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Quality of waters flowing in foothill areas subject to anthropopressure illustrated by the example of the Biała River catchment in southern Poland

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ABSTRACT

The physicochemical parameters of the water of the Biała River and its tributaries were analysed at 11 test points. Some points represented highly urbanized catchment areas while the remaining ones – mixed catchments (with buildings, forest and agricultural areas). The research was conducted from June 2021 to May 2022. Its aim was to identify the pollution of water flowing in developed foothill areas. Basic water quality parameters were determined: C, TDS, COD_{Mn}, Fe, Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-, TKN. During the research period, the parameter values at individual points were very variable (variation over time). Differences in values between points (spatial variation) were also noted. Water quality was related to the development of the catchment area – overall pollution expressed as C or TDS values was greater in highly urbanized catchments and in the lower part of the studied area, but individual substances in high concentrations were also observed locally. It was found that the water was contaminated mainly with organic and biogenic substances.

Keywords: surface water, land development, anthropogenic pressure on the aquatic environment, water pollution.

INTRODUCTION

The expansion of developed areas, especially urbanized ones, significantly affects flowing surface waters [Paul and Meyer, 2001; Marques and Cunico, 2023]. This impact is related not only to the technical transformation of streambeds [Rieck and Sullivan, 2022], i.e. deepening, regulating, sealing, etc., but also to the deterioration of the quality of the flowing water [Ouyang et al., 2006]. Many researchers have conducted investigations on the quality of water in urbanized areas – it is worth giving a few examples. De Mello et al. [2024] examined water quality in catchment areas characterized by different levels of urbanization and found that anthropopressure on the water environment is particularly visible in urban areas and areas without organized wastewater management. Lai et al. [2022] studied changes in the quality of river waters as a result of surface runoff from urbanized areas during light, moderate and heavy rain. They found that the quality of the river water was worse during moderate rainfall than during light and heavy rainfall. The impact of light rainfall on water quality was delayed and short-lived, whereas heavy rainfall had a diluting effect on pollution. Wang et al. [2019] analysed factors affecting the quality of water in urban areas. They discovered that it was determined primarily by the impervious surface index and the average value of investments in land development. Hafsi et al. [2016] conducted a multi-variate analysis of water quality parameters and catchment features, demonstrating that it is possible to determine the urbanization threshold (share of impervious surface) the exceeding of which in investment activities leads to changes in water quality. Many studies have shown that the impact of urbanization on the quality of flowing waters concerns not only the physicochemical parameters of the water, but also the biological features of ecosystems, e.g. biodiversity [Salachna et al., 2022; Salachna and Widuch, 2023]. The aim of the research described in this article was to identify the quality of water flowing in a foothill area characterized by a high degree of land development. Answers were sought to the following questions: 1) does water quality change in the case of permanent anthropogenic impact? 2) do the values of water quality parameters indicate pollution? The answer to the second question will allow assessing whether water resources are degraded already in transitional areas, between poorly developed mountain areas and intensively used highland and lowland areas.

STUDY AREA AND STUDY METHODS

The research was carried out in the Biała River catchment, covering an area of approximately 131 km^2 [Atlas, 2005], located on the northern outskirts of the Polish Carpathians. The upper part of the catchment area is Beskid Śląski Mts and Beskid Mały Mts, while the middle and lower parts are located in Pogórze Śląskie (Silesian Foothills). The catchment designated for research had an area of 118.5 km^2 and was characterized by a high degree of anthropogenic impact on the environment despite its location in a mountainous and foothill region (Figure 1). It is related to the functioning of the city of Bielsko-Biała together with suburban centres in the catchment area subjected to study. To assess the value of water quality parameters, an analysis of the catchment area development was carried out. In particular, the share of various types of urbanized areas in the catchment area was determined. For this purpose, the *SCALGO Live* computer program and the database from the map layer of Land Cover from BDOT10k (date acquired: 2024-05-27) were used.

The quality of water in the Biała River catchment was examined at 11 test points (profiles). They were located both on the main river and the tributaries before their confluence with the main river (Figure 1). The test points had the following designations, names and catchment areas:

- A – Biała River in Mikuszowice – 32.2 km^2,
- 1 – Olszówka Stream – 8.31 km^2,
- 2 – Straconka Stream – 11.26 km^2,
- 3 – Kamienicki Stream – 3.27 km^2,
- 4 – Kamieniczanka Stream – 6.90 km^2,
- B – Biała River in Bielsko-Biała – 71.6 km^2,
- 5 – Niwka Stream – 8.46 km^2,
- 6 – Starobielski Stream – 6.68 km^2,
- 7 – Krzywa Stream – 7.43 km^2,
- 8 – Kromparek Stream – 11.50 km^2,
- C – Biała River in Czechowice-Dziedzice – 118.5 km^2.

In the period from June 2021 to May 2022, 8 measurement series were carried out. Water samples were collected at the points mentioned above on the following dates: 29/06/2021, 01/09/2021, 05/10/2021, 15/11/2021, 16/12/2021, 09/03/2022, 27/04/2022, 17/05/2022. The samples were collected in polyethylene bottles and transported to the water and wastewater laboratory at the University of Bielsko-Biała. On the same day, the following water quality parameters were determined using standard methodology [Eaton et al., 2005]:

- C conductivity (potentiometric method),
- TDS total dissolved substances (potentiometric method),
- COD_{Mn} oxidizability ($KMnO_4$ oxidation + titration method in an acidic medium),
- Fe iron (spectrophotometric method with 1,1 phenanthroline),
- Cl^- chlorides (spectrophotometric method with mercury thiocyanate),

Figure 1. The Biała River catchment area with the location of test points; WTP – wastewater treatment plant

- SO_4^{2-} sulphates (turbidimetric spectrophotometric method),
- PO_4^{3-} phosphates (spectrophotometric method with ascorbic acid),
- NO_3^- nitrates (spectrophotometric method with hydrochloric acid),
- TKN total Kjeldahl nitrogen (mineralization with sulphuric acid and copper + steam distillation + titration method in an acidic environment).

The obtained numerical material from laboratory measurements was subjected to simple statistical analysis due to the small number of measurement series, i.e. 8 (n – 2 = 6). After determining the arithmetic mean and standard deviation of the values of individual parameters at individual test points, correlation and regression analyses were performed. The values of each measured parameter were correlated between study points so as to determine whether changes in the values were similar throughout the area. The Pearson correlation was used due to the linear arrangement of points on the scatter plots. In order to check the trend of changes in parameter values over time, a linear regression analysis was performed.

Table 1. Structure of use of the studied catchment area (based on BDOT10k, May 2024)

Land use form	Percentage of catchment area (%)
Forest, wooded and bushy areas	35.61
– forest	27.54
– woodlet	0.20
– coppices	7.49
– bush/shrubbery	0.38
Agricultural land	24.22
– grasses	18.09
– cultivated land	4.04
– allotment	1.19
– plantation	0.04
– orchard	0.66
– plant nursery	0.20
Building area	35.30
– multi-family	2.47
– single-family	20.41
– industrial-storage	2.74
– shopping and service	0.88
– technical objects	0.48
– other (included square)	8.32
Transport areas	4.0
– road	3.62
– track	0.38
Surface water	0.72
Waste dump	0.10
Unusable land	0.05

RESULTS AND DISCUSSION

Land development structure

Analyses of the catchment area development revealed that the largest share in the entire study area belonged to built-up and transport areas – ca 40%. Slightly less – approximately 36% was covered by woodlands and shrublands. Areas used for agriculture covered less than 25% of the catchment area (Table 1). We can therefore talk about predominance of broadly understood urbanized areas, which is related to the functioning of a large urban centre (the city of Bielsko-Biała) directly at the foot of the mountain ranges.

Catchment areas of particular water quality test points were characterized by various forms of land development. These were mixed catchments, which is particularly visible in the upper part of the Biała River catchment (point A) or in the Straconka Stream catchment (point 2). In some catchments, predominance of a specific form of development was observed, e.g. urbanised areas were predominant in the catchments of the Kamienicki Stream (point 3), Niwka Stream (point 5) and Starobielski Stream (point 6), whereas in the catchment area of the Olszówka Stream (point 1) there was a significant share of woodlands. An interesting catchment is that of the Kromparek Stream (point 8), characterized by a large share of quasi-natural green areas, but in this case we also deal with anthropopressure, among others. in the form of water inflow from the drainage of a nearby expressway. Due to this diversity of subcatchments, spatial diversification of stream water quality parameters can be expected. It should be added that various industrial plants are located throughout the study area, which may influence the quality of the water environment. Undoubtedly, such impact may be exerted by the sewage treatment plant located in the lower part of the catchment area (Figure 1), which receives sewage from the Bielsko-Biała commune and neighbouring communes. The treated sewage is directed to the Biała River.

Variable values

The research revealed large differences in water parameter values both between test points and at individual points during the research period (Table 2). This is indicated not only by the

Table 2. Parameters of water flowing in the Biała River catchment area during the study period – minimum (min), maximum (max), average (av) and standard deviation (SD) values

Research point		C (µS/cm)	TDS (mg/L)	COD_{Mn} (mgO_2/L)	Fe (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	PO_4^{3-} (mg/L)	NO_3^- (mg/L)	TKN (mg/L)
A	min	115	47	2.20	0.08	10.9	11.0	0.07	2.7	0.08
	max	292	120	10.05	0.85	32.0	21.0	0.53	8.4	1.12
	av	209.8	86.1	4.51	0.22	18.0	16.6	0.23	6.5	0.29
	SD	55.7	22.9	2.34	0.24	6.3	3.6	0.13	1.8	0.33
1	min	115	47	3.25	0.07	8.5	9.0	0.09	1.2	0.42
	max	303	124	9.27	0.38	28.0	24.0	0.39	4.6	4.20
	av	245.6	100.8	6.18	0.17	15.8	18.6	0.19	3.0	1.82
	SD	66.4	27.3	2.00	0.11	5.7	4.7	0.09	1.1	1.20
2	min	125	51	1.67	0.02	22.5	9.0	0.09	3.5	0.66
	max	419	172	9.80	0.90	71.0	23.0	0.89	7.0	0.98
	av	289.5	118.5	4.63	0.20	37.7	19.0	0.24	5.3	0.79
	SD	75.9	31.2	2.85	0.28	16.2	4.3	0.25	1.1	0.12
3	min	284	116	2.90	0.07	21.9	23.0	0.10	3.5	0.11
	max	712	292	8.82	0.52	82.9	52.0	0.42	7.8	0.84
	av	552.2	226.2	5.14	0.19	52.7	39.8	0.26	5.1	0.47
	SD	134.2	57.3	2.12	0.17	21.9	10.2	0.12	1.4	0.27
4	min	268	110	2.80	0.06	29.5	22.0	0.06	3.2	0.70
	max	633	259	9.61	0.15	65.1	48.0	0.51	9.3	5.04
	av	556.8	228.3	6.57	0.09	43.1	39.4	0.32	5.3	1.79
	SD	113.2	46.3	2.44	0.03	11.2	7.9	0.15	1.7	1.39
B	min	153	63	1.60	0.03	18.2	16.0	0.13	4.4	0.28
	max	478	196	9.23	0.60	66.0	26.0	0.42	7.4	1.96
	av	303.4	124.4	4.44	0.14	32.4	22.3	0.24	5.8	0.83
	SD	88.2	36.2	2.18	0.18	14.6	3.8	0.12	0.9	0.54
5	min	331	136	2.36	0.02	32.0	25.0	0.15	3.2	0.08
	max	739	303	7.99	0.41	97.0	49.0	0.47	6.5	1.96
	av	639.1	262.1	4.46	0.09	57.6	42.6	0.31	5.0	0.91
	SD	121.6	49.8	1.62	0.12	19.0	7.1	0.09	1.1	0.62
6	min	484	199	3.94	0.18	48.5	43.0	0.27	4.3	0.14
	max	853	350	11.40	1.06	151.5	68.0	1.03	8.0	1.96
	av	769.8	315.6	6.28	0.34	76.9	56.1	0.58	6.0	1.01
	SD	111.5	45.5	2.43	0.27	33.4	8.6	0.23	1.3	0.57
7	min	407	167	2.99	0.16	43.2	40.0	0.16	2.9	0.32
	max	766	314	9.73	0.69	89.0	78.0	0.51	4.9	1.12
	av	696.0	285.4	5.85	0.33	59.4	60.4	0.33	4.1	0.57
	SD	112.4	46.0	2.09	0.16	13.6	11.0	0.13	0.7	0.26
8	min	315	129	2.13	0.02	22.5	23.0	0.12	2.7	0.96
	max	701	287	10.29	2.35	103.5	39.0	0.43	6.1	2.52
	av	463.3	189.9	5.50	1.08	57.5	32.8	0.30	4.6	1.49
	SD	120.3	49.2	2.22	0.67	28.6	4.8	0.10	1.2	0.51
C	min	223	92	6.90	0.27	50.0	16.0	0.18	4.4	0.84
	max	810	332	10.70	0.84	130.6	59.0	1.10	28.2	9.32
	av	614.0	251.9	8.54	0.48	84.1	47.5	0.55	15.3	3.47
	SD	177.3	72.6	1.28	0.17	29.6	14.4	0.31	6.8	2.74

range of extreme values, but also by the standard deviation. A particularly high variability of values during the study period was noted in the case of iron concentration (average concentration for all points and measurement series reached 0.31 mg/L, standard deviation – 0.39 mg/L) and total Kjeldahl nitrogen (average concentration – 1.25 mg/L, standard deviation – 1.38 mg/L).

The analysis of the research results in terms of spatial variability (between test points) allowed concluding that the parameter values increased in the main river from point A to C. This increase resulted from the supply of pollutants with the waters of individual tributaries and from the immediate catchment area of the main river. It can be easily seen in the example chart (Figure 2) – the results of water conductivity (C) and the content of dissolved solids (TDS) were chosen as an example, because these parameters provide information on the presence of various chemical substances in the water. Conductivity indicates the presence of conductive ions from dissolved salts and inorganic compounds. Dissolved substances include all particles in water that are smaller than 2 microns – these may be not only unbound electrolytes, but also dissolved organic matter [Fondriest Environmental, 2014]. The data shows that most substances were contained in the waters of the following tributaries: Kamienicki Stream, Kamieniczanka Stream, Niwka Stream, Starobielski Stream, Krzywa Stream. These tributaries have highly urbanized catchment areas.

The increase in pollutant concentrations between the upper and lower course of the river was observed by many researchers, e.g. Fulazzaky et al. [2010], Liu et al. [2018], Son et al. [2020]. In our own research, the values of all the parameters in the water of the main river at end point C were at least twice higher than at point B. This should not be related only to pollutants from side tributaries. Above point C, in the direct catchment area of the main river, there is a large wastewater treatment plant for the city of Bielsko-Biała and other towns. The treated sewage is discharged into the river, which undoubtedly affects the quality of the water.

The analysis of the variability of parameters in subsequent measurement series between points revealed dependencies only in the case of general water pollution expressed as conductivity and the content of dissolved substances. The correlations have been illustrated by the example of dissolved substances (Table 3). A significant relationship was found between almost all points with the exception of point 8, representing the Kromparek Stream catchment. This catchment area is largely quasi-natural. The analysis of the correlations indicates that an increase or decrease in overall water pollution was observed almost in the entire study area. In other words, it could be assumed that if an increase in the TDS value was found at one point, the same increase would also occur at other points. However, such a conclusion cannot be formulated for individual chemical substances – the correlation analysis revealed that statistically significant relationships occurred rarely, as shown in Table 3 on the example of phosphate concentration. The concentrations of individual substances in the presented studies did not change in a similar way throughout the entire area. Individual substances may be associated with various

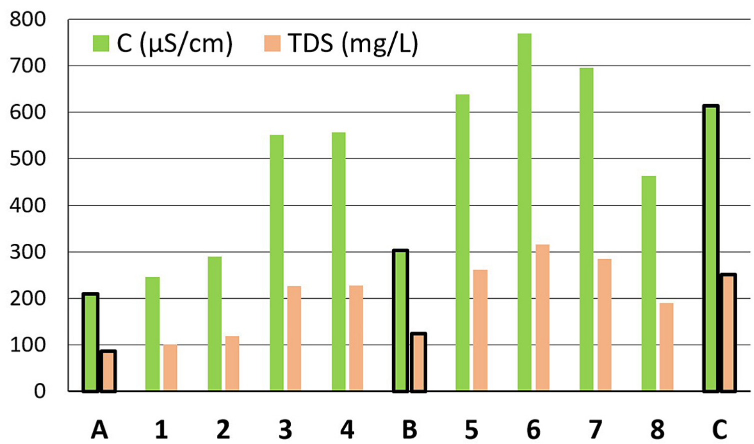

Figure 2. Average values of C and TDS in water at individual points of the Biała River catchment area throughout the study period

Table 3. Correlation of selected parameters between test points during the study period (statistically significant values for $p = 0.05$, $n - 2 = 6$ are in bold)

Correlation coefficient for dissolved substances (TDS)											
	A	1	2	3	4	B	5	6	7	8	C
A		**0.92**	**0.87**	**0.79**	**0.76**	**0.95**	0.70	**0.72**	**0.71**	**0.82**	**0.74**
1	0.52		**0.79**	**0.73**	**0.88**	**0.83**	**0.79**	**0.79**	**0.80**	0.66	**0.81**
2	**0.94**	0.40		**0.83**	**0.84**	**0.95**	**0.89**	**0.85**	**0.87**	**0.82**	**0.84**
3	0.54	**0.81**	0.50		**0.78**	0.65	**0.84**	**0.76**	**0.85**	0.64	**0.78**
4	0.55	0.63	0.59	**0.98**		**0.72**	**0.96**	**0.95**	**0.98**	0.55	**0.90**
B	0.70	0.26	0.67	**0.88**	**0.76**		**0.75**	**0.73**	**0.72**	**0.91**	**0.77**
5	**0.84**	0.29	**0.74**	0.54	0.45	**0.79**		**0.96**	**0.99**	0.64	**0.94**
6	**0.76**	0.61	**0.78**	**0.81**	0.70	0.60	**0.73**		**0.96**	0.57	**0.88**
7	0.54	0.27	0.55	**0.91**	0.57	0.70	**0.79**	**0.85**		0.59	**0.93**
8	0.66	0.49	0.54	0.17	0.17	0.07	0.45	0.60	0.25		**0.77**
C	0.37	0.54	0.08	-0.26	0.11	0.25	0.36	0.17	0.10	0.27	
Correlation coefficient for phosphate concentration (PO_4^{3-})											

forms of anthropopressure in catchments [Jaguś et al. 2012, Li et al. 2021].

An attempt was also made to identify trends or seasonal changes in parameter values at individual points during the research period, but no regularities were found, probably due to uncontrolled short-term inflows of pollutants, the identification of which would be possible under conditions of high sampling frequency.

Pollution

The recorded values of individual water quality parameters discussed below have been related to the limit values of pollution quoted in the literature [Dojlido, 1995] and the Polish legal act regarding the classification of surface water quality [Ordinance, 2021] (Table 4). For the analysed watercourses, standards for streams or small flysch rivers of a silicate nature were adopted on the basis of the geological structure of the area [Ordinance, 2021]. The analysis of TDS values was omitted because the literature does not provide limit values between clean and polluted waters.

The number of water samples that can be considered contaminated in terms of individual parameters is shown in Table 4. The most cases of contamination were found at points 4 (Kamieniczanka Stream), 6 (Starobielski Stream), 8 (Kromparek Stream) and at point C (end point). The recorded water conductivity (C) ranged from 115 to 853 μS/cm, and the value exceeding 330 μS/cm is considered to indicate contamination. In the upper part of the studied catchment (Biała River in Mikuszowice, Olszówka Stream, Straconka Stream), the values occasionally exceeded 300 μS/cm. These are areas with a large share of

Table 4. Number of samples (out of 8) in which the parameter values at individual test points indicated water contamination

Parameter	Contamination limit	A	1	2	3	4	B	5	6	7	8	C
C	330 μS/cm	0	0	1	7	7	3	8	8	8	6	7
COD_{Mn}	4 mgO_2/L	4	7	4	4	6	4	4	7	7	6	8
Fe	1 mg/L	0	0	0	0	0	0	0	1	0	5	0
Cl^-	200 mg/L	0	0	0	0	0	0	0	0	0	0	0
SO_4^{2-}	150 mg/L	0	0	0	0	0	0	0	0	0	0	0
PO_4^{3-}	0.18 mg/L	4	3	3	4	7	3	7	8	7	7	8
NO_3^-	6 mg/L	6	0	3	2	2	3	3	3	0	1	7
TKN	2 mg/L	0	3	0	0	2	0	0	0	0	2	5
Total amount		14	13	11	17	24	13	22	27	22	27	35

forests. However, attention should be paid to the worse quality of water in the Straconka Stream, which may be related to the intensification of development in this catchment. This is an attractive area for single-family housing, where large recreational areas (so-called boulevards) have also been located. Water flowing from highly urbanized areas was contaminated - in the case of the Niwka, Starobielski and Krzywa Streams in each measurement series.

The oxidizability (COD_{Mn}) of the tested samples ranged from 1.6 to 11.4 mgO_2/L. Pure surface waters are characterized by oxidizability reaching up to approximately 4 mgO_2/L. Unfortunately, this value was frequently exceeded at each test point. This indicates an excessive content of organic compounds in the water, which may come from both forest areas, e.g. humic compounds, and urbanized areas, where some of the sewage may be discharged into the environment without treatment. This mainly applies to single-family buildings, where wastewater is also produced outside the house - during various house and garden works. The highest oxidation values were found in the following streams: Olszówka (forest areas, single-family buildings), Kamienieczanka and Starobielski (single-family buildings), as well as at the end point.

The content of iron (Fe) should not exceed 1 mg/L. Concentrations exceeding 2 mg/L are considered by some researchers to pose danger to most fish. Iron in surface waters comes mainly from the leaching of rocks and soils, but it is also an indicator of industrial activity. The vast majority of the tested waters were not contaminated with iron. Pollution was found in the Kromparek Stream (point 8). The catchment area of this stream is not very urbanized. There are arable fields, meadows and wetlands - they are probably the source of iron.

The content of chlorides (Cl^-) and sulphates (SO_4^{2-}) in the tested waters did not indicate contamination with these substances (the limits of concentrations between clean and polluted waters are 200 $mgCl^-/L$ and 150 $mgSO_4^{2-}/L$). The content of chlorides reached up to several dozen mg/L in the upper part of the catchment, whereas in the lower part it periodically exceeded 100 mg/L. The concentration of sulphates did not exceed several dozen mg/L. The highest values were recorded for the Starobielski and Krzywa Streams and at the end point of the catchment. The spatial variation in chloride and sulphate concentrations indicates that their concentration in water in this area is determined by anthropogenic influences.

Phosphate ions (PO_4^{3-}) were present in the tested waters in large quantities despite their natural chemical precipitation from water and sorption in soils and sediments. Water contamination with phosphates (concentrations above the limit value of 0.18 $mgPO_4^{3-}/L$) was found at all test points, especially in the lower part of the catchment, where concentrations frequently reached several tenths of mg/L. The causes of phosphate pollution should be sought in the discharge of household pollutants into the environment, but agricultural activities, including animal breeding, may also be a source of phosphates.

Nitrates (NO_3^-) occur in clean surface waters in concentrations below 6 mg/L. In the studied catchment, this value was often exceeded. The greatest number of exceedances were recorded at the initial point (impact of agricultural areas) and at the end point (impact of sewage discharge from the municipal wastewater treatment plant). It is worth noting that the values at the initial point reached several mg/L, and at the end point even more than 20 mg/L. The lowest concentrations were recorded in the case of the water of the Olszówka Stream (catchment area with a large share of forest).

The concentration of total Kjeldahl nitrogen (TKN), i.e. nitrogen in organic and ammonium compounds, in the tested waters ranged from 0.08 to 9.32 mg/L. The contamination level of 2 mg/L was exceeded only at some points, especially at the end point. It can be assumed that oxidizing conditions prevail in the studied streams, leading to the formation of nitrates. The largest amounts of unoxidized forms of nitrogen were found in the Olszówka Stream (inflow of organic substances from forest areas), the Kamienieczanka and Starobielski Streams (influence of highly urbanized areas), the Kromparek Stream (influence of agricultural areas) and at the end point (influence of the municipal wastewater treatment plant).

The above data analysis indicates that waters flowing in the Biała River catchment are in many cases contaminated with mineral, including biogenic, as well as organic substances. This is confirmed by the assessment of the quality of the Biała River water carried out by the Environmental Protection Inspectorate as part of national environmental monitoring. The Biała River is subject to water quality monitoring, and the control point with the identification number PL01S1301_1695 is located just before the mouth of the Vistula River. In terms of biological parameters, the Biała River is classified as quality class 4 (on a scale from 1 to 5), and its chemical status is rated as 'below good'. According to the general classification, the Biała River is characterized by 'poor water condition' [Environmental Protection Programme 2022].

CONCLUSIONS

Parameters of the water in the Biała River and its tributaries were very variable despite permanent anthropogenic impacts, but the values were not characterized by long-term trends or seasonal changes. Changes in the total content of chemical substances in water were similar throughout the entire study area, but the concentrations of individual substances were generally not correlated between test points - the concentration of individual substances was influenced by catchment conditions. The water in research profiles located in the upper part of the catchment area had better quality than that in the middle and lower parts. Polluted waters were typical of highly urbanized catchments. The poor quality of water in the main river was significantly influenced by the municipal wastewater treatment plant. The development of foothill areas in the Biała River catchment area results in unfavourable quality of water resources. The classification of water as polluted in the conducted research was based mainly on: conductivity, oxidizability, phosphate and nitrate concentrations.

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