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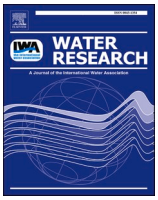

Bioremediation of rapid sand filters for removal of organic micropollutants during drinking water production

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ABSTRACT

Rapid sand filtration (RSF) is used during drinking water production for removal of particles, possible harmful microorganisms, organic material and inorganic compounds such as iron, manganese, ammonium and methane. However, RSF can also be used for removal of certain organic micropollutants (OMPs). In this study, it was investigated if OMP removal in columns packed with sand from full scale RSFs could be stimulated by bioaugmentation (i.e. inoculating RSFs with sand from another RSF) and/or biostimulation (i.e. addition of nutrients, vitamins and trace-elements that stimulate microbial growth). The results showed that removal of PFOA, carbamazepine, 1-H benzotriazole, amidotrizoate and iopamidol in the columns was low (< 20 %). Propranolol and diclofenac removal was higher (50–60 %) and propranolol removal likely occurred via sorption processes, whereas for diclofenac it was unclear if removal was a combination of physical-chemical and biological processes. Moreover, bioaugmentation and biostimulation resulted in 99 % removal of gabapentin and metoprolol after 38 days and 99 % removal of acesulfame after 52 days of incubation. The bioaugmented column without biostimulation showed 99 % removal for gabapentin and metoprolol after 52 days, and for acesulfame after 80 days. In contrast, the non-bioaugmented column did not remove gabapentin, removed < 40 % metoprolol and showed 99 % removal of acesulfame only after 80 days of incubation. Removal of these OMPs was negatively correlated with ammonium oxidation and the absolute abundance of ammonia-oxidizing bacteria. 16S rRNA gene sequencing showed that OMP removal of acesulfame, gabapentin and metoprolol was positively correlated to the relative abundance of specific bacterial genera that harbor species with a heterotrophic and aerobic or denitrifying metabolism. These results show that bioaugmentation of RSF can be successful for OMP removal, where biostimulation can accelerate this removal.

1. Introduction

Intake waters for drinking water production such as surface water, can contain low concentrations (ng/L to μg/L level) of organic micropollutants (OMPs), such as pesticides, pharmaceutically active compounds (PhACs), endocrine disrupting compounds, X-ray contrast media and personal care products (Gros et al., 2009; Houtman, 2010; Jürgens et al., 2002; Kasprzyk-Hordern et al., 2008; Kolpin et al., 2002; Stolker et al., 2004). Despite their low concentrations, some micropollutants are of concern to aquatic organisms and human health, also because the effects of these OMP mixtures are unknown (Schwarzenbach et al., 2006). The regulatory standards for OMPs in drinking water in the Netherlands are low, with for instance a maximum allowed concentration of 0.1 μg/L for individual pesticides and 0.5 μg/L for total pesticides (Anonymous, 2012). In other to comply with legal requirements for OMP concentrations in drinking water, these compounds need to be sufficiently removed during drinking water production. Moreover, when OMP concentrations increase in surface waters in the future (Bernhardt et al., 2017), even more extensive treatment of surface water needs to be implemented.

Rapid sand filtration (RSF) is a process that is applied for decades in drinking water treatment to remove suspended solids, organic carbon, metal oxides and ammonium. There are increasing indications that OMPs, such as pharmaceuticals and pesticides, are biologically removed during RSF (Benner et al., 2013; Feld et al., 2016; Hedegaard and Albrechtsen, 2014; Shimabuku et al., 2019; Vandermaesen et al., 2019; Wang et al., 2021; Zearley and Summers, 2012; Zhou et al., 2022). Physical-chemical processes (i.e. sorption, filtration) and/or biological

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processes (metabolism or co-metabolic nitrification or methane oxidation) are likely responsible for this OMP removal during RSF (Wang et al., 2021). Sorption can occur to the sand of an RSF, but also to the formed metal oxides (Wang et al., 2021).

In a previous study, we found that full scale RSFs from different drinking water treatment plants in the Netherlands showed different OMP removal capacities, which could be due to differences in filter sand and/or the microbial community composition (Di Marcantonio et al., 2020). Therefore, we hypothesized that augmentation of filter sand from RSFs that showed good removal could enhance the removal capacity of RSFs that showed insufficient OMP removal. Bioaugmentation of RSFs was at least successful for the removal of 2, 6-dichlorobenzamide (BAM) (Albers et al., 2015; Horemans et al., 2017a; b). The objective of our study was, therefore, to determine the effect of bioaugmentation on OMP removal in columns packed with filter sand from an RSF that poorly removed certain OMP by adding filter sand from an RSF that showed high OMP removal. In addition, we also studied the effect of biostimulation on OMP removal in our experiments by addition of a nutrient solution (ammonium, nitrate and phosphate) and/or vitamins/trace-elements solution to these columns. This experiment was done with a selection of 10 different OMPs: acesulfame, amidotrizoate, 1-H benzotriazole, carbamazepine, gabapentin, diclofenac, iopamidol, metoprolol, propranolol and perfluorooctanoic acid (PFOA). These OMPs were chosen based on 1) their occurrence and concentration in surface water, 2) their known removal efficiencies during RSF and other treatment processes, 3) the list of guide- and priority substances from the national institute for public health and environment (RIVM) and 4) the differences in molecular properties.

2. Materials and methods

2.1. Experimental set-up

Column studies were performed using filter sand from a full scale RSF that did not remove any OMP (location 6 from Di Marcantonio et al. (2020)) and filter sand from a full scale RSF that removed at least 6 out of 30 detected OMPs, namely cyclamate, caffeine, gabapentin-lactam, metformin, valsartan, and saccharine (location 4 from Di Marcantonio et al. (2020)). For bioaugmentation, sand from location 4 was mixed with sand from location 6 (10% v/v) prior to column packing (inoculum B). The non-bioaugmented column existed solely of sand from location 6 (inoculum I). Column studies were done using four glass columns (100 cm height, 3,5 cm diameter, column volume 770 ml) that were filled up to 80 cm with filter sand. Columns were wrapped with dark styrofoam to protected them from light and temperature fluctuations. The temperature was controlled at 18–20 °C. Column influent water was collected weekly from natural surface water that was the RSF influent water of location 6. This water was filtered (100 μm mesh size) to remove larger particles and stored in one separate stainless-steel tank for each column. Thereafter, these tanks were spiked with OMPs and a nutrient-solution and/or vitamins/trace-elements solution, according to Table 1. The composition of these solutions is given in Table S1 and Table S2. The concentration of ammonium, nitrate and phosphate of the natural surface water was measured over the last years and used to determine the composition of the nutrient solution by complementing the surface water to reach its yearly maximum of 0.8–1 mg/L ammonium, 0.06 mg/L phosphate and 4–6 mg/L nitrate (Figure S1 and Figure S2).

Table 1
Experimental set-up of the column experiments.

	Column 1	Column 2	Column 3	Column 4
OMP mixture	+	+	+	+
Intake water (influent)	+	+	+	+
Nutrient-solution	+	−	+	+
Vitamines/trace-elements solution	+	+	−	+
Bioaugmented	+	+	+	−

The OMP concentrations of the OMP stock solution were analysed before spiking it to the influent water in the stainless-steel tanks at a 1000x dilution (Table S3). The OMP concentrations of the influent water in the tanks were mostly around 10 μg L^{-1} (Table S2), which was 100 to 1000 times the detection limit so that more than 99 % removal could be quantitatively measured. As exceptions, diclofenac was spiked at 0.93 μg L^{-1} and the concentration of amidotrizoate was 25 μg L^{-1}. Diclofenac could therefore only be quantified up to 92 % removal. Diclofenac concentrations were lower due to its low solubility and filtration of the solutions after preparation. PFOA was around 6 ug/L in the influent, while the stock solution contained 7.9 mg/L, probably due to sorption process in the tank. For amidotrizoate, it was unclear why the concentration in the tank influent water was higher than expected from the spiked stock solution. It is unlikely that this is from the concentration in the influent surface water for the RSFs, as these were always at 0 ng/L (data not shown).

The influent water was added at the top of the columns using a Danfos membrane-dosing pump with a constant flow of 3.1 L h^{-1} and a HRT of 15 min. The effluent was collected at the bottom of the column. The column specific details can be found in Table S4. Columns were weekly back-washed to mimic weekly full-scale RSF back-washing and to mitigate pressure build-up due to clogging and microbial activity. Influent and effluent water samples were taken before backwashing at day 0, 10, 24, 38, 52, 66 and 80 for analysis of electric conductivity (EC), pH, temperature, OMP concentrations, ammonium and nitrate.

RSF sand samples (5 gram wet volume) were taken from the column before back-washing at day 10, 24, 38, 52, 66 and 80 from the top of the column using a sterile plastic spoon for analysis of adsorbed OMPs and for microbial community analysis and qPCR. As a proxy for the $t = 0$ sample, sand from the inoculum of the non-bioaugmented column ('inoculum I') and the inoculum of the bioaugmented columns ('inoculum B') was taken before column packing. All sand samples were decanted to remove excess water and immediately stored at −20 °C upon further processing.

2.2. EC, oxygen and temperature

The pH, EC, oxygen concentration and temperature were measured with calibrated sensors. The temperature was measured in the influent tanks with a Testo 110 electrical thermometer (Testo, The Netherlands), the pH was measured using a Radiometer PHM 210 sensor (Radiometer, Denmark), the EC was measured with a Radiometer CDM 83 Conductivity meter (Radiometer, Denmark) and the oxygen concentration was measured using a WTW Oxi 340i membrane electrode (Xylem Analytics, Germany).

The pH, EC and oxygen concentration were measured in a beaker filled with the column influent or effluent. The influent water was collected by completely submerging the beaker in the influent tanks. The effluent sample was collected with a tube maintained below the water level to limit mixing of atmospheric oxygen with the water.

2.3. OMP analysis of water samples

First, internal standards were added to the water samples and subsequently filtered over a 0.2 μm filter. Thereafter, for analysis of acesulfame, amidotrizoate, iopamidol and PFOA, part of the water samples (100 μl) were directly injected into a Accela high performance liquid chromatography (HPLC) system (Thermo Fisher Scientific, Germany) equipped with a Hypersil Gold C18 column (100 mm × 2.1 mm I.D., particle size 1.9 μm; Thermo Fisher Scientific) in combination with a SecurityGuard Ultra guard column (Phenomenex, USA), and coupled to a triple quadrupole Vantage mass spectrometer (Thermo Fisher Scientific).

For analysis of diclofenac, metoprolol, propranolol, benzotriazole,

carbamazepine and gabapentin, another part of the water samples (100 µl) was directly injected into a Shimadzu Nexera X2 HPLC-system (Shimadzu Corporation, Japan) equipped with a Luna Omega Polar C18 column (100 mm × 2.1 mm I.D., particle size 1.6 µm) (Phenomenex, USA) in combination with a SecurityGuard Ultra guard column (Phenomenex, USA), and coupled to a triple quadrupole SCIEX 6500+ mass spectrometer (SCIEX, Canada). Both MS were equipped with a heated electrospray ionization-interface (H-ESI) and measurements were done according to the selected reaction monitoring (SRM) principal. Analysis was executed in a positive and negative ionization mode.

2.4. OMP analysis of solid sand samples

Sand from the inocula and from each column at the end of the experiment was analysed for adsorbed OMPs. Sand was air-dried on paper filters and thereafter, 9 ml of methanol was added to 1 gram of dry sand. Samples were shaken, vortexed and treated with ultrasound. The resulting extract was filtered over 0.2 µm regenerated cellulose filters. Subsequently, 8 ml of the filtered extract was evaporated to a volume of 250 µl. Internal standards and ultrapure water was added to obtain 5 ml per sample. Afterwards, samples were analyzed as described for the water samples. The recovery of the extraction method was not validated, and therefore concentrations are indicative.

2.5. Analytical method validation

The limit of detection (LOD) of each of the ten OMPs was determined by using the standard deviation of the repeatability for the lowest concentration that was detected. The concentrations were calculated using a calibration curve, that was corrected for the internal standard. The limit of quantitation (LOQ) was then determined by using the LOD multiplied by 3 and was rounded up. The LOQ was 0.5 µg L^{-1} for iopamidol, 0.05 µg L^{-1} for amidotrizoate and acesulfame and 0.01 µg L^{-1} for gabapentin, benzotriazole, propranolol, carbamazepine, diclofenac, metoprolol and PFOA. The repeatability and recovery for iopamidol, amidotrizoate, acesulfame and PFOA were determined by spiking drinking water with each OMP at the LOQ and at 1 µg L^{-1} of each compound ($n = 8$), which was analyzed together with the corresponding drinking water blanks. The repeatability and recovery for gabapentin, benzotriazole, propranolol, carbamazepine, diclofenac and metoprolol were determined by spiking drinking water and surface water with each OMP at 0.5 µg L^{-1} ($n = 8$), which were analyzed together with the corresponding drinking and surface water blanks. Recoveries were calculated by comparing the concentrations obtained from external standard calibration with the initial spiking level, after subtraction of the corresponding blank sample. The relative standard deviation (RSD) of the repeatability and recovery can be found in Table S5.

The RSD for reproducibility was also determined for gabapentin (5 %, $n = 9$), benzotriazole (8.3 %, $n = 7$), propranolol (4.1 %, $n = 8$), carbamazepine (4.5 %, $n = 10$), diclofenac (4 %, $n = 12$) and metoprolol (4.9 %, $n = 10$) at 0.5 µg L^{-1} in surface water.

2.6. Nitrate and ammonium

Nitrate concentrations were determined using the colorimetric PANERL method 353.1 (NEMI, 1978). First, nitrate was reduced to nitrite using hydrazine sulfate. All present and formed nitrite reacted with sulfanilamide and naphthyl ethylenediamine (NED) to form a red colored diazo group. Extinction was measured spectrophotometrically at 540 nm. Ammonium was determined using a modified Berthelot reaction (Krom, 1980). Extinction was measured spectrophotometrically at 660 nm.

2.7. Calculations OMP removal rates

Calculations to determine the removal rate of each OMP were done using the formulas described below:

- Hydraulic retention time (HRT) in hours (h) = Column volume (L) / flow (L h^{-1}).
- OMP removal rate (in µg h^{-1}) = [OMP] (µg L^{-1})$_{effluent}$ – [OMP]$_{influent}$ x flow (L h^{-1})
- The volumetric removal rate (in g h^{-1} L^{-1}) = removal rate corrected for column volume (L) (column volume was 770 ml)
- The specific removal rate (in µg h^{-1} g_{sand}^{-1}) = removal rate per gram sand (columns contained around 1400 gr sand)
- HRT_{99} = HRT that was needed for 99 % removal of the OMP in the column influent. The maximum removal percentage and removal rate per OMP was used to calculate the corresponding needed flow for the HRT_{99}.

2.8. Microbial community analysis and qPCR

The microbial community of all collected and frozen sand filter samples was analyzed by 16S rRNA gene amplicon sequencing. DNA extraction and subsequent 16S rRNA gene amplicon sequencing was done on approximately 0.25 gr sand as described previously (Timmers et al., 2022). Spearman correlations were calculated between relative abundances of ASVs and concentrations of ammonia, nitrate, OMPs or other measured parameters such as pH, EC, temperature and time. Differential abundance analyses was performed between bioaugmented columns and the non-bioaugmented column using ANCOM (Lin and Peddada 2020). Significant differences in alpha- and beta-diversity were determined with pairwise Kruskal-Wallis tests and pairwise PERMANOVA tests combined with adonis tests, respectively, as part of the Qiime2 workflow (Bolyen et al. 2019). qPCR was performed on the isolated DNA to determine total bacterial 16S rRNA gene copies, and *amoA* gene copies of ammonia-oxidizing bacteria (AOB) and ammonia-oxidizing archaea (AOA). The qPCR analysis for total bacterial 16S rRNA gene copies has been described by Paulus et al. (2020), whereas the qPCR analysis for the *amoA* genes of AOB and AOA has been described by van der Wielen et al. (2009).

3. Results and discussion

3.1. Hydrophilic OMPs

Acesulfame, gabapentine and iopamidol were not adsorbed to the sand filter material (Table 2) and are relatively hydrophilic OMPs with a negative K_{ow} (Table 3). Both acesulfame and gabapentine were 99 % removed in the columns at the end of the experiment, whereas iopamidol was poorly removed (<20 %) (Table 3).

For acesulfame, 99 % removal was observed between 38 and 52 days for bioaugmented columns that received additional nutrients (column 1 and 3), while the column that did not receive nutrients (column 2) and the column that was not bioaugmented (column 4) showed delayed removal, with 99 % removal between 66 and 80 days (Fig. 1).

Gabapentin was for 99 % removed between 24 and 38 days in the bioaugmented columns that received nutrients (column 1 and 3) while the column that did not receive nutrients (column 2) showed 99 % removal between 38 and 52 days (Fig. 1). Moreover, the column that was not bioaugmented (column 4) did not show any removal of gabapentin till 66 days. At day 80, the last measuring point, a slight increase in removal was observed. Omitting trace-elements/vitamin solution (column 3) did not have any effect on the removal of acesulfame and gabapentin. These results imply that acesulfame and gabapentin were biodegraded. Biological degradation of acesulfame has previously been observed in wastewater treatment plants (Kahl et al., 2018). Our results expand this metabolism towards rapid sand filters for surface water treatment. Biological degradation of gabapentin has been observed in surface water but only under oxic conditions (Henning et al., 2018), as was also the case in our column studies where oxygen was never

Table 2
OMP concentrations in the inoculum sand (I; μg kg^{-1}) and the bioaugmented inoculum sand (B) before packing the columns ($t = 0$) and in the sand of the columns 1–4 after 80 days of incubation.

[OMP] in μg/kg	I ($t = 0$)	B ($t = 0$)	Column 1	Column 2	Column 3	Column 4
Iopamidol	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Amidotrizoate	<LOQ	<LOQ	0.9	1	0.6	0.7
Acesulfame	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Gabapentin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
1-H benzotriazole	0.1	0.2	1.7	1.4	1.2	1.2
Propranolol	<LOQ	<LOQ	12	13	12	7.1
Carbamazepine	<LOQ	<LOQ	1.6	1.8	1.3	1.3
PFOA	0.6	0	43	53	45	47
Diclofenac	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Metoprolol	<LOQ	<LOQ	<LOQ	<LOQ	0.12	<LOQ

depleted (Figure S3). Still, previous column studies with sand filters showed poor removal of gabapentin (Nugroho et al., 2010; Onesios and Bouwer 2012). These findings are in contrast to our study, where high removal of gabapentin during sand filtration of surface water was observed.

3.2. Hydrophobic OMPs

Adsorbed hydrophobic OMP concentrations were measured on the sand of the non-bioaugmented inoculum (inoculum I), the bioaugmentation inoculum (inoculum B) and on the sand of each column after 80 days (Table 2). Although these quantities are indicative, the concentration of propranolol and PFOA was highest at the end of the experiment compared to all other OMPs. The concentration of these two compounds was also higher on the sand of all columns after 80 days as compared to the inoculum material. 1-H benzotriazole, carbamazepine, amidotrizoate and metoprolol concentrations were also higher on the sand after 80 days as compared to the inoculum material. These findings correspond to the hydrophobic character (>log K_{ow}) of these OMP (Table 3). Only diclofenac was not detected in the sand material despite its hydrophobicity.

Since PFOA concentrations were the highest of all OMPs on the sand material at the end of the experiment, it can be concluded that it was mostly removed by adsorption. However, maximum specific removal rates of PFOA from the water phase were lowest of all OMPs (Table 3). An explanation for this apparent discrepancy could be that PFOA was not desorbed during backwashing of the columns during the experiment, but instead accumulated on the sand during the experiment. Other OMPs that sorbed on the sand showed low removal (<10 %) and low specific removal rates, except for propranolol, metoprolol and amidotrizoate (Table 3). Since the amidotrizoate concentration was 2.5 times higher than other OMPs (25 μg L^{-1}, Table S2), the specific maximum removal rate was similar to that of propranolol. Still, the average removal of amidotrizoate was almost zero (0–2.4 %), whereas the maximum removal was 18.5 % (See supplementary data).

Propranolol removal was on average between 40 and 54 % since the beginning of the experiment and removal slowly decreased to around 30–40 % after 80 days in the bioaugmented columns (Fig. 1). The column that was not bioaugmented (column 4) showed only an average of 30 % propranolol removal since the beginning, implying that enhanced biodegradation due to bioaugmentation had a role in proporanolol removal. Nevertheless, the higher adsorbed propanolol concentrations on the sand of the bioaugmented compared to the non-bioaugmented columns (Table 2), indicated that enhanced sorption and not enhanced biodegradation caused the higher propanolol removal. Apparently, the sand in the bioaugmented columns had other physical-chemical properties than the sand in the non-bioaugmented column that allowed better propranolol removal.

Metoprolol removal was already around 40–52 % in all columns at the beginning of the experiment, which implied that metoprolol was initially adsorbed to the sand material. Yet, metoprolol was only sporadically detected on the sand at the end of the experiment (Table 2). This either means that the adsorbed metoprolol must have been biodegraded or completely desorbed during backwashing of the columns. Metoprolol removal increased to 99 % in the columns that were bioaugmented (columns 1 to 3) after 38 days when biostimulated with nutrients and 52 days without addition of nutrients. In contrast, metoprolol removal in the column that was not bioaugmented (column 4) decreased to around 10 % at 38 days and only increased again to 40 % removal after 66 days. These results provide evidence for combined sorption and biodegradation of metoprolol, where biodegradation became the dominant process with time. It has previously been shown that propranolol and metoprolol adsorb well onto aquifer sand during river bank filtration (Bertelkamp et al., 2014) and sorption has been reported before as the dominant removal mechanism for propranolol (Radjenović et al., 2009). Biological degradation of metoprolol has indeed been reported (Petrovic et al., 2009) both under oxic and anoxic conditions (Rubirola et al., 2014; Rutere et al., 2021).

Diclofenac removal was around 40–60 % since the beginning of the experiment and remained relatively stable over time in the bioaugmented columns where vitamins/trace-elements were added (column 1 and 2). In contrast, the bioaugmented column that received no vitamins/trace-elements (column 3) and the column that was not bioaugmented (column 4) showed a decreasing trend in removal after 66 days and 24 days, respectively (Fig. 1). Differences in diclofenac removal between columns are likely due to differences in the microbial communities or in physical-chemical characteristics of the sand, as seemed to be the case for propranolol. Diclofenac was spiked at 0.93 μg/L, which was almost ten times lower than the other OMPs (Table S2). This low concentration of diclofenac resulted in very low specific removal rates which could be a reason why it was below the detection limit on the sand at the end of the experiment. Diclofenac removal has been reported previously with variable results, i.e. 0–94 % removal in different matrices and different liquid or solid retention times (González et al., 2006; Kim et al., 2017; Plósz et al., 2012; Quintana et al., 2005; Radjenović et al., 2009). Diclofenac removal in sand material was reported to be between 10 %−28 % (Onesios and Bouwer, 2012; Zearley and Summers, 2012), whereas river bank filtration showed 60–80 % diclofenac removal (Petrovic et al., 2009).

3.3. Nitrification

Ammonium and nitrate were analyzed in the influent and effluent water samples of all columns at each time point to determine if OMP removal was related to nitrification. Nitrate production was calculated from the observed ammonium removal (Fig. 2B). In the columns where nutrients were added (column 1, 3 and 4), 0.8 mg L^{-1} NH_4^+ and 4 mg L^{-1} NO_3^- were added to the influent water. Column 2 did not receive extra ammonium or nitrate and measured influent concentrations for this column were therefore reflecting the natural concentrations in the surface water, which were 0.5–0.6 mg L^{-1} NH_4^+ and 2.0 mg L^{-1} NO_3^-. Based on the theoretical stoichiometry of nitrification, complete nitrification

Table 3
Characteristics of the OMPs used in this study, the average influent concentrations in the columns ($\mu g\ L^{-1}$) and the removal specifics of the OMP at the time when highest removal was observed. HRT_{99} is the hydraulic retention time (h) that would be needed for 99 % removal of the OMP at the highest removal rate.

OMP	Group	CAS number	MW	pK_a	Log K_{ow}	Average concentration influent (ug/L)	Time at max removal (days)	Max removal (%)	Specific removal rate ($\mu g\ h^{-1}\ gr^{-1}$ sand)	Volumetric removal rate ($\mu g\ h^{-1}\ L^{-1}$)	HRT_{99} (h)
Acesulfame-K	Sweetener	33,665–90–6	163.2	2	−1.33	9.52	52 (C1)	99	0.022	39.36	0.23
Amidotrizoate	X-ray contrast	117–96–4	613.9	–	1.37	24.64	80 (C3)	18.5	0.011	20	1.22
1-H Benzotriazole	Chelating agent	95–14–7	119.1	8.37	1.44	9	10 (C2)	6.5	0.001	2.4	3.52
Carbamazepine	Pharmaceutical	298–46–4	236.3	13.9	2.45	9.46	52 (C4)	5	0.001	2	4.54
Diclofenac	Pharmaceutical	15,307–86–5	296.2	4.15	4.51	0.93	52 (C1)	58.2	0.001	2.56	0.39
Iopamidol	X-ray contrast	60,166–93–0	777.1	10.7	−2.42	8.75	24 (C2)	15.5	0.003	5.6	1.92
Metoprolol	Pharmaceutical	51,384–51–1	267.4	9.7	1.88	8.2	52 (C1)	99	0.018	32.32	0.23
Propranolol	Pharmaceutical	525–66–6	259.3	9.42	3	8.12	10 (C2)	53.6	0.010	18	0.42
Gabapentin	Pharmaceutical	60,142–96–3	171.2	3.7	−1.1	9.04	38 (C1)	99	0.020	36.96	0.23
PFOA (Perfluorooctanoic acid)	PFAS	335–67–1	414.1	1.3 - 2.8	4.81	5.93	38 (C1)	6.25	0.001	1.6	3.64

of 0.5–0.6 mg L^{-1} NH_4^+ would result in 1.7–2.0 mg L^{-1} NO_3^-. Together with the natural presence of 2.0 mg L^{-1} NO_3^-, this would result in 3.7 to 4.0 mg L^{-1} NO_3^-, which was indeed comparable to the measured average nitrate concentration of 4.1 mg L^{-1} NO_3^- in the effluent of column 2.

Columns to which additional nutrients were added, received around 1.3 mg L^{-1} NH_4^+, which is the sum of the naturally present 0.5 mg L^{-1} and the added 0.8 mg L^{-1} NH_4^+. The effluent ammonium concentration was always below the detection limit, implying that all ammonium was oxidized since the beginning of the experiment. Complete nitrification of 1.3 mg L^{-1} NH_4^+ would produce 4.5 mg L^{-1} NO_3^-. This together with the naturally present 2.0 mg L^{-1} NO_3^- and the added 4.0 mg L^{-1} NO_3^- would result in 10.5 mg L^{-1} NO_3^- in the effluent. This expected concentration also corresponded with the measured average concentrations of 11 mg L^{-1} NO_3^- in columns 1, 3 and 4, showing that complete nitrification occurred in all columns during the experiment. However, the NH_4^+ concentrations in the influent decreased with time, which corresponded to an increase in nitrate concentrations in the influent at 80 days. Nitrification activity had thus increased in the influent water during storage in the tanks, and from 24 days onwards most of the nitrification occurred in the tanks and less in the columns (Fig. 2). This nitrification was higher in tanks with additional nutrients. The shift to nitrification activity in the tanks could explain why most oxygen consumption in the columns occurred in the first 24 days of operation and decreased with time (Figure S3). Nitrification could also explain the increase in EC in the tanks over time (Figure S3), because the produced nitrate in the influent water of the feeding tanks (Fig. 2) has a major influence on the EC as anion. The influent water was weekly replenished with non-sterile surface water and, therefore, enabling continuous growth of nitrifiers in the tanks.

The qPCR results of total bacteria, AOB and AOA showed that AOB were highly present in total abundance and relative to total 16S rRNA numbers (average 7.9×10^7 16S rRNA copies g_{sand}^{-1}; 3.2 % of total 16S rRNA copies g_{sand}^{-1}) as compared to AOA, which showed very low abundance (average 4.9×10^5 16S rRNA copies $g_{sand}^{-1;}$ 0.02 % of total 16S rRNA copies g_{sand}^{-1}). This implied that AOB, and not AOA played an important role in nitrification in all columns (Fig. 2 and Figure S4). Column 2 showed different dynamics of the AOB quantification as the other three columns, which was related to the dynamics of the ammonium concentration and therefore also the nitrate production (Fig. 2). Column 2 did not receive the ammonium-containing nutrient-solution, which probably allowed less nitrification in the tank and caused the deviating dynamics of ammonium and AOB. Column 3 showed a dramatic increase in total bacteria, AOA and AOB (Figure S4), which was related to a decrease in the total microbial alpha-diversity (Figure S5). This could possibly be due to heterogenic sampling of the sand, as other chemical parameters did not show this deviation.

3.4. Microbial community analysis and qPCR

To understand if the microbial communities were affected by a continuous high dose of a mixture of ten OMPs, microbial community dynamics were assessed using 16S rRNA gene amplicon sequencing and qPCR on total bacterial 16S rRNA gene copies. Total 16S rRNA gene copies in the sand of columns 1, 2 and 4 slightly decreased during the experiment from approximately 6×10^8 to around 4×10^8 copies gr_{sand}^{-1} (Figure S4). Total 16S rRNA gene copies in the sand of column 3 showed more dynamic behaviour compared to the other columns (Figure S4). Microbial community analysis did not show any significant change in the microbial α-diversity during the runtime of the experiment for each column separately (Figure S5). Column 1, 2 and 3 showed a significantly higher microbial α-diversity than column 4 since the beginning of the experiment (pairwise Kruskal Wallis, $p<0.05$). Principal component analysis (PCA) showed that the microbial community in column 2 and 3 clustered separately from the microbial community in column 1 and 4 (Fig. 3), although the microbial communities in the columns were all significantly different from each other (PERMANOVA pairwise on Bray

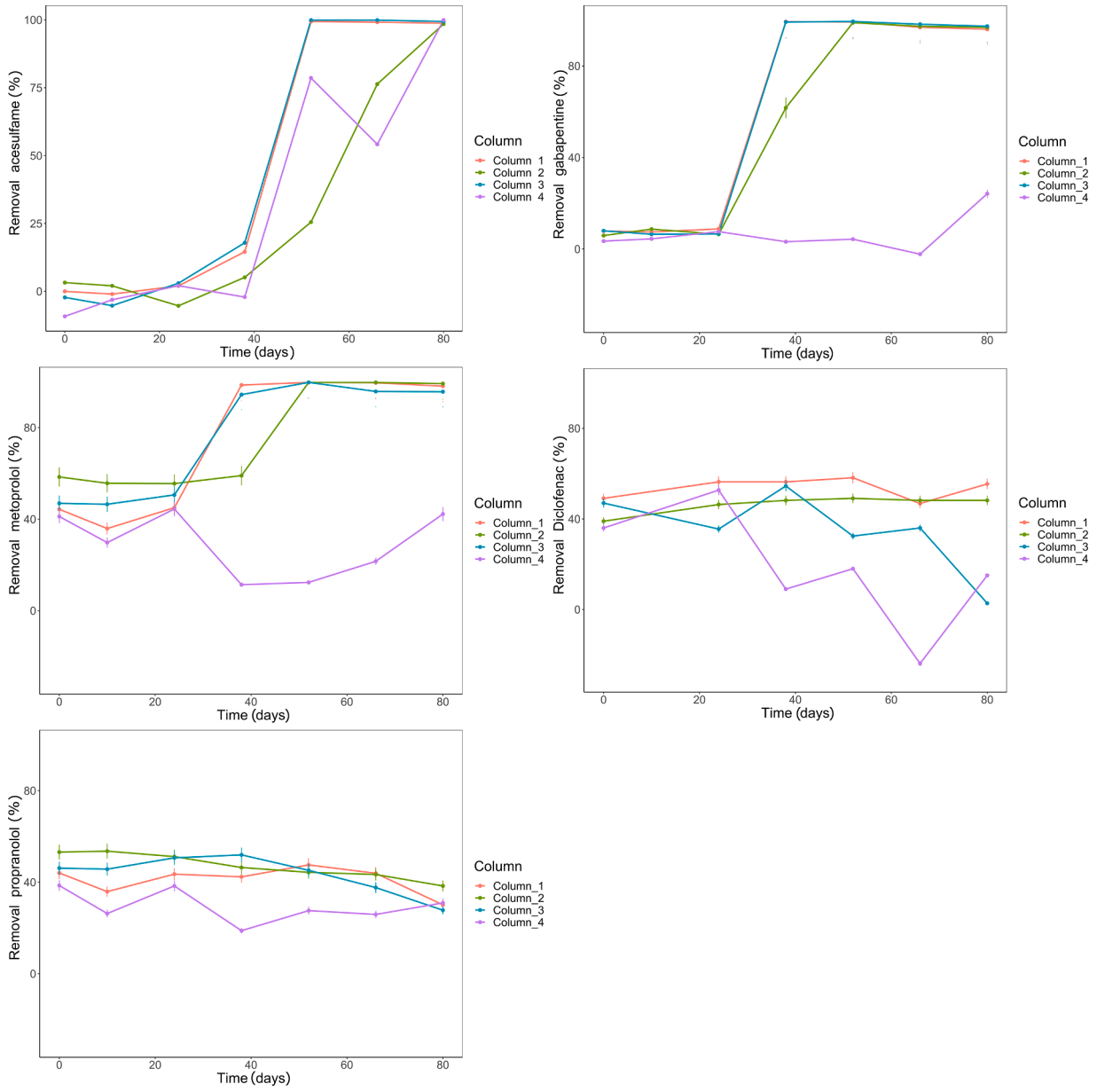

Fig. 1. Removal (%) of acesulfame, gabapentin, metoprolol, diclofenac and propranolol during 80 days of incubation in column 1 (10 % bioaugmented + nutrients + vitamins/trace-elements), column 2 (10 % bioaugmented + vitamins/trace-elements), column 3 (10 % bioaugmented + nutrients) and column 4 (nutrients + vitamins/trace-elements). Standard deviations are RSD for reproducibility (see Section 2.5).

Curtis dissimilarity, $p<0.05$). A significant part of the variation in the microbial community composition could be explained by nutrients (17 %), bioaugmentation (13 %) or vitamins/trace-elements (11 %) (Adonis test, $p<0.05$). The addition of nutrients and vitamins/trace-elements, as was done in column 1 and 4, would therefore explain 28 % of the variance in the microbial community composition, which is much higher than the bioaugmentation effect alone. The qPCR results of total bacteria and ammonia-oxidizing bacteria (AOB) showed that the bacterial community in column 1 and 4 comprised on average 1.7–2.7 % AOB. Columns 2 and 3 showed an average of 4.5–5 % AOB (Fig. 2). The PCA results showed that microbial communities of all columns were more similar in the first 24 days (Fig. 3), after which column 1 and 4 decreased in% AOB, while column 2 and 3 increased in % AOB (Fig. 2). This difference in AOB might, therefore, explain part of the separate clustering of columns 1 and 4 versus columns 2 and 3. The addition of nutrients in combination with vitamins/trace-elements (columns 1 and 4) probably allowed more competitive growth of heterotrophic microorganisms over autotrophic ammonia-oxidizers compared to only addition of vitamins/trace elements (column 2) or only nutrients (column 3). This would also explain why the community composition of the inocula clustered mostly with the community composition of columns 2 and 3 where less changes in the microbial communities occurred as opposed to column 1 and 4. Overall, addition of nutrients and vitamins/trace-elements and to a lesser extent bioaugmentation affected the quantitative and compositional aspects of the microbial communities in the columns during the 80 days incubation period, whereas OMP exposure did not.

OMP removal results demonstrated that biological degradation was an important removal mechanism for at least acesulfame, gabapentine, metoprolol and possibly diclofenac. Differential abundance analysis was performed to identify enriched amplicon sequence variants (ASVs) that might relate to enhanced gabapentin and metoprolol removal in the bioaugmented columns. Spearman correlations were also calculated between time or OMP concentrations and relative abundance of ASVs, to identify ASVs that increased in relative abundance during incubation

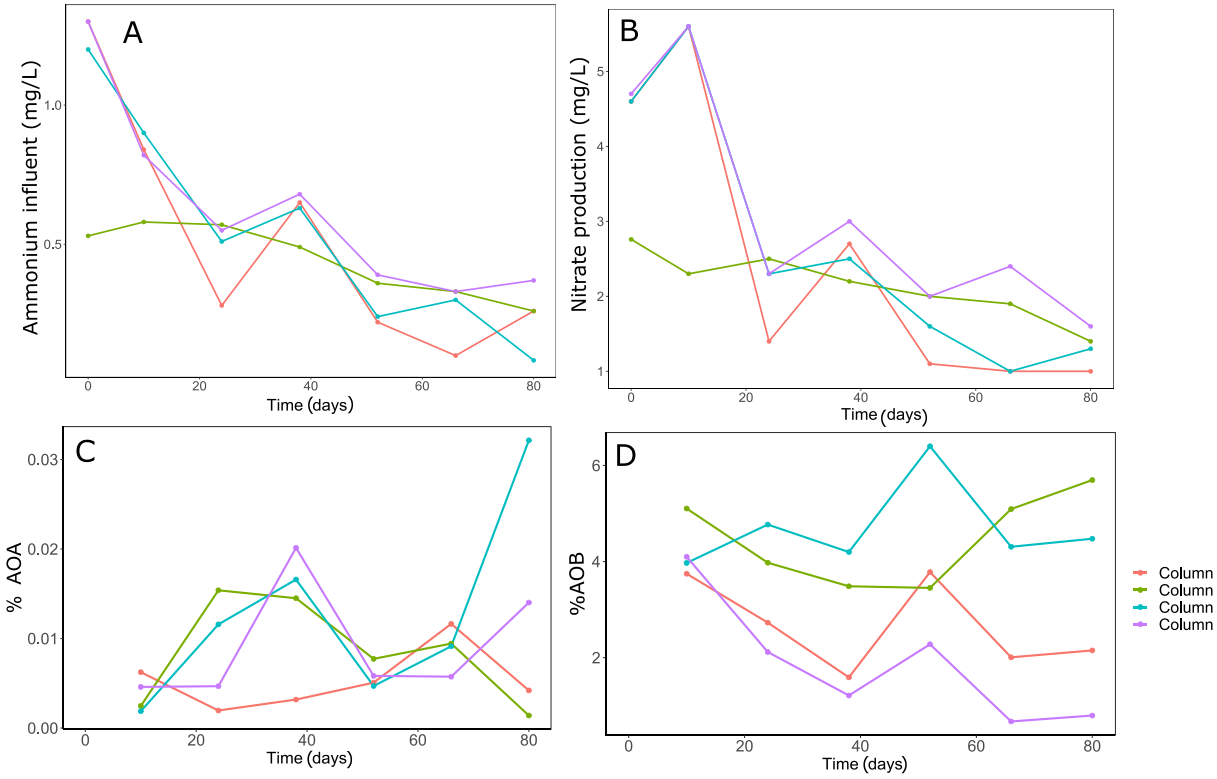

Fig. 2. A) The ammonium concentration (mg L^{-1}) in the influent, B) the nitrate production (mg L^{-1}), C) the percentage of ammonia-oxidizing archaea (AOA) and D) ammonia-oxidizing bacteria (AOB) in column 1 (10 % bioaugmented + nutrients + vitamins/trace-elements), column 2 (10 % bioaugmented + vitamins/trace-elements), column 3 (10 % bioaugmented + nutrients) and column 4 (nutrients + vitamins/trace-elements) during 80 days of operation. Nitrate production (mg L^{-1}) was calculated from the measured ammonium removal.%AOB and%AOA were calculated from amoA gene copies for AOA or AOB to total 16S rRNA gene copies.

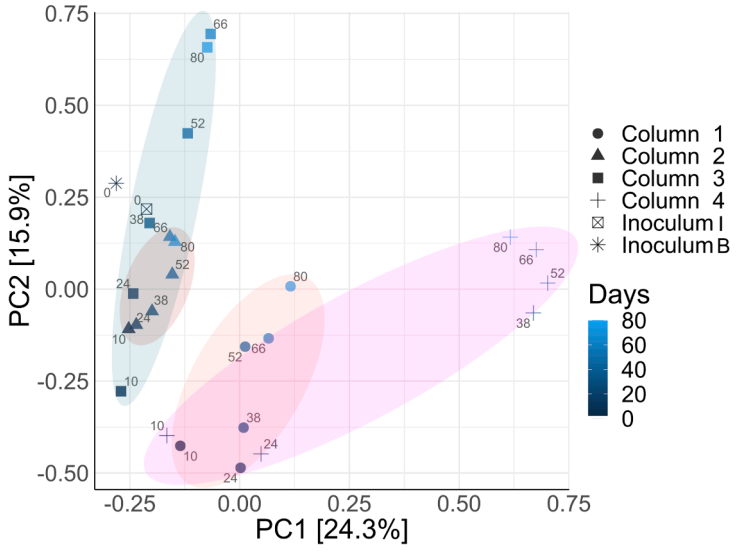

Fig. 3. Principal component analysis (PCA) based on Bray-Curtis dissimilarities of the microbial communities as determined with 16S rRNA gene amplicon sequencing. Different shapes represent different samples and different colours represent incubation time (see legend): Inoculum (Inoculum I), inoculum with bio-augmented material (Inoculum B) and the different columns (column 1–4). Labels at sampling points indicate the sampling day. Principal components 1 and 2 explained 40.2 % of the total variation.

and OMP degradation in all columns. The results of both analyses are presented in Fig. 4 where the ASVs are clustered per genus that showed a positive Spearman correlation (ρ>0.4) with time or acesulfame, gabapentine or metoprolol removal. Some ASVs at genus level, such as JG30-KF-CM45 (order *Thermomicrobiales*), genus 11–24 (class *Blastocatellia*), genus Ab4 (class *Anaerolineae*), genus mle 1–7 (family *Nitrosomonadaceae*) and genera belonging to the family *Methyloligellaceae*, increased in relative abundance during inoculation in all columns. Other genera were relatively more present in the bioaugmented columns, and some of these genera (i.e. genera belonging to *Enthotheonellaceae,*

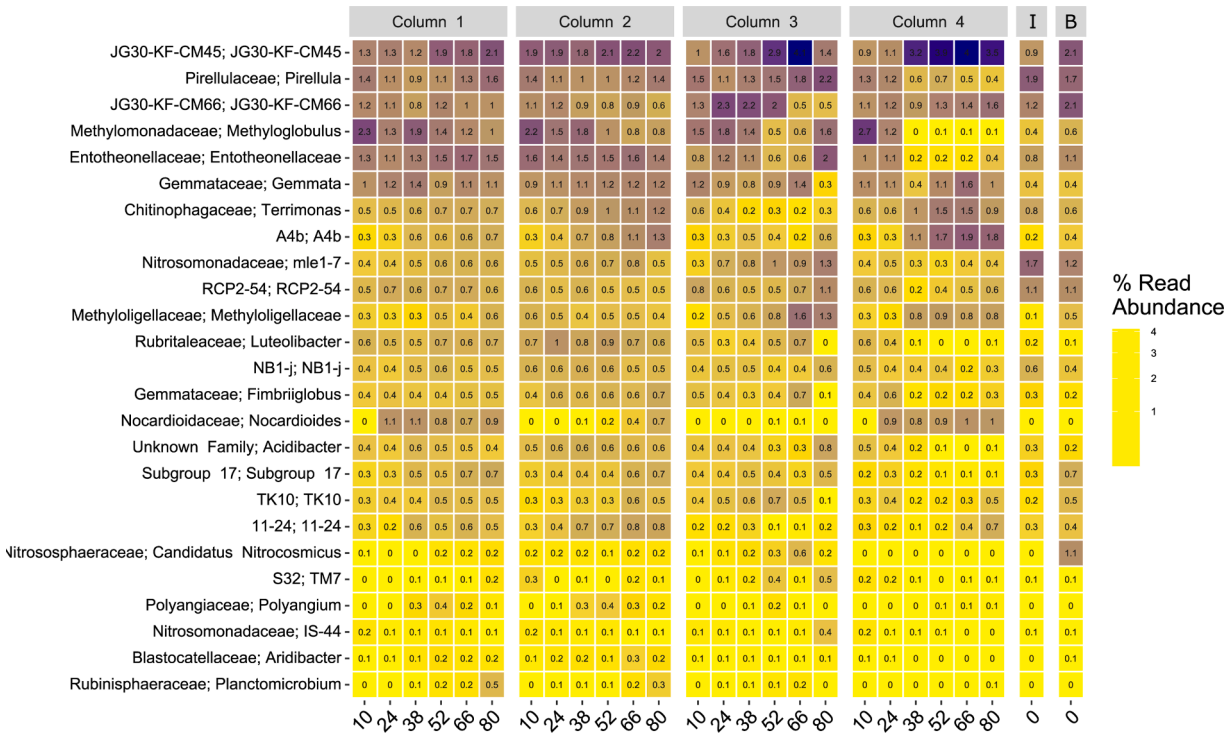

Fig. 4. Heatmap showing the relative abundance (%) of ASVs grouped at genus level for the different columns (1–4), the inoculum (I) and the bioaugmented inoculum (B) at different sampling days. Only ASVs that were differentially abundant in the bioaugmented columns or that showed a spearmann correlations (ρ>0.4) with time or OMP concentrations of metoprolol, gabapentine or acesulfame are shown.

Luteolibacter, cluster NB1-j, *Acidibacter*, Subgroup 17, *Candidatus* "Nitrosocosmicus", *Aridibacter, Pirellula, Fimbriiglobus* and *Planctomicrobium*) only increased in relative abundance during incubation in these bioaugmented columns. Interestingly, where information can be found about the metabolism of described species within these genera, most exhibit an aerobic and heterotrophic metabolism (Table S6). Some of these genera, however, can also use nitrate instead of oxygen as electron acceptor, such as *Aridibacter* and *Pirellula*. We did not find the genus *Chelatococcus* or genera belonging to the families *Phyllobacteriaceae, Methylophilaceae, Bradyrhizobiaceae*, and the genus *Pseudomonas* that were previously reported to be possibly involved in degradation of acesulfame (Huang et al., 2021; Kahl et al., 2018), or the genus *Micrococcus* thought to be involved in the degradation of gabapentin (Kamal et al., 2020).

A positive correlation (ρ>0.4) was also observed between ammonium concentrations and the relative abundance of ASVs belonging to certain genera. These, as expected, included ammonium oxidizing bacteria (AOB) and/or nitrite oxidizing bacteria (NOB) such as *Nitrospira, Nitrosomonas*, and "*Candidatus* Nitrotoga" (Figure S6). Moreover, *Methyloglobulus* (a methane- and methanol oxidizing genus) and *Hyphomicrobium* (contains denitrifying methanol and methylamine oxidizers) also showed this correlation with ammonium concentrations. The absence of methane, the decrease in ammonium oxidation in the columns and the decrease in absolute abundance of AOB after 24 days of incubation (Fig. 2) showed that methanotrophs and nitrifying microorganisms, and possibly methanol oxidizing bacteria, were at least not involved in biological metoprolol, gabapentin and acesulfame degradation, because this degradation increased after the first 24 days. Furthermore, the qPCR results also showed that abundance of AOA and AOB correlated to nitrate production, and not to OMP removal (Fig. 2). Since nitrification occurred mostly in the feed tanks after 24 days, oxygen consumption in the columns was lowered, which could have decreased competition for oxygen between nitrifying microorganisms and potential aerobic heterotrophic OMP degrading microorganisms.

Metoprolol was shown previously to be removed by aerobic heterotrophic microorganisms and ammonium inhibited this removal (Falås et al., 2016). Moreover, metoprolol was not removed using nitrifying cultures (Sathyamoorthy et al., 2013) and nitrification was even inhibited in the presence of metoprolol (Rutere et al., 2021). Acesulfame is metabolically degraded with oxygen or nitrate as electron acceptor and no association with nitrification was confirmed (Castronovo et al., 2017). For diclofenac biodegradation, it has been reported that diclofenac removal was higher after oxic post-treatment with low ammonium content than in activated sludge processes (Falås et al., 2016). Diclofenac has also been reported to be recalcitrant in nitrifying activated sludge (Fernandez-Fontaina et al., 2016). Inhibition of nitrification did however only partly affect removal, showing that probably both ammonium oxidizing bacteria (AOB) and heterotrophic microorganisms were responsible for removal (Tran et al., 2009). These findings are in line with our results that the OMPs, which were biodegraded in the columns with filter sand from full-scale rapid sand filters, were probably degraded heterotrophically with oxygen and/or nitrate as electron acceptor. These microorganisms were limited in nutrients for growth in the columns, while vitamins and trace-elements were not limiting.

3.5. Feasibility and future research

The full scale RSF of inoculum B has an HRT of 0.43 h and the full scale RSF of inoculum I has an HRT of 0.48 h (Petra Scholte, Waternet, pers comm.). Here, we operated the columns at an HRT of 0.25 h (Table S4). Hence, the HRT of both full scale RSFs is longer than used in our study, which means that OMP removal under full scale conditions at concentrations used in this study could be even higher than in our study. The HRT needed for removal of 99 % of the OMPs in our study (HRT_{99}) was also calculated (Table 3). The HRT_{99} values showed that the HRT for acesfulfame, gabapentine and metoprolol could be shortened to 0.2 h. Furthermore, diclofenac and propranolol should be removed for 99 % at the HRT of both full scale filters. For the OMP that showed low removal (e.g. amidotrizoate, 1-H benzotriazole, carbamazepine, iopamidole and PFOA) an HRT of 1.2–4.5 h is needed for 99 % removal. Previous column

experiments showed that higher retention time of 12 h resulted in improved removal (>50 %) of carbamazepine and amidotrizoate (Yoon et al., 2017). Carbamazepine removal during RSF was very low (<2 %) (Zearley and Summers, 2012) and a longer HRT of 4 h was needed for carbamazepine removal during RSF (Zhou et al., 2022), which corresponded to our calculated HRT_{99} of 4.5 h for complete carbamazepine removal (Table 3). RSF, therefore, does not seem to be suitable treatment process for the removal of amidotrizoate, 1-H benzotriazole, carbamazepine, iopamidole and PFOA, but possibly other biological treatment processes (e.g. biological active carbon filtration, slow sand filtration or dune infiltration) might be more suitable to remove these compounds. These results can however not be extrapolated to full-scale, because we used higher concentrations (around 10x higher) than the OMP concentrations that can be found at full scale. Assuming OMP removal would follow first-order kinetics, the HRT that is needed for removal at actual concentrations is probably shorter, but information on degradation kinetics is needed to calculate this exactly. Furthermore, it is possible that at lower OMP concentrations, different micro-organisms are enriched and different enzymes with other affinities for OMPs are active, which also changes degradation kinetics.

For application of bioremediation at full scale RSF for OMP removal, stable performance of the microbial community is important. Grazing, competition with indigenous communities and flushing out of OMP degrading bacteria are processes that could decrease OMP removal (Albers et al., 2015; Daly et al., 2018; Horemans et al., 2017a). In our study, columns were back-washed every week but this did not seem to have an effect on OMP removal and the OMP degrading microbial community. Furthermore, the continous flow, minor temperature fluctuations, increase in EC and dosing of a mixture of ten OMP for 80 days also did not influence OMP removal, nor the microbial community composition.

The results from our column study are promising for implementation of bioaugmentation and/or biostimulation at full-scale RSF for the removal of OMPs. However, future studies need to be performed that focus on 1) the long term effects of bioaugmentation and/or biostimulation; 2) the influence of variations in temporal factors (temperature, nutrients, OMP concentrations, etc.); 3) the influence of variations in HRT; 4) the removal capacity of a broader spectrum of OMPs after bioaugmentation and 5) the operational challenges of bioaugmentation of full scale RSFs. Besides, research should also focus on enrichment and cultivation of OMP-degrading microorganisms, so that the optimal conditions for OMP removal can be studied and bioaugmentation can be performed and monitored more effectively, by identifying and quantifying these microorganisms at full scale RSFs.

4. Conclusions

High removal (99 %) of acesulfame, gabapentin and metoprolol, medium removal (50–60 %) of propranolol and diclofenac and low removal (<20 %) of PFOA, carbamazepine, 1-H benzotriazole, amidotrizoate and iopamidol was observed in columns with sand from full-scale RSFs that were supplemented with bioaugmentation material, nutrients and/or a mixture of vitamins and trace elements. Bioaugmentation and biostimulation were successful strategies to enhance the biological removal of acesulfame, gabapentin, metoprolol and possibly diclofenac in the columns. Bioaugmentation was responsible for the high removal of gabapentin and metoprolol in the columns, whereas biostimulation accelerated this removal by decreasing the lag phase. The removal of these compounds was not associated with microbiological methane, methanol or ammonia oxidation. Indications were obtained that heterotrophic micro-organisms, using oxygen or nitrate as electron acceptor, are involved in biodegradation of acesulfame, gabapentine, metoprolol and possibly diclofenac. These results are promising for the application of bioaugmentation and/or biostimulation at full scale RSFs, but additional research on the influence of other factors on OMP removal is needed before application of bioremediation and/or biostimulation to enhance OMP removal by RSFs can be achieved.

Author's contributions

PHAT performed funding acquisition, conceptualization, formal analysis and curation, investigation, methodology, administration, and writing of the original draft manuscript. WS designed experimental methodology, performed investigation and data analysis, and reviewed and edited the manuscript. MLF performed part of the investigation and reviewed and edited the manuscript, PvdW reviewed experimental conceptualization, investigation, and reviewed and edited the manuscript.

Declaration of Competing Interest

The authors declare no conflict of interest.

There are no financial and personal relationships with other people or organizations that could inappropriately influence (bias) our work.

Data availability

No data was used for the research described in the article.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2023.120921.

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