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Upgrading constructed wetlands using upstream (advanced) oxidation technology to improve the removal of micropollutants and reduce the ecotoxicological risks

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ABSTRACT

This study shows research pathways from the Interreg-EmiSûre project, where several admixtures were studied as substrates for constructed wetlands (CWs), to the Interreg-CoMinGreat project, which proposed a pre-oxidation step to improve the removal of micropollutants, extend CW lifetime, and reduce the surface area. In EmiSûre, CWs (15% of activated carbon and 85% of sand) were installed in Echternach wastewater treatment plant (WWTP) (Luxembourg) achieving 80% removal of most the target compounds. Then, the configuration of these CWs was combined with photo-Fenton in Bliesen WWTP (Germany) at a natural pH; dosing 1.5 mg L^{-1} of iron (Fe^{3+}) (citric acid as the chelating agent); and 20 mg L^{-1} of H_2O_2. Also, UV/H_2O_2 treatment was tested to avoid iron dosage. Diclofenac present in the treated effluent of Bliesen is a key pollutant that poses medium ecotoxicological risks for aquatic life. Its removal in CWs reaches 88%, however, it is known to be very restrictive during the adsorption process. With the pre-oxidation, 52% of diclofenac is removed, resulting in a lower load to be treated by the CWs; therefore, reducing considerably the required surface area. Implementing UV/H_2O_2 treatment as the first step could reduce the CW surface area per PE to 0.19 m^2.

Key words: advanced oxidation processes, constructed wetlands, land reduction, process integration, wetland upgrading

HIGHLIGHTS

- CWs alone significantly reduced micropollutants, achieving a target of 80%.
- Diclofenac is used as a key for its limited adsorption and ecotoxicological risks.
- AOP can remove up to 52% of diclofenac, lowering the load treated by CWs.
- Pre-oxidation with UV/H_2O_2 further reduces CW surface area till 0.19 m^2 per PE.

1. INTRODUCTION

The Water Framework Directive (WFD) implemented in 2000 was the driver in the improvement of the current surface and ground water quality, thanks to the effort of the European Union towards water supply and sanitation. With respect to wastewater treatment, WFD – together with Urban Wastewater Treatment Directive (1991) – was focused on centralized wastewater treatment plants (WWTPs) of settlements with >2,000 inhabitants (European Commission 2000). The context has changed since then, and despite the major advances that have been made, most attention is now turned to micropollutants and the potential effects they can generate in the environment.

WWTPs are specifically designed to depurate the incoming organic loads as well as the nutrients; however, the mechanical and biological treatments are not able to eliminate successfully the micropollutants. Thus, implementation of a quaternary treatment is needed to reach the established standard quality for surface waters (European Commission 2013).

To emphasize the efforts to be taken to avoid the release of micropollutants into the water bodies aiming to mitigate their possible effects, European Commission in October 2022 proposed and updated the Directive concerning Urban Wastewater Treatment and approved it in October 2024 (UWWTD) (European Commission 2024). Among the main aspects to be amended are the following: (1) extending the scope to small agglomerates of 1,000 PE; (2) reinforcing attention to pollutant sources by the making the polluter pay principle; (3) being more restrictive in the discharge limits for nitrogen and phosphorus; (4) addressing micropollutant removal in agglomerates above 150,000 PE.

A large number of research groups worldwide have carried out studies for the development of technologies that were able to tackle this new concern about micropollutants. However, the most sophisticated ones, such as membranes, are not operationally and economically feasible in rural areas with few inhabitants.

A promising solution to overcome the challenge of wastewater management in small populations, sometimes located in remote areas, are natural-based solutions and specifically constructed wetlands (CWs), that have been widely studied due to their low maintenance and operational cost.

CWs are artificial systems designed to simultaneously use natural processes involving wetland vegetation, soils, and their associated microbial community for wastewater purification (Vymazal 2010) with a wide range of applications. Since the mid-2000s, this technology has been extensively studied and applied as a tool for wastewater depuration with excellent results in chemical oxygen demand (COD), phosphorous and nitrogen removal for diverse range of wastewater sources such as domestic, municipal, and industrial wastewater, as well as sludges. The related research and full-scale studies have been exponentially increased over the last two decades, indicating the high potential and dynamic for future exploration and expansion of the system capacity and efficiency. A clear proof of its success is the considerable increase of publications on wastewater treatment by CWs in the last decade (Supplementary material, Figure S1 (blue line)), dealing with the treatment of urban wastewater as well as water from agriculture or even industrial wastewater. Furthermore, recent studies have demonstrated its effectiveness for the removal of pharmaceuticals, considerably higher than those achieved in conventional WWTPs (Zhang *et al.* 2023). For this reason, research works started to focus on micropollutant and pathogen removal; however, these investigations are currently in a first stage (demonstrated by the orange line in Figure S1), and more studies are needed to understand the processes related to the degradation of these pollutants and to determine its potential and possibilities as a quaternary treatment in a conventional WWTP, which is the objective of the present study.

The Greater Region is a cross-border area located in central Europe consisting of Luxembourg, Lorraine (France), Wallonia (Belgium), Rhineland-Palatinate, and Saarland (Germany). The total area is 65,401 km^2 with a current population of 11.8 million inhabitants[1]; however, the population density is really unequal, with <150 inhabitants km^{-2} in the majority of the region's provinces.

This means that, before the new UWWTD, for many of these populations, there was no solution for the micropollutant discharge, which may find in CWs, the perfect downstream technology in WWTP for effluent purification purposes.

In the recent years, significant research efforts were put towards innovative designs and novel modifications of CWs. One of the most important trends is the use of hybrid CW systems combining units with different configurations installed in series to enhance the micropollutant removal efficiency. Tidal flow, combined with horizontal flow CW (Al-Mashaqbeh *et al.* 2024), demonstrates the ability to remove >93% of some micropollutants but <5% of diclofenac. Tang *et al.* (2025) tested six hybrid treatment lines showing that vertical flow–horizontal flow–surface flow treatment train achieved the highest performance and a good developed microbial community.

Despite the numerous advantages of CW and the hybrid systems, a significant limitation is the substantial land area requirements. This spatial demand poses practical challenges (Kushwaha *et al.* 2024), particularly in regions where available land is limited and expensive as Luxembourg. Accordingly, this study also aims to address this critical drawback by exploring strategies to optimize CW by minimizing the required surface while increasing treatment efficiency.

Another strategy to enhance the performance of the CW is the implementation of an oxidative treatment as a pre-CW step, thus the micropollutants remaining after the natural-based solution can be degraded via an advanced treatment. This alternative treatment train has been studied by several authors such as López-Vinent *et al.* (2023, 2024) and Casierra-Martinez *et al.* (2020). However, although the efficiency of micropollutant removal is improved, the need for surface reduction is still unexplored.

Interreg Greater Region – EmiSûre[2] project was developed with the objective to develop cross-border strategies for the management of micropollutants in the tributary basin of the Sûre (a cross-border river between Germany and Luxembourg). The detailed study on CW applications confirmed the ability to remove COD, nitrate, phosphate together with a high

[1] https://www.granderegion.net/En-bref/Chiffres-cles

[2] https://www.emisure.lu/

elimination rate of micropollutants (Venditti *et al.* 2022a) when intensified with the innovative substrate. The questions raised after the completion of EmiSûre led to an even more ambitious follow-up project, the Interreg Greater Region – CoMinGreat,[3] in which main objectives related to CWs were to enhance the removal of some recalcitrant compounds, and to reduce the high surface area required for the natural-based system.

Within this project, a demonstration centre was setup at the Bliesen WWTP (13,000 PE, Federal State of Saarland, Germany), where four micropollutant removal technologies were tested with an innovation of the CW treatment upgrade via a pre-oxidation step included among them.

Advanced oxidation processes (AOPs) are technologies whose common thread is their capability to generate $\cdot OH$, the second strongest known radical that can degrade very recalcitrant organic compounds and even mineralize them. The mechanism for generating these radicals is different depending on the technology.

For UV/H_2O_2, $\cdot OH$ species are produced from the homolytic cleavage of H_2O_2 by absorption of UVC radiation mainly at 254 nm (Reaction 1) (Sánchez-Montes *et al.* 2020):

$$H_2O_2 + hv \rightarrow 2\ ^{\bullet}OH \qquad \text{(Reaction 1)}$$

Another oxidative treatment that has shown to be very effective in removing recalcitrant organic compounds is the photo-Fenton process. It is based on an upgrade of the Fenton reaction (Reaction 2), via the regeneration by UV light of the iron catalyst (Fe^{3+} to Fe^{2+}), while producing a higher amount of $^{\bullet}OH$ (Reaction 3) (Núñez-Tafalla *et al.* 2024a). In photo-Fenton process, solar light can be used as source of irradiation, but if a lamp emitting in the UVC is used, Reaction 1 should also be observed.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + ^{\bullet}OH \qquad \text{(Reaction 2)}$$

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + ^{\bullet}OH + H^+ \qquad \text{(Reaction 3)}$$

The main novelty of this study is the introduction of a pre-oxidation step to CW treatment that aims to increase its applicability, particularly to: (1) enhance the removal rate of those compounds demonstrated as particularly recalcitrant for wetlands, (2) reduce the potential risks associated to micropollutants discharge, and (3) assess the possible reduction of the wetland area.

The purification capacity and the environmental consequences of the implementation of the CW technology and the combination with AOPs, for the specific context of the Greater Region, are described as follows in this article.

2. MATERIALS AND METHODS

2.1. Experimental setup

2.1.1. Description of the CWs tested in the Sûre catchment

The Sûre river crosses three countries, being the physical border between Germany and Luxembourg before entering the Mosel river. The catchment is characterized by rural areas with municipalities mainly connected to small- and medium-sized WWTPs (below 20,000 PE).

Echternach WWTP (maximum capacity 36,000 PE) was chosen because of its good effluent quality and its cross-border character treating around 13,000 PE from Germany, an industrial stream from Luxembourg and representing adequately the catchment. The WWTP has a total sludge retention time (SRT) of 19 days and a hydraulic retention time (HRT) that varies between 26 and 31 h. Two vertical-flow CWs of 11.18 and 12.78 m^2 surface area were installed as quaternary treatment (Figure 1). Both were filled with a mix of 15% activated biochar and 85% sand according to the result obtained in the first stage of EmiSûre at a lower scale. A detailed characterization of the substrate is reported in Brunhoferova *et al.* (2022). The systems were planted with macrophytes known for wetland systems according to the literature: *Phragmites australis*, *Lythrum salicaria,* and *Iris pseudacorus* (Brunhoferova *et al.* 2021) at a density of 25 plants steams per m^2.

[3] https://comingreat.eu/

Figure 1 | Pilot-scale CW installed at Echternach WWTP.

The effluent of the WWTP was used as the influent to the units, pumped, and uniformly distributed over the surface. The feeding strategy generally consisted of six short equally daily water cycles (every 4 h) and the applied hydraulic loading rate (HLR) varied from 100 to 200 L m^{-2} d^{-1}.

Wastewater samples were collected monthly as the influent of the WWTP (24-h composite sample), effluent of the WWTP (24-h composite sample) which is the influent to the vertical-flow CWs and effluent from the vertical-flow CWs (grab samples) to assess the performance of the WWTP and the impact of the CWs, respectively. The pilot plant was operated from October 2019 to January 2021 with an average temperature of 10 °C, approximately 800 mm of rainfall, and 52 days of maximum temperature above 25 °C[4].

2.1.2. From viability to optimization

Figure 2 shows how EmiSûre was started with the testing of new CW substrates to intensify the action capacity to remove micropollutants, validating the results obtained at laboratory-to-pilot scale (real scenario for the Sûre catchment). This led

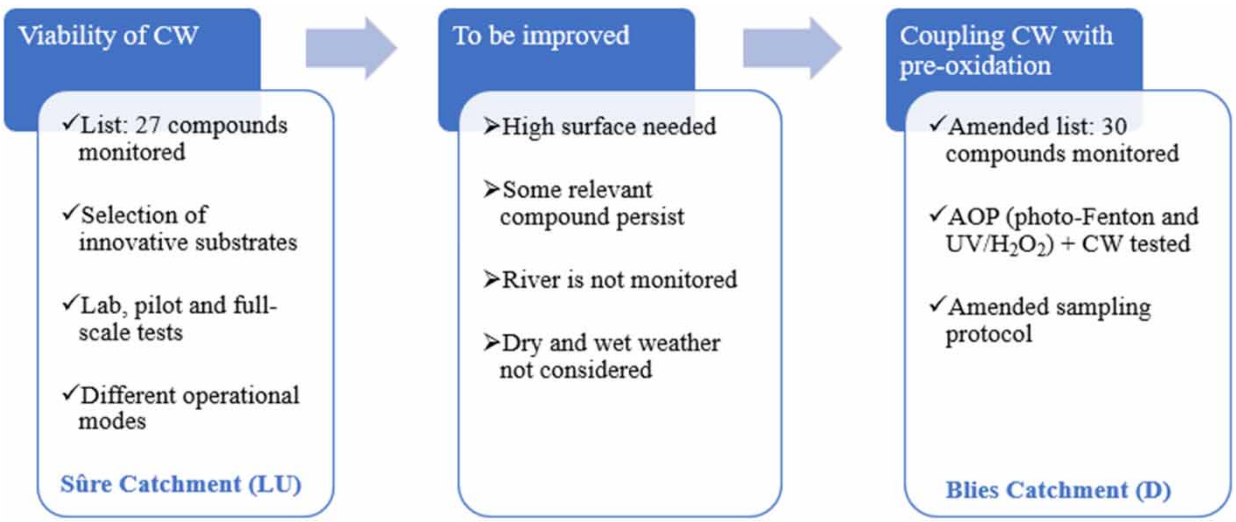

Figure 2 | Simplified flow diagram of the workflow of this study.

[4] https://lustat.statec.lu

to the identification of aspects where improvements can be made, principally the limited removal of certain micropollutants and the high space requirements which were tackled within CoMinGreat, tested at the pilot scale in the Blies catchment. A simplified workflow employed in the last 5 years is presented in Figure 3, which illustrates the evolution of the investigation guiding to the coupling of CWs with an AOP.

2.1.3. Description of the upgraded CWs tested in the Blies catchment

The Blies river flows from Germany and ends in France, being the physical border between Germany and France at the lower extend. It flows through Bliesen, where the WWTP is located (13,000 PE, full domestic wastewater). The CoMinGreat consortium aimed at testing several technologies containerized in a demonstrator center that was installed at Bliesen WWTP and monitored over 1 year of operation. Four treatment alternatives, for the removal of micropollutants, were installed in the demonstrator: (i) CW; (ii) pre-oxidation by AOP followed by CWs; (iii) granular-activated carbon (GAC) columns, and (iv) ozone followed by GAC columns. The main objective was to compare the performance of the four different purification strategies, and especially to evaluate the possible intensification of the CWs previously studied in EmiSûre via a pre-oxidation technology, which can increase its applicability in regions with a high land pressure or scarcity as Luxembourg.

The pilot CW as standalone treatment. (Figure 3) consisted of 1 m^3 of IBC tank configured by two layers of gravel of different sizes as drainage and filled with 15% activated biochar and 85% sand mixed homogenously. The unit is planted at a density of 30 plants steams per m^2 with *P. australis* and *I. pseudacorus* distributed alternately. The system was irrigated 3 times per day during 30 min with WWTP effluent (intermittent regime). The maximum HLR was 400 L m^{-2} d^{-1}. To avoid blockages in the irrigation system due to the frost in the winter season, all the pipes installed outdoors were protected by insulation foam and a heating cord. Samples were collected monthly following the procedure already described for the Sûre site.

Combination of AOP operated at neutral pH and CWs. the UV-pilot system was designed and developed in collaboration with Enviolet GmbH. It consisted of three loops connected in cascade with a 150-W (nominal power) medium pressure lamp, a centrifugal pump (800 L h^{-1}), and a recirculation tank each. The system was operated in a continuous mode, feeding each loop with the overflow of the previous one. The total HRT inside the lamps was 16.5 s (total illumination time), being able to treat up to 19 m^3 per day. The operation was performed at natural pH, to avoid increasing the salinity due to the acidification and later neutralization. Citric acid (from Brenntag) was used as iron chelating agent, and the iron source was a ferric sulphate solution (12%) from Dr Paul Lohman GmbH. The reagents, Fe:Citric acid, already chelated, and H_2O_2 were dosed automatically from two storage tanks of capacity 100 L, connected by one peristaltic pump each. Iron (Fe^{3+}) dosage was set at 1.5 mg L^{-1}, tested with a molar ratio with citric of 1:1 (Fe:Citric acid 0.027:0.027 mM) and 1:2 (Fe:Citric acid 0.027:0.054 mM). H_2O_2 was set at 20 mg L^{-1}. UV/H_2O_2 process was also carried out to avoid the addition of the iron and the subsequent increase in organic matter due to the chelating agent. The downstream CW after AOP consisted of

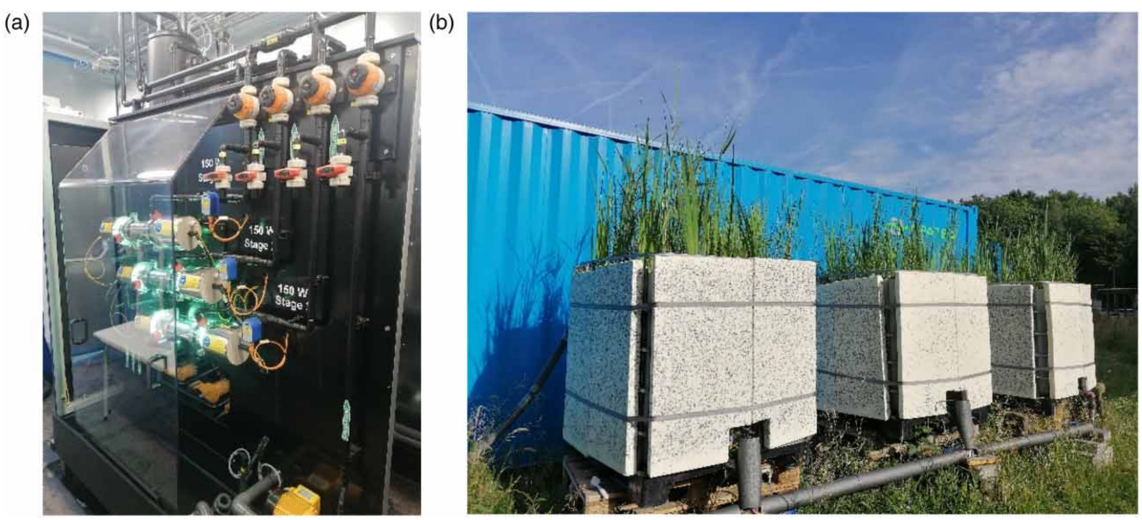

Figure 3 | CoMinGreat demonstration center. (a) AOP system, (b) CWs as standalone treatment (left side) and as AOP downstream technology (right side).

two 1-m^3 IBC tanks with the same configuration as the standalone CW. A full detailed description of the combined system is present in Salmeron *et al.* 2022.

The pilot was operated from November 2021 to October 2022 with an average temperature of 12 °C and approximately 950 mm of rainfall[5]. Samples were collected every month as the influent of the WWTP (24-h composite sample), effluent of the WWTP (24-h composite sample), AOP effluent (grab samples), and vertical-flow CW effluent (grab samples) to assess contribution of the each step for the removal of micropollutants. Residual iron and H_2O_2 in the CW effluent was monitored to avoid discharge of chemicals in the receiving water body.

2.2. Selection of target compounds to be monitored in the Greater Region

In total, 27 micropollutants have been initially selected jointly with the national water authorities (Administration de gestion de l'eau in Luxembourg; Ministerium für Umwelt, Landwirtschaft, Ernährung, Weinbau und Forsten in Rhineland-Palatinate in Germany) to be monitored in the Sûre (Luxembourg) catchment. The list was later amended to 30 compounds for the Blies catchment including contrast media and sucralose as main tracers for pharmaceuticals and domestic wastewater composition, respectively. The target compounds are given in Table 1 according to their CAS number and the lowest Predicted No Effect Concentration (PNEC) values in freshwater (see Section 2.4). The list comprises 20 pharmaceuticals from 10 therapeutic classes known to be excreted in the highest amount in these catchments (i.e. antibiotics, beta-blockers, anti-inflammatories). Moreover, it contains 10 herbicides of emerging concern (i.e. glyphosate and its degradation product, aminomethylphosphonic acid (AMPA)) or with a legal obligation (i.e. carbendazim, diuron, and isoproturon), two fluorosurfactants (i.e. perfluorooctanesulfonic acid (PFOS)), and other compounds known to be especially relevant for the Sûre river (i.e. benzotriazole and tris(2-chloroisopropyl)phosphate) (Gallé *et al.* 2019).

2.3. Analytical methodology

Macropollutants. Common parameters were routinely monitored. COD, total nitrogen, PO_4-P, NH_4-N, and NO_3-N were measured using Hach Lange cuvette tests. Oxidation–reduction potential, pH, and conductivity were determined using WTW (Xylem, UK) sensors.

Chemicals. Iron concentration was measured following ISO 6332 using 1,10-phenanthroline at 510 nm and H_2O_2 was determined according to DIN 38 402 H15 using titanium (IV) oxysulfate at 410 nm, measured with a Hach DR3900 Spectrophotometer.

Micropollutants. They were analyzed by Liquid Chromatography coupled to tandem Mass Spectrometry (LC-MS/MS). It consists of an Agilent 1200 SL LC coupled with an Hybrid Quadrupole-Linear Ion Trap instrument (Sciex 4500 QTrap) with electrospray ionization in positive mode operated in multiple reaction monitoring. All samples were pre-concentrated by solid phase extraction before their injection. The analyses were performed externally (Luxembourg Institute of Science and Technology LIST, Luxembourg) (Venditti *et al.* 2022a). The analysis of the micropollutants results was developed with a conservative approach, thus, the ones detected below their limit of quantification (LOQ) were assumed to be present at their respective LOQ, and the removal was calculated accordingly.

2.4. Data processing

The measured concentrations of micropollutants were compiled and curated to avoid inconsistencies. After that, data were analyzed using Microsoft Excel, where annual averages and standard deviations were calculated for each of the monitored parameters. Subsequently, the data were normalized and the removal efficiencies at each treatment stage were determined relative to the initial concentrations at the treatment inlet (Equation (1)). This approach allowed for a clear assessment of the contribution of each treatment step to the overall removal process.

$$\text{Removal \%} = 100 \times \frac{\text{Conc. influent} - \text{Conc. effluent}}{\text{Conc. influent}} \qquad (1)$$

[5] https://www.saarland.de

Table 1 | List of relevant compounds to be monitored in this study

Class	Substance	CAS number	PNEC[a] [μg L^{-1}]
P-Pharmaceuticals (N#20)			
Anti-inflammatories (3)	Diclofenac (S)(B)	15307-86-5	0.04
	Ibuprofene (B)	15687-27-1	0.011
	Ketoprofen (S)	22071-15-4	2.4
Anaesthetics (1)	Lidocaine (S)(B)	137-58-6	600
Antibiotics (5)	Ciprofloxacin (S)(B)	85721-33-1	0.064
	Clarithromycin (S)(B)	81103-11-9	0.12
	Erythromycin A (S)	114-07-8	0.3
	N4-acetylsulfamethoxazole (S)(B)	21312-10-7	2.38
	Sulfamethoxazole (S)(B)	723-46-6	0.6
Beta-Blockers (3)	Atenolol (S)(B)	29122-68-7	150
	Metoprolol (S)(B)	51384-51-1	8.6
	Propranolol (S)	525-66-6	0.16
Cytostatics (1)	Cyclophosphamide (S)	50-18-0	6.96
Contrast media (2)	Amidotrizoic acid (B)	117-96-4	0.073
	Iomeprol (B)	78649-41-9	0.15
Hormones (3)	Estradiol-beta (B)	50-28-2	0.0004
	Estrone (B)	53-16-7	0.00036
	Ethinylestradiol (B)	57-63-6	0.000037
Lipid regulators (1)	Bezafibrate (S)(B)	41859-67-0	2.3
Psychiatric drug (1)	Carbamazepine (S)(B)	298-46-4	2
H-Herbicides/Pesticides (8)			
	Aminomethylphosphonic acid (AMPA) (S)(B)	1066-51-9	1500
	Deet (S)(B)	134-62-3	88
	Diuron (S)(B)	330-54-1	0.049
	Flufenacet (B)	142459-58-3	0.04
	Glyphosate (S)(B)	1071-83-6	120
	Isoproturon (S)(B)	34123-59-6	0.3
	Mecoprop (S)	7085-19-0	N.A.
	Terbutryn (S)(B)	886-50-0	0.065
Others (8)			
Antimycotic	Carbendazim (S)(B)	10605-21-7	0.44
Corrosion inhibitor (2)	Benzotriazole (S)(B)	95-14-7	19
	Tolyltriazole (S)(B)	29385-43-1	N.A.
Flame retardant (1)	Tris(2-chloroisopropyl)phosphate (TCPP) (S)(B)	13674-84-5	260
Fluorosurfactants (2)	Perfluorooctanesulfonic acid (PFOS) (S)(B)	1763-23-1	0.002
	Perfluorooctanoic acid (PFOA) (B)	335-67-1	0.18
Stimulants (1)	Caffeine (B)	58-08-2	1.2
Sweeteners (1)	Sucralose (B)	56038-13-2	29.7

[a]NORMAN Ecotoxicology Database – Lowest PNECs (February 2025).
(S) and (B) indicate Sûre and Bliese catchment, respectively.
N.A., not available.

2.5. Environmental risk assessment

The potential environmental risk of each single compound was assessed for the Sûre and the Blies catchment based on the risk quotient (RQ) estimated as follows (Equation (2)):

$$RQ = \frac{MEC}{PNEC} \tag{2}$$

It is calculated as a ratio of the measured environmental concentration (MEC) and PNEC data which reflect the ecotoxicity of a molecule on the aquatic (in this case, fresh water) ecosystems.

Because of the complexity and vulnerability of data, this study relies on PNEC values from the literature, using the NORMAN Ecotoxicology Database[6] and other sources. In this study, PNEC was calculated for the treated water effluent, before being discharged into the environment. However, it is important to consider that this effluent will be diluted, in different ratios depending on the flow, when it mixes with the receiving water body. Therefore, the final risk will be proportionally lower.

The risks can be defined into five degrees according to the RQ values: (i) $RQ > 1{,}000$ indicates that the potential ecological risk of the compound is at a very high risk, (ii) $100 < RQ < 1{,}000$ indicates high risk, (iii) $10 < RQ < 100$ indicates that the compound could induce a medium potential risk, (iv) $1 < RQ < 10$ indicates that the compound entails a low risk and finally, (v) $RQ < 1$ indicating negligible risk (Gosset *et al.* 2020).

2.6. Surface estimation of CWs

As the use of CWs for the removal of micropollutants as quaternary treatment is not widely studied yet (as showed in Figure S1), from the best of our knowledge, currently there are no established methods to estimate the required surface for CWs in this particular application. For this reason, keeping a conservative approach, in this study the calculation of the required surface area was based on the organic load (COD) of the WWTP effluent. According to Langergraber *et al.* (2007), to keep a good removal efficiency at temperatures below 12 °C, the organic input to the wetland should not be higher than 20 g COD m^{-2} d^{-1}. The estimation of the surface needed per PE was done according to the following equation (Equation 3):

$$A_{CW,PE} = \frac{COD_e * Q}{COD_{max} * PE} \quad (3)$$

where $A_{CW,PE}$ is the calculated CW area per PE (m^2 PE^{-1}), COD_e the organic load of the effluent to be treated by the wetlands (mg COD L^{-1}), Q is the volume of water to be treated per day (m^3 d^{-1}), and COD_{max} is the maximum input of organic load, meaning 20 g COD m^{-2} d^{-1}.

An alternative approach is proposed to estimate the area required for the purification of the microcontaminants based on the mass of diclofenac removed by CWs in Section 3.3.

3. RESULTS AND DISCUSSION

3.1. Viability of CWs as standalone quaternary treatment in Echternach WWTP

The concentrations of the relevant substances were measured to evaluate the added value of CWs as quaternary treatment with respect to the conventional activated sludge process. The intermittent regime was used as the basis for the operation of CWs because it is known to improve the oxidation–reduction conditions favourable for complete nitrification and elimination of micropollutants. Clogging of the medium has also been demonstrated to be less frequent when compared with continuous flow operation. Among 27 compounds, only 14 were observed in relevant concentrations in the effluent of the WWTPs (>50 ng L^{-1}). The removal of each micropollutant during the full operation was assessed for the quaternary treatment. Results showed, in most of the micropollutants, >80% of removal (regarding the effluent of the WWTP) (Figure 4) with the only exceptions of AMPA and TCPP that are still discharged in relevant concentrations of >2 μg L^{-1}, and PFOS that is highly recalcitrant.

Previous studies have demonstrated that CWs are a powerful technology as quaternary treatment. Filling materials as sand and biochar (Seintos *et al.* 2025) can remove >80% of target compounds such as of ibuprofen, naproxen, triclosan, bisphenol A, diclofenac, and ketoprofen. In this context, the mixed substrate consisting of 15% biochar and 85% sand shows a considerable potential (Salmerón *et al.* 2024), combining high removal performance of >80% with environmental benefits, in line with the results of the present study. Moreover, the use of locally available sands can significantly reduce the carbon footprint, while biochar derived from waste contributes to circular economy objectives (Escolà Casas & Matamoros 2021; Venditti *et al.* 2024).

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[6] https://www.norman-network.com/nds/ecotox/

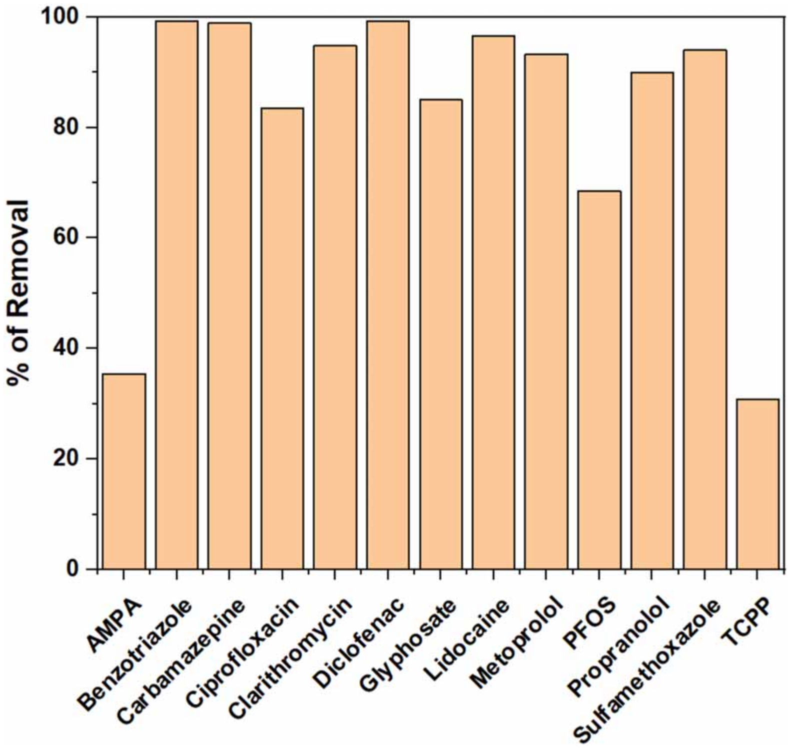

Figure 4 | Removal of micropollutants in the CWs regarding the effluent of Echternach WWTP. Adapted from Venditti *et al.* (2022b).

An evaluation of the environmental risk posed by RQ quanties the impact when a CW is applied as quaternary treatment. Results are shown in Supplementary material, Table S1.

While the effluent of the WWTP is considered equivalent to the CW influent (InCW), the MEC is assumed to be equivalent to the average measured concentrations in the CW effluent during the observation period. Among the compounds, three can be classified as most toxic (PNEC $<0.1\ \mu g\ L^{-1}$), three as an intermediate ecotoxicity ($0.1\ \mu g\ L^{-1} <$ PNEC $<1\ \mu g\ L^{-1}$), and seven as least ecotoxic (PNEC $>1\ \mu g\ L^{-1}$) (Gosset *et al.* 2021).

As seen in Figure 5, a low risk ($1 < RQ < 10$) is found for clarithromycin, ciprofloxacin and medium for diclofenac and PFOS in the effluent of Echternach WWTP. Nine compounds are considered at negligible risk, including carbamazepine, benzotriazole, AMPA, and TCPP. Despite being present in higher concentrations in the effluent, AMPA and TCPP also have a very high PNEC (1,500 and 260, respectively) and, therefore, their discharge has no potential consequences on the environment as pharmaceuticals do.

The results indicate that applying CWs as quaternary treatment reduces the environmental risk posed by micropollutants for >80%. Only PFOS poses low ecotoxicological risk although its concentration was reduced by 68%. The other three compounds of higher risk in the WWTP effluent were reduced to negligible levels. As a result, the number of micropollutants now classified within the negligible risk range increased to 12, including environmentally significant compounds such as diclofenac and ciprofloxacin. Similarly, Herrera-Melián *et al.* (2023) evaluated the environmental risk reduction potential of CWs. With an average 87% of micropollutant removal, three of the five target compounds of their study showed low risk, ibuprofen remained at medium risk, and nicotine at high risk. Chen *et al.* (2022) reported a general decrease in water toxicity levels when studying CWs at a large scale. In alignment with our study, these findings confirm the capacity of CWs to significantly mitigate potentially hazardous compounds from the environment, evidencing their role as active remediation systems rather than a mere removal tool.

According to the above results, it can be confirmed that CWs are a real alternative for the purification of WWTP effluents, achieving high removal rates for most of the relevant compounds, following the new UWWTD objectives. Moreover, CWs demonstrated of being capable of substantially reducing the possible ecotoxicological effects that micropollutants can generate in the receiving environment.

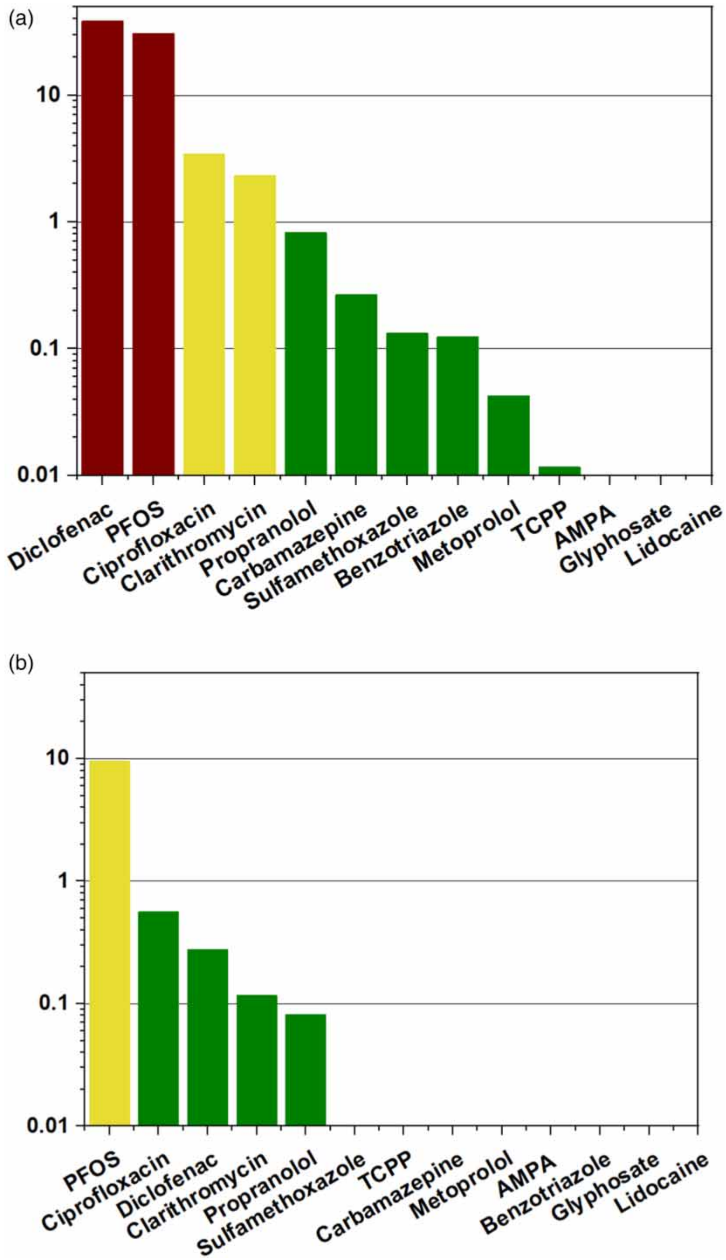

Figure 5 | Ecotoxicological risk of relevant compounds for (a) the effluent of the WWTP and (b) for the effluent of the CW used as quaternary treatment. Micropollutants of medium risk in red, low risk in yellow and negligible risk in green.

3.2. Use of CWs with a pre-oxidative step

3.2.1. Removal of micropollutants

The degradation of eight micropollutants was studied with the purpose of comparing the performance of CWs, as a single treatment and in combination with a previous oxidative process. Benzotriazole, carbamazepine, clarithromycin, and diclofenac were selected for being of relevance in the regulation of Luxembourg, and AMPA, PFOS, and TCPP for being very recalcitrant for their removal in Echternach WWTP. However, PFOS was present in concentrations around 10 ng L^{-1}, and thus could not be monitored.

It is necessary to point out that the presence of some inorganic ions in the water can seriously affect the results obtained in the oxidation process. Bicarbonates are widely recognized as ·OH scavengers (Cavalcante *et al.* 2022) with a reaction rate of

$k_{OH + HCO3-} = 8.5 \times 10^6\ M^{-1}s^{-1}$ (Rath & von Gunten 2024). Bliesen WWTP effluent contains 97–113 mg L^{-1} of bicarbonates, so it was expected that the pre-oxidation step would not be as effective as in other investigations using 'soft' water due to the competition between micropollutants and bicarbonate for the generated radicals.

Removal rates of each microcontaminant throughout the different steps of the proposed treatment trains are reported in Figure 6. Diclofenac is widely recognized in the literature as a limiting factor for adsorption process, even for GAC, one of the best performing and the most powerful substrates. The maximum lifetime of GAC for removing 80% of diclofenac in water effluents is usually around 20,000 bed volumes (Benstoem *et al.* 2017), being necessary to regenerate the adsorbent more often in waters with higher concentrations of this substance. As one of the main removal mechanisms in CWs is adsorption, this compound represents a crucial point. However, diclofenac is reported to be very sensitive to the exposure to a source light and its degradation by photolysis is important (Pérez-Estrada *et al.* 2005). Therefore, when applying an oxidative pre-treatment involving the use of UV light, its degradation pathway occurs very fast, resulting in a lower fraction to be removed by the subsequent CW/adsorption (Núñez Tafalla *et al.* 2022) and potentially increasing their lifetime. When photo-Fenton at molar ratio 1:1 is applied, a very limited removal of micropollutants was observed, for example, diclofenac with the highest ratio of 17%. The low ratio could be related to the low iron dose, selected to minimize its discharge into the receiving water bodies. Moreover, by adding only the chelating agent amount is strictly necessary for the concentration of iron (molar ratio 1:1), and it is probable that the iron was not completely available for reaction with H_2O_2. Marson *et al.* (2022) reported that when using Fe:Citric acid as the iron source, the maximum micropollutant removal efficiency was reached at a molar ratio 1:5. However, even at a low iron dose as the one used in this study (1.5 mg L^{-1}), the citric acid (1:1) means an increase of organic carbon in the treated water of 9.7 mg L^{-1}, which will compete vigorously with the micropollutants for the oxidative radicals and also affect directly the downstream CW. The low iron availability in a molar ratio 1:1 has also been reported by Núñez-Tafalla *et al.* (2024b). In that study, increasing the molar ratio of Fe:Citric acid from 1:1 to 1:2 (iron dose 6 mg L^{-1}) increased the removal of benzotriazole from 14 to 56%, respectively. Therefore, for the following tests, it was decided to continue with a ratio of 1:2, looking for an improvement of the removal of micropollutants while avoiding serious compromise of the effluent quality.

Results of photo-Fenton with a higher molar ratio showed a significant increase in the degradation of diclofenac (62%) and clarithromycin (44%), which considering the high content of bicarbonate in the water matrix meant a high improvement regarding the previous condition tested that can benefit the CW afterwards. Despite the improvement achieved, there were still recalcitrant compounds, such as AMPA, carbamazepine, and TCPP, for which the removal ratio can be increased, and for glyphosate, the removal decreased drastically (from 31% with 1:1 to 7% with 1:2), probably for the competition

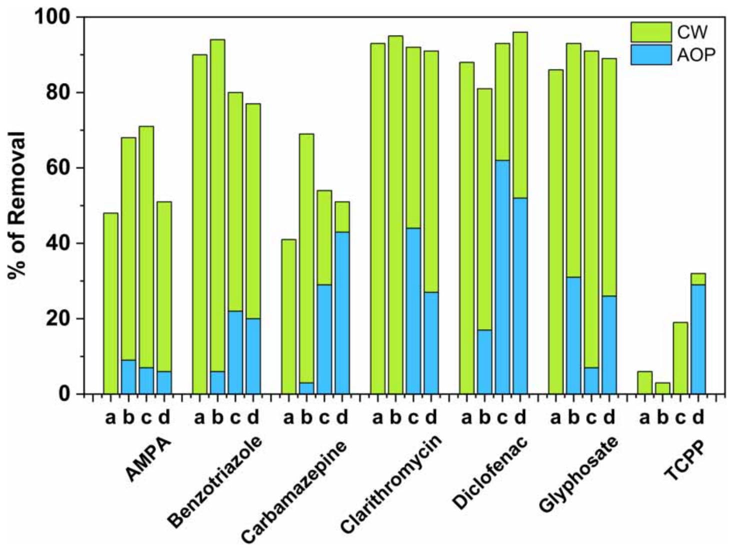

Figure 6 | Percentage of removal in each treatment step for the different treatment trains tested as quaternary treatment. (a) CW standalone; (b) photo-Fenton Fe:Citric acid 1:1 followed by CW; (c) photo-Fenton Fe:Citric acid 1:2 followed by CW; and (d) UV/H_2O_2 followed by CW.

caused by the increase of organics. This shows the necessity to reinforce the oxidative power of the treatment, either by increasing the dose of radiation or the dose of reagents (iron and/or H_2O_2).

Due to the configuration of the UV-pilot system, it was not possible to regulate the flow rate to increase the retention time of the water inside the lamps and thus increase the radiation dose. Additionally, in terms of increased reagent doses, the installation of a natural-based solution as a second step entails certain constraints that must be followed. Iron is a metal that must be minimized in water bodies and, despite CWs have the capacity to remove metals (Pérez-Sirvent *et al.* 2017), increasing iron implies an increase in the organic carbon in the water associated with the chelating agent. As a consequence, the surface area of CWs required grows proportionally, which is contrary to the objective of the present study. It is important to note that no residual iron or H_2O_2 was detected after the CW treatment.

Considering all the boundaries mentioned above, UV/H_2O_2 was proposed as a pre-oxidative treatment. This process is the alternative that generates fewer radicals and whose oxidizing power is lower than all other proposed. However, by avoiding the use of iron, the operation is greatly simplified. It is no longer necessary to add organic compounds that compete for the radicals with the micropollutants, and no additional considerations are needed to increase the surface area for CWs to depurate the organics.

In five of the compounds, the removal achieved by the UV/H_2O_2 process was lower than the one reached by photo-Fenton with Fe:Citric acid (1:2) but significantly higher than with 1:1. Moreover, the removal rate for carbamazepine and TCPP was increased up to 43 and 29%, respectively, the highest removal achieved in this study even when compared with the standalone CWs. Thus, the downstream CW can enhance even more the results obtained.

In general terms, the final elimination of micropollutants after combined treatment is very similar to that achieved by standalone CWs, although, for TCPP, which is very recalcitrant, a considerable improvement is observed. Lei *et al.* (2022) proposed the use of UVC lamp pretreatment to degrade photosensitive compounds prior to CW treatment. This approach reached the 100% removal of mecoprop, sulfamethoxazole, diclofenac, and furosemide thus enhancing the subsequent performance of the CW system; however, the possible land reduction is not considered.

Overall, the combination of AOP and nature-based solutions is widely acknowledged as a promising strategy for water treatment (Xiangyu *et al.* 2025). However, a significant gap persists in the literature regarding studies that transition to full-scale applications. In this context, the findings of the present study provide valuable insights into the practical feasibility and effectiveness of such integrated approaches under real operating conditions.

3.2.2. Risk assessment

Each of the proposed treatment alternatives is assessed comprehensively by the ecotoxicological risk analysis.

In terms of ecotoxicity (Supplementary material, Table S2), as in the Echternach WWTP, for the effluent of Bliesen, the micropollutant with the greatest risk to the environment was diclofenac that entailed a medium risk. Then, clarithromycin poses a low risk, and the rest of the compounds were negligible.

Figure 7 shows graphically the effluent risk without quaternary treatment and after each of the proposed alternatives. For both, standalone CW and in combination with a pre-oxidative step, the final risk reduction is very significant due to the elimination of diclofenac in all the quaternary treatments. For the rest of the compounds, the risk is negligible. The present work has been carried out in real scenario, which implies variations, generally seasonal, in the concentrations of pollutants in the effluent. That is the case for carbamazepine. Its average concentration in the effluent during the pilot operation was found to be 157 ng L^{-1}. However, the testing of the photo-Fenton process 1:2 was carried out in summer, when the population and, therefore, the loads in the influent of the WWTP grow as it is a recreational destination. Consequently, carbamazepine in the effluent rose to 312 ng L^{-1} and although $>$50% is removed, its concentration poses a higher risk than in the rest of the treatment alternatives.

Considering both the degradation of micropollutants and the reduction of the ecotoxic risk involved, it can be confirmed that the combination of CW and pre-oxidation, especially with UV/H_2O_2, is a very suitable solution for the purification of WWTP effluents. Diclofenac plays a main role for ecotoxicity. With the pre-oxidation, the global removal of diclofenac increases and, as most of the elimination takes places in the first step of the treatment train, CW received a lower load that can be easily removed. It is important to note that this risk assessment was conducted based on the effluent itself, that will be discharged into the water body. The dilution of the effluent, which will occur depending on the flow rate of the receiving stream, is expected to significantly reduce the overall risk, potentially by several orders of magnitude.

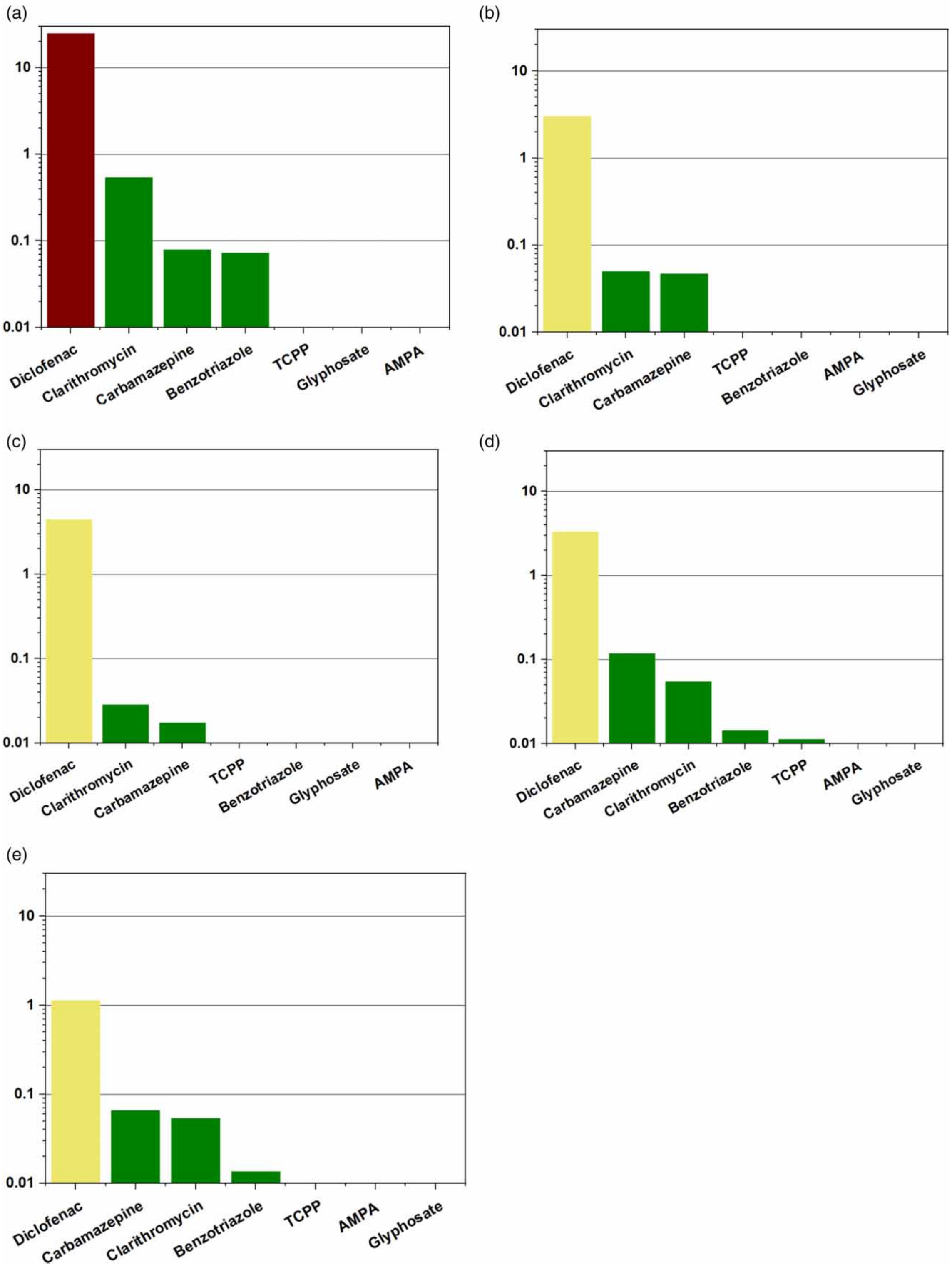

Figure 7 | Ecotoxicological risk associated to each micropollutant in Bliesen WWTP. (a) WWTP effluent; (b) CW standalone; (c) photo-Fenton Fe:Citric acid 1:1 followed by CW; (d) photo-Fenton Fe:Citric acid 1:2 followed by CW; and (e) UV/H_2O_2 followed by CW. Micropollutants of medium risk in red, low risk in yellow and negligible risk in green.

3.3. Calculation of the CW surface requirements

One of the major constraints in the use of CWs is the large space required for their proper performance, which is the main factor to be considered in this study when focusing on their intensification. Traditionally, the calculation of the required area for a CW as main biological treatment step is based on the COD of the influent, with a maximum of 20 g COD m^{-2} d^{-1} according to studies in which wetlands are used to treat sewage with a minimum (mechanical) pretreatment. In the present study, most of the organic matter has already been removed in the biological treatment of the Bliesen WWTP, so the COD is very low and the CW surface area required per PE is substantially lower than in other studies (Table 2). The pre-oxidation is not intended to remove COD, and in the case of photo-Fenton at neutral pH it is increased by the addition of the chelating agent.

The first calculation of the CW surface in Bliesen WWTP was done according to the annual average flow of dry and wet weather, being 5,702.4 m^3 day^{-1} after considering the 20% of infiltration from soil.

When combining UV/H_2O_2 process and CW, it would lead to a reduction of the CW surface of the 12.5%, according to the low COD reduction by the AOP. However, this approach is very rough, as the pre-oxidation degrades significantly some of the micropollutants that pose a high risk for the environment and is very effective for diclofenac removal, the main constraint for adsorption process.

For this reason, a new approach is proposed where diclofenac is taken as the reference micropollutant for the dimensioning the CW as quaternary treatment for municipal wastewater due to the limitations for adsorption process and its high ecotoxicological risk. The annual average concentration of diclofenac in Bliesen WWTP was 1,073 μg L^{-1}. Considering the daily flow of 5,702.4 m^3 and 5,189 m^2 of surface calculated in the first step, means a diclofenac load of 1.18 μg m^{-2} that can be removed by >80% using the CWs alone. Thus, diclofenac is a good reference for the new area estimation based on micropollutant removal. By including a pre-oxidation, the diclofenac load is significantly reduced, which means that the flow treated per m^2 can be increased and the CW surface reduced proportionally (Table 3).

The lowest surface can be installed by photo-Fenton process using Fe:Citric acid (1:2) as the pre-oxidation step. However, the organic load would increase till 64 g COD m^2 d^{-1} and the HLR till 2.9 m^3 m^{-2} d^{-1}, which could lead to problems in the performance of the CW or even lead to clogging. A previous study (Brunsch *et al.* 2018) explored the performance of CWs for the removal of micropollutants with satisfactory results at a HLR of 2.6 m^3 m^{-2} d^{-1}. The HLR of UV/H_2O_2 is below that value and the surface is still significantly lower than applying CW standalone. This fact, together with the simplicity of operation described in previous sections, makes UV/H_2O_2 the best alternative as a complement of CW, improving notably its applicability. Considering Bliesen WWTP, the CW standalone as quaternary treatment would require 5,200 m^2 of land, while combining with UV/H_2O_2, the required surface area could be reduced to around 2,400 m^2. In spatially constrained regions or where land has high cost per square meter, such as Luxembourg, which has a total area of only 2,586 km^2, this

Table 2 | Estimation of CW required surface (in m^2) according to the organic load of the effluent in previous steps

Treatment before CW	Effluent COD (mg L^{-1})	Estimated surface area for the downstream CW (m^2)	Surface area per PE (m^2)
WWTP	18.2	5,189	0.40
Pre-oxidation photo-Fenton Fe:Citric acid (1:1)	19	5,417	0.42
Pre-oxidation photo-Fenton Fe:Citric acid (1:2)	22	6,273	0.48
Pre-oxidation UV/H_2O_2	15.8	4,505	0.35

Table 3 | Calculated design parameters of CW when applied as quaternary treatment including pre-oxidation

	Reduction of diclofenac load (%)	Estimated size (m^2)	g COD m^2 d^{-1}	HLR (m^3 m^{-2} d^{-1})	Surface area per PE (m^2)
Pre-oxidation photo-Fenton Fe Citric acid (1:1)	17	4,307	25	1.3	0.33
Pre-oxidation photo-Fenton Fe:Citric acid (1:2)	62	1,972	64	2.9	0.15
Pre-oxidation UV/H_2O_2	52	2,491	36	2.3	0.19

substantial reduction in land demand significantly enhances the practical feasibility. Besides the land reduction, the combination can also provide a great benefit in terms of increased lifetime of the CW, which must be considered in future investigations.

4. CONCLUSIONS, RECOMMENDATIONS, AND PERSPECTIVE

This study contributes to the development of practical, scalable strategies to enhance the real-world applicability of CWs for micropollutant removal, particularly in regions with varying land availability and population density. Consistent with previous research, the results confirm that CWs are capable of removing >80% of targeted micropollutants from wastewater effluents. More importantly, this study demonstrates that CWs significantly reduce the environmental risks associated with micropollutant discharge, thereby supporting the ecological improvement of receiving water bodies.

One of the key challenges in CW implementation is the substantial surface area typically required for effective treatment. In this context, the intensification of CW performance through pre-oxidation is as a crucial strategy to enhance the feasibility of CWs. The present study shows that the integration of UV/H_2O_2 pre-treatment can reduce the required CW surface by approximately 52%, making this solution significantly more viable for space-constrained urban and peri-urban areas, as the case of Luxembourg. Additionally, the combination with pre-oxidation is expected to prolong the operational lifespan of CWs by reducing the adsorption load, particularly for persistent compounds such as diclofenac.

A further novel contribution of this study is the development of a design approach based on micropollutant loading, using diclofenac as a reference compound, rather than the conventional sizing based on organic matter. This micropollutant-focused approach offers a more structured framework for CW design, addressing a gap that has not been previously solved in literature.

Nonetheless, several limitations must be acknowledged. The surface area requirements and hydraulic loading rates presented in this study are derived from design calculations and literature-based performance data, with limited validation under real-world operational conditions. Additionally, long-term aspects such as potential clogging or seasonal variability of the combined system remain to be fully assessed. Future research should prioritize pilot and full-scale studies to validate the proposed design parameters and to quantify the expected extension of CW operational lifespan when pre-oxidation is applied.

From a practical perspective, the proposed integrated treatment offers a promising and sustainable option for improving water management in small and medium-sized communities. The substantial reduction in land requirements makes this approach highly attractive for space-constrained urban environments. To support broader adoption and policy integration, future studies should also include comprehensive economic analyses and life cycle assessments.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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