

Impact of point source pollutants on the distribution of selected water parameters in the Vistula River in Puławy, Poland

Mateusz Jakubiak¹⁾  , Bartosz Bojarski²⁾ 

¹⁾ AGH University of Science and Technology, Faculty of Mining Surveying and Environmental Engineering, Department of Environmental Management and Protection, al. Mickiewicza 30, 30-059 Krakow, Poland

²⁾ Polish Academy of Sciences, Institute of Ichthyobiology and Aquaculture in Gołysz, Poland

RECEIVED 19.01.2021

REVIEWED 19.04.2021

ACCEPTED 28.05.2021

Abstract: Human activities have a complex and multidimensional impact on water quality. The concentration of inhabitants, production and services intensifies influence of urban agglomerations on water in rivers. Among many sources of surface water pollution, the most important are sewage discharges.

The aim of the research was to determine the effect of point discharge of treated industrial and municipal wastewater on the distribution of selected water chemical parameters in the Vistula River in Puławy. The studies were carried out in 2018–2019. Samplings were collected in five sampling points and tested in the hydrochemical laboratory. The obtained data were statistically analysed to investigate differences between the sampling points. The negative impact of wastewater discharge on the water quality in the Vistula was found. However, the pollution level decreased with the flow of the river. The parameters tested at measurement point located 1200 m below the discharge approached the values recorded above the sewage outfall. The presented observations of changes in the concentration of pollutants indicate the self-purification capacity of a river. However, for each watercourse flowing through urbanized areas, it is an individual feature. It depends on a number of factors and requires regular monitoring studies taking into account hydrochemical analysis of watercourses.

Keywords: point source pollutants, “Rozlewisko” reservoir, urban pollutants, wastewater discharge, water quality, water monitoring, watercourses

INTRODUCTION

Surface waters, rivers in particular, have always been a determinant of settlements location and development. Nevertheless, urbanized areas are characterized by a deficit of water surface in relation to the adjacent areas [STEELE, HEFFERNAN 2014]. Additionally, with the rapid urban expansion and population growth, these areas are being gradually biologically depleted. Therefore, one of the important tasks in the field of nature protection in cities is to preserve surface waters and care for their quality. This protection is important for maintenance of biodiversity and also aesthetic and landscape values [JAKUBIAK, CHMIEŁOWSKI 2020]. Surface waters additionally fulfill the function of ecological corridors in areas subjected to human pressure

[JAKUBIAK, PANEK 2016; 2017]. The Vistula River is one of the most unique and largest ecological corridors in Europe. Due to its natural values, the entire valley of the Vistula has been recognized as a corridor of Pan-European ecological network. The Vistula Valley ecological corridor was divided into sections for the purposes of classification and characterization. The “Central Mazovian section of the Middle Vistula Valley” begins in Puławy, at 372 kilometer of the Vistula. It is a valuable corridor due to the preserved fragments of willow, poplar riparian forests and large riverside areas covered with willow thickets [GACKA-GRZESIKIEWICZ (eds.) 1995; GDOŚ 2002].

Human activity also has a complex and multidimensional impact on water quality. The intensification of that impact is related to urban agglomerations because of the concentration of

inhabitants, production and service activities. Among many sources of surface water pollution, the most important are discharges of contaminated municipal and industrial sewage as well as polluted surface runoff from built-up areas [GOPCHAK *et al.* 2020; MAZUR *et al.* 2016; MAZUR, SITAREK 2020; ZEMELKA 2019]. Environmental protection, including care of water quality, has become an area of priority investment in Poland for the last two decades. Therefore, a dynamic development of sewage networks together with the construction of new sewage treatment plants or modernization and expansion of existing ones are visible in municipal investments. The development of sewage networks is accompanied by an increase of the municipal sewage treatment plants capacity and the use of modern nutrient removal technology. In 2019 in Poland, there were 3,277 municipal wastewater treatment plants operating as elements of sewage networks. The population served by these plants was nearly 29 mln people [GUS 2020]. In some areas, especially urban agglomerations, over 90% of the households is connected to the sewage system. An example is Puławy city, where 95.7% of the population uses the municipal sewage system [SIUDAK, LEWANDOWSKA 2016]. Treatment of industrial and domestic sewage is an essential component of water care, especially in case of rivers in urban agglomerations, where sewage is discharged to the watercourses.

The aim of the research was to determine the effect of point discharge of treated industrial and municipal wastewater on the distribution of selected water chemical parameters in the Vistula River (the section located in Puławy).

MATERIALS AND METHODS

STUDY AREA AND SITE DESCRIPTION

The research area was the Vistula River near the discharge of treated sewage and industrial waters at the border of Puławy and Wólka Gołębska (Fig. 1). The outfall is located at 378.2 kilometer of the Vistula (51°28'10" N, 21°54'59" E). It is 5.7 km below the Puławy Water Gauge (water gauge code: 17870095). According to the classification of WFD Water Body, the research area is located in the WFD Water Body "Vistula from Kamienna to Wieprz" (code PLRW2000212399, type 21 – great lowland river). The Nature 2000 – Special Protection Area "Valley of Middle Vistula" (PLB140004) is located next to the discharge [GDOŚ 2002]. Sewage is discharged to the Vistula through the canal of Zakłady Azotowe Puławy S.A.. Part of this canal is formed as a flow-through water reservoir, called "Rozlewisko". It is used to mix, cool down and clean the effluents before being discharged. It is a semi-natural reservoir, created in the oxbow lake of the Vistula and separated from the river by a flood embankment. The reservoir is a part of the local hydrological system. It is also fed by groundwater and surface runoff from the immediate catchment area. The reservoir is shallow (about 1 m deep) with an area of about 20 hectares and the capacity of about 280 thous. m³. "Rozlewisko" is characterized by a fast flow and high throughput, although there are also stagnant zones [LIGĘZA, SMAL 2003].

The discharge canal of Zakłady Azotowe Puławy S.A. carries industrial waters: treated wastewater, cooling water and effluents from ash pans from Zakłady Azotowe in Puławy together with treated household and industrial wastewater from the MPWiK

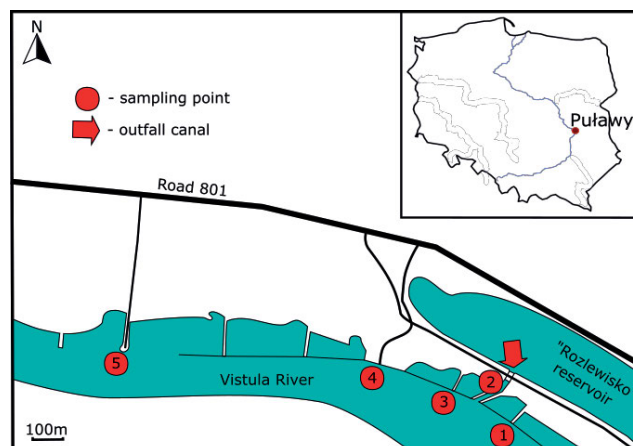


Fig. 1. Research area: location of outfall form "Rozlewisko" reservoir to the Vistula River and five sampling points. Location of Puławy city, Poland; source: own elaboration

Sewage Treatment Plant in Puławy (Pol. Miejskie Przedsiębiorstwo Wodociągów i Kanalizacji „Wodociągi Puławskie”. Production processes at Zakłady Azotowe Puławy S.A. consume approximately 90,000 thous. m³ of water yearly. Process water is abstracted from surface water (the Vistula and Kurówka Rivers) and groundwater intake [Grupa Azoty 2019]. Post-process water and sewage, depending on the source of origin, are treated by Zakłady Azotowe Puławy S.A. mechanically and chemically in the Central Industrial Sewage Treatment Plant (Centralna Oczyszczalnia Ścieków Przemysłowych) or biologically in the Biological Industrial Sewage Treatment Plant (Biologiczna Oczyszczalnia Ścieków Przemysłowych) and the Fecal Sanitary Sewage Treatment Plant (Fekalna Oczyszczalnia Ścieków Sanitarnych). Sewage from the city of Puławy and the municipalities of Końskowola and Żyrzyn are treated mechanically and biologically in the MPWiK Sewage Treatment Plant in Puławy. The installation was modernized in 2015. The biological part includes nitrification, denitrification and dephosphatation, which can be supported by chemical phosphorus precipitation. Approximately 2,400 thous. m³ of sewage is processed yearly in the treatment plant in Puławy. The daily capacity of the plant is 12,650 m³ according to the water permit [MPWiK 2017]. Purified wastewater is discharged through a short outfall canal from "Rozlewisko" to the Vistula.

SAMPLE COLLECTION AND ANALYSIS

The hydrochemical studies were carried out in 2018–2019. Samplings were collected every two months, from June 2018 to April 2019. There were five sampling points: four along the Vistula and one point located at the outfall canal. The first point (No. 1) was located 150 m up the Vistula above the estuary of the outfall canal. Point No. 2 was located in the outfall canal. The next three sampling points were located at the following distances below the estuary of the outfall canal: No. 3 – 100 m, No. 4 – 350 m, No. 5 – 1200 m. Water for analyses was taken from a depth of 30–50 cm below the water table with use of a sampling dipper. Each time, three samples were taken from each sampling point. Water samples in closed bottles were transported to the laboratory for immediate analysis. The P (phenolphthalein) and total alkalinity (methyl orange), pH, total hardness, nitrate

concentration (NO_3^-), phosphate concentration (PO_4^{3-}) and organic carbon concentration (C org.) were measured in the water samples. The P alkalinity and total alkalinity were determined by titration of the tested water sample with $0.1 \text{ mol}\cdot\text{dm}^{-3}$ HCl solution. According to standard procedure the P alkalinity value corresponds to the colour change of phenolphthalein (pH 8.3) and the total alkalinity value corresponds to the colour change of methyl orange (pH 4.3) according to PN-EN ISO 9963-1:2001. The pH value was measured with a 691 pH meter. Total hardness was determined by titration with ethylenediaminetetraacetic acid (EDTA) according to PN-ISO 6059:1999. The concentration of nitrates was determined spectrophotometrically ($\lambda = 415 \text{ nm}$) using the phenol-disulfonic acid (PDSA) procedure. Phosphate concentration was determined by the ammonium molybdate spectrophotometric method ($\lambda = 720 \text{ nm}$). Organic carbon concentration was measured with an IL 550 TOC-TN analyser.

The obtained data did not show normal distribution and therefore the nonparametric Kruskal–Wallis test followed by Dunn–Bonferroni multiple comparison (post hoc) test was performed to analyse statistical differences between the sampling points. The p -values lower than 0.05 were considered statistically significant. The PQStat software were used for data analysis. The results were presented as mean \pm SD.

RESULTS AND DISCUSSION

The pH value in the analysed samples ranged from 7.39 to 8.43 (Tab. 1). In all months of the research the highest value was recorded at the sampling point No. 1 located above the outfall canal, and the lowest – at the sampling point No. 2 at the outfall canal. A gradual increase of the pH value was observed at the next measurement points. The values measured at sampling points 2 and 3 were statistically significantly lower than the values recorded at point 1 (Tab. 2). At point No. 5, the pH value was close or equal to the value at point No. 1 (Tab. 1).

The P alkalinity value in the tested water samples ranged from 0.00 to $12.33 \text{ mg CaCO}_3\cdot\text{dm}^{-3}$ (Tab. 1). Most often it had the highest value at point No. 1, and the lowest at point No. 2. Then it gradually increased. The alkalinity value at point No. 5 was similar or equal (in August and December) to the values measured at point No. 1. The total alkalinity value ranged from 0.00 to $17.50 \text{ mg CaCO}_3\cdot\text{dm}^{-3}$. This parameter showed a similar trend as P alkalinity. The exception was the study carried out in December 2018, when the P alkalinity value was equal to $0.00 \text{ mg CaCO}_3\cdot\text{dm}^{-3}$ at all measurement points (Tab. 1). The values determined at sampling points 2 and 3 were statistically significantly decreased in comparison to the values recorded at point No. 1 (both in the case of P alkalinity and total alkalinity) (Tab. 2).

Total hardness in the analysed water samples ranged from 258.00 to $313.00 \text{ mg CaCO}_3\cdot\text{dm}^{-3}$ (Tab. 1). A uniform trend of changes was not observed. The values fluctuated in individual months. No statistically significant differences in comparison to the sampling point No. 1 were observed during the study (Tab. 2).

The nitrate concentration ranged from 0.75 to $30.62 \text{ mg NO}_3^-\cdot\text{dm}^{-3}$ (Tab. 1). In all research months, the lowest concentration was recorded at the sampling point No. 1 located above the outfall canal, and the highest – at the point No. 2 (in the

outfall canal) – Table 1. The values recorded at the points 2 and 3 were statistically significantly increased in comparison to the concentration measured at the point No. 1 (Tab. 2). A gradual decrease in concentration was observed from point No. 3 up to No. 5. The concentration at point No. 5 was always slightly higher than the values measured at point No. 1 (Tab. 1).

Phosphate concentration ranged from 0.47 to $1.76 \text{ mg PO}_4^{3-}\cdot\text{dm}^{-3}$ (Tab. 1). This parameter showed a similar trend as the nitrate concentration. However, the phosphate concentration in October at sampling point No. 5 was higher than at points nos. 1, 3 and 4 (Tab. 1). Moreover, the statistical analysis showed that the value occurred at the sampling point No. 5 was still higher than the concentration noted above the outfall canal (Tab. 2).

The concentration of organic carbon in the analysed samples ranged from 51.33 to $75.33 \text{ mg C org.}\cdot\text{dm}^{-3}$ (Tab. 1). In all research months, the lowest concentration was found at the sampling point No. 1 above the outfall canal, and the highest – in the outfall canal, at the point No. 2 (Tab. 1). Statistically significantly higher values in comparison to the point No. 1 were noted at the points 2 and 3 (Tab. 2). A gradual decrease in concentration was observed from point No. 3 up to No. 5. At point No. 5 it was close (most months) or equal (June) to the value at point No. 1 (Tab. 1).

The intensification of a wide spectrum of anthropogenic impacts in highly urbanized areas may have a negative effect on the quality of the waters flowing through cities. MICHAŁKIEWICZ *et al.* [2011] showed that the water quality of the Warta River deteriorates along the section where it flows through Poznań city. Both, the electrical conductivity and the concentration of total phosphorus, were higher in the Warta water samples collected at the point located below the city than in the samples from the point above Poznań [MICHAŁKIEWICZ *et al.* 2011]. The results of the presented research show that, despite the flow of water through the additional treatment stage (“Rozlewisko” reservoir), the concentrations of nutrients in the discharge canal were still increased (nitrate nitrogen: $3.97\text{--}6.92 \text{ mg N-NO}_3^-\cdot\text{dm}^{-3}$ and phosphate phosphorus: $0.27\text{--}0.57 \text{ mg P-PO}_4^{3-}\cdot\text{dm}^{-3}$). Moreover, based on the studies of water parameters, it can be said that the hydrochemical parameters of water in the Vistula were above class II according to the classification of WFD Water Body type 21 – great lowland river [Rozporządzenie ... 2019]. In terms of nitrate nitrogen, the results indicate class I of water in the Vistula at the sampling point above the outfall canal form –“Rozlewisko”. The values of nitrate nitrogen in the Vistula are below the range of values ($3\text{--}5 \text{ mg NO}_3^-\cdot\text{dm}^{-3}$) recorded in small watercourses within Vistula river basin in Central Poland [BRYŚIEWICZ *et al.* 2019]. The highest recorded value of total hardness was $297.5 \text{ mg CaCO}_3\cdot\text{dm}^{-3}$, corresponding to class I of surface water quality. The pH value corresponds to class II (7.5–8.4). However, in case of phosphate phosphorus and total organic carbon in all tested water samples from point No. 1 values exceeded several times the limit value ($0.101 \text{ mg P-PO}_4\cdot\text{dm}^{-3}$ and $13.6 \text{ mg C org.}\cdot\text{dm}^{-3}$) for surface water quality class II [Regulation ... 2019]. The values of water parameters in the Vistula also depend on the water quality in the tributaries. BRYŚIEWICZ *et al.* [2019] also showed similar concentration of phosphate phosphorus in studies on small watercourses within Vistula River basin.

The quality of water in rivers can be affected by point [POLICHT-LATAWIEC *et al.* 2013; POLICHT-LATAWIEC, KAPICA 2013] and nonpoint [PYTKA *et al.* 2013] sources of pollution. The most

Table 1. The tested water parameters at five sampling points in all measurement dates (mean \pm SD)

| Parameter | Date | Sampling point 1 (150 m above outfall canal) | Sampling point 2 (outfall canal) | Sampling point 3 (100 m below outfall canal) | Sampling point 4 (350 m below outfall canal) | Sampling point 5 (1200 m below outfall canal) |
|---|---------|--|-------------------------------------|--|--|---|
| pH | 06.2018 | 8.43 \pm 0.01 | 7.59 \pm 0.01 | 8.24 \pm 0.02 | 8.34 \pm 0.00 | 8.36 \pm 0.00 |
| | 08.2018 | 8.41 \pm 0.01 | 7.61 \pm 0.01 | 7.97 \pm 0.01 | 8.18 \pm 0.01 | 8.26 \pm 0.01 |
| | 10.2018 | 8.33 \pm 0.01 | 7.97 \pm 0.01 | 8.22 \pm 0.03 | 8.31 \pm 0.02 | 8.33 \pm 0.01 |
| | 12.2018 | 8.09 \pm 0.01 | 7.40 \pm 0.02 | 7.56 \pm 0.02 | 7.99 \pm 0.01 | 8.02 \pm 0.01 |
| | 02.2019 | 8.29 \pm 0.01 | 7.39 \pm 0.01 | 7.55 \pm 0.01 | 7.99 \pm 0.01 | 8.16 \pm 0.01 |
| | 04.2019 | 8.39 \pm 0.01 | 7.86 \pm 0.01 | 8.17 \pm 0.02 | 8.25 \pm 0.02 | 8.32 \pm 0.01 |
| P alkalinity (mg CaCO ₃ ·dm ⁻³) | 06.2018 | 9.17 \pm 1.44 | 0.00 \pm 0.00 | 4.00 \pm 1.73 | 5.00 \pm 0.00 | 7.50 \pm 0.00 |
| | 08.2018 | 7.50 \pm 0.00 | 0.00 \pm 0.00 | 0.00 \pm 0.00 | 5.00 \pm 0.00 | 7.50 \pm 0.00 |
| | 10.2018 | 12.33 \pm 0.58 | 8.00 \pm 0.00 | 10.00 \pm 0.00 | 12.00 \pm 0.00 | 12.00 \pm 0.00 |
| | 12.2018 | 5.00 \pm 0.00 | 0.00 \pm 0.00 | 0.00 \pm 0.00 | 0.00 \pm 0.00 | 5.00 \pm 0.00 |
| | 02.2019 | 7.50 \pm 0.00 | 0.00 \pm 0.00 | 0.00 \pm 0.00 | 7.50 \pm 0.00 | 10.00 \pm 0.00 |
| | 04.2019 | 12.33 \pm 0.58 | 7.00 \pm 0.00 | 10.00 \pm 0.00 | 12.00 \pm 0.00 | 12.00 \pm 0.00 |
| Total alkalinity (mg CaCO ₃ ·dm ⁻³) | 06.2018 | 16.67 \pm 1.44 | 2.50 \pm 0.00 | 9.17 \pm 1.44 | 12.50 \pm 0.00 | 17.50 \pm 0.00 |
| | 08.2018 | 12.50 \pm 0.00 | 0.00 \pm 0.00 | 2.50 \pm 0.00 | 10.00 \pm 0.00 | 12.50 \pm 0.00 |
| | 10.2018 | 14.33 \pm 0.58 | 10.00 \pm 0.00 | 12.50 \pm 0.00 | 13.00 \pm 0.00 | 13.00 \pm 0.00 |
| | 12.2018 | 0.00 \pm 0.00 | 0.00 \pm 0.00 | 0.00 \pm 0.00 | 0.00 \pm 0.00 | 0.00 \pm 0.00 |
| | 02.2019 | 10.00 \pm 0.00 | 0.00 \pm 0.00 | 2.50 \pm 0.00 | 10.00 \pm 0.00 | 12.50 \pm 0.00 |
| | 04.2019 | 14.33 \pm 0.58 | 10.00 \pm 0.00 | 11.00 \pm 0.00 | 13.00 \pm 0.00 | 13.00 \pm 0.00 |
| Total hardness (mg CaCO ₃ ·dm ⁻³) | 06.2018 | 274.33 \pm 1.15 | 260.00 \pm 0.00 | 260.00 \pm 0.00 | 273.00 \pm 0.00 | 260.00 \pm 0.00 |
| | 08.2018 | 282.00 \pm 1.73 | 270.00 \pm 0.00 | 278.00 \pm 0.00 | 288.00 \pm 0.00 | 267.00 \pm 1.73 |
| | 10.2018 | 290.00 \pm 0.00 | 313.00 \pm 0.00 | 298.00 \pm 0.00 | 285.00 \pm 0.00 | 285.00 \pm 0.00 |
| | 12.2018 | 260.00 \pm 0.00 | 289.33 \pm 1.15 | 278.00 \pm 0.00 | 269.33 \pm 1.15 | 268.00 \pm 0.00 |
| | 02.2019 | 270.00 \pm 0.00 | 258.00 \pm 0.00 | 265.00 \pm 0.00 | 270.00 \pm 0.00 | 268.00 \pm 0.00 |
| | 04.2019 | 298.00 \pm 0.00 | 308.00 \pm 0.00 | 298.00 \pm 0.00 | 285.00 \pm 0.00 | 283.00 \pm 0.00 |
| NO ₃ ⁻ (mg·dm ⁻³) | 06.2018 | 0.75 \pm 0.04 | 17.56 \pm 0.78 | 3.21 \pm 0.20 | 1.83 \pm 0.03 | 1.43 \pm 0.05 |
| | 08.2018 | 4.09 \pm 0.04 | 24.26 \pm 0.55 | 12.35 \pm 0.38 | 6.04 \pm 0.11 | 4.23 \pm 0.13 |
| | 10.2018 | 4.37 \pm 0.04 | 27.65 \pm 0.17 | 10.44 \pm 0.06 | 9.81 \pm 0.03 | 9.79 \pm 0.02 |
| | 12.2018 | 4.62 \pm 0.21 | 26.86 \pm 0.48 | 14.75 \pm 0.44 | 5.64 \pm 0.06 | 5.55 \pm 0.12 |
| | 02.2019 | 4.03 \pm 0.08 | 30.62 \pm 0.89 | 13.25 \pm 0.43 | 7.23 \pm 0.07 | 5.05 \pm 0.08 |
| | 04.2019 | 4.03 \pm 0.12 | 26.86 \pm 0.70 | 16.16 \pm 0.26 | 9.45 \pm 0.29 | 5.94 \pm 0.09 |
| PO ₄ ³⁻ (mg·dm ⁻³) | 06.2018 | 0.48 \pm 0.02 | 0.83 \pm 0.04 | 0.62 \pm 0.03 | 0.55 \pm 0.01 | 0.54 \pm 0.00 |
| | 08.2018 | 0.47 \pm 0.01 | 1.01 \pm 0.04 | 0.81 \pm 0.01 | 0.60 \pm 0.01 | 0.53 \pm 0.02 |
| | 10.2018 | 0.49 \pm 0.04 | 0.88 \pm 0.00 | 0.57 \pm 0.04 | 0.49 \pm 0.01 | 0.76 \pm 0.03 |
| | 12.2018 | 0.50 \pm 0.08 | 1.76 \pm 0.15 | 1.15 \pm 0.03 | 0.96 \pm 0.15 | 0.55 \pm 0.06 |
| | 02.2019 | 0.52 \pm 0.03 | 1.74 \pm 0.09 | 1.28 \pm 0.05 | 0.93 \pm 0.03 | 0.64 \pm 0.05 |
| | 04.2019 | 0.50 \pm 0.02 | 1.16 \pm 0.10 | 0.99 \pm 0.04 | 0.80 \pm 0.02 | 0.59 \pm 0.01 |
| C org. (mg·dm ⁻³) | 06.2018 | 51.33 \pm 0.58 | 64.33 \pm 0.58 | 53.33 \pm 1.15 | 51.33 \pm 0.58 | 51.33 \pm 0.58 |
| | 08.2018 | 51.33 \pm 0.58 | 70.00 \pm 0.00 | 57.33 \pm 0.58 | 54.33 \pm 0.58 | 52.67 \pm 0.58 |
| | 10.2018 | 55.00 \pm 0.00 | 74.67 \pm 0.58 | 58.33 \pm 0.58 | 53.33 \pm 0.58 | 53.33 \pm 0.58 |
| | 12.2018 | 54.00 \pm 0.00 | 75.33 \pm 2.52 | 59.33 \pm 2.52 | 56.00 \pm 1.73 | 55.67 \pm 2.52 |
| | 02.2019 | 53.67 \pm 1.15 | 70.67 \pm 1.15 | 59.00 \pm 0.00 | 54.33 \pm 0.58 | 52.67 \pm 1.15 |
| | 04.2019 | 52.00 \pm 0.00 | 73.33 \pm 0.58 | 58.67 \pm 0.58 | 53.00 \pm 0.00 | 52.33 \pm 0.58 |

Source: own study.

Table 2. The average values of the tested water parameters at five sampling points (mean \pm SD)

| Parameter | Sampling point 1 (150 m above outfall canal) | Sampling point 2 (outfall canal) | Sampling point 3 (100 m below outfall canal) | Sampling point 4 (350 m below outfall canal) | Sampling point 5 (1200 m below outfall canal) |
|---|--|-------------------------------------|--|--|---|
| pH | 8.32 \pm 0.12 | 7.64 \pm 0.22* | 7.95 \pm 0.30* | 8.18 \pm 0.15 | 8.24 \pm 0.12 |
| P alkalinity (mg CaCO ₃ ·dm ⁻³) | 8.97 \pm 2.80 | 2.50 \pm 3.65* | 4.00 \pm 4.64* | 6.92 \pm 4.35 | 9.00 \pm 2.64 |
| Total alkalinity (mg CaCO ₃ ·dm ⁻³) | 11.31 \pm 5.63 | 3.75 \pm 4.64* | 6.28 \pm 4.95* | 9.75 \pm 4.68 | 11.42 \pm 5.55 |
| Total hardness (mg CaCO ₃ ·dm ⁻³) | 279.06 \pm 13.00 | 283.06 \pm 22.58 | 279.50 \pm 15.03 | 278.39 \pm 7.99 | 271.83 \pm 9.33 |
| NO ₃ ⁻ (mg·dm ⁻³) | 3.65 \pm 1.35 | 25.64 \pm 4.21* | 11.69 \pm 4.33* | 6.67 \pm 2.75 | 5.33 \pm 2.55 |
| PO ₄ ³⁻ (mg·dm ⁻³) | 0.49 \pm 0.04 | 1.23 \pm 0.40* | 0.90 \pm 0.27* | 0.72 \pm 0.20* | 0.60 \pm 0.09* |
| C org. (mg·dm ⁻³) | 52.89 \pm 1.53 | 71.39 \pm 3.94* | 57.67 \pm 2.33* | 53.72 \pm 1.64 | 53.00 \pm 1.71 |

* A statistically significant difference ($p < 0.05$) in comparison to sampling point 1.

Source: own study.

common point sources of water pollution are municipal and industrial wastewater discharges. Most often, wastewater is mechanically-biologically treated. In case of the Vistula the point sources of pollution include discharges of mine waters. POLICHT-LATAWIEC and KAPICA [2013] studied the impact of a coal mine on water quality in the Vistula in 2011. Increased concentrations of ammoniacal nitrogen, nitric nitrogen, nitrites, phosphates and total phosphorus were observed at points located below the mine water outlet. Research show that in case of most tested parameters, the level of pollution decreased with the distance from the outlet. A similar trend was observed in subsequent studies (2011–2012) carried out at the same section of the Vistula [POLICHT-LATAWIEC 2014]. Dam reservoirs and the shape of a river bed might also have an effect on rivers chemistry [BOGDAŁ *et al.* 2015; XIAO *et al.* 2020]. BOGDAŁ *et al.* [2015] conducted a study comparing the hydrochemical parameters of the Vistula inflow to the Goczałkowice Reservoir with the parameters of the water flowing out of the reservoir. A lower concentrations of nitrates and ammonium nitrogen (statistically significant) along with phosphates, total phosphorus and total iron (statistically insignificant) were demonstrated in the samples collected at the outflow of the Goczałkowice Reservoir. However, the dam reservoir contributed to the deterioration of the oxygen conditions in the river [BOGDAŁ *et al.* 2015]. A significant part of the research on sources of rivers water quality focuses on the outfall of wastewater treatment. Studies on the impact of sewage discharge from a mechanical-biological treatment plant to rivers indicate an increase of pollution in water. In particular, the concentration of biogens rises in the section of the watercourse below the discharge. For example, the chemical parameters in the Kiecz stream, the receiver of the treatment plant in Tuchola, were deteriorated due to the inflow of sewage. The increase of BOD₅ and concentration of nitrates, nitrites and chlorides was found 100 m below the sewage discharge [LEWANDOWSKA-ROBAK *et al.* 2011]. The discharge from the mechanical-biological wastewater treatment plant also effects in increase of tested parameters values in the San River water (total suspended solids, BOD₅, COD-Cr, sulphates, chlorides, total nitrogen, total phosphorus). However,

all recorded changes in water parameters at measuring points located more than 2 km from the sewage discharge were statistically insignificant [POLICHT-LATAWIEC *et al.* 2013].

CONCLUSIONS

The negative impact of municipal and industrial wastewater (both subjected to treatment processes) discharge on the water quality in the Vistula was found. All tested hydrochemical parameters values, apart from the total hardness, changed in result of contamination by sewage inflow. The pollution level decreased with the flow of the river. The tested parameters at the last measurement point (1200 m below the discharge) approached the values recorded above the sewage outfall. The presented observations of changes in the concentration of pollutants in authors' own research, as well as the results of the above-mentioned studies, indicate the self-purification capacity of a river. However, for each watercourse flowing through urbanized areas, it is an individual feature. It depends on a number of factors and requires regular monitoring studies taking into account the hydrochemical analysis of watercourses.

REFERENCES

- BOGDAŁ A., KOWALIK T., WITOSZEK K. 2015. Effect of the Goczałkowice Reservoir on the changes of water quality in the Vistula River. *Ecological Engineering*. Vol. 45 p. 124–134. DOI 10.12912/23920629/60605.
- BRYSIEWICZ A., BONISLAWSKA M., CZERNIEJEWSKI P., KIERASINSKI B. 2019. Quality analysis of waters from selected small watercourses within the river basins of Odra River and Wisła River. *Rocznik Ochrona Środowiska*. Vol. 21 (2). p. 1202–1216.
- GACKA-GRZESIKIEWICZ E. (ed.) 1995. Korytarz ekologiczny doliny Wisły. Stan – funkcjonowanie – zagrożenia [Ecological corridor of the Vistula valley. Condition – Operation – Threats]. Warszawa. Fundacja IUCN Poland. ISBN 2-8317-0240-2 pp. 196.

- GDOŚ 2002. Natura 2000 – Standardowy formularz danych Dolina Środkowej Wisły [Natura 2000: Standard data form: Valley of Middle Vistula]. PLB140004 pp. 17.
- GOPCHAK I., KALKO A., BASIUK T., PINCHUK O., GERASIMOV I., YAROMENKO O., SHKIRYNETS V. 2020. Assessment of surface water pollution in Western Bug River within the cross-border section of Ukraine. *Journal of Water and Land Development*. No. 46 p. 97–103. DOI 10.24425/jwld.2020.134201.
- Grupa Azoty 2019. Non-financial statement of the Grupa Azoty Group for the 12 months ended December 31th 2018. Tarnów. Grupa Azoty S.A. pp. 46.
- GUS 2020. Bank Danych Lokalnych. Oczyszczalnie ścieków komunalnych [Local Data Bank. Municipal waste water treatment plants]. [Access 15.10.2020]. Available at: bdl.stat.gov.pl/BDL/metadane/podgrupy/222?back=True
- JAKUBIAK M., CHMIEŁOWSKI K. 2020. Identification of urban water bodies ecosystem services. *Acta Scientiarum Polonorum. Formatio Circumiectus*. Vol. 19(3) p. 73–82.
- JAKUBIAK M., PANEK E. 2016. Small water bodies in the valley of the river Rudawa in Krakow – the environmental value. *Geomatics and Environmental Engineering*. Vol. 10 (1) p. 45–57. DOI 10.7494/geom.2016.10.1.45.
- JAKUBIAK M., PANEK E. 2017. Małe zbiorniki wodne w zachodniej części Krakowa [Small water bodies in the western part of Krakow]. Kraków. Wydawnictwa AGH. ISBN 978-83-7464-888-2 pp. 192.
- LEWANDOWSKA-ROBAK M., GÓRSKI Ł., KOWALKOWSKI T., DĄBKOWSKA-NASKRĘT H., MIESIKOWSKA I. 2011. The influence of treated sewage discharged from wastewater treatment plant in Tuchola on water quality of Kicz stream. *Inżynieria i Ochrona Środowiska*. Vol. 14 (3) p. 209–221.
- LIGEŻA S., SMAL H. 2003. Skład granulometryczny osadów dennych zbiornika wód zrzutowych Zakładów Azotowych Puławy [Textural differentiation of bottom sediments in the reservoir of Puławy Nitrogen Fertilizer Factory (SE Poland)]. *Acta Agrophysica*. Vol. 1 (2) p. 271–277.
- MAZUR R., KAŁUŻA T., CHMIŚT J., WALCZAK N., LAKS I., STRZELEŃSKI P. 2016. Influence of deposition of fine plant debris in river floodplain shrubs on flood flow conditions – The Warta River case study. *Physics and Chemistry of the Earth. Parts A/B/C*. Vol. 94 p. 106–113. DOI 10.1016/j.pce.2015.12.002.
- MAZUR R., SITAREK M. 2020. Microbiological bioremediation of the Kamienna Góra dam reservoir. *Acta Scientiarum Polonorum. Formatio Circumiectus*. Vol. 19(1) p. 47–59. DOI 10.15576/ASP.FC/2020.19.1.47.
- MICHAŁKIEWICZ M., MĄDRECKA B., DYSARZ T., JONIAK T., SZELAĞ-WASIELEWSKA E. 2011. Wpływ miasta Poznania na jakość wód rzeki Warty [The influence of the city of Poznań on water quality of the Warta River]. *Nauka Przyroda Technologie*. Vol. 5 (5), #89 p. 1–13.
- MPWiK 2017. Plan rozwoju i modernizacji urządzeń wodociągowych i urządzeń kanalizacyjnych Miejskiego Przedsiębiorstwa Wodociągów i Kanalizacji „Wodociągi Puławskie” Spółka z o.o. in Puławy na lata 2017–2021 [Plan for the development and modernization of water supply and sewage devices of the Municipal Water and Sewage Company “Wodociągi Puławskie” Spółka z o.o. in Puławy for 2017–2021]. Puławy. Miejskie Przedsiębiorstwo Wodociągów i Kanalizacji „Wodociągi Puławskie” Spółka z o.o. pp. 17.
- PN-EN ISO 9963-1:2001 Jakość wody – Oznaczanie zasadowości – Część 1: Oznaczanie zasadowości ogólnej i zasadowości wobec fenoloftaleiny [Water quality – Determination of alkalinity – Part 1: Determination of total and composite alkalinity].
- PN-ISO 6059:1999 Jakość wody – Oznaczanie sumarycznej zawartości wapnia i magnezu – Metoda miareczkowa z EDTA [Water quality – Determination of the sum of calcium and magnesium – EDTA titrimetric method].
- POLICHT-LATAWIEC A. 2014. The effect of saline mine waters discharge from hard coal mine on the ecological state of the Vistula River. *Acta Horticulturae et Regiotecturae*. Vol. 2 p. 43–47. DOI 10.1515/ahr-2014-0011.
- POLICHT-LATAWIEC A., KANOWNIK W., ŁUKASIK D. 2013. Effect of point source pollution on the San River water quality. *Infrastructure and Ecology of Rural Areas*. Vol. 1 (4) p. 253–269.
- POLICHT-LATAWIEC A., KAPICA A. 2013. Wpływ kopalni węgla kamiennego a jakość wody rzeki Wisły [Influence of hard coal mine on water quality in the Vistula River]. *Annual Set the Environment Protection*. Vol. 15 p. 2640–2651.
- PYTKA A., JÓZWIAKOWSKI K., MARZEC M., GIZIŃSKA M., SOSNOWSKA B. 2013. Impact assessment of anthropogenic pollution on water quality of Bochońniczanka River. *Infrastructure and Ecology of Rural Areas*. Vol. 3(2) p. 15–29.
- Rozporządzenie Ministra Gospodarki Morskiej i Żeglugi Śródlądowej z dnia 11 października 2019 r. w sprawie klasyfikacji stanu ekologicznego, potencjału ekologicznego i stanu chemicznego oraz sposobu klasyfikacji stanu jednolitych części wód powierzchniowych, a także środowiskowych norm jakości dla substancji priorytetowych [Regulation of the Minister of Maritime Economy and Inland Navigation of 11 October 2019 on the classification of ecological status, ecological potential, chemical status and the method of classifying the status of surface water bodies as well as environmental quality standards for priority substances]. *Dz.U.* 2019 poz. 2148.
- SIUDAK R., LEWANDOWSKA K. 2016. Program ochrony środowiska dla gminy Miasto Puławy na lata 2016–2020. Załącznik do Uchwały Nr XXXV/328/17 Rady Miasta Puławy z dnia 23 lutego 2017 r. [Environmental protection program for the municipality of the city of Puławy for the years 2016–2020. Annex to Resolution of the City Council of the City of Puławy of February 23, 2017 No. XXXV/328/17]. Suchy Las. Ekostandard Pracowania Analiz Środowiskowych pp. 69.
- STEELE M.K., HEFFERNAN J.B. 2014. Morphological characteristics of urban water bodies: mechanisms of change and implications for ecosystem function. *Ecological Applications*. Vol. 24(5) p. 1070–1084.
- XIAO C., CHEN J., YUAN X., CHEN R., SONG X. 2020. Model test of the effect of river sinuosity on nitrogen purification efficiency. *Water*. Vol. 12(6), 1677. DOI 10.3390/w12061677
- ZEMELKA G. 2019. Contamination and environmental risk assessment of heavy metals in sediments of Dobczyce reservoir and its tributaries – a literature review. *Geomatics and Environmental Engineering*. Vol. 13(1) p. 63–75. DOI 10.7494/geom.2019.13.1.63.