## LOADING THE WATERS OF THE RIVER GWDA WITH BIOGENIC SUBSTANCES WITHIN THE ADMINISTRATIVE BOUNDARIES OF THE TOWN OF PIŁA (NORTH-WEST POLAND)

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The results of hydrochemical tests of the Gwdy river in the area of the town of Piła are presented in this study. The catchment area of the Gwda river comprises the area of 4942.8 km<sup>2</sup>. The surface of catchment area is covered with forest in 43.1%, arable land constitutes 36.5%, and grassland 7.2%. The Gwda river is a right-bank tributary of the Noteć River of IV order. Water samplings were collected in 2009 from three measurement and control points located between 13 and 24 kilometre of the course of the river. During the tests thermal and oxygen conditions were marked and biogenic substances (nitrate acid, ammonia nitrogen, nitrite nitrogen, total nitrogen, total phosphorus and mineral phosphorus). Concentrations of most of the indicators examined qualified the waters of Gwda to the waters of good quality. The indicator whose concentrations exceeded the limit values for the waters of quality was general phosphorus.

Keywords: nitrogen, phosphorus, river Gwda, pollution

#### **INTRODUCTION**

The increasing number of population and the dynamic development of the industry make that the available water resources are shrinking at an alarming rate, and the natural shortage of water is intensified by its heavy pollution [Bajkiewicz-Grabowska and Mikulski 2007, Directive 2000/60/EC]. One of the types of water pollution is anthropogenic pollution, which gets into the waters from point sources. This is mainly household and industrial sewage - mining waters, organized landfill leachate, leaks of pollutants from devices transporting or storing these substances. Another type of the sources of pollution are area sources such as flow from urban areas, roads, unorganized landfill leachates etc. [Ilnicki 2014]. All the above-mentioned pollutants disturb the

biological balance of aquatic environment, are dangerous for living organisms and can be the cause of secondary water pollution [Mikołajczak et al. 2001].

One of the methods specifying the quality of the water of a particular river and deviation from the natural condition are tests of abiotic environment elements [Korol and Kędzia 1993, Byczkowski 1996, Dz. U. Nr 257, poz. 1545]. The quantity of pollutants entering the surface waters can be monitored, among other things, by controlling the quantity of biogenic compounds, which are an important factor in the functioning of the river ecosystems. The content of biogenic compounds in water decreases rapidly in the summer months, when there are mass algal blooms, in other months of the year their level normally increases [Ilnicki 2014]. In this study a preliminary assessment of hydrochemical conditions of the Gwda river is presented based on oxygenation and biogenic compounds and the impact of pollutants evacuated to this river in the area of the town of Piła during vegetation season in 2009.

#### MATERIALS AND METHODS

# Characteristics of the Gwda river and its catchment area

The Gwda River is the river flowing through West Pomeranian and South Pomeranian Lake District with a length of 147 km. Its springs are located at a height of 157 meters a.s.l. west of the village of Biała in West Pomeranian province. It flows through several lakes including Studnica, Wierzchowo and Wielimie. In the central and partially lower course the Gwda flows through forests, mainly pine forests. In this area several smaller or larger tributaries flow to it, among which the most important are Czernica, Szczyra and Głomia (left) and right: Osoka, Czarna, Młynówka, Płytnica, Rurzyca and Piława [Kondracki 2001]. In addition, several smaller, frequently periodically occurring tributaries flow into the Gwdy River [Mikołajczak and Sheremetev 1999]. The total area of the catchment area of the Gwdy covers 4942.8 km<sup>2</sup>, including forests – 43.1%, arable land – 36.5% and grassland – 7.2%. A significant longitudinal slope of the river (0.68‰) was used for energy purposes. Along the course of the river 5 water reservoirs with earth barriers and hydraulic power plants were built. In the upper part of the catchment area lake density is 5–10%, which causes the alignment of flows [Andrzejewski 2000, Melcer and Olejnik 2006, Górecki 2007, Ilnicki et al. 2008].

From point sources the greatest threat to the waters of the Gwda are discharges of pollutants from the area of Piła (more than 75 thousand inhabitants and numerous industrial plants). The sewage from the town are subject to treatment in mechanical – biological treatment plant including the removal of biogenic compounds, and then it is brought into the river or the land [Robakowska et al. 2004].

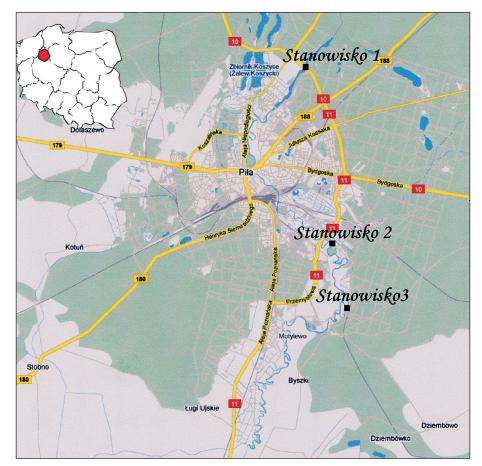


Figure 1. Location of the sampling sites



**Photo 1**. Site 1 – Koszyce (Phot. Grzegorz Oczkowski)

#### Sampling sites

Three measuring sites located between 13 and 24 km of the course of river were established for the implementation of the objective intended, and the section tested is mostly located within the administrative boundaries of the town of Piła. The location of the research area and individual sampling sites is shown in Figure 1.

Site 1 – Koszyce (Photo 1) – located in front of the town, on the bridge of the national road No. 10 Szczecin – Bydgoszcz. Left bank of the river is covered with mixed forest in this place with the predominance of pine, the right bank is waste land turning into pine forest. At a distance of 100 m from the site there are individual buildings. The width of the bed of a river is 25 m. The river at this point flows to the tank Koszyce, the banks are low, wet in some places, at the bottom there is a layer of mud.

- Site 2 Koszyce (Photo 2) was placed at 16 km of the course of river at a distance of 50 m below the outlet of sewage collector of mechanical biological sewage treatment plant. At a distance of 30 m from the site runs a hardly frequented county road. The banks are quite high, they form two-meter high slopes in this place. The width of the bed of the river is 10 m. The site is surrounded by meadows and barren land with single trees growing there.
- Site 3 Kalina (Photo 3) is located at approx. 3 km below the sewage collector, in the forest district of a town. The river forms here a meander with sandy gravelled bottom. The left bank is high, covered with conifer forest, the right one, significantly lower, is covered with meadow vegetation. The river bed is 14 m wide in this place. On the banks you can find submerged vegetation. The nearest buildings are just 500 m below the measuring point.

#### Field and laboratory methods

Hydrochemical methods of the waters of the Gwda river were performed from April to October 2009. Water samples were collected using the Ruttner bucket with a capacity of 3 dm<sup>3</sup> from the centre of the mainstream, the temperature of water was measured using a digital thermometer ST – 9215A/B/C with the accuracy of measurement 0.1 °C. Chemical analyses of the water samples was performed in the laboratory of the Institute of Hydrochemistry and Water Protection ZUT in Szczecin, in accordance with the methods recommended by the Standard Methods [2005] and Hermanowicz et al. [1999], and



Photo 2. Site 2 – Leszków and sewage collector of mechanical – biological sewage treatment plant (Phot. Grzegorz Oczkowski)



Photo 3. Site 3 - Kalina (Phot. Grzegorz Oczkowski)

included the following indicators: dissolved oxygen, mineral phosphorus, total phosphorus, total nitrogen, nitriate nitrogen, ammonia nitrogen, nitrite nitrogen. Calculated from accounting point: oxidation percentage, mineral nitrogen, nitrogen and organic phosphorus.

The assessment of the quality of water was performed comparing the results of the selected physical and chemical parameters of water with the guidelines in the Regulation of the Minister of Environment dated 9 November 2011 [Dz. U. Nr 257, poz. 1545, załącznik 5].

#### **RESULTS AND DISCUSSION**

Temperature has a significant impact on aquatic biocenosis and the course of chemical processes and its increase affects the acceleration of chemical and biochemical processes [Ilnicki et al. 2008, Ilnicki 2014]. The temperature of lothic waters changes faster than that of lenithic waters and depends on: air temperature, temperature of water supplying the river, formation of the river valley, covering of banks and the inflow of sewage (including warmed up waters). Temperature fluctuations in different layers of water in the river are low. Higher temperature of water is in this part of the bed where it flows slower, the lower one is usually in the mainstream. In the flowing waters we have to deal with the increase of temperature with the increase of distance from the source [Bajkiewicz-Grabowska and Mikulski 2007]. The temperature of the waters of the river Gwda throughout the research period changed in accordance with the prevailing climatic conditions. During the whole research period the average temperature of water was 16.7 °C. Minor

variations of the indicator tested on individual sampling sites were observed. It was found that during the whole research period the temperature of water was the lowest in site 1, while the highest values were recorded in site 2 (Table 1), higher temperatures of water recorded in the whole period of research in site 2 in relation to other sites could be the result of the discharge of treated and warmed up sewage in the settlement tank from the treatment plant (Table 1). The inflow of sewage or water with different temperature brings about thermal differences in the cross section of the river. These waters are mixed at a distance from several to a dozen kilometres below the inflow of sewage [Górecki and Melcer 2006, Ilnicki 2014]. Mixing of the waters of the Gwda river is already on approximately 3 km site 3, which is reflected by lower temperature values of water in this site (Table 1). Water temperature is closely related to the oxygen content dissolved. The oxygen content in the waters of the Gwda river during the research period was in a range from  $7.04 \text{ mg O}_{\circ}/\text{dm}^3$  in June 2009 to 10.24 mg O\_{\circ}/\text{dm}^3 in April 2009 and the average from the research period was 8.1 mg  $O_2/dm^3$  (Table 1). In the same periods of 1995 - 1997 the average content of oxygen dissolved in the West Oder River was 11.4 mgO<sub>2</sub>/dm<sup>3</sup>. This parameter was similar in the waters of the East Oder River [Tórz 2002]. Concentrations of oxygen are generally lower below the places of the inflow of sewage containing easily degradable organic substances. This phenomenon appears clearly in case of the sewage of food industry and household sewage [Ilnicki 2014]. The level of oxygen dissolved can also be reduced during the transformation of biogenic compounds [Boers et.al. 1998, Ramirez et.al. 2003, Ramirez et al. 2004]. Tests of the Orli and Rów Polski rivers performed by Melcer and Olejnik [2006] proved that the larger the share of arable land in the catchment area and lower density of forest, the more pollution of waters with compounds of nitrogen and phosphorus. The average concentration of total phosphorus found during tests in the water of the Gwdy river (0.38 mg P/dm<sup>3</sup>) (Table 1) is significantly lower than in the Orli and Rów Polski, despite the presence of large, point pollution sources (Piła, Szczecinek) in the water catchment area of the Gwdy river. The share of arable land in the total area of the catchment area of the Gwda river is approximately twice as smaller than in the catchment area of the compared rivers. It should therefore be concluded

Date	Sampling sites	Dissolved oxygen	Temperature	Oxidation percentage	N-NH4	N-NO <sub>3</sub>	N-NO <sub>2</sub>	Total nitrogen	Mineral nitrogen	Organic nitrogen	Mineral phosphorus	Organic phosphorus	Total phosphorus	Mineral phosphorus
		mgO <sub>2</sub> / dm <sup>3</sup>	٥C	%	mg/dm <sup>3</sup>									
29.04.09	1	9.60	16.4	98.09	0.097	0.706	0.039	1.222	0.842	0.380	0.019	0.304	0.323	0.019
	2	8.16	17.4	85.13	0.445	4.501	0.056	5.662	5.002	0.660	0.061	0.322	0.383	0.061
	3	10.24	17.2	106.39	0.516	0.801	0.096	1.623	1.413	0.210	0.013	0.208	0.221	0.013
29.05.09	1	9.76	15.9	87.66	0.118	0.350	0.082	0.895	0.549	0.346	0.050	0.307	0.357	0.050
	2	9.44	16.5	98.67	0.359	1.839	0.092	3.216	2.290	0.926	0.074	0.266	0.340	0.074
	3	9.60	16.4	96.39	0.194	0.354	0.046	0.769	0.594	0.175	0.066	0.266	0.332	0.066
27.06.09	1	7.36	18.6	98.09	0.464	0.560	0.053	1.435	1.077	0.358	0.210	0.293	0.502	0.210
	2	7.04	19.0	78.70	0.543	1.259	0.053	2.351	1.856	0.495	0.246	0.222	0.468	0.246
	3	8.00	18.9	76.21	0.356	0.454	0.053	0.975	0.863	0.112	0.194	0.249	0.443	0.194
	1	8.16	19.8	86.07	0.126	0.694	0.094	1.405	0.914	0.491	0.106	0.319	0.426	0.106
15.07.09	2	8.00	20.3	89.39	0.248	0.958	0.085	1.765	1.291	0.474	0.119	0.332	0.451	0.119
	3	8.32	20.1	88.51	0.189	0.311	0.092	0.747	0.592	0.155	0.084	0.342	0.426	0.084
31.08.09	1	8.00	17.7	91.69	0.254	0.485	0.003	1.060	0.742	0.319	0.063	0.278	0.340	0.063
	2	7.52	18.8	83.98	0.413	1.427	0.078	3.624	1.918	1.706	0.093	0.375	0.468	0.093
	3	8.16	18.6	80.74	0.182	0.527	0.066	0.946	0.775	0.171	0.081	0.353	0.434	0.081
26.09.09	1	8.16	14.3	87.26	0.311	0.633	0.025	1.005	0.969	0.036	0.142	0.190	0.332	0.142
	2	8.80	15.5	79.70	0.492	1.324	0.059	2.120	1.875	0.245	0.169	0.197	0.366	0.169
	3	7.84	15.2	88.21	0.563	0.568	0.067	1.297	1.199	0.098	0.132	0.192	0.323	0.132
10.10.09	1	8.96	10.5	78.08	0.100	0.404	0.016	0.652	0.519	0.133	0.085	0.239	0.323	0.085
	2	8.32	11.6	80.31	0.350	1.333	0.039	1.984	1.722	0.262	0.096	0.287	0.383	0.096
	3	9.60	11.3	76.50	0.342	0.512	0.043	1.002	0.896	0.107	0.088	0.252	0.340	0.088

Table 1. The values of the parameters in the waters of the Gwda river in sampling sites in 2009

that a decisive influence on the pollution with biogenic compounds are the area sources [Ilnicki et al. 2003, Melcer and Olejnik 2006]. Tests of the Gwda River showed a disturbance of the cycle of phosphorus transformation. The highest average concentration of total phosphorous (0.440 mg P/dm<sup>3</sup>) appeared in the summer and the lowest (0.326 mg P/dm<sup>3</sup>) in the spring. In the autumn the average content of the indicator discussed was 0.345 mg P/dm<sup>3</sup> (Table 1). Seasonal variability in the content of total phosphorous was similar in the waters of the river Gowienica in the years 2001 - 2002 (in the autumn 2001 - 0.340 mg P/  $dm^3$ , in the spring  $2002 - 0.180 \text{ mg P/dm}^3$ , in the summer of 2002 - 0.593 mg P/dm<sup>3</sup>) [Kubiak et al. 2003]. Higher concentration values of total phosphorus and phosphates in the waters of the Gwda river during the summer months could be influenced by increased precipitation, including a large amount of torrential rain. Polluted storm water discharged to urban catchment areas have increased concentrations of phosphates dissolved and total phosphorus [Dondajewska et al. 2009].

Organic nitrogen flows to the waters mainly with eroded particles of soil, but also in the form of a dissolved organic substance. Organic and ammonium forms are introduced into water with untreated sewage, and ammonium and nitrate form from the treatment plant. In surface waters in the vegetation season, usually an organic form of nitrogen is prevalent, sometimes, if it is not fully used by plants the nitrate form. Tests of the waters of the Gwda river performed in vegetation season have shown that dominant form of nitrogen is mineral nitrogen with a significant advantage of nitrates over other forms of (Table 1). The highest concentrations of nitrate nitrogen recorded on site 2 are the remains of sewage treatment (Table 1). The efficiency of the removal of nitrogen and phosphorus in mechanical-biological sewage treatment plants with a three step system of sewage treatment 75 and 87% respectively [Górecki and Melcer 2006].

In rivers the nitric nitrogen dominates over ammonium form. The advantage of nitrate form, which is associated with good oxygenation of river waters and the dominance of nitrification process over denitrification was characteristic for the waters of the Gwdy river during the whole period of research (Table 1) [Tórz 2002]. Concentrations of ammonia nitrogen in the surface waters range from hundredths up to several mg/ dm<sup>3</sup>. During the tests the lowest content of ammonia nitrogen [Dz. U. Nr 257, poz. 1545] was demonstrated than the one provided in the literature in the water of the Gwda river, which ranged from 0.097 to 0.563 mg/dm<sup>3</sup> (Table 1). Its presence in the waters is the resultant of many factors, of which the most important is the inflow of ammonia from point and area source, the stage of the development of vegetation, aerobic and thermal conditions [Allan 1998]. The content of ammonia nitrogen demonstrates significant fluctuations in the course of the year. In the spring, the content of ammonium ions usually high is caused by the low intensity of biological production. Melt waters flowing from the catchment area can cause the maintenance of higher concentrations. In the summer this situation changes when ammonium salts appearing in water are collected by plants in the process of biosynthesis, which causes a drop in the concentration of ammonium nitrogen. In the autumn, when the intensity of biological production in river waters falls there is a lower demand for nitrogen compounds, what results in their higher concentrations [Kubiak et al. 2004]. The tests performed demonstrated seasonal disturbances of the fluctuations in the concentrations of the ammonium nitrogen. The highest, average concentrations of ammonium ions in the water of the river Gwda appeared in June (0.454 mg N/ dm<sup>3</sup>) and September (0.455 mg N/dm<sup>3</sup>). While the lowest ones (0.188 mg N/dm<sup>3</sup>) in July (Table 1).

The nitrite nitrogen is an unstable form. In the clean surface waters the content of nitrites is in thousandths of mg/dm<sup>3</sup>. In polluted waters it can appear in slightly larger quantities. In the waters of the Gwda river the content of nitrite nitrogen fluctuated between 0.003 mg N/dm<sup>3</sup> to 0.096 mg N/dm<sup>3</sup>, which indicates the water of good quality (Table 1).

With the higher temperature of the air and water the processes of organic matter decomposition and the oxidation of ammonia to nitrates are more intense. Another factor affecting the content of biogenic compounds in water is the development of aquatic vegetation, mainly phytoplankton. Temperature plays the most important part here. Tests demonstrated that the content of nitrate nitrogen in the water of the Gwda river depends on

Parameter	Temperature	Oxidation percentage	Dissolved oxygen		
N-NO <sub>3</sub>	0.06	-0.05	-0.14		
N-NH <sub>4</sub>	0.05	0.01	-0.33		
N-NO <sub>2</sub>	0.53	0.28	0.12		
Mineral phosphorus	0.19	-0.44	-0.71		

 Table 2. Correlations of selected indicators in the waters of the Gwda river

the temperature of water only to a small extent (correlation coefficient of r = 0.06) (Table 2).

A slight, inverse relationship between the content of nitrates and percentage oxygenation was also demonstrated (correlation coefficient of r = 0.05) (Table 2). Taking into account a significant forest density of the catchment area of the Gwda river and the fact that the afforestation restricts the inflow of nitrogen to the river [Górecki 2007], it can be assumed that the higher concentrations of nitrates on individual stands are the result of the inflow of pollutants from point sources or feeding from internal resources, which are bottom deposits [Boers et al. 1998].

In the group of indicators, which characterise a physical condition of water the temperature on all test stands research corresponded to the I class of purity (Table 3). In the group of indicators, which characterise aerobic conditions and organic pollutants the oxygen was dissolved on all test stands in the I class of purity. Indicators, which characterised biogenic conditions were within the I or II class of the quality of waters, with the exception of total phosphorus on site 2, where its quantity corresponded to the waters below good status (Table 3). Bad condition of waters is probably the consequence of the discharge of sewage from the collector of mechanical-biological sewage treatment plant.

### CONCLUSIONS

Concentrations of most of the indicators examined qualified the waters of the Gwda to good quality waters. Concentration of oxygen dissolved during the whole period of the tests was high, and thermal conditions of the river Gwda – typical for the flowing waters in moderate climate. The content of biogenic substances in the whole research period qualified waters of the river Gwda to waters of good quality, except total phosphorus. Increased phosphorus concentra-

Parameter	Unit	Min	Max	Mean	Water quality class				
Site 1									
Temperature	O₀	10.5	19.8	16.2	I				
Dissolved oxygen	mgO <sub>2</sub> /dm <sup>3</sup>	7.36	9.76	8.57	I				
Ammonia nitrogen	mg/dm <sup>3</sup>	0.097	0.464	0.210	I				
Kjeldahla nitrogen (N <sub>org</sub> +N <sub>NH4</sub> )	mg/dm <sup>3</sup>	0.233	0.822	0.505	I				
Nitrate nitrogen	mg/dm <sup>3</sup>	0.350	0.706	0.547	I				
Total nitrogen	mg/dm <sup>3</sup>	0.652	1.435	1.096	I				
Phosphates	mg/dm <sup>3</sup>	0.019	0.210	0.096	I				
Total phosphorus	mg/dm <sup>3</sup>	0.323	0.502	0.372	II				
Site 2									
Temperature	O₀	11.6	20.3	17.0	I				
Dissolved oxygen	mgO <sub>2</sub> /dm <sup>3</sup>	7.04	9.44	8.18	I				
Ammonia nitrogen	mg/dm <sup>3</sup>	0.248	0.543	0.407	I				
Kjeldahla nitrogen (N <sub>org</sub> +N <sub>NH4</sub> )	mg/dm <sup>3</sup>	0.612	2.119	1.088	II				
Nitrate nitrogen	mg/dm <sup>3</sup>	0.958	4.501	1.806	I				
Total nitrogen	mg/dm <sup>3</sup>	1.765	5.662	2.960	I				
Phosphates	mg/dm <sup>3</sup>	0.061	0.246	0.123	I				
Total phosphorus	mg/dm <sup>3</sup>	0.340	0.468	0.408	below good status				
Site 3									
Temperature	O₀	11.3	20.1	16.8	I				
Dissolved oxygen	mgO <sub>2</sub> /dm <sup>3</sup>	7.84	10.24	8.82	I				
Ammonia nitrogen	mg/dm <sup>3</sup>	0.182	0.563	0.335	I				
Kjeldahla nitrogen (N <sub>org</sub> +N <sub>NH4</sub> )	mg/dm <sup>3</sup>	0.344	0.726	0.481	I				
Nitrate nitrogen	mg/dm <sup>3</sup>	0.311	0.801	0.504	I				
Total nitrogen	mg/dm <sup>3</sup>	0.747	1.623	1.051	I				
Phosphates	mg/dm <sup>3</sup>	0.013	0.194	0.094	I				
Total phosphorus	mg/dm <sup>3</sup>	0.221	0.443	0.360	II				

 Table 3. Extreme and average values of physical and chemical elements and the class of water quality in the Gwda river on sampling sites

tions in the summer months show partial use of it by autotrophic organisms and increased fertility of waters. Increased concentrations of nitrates recorded during the tests on site 2 could be the result of the inflow of pollutants from sewage treatment plant. These pollutants are diluted, which was visible in the lower values of this parameter in the next sampling site.

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