

VARIABILITY OF VALUES OF PHYSICO-CHEMICAL WATER QUALITY INDICES ALONG THE LENGTH OF THE IWONICZANKA STREAM

Andrzej Bogdał¹, Tomasz Kowalik¹

¹ Department of Land Reclamation and Environmental Development, University of Agriculture in Krakow, Al. Mickiewicza 24–28, 30–059 Kraków, Poland, e-mail: rmbogdal@cyf-kr.edu.pl; rmkowali@cyf-kr.edu.pl

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ABSTRACT

The paper aims at presentation of the effect of changes in the catchment area management on the value of water quality physicochemical indices along the length of the Iwoniczanka stream, which flows through Iwonicz-Zdrój, one of the oldest health resorts in Poland. Analyses of 14 water quality indices were conducted from November 2013 to May 2014 in five measurement points: two situated in the upper course of the stream – in forest areas, two located in the area of Iwonicz-Zdrój town, and one below the rural built-up area. On the basis of the conducted data analysis it was found that the mean values of pH, electrolytic conductivity, sulphates, calcium, total iron and manganese were increasing with the course of flowing water, as evidenced by the water enrichment in substances which had their sources in built-up areas. On average, the highest values of biogenic indices and chlorides but the lowest values of oxygen indices were registered immediately below the location of drain collector from the closed sewage treatment plant, which resulted in pollution of the analysed stream bed with the substances previously drained from the treatment plant. Water flowing through the forest areas had the maximum ecological potential in the built-up areas and due to phosphate concentrations it was classified to class II and then, due to self-purification, returned to the physicochemical parameters appropriate for class I water. The conducted hydro-chemical tests confirmed a significant negative effect of built-up areas on the quality of the flowing waters.

Keywords: water quality parameters, ecological potential, anthropogenic pollution.

INTRODUCTION

Water, which is a natural resource of the natural environment, is prone to pollution at almost each stage of its hydrogeological cycle. It leads to decreasing its quality parameters, and therefore, to reducing the possible utilization of its resources for environmental or economic purposes of people [Roger 1994, Bogdał and Ostrowski 2007, Bulut et al. 2010, Hus and Pulikowski 2011, Kanownik and Rajda 2011].

Water resources are one of the most important environmental components stimulating civilizational and economic development of countries. On the territory of Poland surface water resources are small and irregularly distributed in space and time. For these reasons, while using and shaping

such meagre resources, one should remember to proceed in compliance with the principles of sustainable development, which assume bringing together the resources protection with a complex and multifunctional management of rural areas [Rilp and Hildmann 2000, Koc and Glińska-Leszczuk 2004, Sobczyński and Joniak 2013, Kanownik and Rajda 2011].

Deteriorating state of water quality is the driver of increasingly intensive investigations aiming at understanding the processes occurring in the aquatic environment and associated hydrological characteristics. Important pollution sources of surface waters in the rural areas are, among others, municipal sewage, animal husbandry wastes, precipitations and chemicals used in agriculture [Koc and Glińska-Leszczuk 2004,

Ostrowski et al. 2005, Aydin 2007, Kupiec 2010, Hus and Pulikowski 2011, Kanownik and Rajda 2011, Kowalik et al. 2014, Policht-Latawiec et al. 2014]. Hydrochemistry of rain undergoes constant changes resulting from the location with respect to pollutant emitters, the weather conditions and processes occurring in the atmosphere. On the other hand, changes of physicochemical properties of surface waters, including seasonal changes, are the resultant of the pollutant inflow from anthropogenic sources and natural erosion processes, air and water temperature, plant vegetation, etc. [Hillbricht-Ilkowska 1994, Grosbois et al. 2001, Glińska-Leszczuk 2002, Wiatkowski and Paul 2009, Balcerzak and Rybicki 2011, Kowalik et al. 2014].

The quality of surface waters should be constantly under control, which would allow for possible determining the needs concerning their protection against contamination. It is particularly important in the mountain and highland areas, which determine water management of the lower situated areas of Poland [Szalińska and Dominik 2006, Policht-Latawiec et al. 2014]. For many years point sources of contamination were considered the main cause of deterioration of surface water quality. Over the years, it was noticed that despite its reduction or even elimination, water quality did not improve or got only slightly better. The cause are the pollutants originating from area sources, connected with precipitation and agricultural use of soil. In order to be able to solve the problem of natural environment pollution, it becomes necessary to constantly broaden the knowledge about its functioning, but also about the causes and effects of pollution of the individual environmental components, including waters [Smoroń 1998, Ostrowski et al. 2005, Liberacki and Szafranski 2008, Sojka et al. 2008, Wiatkowski and Paul 2009, Kupiec 2010, Wiatkowski et al. 2012].

The paper aims at presenting the effect of changes in the catchment area management on the value of physicochemical indices of water quality along the length of the Iwoniczanka stream, which flows through Iwonicz-Zdrój, one of the oldest health resorts in Poland.

MATERIAL AND METHODS

The Iwoniczanka stream, whose water quality is the subject of the present paper, flows from the southern slopes of the Przymiarki mountain

range situated by the north-eastern boundaries of Lubatowa village (Podkarpackie voivodship, Poland). It flows through Iwonicz-Zdrój town and through the area of Iwonicz village, flowing into the Lubatówka river at the 11.4 km of its course. On the bases of the physiographic study conducted by the authors it was established that the length of the Iwonicznka stream is 13.92 km and its catchment area is 25.36 km². The Iwonicznka is strongly changed uniform part of surface waters (JCWP) and regarding abiotic factors it is classified to type 12 flysch streams. The area of the Iwoniczanka catchment is situated in the Outer Western Carpathian province (513), within the range of two macroregions: Small Beskidy Mts. (from the south, 513.71) and Bukowskie Foothills (from the north, 513.69). Both physico-geographical units differ with their relief. In the northern part of the catchment, arable lands and grasslands prevail, occupying totally about 60% of the area. Forest complexes located mainly in the southern part of the catchment cause that the afforestation of the area is on the level of 23%. A considerable part of the catchment is occupied by a built-up area (Figure 1); its quite large share makes up 13.9%. In the upper course of the Iwoniczanka stream water is taken for water supply systems. Sewage originating from the localities composing Iwonicz-Zdrój district is drained to a collective sewage treatment plant in Krosno.

Physicochemical water quality indices in the Iwoniczanka stream were investigated from November 2013 to May 2014 in the laboratories of Department of Land Reclamation and Environmental Development, University of Agriculture in Krakow. Samples were collected in five measurement points situated along the length of the Iwoniczanka stream (Figure 1). The first was located at km 4+670 of the stream course, below Iwonicz urban built-up area, the second (km 5+870) between Iwonicz village and Iwonicz-Zdrój town, the third (km 7+080) in Iwonicz-Zdrój town – 20 m below the site where a collector from sewage treatment plans used to be situated until 21 February 2012, the fourth (km 11+540) immediately above Iwonicz-Zdrój built-up area – below the water intake for water treatment plant and the fifth (km 12+040) in the upper part of the catchment (Figure 1). 14 physicochemical indices from the indices group of acidification (pH), oxygen (oxygen saturation degree, dissolved oxygen), biogenic (phosphates – PO_4^{-3} , ammonium nitrogen – N-NH_4^+ , nitrite nitrogen N-NO_2^- , nitrate

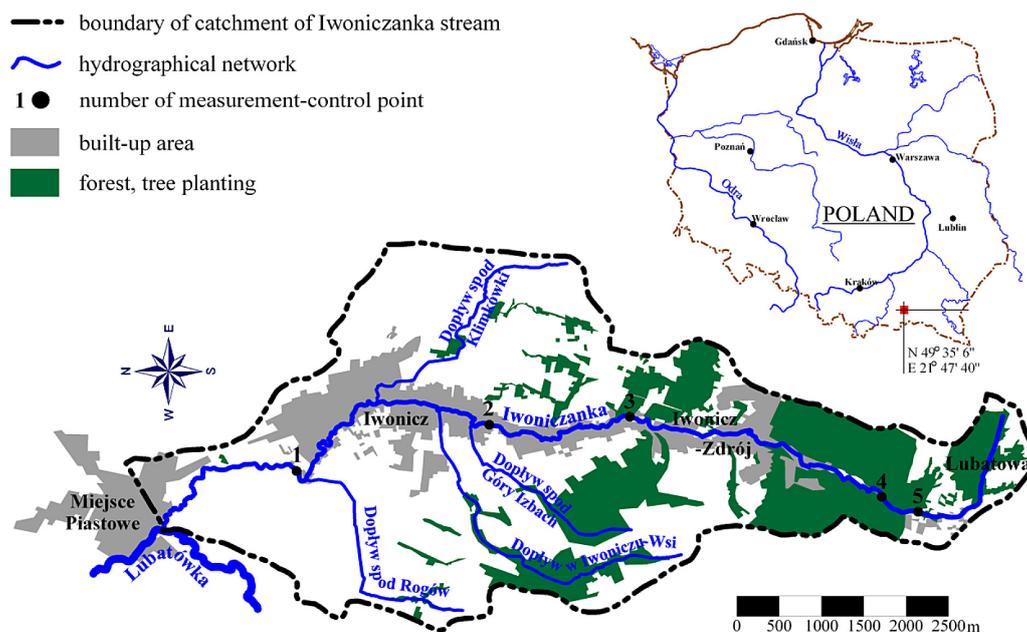


Figure 1. Use and location of the Iwoniczanka stream catchment and location of measurement-control points

nitrogen – N-NO_3^-), salinity (electrolytic conductivity, sulphates SO_4^{2-} , chlorides – Cl^- , calcium Ca^{2+} , magnesium – Mg^{2+}) and metals (total iron – Fe_{total} and manganese – Mn^{2+}) were determined in the water samples using referential methods [Rozporządzenie MŚ 2011].

The minimum and maximum values were determined. Arithmetic mean, standard deviation and variation coefficient were computed for each analysed water quality index. Moreover, the values of the analyzed physicochemical indices were subjected to a detailed statistical analysis, which verified the normality of data distributions by means of Shapiro-Wilk test and the homogeneity of variances in groups using Brown-Forsythe test. Because a number of empirical data groups were compared, out of which no normality of distributions was found for a majority of cases, a non-parametric Kruskal-Wallis test was used for the estimation of the significance of differences between the values of water quality indices tested in different measurement points.

A cluster analysis was conducted on the basis of the obtained physicochemical indices to group the measurement points regarding the similarity of water quality in the Iwoniczanka stream. Estimation of the distances between the clusters was conducted by means of Ward agglomerative method with Euclidean distances, which bases on the analysis of variance and aims at minimizing the sum of squares of any two clusters. The analysis was conducted by means of a licensed

computer software STATISTICA 10, in four variants using:

- oxygen indices (dissolved oxygen, oxygen saturation degree),
- biogenic indices (phosphates, ammonium nitrogen, nitrite and nitrate nitrogen),
- salinity indices (electrolytic conductivity, sulphates, chlorides, calcium and magnesium),
- all 14 analysed physicochemical indices.

Since the analysed water quality indices are stated in various units and have very different range of values, the empirical data were standardized in order to make them comparable and avoid the load phenomenon. The cluster analysis yielded the hierarchy of clusters presented as dendrograms.

The assessment of ecological potential of the Iwoniczanka stream water was made in each measurement-control point in compliance with the Regulation of the Minister of the Environment of 23 October, 2013 on the classification of the uniform parts of surface waters and environmental quality standards for priority substances [Rozporządzenie MŚ 2014].

RESULTS

Mean values of pH, electrolytic conductivity, sulphates, calcium, total iron and manganese (Table 1) were increasing with the course of flowing water in the Iwoniczanka stream. The reason for

Table 1. Statistical parameters describing selected water quality indicators in the Iwoniczanka stream

Water quality indicators	The values specified by standards		Point 1 (km 4+670)			Point 2 (km 5+870)			Point 3 (km 7+080)			Point 4 (km 11+540)			Point 5 (km 12+040)		
	I	II	range mean	SD	CV [%]												
pH	6-8.5	6-9	8.02-8.72 8.38	0.23	3	7.91-8.76 8.33	0.25	3	7.95-8.69 8.26	0.26	3	7.94-8.46 8.26	0.19	2	7.61-8.43 8.12	0.28	4
Oxygen saturation degree	-	-	87-143 110	18	16	84-138 109	17	15	86-135 108	16	15	85-131 109	13	12	84-128 109	14	13
Dissolved oxygen	≥7	≥5	9.50-17.35 12.27	2.42	20	9.84-16.49 12.00	2.19	18	9.22-16.30 11.82	2.20	19	9.87-16.02 11.90	1.96	16	9.83-15.66 11.87	1.89	16
PO ₄ ³⁻	≤0.20	≤0.31	0.052-0.551 0.184	0.154	84	0.090-0.582 0.208	0.159	76	0.140-0.378 0.212	0.085	40	0.000-0.108 0.027	0.035	130	0.000-0.160 0.041	0.052	127
N-NH ₄ ⁺	≤0.78	≤1.56	0.020-0.095 0.059	0.026	44	0.012-0.112 0.052	0.039	75	0.007-0.249 0.081	0.089	110	0.000-0.028 0.006	0.011	183	0.000-0.030 0.012	0.014	117
N-NO ₂ ⁻	-	-	0.011-0.016 0.012	0.002	17	0.011-0.017 0.014	0.002	14	0.012-0.031 0.020	0.007	35	trace values	0.000	0	trace values	0.000	0
N-NO ₃ ⁻	≤2.2	≤5.0	0.369-1.610 1.172	0.478	41	0.468-1.660 1.224	0.438	36	0.860-1.620 1.293	0.272	21	0.044-1.140 0.561	0.458	82	0.016-1.040 0.488	0.426	87
Electrolytic conductivity	≤1000	≤1500	254-660 447	129	29	243-503 403	82	20	230-495 380	84	22	210-419 318	71	22	159-407 295	82	28
SO ₄ ²⁻	≤150	≤250	22.8-40.6 33.6	5.4	16	30.9-39.7 37.0	2.8	8	30.3-38.7 35.5	2.8	8	22.6-33.9 27.3	3.9	14	20.4-31.5 27.0	3.4	13
Cl ⁻	≤200	≤300	13.9-29.0 21.4	6.2	29	13.5-40.2 22.9	9.7	42	11.9-59.7 26.4	15.5	59	3.3-10.0 6.4	2.1	33	2.8-11.0 6.6	2.9	44
Ca ²⁺	≤100	≤200	69.6-91.6 81.7	7.8	10	67.2-89.6 80.3	8.9	11	64.4-89.1 77.1	9.7	13	69.1-82.9 72.7	4.6	6	66.9-81.2 73.8	5.0	7
Mg ²⁺	≤50	≤100	8.8-22.1 16.2	4.7	29	10.2-21.1 16.8	3.6	21	12.3-19.0 16.5	2.6	16	13.2-19.3 16.9	2.2	13	13.1-20.6 17.1	2.6	15
Fe _{total}	-	-	0.13-0.47 0.31	0.12	39	0.09-0.45 0.27	0.12	44	0.09-0.43 0.27	0.13	48	0.12-0.24 0.19	0.04	21	0.12-0.56 0.21	0.15	71
Mn ²⁺	-	-	0.06-0.22 0.14	0.05	36	0.05-0.21 0.13	0.04	31	0.05-0.18 0.11	0.04	36	0.03-0.20 0.09	0.05	56	0.02-0.17 0.09	0.06	67

SD – standard deviation, CV – coefficient of variance, * according to the Minister Decree [Rozporządzenie MS 2014]:

– maximum ecological potential	class I	class II	– good ecological potential
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this state of affairs was surface water enrichment in the substances which have their sources in the built-up areas and their runoffs with precipitation waters from the roads and premises. Along the whole analysed reach of the Iwoniczanka, its water contained similar amounts of oxygen, however on average more advantageous oxygen conditions were in points 1 and 2 (Table 1), which is connected with a higher flow velocity in the regulated river bed. On average highest values of all analysed biogenic indices and chlorides, but the lowest values of oxygen indices were registered in point 3 (Table 1), situated 20 m below the place where 9 months earlier drain collector of low efficient sewage treatment plant used to be located. Despite its closure, water quality in this place is still the worst, which may be due to the Iwoniczanka bed pollution with the substances formerly drained from the sewage treatment plant. It may

be also supposed that with time, both in this place and below it the water quality will improve. The more so, as even now a decrease in biogens concentrations and improvement of oxygen conditions as a result of water self-purification processes may be observed in points 1 and 2 (Table 1).

On the basis of variation coefficient (CV), which is an objective and comparable measure of empirical data deviation from the mean values, it may be inferred about the random variability of water physicochemical characteristics of water. In case of the investigated waters of the Iwonicznaka stream one may speak about a low variability ($CV \leq 20\%$) of pH value, oxygen saturation degree, dissolved oxygen, sulphates and calcium. The greatest dynamics of changes, with some exceptions, was observed for phosphate concentrations and ammonium nitrogen – $CV \geq 60\%$ (Table 1).

Table 2. Comparison of water quality indicators values using non-parametrical Kruskala-Wallis test

pH [-]						Oxygen saturation degree [%]					Dissolved oxygen [mg O ₂ ·dm ⁻³]						
Pkt		1	2	3	4	Pkt		1	2	3	4	Pkt		1	2	3	4
	Me	8.44	8.34	8.26	8.30		Me	111	109	110	111		Me	11.87	11.53	11.36	11.48
2		8.34	1.00			2		109	1.00			2		11.53	1.00		
3		8.26	1.00	1.00		3		110	1.00	1.00		3		11.36	1.00	1.00	
4		8.30	1.00	1.00	1.00	4		111	1.00	1.00	1.00	4		11.48	1.00	1.00	1.00
5		8.13	0.42	1.00	1.00	5		108	1.00	1.00	1.00	5		11.55	1.00	1.00	1.00
PO ₄ ³⁻ [mg·dm ⁻³]						N-NH ₄ ⁺ [mg·dm ⁻³]					N-NO ₂ ⁻ [mg·dm ⁻³]						
Pkt		1	2	3	4	Pkt		1	2	3	4	Pkt		1	2	3	4
	Me	0.145	0.160	0.170	0.015		Me	0.055	0.050	0.040	0.000		Me	0.012	0.014	0.018	0.000
2		0.160	1.00			2		0.050	1.00			2		0.014	1.00		
3		0.170	1.00	1.00		3		0.040	1.00	1.00		3		0.018	0.95	1.00	
4		0.015	0.03	0.01	0.00	4		0.000	0.01	0.04	0.03	4		0.000	0.05	0.01	0.00
5		0.025	0.04	0.04	0.01	5		0.007	0.04	0.04	0.05	5		0.000	0.05	0.01	0.00
N-NO ₃ ⁻ [mg·dm ⁻³]						Electrolytic conductivity [μS·cm ⁻¹]					SO ₄ ²⁻ [mg·dm ⁻³]						
Pkt		1	2	3	4	Pkt		1	2	3	4	Pkt		1	2	3	4
	Me	1.434	1.444	1.296	0.338		Me	454	392	389	307		Me	33.6	37.6	36.1	26.3
2		1.444	1.00			2		392	1.00			2		37.6	1.00		
3		1.296	1.00	1.00		3		389	1.00	1.00		3		36.1	1.00	1.00	
4		0.338	0.03	0.04	0.03	4		307	0.04	0.92	1.00	4		26.3	0.04	0.00	0.03
5		0.350	0.04	0.04	0.02	5		297	0.03	0.34	0.83	5		27.4	0.04	0.00	0.03
Cl ⁻ [mg·dm ⁻³]						Ca ²⁺ [mg·dm ⁻³]					Mg ²⁺ [mg·dm ⁻³]						
Pkt		1	2	3	4	Pkt		1	2	3	4	Pkt		1	2	3	4
	Me	20.5	19.5	21.8	6.2		Me	80.4	80.9	75.9	70.6		Me	16.6	16.6	17.2	17.2
2		19.5	1.00			2		80.9	1.00			2		16.6	1.00		
3		21.8	1.00	1.00		3		75.9	1.00	1.00		3		17.2	1.00	1.00	
4		6.2	0.01	0.01	0.00	4		70.6	0.29	0.76	1.00	4		17.2	1.00	1.00	1.00
5		6.7	0.01	0.01	0.00	5		73.6	0.61	1.00	1.00	5		17.4	1.00	1.00	1.00
Fe _{total} [mg·dm ⁻³]						Mn ²⁺ [mg·dm ⁻³]					Water quality indicator						
Pkt		1	2	3	4	Pkt		1	2	3	4	Pkt		1	2	3	4
	Me	0.36	0.22	0.23	0.19		Me	0.15	0.13	0.11	0.10		Me	Me	Me	Me	Me
2		0.22	1.00			2		0.13	1.00			2		Me	p		
3		0.23	1.00	1.00		3		0.11	1.00	1.00		3		Me	p	p	
4		0.19	1.00	1.00	1.00	4		0.10	0.72	1.00	1.00	4		Me	p	p	p
5		0.15	0.40	1.00	1.00	5		0.10	0.76	1.00	1.00	5		Me	p	p	p

Me – median, p – probability test, * **bold type** indicates significant differences (for $\alpha = 0.05$).

On the basis of the average values of 10 investigated physicochemical indices and values permissible for individual quality classes [Rozporządzenie MŚ 2014] it was established that water in points 1, 4 and 5 had a maximum ecological potential. On the other hand, due to raised phosphate concentrations in points 2 and 3, the water was classified to class II – good ecological potential (Table 1).

Analysis of the empirical data conducted using Kruskal-Wallis test on the significance level $\alpha = 0.05$ revealed, that there are no statistically significant differences between the values of all tested water quality indices in points 1, 2 and 3. The differences between the values of indices noted in points 4 and 5 also proved statistically insignificant (Table 2).

However, clear and statistically higher values were registered between the groups of points (1, 2 and 3 – 4 and 5) for the following indices: phosphates, ammonium nitrogen, nitrite nitrogen, ni-

trate nitrogen, sulphates and chlorides. Moreover, a higher electrolytic conductivity was measured in point 1 than in two points situated in the upper course of the Iwoniczanka, i.e. in points 4 and 5 (Table 2). The results of statistical test confirm the major impact of the area management on water quality, in this case settlements or forest.

Four dendrograms (Figure 2), showing the similarity of water quality in the individual measurement points, were obtained in result of the cluster analysis conducted using Ward method separately for oxygen, biogenic and salinity indices, and jointly for all 14 analysed physicochemical indices. For the oxygen indices, three clusters were obtained at the bond distance on level 2 (Figure 2a): the first comprising only point 1, in which the most advantageous oxygen conditions were noted in the water, the second comprising point 2 and points 4 and 5 in which a medium water saturation with oxygen was noted and the third cluster composed of point 3, where

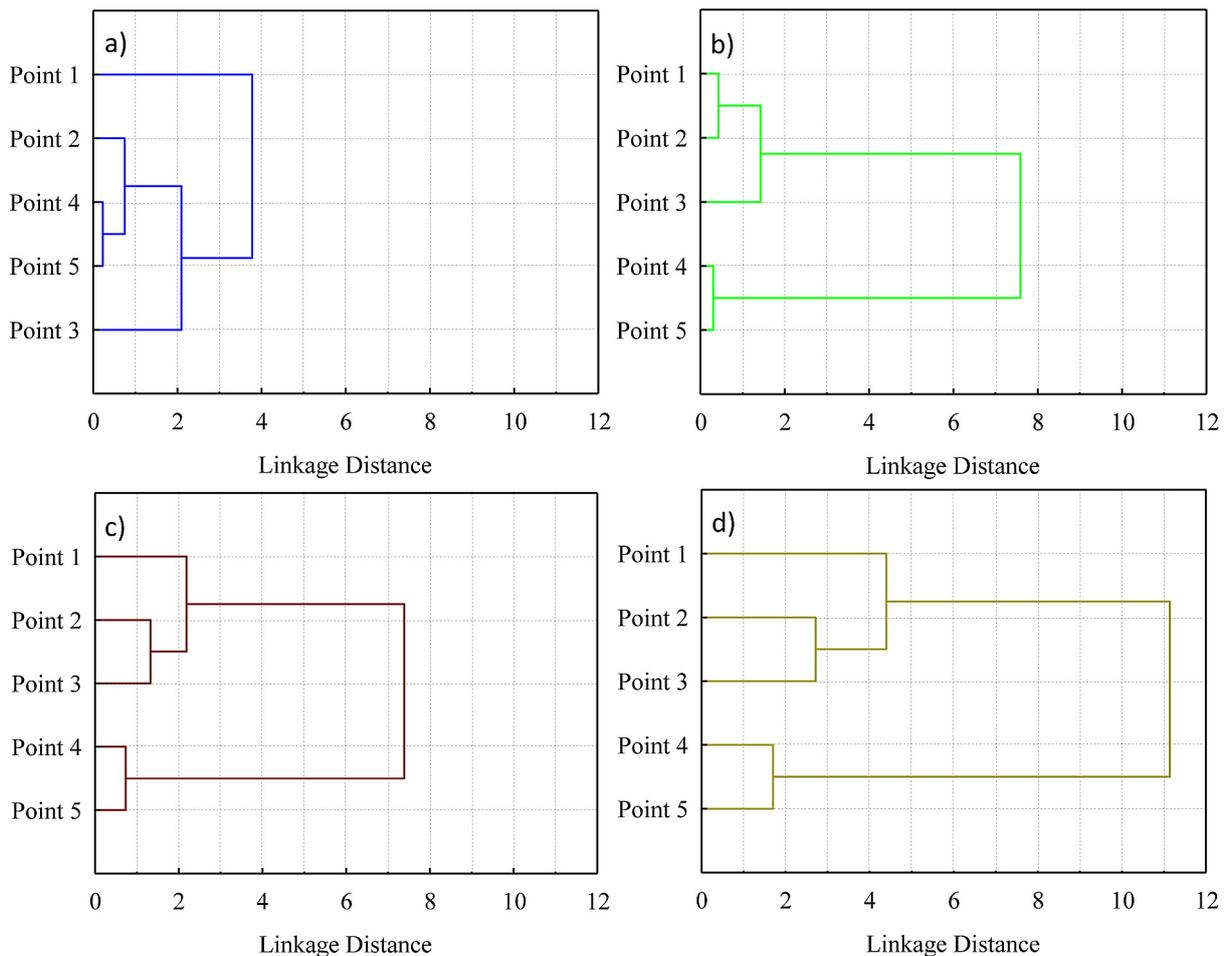


Figure 2. The dendrograms (Ward's method – Eukclidean Distance) showing similarity of surface water quality examined in individual measurement-control points, taking into account the values of: a) oxygen indicators, b) nutrient indicators, c) salinity indicators, d) all examined physicochemical indicators

water containing the least of dissolved oxygen and the least saturated with oxygen was observed. Due to biogenic indices, also at the bond distance on level 2, two clusters formed (Figure 2b): the first comprising points 1, 2 and 3 with quite high biogen concentrations and the second made up of points 4 and 5, in which water contained much lower amounts of biogenic substances. Water salinity was very similar (Figure 2c) in two pairs of measurement-control points – 2 and 3, and in 4 and 5, however, the values of salinity indices were much lower in the second pair of points. Slightly different water salinity occurred in point 1, but it was similar to observed in points 2 and 3. Considering all the tested indices, the similarity of water quality between points was less noticeable than in the previous variants, because only at the bond distance on the level 5, two clusters formed (Figure 2d): the first comprising points 1, 2 and 3 situated in the urban and rural built-up areas, where water had less favourable physicochemical parameters than in points 4 and 5, which were situated in the upper course of the Iwoniczanka river, in forest areas (cluster two).

CONCLUSIONS

The following conclusions can be drawn from the analysis of data obtained over several months of hydrochemical testing of water flowing into the Iwoniczanka stream:

1. Mean values of pH, electrolytic conductivity, sulphates, calcium, total iron and manganese were increasing with the course of flowing water, which was caused by the water enrichment in the substances originating from the built-up areas.
2. On average highest values of biogenic indices and chlorides but the lowest values of oxygen indices were registered immediately below the location of the drain collector of the closed sewage treatment plant, which resulted in the investigated stream bed pollution with the substances formerly drained from the treatment plant.
3. Water flowing through the forest areas had the maximum ecological potential, in the compact urban development areas it was classified to class II because of phosphate concentrations and further, as a result of self-purification it

returned to the physicochemical parameters appropriate for water in class I.

4. The analysis of the collected data revealed a significant impact of built-up areas on the quality of flowing waters.

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