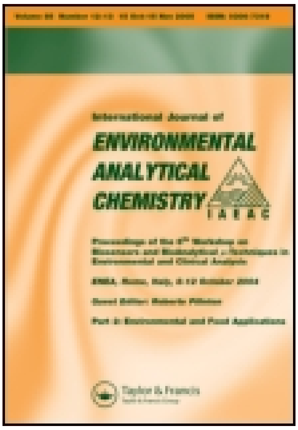

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Evaluation of primary treatment and loading regimes in the removal of pharmaceuticals and personal care products from urban wastewaters by subsurface-flow constructed wetlands

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Evaluation of primary treatment and loading regimes in the removal of pharmaceuticals and personal care products from urban wastewaters by subsurface-flow constructed wetlands

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The ability of several mesocosm-scale horizontal subsurface flow (SSF) constructed wetlands (CW) to remove pharmaceuticals and personal care products (PPCPs) from urban wastewater was assessed in the winter and summer of 2008. As CWs are generally used as secondary or tertiary wastewater treatment systems, their efficacy was compared when fed from two different primary treatment systems, a sedimentation tank and an anaerobic hydrolysis upflow sludge bed reactor (HUSB). The influence of plants (*Phragmites australis*) in the CWs and their feeding regime (continuous flow or batch flow) on PPCP removal were also monitored. One of the CWs was replicated and operated simultaneously in Barcelona and León, Spain, in order to study the effect of environmental conditions on PPCP removal. All systems operated in the open air. The sedimentation tank offered slightly better removal values throughout the experimental period than the HUSB. The presence of *P. australis* enhanced the removal of salicylic acid, galaxolide, tonalide and methyl dihydrojasmonate, but only in summer (when plants were more active). The use of a batch flow or a continuous flow made very little difference to PPCP removal efficiency. When the two mesocosm replicates were compared, temperature proved to be one of the most determining parameters affecting PPCP elimination, with naproxen, ibuprofen, diclofenac, caffeine, galaxolide, tonalide and methyl dihydrojasmonate being removed in SSF-CWs more efficiently at higher temperatures. In general, the most easily removed PPCPs in planted CWs were caffeine (14 ± 74%–84 ± 7% in winter, 98 ± 1%–99 ± 1% in summer), methyl dihydrojasmonate (28 ± 21%–63 ± 17% in winter, 93 ± 2%–98 ± 1% in summer) and salicylic acid (0%–97 ± 4% in winter, 41 ± 40%–89 ± 9% in summer), followed by naproxen (0%–41 ± 16% in winter, 60 ± 18%–95 ± 4% in summer) and ibuprofen (0%–47 ± 26% in winter, 35 ± 12%–99 ± 1% in summer). Other substances experimented lower removal efficiencies, like ketoprofen (4 ± 27%–27 ± 14% in winter, 0%–37 ± 32% in summer), diclofenac (0%–22 ± 22% in winter, 0%–71 ± 8% in summer), carbamazepine (0%–9 ± 100% in winter, 0%–58 ± 21% in summer), galaxolide (0% in winter, 25 ± 14%–87 ± 5% in summer) and tonalide (0% in winter, 32 ± 12%–76 ± 12% in summer).

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1. Introduction

During the first decade of this century, several environmental scientists have focused their attention on the use of constructed wetlands (CWs) for the removal of pharmaceuticals and personal care products (PPCPs) from urban wastewater, these systems having proved efficient and affordable for the purpose [1,2]. However, owing to the risk of clogging, CWs are not usually fed with raw wastewater, but with primary or secondary effluents. Primary treatments are normally simple systems, like septic tanks, Imhoff tanks and/or sedimentation ponds or tanks where most coarse and suspended materials are retained. Secondary treatments are more complex systems where water is more thoroughly cleansed, an example being the biological process with activated sludge in a conventional wastewater treatment plant (WWTP). The ability of WWTPs to remove PPCPs has been recently assessed [3–6]. The coexistence of several micro-environments in CWs allows for a variety of microbiological communities, which might be able to offer different metabolic pathways leading to PPCP degradation, which are still unclear [7]. In addition, other removal processes could take place inside CWs, like adsorption-retention [8], photodegradation [9,10] and plant up-take [11]. Little attention has been paid to which kind of primary treatment is more efficient for PPCP removal from wastewaters. Moreover several operational parameters and design characteristics of CWs, such as feeding regime and the influence of climate, have not been optimised for PPCP removal yet.

In this study, five mesocosm-scale CWs were compared in order to assess their ability to remove PPCPs from urban wastewater. Two different primary treatments (a sedimentation tank (ST) and an anaerobic hydrolysis upflow sludge bed (HUSB)) and two different feeding regimes for the CWs (batch flow and continuous saturation conditions) were studied. One part of the experiment took place simultaneously in two places 800 km apart: Barcelona, a coastal city in NE Spain, and León, an inland city in NW Spain, in order to assess PPCP removal efficiency in identical treatment systems with different environmental conditions. The influence of plant presence was also studied, as were seasonal changes, the systems being monitored in winter and summer 2008. All CWs were operated in the open air.

The PPCPs studied belonged to several groups: analgesic-anti-inflammatory drugs (ketoprofen, naproxen, ibuprofen, diclofenac and salicylic acid), anti-epileptic drugs (carbamazepine), lipid regulators (clofibric acid), diuretic drugs (furosemide), stimulant drugs (caffeine) and fragrances (galaxolide, tonalide and methyl dihydrojasmonate), and were chosen because of their widespread use and high frequency of detection in previous studies [8].

2. Experimental

2.1 *Description of the treatment systems*

A code was created to name every treatment line (Figure 1a). The first letter of the code refers to the location, Barcelona (B) or León (L). After that, the primary treatment is specified (ST or HUSB). Then, the loading regime is mentioned, batch (batch) or continuous saturation (cont) flow. Finally, and only for León CWs, the presence of plants is indicated as planted (p) or unplanted (u).

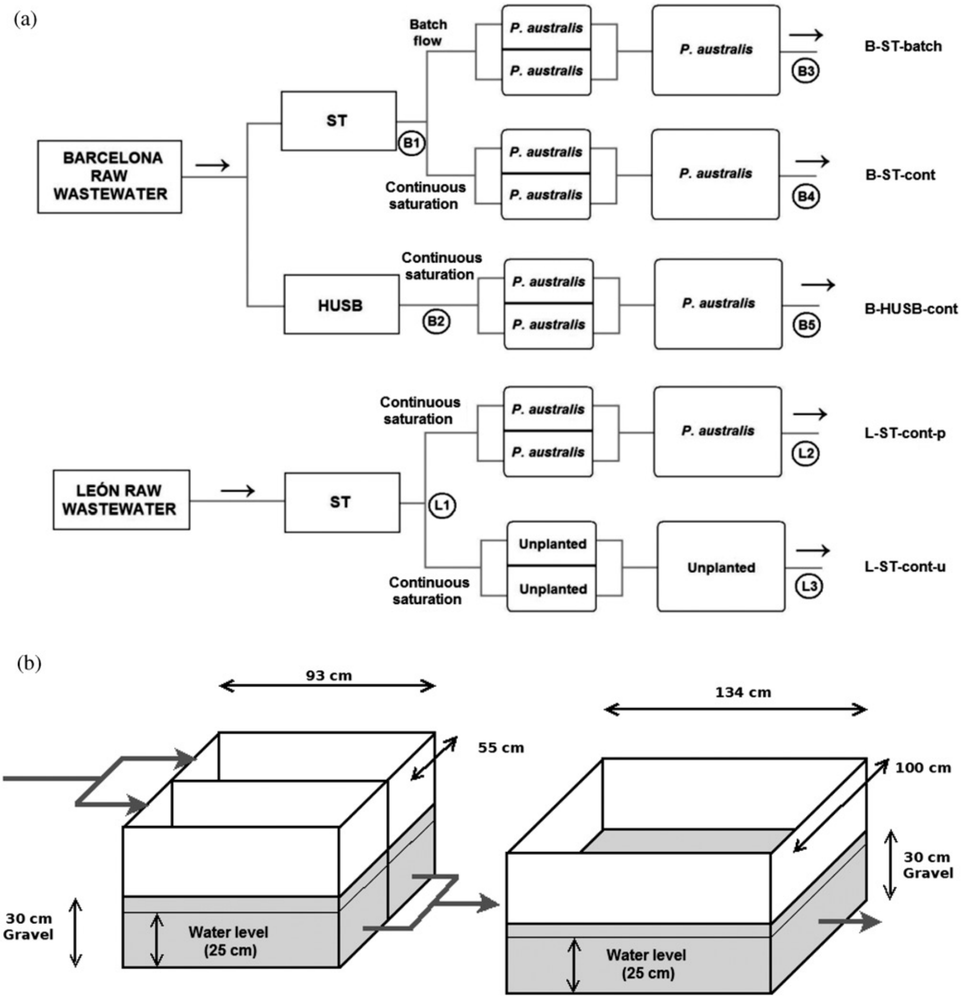


Figure 1. (a) Schematic diagram of all the treatment lines in Barcelona and León. Sampling points are represented by a combination of letters and numbers in circles. (b) Dimensions and structure of a single CW. Primary treatment is not included.

2.1.1 *Barcelona CWs*

Three independent lines of horizontal subsurface flow (SSF) CWs were set up in the open air on the campus of the Technical University of Catalonia (UPC) in Barcelona. The plant was constructed in 2006 and began its operation in February 2007. Each line consisted of two tanks connected in series. The first tank was divided into two parallel compartments; each one 93 cm long, 55 cm wide and 45 cm deep; and filled with a 30 cm-depth layer of siliceous gravel ($d_{10} = 4$ mm). The second tank was 134 cm long, 100 cm wide and 80 cm deep, and was also filled with a gravel layer 30 cm deep. The water depth was 25 cm in all the tanks. Figure 1(b) shows a diagram of these tanks, all of which were made of high-density polypropylene. Young individuals of *Phragmites australis* were collected in nearby wetland areas and planted in each tank with a density of 50 plants m^{-2}. Vegetation coverage was 100% in all these CWs. All lines had a theoretical hydraulic retention time (HRT) of 3.5 days and received the same flow (84 L d^{-1}) and therefore operated with the same hydraulic loading rate (28.5 mm d^{-1}) and a surface organic loading rate of 6 g BOD_5 m^{-2} d^{-1}. The first line (B-ST-batch) was designed to be fed in a batch regime (exactly, alternating batch-unsaturated and saturated phases which lasted 4 days: 2 days filling, 1 day saturated and resting and 1 day unsaturated and resting). The second (B-ST-cont) and third (B-HUSB-cont) lines were designed for continuous saturation regime. Evapotranspiration water losses in each of the three CWs were higher in summer (25–30 L m^{-2} day^{-1}) than in winter (2–10 L m^{-2} day^{-1}). All the treatment lines are schematised in Figure 1(a).

Raw wastewater from a nearby municipal sewer was pumped, coarsely screened and then stored in a distribution tank of 1.2 m^3 and 12 h HRT. This water was used to feed two different primary treatment systems, (a) an ST and (b) an HUSB. The primary-treated water from the ST was piped to the first and the second lines (B-ST-batch and B-ST-cont, respectively). The ST was a PVC cylinder, with an HRT of 2 h (30 cm diameter, 80 cm high). The HUSB primary-treated water was piped to the third line (B-HUSB-cont). The HUSB reactor consisted of a PVC cylinder (30 cm diameter, 190 cm high, 3 h HRT). HUSB reactors are essentially upflow anaerobic sludge bed (UASB) reactors operated at a lower hydraulic retention time in order to promote hydrolysis and avoid methanogenesis [12].

2.1.2 *León CWs*

A replicate of the Barcelona second line (B-ST-cont) was set up in León using the same materials. This part of the experiment took place in the open air within the León WWTP facilities, two lines being created, one of them planted with 50 plants m^{-2} of *P. australis* (L-ST-cont-p) and the other left unplanted (L-ST-cont-u). Wastewater coming out of the primary clarifier of the WWTP was pumped every 30 min and stored in a distribution tank (0.5 m^3; 0.5 h theoretical HRT), from which both lines were fed with a surface organic load of 6 g BOD_5 m^{-2} d^{-1}. The operational principles of a primary clarifier are similar to those of the ST. Both lines worked under continuous saturation conditions and had a theoretical HRT of 3.5 days. Evapotranspiration water losses were about 30 L m^{-2} day^{-1} in the planted line and 5 L m^{-2} day^{-1} in the unplanted line in summer. Evapotranspiration was negligible in winter as water losses were compensated by rainfalls. A schematic diagram of these systems is shown in Figure 1(a). The plant was constructed and began its operation in May 2007.

2.2 *Sampling*

Two sampling campaigns were carried out simultaneously at the two sites, one in winter 2008 ($n = 6$) and the other one in summer 2008 ($n = 6$) with water grab samples collected daily during six consecutive days. Samples were always taken at the same hour (in the morning). Sampling points are indicated in Figure 1(a). For PPCP determination, water samples were collected in one-litre amber glass bottles, which were transported refrigerated (4°C) to the laboratory and processed within 24 hours. In addition, physico-chemical parameters (temperature, conductivity, dissolved oxygen and redox potential) were measured in situ in all samples. Conventional wastewater quality parameters (COD, BOD_5 and NH_3-N) were measured during the experimental period.

2.3 *Analytical methodology*

2.3.1 *Chemicals*

GC grade (Suprasolv) hexane, methanol and ethyl acetate were obtained from Merck (Darmstadt, Germany). Analytical grade sodium hydroxide and hydrogen chloride were supplied by Panreac (Barcelona, Spain). Analytical grade ibuprofen, caffeine, methyl dihydrojasmonate, ketoprofen, salicylic acid, diclofenac, naproxen, clofibric acid, galaxolide, tonalide, furosemide, carbamazepine and dihydrocarbamazepine were purchased from Sigma-Aldrich (Steinheim, Germany). 2,4,5-trichlorophenoxypropionic acid (2,4,5-TPA or fenoprop) was obtained from Riedel-de-Haën (Seelze, Germany). Trimethylsulfonium hydroxide (TMSH) and triphenylamine were purchased from Fluka (Buchs, Switzerland) and the 47-mm 0.7-µm glass fibre filters were purchased from Whatman (Maidstone, UK). Some physico-chemical properties of these compounds are summarised in Table 1.

2.3.2 *COD, BOD_5 and NH_3-N determination*

Water quality parameters (COD, BOD_5 and NH_3–N) were measured according to Standard Methods [13]: the 5220C method for COD, the 5210B method for BOD_5 and the 4500-NH_3 C method for NH_3–N. All reagents were analytical grade.

2.3.3 *Physico-chemical parameters*

Temperature, conductivity, dissolved oxygen and redox potential were measured *in situ* using probes manufactured by WTW (Weilheim, Germany).

2.3.4 *PPCP analytical procedure*

PPCPs in wastewater samples were analysed following a methodology previously described by Matamoros *et al.* [14]. Briefly, all sewage samples, influents and effluents, were filtered through 47-mm 0.7-µm glass-fibre filters and then acidified to pH 2 with concentrated hydrochloric acid. A sample volume of 250 mL was then spiked with 1 µg of a surrogate standard mix (i.e. fenoprop for acidic compounds and dihydrocarbamazepine for neutral ones). The spiked sample was percolated through a polymeric solid-phase extraction cartridge (100 mg Strata X) from Phenomenex (Torrance, CA, USA) previously conditioned with 5 mL of *n*-hexane, 5 mL of ethyl acetate, 10 mL of methanol, and 10 mL of MilliQ water (pH = 2). The sample flow rate through the cartridge was adjusted to approximately 10 mL min^{-1}. Thereafter, the cartridges were allowed to dry for 30 minutes and eluted with 10 mL of hexane/ethyl acetate (1 : 1). The extract was evaporated until ca. 20 µL under a gentle nitrogen stream, and 186 ng of triphenylamine added as an internal standard. Then the vial was reconstituted to 300 µL with ethyl acetate. Methylation of the acidic carboxyl group was performed in a hot GC injector (270°C) by adding 10 µL of TMSH solution (0.25 mol L^{-1} in methanol) to a 50-µL sample before injection. Derivatised samples were analysed in a TRACE GC-MS (Thermo-Finnigan, Dreieich, Germany) in the electron impact mode (70 eV ionisation energy) fitted with a 30-m × 0.25-mm

Table 1. Physico-chemical properties of the target PPCPs.

Substance	CAS number	pK_a	$\log K_{ow}$ (a/b)*	$\log K_{oc}$	Water solubility at 25°C ($mg\,L^{-1}$)	Henry's constant at 25°C ($atm\,m^3\,mol^{-1}$)
Ketoprofen	22071-15-4	4.45	3.12/−0.44	2.459	51 (at 22°C)	2.12×10^{-11}
Naproxen	22204-53-1	4.15	3.18/−0.34	2.543	15.9	3.39×10^{-10}
Ibuprofen	15687-27-1	4.91	3.97/0.45	2.596	21	1.52×10^{-7}
Diclofenac	15307-86-5	4.15	4.51/0.7	2.921	2.37	4.73×10^{-12}
Salicylic acid	69-72-7	2.97	2.26/−2.42	1.379	2240	1.42×10^{-8}
Carbamazepine	298-46-4	–	2.45	3.588	112	1.08×10^{-10}
Caffeine	58-08-2	10.40	−0.07	1	21600	3.58×10^{-11}
Methyldihydrojasmonate	24851-98-7	–	2.98	2.153	280	5.02×10^{-7}
Galaxolide (HHCB)	1222-05-5	–	5.90	4.016	1.75	1.32×10^{-4}
Tonalide (AHTN)	1506-02-1	–	5.70	3.933	1.25	4.22×10^{-5}

Note: Values (pK_a, $\log K_{ow}$, $\log K_{oc}$, Henry's constant and solubility) were obtained from EPIsuite v4.00 [16].
(*) $\log K_{ow}$ for neutral forms of all compounds per $\log K_{ow}$ at pH 8 for acidic compounds.

i.d. × 0.25 μm-DB-5 column (J&W Scientific, Folsom, CA, USA). A volume of 2 μL of sample (dissolved in ethyl acetate) was injected in the splitless mode. All glass material had been previously cleaned with water and acetone and then heated at 450°C during 6 h. Chromatographic conditions, data processing and validation of the methodology are described elsewhere [8]. Limits of quantification ($\mu g\,L^{-1}$) were 0.17 for ketoprofen, 0.71 for naproxen, 0.08 for ibuprofen, 0.19 for diclofenac, 1.05 for salicylic acid, 0.37 for carbamazepine, 1.09 for furosemide, 0.14 for clofibric acid, 0.08 for caffeine, 0.14 for methyl dihydrojasmonate, 0.19 for galaxolide and 0.11 for tonalide.

PPCP metabolites and conjugates were not considered in the analytical method. This could introduce an error in the calculation of removal efficiencies. Only the aqueous fraction of influent and effluent samples was studied. Trace organics associated with solids were not analysed in the samples.

2.4 *Statistics*

Experimental results were statistically evaluated using the SPSS 16 package [15]. Data normality and homoscedasticity were checked with a Shapiro-Wilk W test and a Levene test, respectively. Comparisons of CW efficiencies were performed with Mann-Whitney *U* tests (non-parametric tests). Differences were considered significant when $p < 0.05$.

3. Results and discussion

The experimental set-up of the CWs allowed for the independent comparison of design variables. First of all, both primary treatment systems in Barcelona (ST and HUSB) were studied by comparing their effluent concentrations. Comparing lines B-ST-cont and B-HUSB-cont showed the influence of the nature of primary-treated wastewater on wetland performance, while a comparison of lines B-ST-cont and B-ST-batch enabled us to assess the effect of the loading regime (alternating batch-unsaturated and saturated phases *vs.* continuous saturation conditions). The influence of plants was studied by comparing lines L-ST-cont-p and L-ST-cont-u. PPCP removal efficiency under different environmental conditions was analysed by comparing lines B-ST-cont and L-ST-cont-p, and seasonal influence on PPCP removal was assessed by comparing the efficiency of each treatment line in winter and summer.

3.1 *Wastewater characteristics*

Some PPCPs were not detected in the wastewater samples analysed (furosemide and clofibric acid). Table 2 shows PPCP concentrations at every sampling point in winter and summer 2008.

Influent concentrations were measured at B1, B2 and L1 sampling sites (Figure 1a). In Barcelona, PPCP influent concentrations (B1 and B2) varied from $0.32 \pm 0.05\,\mu g\,L^{-1}$ for tonalide in winter to $70.41 \pm 8.17\,\mu g\,L^{-1}$ for caffeine in summer. The pollutants with the highest influent concentration values were naproxen, ibuprofen, salicylic acid, caffeine and methyl dihydrojasmonate, followed by carbamazepine at 2.02 ± 1.00–$7.43 \pm 4.99\,\mu g\,L^{-1}$. In León, influent concentrations (sampling point L1) were similar to those in Barcelona. Values ranged from $0.37 \pm 0.25\,\mu g\,L^{-1}$ for tonalide and $0.37 \pm 0.10\,\mu g\,L^{-1}$ for diclofenac in summer to $67.34 \pm 25.31\,\mu g\,L^{-1}$ for caffeine in summer. The PPCPs with the highest influent concentrations in León were ibuprofen, salicylic acid, caffeine and methyl dihydrojasmonate. The PPCP occurrence pattern agrees with other studies of European urban wastewater samples [3,17,18]. Effluent concentrations were measured at sampling points B3, B4, B5, L2 and L3 (Figure 1a).

Table 2 also shows COD, BOD_5 and NH_3–N concentrations, as well as some physico-chemical parameters for each sampling point. These characteristics of the influent wastewaters in Barcelona (sampling points B1 and B2) and León (sampling point L1) were slightly different. COD and BOD_5 influent concentrations were higher during winter in León than in Barcelona, but lower during summer. However, in both places winter values were higher than summer ones. COD/BOD_5 ratios are employed to assess the biodegradability of wastewater; the lower this ratio is, the higher the biodegradability. Considering this, influent water data from Table 2 (sampling points B1, B2, L1) indicate that the wastewater of Barcelona was more biodegradable than that of León, and that wastewater was more biodegradable in summer than in winter. Ammonia influent concentrations were similar for both places and did not vary greatly throughout the experimental period. A remarkable aspect of the physico-chemical parameters was the conductivity value of the influent, which was one order of magnitude greater in Barcelona than in León. Even higher conductivity values were found in the effluents of Barcelona in summer (sampling points B3, B4 and B5), which may have been due to a major water loss by evapotranspiration. This difference in conductivity could affect or determine the microbial communities living in CWs.

3.2 *Removal efficiencies in CWs*

As the experiment was run simultaneously in two different places, the influent wastewater was different. Moreover, in Barcelona two lines (B-ST-batch and B-ST-cont) were fed with slightly different wastewater from the other line (B-HUSB-cont), because of different primary treatments. CW performance comparisons were therefore made in all cases by comparing removal efficiencies, and not only effluent concentrations. Removal efficiencies from the liquid phase for all lines (B-ST-batch, B-ST-cont, B-HUSB-cont, L-ST-cont-p and L-ST-cont-u) were calculated using Equation (1).

$$Removal\_efficiency\_(\%) = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

where C_i ($\mu g\,L^{-1}$) is the influent liquid concentration for a given pollutant and C_e ($\mu g\,L^{-1}$) is the effluent liquid concentration for the same pollutant. Only the aqueous fraction of wastewater was analysed. Because of technical reasons, grab samples were collected instead of composite samples. A preliminary test was made in winter 2008 comparing the PPCP concentrations in a grab sample and in a 24 h-composite sample, finding no statistical differences ($p < 0.05$) for most substances. This could be related to the origin of wastewater in León (a big primary settler of a WWTP) and to the storage of wastewater in Barcelona (a tank with 12 h HRT), which would guarantee the homogenisation of water. Evapotranspiration measurements were not considered in Equation (1). The mean influent and effluent concentration values ($n = 6$) for each pollutant were used to calculate removal efficiency at each sampling point in order to minimise variability. PPCP removal efficiencies in winter and summer for each CW are shown in Figure 2.

Table 2. Contaminant concentrations and physico-chemical parameters at each sampling point in winter

	Barcelona					
	B-ST (B1)		B-HUSB (B2)		B-ST-batch (B3)	
	Winter 2008	Summer 2008	Winter 2008	Summer 2008	Winter 2008	Summer 2008
Analgesic anti-inflamatory drugs						
Ketoprofen ($\mu g\,L^{-1}$)	0.57 ± 0.09	0.46 ± 0.20	0.67 ± 0.11	0.46 ± 0.17	0.46 ± 0.06	0.60 ± 0.19
Naproxen ($\mu g\,L^{-1}$)	3.75 ± 2.70	5.42 ± 2.57	5.79 ± 4.64	5.69 ± 2.89	2.62 ± 1.45	< 0.71
Ibuprofen ($\mu g\,L^{-1}$)	18.24 ± 2.69	25.06 ± 7.24	24.11 ± 3.77	25.97 ± 4.49	12.74 ± 3.92	0.31 ± 0.18
Diclofenac ($\mu g\,L^{-1}$)	0.56 ± 0.08	0.76 ± 0.20	0.77 ± 0.09	0.83 ± 0.19	0.60 ± 0.12	0.24 ± 0.02
Salicylic acid ($\mu g\,L^{-1}$)	33.58 ± 19.68	7.28 ± 12.53	31.81 ± 18.03	21.86 ± 17.54	< 1.05	1.36 ± 0.21
Antiepileptic drugs						
Carbamazepine ($\mu g\,L^{-1}$)	4.30 ± 2.44	2.02 ± 1.00	7.43 ± 4.99	2.47 ± 1.57	4.61 ± 1.54	0.97 ± 0.21
Stimulant drugs						
Caffeine ($\mu g\,L^{-1}$)	17.66 ± 4.64	70.41 ± 8.17	14.66 ± 4.39	69.39 ± 7.79	6.95 ± 3.20	0.53 ± 0.06
Fragrances						
Galaxolide ($\mu g\,L^{-1}$)	1.09 ± 0.16	1.30 ± 0.29	2.00 ± 0.78	1.12 ± 0.08	1.93 ± 0.46	< 0.19
Tonalide ($\mu g\,L^{-1}$)	0.32 ± 0.05	0.47 ± 0.07	0.63 ± 0.27	0.39 ± 0.06	0.55 ± 0.16	0.11 ± 0.06
Methyl dihydrojasmonate ($\mu g\,L^{-1}$)	15.52 ± 2.05	20.58 ± 4.22	24.07 ± 6.47	21.86 ± 2.86	5.66 ± 2.42	0.35 ± 0.08
Conventional wastewater quality parameters						
COD ($mgO_2\,L^{-1}$)	262 ± 63	190 ± 21	327 ± 94	200 ± 32	68 ± 7	195 ± 168
BOD_5 ($mgO_2\,L^{-1}$)	145 ± 36	141 ± 32	176 ± 21	154 ± 27	14 ± 5	19 ± 10
NH_3–N ($mg\,L^{-1}$)	18 ± 11	23 ± 2	20 ± 17	25 ± 2	14 ± 6	0.05 ± 0.03
Water physico-chemical parameters						
Temperature (°C)	14.6 ± 2.6	22.6 ± 1.3	14.4 ± 2.4	22.7 ± 1.3	11.7 ± 1.5	22.1 ± 0.7
Conductivity ($\mu S\,cm^{-1}$)	3024 ± 540	3052 ± 80	3017 ± 457	3044 ± 77	3035 ± 259	15823 ± 1015
Dissolved oxygen ($mg\,L^{-1}$)	3.5 ± 1.6	0.1 ± 0.2	2.4 ± 0.8	0.0 ± 0.0	3.5 ± 0.8	0.4 ± 0.3
Redox potential (mV)	124 ± 74	91 ± 33	−90 ± 23	−154 ± 14	−68 ± 14	116 ± 9

2008 and summer 2008. Mean values and standard deviations are shown ($n = 6$).

				León					
B-ST-cont (B4)		B-HUSB-cont (B5)		L-ST (L1)		L-ST-cont-p (L2)		L-ST-cont-u (L3)	
Winter 2008	Summer 2008	Winter 2008	Summer 2008	Winter 2008	Summer 2008	Winter 2008	Summer 2008	Winter 2008	Summer 2008
0.51 ± 0.12	0.24 ± 0.06	0.50 ± 0.08	0.64 ± 0.19	1.79 ± 0.39	<0.17	1.21 ± 0.32	<0.17	1.39 ± 0.35	<0.17
3.27 ± 2.90	<0.31	3.22 ± 2.56	<0.71	3.53 ± 0.91	1.35 ± 0.28	2.06 ± 0.70	<0.71	2.47 ± 0.51	0.79 ± 0.29
17.81 ± 3.81	0.52 ± 1.06	19.49 ± 7.53	1.72 ± 2.86	24.19 ± 8.45	8.38 ± 1.87	11.83 ± 6.34	5.25 ± 0.63	15.36 ± 6.13	7.96 ± 1.55
0.65 ± 0.14	0.20 ± 0.01	0.59 ± 0.13	0.23 ± 0.05	0.83 ± 0.20	0.37 ± 0.10	0.63 ± 0.14	0.37 ± 0.06	0.99 ± 0.93	0.50 ± 0.05
<1.05	1.48 ± 0.61	2.93 ± 2.63	1.29 ± 0.26	9.93 ± 7.72	10.29 ± 4.92	7.01 ± 3.62	1.69 ± 0.79	9.92 ± 7.57	8.69 ± 7.86
3.97 ± 2.52	0.67 ± 0.06	4.14 ± 2.06	0.76 ± 0.15	1.36 ± 0.70	1.52 ± 1.99	0.95 ± 0.76	<0.37	1.06 ± 0.65	<0.37
2.59 ± 0.83	0.43 ± 0.09	3.47 ± 1.44	0.53 ± 0.19	67.34 ± 25.31	22.59 ± 5.21	38.62 ± 8.28	0.39 ± 0.10	18.97 ± 5.70	0.44 ± 0.12
2.73 ± 0.73	<0.19	3.14 ± 1.64	<0.19	0.94 ± 0.26	1.22 ± 0.80	1.13 ± 0.27	0.87 ± 0.44	1.26 ± 0.25	1.14 ± 0.41
0.91 ± 0.25	0.12 ± 0.05	1.08 ± 0.55	<0.11	0.39 ± 0.15	0.37 ± 0.25	0.41 ± 0.10	0.23 ± 0.12	0.44 ± 0.09	0.34 ± 0.12
10.12 ± 1.74	0.36 ± 0.07	14.04 ± 3.38	0.40 ± 0.31	11.55 ± 4.72	3.95 ± 0.89	7.13 ± 3.39	<0.14	7.81 ± 2.26	0.57 ± 0.13
110 ± 7	151 ± 120	128 ± 11	204 ± 204	522 ± 142	106 ± 49	103 ± 14	29 ± 19	102 ± 11	28 ± 9
47 ± 12	42 ± 34	54 ± 16	20 ± 8	208 ± 70	70 ± 33	57 ± 7	12 ± 5	55 ± 8	16 ± 5
17 ± 5	0.02 ± 0.03	16 ± 10	0.02 ± 0.02	20 ± 4	13 ± 2	20 ± 1	7 ± 1	20 ± 1	15 ± 2
11.3 ± 1.4	21.4 ± 0.6	11.5 ± 1.6	21.5 ± 0.6	12.2 ± 0.8	19.2 ± 1.4	5.7 ± 2.3	16.9 ± 1.5	4.5 ± 2.7	17.0 ± 2.5
3117 ± 148	12694 ± 35	3100 ± 150	14602 ± 73	370 ± 289	133 ± 28	345 ± 251	125 ± 8	376 ± 249	118 ± 23
3.5 ± 0.5	0.8 ± 0.1	3.3 ± 0.9	0.1 ± 0.1	0.7 ± 0.3	0.4 ± 0.2	0.4 ± 0.2	0.3 ± 0.2	0.6 ± 0.3	0.2 ± 0.1
−106 ± 10	92 ± 10	−113 ± 12	104 ± 10	−6 ± 114	26 ± 166	−36 ± 122	−102 ± 102	−47 ± 133	−64 ± 115

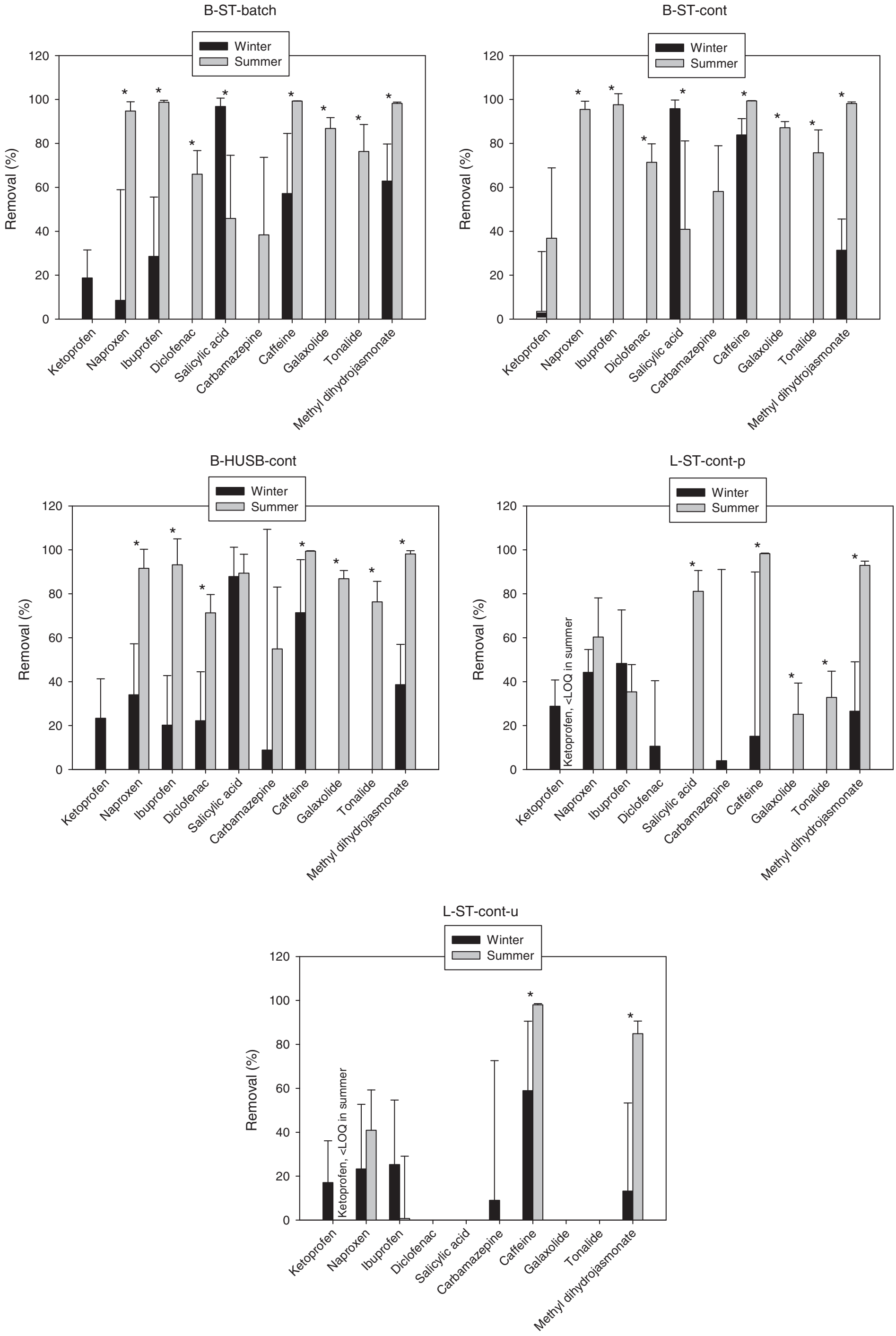


Figure 2. Winter and summer removal efficiencies for each treatment line. Mean values and standard deviations are given. Significant seasonal differences ($p < 0.05$) are marked with an asterisk (*).

Analgesic anti-inflammatory drugs. These five analgesics are ionised at environmental pH, and are highly polar compounds ($\log K_{ow}$ −2.42–0.70, see Table 1). Ketoprofen showed low removal efficiencies (≤37 ± 32%) in all CWs, both in winter and summer. Naproxen removal was low in winter (≤41 ± 16%) in all wetlands, but this situation was reversed in summer, when naproxen removal was clearly higher, especially in Barcelona (≥92 ± 9%), a trend suggesting temperature dependence. A similar trend was observed for ibuprofen, with low removal efficiencies in winter (≤47 ± 26%) in all wetlands, but high removal efficiencies in Barcelona during summer (≥93 ± 12%). Diclofenac showed a similar behaviour, but with lower removal efficiency values in summer (66 ± 11%–71 ± 8% in Barcelona). These four non-steroidal analgesic anti-inflammatory drugs were not easily degraded by the León wetlands (removal efficiencies throughout the whole year of ≤27 ± 14% for ketoprofen, ≤60 ± 18% for naproxen, ≤47 ± 26% for ibuprofen and ≤12 ± 30% for diclofenac). Salicylic acid was satisfactorily removed in winter by the Barcelona CWs (≥88 ± 13%), but during summer only the HUSB line (B-HUSB-cont) kept up these good removal values (89 ± 9%). In León only the planted line (L-ST-cont-p) proved capable of removing salicylic acid (81 ± 10%), and only in summer.

Ketoprofen is not easily eliminated in horizontal SSF-CWs [8]. It has been observed to be better removed in surface flow (SF) CWs [19], as it is photodegradable [10,20,21]. Diclofenac removal in horizontal SSF-CWs is generally low (<50%) [8,22]. However higher efficiencies (65–96%) have been reported in hybrid systems including different kinds of wetlands connected in series [23] and in SF-CWs working as tertiary treatments [19], probably due to the possibility of diclofenac photodegradation [9,24]. Salicylic acid removal in this experiment was low compared with other similar studies [8,25] but this could be explained by the anoxic conditions typically found in horizontal SSF-CWs, since some compounds, like salicylic acid, ibuprofen or diclofenac, are more easily removed in media with high redox potentials [22]. Our results indicate that naproxen, ibuprofen and diclofenac elimination was favoured under summer conditions. This agrees with previous studies where a positive correlation between temperature and naproxen removal was observed and a connection between plant presence (whose activity is higher in summer) and naproxen, ibuprofen and diclofenac elimination was reported [22].

Antiepileptic drugs. Carbamazepine removal efficiency was very low or nearly negligible throughout the experimental period in all CWs. However, the best results were observed in Barcelona in summer (38 ± 35%–58 ± 21%). Carbamazepine is a recalcitrant substance, not easily removed from urban wastewaters by conventional WWTPs [3,6,26] or by CWs [1,19]. However, Dordio *et al.* [27] observed higher eliminations (88% in winter and 97% in summer) in a *Typha* spp. microcosms-CW (HRT 7 days) with a matrix of light expanded clay aggregates, a material known for its sorption abilities. They pointed out that carbamazepine was mainly removed by adsorption onto the substrate and, to a lesser extent, favoured by plant presence. Carbamazepine physico-chemical characteristics support that adsorption mechanism. Hijosa-Valsero *et al.* [22] found a positive correlation between redox potential values and carbamazepine elimination in CWs. High redox potential values (about 100 mV in these SSF-CWs) could be related to vegetal activity. A small contribution of direct plant up-take cannot be discarded considering the $\log K_{ow}$ value of this compound (Table 1), as this process is more probable for those substances with $\log K_{ow}$ values of 1–3.5 [28].

Stimulant drugs. Winter caffeine removal was higher in Barcelona (57 ± 27%–84 ± 7%) than in León (14 ± 74%–59 ± 32%). It was nevertheless easily removed by all wetlands during summer (≥98 ± 1%). Caffeine has been previously observed to be easily removed in CWs [1,8,25], especially in summer [22]. Caffeine could be an easily microbiologically degradable substance. A review carried out by Gokulakrishnan *et al.* [29] revealed that major caffeine degrading strains belonged to *Pseudomonas* and *Aspergillus*. Bacteria degrade this substance predominantly through demethylation but fungi degradation pathways are still unknown [29]. Other removal mechanisms like plant uptake or plant degradation via exudates are possible. Caffeine is a hydrophilic substance (Table 1) and its elimination by adsorption on the gravel bed is not very probable.

Fragrances. The lipophilic fragrances galaxolide and tonalide ($\log K_{ow}$ 5.90 and 5.70, respectively) can adsorb onto solids in CWs [8]. Since only the liquid fraction was analysed in this experiment, the calculated removal efficiencies for these substances could be underestimated. These two fragrances had very similar removal patterns. In winter, they were not removed at all by any treatment system. In summer, they were quite efficiently removed in Barcelona (76 ± 12%–87 ± 5%), but less so in León (33 ± 12% in the planted wetland and 0% removal in the unplanted one). These results are low compared with those of other studies of similar CWs. Removal efficiencies of over 80% were observed by Matamoros and Bayona [8] in a horizontal SSF-CW, but this may have been due to the larger size of their CW (area 55 m^2, HRT 5.4–6.2 days), which would enhance the retention of solids and, as a consequence, the removal of these two fragrances. In that study, these two substances were detected at high concentrations in the gravel, which indicated that sorption onto the organic matter (mostly near the inlet zone) was their main removal mechanism. However, many other simultaneous removal mechanisms may exist. It has been reported that the presence of plants favours galaxolide and tonalide elimination in CWs and that their removal is also influenced by redox potential, suggesting both vegetal and microbiological mediated processes [22]. This could explain the different summer performances in Barcelona and León, since redox potential values were higher in the former locality. Even volatilisation processes could occur, given the Henry's constants of these two substances (Table 1). The hydrophilic fragrance methyl dihydrojasmonate ($\log K_{ow}$ 2.98) had variable removal efficiencies during winter (13 ± 40%–63 ± 17%) but high efficiencies during summer (85 ± 6% for the unplanted wetland and 93 ± 2%–98 ± 1% in the others). Other studies have also proved the easy removal of this fragrance by CWs [8,25], notably during summer [22]. Taking into account its relatively simple chemical structure and the influence of seasonality on its elimination, biodegradation could be one of the most probable removal mechanisms for this fragrance.

Seasonal variations are shown in Figure 2, where winter and summer removal efficiencies of each CW are compared, showing significant differences ($p < 0.05$). In general, removal efficiencies were higher during summer in all the CWs. Evapotranspiration water losses may increase PPCP effluent concentrations in CWs (in particular in summer), thus making removal efficiencies appear to be lower than they really are. In spite of this fact, summer efficiencies were mostly higher than winter ones, proving the beneficial influence of summer conditions on PPCP removal. In Barcelona (B-ST-batch; B-ST-cont and B-HUSB-cont), naproxen, ibuprofen, diclofenac, caffeine, galaxolide, tonalide and methyl dihydrojasmonate were significantly more easily removed in summer, indicating that their removal depends on temperature. On the contrary, in León (L-ST-cont-p and L-ST-cont-u) only salicylic acid, caffeine, galaxolide, tonalide and methyl dihydrojasmonate were significantly more easily removed in summer, whereas naproxen, ibuprofen and diclofenac removal showed no significant seasonal changes.

This difference between localities could be due to the lower average temperatures or to the lower redox potential values in León. The statistical analysis of temperature data is strongly influenced by seasonality, because higher temperatures are registered in summer. In this regard, it may be more accurate to say that summer conditions (e.g. warmth, plant activity and sunlight) enhance the removal of some PPCPs, instead of just attributing this fact to temperature [22]. Microbiological degradation processes are negatively affected by a temperature decrease. Therefore, the main degradation of hydrophilic substances (naproxen, ibuprofen, diclofenac, caffeine and methyl dihydrojasmonate) in the CWs studied appears to follow a predominantly microbiological pathway. It is believed that hydrophobic compounds (galaxolide and tonalide) are removed by sorption onto the organic matter retained in the gravel bed [8]. In our case the seasonality of the removal of hydrophobic substances could be related to the release of hydrophobic compounds in winter and accumulation during summer, when biofilm and plants are more active. Nevertheless, as stated before, biological processes could also play a significant role.

However, in some of the Barcelona treatment lines (B-ST-batch, B-ST-cont), salicylic acid was better removed during winter. It is necessary to point out that the influent concentration of this compound in Barcelona was slightly higher in winter and that the degradation of organic matter in a CW exhibits Monod kinetics, so that, at low concentrations, pollutant removal rates increase with increasing pollutant concentration [30]. In any case, other explanations are possible.

In León, the planted wetland (L-ST-cont-p) was more affected by seasonal changes than the unplanted system (L-ST-cont-u). Salicylic acid, caffeine, galaxolide, tonalide and methyl dihydrojasmonate were removed to a higher extent in the planted system during summer, whereas in the unplanted system only caffeine and methyl dihydrojasmonate had better removal efficiencies in summer. This can be attributable to the very low vegetal activity in temperate regions in winter.

Matamoros *et al.* [19] observed that naproxen and diclofenac removal efficiencies were clearly affected by seasonal changes in a SF-CW, while galaxolide, tonalide, carbamazepine, ibuprofen and ketoprofen removal efficiencies were not affected. In a hybrid CW system (combining several types of treatment systems), Conkle *et al.* [1] did not detect seasonal variations in the removal of ibuprofen and naproxen. However, our results are not directly comparable to those of these authors, since our systems are horizontal SSF-CWs. On the contrary, other authors have assessed mesocosm-scale SSF-CWs, finding seasonal changes for the removal of naproxen, salicylic acid, caffeine, methyl dihydrojasmonate, galaxolide and tonalide [22].

3.3 *Primary treatment of wastewater (ST vs. HUSB)*

Two different primary treatments were used in Barcelona, ST and HUSB, wastewater from the former being fed into line B-ST-cont and from the latter into B-HUSB-cont, the lines being otherwise identical. However, the different nature of these primary treatment systems may have influenced important physico-chemical parameters of wastewater (like redox potential or oxygen concentration), which will be relevant during CW treatment (Table 2). In fact, lower redox potential values (more anaerobic conditions) were detected in the effluent of the HUSB (sampling point B2) than in that of the ST (sampling point B1), while the concentrations of some PPCPs were different in the effluents at the same two sampling points (Table 2). The statistical comparison of contaminant concentrations at points B1 and B2 allowed for the study of both primary treatment performances (Table 2). In winter, the ST produced an effluent with significantly lower ($p < 0.05$) concentrations of galaxolide, tonalide, methyl dihydrojasmonate, ibuprofen and diclofenac. In summer, fewer differences between the primary treatments were observed (only tonalide concentration was significantly lower in the HUSB effluent than in the ST effluent). This could mean that the HUSB performance improves in summer, eliminating its efficiency differences with the ST observed in winter. Hence, the ST would be the most constant treatment system throughout the year.

Comparing the CW removals from lines B-ST-cont and B-HUSB-cont made it possible to study the influence of the nature of the wastewater (physico-chemical parameters and the influent PPCP concentration, Table 2) on their performance. If we consider effluent concentrations of the CWs (points B4 and B5 on Table 2), it is evident that most PPCP concentration values are lower in B-ST-cont (point B4) than in B-HUSB-cont (point B5), both in winter and summer. Concentrations were significantly ($p < 0.05$) lower in B4 for methyl dihydrojasmonate in winter and for ketoprofen and ibuprofen in summer. Therefore, the differences between the primary treatments are small, but the ST offered slightly better results than the HUSB system.

3.4 *Loading regime (alternating batch-unsaturated and saturated phases vs. continuous saturation)*

Lines B-ST-batch and B-ST-cont were fed with the same wastewater, but with different loading regimes, batch flow for the former and a continuous flow for the latter. Batch systems are usually more aerated than continuously saturated systems. However, we noticed no clearly higher dissolved oxygen concentrations or clearly higher redox potential values in the B-ST-batch line (sampling point B3) than in the B-ST-cont line (sampling point B4) (Table 2). Figure 3 shows the removal efficiencies of the two systems in winter and summer 2008. In winter, these systems only showed good removal efficiencies for salicylic acid, caffeine and methyl dihydrojasmonate. Some differences between these systems appeared in winter, when B-ST-batch was more efficient for the removal of methyl dihydrojasmonate, whereas B-ST-cont was more efficient for caffeine. In summer the results of both systems were more similar and removal higher; but B-ST-cont was more efficient for the removal of ketoprofen, although ketoprofen removal values were low in summer, as were those of salicylic acid and carbamazepine. In short, very few differences in PPCP removal efficiencies were observed between batch flow and continuous flow. This evidence agrees with the highly similar oxygen concentration in the CW effluents for both loading regimes (Table 2) and with the high oxygen dependence of PPCP removal efficiency reported for CWs [8].

3.5 *Plant presence*

Lines L-ST-cont-p and L-ST-cont-u were fed with the same primary-treated wastewater, the only difference between them being the presence of plants (*P. australis*) in L-ST-cont-p. The removal efficiency of these two systems was statistically compared in winter and summer (Figure 4). In winter, both systems had very low removal efficiencies for all PPCPs; the unplanted system was more efficient than the planted one for the removal of caffeine. In summer, when plants were more active, the planted system gave the best results

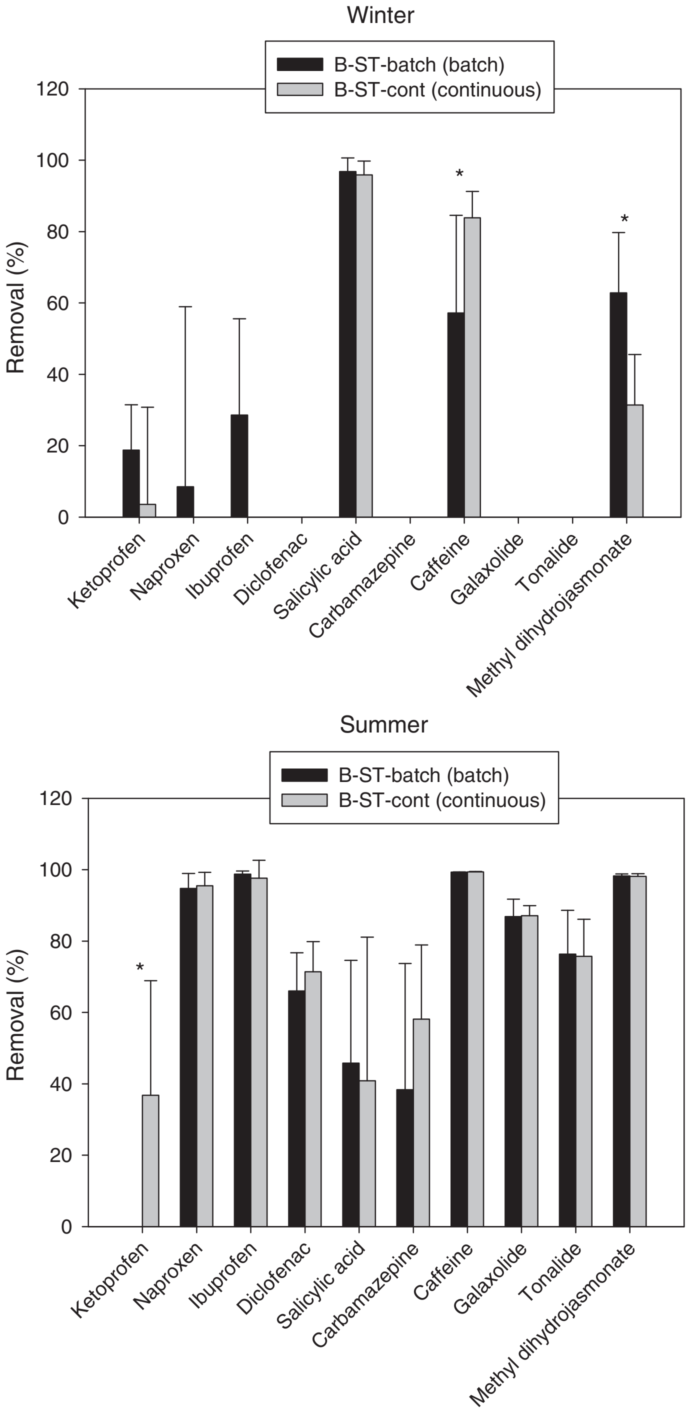


Figure 3. Feeding regime. Comparative removal efficiencies of the batch and continuous lines. Mean values and standard deviations are given. Winter and summer data are represented separately. Any significant differences ($p < 0.05$) between treatment lines are marked with an asterisk (*).

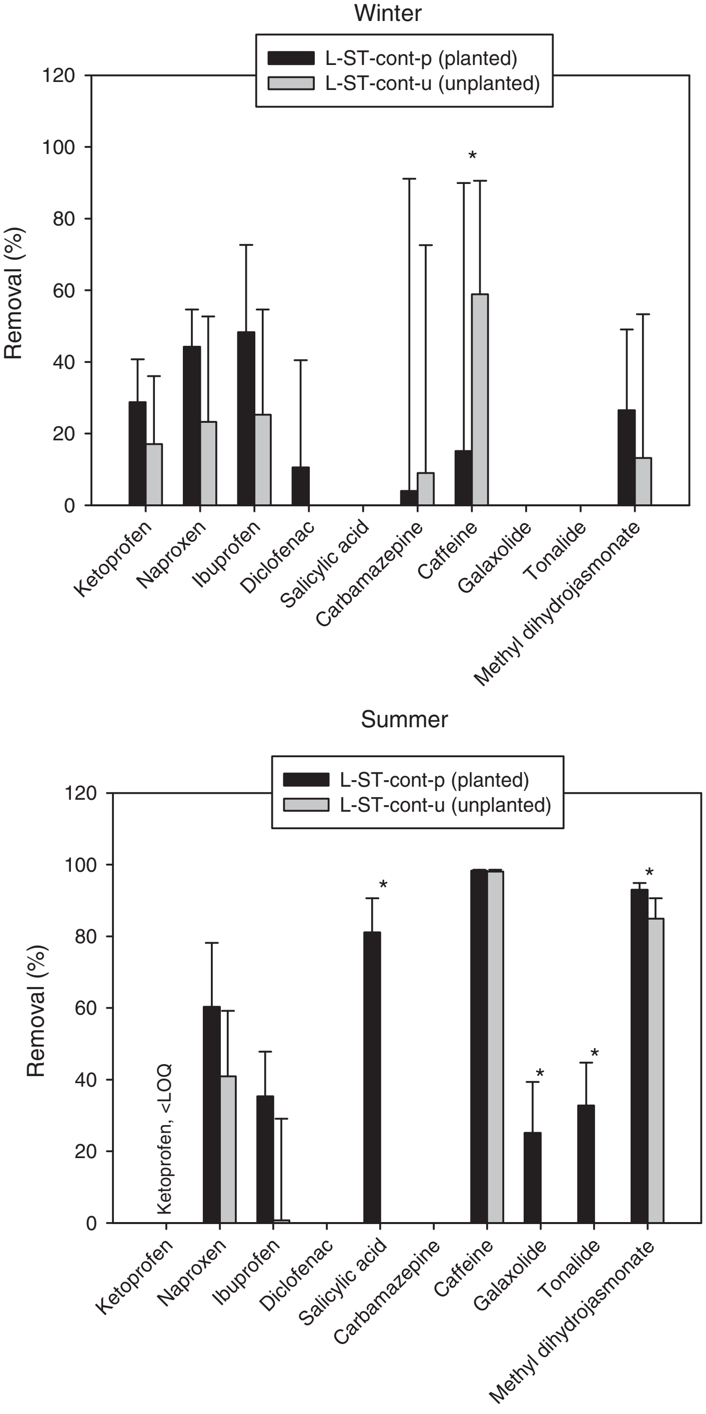


Figure 4. Plant presence. Comparative removal efficiencies of the planted and unplanted lines. Mean values and standard deviations are given. Winter and summer data are represented separately. Any significant differences ($p < 0.05$) between treatment lines are marked with an asterisk (*).

for the removal of salicylic acid, galaxolide, tonalide and methyl dihydrojasmonate. Summer removal efficiencies of ibuprofen, diclofenac, carbamazepine, galaxolide and tonalide were low in both wetlands. It is important to say that PPCP effluent concentrations were lower in the planted than in the unplanted system during summer (Table 2, sampling points L2 and L3), even despite the greater evapotranspiration water losses occurred in the planted CW (which produce a concentration of the compounds).

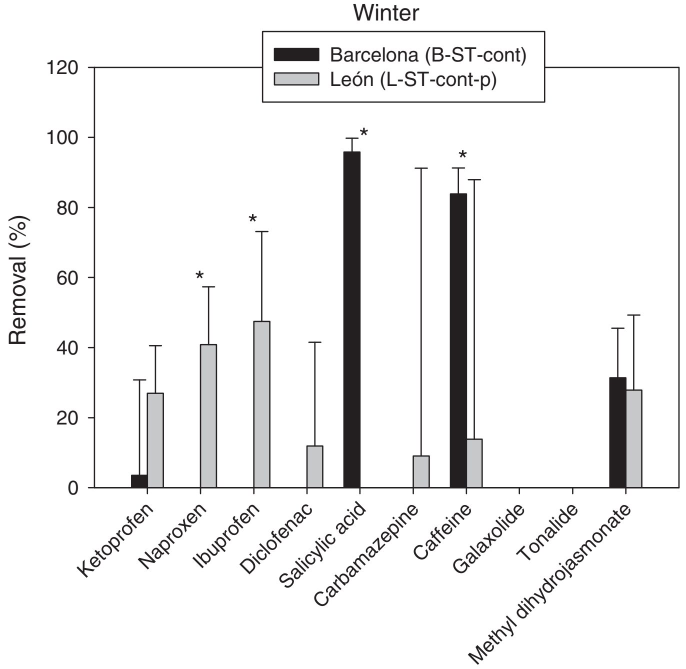
It seems evident that the presence of *P. australis* enhances the removal of salicylic acid, galaxolide, tonalide and methyl dihydrojasmonate. This beneficial influence is only noticeable during summer (when plants are more active) and may be due to either direct effects (e.g. plant uptake or degradation by enzymatic exudates) or indirect ones (e.g. oxygenation by roots that favoured biofilm growth) [11].

3.6 *Environmental conditions (difference between localities)*

Figure 5 shows the comparative removal efficiencies of line B-ST-cont and its replicate in León, line L-ST-cont-p, in winter and summer. Winter removal efficiencies were generally low for both lines, neither of them being able to remove galaxolide or tonalide. The Barcelona line was unable to remove naproxen, ibuprofen, diclofenac and carbamazepine, but was significantly better at removing salycilic acid and caffeine, whereas León performed better with naproxen and ibuprofen. During summer, removal efficiencies were higher, with the Barcelona wetland working significantly better in the removal of naproxen, ibuprofen, diclofenac, caffeine, galaxolide, tonalide and methyl dihydrojasmonate than León, which only worked better on salicylic acid. As mentioned in Section 3.2, the León CW did not work significantly better in summer than in winter for the removal of naproxen, ibuprofen and diclofenac, which is not in agreement with the results of other works [22]; however the low potential values observed during summer in these systems (Table 2) could explain this abnormality.

The differences between the two places depend not only on the nature of wastewater and its PPCP concentration, but also, and significantly, on environmental conditions. Figure 6 offers climate data for the two cities. Evapotranspiration water losses were similar at both localities (see Section 2.1), despite the different relative humidity values (Figure 6). Barcelona has milder and warmer weather, so the PPCPs with temperature-dependent elimination (i.e. naproxen, ibuprofen, diclofenac, caffeine, galaxolide, tonalide and methyl dihydrojasmonate; see Section 3.2) would be more easily removed there and in summer. Figure 5 shows experimental proof of this. In winter, however, naproxen and ibuprofen were degraded more in León, possibly because in winter neither city reached an optimal environmental temperature for the biological degradation of these PPCPs (nitrifying and proteolitic bacteria living in CWs usually reach their optimal activity at 15–25°C [32]). Moreover, in winter environmental and/or physico-chemical factors other than temperature may contribute more to this elimination. A curious and remarkable fact was that salicylic acid was more easily removed in winter in Barcelona and in summer in León, perhaps because salicylic acid can also be a degradation metabolite of acetylsalicylic acid and other compounds with this molecule in their structures (like many cosmetics).

Wastewater nature, vegetal ecotypes, physico-chemical parameters (like dissolved oxygen, redox potential and conductivity) and climate conditions may have induced the presence of different microbial strains in the two places, with greater or lower PPCP degradation capacities. In addition, temperature and insolation could have affected



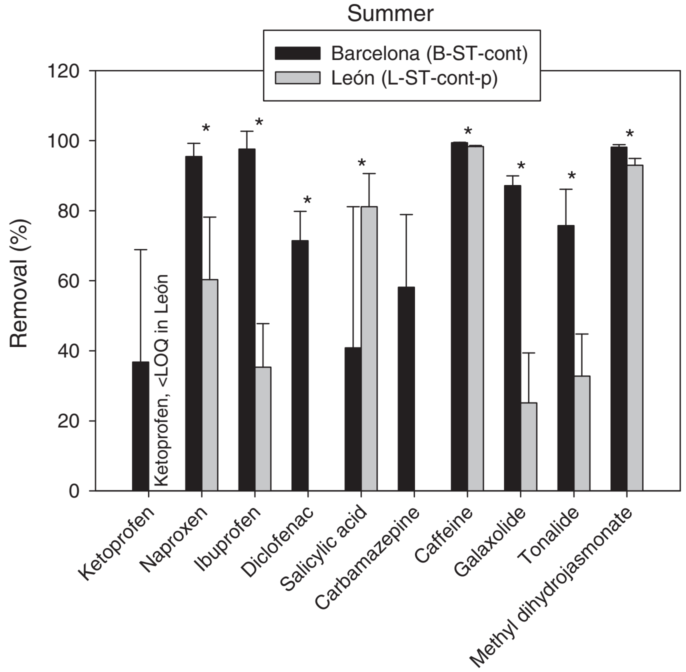


Figure 5. Environmental conditions. Comparative removal efficiencies of the Barcelona B-ST-cont line and its replicate in León. Mean values and standard deviations are given. Winter and summer data are represented separately. Any significant differences ($p < 0.05$) between places are marked with an asterisk (*).

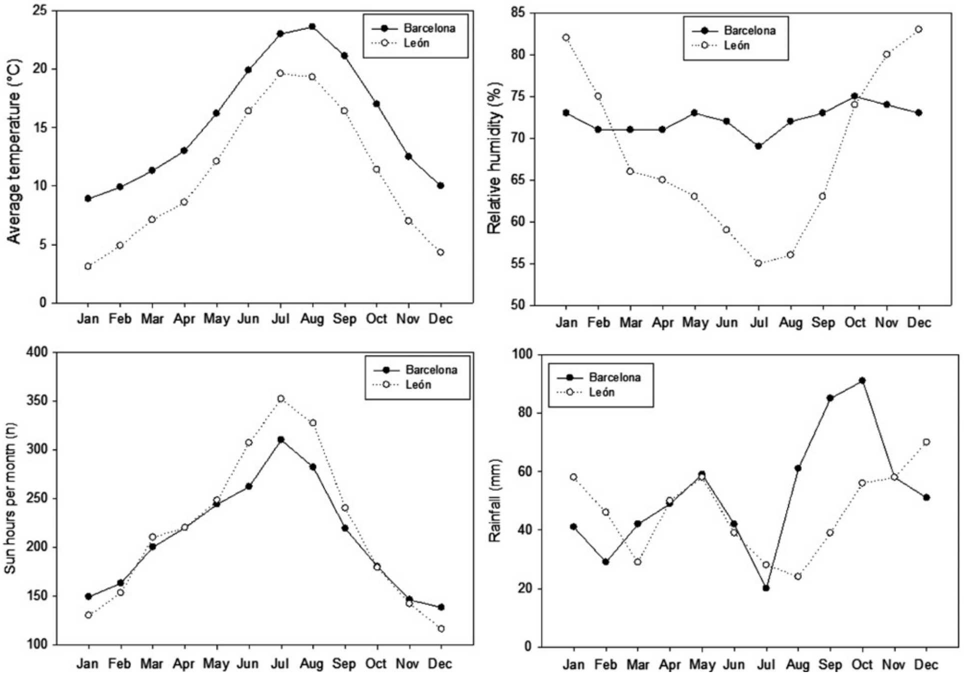


Figure 6. Normal climate values (1971–2000) in the nearest weather stations (Barcelona Airport and the Virgen del Camino Air Base, León). Data taken from the Spanish State Meteorological Office [31].

non-biological elimination processes; and rainfall could have caused changes in effluent concentrations by dilution.

4. Conclusions

Several mesocosm-scale horizontal SSF-CWs were monitored in winter and summer in order to assess their ability to remove PPCPs from urban wastewaters. All of them operated in the open air. The main conclusions of this study are listed below:

- The urban wastewaters studied had PPCP concentrations similar to those of other wastewaters in Europe.
- Some PPCPs, like ketoprofen (0%–37 ± 32%) and carbamazepine (0%–58 ± 21%), were very inefficiently removed in the CWs studied. Other substances had only low removal efficiencies in winter but high removal efficiencies during summer, like caffeine and methyl dihydrojasmonate (10–80% in winter, >80% in summer). The remaining pollutants had different removal efficiencies depending on the characteristics of the CW.
- Two primary treatments were compared for the removal of PPCPs by CWs, namely, an ST and an HUSB. The ST offered slightly better results throughout the experimental period than the HUSB, whose operational performance was temperature-dependent.

- The removal of naproxen, ibuprofen, diclofenac, caffeine, galaxolide, tonalide and methyl dihydrojasmonate in these SSF-CWs was favoured by high temperatures.
- Very few differences in PPCP removal efficiencies appeared when feeding the studied CWs with a batch flow or with a continuous saturation flow.
- The presence of plants (*P. australis*) enhanced the removal of salicylic acid, galaxolide, tonalide and methyl dihydrojasmonate. This beneficial influence was only noticeable during summer (when plants were more active).
- When two replicates of a CW were compared at different places, temperature appeared to be one of the most determinant parameters in PPCP elimination, although not the only one. Other factors like the nature of wastewater, the vegetal ecotypes and physico-chemical parameters may also have contributed to the different performances observed.

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