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D – data interpretation
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F – literature search

Dynamics of physicochemical parameter concentrations in the Graniczna Woda stream water

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Abstract

The paper presents variability of physicochemical parameter concentrations and determined the potential and chemical status of water in the Graniczna Woda stream, the right bank tributary to the Stoła River. The stream catchment area of 41.5 km^2 is covered mainly by forests. A lowland stream flows through part of the Upper Silesia Industrial Region through three districts. A biological-mechanical municipal sewage treatment plant operates in the area of Miasteczko Śląskie, as well as a factory sewage treatment plant of Zinc Plant. The data base used in the papers consisted of the results obtained from the Provincial Inspectorate of the Environmental Protection in Katowice, monthly analyses of water samples collected in the years 2009–2013 in the control-measurement points located by the mouth of the Stoła River. 34 physicochemical indices were analyzed in the paper. Statistically significant upward trends were determined over the period of investigations for values of electrical conductivity (*EC*), total suspended solids, Cl, SO_4, NO_2-N and Zn in the stream water. Statistically significant downward trend was noted for total hardness. It was stated that both the potential and chemical status o the stream water were below good. Exceeded limit values for quality class II determined for oxygen and organic indices (chemical oxygen demand COD-Mn, total organic carbon TOC), salinity (*EC*, SO_4, Cl, Ca, hardness) and biogenic indices and substances particularly harmful for aquatic environment (Zn, Tl) as well as exceeded allowable heavy metal concentrations may evidence a constant inflow of heavy metals to the aquatic environment of the Graniczna Woda stream from municipal and industrial sewage.

Key words: *anthropogenic pollution, heavy metals, physicochemical parameters, Silesia, trend, water quality*

INTRODUCTION

Human activities always involve a more or less serious interference in the natural environment. It may lead to changes on individual elements of the environment, its transformation or disturbance of its natural processes [BOGDAŁ *et al.* 2012; GAŁCZYŃSKA *et al.* 2011; KANOWNIK *et al.* 2013; NOWIŃSKA, ADAMCZYK 2013]. The crucial reason for the undesired changes occurring in water reservoirs and watercourses is their anthropogenic pollution connected with intensified urbanization [JAWECKI *et al.* 2017; KOSIŃSKA, MIŚKIEWICZ 2012; LAMPART-KAŁUŻNIACKA *et al.* 2012; MOSIEJ *et al.* 2007; POLICHT-LATAWIEC *et al.* 2013], intensive agricultural production and industrial activities [GOZZARD *et al.* 2011; KORNAŚ, GRZEŚKOWIAK 2011; KOWALIK *et al.* 2014; PYTKA *et al.* 2013]. One of the most industrialized regions in Poland is Silesian province, where four industrial regions: Silesian region, Częstochowa region, Rybnik region and Bielsko region are situated. The Upper Silesian Industrial Region (GOP) is the area with the greatest concentration of industrial plants in Poland. Its intensive industrialization has been lasting since the turn of the 18th and 19th century. Industrial development in this area was connected with abundant deposits of mineral resources including hard coal, silver, zinc and lead ores. Currently, the main domestic producer of refined zinc and its alloys manufacturing c.a. 80 thousand tons per year (40% of domestic production), refined lead and its alloys (50% of domestic production), Dore's metal (alloy of silver with admixtures of copper, lead and gold) with a minimum 98.5% content of Ag, sulphuric acid and refined cadmium, is "Miasteczko Śląskie" Steelworks operating in Miasteczko Śląskie in the GOP area. Wastes generated in the steelworks technological processes are the source of heavy metals transferred to the environment [CABALA *et al.* 2008].

The paper aimed at an analysis of changeability of selected physicochemical parameters concentrations and determining the potential and chemical status of water in the stream which has its source in the vicinity of zinc smelter in the area of Miasteczko Śląskie district.

CHARACTERISTICS OF THE RESEARCH OBJECT

The Graniczna Woda stream flows through the northern part of the Upper Silesian Industrial Region (GOP) and the districts of Tworóg, Tarnowskie Góry and Miasteczko Śląskie in the Silesia province. It is a lowland gravel-bed stream (abiotic type 18) of the fourth order. It is the right bank tributary to the Stoła River, which is a left bank tributary to the Mała Panew River (Fig. 1). The stream is about 11.7 km long. The terrain through which the Graniczna Woda flows, is located on the borderline of diversified physico-geographical structures. The Opole Plain, stretching to the north is represented by a lowland periglacial landscape, whereas the terrain to the south of the presented area is of an upland character, represented by carbonate rocks of Tarnogóra Hump. The stream catchment area – 41.5 km^2 is mainly covered by forests and to a lesser extent made up by urbanized, industrial and agricultural areas (Fig. 2) [ALEXANDROWICZ 1999; KONDRACKI 2013; KZGW 2014].

Zinc Smelter is operating in the area of Miasteczko Śląskie district with its own mechanical-chemical sewage treatment plan, moreover there is also a mechanical-biological treatment plant treating municipal and industrial sewage. The Graniczna Woda stream is the receiving waters for sewage from both treatment plants. The sewage treatment plant attached to the Zinc Smelter has been operating since 1980. Its throughput is 2880 m^3 daily and its sewage loading rate is not quite 100%. On the other hand, the throughput of the district treatment plant commissioned in 1968 is 2100 m^3 per day. The sewage loading rate of this treatment plant is ca. 43% [PARUSEL 2003].

METHODS OF RESEARCH

The main database used in the paper consisted of the results of monthly assessments of 34 selected physicochemical indices made in the water samples collected from the Graniczna Woda stream in the years 2009–2013 at the control-measurement point by the mouth reach to the Stoła River, at the level of the water gauge in Hanusek village, in Tworóg district (Fig. 1, Fig. 2). The values and concentrations of the parameters from indices group characterizing: physical status, including thermal and physical conditions (the temperature, total suspended solids), oxygen conditions and organic pollutants (dissolved oxygen, biochemical oxygen demand – BOD_5, chemical oxygen demand – COD-Mn, total organic carbon – TOC), salinity (conductivity at 20°C – *EC*, sulphates – SO_4, chlorides – Cl, calcium – Ca, magnesium – Mg, total hardness), acidification (water pH), biogenic conditions (ammonium nitrogen – NH_4-N, total Kjeldahl nitrogen – TKN, nitrate nitrogen – NO_3-N, nitrite nitrogen – NO_2-N, total nitrogen – TN, phosphate phosphorus (V) – PO_4-P, total phosphorus – TP), but also values of the indices from the group of substances particularly harmful to the aquatic environment (arsenic – As, barium – Ba, boron – B, hexavalent chromium – Cr^{6+}, total chromium – Cr, zinc – Zn, copper – Cu, aluminium – Al, thallium – Tl, fluorides – F, volatile phenols, petroleum phenols) and priority substances (cadmium and its compounds, lead and its compounds), characterizing the chemical status of water, were determined in the water samples by means of referential methods [Rozporządzenie MŚ... 2016a] by the Voivodeship Environmental Protection Inspectorate in Katowice.

Basic descriptive statistics, such as minimum and maximum value, arithmetic mean, standard deviation and variation coefficient [STANISZ 2007] were determined for selected indices. Concentrations of As, Cr^{6+}, volatile phenols and petroleum hydrocarbons assessed in many of the analysed water samples were below the limit of quantification, which made impossible determining all descriptive statistics. For these indices only minimum and maximum values were determined and no statistical analyses were conducted.

Water quality (potential) assessment was conducted in the paper in compliance with annexes 5 and 6 to the Regulation of the Minister of Environment dated 21 July 2016 [Rozporządzenie MŚ... 2016b]. The method of interpreting the results of research on quality indices forming physicochemical elements, in case of uniform parts of artificial or strongly changed surface waters, relied on classification of each analyzed index to an appropriate water quality class by comparing the value of arithmetic mean of the index, computed on the basis of the concentrations registered during the period of investigations, with the limit values. Class I denotes the maximum potential, class II – good, whereas non-fulfilment of class I requirements means potential below good. Classification of the che-

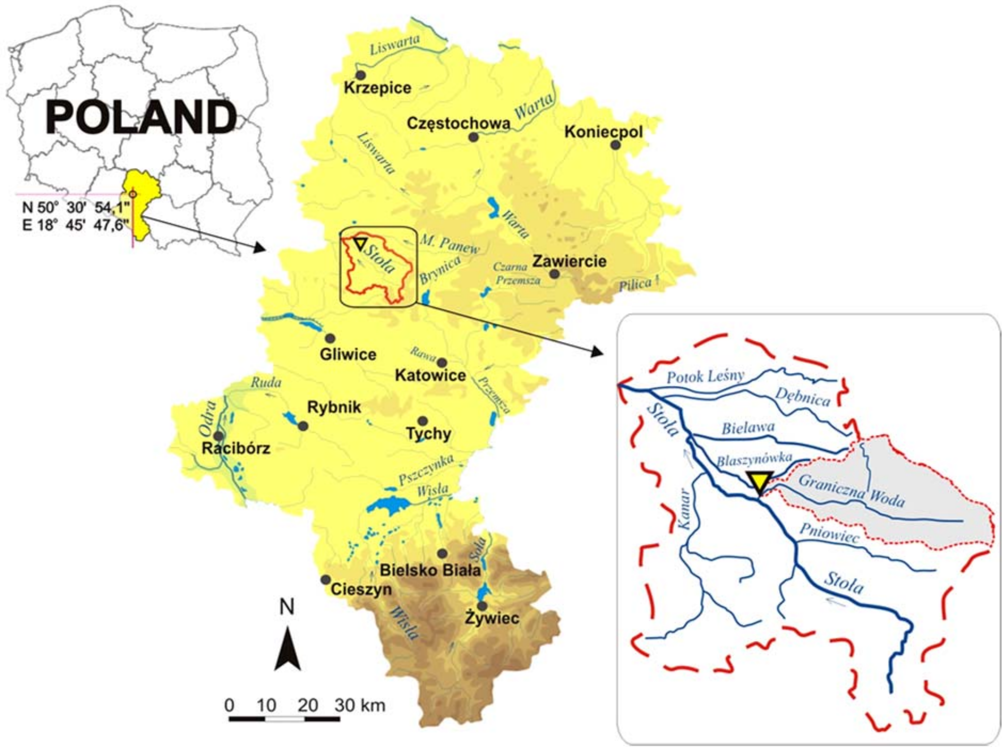

Fig. 1. Location of the measurement – control point in the Graniczna Woda stream catchment; source: own elaboration

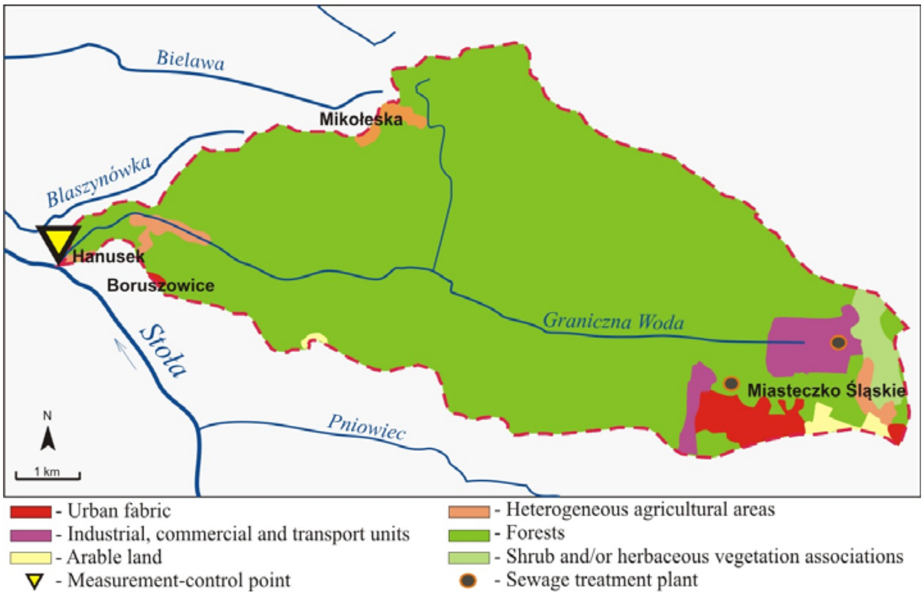

Fig. 2. Forms of land cover in the Graniczna Woda catchment; source: own studies on the basis of CORINE Land Cover 2012 [CLC 2012]

mical status was made according to the annex 9 to the order. It was assumed, that a uniform part of waters had a good chemical status if computed arithmetic mean values of the measurement results and maximum concentrations (the highest registered concentrations of the measured values) did exceed the admissible values of, respectively mean and maximum values determined for the inland surface waters. If water did not meet the above mentioned requirements, it was assumed that it did not reach good chemical status and its status was below good [Rozporządzenie MŚ... 2016b].

Seasonal variability of 28 indices over the period of investigations was determined on the basis of their monthly values in the summer and winter half-year. The material was elaborated in the winter (1.09–30.04) and summer (1.05–31.10) hydrological seasons. Statistical inference was conducted using Mann–Whitney *U* test on the significance level $\alpha = 0.05$ (p-value) to check whether the values of the parameter concentrations differed between the seasons. Median was computed for each parameter.

An analysis of time trend of 28 indices variability over the analyzed 5-year period was conducted by means of Mann–Kendall non-parametric test. The test was selected because of the lack of normality of the analyzed parameters, according to the results of Shapiro–Wilk test. The Mann–Kendal test is usually used in the analyses of climatic changes [AZIZZADEH, JAVAN 2015; KAŹMIERCZAK *et al.* 2014; SKOWERA *et al.* 2015], hydrological analyses [BANASIK *et al.* 2013; MAKSYMIUK *et al.* 2008; RUTKOWSKA, PTAK 2012] water quality analyses [CHANG 2008; HIRSH *et al.* 1991; ROGORA *et al.* 2015; ZELEŇÁKOVÁ *et al.* 2015]. It involves verification of the hypothesis about a lack of trend in data on the basis of a non-parametric correlation coefficient. A non-parametric equivalent of the correlation coefficient used in Mann–Kendall test is the rank correlation coefficient for the data sequence $\{x_1, x_2, ..., x_n\}$ and the sequence of their corresponding time moments $\{1, 2, …, n\}$, known as Kendall's tau coefficient. Kendall's tau coefficient bases on the difference between the number of conforming (in the same order) and non-conforming pairs within the observed data [MAKSYMIUK *et al.* 2008]. The non-parametric rank correlation coefficient in the test is tau (τ) statistics determined by the dependence:

$$\tau = \frac{S}{\frac{n(n-1)}{2}} \tag{1}$$

where: S = Mann–Kendall statistics; n = number of observations; $n(n - 1)$ = possible data pairs.

Tau (τ) statistics assumes values within the [–1; 1] range.

Mann–Kendall statistics of the time sequence is defined on the basis of the equation:

$$S = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \operatorname{sgn}(x_j - x_i) \tag{2}$$

where:

$$\operatorname{sgn}(x_j - x_i) = \begin{cases} 1 \text{ dla } (x_j - x_i) > 0 \\ 0 \text{ dla } (x_j - x_i) = 0 \\ -1 \text{ dla } (x_j - x_i) < 0 \end{cases} \tag{3}$$

n = the number of time sequence elements.

Basing on the standardized test Z statistics defined from the equation:

$$Z = \frac{S - \operatorname{sgn}(S)}{\sqrt{\operatorname{Var}(S)}} \tag{4}$$

where: Var(S) = variance S defined from the equation:

$$\operatorname{Var}(S) = \frac{n(n-1)(2n+5)}{18} \tag{5}$$

probability connected with standardized test Z statistics was computed [KAŹMIERCZAK *et al.* 2014]. Positive values of the statistics evidence the occurrence of the upward trend, whereas the negative values indicate a downward trend [HIRSCH *et al.* 1982]. A change on the significance level $\alpha = 0.05$ (p-value) was assumed as a statistically significant (upward or downward) trend.

RESULTS AND DISCUSSION

The assessment of the Graniczna Woda stream water on the basis of limit concentrations of individual quality indices [Rozporządzenie MŚ... 2016b] revealed that in case of the temperature, dissolved oxygen, magnesium (Mg) and 10 quality indices from the group of substances particularly harmful to the aquatic environment – arsenic (As), barium (Ba), boron (Bo), total chromium (Cr), hexavalent chromium (Cr^{6+}), copper (Cu), volatile phenols, petroleum phenols, aluminum (Al) and fluorides (F), the values admissible for class I were not exceeded (Tab. 1). Mean values of total suspended solids and total phosphorus (TP) concentrations, as well as values of BOD_5 and water pH allowed to classify the water to class II, with good potential (Tab. 1). Concentrations of: total suspended solids exceeded the limit value for class I by 3.3 $mg\cdot dm^{-3}$, total phosphorus by 0.04 $mg\cdot dm^{-3}$, BOD_5 by 0.5 mg O_2 $mg\cdot dm^{-3}$, and water pH value by 0.04. Average concentrations of the other parameters did not meet the requirements for class II. Values admissible for class II were the most exceeded for thallium (Tl), chlorides (Cl), ammonium nitrogen (NH_4-N), total Kjeldahl nitrogen (TKN) and zinc. Values of these indices were many times higher than the allowable values. Mean concentration of thallium – 0.134 $mg\cdot dm^{-3}$ was 67-times higher than the allowable concentration (0.002 $mg\cdot dm^{-3}$). Chloride concentration – 223.9 $mg\cdot dm^{-3}$ was 12-times higher, ammonium nitrogen (NH_4-N) over 10 times, and total Kjeldahl nitrogen (TKN) concentration exceeded the limit value for class II almost 5 times. Mean concentration of zinc (Zn) – 3.58 $mg\cdot dm^{-3}$ was almost 3.5 times higher than the standard value. Moreover, also over 3 times higher than standard values of electrolytic conductivity (*EC*) were registered (Tab. 1). The highest water temperature during the period of investigations – 19.9°C was noted in July 2011 and the highest total suspended solids concentration – 44 $mg\cdot dm^{-3}$ in September 2012 (Tab. 1). The maximum concentrations of the analyzed biogenic indices were registered in September (NO_2-N) and November (NO_3-N) 2011, and in February (TP), in September (TN, NH_4-N, TKN) and November (PO_4-P) 2013. Considering the oxygen indices, their maximum values occurred in March 2009 (COD-Mn) and in 2001 (dissolved oxygen) in May 2010 (TOC) and July 2012 (BOD_5). The maximum values for salinity were registered in April (Mg) and June (Ca, total hardness) 2009, in May (SO_4) and October (Cl) 2012, and in November 2013 (*EC*). The highest water pH 7.7 was noted in February 2010.

Table 1. Assessment results of the potential and chemical status of the Graniczna Woda stream water (abiotic type 18)

Group	Indices	Measurement unit	Limit values for class[1)]		Assessment results of the potential and chemical status		
					range of values		average
			I	II	minimum value	maximum value	
A	temperature	°C	≤ 22	≤ 24	0.2	19.9	9.4
	total suspended solids	$mg·dm^{-3}$	≤ 9.0	≤ 15.7	2.5	44.0	12.3
B	dissolved oxygen	$mg\ O_2·dm^{-3}$	≥ 5.6	≥ 5.3	5.0	13.6	9.1
	BOD_5	$mg\ O_2·dm^{-3}$	≤ 3.0	≤ 4.5	0.5	15.0	3.5
	COD-Mn	$mg\ O_2·dm^{-3}$	≤ 7.3	≤ 9.3	7.7	15.0	12.0
	TOC	$mg\ C·dm^{-3}$	≤ 7.5	≤ 9.8	9.2	41.0	16.9
C	electrolytic conductivity	$µS·cm^{-1}$	≤ 380	≤ 491	160	6600	1463
	sulphates	$mg\ SO_4·dm^{-3}$	≤ 28.8	≤ 82.5	35.0	750.0	214.9
	chlorides	$mg\ Cl·dm^{-3}$	≤ 14.4	≤ 18.2	13.0	1100.0	223.9
	calcium	$mg\ Ca·dm^{-3}$	≤ 76.5	≤ 78.6	76.0	320.0	147.0
	magnesium	$mg\ Mg·dm^{-3}$	≤ 9.2	≤ 11.3	7.4	11.0	8.9
	total hardness	$mg\ CaCO_3·dm^{-3}$	≤ 225.0	≤ 266.0	59.0	769.0	291.6
D	water pH	–	7.4–8.1	6.7–8.1	6.3	7.7	7.0
E	ammonium nitrogen	$mg\ N\text{-}NH_4·dm^{-3}$	≤ 0.19	≤ 0.635	0.66	32.00	6.39
	total Kjeldahl nitrogen	$mg\ N·dm^{-3}$	≤ 1.0	≤ 1.6	1.0	46.0	7.9
	nitrate nitrogen	$mg\ N\text{-}NO_3·dm^{-3}$	≤ 0.7	≤ 2.2	0.44	18.00	2.60
	nitrite nitrogen	$mg\ N\text{-}NO_2·dm^{-3}$	≤ 0.01	≤ 0.03	0.004	0.52	0.07
	total nitrogen	$mg\ N·dm^{-3}$	≤ 2.2	≤ 3.8	1.9	49.0	9.5
	phosphate phosphorus (V)	$mg\ P\text{-}PO_4·dm^{-3}$	≤ 0.065	≤ 0.101	0.025	0.331	0.173
	total phosphorus	$mg\ P·dm^{-3}$	≤ 0.20	≤ 0.33	0.03	1.00	0.24
F	arsenic	$mg\ As·dm^{-3}$	≤ 0.05	≤ 0.05	< 0.01	0.04	–
	barium	$mg\ Ba·dm^{-3}$	≤ 0.5	≤ 0.5	0.06	0.11	0.08
	boron	$mg\ B·dm^{-3}$	≤ 2	≤ 2	0.04	0.37	0.18
	hexavalent chromium	$mg\ Cr^{6+}·dm^{-3}$	≤ 0.02	≤ 0.02	0.0025	< 0.005	–
	total chromium	$mg\ Cr·dm^{-3}$	≤ 0.05	≤ 0.05	0.005	< 0.01	–
	zinc	$mg\ Zn·dm^{-3}$	≤ 1	≤ 1	0.25	31.00	3.58
	copper	$mg\ Cu·dm^{-3}$	≤ 0.05	≤ 0.05	< 0.005	0.009	–
	volatile phenols	$mg·dm^{-3}$	≤ 0.01	≤ 0.01	0.0005	< 0.001	–
	petroleum phenols	$mg·dm^{-3}$	≤ 0.2	≤ 0.2	0.025	< 0.05	–
	aluminum	$mg\ Al·dm^{-3}$	≤ 0.4	≤ 0.4	0.13	1.60	0.38
	thallium	$mg\ Tl·dm^{-3}$	≤ 0.002	≤ 0.002	0.010	0.404	0.134
	fluorides	$mg\ F·dm^{-3}$	≤ 1.5	≤ 1.5	0.22	2.90	1.13
G	cadmium and its compounds	$µg·dm^{-3}$	≤ 0.25[2)] (1.5[3)])		12.0	1060.0	94.82
	lead and its compounds	$µg·dm^{-3}$	≤ 1.2 (14[3)])		5.6	230.0	74.3

– class I maximum potential; – class II good potential; – not fulfilled requirements for class II potential below good; – good chemical status; – chemical status below good

[1)] Mean annual values. [2)] For water hardness class V: ≥200 mg $CaCO_3·dm^{-3}$. [3)] Maximum allowable concentration.
Explanations: Group of indices characterizing: A = physical status, including thermal conditions; B = oxygen (oxygenation) conditions and organic pollutants; C = salinity; D = acidity (acidity status); E = biogenic conditions (nutrients); F = substances particularly harmful to the aquatic environment (specific synthetic and non–synthetic pollutants): G = chemical status (priority substances and other pollutants).
Source: own studies on the basis on Regulation of the Minister of Environment [Rozporządzenie MŚ... 2016b].

The maximum values of a majority of indices from the group of substances particularly harmful to the aquatic environment and all from the group of priority substances were registered in the months of the winter hydrological half-year: in November (As – 2012, Ba – 2010, B – 2011, Zn – 2010), in December (Cd – 2011, Pb – 2013), in January 2009 (F) and in March 2013 (Tl). The maximum copper (Cu) concentrations 0.009 $mg·dm^{-3}$ (Tab. 1) were registered twice – in February and May 2012. During the period of research, the maximum concentrations of Cr^{6+}, Cr, volatile phenols and petroleum hydrocarbons were noted four times in the months of the winter period and four times in the months of the summer period. Aluminum (Al) occurred in the highest concentration (1.60 $mg·dm^{-3}$) in May 2010 (Tab. 1). The stream water did not meet the requirements stated for water of good chemical status because of mean values and maximum concentrations of cadmium (Cd) and lead (Pb). Mean cadmium (Cd) concentrations exceeded the allowable values almost 400 times, whereas lead (Pb) over 60 times. The highest noted concentrations of the measured values of cadmium (Cd) and lead (Pb) exceeded, respectively over 700 and 16-times the admissible values stated for the surface waters (Tab. 1). BOJAKOWSKA and SOKOŁOWSKA [1998] obtained similar results.

Statistical analysis conducted using U Mann–Whitney test revealed, that the values of five parameters significantly differed between seasons (Tab. 2). Statistically significant differences between the summer and winter half-year were registered for: the temperature, dissolved oxygen, calcium (Ca), nitrate nitrogen (NO_3-N) and nitrite nitrogen (NO_2-N). Statistically significant higher concentration of dissolved oxygen was noted in the winter half-year, whereas Ca,

Table 2. Results of U Mann–Whitney significance test of differences between the values of selected physicochemical parameters concentrations in the Graniczna Woda stream water in winter and summer seasons

Indices	Measurement unit	Median		The values of statistics (*Z*)	Probability test (*p*)[1)]
		winter	summer		
Temperature	°C	2.7	15.2	–6.17	<0.001
Total suspended solids	$mg·dm^{-3}$	9.8	9.9	–0.53	0.597
Dissolved oxygen	$mg\ O_2·dm^{-3}$	10.7	7.3	6.06	<0.001
BOD_5	$mg\ O_2·dm^{-3}$	2.2	2.6	–1.33	0.183
COD-Mn	$mg\ O_2·dm^{-3}$	11.5	13.0	–0.81	0.420
TOC	$mg\ C·dm^{-3}$	15.0	17.0	–1.52	0.128
Electrolytic conductivity	$\mu S·cm^{-1}$	935	1050	–1.44	0.149
Sulphates	$mg\ SO_4·dm^{-3}$	165.0	180.0	–1.67	0.094
Chlorides	$mg\ Cl·dm^{-3}$	145.0	175.0	–1.32	0.186
Calcium	$mg\ Ca·dm^{-3}$	100.5	160.0	–2.09	0.037
Magnesium	$mg\ Mg·dm^{-3}$	9.3	8.8	0.32	0.747
Total hardness	$mg\ CaCO_3·dm^{-3}$	255.0	284.0	–1.48	0.140
Water pH	–	7.1	7.0	1.24	0.214
Ammonium nitrogen	$mg\ N\text{-}NH_4·dm^{-3}$	5.30	6.70	–0.88	0.380
Total Kjeldahl nitrogen	$mg\ N·dm^{-3}$	6.1	7.6	0.06	0.954
Nitrate nitrogen	$mg\ N\text{-}NO_3·dm^{-3}$	0.70	1.90	–4.18	<0.001
Nitrite nitrogen	$mg\ N\text{-}NO_2·dm^{-3}$	0.02	0.09	–4.16	<0.001
Total nitrogen	$mg\ N·dm^{-3}$	6.8	9.55	–1.01	0.312
Total phosphorus	$mg\ P·dm^{-3}$	0.21	0.19	0.98	0.329
Phosphate phosphorus (V)	$mg\ P\text{-}PO_4·dm^{-3}$	0.200	0.150	1.08	0.282
Barium	$mg\ Ba·dm^{-3}$	0.08	0.08	1.16	0.246
Boron	$mg\ B·dm^{-3}$	0.13	0.18	–0.21	0.833
Zinc	$mg\ Zn·dm^{-3}$	1.30	1.00	0.78	0.434
Aluminum	$mg\ Al·dm^{-3}$	0.29	0.25	0.68	0.494
Thallium	$mg\ Tl·dm^{-3}$	0.240	0.063	1.47	0.142
Fluorides	$mg\ F·dm^{-3}$	0.78	1.30	–1.45	0.146
Cadmium and its compounds	$\mu g·dm^{-3}$	0.048	0.045	0.36	0.721
Lead and its compounds	$\mu g·dm^{-3}$	0.049	0.049	–0.08	0.936

[1)] Statistical values indicating statistically important differences on the level $\alpha = 0.05$.
Source: own study.

NO_3-N, NO_2-N and the temperature values in the summer period. Also higher, but statistically not proven values were registered for the other oxygen indices, a majority of biogenic and salinity values and total suspended solids. KOWALIK *et. al.* [2012] obtained similar results. In the winter half-year higher values, but statistically not proven were noted for magnesium (Mg), water pH, total phosphorus (TP) and phosphate phosphorus (V) (PO_4-P). Median values of most quality indices from the group of substances particularly harmful to the aquatic environment and from the group of priority substances were higher in the winter half-year. Only boron (B) and fluorides (F) assumed higher values in the summer season, whereas in both half-years median value for barium (Ba) and lead (Pb) was the same, respectively 0.08 $mg·dm^{-3}$ and 0.049 $\mu g·dm^{-3}$ (Tab. 2).

The discussed sequence of values of the analyzed parameters for the years 2009–2013 revealed an upward trend in the stream water for all indices characterizing physical status and biogenic conditions, but also for a majority of the analyzed indices from the group of substances particularly harmful to the aquatic environment and salinity. MIATKOWSKI and SMARZYŃSKA [2014] obtained similar results. Considering the other parameters, the negative results of Mann–Kendall statistics pointed to the occurrence of downward tendencies (Tab. 3).

Statistically significant upward trends were noted for six parameters – total suspended solids, electrolytic conductivity (*EC*), sulphates (SO_4), chlorides (Cl), nitrite nitrogen (NO_2-N) and zinc (Zn). Statistically significant downward trends were observed only for total hardness. Values of zinc (Zn), lead (Pb) and nitrite nitrogen (NO_2-N) concentrations over the period of research revealed definitely the highest random variability. Coefficients of variance were as follows: 205, 164 and 149% (Tab. 3). The lowest coefficient of variance characterized: water pH, magnesium (Mg), barium (Ba) and COD-Mn.

CONCLUSIONS

Quality of the water outflow from a river catchment area to a great extent depends on the dominant land use type [MIATKOWSKI, SMARZYŃSKA 2014]. In forest catchments, at a lack of anthropogenic transformations, pollutant loads carried by watercourses are conditioned mainly by the effect of physiographic and natural factors [KANOWNIK *et al.* 2013; KOWALIK *et al.* 2012]. Although forests and areas covered by bushes constitute a considerable part of the total area of the Graniczna Woda catchment, the obtained results evidence a high anthropogenic pressure on the stream wa ter. It was found, that both the potential

Table 3. Variability measures and rank assessment (Kendall's tau statistics) of the trend of selected physicochemical parameters changes in the Graniczna Woda stream water in 2009–2013

Indices	Measurement unit	Standard deviation $mg \cdot dm^{-3}$	Variation coefficient %	Rank statistics of the trend (Kendall tau)	Test statistic (*Z*)	Probability test (*p*)[1)]	Trend of changes
Temperature	°C	6.5	69	0.080	0.87	0.383	0
Total suspended solids	$mg \cdot dm^{-3}$	9.7	78	0.286	2.86	0.004	↑
Dissolved oxygen	$mg\ O_2 \cdot dm^{-3}$	2.2	24	–0.137	–1.49	0.136	0
BOD_5	$mg\ O_2 \cdot dm^{-3}$	3.4	98	0.145	1.57	0.116	0
COD-Mn	$mg\ O_2 \cdot dm^{-3}$	2.1	17	–0.344	–1.56	0.120	0
TOC	$mg\ C \cdot dm^{-3}$	6.1	36	–0.005	–0.06	0.954	0
Electrolytic conductivity	$\mu S \cdot cm^{-1}$	1211	83	0.350	3.81	< 0.001	↑
Sulphates	$mg\ SO_4 \cdot dm^{-3}$	137.8	64	0.329	3.29	< 0.001	↑
Chlorides	$mg\ Cl \cdot dm^{-3}$	191.9	86	0.221	2.22	0.026	↑
Calcium	$mg\ Ca \cdot dm^{-3}$	81.3	55	0.076	0.35	0.730	0
Magnesium	$mg\ Mg \cdot dm^{-3}$	1.1	12	–0.202	–0.91	0.361	0
Total hardness	$mg\ CaCO_3 \cdot dm^{-3}$	149.2	51	–0.233	–2.53	0.011	↓
Water pH	–	0.3	4	–0.157	–1.71	0.087	0
Ammonium nitrogen	$mg\ N\text{-}NH_4 \cdot dm^{-3}$	4.56	71	0.061	0.67	0.504	0
Total Kjeldahl nitrogen	$mg\ N \cdot dm^{-3}$	6.3	80	0.045	0.49	0.623	0
Nitrate nitrogen	$mg\ N\text{-}NO_3 \cdot dm^{-3}$	3.67	141	0.032	0.35	0.728	0
Nitrite nitrogen	$mg\ N\text{-}NO_2 \cdot dm^{-3}$	0.10	149	0.233	2.34	0.019	↑
Total nitrogen	$mg\ N \cdot dm^{-3}$	6.9	73	0.046	0.50	0.620	0
Total phosphorus	$mg\ P \cdot dm^{-3}$	0.16	69	0.070	0.77	0.444	0
Phosphate phosphorus (V)	$mg\ P\text{-}PO_4 \cdot dm^{-3}$	0.086	50	–0.138	–1.10	0.267	0
Barium	$mg\ Ba \cdot dm^{-3}$	0.01	16	–0.076	–0.41	0.681	0
Boron	$mg\ B \cdot dm^{-3}$	0.09	52	0.239	1.29	0.196	0
Zinc	$mg\ Zn \cdot dm^{-3}$	7.34	205	0.396	2.71	0.006	↑
Aluminum	$mg\ Al \cdot dm^{-3}$	0.36	95	0.136	0.73	0.464	0
Thallium	$mg\ Tl \cdot dm^{-3}$	0.123	92	0.111	0.60	0.550	0
Fluorides	$mg\ F \cdot dm^{-3}$	0.70	62	0.063	0.28	0.777	0
Cadmium and its compounds	$\mu g \cdot dm^{-3}$	155.58	164	–0.037	–0.41	0.685	0
Lead and its compounds	$\mu g \cdot dm^{-3}$	70.8	95	–0.062	–0.28	0.781	0

[1)] The trend significant at $p < 0.05$.
Explanations: ↓ – downward trend; ↑ – upwards trend; 0 = lack of statistically significant trend.
Source: own study.

and chemical status of the stream water were below good. Exceeded limit values for quality class II noted for oxygen and organic indices (COD-Mn, TOC), salinity (*EC*, SO_4, Cl, Ca and total hardness), biogenic indices (except TP) and substances particularly harmful to the aquatic environment (Zn and Tl), as well as exceeded heavy metal concentrations, may evidence a constant inflow of pollutants from municipal and industrial sewage to the Graniczna Woda stream. Statistically significant upward trends were registered over the period of investigations for the values for electrolytic conductivity (*EC*) and total suspended solids concentrations, chlorides (CL), sulphates (SO_4), nitrite nitrogen (NO_2-N) and zinc in the stream water. Statistically significant downward trend was observed for only one parameter – total hardness. Analysis of seasonality revealed, that statistically significantly higher concentrations of nitrite nitrogen (NO_2-N), nitrate nitrogen (NO_3-N), calcium (Ca) and water temperature occurred in the summer rather than winter half-year. Water out flowing with the Graniczna Woda stream may affect water quality in the whole catchment of the Stoła and Mała Panew rivers, therefore further research on the stream water in view of its quality should be continued.

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Dynamika stężeń parametrów fizykochemicznych w wodzie potoku Graniczna Woda

STRESZCZENIE

W pracy przedstawiono zmienność wartości wybranych parametrów fizykochemicznych oraz określono potencjał i stan chemiczny wody potoku Graniczna Woda, prawostronnego dopływu rzeki Stoły. Obszar zlewni potoku, o powierzchni 41,5 km^2, zajmują głównie tereny leśne oraz w mniejszym stopniu tereny zurbanizowane, przemysłowe i użytki rolne. Potok nizinny żwirowy (typ abiotyczny 18) przepływa przez północną część Górnośląskiego Okręgu Przemysłowego oraz gminy Tworóg, Tarnowskie Góry i Miasteczko Śląskie. Na terenie Miasteczka Śląskiego funkcjonuje biologiczno-mechaniczna oczyszczalnia ścieków komunalnych i zakładowa oczyszczalnia ścieków Huty Cynku „Miasteczko Śląskie". Bazę danych wykorzystanych w pracy stanowiły wyniki, pozyskane z Wojewódzkiego Inspektoratu Ochrony Środowiska w Katowicach, comiesięcznych analiz próbek wody pobranej z potoku w latach 2009–2013 w punkcie pomiarowo-kontrolnym usytuowanym w miejscowości Hanusek, przy odcinku ujściowym do rzeki Stoły. W pracy przeanalizowano, zgodnie z obowiązującym rozporządzeniem MŚ z 2016 r., 34 wskaźniki fizykochemiczne. W okresie badań ustalono istotnie statystycznie trendy rosnące wartości przewodności elektrycznej (*EC*) i stężenia zawiesiny ogólnej, chlorków (Cl), siarczanów (SO_4), azotu azotanowego (III) (N-NO_2) oraz cynku (Zn) w wodzie potoku. Statystycznie istotny trend malejący stwierdzono w odniesieniu tylko do jednego parametru – twardości ogólnej. Stwierdzono, że potencjał i stan chemiczny wody potoku były poniżej dobrego. Przekroczone wartości graniczne dla II klasy jakości stwierdzone w przypadku wskaźników tlenowych i organicznych (chemiczne zapotrzebowanie na tlen – ChZT-Mn, ogólny węgiel organiczny – OWO, zasolenia (*EC*, SO_4, Cl, wapń – Ca, twardość ogólna), biogennych (azot amonowy – N-NH_4, azot Kjeldahla, azot azotanowy (V) – N-NO_3, azot azotanowy (III) – N-NO_2, azot ogólny – N, fosfor fosforanowy (V) – P-PO_4) i substancji szczególnie szkodliwych dla środowiska wodnego (cynk – Zn, tal – Tl) oraz przekroczone dopuszczalne wartości stężenia metali ciężkich (ołów – Pb, kadm – Cd), mogą świadczyć o ciągłym dopływie zanieczyszczeń do środowiska wodnego potoku Graniczna Woda ze ścieków komunalnych oraz przemysłowych.

Słowa kluczowe: *jakość wody, metale ciężkie, parametry fizykochemiczne, trend, Śląsk, zanieczyszczenia antropogeniczne*