

Strategies and technological means for minimising organic micropollutant emissions from Tallinn WWTP

ANNEX 5

EMPEREST – ELIMINATING MICRO-POLLUTANTS FROM EFFLUENTS
FOR REUSE STRATEGIES

Tallinn WWTP, 2025



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 5 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.

EMPEREST consortium: Union of the Baltic Cities Sustainable Cities Commission c/o City of Turku (FI), Baltic Marine Environment Protection Commission – Helsinki Commission (HELCOM) (FI), University of Tartu (EE), Berlin University of Technology (DE), Turku University of Applied Sciences (FI), Gdańsk Water Utilities (PL), Water and Sewage Company Ltd of Szczecin (PL), Tartu Waterworks Ltd (EE), Tallinn Water Ltd (EE), “Kaunas water” Ltd (LT), Turku Region Wastewater Treatment Plant (FI), DWA German Association for Water, Wastewater and Waste DWA Regional group North-East (DE), Environmental Centre for Administration and Technology (LT), City of Riga (LV).

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Contract:	EMPEREST – Eliminating Micro-Pollutants from Effluents for Reuse Strategies no. C013
Title:	Strategies and technological means for minimising organic micropollutant emissions from WWTPs Pilot-scale removal of micropollutants at the Tallinn WWTP in Estonia.
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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	SS	suspended solids
AOF	adsorbable organic fluorine	TCOD	total chemical oxygen demand
AOPs	advanced oxidation processes	TN	total nitrogen
A2/O	anaerobic/anoxic/oxic system	TOC	total organic carbon
BOD ₅	biochemical oxygen demand	TP	total phosphorus
COD	chemical oxygen demand	TSS	total suspended solids
DE	Germany	UV	ultraviolet
DF	drum filter	UVA	ultraviolet absorbance
DOC	dissolved organic carbon	UVA254	ultraviolet absorbance at 254
DOM	dissolved organic matter	wt%	weight percentage
EBCT	empty bed contact time	UWWTD	urban wastewater treatment
EE	Estonia	WWTPs	directive
EU	European Union	4-MTB	wastewater treatment plants
FI	Finland	6-MTB	4-methyl-benzotriazole
GAC	granular activated carbon		6-methyl-benzotriazole
GC-MS	gas chromatography-mass spectrometry		
HELCOM	Helsinki Commission		
HMI	human-Machine Interface		
IX	ion exchange		
IXR	ion exchange resin		
LC-MS	liquid chromatography-mass spectrometry		
LC-MS/MS	liquid chromatography-tandem mass spectrometry		
LT	Lithuania		
LV	Latvia		
OC	oxygen concentrator		
OG	ozone generator		
OMPs	organic micropollutants		
PE	population equivalent		
PFAS20	list of twenty PFASs		
PFBA	perfluorobutanoic acid		
PFBS	perfluorobutane sulfonic acid		
PFDA	perfluorodecanoic acid		
PFDoDA	perfluorododecanoic acid		
PFDoDS	perfluorododecane sulfonic acid		
PFDS	perfluorodecane sulfonic acid		
PFHpA	perfluoroheptanoic acid		
PFHpS	perfluoroheptane sulfonic acid		
PFHxA	perfluorohexanoic acid		
PFHxS	perfluorohexane sulfonic acid		
PFNA	perfluorononanoic acid		
PFNS	perfluorononane sulfonic acid		
PFOA	perfluorooctanoic acid		
PFOS	perfluorooctane sulfonic acid		
PFPeA	perfluoropentanoic acid		
PFPeS	perfluoropentane sulfonic acid		
PFTTrDA	perfluorotridecanoic acid		
PFTTrDS	perfluorotridecane sulfonic acid		
PFUnDA	perfluoroundecanoic acid		
PFUnDS	perfluoroundecane sulfonic acid		
PL	Poland		
PLC	programmable logic controller		
PSA	pressure swing adsorption		

1. Introduction

Organic micropollutants (OMPs) in wastewater are increasingly recognized as a pressing environmental and public health issue. Present at trace levels typically in nanograms to micrograms per litre OMPs originate from a wide range of industrial and human-related activities. Despite their low concentrations, they pose significant ecological and health challenges due to their persistence, potential for bioaccumulation, and biological activity.

Wastewater treatment plants (WWTPs) are among the primary point sources of OMPs. While modern WWTPs efficiently remove conventional pollutants like organic matter, nitrogen, and phosphorus, they struggle to eliminate OMPs. This limitation stems from the complex and diverse chemical nature of these contaminants, which often resist conventional treatment methods. Consequently, WWTP effluents may still release biologically active compounds capable of disrupting aquatic ecosystems and contributing to long-term risks for human health.

The persistence of OMPs in treated water signals an urgent need for both technological innovation and regulatory progress. Advanced treatment solutions including ozonation, membrane filtration and powdered or activated carbon adsorption are being tested and refined to target and remove these micropollutants before discharge. However, scaling these approaches requires thorough assessments of efficiency, cost, and environmental sustainability.

To address this issue, the European Union adopted an updated Urban Wastewater Treatment Directive (UWWTD) in November 2024. The directive mandates enhanced nutrient removal and imposed stricter standards for monitoring and eliminating micropollutants. By 2045, WWTPs serving 150,000 population equivalents (PE) or more must implement quaternary treatment to tackle a wide array of micropollutants. Facilities serving agglomerations between 10,000 and 100,000 PE in sensitive areas must also adopt these measures unless a comprehensive risk assessment indicates no substantial public or ecological risk.

This report shares findings from pilot-scale testing of advanced OMP removal technologies using a mobile treatment unit for six months in Tallinn WWTP. The pilot evaluated the effectiveness of ozone oxidation, activated carbon and superfine activated carbon in reducing micropollutant levels in treated wastewater. It also identified the key process parameters that influence removal efficiency. These results support the development of evidence-based strategies for broader implementation of advanced treatment technologies contributing to improved water quality, healthier ecosystems, and reduced human exposure to harmful pollutants.

2. Setup

2.1. Study Site

The pilot test was carried out at the Tallinn Wastewater Treatment Plant (WWTP), the largest municipal facility in Estonia. Located on the Baltic coast, the plant discharges its treated effluent into the Baltic Sea and serves a population equivalent (PE) of approximately 500 000, with an average daily influent flow of around 120 000 m³.

Wastewater enters the plant and first passes through mechanical screens that remove larger debris. These materials are subsequently washed, compacted, and transported to a landfill. Grit brought in by stormwater is separated in grit traps, washed, and used in composting. Fats and oils from grit traps surface are removed (Figure 1).

Next, the water flows into primary sedimentation tanks, where suspended solids are allowed to settle. The resulting raw sludge is directed to the sludge treatment process.

Biological treatment then begins in aeration tanks, where nitrogen compounds are removed. Air is diffused from the bottom of the tanks in large volumes, and methanol is added to promote efficient biological activity. The mixture of wastewater and bacteria continues to secondary sedimentation tanks, where activated sludge is separated. A portion of this sludge is recycled back to the aeration tanks, while the excess is directed to sludge treatment.

Approximately 90% of the treated water is further treated through a biofilter for post-denitrification. The final, thoroughly treated effluent is discharged via a deep-sea outlet extending nearly 3 km into the Bay of Tallinn.

Average concentrations of pollutants in 2024 effluent are as follows:

- Biochemical oxygen demand (BOD7) 3,4 mg BOD7/L
- Total chemical oxygen demand (TCOD) 36 mg COD/L
- Total suspended solids (TSS) 6,6 mg/L
- Total nitrogen (TN) 6,1 mg N/L
- Total phosphorus (TP) 0,33 mg P/L

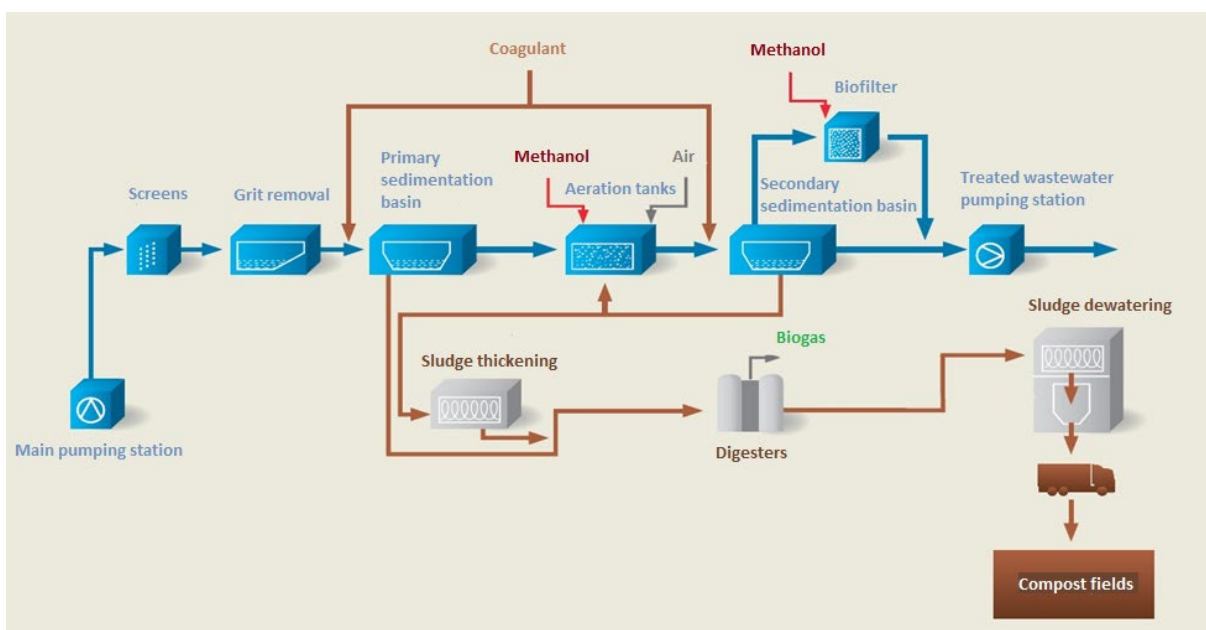


Figure 1. Tallinn WWTP Process Scheme

2.2. Pilot Plant Description

The pilot test was conducted using two mobile pilot containers, designed, and built by Industrial System Engineering, based on a detailed design concept developed collaboratively by Tartu Waterworks Ltd and the University of Tartu (Figure 2).



Figure 2. View of the pilot plant (two sea containers) located at the Tallinn WWTP in Estonia



Figure 3. View of the pilot plant interior

The pilot plant is dedicated to evaluating the removal efficiency of OMPs from water or wastewater. For the pilot testing, Tallinn WWTP used effluent water from the biofilter as the inlet for the pilot equipment. According to the process scheme (Figure 3), the testing equipment is divided into units corresponding to different technological systems.

Effluent of the biofilter is pumped to the first unit, which corresponds to pile cloth media filtration. In pilot, Mecana Pile cloth media filtration (PCMF), which uses drum filter, was tested out. The main aim of the PCMF unit is to remove suspended solids from the water as it flows through the filter cloth into the filter drum, the solids being retained on the filter cloth. The filtered water then flows out of the unit through the rising chamber and finally over an overflow weir to the buffer tank (Mecana Umwelttechnik AG, 2023), which is used in the following technological units of the pilot plant.

The second unit represents the ozonation system, recognized as one of the advanced treatment technologies for eliminating persistent organic micropollutants (OMPs), including pharmaceutical residues. Through oxidation, ozone transforms these contaminants into less harmful substances. The system's ozone consumption is influenced by the specific types and concentrations of pollutants present in the WWTP effluent (Kuusik et al., 2023).

This ozonation system employs pressure swing adsorption (PSA) technology to generate high-purity oxygen on-site. Ambient air is passed through a PSA oxygen generator, which uses selective adsorbents to separate oxygen from other gases. The extracted oxygen is then supplied to the ozone generator, where ozone is produced. To maintain optimal operating temperatures and ensure consistent ozone production, the ozone generation cells are cooled using a closed-circuit water-cooling system. The generated ozone is subsequently injected into the WWTP's effluent stream, where it dissolves and reacts with OMPs, effectively degrading them.

Ozone treated water then proceeds to the third unit, the sand filter (DMF). In the pilot system, the sand filter operates in a downward flow direction during normal filtration, effectively removing any remaining suspended solids and mineral residues. During the backwash cycle, the flow is reversed, i.e water and air is pumped upward to clean the filter media, and the resulting dirty backwash water is discharged through an upper outlet pipe.

Following the sand filter, a buffer tank is used to store water for the remaining treatment steps and serves also as clean backwash water for sand filter.

Fourth unit is divided into 4A and 4B units, which both are granular activated carbon (GAC) filters. Their filtration process and backwash process are similar to sand filtration process. But unlike the sand filter, GAC A and GAC B purpose is to eliminate OMPs and is based on adsorption processes.

Following the GAC A and GAC B, a buffer tank water is used for the previous filter backwashes, and for the following unit five, UV disinfection. As the name suggests, the purpose of UV treatment is to reduce harmful microorganisms and pathogens, thereby safeguarding public health and protecting aquatic ecosystems from waterborne diseases and related environmental impacts.

Additionally, superfine powdered activated carbon (sPAC) was tested in combination with a PCMF system. For this setup, the filter media was replaced with finer cloth to enhance filtration. Effluent from a biofilter was pumped into a mixing tank, where both coagulant and sPAC were dosed proportionally to the water's total organic carbon (TOC) level. After mixing, the sPAC-enriched water was directed to the PCMF unit, where a filtration process like that in Unit one was carried out. Following filtration, the PCMF effluent was once again visibly clear.

The role of sPAC is comparable to that of GAC; however, due to its superfine particle size, sPAC has a significantly larger specific surface area than GAC. This characteristic theoretically enables it to adsorb a greater quantity of OMPs.

The pilot plant is a controlled environment and is designed to automate the process. It is equipped with features to control water flow, level, turbidity with also the option to monitor water temperature, its pH level and electric conductance.

The pilot plant is controlled and monitored by HMI panel (Figure 4). Alternatively, the HMI is also accessible from the HMI webpage using computer web browser, which provides secure remote access to the pilot plant. The computer needs to be in the same network as HMI, alternatively there is also a possibility to use VPN.

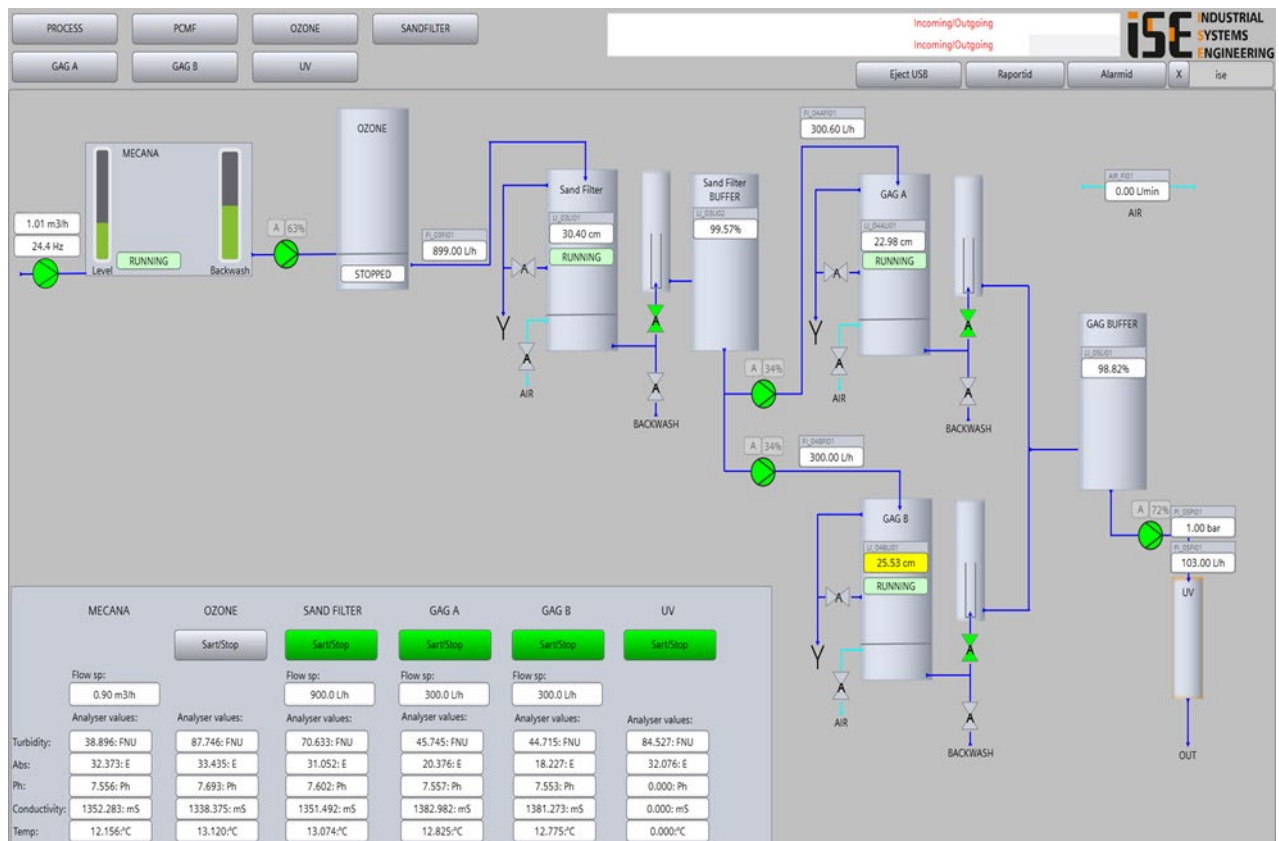


Figure 4. HMI display of the entire SCADA system process

Almost all the visual elements contain an interactive pop up with more details and parameters regarding the element. Additionally, the main process page provides a quick overview of the analyser data, allows specific processes to be turned on or off, and enables the setting of set points.

Furthermore, the on-site plant setup is designed for flexibility, using hoses with cam lock couplings that allow various process steps to be easily connected or rearranged. This adaptability supports more realistic pilot testing and planning, ensuring the system can be tailored to the specific needs and future development plans of each wastewater treatment plant participating in the testing.

All equipment is installed in two sea containers to allow for easy transport and rapid commissioning at any water intake or wastewater treatment plant. Additionally, the containers are insulated to enable testing even in cold weather conditions.

The pilot plant was designed to be highly flexible, allowing for the testing of different treatment processes and evaluating how various process parameters affect treatment efficiency. One of the key features ensuring the high flexibility of the pilot plant is the use of water buffer tanks with overflows and pumps installed before pile cloth media filtration, before ozone oxidation, after sand filter buffer and before UV filtration. These allow each treatment stage to operate at different flow rates. Additionally, bypasses for each treatment stage make it possible to test various treatment process configurations, depending on research needs.

The treatment steps are composed of the following main components:

1. Mecana Pile Cloth Media Filter, type TF05-S-DUPLEX/A4 (PCMF)
Set filter cloth type: Pile Fabric OptiFiber® PES-14
Filter surface area 0.5 m²
max hydraulic capacity 5 m³/h

Buffer tank after PCMF- Essential for maintaining continuous functionality of the following equipment while PCMF undergoes backwash cycle.

2. Ozonetech Rena Vivo A4 ozone system

an ozone contact tank size	50 L
max flow-through	250 L/min
Ozone generator ICT 40 with nominal production of	40 g O ₃ /h
Ozone concentration	135 g/Nm ³
PSA technology-based oxygen generator - Onyx with flow of	6 L/min
Nominal oxygen concentration	93 %

3. Sand filter (DMF)

diameter	0.4 m
surface area	0.126 m ²
filter nozzles	36x0.3= 2.05 cm ²

Filter media: 1.2-2.0 mm coarse sand in the bottom and top layer of Hydro-anthracite N with a grain size of 0.8-1.6 mm.

4. Granular activated carbon (GAC) filters – 2 units

Filter media:	Hydraffin AR 8x30
surface area	0.126 m ²

- a backwash water storage tank

maximum working volume	0.7 m ³
length	1.35 m
width	0.46 m
height	1.3 m

5. Saniray VX-245-6 ultraviolet (UV) lamp

Maximum flow	1 m ³ /h
UV dose	400 J/m ² at 60 % UV transmittance

6. sPAC (superfine activated carbon) - separately tested.

2.1. Experimental setup

Tallinn WWTP operated the pilot plant from 26th of August 2024 to 3rd of February 2025. During this period, testing was carried out in three distinct configurations, each combining different treatment technologies.

Initially, starting on September 2nd, the pilot operated in the following sequence: Biofilter → Drum Filter → Ozonation → Sand Filter → GAC A → GAC B → UV. In November, Tallinn reconfigured the system, connecting the drum filter directly to GAC B, allowing to compare effluent quality with and without ozonation. In January, sPAC was added into the setup.

The combinations tried out were as follows:

- 1) PCMF-O₃-DMF-GAC A-GAC B-UV
- 2) PCMF-O₃-DMF-GAC B-UV
 - a. PCMF-O₃-DMF-GAC A-UV
- 3) sPAC-PCMF

2.2. Analytical Methods

Performance of the examined treatment train was monitored by grab sampling, as well as online sensors. The automatic analysis cell measured parameters such as turbidity, UV₂₅₄, pH, conductivity, and temperature. Figure 5 illustrates the analysis cells.



Figure 5. Automatic analysis cell for multipurpose samples

Manual valves were installed after each treatment stage to facilitate the collection of grab samples for laboratory analysis. These samples were analyzed both in our in-house laboratory and in cross-border laboratories.

Grab samples from every stage were collected once a week during the piloting period. The samples were examined for wastewater quality parameters indicating the content of suspended solids and organic compounds. The list of measured wastewater quality parameters is as follows:

- Suspended Solids
- Total Phosphorus
- Total Nitrogen
- Ammonia
- Phosphates
- UV₂₅₄
- Turbidity
- TCOD
- Dissolved organic carbon (DOC)

Four different OMP analysis on the influent and effluent of pilot plant:

- 13 PFAS compounds
 - PFBA (Perfluorobutanoic acid),
 - PFBS (Perfluorobutanesulfonic acid),
 - PFDA (Perfluorodecanoic acid),
 - PFHpA (Perfluoroheptanoic acid),
 - PFHpS (Perfluoroheptanesulfonic acid),
 - PFHxA (Perfluorohexanoic acid),
 - PFHxS (Perfluorohexanesulfonic acid),
 - PFNA (Perfluorononanoic acid),
 - PFOA (Perfluorooctanoic acid),
 - PFOS (Perfluorooctanesulfonic acid),
 - PFPeA (Perfluoropentanoic acid),
 - PFUdA (Perfluoroundecanoic acid),
 - TFA (Trifluoroacetic acid)
- 12 Pharmaceuticals
 - Amisulpride,
 - Benzotriazole,
 - Candesartan,
 - Carbamazepin,
 - Citalopram (+escitalopram),
 - Clarithromycin,
 - Diclofenac,
 - Hydrochlorothiazide,
 - Irbesartan,
 - Metoprolol,
 - Venlafaxine

3. Results

The requirements for quaternary treatment of discharges from urban wastewater treatment plants the Urban Wastewater Treatment Directive (UWWTD) mandate the removal of specific organic micropollutants that can contaminate water even at low concentrations. These substances must be removed at a minimum efficiency of 80% relative to the influent load. The regulation categorizes these compounds into two groups. Category 1 includes substances that are very easily treatable, such as amisulpride, carbamazepine, citalopram, clarithromycin, diclofenac, hydrochlorothiazide, metoprolol, and venlafaxine. Category 2 comprises substances that can be easily disposed of, including benzotriazole, candesartan, and irbesartan. The concentration of these substances must be measured to verify compliance with the removal targets. (Office of the European Union, 2024)

Tallinn Wastewater Treatment Plant conducted its pilot testing with direct reference to UWWTD, and the selection of analytes for laboratory analysis was based on the listed substances. In addition, Tallinn had previously carried out PFAS analyses and was already aware of which compounds posed the greatest concern in their effluent. Based on this prior knowledge, specific PFAS compounds were selected for analysis during the piloting.

The influent to the pilot plant consisted of effluent water from the biofilter known as post-denitrification station of Tallinn WWTP. The pilot plant consisted of two sea containers. The first container included pile cloth media filtration, while the second contained ozonation, sand filtration, two granular activated carbon (GAC) filters, and a UV treatment unit. The following Table 1 shows the flow rates and parameters recorded from the pilot process.

Table 1. Piloting process parameters during testing. (CT – contact time)

Date	Flow (m ³ /h)						Parameters			
	Drum filter	O ₃	Redox, mV	GAC A	GAC B	UV	Dose O ₃ , %	CT O ₃ , min	CT GAC A, min	CT GAC B, min
18.09.2024	1,8	0,8	n.d.	0,25	0,25	0,1	10%	3,8	24	24
25.09.2024	1,4	0,8	n.d.	0,25	0,25	0,1	20%	3,8	24	24
02.10.2024	1,4	0,8	n.d.	0,25	0,25	0,1	20%	3,8	24	24
09.10.2024	1,7	0,6	n.d.	0,25	0,25	0,1	30%	5,0	24	24
16.10.2024	1,5	0,8	n.d.	0,25	0,25	0,1	30%	3,8	24	24
30.10.2024	1,4	0,7	n.d.	0,25	0,2	0,1	100%	4,3	24	30
20.11.2024	1,2	0,7	n.d.	0,25	0,2	0,1	55%	4,3	24	30
27.11.2024	1,2	0,7	n.d.	0,25	0,2	0,1	55%	4,3	24	30
04.12.2024	1,2	0,7	n.d.	0,25	0,2	0,1	55%	4,3	24	30
12.12.2024	1,3	0,7	n.d.	0,25	0,2	0,1	100%	4,3	24	30
18.12.2025	1,2	0,7	486	0,25	0,2	0,1	100%	4,3	24	30
08.01.2025	1,2	0,7	868	0,25	0,2	0,1	100%	4,3	24	30
15.01.2025	0,6	0,6	950	0,25	0,2	0,1	100%	5,2	24	30
22.01.2025	n.d.	0,5	771	0,25	0,2	0,1	100%	6,0	24	30
03.02.2025	n.d.	0,6	800	0,25	0,2	0,1	100%	5,0	24	30

The pilot testing ran for six months, from September 2024 to February 2025. Throughout the testing period, automatic analyser data was continuously recorded. When operating without disruptions, the pilot system ran 24/7. Samples for PFAS, pharmaceuticals, and other micropollutants were collected up to four times and sent to

external laboratories for analysis. Sampling was conducted at the inlet to establish baseline concentrations, as well as after key treatment stages including ozonation and GAC filtration.

3.1. Removal of Pharmaceuticals

The Table 2 presents pharmaceutical residue concentrations measured in the influent of the pilot plant and across four different sampling dates. All analysed pharmaceuticals were found at least once from the influent except for irbesartan.

Table 2. Pharmaceutical residues found in the pilot plants influent.

Pharmaceutical residues found in the pilot plants influent (ng/L)				
Pharmaceuticals	04.12.2024	17.01.2025	24.01.2025	03.02.2025
Benzotriazole	1600	870	1300	920
4/6-methyl-1H-benzotriazole	2000	74	1000	400
Diclofenac	430	1200	1100	1700
Metoprolol	910	720	900	600
Hydrochlorothiazide	290	180	210	160
Carbamazepine	220	180	210	200
Candesartan	180	82	96	120
Venlafaxine	180	89	100	120
Clarithromycin	n.d.	18	n.d.	47
Citalopram (+escitalopram)	45	28	29	34
Amisulpride	n.d.	31	17	n.d.
Irbesartan	n.d.	n.d.	n.d.	n.d.

The Figure 6 compares the average removal performance of three treatment methods, ozonation combined with granular activated carbon (O_3 + GAC), granular activated carbon alone (GAC), and powdered activated carbon (sPAC). The data show that the O_3 + GAC configuration consistently achieved the highest removal efficiencies across most compounds, particularly for more persistent substances like diclofenac and citalopram. While GAC alone also demonstrated solid performance, its effectiveness was generally lower than the combined treatment. PAC, although simpler to implement, showed more variable results and was less effective for certain compounds.

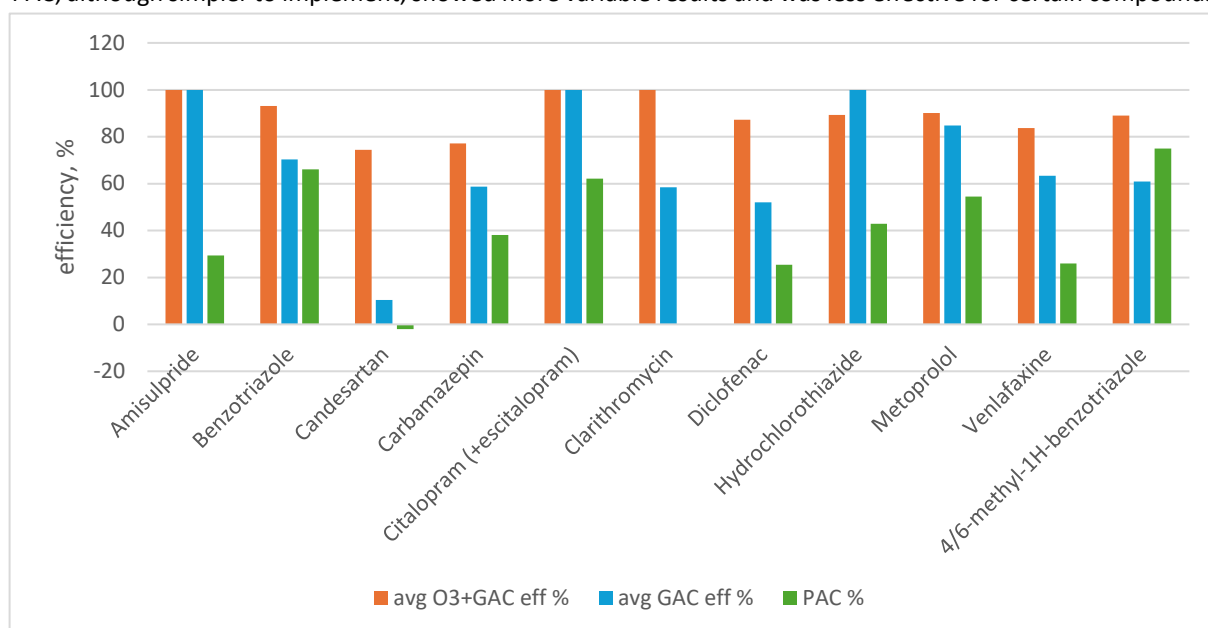


Figure 6. Removal efficiency of pharmaceutical residues from the pilot plant

The high concentration results may also be because sPAC was in operation for only one week and was grab sampled once.

Figure 7 presents the concentrations of twelve pharmaceuticals measured on the 4th of December 2024 at three points in the pilot plant: the inlet, the effluent from the GAC A + O₃ treatment, and the effluent from a separate GAC B. In the influent, benzotriazole and 4/6-methyl-1H-benzotriazole exhibit the highest loads, with diclofenac and metoprolol also present. At the GAC A + O₃ effluent spot, concentrations of nearly all compounds plunge to below detection limits. The parallel GAC B effluent treated without prior ozonation also shows decreases relative to influent but retains higher residuals of persistent substances such as diclofenac.

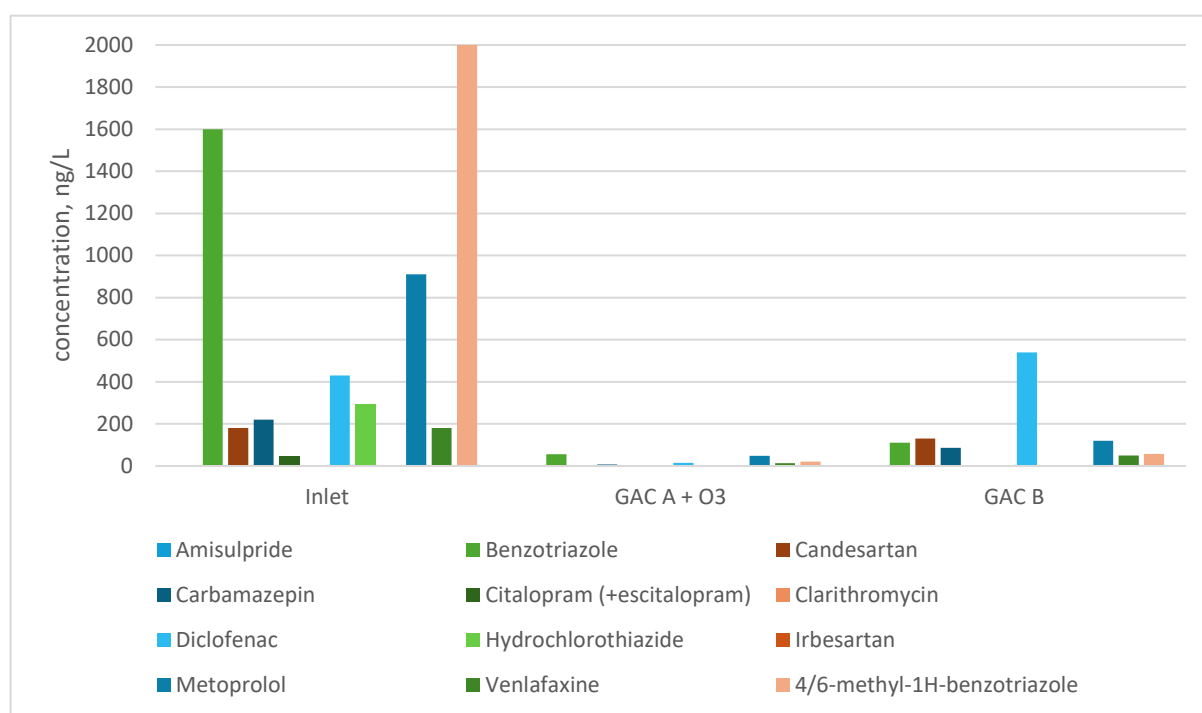


Figure 7. Pharmaceutical Removal Across Treatment Stages on December 4th, 2024

Figure 8 compares pharmaceutical concentrations on the 17th of January 2025 at three points in the pilot plant: the pilot inlet, the effluent from the GAC A + O₃ treatment, and the effluent from a separate GAC B. In the influent, diclofenac, benzotriazole and metoprolol register the highest loads. The combined ozonation and GAC A stage, concentrations of nearly all compounds fall to below detection. The GAC B effluent operated without prior ozonation also shows significant reductions relative to the influent but retains higher residuals of more persistent molecules such as diclofenac.

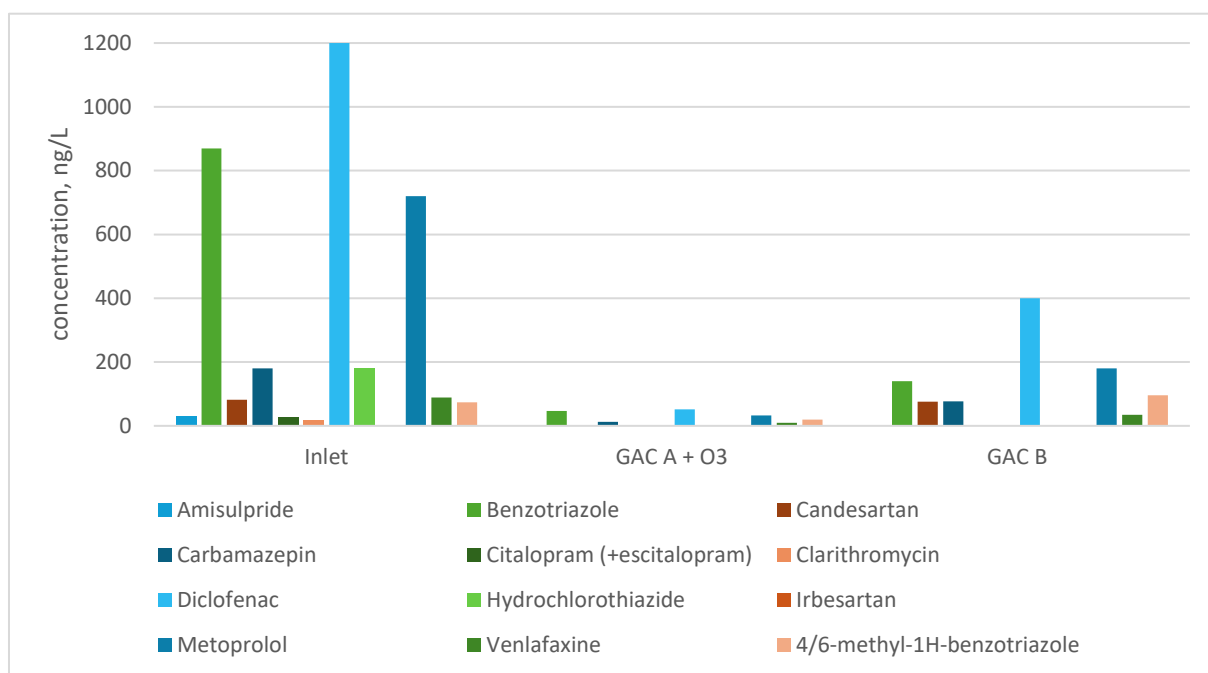


Figure 8. Pharmaceutical Removal Across Treatment Stages on January 17th, 2025

Figure 9 compares the loads of pharmaceuticals measured on the 24th of January 2025 across five different sampling points: the pilot inlet before powdered activated carbon, the sPAC drum filter effluent, the ozonation effluent, the combined GAC A + O₃, and the separate GAC B. At the inlet, diclofenac, metoprolol, benzotriazole and 4/6-methyl-1H-benzotriazole dominate the pharmaceutical burden. Following sPAC, all compounds drop markedly, though diclofenac remain detectable at high levels. Ozonation further reduces concentrations especially for oxidation-sensitive molecules like diclofenac bringing most substances down to low hundreds of units. GAC B effluent stream exhibits the lowest residual concentrations for nearly every compound outperforming the O₃ + GAC A configuration.

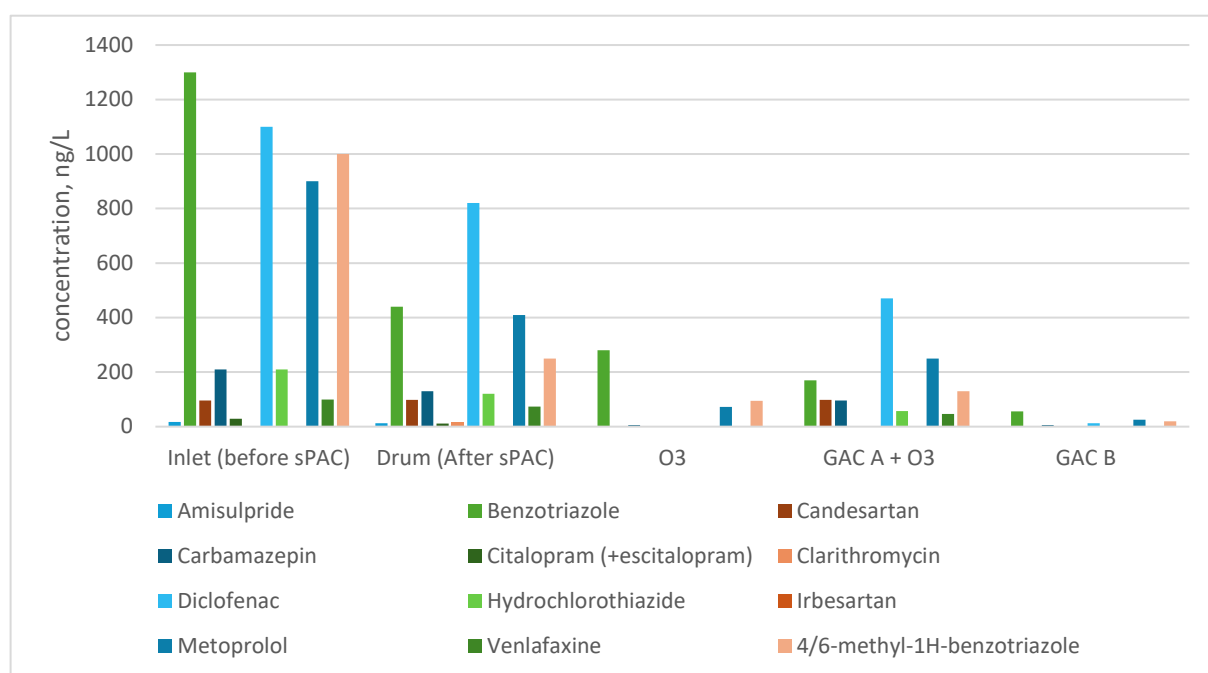


Figure 9. Pharmaceutical Removal Across Treatment Stages on January 24th, 2025

Figure 10 shows pharmaceutical concentrations on the 3rd of February 2025 at three independent sampling points: the pilot inlet, the effluent from the GAC A + O₃ treatment, and the effluent from a separate GAC B. Both treatment steps achieve substantial reductions across all pharmaceuticals, with most residues falling below 100 ng/L. The combined ozonation and GAC A stage, concentrations of nearly all compounds fall to below detection limits except benzotriazole with the value of 49 ng/L. The GAC B effluent also shows significant reductions relative to the influent but retains higher residuals of more persistent molecules. For example, diclofenac stays at the value of 540 ng/L.

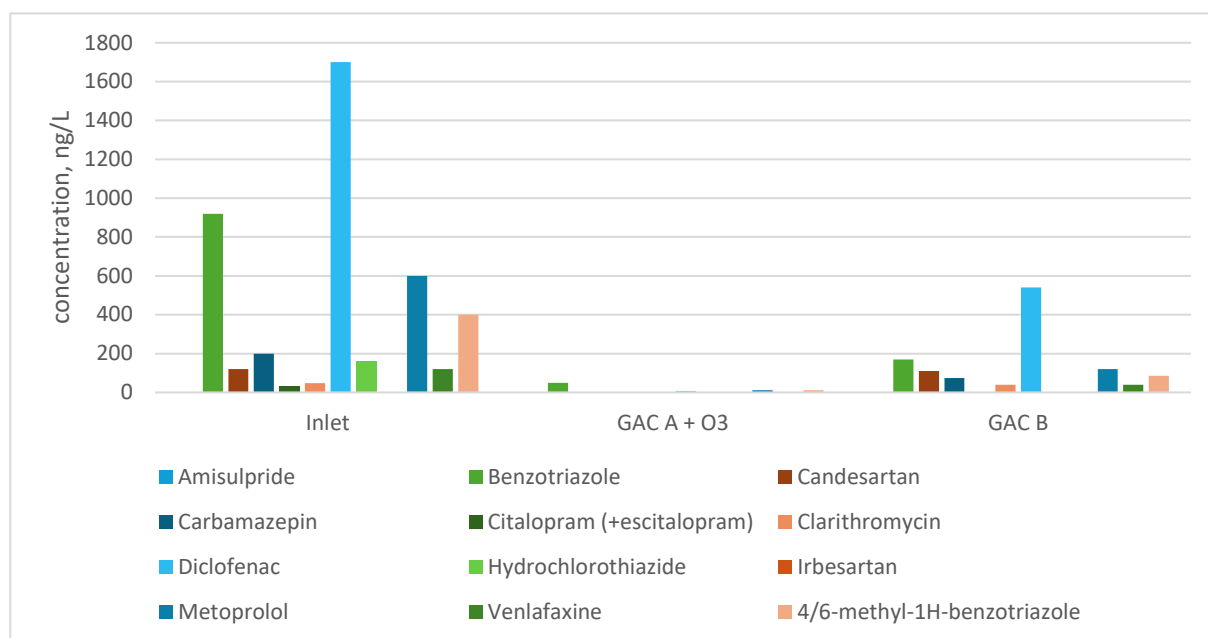


Figure 10. Pharmaceutical Removal Across Treatment Stages on February 3rd, 2025

3.2. Removal of PFAS

The results for PFAS show that removal efficiencies varied significantly depending on both the compound and the treatment method (Figure 11). In general, the O₃ + GAC combination achieved the highest removal rates for most PFAS substances, while ozonation alone showed limited effectiveness. PAC and GAC treatments demonstrated moderate removal, with some compounds showing minimal or even negative removal percentages, indicating potential desorption or analytical variability.

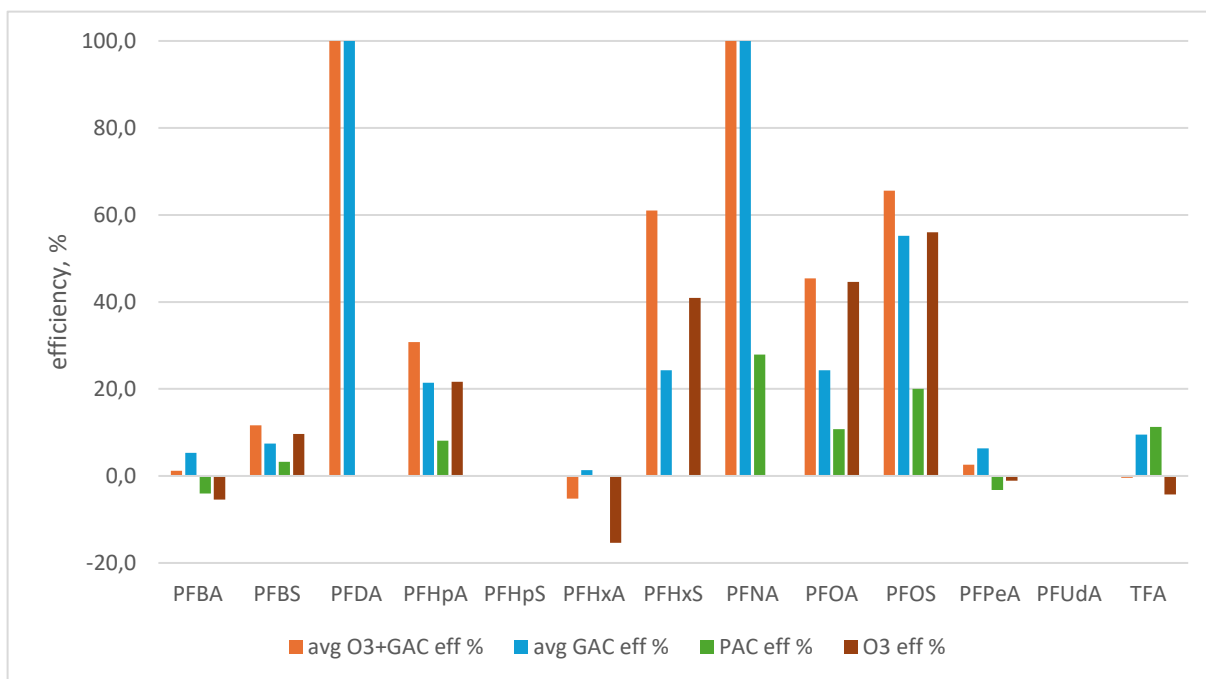


Figure 11. Removal efficiency of PFAS from the pilot plant

PFAS concentrations were measured on the 4th of December 2024 at three independent points (Figure 12): the pilot inlet, the effluent from the combined O₃ + GAC A, and the effluent from the standalone GAC B. At the inlet, PFBS dominates at 17 ng/L. Following ozonation and GAC A, most of PFAS levels drop with PFBS falling to 15 ng/L. After ozonation PFAS compounds like PFHxA and PFPeA levels rise from 8,8 ng/L to 9,3 ng/L and 7,2 ng/L to 7,4 ng/L. The same trend follows for GAC B. PFBS lowers to 15 ng/L and PFHxA levels rise from 8,8 ng/L to 9,9 ng/L.

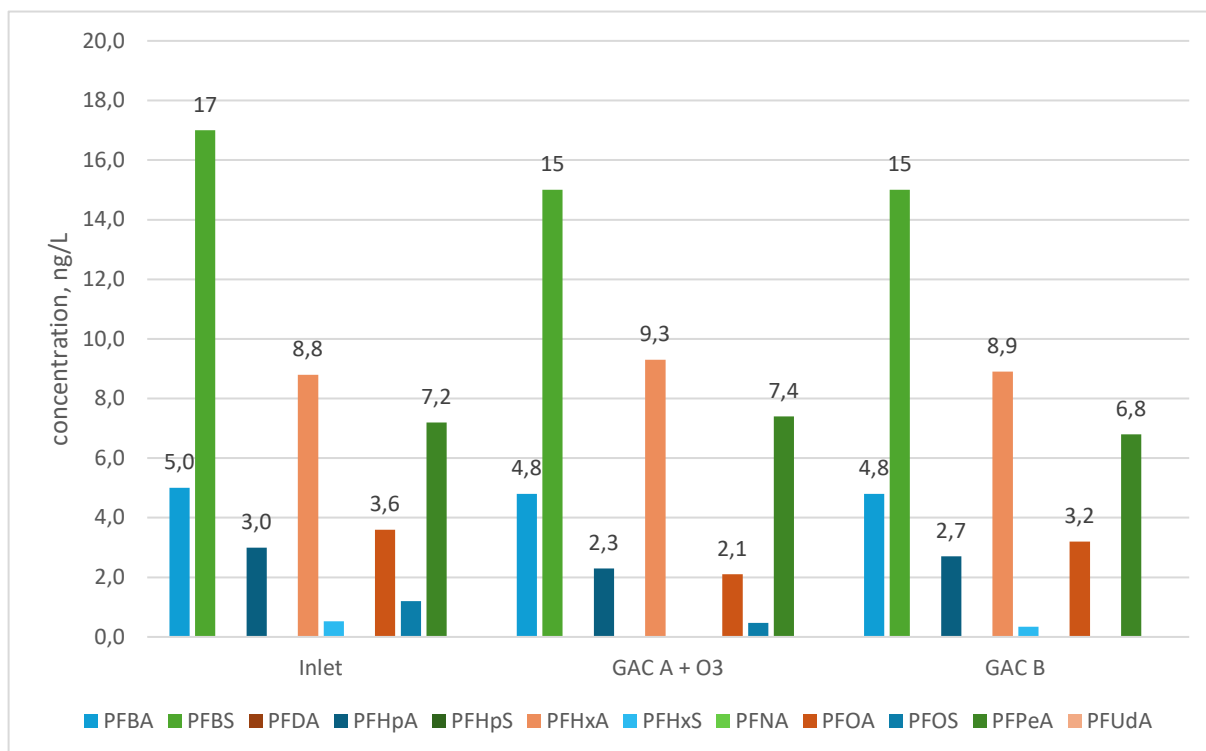


Figure 12. PFAS Removal Across Treatment Stages on December 4th, 2024

Figure 13 from January 17th, 2025, reveals that the combined ozonation and GAC A train outperformed the standalone GAC B treatment. For PFBS, the inlet level of 26 ng/L fell to 22 ng/L after ozonation + GAC A with an 15 % removal, whereas GAC B alone achieved only an 8 % reduction, ending at 24 ng/L. This trend holds for every PFAS compound analysed.

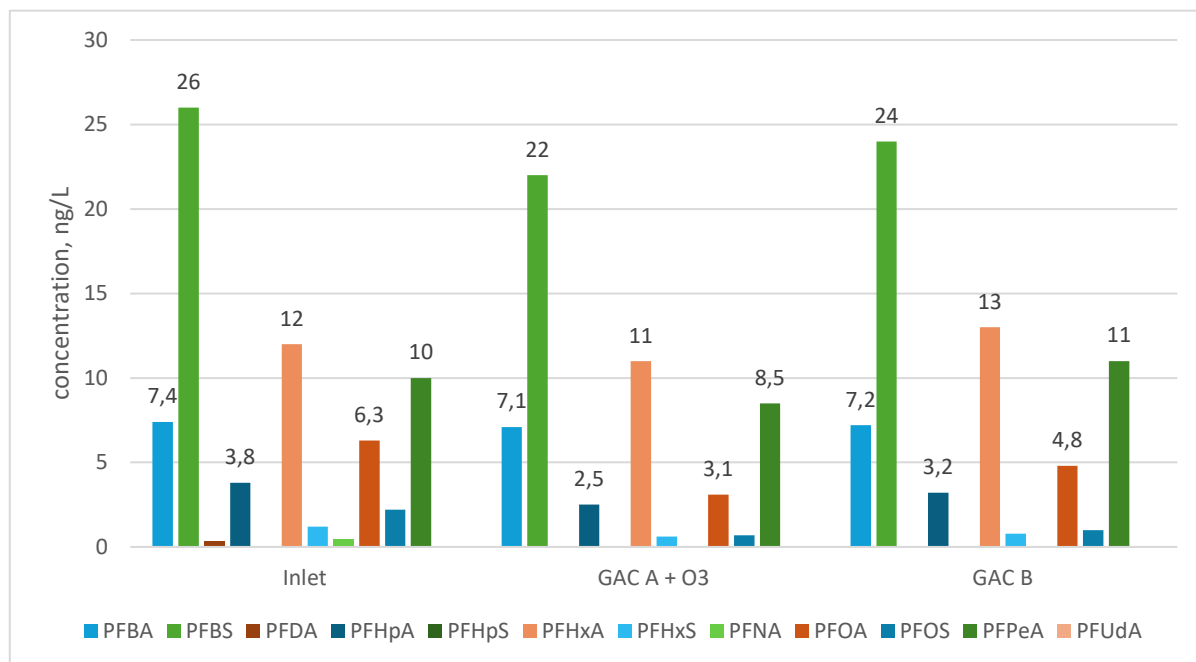


Figure 13. PFAS Removal Across Treatment Stages on January 17th, 2025

The Figure 14 profile from the 24th of January 2025 tracks concentrations across six stages: the pilot inlet, sPAC, ozonation only, combined O₃ + GAC A and standalone GAC B. At the inlet, PFBS again dominates at around 31 ng/L. After sPAC, PFBS lowers to 30 ng/L. Subsequent ozonation further reduced PFBS to 28 ng/L, and standalone granular activated carbon GAC B achieved an additional drop to 26 ng/L. The greatest removal occurred when ozonation was followed by granular activated carbon (O₃ + GAC A), yielding a final PFBS concentration of 25 ng/L.

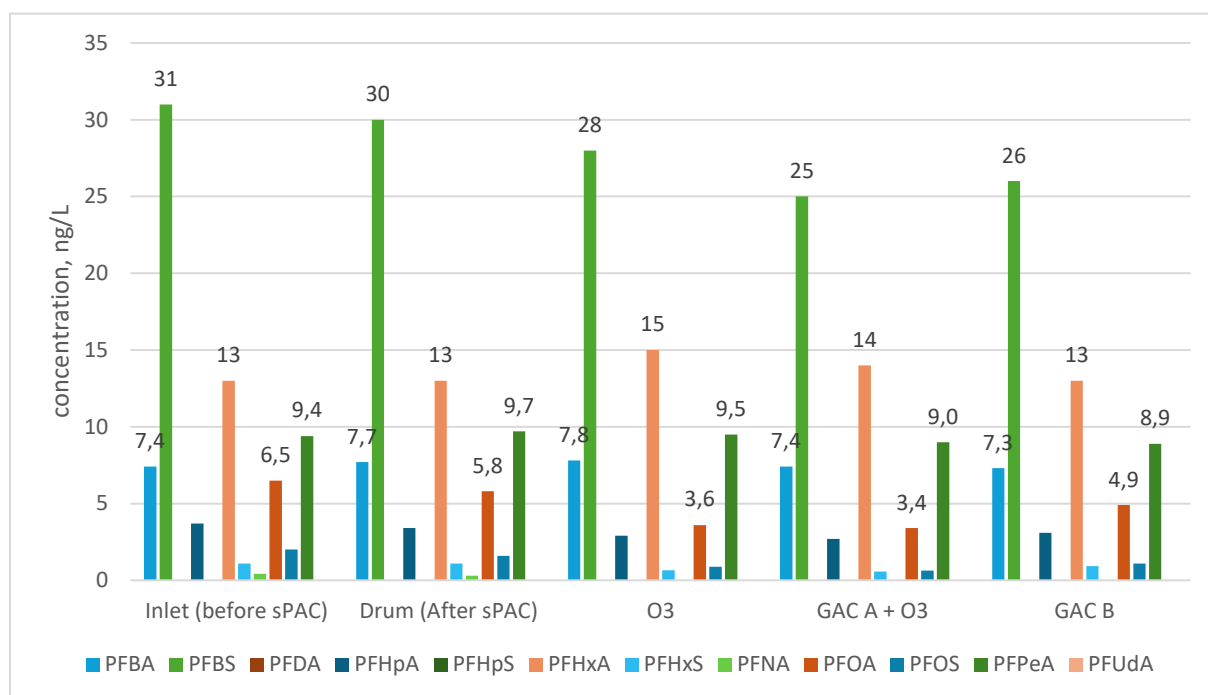


Figure 14. PFAS Removal Across Treatment Stages on January 24th, 2025

Figure 15 shows PFAS concentrations measured on the 3rd of February 2025 at three independent points: the pilot inlet, the effluent from the combined O₃ + GAC A, and the effluent from the standalone GAC B. At the inlet, most notably PFBS dominated with the concentration at 17 ng/L. After the integrated ozonation + GAC A there was no removal. In the standalone GAC B effluent, PFBS even crept up to 18 ng/L. PFHxA exhibited an unexpected profile. The inlet concentration was 9.5 ng/L, which increased to 11 ng/L following the combined ozonation and granulated activated carbon stage and then fell to 8.1 ng/L in the standalone GAC B effluent. The same trend can be said about PFPeA and PFBA treatment.

For certain compounds, such as PFHxA, concentrations may increase during specific treatment steps. While ozonation followed by granular activated carbon generally improves the removal efficiency of many targeted PFAS compounds, it can also result in elevated levels of short-chain PFASs like PFHxA. This six-carbon perfluorohexanoic acid is a known degradation product of short-chain fluorotelomer-based substances, including side-chain fluorinated polymers and fluorosurfactants. The formation of PFHxA during treatment suggests that oxidative processes may transform precursor compounds into more mobile and persistent byproducts. (Anderson et al., 2019)

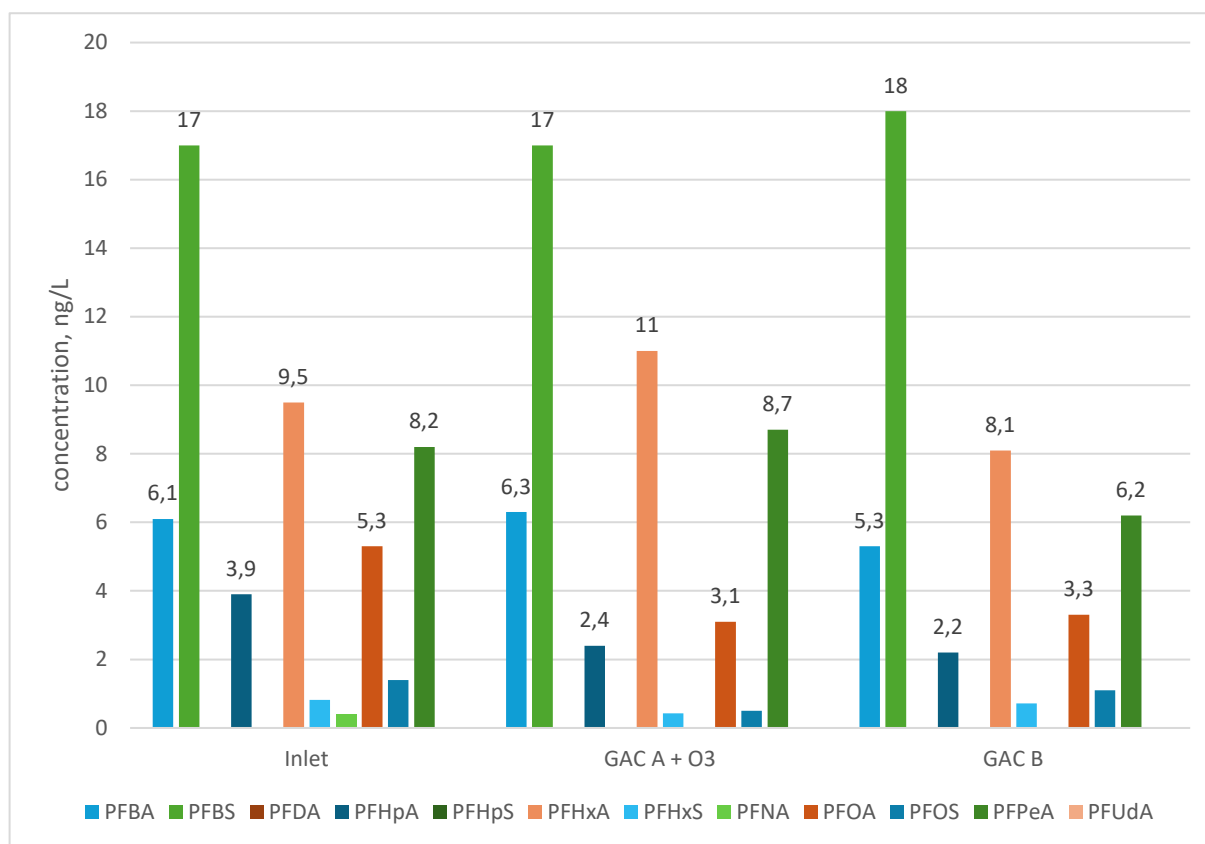


Figure 15. PFAS Removal Across Treatment Stages on February 3rd, 2025

3.2.1. Removal of TFA

In the Figure 16, inlet concentrations remain stable at roughly 700–710 ng/L across January 17th, January 24th, and February 3rd, 2025. After combined ozonation and GAC A treatment, TFA initially drops to 650 ng/L on the 17th of January but then climbs to 720 ng/L on the 24th of January and 760 ng/L on the 3rd of February, both exceeding the pilot's inlet levels. Standalone GAC B produces lower effluent values from the inlet to 570-680 ng/L. This indicates that ozonation not only fails to remove TFA completely but can generate additional TFA from PFAS. As previously mentioned, certain compounds such as trifluoroacetic acid can exhibit increased concentrations during specific stages of treatment. Ozonation can lead to elevated levels of short-chain PFASs like TFA, likely due to the transformation of precursor substances during oxidation.

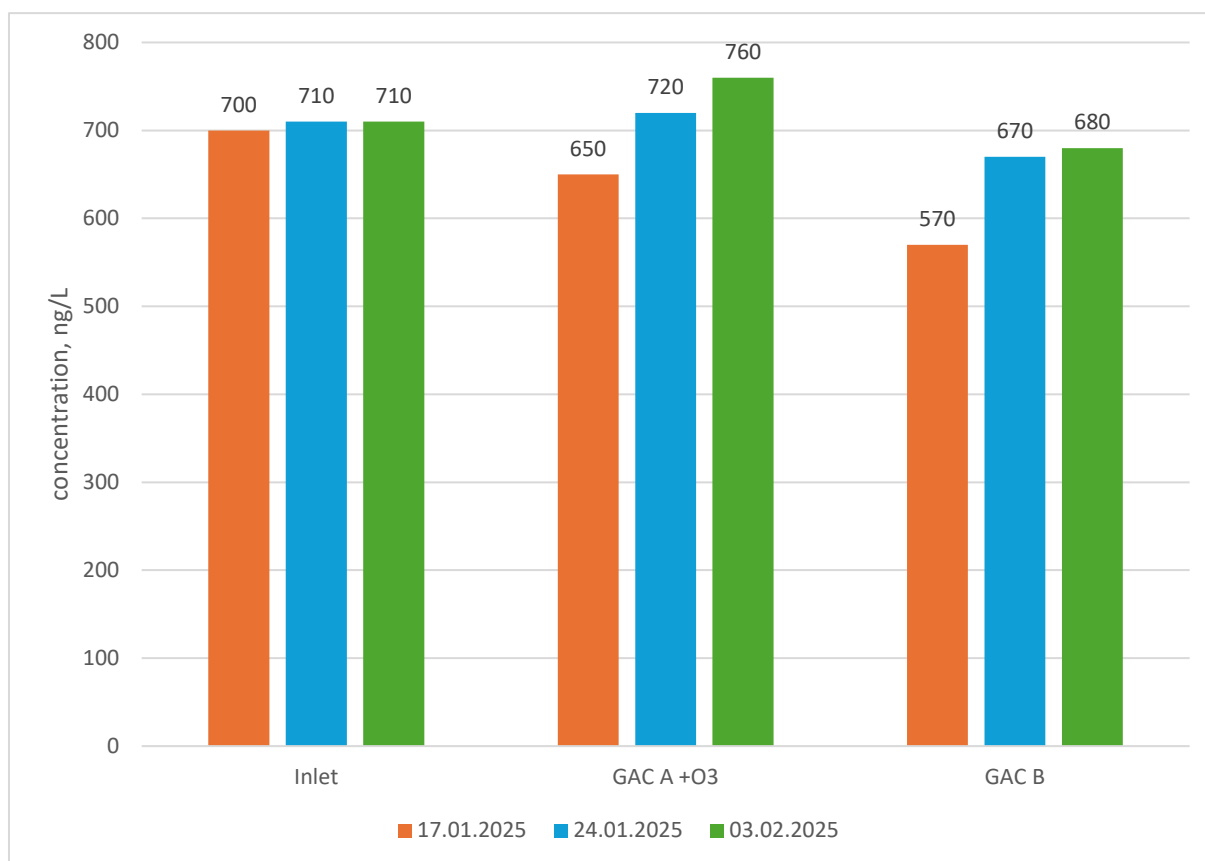


Figure 16. TFA Removal Across Treatment Stages

4. Conclusions

Tallinn Wastewater Treatment Plant conducted its pilot testing from September 2024 to February 2025 and has concluded from the piloting:

- Ozonation followed by granular activated carbon achieved the highest removal efficiencies for both category 1 and 2 pharmaceutical compounds.
- Short-chain PFAS like trifluoroacetic acid and perfluorohexanoic acid showed concentration increase after ozonation, indicating the need for treatment steps specifically targeting these acids.
- PFAS removal showed a need for longer monitoring period with increased sampling frequency and in-depth analyses to fully understand performance trends and optimize treatment strategies.
- Piloting provided site-specific evidence to guide Tallinn WWTP in implementing advanced quaternary treatment in line with the EU's updated Urban Wastewater Treatment Directive (2024/3019).

5. References

Anderson, J. K., Luz, A. L., Goodrum, P., & Durda, J. (2019). Perfluorohexanoic acid toxicity, part II: Application of human health toxicity value for risk characterization. *Regulatory Toxicology and Pharmacology*, 103, 10–20. <https://doi.org/10.1016/J.YRTPH.2019.01.020>

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