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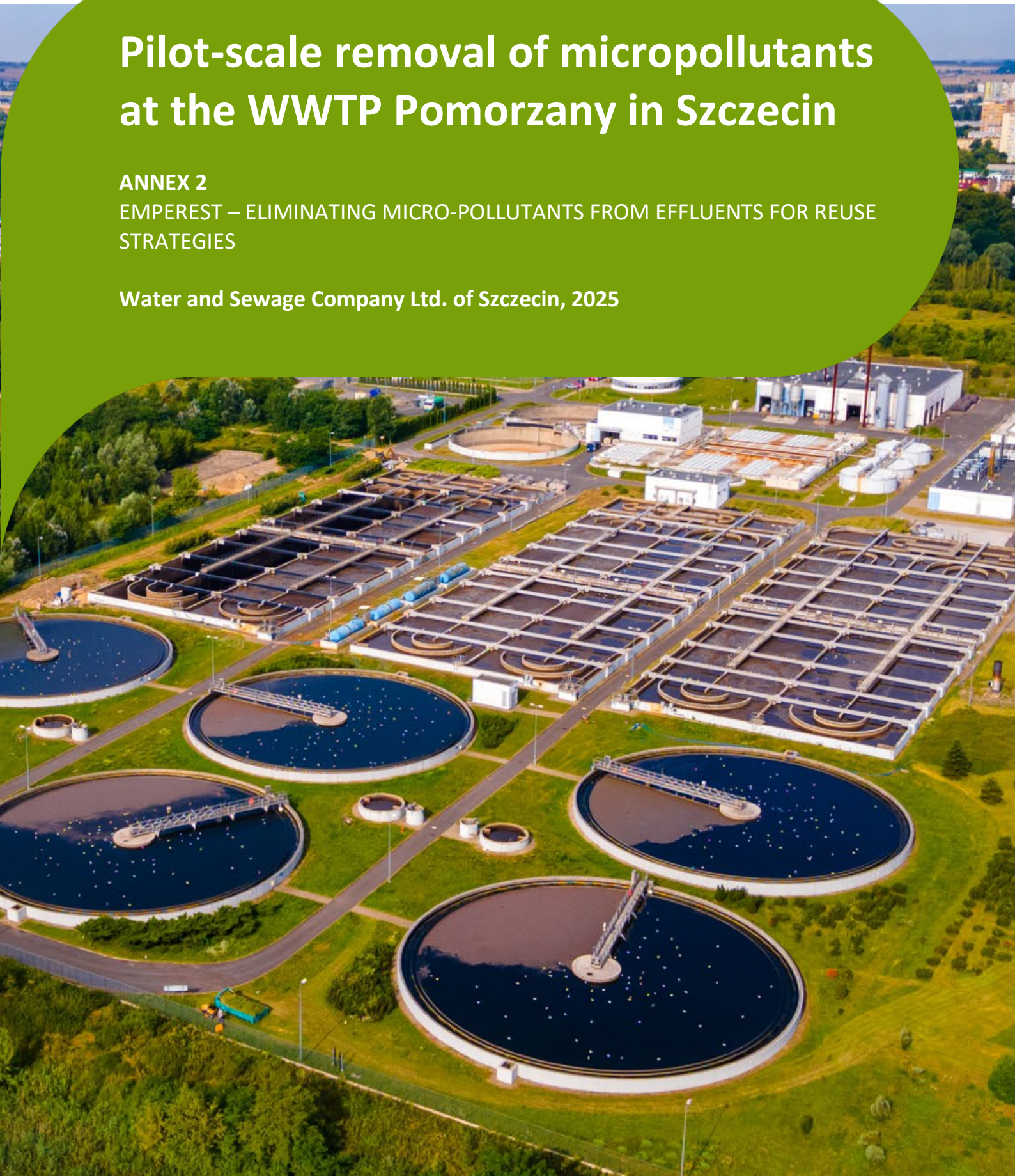
SUSTAINABLE WATERS
EMPEREST

Pilot-scale removal of micropollutants at the WWTP Pomorzany in Szczecin

ANNEX 2
EMPEREST – ELIMINATING MICRO-POLLUTANTS FROM EFFLUENTS FOR REUSE STRATEGIES

Water and Sewage Company Ltd. of Szczecin, 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 2 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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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
AOF	adsorbable organic fluorine
AOPs	advanced oxidation processes
A2/O	anaerobic/anoxic/oxic system
BOD_5	biochemical oxygen demand
COD	chemical oxygen demand
DE	Germany
DF	drum filter
DOC	dissolved organic carbon
DOM	dissolved organic matter
EBCT	empty bed contact time
EE	Estonia
EU	European Union
FI	Finland
GAC	granular activated carbon
GC-MS	gas chromatography-mass spectrometry
HDFDSA	heptadecafluorodecanesulphonic acid
HELCOM	Helsinki Commission
HFPO-DA	hexafluoropropylene oxide-dimer acid
HMI	human-Machine Interface
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
PFAS	group of per- and polyfluoroalkyl substances
PFBA	perfluorobutanoic acid
PFBS	perfluorobutane sulfonic acid
PFDA	perfluorodecanoic acid
PFDoDA	perfluorododecanoic acid
PFDS	perfluorodecane sulfonic acid
PFHpA	perfluoroheptanoic acid
PFHpS	perfluoroheptane sulfonic acid
PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexane sulfonic acid
PFMOBA	perfluoro-4-methoxybutanoic acid
PFMPA	perfluorodecanesulfonic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonic acid
PFPeA	perfluoropentanoic acid
PFPeS	perfluoropentane sulfonic acid
PFSA	perfluoroethoxyethanesulfonic acid
PFTrDA	perfluorotridecanoic acid
PFUnDA	perfluoroundecanoic acid
PL	Poland
PLC	programmable logic controller
PSA	pressure swing adsorption
SS	suspended solids
TCOD	total chemical oxygen demand
TN	total nitrogen
TOC	total organic carbon
TP	total phosphorus
TSS	total suspended solids
UV	ultraviolet
UVA	ultraviolet absorbance
UVA254	ultraviolet absorbance at 254
wt%	weight percentage
UWWTD	urban wastewater treatment directive
WWTPs	wastewater treatment plants
2PFHSA	2-(perfluorohexyl)ethane-1-sulfonic acid sodium salt
4,8-Dioxa	4,8-Dioxa-3H-perfluorononanoic acid
4-MTB	4-methyl-benzotriazole
6-MTB	6-methyl-benzotriazole

1. Introduction

Organic micropollutants (OMPs) in wastewater are an emerging environmental concern due to their widespread presence and adverse effect on human health and the environment. OMPs are defined as trace-level contaminants, typically present in very low concentrations ranging from nanograms to micrograms per litre. They originate from various industrial and human sources and pose significant ecological and health challenges due to their persistence, bioaccumulation potential, and biological activity at low concentrations.

Wastewater treatment plants (WWTPs) are considered one of the main source of OMPs in aquatic environment. Although WWTPs are designed to remove organic matter and nutrients, they are often not fully effective at eliminating micropollutants, which include pharmaceuticals, personal care products, pesticides, hormones, and microplastics. The problem of OMPs in wastewater highlights the need for improved treatment technologies, stricter regulatory measures, and better public awareness regarding the disposal of chemicals and pharmaceuticals. Improvements including advanced oxidation processes, membrane filtration, and activated carbon adsorption are being explored to mitigate this growing threat, ensuring the protection of both human health and aquatic ecosystems.

To better protect human health and the environment, in November 2024, the European Union (EU) adopted the revised Urban Wastewater Treatment Directive (UWWTD), which mandates enhanced nutrient removal and imposes stricter requirements for monitoring and eliminating micropollutants from urban wastewater. Urban WWTPs serving 150,000 population equivalents (PE) or more must implement quaternary treatment to remove a broad spectrum of micropollutants by 2045. The UWWTD also imposes additional quaternary treatment in WWTPs serving agglomerations between 10,000 and 100,000 PE in areas identified as sensitive to micropollutant pollution, unless they demonstrate the absence of environmental or public health risks through risk assessment.

This report presents the results of pilot testing on the removal of organic micropollutants using of a mobile pilot-scale plant, which enables the evaluation of the efficiency of advanced wastewater treatment processes. The pilot test aimed at assessing the potential of cloth filtration, ozone oxidation and activated carbon adsorption to reduce micropollutant emissions with wastewater, as well as determining the process parameters that ensure the highest micropollutant removal efficiency. The results obtained were used to estimate investment and operational costs of a potential full-scale quaternary treatment system for the WWTP Pomorzany in Szczecin, serving 418,000 population equivalents (PE).

2. Materials and methods

2.1. Study site

The pilot tests were conducted at the WWTP Pomorzany, which is one of the largest facilities located upon the Baltic Sea. The average influent flow rate to the plant is approx. 66,000 m^3/d and the pollutant load corresponds to 418,000 population equivalents (PE). The primary treatment line comprises screens, aerated grit chambers and primary sedimentation tanks. The secondary treatment line includes three bioreactors and six circular secondary sedimentation tanks operated in parallel. Configuration of the bioreactors is based on the Anaerobic/Anoxic/Oxic (A^2/O) system. Average concentrations of pollutants in the treated wastewater are as follows:

- Biochemical oxygen demand (BOD_5) 5.4 mg BOD_5/L
- Total chemical oxygen demand (TCOD) 28.6 mg COD/L
- Total suspended solids (TSS) 6.2 mg/L
- Total nitrogen (TN) 7.5 mg N/L
- Total phosphorus (TP) 0.7 mg P/L

2.2. Pilot plant description

The pilot tests were carried out by means of a semi-technical mobile pilot plant constructed by the Probiko-Aqua company, based on a detailed design concept developed by Gdańsk Water Utilities (Figures 1 and 2). The pilot installation consists of the following main units:

- MITA TF2 VM cloth drum filter (DF)
  - POLSTOFF "PILE" type filter cloth with a thickness of 4–5 mm
  - filtration surface 2 m^2
  - max hydraulic capacity 20 m^3/h
- ProO2 Max 795MC pressure swing adsorption (PSA) oxygen concentrator (OC)
  - max gas flow 10 l/min
  - oxygen content at 2 l/min > 93% ± 3%
  - oxygen content at 10 l/min 87 to 93%
- Ozonia CFS-1 2G compact ozone generator (OG)
  - nominal ozone concentration 10 wt%
  - nominal ozone production 55 g O_3/h
- Ozone contact tank
  - diameter 0,705 m
  - height 2,30 m
  - working volume 0,200 – 0,800 m^3
- Gravity filters – 2 units
  - diameter 0,35 m
  - surface area 0,962 m^2
  - filter nozzles vertical slots of the width 0,30 mm
- Backwash water storage tank
  - length 0,120 m
  - width 0,069 m
  - height 0,99 m
  - maximum working volume 0,750 m^3
- Probiko-Aqua Protec 1200 EW ultraviolet (UV) lamp
  - maximum flow 0,70 m^3/h
  - UV dose 400 J/m^2 at 60% UV transmittance
- Air compressor (AC)
  - Airpress oil-free compressor LMO 25-250
  - free air delivery 150 L/min
  - maximum pressure 8 bar

The treatment train is equipped with the following online measuring instruments for process monitoring:

- IFM SM9100 magnetic-inductive water flow meter – 1 unit
- IFM SM7120 magnetic-inductive water flow meter – 6 units
- IFM SA5020 air flow sensor – 1 unit
- IFM PN2098 water level sensors – 8 units
- WTW UV 700 IQ SAC UV absorbance sensors with ultrasound cleaning system – 3 units
- WTW VisoTurb 700 IQ turbidity sensors with ultrasound cleaning system – 2 units

Figure 1. View of the pilot plant during tests at the WWTP Pomorzany in Szczecin.

Figure 2. View of the pilot plant interior.

Online UV absorbance (UVA) and turbidity sensors allow to continuously monitor removal performance of suspended solids an organic compounds. Programmable logic controller (PLC) based control system and Human-Machine Interface (HMI) enable monitoring and control of the devices and processes within the pilot plant. An on-site VPN router provides secure remote access to the pilot plant over cellular networks.

The devices that constitute the treatment train can be operated in various configurations depending on the research needs. All the devices are mounted in a 20-feet high cube shipping container (Figure 1). The way the pilot plant was designed and constructed allows for easy transport and quick commissioning at any water or wastewater treatment plant. Figures 3 – 5 show a process flow diagram displayed on the touch panel HMI.

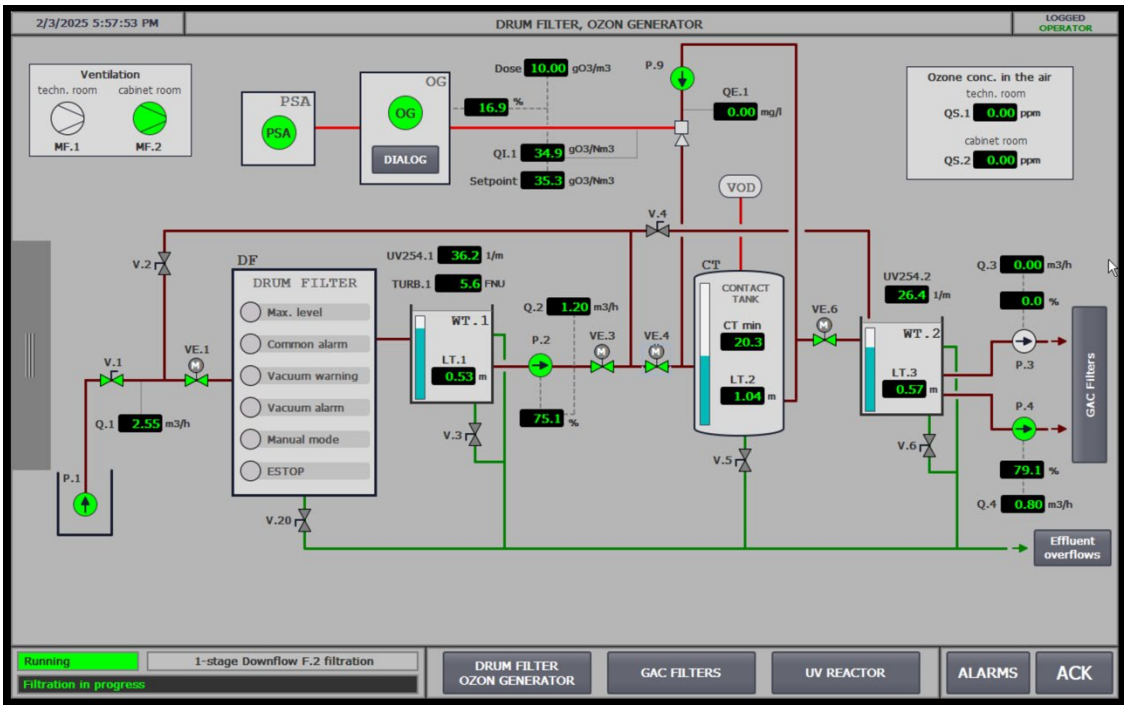

Figure 3. Flow diagram displayed on screen 1 of HMI panel. Labelling of main components of the process train: DF - cloth drum filter, PSA - oxygen concentrator, OG - ozone generator, WT – intermediate process tank, P - process pump, UVA254 – UV absorbance sensor, TURB – turbidity sensor.

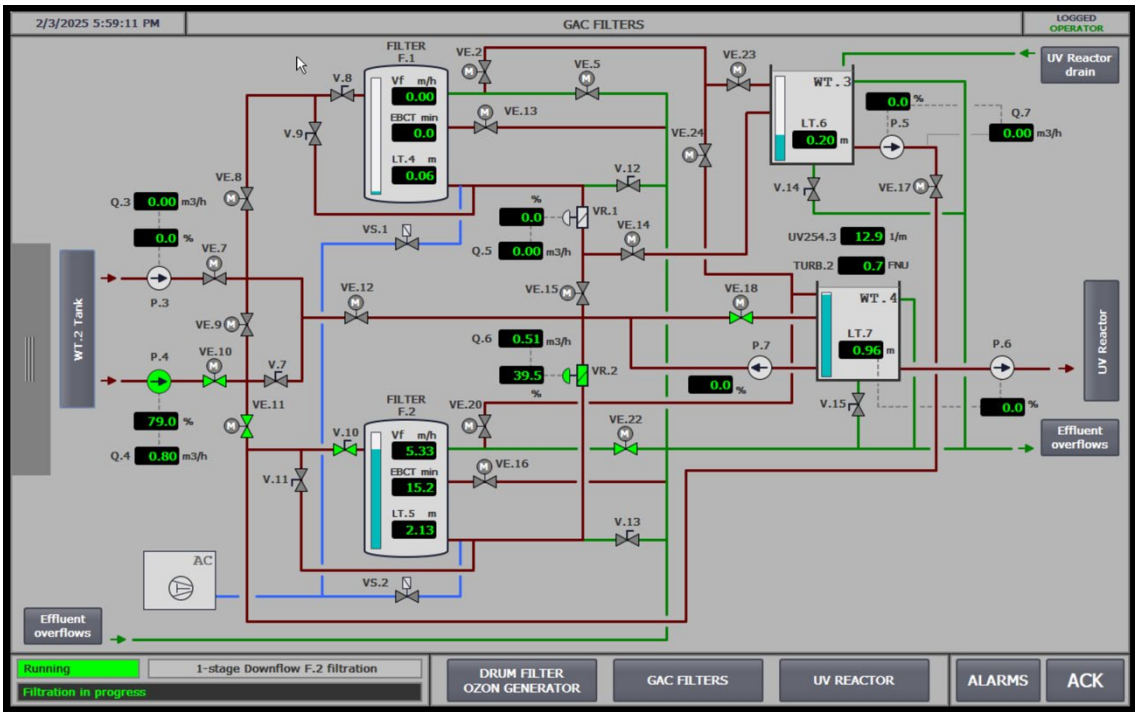

Figure 4. Flow diagram displayed on screen 2 of HMI panel. Labelling of main components of the process train: F – gravity filter, WT.3 - intermediate process tank, WT.4 – backwash water tank, P - process pump, AC - air compressor, UVA254 – UV absorbance sensor, TURB – turbidity sensor.

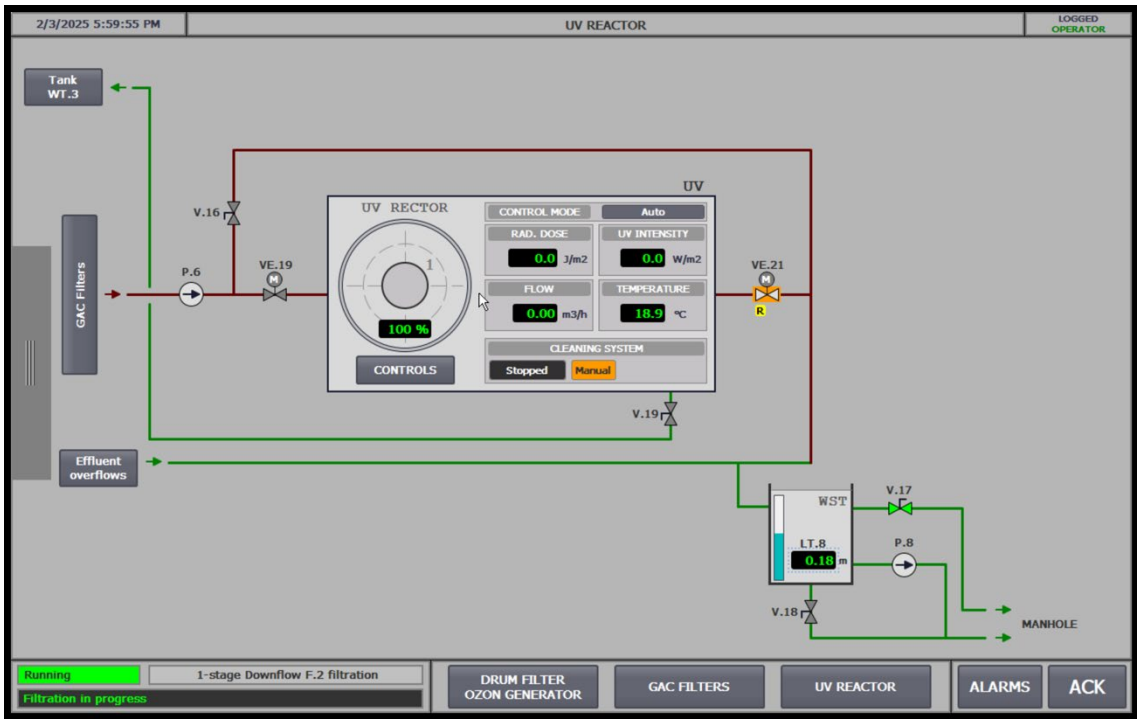

Figure 5. Flow diagram displayed on screen 3 of HMI panel. Labelling of main components of the process train: UV – ultraviolet lamp, WST - backwash and overflow tank.

2.3. Analytical methods

Performance of the examined treatment set was monitored using 24-hour composite and grab sampling, as well as online sensors. Depending on the study period, samples were collected once or twice a week. The samples were examined for wastewater quality parameters indicating the content of suspended solids and organic compounds, including OMPs of emerging concern. The measured micropollutants cover exactly those twelve specified in two groups (8+4) of the the UWWTD for which a minimum removal of 80% is required. The list of measured wastewater quality parameters is as follows:

- TCOD
- BOD5
- Dissolved organic carbon (DOC)
- UVA
- TN
- N-NH4
- N-NO3
- TP
- TSS
- pH
- Bromates
- 23 PFASs:

  perfluorobutanoic acid (PFBA), perfluorodecanesulfonic acid (PFMPA), **perfluoropentanoic acid (PFPeA), perfluorobutane sulfonic acid (PFBS),** perfluoro-4-methoxybutanoic acid (PFMOBA), perfluoroethoxyethanesulfonic acid (PFSA), **hexafluoropropylene oxide-dimer acid (HFPO-DA), perfluorohexanoic acid (PFHxA), perfluoropentane sulfonic acid (PFPeS), perfluoroheptanoic acid (PFHpA), perfluorohexane sulfonic acid (PFHxS),** 4,8-Dioxa-3H-perfluorononanoic acid (4,8-Dioxa), 2-(Perfluorohexyl)ethane-1-sulfonic Acid Sodium Salt (2PFHSA), **perfluoroheptane sulfonic acid (PFHpS), perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), perfluorononanoic acid (PFNA), perfluorodecane sulfonic acid (PFDS),** Heptadecafluorodecanesulphonic acid (HDFDSA),

perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA),

- Twelve micropollutants
  amisulpride, carbamazepine, citalopram clarithromycin, diclofenac, hydrochlorothiazide, metoprolol, venlafaxine, benzotriazole, candesartan, irbesartan, Mixture of 4-methyl-benzotriazole (4-MTB) and 6-methyl-benzotriazole (6-MTB)

TCOD, TOC, DOC, TSS, BOD5, NNH4, NNO3, TN, TP were determined according to the standard laboratory methods. Turbidity was measured according to the nephelometric principle with WTW VisoTurb 700 IQ sensors. Micropollutants were measured using a liquid chromatography-mass spectrometry (LC-MS) method. In order to measure PFASs, liquid chromatography-tandem mass spectrometry (LC-MS/MS) was employed.

3. Results

The pilot plant was fed with effluent sewage of the WWTP Pomorzany. The treatment process consisted of cloth filtration, ozone oxidation and followed by granular activated carbon (GAC). The GAC filter was filled for the first seven series of measurements with WG-12 activated carbon which is dedicated for drinking water and the remaining two series with WG-90 dedicated for the wastewater. The height of both filter beds equalled to 1,35 m.
The pilot tests were conducted over a period of 69 days, since September 27th 2025 to December 4th 2024. The study was arranged in such a way to test both types of granular activated carbons WG-12 and WG-90 as well as different setups of ozone dose, ozone contact time and GAC contact time.

3.1. Tests preparations - determining the optimal process parameters

Tests carried at WWTP Pomorzany were the second of a series in the EMPEREST program and therefore there was a knowledge of approximate parameters that were used at Wschód WWTP in Gdańsk. Moreover the initial results obtained there eventhough they were not completed yet had also been consulted. With such background a plan for tests was developed for nine sampling series. In the course of measurements and after obtaining the first results, further extra sampling series were planned and carried out. Combined plan and realised measurement sampling series is presented in Figure 6.

Activated carbon	Data		dose O3	CT O3	CT GAC
WG 12	27.09.2024	1 sample	6	20	30
	04.10.2024	2 sample	5	30	40
	11.10.2024	3 sample	6	40	20
	18.10.2024	4 sample	8	40	20
	25.10.2024	5 sample	10	40	20
	30.10.2024	6 sample	6	30	30
	08.11.2024	7 sample	8	30	20
WG 90	22.11.2024	8 sample	10	30	20
	27.11.2024	9 sample	8	30	20
	29.11.2024	extra sample	-	-	20
	04.12.2024	extra sample	3	30	20

Figure 6. Preplanned and realised setup for pilot tests at WWTP Pomorzany in Szczecin.

Flow rate to the pilot station was at 1,5 ÷ 2,0 m^3/h.

To assess the efficiency of micropollutant removal, nine series (and two additional with a reduced measurement scope) of wastewater sampling were conducted. Each series used 24-hour composite sampling for which four dedicated automated sampling stations (Figure 7) have been installed at specific points:

- Inlet to the WWTP Pomorzany (raw sewage),
- Inlet to the pilot station (treated sewage=secondary effluent=outlet from the WWTP Pomorzany),
- effluent after drum filter,
- effluent after GAC (outlet from the pilot station).

Apart from mentioned above, grab samples have been used for five series to make measurements after ozonation.

Figure 7. Two of four automated sampling stations at WWTP Pomorzany in Szczecin.

The applied process parameters are in line with the typical ranges used for full-scale quaternary treatment systems, as listed below:

- ozone dose 5 – 10 mg O_3/L or 0.5 – 1.5 mg O_3/mg DOC
- ozone contact time 5 – 30 min
- EBCT of GAC 20 – 40 min, with 20 min often used as a benchmark

Filter cycles of the cloth filter and GAC filter remained constant throughout the pilot test, and equalled to 2h and 24h respectively. Short filter cycle durations were applied to ensure they do not affect the efficiency of micropollutant removal.

Ozone dose	Ozone contact time	GAC contact time	DF filter effluent		ozone oxidation tank effluent	Granular activated carbon filter effluent	
			UV 254 absorbance	turbidity	UV 254 absorbance	UV 254 absorbance	turbidity
6	40	20	21,4	0,7	17,3	6,1	0,5
8	30	20	27,7	1,1	17,2	5,9	0,9
10	30	20	28,1	1,2	19,4	16,7	0,9

Figure 8. UV 254 absorbance and turbidity values during the course of pilot tests at WWTP Pomorzany in Szczecin.

3.2. Removal of TSS, TCOD, DOC, TP and TN

TSS in secondary effluent refer to the portion of solid particles that remain undissolved in the treated wastewater after secondary biological treatment. These solids include organic and inorganic materials such as microbial flocs, colloidal particles, and fine particulate matter that are not fully settled during secondary clarification. Suspended solids removal from secondary effluent significantly decreases ozone demand by reducing direct consumption, minimizing scavenging of hydroxyl radicals, and improving diffusion of ozone into wastewater. This leads to more effective oxidation, enhanced pollutant removal, and reduced formation of undesirable byproducts. Therefore, pre-treatment methods such as filtration are beneficial for optimizing ozonation in wastewater treatment.

As shown in Figure 9÷11, the removal of suspended solids in the cloth drum filter was effective, with a reduction ranging from 60% to 96%. Throughout the entire pilot testing period, TSS concentrations after the drum filter did not exceed 1.4 mg/L, The results confirmed the high efficiency of cloth filtration in removing suspended solids from biologically treated wastewater, thereby positively impacting the reduction of ozone demand. TSS concentration after the subsequent ozone oxidation and GAC filtration remained below 1.0 mg/L.

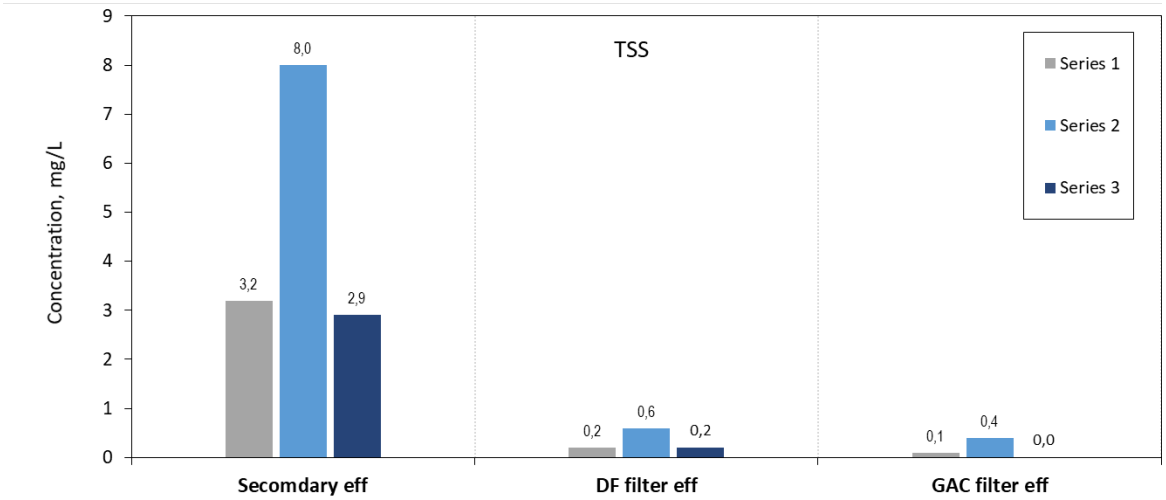

Figure 9. Concentrations of TSS at different stages of wastewater treatment. Process parameters: ozone dose of 6 mg O_3/L, 20, 40, 30 min ozone contact time (for series 1÷3 respectively) and 30, 20, 30 min EBCT of GAC (for series 1÷3 respectively). C = 24-hour composite sample.

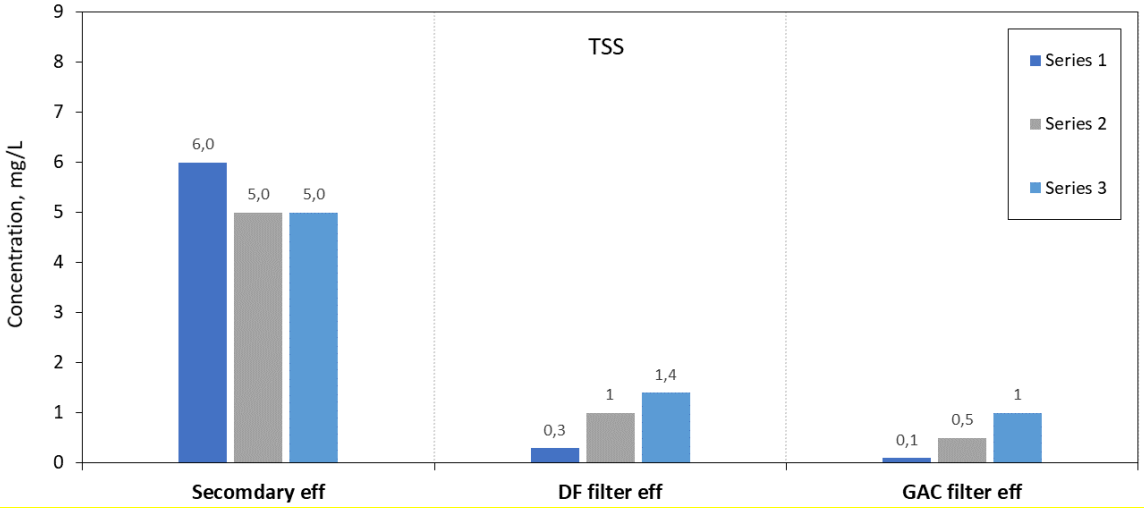

Figure 10. Concentrations of TSS at different stages of wastewater treatment. Process parameters: ozone dose of 8 mg O_3/L, 40, 40, 30 min ozone contact time (for series 1÷3 respectively) and 20 min EBCT of GAC (for series 1÷3). C = 24-hour composite sample.

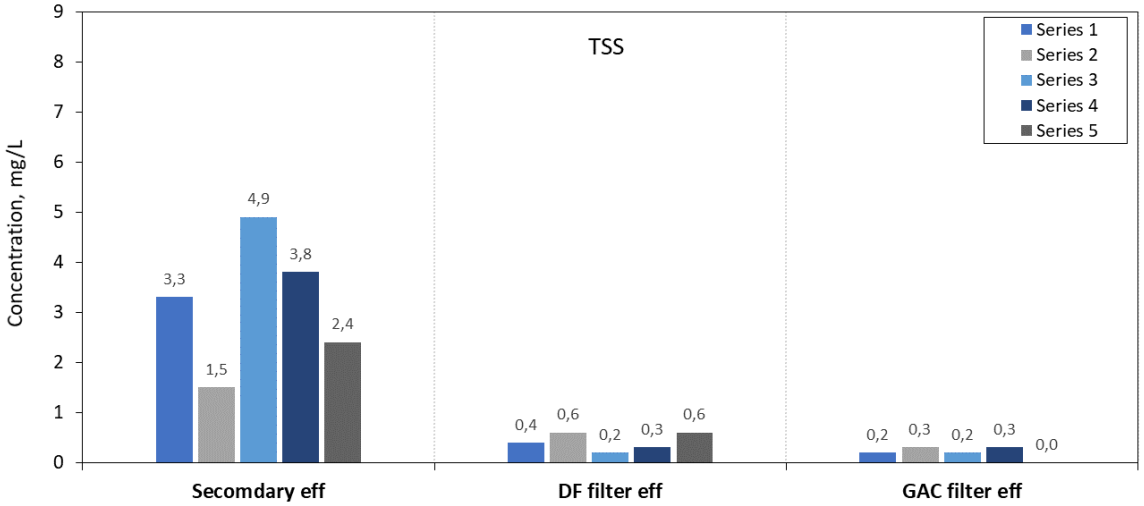

Figure 11. Concentrations of TSS at different stages of wastewater treatment. Process parameters: ozone dose of 10 mg O_3/L, 40, 40, 30, 30, 30 min ozone contact time (for series 1÷5 respectively) and 20 min EBCT of GAC (for series 1÷5). C = 24-hour composite sample.

Secondary effluent from wastewater treatment plants contains a diverse range of residual organic compounds, broadly categorized into biodegradable and non-biodegradable fractions. Biodegradable organics include substances that can still be metabolized by microorganisms, although some remain in the effluent due to limited microbial activity or insufficient retention time during treatment. In contrast, non-biodegradable organics resist biological degradation and often persist through conventional treatment processes, posing environmental risks when discharged into natural water bodies. To evaluate and manage these residuals, a range of analytical metrics is employed. TCOD is commonly used to quantify the total amount of oxidizable organic material in wastewater, encompassing both dissolved and particulate forms. TOC and DOC analyses provide detailed insights into the carbon content of organic matter, with TOC accounting for both particulate and dissolved forms, and DOC representing the dissolved fraction specifically. Since many micropollutants are present in the dissolved phase, DOC is often a key indicator for evaluating the effectiveness of removal strategies.

Accurate characterization of organic fractions in secondary effluent is critical for effective effluent management and helps protect aquatic ecosystems. Metrics such as TCOD, TOC, and DOC provide key insights into residual

organic loading and guide the selection and operation of tertiary treatment processes such as advanced oxidation, activated carbon adsorption or membrane filtration.

Ozonation and GAC filtration are two commonly used and effective methods for removing organic compounds from wastewater. GAC is a porous material with a high surface area that adsorbs organic compounds, including pharmaceuticals, as wastewater passes through the filter. Ozonation is a powerful oxidative water treatment process to degrade organic contaminants through strong oxidative reactions. However, it can be very energy-intensive and may produce byproducts that at high levels as bromates are hazardous and require further treatment. This compound has to be additionally controlled while applying ozone oxidation. Both methods have their advantages and limitations, and their performance can vary depending on the specific pharmaceutical compounds and the wastewater quality.

The combined use of ozonation and GAC filtration is a promising approach for the effective removal of TOC and DOC from secondary effluent. By leveraging the oxidative power of ozone and the adsorptive capacity of GAC, this method enhances the treatment process, ensuring higher water quality and meeting stricter environmental discharge standards.

Figures 12–17 illustrate the removal of organic compounds during the advanced treatment of secondary effluent. The combined process of cloth filtration, ozonation, and GAC filtration resulted in a moderate removal of TCOD, ranging from 60% to 95% and the removal rates of DOC varied between 64% and 90%, respectively. The formation of intermediate oxidation products during ozonation contributes to the persistence of TCOD, since many of them still react with oxidizing agents in standard TCOD tests.

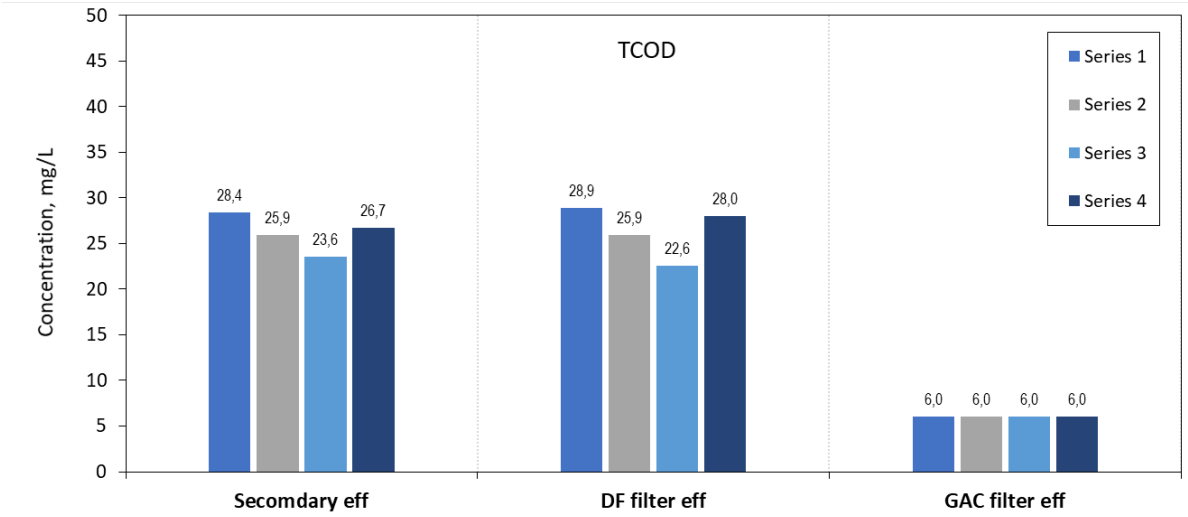

Figure 12. Concentrations of TCOD at different stages of wastewater treatment. Process parameters: ozone dose of 6 mg O_3/L, 20, 40, 40, 30 min ozone contact time (for series 1÷4 respectively) and 30, 20, 20, 20 min EBCT of GAC (for series 1÷4 respectively). C = 24-hour composite sample.

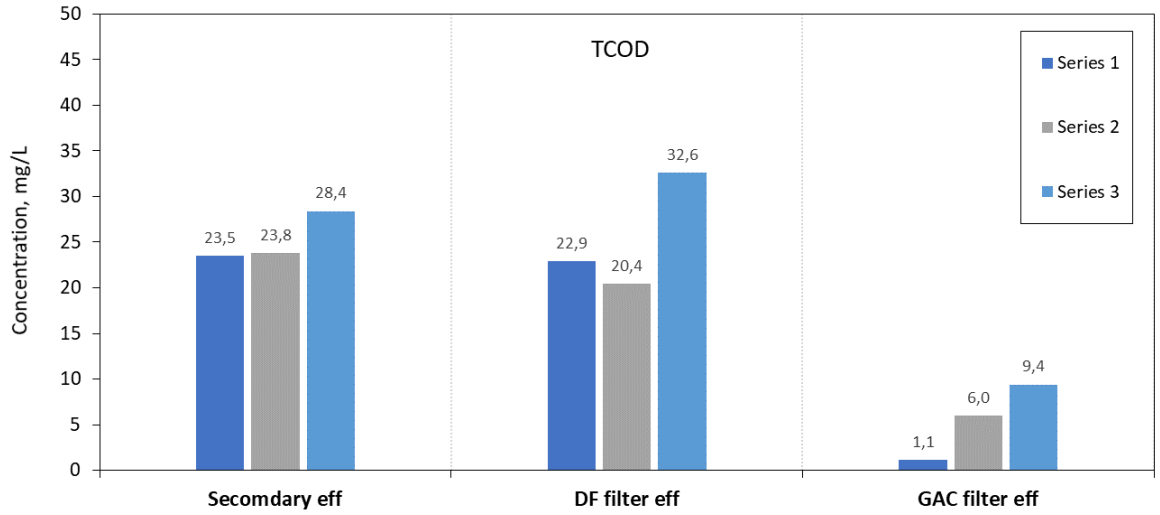

Figure 13. Concentrations of TCOD at different stages of wastewater treatment. Process parameters: ozone dose of 8 mg O_3/L, 40, 40, 30 min ozone contact time (for series 1÷3 respectively) and 20 min EBCT of GAC (for series 1÷3). C = 24-hour composite sample.

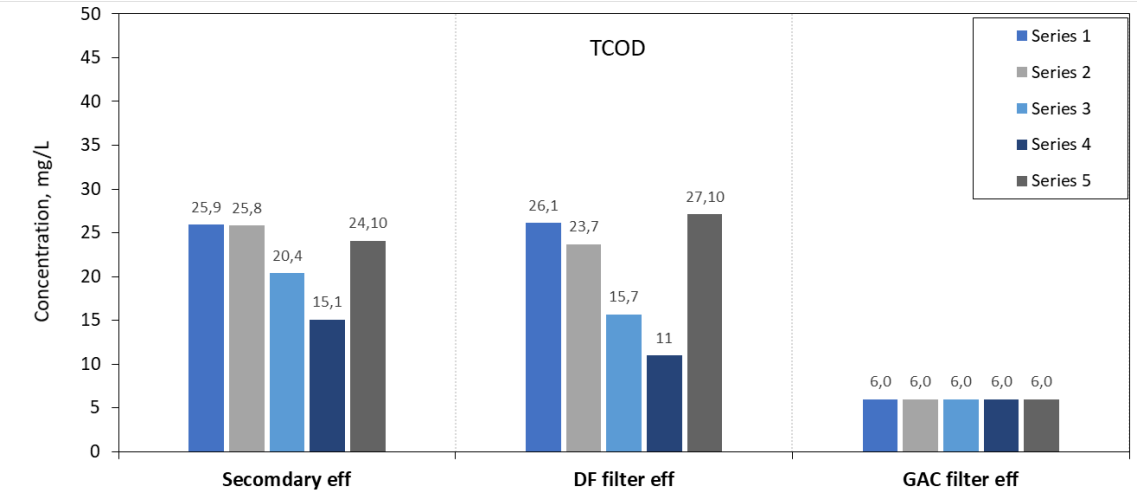

Figure 14. Concentrations of TCOD at different stages of wastewater treatment. Process parameters: ozone dose of 10 mg O_3/L, 40, 40, 30, 30, 30 min ozone contact time (for series 1÷5 respectively) and 20 min EBCT of GAC (for series 1÷5). C = 24-hour composite sample.

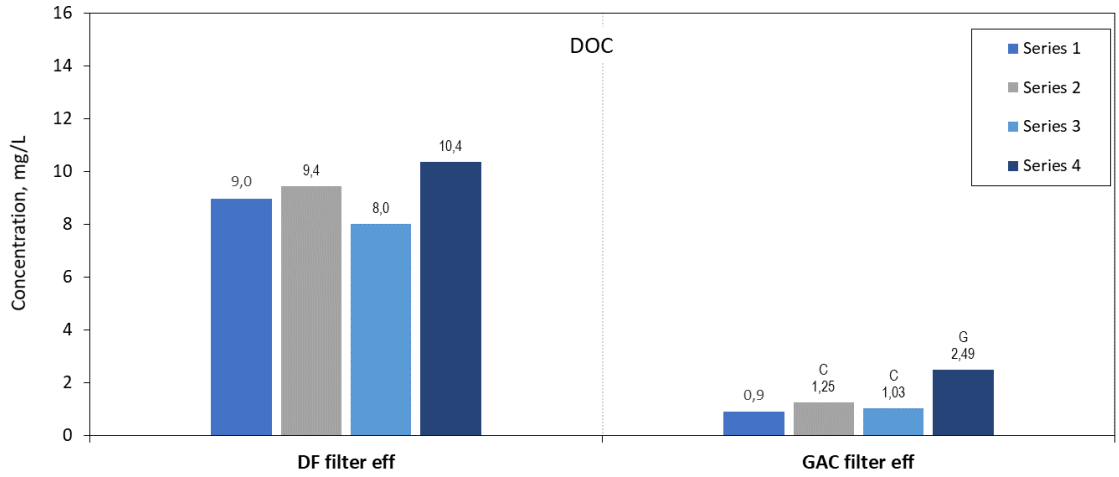

Figure 15. Concentrations of DOC at different stages of wastewater treatment. Process parameters: ozone dose of 6 mg O_3/L, 20, 40, 40, 30 min ozone contact time (for series 1÷4 respectively) and 30, 20, 20, 20 min EBCT of GAC (for series 1÷4 respectively). C = 24-hour composite sample.

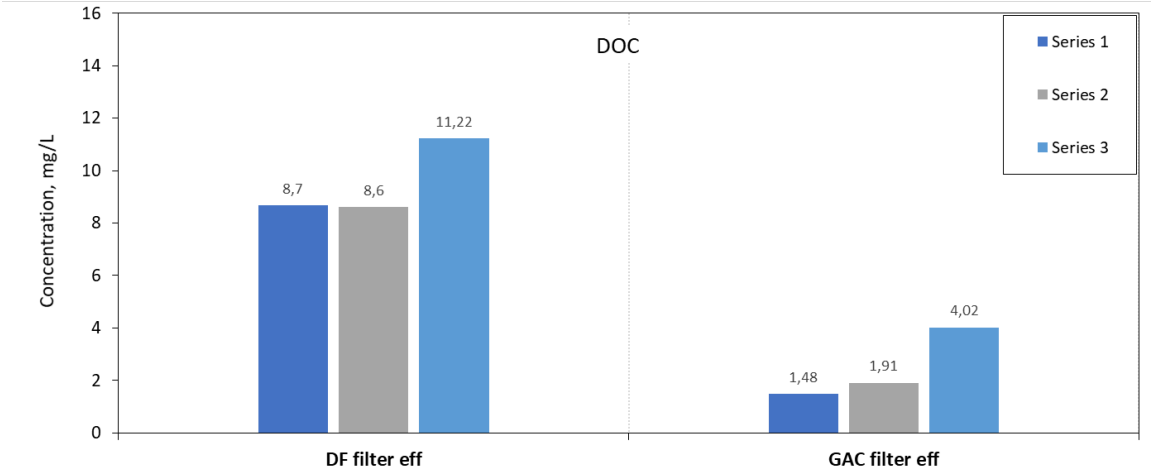

Figure 16. Concentrations of DOC at different stages of wastewater treatment. Process parameters: ozone dose of 8 mg O_3/L, 40, 40, 30 min ozone contact time (for series 1÷3 respectively) and 20 min EBCT of GAC (for series 1÷3). C = 24-hour composite sample.

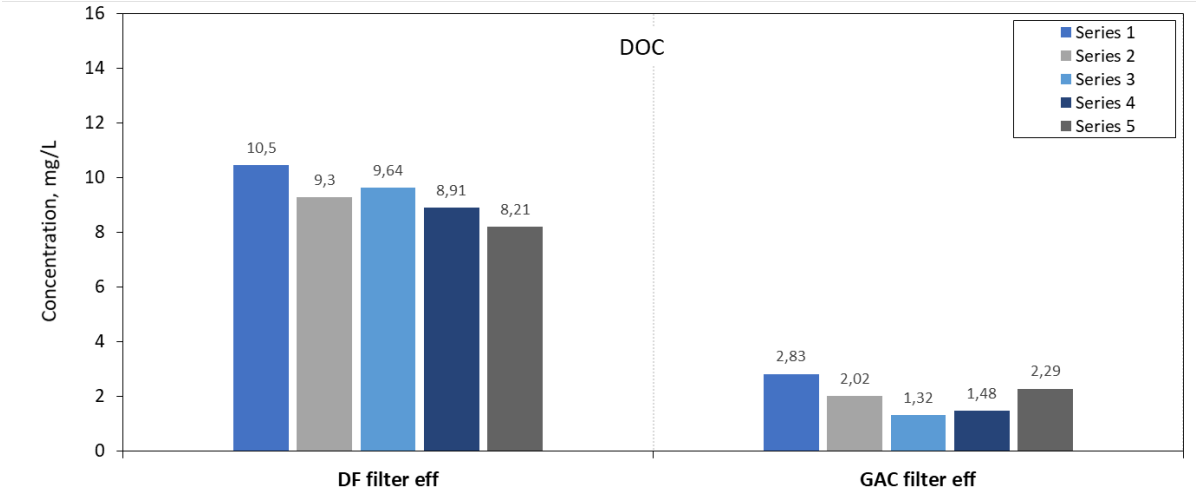

Figure 17. Concentrations of DOC at different stages of wastewater treatment. Process parameters: ozone dose of 10 mg O_3/L, 40, 40, 30, 30, 30 min ozone contact time (for series 1÷5 respectively) and 20 min EBCT of GAC (for series 1÷5). C = 24-hour composite sample.

Apart from TS, TCOD and DOC, measurements of TP and TN reduction have been carried out. Figures 18÷20 present reduction of TP at different stages of a pilot plant whereas Figures 21÷23 present those for TN. The combined process of cloth filtration, ozonation and GAC filtration resulted in a moderate removal of TP, ranging from 17% to 68% and minimum removal of TN which varied between 5% and 35%.

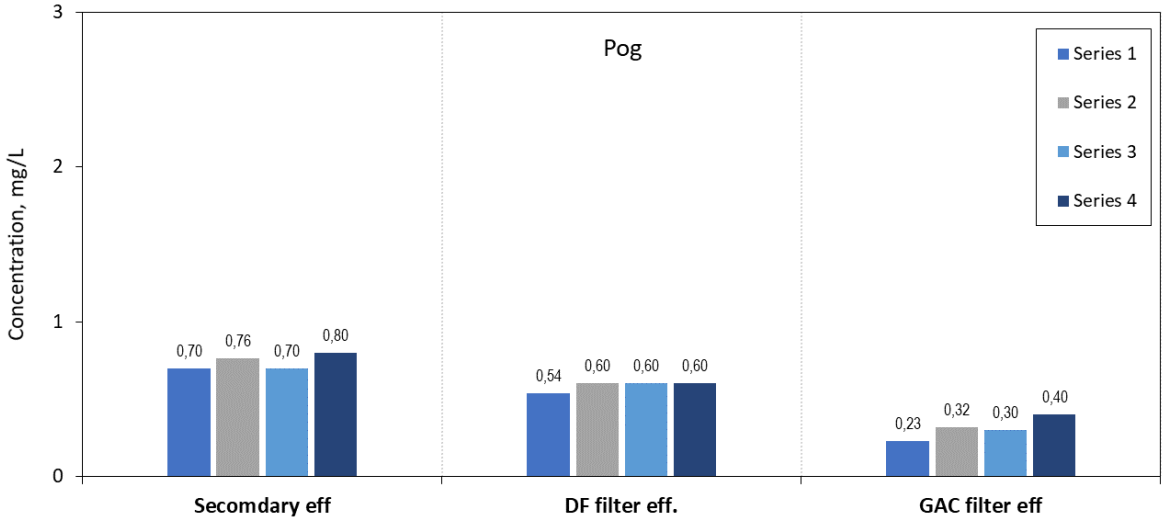

Figure 18. Concentrations of TP at different stages of wastewater treatment. Process parameters: ozone dose of 6 mg O_3/L, 20, 40, 40, 30 min ozone contact time (for series 1÷4 respectively) and 30, 20, 20, 20 min EBCT of GAC (for series 1÷4 respectively). C = 24-hour composite sample.

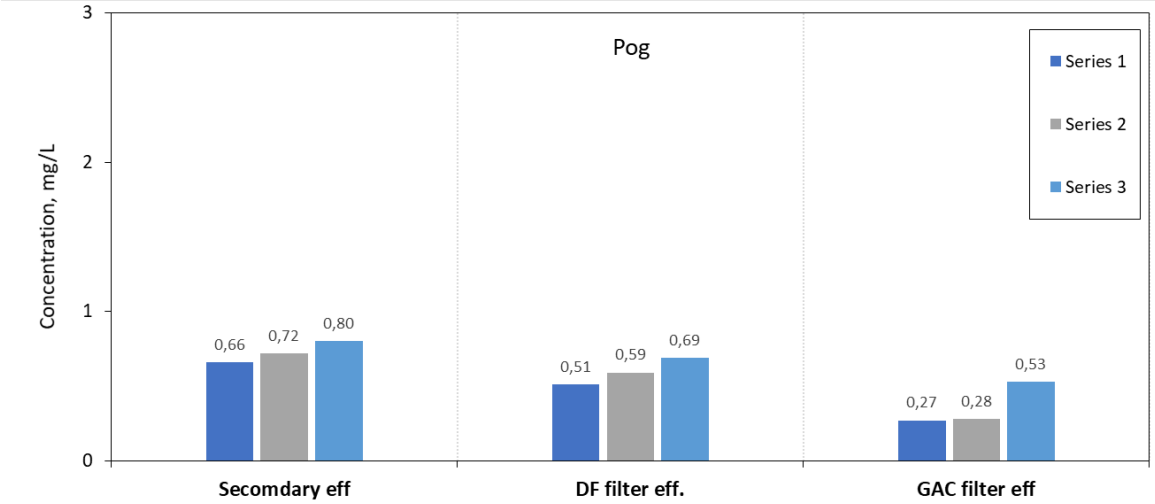

Figure 19. Concentrations of TP at different stages of wastewater treatment. Process parameters: ozone dose of 8 mg O_3/L, 40, 40, 30 min ozone contact time (for series 1÷3 respectively) and 20 min EBCT of GAC (for series 1÷3). C = 24-hour composite sample.

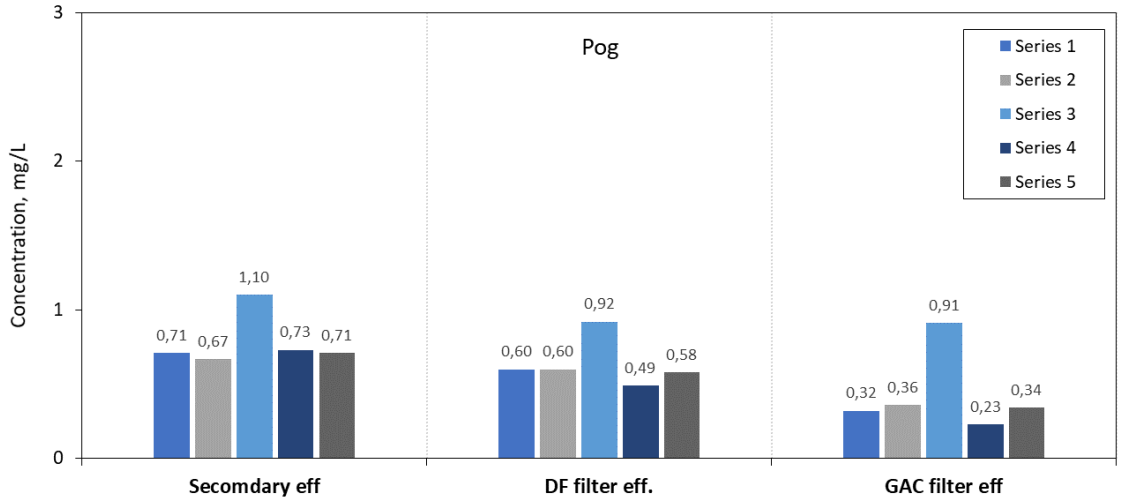

Figure 20. Concentrations of TP at different stages of wastewater treatment. Process parameters: ozone dose of 10 mg O_3/L, 40, 40, 30, 30, 30 min ozone contact time (for series 1÷5 respectively) and 20 min EBCT of GAC (for series 1÷5). C = 24-hour composite sample.

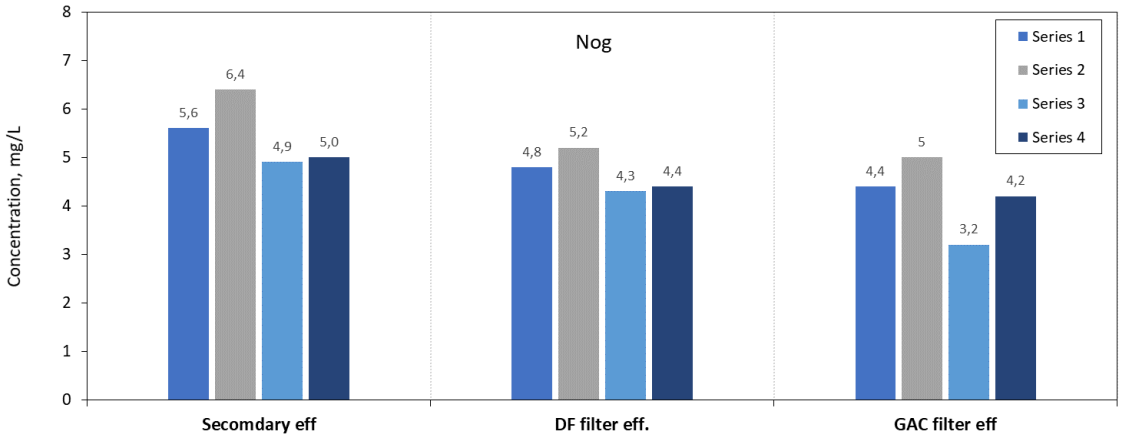

Figure 21. Concentrations of TN at different stages of wastewater treatment. Process parameters: ozone dose of 6 mg O_3/L, 20, 40, 40, 30 min ozone contact time (for series 1÷4 respectively) and 30, 20, 20, 20 min EBCT of GAC (for series 1÷4 respectively). C = 24-hour composite sample.

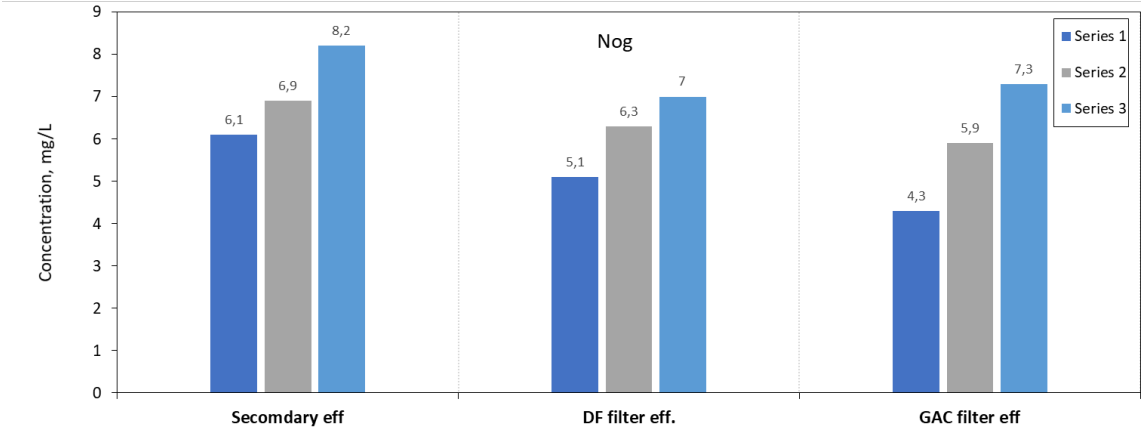

Figure 22. Concentrations of TN at different stages of wastewater treatment. Process parameters: ozone dose of 8 mg O_3/L, 40, 40, 30 min ozone contact time (for series 1÷3 respectively) and 20 min EBCT of GAC (for series 1÷3). C = 24-hour composite sample.

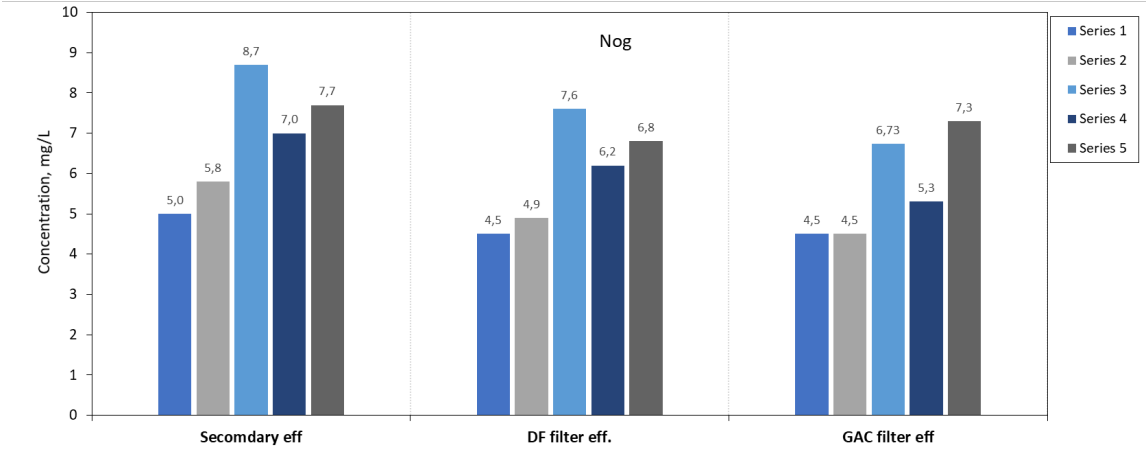

Figure 23. Concentrations of TN at different stages of wastewater treatment. Process parameters: ozone dose of 10 mg O_3/L, 40, 40, 30, 30, 30 min ozone contact time (for series 1÷5 respectively) and 20 min EBCT of GAC (for series 1÷5). C = 24-hour composite sample.

3.3. Removal of PFAS

PFAS are a vast group of synthetic fluorinated compounds with unique, complex properties. These chemicals, characterized by carbon-fluorine bonds, are highly resistant to degradation due to the strength of the carbon-

fluorine bond. Used in a wide range of industrial and consumer products, PFAS enhance resistance to stains, grease, and water. With thousands of distinct compounds, many of which are still being studied, PFAS continue to raise concerns regarding their persistence in the environment and potential health impacts.

The Urban Wastewater Treatment Directive (UWWTD) introduces key measures addressing PFAS, now recognized as emerging pollutants. It mandates comprehensive monitoring of urban wastewater for a broad spectrum of PFAS compounds, beyond a limited subset, to better assess and manage environmental and health risks.

Out of the twenty three PFAS compounds analysed, only eleven – PFBA, PFBS, PFHxA, PFHpA, PFHpS, PFOA, 2PFHSA, PFDA, PFTrDA, PFSA and PFDoDA – were detected in the wastewater samples. The removal efficiency of PFAS during combined ozonation and GAC filtration was erratic at best. There was no clear pattern for all PFAS and concentrations of individual PFAS at different stages of wastewater treatment are presented in Figures 25 – 35. Process parameters for each series is presented on Figure 24.

SERIE	dose O3	CT O3	CT GAC
1	6	20	30
2	6	40	20
3	6	30	30
4	8	40	20
5	8	30	20
6	8	30	20
7	10	40	20
8	10	30	20

Figure 24.. Process parameters for each series: ozone dose in mg O_3/L, ozone contact time in minutes, EBCT of GAC in minutes. 24-hour composite sample for each series.

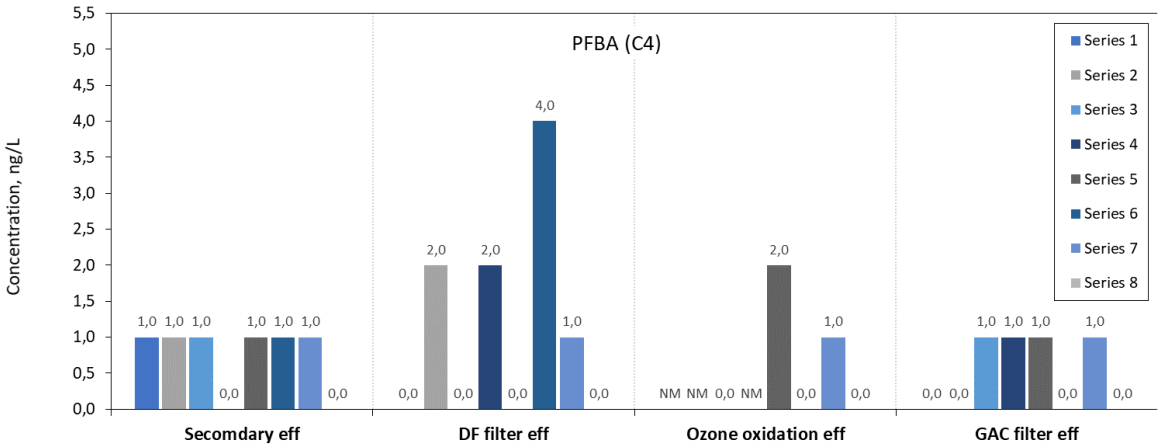

Figure 25. Concentrations of PFBA at different stages of wastewater treatment. Detection level was 1,0 ng/L

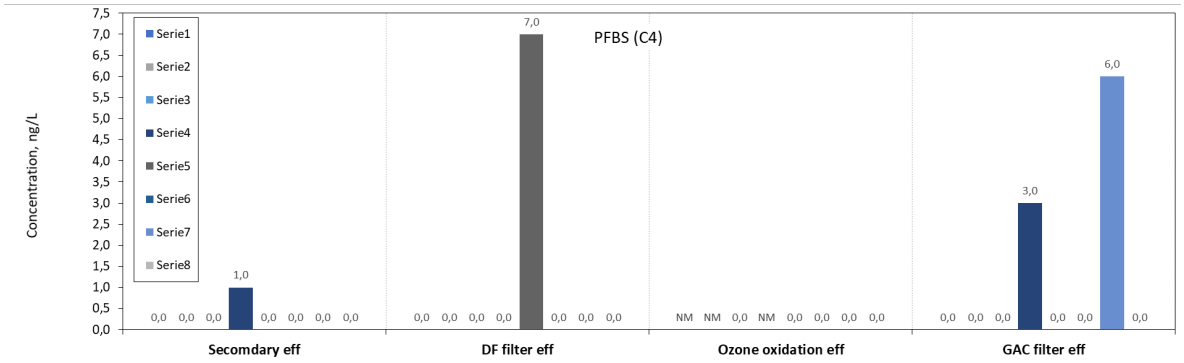

Figure 26. Concentrations of PFBS at different stages of wastewater treatment. Detection level was 1,0 ng/L

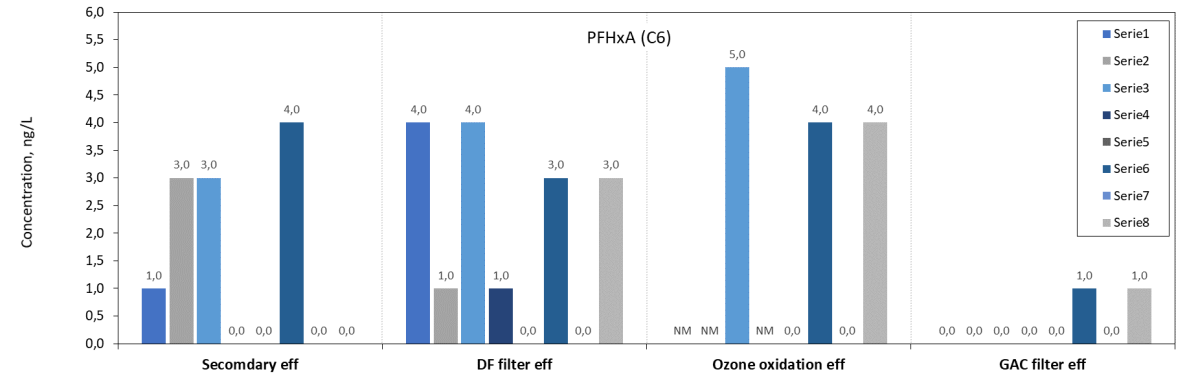

Figure 27. Concentrations of PFHxA at different stages of wastewater treatment. Detection level was 1,0 ng/L

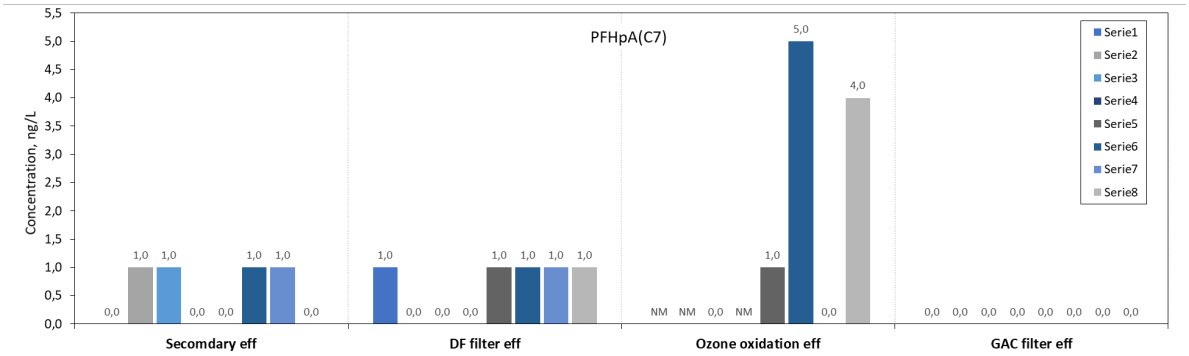

Figure 28. Concentrations of PFHpA at different stages of wastewater treatment. Detection level was 1,0 ng/L

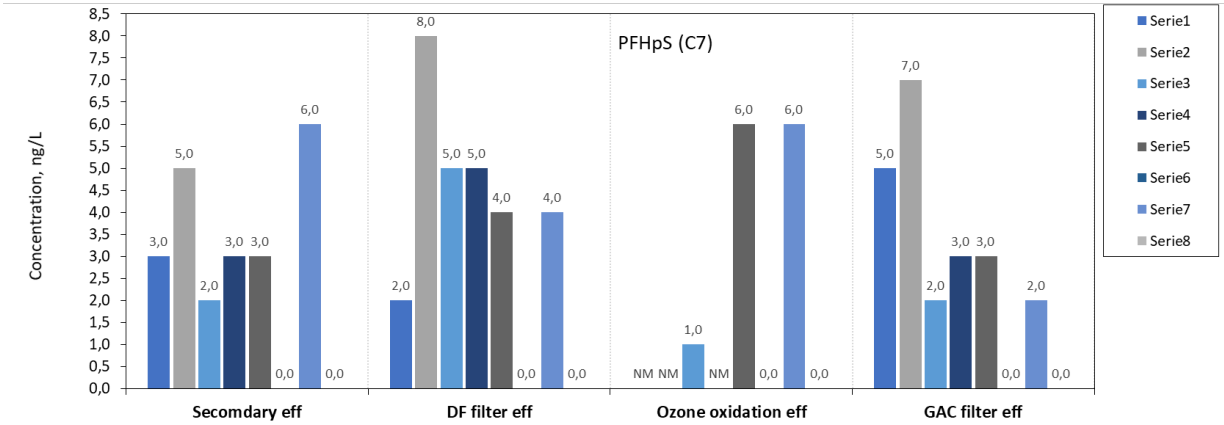

Figure 29. Concentrations of PFHpS at different stages of wastewater treatment. Detection level was 1,0 ng/L

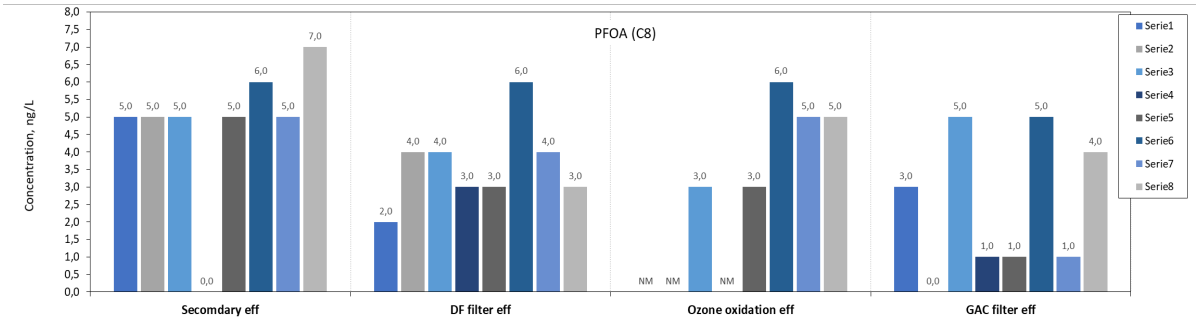

Figure 30. Concentrations of PFOA at different stages of wastewater treatment. Detection level was 1,0 ng/L

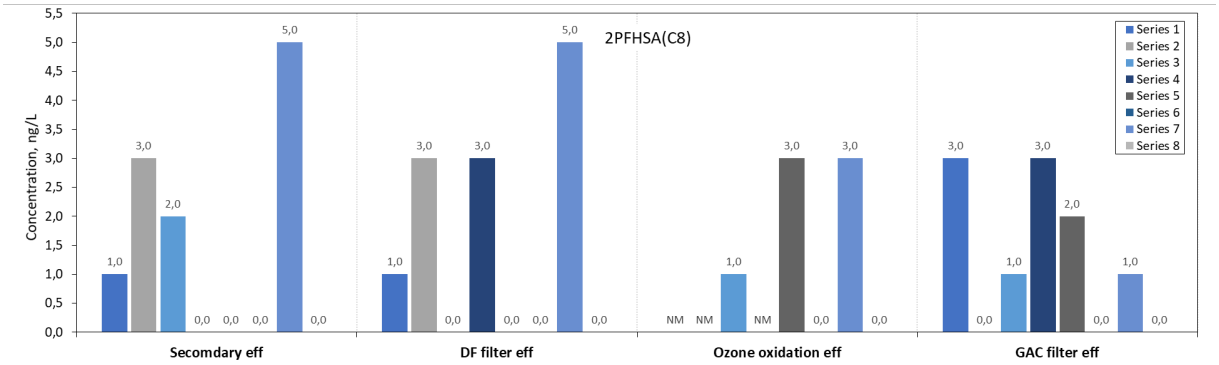

Figure 31. Concentrations of 2PFHSA at different stages of wastewater treatment. Detection level was 1,0 ng/L

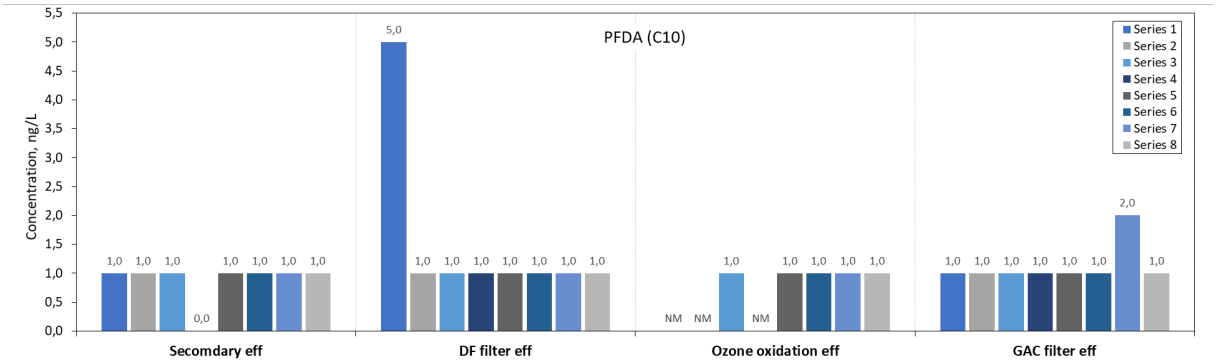

Figure 32. Concentrations of PFDA at different stages of wastewater treatment. Detection level was 1,0 ng/L

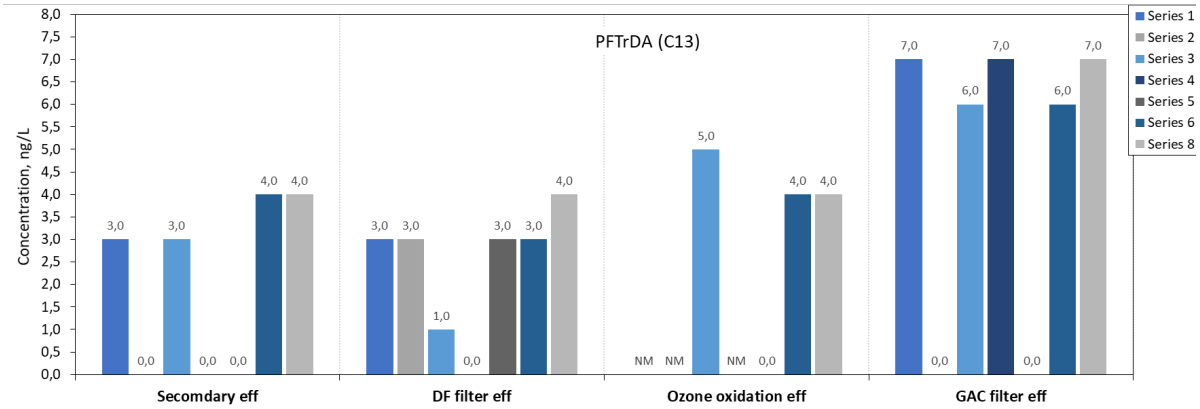

Figure 33. Concentrations of PFDA at different stages of wastewater treatment. Detection level was 1,0 ng/L

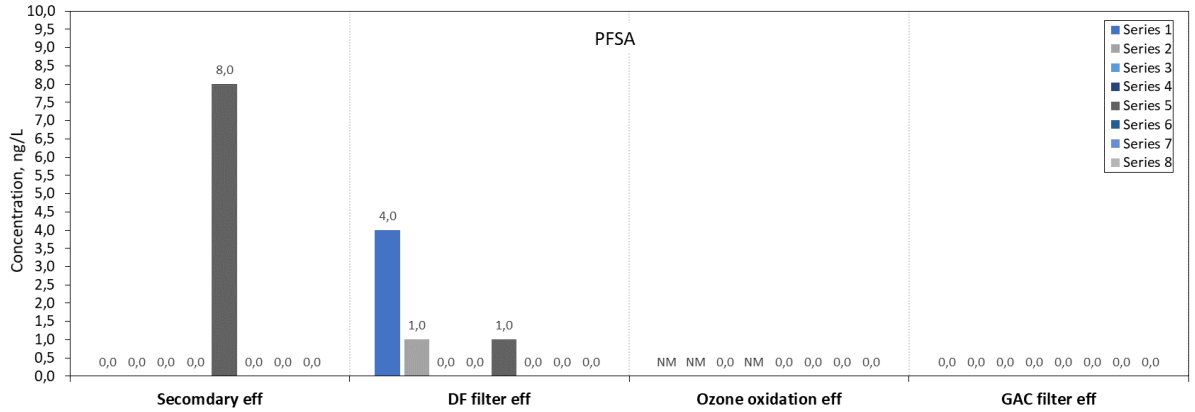

Figure 34. Concentrations of PFDA at different stages of wastewater treatment. Detection level was 1,0 ng/L

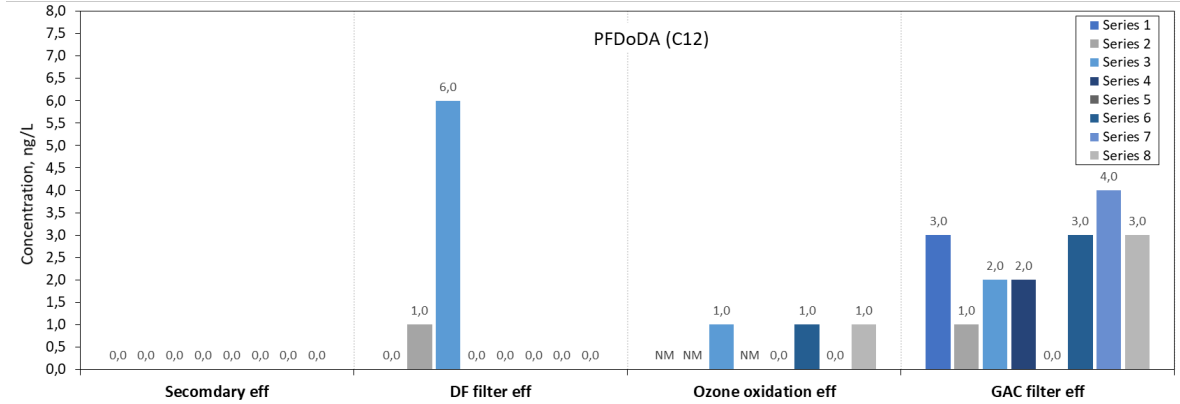

Figure 35. Concentrations of PFDA at different stages of wastewater treatment. Detection level was 1,0 ng/L

With only three short-chain PFAS measured during the pilot tests and PFBS not giving any reliable results it is difficult to clearly say that the results have proven that short-chain PFAS increases gradually after ozonation and/or GAC filtration. It is reflected in Figure 36 which interpretation alone may be misleading without looking specifically at Figure 25 and 27.

The sum of long-chain PFAS as presented on Figure 37 remains more or less at a similar level although similarly to the sum of short-chain PFAS one should be careful to draw any conclusions basing on such a limited data and rather look at specific PFAS as shown on Figure 28 to 35.

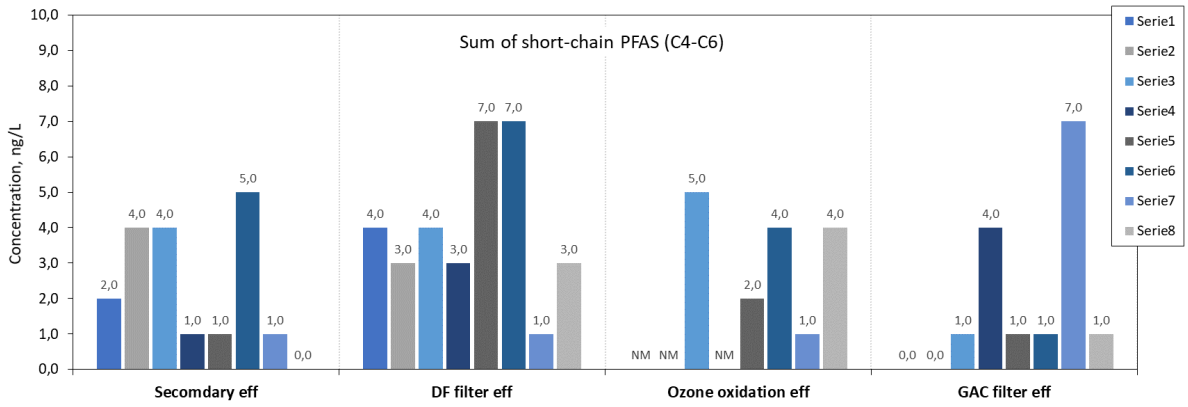

Figure 36. Sum of short-chain PFAS at different stages of wastewater treatment. Detection level was 1,0 ng/L

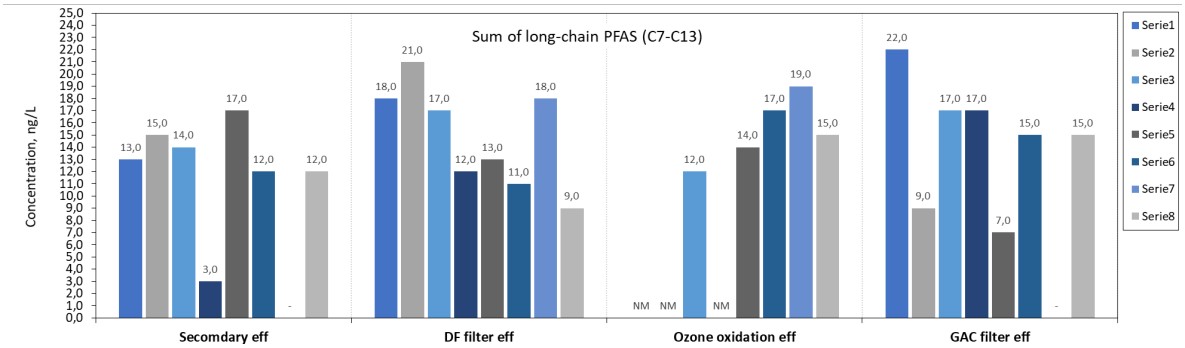

Figure 37. Sum of long-chain PFAS at different stages of wastewater treatment.

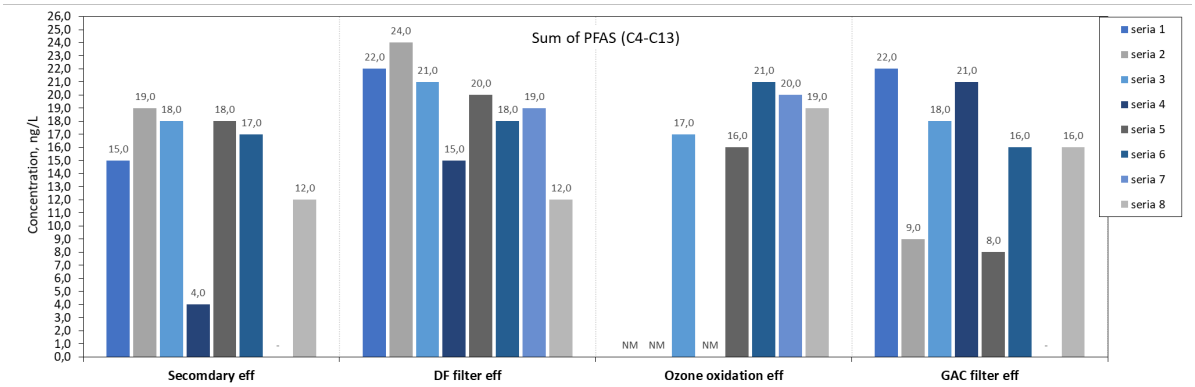

Figure 38. Sum of PFAS at different stages of wastewater treatment.

Since the partial oxidation process may affect PFAS that are not included in laboratory analyses, the number and type of PFAS compounds measured in wastewater samples are crucial for evaluating their removal. PFAS comprise a very large group of substances that can be present in wastewater and analysing only a limited number, for instance 23 as in this case and presented on Figure 38, to assess their removal efficiency might be insufficient — especially when advanced oxidation processes (AOPs), such as ozone oxidation, are used for micropollutant elimination. Longer measurements with more compounds are necessary to formulate trends in their behaviour at different stages of WWTP processes and to draw any representative and solid conclusions which was definitely not possible during the tests carried at WWTP Pomorzany.

3.4. Removal of micropollutants

The new UWWTD defines and describes two major categories of micropollutants to be treated at WWTP. Minimum percentage of removal in relation to the load of the influent is defined as 80%. The percentage of removal shall be calculated on dry weather flow for at least six substances. The number of substances in category 1 shall be twice the number of substances in category 2. Consequently during the pilot tests at WWTP Pomorzany samples and measurements have been also made at the inlet to the WWTP using also 24-hour composite sample as for all other sampling points. The defined micropollutants are:

Category 1 (substances that can be very easily treated):
(i) Amisulprid (CAS No 71675-85-9),
(ii) Carbamazepine (CAS No 298-46-4),
(iii) Citalopram (CAS No 59729-33-8),
(iv) Clarithromycin (CAS No 81103-11-9),
(v) Diclofenac (CAS No 15307-86-5),
(vi) Hydrochlorothiazide (CAS No 58-93-5),
(vii) Metoprolol (CAS No 37350-58-6),

(viii) Venlafaxine (CAS No 93413-69-5);

Category 2 (substances that can be easily disposed of):
(i) Benzotriazole (CAS No 95-14-7),
(ii) Candesartan (CAS No 139481-59-7),
(iii) Irbesartan (CAS No 138402-11-6),
(iv) mixture of 4-Methylbenzotriazole (CAS No 29878-31-7) and 6-methylbenzotriazole (CAS No 136-85-6).

These pharmaceuticals are a significant class of micropollutants found in wastewater. These compounds can be challenging to remove due to their chemical stability and low concentrations. Two common and effective methods for removing pharmaceuticals from wastewater are ozonation and GAC filtration.

The pharmaceuticals analysed during the pilot study belonged to several therapeutic categories: antihypertensives (candesartan, irbesartan, metoprolol, hydrochlorothiazide), antidepressants (citalopram, norfluoxetine, venlafaxine), antipsychotics and mood stabilizers (amisulpride, carbamazepine), antibiotics (clarithromycin), and anti-inflammatory/pain relief agents (diclofenac).

The analysed 4-MBT and 6-MBT are two closely related organic compounds that are methylated derivatives of benzotriazole, a heterocyclic compound with corrosion-inhibiting properties. They are common corrosion inhibitors, particularly for copper and its alloys, and are often found in industrial wastewater. 4-MBT serves also as an essential component within the mixture of aircraft deicing and anti-icing fluids. While both compounds exhibit low acute toxicity, their persistence in aquatic environments raises concerns about long-term ecological impact. Effective removal of 4-MBT and 6-MBT can be achieved using advanced treatment technologies, such as AOPs, activated carbon adsorption, membrane filtration, or electrochemical treatment.

Analytical results confirmed the presence of eleven out of the twelve tested compounds in the wastewater, with irbesartan being the only substance not detected.

The concentrations of individual micropollutants after each stage of wastewater treatment are presented in Figures 39 – 49. Series 1, 2 and 4 were excluded from measurements of ozone oxidation effect. Series 3, 5, 6, 7 and 8 for ozone oxidation effect were using measurements of a grab sample. All other samples used 24-hour composite sample.

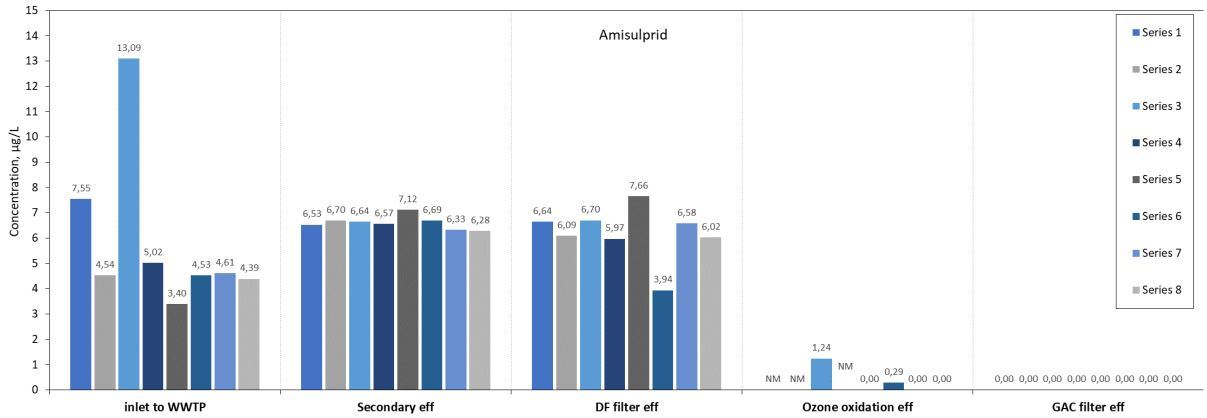

Figure 39. Concentrations of amisulpride at different stages of wastewater treatment.

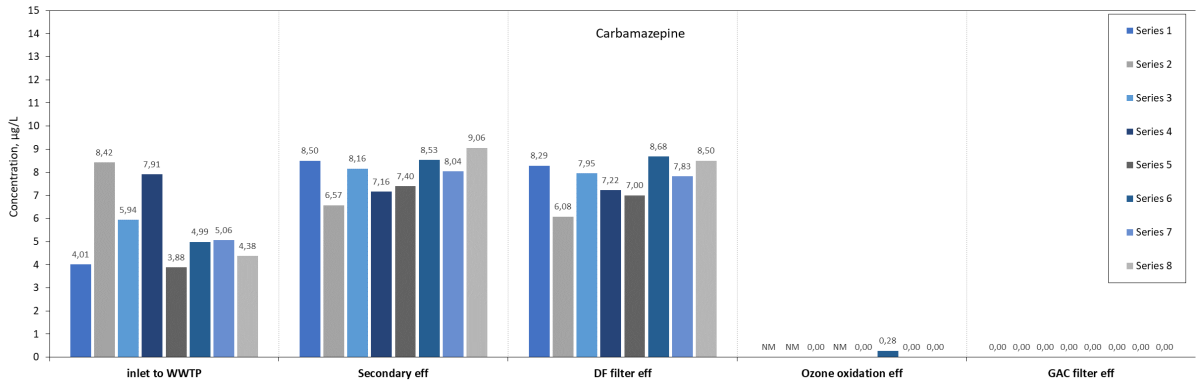

Figure 40. Concentrations of carbamazepine at different stages of wastewater treatment

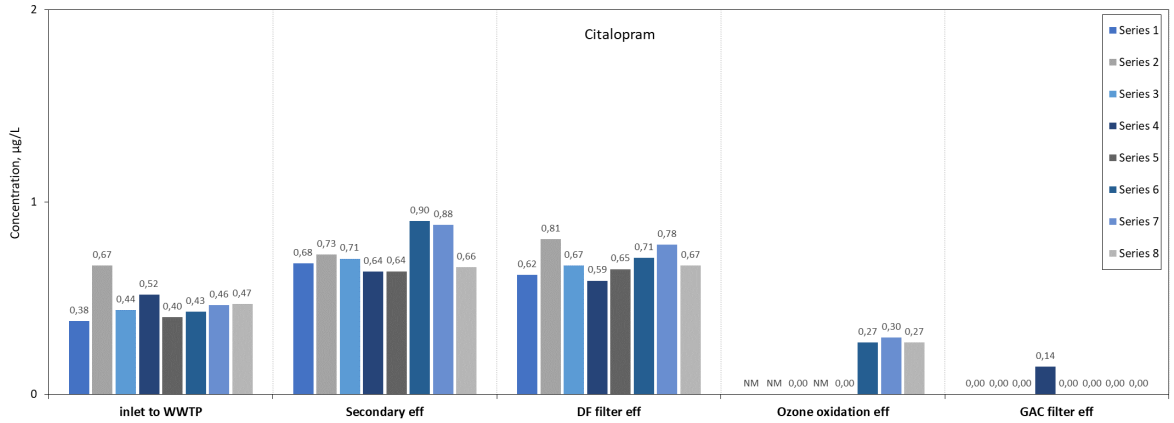

Figure 41. Concentrations of citalopram at different stages of wastewater treatment.

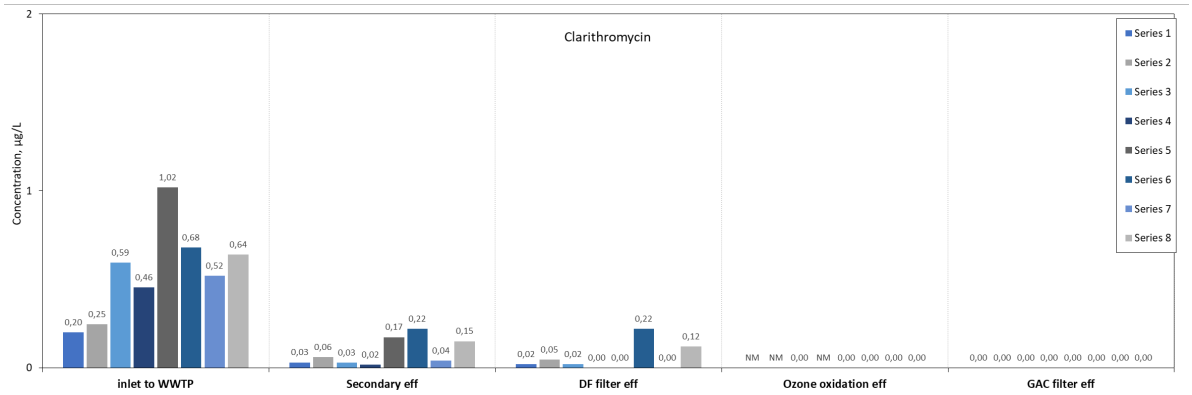

Figure 42. Concentrations of clarithromycin at different stages of wastewater treatment.

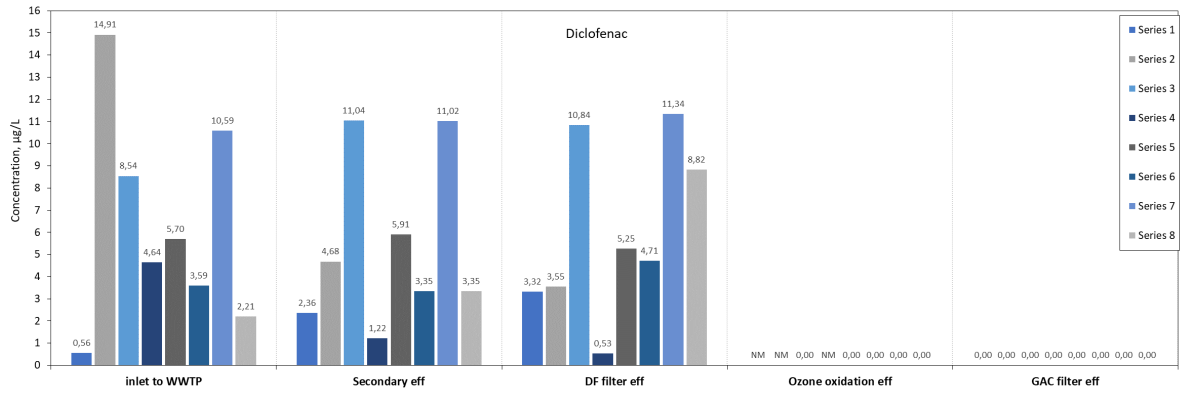

Figure 43. Concentrations of diclofenac at different stages of wastewater treatment.

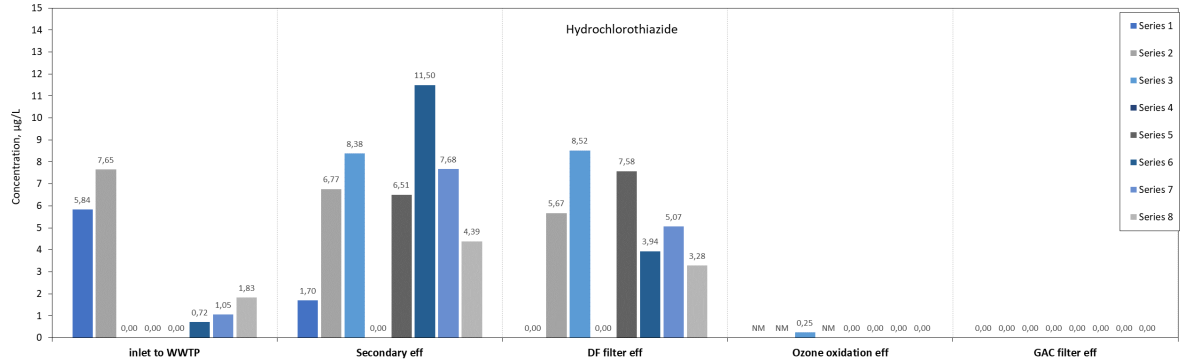

Figure 44. Concentrations of hydrochlorothiazide at different stages of wastewater treatment.

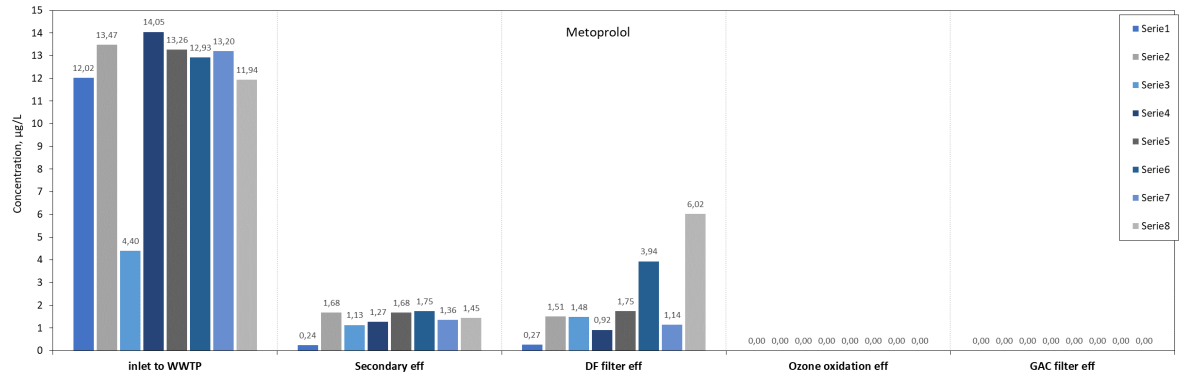

Figure 45. Concentrations of metoprolol at different stages of wastewater treatment.

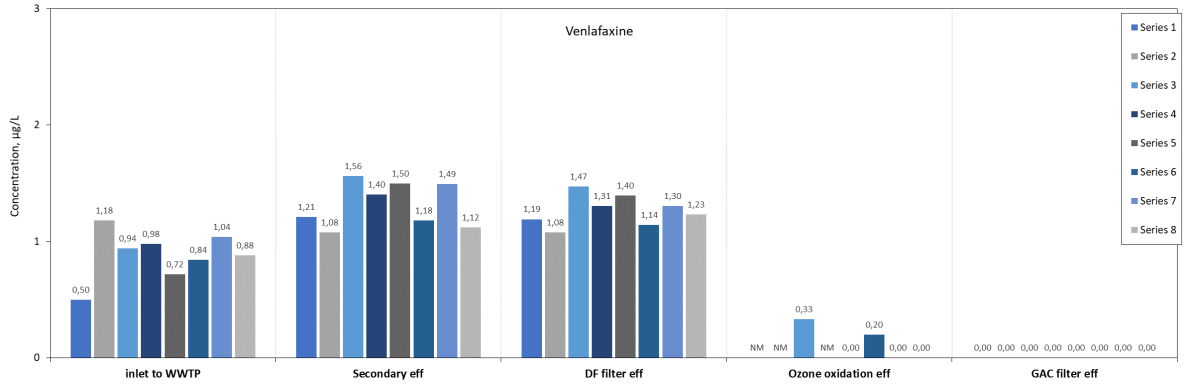

Figure 46. Concentrations of venlafaxine at different stages of wastewater treatment.

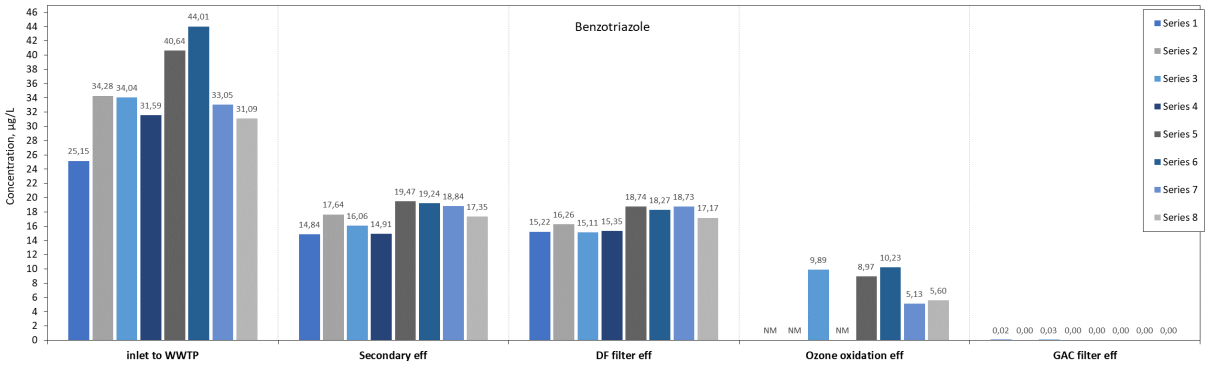

Figure 47. Concentrations of benzotriazole at different stages of wastewater treatment.

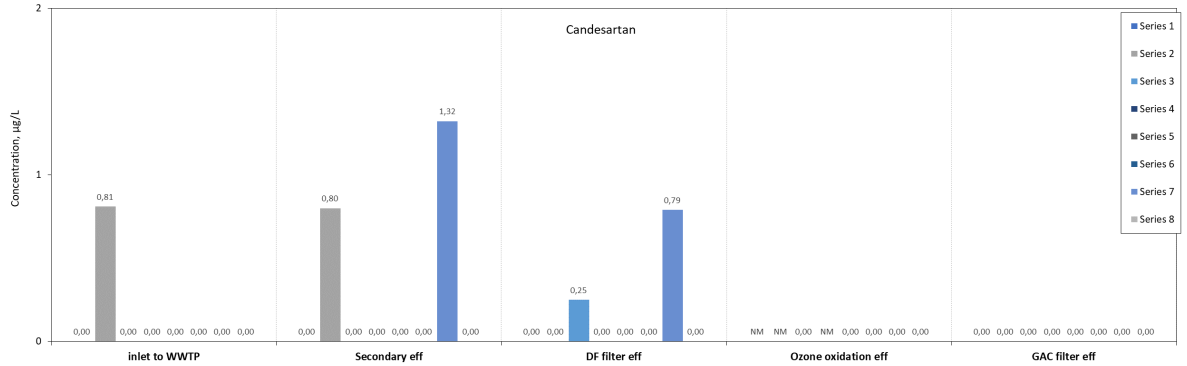

Figure 48. Concentrations of candesartan at different stages of wastewater treatment

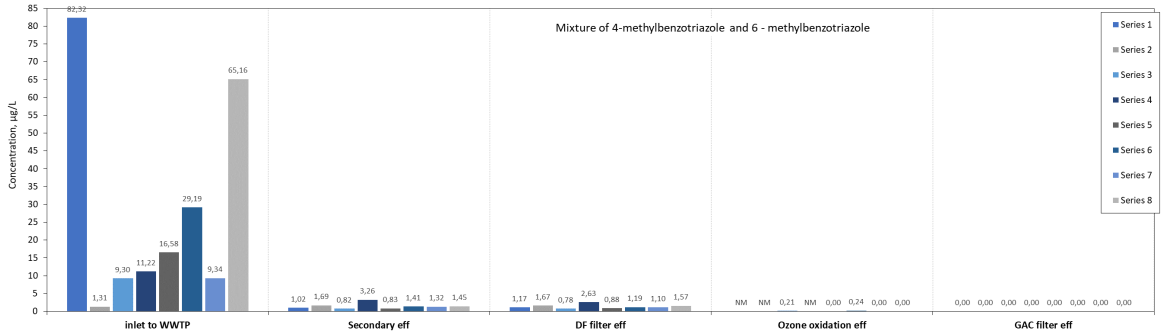

Figure 49. Concentrations of mixture of 4-Methylbenzotriazole and 6-methylbenzotriazole at different stages of wastewater treatment.

As expected, the obtained results confirm very high efficiency of removal of all measured micropollutants by the combination of ozonation and GAC filtration. Ozonation alone achieved very high removal efficiency with exception of citalopram and benzotriazole. After combined ozonation and GAC filtration, the removal efficiency was at the level of 100% for all compounds in all measurement series with the exception of only one sample in series 4 of citalopram.

The highest concentrations at the inlet to the plant were reported for benzotriazole ranging from 25,15 µg/L to 44,01 µg/L. They were also observed at significant values through the following stages of the pilot plant. Values for amisulpride, carbamazepine, diclofenac, hydrochlorothiazide, metoprolol and mixture of 4-methylbenzotriazole and 6-methylbenzotriazole were measured at the average values of 7 to 15 µg/L with two exceptional series for the last one that were very high. The remaining compounds were reported at the values up to 2 µg/L.

4. Conclusions

The following conclusions can be derived from the pilot test conducted at the WWTP Pomorzany in Szczecin/POLAND:

- The mobile pilot plant is a highly cost-effective tool to support upgrading and development of numerous wastewater treatment plants without incurring the high costs of designing and constructing their own pilot installation.
- The values of process parameters i.e. 6, 8 and 10 mg O_3/L ozone dose proved that 6 mg O_3/L is sufficient for removal of micropollutants. This led to the conclusions that further tests with lower values of ozone dose should be carried out to find an optimal dose. Due to the shortage of time consequently only one extra measurement made on 04.12.2024 followed, with ozone oxidation with only 3 mg O_3/L ozone dose. Even that dose proved sufficient. Optimum ozone contact time was established at a level of 30 min EBCT of GAC filter at 20 min. Consequently these values can be used as design parameters for developing a concept of a quaternary treatment stage based on cloth or presumably other types filtration like sand filters followed by ozonation and granular activated carbon filtration.
- Tests carried out at the pilot plant showed although expected yet interesting information in the scope of TP and TN removal. Moderate removal of TP ranging from 17% to 68% and minimum removal of TN which varied between 5% and 35% were reported. This can be important for all installations that struggle with TP and TN removal in the light of new regulations for those cited in UWWTD.
- Results for PFAS compounds removal showed that the amount of measured compounds and their presence or lack of it in wastewater coming to the plant and consequently at following stages of treatment process was not enough to draw solid conclusions. Quite important factor here was the level of detection which was nanograms. Such low concentrations require specific and almost sterile environment for sampling and consequently processing of each probe that even a cloth of goretex a person carrying measurements is dressed in may be enough to jeopardise the whole process. Additionally 24-composite sample could affect the result of PFAS measurement despite all the elements being made of PFAS-free materials.
- The results of the analyses of PFAS compounds in wastewater samples showed discrepancies and a lack of clear quantitative trends. Such inconsistency may result from:
    - Daily changeability of wastewater (rainfall, quality of wastewater brought in trucks)
    - Limited amount of measured PFAS compounds which was only 23 where already several thousand PFAS compounds are already known and used in different sectors of life and those compounds can transform into other compounds.
    - Period of the year the tests were carried out
- The combination of cloth filtration, ozonation and GAC filtration has been proven to have a high removal rate of organic micropollutants. Removal rate of the measured micropollutants equalled to 100% with the exception of only one probe of citalopram.
- The comprehensive analysis of presented laboratory results gives some important facts that one must be aware of:
    - Current number of available laboratories being able to carry PFAS and micropollutant tests is very limited.
    - Time required to get the results is relatively long 2-4 weeks thus making reaction to the results and possible change in parameters very difficult especially under time pressure.

    - Detection levels for PFAS in nanograms and micropollutants in micrograms is very low and there are too many factors that can influence the results. Consequently number of samples must be sufficient enough to reject these clearly burdened with measurement or probing failure and to be able to formulate solid conclusions.

- While looking at the results one must take into consideration that the measurement period was relatively short of only 69 days during Autumn. This does not guarantee the certainty of the same results throughout the whole year when both weather and season can significantly influence what is coming to the WWTP.
- Design process and consequently construction of quaternary step of wastewater treatment is very expensive and must rely on really solid data which means that tests should be carried out for at least one full year to take into account changeability of weather conditions and seasons. Moreover for such purposes at least two different laboratories should carry tests of the same samples.

5. References

Directive (EU) 2024/3019 of the European Parliament and of the Council of 27 November 2024 concerning urban wastewater treatment.

Swinarski, M. (2025). Pilot-scale removal of micropollutants at the Wschód WWTP in Gdańsk. Output 2.3 of the EMPEREST project, co-funded by Interreg Baltic Sea Region. Gdańsk Water Utilities.