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MICROPOLLUTANTS IN COASTAL WASTEWATER: COMPOSITION, DYNAMICS, AND REMOVAL BY OZONATION

DOCTORAL DISSERTATION

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Supervisor

Dr. Mindaugas ŽILIUS (Klaipėda University, Natural Sciences, Ecology and Environmental Sciences – N 012).

Advisor

Assoc. Prof. Dr. Zita Rasuolė GASIŪNAITĖ (Klaipėda University, Natural Sciences, Ecology and Environmental Sciences – N 012).

The doctoral dissertation is defended at the Board of Klaipėda University in Ecology and Environmental Sciences:

Chairman

Assoc. Prof. Dr. Darius DAUNYS (Klaipėda University, Natural Sciences, Ecology and Environmental Sciences – N 012);

Members:

Assoc. Prof. Dr. Olga ANNE (Klaipėda University, Natural Sciences, Ecology and Environmental Sciences – N 012);
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Prof. Habil. Dr. Aneta LUCZKIEWICZ (Gdańsk University of Technology, Poland, Technological sciences, Environmental engineering – T 004);
Dr. Martynas TICHONOVAS (Kaunas University of Technology, Technological sciences, Environmental engineering – T 004).

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Address: Universiteto alley 17, LT-92294, Klaipėda, Lithuania.

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Agnė JUCYTĖ-ČIČINĖ

MIKROTERŠALAI PRIEKRANTĖS VALYKLŲ NUOTEKOSE: SUDĖTIS, KAITA IR PAŠALINIMAS TAIKANT OZONAVIMĄ

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Vadovas

dr. Mindaugas ŽILIUS (Klaipėdos universitetas, gamtos mokslai, ekologija ir aplinkotyra – N 012).

Mokslinis konsultantas

doc. dr. Zita Rasuolė GASIŪNAITĖ (Klaipėdos universitetas, gamtos mokslai, ekologija ir aplinkotyra – N 012).

Daktaro disertacija ginama Klaipėdos universiteto Ekologijos ir aplinkotyros mokslo krypties taryboje:

Pirmininkas

doc. dr. Darius DAUNYS (Klaipėdos universitetas, gamtos mokslai, ekologija ir aplinkotyra – N 012);

Nariai:

doc. dr. Olga ANNE (Klaipėdos universitetas, gamtos mokslai, ekologija ir aplinkotyra – N 012);

doc. dr. Tatjana PAULAUSKIENĖ (Klaipėdos universitetas, technologijos mokslai, aplinkos inžinerija – T 004);

prof. habil. dr. Aneta LUCZKIEWICZ (Gdansko technologijų universitetas, Lenkija, technologijos mokslai, aplinkos inžinerija – T 004);

dr. Martynas TICHONOVAS (Kauno technologijų universitetas, technologijos mokslai, aplinkos inžinerija – T 004).

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Adresas: Universiteto al. 17, LT- 92294, Klaipėda, Lietuva.

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Abstract

Micropollutants, including steroid hormones, phthalate esters, pharmaceutical residues, and polycyclic aromatic hydrocarbons, are by-products of routine human activities. Many of these compounds have endocrine disrupting potential and frequently enter the aquatic environment in measurable quantities, posing risks to organisms and overall ecosystem health. In coastal areas, high seasonal human activity can lead to wastewater generation and pollution beyond the designed capacity of the local wastewater treatment plants (WWTPs). This may result in the increased discharge of micropollutants into the adjacent coastal environments.

This study assessed the impact of seasonal population fluctuations in the Small (Nida) and Large (Palanga) seaside resorts on wastewater quality, nutrients and micropollutants (phthalates and estrogenic potential) before and after treatment in their WWTPs. Secondly, it evaluated the effect of the temporary large public event (Sea Festival) on the same parameters, including individual micropollutant groups of phthalates, hormones (estrone (E1), beta-estradiol (E2)), pharmaceuticals (carbamazepine (CBZ), venlafaxine (VEN)) and polycyclic aromatic hydrocarbons (PAH) in the local WWTP. Finally, the potential of ozonation to reduce persistent pharmaceuticals (CBZ and VEN) and overall pollution in biologically treated wastewater from three coastal WWTPs of Nida, Palanga, and Klaipėda, subjected to different anthropogenic pollution sources, was investigated.

Resident population fluctuations related to seasonal tourism and temporary public event influenced wastewater quantity, quality, and micropollutant dynamics in coastal WWTPs. Pollution loads, including micropollutants, increased ~ 2–5 fold during the high season (June–August) and 2–3 fold during a temporary event. Additionally, as revealed by the seasonal study, an association was detected for tourism indicators with phthalates and estrogenic potential. During tourist season, the average wastewater flow increased by ~200%, compared to the 16% increase during the temporary event. Despite increased loads, all coastal WWTPs effectively reduced conventional pollutants by 65–100%. Nevertheless, nutrient and estrogenically active compound removal was occasionally lower during June–August, particularly in the Small resort WWTP. High overall micropollutant removal rates (74%–100%) were achieved; however, E1 and E2 exceeded their predicted no-effect concentrations, resulting in high environmental Risk Quotient values. Although pharmaceutical dynamics were not affected by the temporary public event, conventional treatment was insufficient to reduce them. As a result, CBZ and VEN persisted at high Risk Quotient values in the effluent discharged to the Baltic Sea. To address this, an ozonation experiment was conducted showing that 5 min of ozonation substantially reduced CBZ and VEN concentrations in biologically treated wastewater from coastal WWTPs, regardless of different pollution profiles.

Key Words

Seasonal tourism, public events, wastewater treatment plants, micropollutants, hormones, pharmaceuticals, polycyclic aromatic hydrocarbons, phthalates, ozonation

Reziumė

Mikroteršalai, įskaitant steroidinius hormonus, ftalatus, farmacinius junginius ir policiklinius aromatinius angliavandenilius (PAHs), yra įprasti šalutiniai antropogeninės veiklos produktai. Daugelis šių junginių pasižymi endokrininę sistemą trikdančiomis savybėmis ir į vandens aplinką dažnai patenka išmatuojamais kiekiais, keldami pavojų vandens ir bendrai ekosistemų sveikatai. Pajūrio zonose didelio intensyvumo sezoninė žmonių veikla gali lemti padidėjusį nuotekų susidarymą ir taršos apkrovas, viršijančias vietinių nuotekų valyklų projektinį pajėgumą. Dėl to gali padidėti mikroteršalų išleidimas į priekrantės aplinką.

Šiame tyrime vertintas Mažojo (Nidos) ir Didžiojo (Palangos) kurortų sezoninių gyventojų skaičiaus svyravimų poveikis nuotekų kiekiui ir kokybei jų nuotekų valyklose. Buvo nustatytos įprastinių teršalų, maistinių medžiagų ir mikroteršalų koncentracijos įskaitant ftalatus ir estrogeninį potencialą nuotekose prieš ir po valymo. Taip pat buvo įvertintas laikino didelio viešojo renginio (Jūros šventės) poveikis nuotekų kiekiui, sudėčiai bei kokybei įtraukiant papildomas atskiras mikroteršalų grupes: ftalatus, hormonus (estroną (E1), beta-estradiolį (E2)), vaistus (karbamazepiną (CBZ), venlafaksiną (VEN)) ir policiklinius aromatinius angliavandenilius (PAHs). Galiausiai buvo ištirtas ozonavimo potencialas siekiant sumažinti patvarius farmacinius junginius (CBZ ir VEN) bei bendrą taršą biologiškai išvalytose nuotekose iš trijų pajūrio nuotekų valyklų – Nidos, Palangos ir Klaipėdos, veikiamų skirtingų antropogeninių taršos šaltinių.

Su sezoniniu turizmu ir laikinu dideliu viešu renginiu susiję gyventojų skaičiaus svyravimai turėjo įtakos nuotekų kiekiui, kokybei ir mikroteršalų dinamikai pajūrio nuotekų valyklose. Taršos apkrovos, įskaitant mikroteršalus, sezono piko metu (birželis–rugpjūtis) padidėjo apie 2–5 kartus, o laikino renginio metu 2–3 kartus. Taip pat sezoninio tyrimo metu nustatytas ryšys tarp turizmo rodiklių ir ftalatų bei estrogeninio potencialo. Intensyvaus turizmo sezonu vidutinis nuotekų srautas padidėjo ~200 %, o laikino renginio metu – 16 %. Nepaisant padidėjusių apkrovų, visos pajūrio valyklos efektyviai sumažino įprastinių teršalų kiekį 65–100 %. Nepaisant to, maistinių ir estrogeninių medžiagų šalinimas birželio–rugpjūčio mėnesiais kartais sumažėjo, ypač Mažojo kurorto nuotekų valykloje. Nors bendras mikroteršalų pašalinimas buvo aukštas (74–100 %), E1 ir E2 viršijo nustatytas prognozuojamas poveikio nesukeliančias koncentracijas, todėl dominavo didelės ekologinės rizikos aplinkai koeficiento reikšmės. Nors laikinas renginys neturėjo įtakos farmacinių medžiagų dinamikai vietinėje valykloje, įprastinis valymas nesumažino jų koncentracijos. Dėl to į Baltijos jūrą išleidžiamose nuotekose liko didelės CBZ ir VEN koncentracijos taip pat aspkaičiuotos didelės ekologinės rizikos koeficiento vertės. Ozonavimo eksperimentas parodė, kad 5 minučių ozonavimo pakako ženkliai sumažinti venlafaksino ir karbamazepino koncentracijas biologiškai išvalytose nuotekose iš pajūrio nuotekų valyklų, nepaisant skirtingo antropogeninės taršos profilio.

Reikšmingi žodžiai

Sezoninins turizmas, masiniai renginiai, nuotekų valyklos, mikroteršalai, hormonai, farmacinės medžiagos, policikliniai aromatiniai angliavandeniliai, ftalatai, ozonavimas

Contents

1

Introduction

Coastal zones are unique ecosystems characterized by high complexity, productivity and biodiversity (Costanza et al., 2014; Barbier et al., 2011; Beck et al., 2001). They play a vital role in global economic growth, generating trillions of dollars annually through key sectors such as fisheries, tourism, and international shipping (Lakshmi et al., 2021). However, these areas are increasingly threatened by pollution from land-based activities and industrial processes (Jägerbrand et al., 2019; Tornero et al., 2016; Häder et al., 2020). Such pollution poses serious risks to the economic sustainability of aquaculture, coastal tourism, and biodiversity (HELCOM, 2019; Dodds et al., 2009). Seasonal and temporary surges in human activity, particularly mass tourism, further exacerbate the delivery of pollution to coastal environments (Rathi et al., 2021; Santos et al., 2022). These pressures are especially pronounced in the Baltic Sea region, one of the most polluted marine areas globally, due to its geographical isolation, limited water exchange, and continuous nutrient and persistent pollutant inputs from inland and anthropogenic sources (Kanwischer et al., 2022).

Coastal tourism, although economically vital and highly dependent on environmental quality, paradoxically drives anthropogenic pollution that undermines its sustainability. Its contribution to micropollutant loads to the environment remains both critical and largely overlooked. In the Baltic Sea region, coastal areas experience a substantial seasonal increase in tourist numbers (Ahmad et al., 2018), some resorts reporting more than a 140-fold increase during summer compared to their permanent population (Povilanskas & Armaitienė, 2010; Razma et al., 2025). Public events, including festivals, concerts, and sports competitions, also cause temporary surges in residential population (Gerrity et al., 2011; Jiang et al., 2014; Andriolo et al., 2023). For instance, during the Sea Festival in Klaipėda (Lithuania), situated in the South East Baltic region, the residential population increases up to 3-fold due to incoming visitors (Kraniauskas et al., 2018). This influx can increase the wastewater load and, consequently, the pollution level, often exceeding the capacity of local wastewater treatment plants (WWTPs) (Ahmad et al., 2018). Even under normal operating loads, traditional wastewater treatment technologies are not optimized to effectively remove certain micropollutants, such as pharmaceutical compounds and hormone residues, which often have endocrine-disrupting properties (Rathi et al., 2021). Recent studies indicate that population surges during peak tourism seasons contribute to higher nutrient discharges (Ji et al., 2024) and micropollutant concentration in wastewater (Phan et al., 2015; Jiang et al., 2014; Ştefănică et al., 2021; Lenart-Boroń et al., 2022). Despite growing awareness of these threats, the impact of population fluctuations on pollution dynamics in coastal WWTPs and their subsequent effects on treatment efficiency and pollutant delivery to coastal ecosystems remain poorly understood.

Micropollutants, particularly endocrine disruptors, such as plasticizers, hormones, pharmaceuticals, and polycyclic aromatic hydrocarbons (PAHs), pose significant risks to aquatic life and human health, potentially leading to cancer, reproductive disorders, and developmental abnormalities. Through accumulation and biomagnification, they may enter drinking water sources and the food web (Benjamin et al., 2017; Beck et al., 2006; Briciu et al., 2009; Zhang et al., 2011). In addition, rising micropollutant levels can also exacerbate eutrophication (Gul et al., 2022; Feijoo et al., 2023), a persistent issue in the Baltic Sea (Preisner et al., 2020). To address this, the attention is increasingly shifting to the implementation of advanced treatment technologies (Bourgin et al., 2018; Tang et al., 2020), which can effectively degrade persistent micropollutants before they enter surface water bodies. However, the practical application of alternative technologies, such as advanced oxidation processes, remains poorly researched, especially in coastal wastewater treatment plants.

The main objectives of this thesis were to evaluate the impact of seasonal population fluctuations on overall wastewater quality and micropollutant concentrations before and after treatment at WWTPs of coastal resorts with different population equivalent (PE). The thesis also examined how excessive pollution impacts conventional treatment processes and whether increased tourism in coastal areas may affect surrounding ecosystems. Furthermore, the thesis examined how a temporary event influences the overall quality and fluctuations in endocrine-disrupting micropollutants at a local WWTP before discharging them into the adjacent Baltic Sea coastal ecosystem. Finally, the thesis evaluated how advanced oxidation treatment, using ozonation, may reduce pharmaceutical contamination and enhance the quality of biologically treated wastewater from coastal WWTPs with different sources of anthropogenic impact. Understanding contamination levels of micropollutants and the tourism-driven pollution influence on conventional wastewater treatment systems is essential for improving management strategies to protect the ecological integrity of the Baltic Sea.

1.1. Aim, objectives and working hypotheses

The present study aims to assess the general wastewater quality, micropollutant composition, and dynamics at coastal WWTPs, with respect to residential population dynamics, and to evaluate the potential of advanced treatment technologies for specific micropollutant removal before discharging them into coastal ecosystems.

The following objectives were defined:

1. To evaluate whether and how seasonal tourism dynamics in coastal resorts influence the wastewater quality and micropollutant (EEQ, PAEs) levels before and after treatment at their WWTPs.
2. To assess the impact of a large temporary public event on the wastewater quality and micropollutant (pharmaceuticals, hormones, PAEs, and PAHs) levels before and after treatment at a coastal city WWTP.
3. To evaluate the potential of ozonation in removing pharmaceuticals from biologically treated wastewater with different anthropogenic impacts.

Hypotheses:

1. The seasonal population surge drives pollution increase, altering the composition and/or dynamics of micropollutants and general contaminants in wastewater. Consequently, elevated organic pollution may exceed the designed population equivalent capacity of coastal WWTPs, reducing treatment efficiency and increasing risks to coastal ecosystems.
2. A large public event temporarily increases wastewater pollution from the city to the coastal WWTP, impairing treatment efficiency and elevating risks to coastal ecosystems.
3. Ozone-based advanced oxidation treatment removes general pollution and pharmaceuticals (VEN, CBZ) similarly in biologically treated wastewater, irrespective of different anthropogenic activities (tourism, residential, or industry).

1.2. Novelty

This thesis examines the long-standing issue of the impact of seasonal tourism (i.e., population fluctuation) on coastal WWTPs discharging to different Baltic Sea compartments and the adjacent aquatic areas. It highlights the role of the resident population as a source of endocrine-disrupting micropollutants to the aquatic environment, an aspect that has received little attention so far. An important finding of this research was the unique non-linear relationship between tourism indicators and estrogenic activity, alongside a strong linear correlation observed with plasticizers, nutrients, and general water quality parameters. This indicates the significant impact of population on the transfer of specific micropollutants to coastal WWTPs, thereby requesting targeted monitoring and mitigation.

To address the complexity of pollutant behavior and treatment potential, this study integrated multiple complementary methodologies, including advanced analytical measurements, biochemical assays, microbiological characterization, and advanced oxidation (AO) processes. The simultaneous application of these diverse techniques enabled an in-depth, multidimensional evaluation of pollutant dynamics and treatment feasibility, representing a novel and comprehensive monitoring and assessment framework. For the first time, mass balance calculations were applied to specific coastal WWTPs to estimate the total pollutant loads discharged into the Baltic Sea and the Curonian Lagoon. This approach also allowed the assessment of the coastal WWTPs pollution management efficiency under varying tourism pressures, providing essential data for planning treatment capacity, regulatory compliance, and adaptive management. Furthermore, ecological risk assessment was carried out, using predicted no-effect concentrations (PNEC) and risk quotient (RQ) metrics. This enables identification and prioritization of micropollutants based on their calculated risk scores for monitoring and regulation, which helps to preserve the local ecosystem, ensuring compliance with environmental quality standards.

Unlike many previous studies, this research covers an extended analytical approach to assess the impact of tourism, incorporating a wide range of parameters, from conventional quality indicators and nutrients to a complex mixture of micropollutants, including plasticizers, hormones, farmaceuticals, and PAHs. Notably, the dynamics of these micropollutants have not been previously explored in coastal WWTPs during seasonal and temporary gatherings. An extensive dataset was collected from two coastal resort WWTPs with PE of 6,700 and 36,000 over the year, providing detailed insights into the temporal variability of these pollutants in response to fluctuating tourism pressures. This study is a foundation for developing evidence-based management strategies and a policy framework for coastal WWTPs.

While ozone application to remove micropollutants from experimental wastewater is a common research topic, this study evaluated its performance under real conditions using effluent samples from three WWTPs exposed to varying levels and types of anthropogenic pressure. These findings offer practical insights for coastal WWTPs considering advanced treatment solutions.

1.3. Scientific and applied significance of the results

An environmental risk assessment based on calculated risk scores revealed that estrogenic compounds and pharmaceuticals caused persistent environmental risk in effluents from coastal WWTPs. The highest risk scores, consistently classified as "high risk" (RQ>1), were associated with estrogenic compounds of 17 beta-estradiol (E2), estrone (E1), and estrogenic equivalent (EEQ). The seasonal dynamic of estrogenic compounds depended on population fluctuation, highlighting the potential human threat to the aquatic environment. Therefore, further studies on the acute and long-term ecological effects of chronic exposure across various marine environments are recommended, especially in the areas affected by larger WWTPs.

The updated Urban Wastewater Treatment Directive (UWWTD), effective from 1 January 2025, requires EU Member States to monitor and reduce 13 priority micropollutants in treated wastewater and mandates quaternary treatment for WWTPs >100,000 PE by 2040, with a target of 80% average removal efficiency. This study evaluated two UWWTD-listed pharmaceuticals, carbamazepine (CBZ) and venlafaxine (VEN), both of which increased in concentration after biological treatment, indicating high persistence. However, the ozonation treatment applied in the experiment described in this thesis enabled the complete removal of CBZ and VEN within 5 min of contact time. These results demonstrate the feasibility of implementing advanced quaternary treatment in three coastal WWTPs with varying anthropogenic pressures, including tourism. While CBZ is not yet included on the Water Framework Directive (WFD) "Watch List", a gap we recommend addressing for more comprehensive monitoring from WWTPs to the receiving waters.

This study presents the first national mass-balance estimation in coastal WWTPs, discharging to the Baltic Sea and Curonian Lagoon, of endocrine-disrupting contaminants included in the EU Water Framework Directive (WFD), surface water "Watch List", and the list of priority hazardous substances. In addition, a novel biochemical method using genetically modified yeast cells was used to assess total estrogenicity. This approach proved cost-effective, less labour-intensive, and more time-efficient than the advanced analytical techniques, offering substantial potential for routine monitoring.

This approach provides a foundation for monitoring programs to include specific micropollutants, such as hormones and pharmaceuticals, and other hazardous substances identified under the UWWTD and WFD, in the effluent and receiving waters. Additionally, conducting comparable pilot-scale and on-site tests is advised to verify ozonation effectiveness in removing priority endocrine-disrupting micropollutants in other national WWTPs with a PE < 100,000.

1.4. Scientific approval

The results of this study were presented at the following conferences:

1. 19th International Conference on Waste Management, 3–4 April 2025, Venice (Italy). "Ozonation as an effective method to remove pharmaceuticals from biologically treated wastewater of different origin" (Oral).
2. 9th International Conference on Environmental Pollution, Treatment, and Protection, 14–16 March 2024, London (UK). "Mass event influence on micropollutant composition and loads before and after treatment in the coastal waste water treatment plant" (Poster).
3. 14th Baltic Sea Science Congress, 21–25 August 2023, Helsinki (Finland). "The seasonal tourists' effect on micropollutants delivery and effluents quality in popular coastal resorts of the Baltic Sea" (Poster)
4. 16th National Conference on Marine Science and Technology "Marine and Coastal Research," 15–17 May 2024, Nida (Lithuania). "Impact of Mass Gatherings on Wastewater Quality and Dynamics: Assessment of Micropollutants, General Pollution Loads, and Treatment Efficiency" (Oral).
5. 15th National Conference on Marine Science and Technology "Marine and Coastal Research," 19–21 April 2023, Dreverna (Lithuania). "Impact of Seasonal Human Fluctuations on Wastewater Dynamics and Quality in Popular Coastal Resorts: Evaluation of Phthalates, Hormones, Nutrients, and Their Removal Efficiency" (Oral).

1.5. Publications

The material of this study was presented in two original publications published in the peer-reviewed scientific journals:

1. Jucyte-Cicine, A., Lorre, E., Petkuviene, J., Gasiunaite, Z. R., Politi, T., Vybernaite-Lubiene, I., Zilius, M., 2024. Coastal wastewater treatment plants as a source of endocrine-disrupting micropollutants: A case study of Lithuania in the Baltic Sea. Marine Pollution Bulletin 200, 116084. https://doi.org/10.1016/j.marpolbul.2024.116084
2. Jucyte-Cicine, A., Lorre, E., Petkuviene, J., Gasiunaite, Z. R., Durcova, E., Vybernaite-Lubiene, I., Zilius, M., 2025. Understanding the impact of the summer Sea Festival on the dynamic of micropollutant delivery to the coastal wastewater treatment plant. Emerging Contaminants 11(2), 100465. https://doi.org/10.1016/j.emcon.2024.100465

1.6. Thesis structure

The dissertation includes nine chapters: an introduction, a literature review, material and methods, results, discussion, recommendations, conclusions, references, a summary in Lithuanian, and annexes. The material is presented in 144 pages, 24 figures, and 28 tables. The dissertation refers to 228 literature sources. It is written in English with an extended summary in Lithuanian.

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1.8. Abbreviations

Abbreviation	Explanation
ACE	Acenaphthene
ACEY	Acenaphtylene
ANT	Anthracene
AO	Advanced oxidation
BBzP	Butyl Benzyl phthalate
BENAA	Benzo(a)anthracene
BENAP	Benzo(a)pyrene
BENBF	Benzo(b)fluoranthene
BENKF	Benzo(k)fluoranthene
BENP	Benzo(g,h,i)perylene
BOD	Biological oxygen demand
CBZ	Carbamazepine
CHR	Chrysene
COD	Chemical oxygen demand
DBP	Dibutyl phthalate
DEHA	Di(2-ethylhexyl) adipate
DEHP	Di(2-ethylhexyl) phthalate
DEP	Diethyl phthalate
DF	Detection frequency
DIB	Dibenzo(a,h)anthracene
DiBP	Di-iso-butyl phthalate
DMP	Dimethyl phthalate
DnBP	Dibutyl phthalate
DOC	Dissolved organic carbon
E1	Estrone
E2	17 beta-estradiol
EEQ	Estrogenic equivalent
EQS	Environmental Quality Standard
FLU	Fluorene
FLUA	Fluoranthene
GC-MS	Gas Chromatography-Mass Spectrometry
IND	Indeno(1,2,3-c,d)pyrene
MDL	Method detection limits
MEC	Measured environmental concentration

Abbreviation	Explanation
MQL	Method limits of quantification
NAP	Naphthalene
PAEs	Phthalic acid esters
PAHs	Polycyclic aromatic hydrocarbons
PE	Population equivalent
PHE	Phenanthrene
PNEC	Predicted no-effect concentration
PYR	Pyrene
RC	Relative contribution
RQ	Risk Quotient
SPE	Solid phase extraction
SPM	Suspended particulate matter
TN	Total Nitrogen
TP	Total Phosphorus
UPLC	Ultra-high-performance liquid chromatography-mass spectrometry
UWWTD	Urban Wastewater Treatment Directive
VEN	Venlafaxine
WFD	Water Framework Directive

2

Literature review

2.1. Coastal pollution from source to ecosystem

Pollution in coastal zones is a long-standing, complex environmental challenge driven by increasing anthropogenic pressures. For decades, nutrient and organic matter inputs, particularly excess nitrogen and phosphorus, have been recognized as key drivers of coastal eutrophication (Smith, 2003). As a result, nuisance harmful algal blooms led to the accumulation of organic matter, oxygen depletion and overall ecosystem degradation (Smith et al., 2009; Wurtsbaugh et al., 2019; Diaz et al., 2008). In addition to nutrients, trace contaminants, called micropollutants, such as pharmaceuticals, have emerged as a more recent environmental concern in coastal zones. Micropollutants are often classified into broad categories such as contaminants of emerging concern and/or endocrine-disrupting chemicals. Among endocrine-disrupting chemicals, hormones, plasticizers, pharmaceuticals, and polycyclic aromatic hydrocarbons (PAHs) have received particular attention due to their persistence, bioaccumulation potential, and adverse ecological impacts (Mishra et al., 2023). Even at trace concentrations, such compounds can disrupt endocrine and reproductive functions, posing risks to aquatic organisms (Aus der Beek et al., 2016; Beck et al., 2006). The increasing detection of these micropollutants in the surrounding environment has prompted intensive research into their sources, transport pathways, accumulation patterns, and ecological consequences in aquatic environments (Phan et al., 2015; Buttiglieri et al., 2016; Lorre et al., 2024; Mahaliyana et al., 2025).

Micropollutants in wastewater mostly originate from daily household activities and industrial discharges (Margot et al., 2015; Anne and Paulauskiene, 2021). Domestic sewage contains detergents, personal care products, grease, and fecal matter. These substances carry micropollutants, including phthalates, steroidal hormones, and pharmaceuticals. In contrast, industrial wastewater introduces distinct contaminants, such as PAHs, depending on the dominant local industries (Chen et al., 2024). Once released into the sewer system, the micropollutant cocktail reaches WWTPs, which are a critical barrier, controlling further micropollutant discharge to the coastal environment (Eggen et al., 2014; Rogowska et al., 2020; Hamid & Eskicioglu, 2012; Di Marcantonio et al., 2022). However, conventional WWTPs were not originally designed to effectively remove micropollutants of concern (Phan et al., 2015; Kumar et al., 2022; Khasawneh & Palaniandy, 2021; Yu et al., 2011). As a result, substantial quantities of micropollutants are often discharged into receiving waters (Hamid & Eskicioglu, 2012; Kasonga et al., 2021; Di Marcantonio et al., 2022).

Depending on their physicochemical properties, micropollutants behave differently in sewer systems. For example, hydrophobic compounds such as phthalates and PAHs tend to adsorb onto suspended solids and be transported over long distances, largely settling during mechanical sedimentation at the WWTPs. While this eliminates PAHs from the water column and protects the environment, their accumulation in sludge creates challenges for safe reuse and disposal (Jiang et al., 2013). On the other hand, hydrophilic substances are transported in the dissolved phase to the biological treatment, where they are partially degraded. After treatment, dissolved and particle-bound micropollutant residues are discharged from WWTPs into surface waters, exhibiting different behaviors, which determine their subsequent environmental fate. Once polar or semi-polar persistent micropollutants such as estrogens enter coastal ecosystems, they tend to bioaccumulate in food webs (Zhao et al., 2019). In contrast, polar compounds such as dimethyl phthalate (DMP) and CBZ exhibit more complex behavior, remaining dissolved in water, facilitating their long-distance transport through aquatic systems. Eventually, these compounds can infiltrate groundwater, where they persist and pose direct risks to human health (Spahr et al., 2020; Elliott et al., 2018).

Recent studies indicate a growing presence of micropollutants across different environmental compartments (Jiang et al., 2014; Ştefãnică et al., 2021; Lenart-Boroń et al., 2022; Zandaryaa and Frank-Kamenetsky, 2021; Mauritsson et al., 2022; Lorre et al., 2024). This trend is especially evident in densely populated coastal areas, which are often affected by seasonal tourism (Zaborska et al., 2019; Sousa et al., 2020). Tourism-driven population surges can substantially increase water use and, consequently, wastewater production, leading to higher pollution levels in coastal areas. For example, persistent micropollutants already accumulated in coastal waters, with large quantities of CBZ reported in the Baltic Sea, where it may persist for several years (Björlenius et al., 2018; Mackuľak et al., 2019), and significant amounts of plasticizers in sediments of the Curonian Lagoon (Lorre et al., 2024. Only a few studies have examined the relationship between population dynamics and micropollutant occurrence. Although some studies traced micropollutant movement from WWTPs to the adjacent coastal areas, they focused primarily on pharmaceutical contamination (Gerrity et al., 2011; Jiang et al., 2014). Despite growing awareness of the presence and the level of micropollutants in coastal ecosystems, knowledge gaps on accumulation and the most affected zones remain. Specifically, there is limited understanding of how micropollutant dynamics in nearby WWTPs respond to seasonal population fluctuations, whether they influence treatment efficiency, and micropollutant discharge into coastal ecosystems.

2.2. Ecological threats of micropollutants

Various micropollutants present significant environmental concerns, particularly natural and synthetic hormones, pharmaceuticals, plasticizers, and PAHs. These substances warrant attention due to their widespread presence in aquatic ecosystems and their documented negative impacts on ecological systems and human health, especially as endocrine-disrupting chemicals (Bergman et al., 2013; Sanganyado et al., 2021; Diamanti-Kandarakis et al., 2009; Aris et al., 2014; Schug et al., 2011). For example, phthalates and PAHs, being hydrophobic, are readily transferred from water to the lipids of organisms (Jiang et al., 2013). While pharmaceutical residues resist biodegradation, they persist in aquatic environments, resulting in prolonged exposure. This increases potential for biomagnification in the food web, elevating risks to marine organisms (Gul et al., 2022). In addition, pharmaceuticals act through multiple biological pathways, indirectly disrupting endocrine functions and impairing the essential ecological functions of natural microbial communities (Alvarino et al., 2014).

Pharmaceuticals have gained growing attention due to their persistence in conventional wastewater treatment and their potential for chronic exposure to aquatic organisms. Carbamazepine (CBZ), a widely used psychiatric pharmaceutical, is one of the most persistent pharmaceuticals commonly used as a tracer for recalcitrant organic pollution. CBZ can impair invertebrates reproduction and delay fish development by interfering with cell cycle regulation and hormonal signalling (Mackuľak et al., 2019; Björlenius et al., 2018). Whereas venlafaxine (VEN), a widely detected antidepressant, disrupts endocrine-related physiological regulation and biotransformation processes in aquatic organisms, potentially impairing reproductive hormone balance (Qu et al., 2018). According to Long et al. (2023), the CBZ and VEN were found to concentrate in benthic macroalgae at levels nearly 24,000 times higher than those measured in the surrounding water. This significant bioaccumulation poses a serious threat to benthic biodiversity, potentially disrupting ecosystem functions and triggering cascading effects throughout aquatic food webs.

Hormones are of particular concern due to their persistence, endocrine-disrupting effects at very low levels and potential drinking water contamination. A large group of hormones is the estrogens, with estradiol (E2) and estrone (E1) as the primary forms. These hormones directly activate estrogen receptors, causing endocrine disruption even at very low concentrations in the nanogram range (Beck et al., 2006; Briciu et al., 2009; Zhang et al., 2011). This disruption impairs reproduction and sexual development in wildlife, leading to altered sex ratios, reduced fertility, and abnormal sexual behavior. Over time, it can destabilize populations and threaten biodiversity (Zhang et al., 2011; Hamid and Eskicioglu, 2012). Although E1 demonstrates a lower potency than E2, it frequently results from microbial breakdown of E1 (Kumar et al., 2010; Hamid & Eskicioglu, 2012). Studies report E1 as the dominant estrogen in effluents and rivers (Loos et al., 2018). Its persistence and physicochemical properties allow trophic transfer, posing risks to human health through contaminated aquatic organisms (Pironti et al., 2021).

Phthalates, a ubiquitous endocrine disruptor, are linked to reproductive, developmental, and cancer-related health and environmental risks. Among the many groups of chemical plasticizers, phthalates (PAEs) are the most widely used in flexible plastics and various consumer products, including medical supplies, perfumes, nail polish, shampoos, lotions, paints, and adhesives (Pereira et al., 2015; Net et al., 2015). Since PAEs do not chemically bind to polymer matrices, they are easily released into the environment, increasing the risk of exposure to humans and wildlife (Russo et al., 2015). Common PAEs, such as DEHP, diethyl phthalate (DEP), and dibutyl phthalate (DBP), have been linked to various health issues, including cancer, developmental abnormalities, and reproductive harm in humans and wildlife (Benjamin et al., 2017). Recent studies also show that elevated PAEs levels negatively affect coral reef invertebrates, hindering development and posing risks to marine biodiversity (Vered et al., 2022). Their persistence in the ecosystem leads to long-term ecological effects (Net et al., 2015).

Among endocrine disruptors, PAHs are highly toxic and persistent, linked to serious environmental and health risks. PAHs tend to sorb onto particulate matter and accumulate in sediments (Maletić et al., 2019). They mostly originate from pyrogenic processes, including the incomplete combustion of coal and petroleum, as well as from petrogenic sources such as crude oil, gasoline, and diesel. Even trace amounts of PAHs are carcinogenic (Saber et al., 2021; Yan et al., 2016; Patel et al., 2020; Suresh et al., 2024) and can often cause indirect endocrine disruption (Chen et al., 2022; Souza et al., 2024; Lee et al., 2017; Zajda et al., 2020; Honda and Suzuki, 2020). For example, benzopyrene exhibits anti-estrogenic and anti-androgenic effects in crustaceans and can impair thyroid function in fish by disrupting thyroid hormone synthesis and signaling pathways (Wen and Pan, 2015; Movahedinia et al., 2018). Due to their persistence and bioaccumulation potential, PAHs can reach harmful concentrations in aquatic organisms, posing risks to human health through seafood consumption (Liu et al., 2023; Qin et al., 2020).

Overall, the micropollutants discussed above pose a significant threat to sensitive coastal ecosystems, as evidenced by their widespread presence and documented harmful effects. Current EU regulations address only a limited number of these compounds. For example, DEHP is the only phthalate regulated, with environmental quality standards (EQS) set for surface waters and enforced across EU countries, alongside several PAHs. Some potentially harmful chemicals, such as VEN, have been added to the EU "Watch List" for continued monitoring, while CBZ remains an exception. Hormones E1 and E2 are listed in the "Watch List" as well and have a predicted EQS defined, although their legal monitoring is not yet enforced. Despite the progress, systematic monitoring of these hazardous substances is important to support effective risk assessment and help future regulatory measures.

Given the concerns and obligation to gather monitoring data for suspected and priority hazardous chemical compounds, proactive risk assessment methods are beneficial for evaluating their environmental impact. A practical approach to assessing the ecological risks posed by endocrine-disrupting compounds involves combining Predicted No-Effect Concentrations (PNECs) with systematic risk-scoring calculations. This framework enables scientists and regulators to quantify and prioritize potential environmental threats.

2.3. Progress in controlling micropollutant contamination

Environmental regulations have progressively evolved in response to the escalating risks of micropollutant contamination; however, the true scale of their release and accumulation remains unknown (Kümmerer et al., 2018). In the recent decade, the European Union (EU) has strengthened its control over micropollutant emissions to the environment in response to escalating ecological and health concerns (Morris et al., 2017; Pedrazzani et al., 2019). Key policies, including the Water Framework Directive WFD, Urban Wastewater Treatment Directive UWWTD, and Drinking Water Directive (DWD), form the backbone of EU water management. To address emerging micropollutant management, the EU "Watch List" the step before adding to the priority hazardous substances list, was established under WFD, which requires systematic monitoring of emerging hazardous pollutants in water bodies. Starting in 2025, WWTPs are expected to comply with stricter discharge limits and expanded monitoring requirements for micropollutants under the updated UWWTD. In accordance with it, in the Baltic region, HELCOM has prioritized pharmaceuticals and other emerging micropollutant groups on its Baltic Sea Action Plan, calling for monitoring and management to address ongoing contamination (HELCOM, 2024, 2025). Despite regulatory advances, the most effective approach to reduce micropollutant contamination remains control at the source, which involves limiting new discharges and replacing harmful substances with safer alternatives. When source control is insufficient, wastewater treatment facilities should modify their discharge protocols and upgrade their infrastructure to remove these contaminants more efficiently.

Micropollutant removal from wastewater is inherently challenging due to its highly complex composition and variable concentrations, influenced by seasonal population fluctuations, industrial discharges, and land-use patterns. Furthermore, the diverse physicochemical properties of micropollutants complicate their efficient and consistent removal to environmentally safe levels. Wastewater treatment typically begins with a mechanical stage, during which most solids are separated, retaining hydrophobic micropollutants, such as PAHs and PAEs. During the subsequent biological treatment stage, which employs activated sludge, micropollutants can be biodegraded to some extent (Ardern et al., 1914). However, its effectiveness in degrading persistent organic micropollutants remains frequently insufficient (Tian et al., 2022; Falås et al., 2016). Many micropollutants, particularly pharmaceuticals, possess physicochemical properties that render them resistant to conventional biological treatment, including low sorption capacity and high chemical stability (Kamaz et al., 2019). Consequently, recalcitrant micropollutants, either parent compounds or degradation byproducts, are discharged from WWTPs into nearby water bodies (Jiang et al., 2013). To address these challenges, novel wastewater treatment technologies are being developed and evaluated.

Advanced wastewater treatment technologies, such as advanced oxidation processes, reverse osmosis, and activated carbon filtration, are considered promising, practical strategies for reducing the discharge of micropollutants into the environment. However, the selection of technology depends on the specific micropollutant being targeted. For example, advanced oxidation and activated carbon filtration demonstrated superior performance in eliminating polar pesticides and pharmaceutical compounds. At the same time, reverse osmosis proved more effective at removing metals and less-polar compounds (El Brahmi et al., 2024). Among advanced oxidation methods, ozonation is the most widely studied non-selective approach, particularly effective in degrading persistent micropollutants. Nevertheless, the efficiency of most advanced treatment technologies can be influenced by the composition of the wastewater matrix, which varies in pollution sources. Industrial wastewater may contain reactive scavengers such as nitrites, whereas domestic wastewater often has high organic content (Chen et al., 2023; Van Gijn et al., 2022).

Coastal WWTPs typically receive complex influent from different pollution sources, including tourism, household, and industrial inputs, depending on the town/resort size. Seasonal population fluctuations pose additional challenges for Coastal WWTPs by altering influent composition and dynamics, potentially reducing treatment efficiency and compromising effluent quality. This variability can also affect the performance of the selected advanced treatment, particularly in degrading persistent micropollutants.

In the Baltic coastal areas of Lithuania, subsurface groundwater discharge may also affect wastewater composition in coastal WWTPs by introducing iron, manganese, and sulfides from anoxic coastal aquifers (Diliūnas et al., 2006; Kitterød et al., 2022). These reduced species can act as ozone scavengers, lowering oxidation efficiency and increasing indirect risk of by-product formation (Luo et al., 2023; Propolsky et al., 2025). Although ozonation is increasingly applied in urban WWTPs worldwide, progress in coastal WWTPs has been less pronounced. Given its non-selective nature to oxidize organic matter, ozonation offers strong potential for WWTPs influenced by diverse anthropogenic pollution. Evaluating the potential of ozonation for removing persistent micropollutants in coastal WWTPs affected by variable pollution sources would provide a solid basis for determining its suitability as a post-biological treatment

3

Material and methods

3.1. Study areas

To explore the relationship between seasonal residential population fluctuation and pollution dynamics in the southeastern Baltic region, three locations with WWTPs were selected (Fig. 1). All three coastal towns serve as tourist destinations, experiencing notable seasonal population surges during summer peak times and are also influenced by different degrees of human activities (Povilanskas and Armaitienė, 2010, 2011; Schernewski et al., 2019). Seasonal population surges may significantly increase wastewater production, affecting pollution levels and treatment efficiency at corresponding WWTPs (see Papers I and II) that discharge to the Baltic Sea or the Curonian Lagoon.

Nida, a small, charming resort town on the Curonian Spit, is a UNESCO World Heritage site (55°18’31”N, 20°59’79”E). With a permanent population of ~2000, Nida experiences a substantial influx of visitors during peak tourist seasons, such as summer and national holidays, when its population surges over 140-fold (Povilanskas and Armaitienė, 2010; Razma et al., 2025). The economy of the town is tourism-focused and its accommodations primarily consist of apartments and guesthouses. The area maintains its pristine environment by remaining free of industrial activity. The Nida WWTP, constructed in 2008, serves with a design capacity of 2,200 $m^3\ d^{-1}$ and the maximum Population Equivalent (PE) of 6,700, based on total Biochemical Oxygen

Demand per day (BOD; 60 g person^{-1} day^{-1}). The facility processes predominantly domestic wastewater through a two-stage treatment system (Luczkiewicz et al., 2019). The treatment begins with mechanical sedimentation (primary treatment), followed by a biological treatment phase (secondary treatment) utilizing activated sludge technology. Wastewater after treatment flows through 150 m underwater pipelines into the Curonian Lagoon. Main information about the WWTPs is summarised in Table 1.

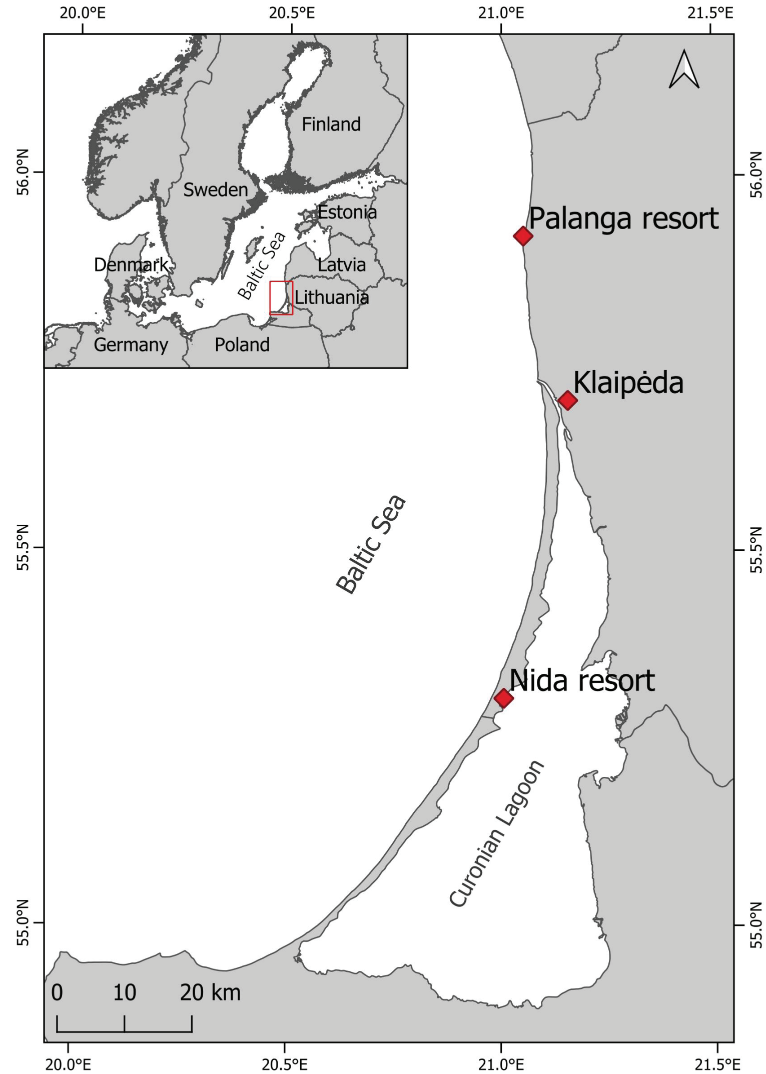

Figure 1. Map showing the geographical location of Nida, Palanga, and Klaipėda on the southeastern Baltic Sea coast.

Palanga, a thriving coastal resort in western Lithuania (55°55’03”N, 21°04’07”E), is a premier vacation destination, attracting domestic and international tourists. While its permanent population is ~18,000 residents, this number experiences dramatic growth (over 37 times) during the peak tourism season (OECD, 2023). The area features extensive hospitality infrastructure, including full-service hotels and amenities, which generate higher influent flows to the WWTP. The Palanga WWTP has been operational since 1993. Starting with mechanical treatment in 2000, it was upgraded to incorporate biological treatment processes. It follows a similar treatment sequence to the Klaipėda and Nida WWTPs (Luczkiewicz et al., 2019). However, this is the only WWTP that occasionally uses chemical flocculants. Similar to Nida resort, there are no large-scale industries. The maximum designed influent capacity and PE of Palanga WWTP are 21,000 $m^3\ d^{-1}$ and 36,000, respectively. Treated effluents are discharged into the coastal waters of the Baltic Sea, approximately 2.15 km from the shore.

Klaipėda, situated in western Lithuania (55°42′12″ N, 21°07′50″ E), is the largest coastal city in Lithuania. While not officially designated as a resort, the city has emerged as a notable tourist destination, particularly during its annual Sea Festival in late July. This three-day event attracts numerous national and international visitors, temporarily increasing the population of ~156,000, up to three times the usual level (Kraniauskas et al., 2018), significantly impacting wastewater management demand. The Klaipėda WWTP has been operational since 1998; it processes 95,000 m^3 daily through a comprehensive system of mechanical sedimentation and biological treatment using activated sludge, followed by final sedimentation before discharge (Luczkiewicz et al., 2019). The facility handles various influent sources, with domestic wastewater constituting approximately 60% of the total flow (pers. comm. AB «Klaipėdos Vanduo», 2024). The maximum designed PE for Klaipėda WWTP is ~305,333. The treated effluent is discharged to the Klaipėda Strait, which is the outflow of the Curonian Lagoon to the Baltic Sea.

Table 1. The main characteristics of the studied wastewater treatment plants (WWTPs) selected in the coastal areas.

WWTP	Projected maximum capacity (m^3 d^{-1})	Maximum PE	Permanent residents	Maximum anticipated population increase	Contribution of industry (%)	Wastewater treatment stages	Receiving water body	Infiltration rate (%)
Nida	2,200 [2]	6,700 [1]	~2,000 [5]	~280,000 [6,8]	0 [1]	Mechanical, biological [1]	Curonian Lagoon [1]	0 [1]
Palanga	21,000 [4]	36,000 [1]	~18,000 [5]	~667,000 [9]	NA [1]	Mechanical, Biological [1]	Baltic Sea [1]	60 [1]
Klaipėda	95, 000 [3]	305,333 [1]	~156,000 [5]	~500,000 [7]	23 [1]	Mechanical, biological [1]	Klaipėda strait/ Curonian Lagoon [3]	44 [1]

Note 1. PE – population equivalent; NA – data not available.

Note 2: Data was taken from:

[1] Luczkiewicz et al., 2019

[2] https://nvanduo.lt/veikla/

[3] Aplinkos apsaugos agentūra (2021)

[4] https://www.palangosvandenys.lt

[5] https://osp.stat.gov.lt/

[6] Povilanskas & Armaitienė, 2010

[7] Kraniauskas et al., 2018

[8] Razma et al., 2025

[9] OECD, 2023

3.2. Study design and sampling strategy

This study employed a comprehensive methodological approach to evaluate how population dynamics influence wastewater composition, micropollutant concentrations, and treatment performance in coastal wastewater treatment plants. The study combined regular seasonal monitoring with targeted sampling during a major temporary public event, capturing both gradual shifts and sudden changes in pollution patterns. In addition, ozonation was selected to evaluate how this advanced treatment technology would mitigate pollution discharged into the coastal environment. Finally, relationships between pollutant dynamics and tourism indicators were analyzed alongside quantitative assessments of removal efficiency and ecological risk.

To answer research questions, the study was designed to capture the dynamics of general pollution and micropollutant levels in wastewater before treatment (influent) and after treatment (effluent), and evaluate the efficiency of ozonation in removing persistent pollutants (Table 2). The study was structured into three main activities conducted during different periods:

1. Seasonal wastewater and effluents monitoring at the two coastal WWTPs (Nida and Palanga) throughout 2022–2023, analyzing pollution dynamics related to tourist fluctuation.

2. Evaluation of the large temporary public event impact on pollution dynamics at the Klaipėda WWTP in July 2023.

3. Experimental application of ozone to remove pharmaceuticals from biologically treated wastewater from different coastal WWTPs (Klaipėda, Nida, and Palanga), considering the diverse pollution sources that may affect removal efficiency.

Table 2. Summary of the study design.

Name of activity	Study period, frequency	Sampling WWTPs	Sample No.	Sample type	Target compound groups	Sample treatment and analytical Method
Seasonal monitoring	03/2022 – 02/2023, monthly	Nida, Palanga	144	Influent and effluent	Total estrogenicity Phthalate esters Quality parameters	SPE, Bioassay SPE, GC-MS/MS Spectrophotometry
Large public event evaluation	18–28 July 2023, daily	Klaipėda	36	Influent and effluent	Estrogens Pharmaceuticals Phthalate esters Polycyclic aromatic hydrocarbons Quality parameters	SPE, LC-MS/MS SPE, GC-MS/MS Spectrophotometry
Micropollutant removal experiment	24–29 July 2024, hourly	Nida, Palanga, Klaipėda	35	Effluent	Pharmaceuticals Quality parameters	Ozone treatment, followed by SPE, LC-MS/MS ICP-MS Spectrophotometry Microbiological assessment

Note: GC-MS – Gas Chromatography coupled with Mass Spectrometry, LC-MS/MS – Liquid Chromatography coupled with Mass Spectrometry, ICP-MS – Inductively Coupled Plasma Mass Spectrometry, SPE – Solid Phase Extraction.

3.2.1. Seasonal pollution monitoring at the coastal WWTPs

To investigate how seasonal changes in resident population affect wastewater quality, pollutant loads and their retention in the WWTPs, we analyzed phthalates and estrogenic potential alongside general wastewater parameters at two coastal resorts with different resident populations. Monthly sampling was conducted at the WWTPs of Nida (hereafter, the Small resort WWTP) and Palanga (hereafter, the Large resort WWTP) from March 2022 to February 2023, covering both the non-tourism season (March–May and September–February) and the peak tourism season (June–August). At each WWTP, samples were collected in triplicate at real time, before treatment (influent) and after treatment (effluent) (Fig. 2). Samples were taken using a stainless-steel sampler and transferred into three 1 L glass bottles for the analysis of 1) phthalates (PAEs) and 2) estrogenic equivalent (EEQ). Additional samples were collected for the nutrients, dissolved and solid matter. Following the collection, EEQ samples were immediately treated with 1% (v/v) methanol to inhibit microbial activity and avoid biodegradation. All samples were transported to the laboratory in a cool box within 2 hours for further processing. During each sampling, air temperature was measured monthly at the WWTPs using a digital thermometer; however, these measurements do not reflect the monthly average for the corresponding resorts.

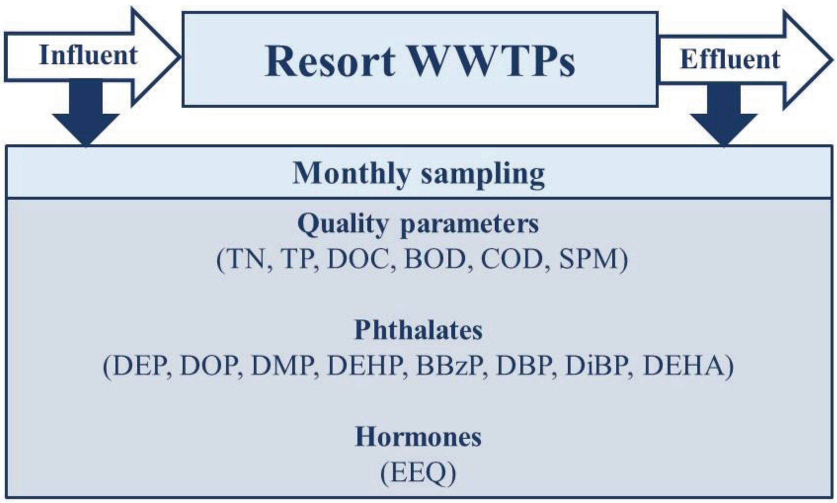

Figure 2. Research workflow of the seasonal study conducted at two coastal resort WWTPs.

3.2.2. The assessment of a temporary event contribution to pollution delivery

The concentration of micropollutants (hormones, PAEs, pharmaceuticals, and polycyclic aromatic hydrocarbons (PAHs)), nutrients, and general quality parameters were analyzed to evaluate the impact of the Sea Festival on pollution dynamics and wastewater treatment efficiency at the Klaipėda WWTP. Influent samples were collected 3 days before, during, and 3 days after the Sea Festival held on the 21–23 July 2023. Effluent samples were collected 48 hours after each influent sampling to ensure the complete treatment process (Fig. 3). Samples were taken in triplicate using a stainless-steel sampler and transferred into three 1 L glass bottles for the analysis of 1) PAEs, 2) PAHs, and 3) hormones and pharmaceuticals. Additional samples were collected for nutrient and solid matter analysis.

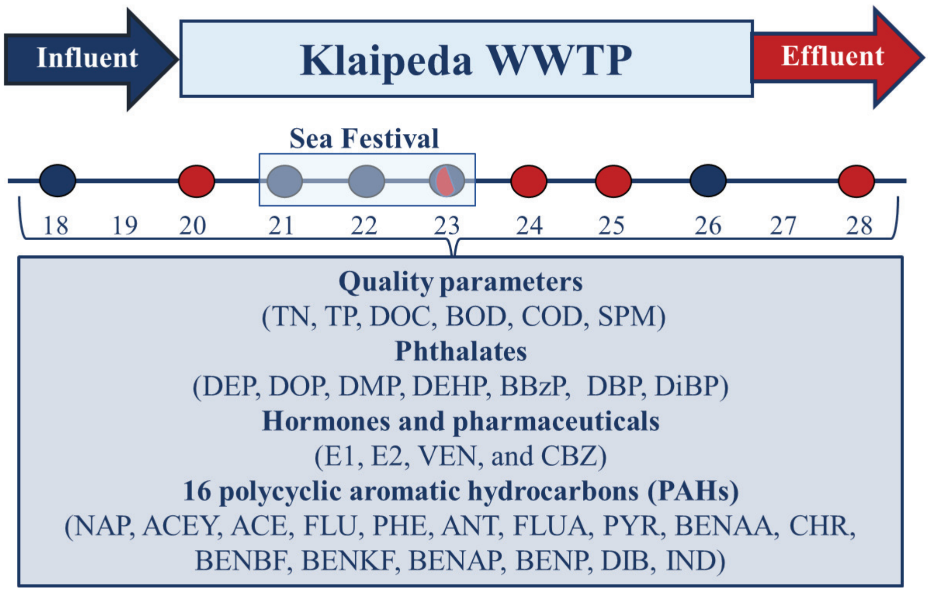

Figure 3. Sampling timeline and research workflow for assessing the impact of a temporal public event at the Klaipėda WWTP. Influent sampling is marked in blue and effluent in red. On July 23rd, both influent and effluent were sampled.

3.2.3. Removal of pharmaceuticals from the biologically treated wastewater using ozonation: batch experiment

The impact of advanced oxidation (AO) using ozone on two pharmaceutical compounds (VEN, CBZ) and the quality of biologically treated wastewater was evaluated experimentally (Table 2). Ozonation was applied to wastewater after biological treatment to optimise ozone consumption and enhance micropollutant decomposition. This approach enabled more targeted oxidation under conditions of lower organic content, thereby reducing ozone demand and minimizing the formation of toxic by-products such as bromate and aldehydes (Derco et al., 2024).

Biologically treated wastewater samples used for the experiment were obtained from three WWTPs representing different pollution profiles: Nida (resort influence), Palanga (resort and residential influence), and Klaipėda (residential, industrial, and resort influence). Detailed features of each WWTP are provided in Table 1. Flow-proportional composite samples (5 L) were collected over 24 hours in sealed plastic containers following mechanical and biological treatment. The batch-mode ozonation system consisted of a stainless-steel ozone reaction chamber with a working volume of 1.6 L. Ozone was generated externally using a dielectric barrier discharge generator and introduced into the reactor through a stainless-steel porous diffusers mounted at the bottom of the chamber. Oxygen generated from the air was used as the feed gas for ozone generation. Excess, non-reacted ozone exited the reactor through a ventilation port located at the top of the chamber. During ozonation, samples were collected at 5-minute intervals through a sampling port located near the bottom of the reactor. After each run, the reactor was emptied and rinsed with demineralized water before being filled with a new wastewater batch.

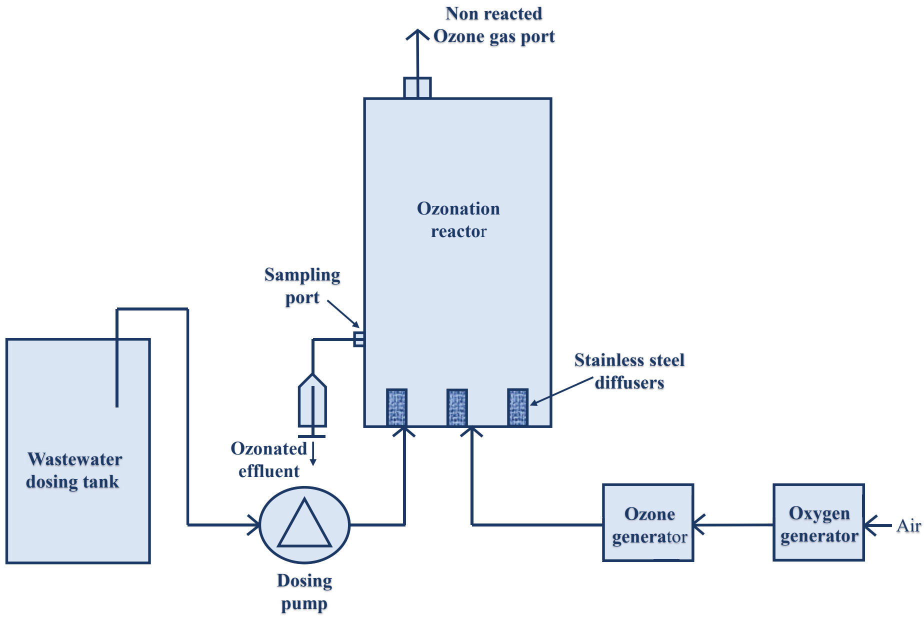

Figure 4. Scheme of a bench-scale ozonation system to degrade pollutants in biologically treated wastewater.

The experimental workflow for pollutant decomposition is presented in Figure 5. Biologically treated wastewater samples from all three WWTPs were subjected to ozonation for 5, 10, and 15 min, respectively. Following the treatment, samples were collected from the reactor for the analysis of pharmaceutical residues and bacterial contamination. General water quality parameters, including DOC, BOD, COD, and SPM, were also measured to assess overall pollution removal efficiency. Additionally, nitrate, bromide and water hardness (Ca, Mg) were measured due to their potential influence on radical scavenging during ozonation. To maintain the required biologically treated wastewater level in the reactor, sampling frequency was reduced; therefore, samples were taken before ozonation (0 min) and after 15 min of the treatment only (Fig. 5). The dissolved ozone concentration was maintained at 7.3 ± 0.7 mg L^{-1} throughout the experiments. This concentration was selected based on the average DOC of effluent from Klaipėda, Nida, and Palanga WWTPs (~13 mg L^{-1}; Papers I and II), ensuring a consistent DOC-to-ozone ratio of approximately 0.5 g O_3/g DOC.

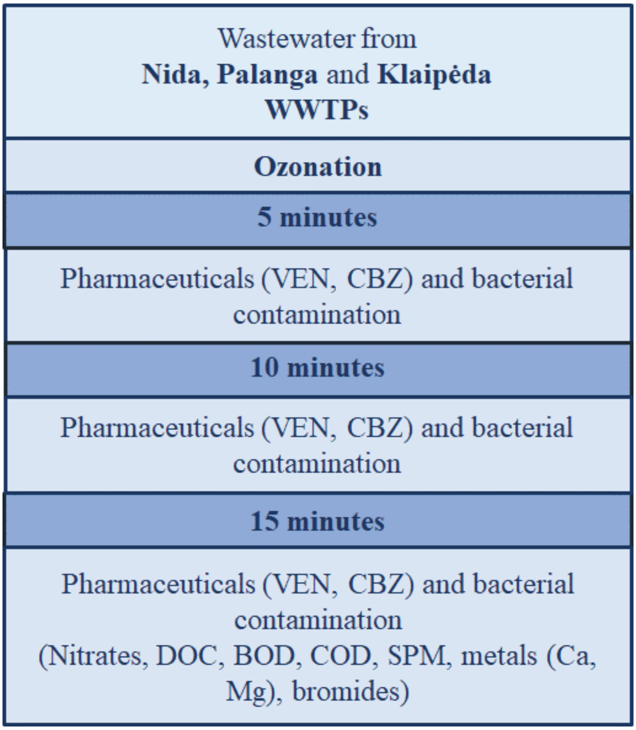

Figure 5. Experimental workflow for assessing the ozonation impact on the biologically treated wastewater quality and pharmaceutical removal in the coastal WWTPs.

3.3. Analytical methods

3.3.1. Hormone and pharmaceutical analysis

Estrogens and pharmaceuticals were extracted following the modified version of the solid phase extraction (SPE) method detailed in Paper I. Before filtration and extraction, the samples were spiked with the internal standard (20 ng L^{-1} for E1 and E2, and 80 ng L^{-1} for VEN and CBZ). Influent and effluent samples (250 mL) were filtered through glass fiber filters (47 mm diameter, 0.7 μm nominal pore size; Frisenette, Denmark). For particulate-bound compounds, retained on the filter, 15 mL of analytical-grade MeOH was used to extract the filter according to the Ecologiena® protocol (Biosense, Japan). The combined filtrates were subjected to solid-phase extraction (SPE) using Oasis HLB cartridges (Waters™, USA), following the procedure described by Ross et al. (2017) with minor modifications. The cartridges were conditioned with 5 mL of analytical-grade methyl tert-butyl ether (MTBE), MeOH, and analytical-grade water, then samples were passed through the cartridges using Chromabond® tubing adaptors at a 2 mL min^{-1} flow rate. After washing with the 2% ammonia solution, compounds were eluted with 10 mL of MTBE. The eluents were stored at -20 °C until the analysis, following the US EPA (Environmental Protection Agency) Method 1698 (EPA, 2007) and Fang et al. (2019). Before the analysis, eluents were dried with nitrogen (N_2) gas at 35 °C and reconstituted with 1 mL of 30% ACN and 70% LC-MS water.

The hormones and pharmaceuticals were analyzed using LC-MS/MS with the Waters Acquity UPLC I-Class/Xevo TQS micro-system (Waters Corp., US). Separation was performed on a reverse phase C18 column (Acquity Premier Peptide BEH C18, 300Å, 1.7 µm 2.1 × 100 mm MVK). Ionized molecules were accelerated through the instrument mass analyzer and separated based on their parent ions mass-to-charge (m/z) ratios (Table 3).

Hormones and their corresponding internal standards were detected and quantified in negative ion mode [M − H] − while pharmaceuticals and their respective internal standards were analyzed in positive ion mode [M + H] + using multiple reaction monitoring (MRM) and single ion recording (SIR). The method parameters for the estrogen analysis were configured as follows: the desolvation temperature was set at 600°C, the ion source temperature was maintained at 150 °C, the target column temperature was set at 40°C, and the sample temperature was adjusted to 10°C. Nitrogen gas was used as the carrier gas (desolvation and cone) at a flow rate of 1200 L/h. A 50 µL injection volume was selected to enhance instrumental sensitivity for estrogen detection. For quantification, an internal standard calibration method based on a minimum five-point calibration curve was used for each estrogen and pharmaceutical compound. The instrumental parameters for pharmaceutical analysis were as follows: desolvation temperature, 200 °C; ion source temperature, 150 °C; column temperature, 60 °C; sample temperature, 20 °C; and injection volume, 10 µL. The recovery rate (%) calculations were conducted by analyzing spiked samples at 20, 130, and 500 ng L^{-1} for E1 and E2, and 50, 100, and 500 ng L^{-1} for CBZ and VEN (n=3 for each analyte). The recovery rates obtained from all spiked experiments varied between 70% and 120% for all compounds (see Table 4). Procedural and instrumental blanks were performed for each sample batch to ensure quality. The procedural blanks were always below the method limits of detection (MDL). The limit of quantification (MQL) was defined at a signal-to-noise ratio of 10:1, while MDL corresponded to a peak height three times the noise level. MQL ranged from 0.1 to 5.0 ng L^{-1}. Control samples were injected and monitored regularly to prevent instrumental variations during LC-MS/MS analysis. The MassLynx software (Waters Corp.) was used for signal acquisition and data handling.

Table 3. Physicochemical properties of targeted pharmaceuticals and hormones.

Name	Acronym	CAS number	Formula	Molecular weight (g mol^{-1})	Log Kow	Target ion (m/z) [a]	Qualifier ions (m/z)[a]
Carbamazepine	CBZ	298-46-4	$C_{15}H_{12}N_2O$	236.3	2.5	237.0	179.0–194.0
Venlafaxine	VEN	93413-69-5	$C_{17}H_{27}NO_2$	277.4	3.2	278.3	260.0–215.0
Estrone	E1	50-28-2	$C_{18}H_{22}O_2$	270.4	3.1	269.1	145.0
17beta-estradiol	E2	53-16-7	$C_{18}H_{24}O_2$	272.4	3.9	271.1	183.1

Note 1: Kow: octanol–water partition coefficient, Data from: PubChem Compound Database (NCBI, 2024)
Note 2: [a] data from: Quanpedia Database (Thermo Fisher Scientific, 2024).

Table 4. The recovery of targeted hormones and pharmaceuticals.

Group of compounds	Analyte name	Recovery %
Hormones	Estrone	120
	17 beta-estradiol	72
Pharmaceuticals	Venlafaxine	88
	Carbamazepine	77

3.3.2. Total estrogenicity assessment

In the laboratory, the samples were passed through Frisenette GF/F filters (100 mL of wastewater and 200 mL of effluent) to collect estrogenically active compounds in both dissolved and particulate-bound phases, which were extracted from the filter using 5 mL of methanol, following the Ecologiena® protocol (Biosense, Japan). The combined filtrates were stored for up to 24 hours at 4 °C before extraction. SPE of samples was performed using Oasis HLB cartridges (Waters™, USA), following a protocol described by Ross et al. (2017) with some modifications. Briefly, the cartridges were sequentially conditioned with 5 mL of analytical grade MTBE, MeOH, and water. The filtrates were then passed through the conditioned cartridges using Chromabond® tubing adaptors at the 2 mL min^{-1} constant flow rate and washed with the 2% ammonia solution. The cartridges were then eluted with 10 mL of MTBE. The obtained eluants were stored at -20 °C until biochemical analysis (up to 40 days) following the recommendations of US EPA Method 1698 (EPA, 2007) and Fang et al. (2019). Before the analysis, the eluents were dried under a gentle N_2 gas stream at 35 °C and reconstituted with 1 mL of 5% MeOH and 95% LC-MS water.

Total estrogenic equivalent in wastewater and effluent samples was assessed using a biochemical "Yeast Estrogen Screen" test (S-YES^{MD}, new_diagnostics GmbH). This assay is based on a genetically modified yeast strain, *Saccharomyces cerevisiae* BJ3505 (McDonnell et al., 1991). Each yeast cell contains two plasmids: one encoding the human estrogen receptor α, which is activated by estrogenically active substances (i.e., E1, E2, EE2), and the other encoding a reporter enzyme β-Galactosidase, which is expressed when its receptor is activated. Consequently, estrogenic substances trigger the receptor plasmids, producing β-Galactosidase associated with the plasmid enzyme. The S-YES^{MD} test was conducted in microtiter plates following the manufacturer's protocol. An aliquot of 80 µL and 30 µL of yeast suspension was added to the microtiter plate wells and incubated for 4 hours at 37 °C while shaking at 500 rpm. In addition, each microtiter plate contained 9-point calibration solutions, ranging from 5 to 400 ng L^{-1}, prepared in analytical-grade water (95%) and methanol (5%). Estrogenic activity was expressed as 17 beta-estradiol (E2) equivalent (EEQ). After incubation, absorbance was measured at 620 nm before and at 580 nm after the addition of Chlorophenol Red-β-D-galactopyranoside (new_diagnostics GmbH) using the Varioshan Lux spectrophotometer (Thermo Fisher Scientific, Finland). Three replicates were used for each sample with a 1:3 dilution. The method detection limit in the laboratory was ≥0.04 ng L^{-1}, and the method quantification limit was ≥0.06 ng L^{-1}.

3.3.3. Analysis of phthalate esters

The extraction of PAEs was performed following the method described in Lorre et al. (2023). The wastewater samples (200 – 500 mL) underwent filtration using pre-combusted (6 h at 500 °C) GF/F glass fiber filters (47 mm diameter, 0.7 µm nominal pore size; Frisenette, Denmark) to separate dissolved and particulate-bound phases. The filtrate was slightly acidified (pH between 2 and 5) and underwent solid-phase extraction (SPE) using C18ec cartridges (Chromabond®, 6 mL/500 mg) at a flow rate of 2 mL min^{-1} under vacuum. After extraction, the cartridges were dried with N_2 and eluted with 2 mL of ethyl acetate. The dried GF/F filters (at 60 °C for 4 h), containing precipitated suspended particulate matter (SPM), were spiked with the internal standard before ultrasonic extraction twice for 10 min with 10 mL of dichloromethane (DCM) using an ultrasonic homogenizer Bandelin Sonoplus HD 4200 equipped with a TS103 probe (BANDELIN electronic GmbH & Co. KG, Germany). DCM was evaporated to dryness, and then PAEs were reconstituted in 1.5 mL of ethyl acetate (EA). Before GC-MS analysis, the extracts were filtered through 0.22 µm PTFE filters (Frisenette, Denmark).

The PAEs were analyzed following the GC-MS method described in Lorre et al. (2023). The GC-MS analysis employed a Shimadzu GC-2010 Plus gas chromatograph with a GC-MS-TQ8040 mass spectrometer (Shimadzu Corp., Japan). Helium served as the carrier gas at 1 mL min^{-1}. The GC injector was operated in splitless mode at 250 °C. The separation occurred on a Rxi-5Sil MS w/Integra-Guard capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness; Restek®, Bellefonte, USA). The temperature program used for PAEs analysis was: 60 °C, held for 2 min; increased to 240 °C at 25 °C/min, held for 2 min; and then to 300 °C at 10 °C/min, held for 3 min. The transfer line and ion source were maintained at 280 °C and 230 °C, respectively. The mass spectrometer operated in time-scheduled single-ion monitoring (SIM) mode, with specific recording ions given in Table 5. LabSolutions (Shimadzu Corp.) software was used for signal acquisition and data handling. The method detection limit (MDL) and method quantification limit (MQL) were calculated as MDL = 3 × Ss and MQL = 10 × Ss for each PAE (Ss – sample standard deviation of replicate spiked sample analyses; n = 10). For PAEs, MQL values ranged from 0.034 to 0.205 µg L^{-1}. Recovery rate (%) calculations were conducted by analyzing spiked samples at 1 µg L^{-1} (dissolved and particulate; n = 10). Recovery rates varied between 70% and 103% (Table 7). Quality control included procedural and instrumental blanks for each sample batch, with procedural blanks consistently below the MDL. Control samples were injected and monitored regularly to control instrumental variations during the GC-MS analysis.

Table 5. Physicochemical properties of the measured phthalates.

	Name	Acronym	Formula	CAS number	Molecular weight (g mol^{-1})	Boiling point (°C)	Vapour pressure[a] (mmHg)	Log K_{ow} [a]	Target ion (m/z)	Qualifier ions (m/z)
1	Dimethyl phthalate	DMP	$C_{10}H_{10}O_4$	131-11-3	194.2	282	2×10^{-3}	1.61	163	194-133
2	Diethyl phthalate	DEP	$C_{12}H_{14}O_4$	84-66-2	222.2	298	1×10^{-3}	2.38	149	177-222
3	Di-iso-butyl phthalate	DiBP	$C_{16}H_{22}O_4$	84-69-5	278.3	327	2.9×10^{-4}	4.11	149	223
4	Dibutyl phthalate	DBP	$C_{16}H_{22}O_4$	84-74-2	278.3	340	2.7×10^{-5}	4.45	149	223-278
5	Butyl Benzyl phthalate	BBzP	$C_{19}H_{20}O_4$	85-68-7	312.4	370	5×10^{-6}	4.59	149	206-312
6	Di(2-ethylhexyl) phthalate	DEHP	$C_{24}H_{38}O_4$	117-81-7	390.6	386	1×10^{-7}	7.50	149	167-279
7	Di(n-octyl) phthalate	DOP	$C_{24}H_{38}O_4$	117-84-0	390.6	380	1×10^{-7}	8.06	149	279-261

Note 1: Kow: octanol–water partition coefficient; CAS: Chemical Abstract System
Note 2: [a]Data from Staples et al., 1997

Table 6. Physicochemical properties of the measured polycyclic aromatic hydrocarbons.

	Name	Acronym	CAS number	Formula	Molecular weight (g mol^{-1})	Boiling point[a] (C°)	Vapour pressure[c] (Pa)	Log Kow[a]	Target ion (m/z)	Qualifier ions (m/z)
1	Naphthalene	NAP	91-20-3	$C_{10}H_8$	128.17	217.9	11×10^{1} (25°C)	3.36	128	127
2	Acenaphtylene	ACEY	208-96-8	$C_{12}H_8$	152.20	280.0	3.9×10^{0} (20°C)	4.08	152	151
3	Acenaphthene	ACE	83-32-9	$C_{12}H_{10}$	154.21	297.0	2.1×10^{-1} (25°C)	4.32	153	154
4	Fluorene	FLU	86-73-7	$C_{13}H_{10}$	166.22	295.0	8.6×10^{-2} (25°C)	4.18	165	166
5	Phenanthrene	PHE	85-01-08	$C_{14}H_{10}$	178.24	340.0	1.3×10^{-1} (25°C)	4.46	178	176
6	Anthracene	ANT	120-12-7	$C_{14}H_{10}$	178.24	339.9	2.3×10^{-3} (25°C)	4.45	178	176
7	Fluoranthene	FLUA	206-44-0	$C_{16}H_{10}$	202.26	384.0	6.7×10^{-4} (25°C)	5.53	202	200
8	Pyrene	PYR	129-00-0	$C_{16}H_{10}$	202.26	404.0	3.3×10^{-4} (25°C)	5.30	202	200
9	Benzo(a)anthracene	BENAA	56-55-3	$C_{18}H_{12}$	228.29	437.6	2.9×10^{-6} (20°C)	5.60	228	226
10	Chrysene	CHR	218-01-9	$C_{18}H_{12}$	228.29	448.0	8.4×10^{-7} (25°C)	5.60	228	226
11	Benzo(b)fluoranthene	BENBF	205-99-2	$C_{20}H_{12}$	252.31	481.0[b]	6.7×10^{-5} (20°C)	6.60	252	250
12	Benzo(k)fluoranthene	BENKF	207-08-9	$C_{20}H_{12}$	252.31	480.0	6.7×10^{-5} (20°C)	6.85	252	250
13	Benzo(a)pyrene	BENAP	50-32-8	$C_{20}H_{12}$	252.31	311.0	7.5×10^{-7} (25°C)	6.00	252	250
14	Benzo(g,h,i)perylene	BENP	191-24-2	$C_{22}H_{12}$	276.32	500.0	1.4×10^{-8} (25°C)	7.00	276	277
15	Dibenzo(a,h)anthracene	DIB	53-70-3	$C_{22}H_{14}$	278.34	524.0	1.3×10^{-8} (20°C)	6.00	278	276
16	Indeno(1,2,3-c,d) pyrene	IND	193-39-5	$C_{22}H_{12}$	276.32	536.0	1.3×10^{-8} (25°C)	7.70	276	274

Note 1: [a] Data from Khiadani (Hajian) and al. 2013
Note 2: [b] Data from ICSC 0721–BENZO(k)FLUORANTHENE from https://inchem.org/documents/icsc/icsc/eics0721.htm
Note 3: [c] Data from Alice Paris, 2017

Table 7. The recovery of the targeted phthalates.

PAEs	Recovery (%)	
	Dissolved phase	Particulate phase
Dimethyl phthalate	105	70
Diethyl phthalate	97	74
Di-iso-butyl phthalate	99	91
Dibutyl phthalate	106	96
Butyl Benzyl phthalate	106	82
Di(2-ethylhexyl) phthalate	107	103
Di(n-octyl) phthalate	104	96

3.3.4. Polycyclic aromatic hydrocarbon analysis

The wastewater samples (200–500 mL) were filtered through pre-combusted (6 h at 500 °C) Frisenette GF/F filters to separate dissolved and particulate-bound phases. The extractions were performed according to the standard EN 16691:2016 (European Committee for Standardization), Water quality, determination of selected PAHs in whole water samples – method using SPE with SPEdisks combined with GC-MS. Briefly, SPE was performed with C18 PAH cartridges (Chromabond®, 6 mL/2000 mg) to extract the PAHs from the water samples. The cartridges were initially conditioned with 20 mL of dichloromethane, 10 mL of acetone, and 20 mL of MilliQ water. The glass bottles containing the samples spiked with internal standard (50 µg L^{-1}) were connected to the conditioned cartridges via Chromabond® tubing adaptors. The water sample was passed through the cartridge at a 25 mL min^{-1} flow rate using a vacuum pump. When all the samples were passed, the sample reservoir was rinsed with 4 mL of water and passed through the adsorbent. After the extraction, the cartridge was dried for 5 min with N_2 and eluted as follows: 5 mL of acetone, 10 mL of dichloromethane, 4 times 5 mL of dichloromethane, and finally, the sample reservoir was rinsed with 15 mL of dichloromethane and passed through the adsorbent. All eluates were passed through a funnel filled with Na_2SO_4 and collected in a glass vessel. The extracts were evaporated to almost dryness under a gentle stream of N_2 at room temperature. The solvent change was performed before the GC-MS analysis by dissolving the remaining extract in 2 mL of analytical grade toluene and evaporating to a volume of less than 0.5 mL. Finally, the extract was transferred to a glass autosampler vial, and the surrogate standard (injection) was added. The GF/F filters containing precipitated SPM were dried at 60 °C for 3 hours before the analysis. The filters were then spiked with the internal standard and ultrasonically extracted twice for 10 min with 10 mL of dichloromethane using an ultrasonic homogenizer Bandelin

Sonoplus HD 4200 equipped with a TS103 probe. Dichloromethane was evaporated to dryness, and PAHs were dissolved in 1 mL of toluene. Before the GC-MS analysis, the extracts were filtered through 0.22 µm PTFE filters.

The PAHs were analyzed following the EN 16691:2016 method using a Shimadzu GC-2010 Plus gas chromatograph coupled to a GC-MS-QP-2020 mass spectrometer. Helium served as the carrier gas at 1 mL min^{-1}. The GC injector was operated in splitless mode at 280 °C. Separation was performed on a Rxi-5Sil MS w/Integra-Guard capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness; Restek®, Bellefonte, USA). The temperature program used for PAHs analysis was: 90 °C, held for 2 min; ramped to 300 °C at 10 °C/min, held for 8 min. The transfer line and ion source were maintained at 280 °C and 300 °C, respectively. The mass spectrometer operated in time-scheduled SIM mode, with specific recording ions given in Table 6. LabSolutions software was used for signal acquisition and data handling. The MQL for PAHs varied from 0.011 to 0.044 µg L^{-1}. Recovery rate (%) calculations were conducted by analyzing spiked samples at 1 µg L^{-1} (dissolved and particulate; n = 10), resulting in recovery rates from 70% to 107% (Table 8). Quality control (QC) measures included procedural and instrumental blanks for each batch, with procedural blanks consistently below the MDL.

Table 8. The recovery of PAHs in the present study.

PAHs	Recovery (%)	
	Dissolved phase	Particulate phase
Naphthalene	107	105
Acenaphtylene	107	102
Acenaphthene	89	95
Fluorene	97	89
Phenanthrene	102	94
Anthracene	102	103
Fluoranthene	103	103
Pyrene	103	91
Benzo(a)anthracene	82	90
Chrysene	89	84
Benzo(b)fluoranthene	73	79
Benzo(k)fluoranthene	70	85
Benzo(a)pyrene	88	101
Benzo(g,h,i)perylene	78	92
Dibenzo(a,h)anthracene	99	105
Indeno(1,2,3-c,d)pyrene	94	87

3.3.5. Analytical determination of general wastewater quality

In the present study, six key wastewater quality parameters were analyzed, including total nitrogen (TN), total phosphorus (TP), dissolved organic carbon (DOC), biochemical oxygen demand (BOD), chemical oxygen demand (COD), and suspended particulate matter (SPM). These parameters were selected as indicators of wastewater composition and treatment efficiency, providing crucial data on nutrient content, organic pollution level, and solid matter concentration. A few additional parameters (bromides, nitrates, metals (Ca, Mg) and bacterial colony count were included to more specifically characterize wastewater quality and better define its influence on the ozonation experiment in the third research task.

In the laboratory, the wastewater and effluent samples for DOC analysis were centrifuged at 4200×g for 5 min to precipitate the suspended matter. The supernatant was then filtered through the Frisenette GF/F filters and analyzed at high temperature (680 °C) according to the guidelines outlined in ISO 20236:2018 (Water quality - Determination of total organic carbon (TOC) and dissolved organic carbon (DOC) after high-temperature combustion). The SPM was collected on the Frisenette GF/F filters, dried at 105 °C to constant weight for 48 hours, and weighed according to EN 872:2005 (Water quality – Determination of suspended solids - Method by filtration through glass fiber filters). TN was analyzed after dilution using the Shimadzu TOC 5000 analyzer (Shimadzu Corp., Japan) with a TN module, following the guidelines outlined in the ISO 20236:2018 method. Additionally, dissolved nitrates (NO_3^-) concentrations were measured with a 4-channel continuous flow analyzer (San^{++}, Skalar, The Netherlands) using standard colorimetric methods (Grasshoff et al., 1983) as described in Vybernaite-Lubiene et al. (2017). Total phosphorus (TP) was determined after digestion and oxidation of the organic phosphorus forms with alkaline per-oxodisulphate acid, then quantified spectrophotometrically following the molybdate method (Koroleff et al., 1983). Biochemical oxygen demand (BOD) over seven days was determined according to the LST EN ISO 1899-2:2000 method, with the addition of allylthiourea. Briefly, the samples were incubated in BOD bottles at 20 °C, and the decrease in dissolved oxygen (O_2) concentration was monitored during 7 days. Dissolved O_2 was determined with an optical sensor connected to a multiparameter benchtop meter WTW Multi 9630 IDS (Xylem Inc., Germany). Chemical oxygen demand (COD) was measured using the sealed-tube method (Macherey-Nagel, Germany) in accordance with ISO 15705:2002. Briefly, 2 mL of the homogenized sample was transferred into the test tube with the prepared reagent (Macherey-Nagel, Germany). The mixture was then heated at 150 °C for 2 h. Afterwards, the concentration was measured spectrophotometrically with MN Nanocolor VIS II (Macherey-Nagel). Additionally, bromide concentrations were determined in accordance with ISO

10304-1:2007 (Water quality) using ion-exchange chromatography performed with a Metrohm 930 Compact IC Flex ion chromatograph.

3.3.6. Metal analysis in the wastewater

The samples from the ozonation experiment were prepared in accordance with LST EN ISO 15587-2:2004, using a closed-type microwave system to perform digestion. A 5 mL aliquot of each sample was taken for analysis. For mineralization, the digestion was conducted at 170°C for 10 min. The analytical method employed allowed for the simultaneous determination of multiple elements. For calcium (Ca) quantification, the samples containing high concentrations were diluted 9-fold before analysis. Magnesium measurements utilized the Kinetic Energy Discrimination mode. Calcium analysis was performed using cold plasma combined with the Dynamic Reaction Cell mode on the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) system (Nexion 2000, Perkin Elmer, USA).

Water hardness was calculated from the concentrations of calcium and magnesium in the samples in mg L^{-1}. Calcium concentration was multiplied by a factor of 2.5, and the magnesium concentration by a factor of 4.1. These conversion factors correspond to the $CaCO_3$ equivalents of calcium and magnesium ions, respectively. The total water hardness was calculated as the sum of both components, representing the combined contribution of calcium and magnesium ions.

3.3.7. Microbiological quantification of colony-forming units

To determine the colony-forming units (CFU) in the wastewater before and after 5, 10 and 15 min of ozonation, samples with bacterial cultures were plated on Plate Count Agar (PCA) medium. The undiluted samples, as well as 1:10 and 1:100 serial dilutions, were prepared. A volume of 100 µL of each bacterial suspension was spread onto the agar surface. The plates were incubated at 37°C for 16–18 hours to allow bacterial growth and colony formation. CFUs were calculated by multiplying the number of colonies counted on an agar plate by the inverse of the dilution factor and dividing by the volume of the culture plated, expressed as: CFU mL^{-1} = (No. of Colonies × Dilution Factor)/ Volume Plated (mL).

3.4. Numerical and statistical analysis

3.4.1. Pollution loading calculation

The mass balance of pollutants entering and leaving the WWTPs was estimated by multiplying the measured analyte concentrations by the monthly or daily corresponding influent or effluent volumes for the same sampling period:

$$L = C \times V$$

where L is the pollutant load, C is the pollutant concentration, and V is the wastewater volume.

The input loads of EEQs and PAEs (paper I) were expressed as g month^{-1} and kg month^{-1}, respectively, while the corresponding output loads were reported in g month^{-1}. Similarly, the input loads of pharmaceuticals (VEN, CBZ) and estrogens (E1, E2) were calculated in g day^{-1}, whereas PAHs and PAEs were expressed in kg day^{-1} (paper II). The output loads for all micropollutants except PAHs (which were not detected in effluents) were reported in g day^{-1}. Most conventional wastewater quality parameters had input loads calculated as t month^{-1} or t day^{-1}, while output loads were reported in kg month^{-1} or kg day^{-1}.

All daily influent and effluent flow data were kindly provided by UAB "Palangos Vandenys," UAB "Neringos Vanduo," and AB "Klaipedos Vanduo".

3.4.2. Risk assessment and predicted no-effect concentration

The predicted no-effect concentration (PNEC) is a widely used metric in environmental risk assessment, representing the maximum concentration of a substance unlikely to cause adverse effects on aquatic organisms (Caldwell et al., 2008). Compounds such as E2 and E1 are known endocrine disruptors that can impact aquatic life at very low concentrations. This study used PNECs to evaluate potential ecological risks posed by micropollutants discharged from the coastal WWTPs to adjacent marine ecosystems. The PNEC values were derived from published chronic toxicity data for sensitive aquatic species, including fish, algae, and invertebrates. A summary of the PNEC values and their corresponding literature sources is provided in Table 9.

Table 9. Predicted no-effect concentration (PNEC) of selected micropollutants.

Micropollutant	PNEC	References
E1	4.0 ng L^{-1}	Loos et al., 2018
E2	0.4 ng L^{-1}	Loos et al., 2018
VEN	90.0 ng L^{-1}	Qu et al., 2018
CBZ	500.0 ng L^{-1}	Oldenkamp et al., 2019
DBP	10.0 µg L^{-1}	ECHA, 2023

Note: E1– estrone, E2 – 17 beta-estradiol, VEN – venlafaxine, CBZ – carbamazepine, DBP – dibutyl phthalate.

To assess the environmental hazard levels of the investigated micropollutants, the risk quotient (RQ) was calculated as the ratio between the measured environmental concentration (MEC) and the PNEC.

$$RQ = \frac{MEC}{PNEC}$$

Ecological risk levels were classified based on RQ values as follows: minimal risk ($RQ < 0.1$), moderate risk ($0.1 \leq RQ < 1$), and high risk ($RQ \geq 1$).

3.4.3. Statistical methods

Due to the limited sample size ($n < 20$), statistical linear relationships among tourism indicators, nutrient concentrations, PAEs levels, and other water quality indicators were assessed using the non-parametric Spearman correlation. Hoeffding's D association statistic was applied to identify the significant non-linear and non-monotonic relationship (Lesley et al., 2011) between EEQ values, environmental variables, temperature, flow rates, tourism indicators, and PAEs levels. This approach accounted for the potential interference from the other compounds; for example, pharmaceutical residues may suppress estrogenic activity (Ezechiáš et al., 2016), resulting in a non-linear response to tourism indicators. All statistical analyses were performed using R software version 4.1.2 and Python 3.12.1. The estrogenic activity in wastewater samples, before and after treatment, was further evaluated using the BioVAL statistical tool (new_diagnostics GmbH, Germany), which supports biochemical data interpretation and calculation. This includes assessing the ability of estrogenic compounds to bind to estrogen receptors. BioVal applies multiple statistical methods based on non-linear response models.

4

Results

4.1. Seasonal impact on pollution dynamics in coastal WWTPs

4.1.1. Seasonal quality of the influent received by the coastal WWTPs

The results presented in this chapter were published in Paper I. In this study, Nida and Palanga represent Small and Large Lithuanian coastal resorts, respectively. The influent discharge from Large and Small resorts followed seasonal patterns, with the peaks during the high-tourism months between June and August.

The seasonal dynamics of the influent were more pronounced at the Small resort, where the average monthly flow rate increased by more than 2-fold, from the non-tourist season (December–February; ~12,081 m^3) to the high tourist season (June to August; ~25,623 m^3). In contrast, the flow rate from the Large resort showed only a slight increase during the tourist season (~286,420 m^3) compared to the non-tourist season (~237,437 m^3). Air temperatures in both resorts showed a clear seasonal pattern, peaking in summer (June–August) and reaching their lowest values in winter (December–February). The average summer air temperature was ~22 °C in both resorts. The highest temperatures were recorded in August at both resorts, 26 °C and 29 °C, respectively, in Small and Large ones; nevertheless, it did not coincide with the highest influent volume produced in the WWTPs of these resorts (Fig. 6). Air

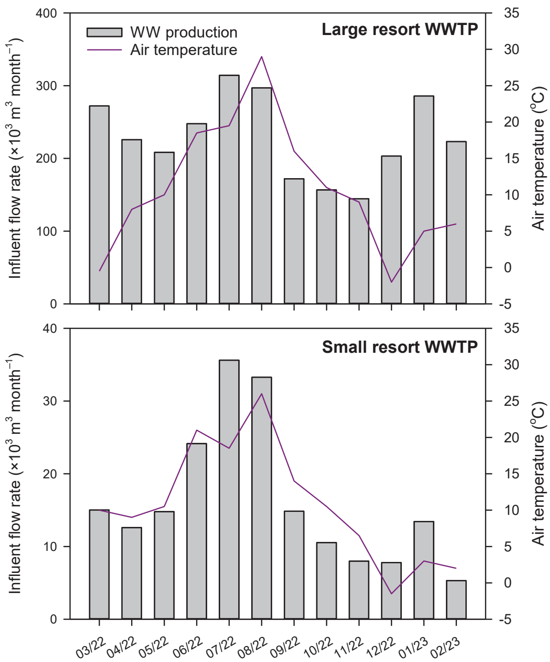

Figure 6. Monthly flow rate from Large (upper panel, Palanga) and Small resorts (bottom panel, Nida), and air temperature (recorded during sampling) at WWTPs, monthly between March 2022 – February 2023. Reprinted from Paper

temperature was significantly correlated with the influent discharge only at the Small resort WWTP ($r=0.87$, $p<0.05$). It was also strongly related to tourism proxies: incoming car count to Small and overnight stays booked at Large resorts. Tourism proxies were significantly correlated with most quality parameters measured in the influent of the resort areas. Among the measured chemical parameters, DOC and nutrients (TN, TP) showed strong correlations with COD and BOD (Fig. 7).

Chemical oxygen demand and BOD in the influent discharged from the resorts varied from 5.4 to 820.3 mg O_2 L^{-1} and 3.9 to 375.0 mg O_2 L^{-1}, respectively, showing obscure seasonal patterns (Fig. 8a, b). Both organic pollution indicators increased from March to July, declining in August in the influent discharged to the Large resort WWTP (Fig. 8a). In contrast, at the Small WWTP, COD and BOD fluctuated throughout the year, with lower values in July and a distinct peak in August (Fig. 8b). The mean COD/BOD ratio (~0.5) indicated moderate influent biodegradability at both WWTPs (Fig. 8a, b). DOC and nutrient (TN, TP) loads exhibited an upward seasonal trend, peaking during the summer months (July–August) in the influent discharged to corresponding WWTPs (Fig. 8c–f). However,

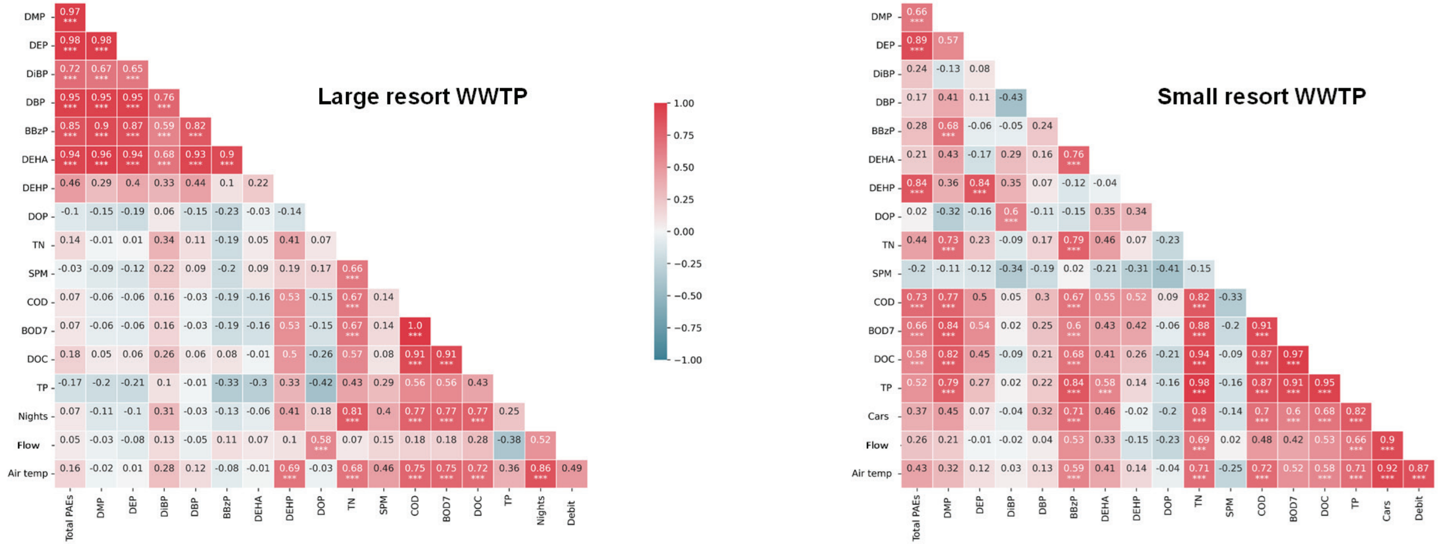

Figure 7. Correlogram for the linear correlations among tourism indicators (requested nights and cars), influent flow rate (debit), and pollutants at WWTPs of Large (left panel) and Small seaside resorts (right panel). Correlograms were built on Spearman correlation matrices. Values labelled by asterisks indicate a significant correlation ($p<0.05$). Correlation strength is in the range of –1 and 1. Blue cells show a negative linear correlation. Reprinted from Paper I

the mean DOC load (n=3) was ~10-fold lower during the tourism season (June–August) at the Small resort WWTP. Mean pre-season (March–May) influent loads of TN (0.7 t month^{-1}) and TP (0.1 t month^{-1}) increased more from the Small resort, with the maximum values reached during August at 5.3 t month^{-1} and 0.7 t month^{-1}, respectively (Fig. 8e, f). Similarly, nutrient loads increased at the Large resort WWTP in July, with TN rising from 10.7 to 26.5 t month^{-1} and TP from 1.4 to 3.6 t month^{-1}. Mean pre-season SPM load (2.8 t month^{-1}) increased during the tourism season (June–August), particularly in August, up to 17.2 t month^{-1} at the Small resort WWTP. At a Large resort WWTP, SPM increased from a pre-season mean of 50.0 to 89.9 t month^{-1} in July. While SPM displayed a more pronounced seasonal increase in the influent at the Small resort WWTP, the elevated load discharge was observed outside the tourism season from the Large resort to the corresponding WWTP, accounting for 68.5 and 62.1 t month^{-1} in November and December, respectively (Fig. 8c, d).

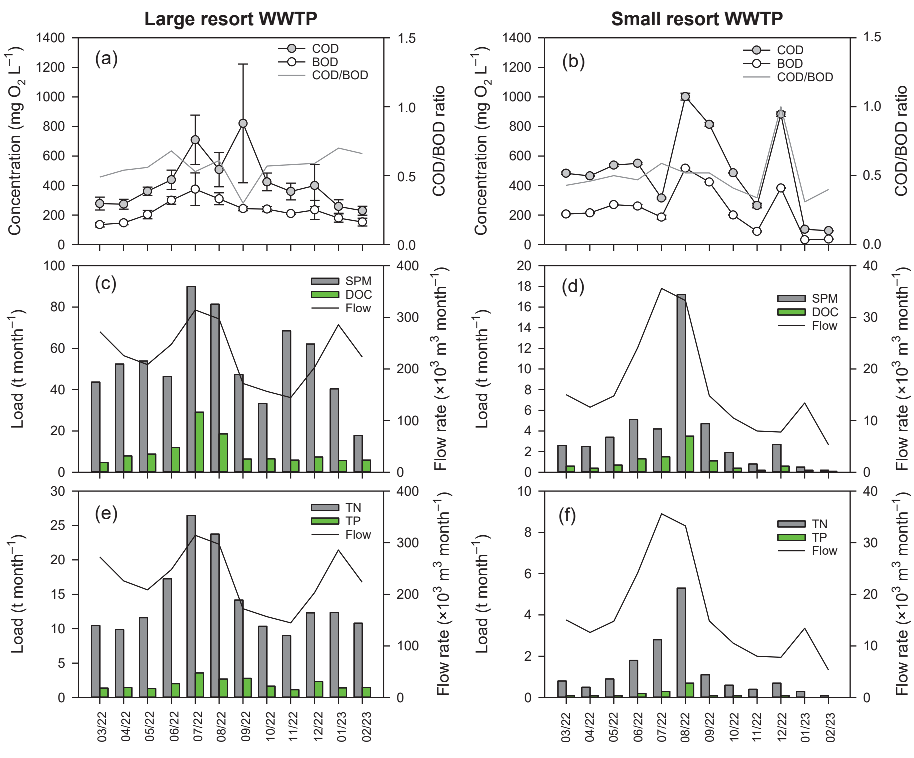

Figure 8. Monthly dynamics of chemical and biochemical oxygen demand and their ratio (a, b), influent flow rate and suspended matter, dissolved organic matter (c, d), and nutrients (e, f) loads in the influent from Large (left panels) and Small resorts (right panels) to their WWTPs during March 2022 – February 2023. Data (only a and b panels) refers to average and standard error (n=3). Reprinted from Paper I.

The yearly mean DOC concentrations (n=12) ranged from 17.4 to 104.0 mg C L^{-1}, while SPM fluctuated more between 37.3 and 516.7 mg L^{-1} in the influent at both WWTPs. Nutrient concentrations were similar between the Small and Large resort WWTPs. TP ranged from 2.3 to 19.1 mg P L^{-1}, while TN varied from 19.4 to 158.0 mg N L^{-1}. Among measured quality parameters, average summer concentrations of DOC (68 mg C L^{-1}) in Large and TN (104.0 mg N L^{-1}) in Small resorts WWTPs showed the most substantial elevations compared to their annual means (42.0 mg C L^{-1} and 65.0 mg N L^{-1}, respectively, DOC and TN; Table 10).

Table 10. Summer and annual concentrations of nutrients and suspended matter in the influent at WWTPs serving Small and Large resorts. Reprinted from Paper I.

Measure	Larger resort WWTP		Small resort WWTP	
	Summer	Annual	Summer	Annual
TN [mg N L^{-1}]	78 (70–80)	61 (38–84)	104 (76–158)	65 (19–158)
TP [mg P L^{-1}]	10 (8–11)	9 (5–16)	12 (8–20)	8 (2–19)
DOC [mg C L^{-1}]	68 (49–93)	42 (17–93)	67 (43–104)	46 (15–104)
SPM [mg L^{-1}]	262 (101–473)	210 (37–473)	240 (227–259)	237 (117–517)

Note 1: TN – total nitrogen, TP – total phosphorus, DOC – dissolved organic carbon, SPM – suspended particulate matter.
Note 2: Data is represented by mean (n=12), and min and max values are provided in brackets. The summer season refers to the June–August.

4.1.2. Micropollutant dynamics and composition in influent

Analysis of individual PAE concentrations in the influent from WWTPs at both resorts showed no clear relationship with increased tourism during warmer months. The measured concentrations of PAEs varied widely from below the analytical limit of quantification to 166.7 µg L^{-1}. At the Large resort WWTP, three dominant PAEs were detected: DBP (11.7 µg L^{-1} on average), DEHP (19.4 µg L^{-1} on average), and DEP (166.7 µg L^{-1} on average). At the Small resort WWTP, lower average concentrations of DBP (4.0 µg L^{-1}), DEHP (78.0 µg L^{-1}), and DEP (42.2 µg L^{-1}) were found (Table S1). The relative contribution (RC) of DEP and DEHP dominated the PAE composition, accounting for ~41% and ~45% of the total amount in the influent delivered to the Large resort WWTP, respectively. At the Small WWTP, DEP accounted for ~30%, while DEHP accounted for ~55%. Overall, DEP predominated in the dissolved phase (>60%), and DEHP was the main component in the particulate–bound phase (>80%) at both WWTPs (Fig. 9).

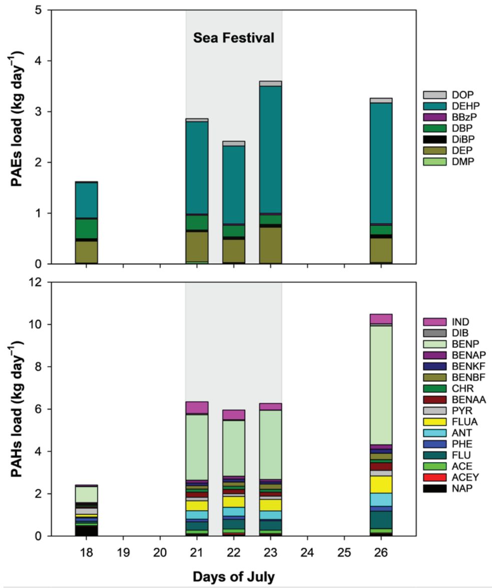

Figure 9. Mean relative contribution of 8 plasticizers in different phases (dissolved [DP], particulate-bound [PP], and total [TP]) in the influent delivered from two coastal resorts to the WWTPs. Relative contribution (%) = (Concentration of individual PAE / ΣPAEs × 100). Reprinted from Paper I.

The DEP, DiBP, DBP, and DEHP exhibited the highest detection frequencies (DF) in influent from both resorts. These PAE congeners displayed distinct distribution patterns between the dissolved (DP) and particulate-bound (PP) phases. While DEP appeared exclusively in the DP, DEHP was predominantly detected in the PP (>97%). DiBP and DBP were consistently found across both phases, with DF exceeding 89% at both WWTPs (Table 11).

Table 11. Mean detection frequency (DF, %) of the individual PAEs in the influent at the WWTPs of Small and Large resorts. Modified from Paper I.

PAEs congener	Phase	WWTP	
		Large	Small
DMP	DP	50	50
	PP	8.3	0
	TP	50	50

PAEs congener	Phase	WWTP	
		Large	Small
DEP	DP	100	100
	PP	0	0
	TP	100	100
DiBP	DP	86	92
	PP	25	25
	TP	89	100
DnBP	DP	100	100
	PP	83	89
	TP	100	100
BBzP	DP	25	8
	PP	33	19
	TP	50	25
DEHA	DP	8	0
	PP	19	8
	TP	17	8
DEHP	DP	100	86
	PP	100	97
	TP	100	97
DOP	DP	50	8
	PP	8	50
	TP	50	58

Note: DP – dissolved phase, PP – particulate-bound phase, TP – total amount (DP+PP).

At the Small resort WWTP, total PAE concentrations in the influent were correlated with organic matter content, as indicated by a stronger correlation with BOD and COD. However, at the Large resort WWTP, total PAEs didn't have a significant ($p > 0.05$) correlation with the influent quality parameters (Fig. 7). At both resorts, tourism activity was closely linked to PAE levels. In particular, total PAEs (DP+PP) and DEHP in the PP showed similarly strong correlation with tourism proxies of car counts incoming to a Small resort ($r = 0.63$, $r = 0.61$, $p < 0.05$), respectively, and overnight stays in the larger resort ($r = 0.68$, $r = 0.81$, $p < 0.05$), respectively (Table 12).

The estimated mean monthly load of total PAEs ($n = 12$) in the influents was higher at the large resort WWTP (~8.6 kg $month^{-1}$) than at the smaller one (~1.7 kg $month^{-1}$). Higher PAEs loads were recorded in August, accounting for 0.9 and 10.5 kg $month^{-1}$, compared to mean pre-season levels of 0.45 and 2.7 kg $month^{-1}$ in the Small and Large resort WWTPs, respectively. At the Small resort WWTP, the increased load was detected in September

(~1.8 kg month^{-1}). Notably, a high load of 42.5 kg month^{-1} was recorded in May at the Large resort WWTP, 4 times higher than the monthly mean load (Fig. 10).

Table 12. The relationship between the total PAEs, DEHP in the particulate phase in influent, and tourism proxies of cars (Small) and overnights (Large) in resorts, measured by Spearman's correlation.

Tourism proxies	PAEs	r_s coefficient	p-value
Overnights	ΣPAEs	0.68	0.015
	DEHP (PP)	0.81	0.002
Cars	ΣPAEs	0.63	0.029
	DEHP (PP)	0.61	0.035

Note 1: ΣPAEs – sum of 8 plasticizers in dissolved + particulate-bound phases, PP – particulate phase.
Note 2: The correlation coefficient (r) indicates the strength and direction of the correlation, ranging from -1 to 1; significance is indicated by $p < 0.05$.

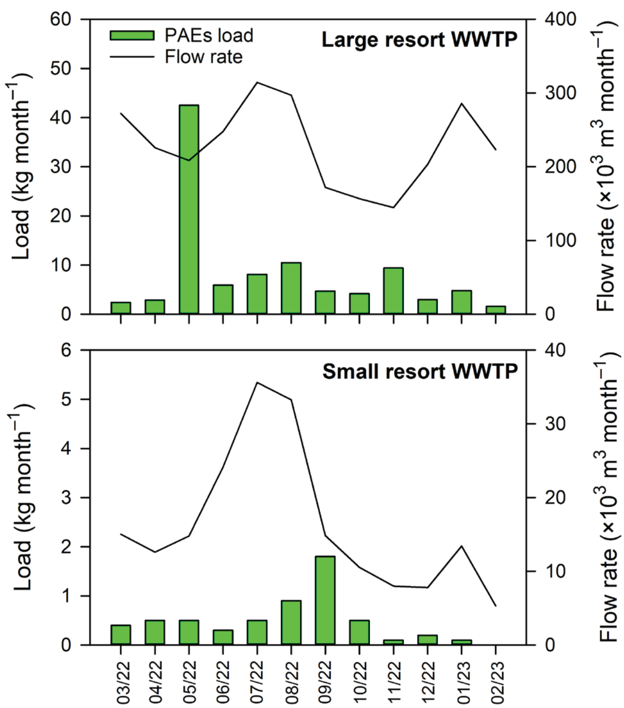

Figure 10. Monthly influent flow rate and load of total PAEs from large and small seaside resorts during March 2022 – February 2023. Reprinted from Paper I.

The level of EEQ in the influent from both resorts varied from 1.0 to 3.7 ng L^{-1}, with the maximum of 4 ng L^{-1} observed at the Small resort WWTP in October (Fig. 11). At this WWTP, EEQ level remained consistent at ~1.5 ng L^{-1} during March–September, then increased up to ~3.0 ng L^{-1} from December to February. The Large resort influent exhibited EEQ fluctuation from ~1.0 ng L^{-1} in July to ~3.8 ng L^{-1} in February. Overall, EEQ concentration in the influents from both resorts was lower in summer (June–August) and higher in colder months, showing an inconsistent seasonal pattern (Fig. 11).

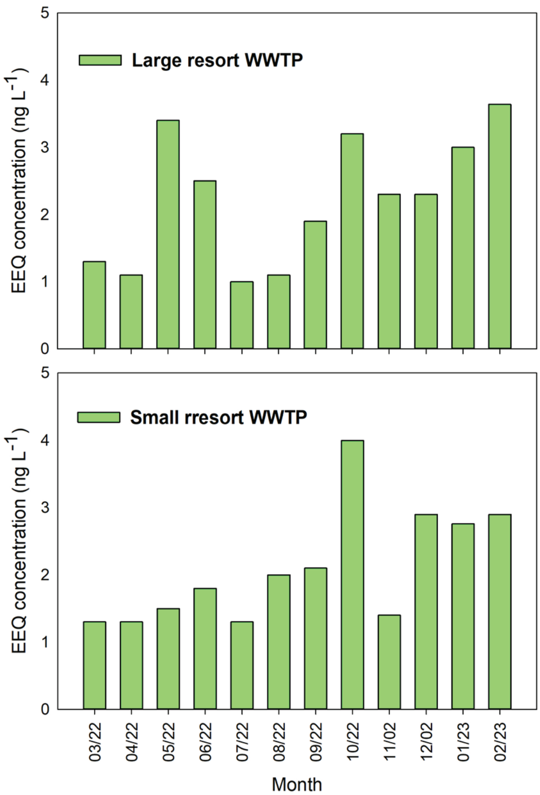

Figure 11. Estrogenic equivalent (EEQ) concentration (ng L^{-1}) in the influent discharged from Small and Large resorts during March 2022 – February 2023.

At the Large resort WWTP, EEQ loads showed no significant correlation ($p > 0.05$) with the tourism proxy, overnight requests, and other examined parameters. In contrast, in the influent of the Small resort WWTP, a significant ($p < 0.05$) non-linear association was found between the EEQ loads and tourism proxy (cars entering), as well as several influent quality parameters, including TN, DOC, BOD, and COD ($p < 0.05$) (Table 13).

Table 13. Non-linear association (Hoeffding's D statistics) between an estrogenic equivalent (EEQ) load and quality indicators, influent flow rate (debit), PAEs levels, tourism indicators (cars, and overnights), and air temperature in the Large and Small wastewater treatment plants (WWTPs). Reprinted from Paper I.

Parameter	Large resort WWTP	Small resort WWTP
TN	r =0.10, p = 0.258	**r = 0.20, p = 0.003**
TP	r = -0.02, p = 0.435	r = 0.04, p = 0.112
DOC	r = -0.06, p > 0.05	**r = 0.08, p =0.044**
BOD7	r = -0.02, p = 0.518	**r = 0.12, p = 0.018**
COD	r = -0.02, p = 0.518	**r =0.12, p = 0.020**
SPM	r = -0.03, p = 0.560	r = -0.07, p > 0.05
ΣPAEs	r = -0.08, p > 0.05	r = 0.02, p = 0.234
Debit	r = 0.03, p = 0.142	r = 0.05, p = 0.086
Air temperature	r = 0.03, p = 0.312	r = 0.06, p = 0.066
Tourism indicators	r = -0.03, p = 0.559	**r = 0.10, p = 0.027**

Note 1: A significant relationship ($p < 0.05$) is shown in bold.
Note 2: The Hoeffding's dependency constant ranges from -0.5 to 1, indicating no association intensity or direction level.

The estimated mean influent EEQ loads at the Small and Large resort WWTPs were 30 and 376 mg month^{-1}, respectively. Seasonal EEQ load dynamics and influent flow rate were more pronounced at the Small resort WWTP, with an EEQ peak in July (~67 mg month^{-1}) and an increase in influent flow rate from 15,000 to 35,611 m^3 month^{-1}. In contrast, the seasonal EEQ pattern at the Large resort WWTP was obscured by high inter-month variability. Elevated EEQ loads were recorded outside the tourism season, specifically in January and February (~800 mg month^{-1}). Although the influent flow rate at Palanga WWTP was highest in July and August, it fluctuated inconsistently throughout the year (Fig. 12).

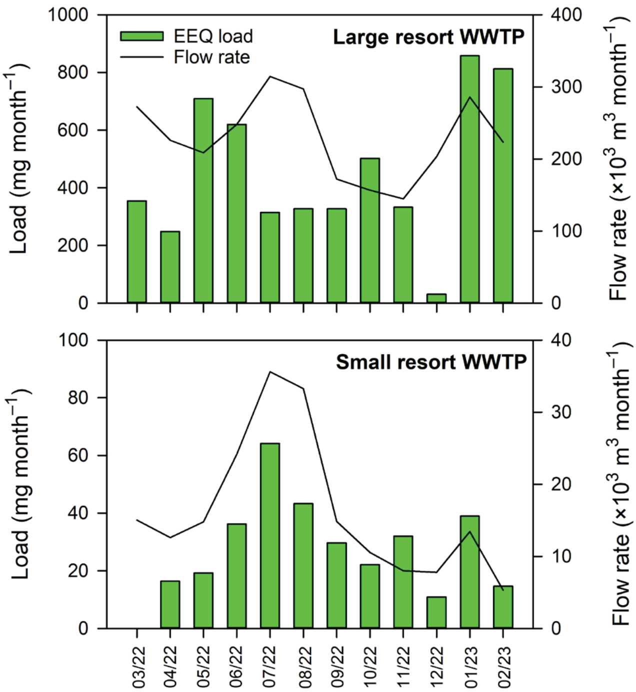

Figure 12. Monthly influent flow rate and load of total estrogenic equivalent (EEQ) from the Large (upper panel) and Small seaside resorts (bottom panel) during March 2022 – February 2023. Reprinted from Paper I.

4.1.3. Pollution retention at the coastal resort WWTPs

Wastewater treatment processes substantially impacted the effluent quality, reducing nutrient (TN, TP), organic matter, and micropollutants in the influent, as summarised in Table 14. Retention refers to the difference between the delivered and discharged loads of material and is estimated as the retained proportion in percentage. While most pollution was retained efficiently, biological treatment had a less pronounced effect on DOC, with mean removals of 73% and 65% at the Large and Small resort WWTPs, respectively. In contrast, the mean load removal of SPM was consistently high, ranging from 89 to 98%. Both WWTPs also achieved high retention of total PAEs, ranging from 81 to 99%. The residual EEQ loads indicated that the annual mean retention after treatment at both WWTPs was ~78%; however, it dropped by up to 15% during the summer season (June–August) (Table 14).

Table 14. The relative amount of nutrients, micropollutants, and suspended matter retained at the coastal WWTPs. Reprinted from Paper I.

Measure	Large resort WWTP (%)		Small resort WWTP (%)	
	Summer	Annual	Summer	Annual
TN	80	80 (55–94)	80	75 (55–94)
TP	85	83 (63–97)	85	83 (63–97)
DOC	79	73 (45–91)	79	65 (49–87)
SPM	92	98 (92–99)	92	89 (67–97)
EEQ	70	77 (40–95)	65	78 (53–98)
ΣPAEs	99	99 (98–100)	81	87 (53–100)

Note 1: TN – total nitrogen, TP – total phosphorus, DOC – dissolved organic carbon, SPM – suspended particulate material, EEQ – estrogenic equivalent, ΣPAEs – (sum of 8 plasticizers in dissolved + particulate-bound phases).
Note 2: Data is represented by mean (n=12), and min and max values are provided in brackets. The summer season refers to the June–August.

The high SPM removal in the influents at both WWTPs resulted in lower effluent BOD, COD, and nutrient concentrations. However, the maximum punctual concentrations of TN and TP reached up to 24.0 mg N L^{-1} and 8.0 mg P L^{-1}, from the Small and Large WWTPs, respectively. General pollution variation was similar across the effluents discharged by the studied WWTPs, with SPM concentrations ranging from 2.0 to 25.0 mg L^{-1} and DOC concentrations from 3.6 to 13.3 mg C L^{-1}. The mean summer (June–August) TN concentration in the effluent from both WWTPs was slightly elevated relative to the annual average (Table 15).

Table 15. Summer and annual concentration of nutrients and suspended matter in the effluents at wastewater treatment plants (WWTPs) of two coastal resorts. Reprinted from Paper I.

Measure	Large resort WWTP		Small resort WWTP	
	Summer	Annual	Summer	Annual
TN [mg N L^{-1}]	16 (15–17)	12 (1–17)	20 (17–24)	13 (5–24)
TP [mg P L^{-1}]	0.6 (0.3–0.8)	2 (0.1–8)	1.4 (0.4–3)	1 (0.3–3)
DOC [mg C L^{-1}]	10 (7–13)	10 (3.6–13)	12 (10–13)	12 (9–13)
SPM [mg L^{-1}]	8 (5–14)	10 (2–24)	4 (3–7)	11 (2–25)

Note 1: TN – total nitrogen, TP – total phosphorus, DOC – dissolved organic carbon, SPM – suspended particulate material.
Note 2: Data is represented by mean (n=12), and min and max values are provided in brackets. The summer season refers to the June–August.

Phthalates showed distinct distribution patterns between the studied WWTPs. The effluent from the Small resort WWTP had DiBP, DBP, and DEHP with the highest relative contributions (RC). In contrast, the Large resort WWTP was dominated by DBP and DEHP. Partitioning between phases differed by compound: DiBP and DBP were mainly present in the dissolved phase (DP), accounting for more than 75% of the total PAE contribution. DEHP was predominantly associated with the particulate phase (PP), accounting for more than 70% of the total PAE contribution. DOP contributed 20% of PAEs in the dissolved phase in the effluent from the Large resort WWTP, but was minimal from the Small resort WWTP. Composition in the total phase (TP) (DP+PP) varied between the WWTPs; at the Small resort WWTP, a higher RC of DiBP and a lower RC of DEHP were found compared to the Large resort WWTP (Fig. 13).

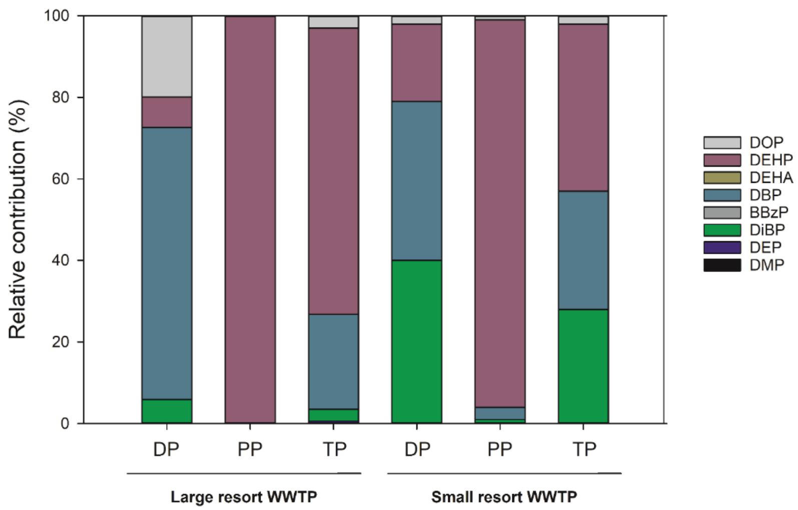

Figure 13. Mean relative contribution of 8 plasticizers in different phases (dissolved [DP], particulate-bound [PP], and total [TP]) in the effluent discharged from the WWTPs of Large and Small coastal resorts, respectively. Relative contribution (%) = (Concentration of individual PAE / ΣPAEs) × 100. Reprinted from Paper I.

Approximately 30% of the effluent samples exceeded the predicted No-Effect Concentrations (PNECs) threshold of 0.4 ng L^{-1} EEQ for E2 (Loos et al., 2018). Risk Quotient (RQ) assessment indicated a consistent potential risk to the aquatic ecosystem throughout the monitoring year at both WWTPs. At the Large coastal WWTP, the effluent samples were evenly distributed between medium risk (50%) and high risk (50%). At the Small WWTP, 42% of samples were classified as high risk, while 58% were classified as medium risk. The concentrations of PAEs did not exceed their PNEC values, indicating a negligible risk to the coastal environment (Table 16).

Table 16. The mean concentration of estrogenic equivalent (EEQ) and exceedance levels relative to the PNEC threshold of 0.4 ng L^{-1} in effluents discharged from the Large and Small resorts (Palanga and Nida, respectively) WWTPs during March 2022 – February 2023. Modified from Paper I.

Date	Large resort WWTP			Small resort WWTP		
	EEQ (ng L^{-1})	Relative exceedance of PNEC (%)	RQ	EEQ (ng L^{-1})	Relative exceedance of PNEC (%)	RQ
03/2022	0.3±0.0	< PNEC	0.8	NA	NA	NA
04/2022	0.4±0.0	0%	1.0	0.4±0.1	0%	1.0
05/2022	0.5±0.0	25%	1.3	0.3±0.1	< PNEC	0.8
06/2022	0.3±0.1	< PNEC	0.8	0.7±0.2	75%	1.8
07/2022	0.6±0.0	50%	1.5	0.7±0.2	75%	1.8
08/2022	0.2±0.0	< PNEC	0.5	0.3±0.1	< PNEC	0.8
09/2022	0.1±0.1	< PNEC	0.3	0.2±0.1	< PNEC	0.5
10/2022	0.5±0.0	25%	1.3	0.3±0.0	< PNEC	0.8
11/2022	0.3±0.0	< PNEC	0.8	0.1±0.0	< PNEC	0.3
12/2022	0.7±0.1	75%	1.8	0.3±0.1	< PNEC	0.8
01/2023	0.8±0.1	100%	2.0	0.5±0.1	25%	1.3
02/2023	0.3±0.1	< PNEC	0.8	0.4±0.1	0%	1.0

Note 1: The RQs for the EEQ were calculated by dividing the measured environmental concentration (MEC) by the PNEC.
Note 2: NA - not available. The data are presented as mean ± standard error.

4.2. Public event impact on pollution dynamics at the coastal WWTP

4.2.1. Nutrient and organic pollution in the influent released from the city to its WWTP

The results presented in this chapter were published in Paper II. Before the festival (July 18th, 2023), the Klaipėda WWTP received ~29,700 m^3 day^{-1} of the influent load. The peak flow occurred on the festival's final day (July 23rd), reaching ~34,500 m^3 day^{-1}. This reflected an increase of 16%, exceeding the average July flow (~32,000 m^3 day^{-1}) by 11%. (Fig. 14). Following the festival, the influent flow rate initially decreased, then fluctuated moderately until exhibiting a sharp and substantial increase on the 31st of July, reaching the highest recorded value of approximately 44,686 m^3 day^{-1}.

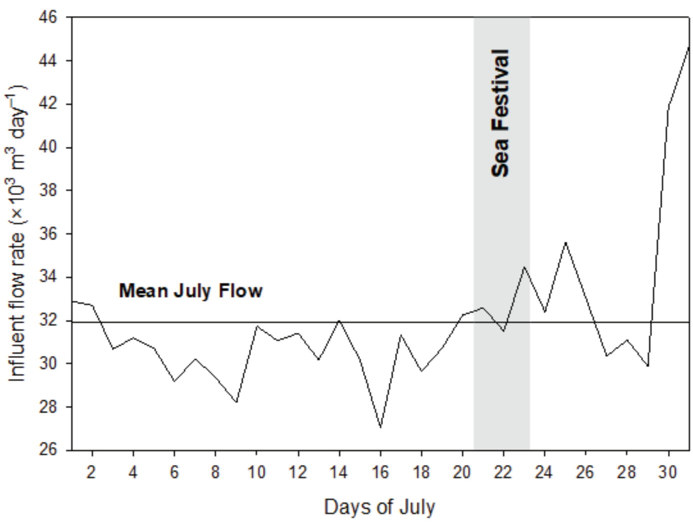

Figure 14. Daily influent flow rate in July 2023 at the Klaipėda WWTP. The Sea Festival period is highlighted in grey (21–23 July 2023). (Reprinted from Paper II)

During the festival (21–23 July), the DOC load received by the Klaipėda WWTP increased from 3.0 t day^{-1} on 18 July to 5.5 t day^{-1} on the festival's first day. Over the subsequent days, the DOC load decreased to ~4.3 t day^{-1}. The initial pre-festival SPM level of 17.3 t day^{-1} increased progressively during the festival, reaching the maximum of 53.6 t day^{-1} on the final day. Nutrient loads also showed a clear upward trend. TN rose from 3.0 to ~ 4.0 t day^{-1} during the first two festival days, reaching 5.5 t day^{-1}

by the last day. Similarly, TP increased incrementally from 0.4 to 0.8 t day^{-1}, reaching 1.0 t day^{-1} on the final day. After the festival, pollution loads decreased but remained above the initial pre-festival levels (Fig. 15).

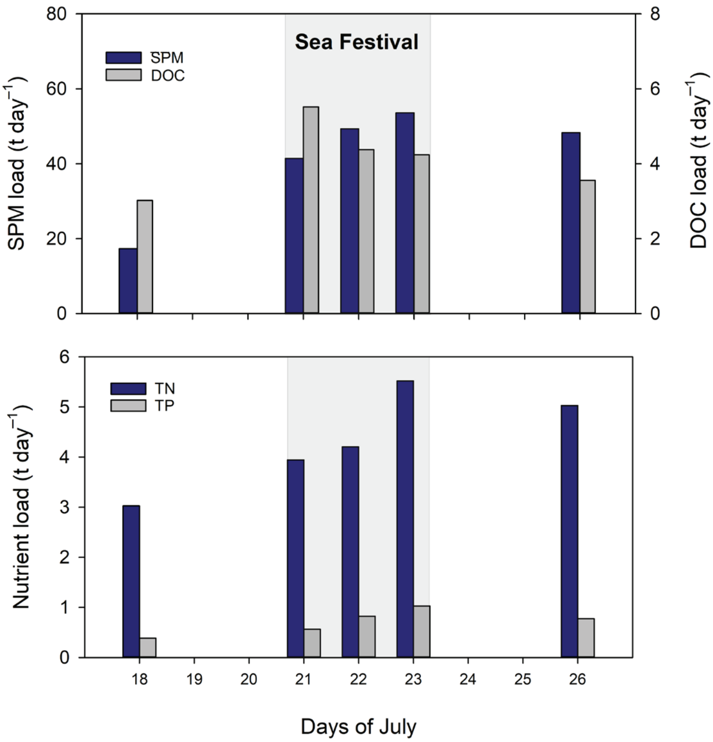

Figure 15. Suspended particulate matter (SPM), dissolved organic carbon (DOC) (upper panel), and nutrient (TN – total nitrogen, TP – total phosphorus; bottom panel) loads in the Klaipėda city WWTP from 18 to 26 July 2023. The Sea Festival period is highlighted in grey (21–23 July). Reprinted from Paper II.

Table 17 presents the mean concentrations of key quality parameters in the influent reaching the Klaipėda WWTP during the Sea Festival (July 21-23). The maximum increases in nutrient concentrations on the final festival day were observed for TN, rising from 121.0 to 160.0 mg L^{-1}, and for TP, increasing from 17.3 to 29.8 mg L^{-1}. The most substantial rise was observed in SPM, from 585.0 to 1565.0 mg L^{-1} on the second day, while DOC reached its highest level of 169.3 mg L^{-1} on the first day. BOD fluctuated between 636.0 and 1408.5 mg O_2 L^{-1}, whereas COD ranged from 1500.0 to 3030.0 mg O_2 L^{-1}, showing no clear festival-related trend. Elevated levels of COD and BOD persisted after the festival, as observed on the 26th of July. In addition, SPM loads exhibited a strong correlation with TN and TP, with correlation coefficients of $r = 0.84$ and $r = 0.89$, respectively ($p < 0.05$) (Fig. S1).

Table 17. The mean punctual concentration of nutrients, biochemical, chemical oxygen demand, and suspended particulate matter in the influent at the Klaipėda WWTP. Reprinted from Paper II.

Date	Quality parameters concentration (mg L^{-1})					
	TN	TP	DOC	COD	BOD	SPM
18/07/23	102.0±0.6	13.0±0.6	101.9±0.3	1500.0±57.7	636.0±26.2	585.0±20.4
21/07/23	121.0±1.5	17.3±1.0	169.3±0.8	2486.0±66.3	993.7±21.1	1270.0±61.2
22/07/23	133.3±5.2	26.2±3.6	138.9±5.7	2431.3±188.1	851.3±54.9	1565.0±93.9
23/07/23	160.0±1.5	29.8±1.1	122.9±1.1	2334.7±294.6	938.3±73.1	1553.0±98.0
26/07/23	152.3±19.3	23.4±5.7	107.8±2.7	3030.0±556.4	1408.5±189.8	1463.0±416.4

Note 1: –total nitrogen, TP – total phosphorus, DOC – dissolved organic carbon, BOD – biochemical oxygen demand, COD – chemical oxygen demand, SPM – suspended particulate matter.
Note 2: The data are presented as mean ± standard error.

4.2.2. Micropollutant dynamics in the influent outflow to Klaipėda WWTP

During the festival (21–23 July), the hormone load in the influent received by the Klaipėda WWTP substantially increased. E2 rose from 0.3 g day^{-1} on 18 July to the maximum of 0.6 g day^{-1} on 22 July, while E1 rose from 2.8 to the maximum of 5.3 g day^{-1} on 23 July. The combined hormone load (E1+E2) peaked from 3.1 to 5.8 g day^{-1} on 23 July and remained elevated at 5.9 g day^{-1} after the festival. Pharmaceutical loads showed no consistent trend. The mean load of CBZ remained between 12.8 and 16.6 g day^{-1} during 18–26 July. Similarly, the mean load of VEN ranged from ~ 3.7 to 4.7 g day^{-1} with total loads of pharmaceuticals (VEN+CBZ) reaching the maximum of ~ 21 g day^{-1} (Fig. 16).

Phthalate loads doubled during the festival, increasing from 1.6 to the maximum of 3.6 kg day^{-1} on the final day, remaining elevated post-festival at 3.3 kg day^{-1}. Among the PAEs, DEP, DBP, and DEHP were the most prevalent. DEHP contributed the most, rising from 0.7 to 2.5 kg day^{-1} on the last day, persisting at 2.4 kg day^{-1} during post-festival days. DEP increased moderately, from 0.4 to 0.7 kg day^{-1}, while DBP load remained relatively stable (0.2–0.4 kg day^{-1}). Similarly, PAH loads increased from 2.4 to the maximum of 6.0 kg day^{-1}. Although most individual PAHs increased, BENP dominated, rising from 0.8 to the maximum of 3.3 kg day^{-1} on the final day. Elevated PAH loads persisted after the event, averaging 10.9 kg day^{-1} (Fig. 17).

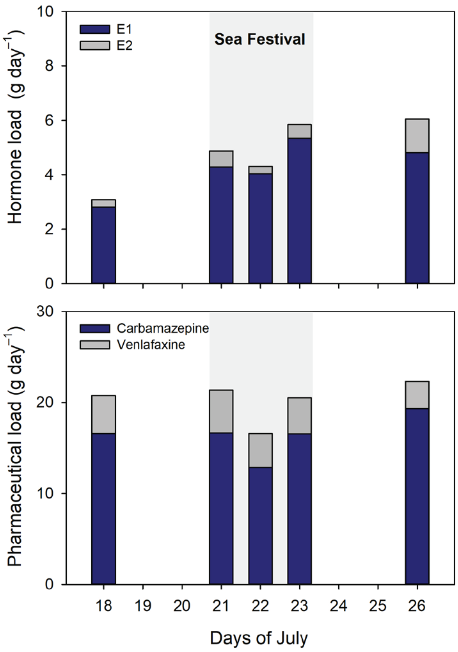

Figure 16. Total loads of hormones (E1 [Estrone] + E2 [17 Beta-estradiol]; upper panel) and pharmaceuticals (VEN [Venlafaxine] + CBZ [Carbamazepine]; bottom panel) to the Klaipėda city WWTP from 18 to 26 July 2023. The Sea Festival period is highlighted in grey (21–23 July 2023). Reprinted from Paper II.

The concentration of the studied micropollutants in the influent at Klaipėda WWTP increased during the festival (21–23 July), except for pharmaceuticals. VEN fluctuated between 90 and 145 ng L^{-1}, whereas CBZ was several-fold higher, averaging ~508 ng L^{-1}. Among hormones, E1 remained within 95–155 ng L^{-1}, while E2 was notably lower with a mean of 17.7 ng L^{-1}, showing sharper fluctuations from ~ 9.0 L^{-1} to a peak of 38 ng L^{-1}. ΣPAEs were present at an average concentration of 84.5 µg L^{-1}, whereas ΣPAHs were at an order of magnitude lower (6.3 µg L^{-1}) (see Table 18).

Most PAEs were frequently detected, at a detection frequency (DF) of 100%, reflecting their persistence in the influent. Although DEHP and DBP had 100 DF in both phases, other PAEs displayed phase-specific distribution. For example, DMP and DiBP were primarily found in the dissolved phase, whereas DOP and BBzP were found in the particulate phase, indicating a strong association with solid particles. Nevertheless, DEP and DiBP were present in the particulate phase with lower DF of 78 and 56, respectively (Table 19).

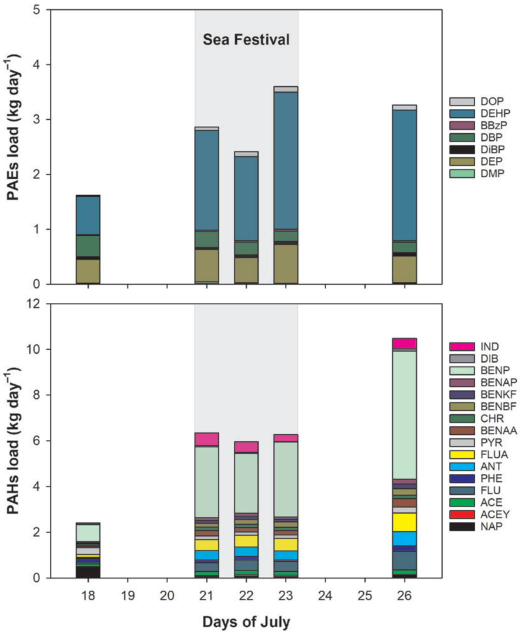

Figure 17. The load of different phthalates (PAEs; upper panel) and polycyclic aromatic hydrocarbons (PAHs; bottom panel) received by the Klaipėda WWTP from 18 to 26 July 2023. The Sea Festival period is highlighted in grey (21–23 July 2023). Reprinted from Paper II.

Table 18. The mean punctual concentration of micropollutants in the influent at the Klaipėda WWTP on 18 – 28 July. Reprinted from Paper II.

Date	Micropollutant concentration					
	VEN (ng L^{-1})	CBZ (ng L^{-1})	E1 (ng L^{-1})	E2 (ng L^{-1})	ΣPAEs (µg L^{-1})	ΣPAHs (µg L^{-1})
18/07/23	142.1±9.3	558.4±35.2	94.9±6.2	9.0±0.03	54.6±5.4	2.4±0.3
21/07/23	145.0±3.7	510.2±37.6	131.6±4.6	17.9±1.0	87.8±4.5	6.3±0.4
22/07/23	118.0±5.3	407.5±19.2	127.9±4.7	8.8±1.7	76.7±3.4	6.1±0.3
23/07/23	115.3±8.8	479.2±26.7	154.8±14.9	14.8±0.8	104.3±10.0	6.0±0.4
26/07/23	90.4±1.0	585.4±4.5	145.7±4.2	37.7±2.1	98.9±10.2	10.6±2.1

Note 1: VEN – venlafaxine, CBZ – carbamazepine, E1 – Estrone, E2 – 17 Beta-Estradiol, ΣPAEs (sum of 7 plasticizers in dissolved and particulate-bound phases), ΣPAHs (sum of 16 polycyclic aromatic hydrocarbons in dissolved and particulate-bound phases).
Note 2: The data are presented as mean ± standard error. MQL – method quantification limit (E2 – 0.1 ng L^{-1}), (PAHs – 0.01 µg L^{-1}).

Table 19. Mean detection frequency (DF, %) of phthalates (PAEs) in the influent at the Klaipėda WWTP. Reprinted from Paper II.

PAEs	Phase	DF (%)
DMP	DP	100
	PP	0
	TP	100
DEP	DP	100
	PP	78
	TP	100
DiBP	DP	100
	PP	56
	TP	100
DnBP	DP	100
	PP	100
	TP	100
BBzP	DP	0
	PP	94
	TP	94
DEHP	DP	100
	PP	100
	TP	100
DOP	DP	0
	PP	100
	TP	100

Note: DP – dissolved phase, PP – particulate-bound phase, TP – total (DP+PP).

A distinct difference in PAH composition was observed between the particulate and dissolved phases. In the particulate phase, the high molecular weight PAH BENP dominated, accounting for 49% of the total PAH load. Only a small amount (6–9%) was contributed by naphthalene (NAP), phenanthrene (PHE), Fluoranthene (FLUA), and pyrene (PYR). Lower-molecular-weight PAHs collectively contributed less than 2% of the total PAH in the particulate phase. The major PAH in the dissolved phase was NAP (57% of PAHs), followed by PHE (17%), Anthracene (21%, ANT), and PYR (5%). The remaining PAHs accounted for less than 2% of the total dissolved phase (Fig. 18).

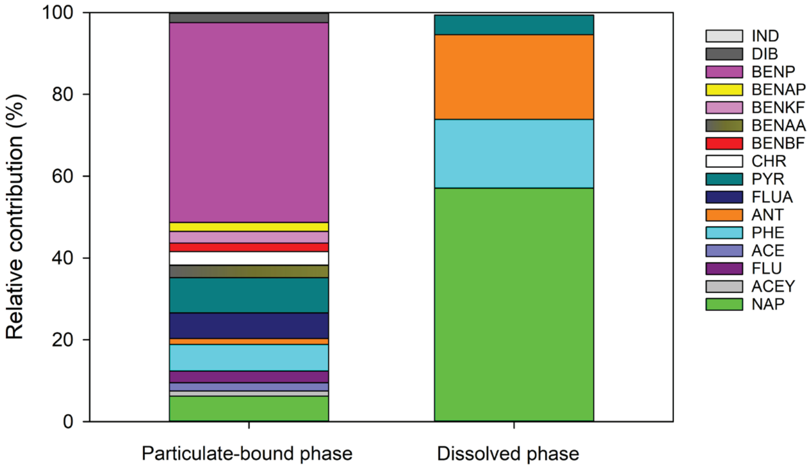

Figure 18. Mean relative contribution of 16 polycyclic aromatic hydrocarbons (PAHs) in dissolved and particulate-bound phases in the influent at the Klaipėda WWTP. Relative contribution (%) = (Concentration of individual PAH/ΣPAHs) × 100. Reprinted from Paper II.

4.2.3. The pollution level in the discharged effluent to the coast

During the festival period (21–23 July), most water quality parameters in the effluent were slightly elevated, except for DOC. Despite this, the Klaipėda WWTP maintained full compliance with the regulatory standards for nutrient and organic matter pollution throughout the monitoring period (July 23–28). TN and TP concentrations were between 5.2–6.4 mg L^{-1} and 0.3–0.5 mg L^{-1}, respectively. Similarly, mean concentrations of organic pollution indicators were low at 53.5, 6.7, and 11.8 mg L^{-1} for COD, BOD, and SPM, respectively (Table 20).

The Klaipėda WWTP demonstrated high performance in removing nutrients and organic matter throughout the monitoring period, though DOC removal was slightly reduced. During the festival period (21–23 July), nutrient and organic pollution retention remained effective, with a slight decrease in DOC elimination. During the Sea festival, the plant achieved near-complete elimination (>95%) of organic pollutants, including nutrients, SPM, BOD, and COD, indicating stable treatment effectiveness (Table 21).

Table 20. The mean punctual concentration of nutrients (TN – total nitrogen, TP – total phosphorus), biochemical (BOD) and chemical oxygen demand (COD), and suspended matter (SPM) in effluents at the WWTP of Klaipėda. Reprinted from Paper II.

Date	Quality parameters concentration (mg L^{-1})					
	TN	TP	DOC	COD	BOD	SPM
Thresholds	15.0 mg L^{-1}	1.0 mg L^{-1}	N/A	Min 75%*	15 mg L^{-1}	25 mg L^{-1}
20/07/23	5.6±0.2	0.3±0.0	18.0±0.2	55.3±0.9	5.1±0.1	8.8±0.7
23/07/23	6.3±0.1	0.4±0.0	16.1±0.9	56.7±0.3	8.3±0.2	15.8±0.2
24/07//23	5.9±0.2	0.5±0.0	16.9±0.4	56.7±0.9	7.8±0.3	12.2±0.5
25/07/23	6.4±0.1	0.5±0.0	16.3±0.2	54.0±0.6	6.7±0.1	12.3±0.4
28/07/23	5.2±0.2	0.5±0.0	16.0±0.1	45.0±0.6	5.4±0.1	10.0±0.3

Note 1: The data are presented as mean ± standard error. The threshold values for parameters are taken from the Wastewater Management Regulation, approved by the Minister of Environment of the Republic of Lithuania (Order No. D1-236, 2023);
Note 2: *removal efficiency; N/A – Not applied.

Table 21. Retention of the relative amount of nutrients (TN – total nitrogen, TP – total phosphorus), dissolved organic matter (DOC), suspended particulate matter (SPM), and changes in biochemical (BOD) and chemical oxygen demand (COD) after treatment at the Klaipėda WWTP. Reprinted from Paper II.

Measure	Retention during Sea Festival (%)	Mean retention during the period (%)
TN	96	95 (95–97)
TP	98	98 (97–99)
DOC	87	85 (82–91)
SPM	99	99 (98–100)
BOD	99	99 (98–100)
COD	99	99 (98–100)

Note 1: The differences between the delivered and discharged loads of matter were used to estimate the proportion of retained material, expressed as a percentage.
Note 2: Data are presented as mean (n=3) for the Sea Festival period and (n=5) for the entire sampling period, and min and max values are provided in brackets.

Micropollutant retention patterns at the Klaipėda WWTP varied across chemical groups. Pharmaceuticals consistently showed positive retention values, ranging from 2.9 to 17.9 g day^{-1}, in some cases exceeding the influent levels. In contrast, hormones, PAEs, and PAHs showed negative values, ranging from –2.3 to –4.8 g day^{-1}, –1.6 to

–3.6 kg day^{-1}, and from –0.1 to –0.4 kg day^{-1}, respectively. Importantly, no changes in micropollutant retention were associated with the festival, as its dynamics followed similar patterns throughout the study period (Fig. 19).

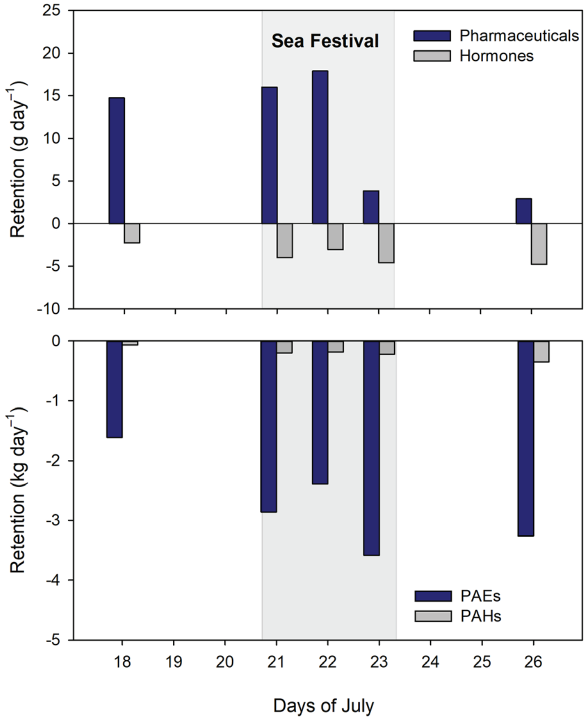

Figure 19. Hormones (E1 + E2), pharmaceuticals (Venlafaxine + Carbamazepine) – upper panel, phthalates (PAEs; the sum of 7 congeners), and polycyclic aromatic hydrocarbons (PAHs; the sum of 16 congeners) – bottom panel, retention in the Klaipėda WWTP from 18 to 26 July 2023. The Sea Festival period is highlighted in grey (21–23 July 2023). Positive values indicate the export of those substances via the effluent released into the surrounding coastal area, while negative values indicate their retention at the WWTP. Reprinted from Paper II.

Following the festival, the total micropollutant discharge with the effluent increased notably, showing a 26% rise from the pre-festival baseline of 45.0 g day^{-1} to 60.6 g day^{-1} following the festival day two. This increase was mainly driven by total PAEs, with a smaller contribution from the pharmaceutical compounds. Specifically, PAEs load rose from 9 g day^{-1} to 25 g day^{-1} while pharmaceuticals (VEN+CBZ) increased from 31 g day^{-1} to 34.4 g day^{-1}. Among PAEs, DEHP was the dominant contributor to the increased load. In contrast, PAHs were not detected at any point during the sampling period. Generally, pharmaceuticals consistently accounted for the largest share of the total micropollutant load, whereas hormones contributed the least. On the other hand, PAEs exhibited the highest temporal variability, while pharmaceutical and hormone loads remained comparatively stable during the study and festival periods (Fig. 20).

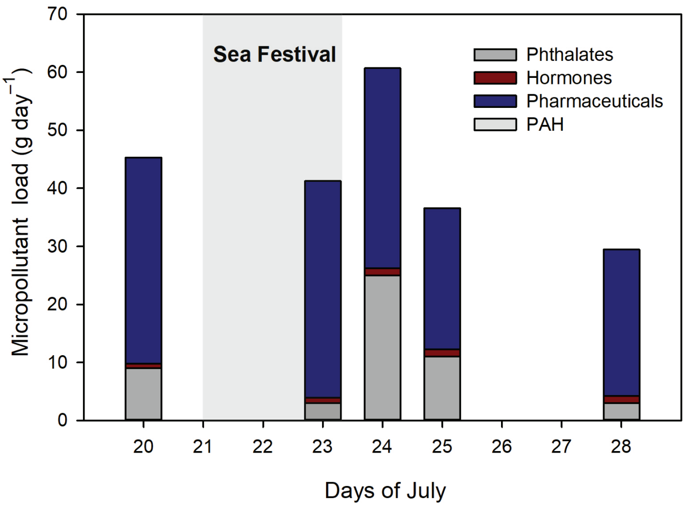

Figure 20. Micropollutant load in the discharged effluent from the Klaipėda WWTP to the coastal area of the Baltic Sea. PAHs – polycyclic aromatic hydrocarbons were not detected. The Sea Festival period is highlighted in grey (21–23 July 2023), and the effluent was produced after 2 days of wastewater treatment (23–25 July 2023). Reprinted from Paper II.

During 20–28 July, the effluent monitoring at the Klaipėda WWTP revealed consistent PNECs exceedances by micropollutants, including hormones and pharmaceutical compounds. The E1 surpassed its PNEC of 0.4 ng L^{-1} by 825%, while E2 exceeded (4 ng L^{-1}) by 8,245%, despite high removal rates at Kaipeda WWTP. Among pharmaceuticals, CBZ exceeded its PNEC of 500 ng L^{-1} by 177%, while VEN surpassed its threshold of 90 ng L^{-1} by 141%. Analysis showed that discharged effluent exhibited the greatest relative PNEC exceedances for hormones, while pharmaceutical concentrations remained consistently above the environmentally safe levels (see Table 22). In this study, individual PAEs did not exceed their PNECs; therefore, they were not included in the further risk assessment.

Table 22. The exceedance of the Predicted No-Effect Concentration (PNEC) threshold value (0.4 ng L^{-1} for estrone [E1], 4 ng L^{-1} for E2 17 Beta-estradiol [E2], 90 ng L^{-1} for Venlafaxine [VEN], 500 L^{-1} for carbamazepine [CBZ]) in the effluents discharged from the Klaipėda WWTP during the period of 20–28 July 2023. Reprinted from Paper II.

Date	Relative exceedance of PNEC (%)			
	E1	E2	VEN	CBZ
20/07/2023	575	<MQL	141	177
23/07/2023	591	<MQL	137	173
24/07/2023	765	1195	128	173
25/07/2023	718	7183	110	106
28/07/2023	825	8245	112	128

Note: MQL – method quantification limit (0.1 ng L^{-1}).

Environmental risk assessment based on Risk Quotient (RQ) analysis revealed that endocrine-disrupting micropollutants (except PAEs) substantially exceeded their PNECs, indicating significant environmental risks (RQ ≥1). The pharmaceutical compounds VEN and CBZ showed moderate RQ values of 1.1-1.8, while hormone E1 showed higher risk levels (RQ ranging from 5.8 to 8.3). E2 showed the highest RQ (13.8), representing the greatest potential risk to the aquatic ecosystems due to effluent discharge (Table 23).

Table 23. The risk quotients (RQ) calculated by the measured environmental concentration (MEC) divided by the Predicted No-Effect Concentration (PNEC) threshold value (0.4 ng L^{-1} for estrone [E1], 4 ng L^{-1} for 17-Beta-estradiol [E2], 90 ng L^{-1} for Venlafaxine [VEN], 500 L^{-1} for carbamazepine [CBZ]) in effluents discharged from the Klaipėda WWTP in the period of 20–28 July 2023. Reprinted from Paper II.

Date	Risk quotients (RQ)			
	E1	E2	VEN	CBZ
20/07/2023	5.8	<MQL	1.4	1.8
23/07/2023	5.9	<MQL	1.4	1.7
24/07/2023	7.7	12.0	1.3	1.7
25/07/2023	7.2	8.5	1.1	1.1
28/07/2023	8.3	13.8	1.1	1.3

Note 1: Risk classification: low risk ≤0.1, medium risk ≥ 0.1≤ 1, high risk ≥1.
Note 2: MQL – method quantification limit (0.1 ng L^{-1}).

4.3. Pollution reduction in biologically treated wastewater using ozone treatment

4.3.1. General characteristics of biologically treated wastewater

Biologically treated wastewater influenced by varying levels of anthropogenic pressure, including residential, and industrial activities, was used in the present study to analyze the effect of ozonation on the decomposition of pharmaceuticals and overall quality. The initial quality before ozonation was characterized, and the results are presented in Table 24. The biologically treated wastewater from the Klaipėda WWTP exhibited the highest BOD/COD ratio (0.20), influenced by the higher BOD concentration. It also contained substantially higher concentrations of several other quality parameters than the Nida WWTP, including bromides (~4-fold), CBZ (3-fold), and water hardness (2-fold), primarily due to the elevated calcium levels. Additionally, the bacterial contamination load in biologically treated wastewater from the Klaipėda WWTP was nearly three times higher than that of the Palanga WWTP. In contrast, the wastewater from the Nida WWTP had the highest COD, SPM, and nitrate concentrations, ~2-, 7-, and 28-fold higher than those from the Palanga WWTP. Overall, DOC and VEN levels were similar in the biologically treated wastewater across the studied WWTPs.

Table 24. Wastewater quality parameters measured before ozonation in the biologically treated wastewater from three coastal WWTPs in Nida, Palanga, and Klaipėda, impacted by different pollution sources, on 24–26 July, 2024.

Parameters	WWTPs		
	Nida	Palanga	Klaipėda
Bromides (mg L^{-1})	0.1	0.3	0.5
Nitrates (mg N L^{-1})	7.2	0.3	0.4
DOC (mg C L^{-1})	14.5	12.4	15.8
Ca (mg L^{-1})	42.6	57.0	90.6
Mg (mg L^{-1})	5.1	16.7	20.8
Ca+Mg (mg L^{-1})	47.7	73.7	111.4
BOD (mg O_2 L^{-1})	8.3	5.2	11.8
COD (mg O_2 L^{-1})	66.5	35.0	59.0
SPM (mg L^{-1})	39.9	5.8	14.7
BOD/COD ratio	0.1	0.2	0.2
CBZ (ng L^{-1})	427.4	1266.5	1519.2
VEN (ng L^{-1})	341.2	361.4	390.0
Microbial count (CFU mL^{-1})	71,000	26,200	74,500

Note: DOC – dissolved organic carbon, BOD – biochemical oxygen demand, COD – chemical oxygen demand, SPM – suspended particulate matter, CBZ – carbamazepine, VEN – venlafaxine.

4.3.2. The ozonation effect on the microbial and general pollution removal

Initial SPM concentrations in the biologically treated wastewater varied substantially among the WWTPs, ranging from 5.8 to 40.0 mg L^{-1}. After 15 min of ozonation, a substantial decrease in SPM was observed in wastewater from all WWTPs, with removal efficiencies ranging from 46.3 to 93.7% (Fig. 21). Despite the wide range of initial concentrations and removal efficiency, final SPM levels converged to similarly low values (2.5–3.13 mg L^{-1}) across all samples from different WWTPs, indicating effective reduction to similar baseline concentrations.

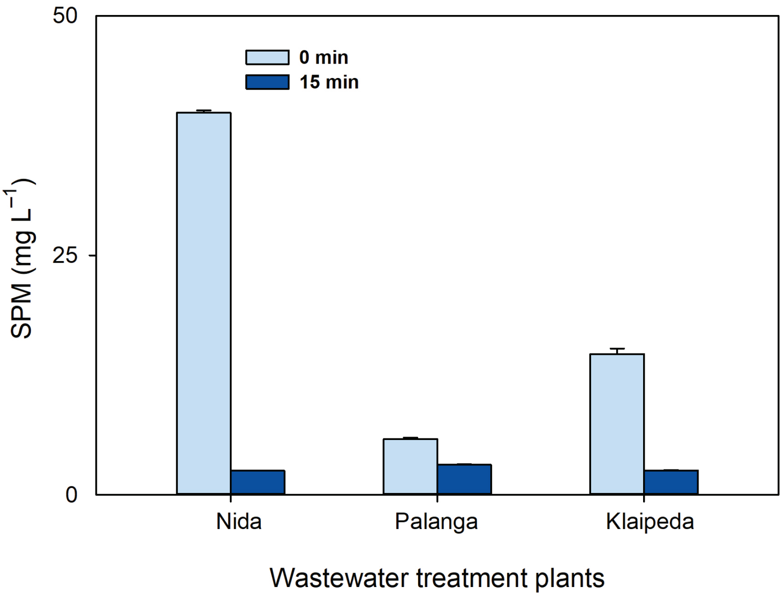

Figure 21. Mean concentration (± standard error, n=2) of suspended matter (SPM) mg L^{-1} in biologically treated wastewater from the Nida, Palanga, and Klaipėda WWTPs before and after 15 min of ozonation (ozone concentration 7 ± 0.7 mg L^{-1}).

Dissolved organic carbon concentration in biologically treated wastewater initially measured from 12.4 to 15.8 mg L^{-1} (Fig. 22a). Following 15 min ozone treatment, DOC concentration remained similar (12.0–15.4 mg L^{-1}) with the Klaipėda WWTP showing the highest concentration. The COD concentration in the same samples ranged from 35.0 to 67.0 mg L^{-1} before ozonation (Fig. 22b). Following ozone treatment, the COD values decreased to 23.0–35.5 mg L^{-1}, representing a 34–65% reduction.

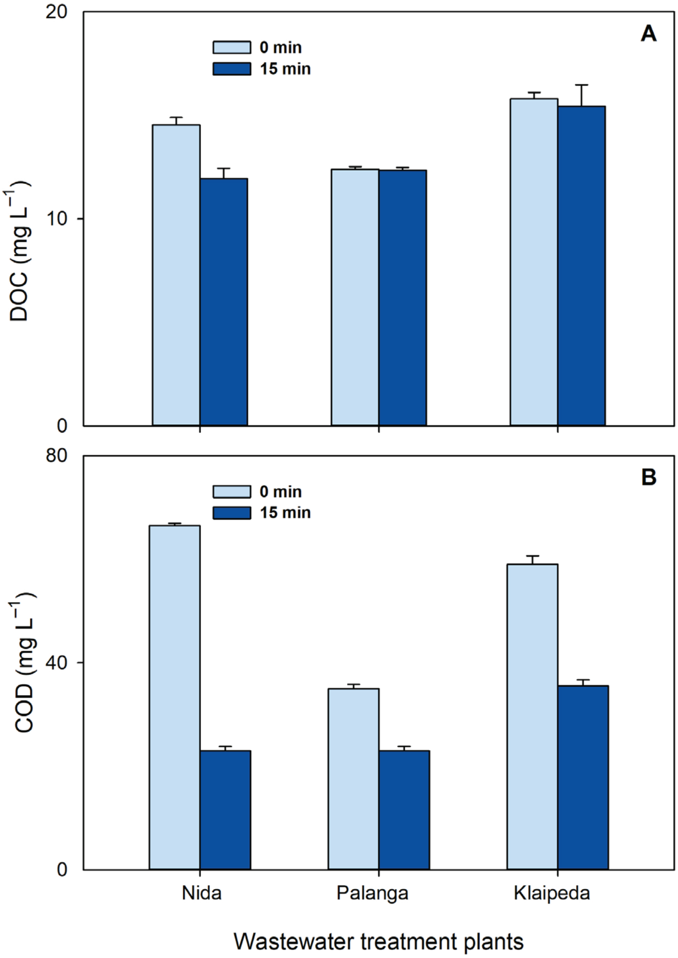

Figure 22. Mean concentration (± standard error, n=2) of dissolved organic carbon (DOC) (upper panel) and chemical oxygen demand (COD) (bottom panel) in the biologically treated wastewater from the Nida, Palanga, and Klaipėda WWTPs before and after 15 min of ozonation (ozone concentration 7 ± 0.7 mg L^{-1}).

Initial bromide concentrations differed among the WWTPs, with the highest levels observed in the Klaipėda WWTP, intermediate levels in Palanga, and the lowest in Nida (Table 24). Following 15 min ozonation, bromide concentrations remained largely unchanged at all WWTPs (0.1, 0.2, and 0.5 mg L^{-1}, respectively in Nida, Palanga and Klaipėda). This indicates that ozonation under the applied conditions did not significantly affect bromide concentrations.

Initial nitrate concentrations varied widely among samples from the different WWTPs, with the highest concentration observed in wastewater from the Nida WWTP (7.2 mg N L^{-1}; Table 24). After 15 min of ozonation, nitrate levels increased in all samples, with variable increases of 15%, 246%, and 184% in the wastewater from Nida, Palanga, and Klaipėda WWTPs, respectively. Despite exhibiting the smallest relative increase in nitrate concentration, the wastewater from Nida WWTP had the highest nitrate concentration after ozonation among the studied WWTPs. Wastewater hardness, calculated as the total calcium and magnesium concentrations, showed only negligible changes after 15 min of ozonation (Fig. S2).

Microbial contamination in the biologically treated wastewater ranged between 26,200 and 74,500 CFU mL^{-1}. A sample volume of 0.1 mL with two replicates of a 1:10 dilution was used. After 5 min of ozonation, microbial contamination was eliminated, with no colonies observed after 10 and 15 min (Table 25). These findings remained consistent across all replicates and sampling times past 5 min, confirming that short-duration ozonation treatment provides fast and complete microbial deactivation.

Table 25. Microbial contamination evaluation based on the average colony-forming unit (CFU) count per mL^{-1} in the biologically treated wastewater from the Nida, Palanga, and Klaipėda WWTPs before (0) and after 5, 10 and 15 min of ozonation.

Microbial contamination	Ozonation min	Nida WWTP	Palanga WWTP	Klaipėda WWTP
CFU mL^{-1}	0	71000	26200	74500
	5	0	0	0
	10	0	0	0
	15	0	0	0

4.3.3. Pharmaceutical levels before and after ozonation

Initial CBZ concentrations across the WWTPs ranged from 1519.2 ng L^{-1} to 427.4 ng L^{-1}, while VEN concentrations ranged from 341.2 ng L^{-1} to 390.0 ng L^{-1} (Table 26). The wastewater from the Klaipėda WWTP contained the highest CBZ and VEN concentrations. Despite a wide variation in initial levels, CBZ was completely decomposed below the detection and quantification limit (<5 ng L^{-1}) in all samples within 5 min of ozonation and remained undetectable after 10 and 15 min. Similarly, VEN concentrations decreased below the limit of quantification (<5 ng L^{-1}) after 5 min of ozonation; however, VEN remained detectable after 10 and 15 min of treatment (Table 25).

Table 26. The mean concentration of pharmaceuticals (ng L^{-1}) in the biologically treated wastewater before ozonation (0 min) and after 5, 10, and 15 min of treatment at the ozone dose of 7 ± 0.7 mg L^{-1} from July 24–26, 2024.

WWTPs	Treatment duration, min				
	Pollutant	0 (ng L^{-1})	5	10	15
Nida	CBZ	427.4±17.1	ND	ND	ND
	VEN	341.2±25.8	<MQL	<MQL	<MQL
Palanga	CBZ	1266.5±41.9	ND	ND	ND
	VEN	361.4±7.9	<MQL	<MQL	<MQL
Klaipėda	CBZ	1519.2±121.1	ND	ND	ND
	VEN	390.0±60.4	<MQL	<MQL	<MQL

Note 1: CBZ – Carbamazepine, VEN – Venlafaxine. Data was collected from the Nida, Palanga, and Klaipėda WWTPs.
Note 2: Results are presented as mean ± standard deviation (SD). MQL - represents method quantification limits (5 ng L^{-1}); ND – not detected.

5

Discussion

5.1. The impact of seasonal tourism on wastewater quality and micropollutant levels at the coastal WWTPs

5.1.1. Seasonal population dynamics affect the influent quality and micropollutant levels

Mass tourism, especially in coastal cities, increases wastewater generation and pollutant loads resulting from daily human activities (Phan et al., 2015; Buttiglieri et al., 2016; Torres-Padrón et al., 2020). The elevated pressure can strain local WWTPs, which are typically designed to handle pollution loads proportional to the expected resident population count.

In this study, two WWTPs serving Baltic coastal resorts of different sizes were examined. During the warmer months (June–August), the influx of visitors from other parts of Lithuania increased the influent flow, nutrient concentrations, organic pollution, and micropollutant loads discharged to the Small resort (Nida) and Large resort (Palanga) WWTPs. The influent production peaked during July and August, coinciding with the highest air temperature and tourism intensity. A strong correlation was observed between tourism proxies and air temperature, reflecting higher water consumption driven by the seasonal influx of visitors, as indicated by the increased number of incoming cars and overnight stays at both resorts. An increased influent volume at the Large resort WWTP was also observed during the colder, off-season months (January-February) of early 2022 and 2023, raising questions about additional factors influencing its dynamics. One possible explanation is the influx of visitors drawn by winter events and celebrations, as Palanga resort remains a popular destination outside the peak tourist season. Another possible explanation is the infiltration of surface and groundwater into the sewer system, which leads to an increased influent load (Palangos Vandenys, pers. comm.). This phenomenon is commonly reported in regions with abundant water resources and high groundwater levels, such as coastal resorts (Luczaj and Masarik, 2015; Sun et al., 2016).

Dissolved organic carbon measurements serve as valuable indicators when evaluating influent pollution dynamics related to population fluctuations (e.g., Katsoyiannis and Samara, 2007). DOC levels during peak summer months were up to five times higher than during the off-season, indicating a substantial increase in dissolved organic pollution during the high tourist activity period. DOC concentration increase corresponded with the higher BOD/COD ratios, suggesting enhanced overall biodegradability of the influent. The Large resort WWTP influent exhibited particularly high BOD/COD ratios, which may indicate dilution of less biodegradable organic compounds due to increased water content from domestic sources or infiltration (Martínez et al., 2003). Alternatively, the elevated ratio could reflect a greater input of readily degradable organic matter resulting from higher human waste production (Liyanage and Yamada, 2017). Conversely, both WWTPs experienced decreased BOD/COD ratios during several colder months. This decrease may be linked to persistent chemical delivery to the sewer system, driven by the increased seasonal infection and associated pharmaceutical usage rates (Kot-Wasik et al., 2016). Additionally, reduced winter temperatures may have slowed biodegradation of micropollutants, resulting in higher concentrations in the WWTPs (Kot-Wasik et al., 2016; Yu et al., 2011).

Nutrient concentrations in the influent from both resorts also increased during the peak tourism period, reflecting intensified loading to the sewer system. Toilets and laundry detergents remain the primary sources of phosphorus, nitrogen, and suspended solids in households (Puijenbroek et al., 2019). With the increasing tourism in the Baltic Sea region (UNWTO, 2023b), associated nutrient pollution is expected to intensify further.

Human activities, primarily beach tourism, are the main source of plastic pollution in coastal resorts (Williams et al., 2016). Since PAEs are not chemically bound to plastic matrices, they can leach easily into the environment and reach WWTPs via surface runoff and domestic sewage (Anne and Paulauskiene, 2021). Our results show a strong correlation between tourism indicators and PAE loads, particularly DEHP in the particulate-bound phase, attached to the suspended matter in the influent from both resorts' WWTPs. This suggests that PAE levels in local sewer systems are directly impacted by tourist activity. Seasonal PAE load increases were more pronounced at the Small resort WWTP, likely due to the variable groundwater infiltration at the Large resort WWTP, where pollution loads may have been overestimated.

The DEHP, DBP, DiBP, DOP, and DEP were the predominant PAE congeners in the influent received by the WWTPs. The Large resort WWTP effluent exhibited an abnormally elevated pre-season total PAE load, primarily due to the increased DEP, DEHP, and DBP outflows. This increase can be linked to the widespread use of plasticizer-containing products during housing renovations and preparing for tourist arrivals. The notably high DEP concentrations detected reflect the extensive use of fragrances and cleaning products during pre-season preparations. Residues from household chemicals may be washed from surfaces, fabrics, and skin into drains, ultimately reaching the sewer system (Koniecki et al., 2011). DEHP and DBP are often associated with refurbishment activities. While DEHP is commonly added to plastics and sealants to enhance flexibility (Anne and Paulauskiene, 2021; Bergé et al., 2013), DBP is frequently found in adhesives, paints, and cleaning agents used in maintenance works (Monti et al., 2022).

Comparing phthalate levels with those estimated in other studies is challenging, as most studies do not distinguish between dissolved and particulate-bound PAEs (e.g. He et al., 2019). Additionally, pre-concentration techniques, which involve partial removal of SPM, can complicate direct comparisons because some PAEs may be lost during this process. PAEs with longer molecular chains, such as DEHP, are predominantly detected in the particulate phase, whereas smaller PAEs are more commonly found in the dissolved fraction (Lorre et al., 2023). The transport and retention of PAEs from resorts to WWTPs can vary depending on these phases. DEHP, the most commonly found phthalate, had an average concentration measured in the influent of this study (34.9 μg L^{-1}) exceeding levels reported in Poland (up to 5 μg L^{-1}) and Denmark (1.2 μg L^{-1}) (Anne and Paulauskiene, 2021), yet comparable to the concentrations in France (52.8 μg L^{-1}) and Spain (47.9 μg L^{-1}) (Martin Ruel et al., 2010).

A significant non-linear association was observed between the tourism proxy of cars and EEQ changes in the influent discharged by the Small resort. Nevertheless, the lack of a clear association between EEQ loads and overnight stays at the Large resort WWTP suggests that the variable influent dilution may have changed micropollutant concentrations. Unexpected increases in EEQ levels were observed during the off-season from both resorts WWTPs, when lower estrogenic activity would normally be expected. This may be explained by reduced microbial degradation of estrogenic compounds at lower temperatures, allowing them to persist during transport through the sewer network (Hao et al., 2024). Furthermore, matrix effects or operational factors, such as the presence of coagulants, may interfere with the bioassay and artificially elevate the measured EEQ, as explained by Tang et al. 2013. Overall, the EEQ concentrations in the influent discharged from the studied coastal resorts (1–4 ng L^{-1}) align with those reported in other European countries, such as Spain (3.3 ng L^{-1}), Portugal (6 ng L^{-1}), and the Czech Republic (1.9 ng L^{-1}) (Aerni et al., 2004; Jarošová et al., 2014).

5.1.2. Wastewater treatment efficiency and effluent quality at the coastal resort WWTPs

Seasonal variability of the influent pollution loads can substantially affect wastewater treatment performance, particularly in regions heavily influenced by tourism. To assess how such fluctuations affect treatment efficiency and effluent quality in the Small and Large resort WWTPs, monitoring was conducted during one year.

Despite being initially designed for smaller populations, both facilities generally maintained stable treatment performance during periods of increased pollutant loading, with occasional exceptions. The concentration of TN and TP after treatment (1–24 mg N L^{-1} and 0.1–8 mg P L^{-1}, respectively) remained within the maximum limits set by the

Ministry of Environment of the Republic of Lithuania (No. D1–236). However, during July, TP concentration in the WWTP of the small resort (3.1 mg P L^{-1}) surpassed the upper limit (2 mg P L^{-1}). Similarly, TN concentrations during the tourism season reached 23.8 mg N L^{-1} and 17.3 mg N L^{-1} in the effluent discharged from both Large and Small resort WWTPs, respectively, surpassing the permitted limits of 15 mg N L^{-1} for the Large resort WWTP and 20 mg N L^{-1} for the Small resort WWTP.

Although nutrient removal at both resorts was generally effective, wastewater treatment efficiency was challenged during the peak tourism period. Moreover, existing EU nutrient discharge standards (Directive 91/271/EEC), including those applied in Lithuania (Ministry of Environment of the Republic of Lithuania, 2006), may not be sufficiently strict to ensure complete ecological protection of aquatic ecosystems or to prevent eutrophication. Lithuania remains particularly vulnerable to eutrophication compared to other European coastal regions (Preisner et al., 2020). Given that riverine nutrient input to the Baltic Sea remains high, additional nutrient loads from coastal areas during seasonal peaks may exacerbate eutrophication and hinder progress toward improving the ecological status of coastal waters. To mitigate eutrophication in the Baltic Sea, stricter nutrient thresholds, especially for TP (0.5 mg L^{-1}), have therefore been recommended (HELCOM, 2021).

Regarding PAE removal, the elimination efficiency of DBP and DEHP was lower in the effluent from the Small resort WWTP. This can be attributed to the higher initial PAE concentration entering the aforementioned WWTP. Additionally, smaller WWTPs may experience reduced biological treatment efficiency due to the shorter influent retention caused by the increased flow rate (Di Marcantonio et al., 2022). The average DEHP concentration in the effluent from both coastal resorts (ND–0.79 µg L^{-1}) was comparable to or lower than levels reported in other countries, including China (0.38–1.32 µg L^{-1}; Wang et al., 2018), Spain (0.39–0.41 µg L^{-1}; Bizkarguenaga et al., 2012), and France (4.2 µg L^{-1}; Martin-Ruel et al., 2010). The study also revealed the reduced EEQ elimination during the peak tourism months (June–August), leading to the average retention of EEQ loads falling below 70%. Previous research has demonstrated that the effectiveness of biological E2 treatment varies widely (38–95%), and can be influenced by factors such as temperature and initial EEQ levels (Colosi and Kney, 2011; Ifelebuegu, 2011).

Despite varying retention rates, most tourism-related pollutants were effectively contained, although removal efficiency differed among specific micropollutants. Assessing the impact of micropollutants on coastal ecosystems remains challenging, as many do not yet have clearly defined environmental quality standard concentration limits. Among the PAEs, DEHP is the only compound officially regulated by the EU (1.3 µg L^{-1}) in coastal waters under the WFD (Directive 2008/105/EC). No environmental quality standard limits are established for specific micropollutants analysed in this study, for example, the most abundant phthalate after DEHP, DBP. Nonetheless, the potential risks can be assessed using the PNEC, in this case 10 µg L^{-1} for the aquatic environment (ECHA, 2023). DBP concentrations observed in the effluents from the Small resort WWTP (ND–5.5 µg L^{-1}) and Large resort WWTP (ND–0.20 µg L^{-1}) remained below the PNEC threshold, indicating no environmental concern. On the other hand, a higher overall mean PAE concentration was found, especially in the effluents from the Small resort WWTP, with a total level reaching 2.0 µg L^{-1}. This emphasizes the role of WWTPs as potential sources of PAEs to the coastal environment (Lorre et al., 2023), contributing to cumulative negative environmental effects. In addition, over 30% of the EEQ concentrations exceeded the proposed environmental quality standard, posing a potential risk to coastal ecosystems. The risk assessment of the effluent discharged from both resorts revealed similar risk distributions and levels throughout the year. The moderate and high-risk categories were equally dominant at both resorts, highlighting potential negative impacts on the surrounding coastal ecosystems.

These findings underscore the need for intensified monitoring, particularly of the EEQ levels before the effluent is discharged into the Baltic Sea and the Curonian Lagoon. Continuous monitoring, combined with stricter regulatory measures, is essential for the effective control and mitigation of the estrogenic compound release into these vulnerable marine environments.

5.2. Impact of a large public event on the wastewater quality and micropollutant levels at the coastal city WWTP

5.2.1. Large public event affects the micropollutant and general pollution levels

Large-scale public gatherings can temporarily affect the volume and quality of wastewater entering treatment plants, particularly in coastal municipalities that receive a high influx of tourists. Temporary population increases typically result in higher organic loads and greater concentrations of various micropollutants (**see first chapter**), potentially compromising treatment effectiveness and increasing contaminant discharge into the coastal environments. During the three-day Sea Festival (21–23 July), Klaipėda experienced an influx of ~500,000 visitors in addition to its resident population of about 156,000, which may significantly impact pollution dynamics in its WWTP.

Despite substantial population growth, this study found moderate effects on the influent load. This can be attributed to the short duration of visitor stays, which led to limited water usage during the event. The Klaipėda WWTP receives influent from multiple sources, including residential and industrial discharges, groundwater infiltration, and rainfall runoff. Consequently, population-driven fluctuations in influent flow may have been obscured by the contributions from other sources. On average, the domestic influent constitutes approximately 60% of the total wastewater flow rate, while industrial sources account for around 23% (pers. comm., "Klaipėdos Vanduo"). The unexpected peak flow observed at the end of July was likely caused by the heavy rainfall in the preceding days, which increased infiltration into the sewer system.

Although the influent flow remained relatively stable, DOC load increased substantially on the first day of the festival, reflecting elevated organic pollution associated with the surge of visitors. This increase was possibly linked to the emptying of portable toilets distributed across the city during the festival ("Klaipėdos Vanduo" pers. comm.), as DOC primarily originates from human waste, including urine and faeces (Seredynska-Sobecka et al., 2011; Liberatore et al., 2016). SPM levels peaked on the final day of the festival, driven by the increased pollution and influent flow. Furthermore, nutrient loads, typically linked to population growth (Bussi et al., 2021), were strongly correlated with SPM, suggesting that particulate matter was the primary carrier of these pollutants.

The indicators of organic pollution, BOD and COD, exhibited wide fluctuations during the studied period and could not be directly attributed to the temporary population increase during the festival. They were approximately twice the values recorded in previous observations from 2015–2016, which reported mean levels of 354 mg O_2

L^{-1} and 732 mg O_2 L^{-1}, respectively (Langas et al., 2019). Elevated pollutant levels may be attributed to the industrial discharges, as industries contribute nearly one-third of the total influent load at the Klaipėda WWTP. This pattern aligns with observations from large WWTPs, where BOD and COD fluctuations are often driven by diverse pollution sources and the complexities of the biodegradation process (McCall et al., 2016; Kim et al., 2019). High SPM, COD, and BOD levels also persisted after the festival on July 26th. This suggests that, over the longer term, the influent quality is governed by more complex processes rather than by external factors only, such as temporary population fluctuations associated with specific events. This observation may also reflect a drawback of the real-time sampling approach, as it may have coincided with elevated domestic organic pollutant loads associated with diurnal variability.

Hormone levels in influent naturally fluctuate as a part of human physiology; therefore, estrogen excretion varies with the age and sex distribution of the population (Hamid and Eskicioglu, 2012). While studies have not investigated steroid hormone levels in influents during temporary large public events (e.g., Gerrity et al., 2011; Jiang et al., 2014), hormone levels estimated in our study were lower than those reported in other locations (566 ng L^{-1} for E1 and 143 ng L^{-1} for E2, Pessoa et al., 2014). However, the substantial increase in estrogen loads observed during the festival highlights the impact of a higher population density. This finding aligns with the study by Phan et al. (2015), in which they reported that peak estrogen levels in the influent coincided with periods of high tourism. Population surges affect estrogen inputs to the sewer system through elevated individual release and by potentially modifying the population's sex and age structure, thereby influencing overall excretion rates. The higher levels of E1 detected can be attributed to microbial E2 transformation, a well-documented process occurring in sewer systems (Almazrouei et al., 2023; Zhao et al., 2020; Zhao et al., 2019).

We hypothesized that population increase during the Sea Festival may potentially affect the influent loading of pharmaceuticals. However, no increase in their loads was observed, despite an increasing consumption trend (OECD, 2023), possibly due to short-term spikes, which might not have been captured during real-time sampling. In general, CBZ concentrations in the influent were higher than those of VEN, likely due to its greater chemical stability (Björlenius et al., 2018; Kim et al., 2019; Mackuľak et al., 2019) and higher prescription dosages. The measured average concentration (745 ng L^{-1}) was comparable to levels previously reported at the Klaipėda WWTP in July (528 ng L^{-1}, Luczkiewicz et al., 2019), confirming its persistent presence. CBZ is widely used in treating epilepsy, neuropathic pain, and bipolar disorder (Bridwell et al., 2022). CBZ and VEN levels in this study were consistent with those reported globally, such as in Israel (955 ng L^{-1} of CBZ, Dvory et al., 2018), the Czech Republic (~490 ng L^{-1} of VEN, Golovko et al., 2014), and Taiwan (30–40 ng L^{-1} of CBZ, Jiang et al., 2014). While these values reflect national pharmaceutical consumption trends

(Le Corre et al., 2012; Baz-Lomba et al., 2016), they do not account for variations during temporary public events.

Phthalic acid esters, a man-made pollutant, exhibited higher loads during the festival, indicating a relationship with the population increase. Pollutant concentrations remained high after the festival ended, indicating ongoing contributions from household and industrial activities. The PAE increases were likely related to the greater use of disposable plastics and personal care products during the event. To the best of our knowledge, this study represents the first investigation of plasticizer level analysis in coastal WWTPs during a temporary large-scale public gathering. The total PAE concentration in the influent (55–104 μg L^{-1}) was within the range reported in other countries, such as China (76.7 μg L^{-1}, Dong et al., 2022) and Vietnam (20.7–405.0 μg L^{-1}, Le et al., 2021), but higher than in some European nations, including Denmark (~1.5 μg L^{-1}) and Poland (~22.0 μg L^{-1}) (Anne and Paulauskiene et al., 2021).

Regarding specific phthalates, DEHP exhibited the highest increase during the festival, consistent with its widespread use as a plasticizer in consumer products such as plastic containers and packaging materials (Bergé et al., 2013; Rowdhwal et al., 2018). Due to its long-chain structure and low solubility in water (Staples et al., 1997), DEHP is highly stable and resistant to biodegradation, which raises the risk of accumulation in various environmental matrices. Its hydrophobic nature results in transport primarily via particulate matter (Lorre et al., 2023). In addition, a moderate increase in DEP concentration was also observed, reflecting the increased influent contamination with perfumes and cosmetic product residues (Koniecki et al., 2011).

During the festival, total PAH consistently exceeded pre-festival levels, presumably due to heightened vehicle traffic, as certain PAH congeners are tracers of vehicle exhaust and fossil fuel combustion (Krugly et al., 2014; Perrone et al., 2014; PubChem, 2024). However, it cannot be solely attributed to transportation due to other interrelated factors. Firstly, the individual PAH, benzo(g,h,i)perylene (BENP), showed the most significant increase in the effluent, a pattern often linked to the presence of surface runoff from urban and industrial areas (Chen et al., 2013; Chen et al., 2019; Suresh et al., 2024). Secondly, PAH loads increased by 40% on July 25th, coinciding with a rainfall event, which may have introduced PAHs from various non-point sources. Persistence of PAHs in the particulate phase confirmed their hydrophobic nature (Ali and Wang, 2021), suggesting that their primary transport pathway into the sewer network was via adsorption onto particulate matter. In comparison, the total PAH levels in this study were significantly lower than those reported in the Jordanian WWTPs (1,200–2,900 μg L^{-1}, Alawi et al., 2018) but higher than those in China (1.1 μg L^{-1}, Tian et al., 2012), although not measured during a temporary large public event.

5.2.2. Wastewater treatment efficiency and pollution discharge to the coastal area impacted by the large public event

Large public events may temporarily affect the ability of coastal WWTPs to maintain effluent quality and regulatory compliance. The Klaipėda WWTP demonstrated effective retention and removal of pollutants, as confirmed by mass balance estimates, particularly for SPM and nutrients. Consequently, the effluent discharged into the Baltic Sea contained daily average nutrient concentrations well within the maximum regulatory limits established by the EU and the Ministry of Environment of the Republic of Lithuania, with TN at 15.0 mg L^{-1} and TP at 2.0 mg L^{-1}. While the treatment process was less effective in retaining DOC, the concentration remained within acceptable limits, indicating the effective management of bulk organic pollution. The reduced biodegradability, reflected in a lower BOD/COD ratio, suggests that readily biodegradable pollutants were successfully removed from the influent. However, non-biodegradable, recalcitrant compounds, including organic micropollutants, such as pharmaceuticals and industrial chemicals, may have remained (Phan et al., 2022).

The results show elevated pharmaceutical concentrations in the effluent during the festival period, contributing to higher loads being discharged into the coastal environment. Notably, CBZ showed a greater increase in concentration than VEN, primarily due to its strong resistance to biodegradation (Mackuľak et al., 2019). CBZ concentrations can potentially increase through microbial deconjugation of glucuronides in wastewater treatment facilities (Joss et al., 2005; Vieno et al., 2007). The detected CBZ concentrations were similar to those reported in other European countries, including France (1.2 µg L^{-1}), Greece (1.0 µg L^{-1}), Italy (0.3 µg L^{-1}), and Sweden (0.9 µg L^{-1}) (Ferrari et al., 2003), even though these levels were not measured during large temporary public events. Importantly, the levels of both pharmaceuticals exceeded the PNEC of 90 ng L^{-1} for VEN and 500 ng L^{-1} for CBZ, raising concerns about their environmental impact (Qu et al., 2018; Oldenkamp et al., 2019). The risk assessment based on RQ measurements showed the persistently high-risk values (>1) for both CBZ and VEN in the effluent released from the Klaipėda WWTP, which may cause adverse effects when reaching the coastal environment. Similarly, while estrogen retention rates were generally high, effluent levels of E1 and E2 remained well above the PNECs and the EU environmental quality standards (Loos et al., 2018), indicating ongoing risks. RQ calculations revealed high risk (RQ > 1), especially for E1 and E2. The persistence of estrogenically active compounds in effluents highlights the challenges faced by WWTPs, which align with findings by Margot et al. (2015). Consequently, WWTPs continue to release active pharmaceutical and hormonal compounds, posing a risk to surrounding coastal ecosystems.

Among the PAEs, DEHP was consistently detected. Nevertheless, it remained within the regulatory limits set by both the Lithuanian Ministry of Environment (<2 µg

L^{-1}) and the EU (1.3 µg L^{-1}) (Net et al., 2015). The highest DEHP concentration was observed on the second festival day, in the levels comparable to those previously recorded in other Lithuanian WWTPs (Lorre et al., 2023). Other PAEs, including BBzP, DMP, and DOP, were removed effectively due to their strong adsorption to particulate matter and subsequent elimination during treatment. The dominance of DBP in the dissolved phase and of DEHP in the particulate-bound phase aligns with previous findings from the Baltic coastal WWTPs (Lorre et al., 2023). Overall, the total PAE concentration detected in the effluent was lower than previously reported in the region (0.1–5.5 µg L^{-1}) (see I paper). This was likely due to more PAEs being adsorbed onto particulate matter and removed via settling in the sludge during treatment. Although PAHs were not detected in the effluent, environmental concerns remain regarding their tendency to accumulate and persist in dried sludge (Lee et al., 2021).

An important study finding was that the total micropollutant load increased in effluent impacted by the festival, which was subsequently discharged into the Baltic Sea. The micropollutant load, consisting of PAEs and pharmaceuticals, increased on the second day of the festival, confirming a direct link to the temporary public event. While pharmaceuticals were mostly discharged with the effluent, the largest portion of PAEs was removed through adsorption onto sludge during the treatment. Nevertheless, PAE loads increased temporarily in the effluent released in relation to the festival, driven by elevated DEHP concentration. These findings highlight the potential ongoing micropollutant discharge and accumulation in the Baltic Sea ecosystem. Therefore, monitoring programs would benefit from incorporating high-frequency sampling during large temporary public events to capture the dynamics of hazardous persistent micropollutant occurrence.

5.3. Ozonation potential for eliminating pollutants from wastewater with different anthropogenic impact

5.3.1. The effects of ozone treatment on the general contamination of wastewater from coastal WWTPs

Ozonation is increasingly recognized as an effective advanced treatment technology for persistent organic pollutants, including pharmaceutical residues in wastewater matrices (von Gunten, 2003; Treguer et al., 2010; Bourgin et al., 2018). Nevertheless, ozonation performance is dependent on wastewater composition and may be adversely affected at coastal wastewater treatment plants receiving influent from diverse anthropogenic sources. As a result, biologically treated wastewater typically contains complex mixtures of residual organic matter and micropollutants, which can influence the effectiveness of ozonation in oxidizing persistent micropollutants (Tang et al., 2020; Merkus et al., 2023; Shin et al., 2025).

To evaluate the implications of complex wastewater matrices, this study assessed ozonation performance in the biologically treated wastewater from three coastal WWTPs (Nida, Palanga, and Klaipėda), which differ in wastewater sources and treatment capacities. DOC was considered one of the key determinants of the ozonation performance, as it reflects the oxidation efficiency of organic matter and governs ozone demand. Notably, DOC concentrations varied slightly among the investigated WWTPs and were within the typical range reported for municipal secondary effluents (Katsoyiannis et al., 2007; Chen et al., 2009). Following 15 min of ozonation, DOC removal remained negligible, consistent with previous studies, which demonstrated that ozonation primarily induces partial oxidation rather than complete mineralization of organic compounds (Phan et al., 2022; Ekblad et al., 2019; Liu et al., 2015). Elevated DOC levels observed in the effluents from the Klaipėda WWTP may suggest the formation of oxygenated transformation products during ozonation, a process known to increase residual DOC while enhancing the biodegradability of wastewater (von Gunten, 2003; Treguer et al., 2010; Bourgin et al., 2018).

Biochemical oxygen demand in the ozone-treated effluent remained stable, except for a slight increase in the effluent from the Palanga WWTP, where initial pollutant loads were up to an order of magnitude lower, likely due to infiltration-induced dilution (Langas et al., 2019). The partial oxidation of persistent organic compounds, such as pharmaceuticals, may have increased the biodegradable organic matter fraction, thereby balancing BOD levels. Further biological degradation was unlikely, as microbial communities were inactivated within 5 min of ozonation, confirming the strong bactericidal effect of ozone reported in other studies (Stange et al., 2019; Epelle et al., 2022). In contrast, higher initial COD levels at the Nida WWTP likely contributed to greater overall COD oxidation, as elevated organic matter enhances ozonation efficiency (Phan et al., 2022; Le Meur et al., 2022). Nevertheless, final COD concentrations were consistently low across samples from all WWTPs, demonstrating the effectiveness of ozonation in reducing chemical pollution from diverse types of biologically treated wastewater. Consequently, the increased biodegradability (BOD/COD) ratio, particularly in the ozone-treated effluent from the Nida WWTP, highlights the need for an additional post-ozonation biological treatment step before discharge to the coastal environment.

Suspended particulate matter concentrations varied widely among the biologically treated wastewater samples, reflecting differences in their initial composition, with the highest levels observed in the effluent from the Nida WWTP. Despite this variability, ozonation applied at the same treatment length and intensity resulted in similar SPM reductions across all WWTPs. This indicates that the oxidative degradation of organic matter flocs effectively destabilized particulate structures, promoting disaggregation and subsequent removal, thereby greatly improving the quality of biologically treated wastewater (García et al., 2020). This finding suggests that the SPM reduction may limit the role of particles as vectors for hydrophobic micropollutants, thereby reducing their transport through WWTPs and potential discharge into coastal environments.

Overall, scavengers present in wastewater matrices can reduce ozonation efficiency by consuming reactive ozone species, particularly hydroxyl radicals, thereby limiting their availability for oxidation of organic contaminants (Morrison et al., 2023). Bromide acts as an important scavenger and can be oxidized to bromate, a potentially harmful by-product. The highest initial bromide concentrations were observed in the biologically treated wastewater from the Klaipėda WWTP, likely reflecting the industrial influence (Soltermann et al., 2017). Despite the considered high ozone dose applied, bromide concentrations remained largely unchanged across the WWTPs, except for a slight decrease at the Palanga WWTP. It could be attributed to lower DOC levels, which may have allowed limited bromide oxidation. In contrast, higher DOC concentrations from the Klaipėda and Nida WWTPs likely induced competition for ozone, thereby inhibiting bromide oxidation (von Gunten, 2003; Chon et al., 2015; Soltermann et al., 2017). The initial nitrate level, another potential scavenger, varied substantially among the WWTPs, with the highest levels detected and remaining after ozonation at the Nida WWTP. Following ozonation, nitrate concentrations increased at all sites, due to oxidation of residual ammonia, as previously reported by Chuang and Mitch (2017).

5.3.2. Ozonation rapidly removes pharmaceuticals in the effluent from coastal WWTPs

The decomposition of persistent pharmaceuticals (CBZ and VEN) by ozonation was investigated in this study, showing different variation patterns across the biologically treated wastewater from the study coastal WWTPs. CBZ concentrations ranged widely from 427.4 ng L^{-1} in the small resort of Nida to 1519.2 ng L^{-1} in the large coastal city of Klaipėda, reflecting differences in population size. In contrast, VEN concentrations showed limited spatial variability, ranging from 341.2 to 390.0 ng L^{-1} across the coastal WWTPs. The measured CBZ and VEN concentrations were comparable to those reported in other countries. For instance, CBZ concentrations in the German WWTP effluents ranged from 600 to 950 ng L^{-1} (Tixier et al., 2003). Similarly, VEN concentrations observed in this study were comparable to those reported in secondary effluents from Tehran (184.9 ng L^{-1}; Golbaz et al., 2023) and Portugal (272 ng L^{-1}; Santos et al., 2013).

In the present study, ozonation was conducted using the bench-scale system with an ozone production rate of 7.3 ± 0.7 mg L^{-1}, which enabled rapid decomposition of CBZ and VEN. The concentration of CBZ decreased to below detection limits after

5 min of contact time, with the effect maintained after 10 and 15 min, indicating significant structural degradation. In contrast, VEN exhibited slower degradation kinetics; its concentration decreased substantially after 5 min of ozonation, remaining detectable after 10 and 15 min, consistent with previous studies reporting its moderate resistance to oxidation due to its chemical structure (García et al., 2020; von Gunten, 2003).

Industrial-scale ozonation reactors typically require retention times of 20–30 min to achieve effective micropollutant oxidation (Abromaitis et al., 2024). However, the results of this study demonstrate that significantly shorter ozonation contact time was sufficient to completely remove CBZ and substantially reduce VEN under the investigated conditions. This finding highlights the feasibility of applying short ozone retention times, particularly at moderate initial micropollutant concentrations, thereby reducing operational costs and energy consumption associated with ozone generation. Furthermore, composition variations of biologically treated wastewater among the studied WWTPs did not adversely affect the ozonation efficiency for persistent micropollutant removal. Therefore, this study provides a basis for future investigations into short-contact ozonation as an effective and sustainable post-biological treatment option for coastal wastewater treatment plants.

6

Recommendations

This research provides new perspectives on the impacts of temporary and seasonal population increases on pollution patterns in the coastal WWTPs along the Lithuanian shoreline. The study highlights the limitations of conventional wastewater treatment and the resulting accumulation of micropollutants within treatment systems. Overall, the findings underscore the need for further investigation into the long-term effects of micropollutants released via the treated effluent, as well as the feasibility of introducing advanced treatment steps and stricter regulatory frameworks to mitigate the environmental impacts of fluctuating human activity on coastal ecosystems.

1. Hormones and pharmaceuticals exceeded their respective PNEC values in all effluent samples, resulting in high risk quotients (RQ > 1) that may endanger the Baltic Sea ecosystem. We recommend targeted monitoring of E1, E2, CBZ, and VEN near wastewater discharge points to assess trends and enhance environmental protection.
2. Ozonation successfully decomposed pharmaceuticals in biologically treated wastewater from the coastal WWTPs. Further research should focus on optimizing ozone exposure time and dosage based on the initial micropollutant concentrations and evaluate additional suspected and priority hazardous contaminants.

7

Conclusions

The thesis outcomes are integrated into the following conclusions:

1. Seasonal increases in coastal tourism significantly influenced wastewater pollution dynamics at both Small and Large resort WWTPs. During the peak tourist period, the load of specific micropollutants, including estrogenically active compounds (only Small resort WWTP) and total PAEs, as well as nutrient and suspended matter pollution, increased substantially. Although overall pollution levels were generally managed, the retention effectiveness depended on the treatment capacity of each WWTP. The Small resort WWTP proved more sensitive to seasonal tourism fluctuations, resulting in relatively higher pollutant discharges to the coastal ecosystem.
2. Temporary population gathering during the Sea festival affected influent quantity and quality, including micropollutants loads (PAEs, PAHs and hormones) at Klaipėda WWTP, except for pharmaceuticals. Despite an increase in the mean wastewater flow, general pollution indicators in treated effluent remained within regulatory limits. However, the removal of micropollutants, particularly CBZ and VEN, was low or even negative due to biological transformation at the WWTP, resulting in elevated discharges of these compounds into the marine environment, raising concerns about their potential accumulation in the Baltic Sea.

3. Micropollutants, including pharmaceuticals and hormones, exceeded their PNEC values in the effluents from all coastal WWTPs during both the tourism season and the Sea festival. In particular, effluents from the Klaipėda WWTP consistently showed high ecological risk (RQ > 1) for pharmaceuticals (CBZ, VEN) and hormones (E1, E2), indicating a potential threat to the adjacent Baltic Sea coastal ecosystem.
4. Ozonation rapidly decomposed persistent pharmaceuticals in the biologically treated wastewater regardless of different anthropogenic influences. CBZ and VEN were substantially reduced within 5 min. After 15 min of ozonation, COD and SPM concentrations decreased notably, substantially improving overall effluent quality.

8

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9

Summary in Lithuanian

ĮVADAS

Europos Sąjungos mastu keliami ambicingi tikslai mažinti vandens taršą pavojingomis medžiagomis – mikroteršalais ir ilgainiui visiškai nutraukti jų patekimą į ekosistemas kaip nustatyta Bendrosios vandens politikos direktyvoje (Direktyva 2000/60/EB) ir prioritetinių pavojingųjų medžiagų Direktyvoje (Direktyva 2013/39/ES) (Loos et al., 2018; Morris et al., 2017; Pedrazzani et al., 2019). Šios medžiagos į aplinką patenka iš įvairių stacionarių ir pasklidųjų taršos šaltinių, tačiau didžiausi jų kiekiai siejami su miesto nuotekų valymo įrenginiais (Jiang et al., 2014; Sftefănică et al., 2021; Lenart-Boroń et al., 2022). Šiuo metu daugumoje nuotekų valyklų taikomi standartiniai mechaniniai bei biologiniai nuotekų valymo metodai, kurie dažnai nėra pajėgūs visiškai pašalinti nuotekose esančius mikroteršalus (Tian et al., 2022; Falås et al., 2016). Dėl to šios medžiagos patenka į paviršinius vandens telkinius (Jiang et al., 2013), kaupiasi aplinkoje bei gyvuosiuose organizmuose, sukeldamos pavojų vandens ekosistemoms (Bergman et al., 2013; Sanganyado et al., 2021; Diamanti-Kandarakis et al., 2009; Aris et al., 2014; Schug et al., 2011).

Ypatingas iššūkis kyla pajūrio kurortuose, kuriuose turizmo sezono bei laikinų masinių žmonių susibūrimų metu nuotekų srautas gali ženkliai padidėti, o jų sudėtis bei kokybė – pakisti (Gerrity et al., 2011; Rathi et al., 2021; Santos et al., 2022). Esant padidėjusiam nuotekų kiekiui bei užterštumui, gali būti viršytas projektinis nuotekų valyklų pajėgumas (Ahmad et al., 2018), o į Baltijos jūrą ar Kuršių marias išleidžiamos nuotekos gali kelti grėsmę jautrioms vietos ekosistemoms (Ji et al., 2024; Phan et al., 2015). Net ir esant įprastinėms eksploatacinėms apkrovoms, tradicinės nuotekų valymo technologijos nėra pritaikytos efektyviai pašalinti tam tikrus mikroteršalus, pavyzdžiui, farmacinių junginių bei hormonų likučius, kurie dažnai turi endokrininę sistemą veikiančių savybių (Rathi et al., 2021). Šios medžiagos trikdo vandens organizmų hormoninę pusiausvyrą, o per maisto grandinę gali neigiamai paveikti ir žmonių populiaciją (Benjamin et al., 2017; Beck et al., 2006; Briciu et al., 2009; Zhang et al., 2011).

Atsižvelgiant į šias grėsmes, pastaruoju metu vis daugiau dėmesio skiriama pažangiųjų nuotekų valymo technologijų diegimui (Bourgin et al., 2018; Tang et al., 2020), tačiau jų taikymo galimybės praktikoje, ypač pajūrio regionų nuotekų valyklose, išlieka nepakankamai ištirtos.

Šiame darbe analizuojamas sezoninio turizmo ir trumpalaikių masinių žmonių susibūrimų poveikis nuotekų kiekiui bei kokybei prieš ir po biologinio valymo pajūrio nuotekų valyklose. Taip pat vertinamas pažangiosios oksidacijos proceso – ozonavimo – efektyvumas mažinant farmacinių medžiagų koncentraciją ir bendrąjį biologiškai išvalytų nuotekų užterštumą skirtingų taršos šaltinių veikiamose pajūrio nuotekų valyklose. Tikimasi, kad tyrimo rezultatai prisidės prie tvaresnių vietinių nuotekų tvarkymo sprendimų diegimo, jautrių pajūrio ekosistemų apsaugos ir Europos Sąjungos aplinkosauginių tikslų įgyvendinimo.

Tyrimo tikslas ir pagrindiniai uždaviniai

Šio tyrimo tikslas – įvertinti gyventojų skaičiaus svyravimo įtaką bendrajai nuotekų kokybei, mikroteršalų sudėčiai ir dinamikai priekrantės nuotekų valyklose, įvertinti pažangiosios valymo technologijos potencialą pašalinti patvariuosius mikroteršalus prieš išleidžiant nuotekas į priekrantės ekosistemas. Tikslui pasiekti buvo iškelti šie uždaviniai:

1. įvertinti, ar ir kaip sezoninė turizmo dinamika pajūrio kurortuose veikia nuotekų kokybę ir mikroteršalų (estrogeninio potencialo, ftalatų) lygį prieš ir po valymo nuotekų valyklose;
2. įvertinti masinio renginio poveikį nuotekų kokybei ir mikroteršalų (farmacinių medžiagų, hormonų, ftalatų ir policiklinių aromatinių angliavandenilių) lygiui prieš ir po valymo pajūrio miesto nuotekų valykloje;
3. įvertinti ozonavimo potencialą pašalinti farmacines medžiagas iš biologiškai išvalytų nuotekų su skirtingu antropogeninės taršos profiliu.

Darbo naujumas

Šioje disertacijoje nagrinėjamas turizmo sezoniškumo poveikis priekrantės nuotekų valykloms, išleidžiančioms nuotekas į Baltijos jūrą ir gretimas ekosistemas. Pabrėžiamas populiacijos, kaip reikšmingo endokrininę sistemą ardančių mikroteršalų šaltinio, vaidmuo – šis aspektas iki šiol mažai nagrinėtas. Svarbus šio tyrimo rezultatas – nustatytas unikalus netiesinis ryšys tarp turizmo rodiklių ir estrogeninio potencialo reikšmių, taip pat stipri tiesinė koreliacija su plastifikatoriais, maistinėmis medžiagomis ir bendraisiais vandens kokybės parametrais. Šie rezultatai rodo reikšmingą populiacijos poveikį specifinių mikroteršalų pernašai į priekrantės nuotekų valyklas ir suteikia pagrindą tiksliniam stebėjimui bei efektyvesnių taršos mažinimo priemonių taikymui.

Siekiant įvertinti sudėtingą taršos dinamiką ir nuotekų valymo potencialą, šiame tyrime buvo integruotos kelios viena kitą papildančios metodikos, apimančios pažangius analitinius metodus, biocheminius tyrimus, mikrobiologinę analizę ir pažangiosios oksidacijos procesus. Šių skirtingų metodų taikymas leido atlikti išsamų, daugiakomponentį teršalų dinamikos bei šalinimo galimybių vertinimą. Pirmą kartą konkrečioms priekrantės nuotekų valykloms buvo pritaikyti masės balanso skaičiavimai, siekiant įvertinti bendrą į Baltijos jūrą ir Kuršių marias išleidžiamų teršalų kiekį. Šis metodas leido įvertinti priekrantės nuotekų valyklų taršos suvaldymo efektyvumą, esant skirtingoms sezoninėms apkrovoms. Be to, buvo atliktas ekologinės rizikos vertinimas, taikant prognozuojamas poveikio nesukeliančias koncentracijas ir rizikos koeficientus. Tai leido identifikuoti ir suskirstyti mikroteršalus pagal apskaičiuotas rizikos koeficiento reikšmes, sudarant pagrindą tiksliniam stebėsenos ir reguliavimo prioritetų nustatymui bei prisidedant prie vietinių ekosistemų apsaugos ir aplinkos kokybės standartų laikymosi užtikrinimo.

Skirtingai nuo daugelio ankstesnių tyrimų, šiame darbe taikomas išplėstinis analitinis požiūris turizmo poveikiui įvertinti, apimantis platų parametrų spektrą – nuo įprastų vandens kokybės rodiklių ir maistingųjų medžiagų iki sudėtingo mikroteršalų mišinio, įskaitant plastifikatorius, hormonus, farmacinius preparatus ir policiklinius aromatinius angliavandenilius. Šių mikroteršalų dinamika priekrantės nuotekų valyklose sezoninių ir (ar) laikinų gyventojų susibūrimų metu iki šiol nebuvo sistemiškai tirta. Dviejose skirtingo dydžio pajūrio kurortų nuotekų valyklose surinkti išsamūs duomenys atskleidė turizmo sezoniškumo įtaką teršalų dinamikai; ši informacija galės būti naudojama įrodymais grįstoms mikroteršalų valdymo strategijoms kurti.

Ozono taikymas mikroteršalams šalinti dažnai nagrinėjamas eksperimentiniuose tyrimuose, tuo tarpu šiame darbe įvertintas ozonavimo efektyvumas realiomis sąlygomis, naudojant biologiškai išvalytų nuotekų mėginius iš trijų pajūrio nuotekų valyklų, veikiamų skirtingų antropogeninės taršos šaltinių. Gauti rezultatai suteikia praktinių įžvalgų pajūrio nuotekų valykloms, svarstančioms pažangiųjų valymo technologijų diegimą.

Rezultatų mokslinė ir praktinė reikšmė

Ekologinės rizikos vertinimas parodė, kad estrogeniniai junginiai ir farmacinės medžiagos kelia nuolatinę ekologinę grėsmę į priekrantės zoną išleidžiamose valytose nuotekose. Didelės rizikos kategorijai (RQ > 1) priskirtos vertės siejamos su beta-estradioliu, estronu ir estrogeniniu ekvivalentu. Estrogeninių junginių sezoninė dinamika buvo susijusi su sezoniniais populiacijos svyravimais, todėl rekomenduojami tolimesni lėtinio ir ūmaus ekologinio poveikio tyrimai įvairiuose paviršiniuose vandenyse, ypač teritorijose, veikiamose didesnio pajėgumo nuotekų valyklų.

Atnaujintoje Europos Sąjungos miesto nuotekų valymo direktyvoje, įsigaliojusioje nuo 2025 m. sausio 1 d., reikalaujama, kad valstybės narės stebėtų ir mažintų 13 prioritetinių mikroteršalų koncentracijas išvalytose nuotekose. Direktyva taip pat įpareigoja iki 2040 m. įdiegti pažangųjį nuotekų valymą valyklose, kurių populiacijos ekvivalentas viršija 100 000, siekiant ne mažesnio kaip 80 % vidutinio mikroteršalų pašalinimo efektyvumo. Šiame tyrime buvo vertinti du į šį sąrašą įtraukti farmaciniai junginiai – karbamazepinas ir venlafaksinas, kurių koncentracijos po biologinio valymo padidėjo. Pritaikius ozonavimą, šie junginiai buvo visiškai pašalinti per 5 min. Gauti rezultatai rodo, kad pažangusis valymo etapas potencialiai gali būti įdiegtas pajūrio nuotekų valyklose, veikiamose skirtingo pobūdžio antropogeninės taršos, įskaitant sezoninį turizmą. Nors karbamazepinas dar nėra įtrauktas į Europos Sąjungos bendrosios vandens politikos direktyvos prioritetinių pavojingų medžiagų sąrašą, rekomenduojama šią spragą užpildyti, siekiant išsamesnio monitoringo nuotekų valyklose ir paviršiniuose vandenyse.

Šiame tyrime pirmą kartą nacionaliniu mastu pateikiamas endokrininę sistemą ardančių mikroteršalų, įtrauktų į Europos Sąjungos bendrosios vandens politikos direktyvos stebimųjų bei prioritetinių pavojingųjų medžiagų sąrašą, kurie patenka į Baltijos jūrą ir Kuršių Marias, masės balanso įvertinimas. Be to, bendram estrogeniniam aktyvumui įvertinti buvo pritaikytas inovatyvus biocheminis metodas, pagrįstas genetiškai modifikuotomis mielių ląstelėmis. Skirtingai nuo instrumentinių analitinių metodų, jis reikalauja mažesnių darbo ir laiko sąnaudų, todėl gali būti taikomas rutininėje stebėsenoje.

Šio tyrimo rezultatai pagrindžia hormonų, farmacinių junginių ir kitų ES direktyvose nurodytų stebimųjų bei prioritetinių pavojingų medžiagų įtraukimą į stebėsenos programas nuotekose ir paviršiniuose vandenyse. Be to, rekomenduojama atlikti bandomuosius ozonavimo veiksmingumo šalinant prioritetinius endokrininę sistemą ardančius mikroteršalus tyrimus kitose nuotekų valyklose, kurių populiacijos ekvivalentas > 100 000.

Rezultatų aprobavimas

Šio tyrimo rezultatai buvo pristatyti šiose mokslinėse konferencijose:

1. 19-oji tarptautinė atliekų tvarkymo konferencija, 2025 m. balandžio 3–4 d., Venecija (Italija). "Ozonation as an effective method to remove pharmaceuticals from biologically treated wastewater of different origin" (žodinis pranešimas).
2. 16-oji nacionalinė jūrų mokslo ir technologijų konferencija „Jūros ir krantų tyrimai", 2024 m. gegužės 15–17 d., Nida (Lietuva). „Masinio susibūrimo poveikis nuotekų kokybei bei dinamikai įvertinant mikroteršalų, bendrosios taršos kiekius ir išvalymo efektyvumą" (žodinis pranešimas).
3. 9-oji tarptautinė aplinkos taršos, tvarkymo ir apsaugos konferencija, 2024 m. kovo 14–16 d., Londonas (Jungtinė Karalystė). "Mass event Influence on micropollutant composition and loads before and after treatment in the coastal waste water treatment plant" (stendinis pranešimas).
4. 14-asis Baltijos jūros mokslo kongresas, 2023 m. rugpjūčio 21–25 d., Helsinkis (Suomija). "The seasonal tourists› effect on micropollutants delivery and effluents quality in popular coastal resorts of the Baltic Sea" (stendinis pranešimas)
5. 15-oji nacionalinė jūrų mokslo ir technologijų konferencija „Jūros ir krantų tyrimai", 2023 m. balandžio 19–21 d., Dreverna (Lietuva). „Poilsiautojų poveikis nuotekų dinamikai, kokybei ir išvalymo efektyvumui pajūrio kurortuose, įvertinant ftalatus, hormonus ir maistines medžiagas" (žodinis pranešimas).

Baigiamojo darbo struktūra

Disertaciją sudaro dešimt skyrių: įvadas, literatūros apžvalga, metodologija, rezultatai, diskusija, rekomendacijos, išvados, literatūros sąrašas, santrauka lietuvių kalba ir priedai. Disertacijos apimtis yra 144 puslapiai, iliustruota 24 paveikslais ir 28 lentelėmis. Disertacijoje pateikiamos nuorodos į 228 literatūros šaltinius. Darbas parašytas anglų kalba su išplėstine santrauka lietuvių kalba.

TYRIMŲ MEDŽIAGA IR METODAI

Gyventojų dinamikos įtaka taršai pajūrio nuotekų valyklose

Bendrieji nuotekų kokybės parametrai

Siekiant įvertinti nuotekų sudėtį ir išvalymo efektyvumą buvo analizuojami nuotekų kokybės parametrai: bendrasis azotas ir fosforas, ištirpusi organinė anglis, biologinis ir cheminis deguonies sunaudojimas bei suspenduotoji medžiaga. Buvo taikomi standartizuoti ISO ir EN metodai. Ištirpusi organinė anglis bei bendrasis azotas buvo analizuojamas po deginimo aukštoje temperatūroje pagal ISO 20236:2018 standartą. Suspenduotoji medžiaga buvo įvertinta gravimetrine analize pagal EN 872:2005 standartą, o bendrasis fosforas po oksidacijos šarmine peroksodisulfato rūgštimi kiekybiškai įvertintas spektrofotometrijos būdu, taikant molibdato metodą (Koroleff ir kt., 1983). Biocheminis deguonies sunaudojimas (per septynias dienas) buvo nustatytas pagal LST EN ISO 1899-2:2000 standartą, pridedant alitiokarbamido. Cheminis deguonies sunaudojimas buvo matuojamas sandaraus vamzdelio metodu (Macherey-Nagel, Vokietija) pagal ISO 15705:2002 standartą.

Teršalų masės balanso skaičiavimai

Taršos kiekis nuotekose prieš ir po valymo buvo įvertintas padauginus koncentraciją iš nuotekų kiekio kubiniais metrais, naudojant pajūrio nuotekų valyklų pateiktus nuotekų srauto duomenis. Apkrovos įtekančiose ir ištekančiose nuotekose buvo išreikštos atitinkamais kiekio bei laiko vienetais, priklausomai nuo cheminių junginių klasės ir mėginių ėmimo dažnio.

Rizikos aplinkai vertinimas

Į priekrantės aplinką išleidžiamų mikroteršalų ekologinė rizika buvo įvertinta naudojant prognozuojamas poveikio nesukeliančias koncentracijas, žemiau kurių neigiamas poveikis vandens organizmams yra mažai tikėtinas, bei rizikos koeficientus, apskaičiuotus pagal realių išmatuotų teršalų koncentracijų ir jiems specifinių prognozuojamų poveikio nesukeliančių koncentracijų santykį. Remiantis rizikos koeficiento vertėmis, rizikos lygis buvo klasifikuojamas kaip minimalus, vidutinis arba didelis.

Statistinė analizė

Dėl mažo imties dydžio statistinė analizė atlikta naudojant neparametrinius metodus, taikant Spearmano koreliaciją tiesiniams, ryšiams ir Hoeffdingo D netiesiniams ir nemonotoniniams ryšiams tarp vandens kokybės parametrų, mikroteršalų ir turizmo rodiklių. Estrogeninis aktyvumas prieš ir po nuotekų valymo buvo įvertintas naudojant „BioVAL“ statistikos programą. Visa statistinė analizė atlikta naudojant R programinės įrangos versiją i3864.1.2 ir Python 3.12.1.

Sezoninis tyrimas

Norint įvertinti sezoninio gyventojų skaičiaus svyravimo poveikį nuotekų kokybei ir valymo efektyvumui, buvo analizuojami ftalatų kiekiai, estrogeninis potencialas ir bendrieji nuotekų kokybės parametrai prieš ir po valymo dviejose pajūrio kurortų nuotekų valyklose. Mėginiai buvo imami kas mėnesį mažo (Nidos) ir didelio (Palangos) kurorto nuotekų valyklose 2022 m. kovo – 2023 m. vasario laikotarpiu, tiek ne turizmo sezono metu (kovas–gegužė ir rugsėjis–vasaris), tiek intensyviausiu vasaros sezono laikotarpiu (birželis–rugpjūtis). Kiekvienoje valykloje realiuoju laiku buvo paimti trys nuotekų mėginiai prieš valymą ir trys – po valymo. Mėginiai buvo surinkti naudojant nerūdijančiojo plieno semtuvą ir perpilti į tris 1 L talpos stiklinius indus, skirtus ftalatų ir estrogeninio potencialo analizei. Papildomai buvo paimti mėginiai maistingųjų medžiagų, ištirpusių ir kietųjų dalelių tyrimams.

Estrogeninio potencialo analizei skirti mėginiai buvo apdoroti 1 % metanolio tirpalu siekiant sumažinti mikroorganizmų aktyvumą ir išvengti biodegradacijos. Visi mėginiai per valandą buvo transportuoti į laboratoriją šaltkrepšyje tolimesnei analizei. Laboratorijoje bendras estrogeninis potencialas nuotekų mėginiuose prieš ir po valymo buvo nustatytas naudojant kietosios fazės ekstrakciją ir biocheminę analizę. Mėginiai buvo filtruojami, siekiant surinkti tiek ištirpusius, tiek su dalelėmis surištus estrogeninius junginius, kurie buvo ekstrahuoti metanoliu. Vėliau kietosios fazės ekstrakcija buvo atlikta naudojant „Oasis HLB“ kasetes, nuotekų mėginius leidžiant pastoviu srautu bei pasirinktus junginius išplaunant metiltretbutil eteriu. Ekstraktai buvo laikomi -20 °C temperatūroje, po to džiovinami azoto dujomis, o likusi kietoji medžiaga ištirpinama tirpiklyje prieš analizę. Estrogeninis aktyvumas buvo kiekybiškai įvertintas naudojant modifikuotomis mielėmis pagrįstą biocheminę analizę, kuomet reaguojant į estrogeninius junginius gaminama β-galaktozidazė. Tyrimas buvo atliktas mikrotitravimo lėkštelėse su kalibruotais estrogenų standartais, absorbcija buvo matuojama spektrofotometriškai prieš ir po substrato pridėjimo. Buvo analizuojami trys kiekvieno mėginio pakartojimai. Metodo aptikimo riba buvo ≥0,04 ng L^{-1}, kiekybinio nustatymo riba – ≥0,06 ng L^{-1}.

Jūros šventės įtaka

Norint įvertinti laikino didelio žmonių susibūrimo poveikį taršos dinamikai ir nuotekų išvalymo efektyvumui Klaipėdos nuotekų valykloje, 2023 metais Jūros šventės metu buvo analizuojamos keturios mikroteršalų grupės (hormonai, ftalatai, farmacinės medžiagos ir policikliniai aromatiniai angliavandeniliai), maistingosios medžiagos ir bendrosios taršos rodikliai. Nuotekų mėginiai buvo imami tris dienas prieš šventę, jos metu ir tris dienas po jos. Išvalytų nuotekų mėginiai buvo imami praėjus 48 valandoms po kiekvieno nevalytų nuotekų mėginio surinkimo, siekiant atspindėti pilną nuotekų išvalymo proceso ciklą. Mėginiai buvo renkami naudojant nerūdijančiojo plieno semtuvą ir perpilami į tris 1 L talpos stiklinius indus. Papildomai buvo surinkti mėginiai maistinių medžiagų ir kietųjų dalelių tyrimams.

Mikroteršalų išskyrimui buvo taikomas filtravimas ir kietosios fazės ekstrakcija, naudojant „Oasis HLB“ ir „C18“ kasetes. Su kietosiomis dalelėmis susijungę mikroteršalai buvo ekstrahuojami tirpikliais: estrogenams ir farmacinių medžiagų likučiams naudotas metanolis, o ftalatams ir policikliniams aromatiniams angliavandeniliams – ultragarsinė ekstrakcija dichlormetanu. Kiekybinė estrogenų ir farmacinių medžiagų likučių analizė atlikta naudojant skysčių chromatografijos ir masių spektrometrijos metodą. Estrogenai buvo analizuojami neigiamų, o farmacinių medžiagų likučiai – teigiamų jonų režimu, taikant daugybinių reakcijų stebėseną. Kalibravimas buvo atliktas naudojant vidinius standartus, sudarant ne mažiau kaip penkių taškų kalibracines kreives. Mikroteršalų atgavimo vertės eksperimentiniuose bandymuose siekė 70–120 %. Kokybės kontrolė apėmė procedūrinių ir instrumentinių bandinių stebėseną bei kontrolinių mėginių analizę. Aptikimo ir kiekybinio nustatymo ribos svyravo nuo 0,1 iki 5,0 nanogramų litre. Ftalatai ir policikliniai aromatiniai angliavandeniliai buvo analizuojami naudojant dujų chromatografiją ir masių spektrometriją, taikant nepadalintą injekciją ir individualaus jono stebėsenos režimą. Ftalatų atgavimo vertės siekė 70–103 %, o policiklinių aromatinių angliavandenilių 70–107 %. Kiekybinio nustatymo ribos policikliniams aromatiniams angliavandeniliams svyravo nuo 0,034 iki 0,205, o ftalatams nuo 0,011 iki 0,044 mikrogramų litre.

Ozonavimo pritaikymas taršos mažinimui biologiškai išvalytose nuotekose

Bendrieji nuotekų kokybės parametrai

Vandens kietumui nustatyti, mėginiai buvo skaidomi uždarame inde mikrobangų krosnelėje pagal LST EN ISO 15587-2:2004 standartą, o koncentracijos nustatytos induktyviai susietosios plazminės masių spektrometrijos metodu. Bromidų koncentracija buvo nustatyta pagal LST EN ISO 10304-1:2009, naudojant jonų mainų chromatografiją. Mikrobiologinis užterštumas įvertintas pagal kolonijas sudarančių vienetų skaičių prieš ir po ozonavimo, sėjant mėginius iš kelių praskiedimų ir inkubuojant 37 °C temperatūroje. Ištirpusių nitratų koncentracija nustatyta taikant standartinius kolorimetrinius metodus (Grasshoff ir kt., 1983), kaip aprašyta Vybernaitė-Lubienė ir kt. (2017).

Patvariųjų farmacinių medžiagų šalinimo eksperimentas

Ozonavimo poveikis farmacinėms medžiagoms (karbamazepinui ir venlafaksinui) bei bendriesiems nuotekų kokybės parametrams po biologinio valymo buvo įvertintas eksperimentiškai. Mėginiai buvo surinkti iš trijų nuotekų valyklų, veikiamų skirtingų taršos šaltinių: Nidos (turizmo poveikis), Palangos (namų ūkių ir turizmo poveikis) ir Klaipėdos (namų ūkių, pramonės ir turizmo poveikis). Sudėtiniai 24 val. mėginiai (5 l) buvo paimti po mechaninio ir biologinio valymo, naudojant sandarius plastikinius indus.

Ozonavimo reaktoriuje nuotekos buvo ozonuojamos 15 minučių. Mėginiai farmacinių medžiagų ir bakterinės taršos analizei buvo paimti prieš ozonavimą (0 min), praėjus 5, 10 ir 15 minučių. Bendriesiems kokybės parametrams (vandens kietumui, nitratams, ištirpusiai organinei angliai, cheminiam ir biologiniam deguonies sunaudojimui, bromidams, suspenduotai medžiagai) nustatyti mėginių ėmimo dažnis sumažintas, siekiant išlaikyti optimalų skysčio lygį reaktoriuje; jie buvo paimti ir paruošti analizei tik prieš ozonavimą (0 min) ir po 15 minučių ozonavimo. Ištirpusio ozono koncentracija buvo palaikoma 7 ± 0,7 mg L^{-1}. Ji parinkta remiantis vidutine ištirpusios organinės anglies koncentracija valytose nuotekose trijose pajūrio valyklose (~13 mg L^{-1}; I ir II straipsniai), užtikrinant reikiamą ozono ir ištirpusios organinės anglies santykį (~0,5 g O_3 g^{-1} DOC).

REZULTATAI IR JŲ APTARIMAS

Sezoninis tyrimas

Sezoninės populiacijos kaitos įtaka nuotekų kokybės dinamikai

Sezoninis turizmas lemia išaugusį nuotekų srautą ir antropogeninės taršos kiekį pajūrio kurortų nuotekų valyklose (Phan ir kt., 2015; Buttiglieri ir kt., 2016; Torres-Padrón ir kt., 2020). Padidėjusi apkrova gali apsunkinti valyklų darbą, kurios paprastai suprojektuotos apdoroti teršalų kiekį, proporcingą numatomam nuolatinių gyventojų skaičiui (populiacijos ekvivalentui). Viršijant šias ribas, išvalymo efektyvumas gali sumažėti (Gerrity ir kt., 2011; Jiang ir kt., 2014; Kim ir kt., 2019), todėl į pajūrio aplinką gali patekti didesni teršalų kiekiai. Šiame tyrime buvo analizuojamos dviejų skirtingo dydžio pajūrio kurortų nuotekų valyklos.

Sezoninį populiacijos padidėjimą lėmė lankytojai, atvykstantys į pajūrį šiltuoju metų laiku birželio–rugpjūčio mėn. Mažojo kurorto išleidžiamų nuotekų srautas vasaros sezono metu padidėjo apie 200 %. Tuo tarpu Didžiajame kurorte nuotekų srauto padidėjimas siekė tik apie 16 % (6 pav.). Gali būti, kad toks nežymus padidėjimas yra susijęs su paviršinio ir gruntinio vandens infiltracija į nuotekų tinklus („Palangos vandenys“, asmeninis komentaras, 2023 m. balandžio 7 d.). Infiltracija yra dažnas reiškinys, kai gruntinio vandens lygis yra aukštas, pavyzdžiui, pajūrio nuotekų valyklose (Luczaj ir Masarik, 2015; Sun ir kt., 2016).

Oro temperatūra abiejuose kurortuose vasaros metu vidutiniškai buvo apie 22 °C. Rugpjūtį aukščiausia temperatūra siekė 26 °C Mažajame ir 29 °C Didžiajame kurorte (6 pav.). Temperatūra abiejuose kurortuose koreliavo su turizmo rodikliais – įvažiavusių automobilių Mažajame ir nakvynių skaičiumi Didžiajame kurorte (7 pav.).

Cheminio ir biologinio deguonies sunaudojimo santykis įtekančiose nuotekose vasarą atitiko vidutinį biologinį skaidumą (~0,5) (7 pav.). Šio santykio sumažėjimas šaltojo sezono metu galėjo būti susijęs su padažnėjusiomis sezoninėmis infekcijomis ir dėl to su išaugusiu vaistų likučių patekimu į nuotekas (Kot-Wasik ir kt., 2016).

Ištirpusios organinės anglies koncentracija dėl išaugusios organinės taršos šiltuoju sezono metu buvo apie penkis kartus didesnė nei šaltuoju sezonu (8 pav.). Sezoniškumas taip pat veikė įtekančių maistingųjų medžiagų kiekį. Mažojo kurorto nuotekų valykloje bendrojo azoto ir fosforo apkrovos padidėjo apie septynis kartus, o Didžiojo – daugiau nei du kartus (8 pav.). Suspenduotos medžiagos kiekis šiltojo sezono metu taip pat reikšmingai išaugo. Mažajame kurorte rugpjūčio mėnesį jis padidėjo apie šešis kartus, o Didžiajame kurorte – apie du kartus (8 pav.). Šiuos svyravimus galimai lėmė išaugęs įtekančių buitinių nuotekų kiekis. Tualetai ir skalbimo priemonės laikomi pagrindiniais fosforo, azoto ir suspenduotų dalelių šaltiniais (Puijenbroek ir kt., 2019). Didėjant turistų skaičiui Baltijos jūros regione (UNWTO, 2023b), tikėtina, kad antropogeninė tarša taip pat augs.

Populiacijos sezoniškumo įtaka mikroteršalų dinamikai nuotekose

Žmonių veikla, ypač paplūdimio turizmas, yra pagrindinis plastiko taršos šaltinis pajūrio kurortuose (Williams ir kt., 2016). Kadangi ftalatai nėra chemiškai sujungti su plastiko matrica, jie lengvai patenka į aplinką ir pasiekia nuotekų valymo įrenginius per paviršines bei buitines nuotekas (Anne ir Paulauskienė, 2021). Ftalatų apkrovoms į abiejų kurortų nuotekų valyklas būdingas ryškus sezoniškumas, glaudžiai susijęs su turizmo intensyvumu. Vidutinė mėnesinė ftalatų apkrova buvo reikšmingai didesnė Didžiojo kurorto nuotekų valykloje (~8,6 kg mėn^{-1}), tuo tarpu Mažajame kurorte siekė tik apie 1,7 kg mėn^{-1} (10 pav.). Didžiausios apkrovos užfiksuotos intensyvaus turizmo sezono metu, rugpjūčio mėnesį jos siekė 0,9 kg mėn^{-1} Mažojo ir 10,5 kg mėn^{-1} – Didžiojo kurorto nuotekų valyklose (10 pav.). Išskirtinai didelė ftalatų apkrova (42,5 kg mėn^{-1}), keturis kartus viršijanti metinį vidurkį (10 pav.), galėjo būti susijusi su pasirengimu sezonui: intensyviais remonto ir renovacijos darbais, kurių metu naudojamos plastifikatorių turinčios statybinės medžiagos ir buitinė chemija. Chemikalų likučiai gali būti nuplauti nuo paviršių, tekstilės gaminių ir odos ir patekti į nuotekų tinklus (Koniecki ir kt., 2011).

Abiejų kurortų nuotekose nustatyta stipri koreliacija tarp turizmo rodiklių (transporto priemonių srauto bei nakvynių skaičiaus) ir ftalatų apkrovos (7 pav.). Suminė ftalatų bei suspenduotoje medžiagoje aptikto di(2-etilheksil)ftalato apkrova reikšmingai koreliavo su transporto priemonių srautu Mažajame kurorte ir su nakvynių skaičiumi didžiajame kurorte. Tai rodo tiesioginį ryšį tarp populiacijos ir ftalatų patekimo į pajūrio nuotekų valyklas (12 lent.). Mažajame kurorte bendra ftalatų koncentracija įtekančiose nuotekose reikšmingai koreliavo su organinių medžiagų kiekiu (7 pav.). Didžiajame kurorte tokia priklausomybė nenustatyta, tikėtina, dėl gruntinio vandens infiltracijos, galėjusios praskiesti nuotekas ir iškreipti taršos apkrovų vertinimą.

Estrogeninio potencialo apkrovų dinamika įtekančiose nuotekose dar aiškiau atskleidė sezoninius skirtumus tarp tiriamų valyklų. Mažojo kurorto nuotekų valykloje nustatyta ryški sezoninė dinamika, didžiausia apkrova, fiksuota liepos mėnesį (~67 mg mėn^{-1}) (11 pav.), sutapo su padidėjusiu nuotekų srautu ir turistų skaičiumi. Taip pat nustatyta reikšminga netiesinė estrogeninio potencialo priklausomybė nuo į Mažąjį kurortą įvažiavusių mašinų skaičiaus bei nuotekų kokybės parametrų (13 lent.). Didelė mėnesinė variacija būdinga Didžiojo kurorto estrogeninio potencialo vidutinei mėnesinei koncentracijai (11 pav.). Abiejų kurortų nuotekų valyklose buvo nustatytas estrogeninio potencialo apkrovos padidėjimas ne sezono metu (12 pav) gali būti siejamas su sumažėjusia estrogeninių junginių biodegradacija žemesnėje temperatūroje (Hao ir kt., 2024).

Taršos sulaikymas pajūrio kurortų valyklose

Šiame tyrime buvo siekiama įvertinti, kaip sezoniniai taršos svyravimai nuotekose iš Mažojo ir Didžiojo kurorto veikia išvalymo efektyvumą ir nuotekų kokybę. Tiek Mažojo, tiek Didžiojo kurorto nuotekų valyklos reikšmingai pagerino išleidžiamų nuotekų kokybę, pasiekdamos aukštą suspenduotų, maistingųjų, organinių medžiagų bei dalies mikroteršalų pašalinimo efektyvumą (89–98 %) (14 lent.). Nepaisant gerų vidutinių bendrosios taršos pašalinimo rodiklių, turizmo sezono metu birželio–rugpjūčio mėnesiais išaugus teršalų apkrovoms maistingųjų medžiagų pašalinimo efektyvumas sumažėjo. Bendrojo azoto ir fosforo koncentracijos liepos ir rugpjūčio mėnesiais keletą kartų viršijo išleidimo į gamtinę aplinką normas. Tačiau Europos Sąjungoje galiojančios maistingųjų medžiagų taršos ribinės vertės (Direktyva 91/271/EEB) vis dar neužtikrina visiško eutrofikacijos rizikos pašalinimo. Lietuvos pajūrio zonos išlieka ypač pažeidžiamos eutrofikacijos procesų (Preisner ir kt., 2020). Siekiant mažinti eutrofikaciją Baltijos jūroje, rekomenduojama taikyti griežtesnę bendrojo azoto išleidimo normą (0,5 mg L^{-1}) (HELCOM, 2021).

Ftalatų pašalinimo efektyvumas taip pat buvo aukštas (81–99 %) (14 lent.), tačiau išleidžiamose nuotekose nustatytos koncentracijos skyrėsi tarp Mažojo ir Didžiojo kurortų nuotekų valyklų (S1 lent.). Nustatyta, kad kai kurių ftalatų pašalinimo efektyvumas Mažojo kurorto nuotekų valykloje buvo mažesnis, galimai dėl trumpesnio įtekančių nuotekų sulaikymo laiko, kurį lėmė padidėjęs hidraulinis srautas (Di Marcantonio ir kt., 2022). Iš Mažojo kurorto nuotekų valyklos išleidžiamose nuotekose buvo nustatyta didesnė bendra vidutinė ftalatų koncentracija, siekusi 2,0 μg L^{-1} ir galinti prisidėti prie ftalatų apkrovos priekrantėje.

Estrogeninio potencialo metinė sulaikymo vertė siekė apie 78 %, tačiau vasarą (birželio–rugpjūčio mėn.) efektyvumas sumažėjo iki <70 % (14 lent.). Daugiau kaip 30 % išmatuotų estrogeninio potencialo verčių viršijo prognozuojamą poveikio nesukeliančios koncentracijos ribą (0,4 ng L^{-1}; Loos ir kt., 2018), o rizikos vertinimas parodė dominuojančią vidutinę bei didelę riziką aplinkai (16 lent.). Abi nuotekų valyklos pakankamai efektyviai šalino taršą, tačiau intensyvaus turizmo sezono metu išaugusios apkrovos lėmė didesnį maistinių medžiagų ir estrogeninį potencialą turinčių mikroteršalų patekimą į priekrantės ekosistemas.

Didelio žmonių susibūrimo įtaka nuotekų užterštumui

Į pajūrio nuotekų valyklą įtekančių nuotekų kokybės pokyčiai

Dideli viešieji renginiai turistiniuose pajūrio miestuose gali laikinai padidinti nuotekų kiekį ir taršą, todėl gali sumažėti nuotekų išvalymo efektyvumas ir padidėti į priekrantės ekosistemas išleidžiamų teršalų kiekis. Šiame darbe buvo analizuojama Jūros šventės įtaka teršalų dinamikai įtekančiose ir ištekančiose nuotekose bei išvalymo efektyvumui pajūrio miesto nuotekų valykloje. Jūros šventės laikotarpiu, 2023 m. liepos 21–23 dienomis, apie 156 000 nuolatinių gyventojų turinčioje Klaipėdoje preliminariai apsilankė apie 500 000 turistų. Nepaisant žmonių antplūdžio, bendras nuotekų įtekėjimo srauto padidėjimas Klaipėdos nuotekų valykloje nebuvo ryškus, galimai dėl riboto vandens sunaudojimo šventės metu. Prieš šventę įtekančių nuotekų srautas siekė apie 29 700 m^3 per parą, o paskutinę šventės dieną padidėjo iki 34 500 m^3 per parą (14 pav.). Tai sudarė 16 % augimą ir 11 % viršijo vidutinį liepos mėnesio nuotekų srautą.

Į Klaipėdos nuotekų valyklą nuotekos patenka iš įvairių šaltinių: gyvenamųjų būstų (apie 60 % viso srauto), pramonės (apie 23 %) bei lietaus nuotekų ir gruntinio vandens infiltracijos (asmeninis komentaras „Klaipėdos vanduo“, 2023 m. lapkričio 11 d.). Šie skirtingi šaltiniai galėjo nustelbti nuotekų srauto pokyčius, susijusius su trumpalaikiu populiacijos padidėjimu šventės metu.

Ištirpusios organinės anglies apkrova padidėjo nuo 3,0 iki 5,5 t per parą pirmąją šventės dieną (15 pav.), dėl laikinų šventės metu naudojamų biotualetų ištuštinimo (asmeninis komentaras „Klaipėdos vanduo“, 2023 m. lapkričio 11 d.), kadangi pagrindinis šios anglies šaltinis yra šlapimas ir išmatos (Seredynska-Sobecka ir kt., 2011; Liberatore ir kt., 2016). Suspenduotos medžiagos apkrova proporcingai augo kiekvieną šventės dieną nuo 17,3 iki 53,6 t per parą (15 pav.). Maistingųjų medžiagų apkrovos, kurios paprastai susijusios su gyventojų skaičiaus augimu (Bussi ir kt., 2021), taip pat padidėjo. Bendrasis azotas padidėjo nuo 3,0 iki 5,5 t per parą, o bendras fosforas – nuo 0,4 iki 1,0 t per parą (15 pav.). Taip pat nustatyta stipri koreliacija tarp suspenduotų ir maistingųjų medžiagų kiekių – bendrojo azoto ir fosforo (atitinkamai $r = 0,84$, $r = 0,89$; $p < 0,05$) (S1 pav.). Tai rodo, kad kietosios dalelės buvo glaudžiai susijusios su azoto ir fosforo pernaša nuotekose. Jūros šventė sukėlė trumpalaikį organinės taršos, suspenduotos medžiagos ir maistingųjų medžiagų apkrovos padidėjimą, tačiau poveikis įtekančių nuotekų kiekiui buvo mažiau ryškus.

Mikroteršalų dinamika nuotekose

Laikinas žmonių skaičiaus padidėjimas didelių viešųjų renginių metu dažnai siejamas su didesniais į nuotekų valyklas patenkančiais organinės taršos bei mikroteršalų kiekiais (Jiang ir kt., 2014; Gerrity ir kt., 2011). Jūros šventės laikotarpiu į Klaipėdos nuotekų valyklą įtekančiose nuotekose tirtų mikroteršalų (hormonų, ftalatų, policiklinių aromatinių angliavandenilių) kiekiai ženkliai padidėjo, išskyrus farmacinių medžiagų likučius (16 pav.). Aptiktas žymus estrogeninių hormonų kiekio padidėjimas patvirtina ankstesnių tyrimų išvadas apie didžiausią jų kiekį nevalytose nuotekose intensyvaus turizmo laikotarpiu (Phan ir kt., 2015). Dėl didelio šiame tyrime analizuoto farmacinio junginio karbamazepino cheminio stabilumo ir atsparumo biodegradacijai (Björlenius ir kt., 2018; Kim ir kt., 2019; Mackuľak ir kt., 2019) jo koncentracija nuotekose prieš valymą buvo vidutiniškai penkis kartus didesnė nei venlafaksino (18 lent.).

Bendras ftalatų kiekis Jūros šventės metu išaugo daugiau nei du kartus. Labiausiai padidėjo di(2-etilheksil)ftalato kiekis (17 pav.), tikėtina, dėl jo kaip plastifikatoriaus naudojimo įvairiuose gaminiuose, pavyzdžiui, plastikiniuose induose ir pakavimo medžiagose (Bergé ir kt., 2013; Rowdhwal ir kt., 2018). Policiklinio aromatinio angliavandenilio benzo(g,h,i)perileno kiekis padidėjo daugiau kaip keturis kartus (17 pav.). Šio junginio pernaša į nuotekų valyklas dažnai siejama su paviršinėmis nuotekomis iš miesto ir pramonės zonų (Chen ir kt., 2013; Chen ir kt., 2019; Suresh ir kt., 2024). Šio tyrimo duomenys patvirtino, kad didelės molekulinės masės policikliniai aromatiniai angliavandeniliai dominuoja suspenduotoje fazėje (18 pav.). Tai reiškia, kad pagrindinis jų pernašos į nuotekų valyklas mechanizmas yra adsorbcija ant kietųjų dalelių.

Nuotekų kokybė po biologinio valymo

Nustatyta, kad didelio viešojo renginio metu Klaipėdos nuotekų valykla stabiliai mažino taršą ir užtikrino nuotekų kokybės atitiktį aplinkosaugos reglamentams (20 lent.). Suspenduotų ir maistingųjų medžiagų kiekių, cheminio bei biologinio deguonies sunaudojimo koncentracijos prieš ir po valymo masės balanso analizė patvirtino nuolatinį aukštą išvalymo efektyvumą (21 lent.). Maistingųjų medžiagų, kurios yra pagrindinė eutrofikacijos priežastis (Smith, 2003), koncentracijos nuotekose buvo ženkliai žemesnės nei Europos Sąjungos ir Lietuvos Respublikos aplinkos ministerijos nustatytos didžiausios leistinos normos (15,0 mg L^{-1} bendram azotui ir 2,0 mg L^{-1} bendram fosforui) (20 lent.).

Tuo tarpu bendras mikroteršalų kiekis su valytomis nuotekomis išleistas į Baltijos jūrą padidėjo (20 pav.). Farmacinių medžiagų karbamazepino ir venlafaksino koncentracijos išleidžiamose nuotekose viršijo prognozuojamas žalos nesukeliančios koncentracijos vertes: 90 ng L^{-1} venlafaksinui ir 500 ng L^{-1} karbamazepinui (Qu ir kt., 2018; Oldenkamp ir kt., 2019) (22 lent.). Rizikos vertinimas, parodė, kad tiek karbamazepino, tiek venlafaksino koncentracija išleidžiamose nuotekose turėjo aukštą rizikos koeficiento vertę (>1) (23 lent.), kuri rodo galimą neigiamą poveikį priekrantės aplinkai. Nors šioje studijoje tirtų hormonų sulaikymas nuotekų valykloje buvo aukštas (19 pav.), tačiau estrono bei beta-estradiolio koncentracija nuotekose po valymo labiausiai viršijo jų prognozuojamas žalos nesukeliančias koncentracijas (atitinkamai 4,0 ng L^{-1} ir 0,4 ng L^{-1}) (22 lent.) (Loos ir kt., 2018). Estronas ir beta-estradiolis taip pat pateko į didelės ekologinės rizikos kategoriją (RQ > 1) (23 lent.). Tuo tarpu individualių ftalatų koncentracijos neviršijo jiems nustatytų prognozuojamų žalos nesukeliančių koncentracijos verčių, tačiau bendras ftalatų kiekis, išleistas su valytomis nuotekomis Jūros šventės metu, laikinai padidėjo (20 pav.), daugiausiai dėl išaugusios di(2-etilheksil)ftalato koncentracijos. Nors policikliniai aromatiniai angliavandeniliai nuotekose po valymo nebuvo aptikti, jie gali kauptis nuotekų dumble (Lee ir kt., 2021). Tyrimo duomenys parodė ne tik laikiną tam tikrų mikroteršalų išleidimo padidėjimą, bet ir nuolatinį jų patekimą į pajūrio ekosistemas bei galimybę jose kauptis. Todėl į stebėsenos programas būtų naudinga įtraukti išleidžiamų nuotekų monitoringą didelių viešųjų renginių metu, siekiant detaliau ištirti pavojingų patvariųjų mikroteršalų dinamiką.

Taršos mažinimo eksperimentas taikant pažangiosios oksidacijos metodą

Bendroji nuotekų kokybė prieš ir po ozonavimo

Ozonavimas yra veiksmingas pažangiosios oksidacijos būdas patvariesiems organiniams teršalams, pavyzdžiui, farmacinių medžiagų likučiams šalinti (von Gunten, 2003; Treguer ir kt., 2010; Bourgin ir kt., 2018). Tačiau į pajūrio nuotekų valyklas nuotekos dažnai patenka iš įvairių šaltinių, todėl po biologinio valymo jose gali būti įvairi teršalų likučių matrica, kuri gali neigiamai paveikti mikroteršalų šalinimą ozonavimo būdu (Merkus ir kt., 2023; Tang ir kt., 2020; Shin ir kt., 2025). Šiame tyrime buvo įvertintas ozonavimo poveikis biologiškai išvalytoms nuotekoms iš Nidos, Palangos ir Klaipėdos pajūrio nuotekų valyklų. Nuotekų kokybė įvertinta matuojant bendrosios taršos ir kitus parametrus, kurie gali turėti įtakos ozonavimo efektyvumui (24 lent.).

Biologiškai išvalytos nuotekos iš trijų pajūrio nuotekų valyklų (Nidos, Palangos ir Klaipėdos) skyrėsi savo kokybe. Biologiškai išvalytose nuotekose iš Klaipėdos valyklos nustatyta didesnė bromidų koncentracija bei vandens kietumas, beveik tris kartus didesnė bakterinė tarša. Nidoje nustatytas didžiausias cheminis deguonies sunaudojimas, suspenduotos medžiagos ir nitratų koncentracijos (24 lent.).

Ozonavimas ženkliai pagerino biologiškai išvalytų nuotekų iš Nidos, Palangos ir Klaipėdos pajūrio nuotekų valyklų bendrąją kokybę, nepaisant skirtingos pradinės teršalų matricos ir koncentracijos. Po 15 minučių ozonavimo ištirpusios organinės anglies koncentracija iš esmės nepakito, galimai dėl įvykusios ribotos visiškos mineralizacijos (21 pav.). Moksliniuose tyrimuose nurodoma, kad ozonavimas retai visiškai mineralizuoja ištirpusią organinę anglį, tačiau dažniau susidaro tarpiniai oksidacijos produktai (von Gunten, 2003; Bourgin it kt., 2018; Phan ir kt., 2022). Po ozonavimo ženkliai nesikeitė ir bromidų koncentracija, galimai nesusidarė pavojingi šalutiniai oksidacijos produktai. Tuo tarpu cheminio deguonies sunaudojimo bei suspenduotos medžiagos koncentracija po ozonavimo ženkliai sumažėjo (21–22 pav.). Dėl stipraus ozono antimikobinio poveikio (Stange ir kt., 2019; Epelle ir kt., 2022) mikrobinė tarša buvo visiškai pašalinta po penkių ozonavimo minučių (25 lent.). Taigi, nustatyta, kad nepaisant skirtingos nuotekų sudėties matricos bei pradinių koncentracijų ozonavimas biologiškai išvalytose nuotekose iš pajūrio valymo įrenginių efektyviai sumažino patvariuosius mikroteršalus, organinę, kietųjų dalelių ir mikrobinę taršą.

Ozonavimo poveikis patvariųjų mikroteršalų mažinimui

Šiame tyrime buvo analizuojamas ozonavimo poveikis patvariųjų farmacinių medžiagų (venlafaksino ir karbamazepino) sumažinimui biologiškai valytose nuotekose iš trijų pajūrio nuotekų valyklų (Nidos, Palangos ir Klaipėdos), veikiamų skirtingų taršos šaltinių. Ozonavimas ženkliai sumažino tirtų patvariųjų farmacinių junginių koncentraciją, nepaisant skirtingos pradinės teršalų matricos ir koncentracijos biologiškai išvalytose nuotekose.

Venlafaksino koncentracija biologiškai išvalytose nuotekose iš visų valyklų buvo labai panaši: Klaipėdoje – 390,0 ng L^{-1}, Palangoje – 361,4 ir Nidoje – 341,2 ng L^{-1}. Po penkių minučių ozonavimo ji nukrito žemiau kiekybinio nustatymo ribų (26 lent.), tačiau liko aptinkama po 10 ir 15 minučių, patvirtinant tyrimuose aprašytą vidutinio laipsnio venlafaksino cheminės struktūros atsparumą oksidacijai (García ir kt., 2020; von Gunten, 2003). Nepaisant didesnio karbamazepino koncentracijų skirtumo tarp nuotekų valyklų (Klaipėdoje – 1519,2 ng L^{-1}; Palangoje – 1266,5 ng L^{-1}; Nidoje – 427,4 ng L^{-1}), po penkių minučiu ozonavimo karbamazepinas nebebuvo aptiktas (26 lent.). Poveikis išliko po 10 ir 15 minučių ozonavimo, galimai dėl visiškos struktūrinės degradacijos. Pramoniniams ozonavimo reaktoriams paprastai reikia 20–30 minučių, kad mikroteršalai būtų efektyviai oksiduoti (Abromaitis ir kt., 2024). Tačiau šio tyrimo rezultatai parodė, kad trumpesnis ozonavimo laikas buvo pakankamas visiškai pašalinti karbamazepiną ir ženkliai sumažinti venlafaksiną. Trumpesnis ozonavimo laikas ypač esant žemoms arba vidutinėms pradinėms mikroteršalų koncentracijoms galėtų sumažinti su ozono gamyba susijusias eksploatavimo išlaidas ir energijos suvartojimo kaštus.

REKOMENDACIJOS

Šis tyrimas atskleidė sezoninio turizmo ir laikinų žmonių susibūrimų įtaką taršai bei jos išvalymui pajūrio nuotekų valyklose, įprastinio nuotekų valymo metodo trūkumus šalinant mikroteršalus. Išlieka poreikis toliau tirti ilgalaikį su valytomis nuotekomis išleidžiamų mikroteršalų poveikį ir galimybę diegti papildomus pažangiojo valymo etapus, siekiant sušvelninti žmogaus poveikį priekrantės ekosistemoms.

1. Hormonai bei farmacinės medžiagos viršijo prognozuojamų poveikio nesukeliančių koncentracijų vertes, todėl apskaičiuoti dideli rizikos koeficientai (>1) patvirtino galimą ekologinę grėsmę Baltijos jūros ekosistemoms. Todėl rekomenduojama tikslingai stebėti estrono, beta-estradiolio, karbamazepino ir venlafaksino koncentraciją šalia nuotekų išleistuvų tiek Baltijos jūroje, tiek Kuršių mariose. Tai padėtų įvertinti ilgalaikes tendencijas ir prisidėtų prie aplinkos apsaugos.

2. Ozonavimas efektyviai suskaidė patvariasias farmacines medžiagas karbamazepiną ir venlafaksiną biologiškai išvalytose nuotekose iš skirtingų pajūrio nuotekų valyklų. Nepaisant to, būtini tolimesni tyrimai ozonavimo trukmei ir ozono dozei optimizuoti, atsižvelgiant į pradinę mikroteršalų koncentraciją bei įtraukiant platesnį prioritetinių mikroteršalų spektrą.

IŠVADOS

1. Turizmo sezoniškumas turėjo didelę įtaką nuotekų taršos dinamikai nuotekų valyklose tiek Mažajame, tiek Didžiajame pajūrio kurorte. Turizmo piko metu tiek specifinių mikroteršalų – ftalatų, estrogeninių junginių (tik Mažojo kurorto nuotekų valykloje), tiek maistingųjų bei suspenduotų medžiagų kiekis ženkliai išaugo. Nors bendroji tarša daugeliu atvejų buvo pakankamai gerai išvaloma, Mažojo kurorto nuotekų valykla buvo jautresnė sezoniniams gyventojų skaičiaus svyravimams, dėl to į Baltijos jūrą buvo išleidžiami didesni organinių medžiagų bei mikroteršalų kiekiai.
2. Laikinas gyventojų susibūrimas Jūros šventės metu paveikė į Klaipėdos nuotekų valyklą patenkančių nuotekų kokybę. Įtekančiose nuotekose padidėjo visų tirtų mikroteršalų (hormonų, ftalatų, policiklinių aromatinių angliavandenilių) kiekiai, išskyrus farmacines medžiagas. Miesto valykla viso tyrimo laikotarpiu stabiliai mažino taršos lygį, užtikrindama aukštą bendrąjį išvalymo efektyvumą. Tačiau farmacinių medžiagų šalinimo efektyvumas buvo žemas, todėl padidėjo šių junginių išleidimas į priekrantę, galimai didinantis jų kaupimąsi Baltijos jūroje.
3. Mikroteršalų, įskaitant farmacines medžiagas ir hormonus, koncentracijos išleidžiamose nuotekose iš visų tirtų pajūrio valyklų visu tyrimo laikotarpiu, apimančiu tiek turizmo sezoniškomo, tiek Jūros šventės įtakos vertinimą, viršijo specifines prognozuojamas poveikio nesukeliančios koncentracijos vertes. Buvo nustatytos galimą neigiamą poveikį Baltijos jūros ekosistemai rodančios aukštos (> 1) hormonų (estrono ir beta-estradiolio) bei farmacinių medžiagų (karbamazepino ir venlafaksino) ekologinės rizikos koeficientų vertės nuotekose, išleidžiamose iš Klaipėdos nuotekų valyklos.
4. Nepaisant skirtingo antropogeninio poveikio, ozonavimas greitai ir efektyviai sumažino patvariųjų farmacinių medžiagų koncentraciją biologiškai išvalytose nuotekose. Karbamazepino ir venlafaksino koncentracija ženkliai sumažėjo po penkių minučių. Po penkiolikos minučių reikšmingai sumažėjo cheminio deguonies sunaudojimo ir suspenduotos medžiagos koncentracijos, todėl ženkliai pagerėjo bendroji nuotekų kokybė.

CURRICULUM VITAE

Agne Jucyte-Cicine was born on October 17, 1986, in Gargzdai, Lithuania. She began her academic journey in 2005 at Kaunas University of Technology, where she pursued a bachelor's degree in Applied Chemistry, graduating in 2009. She continued her studies and obtained a master's degree in Applied Organic Chemistry in 2011. For her master's thesis, Agne explored the applicability of natural essential oils in leather conservation. During her master's studies, she completed two internships, one in Hungary and another in Switzerland, gaining hands-on experience in cosmetic product development and analytical quantification techniques in water and soil laboratories. Her academic path provided a strong foundation in organic chemistry and analytical methodologies, equipping her with expertise in laboratory analysis and quality testing within pharmaceutical manufacturing environments. In April 2021, Agne began her PhD studies at Klaipėda University, focusing on the quantification of micropollutants in wastewater, particularly in areas affected by seasonal and temporary tourism surges. Her research involved analyzing four types of endocrine-disrupting micropollutants: phthalates, estrogens, pharmaceuticals, and polycyclic aromatic hydrocarbons in wastewater from three different-sized coastal resorts along the Baltic Sea coast in Lithuania. Throughout her PhD, Agne worked as a laboratory engineer, a lecturer at the Maritime Academy and a teacher at a local school. Additionally, she participated in several projects, including European Union-funded initiatives and her idea-based project, which she submitted for Inostart funding. Her research interests focus on the composition and dynamics of micropollutants in wastewater, particularly in different anthropogenic activities representing coastal Baltic Sea WWTPs during the increased pressure due to seasonal and/or temporary tourism.

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Annexes

*Table S1***.** The concentration (average ± standard error) of plasticizers in the wastewater and effluents at the two wastewater treatment plants (WWTPs) of seaside resorts during March 2022 – February 2023. Reprinted from paper I.

Date	Palanga resort WWTP															
	Concentration in wastewater (μg L^{-1})								Concentration in effluent (μg L^{-1})							
	DMP	DEP	DiBP	DBP	BBzP	DEHA	DEHP	DOP	DMP	DEP	DiBP	DBP	BBzP	DEHA	DEHP	DOP
03/2022	ND	2.6±0.0	0.8±0.0	0.4±0.0	0.1±0.0	0.1±0.0	3.4±0.3	1.4±0.0	ND	ND	ND	ND	ND	ND	ND	ND
04/2022	ND	3.5±0.1	0.2±0.1	0.8±0.2	0.2±0.0	ND	8.0±0.2	0.1±0.0	ND	ND	ND	ND	ND	ND	ND	ND
05/2022	5.1±2.3	166.7±72.2	2.3±1.1	11.7±4.7	0.7±0.1	0.6±0.2	16.6±0.8	0.2±0.0	ND	ND	ND	ND	ND	ND	0.1±0.0	ND
06/2022	0.2±0.1	9.6±3.4	ND	0.4±0.2	ND	ND	13.3±1.1	0.2±0.0	ND	ND	ND	ND	ND	ND	0.1±0.0	ND
07/2022	0.3±0.0	9.0±0.3	1.2±0.0	1.0±0.1	0.2±0.2	ND	13.7±0.9	0.3±0.0	ND	ND	ND	ND	ND	ND	0.3±0.1	0.1±0.0
08/2022	ND	13.1±1.1	1.7±0.2	2.1±1.5	ND	ND	17.3±0.3	1.1±0.1	ND	ND	ND	ND	ND	ND	0.1±0.0	ND
09/2022	0.1±0.0	6.6±0.7	1.1±0.1	3.6±1.6	ND	ND	15.9±2.2	0.2±0.0	ND	ND	ND	0.1±0.0	ND	ND	ND	ND
10/2022	ND	9.0±0.5	1.1±0.1	1.3±0.4	ND	ND	15.3±0.5	0.1±0.0	ND	ND	0.2±0.2	0.2±0.0	ND	ND	0.2±0.0	ND
11/2022	0.2±0.0	43.0±0.5	0.6±0.0	1.7±0.1	0.1±0.0	ND	19.4±1.4	0.2±0.0	ND	ND	ND	0.1±0.0	ND	ND	ND	ND
12/2022	0.2±0.0	8.8±1.2	0.7±0.1	0.6±0.1	ND	ND	4.3±0.3	ND	ND	ND	ND	0.2±0.0	ND	ND	0.1±0.0	ND
01/2023	ND	3.3±0.1	0.7±0.0	1.1±0.2	ND	ND	10.1±0.1	1.6±0.1	ND	ND	ND	ND	ND	ND	0.1±0.0	ND
02/2023	ND	3.1±0.2	0.7±0.6	0.6±0.0	0.2±0.0	ND	2.3±0.4	ND	ND	ND	ND	ND	ND	ND	ND	ND

Note**:** ND - below the detection limit of the method.

Date	Nida resort WWTP															
	Concentration in wastewater (µg L^{-1})								Concentration in effluent (µg L^{-1})							
	DMP	DEP	DiBP	DBP	BBzP	DEHA	DEHP	DOP	DMP	DEP	DiBP	DBP	BBzP	DEHA	DEHP	DOP
03/2022	ND	3.7±0.1	1.0±0.1	1.2±0.1	0.1±0.0	0.3±0.0	16.3±0.6	2.0±0.2	ND	ND	2.9±0.1	1.0±0.1	ND	ND	0.6±0.1	0.1±0.0
04/2022	0.1±0.0	3.7±0.1	2.0±1.8	2.2±0.8	0.2±0.2	ND	28.5±15.5	2.1±0.1	ND	ND	0.3±0.1	0.4±0.1	ND	ND	0.8±0.9	ND
05/2022	0.2±0.0	10.2±0.1	0.1±0.0	2.6±0.5	0.2±0.0	ND	17.3±0.8	0.2±0.0	ND	ND	0.6±0.7	1.6±1.0	ND	ND	0.6±0.4	ND
06/2022	ND	1.7±0.1	0.6±0.0	0.5±0.0	ND	ND	10.8±1.3	0.5±0.0	ND	ND	0.6±0.1	5.5±0.7	ND	ND	0.3±0.1	ND
07/2022	ND	7.0±0.9	1.2±0.2	1.0±0.2	ND	ND	4.1±0.2	ND	ND	ND	0.3±0.1	0.2±0.1	ND	ND	0.3±0.1	0.2±0.1
08/2022	0.4±0.1	7.0±0.2	1.8±0.0	4.0±2.8	ND	ND	12.2±1.9	0.5±0.2	ND	ND	0.4±0.0	0.2±0.0	ND	ND	0.4±0.1	ND
09/2022	0.3±0.1	42.2±4.4	1.1±0.2	1.9±0.2	ND	ND	78.0±20.9	0.3±0.0	ND	ND	ND	ND	ND	ND	0.5±0.1	ND
10/2022	ND	5.9±0.1	1.3±0.0	2.3±1.3	ND	ND	40.1±3.1	2.4±0.3	ND	ND	ND	ND	ND	ND	0.3±0.0	ND
11/2022	0.1±0.0	3.6±0.1	0.6±0.0	0.9±0.5	ND	ND	6.1±5.3	ND	ND	ND	0.2±0.1	0.8±0.5	ND	ND	0.8±0.4	ND
12/2022	0.2±0.0	10.9±1.3	0.8±0.1	1.0±0.3	ND	ND	9.3±1.5	ND	ND	ND	0.4±0.0	0.3±0.0	ND	ND	0.7±0.1	ND
01/2023	ND	1.6±0.1	0.4±0.0	0.4±0.0	ND	ND	2.7±0.2	ND	ND	ND	0.3±0.0	0.2±0.0	ND	ND	0.2±0.0	ND
02/2023	ND	2.7±0.1	0.7±0.6	0.8±0.0	ND	ND	2.4±0.1	ND	ND	ND	1.1±0.9	0.1±0.0	ND	ND	0.4±0.0	ND

Table S2. Tourism indicators measured by incoming car counts and overnight stays in Nida and Palanga in March 2022 and February 2023, as proxies for tracking population increases relative to permanent residents, based on the data provided by the Nida and Palanga councils.

Month	Cars arrived in Nida	Overnights in Palanga
March	5692	49946
April	7271	53697
May	12013	67622
June	13912	133853
July	16178	236465
August	22898	326880
September	8725	94670
October	6573	38666
November	2867	65457
December	2805	50820
January	2624	50989
February	3736	59903

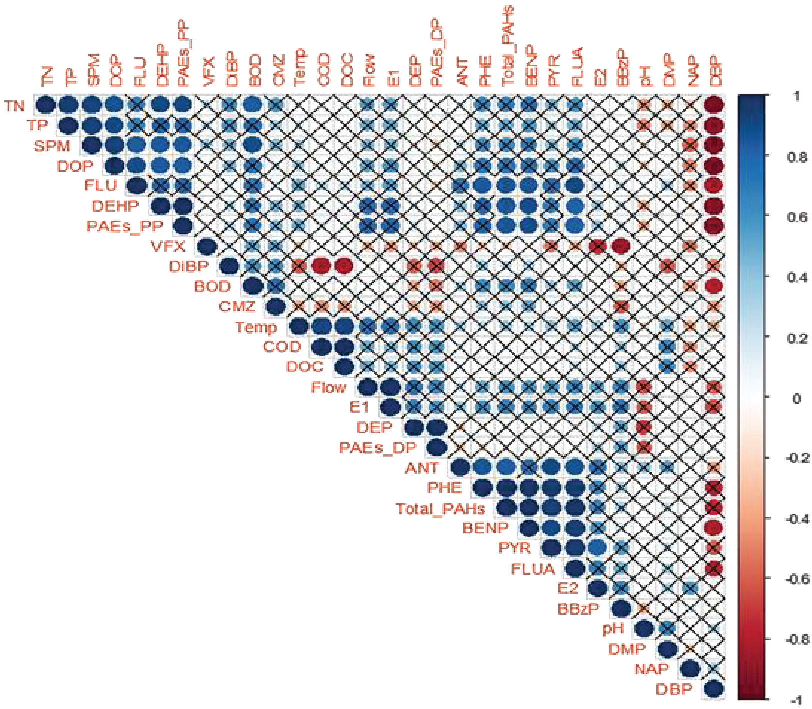

Figure S1. Correlogram for Spearman's linear correlation among all measured parameters: wastewater flow rate, chemical quality indicators, and micropollutants at the Klaipėda WWTP.

Note 1: Correlograms were built on Spearman correlation matrices. Values crossed out by (X) indicate an insignificant correlation (p>0.05).
Note 2: Correlation strength is in the range of –1 and 1. Blue cells show a positive linear correlation.

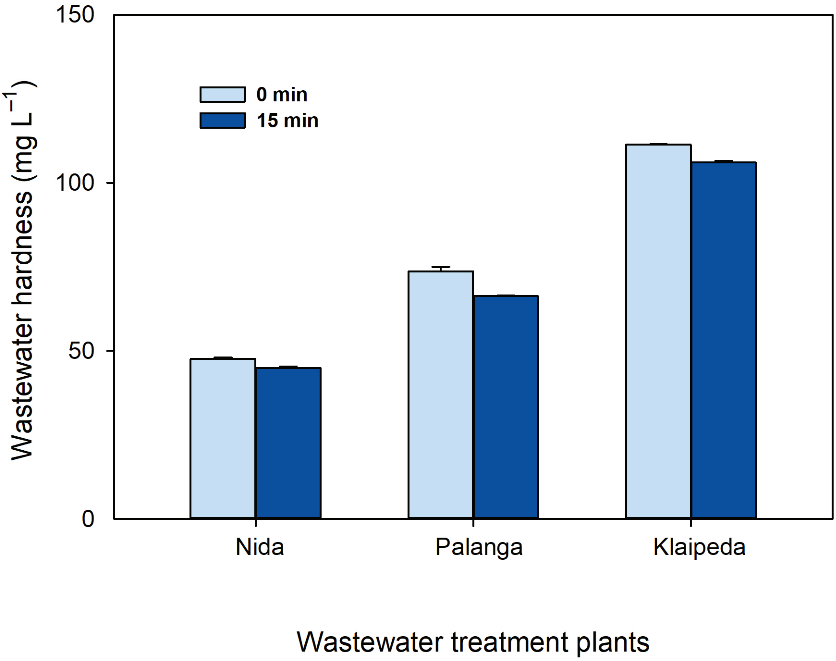

Figure S2. The mean (average ± standard error, n=2) concentration of wastewater hardness (Ca^{2+} + Mg^{2+} ions) mg L^{-1} in biologically treated wastewater from 24 – 26 July, before and after 15 min of ozonation treatment at 7 ± **0.7** mg L^{-1} ozone concentration at Nida, Palanga, and Klaipėda WWTPs.

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Klaipėdos universiteto leidykla, Herkaus Manto g. 84, 92294 Klaipėda
Tel. (0 46) 398 891, el. paštas: leidykla@ku.lt, interneto adresas: http://www.ku.lt/leidykla/
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