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Vertical-flow constructed wetlands as a sustainable on-site greywater treatment process for the decrease of micropollutant concentration in urban wastewater and integration to households' water services

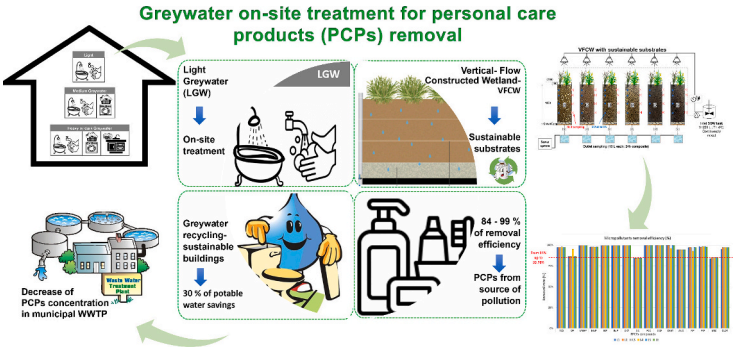
Fernanda Cristina Muniz Sacco [a,*], Silvia Venditti [a], Paul Wilmes [b], Heidrun Steinmetz [c], Joachim Hansen [a]

[a] University of Luxembourg, Faculty of Science, Technology and Medicine (FSTM), rue Richard Coudenhove-Kalergi 6, L-1359 Luxembourg, Luxembourg
[b] University of Luxembourg-LCSB, Avenue des Hauts Fourneaux 7, L-4362 Esch-sur-Alzette, Luxembourg
[c] RPTU Kaiserslautern-Landau, Gottlieb-Daimler-Straße, 67663 Kaiserslautern, Germany

HIGHLIGHTS

- On-site greywater treatment can save at least 30 % of potable water.
- Vertical-flow constructed wetlands are sustainable option for greywater treatment.
- Biochar produced in a circular way is suitable as supporting material in wetlands.
- Personal care products can be removed by on-site greywater treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Micropollutant removal from effluent of conventional wastewater treatment has recently become one of the most discussed topics in the design and operation of wastewater treatment plants (WWTPs). This is due to the need to add a post-treatment step to the conventional processes to comply with stricter quality standards for effluents as outlined in the revised Urban Wastewater Treatment Directive (UWWTD). The adoption of on-site or decentralized greywater (GW) treatment in sustainable buildings using vertical-flow constructed wetlands (VFCWs) is a promising direction. It represents an interesting alternative for the removal of micropollutants at the source of pollution, such as personal care products (PCPs) and some pharmaceuticals which are mainly present in this wastewater fraction. Additionally, the treated greywater could be used in households' water services which do not require potable water quality, thus saving drinking water. In this context, this work compares the results of micropollutant removal from projects using VFCWs as a polishing step of WWTPs effluent, as a centralized solution, to the results from a decentralized GW treatment. The results show that VFCWs can remove the investigated micropollutants (Diclofenac and DEET) with an efficiency of >90 %, in both centralized and decentralized treatments. The admixture biochar from plant residues and from cellulose-toilet paper proved to be

* Corresponding author.
E-mail address: fernanda.muniz@uni.lu (F.C. Muniz Sacco).

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a promising substitute for the mineral zeolite when mixed with sand to remove PCPs from GW and, therefore, a circular economy concept can be applied to this technology.

1. Introduction

Personal care products (PCP) and pharmaceuticals are among the micropollutants present in surface waters. They represent a potential risk to aquatic ecosystems due to the high quantities routinely released and their generally low biodegradability. They may be released partially or totally untreated from the main anthropogenic point sources of pollution which are urban conventional wastewater treatment plants (WWTPs), presently not designed to remove micropollutants (European Parliament and the Council of the European Union, 2013; Lyndall et al., 2017; Katsikaros and Chrysikopoulos, 2021).

The European Commission (EC) aimed to improve the protection of the aquatic environment by promoting the upgrade of the existing WWTPs with a post-treatment step. To do so, the EC has defined a Water Framework Directive (WFD) identifying compounds of concern through the so-called watch list (Loos et al., 2024) and requiring member states their mandatory monitoring (European Parliament and the Council of the European Union, 2013). The first watch list was launched in 2015 and then updated every two years. The last version of the watch list, the fourth one (Cortes et al., 2022), introduced the UV filter agents avobenzone (Chemical Abstracts Service-CAS 70356-09-1), octocrylene (CAS 6197-30-4) and oxybenzone (CAS 131-57-7) for the first time underlining the significance of monitoring PCPs.

This approach, which had been applied in a precautionary manner for the water protection following the aforementioned watch list since 2015, was recently introduced as a mandatory requirement by the EC in the revised Urban Wastewater Treatment Directive (European Commission, 2023). As such, agglomerations above 10,000 PE should achieve an 80 % minimum removal in relation to the load of the influent for at least 6 of the 12 selected compounds with the anti-inflammatory diclofenac (CAS N0 15307-86-5) among them.

While these above-mentioned compounds are currently regulated against, attention must be given to other chemicals that might become more prevalent in the future, such various organic chemicals which are included in PCPs and commonly used in daily human life, such as insect repellents, perfumes, soaps, lotions, and toothpaste. These substances are subsequently rinsed off in showers, bathtubs, and hand sinks, ultimately entering household wastewater streams.

Household wastewater can be divided into two major streams (Noutsopoulos et al., 2018): blackwater (BW) which is the wastewater from toilets, mainly composed of faeces and urine, and greywater (GW), wastewater from bathtubs, showers, hand basins, dishwashers, laundry machines and kitchen sinks (Christova-Boal et al., 1996; Ottoson and Stenström, 2003; Faggiano et al., 2022).

The GW fraction can be also separated into three fractions: light GW which is the wastewater from showers and bathtubs + hand sinks, medium GW, wastewater from showers and bathtubs + hand sinks + laundries, and heavy or dark GW which is composed of water from showers and bathtubs + hand sinks + laundries + kitchen sinks and dish washers. The dark GW is considered as a highly polluted fraction with higher organic carbon loads (biochemical oxygen demand-BOD and chemical oxygen demand-COD), suspended solids and surfactants when compared to other GW fractions (Friedler, 2004; Noutsopoulos et al., 2018).

PCPs are mainly present in the GW fraction and composed of foaming agents and volatile compounds which are not easily removed in conventional processes of wastewater treatments (Faggiano et al., 2022). Thus, additional effluent polishing, such as the use of activated carbon filtration, advanced oxidation processes, ozonation, etc., would be required for removing these substances.

Therefore, decentralized or on-site GW treatment could be a good alternative to decrease the concentration of some of these pollutants at the source (Santasmasas et al., 2013; Zraunig et al., 2019; Subramanian et al., 2020). Furthermore, potable water could be saved due to the reuse of the treated GW for non-drinking purposes.

In Luxembourg, the average daily potable water consumption in households is 132 L per person, which corresponds to 60 % of total consumption in the country. From this amount, only 4 % is used for drinking and cooking, while 27 % is used for flushing toilets which do not need such high-quality water (AGE, 2023; VDL-Luxembourg, n.d.). Therefore, by reusing the treated GW for toilet flushing, at least 27 % of potable water could be saved. For this, the implementation of demonstration projects for GW reuse in buildings for toilet flushing and irrigation is already part of the circular economy strategy in the country (Schosseler et al., 2021).

In this case, knowing that 27 % of potable water consumption is used for flushing toilets, which after being used is called BW fraction, we can consider that most of the households' wastewater, around 70 %, is called GW fraction. Therefore, utilising lightly polluted GW for flushing toilets would satisfy the purpose of its use and necessitate a more practical and cost-effective treatment (Friedler, 2004; Noutsopoulos et al., 2018).

Although the GW is less polluted (Eriksson et al., 2002) and has a lower load of faecal pathogenic organisms than the BW (Oron et al., 2014; Faggiano et al., 2022), several other pollutants are present in such streams such as the aforementioned PCPs, organic matter, nitrogen, phosphorus, sulphur, surfactants, heavy metals and others (Noutsopoulos et al., 2018). Therefore, the GW must be treated before being reused in households as the final quality required of the water will vary according to the purpose of reuse.

The efficiency of vertical-flow constructed wetlands (VFCWs) in removing pharmaceuticals from urban WWTPs' effluent in centralized treatments (Brunhoferova et al., 2021; Venditti et al., 2022) as well as surfactants and PCPs from GW by using decentralized on-site treatment (Ramprasad and Philip, 2016; Nguyen et al., 2019; Morandi et al., 2021) has already been demonstrated in laboratory and pilot scale studies.

Most studies of GW treatment with VFCWs highlight the main benefits as the removal of macropollutants and savings in drinking water due to reuse of treated water (Arden and Ma, 2018; Boano et al., 2020; Morandi et al., 2021). Although the removal of pharmaceuticals and PCPs from GW has been previously studied (Ramprasad and Philip, 2016; Zraunig et al., 2019), the possible reduction in the micropollutant concentration in urban WWTPs' influent due to their removal at the pollution source still needs to be explored, and this is discussed here.

The substitution of the conventional gravel and sand by other materials in VFCWs, through the use of zeolite (Du et al., 2020), lava sand (Morandi et al., 2021) and biochar from plant residues (Brunhoferova et al., 2022; El Barkaoui et al., 2023) have recently been tested to increase the efficiency of pollutant removal. Those studies have, however, not yet completely explored the use of alternative admixtures such as the biochar from cellulose-toilet paper recovered from wastewater.

In this context, the objectives of this work are: i) evaluate the PCP removal from GW using VFCWs filled with substrates composed of sand and the admixtures mineral zeolite, biochar from plant residues, and the alternative biochar from cellulose-toilet paper; ii) compare the results from i), with a focus on the pharmaceutical-anti-inflammatory diclofenac (DCF) and the insect repellent-N,N-diethyl-meta-toluamide (DEET), to those from other projects using VFCWs as a polishing step of WWTPs effluent; and iii) based on results from i) and ii), estimate the potential reduction in micropollutant concentration in urban WWTPs influent due to the on-site GW treatment.

2. Material and methods

2.1. Experimental design and operation

2.1.1. VFCW as a decentralized treatment for GW

The lab-scale investigation of the project titled 'Removal of personal care products from microbial processes in constructed wetlands for greywater recycling in sustainable buildings' (ReCare) simulates a decentralized GW treatment using a vertical-flow constructed wetland (VFCW). This was carried out with 6 columns which are called here lysimeters (L) and made of plexiglass (Europlex company, Belgium) with the dimensions of 29 cm (inner diameter), 115 cm (height) and 71 L (volume).

The lysimeters were filled with different substrates with drainage at the bottom composed of a 10 cm gravel layer (diameters coarse 4–8 mm and fine 2–8 mm), without an aeration system (neither active nor passive), as follows: L1: 85 % sand +15 % zeolite, L2: 95 % sand +5 % zeolite, L3: 85 % sand +15 % activated biochar from plant residues, L4: 95 % sand +5 % activated biochar from plant residues, L5: 85 % sand +15 % activated biochar from cellulose-toilet paper recovered from wastewater, and L6: 95 % sand +5 % activated biochar from cellulose-toilet paper recovered from wastewater (Fig. 1). The substrates had been previously mixed by the SME Klimafarmer (Germany). According to the given technical information, the diameters of the admixtures separately are: sand (Liapor UKS): 0–3 mm, zeolite (Zeogran K80): 0.5–1.0 mm, and biochar: 1–5 mm.

The production process of biochar from cellulose-toilet paper, recovered from wastewater through WWTP screenings, was preceded by dewatering, drying, and pelletizing. The pelletized material was then processed following the same steps employed to produce biochar from plant residues. As per the supplier's specifications, the process entailed carbonization at temperatures from 600 to 800° C for 2 to 6 h in a continuous mode. Afterwards, the biochar was biologically activated by anaerobic fermentation using nutrients and fermentative microorganisms at temperatures from 25 to 35° C for 2–4 weeks.

All lysimeters were planted with the same mix of plants: *Phragmites australis* and *Iris pseudacorus*, and automatically illuminated 8 h per day by UV lamps to simulate the daylight. *Iris pseudacorus* was chosen based on its proven good pollutant removal performance in the previous projects discussed in this study and for the system biodiversification.

The selection of *Phragmites australis* was based on the literature review, considering the removal of the PCP compounds selected in this study. Regardless of types of constructed wetlands, retention times or other factors, *Phragmites australis* presented the best removal performance (Al-Baldawi et al., 2021).

P. australis performance in removing pollutants, as suggested by Chen et al. (2016), is due to good oxygen transfer provided by its large root system along the soil depth which provides greater microorganism growth and biofilm development, and, consequently, enhancing the biodegradation process. This explains why *P. australis* was classified as efficient for the phytoremediation of agrochemicals, especially herbicides in studies of agricultural farms (Schröder et al., 2005) and removal of pharmaceuticals under hydroponic studies (Kotyza et al., 2010).

In this first part of the ReCare project, the lysimeters were fed simultaneously and intermittently with light synthetic greywater (LSGW) in a vertical-flow mode at a frequency of three times per day for 30 min, as described in the Fig. 1. The inflow rate of 7.2 L d^{-1} was pumped by using six-headed pumps (Watson Marlow, Belgium), automatically timer controlled. The Hydraulic Loading Rate (HLR) was 100 L d^{-1} m^{-2}. Dissolved oxygen sensors (PreSens, Germany) were also internally installed at different depths in all lysimeters, which allowed the instantaneous measurement of oxygen concentrations when needed.

Synthetic greywater was used in this study for several reasons. Firstly, GW composition varies with year seasons, people habits, countries, and other factors. Additionally, the chemical composition of PCPs is dependent on brands, countries, and so on. Therefore, the use synthetic GW ensures the reproducibility of the achieved results.

The LSGW recipe (adapted from Diaper et al., 2008; Hourlier et al., 2010; Ziemba et al., 2018) was composed of: sodium dodecyl sulfate ($C_{12}H_{25}NaO_4S$): 40 mg L^{-1}, glycerol ($C_3H_8O_3$): 159.0 μL L^{-1}, lactic acid ($C_3H_6O_3$): 83.0 μL L^{-1}, sodium bicarbonate ($NaHCO_3$): 70.0 mg L^{-1}, and sodium sulfate (Na_2SO_4): 50.0 mg L^{-1}.

The ingredients were diluted in tap water and stored in a tank of 220 L (Lely Center, Greece), which was continuously mixed and refrigerated at 4° C to avoid microorganism growth and ensure the stability of macropollutant concentration in the influent-LSGW. The stability of the

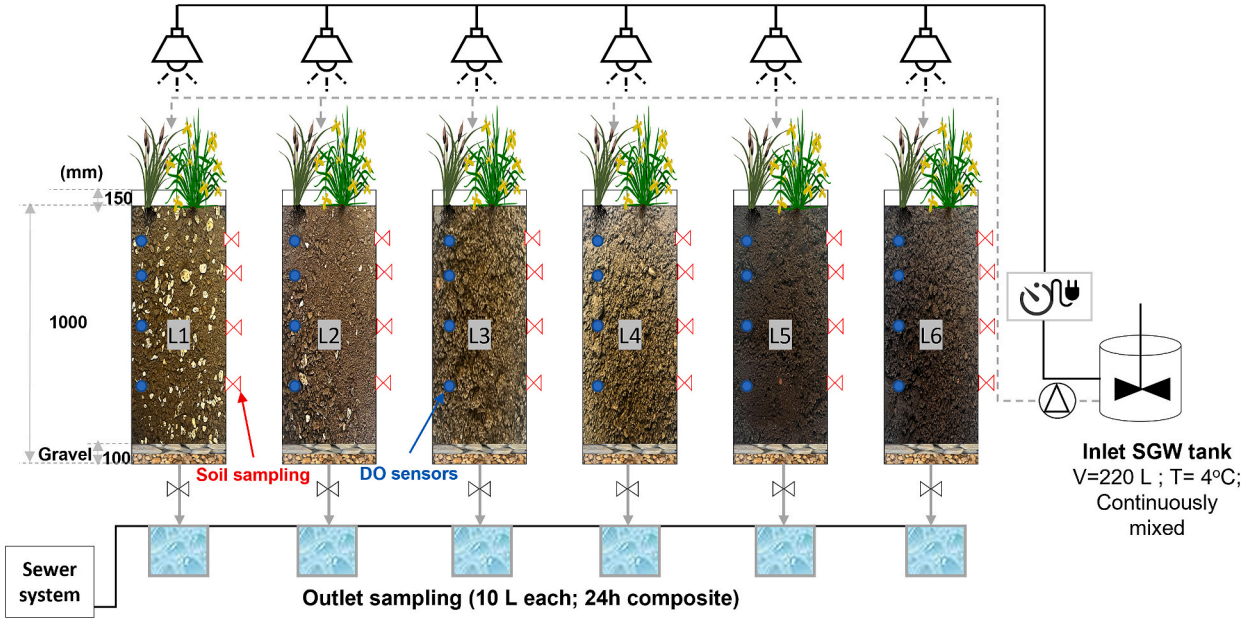


Fig. 1. Schematic diagram of the laboratory scale of the ReCare project. The influent direction to the lysimeters (L) is indicated by the grey dashed lines, and the effluent sampling is indicated by the grey solid lines (L1: 85 % sand +15 % zeolite, L2: 95 % sand +5 % zeolite, L3: 85 % sand +15 % activated biochar from plant residues, L4: 95 % sand +5 % activated biochar from plant residues, L5: 85 % sand +15 % activated biochar from cellulose-toilet paper recovered from wastewater, and L6: 95 % sand +5 % activated biochar from cellulose-toilet paper recovered from wastewater).

main parameters' concentration during one week was tested (Fig. A1, Supplementary information) and the mean values ± standard deviation (in mg L^{-1}), based on sampling campaigns ($n = 15$) were: chemical oxygen demand (COD): 488.10 ± 8.24, total organic carbon (TOC): 129.92 ± 1.76, inorganic carbon (IC): 26.44 ± 0.45, total nitrogen (TN): 4.80 ± 0.09 and nitrate (NO_3^--N): 4.79 ± 0.07.

After the lysimeters had achieved steady conditions (29 days of operation and when the values of macropollutants analyses were stable in the lysimeters' outlet) the influent-LSGW was spiked, in the concentration of 5 μg L^{-1} (Table 1) , with the selected micropollutant compounds (TechLab, France): Triclosan (TCS), Octylphenol (OP), Mono(2-ethylhexyl) phthalate (MEHP), Methylparaben (MeP), Ethylparaben (EtP), Butylparaben (BuP), Oxybenzone (OXY), Octocrylene (OC), Fluconazole (FCZ), Diclofenac (DCF), N,N-diethyl-meta-toluamide (DEET), Avobenzone (AVO), Nonylphenol (NP), Propylparaben (PrP), Miconazole (MIZ), Clotrimazole (CLOT).

The sampling campaigns and monitoring were based on established protocols, which are detailed in the analytical methods section, to follow and control the stability of macropollutants' concentration (COD, TOC, IC, TN, and NO_3^--N) in the influent-LSGW (Fig. A2, Supplementary information). The removal performance of the lysimeters, detailed in Section 2.3. Calculation of pollutant removal efficiency was based on an analysis of the composite sample of effluents collected over a 24-hour period.

The initial condition of the different substrates was externally analyzed to characterize the Brunauer–Emmett–Teller (BET) surface area (3P Instruments GmbH & Co. KG) and cations exchange capacity (CEC) (AGROLAB Agrar und Umwelt GmbH). This helps to evaluate possible changes in soil adsorption capacity within the time frame of the project due to the removal of pollutants from inlet-LSGW (Table B1, Supplementary information).

The design of the setting allows a comparison of the substrates under controlled conditions. Thus the growth of microrganisms and their function can be evaluated without interference of other factors (i.e. season, indigenous bacteria etc).

The number of sampling campaigns (n) considered for the calculation of the average removal efficiency in this paper was 15 for macropollutants and 7 for micropollutants. The operation period considered was 108 days (after reaching steady conditions), in which 777.6 L of water were treated per lysimeter.

2.1.2. VFCW as a centralized treatment for urban WWTP effluent

For the further comparative analyses, data from previous projects using VFCWs to remove pharmaceuticals from effluent of centralized urban WWTPs, as a polishing step, were compared to those from the ReCare project in which VFCWs have been used for the PCP removal from GW, as a decentralized treatment.

For the comparative data analysis, the following common information was used: vertical-flow mode operation of the CWs; substrates employed in the VFCWs: sand mixed with the admixtures- i) mineral zeolite and ii) biochar, ii-a) from plant residues and ii-b) from cellulose-toilet paper recovered from wastewater; mix of plants: *Phragmites australis* and *Iris pseudacorus*; as well as the target compounds, which in this case were: diclofenac (DCF) and DEET.

One of the previous studies compared in this paper is the EmiSûre project, funded by the Interreg Greater Region. Its laboratory-scale design and operation closely resembled those employed in the current ReCare project, described in Section 2.1.1 VFCW as a decentralized treatment for GW, except for the type of treated water. In this project, synthetic wastewater was used to mimic treated effluent from urban WWTPs.

The operation time in the EmiSûre project was 357 days, during which 2797 L of water were treated. Mineral zeolite and biochar from plant residues were tested as admixtures mixed with sand to improve the removal performance of 27 targeted emerging contaminants using VFCWs (Venditti et al., 2022).

Another comparative project is the North-West European Interreg project WOW! (Wider business Opportunities for raw materials from Wastewater – NWE project number 619). In the supplementary project to WOW! – called WOW! Capitalisation, the biochar from cellulose-toilet paper recovered from wastewater, after being biologically activated, was compared to biochar from plant residues, as admixtures mixed with sand, to enhance micropollutant removal in VFCWs.

In the WOW! Capitalisation project, the laboratory setup was designed in mesocosms scale with 20 L reactors, filled with the tested substrates, containing a 10 cm drainage material at the bottom and without artificial aeration system. In this case, real treated effluent from a local urban WWTP was pumped at HLR of 0.023 m^3 d^{-1} m^{-2} of irrigated surface for 30 min and 2 times per day (Venditti et al., 2023). The test lasted 78 days and 148.5 L of wastewater were treated per mesocosm.

2.2. Analytical methods

In the current study, the water quality parameters were monitored by time series analyses performed without replicates (Sefer et al., 2016) and only were measured in duplicates or triplicates when unexpected values were obtained due to sampling errors or others.

The main parameters were measured weekly in fresh samples of influent-LSGW and effluents-L1, L2, L3, L4, L5 and L6: for COD and

Table 1
List of the target Pharmaceuticals and PCP compounds which are mainly present in the greywater fraction.

Category	Group	Sub-group	Compound	CAS number	Abbreviation
Pharmaceuticals	Anti-inflammatories		Diclofenac	15307-86-5	DCF
	Antimycotics		Clotrimazole	23593-75-1	CLOT
			Fluconazole	86386-73-4	FCZ
			Miconazole	22916-47-8	MIZ
	Antiseptics		Triclosan	3380-34-5	TCS
	Insect repellent		N,N-diethyl-meta-toluamide or diethyltoluamide	134-62-3	DEET
PCPs	Preservatives	Parabens	Methylparaben	99-76-3	MeP
			Ethylparaben	120-47-8	EtP
			Propylparaben	94-13-3	PrP
			Butylparaben	94-26-8	BuP
		Phthalates	Di(2-ethylhexyl) phthalate (metabolites):	117-81-7	DEHP
			Mono(2-ethylhexyl) phthalate	4376-20-9	MEHP
			Mono(2-ethyl-5-hydroxyhexyl) phthalate	40321-99-1	5OH-MEHP
			Mono(2-ethyl-5-oxohexyl) phthalate	40321-98-0	5oxo-MEHP
	Surfactants	Non-ionic surfactants	Nonylphenol	84852-15-3	NP
			Octylphenol	1806-26-4	OP
	UV-filters		Avobenzone	70356-09-1	AVO
			Octocrylene	6197-30-4	OC
			Oxybenzone	131-57-7	OXY

NO_3^--N Hach Lange test cuvettes (LCK 1414, 314, 514 and 339) were used following the manufacturer's protocol (HACH, n.d.). However, due to low concentration of macropollutants in the effluents, analyses of TOC and TN were also performed using TOC/TN analyzer equipment (SHIMADZU; model TOC-L CPN).

This model of equipment utilizes the direct or Non Purgeable Organic Carbon (NPOC method) in which the TOC is directly determined as NPOC (TOC = NPOC). The samples are acidified using a mineral acid (for instance HCL) to a pH < 2, to completely convert carbonates and hydrogen carbonates into carbon dioxide, which will be removed from the sample via a sparge gas; then the direct NPOC is measured via oxidation of the remaining organic carbon to CO_2, and finally, the NDIR detection (Shimadzu, n.d.).

The high sensitivity of TOC analysis (Aguilar-Torrejón et al., 2023) allows the replacement of COD in urban wastewater analysis. Their relation can be represented by the following formulas: COD = 49.2 + 3.00 * TOC for urban wastewater influent and COD = 7.25 + 2.99 * TOC for its effluent (Dubber and Gray, 2010).

Moreover, other measurements such as electrical conductivity (EC) and pH were taken with conventional WTW devices (Xylem, UK) to better understand the behavior of the lysimeters within the time frame of the project (Figs. C1 and C2, Supplementary information).

Analysis of pharmaceuticals and PCPs was performed, and for this, the samples were filtered through a 0.45 μm pore size glass fiber filter, frozen and prepared for the external analysis of the target micropollutants (Table 1) at the Luxembourg Institute of Science and Technology-LIST.

Micropollutants were selected according to the following criteria (Table E1, Supplementary information): i) those compounds included in personal care products widely used in daily human life. This includes toothpaste, shampoo and cosmetics that are present in considerable quantities and which contain preservatives such as parabens; ii) those known to be persistent and potentially toxic for the aquatic environment, such as nonylphenol and UV-filters, and others even if not routinely used, like insect repellents (DEET) and anti-inflammatory cream (diclofenac). Compounds meeting the criteria but for which a robust analytical detection method is not available were further excluded.

The quantification of target pharmaceuticals and PCPs was performed by Liquid Chromatography and Tandem Mass Spectrometry (LC-MS/MS) on an Infinity II U-HPLC coupled to 6495 triple-quadrupole MS (Agilent). The MS was operated in positive and negative Electrospray Ionisation (ESI) mode. The analytical column was a Phenomenex Kinetex Biphenyl 150 × 2.1 mm (2.6 μm particle size). The mobile phases used in positive mode were deionized (DI) water and methanol, both buffered with 0.1 % formic acid, and 5 mM ammonium acetate and methanol in negative mode. The flow rate was 300 μL min^{-1} and the column temperature was 40 °C.

The injection volume was 100 μL, allowing the direct analysis of greywater samples without prior preconcentration. The quantification of target compounds was obtained by matrix-matched internal calibration, based on standards and quality check samples prepared in synthetic greywater. The limit of quantification (LOQ) of each compound is detailed in Table 2.

2.3. Calculation of pollutant removal efficiency

The calculation of the removal efficiencies (RE) for macro and micropollutants, in percentage (%), was based on the concentration values (mass divided by the volume) in influent samples (C_0) and in a composite sample of effluents collected over a 24-hour period (C), applying the following formula: RE (%) = [(C_0-C)]/[C_0*100].

For the calculation of RE (%) for the target micropollutants compounds, a conservative approach was adopted in line with the literature studies (Schulze-Hennings and Pinnekamp, 2013; Bourgin et al., 2018). Compounds detected below LOQ are assumed to be present at their respective LOQ equal to the maximum concentration in the water sample. In that way, a minimum removal efficiency value is calculated accordingly. This implies that higher removal rates can be expected for those compounds having higher LOQ.

3. Results and discussion

3.1. VFCW as a decentralized treatment for GW (ReCare project)

3.1.1. Macropollutant removal

The treated GW must eventually fulfil the water quality standards for the purpose of reuse, and therefore, in the ReCare project the macropollutant removal was also monitored.

The efficiencies of the VFCWs of removing the main macropollutants

Table 2
Spike test of pharmaceutical and personal care products (PPCPs): average concentration of main compounds and standard deviation (in ng L^{-1}) in the influent of the light synthetic greywater (LSGW) and the composite sample of lysimeters effluents collected over a 24-hour period (108 days of operation and 777.6 L of treated water per column; n = sampling campaigns). The limit of quantification (LOQ) is also presented.

Compounds	Limit of quantification (LOQ) - ng L^{-1}	Mean values ± std. dev. (ng/L)						
		Influent	Effluent					
		n = 11	n = 7					
		LSGW	L1	L2	L3	L4	L5	L6
TCS	100	3261 ± 1881	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
OP	100	2016 ± 1764	<LOQ	<LOQ	<LOQ	167 ± 92	<LOQ	<LOQ
NP	100	4473 ± 1533	123 ± 43	102 ± 3	112 ± 16	323 ± 147	100 ± 0	119 ± 45
MEHP	25	6759 ± 1974	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
5-OH-MEHP	25	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
5-oxo-MEHP	25	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
MeP	100	6481 ± 2087	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
EtP	25	4298 ± 489	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BuP	25	4546 ± 271	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
OXY	10	3321 ± 231	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	10 ± 1
OC	100	1530 ± 2078	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
MIZ	25	536 ± 407	41 ± 11	32 ± 8	33 ± 8	33 ± 8	32 ± 8	32 ± 8
FCZ	10	5171 ± 991	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DCF	10	3877 ± 464	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DEET	10	5250 ± 457	<LOQ	<LOQ	<LOQ	191 ± 409	<LOQ	<LOQ
CLOT	25	4256 ± 3819	43 ± 27	25 ± 6	<LOQ	<LOQ	<LOQ	<LOQ
AVO	100	2375 ± 2571	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PrP	25	7432 ± 3583	157 ± 68	251 ± 201	171 ± 34	167 ± 14	149 ± 76	196 ± 133

from the inlet-LSGW within the analyzed period are presented in the Fig. 2, and TOC was removed by around 100 % in all lysimeters. In the case of NO_3^--N, which was the main fraction of the TN, based on the time series sampling (n = 15), a removal efficiency of at least 73 % was reached (L3 at 108 days). The overall average removal efficiencies of NO_3^--N with standard variation were L1: 94 ± 4 %, L2: 96 ± 4 %, L3: 91 ± 5 %, L4: 89 ± 7 %, L5: 97 ± 2 % and L6: 85 ± 5 %.

The average concentration values of COD, TOC, TN and NO_3^--N in the effluent of the lysimeters with their respective standard deviation are shown in the Table D1, Supplementary information. The average values of COD varied from a minimum value of 5.33 ± 1.02 mg L^{-1} (L2) up to 9.29 ± 3.83 mg L^{-1} (L3); and for NO_3^--N, the values varied from 0.15 ± 0.08 mg L^{-1} (L5) up to 0.74 ± 0.15 mg L^{-1} (L6).

The COD removal from inlet LSGW, regardless of the type of substrate, provided higher effluent quality with lower concentrations values than the ones obtained in GW treatment using CW from the literature review (Ramprasad and Philip, 2016; Arden and Ma, 2018; Boano et al., 2020; Morandi et al., 2021), which highlights the promising application of the studied substrates in GW treatment aiming at further water reusing. The good performance in COD removal is mainly related to the known aerobic condition within VFCWs.

The same good performance was achieved for the NO_3^--N removal. Due to the aerobic conditions in a VFCW, nitrate removal is probably not caused by denitrification but by plant uptake since plants assimilate nitrate as a preferred nitrogen compound.

The measurement of electrical conductivity (EC) allowed the monitoring of the behavior of the lysimeters within the analyzed period of 108 days (Fig. C1, Supplementary information). The average value of EC in the effluent lysimeters (882 µS cm^{-1}) was higher than the influent LSGW (484 µS cm^{-1}). This may be related to the leaching of salts from substrates due to sorption processes when removing minerals from the inlet LSGW. It could be also attributed to the leaching of soluble salts and free cations as it was already observed in the soil characterization (Table B1, Supplementary information), in which the base saturation (%) was higher than 100 % for all analyzed substrates (Tomašić et al., 2013).

It is important to mention that for water reuse additional disinfection processes are required to achieve water quality standards (The European Parliament and the Council, 2020). However, they were not part of the scope of this study.

3.1.2. *Micropollutant removal*

The removal efficiencies for the target pharmaceuticals and PCP compounds using VFCWs for GW treatment in the ReCare project are presented in the Fig. 3. The results are very consistent and present very low standard variation. The lysimeters obtained similar performance of

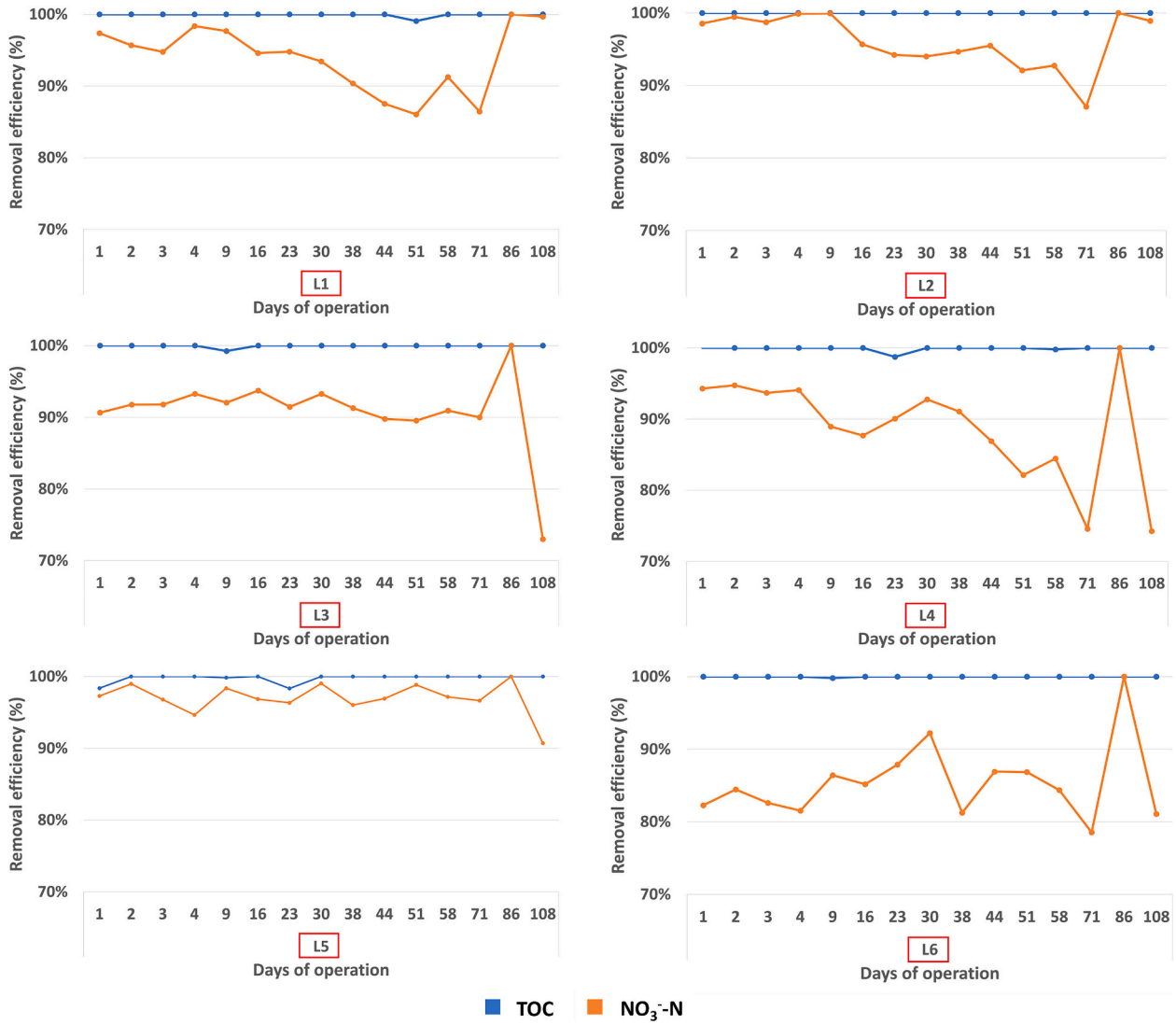
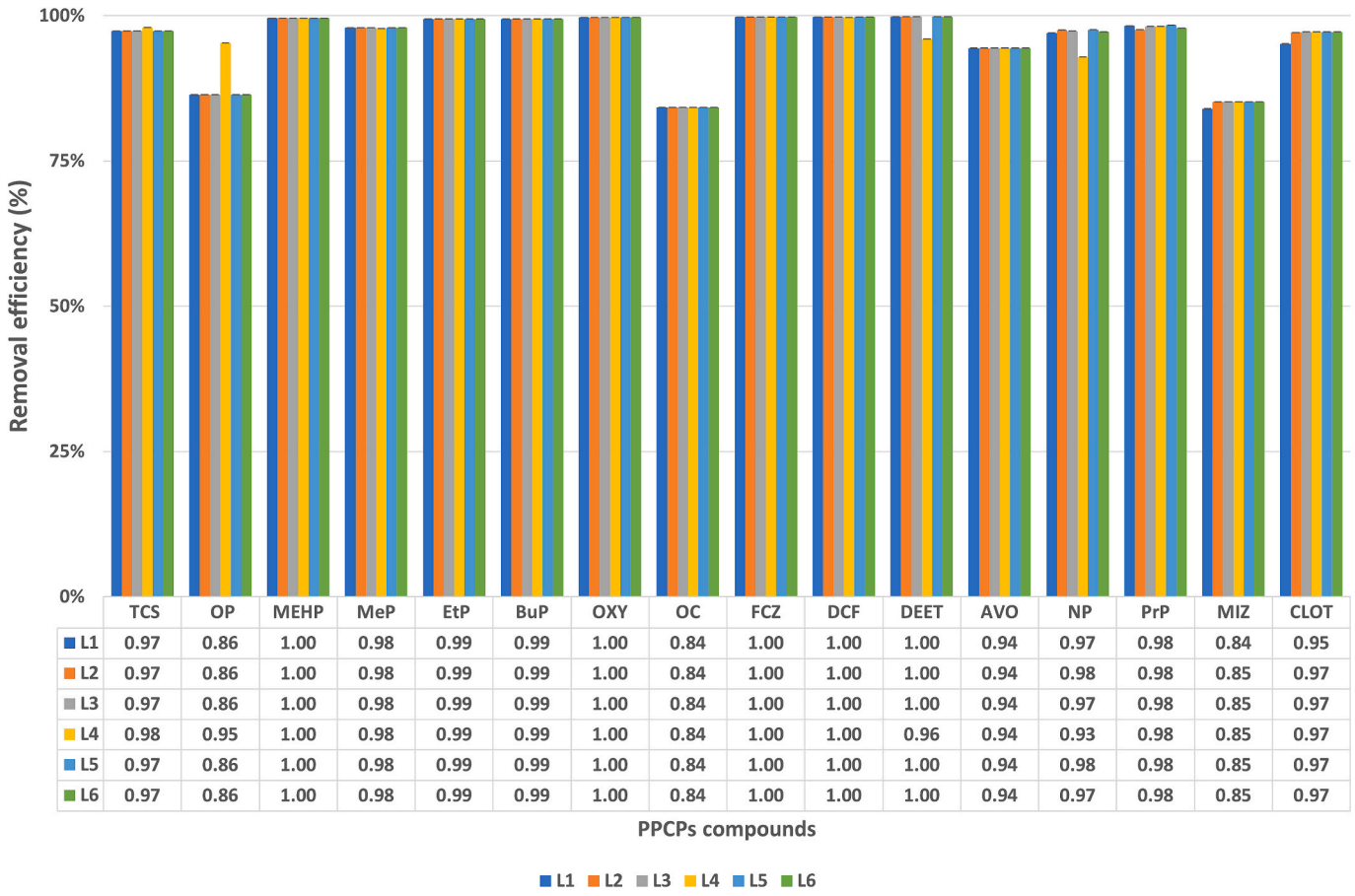


Fig. 2. Macropollutant removal efficiency (%) from light synthetic grey water (LSGW) in the composite sample of lysimeters effluents (L1-L6) collected over a 24-hour period. ReCare project: sampling campaigns (n = 15), duration of 108 days in which 777.6 L of water were treated per lysimeter.



	TCS	OP	MEHP	MeP	EtP	BuP	OXY	OC	FCZ	DCF	DEET	AVO	NP	PrP	MIZ	CLOT
L1	0.97	0.86	1.00	0.98	0.99	0.99	1.00	0.84	1.00	1.00	1.00	0.94	0.97	0.98	0.84	0.95
L2	0.97	0.86	1.00	0.98	0.99	0.99	1.00	0.84	1.00	1.00	1.00	0.94	0.98	0.98	0.85	0.97
L3	0.97	0.86	1.00	0.98	0.99	0.99	1.00	0.84	1.00	1.00	1.00	0.94	0.97	0.98	0.85	0.97
L4	0.98	0.95	1.00	0.98	0.99	0.99	1.00	0.84	1.00	1.00	0.96	0.94	0.93	0.98	0.85	0.97
L5	0.97	0.86	1.00	0.98	0.99	0.99	1.00	0.84	1.00	1.00	1.00	0.94	0.98	0.98	0.85	0.97
L6	0.97	0.86	1.00	0.98	0.99	0.99	1.00	0.84	1.00	1.00	1.00	0.94	0.97	0.98	0.85	0.97

Fig. 3. Removal efficiency (%) of pharmaceuticals and personal care products (PCPs) from light synthetic grey water (LSGW) in the composite sample of lysimeters effluents collected over a 24-hour period: average values in percentage. Error bars indicate the deviation in the performed analyses between the sampling campaigns ($n = 7$). Abbreviations: Triclosan (TCS), Octylphenol (OP), Mono(2-ethylhexyl) phthalate (MEHP), Methylparaben (MeP), Ethylparaben (EtP), Butylparaben (BuP), Oxybenzone (OXY), Octocrylene (OC), Fluconazole (FCZ), Diclofenac (DCF), N,N-diethyl-meta-toluamide (DEET), Avobenzone (AVO), Nonylphenol (NP), Propylparaben (PrP), Miconazole (MIZ), Clotrimazole (CLOT). When the concentration is below LOQ, the given % efficiency corresponds to the minimum efficiency which was calculated using the compound's LOQ.

removal for the majority of the micropollutant compounds, with average efficiencies from 94 % up to 99 %.

This was already expected, based on the initial characterization of the substrates (S1, S2, S3, S4, S5 and S6) (Table B1, Supplementary information), in which their values of potential cation exchange capacity were very similar. Therefore, the main mechanisms of pollutant removal were favoured, such as soil adsorption, plant uptake and biodegradation.

Ramprasad and Philip (2016) obtained similar results testing VFCWs to remove other PCP compounds from GW, such as trimethyl amine (TMA): 98 %, propylene glycol (PG): 95 % and sodium dodecyl sulphate (SDS): 89 %, proving the promising application of this technology for the removal of these micropollutants at the source of pollution.

Lysimeter L4 was an exception because the micropollutant removal efficiency was different than the other lysimeters for some compounds, e.g., the average removal of octylphenol (OP) obtained by L4 was 95 %, while for other lysimeters only 86 %. For the latter, outliers may be related to analytical uncertainties or substrate sorption processes that can be better understood with longer operation of the system.

Among the target micropollutants, the lowest average removal efficiencies were obtained for the UV-filter compound octocrylene (OC: 84 %), antimycotic-miconazole (MIZ: 85 %) and surfactant-octylphenol (OP: 88 %). These results may be partially attributed to their low absolute concentrations in influent samples and their high variability (expressed by the standard deviation) when compared to other compounds. One possible explanation for this could be the degradation of the analyzed compounds in the inlet tank during batch feeding. Other factors such as the solubility of the analyte in the stock solution or of the stock solution in LSGW may also play a significant role.

Lastly, analytical methods often present difficulties in their quantification (Filho et al., 2024), expressed with higher LOQ for both OC and OP. As such, and because a conservative approach has been adopted using LOQ as equal to the maximum concentration possible in the water sample, the average removal efficiencies of OC, MIZ and OP should be cautiously interpreted and considered as the minimum possible values.

In the Table 2, the average concentration of micropollutant compounds (in ng L^{-1}) in the influent-LSGW was compared to the composite sample of lysimeters effluents collected over a 24-hour period. For some of them, despite a removal efficiency of below 90 %, such as OC, the effluent concentration was still below the limit of quantification (LOQ). This excludes the preservative-Propylparaben (PrP), which in spite of its high removal efficiency, had concentrations in the lysimeters-effluent which were always higher than the LOQ.

Therefore, considering that the substrates of ReCare presented similar removal efficiencies for the selected pharmaceuticals and PCPs when treating LSGW, one of the main selection criteria to upscale the technology could be the sustainability aspect. However, for this, more and targeted studies over the years must be conducted to evaluate the longevity and assess the life cycle of the proposed substrates.

3.2. Comparative analyses of VFCWs: decentralized and centralized treatments

As detailed in the Section 2.1.2 VFCW as a centralized treatment for urban WWTP effluent, data analyses were performed to compare results from previous projects. These studies using VFCWs as a polishing step of effluents in centralized urban WWTPs were compared with the ReCare project in which VFCWs have been used as decentralized on-site GW treatment to remove the target micropollutant compounds diclofenac (DCF) and DEET.

Concentrations of DCF and DEET in the influent and effluent were studied within the wastewater matrices LSGW-light synthetic greywater, SEWWT-synthetic treated effluent from urban WWTPs, and REWWT-real treated effluent from urban WWTPs. These concentrations are available in Table 3. For this, VFCWs filled with different admixtures and mixed with sand were compared, such as zeolite and biochar from plant residues and from cellulose-toilet paper. The respective removal efficiencies in the tested scenarios are shown in Fig. 4. The calculated efficiency can be considered as the minimum possible when effluent concentrations are found below LOQ (10 ng L^{-1} for both DCF and DEET).

Overall, the VFCW effluents (Table 3), when treating LSGW, presented stably (with low standard deviations) concentrations for both, DCF and DEET, and always lower than the LOQ for most of the analyzed substrates. The one exception was the one with 5 % activated biochar from plant residues +95 % sand, which presented effluent with high concentrations for DEET and with high standard deviation (191 ± 409 ng L^{-1}). This may be related to analytical errors or substrate adsorption capacity, and further investigations will be performed.

As expected, synthetic wastewaters offer more stable conditions to the experimental studies than real ones, due to the higher variability of pollutant daily loads in real wastewater. However, when comparing only the two types of synthetic wastewaters, LSGW ($n = 7$) and SEWWTP ($n = 19$), the box-plots for the distribution of the obtained removal efficiencies for the target micropollutants throughout the campaigns (n) presented lower values heterogeneity for LSGW (Fig. 4).

The possible reasons for this can be the higher concentration of COD in the inlet of LSGW (488 mg L^{-1}) compared to the one in the SEWWTP (60 mg L^{-1}), which may offer better conditions for microorganism growth, and then, improve the nutrients taken up by plants. Another possible explanation for this can be the duration of the experiments, which was higher for the case of the SEWWTP (357 days of operation). Therefore, further assessment of the sorption processes of the different substrates must be investigated due to possible saturation of soil cation exchange capacity after removing pollutants from wastewater for a long period.

3.2.1. VFCWs with zeolite and biochar from plant residues treating LSGW and SEWWT

Biochar is mainly produced from biomass materials, such as agricultural residues, plant residues, animal and human waste, etc., and used to improve the soil quality and biological processes in CWs (Ji et al., 2022). In this section, its performance in removing the target pollutants DCF and DEET from wastewater is compared to the performance of the natural mineral zeolite, which comes from the natural environment.

The comparison of the lab-scale VFCWs with the substrates, i) 15 % zeolite +85 % sand and ii) 15 % activated biochar from plant residues +85 % sand, in the scenario 1- Fig. 4, shows that both substrates presented very close minimum mean removal efficiencies for DCF (99.8 and 99.9 %) regardless of the type of synthetic wastewater, LSGW and SEWWT, with effluent values lower than LOQ (Table 3). Concerning DEET removal, very close removal efficiencies in the substrates were achieved, >99 % for both types of water (Fig. 4), with effluent values a little higher than LOQ in SEWWT (14 ± 13 ng L^{-1}) (Table 3).

There was a good performance of using biochar substrate in CWs to remove pharmaceuticals and PCPs from wastewater, achieving a removal efficiency of >99 %. This is mainly attributed to two different biochar functions: i) promotion of development and growth of microorganisms, and thus, enhancing of biodegradation processes, and ii) enhancement of the adsorption process due to the increase of cation exchange capacity. For this, the biochar has recently been used in CWs to improve the efficiency of pollutant removal (Hu et al., 2022; El Barkaoui et al., 2023).

Therefore, activated biochar admixtures, produced in a circular economy approach, could be more sustainable alternatives to be used in CWs compared to the natural mineral material zeolite.

3.2.2. VFCWs with biochar from plant residues and biochar from cellulose-toilet paper treating LSGW and REWWT

Biochar is of key interest in increasing the sustainability of VFCWs. In previous comparisons, 15 % of 15 % of zeolite could be replaced by 15 % of activated biochar from plant residues. Scenario 2 in Fig. 4 compares the activated biochar from plant residues to the activated biochar from cellulose-toilet paper, at a 5 % fraction completed with 95 % of sand. The innovative biochar from cellulose-toilet paper, recovered from wastewater, presented good efficiencies for the removal of pharmaceuticals in mesocosms tests (Venditti et al., 2023).

Table 3
Concentration of DCF and DEET in the influent samples and the composite sample of effluents collected over a 24-hour period using VFCWs with different substrates and types of wastewaters (RLGW: real light greywater; REWWT: real effluent of wastewater treatment; LSGW: light synthetic greywater; SEWWT: synthetic effluent of wastewater treatment). The mean and standard deviation values are given in ng L^{-1} and n is the number of sampling campaigns performed in the analysis. The limit of quantification (LOQ) is also presented.

Compounds	Limit of quantification (LOQ) - ng L^{-1}	Effluent	Influent	Effluent	Influent-VFCWs		
		RLGW	REWWT	REWWT	LSGW	REWWT	SEWWT
		n = 1	n = 4	n = 4	n = 11	n = 4	n = 19
DCF	10	174	1380 ± 870	823 ± 330	3877 ± 464	823 ± 330	4596 ± 970
DEET	10	142	793 ± 643	131 ± 69	5250 ± 457	131 ± 69	2490 ± 532

Compounds	Effluent-VFCWs (Laboratory scale)							
	15% zeolite + 85% sand		15% activated biochar from plant residues + 85% sand		5% activated biochar from plant residues + 95% sand		5% activated biochar from cellulose-toilet paper + 95% sand	
	LSGW	SEWWT	LSGW	SEWWT	LSGW	REWWT	LSGW	REWWT
	n = 7	n = 19	n = 7	n = 19	n = 7	n = 5	n = 7	n = 5
DCF	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	37 ± 57
DEET	<LOQ	14 ± 13	<LOQ	16 ± 12	191 ± 409	12 ± 10	<LOQ	56 ± 84

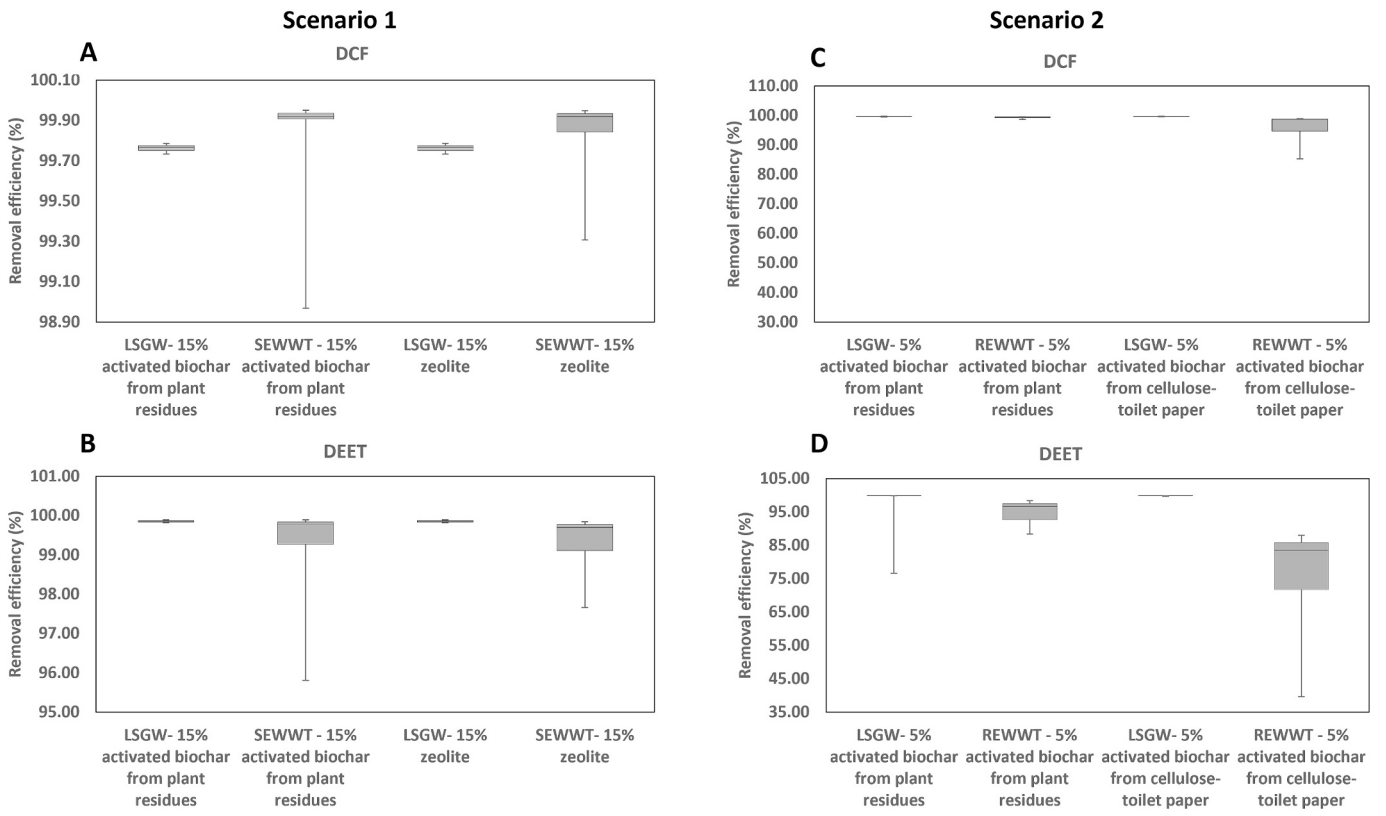


Fig. 4. Removal efficiency of DCF and DEET: scenario1: activated biochar from plant residues and zeolite treating LSGW (n = 7) and SEWWT ($n = 19$) for A (DCF) and B (DEET); scenario2: activated biochar from plant residues and activated biochar from cellulose-toilet paper treating LSGW (n = 7) and REWWT ($n = 5$) for C (DCF) and D (DEET). LSGW (light synthetic greywater), SEWWT (synthetic effluent of wastewater treatment), REWWT (real effluent of wastewater treatment). When the concentration is below LOQ, the given % efficiency corresponds to the minimum efficiency which was calculated using the compound's LOQ.

In this case, the REWWT was compared to the LSGW. The LSGW presented similar removal efficiencies for both types of substrates (mean values of 99.7 % and 98.5 %, DCF and DEET, respectively), as shown in the Fig. 4, which were a little higher and with lower value heterogeneity than REWWT (mean values of 97.4 % and 88.0 %, respectively). The activated biochar from cellulose-toilet paper when treating REWWT, besides higher value heterogeneity (Fig. 4), presented effluent values above the LOQ, for both micropollutants (DCF: 37 ± 57 ng L^{-1} and DEET: 56 ± 84 ng L^{-1}) (Table 3).

To summarize, the substrates: i) 5 % activated biochar from plant residues +95 % sand and ii) 5 % activated biochar from cellulose-toilet paper +95 % sand presented very similar removal efficiencies for DFC and DEET in lab-scale VFCWs treating LSGW. For REWWT, substrates with biochar from plant residues presented better results than those of cellulose-toilet paper.

Besides the biochar production processes, a good quality biochar is obtained from sources which are richer in carbon and low content of mineral matter. These provide large pore volume and high specific surface area to effectively remove pollutants from wastewater, as well as the type and operation mode of the CWs and the choice of plants contribute to the overall removal performance (El Barkaoui et al., 2023).

3.3. VFCWs as a decentralized GW treatment for the decrease of micropollutant concentration in urban WWTP influent

The average removal efficiencies for DCF and DEET in the case-study WWTP considered in this study using the conventional mechanical and biological processes were 45.6 % and 89.6 % respectively ($n = 4$). Moreover, the effluent concentrations were higher than LOQ for both micropollutants, DFC: 823 ± 330 ng L^{-1} and DEET: 131 ± 69 ng L^{-1} (Table 3). This indicates the need of a post-treatment step when 80 % removal must be achieved.

Results of micropollutant removal efficiencies obtained in the ReCare project when treating the LSGW were mean values of 99.7 % and 99.2 %, for both, DCF and DEET respectively, regardless of the type of substrate. Considering the concentration of these micropollutants in RLGW (174 and 142 ng L^{-1}, respectively), a rough estimation showed that around 13 % and 18 % of the concentration of the DCF and DEET, respectively, could be reduced from the inlet of our case-study WWTP using an on-site LGW treatment (Table 4). This is in comparison to a usual concentration of 1380 ± 870 and 793 ± 643 ng L^{-1}, DCF and DEET, respectively.

This highlights that the LGW is not the major source of these two pollutants in the influent of WWTP. Consequently, other household wastewater fractions should be investigated, such as blackwater for the case of DCF, mainly urine fraction, and other sources for DEET, in which the concentration is higher than the one allowed in insect repellent products for human skin application.

In a similar study, Revitt et al. (2011) demonstrated the benefit of a decentralized GW treatment in reducing loads of some heavy metals, such as benzene, nickel (Ni) and lead (Pb) and the hazardous substances-cadmium (Cd) and 4-nonylphenol (4-NP), in centralized WWTPs sewage sludge, which could then help to meet the European Directive 86/278/EEC for agricultural uses as biosolids for soil conditioning (European Commission, 1986).

In this context, further analyses are highly recommended, especially concerning the properties of the target PCPs. Other PCP compounds studied in the ReCare project, listed in the Table 1, varied in their removal efficiencies from a minimum 84.2 % to a maximum 99.8 %. Recognizing that these pollutants are mainly present in the GW fraction because they are part of our skincare daily routine, e.g., the UV filters, VFCWs as a decentralized GW treatment for their concentration

Table 4
Estimation of the decrease of the target micropollutants DCF and DEET in the inlet WWTP using an on-site GW treatment. RLGW (real light greywater), LSGW (light synthetic greywater). The mean and standard deviation values are given in ng L^{-1} and n is the number of sampling campaigns performed in the analysis. When the concentration is below LOQ, the given % efficiency corresponds to the minimum efficiency which was calculated using the compound's LOQ.

	n	Mean values				
		DFC	Std. dev.	DEET	Std. dev.	Unit
Concentration of target micropollutants in RLGW	1	174	–	142	–	ng L^{-1}
Concentration of target micropollutants in municipal WWTP	4	1381	870	793	643	ng L^{-1}
Participation of target micropollutants from RLGW in municipal WWTP	–	12.6	–	17.97	–	%
Removal efficiency of target micropollutants from LSGW-ReCare project	7	99.8	0.01	99.2	1.43	%
Estimated decrease of target micropollutants concentration in WWTP when treating LGW (on-site)	–	12.6	–	17.8	–	%

reduction in urban WWWT influent might be more important. Therefore, this warrants further investigations.

4. Conclusions

VFCWs can remove the investigated micropollutants very well, usually with an efficiency of >90 % if the filter materials are modified by adding supporting admixtures. This is possible both for greywater and as polishing step for micropollutant removal from the effluent of urban WWTPs. The biochar from plant residues and from cellulose-toilet paper have proven to be promising to substitute the mineral zeolite and therefore, a circular economy concept could be also applied to this technology.

Additional studies on the main pollutants' removal mechanisms and properties of PCP compounds are highly recommended. These studies could support the choice of most appropriate substrates for the removal of target PCP compounds, as well as the expected longevity of this technology based on the saturation of soil capacity, which implies soil sorption processes.

This opens up a wide range of possibilities for the treated greywater reuse, which includes toilet flushing, irrigation purposes in green urban areas and others. Nevertheless, further questions need to be clarified in long-term tests with greywater to ensure the safety of its reuse, e.g., legal framework for the decentralized treatment and its reuse. Furthermore, solutions must be found, such as how to deal with households which are not prepared yet for the wastewater separation. This may imply in some additional costs, and aspects like responsibility for installations, transition from centralized to decentralized solutions.

CRediT authorship contribution statement

Fernanda Cristina Muniz Sacco: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Silvia Venditti:** Writing – review & editing, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Paul Wilmes:** Writing – review & editing. **Heidrun Steinmetz:** Writing – review & editing. **Joachim Hansen:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.174310.

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