Using integrative samplers to estimate the removal of pharmaceuticals and personal care products in a WWTP and by soil aquifer treatment enhanced with a reactive barrier

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HIGHLIGHTS

- Integrative passive sampling proved useful to assess PPCPs in wastewater.
- Soil Aquifer Treatment achieves an efficient removal of PPCPs in conventional WWTPs.
- Carbamazepine and its epoxy- metabolite were extensively removed during SAT.
- Treatment parameters should be controlled to degrade a broad range of contaminants.
- It can be foreseen that SAT has large application prospects in wastewater reclamation.

GRAPHICAL ABSTRACT
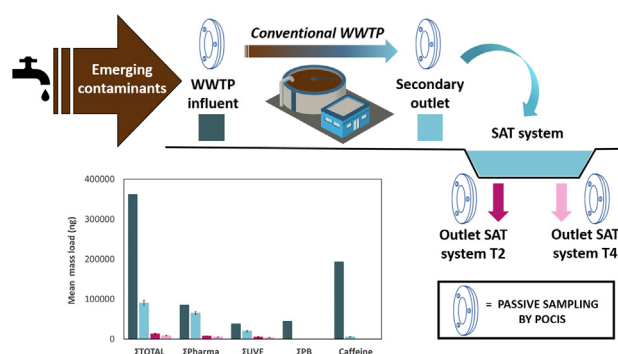
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ABSTRACT

The need and availability of freshwater is a major environmental issue, aggravated by climate change. It is necessary to find alternative sources of freshwater. Wastewater could represent a valid option but requires extensive treatment to remove wastewater-borne contaminants, such as contaminants of emerging concern (CECs). It is urgent to develop not only sustainable and effective wastewater treatment techniques, but also water quality assessment methods. In this study, we used polar organic chemical integrative samplers (POCIS) to investigate the presence and abatement of contaminants in an urban wastewater treatment plant (WWTP) and in soil aquifer treatment (SAT) systems (a conventional one and one enhanced with a reactive barrier). This approach allowed us to overcome inter-day and intraday variability of the wastewater composition. Passive sampler extracts were analyzed to investigate contamination from 56 pharmaceuticals and personal care products (PPCPs). Data from the POCIS were used to estimate PPCPs' removal efficiency along the WWTP and the SAT systems. A total of 31 compounds, out of the 56 investigated, were detected in the WWTP influent. Removal rates along WWTP were highly variable (16-100 %), with benzophenone-3, benzophenone-1, parabens, ciprofloxacin, ibuprofen, and acetaminophen as the most effectively removed chemicals. The two SAT systems yielded much higher elimination rates than those achieved through the primary and secondary treatments together. The SAT system that integrated a reactive barrier, based on sustainable materials to promote

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enhanced elimination of CECs, was significantly more efficient than the conventional one. The removal of the recalcitrant carbamazepine and its epoxy- metabolite was especially remarkable in this SAT, with removal rates between 69–81 % and 63–70 %, respectively.

1. Introduction

Incomplete removal of organic pollutants in wastewater treatment plants (WWTPs) is the main reason for the wide distribution of these substances in the environment. Many of these compounds are considered contaminants of emerging concern (CECs), because of their poor (bio) degradability, potential toxicity, (bio)accumulation, and biomagnification through the food web. In fact, these substances are classified as pseudo-persistent pollutants because they are continuously introduced into the environment at rates that cannot be matched by degradation, so that they look as persistent. CECs encompass a wide range of substances, including pharmaceuticals, personal care products (PCPs), hormones, biocides and pesticides, among many others.

Pharmaceutical residues are typically present in the environment, but it is still unclear whether the levels of these compounds in natural waters can cause undesired physiological effects in wildlife. Research has shown that several regularly used pharmaceuticals are endocrine-disrupting compounds (Veldhoen et al., 2014). Still, so far, the major concern is their contribution to the development of antibiotic resistance (Kim and Aga, 2007; Richardson and Kimura, 2011).

Sunscreens, frequent in wastewater from tourist areas, are also a source of concern. For example, benzophenone-3 (BP3), the most frequently used ultraviolet filter (UVF) in the world (Downs et al., 2022) is toxic to the larval stages of coral and fish and it is known to induce a multigenerational toxic effect from a single exposure (Downs et al., 2016; Kim et al., 2014; Lucas et al., 2021).

Benzotriazoles are high-production volume manufactured chemicals and are used as UV stabilizers in plastic materials, among others. They have been frequently reported in the environment, even in Antarctica (Domínguez-Morueco et al., 2021), as they are only partially removed during conventional wastewater treatments (Asimakopoulos et al., 2013; Molins-Delgado et al., 2015, 2017). Ecotoxicity studies showed their endocrine-disrupting properties, impairing neurotoxicity and hepatotoxicity in different fish species (Liang et al., 2017; Tangtian et al., 2012).

The occurrence of parabens (PBs) in the environment is also a source of concern as they have been found to display endocrine-disrupting activity including a decrease in testosterone and alterations in the reproductive tract of male rodents (Oishi, 2002a, 2002b) as well as carcinogenicity (Charles and Darbre, 2013). Several studies also revealed that PBs bioaccumulate in invertebrates and adipose tissue from birds and fishes, and can biomagnificate through the food web (Gago-Ferrero et al., 2013). Thus, removing PPCPs from water bodies is important for human and environmental health.

Several factors drive the removal of pollutants in WWTPs, including physicochemical properties of the pollutant, hydraulic retention time (HRT) and configuration and operating conditions (pH, T^a) of the WWTP. The need to operate on such a diverse group of contaminants in a broad range of concentrations (from low ng L^{-1} to µg L^{-1}) and physicochemical properties requires the application of non-specific technological solutions. Several wastewater treatment technologies are applied for CECs removal, ranging from conventional activated sludge (CAS) (Tiwari et al., 2017) to membrane bioreactors (MBR) (Besha et al., 2017), or advanced oxidation processes (AOPs) (Grandclément et al., 2017). Nature-based solutions, such as constructed wetlands, have also been applied (Gorito et al., 2017). However, none of them is able to efficiently remove CECs. Consequently, it is still necessary to introduce new strategies in wastewater treatment, to enhance the CECs removal from wastewater.

Advanced treatment technologies for CECs removal require either the addition of chemicals, which often generate toxic disinfection by-products, and/or high costs, which hinder their application (Valhondo and Carrera, 2019). Compared to conventional techniques currently applied, Managed Aquifer Recharge (MAR) through infiltration basins achieves an improvement in the water quality, decreasing the concentration of suspended solids, nutrients, organic matter, pathogens and CECs (Elkayam et al., 2018; Regnery et al., 2015), with low energy demand and no toxic chemicals. Soil Aquifer Treatment (SAT) is a particular case of MAR in which reclaimed water from WWTPs is recharged through the vadose zone, reducing the generation of waste streams (Amy and Drewes, 2007) and supporting a circular economy approach. The implementation of permeable reactive barriers to favour sorption and to promote the growth of diverse microbial communities has proven increase the removal of several CECs during MAR/SAT operations (Valhondo et al., 2014, 2015, 2020a). This allows achieving the improvement of water quality in short times, which facilitates its application as a tertiary treatment (Valhondo et al., 2020a, 2020b). Beyond contaminant removal, MAR helps in recovering aquifer levels and, thus, hyporheic exchange in rivers and the associated ecosystem services.

Demonstrating the effectiveness of any treatment approach in removing pollutants over time is not straightforward. In fact, the analytical methods for the determination of trace contaminants in wastewater are usually based on spot sampling or, at best, 24-h integrated samples. These approaches provide the instantaneous or short-time concentrations of the pollutants but suffer from the uncertainty of longer-term fluctuations. An effective alternative is the use of integrative sampling approaches, in particular passive sampling. Its use for continuous pollutant monitoring in water matrices has expanded in recent years. Passive sampling devices get in dynamic contact with large volumes of water, with exposure periods that can reach 4–5 weeks. They allow the in-situ pre-concentration of ultratrace compounds, providing benefits also from a practical point of view (no energy required, easy handling, and low cost) (Magi et al., 2018). The final result deriving from passive sampling represents the time weighted average concentration (TWA), which is valuable for ecological risk assessment due to chemical stressors. Instead, obtaining TWA from spot sampling requires frequent sampling and a large number of analyses, thus becoming costly and time-consuming. Passive sampling is based on the diffusive flux of an analyte from water to the receiving phase of the sampler. This flux is driven by the difference between the chemical potential of the analyte in the two media. POCIS (Polar Organic Chemical Integrative Sampler) consists of a sorbent phase, sandwiched between two membranes, able to sequester and concentrate contaminants with logK$_{OW}$ values in the range 1–4. POCIS have been used for sampling of pharmaceuticals and personal care products (PPCPs) in different water matrices, including wastewater (Alvarez et al., 2004; Di Carro et al., 2018; Liscio et al., 2009; Magi et al., 2018; Tanwar et al., 2015).

In this context, the goal of the present study is to assess the capability of POCIS to help in a more reliable estimation of CECs removal in wastewater treatments. To this end, a WWTP, located in Palamós, Girona (Spain), treating urban wastewater from several municipalities and a hospital, was selected to study the CECs removal throughout the WWTP, by deploying POCIS at the inlet and outlet. This facility is provided with pilot-scale SAT systems fed with the WWTP outflow. The evaluation of CECs removal in two SAT systems (one with and one without reactive barrier) was included in the study to identify the additional pollutants elimination that this technology can provide, compared to the classical secondary treatment.

2. Experimental

2.1. Chemicals and reagents

The 56 CECs selected for investigation in the present study are relevant for treated wastewater reuse in SAT and agricultural irrigation, for public

health, and for environmental safety. For the selection, we followed the recommendations of the NEREUS COST Action for urban water reuse (European Cooperation in Science and Technology, 2022) and the EU Watch List (2015/495 and 2015, 2015). In addition, we considered the particular characteristics of the selected WWTP, which treats urban wastewater from 10 municipalities and one hospital. Thus, the target analytes include PPCPs belonging to different compound classes, i.e., antibiotics, anti-inflammatories, UV filters, benzotriazoles, and parabens, among others. The specific target compounds and their physicochemical properties are listed in Table S1 of the Supporting Information (SI).

The analytical standards of the target PPCPs as well as the isotopically labelled analytical standards, used as surrogate and internal standards, were of analytical grade (>98 %).

Benzophenone-3 (oxybenzone, BP3); benzophenone-1 (BP1); benzophenone-4 (BP4); 4-hydroxybenzophenone (4HB); 4,4′-dihydroxybenzophenone (4DHB); avobenzone (AVO); 2-(2-benzotriazol-2-yl)-p-cresol (UVP); 5,6-dimethyl-1H-benzotriazole (DMBZT); nalidixic acid (NDX); oxolinic acid (OXL); tetracycline (TCY); succynil-sulfathiazole (S-STZ); sulfadiazine (SDZ); N4-acetylsulfadiazidine (acSDZ); sulfamerazine (SMR); N4-acetylsulfamerazine (acSMR); N4-acetylsulfamethazine (acSMZ); sulfamethoxazole (SMX); N4-acetylsulfamethoxazole (acSMX); sulfamethoxypyridazine (SMPZ); sulfapyridine (SPY); N4-acetylsulfapyridine (acSPY); sulfaquinoxaline (SQX); sulfathiazole (STZ); sulfisomidine (SMD); sulfadimethoxine (SDM); trimethoprim (TMP); acetaminophen (APH, also known as paracetamol); atenolol (ATL); gemfibrozil (GFZ); ketoprofen (KPF); mefenamic acid (MFA); carbamazepine (CBZ); norfluoxetine (norFXT); ofloxacin (OFX); ciprofloxacin (CFX); caffeine (CFF); ibuprofen (IBU); salicylic acid (SCY); diclofenac (DCF); diclofenac-13C (DCF-13C); methyl paraben (MePB); propyl paraben (PrPB); benzyl paraben (BePB); butyl paraben (BuPB) and benzophenone-(carbonyl-13C) (BP-13C) were purchased from Sigma Aldrich (Darmstadt, Germany).

Benzophenone-2 (BP2); 2,2′-hydroxy-4-methoxybenzophenone (DHMB); ethyl-4-(dimethyl-amino) benzoate (EtPABA); ethylhexyl methoxycinnamate (EHMC) and 1H-benzotriazole (BZT) were purchased from Merck (Darmstadt, Germany).

2-Hydroxy-4-methoxy-2′,3′,4′,5′,6′-d5 (BP3-d5); (±)-3-(4-methylbenzylidene-d4) camphor (4MBC-d4); 1H-benzotriazole-4,5,6,7-d4 (BZT-d4); flumequine-13C3 (FLU-13C3); trimethoprim-d3 (TMP-d3); carbamazepine-d10 (CBZ-d10); mefenamic acid-d_3 (MFA-d3); caffeine-d3 (CFF-d3); ibuprofen-d3 (IBU-d3); salicylic acid-d_6 (SCY-d6); diclofenac-d4 (phenyl-d4) (DCF-d4); benzyl paraben-d4 (BePB-d4) and 5-(2,5-dimethylphenoxy)-2,2-bis(trideuteriomethyl)pentanoic acid (GMZ-d6) were supplied by CDN isotopes (Quebec, Canada).

5-Methyl benzotriazole (MeBZT) was obtained from TCI (Zwijndrecht, Belgium). 4-Methylbenzylidene camphor (4MBC) was provided by Dr. Ehrenstorfer (Augsburg, Germany). Flumequine (FLU); N-desmethylvenlafaxine (N-desVFX); carbamazepine 10,11-epoxy (CBZ-E); sulfamethazine-d4 (SMZ-d4) and acetaminophen-d4 (APH-d4) were provided by Toronto Research Chemicals (Toronto, Canada). Oxytetracycline (O-TCY) and naproxen (NPX) were purchased from Honeywell Fluka (Wabash, MA, USA).

Water, methanol (MeOH), and acetonitrile (ACN) of MS-grade were obtained from J.T. Baker (Deventer, The Netherlands), and the nitrogen (99.995 % purity) and argon (99.99 % purity) were supplied by Air Liquide (Barcelona, Spain). Ethanol (EtOH), acetone, formic acid (FA), and ammonium acetate were purchased from Merck (Darmstadt, Germany).

Stock solutions of individual standards and intermediate mix standards solutions containing all analytes (1 mg L^{-1}) were prepared in MeOH. Standard working solutions were daily prepared at appropriate concentrations. Standards solutions were stored in the dark at −20 °C.

2.2. Site description

The selected WWTP is located in Palamós (Girona), on the north of the Spanish Mediterranean coast. The design flow of the facility is 33.000 m^3/day, or 165.450 Eqs/inh., with an HRT of some 24 h. The

area is a touristic hotspot, with a daily influent during the summer months (25.000–30.000 m^3) that doubles that of the winter months (12.000–14.000 m^3). Two pre-treatment lines remove solid waste, grease, and supernatants from inlet water before it flows to the primary treatment. The primary treatment consists of three circular decanters; all operate during the summer, while only two operate during the rest of the year. The secondary biological treatment consists of a conventional activated sludge (CAS) treatment followed by three clarifiers.

A pilot-scale SAT system was installed in the WWTP in 2017 to evaluate the efficiency of reactive barriers to enhance SAT water quality improvement of the secondary treatment effluent. Each SAT system comprises an infiltration basin (1.5 m-long × 2.38 m-wide) overlying a 1.15 m- unsaturated zone, followed by an aquifer (15 m-long × 2.38 m-wide × 1.5 m-high) made up of fine sand (ø = 0.1–0.2 mm). A dosing pump (PRIUS) controls the flow into each system and the elevation of the discharge pipe, which collects the water in the deepest part of the aquifer, controls the outlet of each system. One of the systems (SAT system T2) is a conventional SAT, with the unsaturated zone filled with sand. A reactive barrier was installed in SAT system T4. The reactive barriers consist of approximately 50 % (in volume) of organic substrates (vegetal compost or woodchips), which provide sorption sites and release dissolved organic carbon into the flowing water to favour the development of diverse redox regions with diverse microbial communities, 50 % (in volume) of sand, which provides strength, and a little amount of clay to increase the types of sorption sites. A detailed description of the pilot SAT systems can be found in Valhondo et al. (2020b). SAT systems were operated under the same conditions during the POCIS deployment period, fed with a comparable flow of the effluent of the secondary treatment and allowing plants to grow freely in the recharge areas, thus displaying ideal conditions to compare the removal of CECs between the two systems.

2.3. POCIS assembly

The passive samplers used in this study were developed by Alvarez et al. (2004) to collect and pre-concentrate polar organic compounds. POCIS were assembled in our laboratories by reproducing the characteristics of the commercial type (200 mg sorbent material and 45.8 cm^2 as sampler surface area). Polyethersulfone (PES) membranes (0.1-μm pore size, 150-μm thickness) were obtained from Pall Italia (Buccinasco, Italy) and Oasis hydrophilic-lipophilic balanced (HLB) sorbent phase (60-μm particle size) from Waters (Vimodrone, Italy). PES membranes were washed in water/MeOH (80:20 v/v) for 24 h and with MeOH for 24 h, prior to use. After drying, 200 mg of the HLB sorbent was enclosed between two membranes. The membranes were then compressed between two stainless steel rings, fixed with nuts, and provided with specific holes for the placement (Fig. 1). POCIS were stored at −20 °C until deployment.

2.4. Experiment setup and POCIS deployment

Seven POCIS were placed at different points of the WWTP to monitor the water-borne pollutants along the treatments. Passive sampling could suffer from low reproducibility; therefore, duplicate deployment was performed where possible. Specifically, the following setup was designed (Fig. 2): one POCIS at the inlet of the plant (referred hereafter as "WWTP influent"), namely where the stream of non-treated wastewater (influent) arrives; two POCIS at the outlet of the secondary treatment (referred hereafter as "Secondary outlet"), which is also the influent to the SAT systems; two POCIS at the outlet of the reference system (referred hereafter as "Outlet SAT T2"), and two POCIS at the outlet of the T4, the one operated with the reactive barrier (referred hereafter as "Outlet SAT T4").

All samplers were located inside stainless-steel cages to protect the membranes from accidental impacts. The cages were immersed in the water to obtain a water flow parallel to the membranes; this ensured chemicals accumulated in the samplers by diffusion, avoiding a rapid saturation of the solid phase contained in the POCIS (Fig. S1). Indeed, the chemicals must diffuse from water through the semipermeable membrane
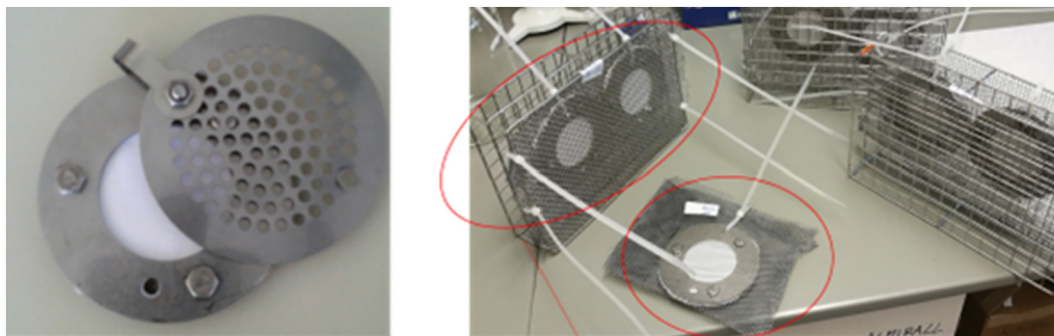
Fig. 1. Assembly for the deployment of the passive samplers into the metallic grid to protect the membranes.

with the only driving force of chemical potential gradient, excluding the "physical filter" behaviour.

The POCIS were deployed for 14 days (from January 18th to February 1st, 2018) to account for temporal fluctuations in concentrations. After the scheduled deployment time, the devices were recovered from the sites (Fig. S2), removed from the cages, and gently rinsed with deionized water to clean the surfaces. Then, they were wrapped in aluminium foil and stored at − 20 °C until further processing.

2.5. POCIS processing and LC-MS/MS analysis of PPCPs

The samplers were thawed and dismantled; with the aid of HPLC-grade water, the HLB sorbent was carefully transferred into a 1 cm i.d. glass cartridge, provided with a polytetrafluoroethylene (PTFE) frit and glass wool, to prevent phase loss. The solid phase was dried for 30 min under vacuum. An aliquot of 10 μL of a solution of the internal standard diclofenac-C^{13} at a concentration of 50 mg L$^{−1}$ was added to the sorbent and dried for 30 min under vacuum. Then, an elution with 50 mL of acetone was performed to recover the sorbed analytes and further evaporated to dryness using a rotary evaporator. The residue was reconstituted in 1 mL of MeOH and, if not immediately analyzed, stored at − 20 °C. An aliquot of this sample was diluted 1:50 with MeOH/water, 50:50 (v/v) and analyzed by LC-MS/MS.

Separation and detection of the target PPCPs were performed by online SPE-LC-MS/MS in a Symbiosis™ Pico instrument from Spark Holland (Emmen, The Netherlands) coupled to a 4000 Q TRAP™ hybrid quadrupole-linear ion trap-MS analyzer from Applied Biosystems-Sciex (Foster City, California, USA), following the method by Vassalle et al. (2020). Briefly, analytes separation was carried out with a Hibar Purospher® STAR® HR R-18 ec. (50 mm × 2.0 mm, 5 μm, Merck) column. The mobile phase consisted of a mixture of HPLC-grade water and ACN, both with 0.1 % of formic acid. MS/MS detection was carried out in positive and negative electrospray ionization (ESI+, ESI−) modes under selected reaction monitoring (SRM). Two major characteristic fragments of the precursor molecular ion were recorded per analyte for enhanced sensitivity and selectivity. The most abundant transition was selected for quantification, whereas the second most abundant was used for analyte confirmation. Fragmentation voltage and collision energy were optimised for each transition. The isotope dilution approach was used for quantification. The instrumental limits of detection (ILOD) and instrumental limits of quantification (ILOQs) were calculated as pg injected in the LC-MS/MS system using matrix-matched standards. The ILODs were in the range 3.5–11 pg for UVFs, 0.0004–3.7 pg for paraben preservatives (PBs), 0.3–0.8 pg for pharmaceuticals (Pharma) and 0.001 pg for CFF. The complete list of ILODs and ILOQs can be consulted in Table S2.

2.6. Determination of PPCPs removal by the passive sampling approach

The amount of chemicals found in the sorbent phase after POCIS deployment correlates with their TWA concentration in water. To provide this concentration, a kinetic constant, called sampling rate (R_S), needs to be estimated (Di Carro et al., 2014). Still, the knowledge of TWA
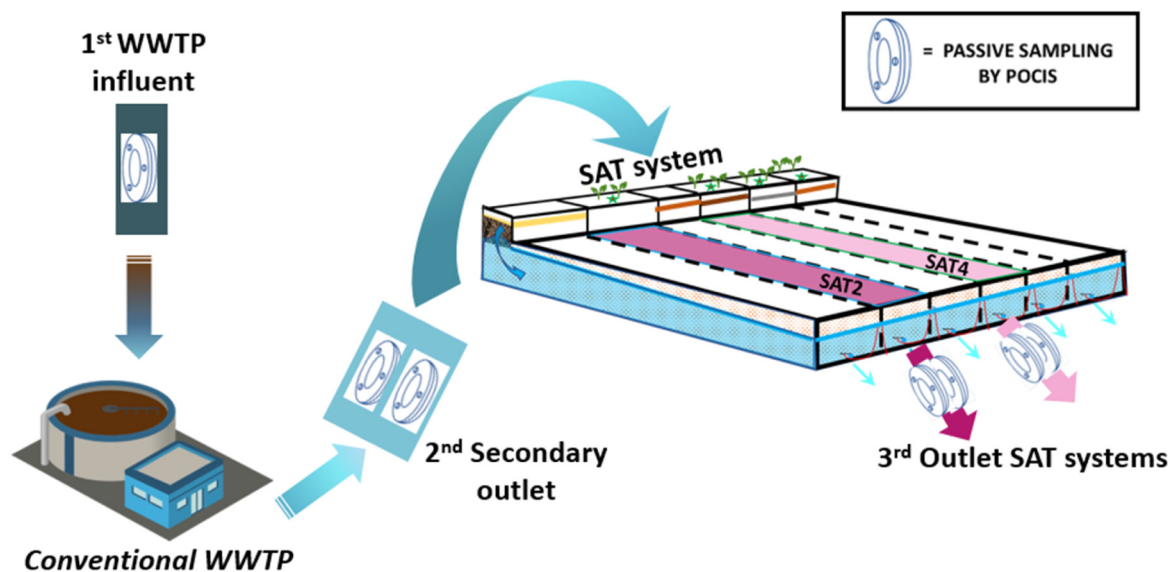

Fig. 2. Experimental setup of the POCIS deployment in the WWTP.

concentrations was not essential in this work because the interest was in the reduction of TWA along the system, which is proportional to the reduction in mass retained. Thus, only the absolute ng of chemicals sampled per POCIS were considered. By comparing the analytes mass in POCIS deployed in the different sites of a WWTPs, information about the abetment of chemicals after specific treatments was obtained. In particular, the removal ratios (RE%) for the selected PPCPs along the WWTP and in the SAT systems T2 and T4 were calculated as the ratio between analyte masses determined in the POCIS at the inlet and at the outlet of the secondary and SAT systems considered.

3. Results and discussion

3.1. Overall results

Data obtained from the analysis of the POCIS extracts were used to determine the presence of the considered contaminants at the various stages of the wastewater treatment. Due to the complex sorption mechanism of the different chemical classes onto the POCIS sorbent, as well as probable fluctuations in the site's conditions (flow, pH, temperatures), a certain degree of variability was expected in the accumulation of the analytes in the duplicated deployments (Alvarez et al., 2014). Nevertheless, results characterized by a relative standard deviation (RSD) >30 %, related to the analyte mass sampled by the duplicated POCIS, had low reliability and were considered with caution.

Thirty-two out of the 56 considered analytes were detected in at least one of the POCIS extracts, 31 of them in the WWTP influent. Full quantitative results are provided in Table S3, expressed as the mass in ng per POCIS of each compound. Fig. 3 displays the chromatogram of the most intense peaks of the extract deriving from the POCIS deployed at the WWTP influent.

It is important to remark that higher sampled amounts of particular contaminants may not necessarily represent a higher concentration in water. Indeed, the amount of a chemical sampled by the POCIS depends on both its concentration in water and the sampling rate (R_S). If two substances have the same water concentration but one has a larger R_S, this will result in a higher sampled amount for the latter. Therefore, direct comparison among the amounts of the different substances detected is possible only for those chemicals characterized by similar R_S.

The contaminant TWA concentrations in the different points of the WWTP could not be calculated, because the specific R_S are not available. Still, information about the abatement of chemicals after the specific treatments could be retrieved by comparing the mass of the analyte adsorbed on the POCIS deployed before and after the treatment. In fact, since these amounts reflect average concentrations over the sampling period, they are more informative than those obtained by spot sampling (Mirasole et al., 2016).
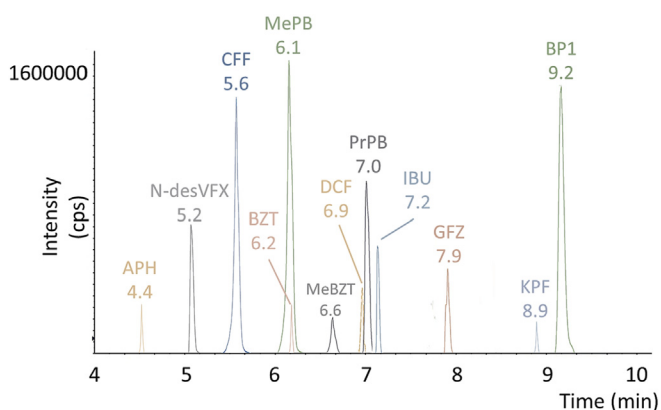

Fig. 3. Reconstructed MS/MS chromatogram of most intense peaks from the POCIS deployed at the WWTP influent.

For the CAS treatment of the selected WWTP, the expected main removal mechanisms of CECs were biodegradation and sorption. Long hydraulic and sludge retention times may foster the growth of slow-growing bacteria, thus improving the removal of many CECs such as DCF and, erythromycin (Fernandez-Fontaina et al., 2012; Suarez et al., 2010). Temperature is also a key factor driving the removal of CECs, as higher removal rates are reported between 15 and 20 °C compared to <10 °C (Castiglioni et al., 2006; Vieno et al., 2005). In our study the deployment was from January 18th to February 1st, when mean temperatures in the systems were between 12.3 and 13.6 °C, while water in the secondary outlet range between 13 and 15.4 °C.

Fig. 4 displays the single CECs mass load calculated for the POCIS at the WWTP influent and the Secondary outlet. Overall, highly variable removal rates were observed for the wide range of selected PPCPs, which is in agreement with the classification of CECs made by Suarez et al. (2010), according to the elimination potential under different biological conditions: highly removed under aerobic and anoxic conditions (e.g. IBU, 95 % removed); highly removed under aerobic but hardly removed under anoxic conditions (e.g. DCF, not removed); recalcitrant to biological degradation (e.g. CBZ, not removed). The CECs' abatement was further estimated in the pilot SAT systems T2 and T4 to assess their removal efficiency.

Considering the total mass of contaminants, a significant reduction of the concentration in water was observed going from the WWTP inlet to the secondary treatment outlet and the SAT treatment outlet; a difference was also observed between the residual contamination present after T2 and T4, showing a general higher efficacy of the reactive barrier components to retain and/or degrade the PPCPs. By looking at the total amount grouped by chemical classes, namely Pharma, UVF, PBs and CFF, the same reduction trend was generally observed, as shown in Fig. S3. However, some compounds inside the classes showed peculiar behaviour, as shown in Fig. 4, that presents the mass load of many CECs at the WWTP influent and effluent. For example BP3 or APH were completely removed after the WWTP treatment, while other UVFs or pharmaceuticals were only partially or not removed. Table 1 summarizes the calculated RE% for each detected contaminant between the WWTP influent and the secondary outlet, and between the secondary outlet and the Outlet of SAT systems T2, without reactive barrier, and T4, with reactive barrier. Complete removal from the WWTPs inlet to the outlet of the secondary treatment was observed only for BP3, the parabens group, and APH.

3.2. Occurrence and fate of pharmaceuticals

Within the pharmaceuticals class, 21 compounds were detected at the WWTP influent, including some fluoroquinolones, sulphonamides, and trimethoprim (antibiotics), the lipid regulator GFZ, the anti-inflammatories MFA, NPX, IBU, KPF, and DCF, the analgesic APH, the anticonvulsant CBZ and its major metabolite CBZ-E, the β-blocker ATL, the antidepressant metabolite norFXT, and the stimulant CFF. A rather wide range of quantities was measured, from tens of ng for MFA to hundreds of μg for CFF, which alone accounted for 53 % of the total mass analyzed at the WWTP influent (Fig. 4). As already mentioned, this indicates a wide range of water concentrations, as well as POCIS R_S.

Only 23 % of the total mass of pharmaceuticals was eliminated by the primary and secondary treatments, thus confirming that conventional WWTPs are not suitable to eliminate pharmaceuticals from wastewater (Krzeminski et al., 2019). The only exception was APH, not detected in the secondary effluent. A wide range of removal rates was observed, from 16 % (KPF) to 97 % (CFF). For antibiotics, the highest RE% was obtained for CFX, whereas the others were characterized by quite low removals. Anti-inflammatories showed high RE%, especially IBU (>95 %). Within the target pharmaceuticals, the anticonvulsant CBZ was the least removed, which was expected, being this neutral substance one of the most critical compounds monitored worldwide. This behaviour has been attributed to its chemical stability and hydrophilicity (log Kow <3) (Nakada et al., 2006). The analytes OFX, several sulphonamides, TMP, CBZ, CBZ-E, ATL, and N-desVFX showed a greater mass at the secondary outlet than at the
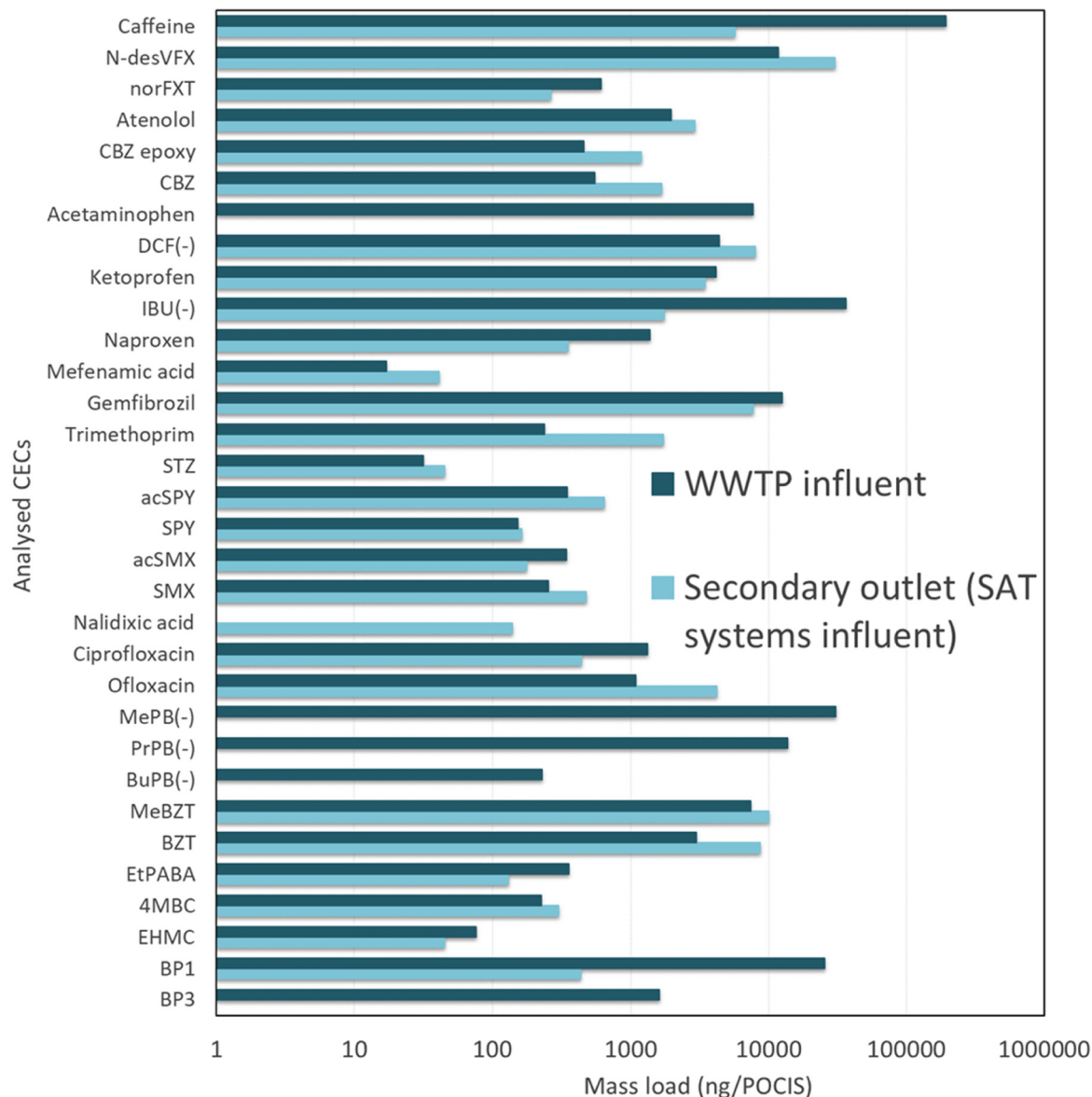
Fig. 4. Mass load (in log scale) determined in the POCIS deployed at the WWTP influent and the Secondary outlet (SAT systems influent) streams of the WWTP.

influent (negative RE%); this phenomenon has been observed in other studies (Behera et al., 2011; Jones et al., 2017). It is usually explained by the reconversion of transformation products into the parent compounds (e.g. by de-conjugation or other transformation processes taking place during the treatment) (Krzeminski et al., 2019).

Effective removal of most pharmaceuticals was observed along the SAT systems: approximately 90 % of the total mass measured at the secondary outlet was depleted. The RE% of SAT systems was compound-dependent (Table 1). SAT system T4 performed better than SAT system T2, accounting for 1.2 to 2.6-folds higher removals. Fig. 5 depicts the load of chemicals sampled at the outlet of SAT systems T2 and T4.

In detail, fluoroquinolones, quinolones, the antibiotic TMP, the β-blocker ATL, the anti-depressant N-desVFX, and CFF were completely removed by both T2 and T4 SAT systems, proving the efficiency of such technology to remove many of the pharmaceuticals present in WWTP outflow. For the rest of them, RE% were in the range of 23 %–91 %.

Among sulphonamides, the SMX mass significantly increased during SAT, while the acSMX mass slightly increased or remained constant, compared to the secondary outlet. These data might suggest an interconversion between the acetylated and non-acetylated forms of sulphonamides

through the steps of the wastewater treatment. A "back transformation" of SMX metabolites was indeed observed in previous studies (Bonvin et al., 2013; Göbel et al., 2005). As for SPY and acSPY, the first remained constant during all WWTP stages, while the second was characterized by a complete removal through the SAT systems. Nevertheless, it is worth noting that the RSD of the two POCIS deployed after the SAT systems were rather high for SMX, acSMX, and SPY. The sulphonamide STZ represents a particular case, being the only compounds for which SAT system T2 showed a better removal efficiency than T4. Its mass was rather low in all samples but completely absent in the POCIS deployed at the outlet of SAT system T2.

The anti-depressant metabolite norFXT decreased from the WWTP influent to the secondary outlet, but was then found at approximately constant mass after SAT. NorFXT is the human metabolism product of the fluorinated antidepressant fluoxetine administered in racemic form. This demethylated active metabolite, even more than the parent compound, is produced in the human body as two enantiomers (Stokes and Holtz, 1997), which act differently, being the (S)-NFLX the more potent regarding its inhibition capacity on serotonin production (Fuller et al., 1992). The apparent inefficacy of the SAT systems might be explained by previously

Table 1

Estimated mass removal (RE%) of the single contaminants detected in the WWTP influent through primary + secondary treatments and through SAT systems.

% removal					
Family group	Compound	Acronym	Inlet/secondary outlet	Secondary outlet/MAR outlet T2	Secondary outlet/MAR outlet T4
Personal care					
Ultraviolet filter	Benzophenone-3	BP3	100	–	–
Ultraviolet filter	Benzophenone-1	BP1	98.3	100	100
Ultraviolet filter	3-(4-Methylbenzilidene) camphor	4MBC	−33.7	100	100
Ultraviolet filter	Ethyl 4-aminobenzoate	EtPABA	63.5	100	100
Ultraviolet filter	1,2,3-Benzotriazole	BZT	−191.1	58	67.7
Ultraviolet filter	Methyl-benzotriazole	MeBZT	−36.1	85	91.5
Paraben	Butylparaben	BuPB(−)	100	–	–
Paraben	Propylparaben	PrPB(−)	100	–	–
Paraben	Methylparaben	MePB(−)	100	–	–
Pharmaceuticals					
Antibiotic	Ofloxacin	OFX	−287.7	100	100
Antibiotic	Ciprofloxacin	CFX	67	100	100
Antibiotic	Nalidixic acid	NDX	–	100	100
Antibiotic	Sulfamethoxazole	SMX	−88	−313.9	−192
Antibiotic	N^4-Acetylsulfamethoxazole	acSMX	48.2	−51.1	41.3
Antibiotic	Sulfapyridine	SPY	−7.6	−0.4	27.5
Antibiotic	Acetylsulfapyiridine	acSPY	−84.2	100	100
Lipid regulator	Sulfathiazole	STZ	−40.1	100	56.4
Anti-inflammatory	Trimethoprim	TMP	−625	100	100
Anti-inflammatory	Gemfibrozil	GFZ	38.3	84.7	89.7
Anti-inflammatory	Mefenamic acid	MFA	−140.5	84.2	87.5
Anti-inflammatory	Naproxen	NPX	74.7	−33	25.1
Anti-inflammatory	Ibuprofen	IBU(−)	95.2	91.3	100
Anti-inflammatory	Ketoprofen	KPF	16	52.2	81.8
Anti-inflammatory	Diclofenac	DCF(−)	−82.6	88.1	91.1
Analgesic	Acetaminophen	APH	100	–	–
Anti-epileptic	Carbamazepine	CBZ	−206.3	69	80.9
Anti-epileptic	Carbamazepine-epoxy	CBZ-E	−161.5	63.3	70.4
β-blocker	Atenolol	ATL	−49.1	100	100
Anti-depressant	Norfluoxetine	norFXT	56.6	−5.9	23.3
Anti-depressant	*N*-desmethylvenlafaxine	N-desVFX	−156.1	100	100
Stimulant	Caffeine	CFF	97.1	100	100

reported evidence showing that the degradation pattern and the enantioselectivity depend to a large extent on the microorganism phylogenies (Ribeiro et al., 2014). Accordingly, SAT microbial communities would be quite less effective at biodegrading norFXT than the microorganisms from the activated sludge of the secondary treatment. Nevertheless, the slight loss of mass observed in SAT system T4, although not in T2, is consistent with the expected effect of the reactive barrier, which should promote the development of diverse microbial communities, possibly favouring norFXT removal.

Regarding the remaining detected analytes, namely GFZ, all anti-inflammatories, and the two anti-epileptic drugs, the mass measured at T4 outlet was always lower than at T2, with the highest difference in the abatement extent for KPF. However, the complete removal of these

Fig. 5. Mean mass load of the selected CECs in the outlet stream of the SAT systems T2 (operated without reactive barrier) and T4 (operated with reactive barrier). Both systems were recharged with the secondary treatment outlet of the WWTP.

substances was not observed, except for IBU in T4. The removal of NPX in the SAT systems was quite low: only 23 % was achieved in T4 (compared to 80–100 % of the other NSAIDs), while a negative removal was observed in T2. The NPX degradation extent has been reported to be notoriously poor through conventional wastewater treatments. This is due to its molecular structure with the presence of two aromatic rings, providing high stability and resistance to microbial degradation. Research carried out so far shows that usually only one probable microbiological transformation process occurs for NPX, in which the aromatic rings are not cleaved (Domaradzka et al., 2015). Only a few bacterial strains have provided full NPX degradation (Guzik and Wojcieszyńska, 2020). Thus, most likely, the microbial communities present in the SAT systems did not provide an increased potential to degrade NPX than those present in the activated sludge of the secondary biological treatment. Despite that, removal in T4 was higher than in T2, which again indicates that the reactive barrier installed in T4 induces a change in the microbial community formed (Hellman et al., 2022), making SAT system more efficient. The fate of NPX in the environment is known to be driven not only by biodegradation but also by adsorption (Liu et al., 2019; Martínez-Hernández et al., 2016) which is strongly dependent on pH. As the molecule has a carboxylic acid group that is deprotonated at environmental pH (range 5–8), NPX is present in the environment mostly in its anionic form. In this form, the electrostatic interaction of NPX with the negatively charged natural organic matter and clay of the soil is difficult (Liu et al., 2019). Most likely this low sorption onto the reactive barrier material might contribute to the reduced removal observed for NPX in the SAT system as compared to that in the WWTP. An implication is that the reactive barrier performance might be increased by adding positively charged surfaces, which would act as sorption sites for anions.

Special attention has to be drawn to the removal achieved for the recalcitrant CBZ and its epoxy-metabolite; both showed negative removal rates at the secondary outlet, while SAT systems displayed removals higher than 50 %. T4 exhibited an improvement in the removal of these two
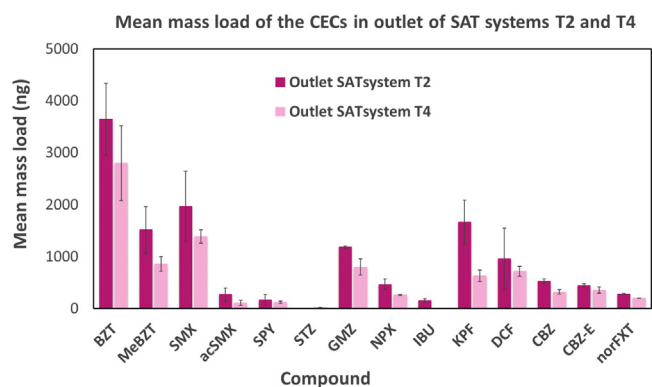
substances compared to T2, indicating that the presence of the reactive barrier boosted the elimination of these two recalcitrant pharmaceuticals. CBZ is a neutral anticonvulsant known to be recalcitrant at conventional WWTPs (Joss et al., 2006). The increased removal efficiency in the SAT systems might be the result of the largest hydraulic retention time, around 15 days, according to previously reported results in a batch study (Li et al., 2015). Furthermore, at the pH of the system, carbamazepine and derivatives are in their neutral (uncharged) form, which allows a stronger interaction with the organic matter and clay in the barrier material.

3.3. Occurrence and fate of personal care products

Five out of the 10 UVFs analyzed were detected in the WWTP influent, i.e. BP3, BP1, EHMC, 4MBC, and EtPABA. BP1 is the major metabolite of BP3 in different organisms, including humans (Zhang et al., 2021). It is not listed among the permitted UVFs in the EU legislative framework on cosmetic products (European Parliament and the Council of the European Union, 2009), but it can be used as an additive in materials intended to enter in contact with food to protect the product from UV radiation. This application would most likely contribute to its occurrence, as a quite high mass was detected at the WWTP influent (approximately 20 μg), almost 16-fold more than that of the BP3. Still, the value for BP3 was rather high; this result was expected, as it is the most used UVF in sunscreen formulations, constituting up to a 6 % (in mass) of the product (European Comission, 2022). It is worth mentioning that the high level of BP3 measured is of concern.

The other detected sunscreens were EtPABA and 4MBC and EHMC, which have been frequently reported globally, being among the most used together with BP3 and octocrylene (Tsui et al., 2014). EHMC is not listed in Table 1 because of the large RSD of the secondary and T2 outlet, but had been fully eliminated after T4. EtPABA and 4MBC were not eliminated during the WWTP, but were fully removed in both SAT systems.

Two benzotriazoles out of the 4 analyzed were detected at the WWTP influent at quite a high level, approximately 3 and 7 μg for BZT and MeBZT, respectively. In this study we considered the paraben preservatives and alkyl esters of the ρ-hydroxybenzoic acid (PABA) within the group of personal care and hygiene products, but we could have also included in the pharmaceuticals group. They are present in medicines to prevent the growth of microorganisms and fungi, thus increasing the shelf life of the products. As their alkyl chain increases, so does the antimicrobial activity of the PABA derivative, but its water solubility decreases. Therefore, MePB and PrPB are the most extensively used (Błedzka et al., 2014). This explains the high mass of MePB and PrPB, determined in this study, approximately 30 and 14 μg, respectively. On the other hand, as expected, BuPB was found at a low concentration (around 200 ng) and BePB was not detected.

PBs were fully removed by the primary and secondary treatments. UVFs were characterized by an overall mass reduction of 48 % from the WWTP influent to the secondary outlet. BP3 was completely depleted, while 63 % and 98 % removals were reached for EtPABA and BP1, respectively. 4-MBC showed a negative removal ratio suggesting that derivative species (metabolites, conjugated forms and other transformation products) present in the influent could transform back to the parent compound during the treatment. This was also the case with the two BZTs determined. Compounds such as 5,6-dimethyl-1-benzotriazole and 5-chloro-benzotriazole are biotransformed into MeBZT and ultimately BZT through demethylation and dechlorination consecutive processes (Molins-Delgado et al., 2015) that could have occurred in the influent waters. As already mentioned, EHMC was considered an exception among UVF; a very low amount of it was sampled at the inlet and the high relative standard deviation between the duplicated POCIS in the other sampling points hinders the interpretation of the results.

The RE% of the PCPs at the outlet of the SAT systems is reported in Table 1. The 71 % and 83 % of the overall UVFs mass was depleted by T2 and T4, respectively. Among them, BP3, BP1, 4MBC, and EtPABA were efficiently removed by both T2 and T4. Regarding BZT and MeBZT, a higher depletion was observed along T4, compared to T2 (1.3 and 1.8-folds higher

for BZT and MeBZT, respectively). Still, both compounds were present in the outlets of the SAT systems, indicating that the removal was incomplete. In particular, due to an initial negative removal going from the WWTP influent to the secondary outlet, the 100 % of the BZT sampled at the WWTP influent was also detected in the outlet of SAT system T4. Overall, this was the only case of concern, due to the effects of this substance in the environment, while a significant decrease in all other substances was observed in the SAT systems.

It is worth noting that the removal achieved in the studied WWTP relies on two treatments, the primary and the biological. In the pilot SAT, the elimination is achieved solely through the soil-aquifer passage, and in the case of T4, upon the stimulation of natural degradation obtained by providing extra organic carbon to the microbial communities grown by means of the reactive barrier.

4. Conclusions

The application of integrated sampling at WWTPs with POCIS represents a useful approach to assess the removal efficiency of selected PPCPs in an urban WWTP and in a pilot-scale SAT systems and to compare the removals obtained in a conventional SAT (T2) versus a system with a reactive barrier made up of sand, vegetal compost (to favour sorption and as an organic carbon source to foster the growth diverse microbial communities), and clay (T4). The removal rates for PPCPs achieved in the WWTP agreed with reported data in the literature. The contaminants abatement obtained by the SAT systems was notably greater in the system operating with the reactive barrier in comparison to the conventional one, due to the enhanced degradation provided by the microbial communities formed. Overall, the removal efficiency provided by both SAT systems were higher than that achieved in the two wastewater treatments applied in the WWTP. Important improvements were observed for GFZ (from 38 % to 90 %) and KPF (from 16 % to 82 %). This improvement was especially remarkable in the case of the recalcitrant CBZ and its major human metabolite (CBZ-E), for which removals of 81 % and 70 %, respectively, were achieved by SAT system T4. Nevertheless, lower removal was attained for acSMX (48 %–41 %), norFXT (57 %–26 %), and NPX (74 %–25 %).

These outcomes demonstrate that SAT is effective and efficient. Detailed analysis suggests that further improvements can be gained by increasing the variety of sorption sites, ideally including positively charged sites. This could be achieved by creating aerobic zones, so as to favour the precipitation of ferric oxides. We conjecture that increasing residence times, which were of only 15 days in the tested SAT systems, would also help. This could be allowing a longer travel distance in the aquifer (15 m at our pilot sites).

An overall improvement (namely a reduction in the final contaminants mass) was observed by combining the WWTP secondary treatment with SAT, in comparison with the sole secondary treatment. Consequently, SAT systems implemented with a natural reactive barrier constitute a sustainable alternative to advanced tertiary wastewater treatments from both the environmental and economic viewpoints. SAT systems would contribute to combat the continuous release of pharmaceuticals and personal care and hygiene products into the aquatic environment.

CRediT authorship contribution statement

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Lurdes Martínez-Landa: Term, conceptualization, methodology, investigation, resources, writing –original draft, writing - review & editing, visualization, funding acquisition.

Jesús Carrera: Conceptualization, writing-review & editing, funding acquisition.
Marina Di Carro: Term, conceptualization, writing-review & editing, supervision, funding acquisition.
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M. Silvia Diaz-Cruz: Term, conceptualization, methodology, validation, resources, writing-review & editing, supervision, project administration, funding acquisition.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.161466.

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