

Evaluation of the middle course of the Oder River contamination

Ocena zmian poziomu zanieczyszczenia Odry w środkowym jej biegu

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Studies of water quality changes in the Oder River in its middle course near the city of Wrocław, mainly concerning the content of organic substances, were conducted between the years 2017-2022. Over the period of five years, no significant worsening of the Oder River water quality has been observed with respect to the total organic carbon content, however, an increase in the concentrations of specific organic contaminants from the PFAS group was observed. An intense seasonal algae growth was found in spring and late summer, and the number of algae has increased with time. Diatoms are the most abundant algae type. Water from the Oder River contains large amounts of biogens (nitrates and phosphates), which promote microorganism growth in water.

Key words: Oder River, micropollutants, perfluoroalkyl acids, algae

Badania zmian jakości wody Odry prowadzone były w środkowym jej biegu koło Wrocławia w latach 2017-2022. W okresie badań nie stwierdzono istotnych zmian zawartości substancji organicznych zarówno w zakresie ogólnego węgla organicznego, jak też analizowanych mikrozanieczyszczeń. W Odrze stwierdzono zakwit glonów w okresie wiosennym i późnego lata, a liczebność mikroorganizmów rosta w kolejnych latach, wśród których dominowały Okrzemki. Stwierdzona duża zawartość substancji biogennych w wodzie mogła przyczynić się do rozwoju mikroorganizmów, w tym glonów.

Słowa kluczowe: Odra, mikrozanieczyszczenia, kwasy perfluorowane, glony

Introduction

Much more attention is currently being paid to the monitoring of water quality worldwide. This is due to the decrease in water resources, within the area with a water deficit that has been increasing annually, and the identification of an increased number of contaminants present in water [1,2]. The increase in the analysis range and the areas subjected to continuous monitoring contributes to a greater increase in costs connected with the monitoring, which is still smaller than those that could potentially arise from ecological catastrophes connected to river contamination [1]. The development of civilization has contributed to the pollution of water worldwide with anthropogenic substances, whose presence has a negative impact on the ecosystem as well as on the people using the water sources. Consequently, there is an increase in the number of substances subjected to both continuous and

preventive monitoring [3,4]. Due to human activity, pesticides [5,6], pharmaceuticals [7,8], and perfluorinated organic compounds are present in natural water sources, especially on the water surface [9-11]. The type and number of contaminants present in water depends on the level of region's industrialization, their land use of the watershed and types of water [12-15]. The main source of surface water pollution worldwide is wastewater introduced into these waters, which is often insufficiently treated. Therefore, the range and frequency of monitoring should be determined individually for every river.

In order to simplify the suitability of water for household or industrial use worldwide, water quality indexes (WQI), which describe the water quality, are used [16,17]. However, most often WQIs are based on basic water quality indicators and do not consider specific contamination, e.g., organic substances [18]. They also do not supply information concerning

the effects on the water ecosystem and potential hazards to humans.

Therefore, it is justified to monitor both basic water quality parameters, as well as specific contaminations stemming from the characteristics of a watershed river [WHO]. Currently, it is also important to evaluate the contaminant's pathway of migration between the components of the environment, and the possibility of individual contaminant's transport. An important component of water quality evaluation is the analysis of permanently migrating substances. The last few years have indicated an increase in PFAS concentrations in natural waters, which are toxic to humans and water organisms [19-20]. Due to the growing problem of PFC concentrations in the environment, their specific qualities, and the lack or limited effectiveness of their removal in wastewater or drinking water treatment for human consumption, many countries have started legal acts concerning PFCs in the environment. In the current

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Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption, the range of analysis for water taken for consumption has been expanded by the addition of mandatory parameters connected to, among others, compounds from the PFAS group [21].

Therefore, it was justified to conduct long-term studies of water quality trends in the Oder River, especially after the ecological catastrophe that took place in August 2022. A long-term evaluation of water quality allows us to determine the amount and types of contaminants present in this river and indicate potential sources of contamination. At the same time, it was justified to analyze substances specific to the Oder water, especially in the ranges of perfluorinated organic substances, due to a lack of information concerning their content in Polish rivers.

Methodology

Monitoring of water quality in the Oder River was performed in its middle course near the city of Wrocław (fig.1) within the locality of Ratowice, where a monitoring station of the Municipal Water and Sewerage Company of Wrocław is located. Oder water quality is monitored because it can infiltrate the



Figure 1.
Location of the monitoring point [22]
Rys. 1. Lokalizacja punktu monitoringu

resource water which is intake into Wrocław's supply system.

Studies in water quality changes, mainly concerning the content of organic substances, were conducted between 2017-2022, with samples being taken twice per month. Long-term monitoring in one area allows us to assess the tendency in water quality changes, especially specific micropollutants.

The range of analysis encompassed: temperature, pH, specific conductivity, color intensity, turbidity, the concentration of total organic carbon, ammonium ion, nitrates (V), phosphates, chlorides, and phosphate and UV absorbance at 254 nm (as a measure of refractive organic sub-

stance content). All analysis was performed in accordance with the Polish Norms. The total count of psychrophilic and mesophilic organism was analyzed by culture methods in accordance with the current Polish standards (PN-EN ISO 6222). The samples for zoo hydrological analysis were taken three times during August 2022. Water has been taken into the glass box and transferred onto a mesh, After transferring 30 dm³ of water from the mesh collector they were taken for analysis. 1 cm³ was analysed under a microscope. The microorganisms observed in 10 areas, were calculated and taxa marked.

Furthermore in the fourth sample (in the years 2019 and 2020) a measurement of perfluoroalkic acid concentrations: perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodekanoic acid (PSDA), perfluoroundekanoic acid (PFUDA), perfluorododekanoic acid (PSGoA), Perfluorobutanesulfonic acid (PFBS), Perfluorohexanesulfonic acid (PFHxS), perfluorooctanesulfonic acid (PFOS) and an analysis of Polycyclic aromatic hydrocarbons (PAHs), chosen halogen and non-halogen volatile organic substances, benzene, toluene, methylbenzene and xylene were carried out. This analysis was added after the pub-

lis was performed with the use of an Ultimate 3000 Dionex fluid chromatographer, equipped with a DAD detector. The detection level used was 254 nm. A Shodex OHPak SB-803 HQ polymer column was used, with a particle size of 13 µm and dimensions of 8 x 300 mm with a Shodex, OHPak SB-G 6B pre-column, with a particle size of 10 µm and dimensions of 6 x 50 mm. Changes in the concentration of molecules with a specific size were found by observing changes in peak area in chromatographs.

An extended range of analysis concerning organic contamination was performed for chosen water samples.

In period of intense fish death in the Oder River in August of 2022, a qualitative analysis of phytoplankton was performed, along with a determination of algal species present (water sample hydrobiological analysis). The analysis was repeated three times in the period 5-15th August 2022. This analysis was added to the monitoring of the Oder River because the presence of algae was listed as the main reason for the Oder disaster.

Results

Ranges and average values of monitored water quality parameter in water samples from the Oder River are shown in table 1.

The water quality monitoring in this study confirmed the variability in water quality parameters, especially concerning biogenic substances (nitrates (V)) and chlorides. The concentration of chlorides was directly proportional to water conductivity (fig.2), which testifies that chlorides are the

Table1. Ranges and average values of analyzed parameters during continuous monitoring
Tabela 1. Zakresy i średnie wartości analizowanych parametrów ciągłego monitoringu

		min	max	Avg.
Temp.	°C	0.1	26	12.1
pH		7.4	8.8	7.9
Conductivity	µS/cm	520	2,260	1,234
Turbidity	NTU	0.3	78.0	15.5
Color	g/m ³	10	22	15
UV ₂₅₄	m ⁻¹	4.2	18.9	11.8
TOC	gC/m ³	3.62	8.92	6.01
NH ₄ ⁺	g/m ³	0.05	0.89	0.23
NO ₃ ⁻	g/m ³	3.6	20.1	10.6
PO ₄ ⁻³	g/m ³	0.00	1.91	0.25
Chlorides	g/m ³	78	525	250
Sulfates	g/m ³	50	130	90
TMC22°C (Total microbial count)	cfu/cm ³	1,100	69,000	10,749
TMC37°C	cfu/cm ³	390	21,000	4,286

lication proposal of water directive for drinking water [21] to assess the risk of pollution infiltration.

The determination of PFAs was performed with the use of isotope dissolution in fluid chromatography together with tandem mass spectrometry ID-LC-MS/MS with a triple quadrupole analyzer with a QTrap 3200 AB Sciex reaction chamber. Electrospray ionization (ESI) was used. The gas chromatography method connected to a mass detector was used to determine volatile organic compounds and benzene, toluene, methylbenzene and xylene presence.

The molecular size distribution was detected with a Size Exclusion Chromatograph (SEC). The chromatographic analy-

main salt with respect to the salinity of the Oder River. At the same time, an increasing trend of these ions was identified during the monitoring period, which results from the dumping of increasing amounts of salinized wastewater [23] a decrease in the amount of water flowing in the Oder River [24] and regularly occurring hydrological droughts [25, 26].

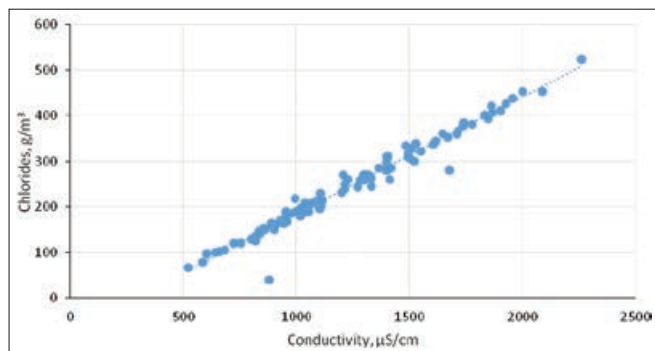


Fig. 2. Relationship between chloride concentration and water conductivity in 2017-2022
Rys. 2. Zależność pomiędzy stężeniem chlorków a przewodnością wody w okresie 2017-2022 r.

The chloride content increased during the period from 2017 to 2019, while in January 2020 a significant decrease was found in their concentration, following a repeated increase up to the end of 2022. During the Oder mortality event in August 2022, an increase in the water conductivity was found, however below a level attesting to organic organisms' toxicity [27].

During the monitoring period, the highest nitrate (V) concentration was found in winter, with the lowest being found in summer (fig. 3), which may be connected with their assimilation by microorganisms during periods of increased water temperature. Such a relationship was not found for phosphates, whose concentration during the entire study period was characterized by low variability in a few samples during the winter of 2020. Similar variability of nitrates (V) and phosphates are presented in 12 Oder monitoring points, presented in the assessment of state surface water in Poland implemented by the Main Inspectorate of Environmental Protection [28]. It shows that the monitoring of one point can be representative for the whole river, because the tendency of long period changes is similar from the source to the

mouth of the river, but the level of contamination can be different.

During the monitoring period, a low variability was found in total organic carbon content (fig. 4), and no significant increase in TOC content was found, which would suggest that there were no dumps of untreated or insufficiently treated wastewater. A significantly larger variability was

found for refractive substances absorbing UV 254 nm wavelength. No relationship was found between the values of these parameters, which indicates that unsatu-

Fig. 4. Variability in TOC content during the monitoring period
Rys. 4. Zmienność OWO w okresie monitoringu

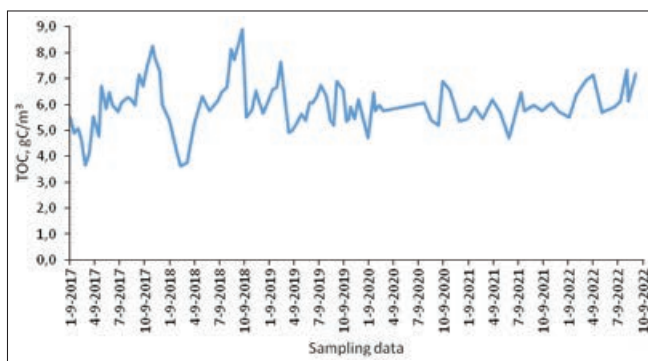


Fig. 5. Relationship between color intensity and UV absorbance
Rys. 5. Zależność pomiędzy intensywnością barwy i absorancją UV

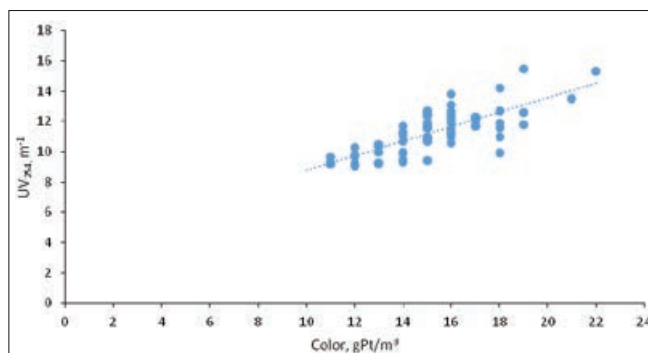
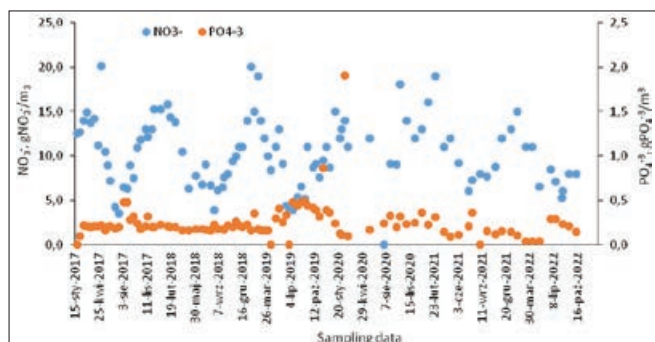


Fig. 3. Variability in biogenic substance content during the monitoring period
Rys. 3. Zmienność zawartości substancji biogenych w okresie monitoringu



rated organic compounds do not dominate the entire organic compound content. However, UV₂₅₄ absorbance was directly proportional to the color intensity (fig. 5), which affirms the domination of humic substances among refractive substances, because, as Linnik et al. have shown [29], humic substances are the deciding factor for surface watercolor.

Results of research of Odra river organic pollution [30] presented seasonal variability and increase concentration of BOD₅ with the distance from source of river.

The substance with molecular mass of 1.8-2.0 kDa (average concentration 21.4 µg/dm³), dominated among other organic substances present in the Oder River, with an insignificantly smaller concentration being found for molecules with 2.5-3.0 kDa mass (17.2 µg/dm³). Compounds with smaller molecular masses were in the minority with concentration similar to the analysis error. It means that organic compounds in the Oder River water were composed of medium and high molecular

weight. A sample chromatogram of molecular size distributions is found in fig. 6.

No halogenic or non-halogen volatile organic substances were found in any of the analyzed water samples. No presence of BETX was discovered. This means that the Oder River water is not contaminated by any specific and toxic organic substances, and despite hydrological flow changes and the dumping of significant amounts of wastewater, this problem does not arise.

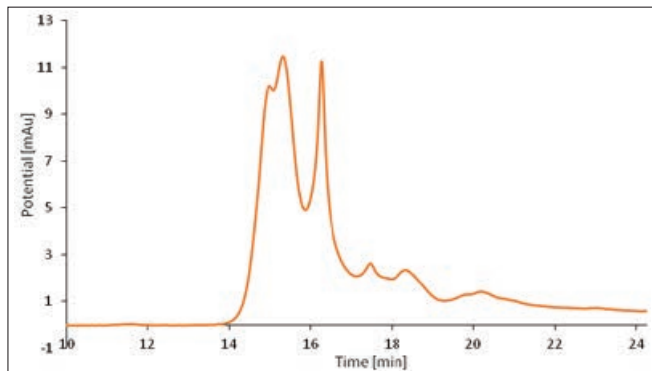


Fig. 6. Sample chromatogram of molecular size distributions in Oder River water
Rys. 6. Przykładowy chromatogram rozkładu wielkości cząstek molekularnych w Odrze

number being in the August-September timeframe. The number of algae from the time period of highest contamination of the Oder i.e. in August 2022 are shown in table 3. This shows that the dominating group was diatoms, especially *Stephanodiscus spp.* On the other hand, golden algae, whose excessive numbers have been indicated as the cause for the mass mortality of fish in the Oder made up (sum of analyzed species) up to 10% of all algae present in water, which, according to Nich-

However, perfluorinated organic substances were found to be present (tab. 2). It was found that the average concentration of analyzed perfluorinated acids increased in the year 2020 in comparison to the previous year. The concentration of these substances in the waters, including those intended for consumption, is monitored based on Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 [21] and therefore an increase in their concentration may signify insufficient elimination during wastewater treatment or an increase in their use, unlike PFBS and PFHxS whose concentration has decreased. These compounds are used to produce substances for impregnating textiles, furniture and wood.

Table 2. A comparison of average PFAS concentrations in the years 2019-2020.

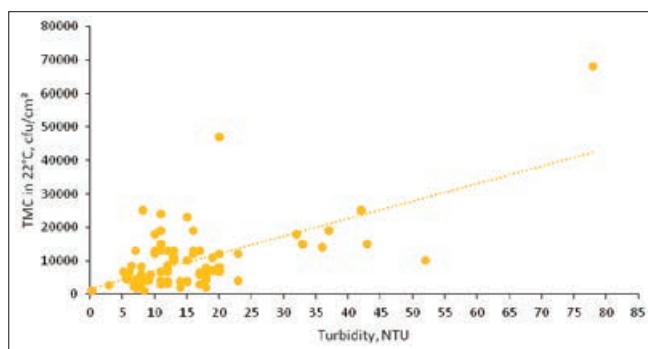
Tabela 2. Porównanie średniej zawartości wybranych kwasów perfluorowanych w latach 2019 i 2020

Compound [ng/dm ³]	2019	2020
PFBA	0.687	8.020
PFPA	0.423	0.834
PFHxA	0.268	0.364
PFHpA	0.214	0.712
PFOA	0.615	3.820
PFNA	0.143	1.136
PFDA	0.211	0.966
PFBS	1.900	0.266
PFHxS	0.320	0.196
PFOS	0.835	13.240

Analysis of the bottom sediments in the Oder River [31] shows the presence of organotin, which is toxic, and testifies of anthropogenic contamination and the possibility of organic compound accumulation in the bottom sediments.

The variability in the values of water quality parameters, mainly turbidity, was connected with the variation in the total numbers of microorganisms (TMC) and their metabolic activity. During the entire study period, the TMC count at 22°C was directly proportional to water turbidity (fig. 7). The number of mesophilic microorganisms was

Fig. 7. Relationship between water turbidity and the total number of microorganisms
Rys. 7 Zależność pomiędzy mętnością wody a ogólną liczbą mikroorganizmów



on average 3.2 times larger than the number of psychrophilic organisms. Only in three samples, the number of psychrophilic bacteria was larger than the number of mesophilic bacteria (fig. 8).

During periods of rapid temperature increase, an intense growth of algae and cyanobacteria was found, with the largest

number of psychrophilic organisms. Only in three samples, the number of psychrophilic bacteria was larger than the number of mesophilic bacteria (fig. 8). During periods of rapid temperature increase, an intense growth of algae and cyanobacteria was found, with the largest

Fig. 8. Variability of psychrophilic and mesophilic microorganisms content

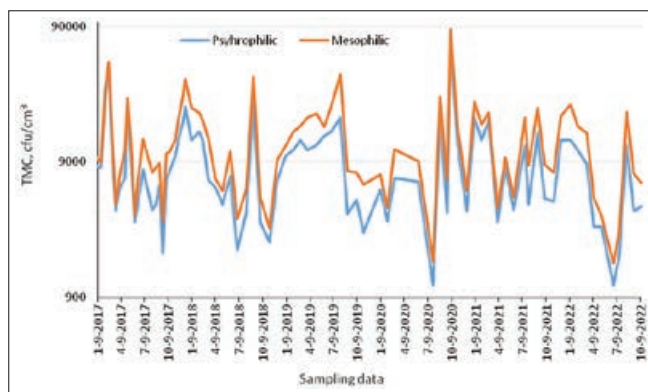


Table 3. Number of individual groups of phytoplankton in Oder River water in August 2022.
Tabela 3. Liczebność poszczególnych grup fitoplanktonu w Odrze w sierpniu 2022

Type of Microorganism	Number in 1 dm ³	Total number of microorganisms, %
<i>Melosira granulata</i>	920	8.6
<i>Stephanodiscus</i>	4 496	41.8
<i>Chrysophyceae</i>	1 104	10.2
<i>Pediastrum duplex</i>	1 288	12.0
<i>Eururela elegance</i>	368	3.4
<i>Microcystis aeruginosa</i>	920	8.6
<i>Scenedesmus quadricauda</i>	368	3.4
<i>Scenedesmus armatus</i>	184	1.7
<i>Mastigophora</i>	368	3.4
<i>Nitzschia holsatica</i>	184	1.7
<i>Synedra ulna</i>	184	1.7
<i>Korattella cochlearia</i>	184	1.7
<i>Synchaeta kitinia</i>	184	1.7

compared to different times, and in different areas of river.

Conclusions:

The results of the monitoring have allowed for the formulation of the following conclusions:

- Over the period of five years no significant worsening of the Oder River water quality has been observed with respect to the total organic carbon content, however, an increase in the concentrations of specific organic contaminants from the PFAS groups was observed.
- The color intensity and UV₂₅₄ absorbance was determined by the presence of humic substances in water. Among organic substances, large molecular compounds dominated, which are susceptible to removal during the coagulation process.
- An intense seasonal algae growth was found in spring and late summer, and the number of algae has increased with time. Diatoms are the dominant algae type in the Oder River around Wrocław city.
- Water from the Oder River contains large amounts of biogens (nitrates and phosphates), which promote growth of microorganisms in water.
- A constant increase in water salination has been found, which confirms the dumping of salinated wastewater into the river.

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