SYLWAN 166 (579): 579-592, September 2022
https://doi.org/10.26202/sylwan.2022018
Journal homepage: https://sylwan-journal.pl

ORIGINAL PAPER

Diversity of physicochemical parameters of waters in Vistula River headwater area after spruce dieback in the Beskidy Mountains

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ABSTRACT

The research was conducted in July 2018 in the Barania Góra massif in the Silesian Beskids. Water samples were taken from the springs and watercourses of the Biała Wisełka and Czarna Wisełka Rivers, comprising the headwaters of the largest river in Poland, the Vistula. A total of 69 water samples was collected: 15 from the springs and 20 from the watercourses of the Biała Wisełka; 11 from the springs and 23 from the watercourses of the Czarna Wisełka. Water samples were collected mainly within the Barania Góra nature reserve. The Reserve was established in 1953 to protect and observe the processes taking place in the various climatic and vegetation zones of the Silesian Beskids and to preserve the spring area of the Vistula in its natural state. Laboratory work was performed at the Laboratory of Geochemistry of the Forest Environment and Land Intended for Reclamation of the University of Agriculture in Krakow. In the water samples collected, pH (Elmetron CX-741 multifunction instrument), conductivity (Elmetron CPC-551 conductometer) and concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, NH_4^+, NO_3^-, HCO_3^-, Na^+, and K^+ ions were measured (DIONEX 5000 chromatograph). The research aims to explore the differences in the physicochemical parameters and the water quality of the Vistula spring area, including the differences between the Biała Wisełka and Czarna Wisełka supply areas. The spring areas of Czarna Wisełka and Biała Wisełka differ in geological structure, soil type and subtype, topography, exposure, forest habitat type, and tree-stand species composition. Additionally, the spring area of Czarna Wisełka and the upper portions of the spring area of Biała Wisełka were affected by the defeat of the dieback of spruce stands. These environmental factors are apparent in the different chemical compositions of the watercourses and springs of the two catchments. Lower pH, conductivity, and concentrations of Ca^{2+}, Mg^{2+}, Cl^-, NH_4^+, NO_3^-, HCO_3^-, Na^+, and K^+ ions in both springs and watercourses were recorded in the Czarna Wisełka catchment.

KEY WORDS

forest catchments, water chemistry, spruce dieback, Beskidy Mts.

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Received: 21 March 2022; Revised: 14 December 2022; Accepted: 15 December 2022; Available online: 25 January 2023

Introduction

The Vistula is the longest river in Poland and the longest tributary of the Baltic Sea. The spring area of the Vistula is located on the western and southwestern slopes of Barania Góra in the Silesian Beskid. Industrial pollution affects this area, mainly from the Katowice complex, the Rybnik Coal District, and the Ostrava region (in the Czech Republic). The average annual load of sulphur oxides (SO_4^{2-}) in the years 1999-2012 in the Silesian Beskid was almost 25 kg/ha, while nitrogen compounds (NO^{2-}+NO^{3-}) were over 4 kg/ha (Zołotajkin *et al.*, 2014). The acidic deposition of large amounts of nitrogen and sulphur compounds and the conversion from multispecies stands with fir, beech, and spruce into spruce monocultures of foreign origin (carried out by the Habsburgs in the 19th century) contributed to the spruce dieback over a large area in the Beskidy Mountains (Małek *et al.*, 2012; Małek and Krakowian, 2012). Additionally, these stands were affected by the outbreak of the spruce bark beetle *Ips typographus* (L.) and infestation by fungal pathogens, mainly *Armillaria* spp. (Grodzki, 2010). The results of these factors, among others, were significant deforestation in Skrzyczne and Barania Góra. The spring area of the Vistula has been protected as a nature reserve since 1953; therefore, no cuts or artificial forest regeneration were performed there, but the area also was affected by the decay of spruce trees, resulting in the accumulation of large amounts of slowly decaying deadwood. The main element influencing the water chemistry of springs and initial river runs is the geological structure (Walling and Webb, 1980; Holloway and Dahlgren, 2001). The altitude (Kendall *et al.* 1999, Stottlemyer 2001) and soil cover (Mulder *et al.*, 1995; Siwek *et al.*, 2017) also have significant influences. These elements, however, remained unchanged, unlike other important factors influencing the water's physicochemical parameters, such as vegetation (including species composition and stands' ages). The area studied is comprised of Carpathian flysch. It is dominated by a shallow-water circulation system; thus, the springs and initial sections of rivers and streams react quickly to environmental changes.

This study aims to determine the effects of spruce-stand decay on the physicochemical parameters and chemical composition of the waters of the Vistula spring area.

Research area

The research was performed in the spring area of the Vistula in the upper parts of the Biała Wisełka and Czarna Wisełka catchments of the Silesian Beskid (Fig. 1). This area is located in the Barania Góra reserve, within the city of Wisła in the Silesian Voivodeship, and it stretches along a wide belt on the western side of the main ridge of the Silesian Beskid, reaching the peak of Barania Góra (1220 m above sea level). The reserve was established in 1953 to preserve the forest areas in Barania Góra, where the Vistula River originates, in their natural state for scientific and sociocultural reasons. In terms of geology, the spring area of Biała Wisełka is comprised of more fertile soil-forming sandstones with interlayers of the lower Istebna slate, while the spring area of Czarna Wisełka is comprised of semi-coarse and coarse sandstones with interlayers of quartz conglomerates (Maciaszek and Zwydak, 1998).

In the Biała Wisełka catchment area, the western (40.9%) and northern (32.4%) exposures of the slopes dominate, while in the Czarna Wisełka catchment area, the dominant exposures are southern (44.6%) and western (29.9%) (Astel *et al.*, 2008). Both areas studied were affected by the disaster of the spruce tree decay, but more severely in the Czarna Wisełka catchment area, where spruce was the dominant species in the entire area. Additionally, a significant part of the Biała Wisełka spring area was covered by beech stands (Fig. 2 and 3). The samples collected in

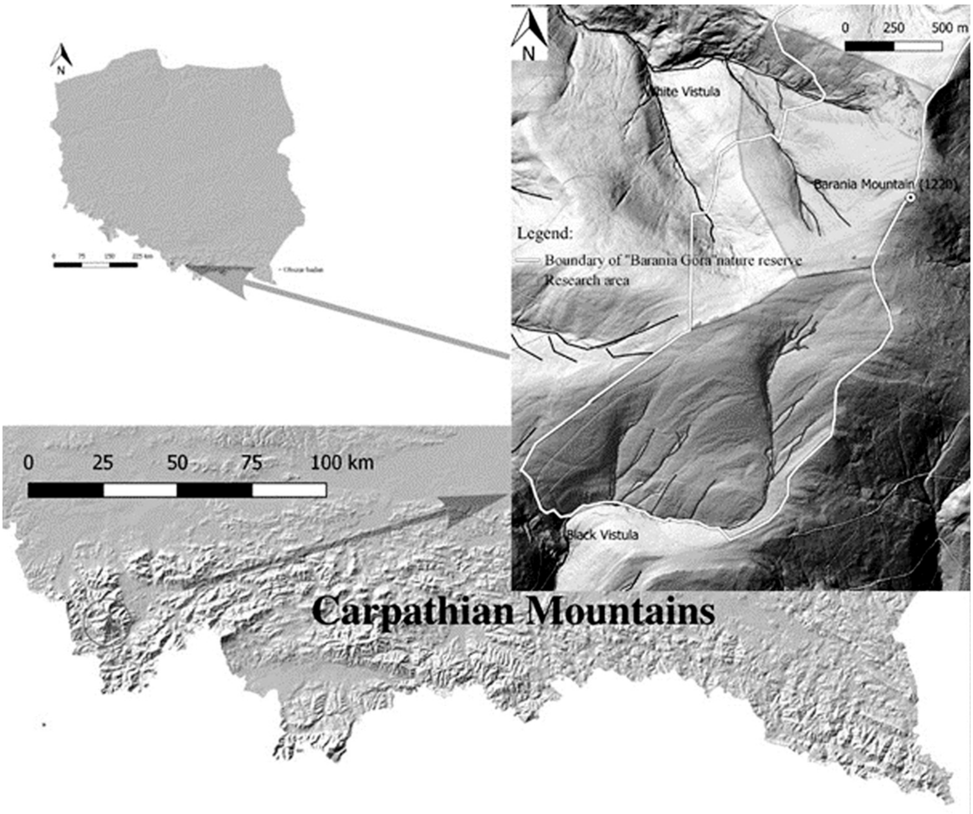

Fig. 1.
Location of the research area (White Vistula - Biała Wisełka, Black Vistula - Czarna Wisełka, Barania Mountain – Barania Góra)

2004 and 2018 were located near the top of the Biała Wisełka and Czarna Wisełka catchments, but the location of all water intake points from 2004 and 2018 do not coincide (Fig. 3). In 2004, 15 points on the Czarna Wisełka watercourses and 18 points on the Biała Wisełka watercourses were used for analyses, in 2018, respectively, 23 and 20 points. Compared to 2004, points sampled in June were taken into account, with the water level defined by the authors as medium (Astel *et al.*, 2008). The water intake points sampled by Kasza (1986) on both the Biała Wisełka and Czarna Wisełka were located in the lower parts of the catchments near the Wisła-Czarne reservoir, similar to the findings of Wróbel (1995) in the Biała Wisełka catchment area; therefore, they are treated as indicative. Sample collection by Wróbel in the Czarna Wisełka was located in the upper part of the catchment.

The average daily rainfall in July 2018 at the IMGW (Institute of Meteorology and Water Management) Wisła Malinka and Istebna Stecówka stations was 3.29 mm based on measurements from the following days: July 1, 6, 8, 9, and 10 at Wisła Malinka and July 1, 6, and 10 at Istebna Stecówka. Water samples were taken on July 7, 9, and 10, 2018. The average daily precipitation in June 2004 at IMGW Wisła Malinka and Istebna Stecówka stations was 4.58 mm based on measurements from the following days: June 20, 21, 23, 24, and 26 at Wisła Malinka and June 20, 21, 23, 24, 25, and 26 at Istebna Stecówka. Water samples were taken on June 24 and 25, 2004 (IMGW, 2004, 2008; Astel *et al.*, 2008).

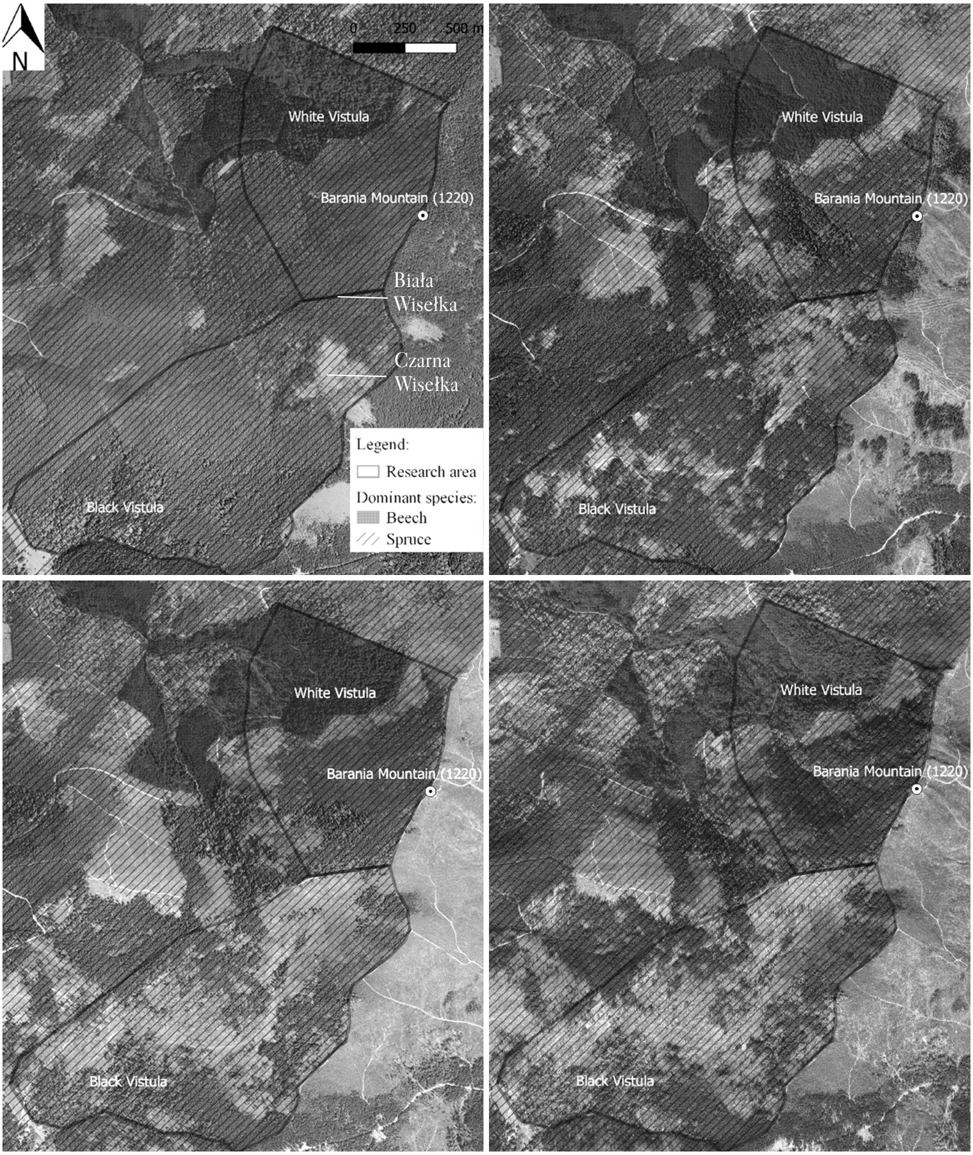

Fig. 2.

Changes in the land cover in the research area. Orthophoto maps successively from 2004, 2010, 2016, and 2018. Sources: Qgis plugin: Archive Ortophotomap; explanations as in Fig. 1

Terrain and laboratory work

As part of the research, 69 water samples were collected for analysis, including 35 in the Biała Wisełka catchment (15 from the springs and 20 from the watercourses) and 34 in the Czarna Wisełka catchment (11 from the springs and 23 from the watercourses). Water samples were collected in July 2018, when water levels were average, in 120 ml polyethylene bottles. All but 10 samples were collected within the Barania Góra reserve (Fig. 3). After the water samples were transported to the Laboratory of Geochemistry of the Forest Environment and Areas Intended for Reclamation

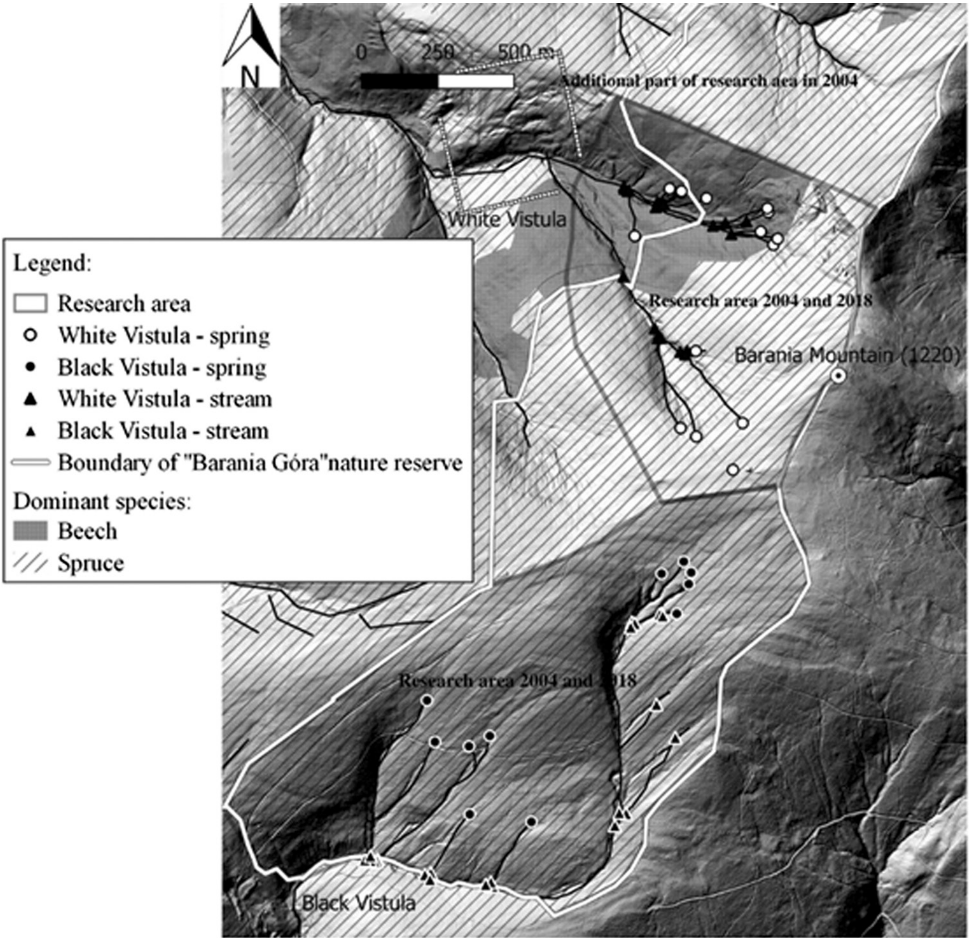

Fig. 3.
Location of water sampling points in the springs and streams of Biała Wisełka (White Vistula) and Czarna Wisełka (Black Vistula)

of the University of Agriculture in Krakow, the following measurements were made in the collected water samples: pH (Elmetron CX-741 multifunctional device), conductivity (SEC; Elmetron CPC-551 conductometer at 21°C), and concentrations of common ions: Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, NH_4^+, NO_3^-, Na^+, and K^+ (DIONEX 5000 chromatograph). The HCO_3^- concentration was calculated from IC (inorganic carbon) measured by a Shimadzu TOC-VCPH Total Organic Carbon Analyzer. The following statistical measures were used to characterize the chemical composition of the waters of streams and springs: arithmetic mean, minimum value, maximum value, and standard deviation. To determine the significance of the differences between the chemical composition of the Biała Wisełka and Czarna Wisełka water and watercourses, the nonparametric Mann-Whitney U test was used at $\alpha=0.05$.

Results

Both in the springs and streams of Biała Wisełka, higher mean concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-}, Na^+, K^+, HCO_3^-, and NO_3^- as well as higher pH and specific electrolytic conductivity were recorded. The differences in ion concentrations, both in the springs and watercourses, were statistically significant. The mean concentration of Cl^- was comparable in the watercourses and springs of Czarna Wisełka and Biała Wisełka. Only the average concentration of NH_4^+ ions in the springs of Czarna Wisełka was higher than in the springs of Biała Wisełka; however, these differences were not statistically significant (Table 1).

The lowest mean pH (5.18) was recorded in the springs of Czarna Wisełka, and the highest mean pH (6.74) was recorded in the streams of Biała Wisełka. Cation concentrations in the streams and springs of the Biała Wisełka were higher than those from Czarna Wisełka. For the springs of Biała Wisełka, the mean Ca^{2+} concentration was more than seven times higher (2.64 $mg \cdot dm^{-3}$) compared to Czarna Wisełka, where the average Ca^{2+} concentration was 0.35 $mg \cdot dm^{-3}$. On the other hand, in the watercourses, the mean Ca^{2+} concentration was more than five times higher in Biała Wisełka at 2.05 $mg \cdot dm^{-3}$, compared to the Czarna Wisełka at 0.36 $mg \cdot dm^{-3}$. The average concentration of Mg^{2+} in the springs and streams was three times higher in the Biała Wisełka at 0.81 $mg \cdot dm^{-3}$ in the springs and 0.63 $mg \cdot dm^{-3}$ in the streams, compared to the Czarna Wisełka at 0.22 $mg \cdot dm^{-3}$ in the spring and 0.21 $mg \cdot dm^{-3}$ in the streams. Higher mean values of NO_3^- and SO_4^{2-} ions also were recorded in Biała Wisełka. The maximum NO_3^- concentration in the study area was 5.66 $mg \cdot dm^{-3}$ for the Biała Wisełka watercourses and SO_4^{2-} 28.02 $mg \cdot dm^{-3}$.

Over the past several decades, changes in the chemical composition of the waters of the Czarna Wisełka and Biała Wisełka watercourses have been noticeable (Table 2). An increase in NH_4^+ concentration in surface waters was observed, compared to previous periods. In 2018, in Czarna Wisełka, the concentration of NH_4^+ was 1.06 $mg \cdot dm^{-3}$ and in Biała Wisełka 2.48 $mg \cdot dm^{-3}$, compared to 2004, where this value was 0.29 $mg \cdot dm^{-3}$ for Czarna Wisełka and 0.11 $mg \cdot dm^{-3}$ for Biała Wisełka. Between the studies conducted by Kasza (1986) and the studies by Wróbel (1995), concentrations of NO_3^- ions decreased, but increased in subsequent periods. In 2018, concentrations of NO_3^- ions in Biała and Czarna Wisełka were 2.64 $mg \cdot dm^{-3}$ and 0.69 $mg \cdot dm^{-3}$, respectively, whereas, in 2004, they were 1.78 and 0.58 $mg \cdot dm^{-3}$. There also was a clear decrease in the concentrations of Ca^{2+} and Mg^{2+} in the waters of both Biała Wisełka and Czarna Wisełka watercourses. Compared to 2004, the concentration of Mg^{2+} in the watercourses of Biała Wisełka was more than two times lower (0.63 $mg \cdot dm^{-3}$), whereas Ca^{2+} was more than three times lower (2.05 $mg \cdot dm^{-3}$). In the waters of the Czarna Wisełka, the concentrations of Mg^{2+} and Ca^{2+} were also lower compared to the previous periods. Compared to 2004, the concentration of Mg^{2+} was 0.21 $mg \cdot dm^{-3}$, more than two times lower; the concentration of Ca^{2+} was 0.36 $mg \cdot dm^{-3}$, six times lower.

Samples from the Czarna Wisełka watercourses located in stands where the process of spruce dieback has not yet been clearly visible were characterized by lower average concentrations of NO_3^- and NH_4^+, 0.49 and 0.17 $mg \cdot dm^{-3}$, respectively, compared to samples collected in the forested area, where NO_3^- was 0.92 $mg \cdot dm^{-3}$ and NH_4^+ 2.03 $mg \cdot dm^{-3}$, 11 times higher. Samples located in beech stands (Biała Wisełka) were characterized by higher average pH and higher average concentrations of Mg^{2+}, Ca^{2+}, NH_4^+, and SO_4^{2-} compared to samples in areas of spruce stands in the Czarna Wisełka and Biała Wisełka. The highest average concentration of NO_3^- was in watercourses located in spruce stands in the Biała Wisełka (4.23 $mg \cdot dm^{-3}$) and for NH_4^+ in watercourses located in the Biała Wisełka beech stands (2.94 $mg \cdot dm^{-3}$) (Fig. 3, Table 3).

Discussion

Higher concentrations of such ions as Ca^{2+}, Mg^{2+}, SO_4^{2-}, Na^+, K^+, and HCO_3^- in the waters of the Biała Wisełka result from differences in the geological structure. The Biała Wisełka catchment

Table 1.

Descriptive statistics for the concentrations of selected chemical parameters as well as the pH and conductivity (SEC) in the Vistula spring area. Abbreviations: CWZ (Czarna Wisełka springs), BWZ (Biała Wisełka springs), CWC (Czarna Wisełka watercourses), BWC (Biała Wisełka watercourses); italic print – statistically significant differences in the springs and watercourses between Czarna and Biała Wisełka; bold print – statistically significant differences in the watercourses between Czarna and Biała Wisełka

Abbrev	Statistics	pH	SEC	HCO_3^-	Ca^{2+}	Mg^{2+}	Na^+	NH_4^+	K^+	Cl^-	NO_3^-	SO_4^{2-}
			[μS/cm]	[mg·dm^{-3}]								
CWZ	Mean	*5.18*	*38.45*	*4.39*	*0.35*	*0.22*	*2.22*	1.45	*0.80*	1.83	*1.31*	*7.58*
	St. dev.	0.70	8.28	1.54	0.24	0.17	0.27	1.42	0.72	1.00	1.39	2.37
	Min.	4.43	24	2.02	0.07	0.04	1.81	0.02	0.37	1.03	0.05	3.55
	Max.	6.31	54	7.12	0.99	0.67	2.55	3.26	2.97	4.90	4.13	11.05
BWZ	Mean	*6.42*	*73.27*	*13.40*	*2.64*	*0.81*	*2.96*	1.18	*0.99*	1.88	*2.53*	*15.05*
	St. dev.	0.71	27.54	11.76	1.80	0.47	0.64	0.86	0.32	0.52	1.26	4.87
	Min.	4.59	32	2.29	0.27	0.15	2.17	0.42	0.49	1.22	0.72	9.63
	Max.	7.21	129	45.41	6.25	1.77	4.87	3.03	1.98	3.52	5.42	28.02
CWC	Mean	*5.41*	*30.96*	*2.93*	*0.36*	*0.21*	*2.34*	**1.06**	*0.50*	1.49	*0.69*	*7.91*
	St. dev.	0.60	6.08	0.83	0.26	0.12	0.30	1.13	0.17	0.35	1.11	1.76
	Min.	4.45	24	1.79	0.04	0.05	1.88	0.05	0.25	0.95	0.05	3.01
	Max.	6.5	47	4.55	1.21	0.49	3.05	3.48	0.87	2.33	5.62	11.93
BWC	Mean	*6.74*	*77.35*	*13.94*	*2.05*	*0.63*	*2.70*	**2.48**	*0.83*	1.48	*2.64*	*14.54*
	St. dev.	0.29	20.12	8.55	0.81	0.17	0.45	0.81	0.14	0.39	1.38	3.08
	Min.	5.71	38	1.59	0.62	0.37	2.21	0.97	0.59	0.96	0.66	9.59
	Max.	7.12	117	29.55	3.65	1.03	4.03	4.20	1.14	2.59	5.66	21.25

Table 2.

Comparison of selected physicochemical parameters of the Czarna Wisełka and Biała Wisełka streams in different periods: 2018 – current research, 2004 – Astel et al. (2008), 1993 – Wróbel (1995), 1976-1984 – Kasza (1986)

Physicochemical parameter	Research period	Value	Czarna Wisełka		Biała Wisełka	
pH	2018	mean	5.4		6.7	
		min / max	4.5	6.5	5.7	7.1
	2004	mean	4.2		6.8	
		min / max	3.8	7.4	6.3	7.8
	1993	single sampling	5.46		7.2	
NH_4^+ [$mg \cdot dm^{-3}$]	2018	mean	1.06		2.48	
		min / max	0.05	3.48	0.97	4.2
	2004	mean	0.29		0.11	
		min / max	0.002	1.31	0.002	0.86
	1993	single sampling	0.154		0.123	
	1976-1984	mean	0.103		0.076	
		min / max	0.15	0.4	0	0.3
NO_3^- [$mg \cdot dm^{-3}$]	2018	mean	0.69		2.64	
		min / max	0.05	5.62	0.66	5.66
	2004	mean	0.58		1.78	
		min / max	0.16	1.21	0.59	4.06
	1993	single sampling	0.488		0.969	
	1976-1984	mean	1.28		1.67	
		min / max	0.15	2.7	0.68	2.58
Ca^{2+} [$mg \cdot dm^{-3}$]	2018	mean	0.36		2.05	
		min / max	0.04	1.21	0.62	3.65
	2004	mean	2.22		7.9	
		min / max	0.86	5.44	1.87	14.55
	1993	single sampling	3.43		13.4	
	1976-1984	mean	6.8		12.7	
		min / max	3.2	13.2	4.7	17.5
Mg^{2+} [$mg \cdot dm^{-3}$]	2018	mean	0.21		0.63	
		min / max	0.05	0.49	0.37	1.03
	2004	mean	0.57		1.45	
		min / max	0.23	1.69	0.52	2.7
	1993	single sampling	1.47		2.3	
	1976-1984	mean	4.0		3.8	
		min / max	0.4	6.9	2.0	9.5
SO_4^{2-} [$mg \cdot dm^{-3}$]	2018	mean	7.91		14.54	
		min / max	3.01	11.93	9.59	21.25
	2004	mean	8.11		13.09	
		min / max	5.41	11.04	8.79	19.40

Table 3.
Selected physicochemical parameters of water in the catchments of Biała Wisełka and Czarna Wisełka depending on forest stands

Stream	Location	Statistics	Number of samples	pH	SEC [µS/cm]	Ca^{2+} [mg·dm^{-3}]	Mg^{2+} [mg·dm^{-3}]	NH_4^+ [mg·dm^{-3}]	NO_3^- [mg·dm^{-3}]	SO_4^{2-} [mg·dm^{-3}]
Czarna Wisełka	deforestation area/upper samples/spruce stand	mean	11	5.31	33	0.33	0.17	2.03	0.92	7.91
		st. dev.		0.65	7.57	0.35	0.13	0.92	1.56	1.73
		min.		4.45	24	0.04	0.05	0.29	0.07	5.96
		max.		6.31	47	1.21	0.42	3.48	5.62	11.93
	forested area/lower samples/spruce stand	mean	12	5.51	29	0.39	0.25	0.17	0.49	7.91
		st. dev.		0.53	3.66	0.13	0.08	0.10	0.25	1.79
		min.		4.56	26	0.21	0.15	0.05	0.05	3.01
		max.		6.50	40	0.75	0.49	0.40	0.84	9.43
Biała Wisełka	beech stand	mean	13	6.85	90	2.59	0.68	2.94	1.79	15.88
		st. dev.		0.15	9.79	0.39	0.17	0.56	0.69	2.82
		min.		6.57	81	2.04	0.43	2.18	0.66	12.01
		max.		7.12	117	3.65	1.03	4.20	3.07	21.25
	spruce stand	mean	7	6.53	53	1.06	0.54	1.61	4.23	12.07
		st. dev.		0.37	9.35	0.27	0.12	0.42	0.80	1.71
		min.		5.71	38	0.62	0.37	0.97	3.05	9.59
		max.		6.94	63	1.29	0.69	2.26	5.66	14.57

is built of geological formations with a higher content of macro-elements, resulting in greater soil fertility in this area, compared to the Czarna Wisełka, which has lower pH, fewer alkaline ions, and is more acidic (Table 1). The diversity of the soils of the Biała Wisełka and Czarna Wisełka catchments has been described in detail by Maciaszek and Zwydak (1998) and Astel *et al.* (2008). The vegetation cover also may influence the higher concentrations of Ca^{2+} and Mg^{2+} ions and higher pH in the waters of Biała Wisełka, which is partially covered by a beech stand. Małek *et al.* (2010) and Jasik *et al.* (2017) indicate that the spring water chemistry has been modified by the tree species growing in the supply area. They noted higher Ca^{2+} and Mg^{2+} ion concentrations and higher pH in beech stands or with beech admixture than in spruce stands. Apart from the ions mentioned above, the concentrations of NH_4^+ also were higher in the watercourses of the Biała Wisełka and the concentrations of NO_3^- were higher in both the watercourses and the springs of the Biała Wisełka. Higher concentrations of NO_3^- and SO_4^{2-} ions in the watercourses and springs of the Biała Wisełka may be related to the greater exposure of this area to air pollution. Godzik and Kiszka (1995) noted higher mean sulphur concentrations in the thalli of *Hypogymnia physodes* (L.) Nyl. and spruce bark in the Biała Wisełka catchment. Astel *et al.* (2008) associate higher concentrations of NO_3^- ions in the Biała Wisełka catchment with the dominant northwestern exposure, and thus a shorter and less-intense vegetation period compared to the Czarna Wisełka catchment, with southwestern exposure.

The decay of spruce stands in the study area was spread over time, with the beginnings of intensive dieback recorded in 2003 (Fig. 2). Both naturally occurring deforestation and that resulting from forest management are associated with an increased outflow of NO_3^- ions from the catchment (Houlton *et al.*, 2003; Kopacek *et al.*, 2017; Sajdak *et al.*, 2021). Depending on the intensity of the decay, the size of the analysed stand, and the location of the study area, it can take from several months to two years for the concentration of NO_3^- ions in surface waters to increase as a result of deforestation (Likens *et al.*, 1969; Martin *et al.*, 1986; Houlton *et al.*, 2003; Wang *et al.*, 2006; Siemion *et al.*, 2011; Żelazny *et al.*, 2017). In the above-mentioned studies, the time for the NO_3^- concentration to return to the baseline state, *i.e.* before the removal of part or all of the stand or the natural disturbance, ranged from several months to four years.

Research carried out in the Tatra Mountains by Żelazny *et al.* (2017) and Kosmowska *et al.* (2018) indicate a severalfold increase in NO_3^- concentration in catchments draining deforested slopes compared to forested ones. These authors measured 15.44 and 13.84 $mg \cdot dm^{-3}$ NO_3^- in waters flowing out of deforested slopes after the wind breakage, 6.17 and 6.09 $mg \cdot dm^{-3}$ for deforested slopes as a result of bark beetle outbreak, and 3.26 and 4.40 $mg \cdot dm^{-3}$ for forested slopes. In the Silesian Beskid (Kosmowska *et al.*, 2018), the measurement for deforested slopes was 5.14 $mg \cdot dm^{-3}$ NO_3^-, and for forested slopes, it was 2.30 $mg \cdot dm^{-3}$. In the Biała Wisełka and Czarna Wisełka catchments, we observed an increase in NO_3^- concentration compared to 2004, which was expected in connection with the decay of spruce stands in the study area. However, this increase was small compared to the above-mentioned authors' results, perhaps because the decay process took several years and was not a single, violent event, such as deforestation caused by windfalls. Moreover, a new generation of the forest currently is growing in the research area, through which the nitrates necessary for growth are assimilated.

Decreasing concentrations of Ca^{2+} and Mg^{2+} in the Biała Wisełka and Czarna Wisełka watercourses may be related to the long-term deposition of pollutants in the study area. Despite decreasing emissions of pollutants into the atmosphere (Statistical Office in Katowice, 2018), their impacts have been visible in ecosystems for many years (Kosmowska *et al.*, 2016; Likens *et al.*, 2021). In forest catchments with excessive sulphur and nitrogen deposition, the negative impacts on soil and groundwater are noticeable. The results include acidification intensification, visible especially in coniferous stands, and leaching of Mg^{2+} and Ca^{2+} out of the tree-root systems. The increased outflow of these ions from the catchment area leads to a reduction in the Mg^{2+} and Ca^{2+} pool available for plants in the soil and a reduction in their concentration in surface waters flowing out of the catchment (Likens *et al.*, 1998; Jóźwiak and Kozłowski 2004; Likens *et al.*, 2021). In the catchment area of Biała Wisełka, water flowing in beech stands contained 8 times more Ca^{2+} and 4 times more Mg^{2+} compared to spruce stands from Czarna Wisełka. Within the Biała Wisełka catchment, this difference was less (respectively 2.5 times more for Ca^{2+} and 1.5 for Mg^{2+})

Likens *et al.* (2021) indicate that the types of disturbances affecting the catchments have short-term effects on the chemical compositions of waters, such as in the cases of hurricanes, hail, or drought, or long-term effects on the chemical compositions of waters, as in the case of acid deposition. When various perturbations overlap over time, they can produce unexpected long-term or short-term responses in water chemistry. Probably the greatest impact was at the time of intensive decomposition of spruce stands, and now there is a visible change in the water composition, with a greater share of ammonium ions reacting with humic acids as a result of the decomposition of accumulated organic matter.

Conclusions

- Compared to the studies conducted in the Beskidy and Tatra Mountains, the outflow of NO_3^- ions is not so clear, although the concentration of these ions has increased compared to 2004 (*i.e.* the period prior to deforestation). Higher concentrations of NO_3^- in waters were recorded in the part of the Biała Wisełka catchment covered with spruce stands.
- Compared to the previous periods, a significant decrease in Mg^{2+} and Ca^{2+} ion concentrations in the Biała Wisełka and Czarna Wisełka watercourses can be observed. Excessive pressure of industrial pollution on the study area can cause increased outflow of Mg^{2+} and Ca^{2+} ions from the catchment area and, thus, the depletion of the pool of these ions available in the soil.
- The increase in the concentration of NH_4^+ ions compared to previous years results from the ongoing process of organic-matter decomposition and is most visible in the area after the decomposition of spruce stands.

Authors' contribution

M.J. – study investigation, writing manuscript, data analysis, methodology; M.B. – study investigation, writing manuscript, data preparation and analysis, visualisation.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding source

This work was supported by the Ministry of Science and Higher Education of the Republic of Poland (SUB/040012/D019).

Acknowledgements

Special thanks to Iwona Skowrońska for providing chemical analysis and Anna Bała, Natalia Juszczak, and Łukasz Kuźniar for helping with sampling.

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STRESZCZENIE

Zróżnicowanie parametrów fizykochemicznych wód obszaru źródliskowego Wisły po rozpadzie drzewostanów świerkowych w Beskidach

Badania przeprowadzono w lipcu 2018 roku w masywie Baraniej Góry, w Beskidzie Śląskim. Próbki wody zostały pobrane ze źródeł i cieków Białej i Czarnej Wisełki, dających początek największej rzece w Polsce – Wiśle (ryc. 1). Kwaśna depozycja dużych ilości związków azotu i siarki oraz dokonana przez Habsburgów w XIX wieku przebudowa z wielogatunkowych drzewostanów z udziałem jodły, buka i świerka na monokultury świerkowe obcego pochodzenia przyczyniły się do wystąpienia w Beskidach klęski zamierania świerczyn na dużym obszarze (Małek i in. 2012; Małek, Krakowian 2012). Dodatkowo drzewostany te zostały dotknięte gradacją kornika drukarza *Ips typographus* (L.), a także porażeniem przez patogeny grzybowe, głównie z rodzaju *Armillaria* spp. (Grodzki 2010). Efektem tych zjawisk były olbrzymie wylesienia, m.in. w rejonie Skrzycznego i Baraniej Góry. Łącznie pobrano 69 próbek wody, z czego 15 ze źródeł i 20 z cieków Białej Wisełki oraz 11 ze źródeł i 23 z cieków Czarnej Wisełki (ryc. 3). Próbki wody zostały pobrane głównie w obrębie rezerwatu Barania Góra, utworzonego w 1953 roku w celu ochrony i obserwacji procesów zachodzących w poszczególnych piętrach klimatyczno-roślinnych Beskidu Śląskiego, a także zachowania obszaru źródliskowego Wisły w stanie naturalnym. Prace laboratoryjne wykonano w Laboratorium Geochemii Środowiska Leśnego i Terenów Przeznaczonych do Rekultywacji Uniwersytetu Rolniczego w Krakowie. W pobranych próbkach wody mierzono pH (przyrząd wielofunkcyjny Elmetron CX-741), przewodność elektrolityczną właściwą (konduktometr Elmetron CPC-551) oraz stężenie jonów Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, NH_4^+, NO_3^-, HCO_3^-, Na^+ i K^+ (chromatograf DIONEX 5000). Celem badań było poznanie zróżnicowania parametrów fizykochemicznych wód źródeł i cieków obszaru źródliskowego Wisły, w tym różnic między obszarami

zasilającymi Białej i Czarnej Wisełki. Obszary źródliskowe obu Wisełek różnią się budową geologiczną, typem i podtypem gleby, ukształtowaniem terenu, wystawą, siedliskowym typem lasu oraz składem gatunkowym drzewostanu (ryc. 3). Dodatkowo obszar źródliskowy Czarnej Wisełki oraz partie szczytowe obszaru źródliskowego Białej Wisełki zostały dotknięte klęską zamierania drzewostanów świerkowych (ryc. 2). Wymienione czynniki środowiskowe uwidaczniają się w odmiennym składzie chemicznym cieków i źródeł obu zlewni. Niższą wartość pH, przewodności elektrolitycznej właściwej oraz stężenia jonów Ca^{2+} i Mg^{2+}, a także SO_4^{2-}, Cl^-, NO_3^-, HCO_3^-, Na^+ i K^+, zarówno w źródłach, jak i ciekach, zanotowano w zlewni Czarnej Wisełki (tab. 1). W porównaniu do badań prowadzonych w Beskidach i Tatrach odpływ jonów NO_3^- nie jest tak wyraźny, aczkolwiek stężenie tych jonów uległo podwyższeniu w porównaniu z 2004 rokiem, czyli okresem przed wylesieniem. W porównaniu z poprzednimi okresami można zauważyć znaczne zmniejszenie wartości stężenia jonów Mg^{2+} i Ca^{2+} w ciekach Białej i Czarnej Wisełki (tab. 2).