

## **Imprint**

This publication has been developed within the project **EMPEREST – Eliminating Micro-Pollutants from Effluents for Reuse Strategies,** co-financed by the Interreg Baltic Sea Region Programme 2021–2027, and helping to drive the transition to a green and resilient Baltic Sea region.

This report forms Annex 6 of the overarching study "Strategies and technological means for minimising organic micropollutant emissions from WWTPs". Each annex presents a site-specific sub-study conducted within the broader framework.

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# **Project note**

The EMPEREST project supports local authorities, service providers and policy-making community in finding ways to reduce PFAS (Per- and polyfluoroalkyl substances) and other organic micropollutants from the water cycle. The project has four activity strands to fulfil its aims. First, in close cooperation with HELCOM EMPEREST prepares methodological recommendations to monitor PFAS group in the aquatic environment. Second, local authorities address the subject on the city level by developing a PFAS risk assessment framework to identify and assess PFAS-related risks and propose relevant risk mitigation strategies. Third, EMPEREST supports water utilities in making informed decisions about cost-effective treatment strategies and investments for removing micropollutants from wastewater. Finally, capacity building takes place for both local authorities and public service providers to inform them about the recent developments in the field and train them with tailored materials and tools.

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## List of Abbreviations

• •			
AC	air compressor	PFTrDA	perfluorotridecanoic acid
AOPs	advanced oxidation processes	PFTrDS	perfluorotridecane sulfonic acid
BOD <sub>7ATU</sub>	biochemical oxygen demand, 7 days	PFUnDA	perfluoroundecanoic acid
$COD_{Cr}$	chemical oxygen demand, dichromate	PFUnDS	perfluoroundecane sulfonic acid
DE	Germany	PL	Poland
EBCT	empty bed contact time	PLC	programmable logic controller
EE	Estonia	SS	suspended solids
EU	European Union	TFA	trifluoroacetic acid
FI	Finland	TFMS	trifluoromethanesulfonic acid
GAC	granular activated carbon	TN	total nitrogen
GC-MS	gas chromatography-mass spectrometry	TOC	total organic carbon
HELCOM	Helsinki Commission	TP	total phosphorus
LC-MS	liquid chromatography-mass spectrometry	TSS	total suspended solids
LC-MS/MS	liquid chromatography-tandem mass spectrometry	UV	ultraviolet
LT	Lithuania	UVA	ultraviolet absorbance
LV	Latvia	UVA254	ultraviolet absorbance at 254
OC	oxygen concentrator	UWWTD	urban wastewater treatment
OG	ozone generator		directive
OMPs	organic micropollutants	<b>WWTPs</b>	wastewater treatment plants
PE	population equivalent	4-MTB	4-methyl-benzotriazole
PFAS30	list of thirty PFASs	6-MTB	6-methyl-benzotriazole
6:2 FTS	1H,1H,2H,2H-Perfluorooctane sulfonate		,
8:2 FTS	1H,1H,2H,2H-Perfluorodecanesulfonate		
4:2 FTS	1H,1H,2H,2H-Perfluorodecanesulfonate		
8:2 FTUCA	8:2 Fluorotelomer unsaturated carboxylic acid		
PFBA	perfluorobutanoic acid		
PFBS	perfluorobutane sulfonic acid		
PFBSA	Perfluorobutanesulfonamide		
PFDA	perfluorodecanoic acid		
PFDoA	perfluorododecanoic acid		
PFDoS	perfluorododecane sulfonic acid		
PFDS	perfluorodecane sulfonic acid		
PFEtS	perfluoroethanesulfonic acid		
PFHpA	perfluoroheptanoic acid		
PFHpS	perfluoroheptane sulfonic acid		
PFHxA	perfluorohexanoic acid		
PFHxS	perfluorohexane sulfonic acid		
FHxSA	Perfluoro-1-hexanesulfonamide		
PFHxDA	Perfluorohexadecanic acid		
PFNA	perfluorononanoic acid		
	perfluorononane sulfonic acid		
PFNS	perfluorooctanoic acid		
PFOA	·		
PFODA	Perfluorooctanedecanoic acid		
PFOS	perfluorooctane sulfonic acid		
PFOSA	Perfluorooctane sulfonamide		
PFPeA	perfluoropentanoic acid		
PFPeS	perfluoropentane sulfonic acid		
PFPrA	perfluoropropanoic acid		
PFPrS	perfluoropropanesulfonic acid		
PFTA	Perfluorotetradecanoic acid		

## 1. Introduction

Organic micropollutants (OMPs) are trace-level contaminants that pose a growing concern on environment and human health. Commonly originating from pharmaceuticals, personal care products, pesticides, hormones, microplastics and industrial compounds, OMPs are widespread and persistent in the environment. They can be harmful to the environment and health due to their bioaccumulation potential and biological activity even at very low concentrations.

Wastewater treatment plants are designed to remove nutrients and organic matters from wastewater, but the currents methods are ineffective in removing micropollutants. Therefore, most of them end up in the aquatic environment through wastewater treatment plants, which underlines the urgent need for more efficient treatment technologies and regulatory measures.

The European Union adopted the revised Urban Wastewater Treatment Directive (UWWTD) in November 2024. It aims to strengthen environmental and public health protection by enhancing the efficiency of wastewater treatment. Key updates to the directive focus on stricter removal of nutrients and mandatory requirements for the elimination of OMPs. UWWTD requires wastewater treatment plants with 150,000 PE and plants over 10,000 PE that discharge into high-risk areas, must implement quaternary treatment for the removal of micropollutants. This report presents the results of a mobile pilot-plant in Turku to evaluate the removal of micropollutants from wastewater. The aim of the pilot study was to assess the removal efficiency of ozonation and activated carbon treatments individually and in combination, in removing micropollutants.

Turku regional wastewater treatment plant's objective was to identify the optimal contact time for activated carbon, as it represents the most feasible large-scale solution for the cave-based treatment plant. The results of the study serve to support this full-scale quaternary treatment investment plan.

## 2. Setup

## 2.1. Study site

The pilot testing was conducted at the Turku Region WWTP in Finland. The average influent flow rate to the plant is approximately 90 000 m<sup>3</sup>/d and the pollutant load corresponds to 343 000 population equivalents (PE). Turku Region WWTP is a four-lane WWTP based on mechanical, chemical and biological treatment. It comprises screens, sand separation, primary clarification phase, aeration phase, secondary clarification phase, sand filtration and UV treatment.

Average concentrations of pollutants in the treated wastewater are as follows:

Biochemical oxygen demand (BOD<sub>7ATU</sub>)
Chemical oxygen demand (COD<sub>cr</sub>)
Total suspended solids (TSS)
Total nitrogen (TN)
Total phosphorus (TP)
3,3 mg/l
6,7 mg/l
0,12 mg/l

## 2.2. Pilot plant description

The pilot test was carried out by means of a semi-technical mobile pilot plant is designed and constructed by University of Tartu, Institute of Chemistry & Tartu Waterworks Ltd. The pilot installation consists of the following main units:

• MECANA Pile cloth media filter

Filter cloth type: Pile Fabric OptiFiber PES-14 filtarion surface  $0,50 \text{ m}^2$  max hydraulic capacity  $5 \text{ m}^3/\text{h}$ 

Mellifiq Ozonetech ICT-40 Ozone generator

nominal ozone concentration 135 g/Nm³ nominal ozone production 8-40 g/h

Mellifiq Ozonetech Topaz Ozone consentrator

max gas flow 10 l/min oxygen content 95 %

Ozone contact tank

volume 50 l height 70 cm max hydraulic capacity  $1 \text{ m}^3/\text{h}$ 

• Filters – Sand filter and 2 Granulated Activated Carbons

diameter 0,35 m surface area 0,096 m² max hydraulic capacity 1 m³/h

Mellifiq Saniray ultraviolet lamp

max hydraulic capacity 1 m<sup>3</sup>/h

Backwash storage tank

length 1,35 m width 0,46 m height 1,3 m maximum working volume 0,7 m³

• Aireco air compressor

free air delivery 245 l/min maximum pressure 8 bar

The pilot plant is equipped with the following online measuring instruments for process monitoring:

- IFM SM6100 magnetic-inductive water flow meter 2 units
- IFM SM7120 magnetic-inductive water flow meter 2 units
- +GF+ Signet 2551 display Magmeter magnetic water flow meter 2 units
- IFM SA5020 air flow sensor 1 unit
- Aplisens PCE-28 water level sensor 8 units
- Sicon M Multi-Channel control unit
- Sigrist ColorPlus 2 Absorption Measuring instrument
- AquaScat S turbidity sensor 1 unit
- conductivity/temperature sensor
- pH sensor
- redox sensor



Figure 1: View of the pilot plant located at the Turku region WWTP

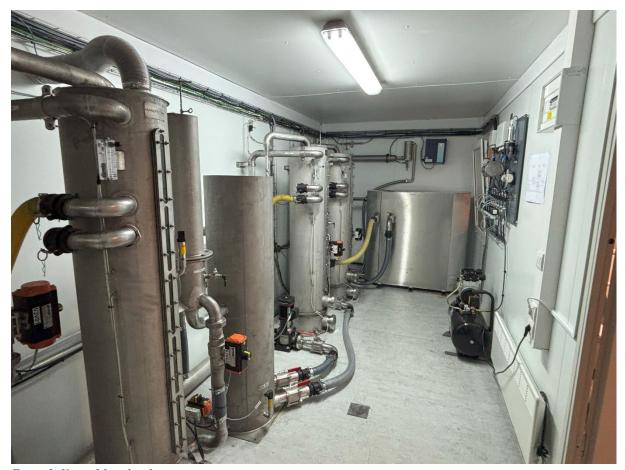


Figure 2: View of the pilot plant interior

## 2.3. Analytical methods

Performance of the examined treatments was monitored by online sensors and grab sampling. The samples were collected twice a week and were analysed for micropollutants, and selected samples were analysed also for other wastewater quality parameters. The measured micropollutants were the ones specified in the UWWTD and 30 PFAS compounds.

The list of measured wastewater quality parameters is as follows:

- Ten pharmaceuticals (Specified in the UWWTD, minimal removal 80 % is required)
  - o 4/6-methyl-1H-benzotriatzole
  - o Amisulpride
  - o Benzotriazole
  - o Diclofenac
  - Hydrochlorothiazide
  - o Irbesartan
  - Candesartan
  - Carbamazepine
  - Clarithromycin
  - Metoprolol
  - Citalopram (+escitalopram)
  - Venlafaxine
- Two benzotriazoles (Specified in the UWWTD, minimal removal 80 % is required)
  - o 4/6-methyl-1H-benzotriatzole
  - Benzotriazole
- PFAS 30-compounds
  - o 1H,1H,2H,2H-Perfluorooctane sulfonate (6:2 FTS)
  - 1H,1H,2H,2H-Perfluorodecanesulfonate (8:2 FTS)
  - o 1H,1H,2H,2H-Perfluorodecanesulfonate (4:2 FTS)
  - o 8:2 Fluorotelomer unsaturated carboxylic acid (8:2 FTUCA)
  - Perfluorooctanedecanoic acid (PFODA)
  - o Perfluorooctanoic acid (PFOA)
  - Perfluorooctane sulfonate (PFOS)
  - o Perfluorobutanoic acid (PFBA)
  - Perfluorobutanesulfonate (PFBS)
  - Perfluorodecanoic acid (PFDA)
  - Perfluorodecanesulfonic acid (PFDS)
  - Perfluorododecanoic acid (PFDoA)
  - Perfluorododecanesulfonic acid (PFDoS)
  - Perfluorohexanoic acid (PFHxA)
  - Perfluorohexanesulfonate (PFHxS)
  - Perfluoroheptanoic acid (PFHpA)
  - Perfluoroheptanesulfonate (PFHpS)
  - Perfluorohexadecanic acid (PFHxDA)
  - Perfluorononanoic acid (PFNA)
  - o Perfluorononanesulfonic acid (PFNS)
  - o Perfluoropentanoic acid (PFPeA)
  - Perfluoropentanesulfonic acid (PFPeS)
  - Perfluorotetradecanoic acid (PFTA)

- o Perfluorotridecanoic acid (PFTrDA)
- Perfluorotridecanesulfonic acid (PFTrDS)
- o Perfluoroundecanoic acid (PFUnDA)
- Perfluoroundecanesulfonic acid (PFUnDS)
- Perfluoro-1-hexanesulfonamide (FHxSA)
- Perfluorooctane sulfonamide (PFOSA)
- Perfluorobutanesulfonamide (PFBSA)

#### PFAS short chain

- PFEtS (Perfluoroethanesulfonic acid)
- o PFPrA (Perfluoropropanoic acid)
- o PFPrS (Perfluoropropanesulfonic acid)
- TFA (Trifluoroacetic acid)
- o TFMS (Trifluoromethanesulfonic acid)
- CODcr
- Suspended solids
- TOC
- Bromate
- Bromide
- Terbutryn

The samples were analyzed in a laboratory accredited according to the ISO/IEC 17025:2017 standard. Most of the laboratory analysis methods used were standard methods and were accredited for the wastewater matrix. Pharmaceuticals and PFAS compounds were determined using a liquid chromatography-tandem mass spectrometry (LC-MS/MS). The concentrations of herbicides (including terbutryn) were determined using a gas chromatography-mass spectrometry (GC-MS).

#### 3. Results

The pilot plant was fed with secondary effluent of the Turku Region WWTP. There were two possible parallel treatment trains: first treatment line consisted of Pile cloth media filter (PCMF), ozone oxidation (O<sub>3</sub>) followed by Dual media sandfilter (DMF) followed by Granular activated carbon (GAC) followed by UV-treatment. Second treatment line consisted of Granular activated carbon (GAC) followed by UV-treatment. These treatment trains were possible to operate parallel at the same time.

The DMF were filled with two different grain sized sand: at the bottom of the filter coarse sand 1,2-2,0 mm grain size, at the top Hydro-anthracite N 0,8-1,6 mm grain size. GAC filters were filled with Hydraffin AR 8x30 granular activated carbon. Height of the GAC beds were 0,84 m.

The pilot testing was conducted over a period of 15 weeks, from March 10, 2025, to June 19, 2025. During testing period 1 the focus of the study was comparison of the two parallel lines and determining the optimal contact time for GAC filtration. Period 2 focused on removal efficiency of the GAC filters with sandfilter prior. Samples were taken twice a week: one with standard settings for contact times and other with different contact times. Herbicides were tested twice during piloting, but they were not detected on the samples.

## 3.1. Testing Period 1: Two parallel lines

The first week of the piloting were conducted with the PCMF, after that without it. First testing period with two parallel lines were conducted during piloting weeks 2 to 9.

During testing period 1 the flow to GAC filters were varied to find the optimal contact time without compromising the removal efficiency of the micropollutants. Every piloting week the first sample day were conducted with standard settings: flow to  $O_3$  600 l/h with the contact time of 5 minutes, and the flow to GAC filters 250 l/h with the contact time of 19,4 minutes. The other sample day the settings varied, the focus of the study was mostly on finding the optimal contact time for the GAC. Contact times were tested between 10,8 minutes and 32,3 minutes. Contact time for the  $O_3$  were mostly 5 minutes during the whole piloting period, one sample were tested with 10 min contact time. One sample during this period was tested without the  $O_3$ .

The sample points were pilot influent, O<sub>3</sub> +DMF effluent, GAC A effluent and GAC B effluent.

#### **BASIC TEST RUNS TWO PARALLEL LINES - SAME INFLUENT WATER**

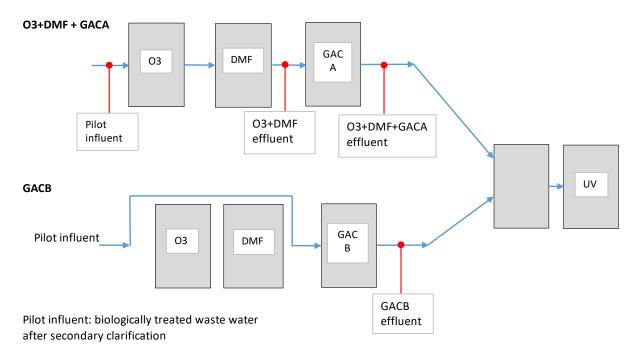


Figure 3: Period 1: parallel lines flowchart

This period was divided in 5 series based on GAC filter contact times:

Series 1 GAC EBCT: 19,4 min (8 sample days)
Series 2 GAC EBCT: 32,3 min (1 sample day)
Series 3 GAC EBCT: 24,2 min (3 sample days)
Series 4 GAC EBCT: 13,8 min (2 sample days)
Series 5 GAC EBCT: 10,8 min (3 sample days)

The dosing of ozone was not adjustable due the limitations of equipment, and the dose was calculated based on redox-sensor value.

Table 1: Operation parameters during period 1

	11.3.2025	12.3.2025	18.3.2025	19.3.2025	25.3.2025	26.3.2025	1.4.2025	2.4.2025	8.4.2025	9.4.2025	15.4.2025	16.4.2025	23.4.2025	24.4.2025	6.5.2025	7.5.2025	13.5.2025	14.5.2025
O₃ dose (mgO₃/L)	0,157	0,166	0,232	0,208	0,21	0,2	-	0,191	0,188	0,226	0,278	0,218	1,1	0,467	2,12	1,77	1,57	1,11
CT O₃ (min)	4,8	4,8	5	5	5	5	-	5	5	10	5	5	5	5	5	5	5	5
EBCT GAC A (min)	24,2	24,2	24,2	19,4	19,4	10,8	19,4	32,3	19,4	19,4	19,4	10,8	19,4	13,8	19,4	10,8	19,4	13,8
EBCT GAC B (min)	-	-	24,2	19,4	19,4	10,8	19,4	32,3	19,4	19,4	19,4	10,8	19,4	13,8	19,4	10,8	19,4	13,8

## 3.1.1. Removal of suspended solids, COD<sub>Cr</sub> & TOC

Suspended solids refer to matter that remains in solid particle form and does not dissolve in water after the biological treatment process. These solids include both organic and inorganic substances, such as microbial flocs, colloidal particles, and fine particulates that do not fully settle during the secondary sedimentation phase.

In figure 4 is shown the amount of suspended solids on each sample point. Sample days 1.4.2025, 8.4.2025 and 15.4.2025 the pilot influent water contained abnormally high level of suspended solids, which was caused by a failure of the secondary clarification tank's axle and the resulting maintenance activities. GAC B filtration couldn't filtrate all this high amount of suspended solids and low doses was detected on the samples.

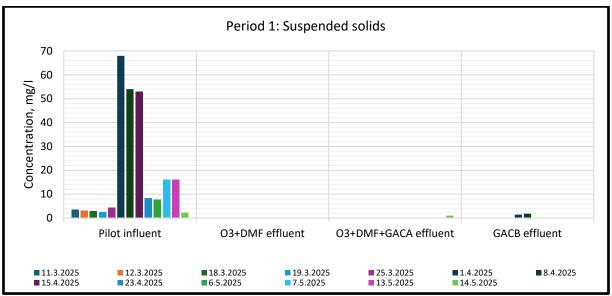


Figure 4: Concentration of suspended solids on each sample points

TOC (Total Organic Carbon) and COD<sub>Cr</sub> (Chemical Oxygen Demand, dichromate) are essential indicators for assessing organic load in wastewater treatment. Wastewater contains both biodegradable and non-biodegradable organic matter. TOC measures the total quantity of organic carbon, while COD indicates the amount of oxygen required for the chemical decomposition of this organic material. On figure 5 is shown COD<sub>Cr</sub> on each sample point, on figure 6 is shown the TOC on each sample point.

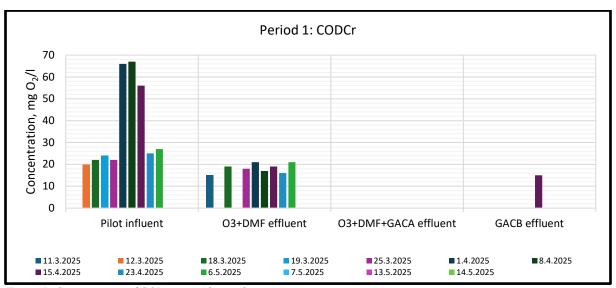


Figure 5: Concentration of CODCr on each sample point

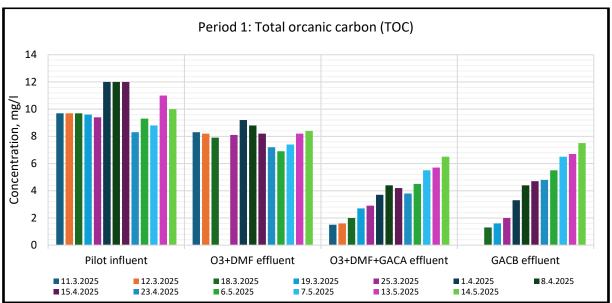


Figure 6: Concentration of TOC on each sample point

## 3.1.2. Removal of Pharmaceuticals

The presence of pharmaceuticals in wastewater is a critical environmental issue due their impact on nature and biodiversity. Conventional wastewater treatment methods are ineffective in removing them from wastewaters, whereas GAC filtration and ozonation have proven to be effective techniques.

During piloting, ten pharmaceuticals listed as indicators in the UWWTD were analysed. The pharmaceuticals belonged to different categories: antidepressants (citalopram, venlafaxine), antipsychotics and mood stabilizers (amisulpride, carbamazepine), antibiotics (clarithromycin), antihypertensives (candesartan, irbesartan, metoprolol, hydroclorothiazide) and anti-inflammatory/pain relief agents (diclofenac).

On this period in pilot influent, hydrochlorothiazide was found at the highest concentrations, ranging from 0,72  $\mu$ g/l to 2,10  $\mu$ g/l. Also, significant concentration was measured for candesartan (1,0  $\mu$ g/l to 1,8  $\mu$ g/l), diclofenac (0,41  $\mu$ g/l to 1,8  $\mu$ g/l), and venlafaxine (0,48  $\mu$ g/l to 0,85  $\mu$ g/l). Irbesartan was not detected during this period, other pharmaceutical concentrations ranged from 0,01  $\mu$ g/l to 0,49  $\mu$ g/l.

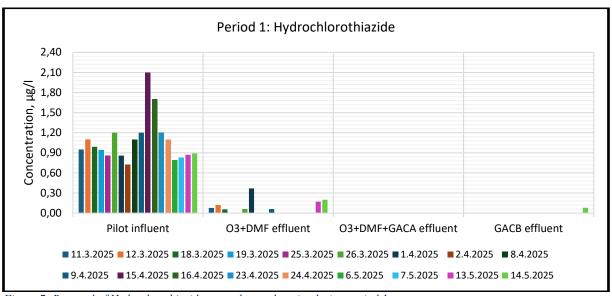


Figure 7: Removal of Hydroclorothiazide on each sample point during period 1

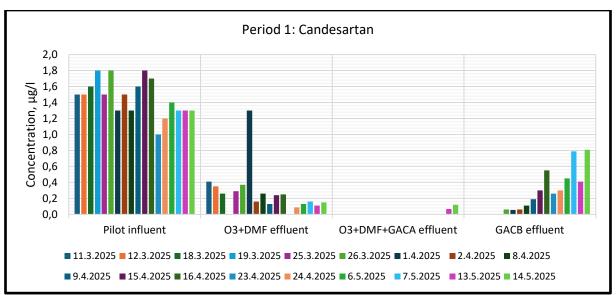


Figure 8: Removal of Candesartan on each sample point during period 1

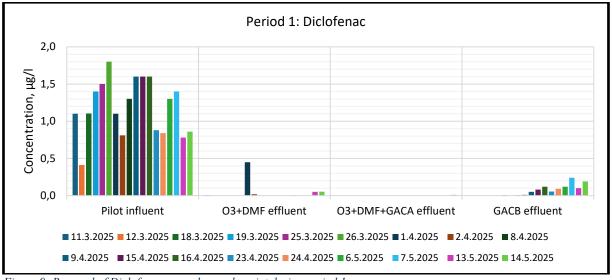
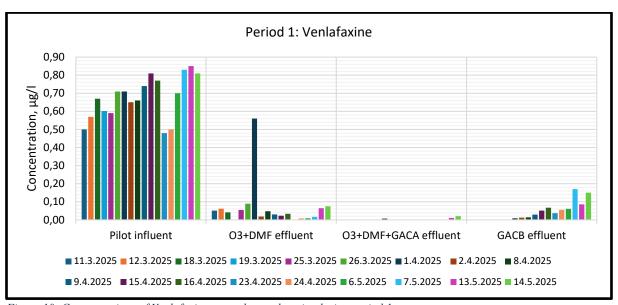


Figure 9: Removal of Diclofenac on each sample point during period 1



 $Figure\ 10:\ Concentrations\ of\ Venla faxine\ on\ each\ sample\ point\ during\ period\ 1$ 

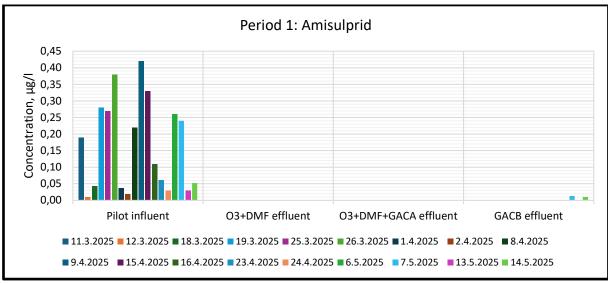


Figure 11: Concentrations of Amisulpride on each sample point during period 1

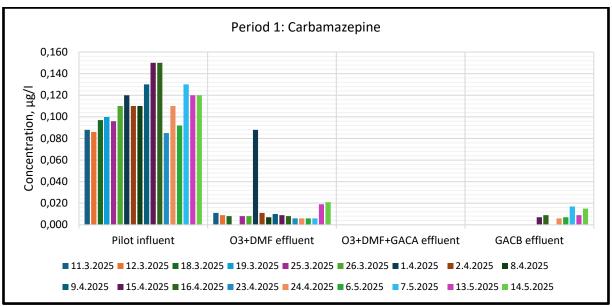


Figure 12: Concentrations of Carbamazepine on each sample point during period 1

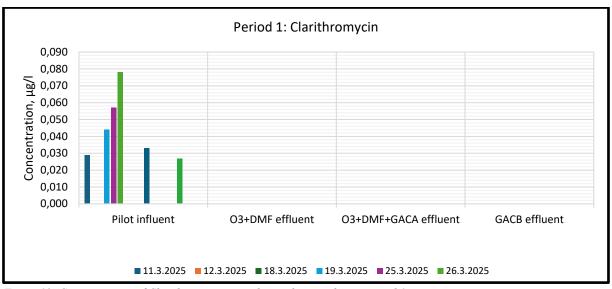


Figure 13: Concentrations of Clarithromycin on each sample point during period 1

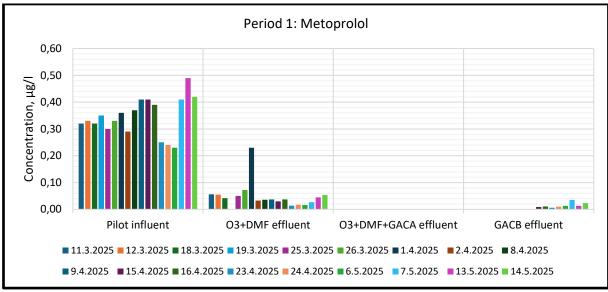


Figure 14: Concentrations of Metoprolol on each sample point during period 1

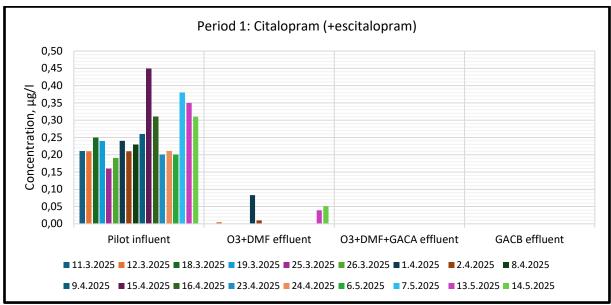


Figure 15: Concentrations of Citalopram on each sample point during period 1

Parallel line 1 the removal efficiency of  $O_3$  +DMF on pharmaceuticals ranged between 75 % to 100 % (figure 16). Dose of the  $O_3$  ranged from 0,16 mg/l to 2,12 mg/l, with one sample day without  $O_3$  (1.4.2025), what shows as high concentration of most of the pharmaceuticals. As shown on figures above (7-15) the dose of  $O_3$  didn't make a big difference, the concentrations on  $O_3$  +DMF effluents were similar, regardless of the dose. Highest doses (1,1 mg/l to 2 mg/l) of  $O_3$  were on 4 last sample days.

Series on figures 16-18 are collected based on the GAC contact time. Removal efficiency on each series is calculated from average efficiency of each contact time. The contact times were varied during the period, and the removal efficiency decreased over time as the GAC filters got saturated and affected on many different series.

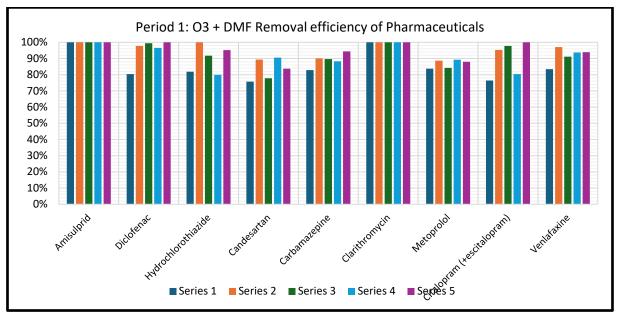


Figure 16: Removal efficiency of parallel line 1:  $O_3$  + DMF on pharmaceuticals, series divided based on GAC contact to determine the  $O_3$  + DMF effect prior GAC filtration

Parallel line 1 with  $O_3$  + sandfiltration prior GAC filtration removal efficiency of pharmaceuticals (figure 17) was 100 % during this period with GAC contact time 32,3 min (series 2), 24,4 min (series 3) and 10,8 min (series 5). With most used GAC contact time 19,4 min (series 1) the removal efficiency of Candesartan and Venlafaxine started to decrease at the end of this period, but the removal efficiency stayed over 95 %. With contact time 13,8 min (series 4) the removal efficiency of Diclofenac, Candesartan and Venlafaxine decreased down to 90 %.

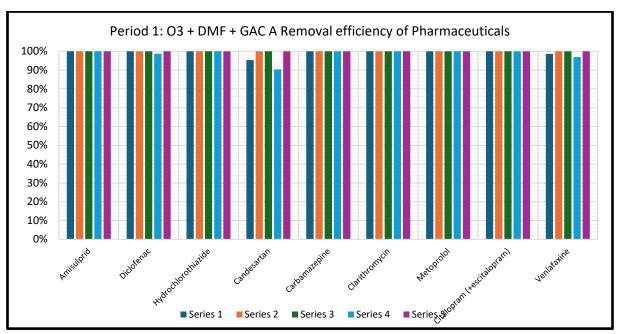


Figure 17: Removal efficiency of parallel line 1: O<sub>3</sub> + DMF + GAC A on pharmaceuticals. GAC contact times: Series 1: 19,4 min, Series 2: 32,3 min, Series 3: 24,2 min, Series 4: 13,8 min, Series 5: 10,8 min.

With parallel line 2 with only GAC filtration the removal efficiency of pharmaceuticals (figure 18) during this period were 100 % with GAC contact time 24,2 min (series 3) and 95-100 % with GAC contact time 32,3 min. Clarithromycin and Citalopram seemed to be easiest to remove and the removal efficiency stayed 100 % during this whole period, regardless of the GAC contact time. With most used GAC contact time 19,4 min the removal efficiency of pharmaceuticals was 80-100 % during this period.

But as seen above on figures 6-14 the GAC B filters removal efficiency decreased over the time as the GAC B filter became saturated without filtration prior. First sign of the GAC B filter (parallel line 2) starting to lose its adsorption capacity was only after 800 bed volumes, as the Candesartan was detected on the effluent. After that the concentration of Candesartan on GAC B effluent increased steadily on every sample and also other pharmaceuticals begin to appear on the samples on low concentrations.

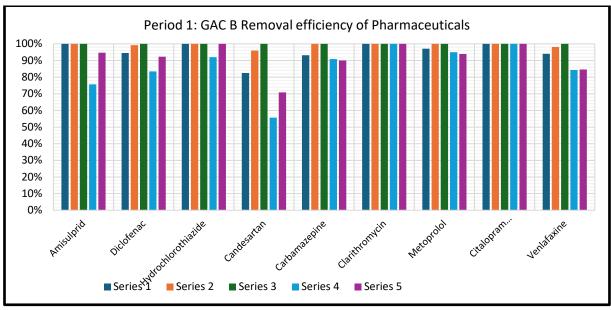


Figure 18: Removal efficiency of parallel line 2: GAC B on pharmaceuticals. GAC contact times: Series 1: 19,4 min, Series 2: 32,3 min, Series 3: 24,2 min, Series 4: 13,8 min, Series 5: 10,8 min.

On figure 19 is shown the removal efficiency of parallel line 1 on Candesartan during time with GAC contact time of 19,4 minutes. On figure 20 is shown the removal efficiency of parallel line 2 on Candesartan during time with same contact time 19,4 minutes. The combination of  $O_3$  and GAC kept the removal efficiency longer than just GAC, which got saturated quickly over time.

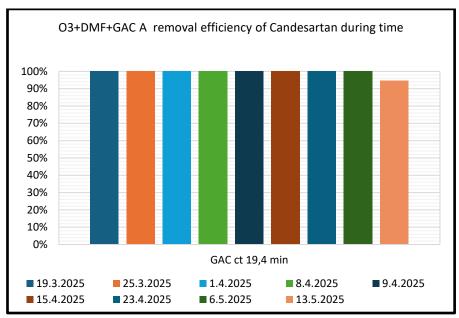


Figure 19: Removal efficiency of Candesartan on parallel line 1: O<sub>3</sub> +DMF+GAC with GAC contact time 19,4 min during time

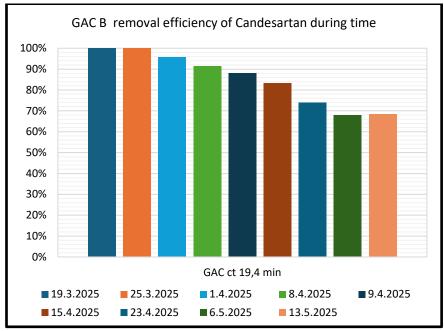


Figure 20: Removal efficiency of Candesartan on parallel line 2: GAC with GAC contact time 19,4 min during time

#### 3.1.3. Removal of benzotriazoles

Benzotriazoles are aromatic heterocyclic compounds, which are highly used industrially due their chemical stability and corrosion inhibiting properties. The derivates of benzotriazole, such as mixture of 4/6 -methyl- 1H-bentzotriatzole is also a component of de-icing and anti-icing fluid, highly used in aircrafts. Benzotriazoles are highly persistence in aquatic environments and raise concerns about their ecological impacts.

During piloting two benzotriazoles listed as indicators in UWWTD were analysed.

On this period in pilot influent the concentration of Benzotriazole ranged from 0,89  $\mu$ g/l to 2,80  $\mu$ g/l. The concentration of mixture of 4/6 -methyl- 1H-bentzotriatzole ranged from 0,47  $\mu$ g/l to 1,70  $\mu$ g/l.

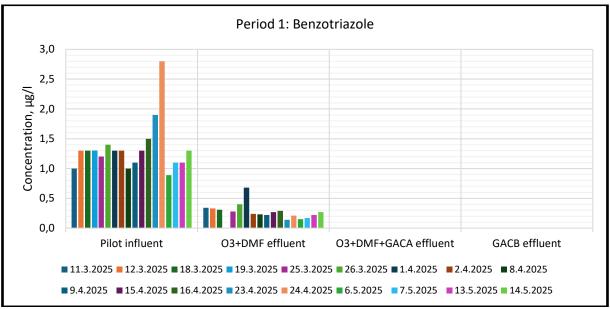


Figure 21: Concentrations of Benzotriazole on each sample point during period 1

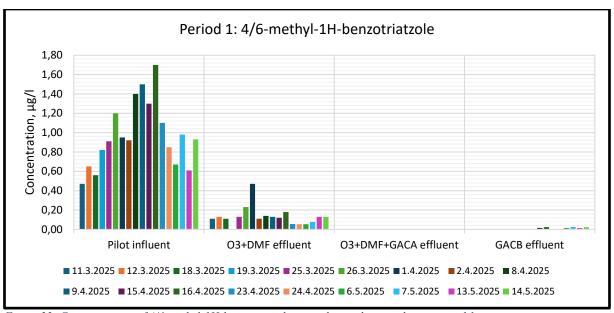


Figure 22: Concentrations of 4/6-methyl-1H-benzotriatzole on each sample point during period 1

Removal efficiency of  $O_3$  + DMF on benzotriazole and mixture of 4/6 -methyl- 1H-bentzotriatzole was between 72 % and 90 % during this period (figure 21)

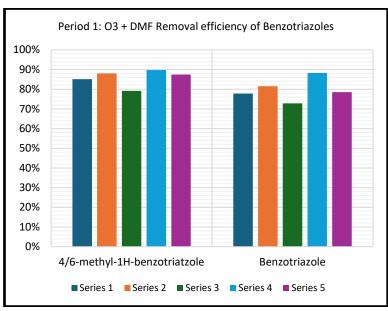


Figure 23: Removal efficiency of parallel line 1:  $O_3$  + DMF on Benzotriazoles, series divided based on GAC contact to determine the  $O_3$  + DMF effect prior GAC filtration

The removal efficiency of parallel line 1 with  $O_3$  +DMF+GAC filtration was 100 % on both Benzotriazole and the mixture of 4/6 -methyl- 1H-bentzotriatzole (figure 23).

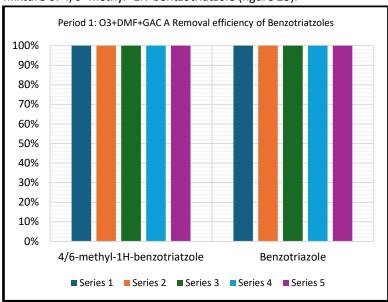


Figure 24: Removal efficiency of parallel line 1: O<sub>3</sub> + DMF + GAC A on benzotriazoles. GAC contact times: Series 1: 19,4 min, Series 2: 32,3 min, Series 3: 24,2 min, Series 4: 13,8 min, Series 5: 10,8 min.

The removal efficiency of parallel line 2 with only GAC filtration was 100 % on Benzotriazole during this period, but with the mixture of 4/6 -methyl- 1H-bentzotriatzole decreased slightly with GAC contact times under 20 minutes (Series 1, 4 and 5). (figure 25).

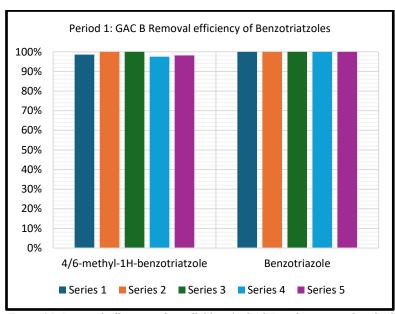


Figure 25: Removal efficiency of parallel line 2: GAC B on benzotriazoles. GAC contact times: Series 1: 19,4 min, Series 2: 32,3 min, Series 3: 24,2 min, Series 4: 13,8 min, Series 5: 10,8 min.

#### 3.1.4. Removal of PFAS

PFAS compounds are partially or fully fluorinated organic substances originating from human activity. They are widely used in industrial- and consumer products due to their water- stain- and grease repellent properties. PFAS compounds are extremely persistent and do not degrade in the environment through biological, chemical or physical processes. PFAS compounds accumulate in the environment and living organisms and may pose various harmful effects. In the new UWWTD, PFAS compounds are identified as harmful substances and key measures are introduced to limit the PFAS pollution into the environment.

Out of 30 PFAS compounds analysed, only 11 compounds were detected, and in pilot influent only 9 PFAS compounds. 8:2 FTS and PFBA appeared after Ozonation. Concentrations in pilot influent ranged from 6 ng/l to 17 ng/l.

GAC filtration appeared to be more efficient on PFAS removal than ozonation. Only with some of compounds the  $O_3$  prior GAC increased slightly the removal efficiency, such as PFOS, PFOA, PFHpA and PFHxS. GAC filtration without  $O_3$  prior was more efficient with PFBA.

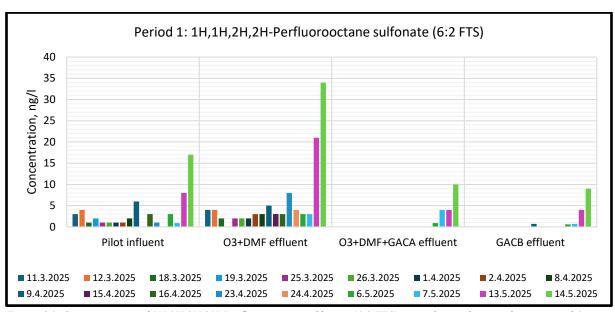


Figure 26: Concentrations of 1H,1H,2H,2H-Perfluorooctane sulfonate (6:2 FTS) on each sample point during period 1

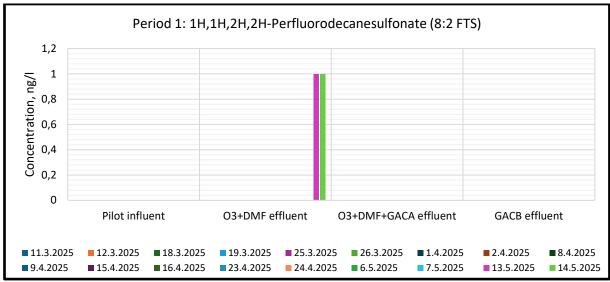


Figure 27: Concentrations of 1H,1H,2H,2H-Perfluorodecanesulfonate (8:2 FTS) on each sample point during period 1

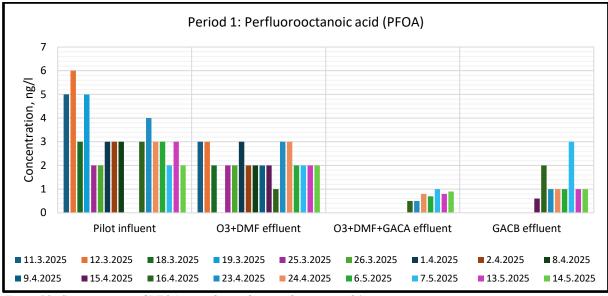


Figure 28: Concentrations of PFOA on each sample point during period 1

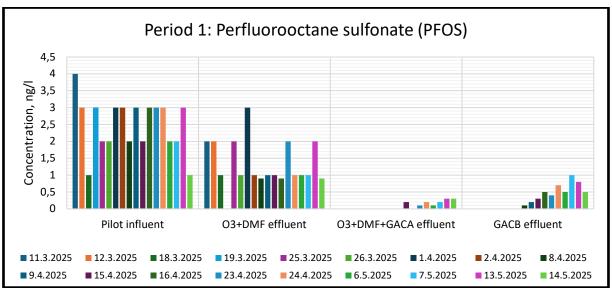


Figure 29: Concentrations of PFOS on each sample point during period 1

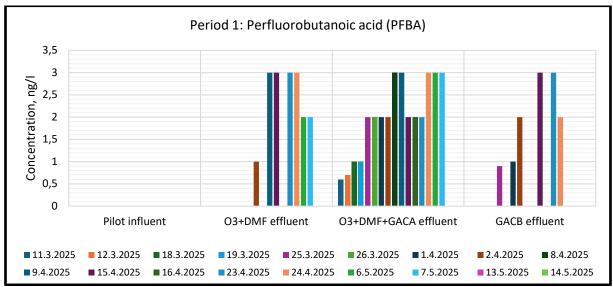


Figure 30: Concentrations of PFBA on each sample point during period 1

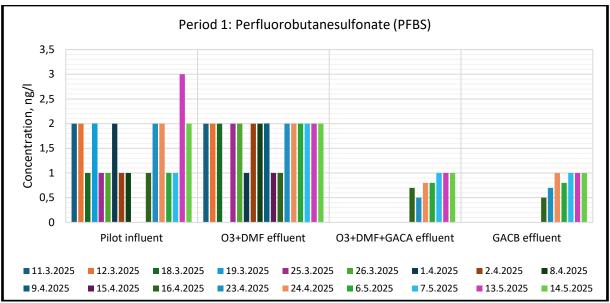


Figure 31: Concentrations of PFBS on each sample point during period 1

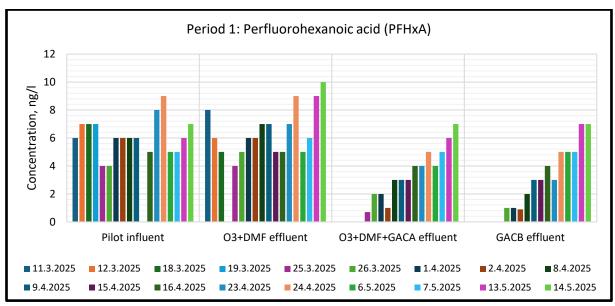


Figure 32: Concentrations of PFHxA on each sample point during period 1

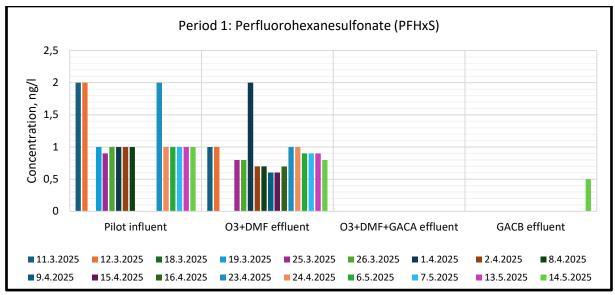


Figure 33: Concentrations of PFHxS on each sample point during period 1

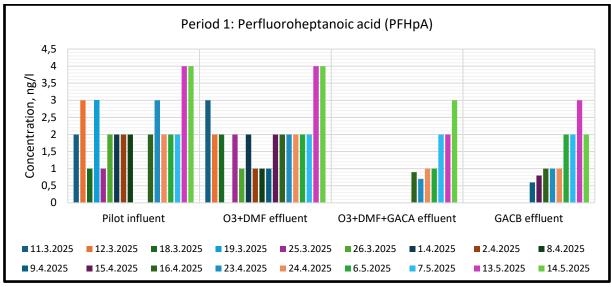


Figure 34: Concentrations of PFHpA on each sample point during period 1

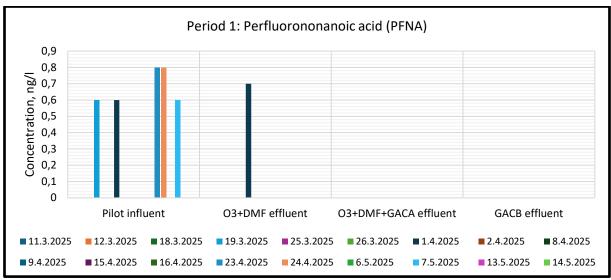


Figure 35: Concentrations of PFNA on each sample point during period 1

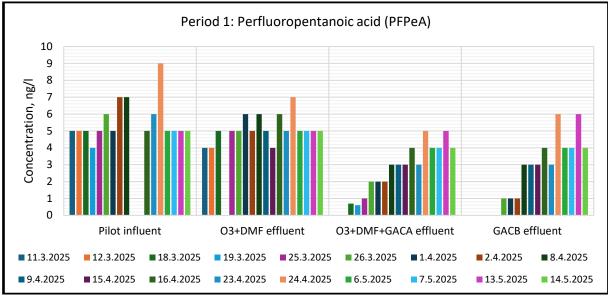


Figure 36: Concentrations of PFPeA on each sample point during period 1

Short chain PFAS compounds were analysed four times during this period. Out of 5 short chain PFAS compounds analysed, 3 compounds were detected. Concentration of TFA (figure 37) on Pilot influent ranged from 620 ng/l to 650 ng/l and the concentration increased after ozonation, ranging from 640 ng/l to 710 ng/l on  $O_3$  + DMF effluent. GAC after  $O_3$  +DMF was not efficient on removing the TFA after Ozonation and the concentration on  $O_3$  +DMF+GAC effluent was same or higher than after  $O_3$  +DMF. Parallel line 2 with only GAC filtration the removal efficiency was slightly better, but only 2 % to 11 %.

Other detected short chain PFAS compounds were PFPrA and TFMS. With PFPrA the concentration (figure 38) on Pilot influent ranged between 0 ng/l to 5 ng/l and removal efficiency of  $O_3$  +DMF varied from negative to 100 %. The GAC removal efficiency was between negative and 12 %.

With TFM (figure 39) the concentration on Pilot influent ranged between 8,4 ng/l to 9,1 ng/l and the Ozonation increased the concentration slightly. The GAC filtration removal efficiency on parallel line 1 was up to 20 % in the beginning, but over time got saturated and removal efficiency became negative. Parallel line 2 with only GAC filtration the removal efficiency of TFMS was up to 45 % on the beginning, but over time decreased down to 6 %.

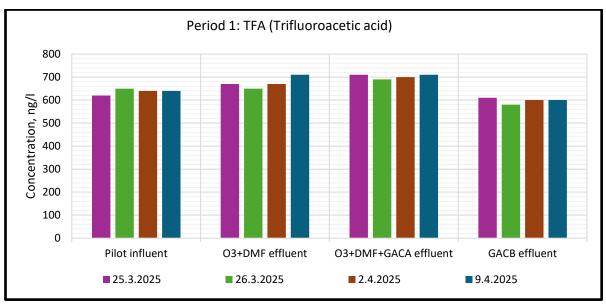


Figure 37: Concentrations of TFA on each sample point during period

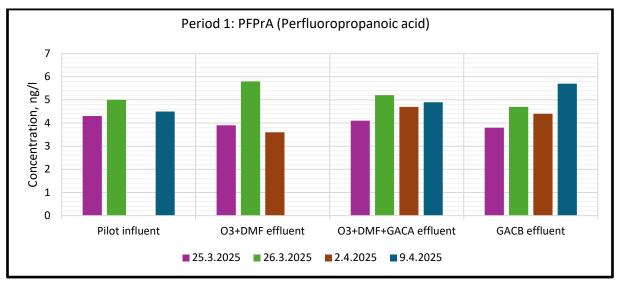


Figure 38: Concentrations of PFPrA on each sample point during period

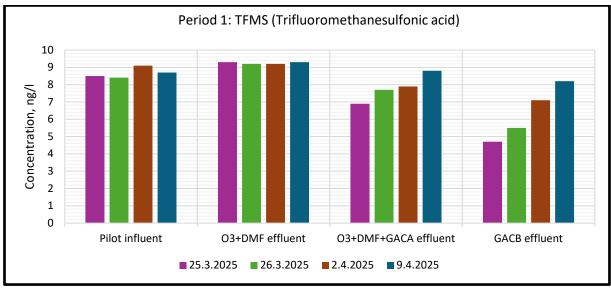


Figure 39: Concentrations of TFMS on each sample point during period

## 3.2. Testing period 2: One line

Second testing period with one line were conducted during piloting weeks 10 to 13. Piloting weeks 10, 11 and 13 were conducted without the  $O_3$ : the treatment train were DMF, then divided to GAC A and GAC B filters followed by UV. Piloting week 12 was conducted with the  $O_3$  prior the DMF. On weeks 10 and 11 the focus was to use only sandfiltration prior GAC filtration to determine the difference between the GAC filtrations after they have been saturated differently. Weeks 12 and 13 were planned to be with  $O_3$ , but due the malfunction of the  $O_3$  generator only week 12 the  $O_3$  was used.

On testing period 2 the main focus was to see if the removal efficiency on GAC B filter can be restored with additional filtering prior.

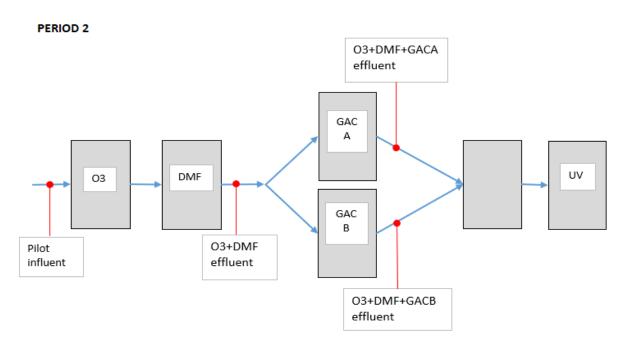


Figure 40: Period 2 flowchart

This period was divided in 3 series based on GAC filter contact times:

Series 1 GAC EBCT: 19,4 min (4 sample days)
Series 2 GAC EBCT: 32,3 min (2 sample day)
Series 3 GAC EBCT: 13,8 min (2 sample days)

Ozone was used on sample days 10.6.2025 and 11.6.2025 and contact time was 5 minutes.

Table 2: Operation parameters during period 2

	20.5.2025	21.5.2025	3.6.2025	4.6.2025	10.6.2025	11.6.2025	17.6.2025	18.6.2025
O <sub>3</sub> dose (mgO <sub>3</sub> /L)	-	-	ı	-	0,146	0,144	-	-
CT O₃ (min)	-	-	-	-	5	5	-	-
EBCT GAC A (min)	19,4	32,3	19,4	13,8	19,4	32,3	19,4	10,8
EBCT GAC B (min)	19,4	32,3	19,4	13,8	19,4	32,3	19,4	10,8

## 3.2.1. Removal of suspended solids and TOC

On this period the suspended solids and TOC were analysed on each sample day. On figure 41 is shown the amount of suspended solids on each sample point. On this period there was no abnormal levels of suspended solids on Pilot influent. On figure 42 is shown TOC on each sample point.

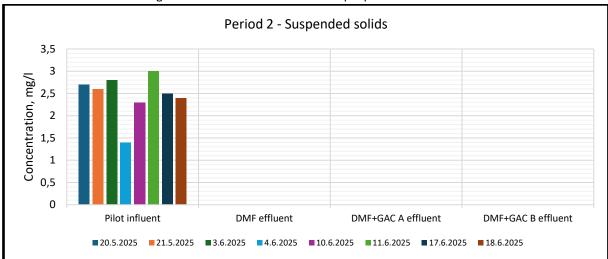


Figure 41: Concentration of suspended solids on each sample point

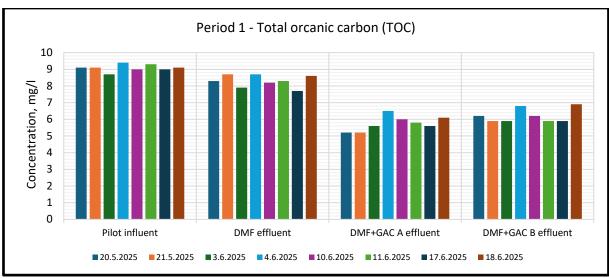


Figure 42: Concentration of TOC on each sample point

#### 3.2.2. Removal of Pharmaceuticals

On this period in Pilot influent hydrochlorothiazide was found at the highest concentrations, ranging from 0,45  $\mu$ g/l to 2,40  $\mu$ g/l. Also, significant concentration was measured for candesartan (1,1  $\mu$ g/l to 1,7  $\mu$ g/l), diclofenac (0,95  $\mu$ g/l to 1,6  $\mu$ g/l), and venlafaxine (0,92  $\mu$ g/l to 1,1  $\mu$ g/l). Irbesartan and clarithromycin was not detected during this period, other pharmaceutical concentrations ranged from 0,021  $\mu$ g/l to 0,48  $\mu$ g/l. O<sub>3</sub> was only used on sample days 10.6.2025 and 11.6.2025.

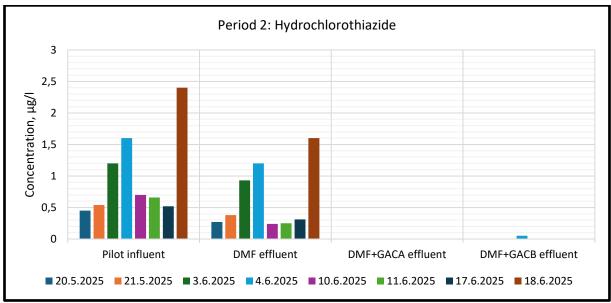


Figure 43: Concentrations of Hydroclorothiazide on each sample point during period 2

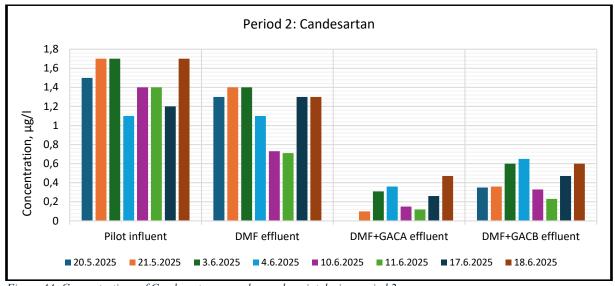


Figure 44: Concentrations of Candesartan on each sample point during period 2

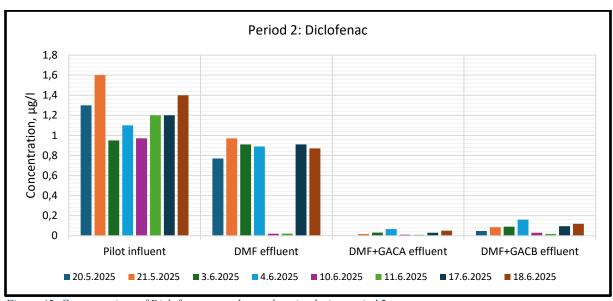


Figure 45: Concentrations of Diclofenac on each sample point during period 2

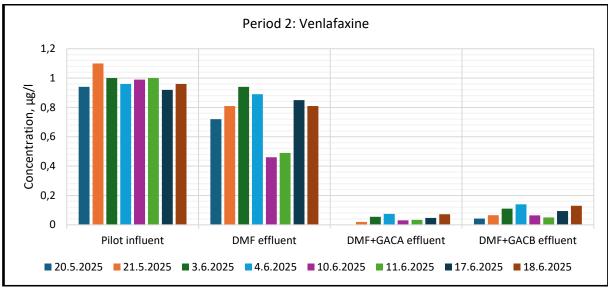


Figure 46: Concentrations of Venlafaxine on each sample point during period 2

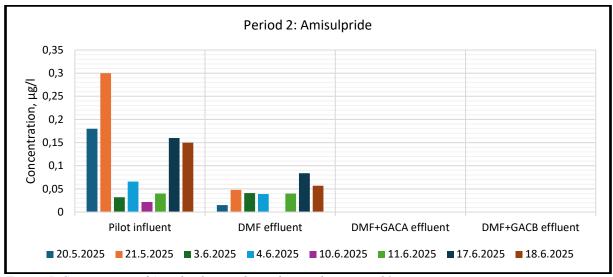


Figure 47: Concentrations of Amisulpride on each sample point during period 2

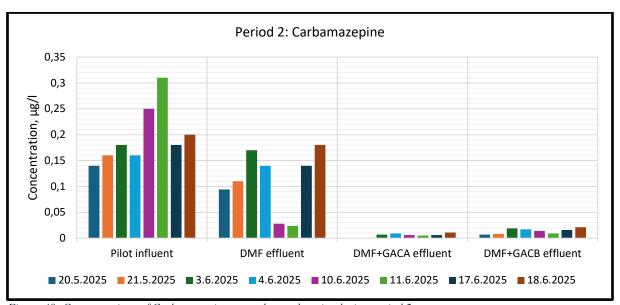


Figure 48: Concentrations of Carbamazepine on each sample point during period 2

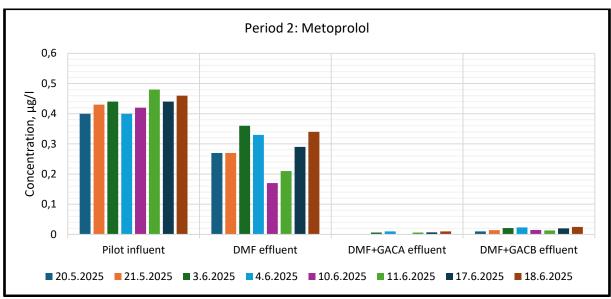


Figure 49: Concentrations of Metoprolol on each sample point during period 2

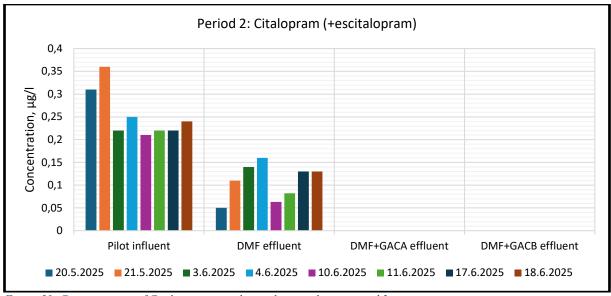


Figure 50: Concentrations of Citalopram on each sample point during period 2

 $O_3$  was only used on one sample day on series 1 and one sample day on series 2, other samples only DMF was used prior GAC filtrations.

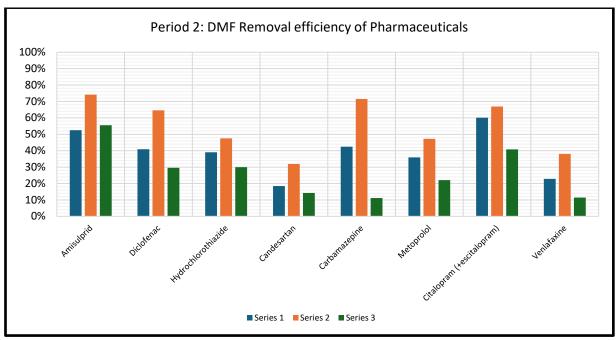


Figure 51: Removal efficiency of DMF on pharmaceuticals, series divided based on GAC contact to determine the DMF effect prior GAC filtration

The removal efficiency of pharmaceuticals was more equal between the two GAC filters in this period, but the prior load and saturation of GAC B filter made it less efficient. The longest GAC contact time of 32,3 min (series 2) was most efficient, but the differences between different contact times were in 5 % range, except candesartan. Candesartan turned out to be the most difficult to remove and needed the longest GAC contact time.

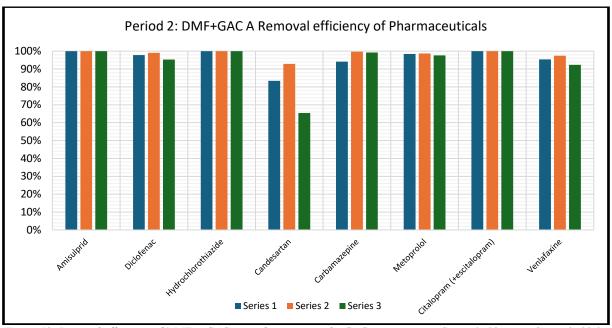


Figure 52: Removal efficiency of DMF + GAC A on pharmaceuticals. GAC contact times: Series 1: 19,4 min, Series 2: 32,3 min, Series 3: 13,8 min

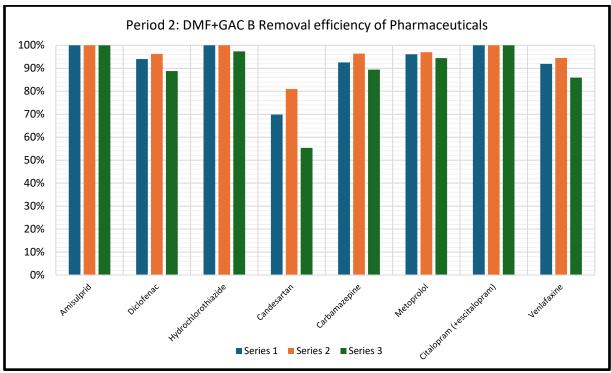


Figure 53: Removal efficiency of DMF + GAC B on pharmaceuticals. GAC contact times: Series 1: 19,4 min, Series 2: 32,3 min, Series 3: 13,8 min

### 3.2.3. Removal of benzotriazoles

On this period in Pilot influent the concentration of Benzotriazole ranged from 0,96  $\mu$ g/l to 1,50  $\mu$ g/l. The concentration of mixture of 4/6 -methyl- 1H-bentzotriatzole ranged from 0,49  $\mu$ g/l to 1,20  $\mu$ g/l.

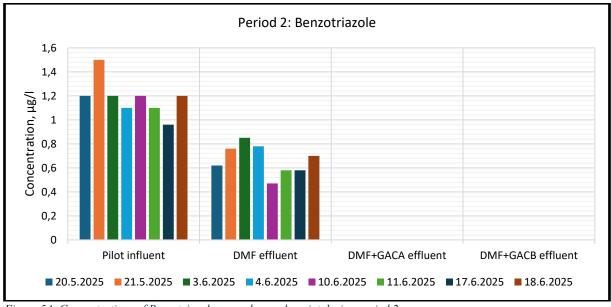


Figure 54: Concentrations of Benzotriazole on each sample point during period 2

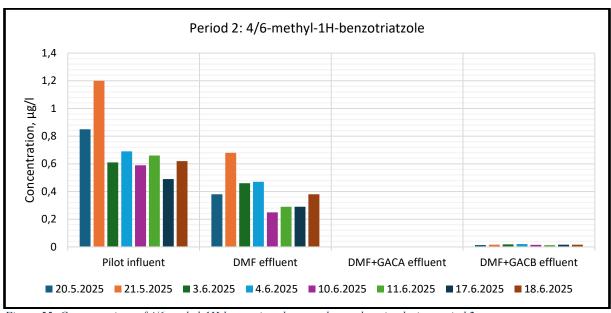


Figure 55: Concentrations of 4/6-methyl-1H-benzotriatzole on each sample point during period 2

The removal efficiency of DMF on Benzotriazole and the mixture of 4/6 -methyl- 1H-bentzotriatzole was under 50 %.

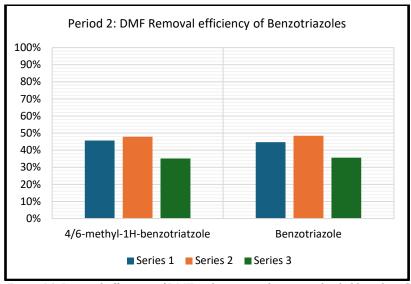


Figure 56: Removal efficiency of DMF on benzotriazoles, series divided based on GAC contact to determine the DMF effect prior GAC filtration

GAC filtration turned out to be highly effective on removal of benzotriazoles: removal efficiency of DMF+GAC A filter was 100 % on both on Benzotriazole and the mixture of 4/6 -methyl- 1H-bentzotriatzole. DMF+GAC B filtration removal efficiency was 100 % on benzotriazole and 97-98 % on the mixture of 4/6 -methyl- 1H-bentzotriatzole.

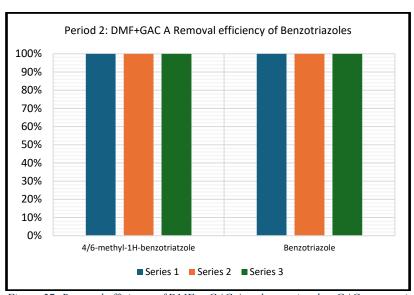


Figure 57: Removal efficiency of DMF + GAC A on benzotriazoles. GAC contact times: Series 1: 19,4 min, Series 2: 32,3 min, Series 3: 13,8 min

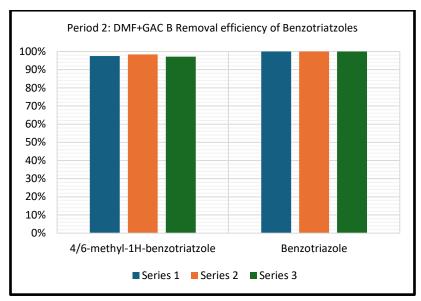


Figure 58: Removal efficiency of DMF + GAC B on benzotriazoles. GAC contact times: Series 1: 19,4 min, Series 2: 32,3 min, Series 3: 13,8 min

#### 3.2.4. Removal of PFAS

Out of 30 PFAS compounds analysed, only 12 compounds were detected during this period. In Pilot influent only 11 PFAS compounds, since PFBA appeared only in one sample on GAC A effluent. Concentrations in Pilot influent ranged from 5 ng/l to 18 ng/l.

Although the GAC B filter was saturated during period 1, its removal efficiency was similar or slightly better than GAC A filter during this period with DMF prior.

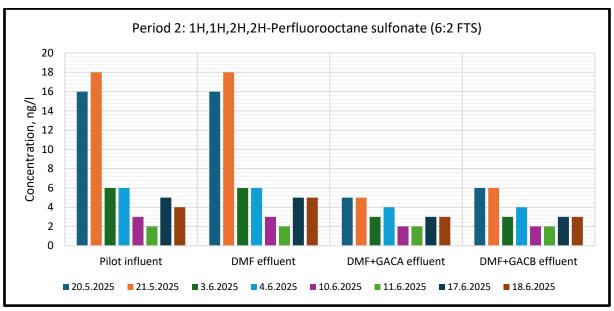


Figure 59: Concentrations of 1H,1H,2H,2H-Perfluorooctane sulfonate (6:2 FTS) on each sample point during period 2

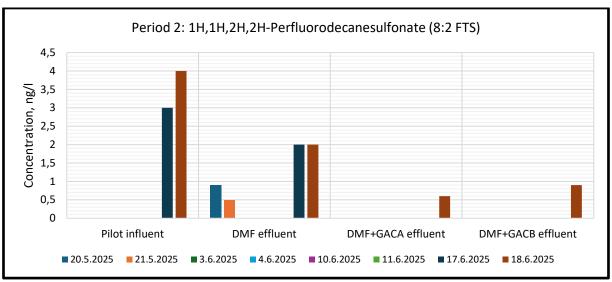


Figure 60: Concentrations of 1H,1H,2H,2H-Perfluorodecanesulfonate (8:2 FTS) on each sample point during period 2

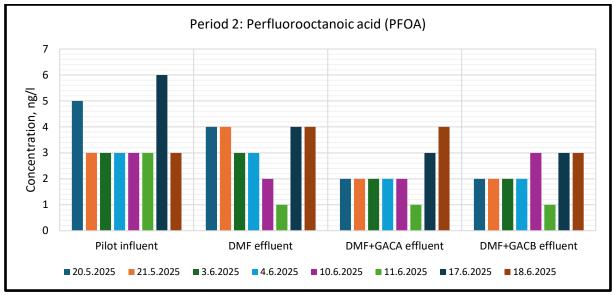


Figure 61: Concentrations of PFOA on each sample point during period 2

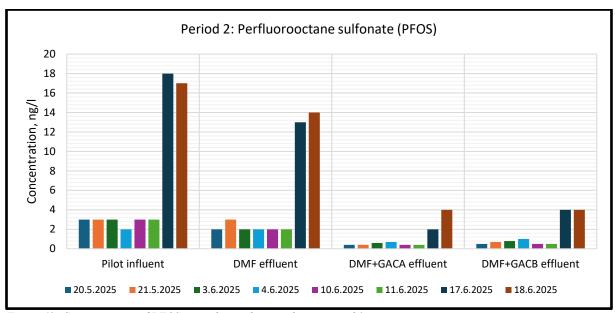


Figure 62: Concentrations of PFOS on each sample point during period 2

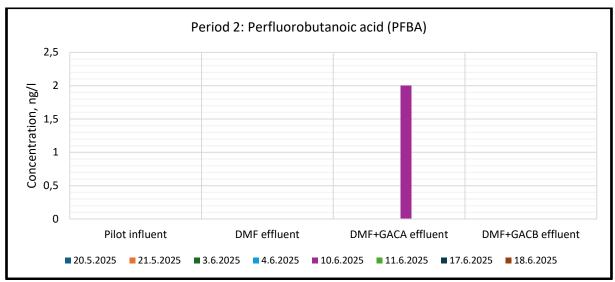


Figure 63: Concentrations of PFBA on each sample point during period 2

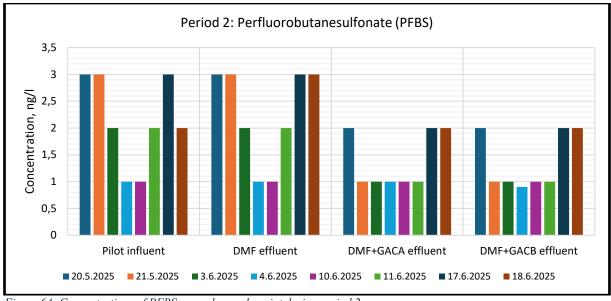


Figure 64: Concentrations of PFBS on each sample point during period 2

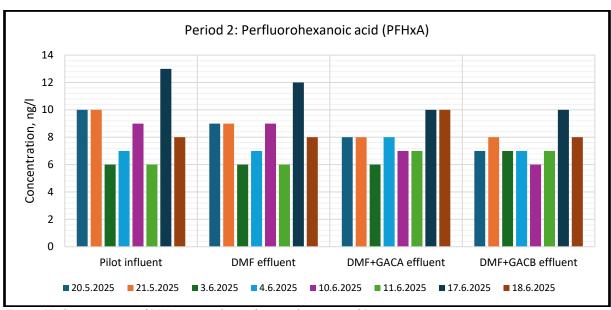


Figure 65: Concentrations of PFHxA on each sample point during period 2

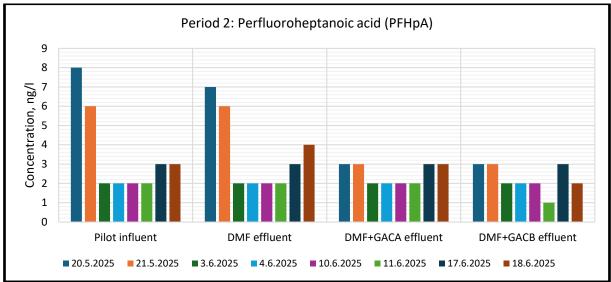


Figure 66: Concentrations of PFHpA on each sample point during period 2

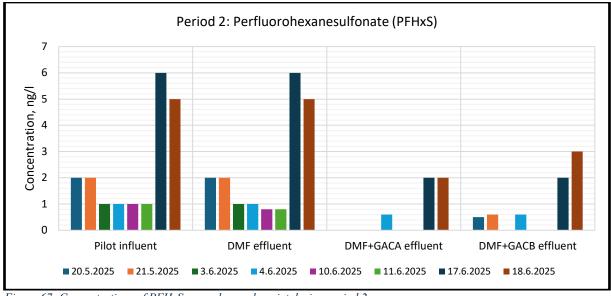


Figure 67: Concentrations of PFHxS on each sample point during period 2

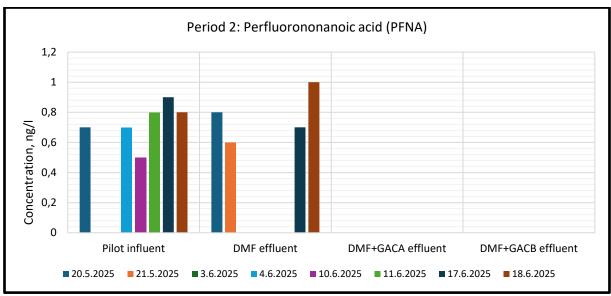


Figure 68: Concentrations of PFNA on each sample point during period 2

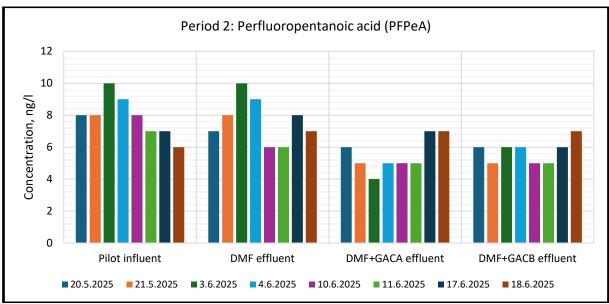


Figure 69: Concentrations of PFPeA on each sample point during period 2

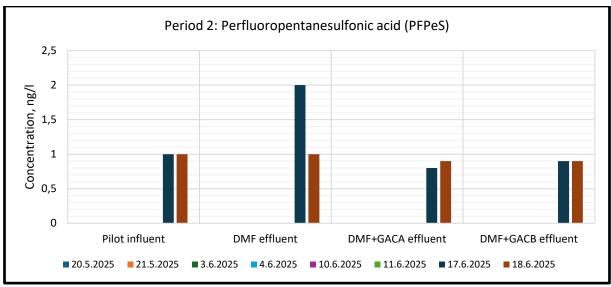


Figure 70: Concentrations of PFPeS on each sample point during period 2

Short chain PFAS compounds were analysed two times during this period. Out of 5 short chain PFAS compounds analysed, 3 compounds were detected. Concentration of TFA (figure 71) on Pilot influent ranged from 710 ng/l to 720 ng/l. Ozonation was used on 10.6.2025 and it shows on DMF effluent that the TFA concentration increased by 80 ng/l, while on sample day 3.6.2025 ozonation was not used and the TFA concentration increased only 10 ng/l. With GAC filtrations the removal efficiency of TFA was negative, except when  $O_3$  was not used on sample day 3.6.2025 the line DMF+GAC B did remove about 5 % of TFA.

Other detected short chain PFAS compounds were PFPrA and TFMS. With PFPrA the concentration (figure 72) on Pilot influent was 0 ng/l, but it was detected on DMF effluent when O<sub>3</sub> was used on 10.6.2025. The DMF+GAC A line could not remove it, but on the DMF+GAC B line PFPrA was not detected.

With TFMs (figure 73) the concentration on Pilot influent ranged between 6,8 ng/l to 7,7 ng/l and the concentration increased on DMF effluent whether  $O_3$  was used or not. The GAC filtrations removal efficiency was also negative.

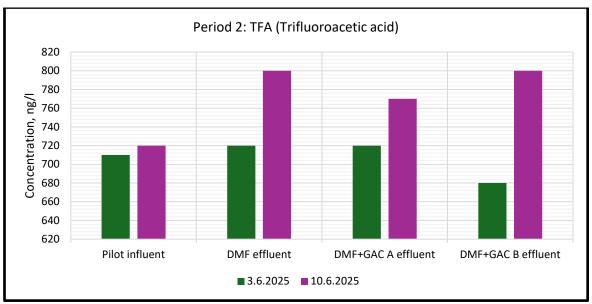


Figure 71: Concentrations of TFA on each sample point during period 2, Ozonation was used on 10.6.2025

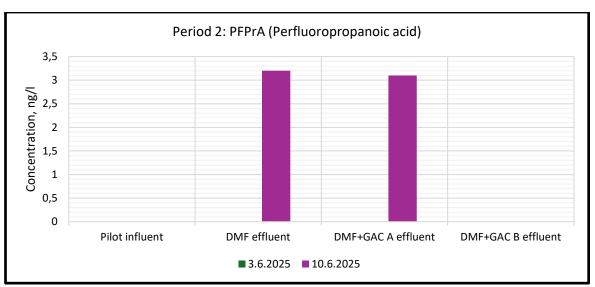


Figure 72: Concentrations of PFPrA on each sample point during period 2

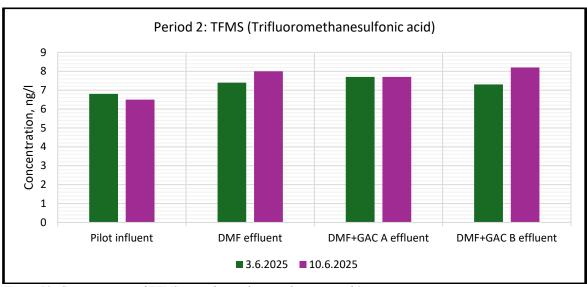


Figure 73: Concentrations of TFMS on each sample point during period 2

## 4. Conclusions

The Pilot tests conducted at the Turku region WWTP have led to the following conclusions:

- The mobile Pilot plant is valuable tool to test different solutions for quaternary treatments and to support full-scale investment plans.
- GAC filtration is highly effective on removing the pharmaceuticals listed as indicators in UWWTD, but it gets saturated fast without any filtration prior.
- GAC contact time should be 20 minutes or more for efficient removal of pharmaceuticals and benzotriazoles and even longer contact time improves the removal efficiency of PFAS.
- O<sub>3</sub> prior GAC filtration improves the removal efficiency of the 30 PFAS compounds analysed, but at the same time it increases the concentration of short chain PFAS compounds (such as TFA) and potentially other, un-analysed PFAS compounds.