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SUSTAINABLE WATERS
EMPEREST

Pilot-scale removal of micropollutants at the Wschód WWTP in Gdańsk

ANNEX 1
EMPEREST – ELIMINATING MICRO-POLLUTANTS FROM EFFLUENTS FOR REUSE STRATEGIES

Gdańsk Water Utilities, 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 1 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).

Contract:	EMPEREST – Eliminating Micro-Pollutants from Effluents for Reuse Strategies no. C013
Title:	Pilot-scale removal of micropollutants at the Wschód WWTP in Gdańsk.
Version:	v. 2.0, June 2025
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Cover photo:	Gdansk Water Utilities (GIWK), photo by aeromedia.pl
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How to cite:	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.

Project note

The EMPEREST project supports local authorities, service providers and policy-making community in finding ways to reduce per- and polyfluoroalkyl substances (PFAS) 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
CIC	combustion ion chromatography
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
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
PFAS	per- and polyfluoroalkyl substances
PFAS20	list of twenty per- and polyfluoroalkyl substances
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
PFTrDA	perfluorotridecanoic acid
PFTrDS	perfluorotridecane sulfonic acid
PFUnDA	perfluoroundecanoic acid
PFUnDS	perfluoroundecane sulfonic 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
U.S.	United Sates
US EPA	U.S. Environmental Protection Agency
UV	ultraviolet
UVA	ultraviolet absorbance
UVA_{254}	ultraviolet absorbance at 254
wt%	weight percentage
UWWTD	Urban Wastewater Treatment Directive
WWTPs	wastewater treatment plants
4-MTB	4-methyl-benzotriazole
6-MTB	6-methyl-benzotriazole

INTRODUCTION

Organic micropollutants (OMPs) in wastewater are an increasingly recognized environmental and public health 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 among the principal point sources of OMPs. Although modern WWTPs are effective at removing conventional pollutants such as organic matter, nitrogen, and phosphorus, they often fall short in eliminating OMPs. This shortcoming is due to the diverse chemical structures and properties of OMPs, which make them resistant to traditional treatment processes. As a result, effluents discharged from WWTPs may still contain a cocktail of biologically active compounds that can disrupt aquatic ecosystems and pose long-term health risks to humans through environmental exposure.

The persistence of OMPs in treated wastewater underscores the urgent need for both technological and regulatory advancements. Advanced treatment methods such as ozonation, membrane filtration, activated carbon adsorption, and ion exchange are being actively researched and piloted to address this challenge. These technologies aim to complement existing wastewater treatment processes by targeting and degrading or capturing micropollutants before discharge. However, scaling up these solutions requires careful evaluation of their efficiency, cost, and environmental sustainability.

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 (European Union, 2024). 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 a comprehensive risk assessment shows no significant public or ecological risk.

This report presents the results of pilot testing on the removal of organic micropollutants by means of a mobile pilot-scale plant, designed to evaluate the efficiency of advanced wastewater treatment processes. The aim of the pilot tests was to assess the potential of ozone oxidation, activated carbon adsorption, and ion exchange for reducing micropollutant emissions in treated wastewater, as well as to determine the process parameters that ensure the highest removal efficiency. The results of the pilot test will contribute to the development of evidence-based strategies for the broader implementation of advanced treatment technologies, ultimately supporting the EU's objectives of safeguarding water quality, protecting aquatic ecosystems, and minimizing human health risks associated with micropollutant exposure.

MATERIALS AND METHODS

Study site

The pilot test was conducted at the Wschód WWTP in Gdańsk (Poland), one of the largest facilities located on the Baltic Sea. The plant receives municipal wastewater and has an average influent flow rate of approximately 107,000 m^3/day. Industrial wastewater accounts for approximately 10% of the total influent to the plant. The pollutant load entering the plant corresponds to 922,000 PE.

The primary treatment line includes four screens, four aerated grit chambers, and three primary settling tanks. The biological treatment process comprises six bioreactors configured according to the Anaerobic/Anoxic/Oxic (A2/O) system, and twelve circular secondary clarifiers.

Average concentrations of pollutants in the secondary effluent are as follows:

- Biochemical oxygen demand (BOD_5) 2.7 mg BOD_5/L
- Total chemical oxygen demand (TCOD) 33 mg COD/L
- Total suspended solids (TSS) 4.6 mg/L
- Total nitrogen (TN) 8.7 mg N/L
- Total phosphorus (TP) 0.3 mg P/L

Pilot plant description

The pilot test was 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 plant is dedicated to evaluating the removal efficiency of OMPs from water or wastewater.

The treatment train is composed of the following main components:

- MITA TF2 VM cloth drum filter (DF)
  - POLSTOFF "PILE" type filter cloth with a thickness of 4–5 mm
  - filtration surface 2,0 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 2.0 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
- an ozone contact tank
  - working volume 0,200 – 0,800 m^3
- gravity filters – 2 units
  - diameter 0,350 m
  - surface area 0,096 m^2
  - filter nozzles vertical slots 0,30 mm
- a backwash water storage tank
  - maximum working volume 0,750 m^3
- Grundfoss CM 3-2 backwash pump
  - rated flow 3,1 m^3/h
  - rated head 13.3 m
- Airpress LMO 25-250 air compressor (AC)
  - oil-free compressor
  - free air delivery 150 L/min
  - maximum pressure 8 bar
- Probiko-Aqua Protec 1200 EW ultraviolet (UV) lamp
  - maximum flow 0,700 m^3/h
  - UV dose 400 J/m^2 at 60% UV transmittance

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

- IFM SM9100 magnetic-inductive water flow meter
- IFM SM7120 magnetic-inductive water flow meter – 6 units
- IFM SA5020 air flow sensor
- 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

The online UV absorbance (UVA) and turbidity sensors allow continuous monitoring of the removal performance of suspended solids and organic compounds.

Figure 1. View of the pilot plant located at the Wschód WWTP in Gdańsk.

Figure 2. View of the pilot plant interior.

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. Figures 3 – 5 show a process flow diagram displayed on the touch panel HMI. An on-site VPN router provides secure remote access to the pilot plant over cellular networks.

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 intermediate tanks with overflows and pumps installed after cloth filtration, ozone oxidation, and granular media 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.

All the devices are mounted in a 20-feet high cube shipping container to ensure easy transport and quick commissioning at any water intake or wastewater treatment plant (Figure 1).

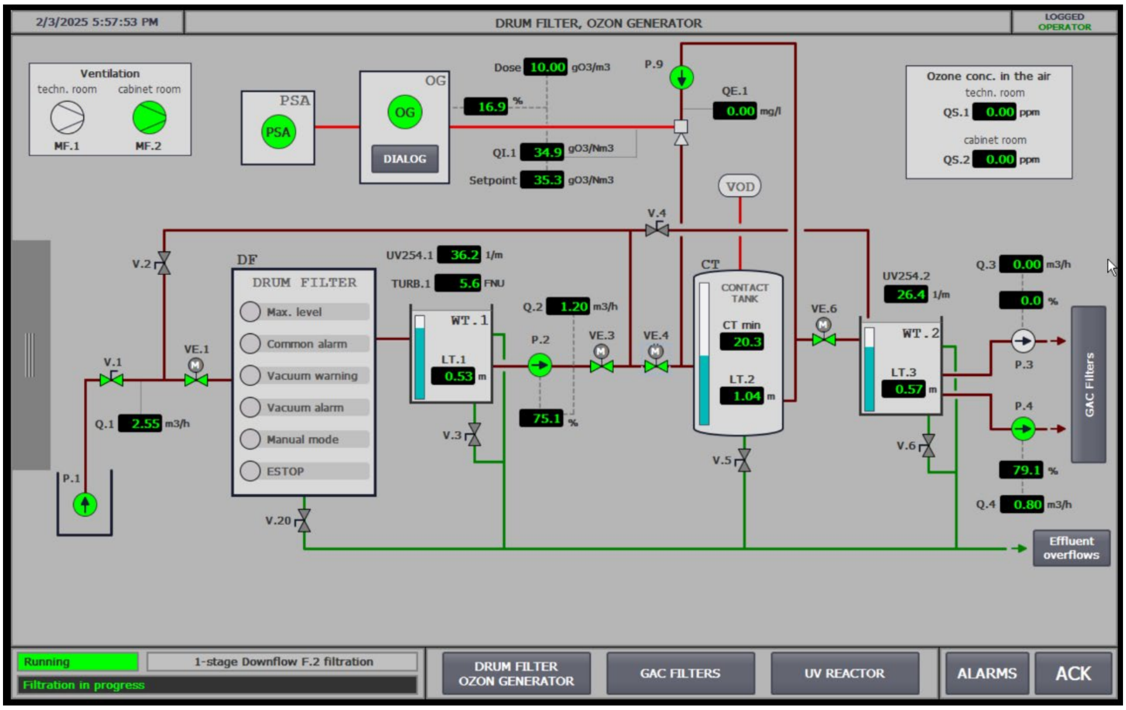


Figure 3. Flow diagram displayed on screen 1 of HMI panel. Labelling of main components of the process train: DF - cloth drum filter, PSA - oxygen concentrator, OG - ozone generator, WT – intermediate process tank, P - process pump, UV254 – UV absorbance sensor, TURB – turbidity sensor.

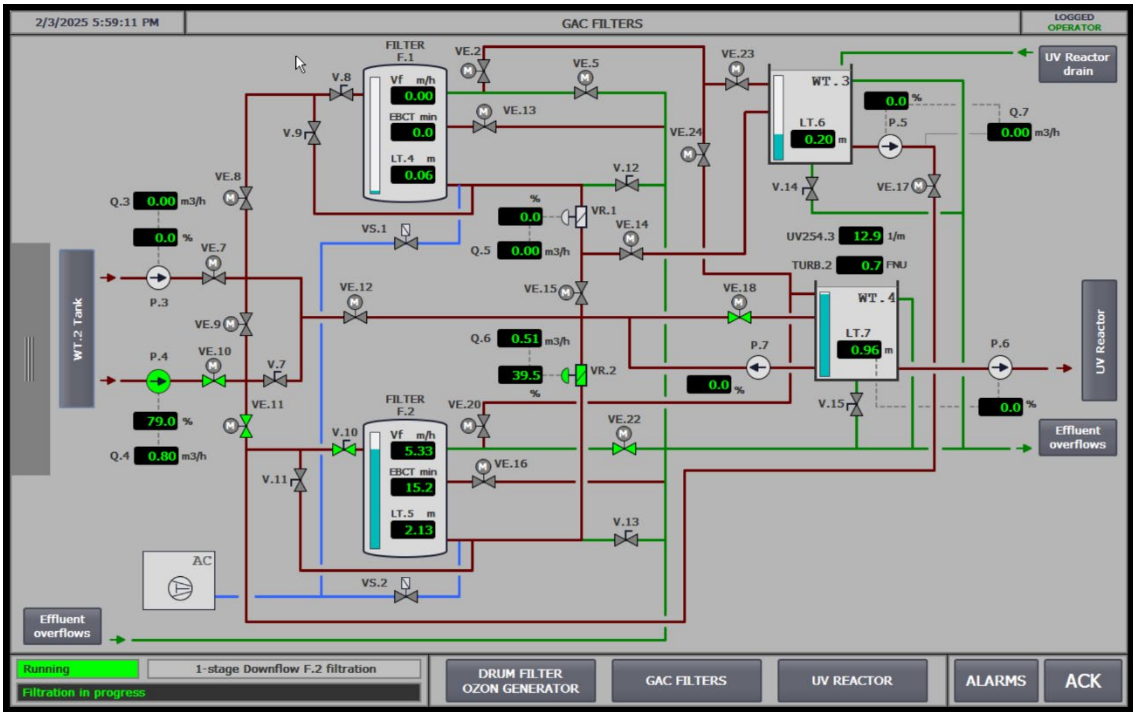


Figure 4. Flow diagram displayed on screen 2 of HMI panel. Labelling of main components of the process train: F – gravity filter, WT.3 - intermediate process tank, WT.4 – backwash water tank, P - process pump, AC - air compressor, UV254 – UV absorbance sensor, TURB – turbidity sensor.

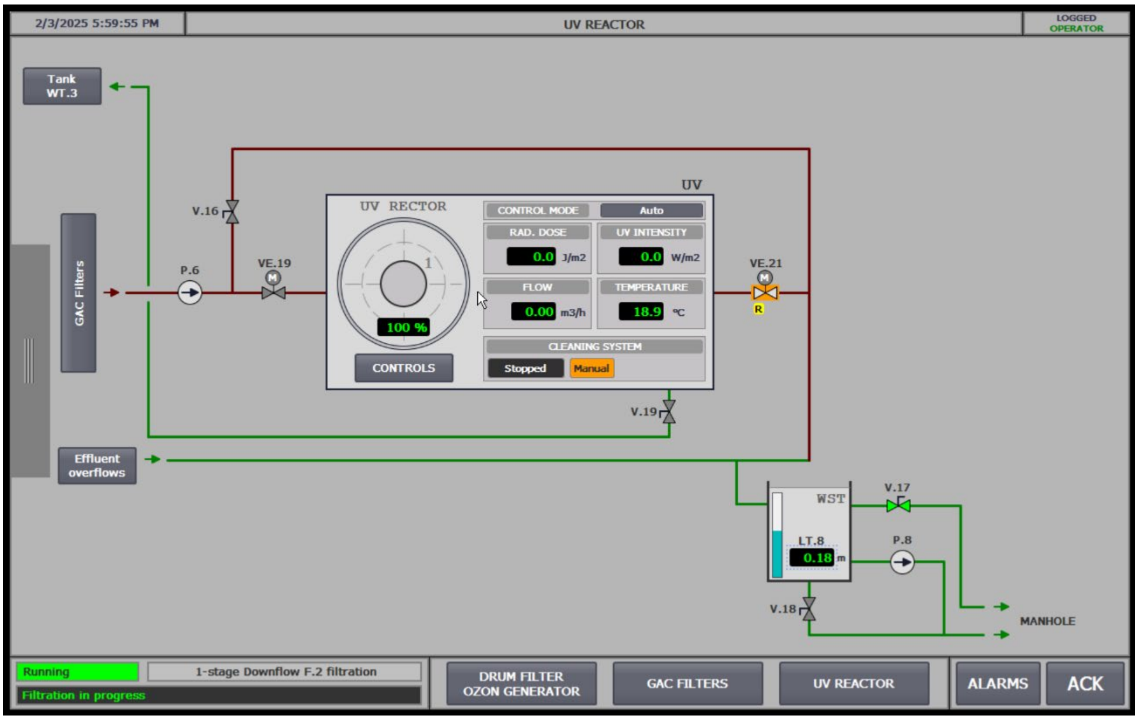


Figure 5. Flow diagram displayed on screen 3 of HMI panel. Labelling of main components of the process train: UV – ultraviolet lamp, WST - backwash and overflow tank.

Analytical methods

Performance of the examined treatment process was monitored using 24-hour composite and grab sampling, as well as the online UVA and turbidity sensors. Samples were collected twice a week and analysed for wastewater quality parameters indicating the presence of suspended solids and organic compounds, including OMPs. The monitored OMPs include those listed in the UWWTD, for which a minimum removal of 80% is required (highlighted in bold), except for benzotriazole (European Union, 2024).

The following parameters were measured to assess wastewater quality:

- TCOD
- Total organic carbon (TOC)
- Dissolved organic carbon (DOC)
- UVA
- TSS
- Turbidity
- 20 per- and polyfluoroalkyl substances (PFAS20)
  perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorobutane sulfonic acid (PFBS), perfluorohexanoic acid (PFHxA), perfluoropentane sulfonic acid (PFPeS), perfluoroheptanoic acid (PFHpA), perfluorohexane sulfonic acid (PFHxS), perfluorooctanoic acid (PFOA), perfluoroheptane sulfonic acid (PFHpS), perfluorononanoic acid (PFNA), perfluorooctane sulfonic acid (PFOS), perfluorononane sulfonic acid (PFNS), perfluorodecanoic acid (PFDA), perfluorodecane sulfonic acid (PFDS), perfluoroundecanoic acid (PFUnDA), perfluoroundecane sulfonic acid (PFUnDS), perfluorododecanoic acid (PFDoDA), perfluorododecane sulfonic acid (PFDoDS), perfluorotridecanoic acid (PFTrDA), perfluorotridecane sulfonic acid (PFTrDS)
- 11 pharmaceuticals
  diclofenac, **clarithromycin**, **candesartan**, **hydrochlorothiazide**, **metoprolol**, **irbesartan**, **venlafaxine**, **citalopram**, norfluoxetine, **amisulpride**, **carbamazepine**

- 2 estrogens
  beta-estradiol, 17α-ethynylestradiol
- 3 herbicides
  terbutryn, isoproturon, diuron
- 2 phenols
  bisphenol A, bisphenol S
- **Mixture of 4-methyl-benzotriazole (4-MTB) and 6-methyl-benzotriazole (6-MTB)**

TCOD, TOC, DOC and TTS were determined according to the standard methods. Ultraviolet absorbance at a wavelength of 254 nanometres (UVA_{254}) was measured with WTW UV 700 IQ SAC sensors. Turbidity was measured according to the nephelometric principle with WTW VisoTurb 700 IQ sensors.
The concentrations of estrogens and bisphenol A were determined using a gas chromatography-mass spectrometry (GC-MS) method, while pharmaceuticals, bisphenol S, 4-MTB, 6-MTB, and herbicides using a liquid chromatography-mass spectrometry (LC-MS) method. In order to measure PFAS, liquid chromatography-tandem mass spectrometry (LC-MS/MS) was employed.

RESULTS

The pilot plant was fed with secondary effluent of the Wschód WWTP. The treatment process train consisted of cloth filtration, ozone oxidation, and granular activated carbon (GAC) filtration, followed by ion exchange (IX), as shown in Figure 6.

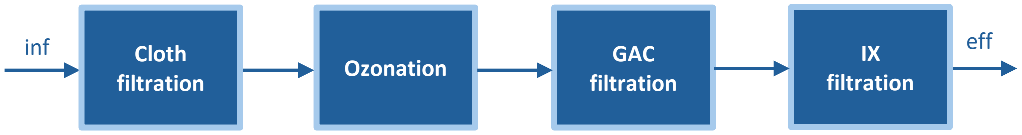


Figure 6. Configuration of the treatment process during the pilot test conducted at the Wschód WWTP in Gdańsk.

The GAC filter and the IX filter were filled with Grand Activated WG-12 activated carbon and DuPont Amberlite^{TM} PSR2 Plus ion exchange resin (IXR), respectively. The height of both filter beds equalled to 1,35 m.

The pilot test was carried out over a 73-day period, from April 29 to July 11, 2024. The duration of the pilot test was divided into two consecutive periods: **Period 1** focused on determining the optimal ozone dose, ozone contact time and empty bed contact time (EBCT) for GAC filtration, and **Period 2** evaluated the efficiency of organic micropollutant removal with ozonation, GAC filtration and IX filtration.

TESTING PERIOD 1 - determining the optimal process parameters

UVA_{254} measurements are used as a surrogate parameter for measuring the presence of dissolved organic matter (DOM) which absorb light at this wavelength. The correlation between the removal of OMPs and the decrease of UVA_{254} is a subject of interest in water treatment research and monitoring, as both metrics are indicators of water quality and treatment efficiency (Wittmer et al., 2015). Real-time UVA_{254} measurements have been proven suitable for monitoring and controlling micropollutant removal processes. For comprehensive assessment, UVA_{254} should be complemented by direct OMP analysis.
Considering good correlation between the removal of organic micropollutants and the decrease of UVA_{254}, the optimal ozonation and GAC filtration parameters were determined by assessing average daily reductions of UVA_{254} for various ozone doses, ozone contact times, and EBCTs in the GAC filter. The results obtained are presented in Figures 7 – 10.
Ozone alone, at a dose of 6 mg O_3/L and a contact time of 15 minutes, resulted in a of UVA_{254} reduction of less than 1%. When the contact time was extended from 15 to 30 and 40 minutes, the reduction of UVA_{254} increased

significantly to 21–23% and 20–26%, respectively (Figure 7). Ozone oxidation followed by GAC filtration further improved UVA_{254} reduction to 48–74%, depending on the combined values of ozone contact time and EBCT (Figure 8). Since the difference in results between the 30-minute and 40-minute ozone contact time was insignificant, the 30-minute contact time was determined as the optimal one.

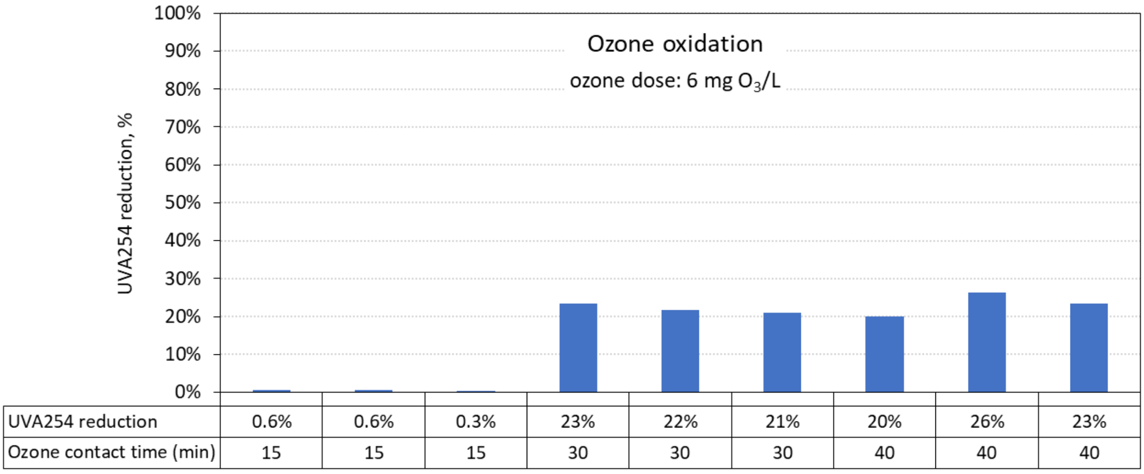


Figure 7. Average daily UVA_{254} reduction for ozone dose of 6 mg O_3/L and ozone contact times of 15, 30, 40 min.

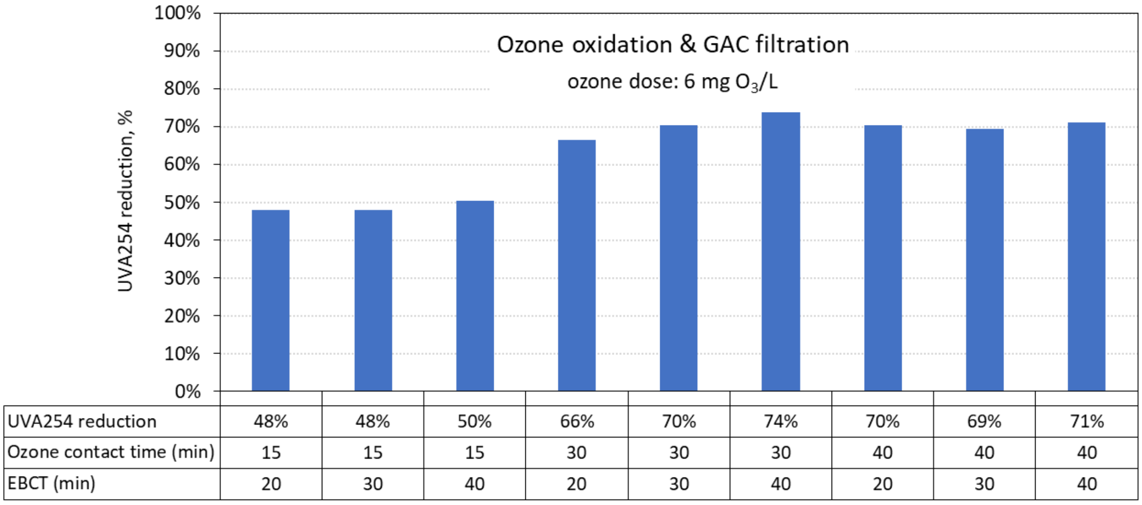


Figure 8. Average daily UVA_{254} reduction for ozone dose of 6 mg O_3/L, ozone contact times of 15, 30, 40 min, and EBCTs of 20, 30, 40 min.

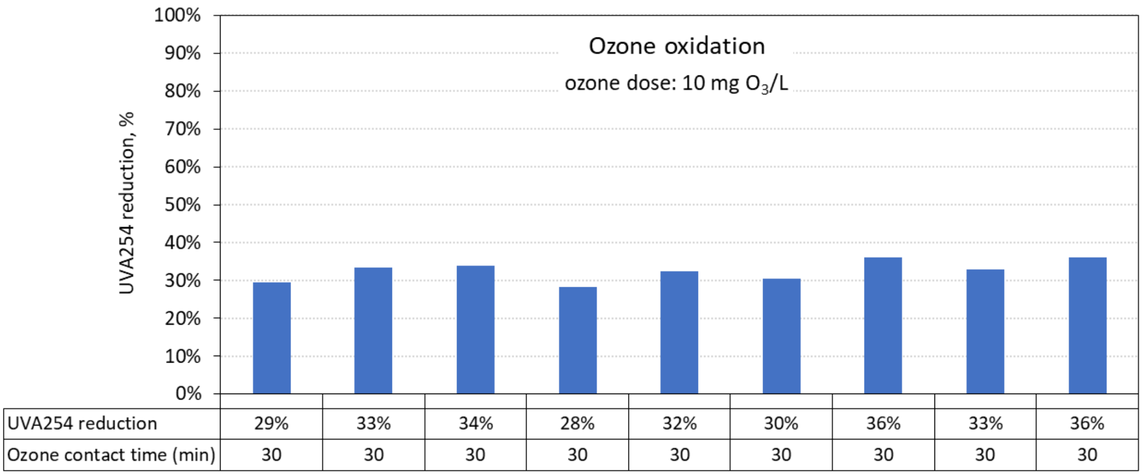
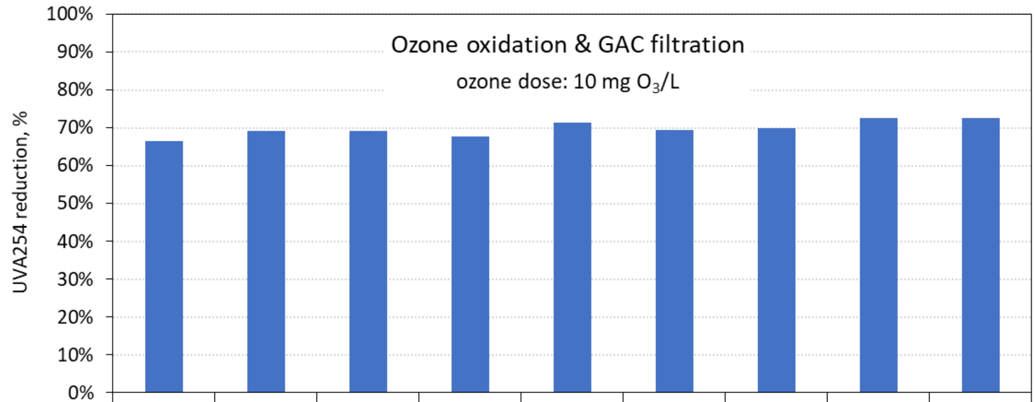


Figure 9. Average daily UVA_{254} reduction for ozone dose of 10 mg O_3/L, ozone contact time of 30 min.



UVA254 reduction	67%	69%	69%	68%	71%	70%	70%	73%	73%
Ozone contact time (min)	30	30	30	30	30	30	30	30	30
EBCT (min)	20	20	20	30	30	30	40	40	40

Figure 10. Average daily UVA_{254} reduction for ozone dose of 10 mg O_3/L, ozone contact time of 30 min, and EBCTs of 20, 30, 40 min.

When ozone alone was applied at a higher dose of 10 mg O_3/L with a contact time of 30 minutes, the reduction of UVA_{254} increased and ranged from 28% to 36% (Figure 9). When combined with GAC filtration, the reduction was even higher, ranging from 67% to 73% (Figure 10).
Among the tested combinations of ozone oxidation and GAC filtration parameters, an ozone dose of 10 mg O_3/L, an ozone contact time of 30 min, and an EBCT of 20 minutes for GAC filter were identified as the optimal conditions for OMPs removal during Testing Period 2. The EBCT for the IX filter was set at the typical value of 30 minutes.

TESTING PERIOD 2 - evaluating the efficiency of organic compounds removal

To evaluate micropollutant removal efficiency, five sampling campaigns were carried out to measure wastewater quality following ozonation, GAC filtration, and IX filtration. The key operational parameters for all sampling series were as follows:

- Flow rate of the drum filter — 2,25 m^3/h
- Ozone dose
  - sampling series 1, 2, 4, 5 — 1,0 mg O_3/mg DOC or 10 mg O_3/L
  - sampling series 3 — 1,2 mg O_3/mg DOC or 10 mg O_3/L
- Ozone contact time — 30 min
- EBCT of GAC filter — 20 min
- EBCT of IX filter — 30 min

The applied process parameters fall within the typical ranges used in full-scale quaternary treatment systems, as listed below:

- ozone dose — 0.5 – 1.5 mg O_3/mg DOC or 5 – 15 mg O_3/L
- ozone contact time — 5 – 30 min
- EBCT of GAC filter — 10 – 40 min, with 20 min often used as a benchmark
- EBCT of IX filter — 10 – 40 min

Filter cycles of the cloth filter, GAC filter and IX filter remained constant throughout the pilot test, and equalled to 4, 24 and 72 hours, respectively. Short filter cycle durations were adopted to ensure they do not affect the removal of micropollutant.

Among all the analysed micropollutants, no presence of estrogens (beta-estradiol and 17α-ethynylestradiol) or phenols (bisphenol A and bisphenol S) was detected. For the remaining groups of micropollutants, the presence of all or some of the analysed compounds was observed. Details on the measured concentrations of micropollutants are presented in the following sections of the report.

Removal of TSS, TOC, and DOC

TSS in secondary effluent include organic and inorganic materials such as microbial flocs, colloidal particles, and fine particulate matter that are not fully settled during secondary clarification. Effective removal of suspended solids from secondary effluent significantly lowers 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 (Liu et al., 2019).

As shown in Figure 11, the removal of suspended solids in the cloth drum filter was efficient, with a reduction ranging from 26% to 62%. Throughout the entire pilot testing period, TSS concentrations after the drum filter did not exceed 3 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.

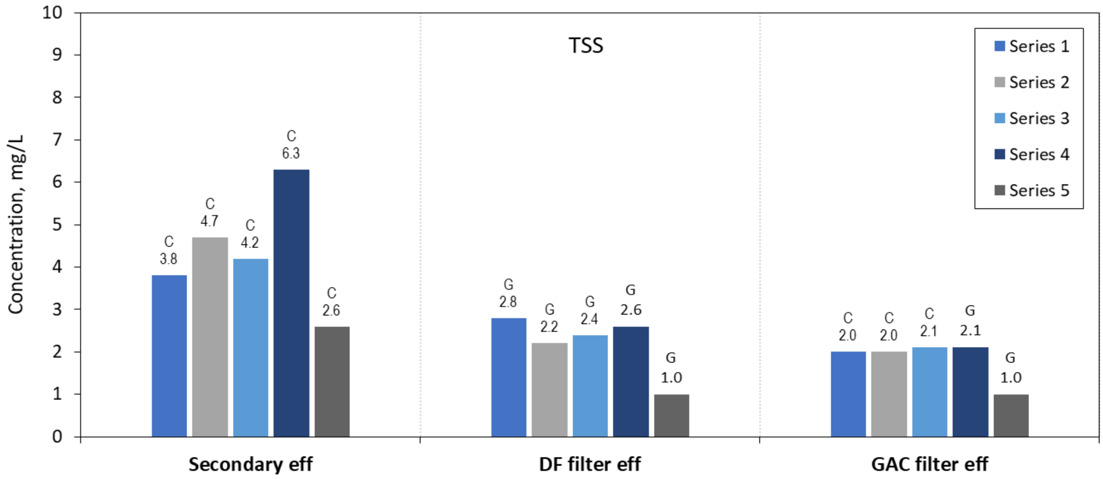


Figure 11. Concentrations of TSS at different stages of wastewater treatment. Process parameters: ozone dose of 10 mg O_3/L, 30 min ozone contact time, and 20 min EBCT of GAC. C = 24-hour composite sample; G = grab sample.

Secondary effluent from WWTPs 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. 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 matter in wastewater, encompassing both dissolved and particulate forms. SCOD specifically measures the fraction of TCOD associated with dissolved organic compounds, excluding particulate form. In parallel, 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, SCOD, TOC, and DOC provide key insights into residual organic loading and guide the selection and operation of quaternary 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 (Knopp et al., 2016). GAC is a porous material with a high surface area that adsorbs organic compounds, including pharmaceuticals. 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 require further treatment. Both methods have their advantages and limitations, and their performance can vary depending on the specific pharmaceutical compounds and the wastewater quality.

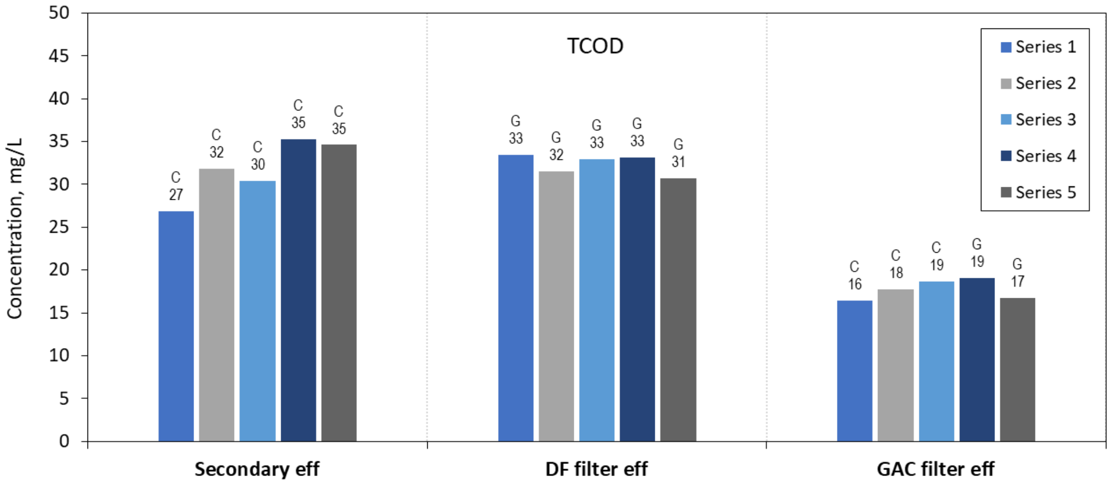


Figure 12. Concentrations of TCOD at different stages of wastewater treatment. Process parameters: ozone dose of 10 mg O_3/L, 30 min ozone contact time, and 20 min EBCT of GAC. C = 24-hour composite sample; G = grab sample.

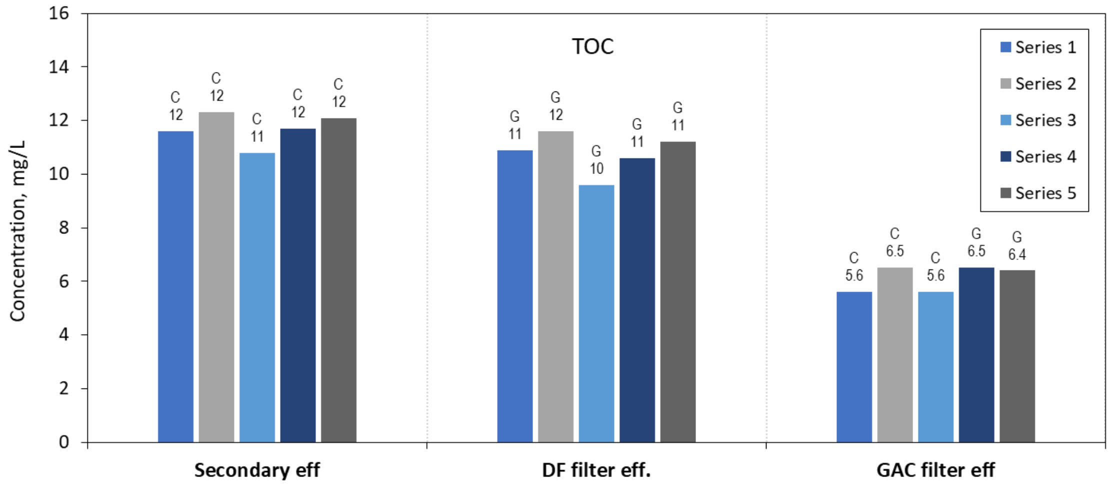


Figure 13. Concentrations of TOC at different stages of wastewater treatment. Process parameters: ozone dose of 10 mg O_3/L, 30 min ozone contact time, and 20 min EBCT of GAC. C = 24-hour composite sample; G = grab sample.

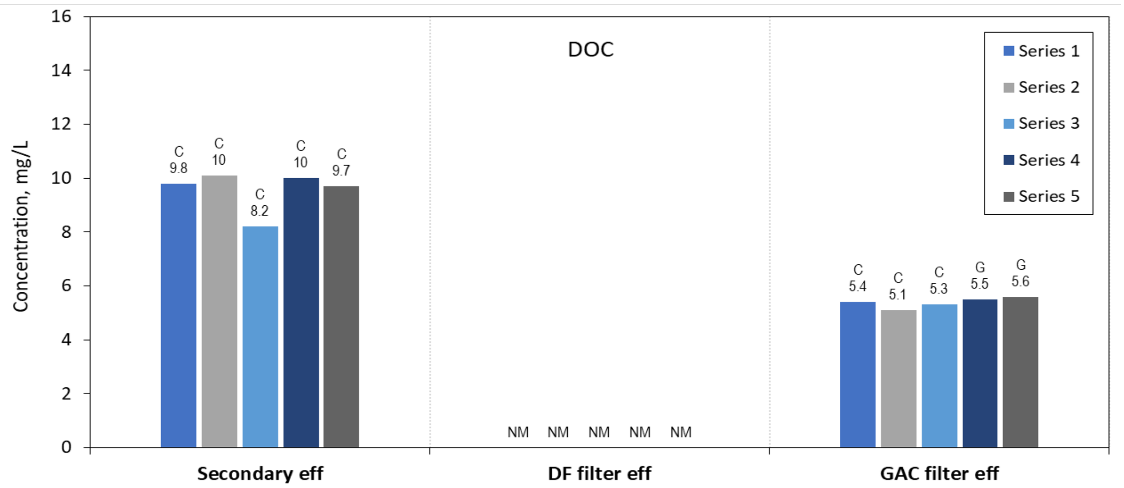


Figure 14. Concentrations of DOC at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, and 20 min EBCT of GAC. C = 24-hour composite sample; G = grab sample; NM = not measured.

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 12–14 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 39% to 52%. The removal rates of TOC and DOC varied between 52%–68% and 35%–50%, respectively. The slightly better removal of TOC compared to TCOD can be explained by the fact that TOC measures only the carbon content, not its reactivity, whereas TCOD reflects the remaining oxidation potential. 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.

Removal of pharmaceuticals

Pharmaceuticals are a significant class of micropollutants found in wastewater. These substances can contaminate water sources, harming aquatic life and disrupting ecosystems. Even in low concentrations, they may affect reproduction, growth, and behaviour in wildlife, posing long-term ecological risks. Some compounds can also contribute to the development of antibiotic-resistant bacteria.

Pharmaceuticals can be challenging to remove from wastewater due to their chemical stability and low concentrations. Common and effective methods include advanced oxidation processes (AOPs), GAC filtration, membrane filtration, and IX filtration (Angeles et al., 2020).

The pharmaceuticals analysed during the pilot test 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). Analytical results confirmed the presence of ten out of the eleven tested compounds in the wastewater, with norfluoxetine being the only substance not detected.

The concentrations of individual pharmaceuticals after each stage of wastewater treatment are presented in Figures 15 – 24. In the secondary effluent, diclofenac was found at the highest concentrations among all the pharmaceuticals, ranging from 1,560 ng/L to 2,920 ng/L. In some sampling series, concentrations exceeding 1,000 ng/L were measured for carbamazepine (790 – 1,490 ng/L), clarithromycin (41 – 1,410 ng/L), and candesartan (444 –1,750 ng/L). For the remaining pharmaceuticals, concentrations ranged from 1.9 ng/L to 440 ng/L.

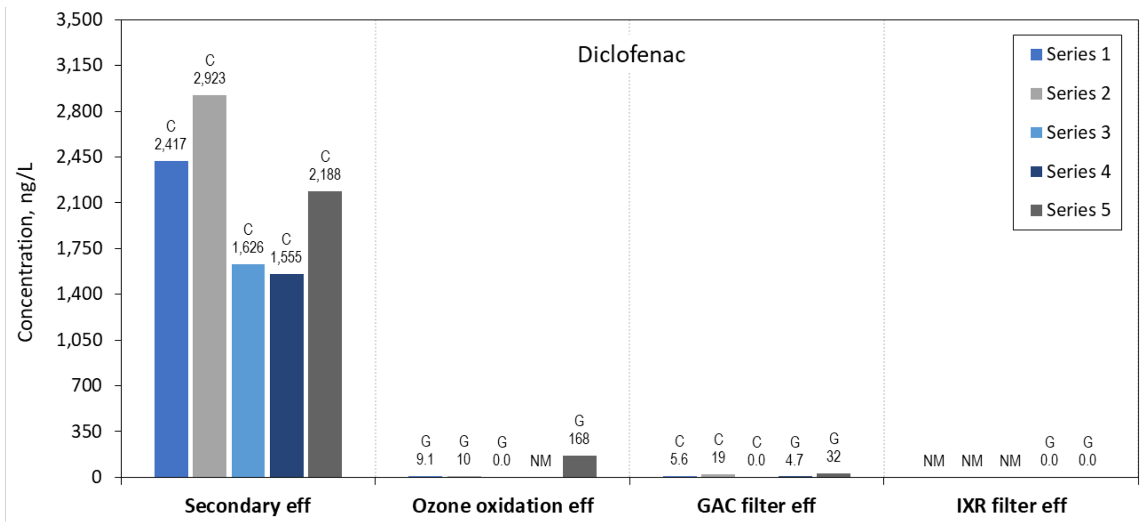


Figure 15. Concentrations of diclofenac at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample; NM = not measured.

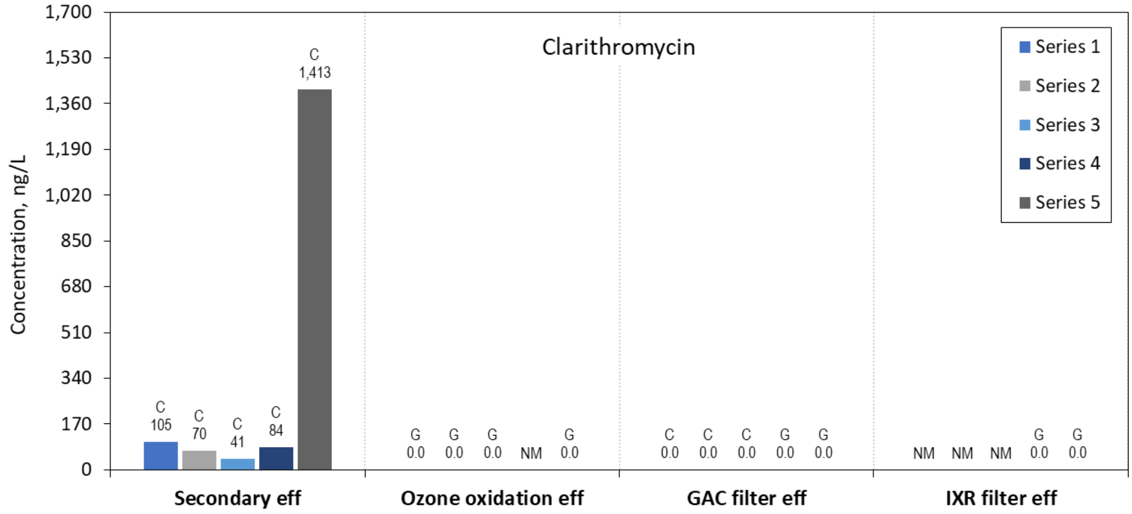


Figure 16. Concentrations of clarithromycin at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample; NM = not measured.

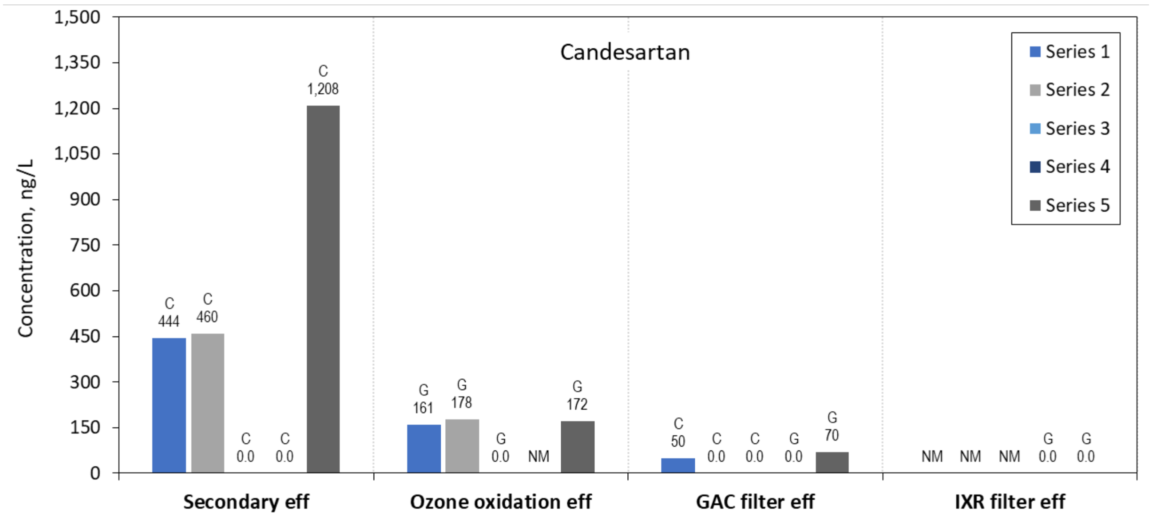


Figure 17. Concentrations of candesartan at different stages of wastewater treatment Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample; NM = not measured.

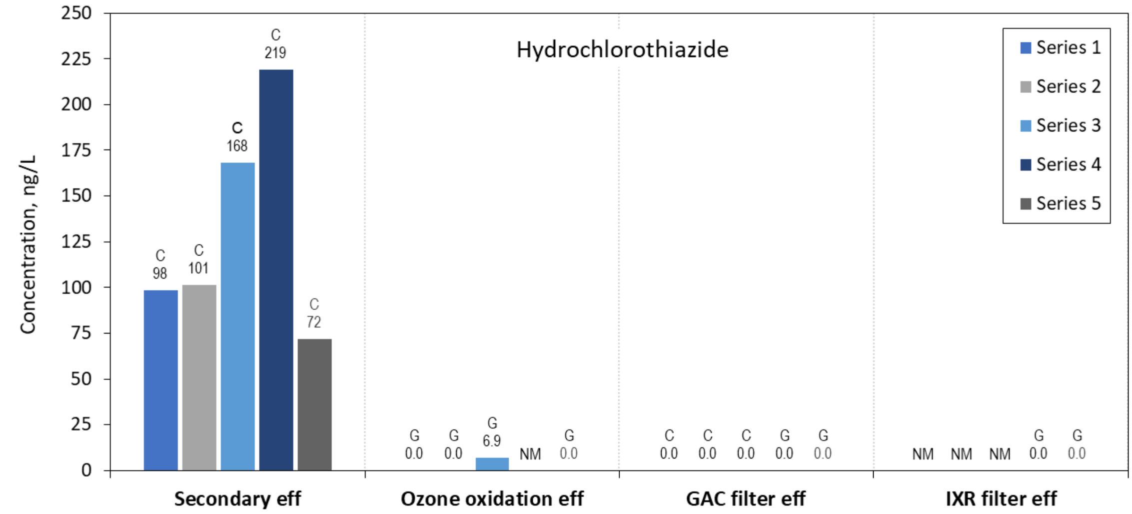


Figure 18. Concentrations of hydrochlorothiazide at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample; NM = not measured.

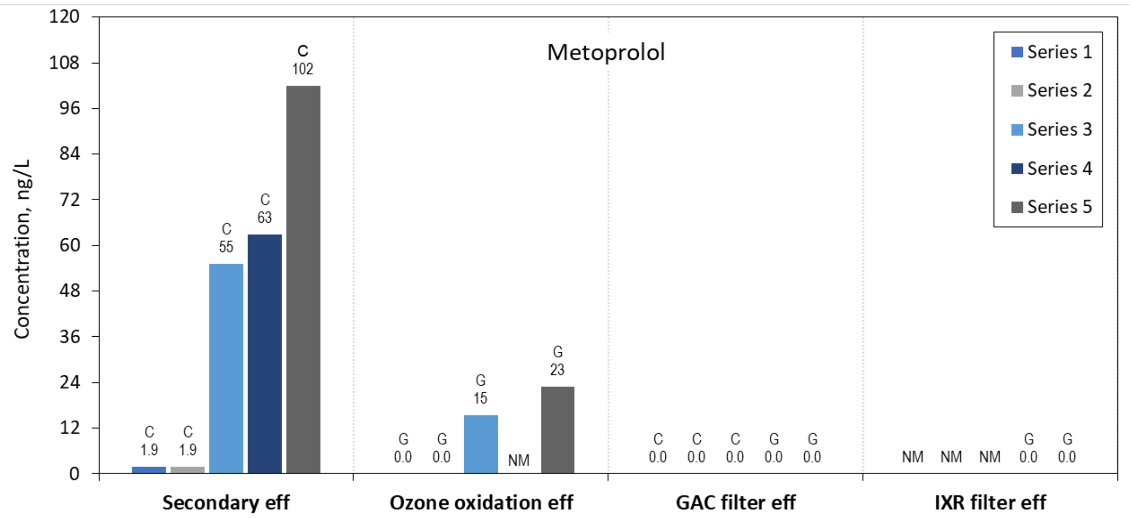


Figure 19. Concentrations of metoprolol at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample; NM = not measured.

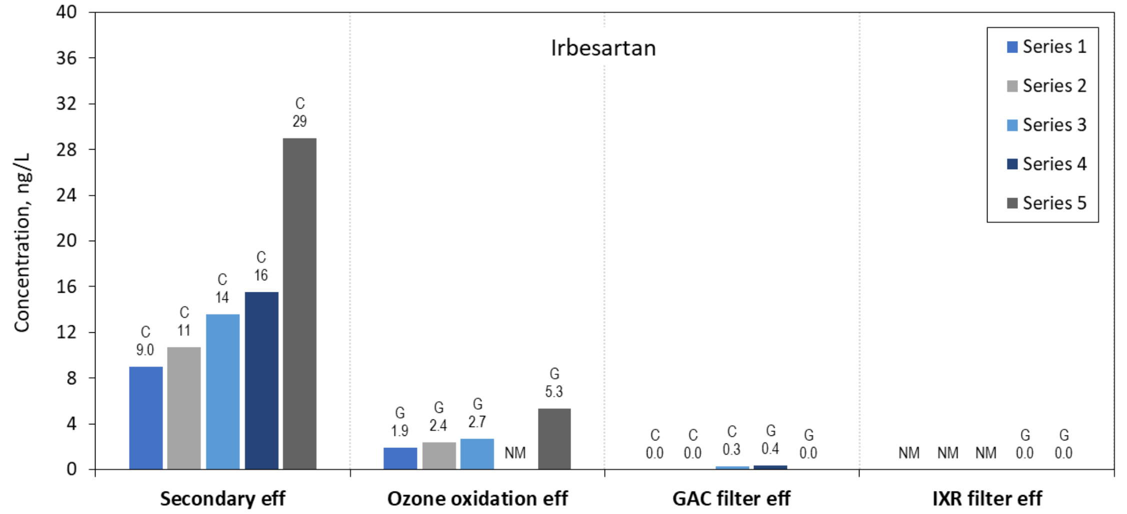


Figure 20. Concentrations of irbesartan at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample; NM = not measured.

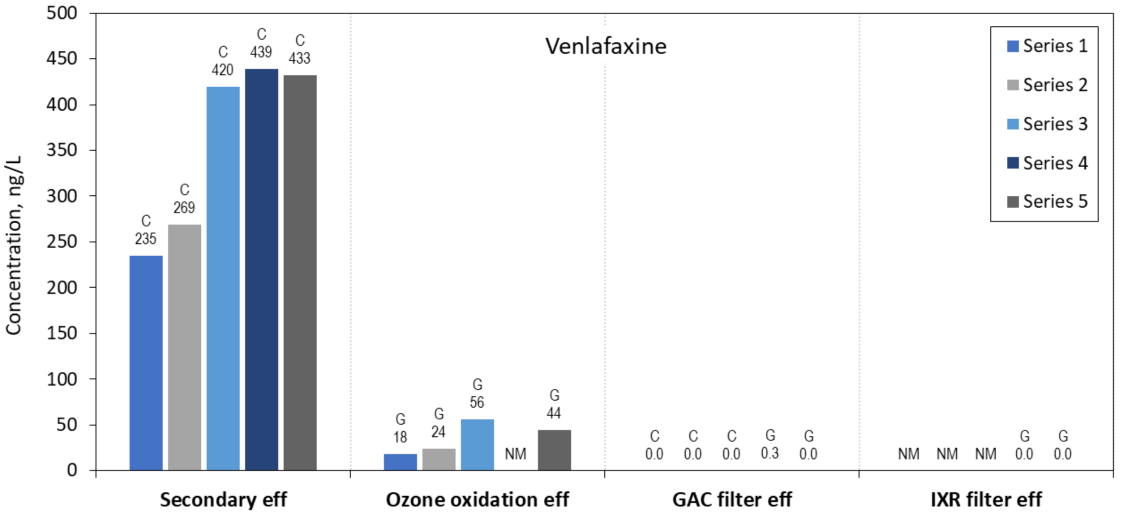


Figure 21. Concentrations of venlafaxine at different stages of wastewater treatment Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample; NM = not measured.

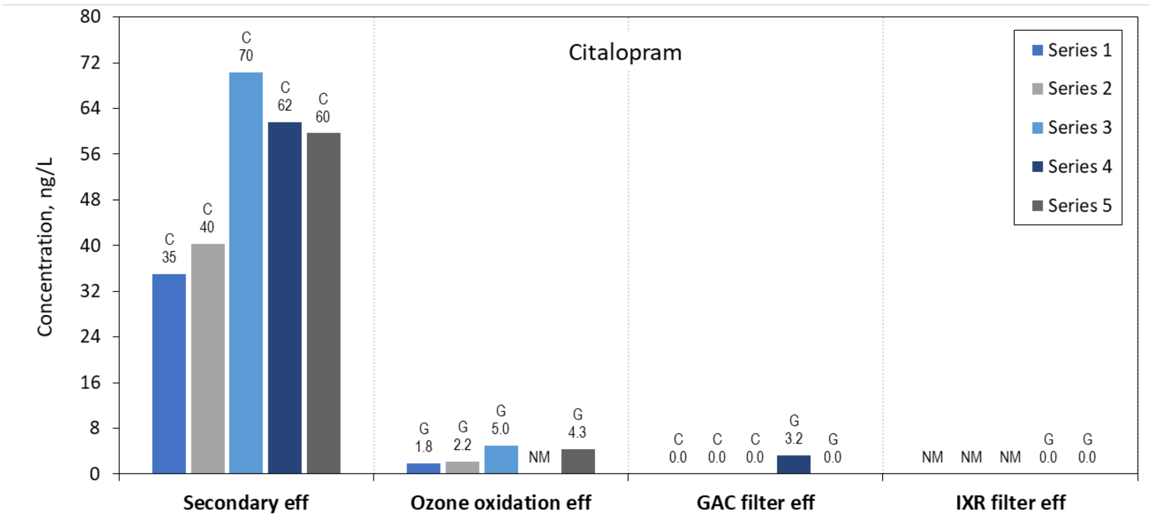


Figure 22. Concentrations of citalopram at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample; NM = not measured.

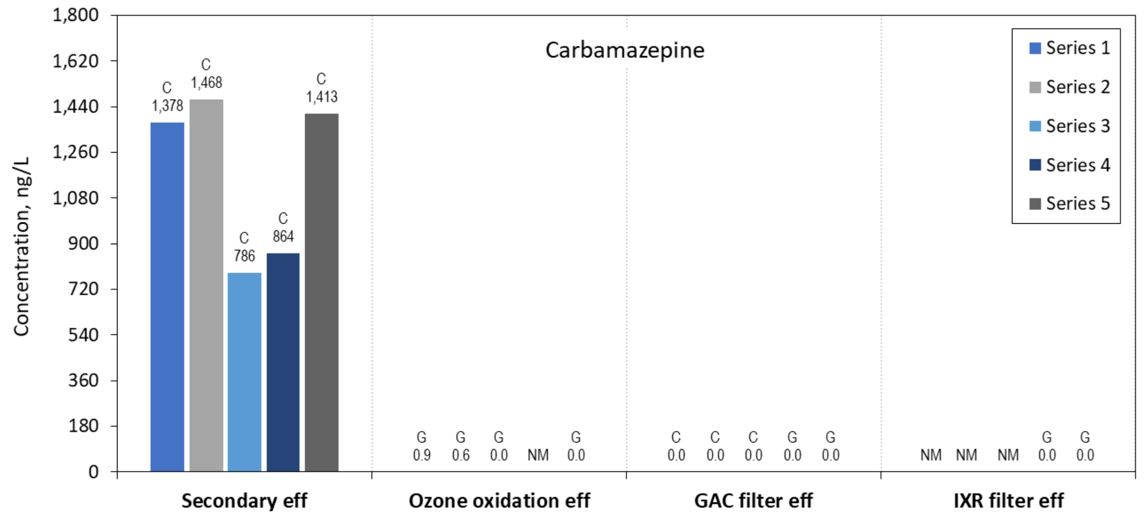


Figure 23. Concentrations of carbamazepine at different stages of wastewater treatment Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample; NM = not measured.

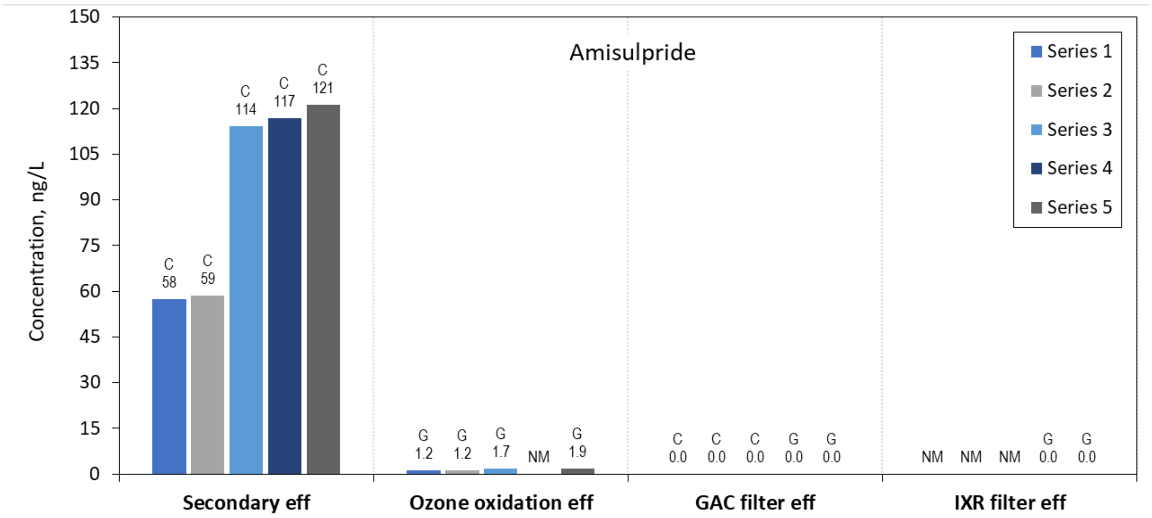


Figure 24. Concentrations of amisulpride at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample; NM = not measured.

As expected, the obtained results confirm very high efficiency of pharmaceutical removal by the combination of ozonation and GAC filtration. Ozonation alone achieved a high removal efficiency ranging from 61% to 100%, depending on the specific compound (Figure 25). After combined ozonation and GAC filtration, the removal efficiency was significantly higher, from 89% to 100% (Figure 26). For most compounds, a 100% removal was observed in all measurement series. The application of IX filtration following combined ozonation and GAC filtration resulted in complete removal of all pharmaceuticals (Figure 27).

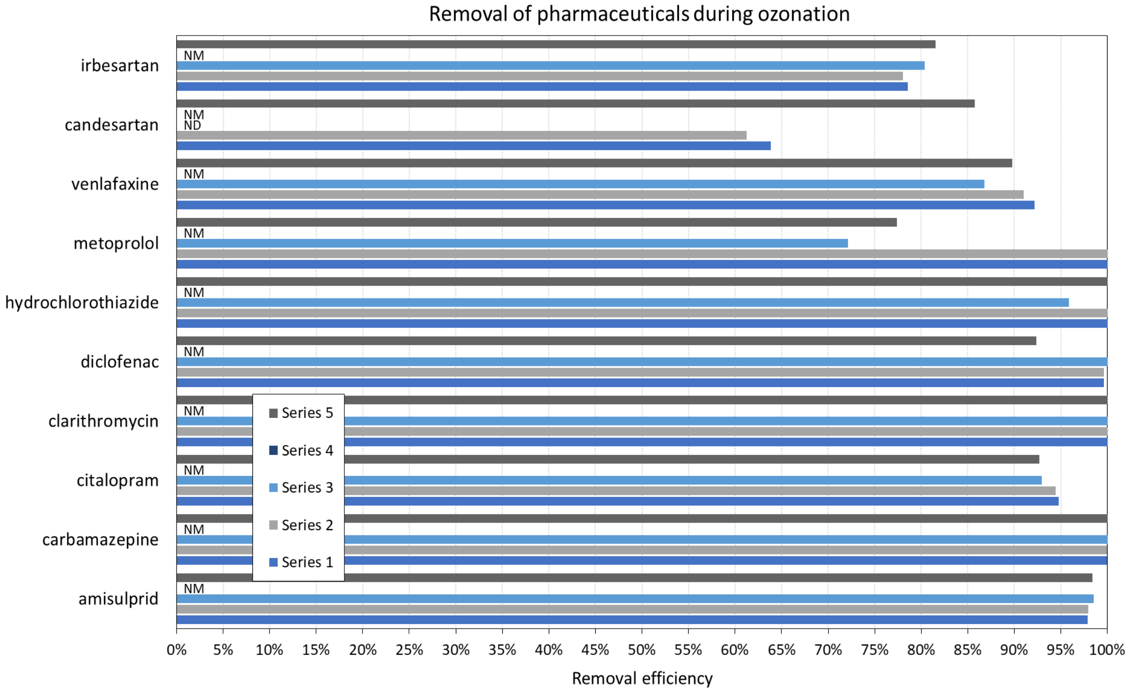


Figure 25. Removal efficiency of pharmaceuticals after ozonation. C = 24-hour composite sample. G = grab sample; NM = not measured; ND = not detected.

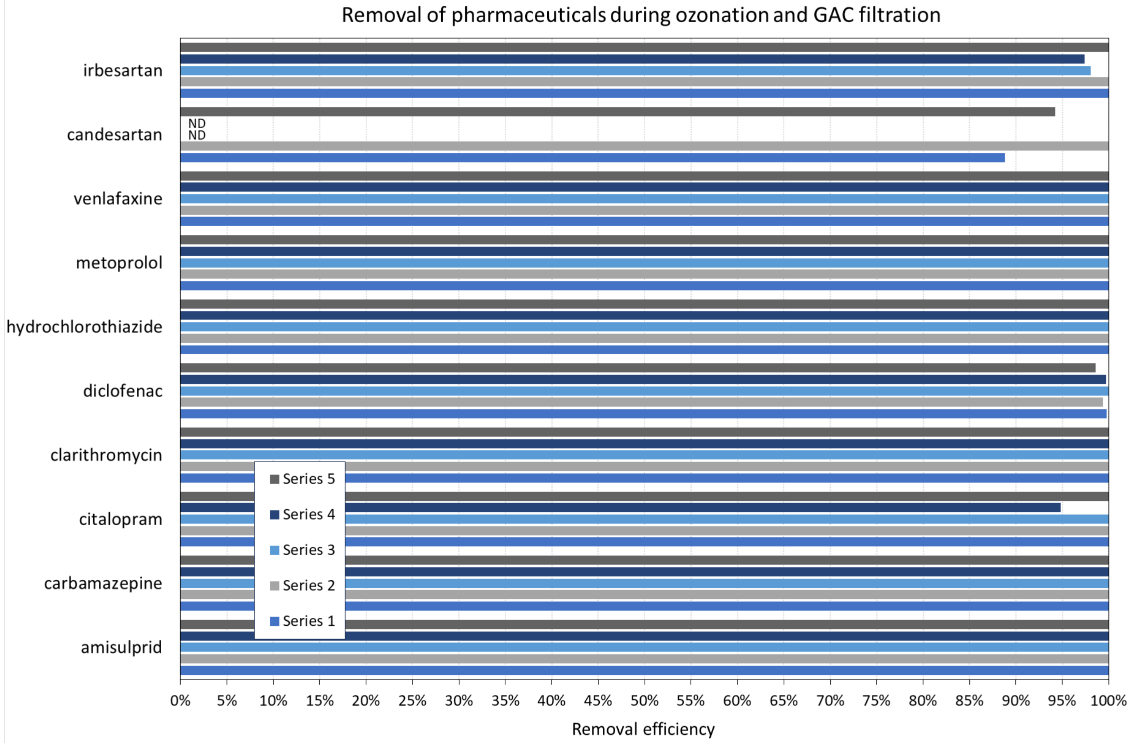


Figure 26. Removal efficiency of pharmaceuticals after combination of ozonation and GAC filtration. C = 24-hour composite sample; G = grab sample; ND = not detected.

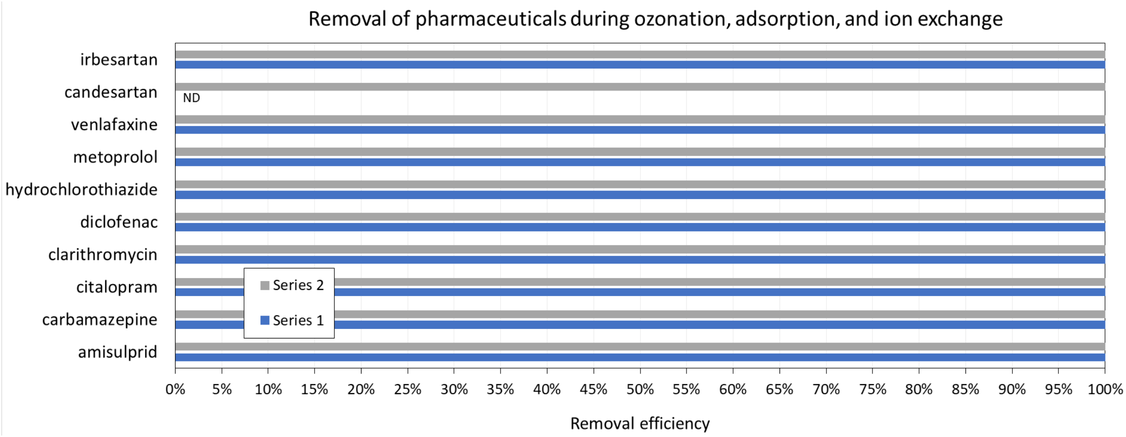


Figure 27. Removal efficiency of pharmaceuticals after combination of ozonation, GAC filtration and IX filtration. C = 24-hour composite sample; G = grab sample; ND = not detected.

Removal of herbicides

Herbicides are chemicals used to manage or eliminate unwanted vegetation. Commonly applied in agriculture and urban landscaping, they can enter water systems through surface runoff, leaching, or industrial discharge. The herbicides analysed during the pilot test, i.e. terbutryn and isoproturon, are selective herbicides widely used in agriculture to control broadleaf and grassy weeds. Terbutryn is also applied as an aquatic herbicide for managing submerged and floating weeds, as well as algae, in water bodies. Belonging to the triazine and phenylurea chemical classes respectively, both compounds are known for their high environmental persistence and mobility, which makes them significant contaminants in water systems. They pose risks to aquatic ecosystems and drinking water quality. Therefore, their removal from wastewater is essential to prevent ecological disruption and ensure compliance with water quality standards.
Effective treatment techniques include activated carbon adsorption, AOPs, and membrane filtration (Saleh et al., 2020).

The measured concentrations of terbutryn varied from 30 ng/L to 50 ng/L (Figure 28). In all sampling series, terbutryn was completely removed by ozonation followed by activated carbon adsorption, while ozonation alone resulted in removal efficiencies between 66% and 100%. Isoproturon was detected at significantly lower concentrations, i.e. below 0.9 ng/L, compared to terbutryn and was completely removed from wastewater by ozonation alone (Figure 29).

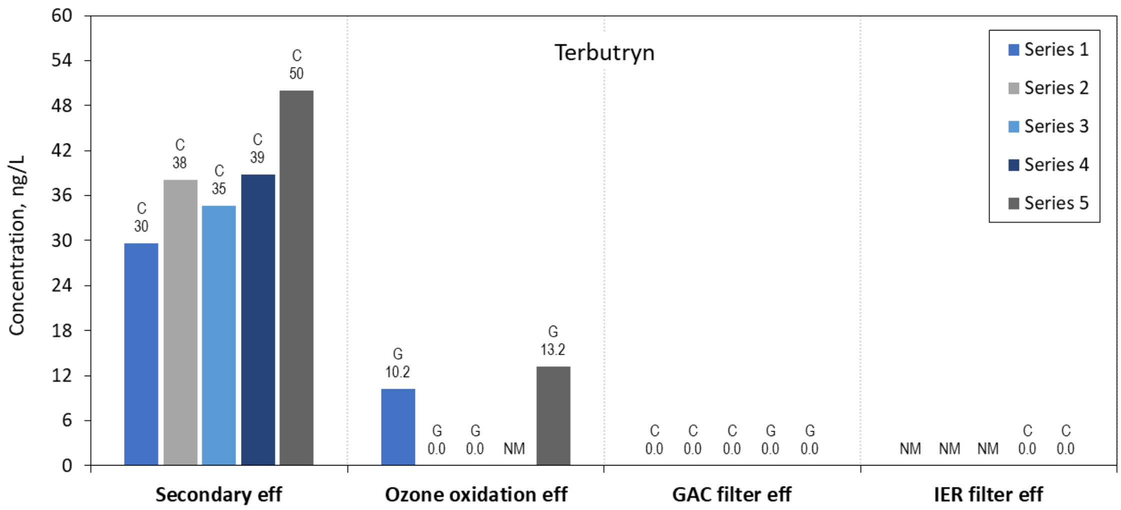


Figure 28. Concentrations of terbutryn at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample; NM = not measured.

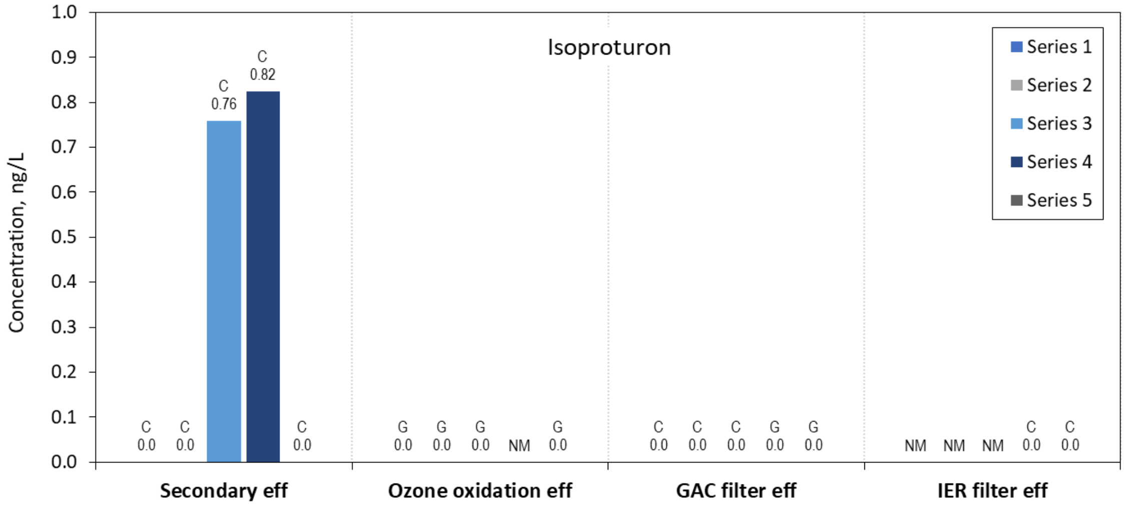


Figure 29. Concentrations of isoproturon at different stages of wastewater treatment. Process parameters: ozone dose 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample; NM = not measured.

Removal of 4-MBT and 6-MBT

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 de-icing 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 from wastewater can be achieved using AOPs, activated carbon adsorption, membrane filtration, or electrochemical treatment (Ferre et al., 2025).

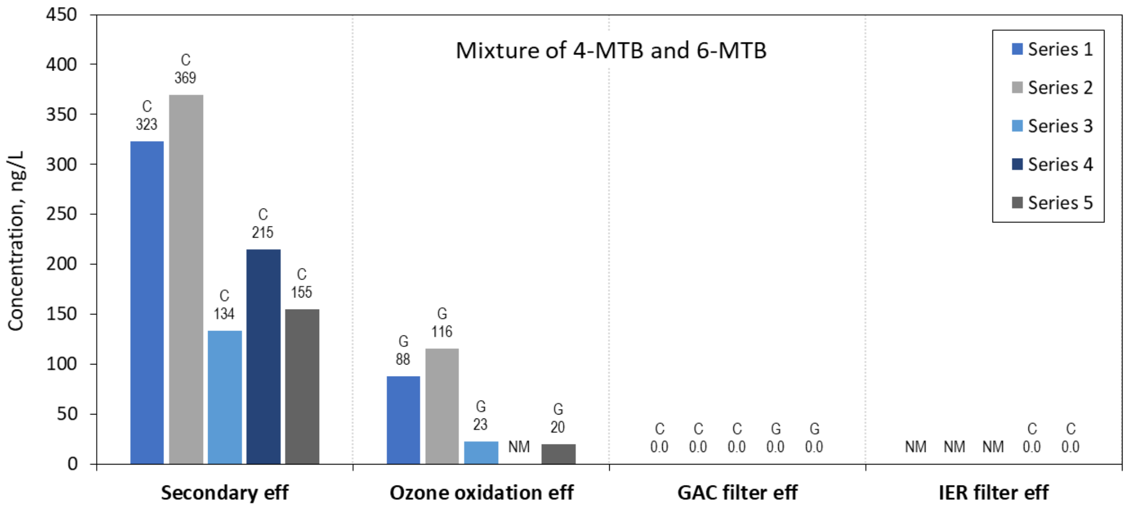


Figure 30. Concentrations of mixture of 4-MTB and 6-MTB at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample; NM = not measured.

The detected concentrations of the sum of 4-MBT and 6-MBT in the secondary effluent ranged from 134 ng/L to 369 ng/L (Figure 30). The removal efficiency of 4-MBT and 6-MBT during the ozonation process alone varied from 69% to 87%. After the combined ozonation and activated carbon adsorption, removal reached 100% in all sampling series.

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 water, grease, oil, stain, and heat. 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 (Ahrens et al., 2014).

PFAS are increasingly recognized as a major environmental and public health concern across the European Union. In response, the revised UWWTD introduces important new provisions to address PFAS, particularly in the context of their discharge into sensitive environments. The UWWTD requires mandatory monitoring of PFAS at the inlets and outlets of urban WWTPs in agglomerations of 10,000 PE or more, when the treated wastewater is discharged into catchment areas used for drinking water abstraction. This targeted approach focuses efforts where the risk of human exposure through drinking water is highest.

The directive also expands the scope of monitoring to include a broad range of PFAS compounds, going beyond a narrow subset. This shift acknowledges the diversity and persistence of PFAS as a chemical group and supports better-informed risk assessments. By 2027, the European Commission is expected to establish standardized methods for measuring both “PFAS Total” and “Sum of PFAS” in wastewater. Member States will have the flexibility to apply one or both parameters, aligning monitoring practices with national priorities and technical capabilities. These developments mark a significant step toward controlling PFAS emissions at their source and protecting both environmental and public health.

Several treatment technologies, such as GAC filters, IX resins, and reverse osmosis, have shown promise in the removal of PFAS. Thermal destruction and AOPs are emerging technologies aimed at breaking down PFAS, though they are often costly and still under development (Sanzana et al., 2025).

Out of the PFAS20 analysed during the pilot test, only six – PFBA, PFBS, PFPeA, PFHxA, PFHxS, and PFOA – were detected in the wastewater samples. It should be emphasised that the measured PFAS concentrations in the wastewater entering the pilot plant throughout the entire pilot testing period were very low, ranging from 1.0 to 5.6 ng/L. The concentrations of individual PFAS at different stages of wastewater treatment are presented in Figures 31 – 36.

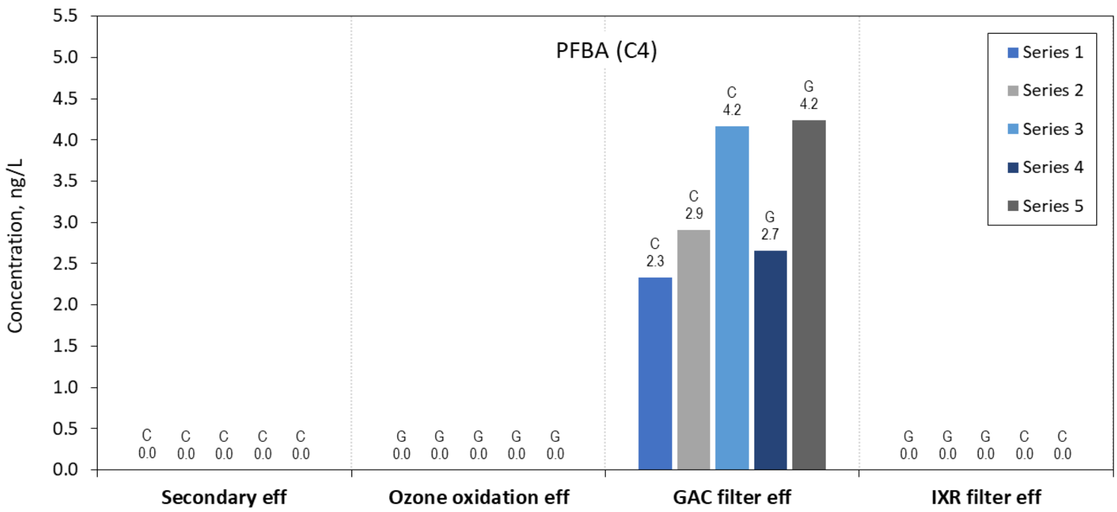


Figure 31. Concentrations of PFBA at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample.

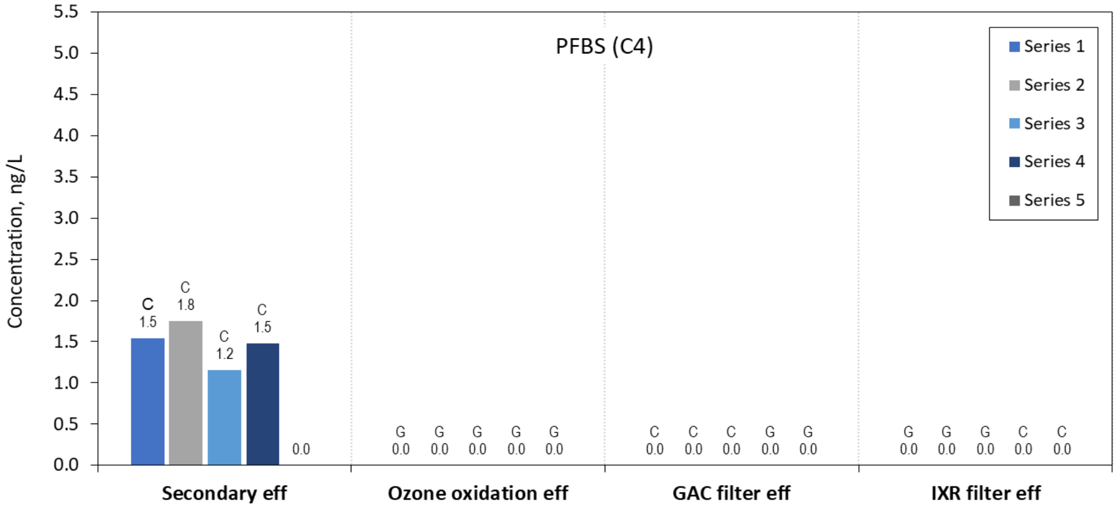


Figure 32. Concentrations of PFBS at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample.

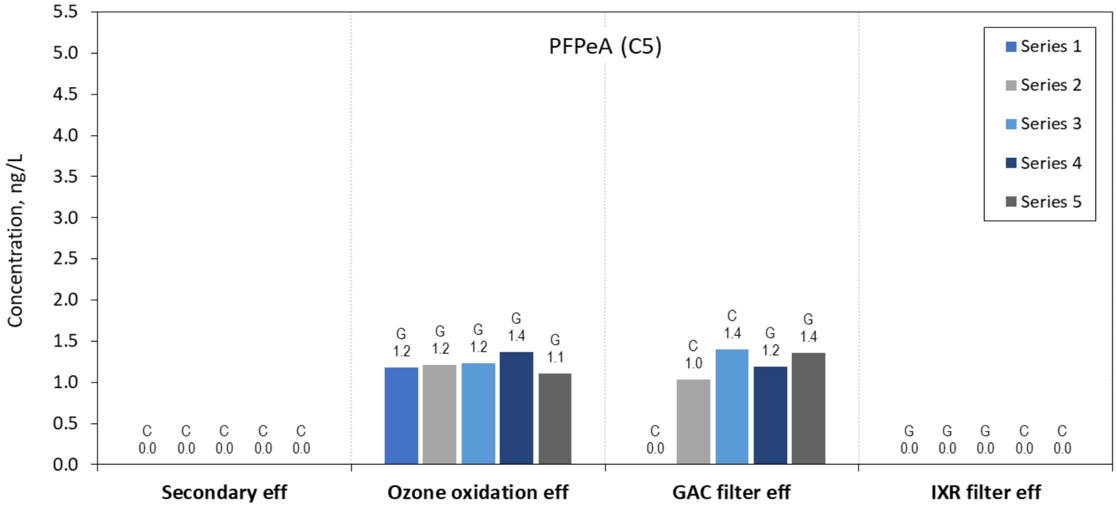


Figure 33. Concentrations of PFPeA at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample.

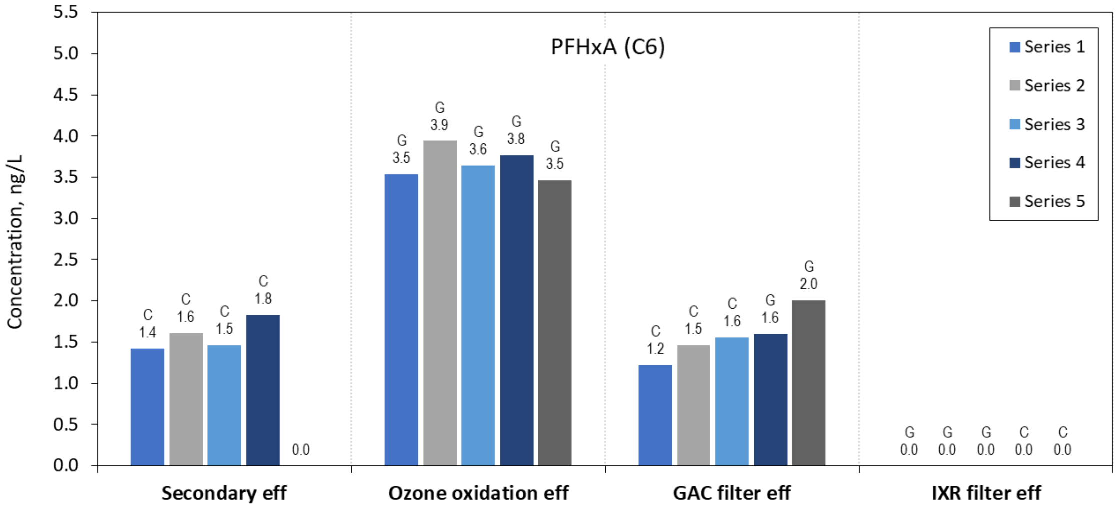


Figure 34. Concentrations of PFHxA at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample.

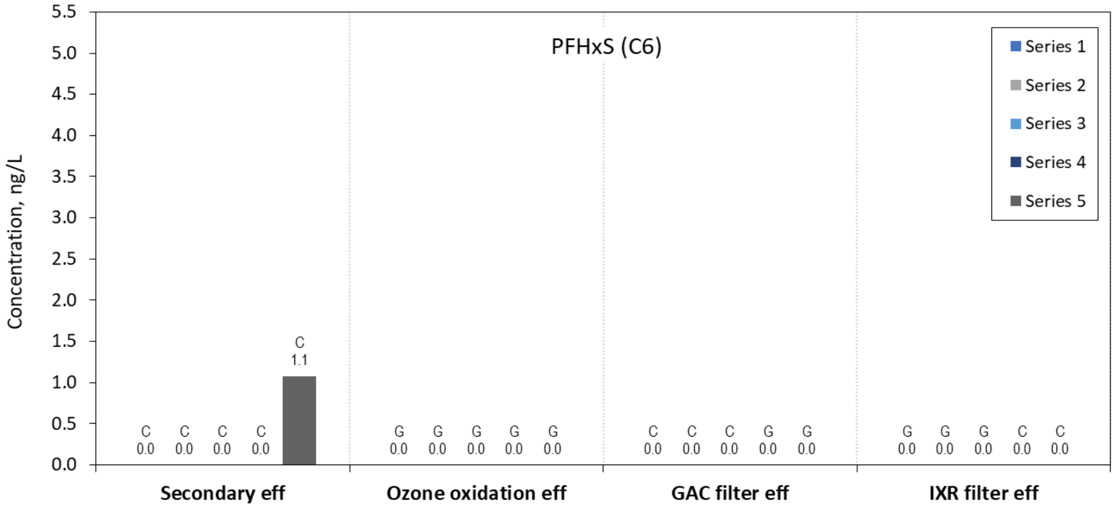


Figure 35. Concentrations of PFHxS at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample.

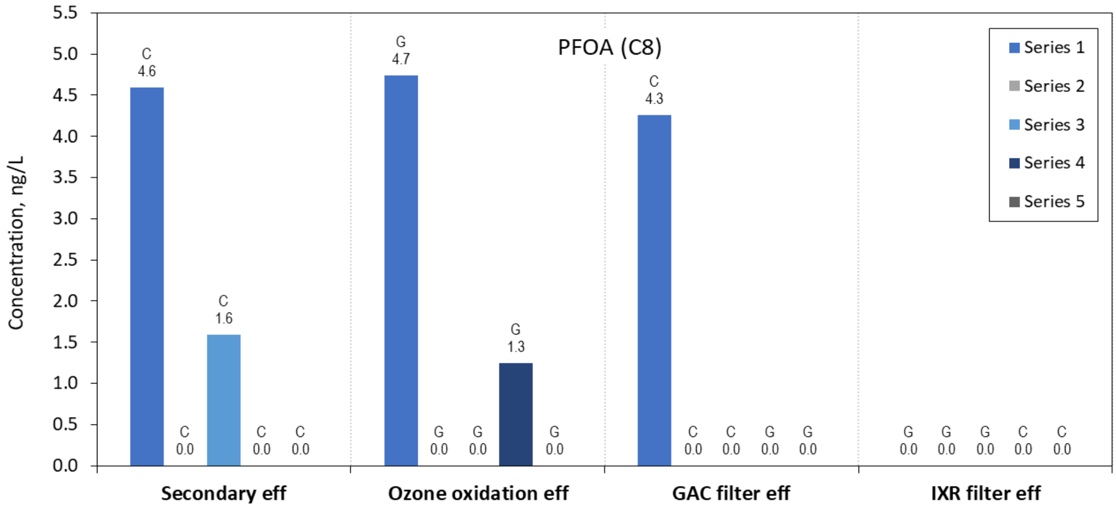


Figure 36. Concentrations of PFOA at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample.

The removal efficiency of PFAS during combined ozonation, GAC filtration and IX filtration was 100% in each sampling series. However, assessing PFAS removal at the earlier treatment stages, i.e. after ozonation and GAC filtration, was not possible, as certain PFAS compounds, i.e. PFBA and PFPeA, appeared only after these processes (Figure 31 and 33). These compounds were not detected in the secondary effluent or in the ozone oxidation effluent. Moreover, the concentration of PFHxA increased after ozonation (Figure 34).

As shown in Figure 37 and Figure 38, the sum of short-chain PFAS increases gradually after ozonation and GAC filtration, while the sum of long-chain PFAS remains relatively constant. This may be explained by the partial oxidation of PFAS (Gagliano et al., 2020; Trojanowicz et al., 2018), leading to an increase in short-chain PFAS formed from long-chain PFAS not included in the laboratory analysis. The degradation of PFAS is primarily driven by highly reactive hydroxyl radicals generated during ozone decomposition. Furthermore, one of the most commonly detected PFAS after ozonation of wastewater is PFHxA and PFBS (Pisarenko et al., 2025). Activated carbon can potentially accelerate this process when combined with ozone, acting as a catalyst that enhances the formation of reactive oxygen species (Sánchez-Polo et al., 2005). Additionally, the composition of the wastewater matrix may promote the generation of various radicals during ozone exposure. These species can attack the strong carbon-fluorine bonds, resulting in the formation of shorter-chain PFAS. The extent of PFAS degradation depends on factors like types of PFAS compounds present in wastewater, ozone concentration, reaction time, pH, and temperature.

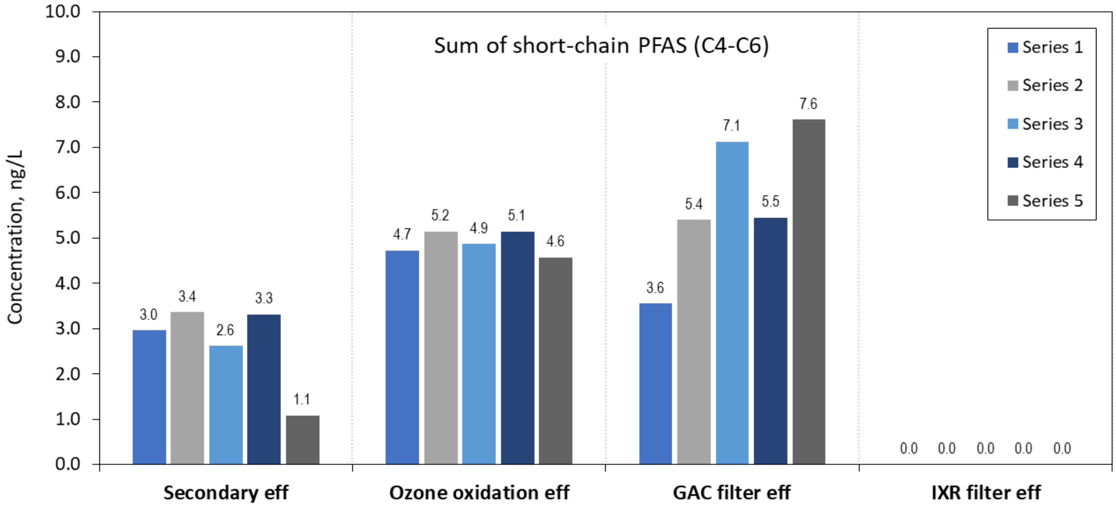


Figure 37. Sum of short-chain PFAS at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample.

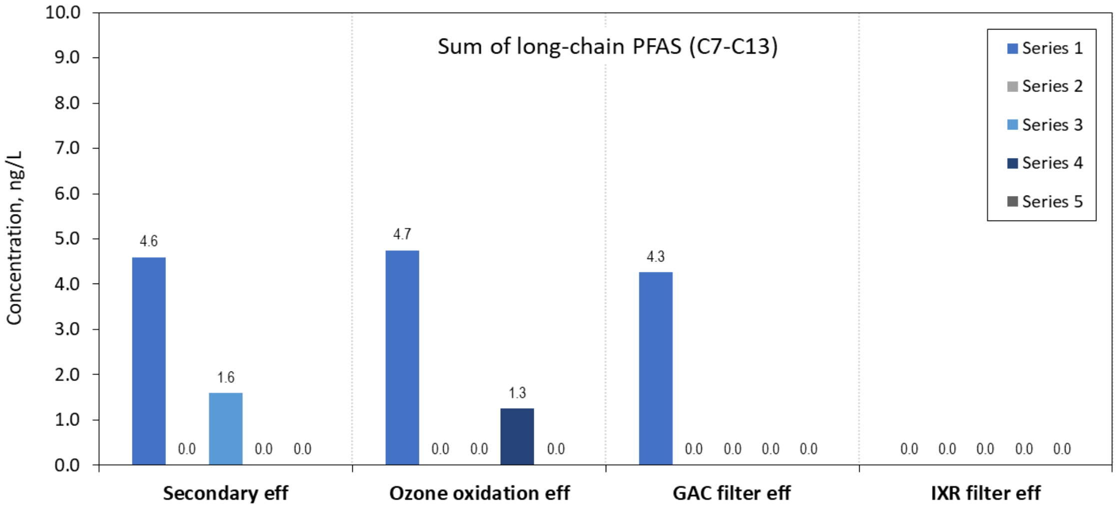


Figure 38. Sum of long-chain PFAS at different stages of wastewater treatment. Process parameters: ozone dose of 1,0 mg O_3/mg DOC (series 1, 2, 4, 5) and 1,2 mg O_3/mg DOC (series 3), 30 min ozone contact time, 20 min EBCT of GAC, and 30 min EBCT of IXR. C = 24-hour composite sample; G = grab sample.

Because partial oxidation may transform PFAS not included in laboratory analyses into compounds that are part of the monitored group, the selection of PFAS types and the number of compounds measured in wastewater samples is critical for an accurate assessment of their removal. Given that PFAS encompass a wide range of compounds, focusing analysis on only a limited number, e.g., 24 or 40, could overlook important compounds, making it insufficient to fully evaluate removal efficiency. Accurate evaluation of PFAS removal requires analytical methods capable of broadly detecting a wide range of PFAS and measuring their total concentration, particularly when AOPs are used to treat OMPs.

The U.S. Environmental Protection Agency (US EPA) has published Method 1621, "Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC)", that offers fast and reliable screening for organic fluorine, setting a new standard in analytical precision. The method measures the aggregate concentration of organofluorines (molecules with a carbon-fluorine bond). When it comes to wastewater, the most common sources of organofluorines are PFAS and non-PFAS fluorinated compounds such

as certain pesticides and pharmaceuticals. The method tells the user that organofluorines are present but cannot identify which specific organofluorines are present. The strength of the method is that it can broadly screen for thousands of known PFAS compounds at the part-per-billion level in water samples (US EPA, 2024).
The EPS's Office of Water led a multi-laboratory validation study of Method 1621. The results of the validation study were used to finalize the method and develop formal performance criteria. However, the use of Method 1621 is not compulsory at the national level in the U.S. until it has been formally adopted by the US EPA through rulemaking.

CONCLUSIONS

Pilot testing is an essential step in the development and implementation of a full-scale quaternary treatment in wastewater treatment systems. This advanced treatment, which typically includes processes such as advanced oxidation, activated carbon adsorption, membrane filtration, or ion exchange, is designed to remove residual OMPs that remain after primary, secondary, and tertiary treatments. Given the complexity and cost associated with these technologies, pilot testing plays a critical role in ensuring their effectiveness, feasibility, and sustainability before full-scale implementation.
A pilot system enables the determination and adjustment of key operational parameters, such as chemical dosage, contact time, and hydraulic loading rates, as well as the evaluation of the performance of proposed treatment technologies under actual site-specific conditions. This allows for process optimization tailored to the specific wastewater matrix, which is crucial for achieving the desired removal efficiencies and ensuring consistent treatment results. In addition to performance assessment, pilot testing provides valuable empirical data that inform and validate the design of full-scale systems. Accurate data on removal efficiencies and operational parameters support sound engineering decisions related to equipment sizing, system layout, and process control. This significantly reduces the risk of design flaws, operational inefficiencies, or costly modifications after full-scale implementation.

Pilot testing carried out at the Wschód WWTP in Gdańsk confirmed the high effectiveness of combined cloth filtration, ozonation and activated carbon filtration in the removal of organic micropollutants. Among the tested combinations of ozone oxidation and GAC filtration parameters, an ozone dose of 10 mg O_3/L, an ozone contact time of 30 minutes, and an EBCT of 20 minutes for GAC filter were identified as the optimal conditions for OMP elimination. Under these conditions, micropollutants regulated by the UWWTD were removed with efficiencies ranging from 89% to 100% after the combination of ozonation and GAC filtration. The application of IX filtration with a 30-minute contact time, following GAC filtration, resulted in the complete removal of all monitored micropollutants.

Ozonation alone achieved a high removal efficiency of pharmaceuticals ranging from 61% to 100%, depending on the specific compound. After the combination of ozonation and GAC filtration, the removal efficiency of pharmaceuticals was significantly higher, from 89% to 100%.
Herbicides were completely removed by ozonation followed by GAC filtration, whereas ozonation alone resulted in removal efficiencies between 66% and 100%.
Removal of 4-MBT and 6-MBT during ozonation alone ranged from 69% to 87%, while after the combined ozonation and GAC filtration reached 100%.

PFAS removal was 100% following combined ozonation, GAC, and IX filtration. However, removal at earlier treatment stages could not be confirmed, as some PFAS compounds appeared only after ozonation or GAC filtration likely due to the partial oxidation of long-chain PFAS into shorter-chain forms. These transformations can produce PFAS not initially present or included in the analysis, making the selection of appropriate target compounds critical for accurate removal assessment. Therefore, to reliably evaluate PFAS removal, analytical methods that broadly screen a wide range of PFAS and quantify their aggregate concentration should be employed, especially when AOPs are used to treat OMPs.

Due to the short pilot testing period and the limited number of wastewater samples analyzed, it is recommended to conduct additional supplementary pilot tests to gather more data on the removal efficiency of OMPs.

Although constructing a mobile pilot plant involves high initial costs, it is a highly cost-effective tool to support upgrading and development of numerous wastewater treatment plants without incurring the high costs of constructing their own pilot installation.

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