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Assessing the impact of micropollutants mitigation measures using vertical flow constructed wetlands for municipal wastewater catchments in the greater region: a reference case for rural areas

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ABSTRACT

The present research aims at giving an approach to the issue of surface water contamination due to micropollutants in rural areas. The catchment of the Sûre river was selected as a reference case for the Greater Region, characterized mainly by settlements with low population density, small water bodies and small- to medium-sized wastewater treatment plants (WWTPs). For these WWTPs, conventional technical solutions for micropollutants elimination are not suitable; therefore, an adapted mitigation strategy is needed to prevent the impact of micropollutants, especially during the dry season. As a suitable alternative to more intensive technologies, Constructed Wetlands (CW) in Vertical Flow (VF) configuration have been successfully tested over one-year period and the elimination rate of 27 micropollutants was quantified. Emission reduction by VF was then considered in a static mass balance model that calculates the longitudinal concentrations profile for the entire river catchment. The EmiSûre approach which focuses on river quality (concentrations of pollutants) instead of emitted loads, effectively allowed to simulate adopted measures *a priori* and resulted efficient to support decision-makers with WWTPs upgrade scenarios.

Key words: constructed wetlands, emission measures, EmiSûre model, micropollutants

HIGHLIGHTS

- A novel approach is applied to assess mitigation measures for micropollutants elimination in rural areas.
- Constructed wetlands are promising for micropollutants elimination.
- Emission reductions by Constructed Wetlands are considered in a static mass balance model.
- The selection of the WWTPs resulted in a significant load reduction.
- The EmiSûre model successfully serves as a valuable tool for decision-makers.

1. INTRODUCTION

Although in the last twenty years the need to minimize micropollutant emission has found a consensus in the upgrade of conventional Wastewater Treatment Plants (WWTPs) with advanced technologies (Eggen *et al.* 2014; Falås *et al.* 2016), a proper solution in which way small and medium-sized WWTPs in rural settlements should be upgraded is still needed.

Mitigation strategies have been focused mainly on large WWTPs where the highest ratio of mass reduction to cost (cost-effectiveness) can be applied with end-of-pipe solutions. For those existing WWTPs, the implementation of intensive technologies demonstrated to lead to high long-term investment with consequent additional energy consumption (UBA 2009).

Micropollutants released from small WWTPs located in rural areas can also lead to critical concentrations in the receiving waters mainly due the limited dilution factor and eventually to the more vulnerable hydrology of the rivers. Surface waters in rural areas often present concentrations of pollutants exceeding the Environmental Quality Standards (EQSs) values, which makes it necessary to introduce measures for achieving and maintaining *good water status* as the main principle of the Water Frame Directive (EC 2013).

In this paper, we propose an approach to such cases and particularly urgent for the Greater Region (German federal states Rhineland-Palatinate and Saarland, the Grand Duchy of Luxembourg, regions Wallonia and Lorraine from Belgium and France respectively) characterized mainly by rural areas with low population density and small water bodies with limited dilution especially during summer. Among the possible rivers, the Sûre has been selected as a representative case being the border between Luxembourg and Germany and connecting a total of 286 WWTPs in its catchment.

Because intensive technologies are not affordable to be applied to small WWTPs, nature-based solutions such as Constructed Wetlands (CWs) are here considered as a potential alternative for micropollutants removal.

The complexity of the multiple mechanisms (i.e. sorption, photodegradation, phytodegradation, and bioremediation) acting together in the removal of pollutants and the fact that the efficiency can be enhanced via the targeted influence of some of them (i.e. selection of substrate to influence sorption) has been an object of previous studies (Li *et al.* 2014; Ilyas & van Hullebusch 2019; Ilyas *et al.* 2020). However, the lack of data available for their application as post-treatment did not help to trust their viability.

The main objective of this study is thus to assess the impact of micropollutant removal measures in the Sûre catchment when post-treatment steps are applied and to offer a model approach for catchments of similar characteristics.

A pilot case study with CW in Vertical Flow (VF) configuration was conducted to define the occurrence of micropollutants for a WWTP that collects industrial and domestic streams from both Germany and Luxembourg and to assess its removal efficiencies as those achieved with the implementation of the post-treatment step.

Emission reduction by VF was thus considered for WWTP $<$10,000 PE in a mass balance model (named EmiSûre model) that calculates longitudinal concentrations profile for the entire river catchment by superimposing the point emissions of the WWTPs and the degradation mechanisms occurring in the water bodies. The model is designed to support decisions on the allocation and choice of additional treatment steps on a regional level. Our criterion for the assessment of beneficial effects is not the load reduction but the impact on micropollutants concentrations in the entire river network. Field sampling data have been used to calibrate the model for relevant pollutants like diclofenac and carbamazepine, and to verify its accuracy.

The model not only predicts spatially resolved exposure concentrations for micropollutants identifying river sites with elevated concentrations but also visualizes the impact of adopted measures *a priori* for compounds that are relevant for the Sûre river. This allows decision-makers to evaluate WWTPs upgrade scenarios without the time and cost-intensive measurement campaigns.

2. MATERIALS AND METHODS

2.1. Selection of target compounds

The current study monitors 27 micropollutants of different use: 14 pharmaceuticals from 6 therapeutic classes known to be excreted in the highest amount in the Sûre catchment (i.e. antibiotics, beta-blockers, anti-inflammatories), 9 herbicides of emerging concern (i.e. glyphosate and its degradation product, AMPA) or with a legal obligation (i.e. carbendazim, diuron, and isoproturon), 2 fluorosurfactants with low EQS (i.e. 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). These compounds are listed (Table 1) according to their CAS number and EQS values. Mean daily loads were calculated for 9 selected substances for all river segments represented in the model. They are marked as (M) in the table.

2.2. Experimental unit set-up

2.2.1. Characteristics of the Sûre catchment

With its 173 km length, the Sûre river crosses three countries, rising from the Ardennes (Belgium), being the physical border between Germany and Luxembourg before emptying into the Mosel. The catchment is characterized by rural areas with municipalities connected to small and medium-sized WWTPs (below 50,000 PE).

2.2.2. Location of the pilot: the WWTP of Echternach

A CW-pilot plant was installed at the WWTPs of Echternach (Luxembourg). This WWTP was chosen because of its good effluent quality (i.e. macropollutant values complying with the national legislation for limits of discharge) and its cross-border character treating 12,500 PE from Germany out of 36,000 PE capacity representing adequately the catchment. The conventional activated sludge system consists of a primary clarifier (V=ca. 380 m^3) and two aerated reactors (V=ca. 4,500 m^3 each) integrated with secondary sedimentation (V=ca. 3,800 m^3), for a total Sludge Retention Time (SRT) of 19

Table 1 | List of compounds

Compound	CAS number	Therapeutic Group/Use	AA-EQS[a] Chronic quality standard [ug l^{-1}]
Pharmaceuticals			
Atenolol	29122-68-7	Beta-Blocker	150
Bezafibrate	41859-67-0	Lipid regulator	2.3
Carbamazepine (M)	298-46-4	Psychiatric drug	2
Clarithromycin (M)	81103-11-9	Antibiotic	0.12
Ciprofloxacin	85721-33-1	Antibiotic	0.089
Cyclophosphamide	50-18-0	Cytostatic	NA
Diclofenac (M)	15307-86-5	Anti-inflammatories	0.05
Erythromycin A	114-07-8	Antibiotic	NA
Ketoprofen	22071-15-4	Anti-inflammatories	NA
Lidocaine	137-58-6	Anaesthetic	NA
Metoprolol	51384-51-1	Beta-Blocker	8.6
Propranolol	525-66-6	Beta-Blocker	0.16
N4-acetylsulfamethoxazole	21312-10-7	Metabolite	NA
Sulfamethoxazole (M)	723-46-6	Antibiotic	0.6
Pesticides/Herbicides etc.			
Carbendazim	10605-21-7	Fungicide	0.44
DEET	134-62-3	Insect repellent	88
Diuron	330-54-1	Algaecide	0.07
Isoproturon	34123-59-6	Algaecide	0.64
Terbutryn	886-50-0	Herbicide	0.065
Mecoprop (MCPP)	7085-19-0	Algaecide	3.6
Tolyltriazole (M)	29385-43-1	Fertilizer	NA
Glyphosate	1071-83-6	Herbicide	120
Aminomethylphosphonic acid (AMPA)	1066-51-9	Degradation product	1500
Fluorosurfactants			
Perfluorooctanesulfonic acid (PFOS) (M)	1763-23-1	Surfactant	0.002
Perfluorooctanoic acid (PFOA)	335-67-1	Surfactant	NA
Others			
Benzotriazole (M)	95-14-7	Corrosion inhibitor	240
Tris(2-chloroisopropyl)phosphate (TCPP) (M)	13674-84-5	Flame retardant	NA

[a]https://www.ecotoxcentre.ch/expert-service/quality-standards/proposals-for-acute-and-chronic-quality-standards/.

d and a Hydraulic Retention Time (HRT) that varies between 26 and 31 hrs. The plant made also use of the grid, sand, and grease trap preceding the primary clarifier.

2.2.3. Description of the VF and sampling design

Two constructed wetlands (VF1 and VF2) of subsurface vertical flow configuration at pilot scale were evaluated as post-treatment steps for the removal of micropollutants. VF1 and VF2 exhibit a surface area of 11,18 m^2 and 12,78 m^2 respectively and were filled with a mix of sand (grain size 0–3 mm, Liapor, Germany) and 15% activated biochar as supporting material (grain size 2–5 mm, Palaterra, Germany), previously demonstrated to be suitable for this application (Venditti *et al.* 2022).

The systems were planted with macrophytes typical of constructed wetland environment *Phragmites australis*, *Lythrum salicaria* and *Iris pseudacorus* (Brunhoferova *et al.* 2021) at a density of 25 plants steams per m^2. The effluent of the WWTP was used as influent to the units, pumped, and uniformly distributed over the surface. At each loading in the intermittent regime, the wastewater flooded the wetland surface, percolated by gravity through the wetland body, and collected in a 50 l plastic tank placed outside each unit. The feeding strategy generally consisted of six short equally daily water cycles (every 4 hrs) and the applied Hydraulic Loading Rate (HLR) varied from 100 to 200 $l\ m^{-2}\ d^{-1}$.

Several sampling campaigns took place over 14 months of operation to:

– characterize the contribution of the industrial (I) and the cross-border streams (both Luxembourgish, LU and German, DEU) into the influent: 24 hrs composite samples of each stream were collected in a time-proportional regime during two measurement campaigns;
– determine the occurrence of micropollutants and assess the efficiency of the conventional activated sludge treatment step: the raw wastewater (IN) was sampled after the mixing of the three streams and before entering the primary clarifier while effluent samples (EF) were collected after the secondary sedimentation. Four regular campaigns of 24 hrs composite samples were carried out. Following the guidelines of (Koms 2021), two extended campaigns were additionally performed collecting 72 hrs composite samples for IN and EF samples. In both regular and extended campaigns, a delay of 24 hrs between IN and EF was considered to reflect the WWTP's HRT.
– assess the feasibility of VF wetland as post-treatment: grab samples (VF1 and VF2) were taken from 50 l volume after the units and related to the effluent of the WWTP.

A schematic of the sampling is presented in the Supporting Information.

2.2.4. Analytical methodology

Macropollutants. Common parameters were routinely monitored. COD, TN, PO_4-P, NH_4-N, and NO_3-N were measured with Hach Lange cuvette tests. Oxidation-reduction potential, pH, and conductivity were collected with conventional WTW (Xylem, UK) Sensors.

Micropollutants. The analyses of the pharmaceuticals were performed externally (Luxembourg Institute of Science and Technology LIST, Luxembourg) and the methodology has been previously described (Venditti *et al.* 2022).

2.2.5. Calculation methods

To compare the contribution of industrial, Luxembourgish, and German wastewater streams into the WWTP inlet, the mass loads (MLs in $g\ d^{-1}\ PE^{-1}$) of relevant compounds have been calculated according to the following equation:

$$ML = \frac{C*Q}{PE}$$

where C is the measured pollutant concentration in $ng\ l^{-1}$, Q is the daily flow $l\ d^{-1}$.

Per capita specific loads of 60 g BOD5, 120 g COD, and 11 g TKN per capita and day are assumed.

To determine the efficiency of each treatment step, the elimination (E in %) of each compound has been calculated as:

$$E = \frac{(C0 - C)}{C0} * 100$$

where C is the effluent and C_0 is the influent concentration. The eliminations were calculated for each campaign and then an average was considered.

2.3. Modelling relevant compounds with the EmiSûre model

2.3.1. General model approach

In the EmiSûre project, a mass balance model tailored for the application in the Greater Region was developed. The model calculates geo-referenced concentrations in surface waters taking into account point emissions from WWTPs and Combined Sewer Overflows (CSO). Concentrations are simulated in a stationary way for mean minimal and mean annual flow conditions separately. Emissions of WWTPs are expressed as average substance-specific loads (L(S) in $g\ d^{-1}$). To calculate these point emissions, the model uses the population equivalents (PE) connected to each WWTP (P_{WWTP} in I) and per-capita loads (l(s) in $g\ I^{-1}\ d^{-1}$) in the influent of the WWTPs for each considered substance S. Wastewater treatment is modeled as a constant removal process whose removal efficiencies are depending on the type of applied treatment (conventional WWTP f_{WWTP}, advanced treatment process f_{ATP} in %) and the considered substance S.

To estimate the influence of CSO events on surface water quality, a CSO discharge factor ($f(S)_{CSO}$ in %) was established. It expresses the proportion of a substance, which enters the surface waters by CSO discharge and thus does not pass the WWTP.

The general model approach is illustrated in Figure 1.

The surface water network is represented by river segments between nodes i. The nodes are defined by load and concentration changes in the river (e. g. point emissions). Each segment is assigned to a flow rate (e. g. mean annual flow) and the corresponding flow velocity. The loads are calculated for each river segment based on a steady-state mass-balance approach. Emitted loads are introduced at the beginning of each river segment ($L(S)_i$). The loads at the end of each river segment ($L(S)_{i+1}$) are calculated taking into account the transformation of the compounds: a first-order reaction kinetic is assumed using a loss constant ($k(S)$ in h^{-1}) specific for each substance and the hydraulic retention time (HRT in s) in the river segment.

Assuming constant emissions (mass per time) from wastewater systems the calculated loads represent average annual conditions (Knerr *et al.* 2020).

2.3.2. Model setup

A total river system length of 899 km (which includes Sûre and all tributaries) was represented and divided into 568 individual segments. The segment-specific flow was included based on historical time series from 29 gauges in the catchment. Information on the range of flow conditions was included by implementing mean annual flow and mean minimal annual flow conditions. The model includes all 286 WWTPs of the catchment and the associated CSOs. All drainage systems in the catchment were considered as combined system, since 97% of the sewer in the catchment represent combined sewer systems. Uniform input data concerning substance-specific loads have been applied all over the catchment. Data for substance-specific loads, removal efficiencies in WWTPs, etc. were taken from literature as mean values. Model input data and used literature are listed in the Supplementary Information.

2.3.3. Assessment of receiving water concentrations

If model predictions for pollutant loads do not significantly deviate from calculated loads using measured data, a Predicted Environmental Concentration (PEC(S)) for the substance S can be calculated. To this end, daily loads ($L(S)_i$ in kg d^{-1}) were divided by daily flows (Q_i in $m^3\ d^{-1}$) in the river. Mean annual flow conditions were used to account for average concentrations, mean minimal flow conditions were used to account for minimum dilution and accordingly maximum concentrations in the waters. Emissions from CSOs have been included in the simulation only for mean annual flow.

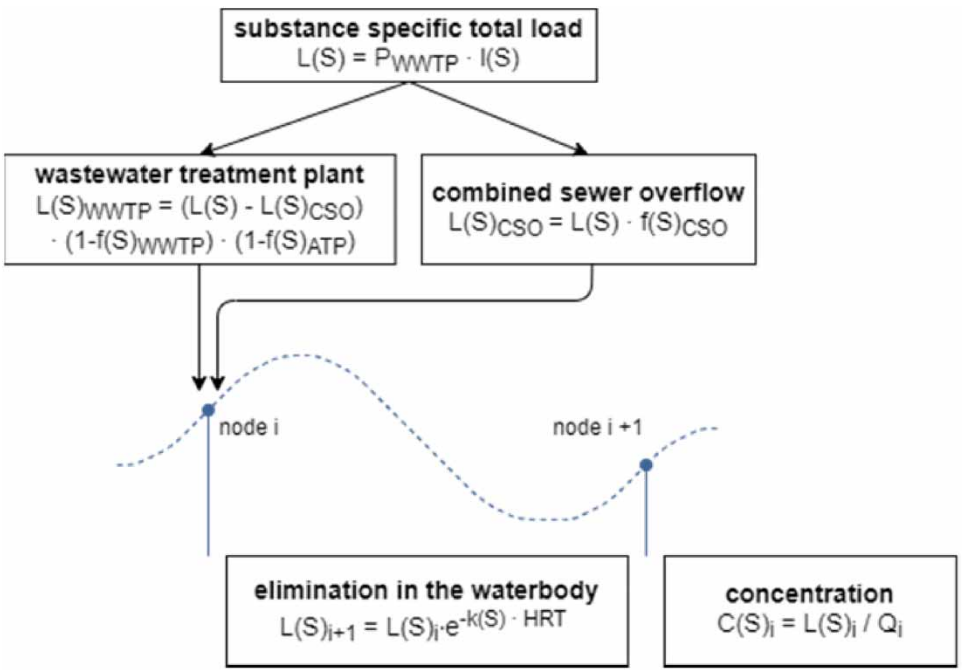

Figure 1 | General model approach.

Pollutant concentrations were assessed based on the so-called Contamination Factor (CF). This is the ratio of the calculated water concentrations (PEC(S)) and Water Quality Criteria (WQC(S)) defined for each substance. As WQC, concentrations excluding chronic damage or short-term toxicity of aquatic organisms were chosen. For WQS, values defined in the Directive 2013/39/EU (EC 2013) and in the German water surface act (OGewV 2016) were used. Annual Average Environmental Quality Standards (AA-EQS) were combined with mean flow conditions and Maximal Acceptable Concentrations (MAC-EQS) were combined with minimal flow conditions. Most of the substances identified in the Sûre river catchment are currently not regulated legally. For this reason, replacement values taken from the literature (e. g. Predicted No Effect Concentration (PNEC(S)) was used. The results are displayed in form of color-coded maps for mean annual and mean minimal annual flow conditions in the river system. Hence, river segments with CF >1, which means concentrations higher than WQC(S) can easily be identified.

2.3.4. Minimizing emission: strategies

To avoid any exceedance of a WQS WWTPs will be upgraded with additional treatment steps in the model regardless of their design capacity. To examine the influence of the WWTP upgrade, the simulation starts at the first WWTP in a river where the WQC is exceeded the downstream. The effect of the WWTP upgrade is then evaluated step by step downstream, taking into account the capacity of the rivers. The procedure is repeated for all rivers. For WWTPs with a design capacity >10,000 PE ozonation or activated carbon filtration were chosen as post-treatment technology. For WWTPs with a design capacity of <10,000 PE constructed wetlands were applied with the experimental results of EmiSûre as input data. To minimize water concentrations, other measures such as source-oriented measures (consumption reduction, substitution, etc.) can be considered.

3. RESULTS AND DISCUSSION

3.1. Feasibility of VF on enhanced removal strategy

3.1.1. Occurrence and removal efficiencies in the WWTP of Echternach

All the streams contributing to the WWTP's influent were characterized in terms of their physicochemical parameters (Table 2). The German daily flow resulted to be almost 2 and 4 times the industrial and Luxembourgish streams respectively. High BOD and COD values suggested wastewater polluted with nonbiodegradable contaminants originating from anthropogenic activities driven by the local industry (automotive and composite materials factories etc). Likewise, relevant concentrations of Na, K, Ca, and conductivity as indicators of high dissolved solids or minerals were also observed in the industrial stream.

The presence of micropollutants in the WWTP's influent was evaluated by tracking back to their origin within the three streams. Micropollutants can get into surface water also out of emissions from industrial processes which may use chemicals

Table 2 | General parameters and macropollutants concentrations in 24 hrs composite samples, $N=6$

Parameter	I	LU	DEU
Q ($m^3\ d^{-1}$)	628	1,510	2,560
PE BOD	10,571	2,869	12,971
COD (mg L^{-1})	1,780	200	545
BOD (mg L^{-1})	1,010	114	304
TN (mg L^{-1})	26	27	44
Ammonia (mg L^{-1})	8.5	17	28
Ptot (mg L^{-1})	9.3	3.2	4.2
Na (mg L^{-1})	279	60	53
K (mg L^{-1})	76	12	16
Ca (mg L^{-1})	53	100	82
Conductivity (uS cm^{-1})	1699	1068	1008

as adjuvants in their operations. Chemicals adjuvants range from complexing agents, surfactants, and preservatives that are not usually used in private households.

When looking at the daily unit mass loads per inhabitant (Table 3) calculated per PE, only 7 substances out of the 27 monitored micropollutants were detected in non-relevant concentrations:

- the antifungal carbendazim together with diuron, isoproturon, terbutryn (Bollmann *et al.* 2014), and MCPP registered as herbicides, forbidden in agriculture but still used as biocides or fungicides in roof paints, outside wall paints, and coating. Their content below the Limit of Quantification (LOQ) indicates that WWTP is not relevant sources of emission. The presence of these contaminants in some European rivers can thus be explained by the diffuse pollution from stormwater run-off (Quednow & Püttmann 2009);
- the cytostatic cyclophosphamide, usually administrated in low amount if compared to other medicaments of this type (i.e. 5-fluorouracil). Only 10% of the administrated active ingredient is excreted unchanged via urine while metabolites and transformation products are not considered in this study;
- the antibiotic erythromycin: among macrolides, this antibiotic mostly suffers from analytical detection problems. Also, only 5% of the administrated active ingredient is excreted unchanged via urine.

Table 3 | Mass loads of 20 relevant compounds [g d^{-1} PE^{-1}] in 24 hrs composite samples for industrial, Luxemburgish, and German wastewater streams, $N=6$

Parameter	I [g d^{-1} PE^{-1}]	LU [g d^{-1} PE^{-1}]	DEU [g d^{-1} PE^{-1}]
Atenolol	0.0013	0.4750	0.1697
Bezafibrate	0.0179	0.0032	0.0081
Carbamazepine	0.0009	0.2916	0.1995
Clarithromycin	0.0009	0.2916	0.1995
Ciprofloxacin	0.0003	0.3747	0.0408
Cyclophosphamide	<LOQ	<LOQ	<LOQ
Diclofenac	0.0234	1.4847	0.7102
Erythromycin	<LOQ	<LOQ	<LOQ
Ketoprofen	0.0002	0.1388	0.0358
Lidocaine	0.0002	0.0322	0.0205
Metoprolol	0.0289	0.0496	0.2211
Propranolol	0.0008	0.1475	0.0056
N-acetyl sulfamethoxazole	0.0003	0.3296	0.2645
Sulfamethoxazole	0.0004	0.1347	0.1171
Benzotriazole	0.0179	0.0032	0.0081
Carbendazim	<LOQ	<LOQ	<LOQ
DEET	0.0077	0.0979	0.0781
Diuron	<LOQ	<LOQ	<LOQ
Isoproturon	<LOQ	<LOQ	<LOQ
Terbutryn	<LOQ	<LOQ	<LOQ
MCPP	<LOQ	<LOQ	<LOQ
TCPP	0.1509	2.3187	3.4719
Tolyltriazole	0.0280	1.0229	0.4078
Glyphosate	0.0044	0.0816	0.0730
AMPA	1.0337	0.2211	0.1358
PFOS	0.0133	0.0101	0.0067
PFOA	0.0050	0.0081	0.0069

For the remaining 20 relevant compounds, the industrial stream resulted being the main source of AMPA, bezafibrate, and PFOS while micropollutants of medical use appeared minimal (i.e. atenolol, carbamazepine, diclofenac, etc). Contrary, both Luxembourgish and German domestic wastewater streams significantly contribute to micropollutants like benzotriazole, diclofenac, TCPP, and tolytriazole. As AMPA usually co-occurs with glyphosate, their transport is traditionally described together. However, previous researchers (Grandcoin *et al.* 2017) indicated industrial phosphonate chelating agents as an alternative source of AMPA which is in line with the strong contribution of the industrial stream identified in this study. It is interesting to observe that among beta-blockers, atenolol and propranolol seemed to be more administrated in Luxembourg with mass loads 3 and 26 times higher than in Germany, respectively. Contrary, metoprolol resulted being 4 times higher in Germany than in Luxembourg.

The concentration of the relevant substances was also measured to assess the removal in conventional WWTP treatment steps (Table 4).

For a few compounds, the effluent concentrations were higher than the influent ones. The reasons for that could be linked to the experimental methodology (i.e. analytical and sampling) or the fate mechanism of the single compound:

- carbamazepine and lidocaine are known to be persistent and hardly removed (Falås *et al.* 2016; Gallé *et al.* 2019) in Conventional Activated Sludge (CAS) treatments. Additionally, carbamazepine metabolites can build back to the parent compound (Ternes 1998; Bahlmann *et al.* 2014; Scheurer *et al.* 2015). A zero removal is thus assumed;
- the acetyl functional group of N-acetyl sulfamethoxazole breaks during the wastewater treatment process, generating the mother compound (sulfamethoxazole)(Göbel *et al.* 2005);
- AMPA is a degradation product of glyphosate and/or phosphonates. As such, its fate has to be related to the parent compounds (Grandcoin *et al.* 2017).

Table 4 | Average concentrations (Min-Max) measured during the observation period (14 months) for 20 relevant compounds [ng l^{-1}] and WWTP removal efficiencies (%), $N=12$

Compound	IN [ng l^{-1}]	EF [ng l^{-1}]	Elimination (%)
Atenolol	323 (65–680)	43 (24–65)	70
Bezafibrate	130 (57–268)	29 (8–60)	73
Carbamazepine	578 (129–1,262)	529 (96–1,290)	0
Clarithromycin	504 (64–1,015)	276 (61–583)	33
Ciprofloxacin	654 (145–3,229)	218 (147–357)	37
Diclofenac	2,109 (302–4,070)	1,523 (481–2,508)	<20
Ketoprofen	111 (15–211)	10 (4–29)	85
Lidocaine	92 (20–151)	122 (32–231)	0
Metoprolol	524 (175–1,150)	363 (202–720)	<10
Propranolol	167 (27–352)	131 (31–265)	<10
N-acetyl sulfamethoxazole	244 (33–658)	10 (4–28)	93
Sulfamethoxazole	165 (4–562)	79 (18–176)	−34
Benzotriazole	4,905 (1,180–10,285)	2,337 (1,049–3,493)	41
DEET	371 (46–1,845)	40 (19–59)	75
TCPP	3,151 (1,320–5,851)	3,002 (1,076–5,218)	<10
Tolyltriazole	1,487 (590–2,602)	1,000 (505–1,337)	<20
Glyphosate	100 (23–196)	127 (60–193)	−27
AMPA	2,341 (825–4,650)	4,079 (1,500–9,460)	−74
PFOS	120 (10–413)	61 (5–246)	22
PFOA	20 (5–50)	15 (4–47)	0

Benzotriazole, TCPP, AMPA, diclofenac, and tolyltriazole were detected as the most abundant in the WWTP influent exceeding 1,000 ng l^{-1} average concentrations. Among them, TCPP, diclofenac, and tolyltriazole were poorly removed while benzotriazole showed a moderate removal together with the antibiotic's ciprofloxacin and clarithromycin.

3.1.2. Performance of VF

The intermittent regime was used as the basis for the operation of VF1 and VF2 because it is known to improve the oxidation-reduction conditions favorable for complete nitrification and elimination of micropollutants. Clogging of the medium has also been demonstrated to be less frequent if compared with continuous flow operation. Among 27 compounds, only 15 were considered relevant in the effluent of the WWTP as influent to VF1 and VF2. An average concentration and removal were considered for the post-treatment step.

Results show (Table 5) high removal efficiencies for most relevant compounds with the only exception of AMPA and TCPP which are still discharged in relevant concentrations. These results confirm those already achieved in a previous pilot installed in a WWTP with less than 10,000 PE, operated for 6 months (Venditti *et al.* 2022).

When relative contributions of the two treatment steps are considered (conventional WWTP and post-treatment with VF, Figure 2) to the overall elimination of the selected compounds, the VF results to be determined in the elimination of persistent compounds (i.e. carbamazepine and lidocaine), antibiotics (especially clarithromycin and ciprofloxacin), diclofenac, benzotriazole, and tolyltriazole. The overall removal of TCPP results to be however still poor. The use of a VF for the WWTP of Echternach allows complying with the 80% removal threshold for the four mandatory compounds defined by the Luxembourgish Water Administration diclofenac, carbamazepine, clarithromycin, and benzotriazole (Administration de Gestion de l'eau 2020) with the average removal rate of 99, 99, 97 and 100% respectively.

3.2. Modelling loads and concentrations of micropollutants in the Sûre

3.2.1. Mean annual loads

Mean daily loads were calculated for 9 selected substances for all river segments represented in the model. The selection followed the methodology proposed in (Knerr *et al.* 2020) and represents the substances that can be predicted with the model approach reliably. To evaluate the validity of the setup predicted loads were compared with loads calculated from measurements. For this purpose, data from different monitoring campaigns, carried out by the local authorities were used.

Table 5 | Average concentrations (Min-Max) measured during the observation period (14 months) for 15 relevant compounds [ng L^{-1}] and VF removal efficiencies (%), $N=12$

Compound	IN VF [ng l^{-1}]	EF VF [ng l^{-1}]	Elimination VF (%)
Carbamazepine	529 (96–1,290)	6 (4–13)	98
Clarithromycin	276 (61–583)	14 (3–43)	95
Ciprofloxacin	218 (147–357)	36 (5–178)	92
Diclofenac	1,523 (481–2,508)	11 (4–31)	99
Lidocaine	122 (32–231)	4 (3–20)	97
Metoprolol	363 (202–720)	24 (5–80)	93
Propranolol	131 (31–265)	13 (5–42)	88
N-acetyl sulfamethoxazole	10 (4–28)	4 (3–5)	45
Sulfamethoxazole	79 (18–176)	5 (4–7)	89
Benzotriazole	2,337 (1,049–3,493)	17 (8–39)	99
TCPP	3,002 (1,076–5,218)	2,075 (707–5,761)	26
Tolyltriazole	1,000 (505–1,337)	11 (4–41)	99
Glyphosate	127 (60–193)	19 (5–49)	85
AMPA	4,079 (1,500–9,460)	2,634 (66–5,720)	25
PFOS	61 (5–246)	19 (5–67)	62

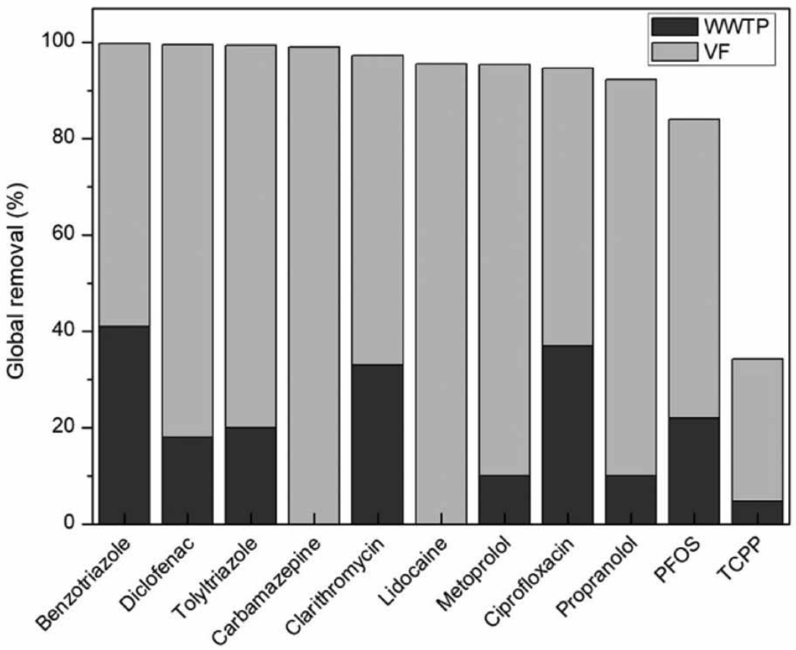

Figure 2 | Relative contributions of the VF and the WWTP to the overall global average removal efficiencies.

Additionally, a measuring campaign in the rivers of the Sûre for the selected micropollutants (see Table 1) was carried out in this study.

The comparison of predicted vs calculated daily loads for the pharmaceuticals diclofenac and carbamazepine is plotted in Figure 3. The results show that the model reflects the loads in the rivers very well for these two substances, because of their constant consumption in the catchment throughout the year and in all regions. The maximal deviation for these two substances was around a factor of two and therefore in the same range as in comparable studies (Ort *et al.* 2009) (Alder *et al.* 2010).

Similarly, good agreements were achieved for benzotriazole, clarithromycin, sulfamethoxazole, TCPP, PFOS, and tolyltriazole. However, for these substances predicted loads were evaluated against a reduced number of measurements because these substances were often not detectable in the river samples (Supplementary Information).

Metoprolol is overestimated at Luxembourg monitoring sites, while at German monitoring sites a good agreement was achieved. This is probably due to variations in regional differences in prescribing behavior for this drug (Supplementary Information).

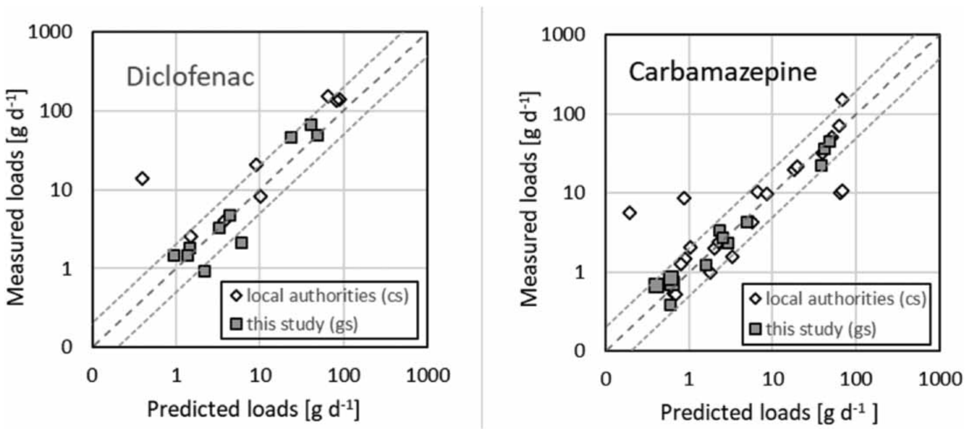

Figure 3 | Model prediction vs measured daily diclofenac and carbamazepine loads (cs=composite samples, gs grab samples).

3.2.2. Water contamination

Figure 4 illustrates the Sûre River catchment including all modeled WWTPs (left) and the status quo for diclofenac in form of a CF-map for mean annual flow conditions in the river system (right). As WQC, the proposed AA-EQS, recommended by the Ecotox center of Switzerland (see Table 1), was applied.

CF >0 is obtained in all waters affected by the effluent of WWTPs. The PEC exceeds the proposed AA-EQS for diclofenac of 0.05 $\mu g\ L^{-1}$ in.14% of the represented river segments. High diclofenac concentrations with CF >2 are partly encountered in upper reaches due to low dilution (e.g. river Wiltz, river Nims) and in particular in rivers, which are highly loaded by the discharge of micropollutants (e.g. river Alzette) due to the higher urban connections.

In the Sûre river itself, CF is below 0.5 in.about 82% and $0.5 \leq CF < 1.0$ in.about 16% of the total river length. However, this does not imply that diclofenac concentrations in the Sûre river always stay below the estimated WQC of 0.05 $\mu g\ L^{-1}$. Besides diclofenac only PFOS exceedance of the estimated WQC was observed in the model results.

3.2.3. Immission-based reduction strategy

The model was used to develop strategies that avoid any exceedance of WQS. We focused on diclofenac because compared to PFOS, diclofenac is eliminated with high efficiency in post-treatment steps. Thus, diclofenac represents a sensitive parameter for the selection of WWTPs to be upgraded.

The result of the applied immission-based reduction strategy for diclofenac is plotted in Figure 5 (right). The upgraded WWTPs are highlighted in Figure 5 (left). Elimination of 94% is assumed for ozonation and 83% for activated carbon filters corresponding to the treatment efficiency found in the literature *et al.*, 2012) (Abegglen & Siegrist 2012; Margot *et al.* 2013; Götz *et al.* 2015). For constructed wetlands, an elimination of 99% was used, corresponding to the findings of this study.

An upgrade of smaller WWTPs in the upper reaches of the river is necessary to avoid any exceedance of WQC. This has also a positive impact on the downstream water bodies and additionally on the evaluation of WWTPs further downstream. To avoid the exceedance of the proposed AA-EQS for diclofenac, a minimum of 12 WWTPs would have to be upgraded. This includes one WWTP with a design capacity of less than 10,000 PE (Junglister/LU) and four WWTPs with a design capacity of less than 5,000 PE (Garnich, Huldange Stackburren, Clemency in LU and Weinsheim in DEU).

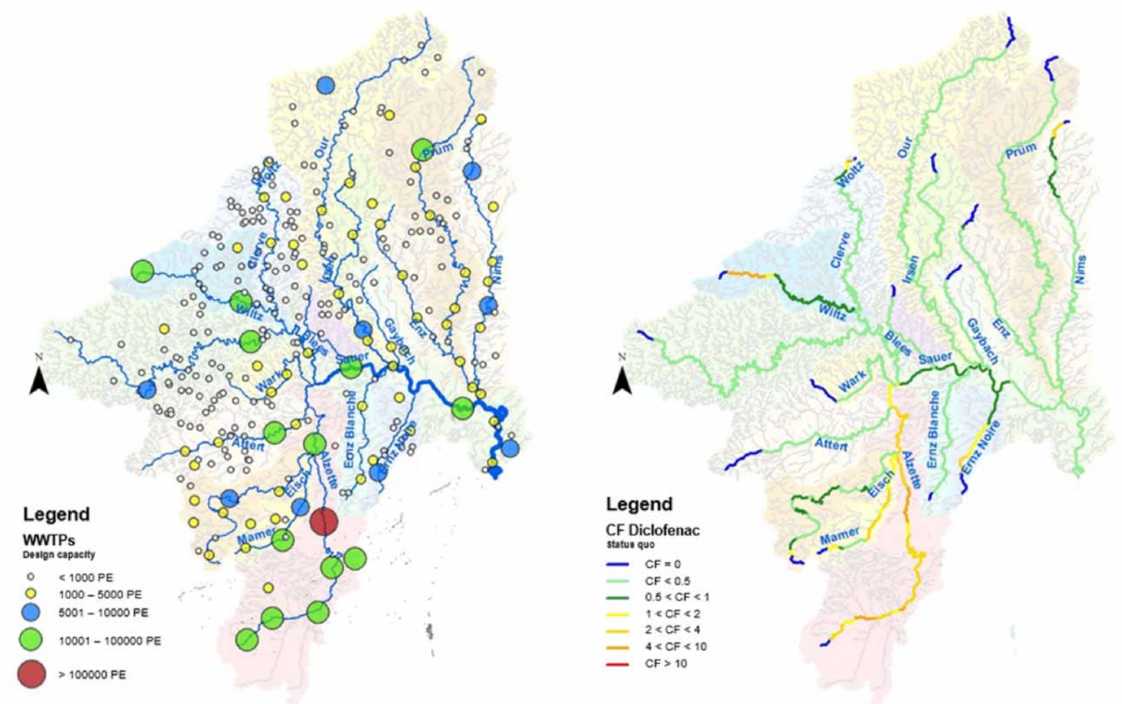

Figure 4 | Sûre River catchment including all modeled WWTPs (left) and the ratio of predicted diclofenac concentrations and proposed AA-EQS for mean annual flow (right).

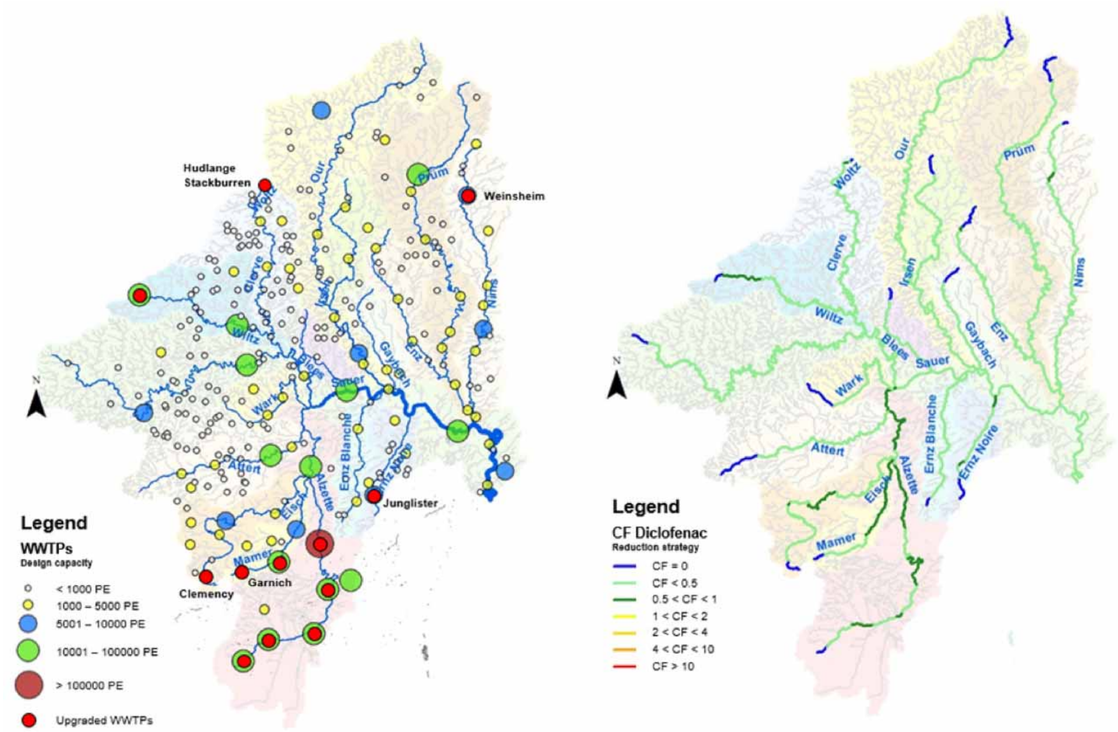

Figure 5 | Upgraded WWTPs (left) and the ratio of predicted diclofenac concentrations and proposed AA-EQS for mean annual flow for the emission-based reduction strategy (right).

The selection of WWTPs to be upgraded is bases on the resulting concentrations for diclofenac downstream of each WWTPs at mean annual flow conditions. Furthermore, diclofenac allows to evaluate of the quality-related benefit in the river catchment via the additional kilometers with CF <1 (Table 6). PFOS as the second parameter with exceedances in the current state cannot be used for this purpose, since PFOS shows an inefficient elimination by ozonation (5%) and activated carbon filters (55%) (Pinnekamp & Markel 2008).

However, other factors are also important for the overall assessment of measures, such as the load reduction at the outlet of the catchment. Table 6 describes the resulting load reduction at the mouth of the Sûre river (load-related) and the portion of the water system with CF <1 (quality-related). Even if substances, such as benzotriazole or tolyltriazole are not relevant in terms of a quality-related evaluation, the upgrade of WWTPs results in a significant load reduction in the catchment and thus also in the downstream waters. The total load reduction potential is significantly higher since only a small number of substances found in the rivers were modelled.

Table 6 | Load- and quality-related comparison at mean annual flow conditions (WQS are exceeded only for diclofenac and PFOS)

Substance	quality-related benefit additional km with CF <1 [km]	load-related benefit Resulting in overall load reduction [g d^{-1}]
Benzotriazole	0	−498
Carbamazepine	0	−29
Clarithromycin	0	−17
Diclofenac	118	−21
Sulfamethoxazole	0	−4,8
Tolyltriazole	0	−165
PFOS	0	−0,1
TCPP	0	−38

4. CONCLUSIONS, RECOMMENDATIONS, AND PERSPECTIVE

Implementing water protection policies for catchments in rural areas, generally requires the know-how of different specialists from the identification of relevant pollutants to the subsequent implementation of measures. In this study, we attempted to give the means to decision-makers of the Greater Region with dominant rural areas and beyond.

Considering the Sûre catchment representative, a mass balance model has been developed, successfully used, and evaluated with measured field concentrations to first assess the status quo of the catchment and then predict concentrations of relevant compounds (i.e. diclofenac and PFOS in this case). The developed model is a simplified approach for decision making on upgrading of WWTPs that neglects dynamics of CSOs. It should not transfer to substances that mainly originate from surface runoff.

In parallel, constructed wetlands in vertical flow configuration have been tested and resulted to be efficient in the removal of micropollutants complying with local regulations for discharge. The experimental results in terms of removal efficiencies for the relevant compounds have been used as input data for the EmiSûre model when a catchment management scenario was utilized such as upgrading WWTP >10,000 PE with activated carbon filtration and ozonation, and constructed wetlands in vertical flow configuration for WWTP <10,000 PE. When looking at the effect of the measure, the selection of the WWTPs to be upgraded resulted in a significant load reduction in the catchment and thus in the downstream waters.

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DATA AVAILABILITY STATEMENT

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

CONFLICT OF INTEREST STATEMENT

The authors declare there is no conflict.

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