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Behaviour of 27 selected emerging contaminants in vertical flow constructed wetlands as post-treatment for municipal wastewater

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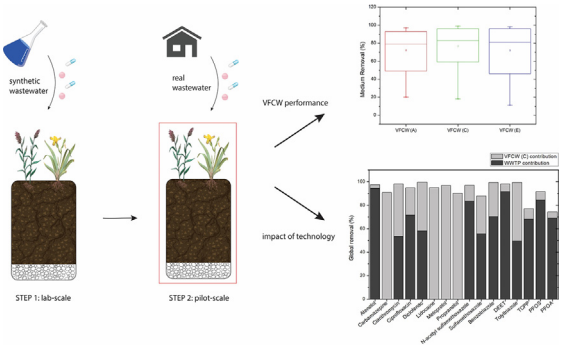
HIGHLIGHTS

- Unconventional substrates are suitable in wetlands for micropollutants elimination.
- The use of activated biochar versus sand/zeolite resulted in a higher efficiency.
- Persistent compounds (i.e. carbamazepine) are well eliminated (>90%).
- The amount of contaminant adsorbed per gram of substrate is quantified.
- Vertical Flow Constructed Wetlands is a promising post-treatment step.

GRAPHICAL ABSTRACT



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ABSTRACT

Six substrates (i.e. sand enriched with activated or non-activated biochar or zeolite in different ratios) were tested in Vertical Flow Constructed Wetlands (VFCWs) planted with *Phragmites australis* and *Iris pseudacorus* for the removal of 27 emerging contaminants from municipal wastewater. The laboratory investigation under controlled conditions (spiked constant concentrations in synthetic wastewater) lasted 357 days and proved VFCWs being able to provide excellent effluent quality in terms of both macro - and micropollutant elimination. Because overall removal efficiencies exceeded 90% in most of the cases, significant differences among the substrates were not detectable. For compounds with medium elimination (i.e. AMPA) the type of substrate seemed to play a strong role and the maximum amount of active ingredient adsorbed per amount of substrate has been quantified (i.e. 0.77 μg of AMPA per g of 30% biochar mixed with sand). Three of the most promising substrates from laboratory where thus selected to be tested under real conditions (fluctuation in concentration, variable temperature). As result, VFCWs with 15% activated biochar mixed with sand proved to be effective in the removal of 18 emerging contaminants and complying with national discharge standards for 4 selected compounds.

1. Introduction

The occurrence of emerging contaminants (also known as micropollutants, MPs) in surface water has been increasing over the last decades resulting in potential risk for aquatic and terrestrial ecosystems (Pal et al., 2010). Hence, the European Commission (EC) decided to identify those substances that could delay or hamper the achievement of a *good ecological and chemical status* for both ground and surface waters as main principle of the Water Framework Directive (2000/60/EC) to be reached by 2027 (EC, 2019). With the so-called Watch List (EC, 2015; EC, 2018), the Commission Implementing Decision made it finally mandatory for all EU member states to monitor 17 compounds, among them the antibiotics azithromycin, clarithromycin and erythromycin.

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Because of their anthropogenic origin, emerging contaminants are mainly released by Wastewater Treatment Plants (WWTPs) which demonstrated to be inefficient (Falås et al., 2016) in the removal of the most persistent. Consequently, some countries have set up more strict national discharge standards, started to plan and implement additional treatment steps identifying urban areas which are significant point sources in the river basin they are located in. As example, the Swiss government identified 100 out of the 700 national WWTPs that will be supported with a post-treatment in order to achieve an overall average of 80% removal of selected organic compounds (Eggen et al., 2014). Likewise, Germany progressed upgrading 30 WWTPs for MPs elimination (Metzger et al., 2020) with the regions of North Rhine-Westphalia and Baden-Wuerttemberg (Koms, 2021) as front runners. Following this example, Luxembourg released a guideline (Administration de Gestion de l'eau, 2020) for those WWTPs that have been selected to be upgraded with a post-treatment. The effluent quality has to achieve 80% removal for each compound namely diclofenac, carbamazepine, clarithromycin and benzotriazole with the option of adding to the permit substances that are relevant for the respective WWTP when measured above Environmental Quality Standards (EQSs) in the receiving surface waters. Till now, the majority applied common technologies such as Activated Carbon Filtration (both powdered, PAC and granulated, GAC) and Ozone.

However, as the upgrading of WWTPs for MPs elimination is a long-term investment that would affect additional energy consumption of about 30% (UBA, 2009), some regional studies tried to identify suitable alternative especially for small and medium-sized WWTPs (i.e. less than 20,000 PE). Due to their low investment and operation cost combined with good effluent quality, Constructed Wetlands (CWs) are a promising additional step for micropollutants removal.

CWs are nature-based wastewater treatment processes in which the synergy of multiple mechanisms acting simultaneously (i.e. sorption, photodegradation, phytodegradation, and biodegradation) demonstrated to enhance the removal of heavy metals, organics and nutrients (Galletti et al., 2010; Haarstad et al., 2012). When applied as decentralized treatment for hospital/domestic wastewater and grey water, CWs showed satisfying removal of pharmaceuticals and personal care products (Verlicchi et al., 2012; Ávila et al., 2014; Verlicchi and Zambello, 2014) but very little is known about their application as post-treatment. Comprehensive reviews (Li et al., 2014; Ilyas and van Hullebusch, 2019; Ilyas et al., 2020) collected and processed a large number of data highlighting high variability in removal rate values with significant standard deviations.

A better understanding of the key factors influencing the removal of MPs in a CW environment would help to select the appropriate configuration (i.e. surface and subsurface flow, vertical and horizontal) and eventually its operating parameters (i.e. aerobic/anaerobic conditions, intermittent or alternating operation mode, hydraulic retention time and so on). Whether such configuration could impact the removal of individual MP is however associated with the nature of the MP itself.

Because of their hydrophobic nature or electrostatic reactions, some MPs would have a better tendency to be attached on the soil (Carmo et al., 2000) and thus the selection of the filling material would determine the efficiency of the configuration towards those compounds. Sorption may occur via absorption (hydrophobic interactions characterized by the octanol-water partition factor, Log*Kow*) and adsorption (electrostatic interactions characterized by the dissociation constant, p*Ka*): compounds with high Log*Kow* (hydrophobic) have intuitively more affinity for the solid fraction (Sipma et al., 2010). This is the case of the musk fragrance tonalide (Ávila et al., 2014) removed up to 80%, the antibiotic class of fluoroquinolones, namely ciprofloxacin and ofloxacin (Verlicchi et al., 2012) and macrolides, namely azithromycin and clarithromycin (Verlicchi and Zambello, 2014).

Then, as CWs are exposed to sunlight photochemical reactions are expected to be relevant for those compounds considered photosensitive like fluoroquinolones (Jia et al., 2012) thus seasonal variation could strongly influence their removal (Matamoros et al., 2008, Stefanakis and Tsihrintzis, 2012, Verlicchi and Zambello, 2014; Rühmland et al., 2015). Photodegradation is however negligible with subsurface flow CW especially in vertical configuration where the surface exposed to sunlight is smaller. Photolysis of diclofenac has also been previously observed (Zhang et al., 2018) and seemed to be more dominant in unplanted wetlands with subsurface flow configuration.

If planted, CWs can act via plant uptake of MPs depending on type of plant (Brunhoferova et al., 2021), plant density and plant root amounts. The role of plant uptake is generally known to be combined with those of biodegradation and strongly affected by seasonal variation (Joner and Leyval, 2009; Hijosa-Valsero et al., 2010; Nuel et al., 2018). The presence of microbial community structures near the plant roots (rhizosphere) in co-habitat with Mycorrhiza fungi could enhance the whole biodegradation mechanism. For emerging contaminants which are persistent and not easily biodegradable, the configuration of CWs and the operation conditions may play a great role in their degradation while for contaminants already biodegradable the impact will be minimal.

Without doubt, the complexity of all simultaneous mechanisms and the limited number of studies on these topics has been detrimental in advancing knowledge and trust in the feasibility of CWs for removal of emerging contaminants.

In this context, the Interreg Greater Region project EmiSûre (Développement de stratégies visant à réduire l'introduction de micropolluants dans les cours d'eau de la zone transfrontalière germano-luxembourgeoise) aimed to exploit the potential of CWs for the mitigation of MPs in rural areas with characteristics similar to the Sûre catchment, a river on the border between Luxembourg and Germany.

The main objectives of this study are thus: (1) to conduct a robust investigation on 27 representative emerging contaminants using laboratory tests under controlled conditions (2) to draw conclusions about possible (and most dominant) removal mechanisms with respect to the individual compound (3) to validate and prove CWs in Vertical subsurface Flow (VF) configuration as polishing treatment for small and medium sized wastewater treatment effluents.

2. Materials and methods

2.1. Selection of target compounds

The comprehensive list of compounds monitored in this study is the result of a joined agreement between the partners of the Interreg Greater Region project 'EmiSûre', among them decision makers (Administration de gestion de l'eau in Luxembourg, Ministerium für Umwelt, Landwirtschaft, Ernährung,Weinbau und Forsten in Rheinland-Pfalz in Germany), WWTP operators (Syndicat Intercommunal de Dépollution des Eaux résiduaires du Nord SIDEN and de l'Est SIDEST both in Luxembourg, and Entsorgungsverband Saar in Germany) and scientists (University of Luxembourg and University of Kaiserslautern in Germany). The 27 compounds (Table **1**) were selected taking into account: a) those known to be excreted in the highest amount (in the case of pharmaceuticals: antibiotics, beta-blockers, analgesics etc), b) those known with the highest eco-toxicity (i.e. cytostatics), c) those known to be under observation (i.e. macrolides) or with legal obligations (i.e. isoproturon, diuron), d) those known to be especially relevant for the Sûre river and already monitored in previous projects (i.e. benzotriazole, tolyltriazole and tris(2-chloroisopropyl)phosphate) (Gallé et al., 2019).

2.2. Experimental design

2.2.1. Lab-scale wetlands set up

The vertical-flow lab scale-wetlands (lysimeters) consist of six plexiglass columns (Europlex, Belgium) having same dimensions (inner diameter 29 cm, height 115 cm) and set up to investigate the impact of a substrate in the removal of MPs from synthetic wastewater used as influent.

The columns are successively filled, from the bottom to the top, with a 10 cm layer of gravel acting as drainage (5 cm of coarse 4–8 mm and 5 cm of fine 2–8 mm), a 90 cm of packing substrate (Fig. 1).

Table 1
List of compounds.

Application	Compound	CAS number	Therapeutic group/use	AA-EQS* Chronic quality standard (ug L^{-1})	Spiked concentrations (ug L^{-1})***	Selection criteria
Pharmaceuticals and metabolites	Atenolol	29,122-68-7	Beta Blocker	150	5	Highly prescribed.
	Bezafibrate	41859-67-0	Lipid regulator	2.3	5	Highly biodegradable.
	Carbamazepine	298-46-4	Psychiatric drug	2	2	Mainly excreted as hydroxylated metabolite. Control compound.
	Clarithromycin	81103-11-9	Antibiotic	0.12	5	Present in the Watch List (EU) 2015/495 of 20 March 2015 (EC, 2015).
	Ciprofloxacin	85721-33-1	Antibiotic	0.089	5	Present in the Watch List (EU) 2018/840 (EC, 2018)
	Cyclophosphamide	50-18-0	Cytostatic	NA**	5	High eco-toxicity impact.
	Diclofenac	15307-86-5	Analgesic/anti-inflammatories	0.05	5	Present in Directive 2013/39/EU.
	Erythromycin A	114-07-8	Antibiotic	NA	5	Present in the Watch List (EU) 2015/495 of 20 March 2015 (EC, 2015).
	Ketoprofen	22071-15-4	Analgesic/anti-inflammatories	NA	5	Highly prescribed. Found in surface waters.
	Lidocaine	137-58-6	Anaesthetic	NA	5	Highly prescribed. Found in surface waters.
	Metoprolol	51384-51-1	Beta Blocker	8.6	5	Highly prescribed.
	Propranolol	525-66-6	Beta Blocker	0.16	5	Highly prescribed. Found in concentrations above EQS.
	N4-acetylsulfamethoxazole	21312-10-7	Metabolite of Sulfamethoxazole	NA	2	For mass balance.
	Sulfamethoxazole	723-46-6	Antibiotic	0.6	2	Old antibiotic, still in use. Scientific data available.
Pesticides/Herbicides	Carbendazim	10605-21-7	Fungicide	0.44	1	Very persistent.
	DEET	134-62-3	Insect repellent	88	2	Very persistent.
	Diuron	330-54-1	Herbicide	0.07	1	Present in Directive 2018/105/E (EC, 2018).
	Isoproturon	34123-59-6	Herbicide	0.64	1	Present in Directive 2018/105/E (EC, 2018).
	Terbutryn	886-50-0	Herbicide	0.065	2	Very persistent.
	Mecoprop (MCPP)	7085-19-0	Herbicide	3.6	1	Found in surface waters.
	Tolyltriazole	29385-43-1	Fertilizer	NA	2	Highly used. Most abundant in WWTPs discharging in the Sûre river.
	Glyphosate	1071-83-6	Herbicide	120	5	Under discussion.
	Aminomethylphosphonic acid (AMPA)	1066-51-9	Degradation product	1500	5	Under discussion.
Fluorosurfactants	Perfluorooctanesulfonic acid (PFOS)	1763-23-1	Surfactant	0.002	2.5	Priority compound.
	Perfluorooctanoic acid (PFOA)	335-67-1	Surfactant	NA	2.5	Of political concern.
Corrosion inhibitor	Benzotriazole	95-14-7	Corrosion inhibitor/Antiviral	240	5	Highly used. Most abundant in WWTPs discharging in the Sûre river.
Flame retardant	Tris(2-chloroisopropyl) phosphate (TCPP)	13674-84-5	Flame retardant	NA	5	Highly used. Most abundant in WWTPs discharging in the Sûre river.

* https://www.ecotoxcentre.ch/expert-service/quality-standards/proposals-for-acute-and-chronic-quality-standards/.
** NA: "not available" in the Ecotoxcentre database.
*** spike in the synthetic wastewater prepared for the lab-scale wetlands of this study.

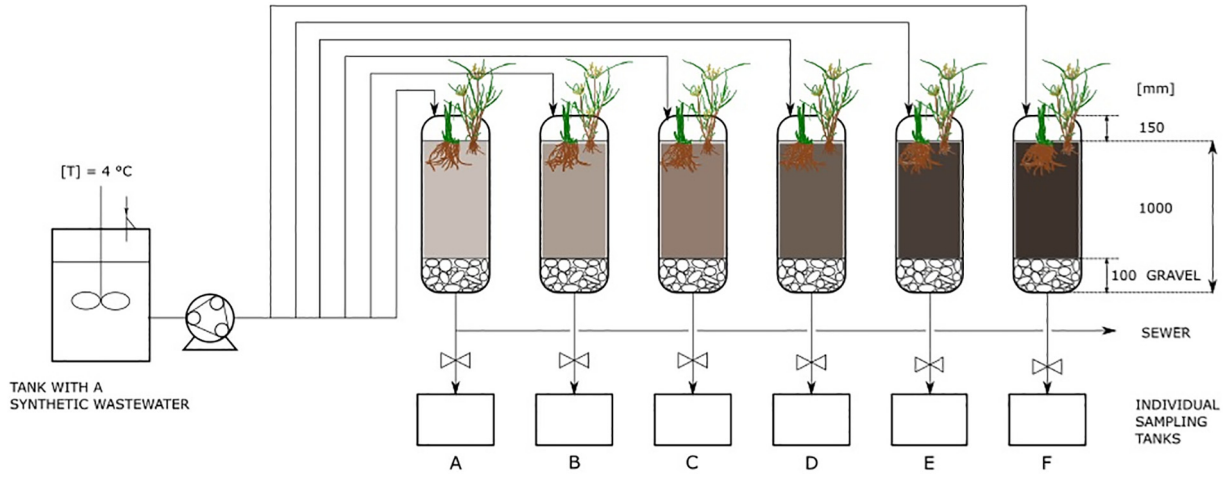

Fig. 1. Schematic of the laboratory installation (sand 100% (Column A), biochar 30% and sand (Column B), activated biochar 15% and sand (Column C), activated biochar 30% and sand (Column D), zeolite 15% and sand (Column E) and zeolite 30% and sand (Column F)).

Each column is planted with macrophytes well applied in common wetland configurations (Kadlec and Wallace, 2008; Huang et al., 2019), *Phragmites australis* and *Iris pseudacorus*, combining the benefit to have long and short roots respectively.

By providing a more developed aerial and underground roots suitable for biofilm, *P. australis* seemed to be especially favourable in the removal of pharmaceuticals (Verlicchi et al., 2013; Zhang et al., 2017). *I. pseudacorus* was selected mostly because of its strong environmental adaptability and stress resistance, but also for the reported high pollutant removal efficiencies (i.e. metals) (Huang et al., 2018).

Biochar (produced from plants by Palaterra, Germany) and zeolite (high sorption capacity from Zeobon, Germany) are mixed with a sand (Liapor, Germany) that serves as support (Table S0, Supplementary information) according to the following composition: sand 100% (Column A), biochar 30% and sand (Column B), activated biochar 15% and sand (Column C), activated biochar 30% and sand (Column D), zeolite 15% and sand (Column E) and zeolite 30% and sand (Column F). The biochar can be activated by fermentation inoculating microorganisms such as Lactobacillus, Rhodopseudomonas and Saccharomyces. Column A is used as reference case, while biochar is compared with zeolite and activated biochar at the same ratios (Columns B, F and D, respectively). If the activation of biochar would show better performances, a reduction in the percentage of the cost-intensive substrate can be evaluated (Column C) in comparison to zeolite (Column E) for a better financial assessment.

The columns are operated in down flow mode and fed simultaneously and intermittently at the same flow rate, with the same synthetic wastewater influent. This results in a similar Empty Bed Contact Time (EBCT), Hourly Space Velocity (HSV) and Hydraulic Loading Rate (HLR) for each column. To ensure comparable results, a high precision six headed pump is used (Watson Marlow, Belgium). The influent synthetic wastewater is pumped at an HLR of 100 L d^{-1} m^{-2} (resulting in 0.00116 L s^{-1} m^{-2}) for 30 min, 3 times per day. This results in EBCT of 9 days, HSV of 216 h and HLR of 0.004 nr h^{-1} (with nr defined as m^3 treated wastewater m^{-3} bed volume). Converted to flow rate per column, this gives 7.07 L d^{-1}. The pump is remotely regulated by a digital signal to feed columns as required. Dissolved oxygen concentrations were measured in situ using non-invasive oxygen sensors (PreSens, Germany) mounted at discrete depths across the lab-scale wetlands.

To mimic natural sunlight and to enable photodegradation, UV lamps (Megaman LED) are installed to provide 8 h per day of light (10 a.m. to 6 p.m.).

The standard synthetic wastewater recipe Standard OECD 303 A has been adapted to meet the final values (effluent concentrations) of COD, TN, PO_4-T and NO_3-N typical of a small/medium-sized WWTP. Tap water is mixed with 45 mg L^{-1} peptone, 35 mg L^{-1} meat extract and 8 mg L^{-1} urea, 3 mg L^{-1} of KH_2PO4 as P source. This results in COD of 60 mg L^{-1}, TN of 15 mg L^{-1}, PO_4-P of 2.5 mg L^{-1}, NO_3-N of 5 mg L^{-1}. The influent water is stored in a 225 L reservoir tank (Lely Center, Greece), and continuously mixed to ensure the solution is homogenous. The tank is kept at a constant temperature of 4 °C to minimize the formation of biofilm.

The experiment is conducted during 475 days and the synthetic wastewater spiked with the target contaminants (high purity standards TechLab, France) (1 to 5 μg L^{-1}, Table 1) after the system has reached steady conditions (last 357 days). In none of the lysimeters the biofilm has been inhibited. A sampling and monitoring protocol was established. Influent grab samples were taken weekly from the storage tank to verify the stability of synthetic influent as the spiked analyte concentrations. Effluent samples from the lysimeters were taken as 24 h composite sample once a week.

For most spiked compounds, concentrations are in the same order of those found in the effluents of the WWTPs discharging in the Sûre river (i.e. 3 μg L^{-1} benzotriazole and diclofenac, 2 μg L^{-1} tolyltriazole in a 36,000 PE WWTP effluent) (Gallé et al., 2019). Chemo-physical properties of target compounds are given in Table S1 (Supplementary information).

2.2.2. Pilot-scale wetlands set up (Reisdorf)

The biological sewage treatment plant of Reisdorf-Wallendorf was commissioned from the Syndicat Intercommunal de Depollution des Eaux Residuaires du Nord (SIDEN) and the Südeifelwerke Irrel AöR in Reisdorf. It is the first Biological Combined System (BIOCOS) within the project "Internationale Abwassergruppe Untere Our" and it came operational in June 2012. It has a capacity of 4600 PE and discharges in the Sûre river fulfilling the qualification of an innovative project (high stability, space-saving and energy efficiency) and complying with the national law restrictions for the discharge. For this, it has been considered an excellent candidate to further test the three most promising substrates of the lab scale lysimeters under real conditions.

Three cubic tanks resulting in 1 m^2 surface area each were established and operated for 6 months. The vertical flow wetlands contained from bottom to top two layers of gravel as drainage system, a substrate (sand 100% in VFCW(A), activated biochar 15% and sand in VFCW(C), zeolite 15% and sand in VFCW(E)) and finally a peat layer for insulation (Fig. 2).

The units were planted immediately after their establishment at a density of 25 plants steams per m^2 with common reeds *Phragmites australis* and *Iris pseudacorus*, distributed alternatively. The effluent of the WWTP was used as influent to the units, pumped and distributed through a perforated plastic pipe. This pipe was placed above the wetland, lying on the peat layer in a serpentine configuration in order to ensure the most uniform water distribution. At each loading (in up-down intermittent regime), the wastewater flooded the wetland surface, drained by gravity through the wetland body and collected in a 35 L plastic tank placed at bottom of each unit.

The feeding strategy consisted on three equal daily water cycle (every 8 h for 30 min) for an applied HLR of 180 L d^{-1} m^{-2} (months 1 to 2), 230 L d^{-1} m^{-2} (month 3 to 4) and finally 300 L d^{-1} m^{-2} (month 5 to

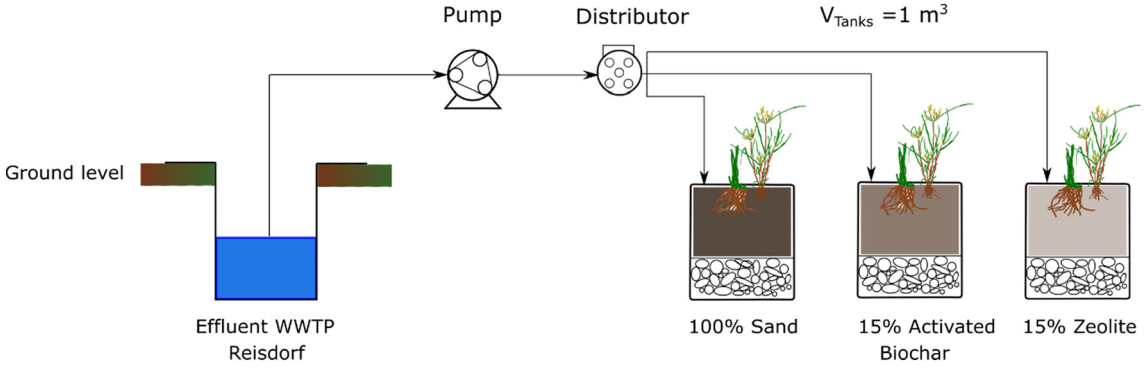

Fig. 2. Schematic of the installation in Reisdorf.

6). The Organic Loading Rate (OLR) ranged from 1.3 to 119 g COD d^{-1} m^{-2} during the 6 months of operation.

Wastewater samples were monthly collected as influent of the WWTP (24 h composite sample), effluent of the WWTP (24 h composite sample) which is the influent to the three vertical flow wetlands and effluent from the three vertical flow wetlands (grab samples) in order to assess the performance of the WWTP and the impact of the VFCW respectively.

2.3. Analytical methods

2.3.1. 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) probes.

2.3.2. Micropollutants

The analyses of the pharmaceuticals were performed externally (Luxembourg Institute of Science and Technology LIST, Luxembourg) in two steps: enrichment by Solid Phase Extraction (SPE) and analysis of the SPE extracts by LC–MS/MS. The analytical method found in the literature (Schröder et al., 2010) was adapted to the specific compounds (Table S2, Supplementary information): acid (pH 3) for X-ray media with resin-based sorbent ENV + cartridges and OASIS reversed-phase sorbent Hydrophilic Lipophilic Balanced (HLB) cartridges for all the other compounds. The methanol extracts were then rebuilt according to specific recoveries compound related into acetonitrile (i.e. ciprofloxacin, clarithromycin, erythromycin, lidocaine, sulfhametoxazole) or methanol (i.e. all the others) before being analysed by LC-MS/MS, an Agilent 1200 SL coupled with a Sciex Qtrap 4500 triple quadrupole with electrospray ionization (ESI) in positive mode. The analysis of glyphosate and AMPA were performed using chemical derivatization and on-line SPE-LC-MS/MS.

3. Results and discussion

3.1. Behaviour of MPs under controlled conditions (lab-scale investigation)

The six lysimeters planted with common reeds were operated under the same conditions but with different substrates for over 357 days.

Macropollutants' data (Table S3 in Supplementary information) indicates that the system is able to provide a consistently high COD removal efficiency (above 90%) with concentrations below 5 mg L^{-1} and excellent stable effluent quality with both pH and conductivity uniform.

The lysimeters had a poor but constant TN (around 12%) removal, which was expected as the CWs were operated mainly under aerobic conditions, so no denitrification took place. The excellent reduction of ammonia NH_4-N (effluent concentrations below an average value of 0.05 mg L^{-1}) together with the nitrate NO_3-N increase (effluent concentrations with average value of 7 mg L^{-1}), implicates well working nitrification process of autotrophic bacteria in all units. These findings are confirmed from consumed dissolved oxygen along the depth of the lysimeters monitored with in situ not invasive sensors which can also be related to enhanced oxygen transfer to the plant roots. Macro redox zones were not identified and oxidation-reduction potential was found continuously high confirming that an aerobic environment prevails in vertical flow wetland configurations (Erdirencelebi and Koyuncu, 2017).

Phosphorus removal efficiency was relevant with the highest reduction observed in Column A. This can be explained by the nature of the sand, known to be rich in Fe. Phosphorus may be retained from the substrate due to precipitation with Fe rather than adsorbed. Lysimeters with higher volume of sand are thus performing better (i.e. A, C and D) in terms of phosphorus removal. Removal values are lower in non-activated biochar (Column B) where phosphorus was initially released (Fig. S.3 in Supplementary information) and a negative removal rate observed. A standard isotherm test was carried out to confirm the result. As consequence, it was concluded that increased concentration of phosphorus in effluent was deriving from the substrate composition itself. The biochar used in this study was in fact produced through a medium temperature pyrolysis of plants (600–800 °C). After that, biochar results as a carrier of the phosphorus of the plants which can be released in the lysimeter effluent by leaching. When activated by fermentation, the phosphorus present in the biochar is used from the activating bacteria and thus not released into the effluent.

The results also show increased effluent conductivity values for all lysimeters mainly due to the substrate-biofilm interactions, which results in soluble salt release.

Micropollutants' eliminations are evaluated especially with respect to the type of substrate. The individual contribution of the different removal mechanisms (sorption, bio-, phyto- and photodegradation) is not further investigated as this investigation only examines the concentration of contaminants in water phase and neglects the characterisation of biofilm or plant tissues. The global eliminations are discussed and an attempt to determine possible driving elimination process is made.

Overall, the results showed high removal efficiencies (above 90%) across the six lysimeters. The performance of the treatment step can be clustered based on compound behaviour as following (Table 2, S.4 in Supplementary information):

- Compounds with high and stable elimination for 16 out of the 27 spiked MPs

Among them, compounds known to be persistent or difficult to be removed in conventional activated sludge systems because poorly biodegradable (i.e diclofenac, carbamazepine, diuron with less than 20% removal) (Falås et al., 2016) showed a stable elimination profile over one-year observation time. A recent study indicated carbamazepine as removed primarily by adsorption to the surface of activated carbon and biochar. A negligible elimination of this compound was previously observed in vertical flow reeds operated with conventional gravel or sand biofilter (Dalahmeh et al., 2018). As differences among the substrates are not detectable, the elimination of those compounds seems to finally benefit from a biological removal mode driven by organisms (bacteria, fungi supported by enzymes, bio-tissues) and including biotransformation, biosorption, bioaccumulation, bioprecipitation and biosolubilisation. The operation of studied lysimeters resulted in enhanced elimination through adsorption due to the prevalent aerobic conditions. The presence of active biofilm may potentially extend the lifetime of the adsorbent material and allows longer and stable elimination.

- Compounds with high but unstable elimination for 6 out of the 27 spiked MPs

Compounds show still high average rates but fluctuating over the observation time. In the case of TCPP (Fig. 3) the elimination was especially efficient in the activated biochar and zeolite-based lysimeters.

In absence of an activated biofilm (Column B), the adsorption of TCPP declined probably due to the completion for adsorption surface between organic matter and the other micropollutants. TCPP resulted to be eliminated in smaller extend with the sand substrate (Column A) and those lysimeters where the proportion of sand towards adsorbing material was higher (Columns C and E).

This may be related to the smaller specific surface area of sand in comparison with to the sand mixed with biochar or zeolite.

- Compounds with medium elimination for the remaining 5 spiked MPs

Differences can be detected among the substrates with a general tendency towards better performances for activated biochar and zeolite-based lysimeters. While glyphosate is highly removed from all substrates during the observation time in line with literature as it is known to be adsorbed by clays and organic matter (Aparicio et al., 2013), the adsorption of its metabolite AMPA declined towards lower elimination rates (Fig. 4 and Fig. 5).

Table 2
: Elimination rates in the lysimeters.

	Compound	Column A			Column B			Column C			Column D			Column E			Column F		
		Min	Max	Average	Min	Max	Average	Min	Max	Average	Min	Max	Average	Min	Max	Average	Min	Max	Average
high and stable elimination	Atenolol	94.6	99.7	99	89.1	99.7	98.7	89.2	99.7	98.6	95.8	99.7	99	98.6	99.7	99.3	94.9	99.7	98.9
	Bezafibrate	96.4	100	99.6	99	100	99.8	96.3	100	99.6	97	100	99.7	99.5	100	99.9	92.6	100	99.4
	Carbamazepine	96.9	99.9	99.6	93.8	99.9	99.5	99.5	99.9	99.8	95.3	99.9	99.6	99.2	99.9	99.8	91.5	99.9	99.3
	Clarithromycin	91.5	99.9	98.5	81.7	99.9	98.4	90.3	99.9	98.7	95.5	99.9	99.1	97.9	99.9	99.4	89.2	99.9	98.7
	Diclofenac	96.1	100	99.5	98.8	100	99.8	98.8	100	99.8	98.2	100	99.8	98.8	100	99.8	92	100	99.3
	Ketoprofen	98	100	99.7	98.7	100	99.8	98.7	100	99.9	97.5	100	99.7	96.2	100	99.7	91.9	100	99.3
	Lidocaine	96.8	100	99.7	98.7	100	99.9	98.8	100	99.9	98.6	100	99.8	98.7	100	99.9	91.6	100	99.2
	Metoprolol	92.1	100	99.2	98.7	100	99.8	99.2	100	99.9	96.2	100	99.7	99.2	100	99.9	82.6	100	98.9
	Propranolol	95.6	99.9	99.5	98.4	100	99.8	98.4	99.9	99.8	98.2	100	99.8	98.4	100	99.8	92.7	100	99.5
	Benzotriazole	92.4	99.9	98.7	96.5	99.9	99.2	96.8	99.9	99.2	93.8	99.9	99.1	86.4	99.9	98.6	-60.6(90)	99.9	90(98.3)
	Carbendazim	96.8	99.9	99.5	98.5	99.9	99.6	98.9	99.8	99.6	99.5	99.9	99.7	86.5	99.8	98.2	90.7	99.9	99.1
	Diuron	94.9	99.8	99.2	95	99.8	99.4	95.2	99.8	99.4	94.6	99.8	99.4	95	99.8	99.4	90.5	99.8	98.9
	Isoproturon	92.1	99.8	99.2	92	99.8	99.3	92.3	99.8	99.3	91.2	99.8	99.2	92	99.8	99.3	90.7	99.8	98.8
	Terbutryn	96.6	99.9	99.5	96.5	99.9	99.7	96.6	99.9	99.7	96.2	99.9	99.6	96.5	99.9	99.6	-71(95.7)	99.9	91(99.4)
	Tolyltriazole	96.5	99.9	99.5	96.5	99.9	99.6	96.6	99.9	99.6	96.1	99.9	99.6	96.5	99.9	99.6	90	99.9	99
	Glyphosate	98.2	99.9	99.7	99.4	99.9	99.8	99.4	99.9	99.9	98.3	99.9	99.8	94.1	99.9	99.6	95.3	99.9	99.4
high but unstable elimination	Ciprofloxacin	75.3	99.7	95.3	77.9	99.7	96.1	74.9	99.7	96.1	76.2	99.7	96.2	75.7	99.7	96.2	75.7	99.7	94.2
	Erythromycin A	93.5	99.8	98.2	95.5	99.8	98.3	95.7	99.8	98.4	95.8	99.8	98.4	95.5	99.8	98.4	92.3	99.8	98.2
	N-acetyl sulfamethoxazole	7.3	88	76.4	5.6	88.5	76.2	4	87.3	75.8	7.3	88.7	76.2	15.3	88.4	76.2	12.1	89.3	76.7
	Sulfamethoxazole	97.8	99.9	99.6	96.9	99.9	99.6	97.8	99.9	99.7	97.4	99.9	99.6	97.7	99.9	99.7	93.6	99.9	99.2
	DEET	96.9	99.9	99.4	93.8	99.9	98.6	95.8	99.9	99.3	98	99.9	99.4	97.7	99.9	99.4	50.8	99.9	95.8
	TCPP	62.1	96.4	86.6	-36(28.5)	96.2	79.9(85)	66.1	97.4	89.2	77.9	98	90.4	72.7	98.6	89.8	26	98.4	88.2
medium elimination	Cyclophosphamide	3.2	99.9	77.1	9.9	98.1	57.6	30.4	99.6	74.3	41.2	99.6	80.3	18	100	76.9	-3(6.7)	100	62(65.9)
	MCPP	88.8	99.8	98.6	61.5	97.6	87.7	94.3	99.7	98.6	91.7	99.7	99	89.7	99.8	98.8	72.5	99.8	94.8
	AMPA	21	99.3	78.6	9.4	94.8	55.6	17.1	98.5	73.7	29.8	98.4	70	39.6	99.3	83.7	-55	99.3	69 (75.6)
	PFOS	17.2	99.9	89.5	-15.1	99.7	66.1	29	99	85.9	46.7	99.9	87	-20	99.9	89.3	-94.8	99.8	82.2
	PFOA	-33.4	96.6	51.4	-43.4	93.3	35.6	-28.7	93.6	42.4	-25.6	89.6	45.7	-33.1	95.8	51.3	-66.5	99.9	54.8
	Average/Substrate			**94**			**91**			**94**			**94**			**95**			**93**

Glyphosate is expected to be rapidly released from these adsorption sites by the competence with inorganic phosphates (Aparicio et al., 2013; Wang et al., 2016). The microflora present in the substrate would then degrade glyphosate to AMPA as metabolite which would ideally accumulate in the substrate giving preference to sorption mechanism (Aparicio et al., 2013; Wang et al., 2016).

AMPA in fact contains phosphate known to be adsorbed onto mineral surface (Nowack and Stone, 2006). The elimination of AMPA is progressively decreasing showing a path independent from the constant load of the feeding and suggesting a limited capacity for the selected substrates towards this compound. Generally, zeolite-based substrates showed a better affinity which can be boosted from the higher cation exchange capacity of this material.

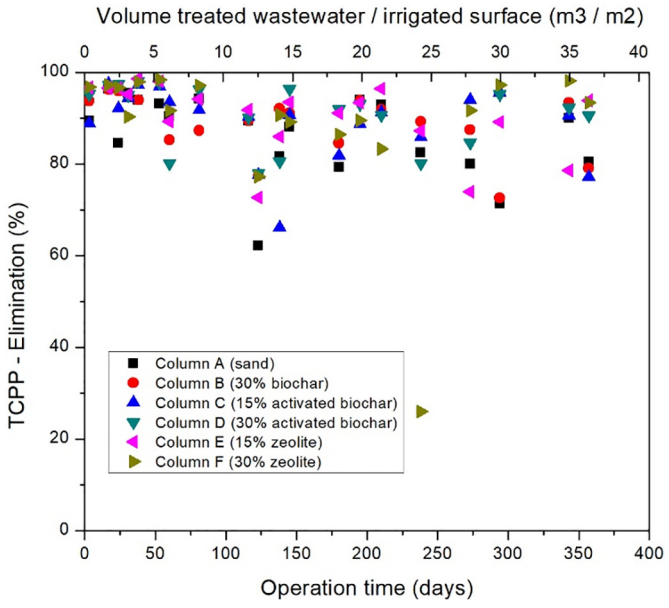

Fig. 3. Elimination of TCPP in the lysimeters treating synthetic wastewater during 357 days.

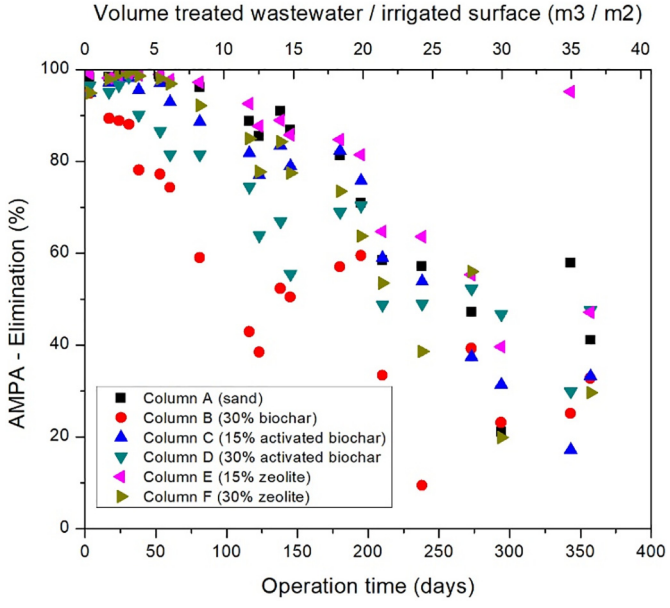

Fig. 4. Elimination of AMPA in the lysimeters treating synthetic wastewater during 357 days.

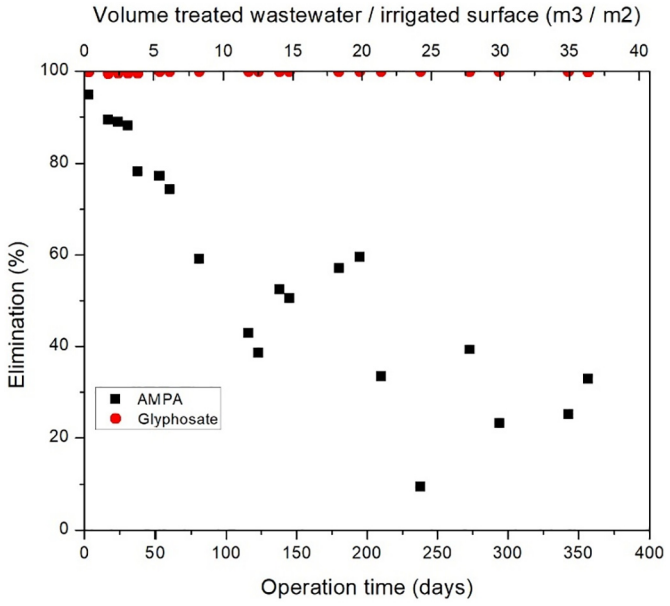

Fig. 5. Elimination of AMPA towards glyphosate in Column B treating synthetic wastewater during 357 days.

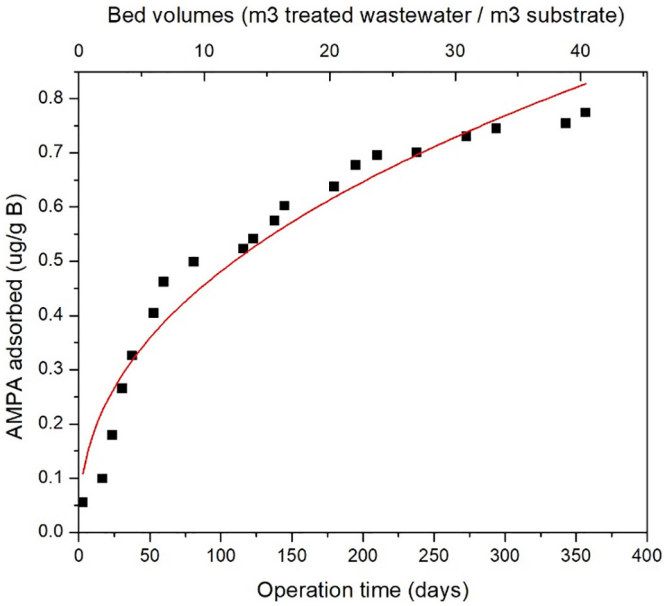

Fig. 6. Breakthrough curve of AMPA in biochar based lysimeter treating synthetic wastewater during 357 days. Spiked concentration: 5000 ng L^{-1}.

Some understanding about the possible sorption process can be derived by exploring how experimental data may fit one of the most popular models, the Freundlich one. The Freundlich equation has an empirical origin, but can be derived from the Langmuir isotherms and thus it is able to describe the complexity of the sorption process (Chowdhury et al., 2012). In this case, the excellent fit to the Freundlich equation reflects the heterogeneity of the sorbent material as well as possible interactions between the adsorbed molecules.

The adsorption of AMPA to the surface of these materials can be described Eq. (1), which defines the relation between the loading q of the substrate (amount of adsorbate adsorbed per g of adsorbent) (Samarghandi et al., 2014) and the operation time at which the effluent concentration is measured. K and n can denote the adsorption parameters.

$$q = \mathrm{K}\, T^{1/n} \tag{1}$$

Breakthrough is shown as function of the lysimeters operation time and the adsorbed concentrations are normalized by the weight of the individual substrate (cumulative curve, Fig. 6). After 250 days of operation AMPA broke through to 60% defined as c/c0 (Benstoem et al., 2017) where c is the effluent and c0 the influent concentration, and equivalent to 40% elimination.

Cyclophosphamide and MCPP depicted similar behaviour (S5 in Supplementary information). Adsorption parameters for the three compounds mentioned above are collected in Table 3.

The reproducibility of the data used to generate the adsorption coefficients can be judged by means of the regression coefficient (square of the Pearson Product-Moment Correlation Coefficient) R_2. The closer to 1 the value is then the more reproducible the data used to calculate.

The value of the adsorption constant (K, denoted as capacity factor) can be useful in gauging the difference in the adsorption capacity of a given material for a range of compounds or the adsorption capacity of a given compound for a range of materials, as long as the exponent value (1/n, denoted as intensity parameter) is relatively constant (Dordio et al., 2011). The heterogeneity of K and n however does not allow an immediate comparison among the substrates.

Considering that the individual compound kinetic follows a pseudo-first order approximation along the time of operation, the exponential distribution of each compounds with respect to the individual substrates has been determined by curve fitting using the data in Table 3 so that the results of the substrates can be easily compared (Fig. 7 and S6 in Supplementary information).

According to the only coefficient displayed in Table 3, AMPA seems to be well adsorbed in lysimeters A and C with higher K at given n. However, from the modelled degradation kinetic, column E depicted a slightly better performance by having lower calculated K and n coefficients. Once the plateau has been reached after 250 days of operation, Column B has treated 2.7 m^3 of synthetic wastewater adsorbing around 0.77 μg of AMPA per g of substrate in comparison to 1 μg of AMPA adsorbed per g of A and C. Similarly, cyclophosphamide showed a slight preference for Column C, 1 μg of active ingredient has been adsorbed per g of substrate C in comparison to 0.7 μg adsorbed per g of B. MCPP showed the lowest affinity for adsorption reaching 0.2 μg of active ingredient adsorbed per g of substrates with the only exception of B and F.

PFOS (Fig. 8) showed high and stable eliminations during the first 100 days of operation and a general decay thereafter, with lower elimination in the sand (Column A) and non-activated biochar (Column B). This may indicate that the removal mechanism for this compound is a combination of adsorption and biodegradation as high elimination are observed when a higher percentage in volume of activated biochar is applied (from Column C to D). PFOA (Fig. 9) confirmed a similar behaviour depicting a low elimination for sand and non-activated biochar towards better removal when higher percentage in volume of activated biochar is applied. Still biological degradation may be less effective for PFOA in comparison to PFOS.

For both compounds the effluent of the lysimeters contained in few occasions (after 138 and 273 days of operation) higher concentration of active ingredient in comparison to the influent (Fig. 10).

Such negative removal can be explained by desorption of the accumulated compounds on the substrates which can be only temporary retained. The rapid increase in elimination thereafter suggests a 'regeneration' of the sorption site newly available. Similar behaviour has been observed in a previous study (Wang et al., 2018).

3.2. Behaviour of MPs under variable conditions (pilot-scale investigation)

3.2.1. Occurrence and removal efficiencies of 27 selected MPs in the WWTP of Reisdorf

The occurrence of the 27 selected compounds was investigated at the influent and effluent of WWTP Reisdorf in order to validate laboratory results and evaluate the removal efficiencies and the impact of a possible polishing

Table 3
Adsorption parameters of mentioned compounds after adsorption from synthetic wastewater on sand 100% (Column A), biochar 30% and sand (Column B), activated biochar 15% and sand (Column C), activated biochar 30% and sand (Column D), zeolite 15% and sand (Column E) and zeolite 30% and sand (Column F).

	AMPA				Cyclophosphamide				MCPP			
	K	n	1/n	R_2	K	n	1/n	R_2	K	n	1/n	R_2
Column A	0.0630	2.0303	0.4925	0.9599	0.0630	2.0303	0.4925	0.9599	0.0039	1.4682	0.6811	0.9908
Column B	0.0677	2.3482	0.4259	0.9456	0.0626	2.2585	0.4428	0.9741	0.0042	1.5286	0.6542	0.9879
Column C	0.0635	2.0656	0.4841	0.9566	0.0598	2.0413	0.4899	0.9791	0.0039	1.4686	0.6809	0.9909
Column D	0.0626	2.1112	0.4737	0.9629	0.0521	1.9141	0.5224	0.9868	0.0038	1.4613	0.6843	0.9911
Column E	0.0581	1.9515	0.5124	0.9692	0.0605	2.0259	0.4936	0.9786	0.0039	1.4647	0.6827	0.9909
Column F	0.0695	2.1449	0.4662	0.9437	0.0686	2.2824	0.4381	0.9739	0.0036	1.5481	0.6460	0.9597

step with VFCWs. Average concentrations of each compound together with WWTP removal efficiencies are reported in Table 4. The standard deviation quantifies the high variability between sampling days with respect to the number of analysed samples (N).

Among 27 MPs, 7 compounds were not detected in relevant concentrations in both influent and effluent of the WWTP due to the following possible reasons:

- cyclophosphamide: among cytostatics, cyclophosphamide is not the most administrated one and presents a number of metabolites and transformation products not considered in this study. Only 10% of the administrated active ingredient is excreted unchanged via urine;
- erythromycin: among macrolides this antibiotic mostly suffers from analytical detection problem. Also, only 5% of the administrated active ingredient is excreted unchanged via urine;
- carbendazim: the EC does not approve carbendazim as an active substance for use of biocidal products of product-type 9 reducing strongly its application;
- diuron: the use of this substance has been limited by the EC and is under assessment as endocrine disruptive;
- isoproturon: the application was not renewed from the EC in 2016 due to its eco-toxicity relevance and carcinogenic potential;
- terbutryn: the low concentration indicates that wastewater treatment plants are not relevant sources of emission; however higher concentrations can be expected in summer during the main season of pesticide use. A possible high level in surface bodies must be thus related to other factors (i.e. Combined Sewer Overflow (CSO), diffuse emission from agriculture etc);
- MCPP: concentration of mecroprop are varying starting with the use (manufacturer garden and household) and with climate changes (increased temperatures, seasonal variability, humidity and rainfalls).

As consequence, it was not possible to calculate the WWTP removal efficiency (n.c. not calculated) for the compounds mentioned above (Table 4).

For 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 to 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 treatments. Additionally, its metabolites can build back to the parent compound (Ternes, 1998; Bahlmann et al., 2014; Scheurer et al., 2015). A zero removal is thus assumed;
- metoprolol and propranolol are usually present in wastewater in highly varying concentrations because used irregularly from the patients compared to their companion atenolol, affecting severely the interpretation of the results;
- AMPA is a transformation product of glyphosate and thus its fate has to be related to its parent compound.

Benzotriazole, TCPP, glyphosate, diclofenac, tolyltriazole and DEET were detected as the most abundant in the WWTP influent exceeding 1000 ngL^{-1} average concentrations. Among them:

- DEET was highly removed (over 90%), together with atenolol, bezafibrate and ketoprofen;

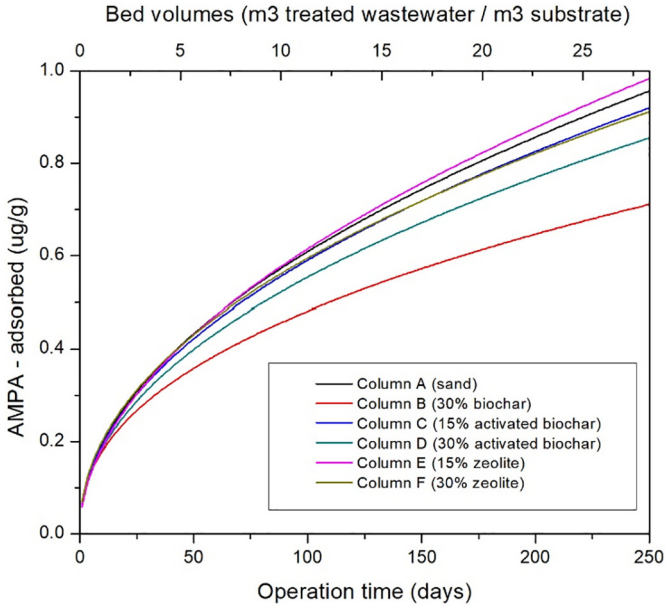

Fig. 7. Modelled AMPA degradation kinetics in lysimeters treating synthetic wastewater during 250 days. Spiked concentration: 5000 ng L^{-1}.

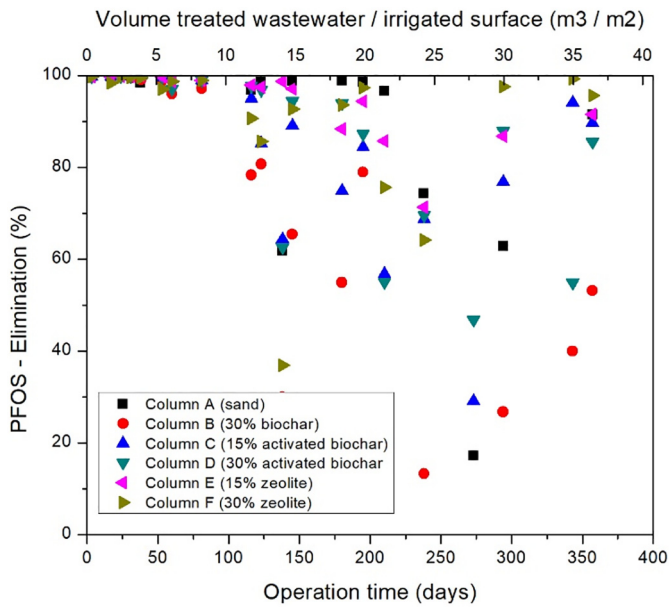

Fig. 8. Elimination of PFOS in the lysimeters treating synthetic wastewater during 357 days.

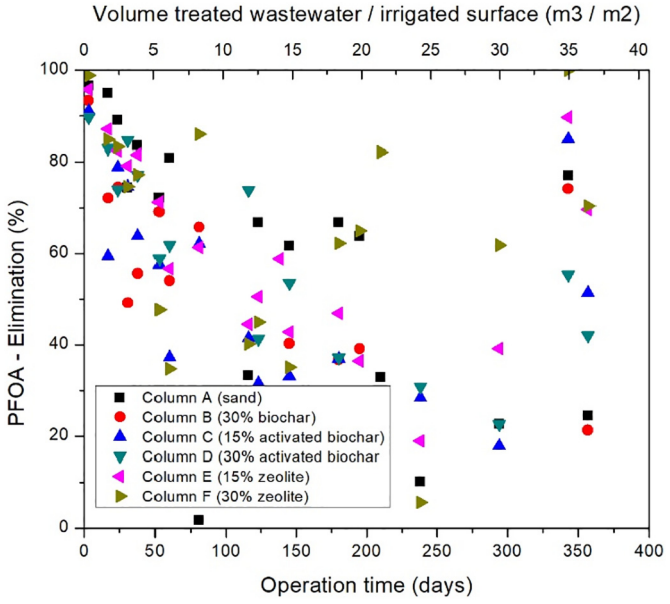

Fig. 9. Elimination of PFOA in the lysimeters treating synthetic wastewater during 357 days.

- benzotriazole, TCPP, tolyltriazole and diclofenac where moderately removed (40% < removal < 90%), together with the highly administrated antibiotics clarithromycin and ciprofloxacin.

High removal efficiencies are not always related to low final concentrations of the selected compounds thus the need of a polishing step has to be contextualised.

WWTP effluent concentrations of TCPP, tolyltriazole, diclofenac are relevant. Clarithromycin, discharged with an average concentration of 168 ng L^{-1} from Reisdorf WWTP, has been introduced in the Watch List (EC) 2015/495 (2015) (EC, 2015) with an AA-EQS. 90 ng L^{-1}.

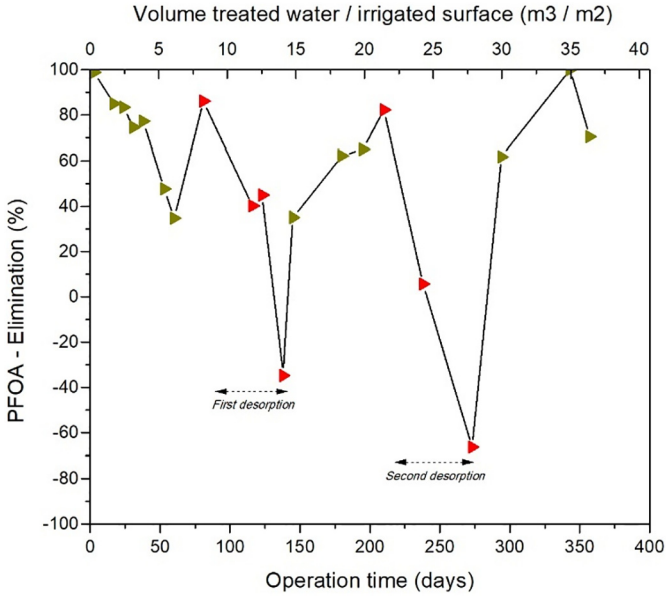

Fig. 10. Elimination of PFOA in Column F (30% zeolite) treating synthetic wastewater during 357 days: two desorption events are identified and displayed with red data points (138 days, 273 days). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 4
Average concentrations (±Std) measured during the observation period (6 months) for 27 compounds (ng L^{-1}) and WWTP removal efficiencies (%), $N = 11$.

Compound	WWTP		
	Influent (ngL^{-1})	Effluent (ngL^{-1})	Removal (%)
Atenolol	912 ± 258	50 ± 23	95
Bezafibrate	736 ± 137	16 ± 11	98
Carbamazepine	120 ± 119	139 ± 12	0
Clarithromycin	360 ± 172	168 ± 25	54
Ciprofloxacin	537 ± 307	152 ± 89	72
Cyclophosphamide	<LOQ	<LOQ	n.c.
Diclofenac	2374 ± 946	995 ± 446	58
Erythromycin	<LOQ	<LOQ	n.c.
Ketoprofen	215 ± 149	10 ± 10	95
Lidocaine	59 ± 22	72 ± 50	0
Metoprolol	323 ± 126	367 ± 149	n.c.
Propranolol	41 ± 35	78 ± 37	n.c.
N-acetyl sulfamethoxazole	139 ± 306	23 ± 27	83
Sulfamethoxazole	133 ± 277	59 ± 57	56
Benzotriazole	5308 ± 1336	1571 ± 701	70
Carbendazim	<LOQ	<LOQ	n.c.
DEET	1279 ± 1090	108 ± 11	92
Diuron	<LOQ	<LOQ	n.c.
Isoproturon	<LOQ	<LOQ	n.c.
Terbutryn	<LOQ	<LOQ	n.c.
MCPP	<LOQ	<LOQ	n.c.
TCPP	9672 ± 2589	3076 ± 1080	68
Tolyltriazole	1508 ± 424	761 ± 212	50
Glyphosate	1297 ± 2508	477 ± 840	63
AMPA	1175 ± 263	2195 ± 1001	−87
PFOS	96 ± 25	15 ± 16	84
PFOA	39 ± 15	12 ± 9	69

3.2.2. Removal efficiencies of 27 selected MPs in the pilot-scale installation of Reisdorf

Table 5 reports the average removal efficiencies of each investigated compound where the three substrates are applied over 180 days of operation. The influent to the three VFCWs is equal to the WWTP effluent. Among 27 micropollutants, 18 compounds were considered relevant.

When the average removal rate is compared (Fig. 11), the substrate with activated biochar (VFCW(C)) shows the best removal rates towards the selected compounds with special attention to the highly administrated antibiotics (clarithromycin and ciprofloxacin), beta-blockers, diclofenac and tolyltriazole.

Overall, none of the VFCWs was able to remove further the flame retardant TCPP. A relevant concentration in the effluent is detected (above 2000 ng L^{-1}). Same conclusion for AMPA which has to be related to its parent compound glyphosate.

When compared with the results of real matrix, laboratory experiments show to be a robust approach that can give indications for compounds not relevant in our domestic wastewater (i.e. isoproturon, diuron, etc.) but that may be relevant for CSOs and run off waters. Eliminations for activated biochar substrate in both synthetic and wastewater matrices are selected paying attention to those compounds present in relevant concentrations in the effluent of the WWTP of Reisdorf and classified as compounds with high and stable elimination for the lab-scale lysimeters. This selection allowed to compare the removal elimination in wastewater matrix with the stable average removal elimination from laboratory scale (Fig. 12).

Results show:

- excellent agreement (delta less than 6%) between laboratory and pilot plant for benzotriazole, clarithromycin, diclofenac, glyphosate, lidocaine, metroprolol, propranolol, tolyltriazole;
- a good agreement (delta between 6 and 25%) for AMPA, carbamazepine, ciprofloxacin and DEET;
- a medium/low agreement (delta higher than 30%) for the others;

which can indicate potentially high removal efficiencies also for those compounds (bezafibrate, carbendazim, diuron, isoproturon, ketoprofen) not

Table 5
Average concentrations (±Std) measured during the observation period (6 months) for 18 compounds (ng L^{-1}) and VFCWs efficiencies (%), $N = 11$.

Compound		VFCW(A)		VFCW(C)		VFCW(E)	
	Influent (ngL^{-1})	Removal (%)	Effluent (ngL^{-1})	Removal (%)	Effluent (ngL^{-1})	Removal (%)	Effluent (ngL^{-1})
Atenolol	50 ± 23	49	25	54	23	53	24
Carbamazepine	139 ± 12	79	29	92	11	84	22
Clarithromycin	168 ± 25	93	12	96	7	96	7
Ciprofloxacin	152 ± 89	78	33	82	28	81	29
Diclofenac	995 ± 446	97	25	99	12	98	21
Lidocaine	72 ± 50	94	4	96	3	96	3
Metoprolol	367 ± 149	92	31	97	10	96	16
Propranolol	78 ± 35	91	7	94	4	94	4
N-acetyl sulfamethoxazole	23 ± 27	77	5	83	4	79	5
Sulfamethoxazole	59 ± 57	24	45	73	16	11	53
Benzotriazole	1571 ± 701	93	111	98	28	95	76
DEET	108 ± 11	64	39	78	24	46	58
Tolyltriazole	761 ± 212	97	24	99	9	98	18
Glyphosate	477 ± 840	96	17	93	35	94	27
AMPA	2195 ± 1001	81	414	59	894	71	639
TCPP	3076 ± 1080	29	2172	28	2219	30	2149
PFOS	15 ± 16	48	8	45	8	44	8
PFOA	12 ± 9	20	10	18	10	29	9
Total average removal (%)		71		76		71	
Total average removal excluding Fluoro-surfactant (%)		75		81		74	

present in relevant concentrations in the effluent of the WWTP of Reisdorf but classified as compounds with high and stable elimination for the lab-scale lysimeters.

For compounds like ciprofloxacin and DEET high elimination can still be expected with a lower magnitude compared to laboratory results. For TCPP the impact of the matrix seemed to be higher and the competition between sorption and biodegradation stronger.

Among the compounds with medium elimination only AMPA seems to be present in relevant concentrations in the effluent of the WWTP of Reisdorf. To model the overall elimination of AMPA a single exponential function along the operation time is used. According to the modelled global degradation kinetics, AMPA seemed to be equally adsorbed from sand mixed to activated biochar 15% in both synthetic and real wastewater matrices (similar slope of the curve, S7 in Supplementary information).

3.2.3. Relative contributions of conventional WWTP and VFCW to the removal of relevant MPs

The removal contributions of the two treatment steps (conventional WWTP and additional treatment step VFCW) to the overall elimination of the selected compounds (Fig. 13) is especially reflected in the final effluent concentrations discharged in the receiving river.

The VFCW (C) resulted to be:

- the dominant treatment in the elimination of those compounds that are known to be persistent and hardly removed in Conventional Activated Sludge treatments (i.e. carbamazepine and lidocaine);
- a strong contributor in the elimination of antibiotics (especially clarithromycin and ciprofloxacin), diclofenac, benzotriazole and tolyltriazole;
- a not significant contributor in the elimination of those compounds highly degraded from the WWTP (i.e. atenolol, DEET, TCPP and fluorosurfactants).

In a regulatory perspective, the use of a VFCW for the WWTP of Reisdorf allows to comply with the 80% removal threshold for the four mandatory compounds defined by Luxembourgish Water Administration diclofenac, carbamazepine, clarithromycin and benzotriazole (Administration de Gestion de l'eau, 2020) with the average removal rate of 99, 92, 96 and 98% respectively.

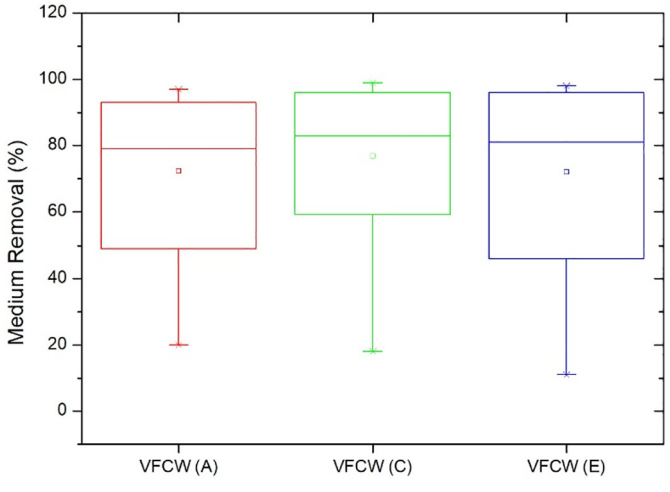

Fig. 11. Average removal efficiencies of the three VFCWs.

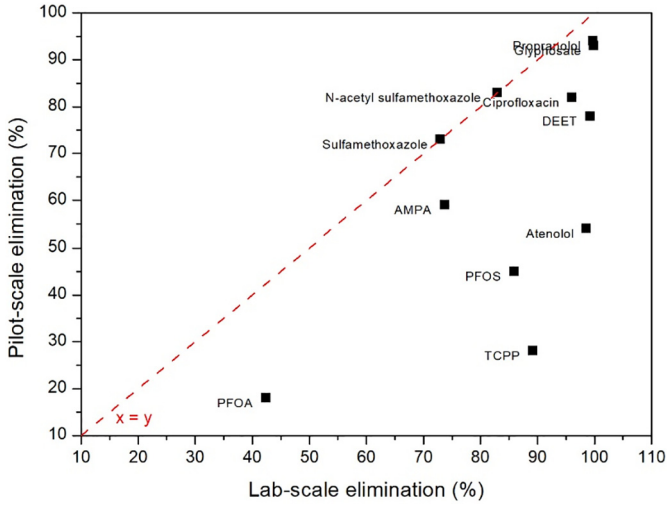

Fig. 12. Pilot versus Lab-scale data (above 95% elimination not displayed).

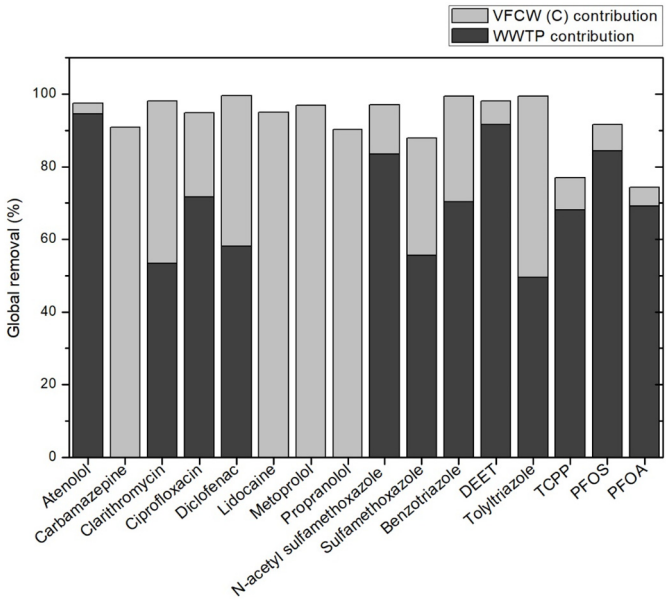

Fig. 13. Relative contributions of the VFCW(C) and the WWTP to the overall global average removal efficiencies.

4. Conclusions

On the basis of the data set collected from running one year six lysimeters in laboratory's controlled conditions and six months three VFCWs under real variable conditions, the following conclusions are drawn:

- Generally, the majority of the selected compounds showed a high and stable removal over the observation time. In particular, compounds known to be persistent (i.e. carbamazepine and diclofenac) are proven to be well degraded in a VFCW configuration due to the chosen substrate affine to biosorption and alternative feeding regime. TCPP shows evidence of being more vulnerable as high concentrations are still detected making difficult to have conclusive statement about the most dominant mechanism for its degradation. Few compounds (i.e. AMPA and cyclophosphamide) rather showed to be poorly removed suggesting sorption as their driving mechanism. A curve fitting approach demonstrated to be a valid method to describe the process and quantify the maximum amount of active ingredient adsorbed per amount of substrate used. Column B with activated biochar has treated 2.7 m3 of synthetic wastewater adsorbing around 0.77 μg of AMPA per g of substrate in comparison to 1 μg of AMPA adsorbed per g of substrate present in columns A and C respectively.
- The occurrence and removal of selected compounds was evaluated in a VFCW configuration under real conditions. The removal of relevant emerging contaminants was higher in activated biochar substrate and confirmed good alignment with laboratory results. This comparison clearly highlights not only the robustness of laboratory scale findings but also allows to extend conclusions about compounds that are not relevant in municipal wastewater but that may be relevant for example for CSO. It is the case of biocides that are reversed in surface water via bioleaching during rain events (i.e. diuron, isoproturon etc) and that could be treated with a VFCW.
- The need end feasibility of a VFCW as polishing step to remove relevant emerging contaminants from the effluent of a conventional wastewater treatment plant has been demonstrated: more than 80% removal has been achieved for more persistent (i.e. carbamazepine and diclofenac), highly used (i.e. benzotriazole) and eco-toxic relevant compounds.

CRediT authorship contribution statement

Silvia Venditti: Writing – original draft preparation, Writing – reviewing and editing, Formal analysis, Methodology, Conceptualization, Investigation, Visualization, Data curation. **Hana Brunhoferova**: Writing – reviewing and editing, Formal analysis, Methodology, Conceptualization, Investigation, Visualization, Data curation. **Joachim Hansen**: Supervision, Funding acquisition, Project administration, Writing – original draft preparation, Writing – reviewing and editing.

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.

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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.2022.153234.

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