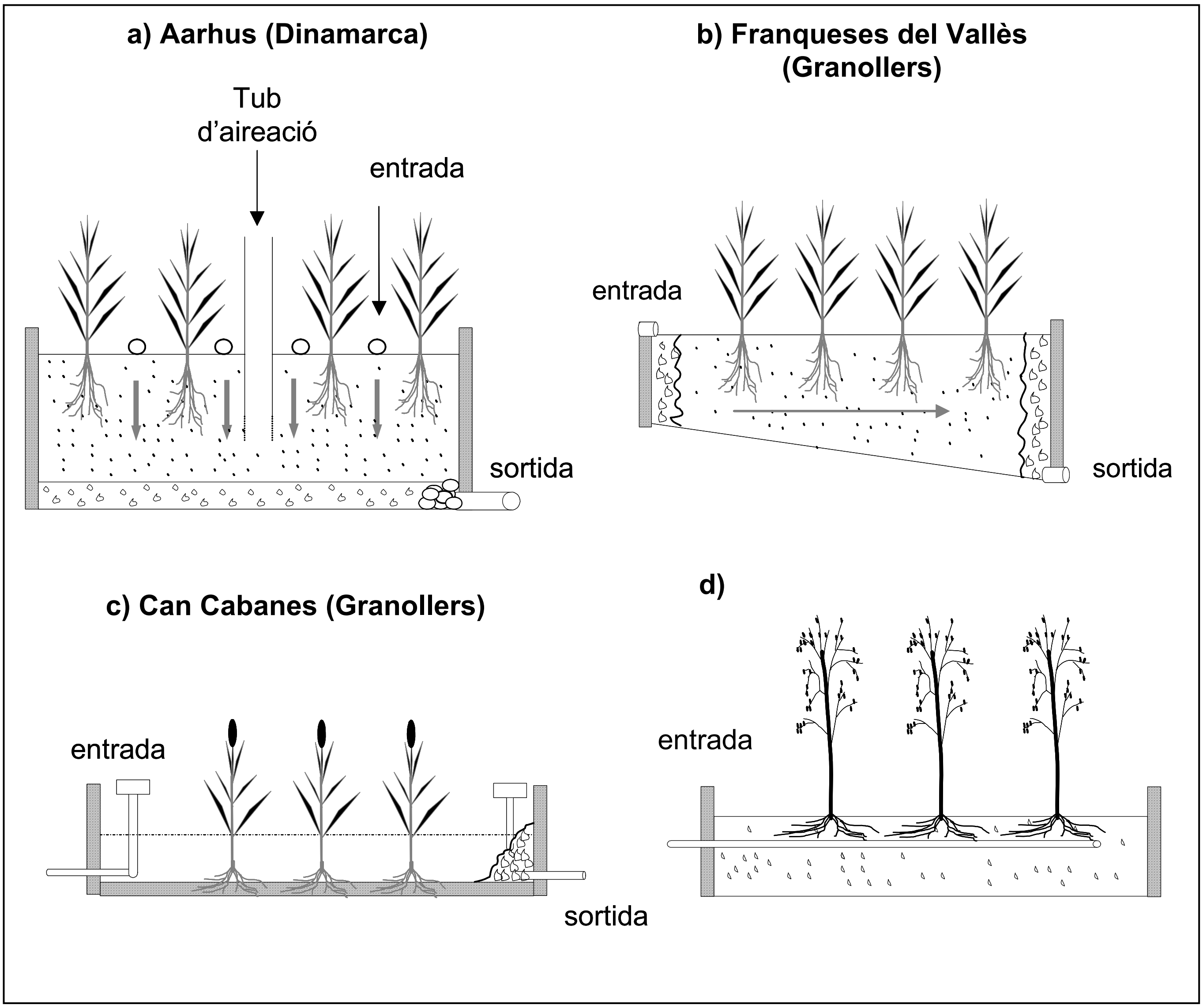


Figura 1. Classificació típica dels aiguamolls construïts. a) flux vertical (VF), b) flux horitzontal (HF), c) flux superficial (SF) i d) sistemes de salzes. Les fletxes indiquen la direcció del flux.

Avantatges i inconvenients dels aiguamolls construïts

Tal i com queda palès a l'estudi realitzat per Garcia i col·laboradors(3), hi ha una sèrie d'avantatges i inconvenients que sorgeixen a l'hora de comparar aquests sistemes amb EDARs convencionals.

AVANTATGES

- El baix cost d'explotació i el baix consum energètic que requereixen.
- La baixa producció de residus, només es generen fangs en el decantador primari instal·lat abans dels aiguamolls.

- L'impacte ambiental és molt reduït i molts cops resulta fins i tot beneficiós, poden, recuperar zones humides (com a exemple l'estany Europa, als aiguamolls de l'Empordà) i incrementar la biodiversitat al mateix temps que s'integren en el paisatge.

INCONVENIENTS

- La necessitat d'àrees superficials molt més grans.
- La dificultat d'arribar a un compromís entre el disseny i el tipus d'aigua residual. Les aigües residuals i les condicions ambientals no són totes iguals; els paràmetres de disseny que són òptims en unes latituds en altres poden no ser-ho.
- La colmatació del sistema pot afectar negativament durant el període d'explotació.
- La dificultat en redissenyar el sistema en cas de que la seva eficiència no sigui l'esperada.

En tot i això, es considera com la tecnologia disponible més adequada pel tractament d'aigües residuals urbanes de petites poblacions.

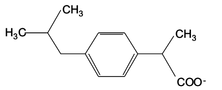
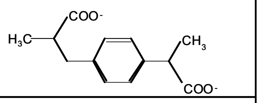
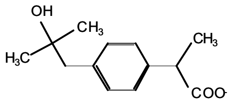
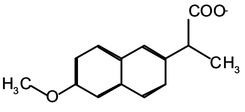
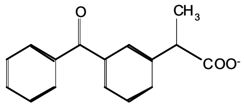
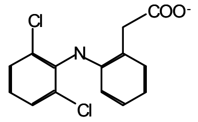
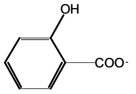
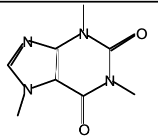
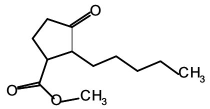
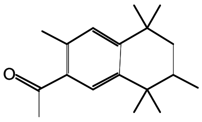
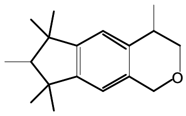
Fàrmacs i productes d'higiene personal

En l'última dècada s'han començat a estudiar els efectes que els fàrmacs i els productes d'ús personal poden tenir al medi ambient. Aquesta aproximació ha estat possible gràcies a dues premisses. La primera d'elles és l'elevat consum que d'aquests compostos s'ha anat produint al llarg dels últims anys, i la segona, fa referència al desenvolupament de tècniques analítiques que han pogut fer factible l'anàlisi d'aquests compostos a nivells traça en el medi aquàtic.

L'ús dels fàrmacs s'ha estès dràsticament des de que el segle passat Alexandre Fleming descobrís la penicil·lina. En l'actualitat existeixen una gran diversitat de fàrmacs i productes d'ús personal. La taula 1 recull algun dels compostos que hom pot trobar en el medi ambient. Des de l'ibuprofèn, analgèsic per excel·lència en els inicis del nou mil·lenni, fins la cafeïna, distribuïda àmpliament per tot el globus terrestre com a estimulant des de temps immemorials.

A més, s’ha de sumar la presència de compostos d’ús personal, d’ús molt més estès. Per exemple, als inicis dels anys 90, el consum era de 550.000 tones només a Alemanya(4). L’ús de les fragàncies, s’ha incrementat en els darrers anys. Així, la galaxolida i la tonalida formen part de les fragàncies més emprades i s’ha estimat que anualment a Europa s’utilitzen més de 2000 tones(5).

TAULA 1. Estructures, propietats físico-químiques i concentracions de fàrmacs i productes d’higiene personal.

Nom comercial/CAS	pka	log Kow	Aigua residual fresca (µg L^{-1})[a]	funció	Estructura
Ibuprofèn 15687-27-1	4.31	3.97	3.70	Analgèsic/ antiinflamatori	
Carboxi-ibuprofèn	--	--	--	Metabòlit de l’ibuprofèn	
Hidroxi-ibuprofèn 51146-55-5	--	--	--	Metabòlit de l’ibuprofèn	
Naproxèn 22204-53-1	4.2	3.18	3.28	Analgèsic/ antiinflamatori	
Ketoprofèn 22071-15-4	4.45	3.12	0.60	Analgèsic/ antiinflamatori	
Diclofenac 15307-86-5	4.2	4.51	3.02	Analgèsic/ antiinflamatori	
Àcid Salicílic 69-72-7	3.5	2.26	57.0	Metabòlit de l’àcid salicílic	
Cafeïna 58-08-2	--	0.16	230	estimulant	
Metill dihidrojasmonat 24851-98-7	--	3.0	4.48	Fragància	
Galaxolida 1506-02-1	--	5.7	2.89	Fragància	
Tonalida 1222-05-5	--	5.9	1.37	Fragància	

[a] recull de dades de diferents EDARs

Un cop els fàrmacs són ingerits i desenvolupen la seva funció en l'organisme, són eliminats, ja sigui directament sense cap modificació, o a través de l'òrgan de detoxificació per excel·lència, el fetge. En ell es produeix la biotransformació d'una part dels fàrmacs, bé sigui per oxidació, reducció, hidròlisi o conjugació (àcid glucurònic, sulfats d'èter, acetilacions, conjugació amb glicocols o metilacions). Les vies d'eliminació poden ser bé pulmonars (això es dóna pels fàrmacs més volàtils), renals, o a través del tub digestiu(6). Finalment, sigui per la via que sigui, aquests compostos acaben al clavegueram i d'aquí a les EDARs i al medi on romandran més o menys temps en funció de la seva recalcitrància. Les concentracions varien entre desenes de ppbs en l'aigua residual fresca (taula 1) fins a centenars o desenes de ppt en rius i rieres (7,8). Cal destacar la detecció d'aquests compostos en aigües de beguda(4), així com la seva presència el Mar del Nord on es va identificar l'àcid clofíbric (9).

Entre els productes d'higiene personal, com ja s'ha comentat, la galaxolida i tonalida es troben entre els més estesos. Aquests compostos tenen una alta hidrofobicitat (taula 1), amb valors de la constant octanol aigua (Kow) de l'ordre dels pesticides organoclorats i els PCBs. Això possibilitaria la seva bioacumulació, per exemple en truites criades en llacunes d'estabilització (10).

El conjunt d'aquestes molècules (fàrmacs i productes d'higiene personal) s'inclouen dintre del grup dels contaminants emergents i són objecte d'un estudi exhaustiu degut, no tant a la seva toxicitat i recalcitrància, ja que aquestes en general són baixes, si no a la seva contínua aportació al medi. Tot plegat fa que se'ls consideri com a compostos pseudopersistents, podent arribar a causar efectes en el medi que tot just ara es comencen a conèixer(11). Per exemple, l'efecte disruptor endocrí ja ha estat demostrat, a nivells de ng/L, per compostos com l'etinilestradiol contingut en els anticonceptius orals(12). A més, s'han de considerar els efectes interactius - incloent additivitat, antagonisme i sinergia - que poden incrementar o decréixer els efectes potencials en el medi ambient(13). Per exemple un estudi dut a terme per Cleuvers i col·laboradors(14) demostra que la toxicitat causada per una mescla de diferents analgèsics (mitjançant el test de toxicitat de *Daphnia magna*) és més elevada que la que s'esperaria per la simple addició dels efectes dels fàrmacs antiinflamatoris individuals.

En relació als productes d'higiene personal, aquests efectes adversos han estat demostrats a través de les fragàncies abans descrites, aquestes donen lloc a la inhibició dels transportadors de resistència a xenobiòtics (multixenobiotic resistance, MXR)(15). Així doncs, els organismes que viuen sota aquesta pressió podrien ser més sensibles a la presència de tòxics que no els que no hi estan sotmesos.

Un cop feta aquesta breu introducció als aiguamolls construïts i als contaminats emergents, el present treball té com a objectiu donar a conèixer les possibilitats d'aquests sistemes a l'hora d'eliminar aquests contaminats de les aigües residuals. Per això es compararan aiguamolls de diferent configuració: flux horitzontal, superficial i vertical.

Cal comentar, que tot i haver-hi molta recerca al voltant de la eliminació d'aquests compostos en EDARs convencionals, aquesta és molt reduïda en aiguamolls construïts, essent el present treball pioner dintre d'aquest camp.

Comportament dels compostos emergents en aiguamolls construïts

El paper de l'oxigen en la eliminació de contaminants

Pel que fa l'eficiència d'eliminació de la majoria de fàrmacs i productes d'higiene personal en els aiguamolls construïts, aquesta va estretament lligada a la quantitat d'oxigen present en aquests i, per tant, a les vies metabòliques predominats en cada cas. Aquesta premissa ve recolzada per diferents experiments duts a terme en aiguamolls construïts de Catalunya i Dinamarca.

El primer d'aquests estudis compara dos aiguamolls de flux horitzontal, preferentment anaerobis, amb diferents profunditats de la làmina d'aigua (0.27 m i 0.5 m). Les concentracions d'oxigen dissolt a la sortida, als dos sistemes eren inferiors a 1 mg/l, no obstant les eficiències d'eliminació de contaminats emergents, en general, varen resultar ser més elevades a l'aiguamoll més somer que al més profund (taula 2). La principal diferència entre els dos sistemes rau en les rutes metabòliques que hi tenen lloc; el sistema més profund amb condicions típicament anaeròbies, té la sulfatoreducció com a ruta principal a l'hora d'eliminar la matèria orgànica (o sigui, utilitza el sulfat com a acceptor d'electrons). En canvi, al sistema somer coexistien les vies sulfatoreductives amb les de nitrificació, la qual cosa dóna a entendre que dintre de l'aiguamoll somer hi ha certa presència d'oxigen. No obstant, aquest és emprat ràpidament per a la formació de nitrats i per això no és detectat a la sortida. Així doncs, aquest primers resultats mostren la importància de l'oxigen per eliminar aquests tipus de compostos.

Més endavant es confirmarien aquestes teories mitjançant el mostreig en aiguamolls de flux superficial, sistemes estrictament aerobis, i en els quals s'hi esperaren altes eliminacions tal i com es mostra en la taula 2 (SF). No obstant, i degut a l'elevat temps de residència dels compostos en aquest sistema (un mes de terme mig) no es poden fer afirmacions estrictes i comparatives amb els sistemes anteriors, amb un temps de residència inferior a una setmana.

Per tal de testimoniar la importància que l'oxigen té en l'eliminació d'aquests compostos es va realitzar el mostreig en aiguamolls construïts de flux vertical (estrictament aerobis), amb un temps de residència al voltant d'hores. A la taula 2 es mostren les elevades eliminacions que presenten els sistemes de flux vertical (VF) en relació als sistemes horitzontals. Aquesta diferència, rau novament, en la diferència de rutes metabòliques d'ambdós sistemes. Als sistemes verticals les vies aeròbiques són predominants . Tal i com es coneix, les rutes aeròbies, en general, són més eficients a l'hora de degradar la matèria orgànica que les anaeròbies (sulfatoreducció, metanogèsis, desnitrificació, etc.) i sembla ser que també ho serien a l'hora d'eliminar els contaminants emergents.

La importància de la vegetació

Segons el que s'ha descrit abans, es podria dir que els aiguamolls de flux vertical semblen ser els més eficients per tal d'eliminar fàrmacs i productes d'ús personal. De fet, aquests provenen dels anomenats filtres d'arenes, d'una llarga tradició a França. Estudis recents han demostrat que a l'hora de tractar aigües residuals, els sistemes plantats són més eficients que els no plantats(16). Això és degut a dos fenòmens. El primer d'ells és l'augment del transport d'oxigen de l'atmosfera al sòl, bé sigui gràcies a les arrels de les plantes o als moviments mecànics de les tiges que esquerden el sòl. El segon fenomen està relacionat amb el creixement de biofilm al voltant dels rizomes i que hom pensa que ajuda a incrementar la biodegradació.

En aquest context, s'ha realitzat un estudi comparatiu de les eficiències en l'eliminació de contaminants emergents en sistemes plantats i no plantats, obtenint millors eficiències en els sistemes amb plantes (taula 2, VF *vs*. Filtre de sorres). Els resultats confirmen allò que ja es sabia per a la matèria orgànica i donen una relació directa entre l'eliminació de contaminants emergents i la matèria orgànica.

Cinètiques d'eliminació de contaminants: El cas de Les Franqueses del Vallès

Per tal d'aprofundir en el modelat del comportament dels contaminants emergents en els aiguamolls construïts, hom empra els paràmetres cinètics de degradació de la matèria orgànica tot considerant l'aiguamoll com un reactor de flux de pistó. Per aconseguir-los hi ha dues aproximacions possibles, incrementar la càrrega hidràulica a l'entrada del sistema o bé recollir mostres a diferents distàncies de l'entrada dels sistemes.

Tot seguint aquesta segona opció, la figura 3 mostra un exemple dels quatre comportaments trobats als aiguamolls subsuperficials de flux horitzontal situats a les Franqueses del Vallès(17). Aquests comportaments són els següents: grup I, compostos fàcilment eliminables (cafeïna, àcid salicílic, metil dihidrojasmonat, ibuprofèn i un dels seus productes de degradació durant el metabolisme humà, l'hidroxi-ibuprofèn; grup II, compostos moderadament eliminables (naproxèn i carboxi-ibuprofèn); grup III, compostos recalcitrants (ketoprofèn, diclofenac, àcid clofíbric i carbamazepina), i finalment, el grup IV, compostos que s'eliminen per interaccions hidrofòbiques amb la matèria orgànica que conté l'aiguamoll (galaxolida i tonalida).

El grup I, amb una relació exponencial en front de la distància, respon a una cinètica d'eliminació de primer ordre. Aquests, a més són els més sensibles als canvis, com ara la colmatació.

El grup II respon a una cinètica d'ordre zero, essent la seva eliminació proporcional a l'àrea de l'aiguamoll.

En quant als compostos recalcitrants (grup III), aquests no experimenten cap tipus de retenció dintre del sistema. Possiblement degut a la seva hidrofilicitat i poca degradació, tal i com ja és esmentat en treballs anteriors d'EDARs(18).

Finalment, per als compostos que s'eliminen per interaccions hidrofòbiques (grup IV) es pot copsar perfectament com aquesta eliminació es dóna bàsicament a la primera part del sistema, que és on es reté la matèria orgànica (19). Per tal de confirmar aquesta hipòtesi, es van estudiar els compostos retinguts en l'aiguamoll, obtenint les concentracions més elevades per a les fragàncies (galaxolida, 850 µg Kg^{-1}) en la part proximal del sistema, mentre els altres compostos apareixien a nivells molt més baixos (ibuprofèn, 6 µg Kg^{-1}).

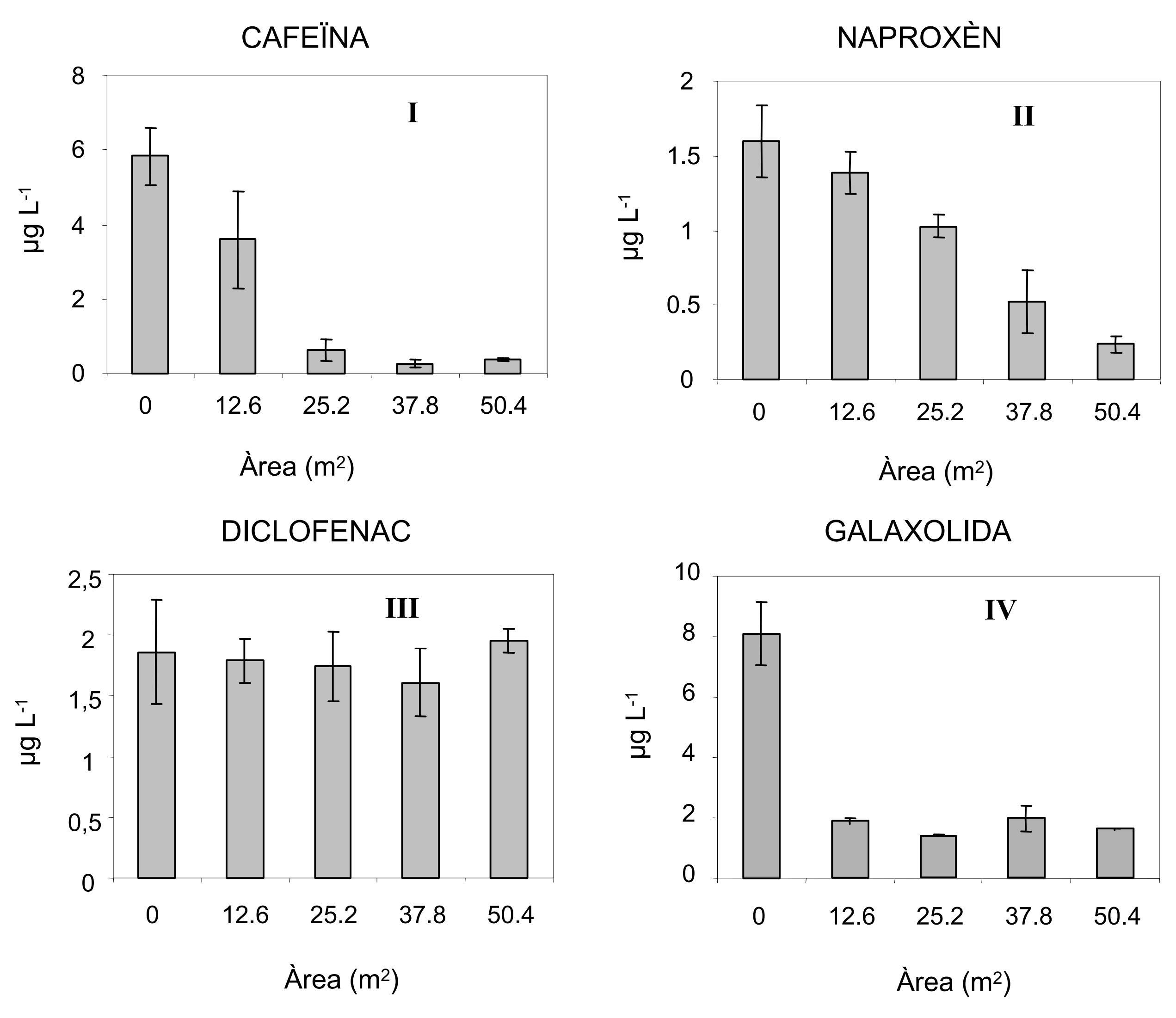


Figura 3. Exemple dels quatre comportaments diferents dels fàrmacs i productes d'higiene personal durant el seu pas pels aiguamolls construïts. L'eix vertical correspon a la concentració de cada compost i l'eix horitzontal representa l'àrea de l'aiguamoll (el punt 0 m^2 correspon a l'entrada , el següents tres els piezòmetres i la sortida el punt 50.4 m^2). La desviació estàndard correspon a un mostreig diari d'una setmana de durada (n=5)

El problema de la colmatació

Dintre de tots els problemes que poden afectar als sistemes de flux subsuperficial (vertical o horitzontal), la colmatació, per la retenció de la matèria orgànica i el desenvolupament excessiu de biofilm, és dels més greus. Quan un d'aquests sistemes es colmata el primer dels efectes és la presència d'aigua en la part superficial del sistema. Aquest efecte pot ser perjudicial per tres raons; la proliferació de mosquits degut a l'aigua estancada, la mala olor que aquesta genera, i una tercera relacionada amb la disminució del procés de tractament de les aigües residuals. Aquest últim efecte s'ha pogut comprovar en un estudi fet als aiguamolls de flux subsuperficial situats a Les Franqueses del Vallès (Granollers). Estudiant l'eliminació de compostos emergents al llarg de dos anys, s'ha vist que quan els processos de colmatació apareixen, les eficiències d'eliminació disminueixen significativament. Per exemple en el cas de l'ibuprofèn aquesta disminució pot arribar a ser superior al 40%.

Aiguamolls construïts vs. EDARs

Quan es comparen aquests dos tipus de sistemes, s'ha de tenir en compte la complexitat de les EDARs en comparació els aiguamolls. Les EDARs consten d'un seguit de processos seqüencials, tant químics com biològics; en canvi els aiguamolls aconsegueixen realitzar els mateixos en un sòl pas. Si comparem les eficiències d'eliminació (taula 2) podem veure com aquestes són molt similars tot i que els requeriments energètics dels aiguamolls són molt més baixos (molts cops nuls) que els necessaris a les EDARs convencionals.

TAULA 2. percentatges d'eliminació de fàrmacs i productes d'higiene personal en aiguamolls flux horitzontal, flux vertical i flux superficial. Comparativa amb EDARs.

Compostos	**HF**		**VF**	**SF**	**Filtre de sorres**	**EDARs**
Fàrmacs	0.50 m	0.27 m				
Àcid salicílic	77	92	98	-	98	99
Ibuprofèn	17	71	98	96	90	60-70/90
OH-Ibuprofèn	20	67	99	-	85	95
CA-ibuprofèn	25	94	99	-	95	95
Naproxèn	47	85	88	91	80	40-55/66
Diclofenac	0	0	73	96	76	9-75/17
Ketoprofèn	0	0	-	99	-	48-69
Cafeïna	85	94	99	-	98	99
Àcid clofíbric	0	0	-	36	-	34/51
Carbamazepina	26	16	-	29	-	7/8
Compostos d'higiene personal						
Metil dihidrojasmonat	61	99	99	-	98	98
Galaxolida	80	85	83	90	80	70-85/89
Tonalida	87	87	73	87	70	75-89/88
Oxigen dissolt (mg/L)	1	1	9	10	6	-

HF, aiguamoll horitzontal de flux subsuperficial (les Franqueses del Vallès, Granollers); **VF**, aiguamoll vertical de flux subsuperficial (Aarhus, Dinamarca); **SF**, aiguamoll de flux superficial (Can Cabanes, Granollers); EDARs convencionals de llots activats situades en Espanya, Alemanya i Brasil.

El futur dels aiguamolls construïts a Catalunya

A partir dels resultats anteriors, queda ben palès que en quan a l'eficiència per tal d'eliminar fàrmacs i productes d'higiene personal, els aiguamolls construïts presenten eficiències semblants a les EDARs. El seu ús però, està condicionat a la existència de sòl, ja que per terme mig es requereixen de 4 a 5 m^2 per habitant equivalent. Per tant aquests tipus de sistemes es limita a petites poblacions amb dificultats per connectar-se a un sistema centralitzat d'EDARs. Avui en dia, l'ACA disposa d'unes 13 plantes en funcionament arreu de Catalunya, la seva totalitat corresponen a sistemes de flux horitzontal combinades amb llacunatge i aiguamolls superficials. En vista dels resultats explicats anteriorment, seria més convenient intentar introduir els sistemes de flux vertical o híbrids (vertical-horizontal) a les nostres contrades per intentar arribar a rendiments més satisfactoris, almenys pel que fa als contaminants emergents. Tot i això, es requereixen més estudis per tal d'arribar a confirmar aquestes hipòtesis, ja que fins ara els sistemes verticals es construeixen en climes diferents al mediterrani.

Abreviatures

HF, flux horitzontal

VF, flux horitzontal.

SF, flux superficial.

SSF, flux subsuperficial.

EDARs, estacions depuradores d'aigües residuals.

PCBs, bifenils policlorats

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