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IMPACT OF DEFORESTATION ON WATER CHEMISTRY IN THE WESTERN TATRAS AND BESKID ŚLĄSKI RANGE IN THE POLISH CARPATHIANS

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ABSTRACT

The article describes the research into the impact of deforestation on the values of physicochemical traits and chemical composition of waters which drain the catchments covered with forest, and those that have been deforested, in the western part of Polish Carpathians. The research was carried out in independent catchments in the Skrzyczne massif in the Beski Śląski (Silesian Beskid Range) in 2013-2014, and in the Kościeliska Valley in the Western Tatras in 2015–2016. During field studies, water samples were collected monthly in catchments with various degrees of deforestation, and the physicochemical characteristics of water were measured (pH, EC, T,...). In the laboratory, the chemical composition of water, specifically the content of 14 ions (Ca²⁺, Mg²⁺, Na⁺, K⁺, NH₄, Li⁺, HCO₃, SO₄²⁻, Cl⁻, NO₇, NO₇, PO₃³⁻ Br⁻, F⁻), was determined by means of ion chromatography (DIONEX 2000). The conducted research has shown the impact of deforestation on the value of physical and chemical traits and chemical composition of water. Deforestation of the slopes caused changes in the structure of the chemical composition of water, especially in the area of correlations between anions. In the Tatras, in the basins deforested as a result of windfall, a significant increase in the proportion of NO₂ (% mval · dm⁻³) in the anionic element of the chemical composition of water was observed, and in the Beskid Śląski, in catchments deforested due to the tree stand decay associated with the imission of pollutants, a significant increase in SO₂² (% mval · dm⁻³) and a significant decrease in HCO₇ (% mval · dm⁻³) in the anionic structure of the chemical composition of waters was observed. These examples document the extremely important role played by forests, which cover mountain slopes, in the hydrochemical functioning of the catchment. In the spatial aspect, there is an unusual phenomenon of hydrochemical mosaicism consisting in the occurrence of different relationships between anions, especially hydrogen carbonates, sulphates and nitrates.

Keywords: stream-water chemistry, deforestation, nitrate concentration, sulfate concentration

INTRODUCTION

The chemical composition of surface waters is shaped by a number of processes occurring throughout the catchment, and the physical and chemical properties of water occurring in nature change under the influence of transformations in the surrounding natural environment (Chełmicki 2012). According to Czop et al. (2008) even small changes in local development conditions in the area of the spring, or in the area of

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their feeding zone, may have a strong impact on the chemical composition of waters.

The massive dying of spruce stands in mountain areas observed in recent years prompts research, due to the unique functions that forests perform in the natural environment. Deforestation of mountain slopes can be the result of anthropogenic or natural activities. In the western part of the Polish Carpathians, large-scale deforestation of anthropogenic nature has been observed for several decades. Spruce forests in the Tatra and Beskidy mountains struggle with many threats to tree stands, which are often referred to as catastrophic threats. The factors with the most important influence on the forest economy include the gradation of the bark beetle Ips typographus, together with the Pityogenes chalcographus (European spruce bark beetle), as the damaged trees create the ideal conditions for their development (Grodzki, Guzik 2009), and mountain winds, which contribute to the so-called windfalls. The last catastrophic phenomenon in the Tatra National Park took place in 2013, when a hurricane wind with the speed of up to 200 km per hour destroyed between one and two hundred thousands of trees. In turn, the Beskid Śląski range, in the 1980–1990s was exposed to strong anthropogenic impacts associated with the immission of pollutants from Silesia, as a result of which forest stands were damaged to a large extent. In the western Polish Carpathians, deforestation of varying origin can be identified. Slow decay of tree stands is observed as a result of long-term pollution; also, violent deforestation occurs sometimes due to strong winds.

The aim of the presented study was to determine the impact of deforestation on the values of physical and chemical characteristics and chemical composition of water that is draining both the forested and the deforested catchments.

MATERIAL AND METHODS

The research was carried out in the western part of Polish Carpathians, in the Kościeliska Valley, in Western Tatras, and in the Skrzyczne massif in the Beskid Śląski (Silesian Beskid range).

In order to determine the impact of deforestation on the chemical composition of water, for research purposes, twelve independent catchments were selected (see: Fig. 1), including six independent catchments in the Tatra National Park, in the Kościeliska Valley, in the catchment of Kościeliski Potok (stream), and another six the Silesian Beskids in the Skrzyczne massif in the Malinowski Potok (stream) and Leśnianka catchments, representing deforestation of varying origin. In the Tatras, three catchments covered with forest were selected for research: Kończysta Turnia (F KT), Krowi Żleb (F KR), and Wściekły Żleb (F WŻ), as well as three deforested catchments: one catchment deforested as a result of bark beetle gradation – Wściekły Żleb (DB WZ), and two catchments deforested as a result of windfall - Wściekły Żleb (DW WŻ) and Pośrednia Kopka (DW PK). In the Beskid Ślaski – two catchments covered with forest were selected: Hala Jaśkowa (F_HJ) and Leśnianka (F_L), as well as four deforested catchments: Pod Malinowska Skała (DA PMS), Kopa Skrzyczańska (DA_KS), and Małe Skrzyczne (DA MS), including one covered with young forest – Malinowska Skała (DA YF MS).

Field studies were conducted once a month: from November 2015 to October 2016 in the Tatras, and from November 2013 to October 2014 in the Beskid Śląski. Temperature, electrolytic conductivity (PEW $_{25^{\circ}\text{C}}$), and water pH were measured in the field, and water samples were taken.

In the Hydrological and Chemical Laboratory within the Institute of Geography and Spatial Management at the Jagiellonian University in Kraków, chemical composition of water was determined using the method of ion chromatography (DIONEX 2000), covering the range of main ion concentrations: Ca2+, Mg²⁺, Na⁺, K⁺, HCO₃⁻, SO₄²⁻, Cl⁻, nutrients: NO₃⁻, NO₂⁻, NH₄, PO₄ and micronutrients: Li⁺, F⁻ i Br⁻. The main ions and NO₃ were selected for the interpretation, while the remaining ions were omitted from the tabular reports due to their low concentration, often below the limit of detection. Water mineralization (M.) was calculated as the sum of the determined ions. The chemical composition of waters was characterized by the arithmetic average (avg.) in the range of ion concentration (mg \cdot dm⁻³), and their share (% mval \cdot dm⁻³) in the chemical composition of water. The variability of the chemical composition was described with the coefficient of variation (Cv), expressing the quotient of the standard deviation to the mean value expressed as a percentage, and presented graphically in the form of box charts.

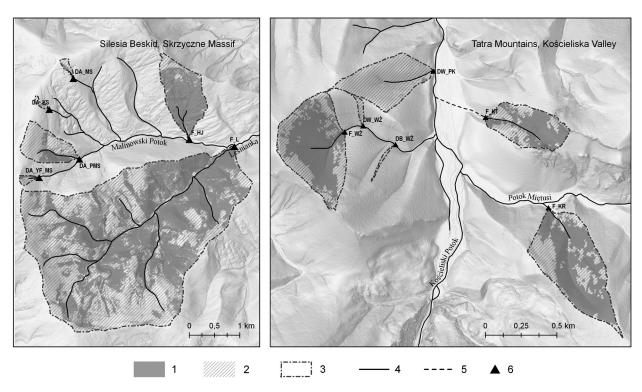


Fig. 1. Study area: 1 – forested areas, 2 – deforested areas, 3 – catchment boundaries, 4 – permanent streams, 5 – periodical streams, 6 – catchment-closing sections, water sampling locations

RESEARCH RESULTS AND DISCUSSION

The streams draining both the forested and the deforested Tatra catchments in the Kościeliska Valley are characterized - according to the division proposed by Pazdro and Kozerski (1990) - with a weakly alkaline reaction. A more diverse correlations occur in the Beskid Slaski, where streams draining the forested catchments located on the slopes of the Skrzyczne massif are similar to Tatra waters in terms of pH, and they also count among weakly alkaline waters, while the streams draining the higher-located, marshy, deforested catchments of the Skrzyczne massif are much more acidified, they have a lower pH and count among medium acidic waters. In terms of water mineralization, waters in the Tatras are more mineralized, and they belong to the freshwater class, whereas the waters in the Beskid Ślaski are poorly mineralized, and they belong to the so-called ultra-fresh waters (see: Table 1).

Analyses of the chemical composition of water in catchments located in the Kościeliska Valley tend

to show the highest concentration of calcium among all cations, followed by substantially lower average concentration of Mg²⁺, Na⁺ i K⁺ ions. The sequence of average concentrations of major cations in decreasing order is: Ca>Mg>Na>K (see: Table 2). In the Skrzyczne massif, the most common sequence of cations is different. Typically, the concentration of Ca²⁺ is the highest (just like in Tatra waters), while the second highest is sodium, whose concentration is usually higher than magnesium: Ca>Na>Mg>K (see: Table 2). The change in the sequence of cations results from differences in the geological structure of the catchment. The Tatra drainage catchments are made of carbonate sedimentary rocks (limestones, dolomites, marls), whereas the catchments in the Beskid Śląski are made of Carpathian flysch, with the dominance of sandstones and slates, sometimes with inserts of other sedimentary rocks.

In the case of anions, there is definitely more variation in terms of concentrations. Bicarbonate ions showed the highest concentration in the drainage wa-

Table 1. Average pH, EC_{25°C}, and M_t values in stream water

						p]	H	EC _{25%}	С	\mathbf{M}_{t}	
	Land c	over	Region	Catchment	ID	\overline{x}	Cv	\overline{x}	Cv	\overline{x}	Cv
						(pH)	[%]	[μS·cm ⁻¹]	[%]	[mg·dm ⁻³]	[%]
				Krowi Żleb	F_KR	8.20	2.6	321.7	1.3	275.4	1.1
	_		Total	Kończysta Turnia	F_KT	8.01	2.6	304.1	8.2	262.4	8.0
	E		Tatry	Wściekły Żleb	F_WŻ	7.72	2.4	302.3	8.1	258.6	8.0
	Forested (F)			Average	value	7.98	2.5	309.4	5.9	265.5	5.7
	ore			Hala Jaśkowa	F_HJ	7.32	1.6	69.8	9.5	51.4	11.9
	_		Beskid Śląski	Leśnianka	F_ L	7.37	1.9	76.2	6.3	56.7	7.4
			Siąski	Average	value	7.34	1.7	73.0	7.9	54.0	9.6
				Pośrednia Kopka	DW_PK	8.03	3.0	331.2	8.7	285.4	9.1
	Wind	fall (W)	Tatry	Wściekły Żleb	DW_WŻ	8.09	3.5	307.3	5.2	264.0	7.5
			rany	Average	value	8.06	3.2	319.2	6.9	274.7	8.3
<u> </u>	Bark b	eetle (B)		Wściekły Żleb	DB_WŻ	8.07	3.2	273.2	4.0	237.2	3.7
Deforested (D)	ıre (A)			Kopa Skrzyczańska	DA_KS	5.81	1.5	40.0	3.0	23.9	5.7
ore	essı		Beskid	Małe Skrzyczne	DA_MS	6.45	1.5	49.3	5.1	35.2	9.7
Def	Anthropogenic pressure (A)		Śląski	Pod Malinowską Skałą	DA_PMS	7.37	1.7	83.6	7.3	61.2	6.3
	godo			Average	value	6.54	1.6	57.6	5.1	40.1	7.2
	Anthro	Young fo	orest (YF)	Malinowska Skała	DA_YF_MS	7.14	1.4	74.3	8.6	53.7	6.1

ters of both forested and deforested catchments in the Kościeliska Valley as well as forested catchments of the Skrzyczne massif. The occurrence of the highest SO₄²⁻ concentration among anions in the deforested catchment (DA_KS) of the Skrzyczne massif is extremely interesting (see: Table 2). The analysis of average concentrations of bicarbonates, depending on the extent of forest cover, shows almost twice as high concentrations of these ions (average = $26.36 \text{ mg} \cdot \text{dm}^{-3}$) in the water from forest-covered catchments, compared to the water from deforested catchments (average = 14.2 mg·dm⁻³) in the Silesian Beskids. The analysis of nitrate concentrations, depending on the extent of forest cover, clearly shows that in the Tatras, in the deforested waters of the basin, the concentration of nitrates (average = $13.84 \text{ mg} \cdot \text{dm}^{-3}$) is several times higher than in non-deforested catchments (average = 4.40 mg·dm⁻³). In deforested catchments, there is also

a clear variation in average concentrations of nitrates depending on the type of deforestation. The concentration of nitrates is about twice as high (average = $13.84 \text{ mg} \cdot \text{dm}^{-3}$) in drainage catchments deforested as a result of windfall than in the basin deforested by the bark beetle (6.09 mg·dm⁻³) (see: Table 2). In the Beskid Śląski, the average concentration of nitrates in water from deforested catchments is twice as high (mean = $5.14 \text{ mg} \cdot \text{dm}^{-3}$), than in the forested catchments (average = $2.30 \text{ mg} \cdot \text{dm}^{-3}$) (see: Table 2)

The consequence of deforestation is a change in the sequence of average concentrations of anions, which presents as follows: in the Kościeliska Valley, in catchments covered with forest it is HCO₃>SO₄>NO₃>Cl, in the deforested catchments it is HCO₃>NO₃>SO₄>Cl whereas in more diversified in waters in the Skrzyczne massif it is SO₄>NO₃>HCO₃>Cl or HCO₃> NO₃>SO₄>Cl.

Table 2. Average concentration (\overline{x}) and coefficient of variation (Cv) of ions [$mg \cdot dm^{-3}$] in stream water

Land cover Region Catchment ID					Ca^{2+}	2+	${f Mg}^{2^+}$.2÷	$\mathbf{N}\mathbf{a}^{\scriptscriptstyle +}$	+_	$\mathbf{K}^{\scriptscriptstyle{+}}$		HCO_3^-	3-	SO_4^{2-}	٨.	NO_3^-	3-	C	_
Carchment Region Catchment ID					 x	Cv	x	Cv	Iχ	Cv	 x	Cv	 x	Cv	X	Cv	Iχ	Cv	ıχ	C
Tarry Timina F.KT 88.02 85 5.07 13.7 0.67 16.9 0.54 8.3 1866 8.2 5.98 2.55 4.89 2.09 0.60	Land cove		Catchment	a	[⁶⁻ mb · gm]	[%]	[*-mb · gm]	[%]	[-mb · gm]	[%]	[mg · gm]	[%]	[_E -mb · gm]	[%]	[⁶ -mb · gm]	[%]	[mg · gm]	[%]	[_E -mb · gm]	[%]
Tarry Tarr			Krowi Żleb	F_KR	41.64	3.1	18.74	3.9	0.23	8.8	0.36	5.4	204.0	1.0	6.74	12.6	3.08		0.51	8.6
Mindfull Misciekky F_WZ 60.18 78 2.99 25.2 0.84 77.3 0.45 9.9 180.7 87 764 23.7 5.22 444 0.56 2.70 2.70 2.70 2.85 2.70 2.85 2.8	(Tatry	Kończysta Turnia	F_KT	58.02		5.07	13.7	0.67	16.9	0.54	8.3	186.6	8.2	86	\sqrt{\sqrt{\chi}}	4.89	20.9	09.0	38.6
Average value S.2.8 6.5 8.93 14.3 0.58 16.3 0.44 7.9 190.4 6.0 6.79 19.6 4.40 24.6 0.56 Reskid Hala F.H. 9.63 11.2 1.40 11.5 1.74 8.0 0.86 9.7 25.82 16.9 8.98 4.7 1.68 27.7 1.26 Average value 9.94 9.5 1.2 1.40 11.5 1.74 8.0 0.86 9.7 25.82 16.9 8.98 4.7 1.68 27.7 1.26 Average value 9.94 9.5 1.52 9.7 1.92 8.6 0.83 10.5 10.29 5.2 2.30 22.8 1.99 Average value 0.94 9.5 1.52 9.7 1.92 8.6 0.83 10.5 10.29 8.2 1.90 1.90 Average value 0.94 9.5 1.52 9.7 1.92 8.6 0.83 1.95 1.94 9.7 1.92 8.6 0.83 1.95 1.94 9.7 1.92 1.94 Average value 0.94 8.2 1.40 0.75 1.75 1.75 1.94 9.7 1.95 1.94 9.7 Average value 0.94 8.7 1.92 1.95 1.95 1.94 1.95 1.95 1.95 1.95 1.95 Bark beetle Wisciekly DB_WZ 24.67 3.7 2.85 1.61 0.75 1.57 0.41 1.94 1.95 1.95 1.95 1.95 1.95 1.95 1.95 Bark beetle Wisciekly DB_WZ 24.67 3.7 2.85 1.61 0.75 1.57 0.41 1.95 1.95 1.95 1.95 1.95 1.95 Bark beetle Wisciekly DB_WZ 24.67 3.7 2.85 1.61 0.75 1.57 0.41 1.95 1.95 1.95 1.95 1.95 1.95 1.95 Bark beetle Wisciekly DB_WZ 24.67 3.7 2.85 1.61 0.75 1.57 0.41 1.95 1.95 1.95 1.95 1.95 1.95 1.95 Bark beetle Wisciekly DB_WZ 24.67 3.7 2.85 1.61 0.75 1.57 0.41 1.95 1.	T) bət		Wściekły Żleb	F_WŻ	60.18	7.8	2.99	25.2	0.84	27.3	0.43	6.6	180.7	8.7		23.7		44.4	0.56	41.9
Hala	ores		Average	value	53.28	6.5	8.93	14.3	0.58	16.3	0.44	7.9	190.4	0.9				24.6	0.56	29.7
Mindfall Average value P.J. 10.26 7.9 1.65 7.9 2.10 9.2 0.80 11.3 26.90 13.1 11.60 5.8 2.84 18.0 0.99 18.0 19.2 1.99 1.	FO	Beskid		F_HJ	9.63	11.2	1.40	11.5	1.74	8.0	98.0	9.7	25.82	16.9	86.8	4.7		27.7	1.26	4.0
Mindfall Misciekly DM_DK 65.69 8.2 3.46 24.5 1.05 8.6 0.84 1.52 1.54 1.55 1.04 1.55 1.04 1.05		Śląski		H.L	10.26	7.9	1.65	7.9	2.10	9.2	0.80	11.3	26.90	13.1	11.60	5.8		18.0	0.93	24.
Windfall (W) Pośrednia (W) DW_PK (55.69) 8.2 3.46 24.5 1.06 35.0 0.54 16.5 194.8 9.7 8.00 32.6 10.95 36.8 0.73 Windfall (W) Wsciekly (B) DW_WZ 60.96 6.8 3.03 16.5 0.70 17.8 0.51 12.4 184.0 9.1 7.97 28.9 13.84 37.6 0.79 Bark beetle (B) Wściekly DB_WZ 54.67 5.7 2.85 16.1 0.75 15.7 0.41 12.4 184.0 9.1 7.97 28.9 13.84 37.6 0.79 Rath beetle (B) Wściekly DB_WZ 54.67 5.7 2.85 16.1 0.75 15.7 0.41 12.4 184.0 9.1 7.97 28.9 13.8 37.6 3.29 1.30 4.3 6.65 3.20 1.31 4.3 6.65 1.24 18.3 7.1 28.1 1.39 1.2 8.21 4.3 1.31 4.3		•	Average	value	9.94	9.5	1.52	9.7	1.92	9.8	0.83	10.5	26.36		10.29	5.2		22.8	1.09	14.
Windfall Tatry Average value 63.33 7.5 3.24 20.5 0.70 17.8 0.51 8.3 173.2 8.5 7.94 25.3 16.74 38.5 0.85 Bark beetle Skrzy-czae DA_KS 2.467 5.7 2.85 16.1 0.75 15.7 0.41 12.4 165.14 3.7 6.62 17.2 6.09 17.8 0.59 Beskid Pod Skraye value 7.55 5.4 1.05 6.8 1.38 0.70 28.1 26.8 3.41 26.8 3.41 2.4 3.41 3.4		;	Pośrednia Kopka		69:59	8.2	3.46	24.5	1.06	35.0	0.54	16.5	194.8	9.7	8.00	32.6	10.95	36.8	0.73	38.
Average value 63.33 7.5 3.24 20.5 12.4 184.0 9.1 7.97 28.9 13.84 37.6 0.79 (B) Aksciekly DA_KS 54.67 5.7 2.85 16.1 0.75 15.7 0.41 12.4 165.14 3.7 6.62 17.2 6.09 17.8 0.59 Skrzy- czańska DA_KS 3.90 3.8 0.83 5.9 1.30 4.3 0.65 33.2 2.15 49.8 10.10 4.6 4.35 12.6 0.61 Skrzyczne Beskid Słąski Skała DA_MS 6.61 5.6 0.82 7.2 1.23 4.2 0.60 41.6 13.39 21.2 8.34 2.9 3.29 9.2 0.82 Słąski Gross Skała Pod Average value 7.55 5.4 1.05 6.8 1.38 7.4 0.65 34.3 14.12 26.9 9.43 4.9 5.14 13.4 0.78 Walinowska Forest	windi (W)		Wściekły Żleb	DW_WŻ		8.9	3.03	16.5	0.70	17.8	0.51	8.3	173.2	8.5	7.94	25.3	16.74	38.5	0.85	33.2
Bark beetle		•	Average	value	63.33	7.5	3.24	20.5	0.88	26.4	0.52	12.4	184.0	9.1	7.97		13.84	37.6	0.79	35.
Kopa Skrzy- DA_KS 3.90 3.8 0.83 5.9 1.30 4.3 0.65 33.2 2.15 49.8 10.10 4.6 4.35 12.6 0.61 0.61 Male	Bark be (B)	etle	Wściekły Żleb	DB_WŻ	54.67	5.7	2.85	16.1	0.75	15.7	0.41	12.4	165.14	3.7	6.62	17.2	60.9	17.8	0.59	14.
Beskid Pod Skrzyczne DA_MS 6.61 5.6 0.82 7.2 1.23 4.2 0.60 41.6 13.39 21.2 8.34 2.9 3.29 9.2 0.82 0.82 0.82 0.82 0.70 28.1 26.82 9.7 9.85 7.2 7.78 18.3 0.78 0.82 0.70 28.1 26.82 9.7 9.85 7.2 7.78 18.3 0.78 0.82 0.83 0.82 0.83 0.83 0.84 0.84 0.85 0.84 0.85 0.84 0.85 0.84 0.85 0.84 0.85 0.84 0.85 0.84 0.85 0.84 0.85 0.84 0.85			Kopa Skrzy- czańska	DA_KS	3.90	3.8	0.83	5.9	1.30	4.3	0.65	33.2	2.15	49.8	10.10	4.6	4.35	12.6	0.61	16.8
Beskid Pod Sląski Malinowską DA_PMS 12.13 6.8 1.49 7.3 1.61 13.8 0.70 28.1 26.82 9.7 9.85 7.2 7.78 18.3 0.78 Young forest Average value 7.55 5.4 1.05 6.8 1.38 7.4 0.65 34.3 14.12 26.9 9.43 4.9 5.14 13.4 0.74 Young forest Skała Malinowska MS 0.83 6.9 1.64 8.1 1.63 5.6 0.69 14.0 20.17 11.2 8.49 4.3 10.52 9.9 0.68			Małe Skrzyczne	DA_MS	6.61	5.6	0.82	7.2	1.23		09.0	41.6	13.39	21.2	8.34		3.29		0.82	17.:
Young forest Average value 7.55 5.4 1.05 6.8 1.38 7.4 0.65 34.3 14.12 26.9 9.43 4.9 5.14 13.4 0.74 Young forest Malinowska DA_YF 9.83 6.9 1.64 8.1 1.63 5.6 0.69 14.0 20.17 11.2 8.49 4.3 10.52 9.9 0.68 (YF) (YF)	ıq əinəgoqo	Beskid Śląski	ı		12.13	8.9	1.49	7.3	1.61	13.8	0.70	28.1	26.82	9.7	9.85	7.2	7.78	18.3	0.78	25.
Young Malinowska DA_YF_ 9.83 6.9 1.64 8.1 1.63 5.6 0.69 14.0 20.17 11.2 8.49 4.3 10.52 9.9 0.68 (YF)	nthro		Average	value	7.55	5.4	1.05	8.9	1.38	7.4	9.65	34.3	14.12	26.9	9.43	4.9	5.14	13.4	0.74	20.
		ung rest 7F)	Malinowska Skała	DA_YF_ MS	9.83	6.9	1.64	8.1	1.63	5.6	69.0	14.0	20.17	11.2	8.49		10.52	6.6	99.0	22.0

The analysis of the structure of chemical composition of watercourses draining the forested and the deforested catchments shows particularly large variations in terms of anions. In the Tatras, the share of NO₃ in the structure of chemical composition of water draining the catchments deforested as a result of windfall is on average 3.3% mval·dm⁻³; it is over three times higher than in the forested catchments, with the average of 1.1% mval·dm⁻³, and almost twice as large as in the catchments affected by the bark beetle with the average of 1.7% mval·dm⁻³ (see: Table 3, Fig. 2). In the Beskid Śląski, the share of SO₄- ions in the structure of chemical composition of water draining the catchments deforested as a result of pollution is on average 21.0% mval·dm⁻³ which makes it twice as high as in forested catchments, where the average is 14.8% mval·dm⁻³ (see: Fig. 2). The average share of NO₃ is almost three times higher in the water from the deforested catchment (average = 8.0% mval·dm⁻³) compared to forested areas (average = 2.5% mval·dm⁻³). In turn, the average share of HCO₂ ions in the chemical composition of waters is almost twice as high in forested catchments (with the average of 30.3% mval·dm⁻³), than in the deforested catchments (with the average of 18.7% mval·dm⁻³). It is worth noting that in the basin of deforested, but almost entirely overgrown young forest, the share of HCO₃ in the structure of chemical composition of water increases significantly (with the average of 23.6% mval·dm⁻³), whereas the share of SO₄²- decreases (with the average of 12, 2% mval·dm⁻³). (see: Table 3).

The consequence of deforestation in both the Tatras and in the Beskid Slaski range is the change of the anion sequence within the structure of the chemical composition of waters in these areas. The proportion of NO₃ ions in the structure of the chemical composition of waters draining the deforested catchments of the Tatras was so large that the sequence of anions from the natural sequence HCO₃>SO₄>NO₃>Cl occurring in the waters in this area changed to the sequence HCO₃>NO₃>SO₄>Cl. In the Beskid Śląski, a large proportion of SO₄²⁻ ions in the structure of the chemical composition of waters draining deforested catchments has changed the sequence of anions from HCO₃>SO₄>NO₃>Cl, which dominates in waters from forested catchments, to SO₄>HCO₃>NO₃>Cl, dominant in waters from the deforested catchment, or HCO₃>SO₄=NO₃>Cl in the catchment where secondary reforestation of the slopes was observed.

Extremely interesting is the occurrence of very low concentrations of bicarbonates in the drainage waters of the deforested areas of the Malinowski Stream catchment, near the ridge, in the Beskid Śląski range (DA KS catchment). In this part of Carpathian flysch there is an exceptional sequence of anions, where the concentration of bicarbonates and their share in the chemical composition is small, and it is expressed by the sequence of SO₄>NO₃>HCO₃>Cl. This is an unusual hydrochemical phenomenon, because as a rule in a temperate climate in sedimentary rocks, the dominant anion should be bicarbonates. The negligible share of bicarbonates in the chemical composition of water probably indicates a disturbance of the relationship between carbon dioxide occurring in the soil and bicarbonates. In the Carpathian flysch, bicarbonates are generally the dominant ions among anions (Drużkowski, Szczepanowicz 1988; Maultz 1972; Welc 1985; Żelazny 1995, 2005; Siwek 2012, Żelazny et al. 2017). This is also confirmed by the above studies, carried out in the Kościeliska Valley and in the forested areas of the Skrzyczne massif catchment, as well as several years of studies of 23 streams in the Polish Tatras, whereby M. Żelazny (2012) has demonstrated the predominance of bicarbonates among the anions, in the chemical composition of the water regardless of the hydro-meteorological and lithological conditions. The dominance of sulphates over bicarbonates in the structure of the chemical composition of waters was shown by Michalik (2008) and Michalik et al. (2012) in waters from springs in the Świętokrzyskie Mountains, as well as by Kosmowska et al. (2015) and Kosmowska et al. (2016) in the Malinowski Stream catchment in the Beskid Śląski. This is linked to the accumulation of pollutants in the soil as a result of the emission of pollutants from Silesia and their depositing in mountainous catchments, after which it is possible to observe their leaching from the soil solution. Thus, the presence of sulphates in high concentrations and their significant share in the structure of chemical composition Therefore, the high saturation of sulphates, and their significant share in the chemical composition of water can be associated with an anthropogenic factor. The much higher proportion of sulphates in the chemical composition of water is also

Table 3. Average concentration (\bar{x}) and coefficient of variation (Cv) of the ions content [% mval · dm⁻³] in stream water

	,																			
					Ű	Ca^{2+}	Ĭ	${ m Mg}^{2^+}$	\mathbf{Na}^{+}	+_	$\mathbf{K}^{\scriptscriptstyle{+}}$	+	HCO_{3}^{-}	3	\mathbf{SO}_4^{2-}	ı	NO_3^-	1	ū	
					lχ	Cv	lχ	Cv	lχ	Cv	lχ	Cv	lχ	Cv	lχ	Cv	lχ	Cv	Iχ	$C_{\mathbf{v}}$
	Land cover	Region	Catchment	a	[% mval · dm-3]	[%]	[% mval · dm-3]	[%]	[% mval · dm-8]	[%]	[°-mb · lavm %]	[%]	[8-mb · Isvm %]	[%]	[% mval · lavm %]	[%]	[°-mb · lsvm %]	[%]	[*-mb · lsvm%]	[%]
			Krowi Żleb	F_KR	28.5	1.5	21.2	2.1	0.1	5.4	0.1	5.8	47.1	9.0	2.0 1	12.1	0.7	8.3	0.2	8.7
	(*	Tatry	Kończysta Turnia	F_KT	43.2	1.0	6.2	9.9	0.4	11.0	0.2	9.3	46.6	1.4	1.9 1	18.8	1.2 2	25.3	0.3	43.6
	1) b		Wściekły Żleb	F_WŻ	45.6	1.8	3.7	19.8	9.0	20.2	0.2	12.8	45.9	1.8	2.4 1	18.6	1.3 5	50.7	0.2	48.0
	resto		Average value	alue	39.1	1.4	10.4	9.5	9.4	12.2	0.2	9.3	46.5	1.3	2.1 1	16.5	1.1	28.1	0.2	33.4
	Foi		Hala Jaśkowa	F_HJ	34.6	1.1	8.3	2.2	5.5	4.6	1.6	5.1	31.2	5.7	14.0 1	10.8	2.0 2	20.9	2.7	13.2
		Beskid Ślaski	Leśnianka	F_L	33.7	1.5	8.9	1.7	0.9	7.7	1.3	9.6	29.4	6.5	15.6	8.4	3.1 2	20.1	1.8	27.4
		and a second	Average value	alue	34.1	1.3	9.8	1.9	5.7	6.1	1.4	7.3	30.3	6.1 1	14.8	9.6	2.5 2	20.5	2.2	20.3
	Wiatrolom		Pośrednia Kopka	DW_PK	45.3	1.8	3.9	17.2	9.0	27.4	0.2	23.8	8.44	2.7	2.3 2	24.5	2.5 4	40.7	0.3	40.4
	Windfall (W)	Tatry	Wściekły Żleb	DW_WŻ	45.6	1.3	3.7	14.8	0.5	13.2	0.2	6.7	43.0	4.0	2.5 1	17.8	4.1 3	38.9	0.4	33.6
		•	Average value	alue	45.4	1.5	3.8	16.0	0.5	23.0	0.2	15.2	43.9	3.3	2.4 2	21.1	3.3 3	39.8	0.3	37.0
	Bark beetle (B)	_	Wściekły Żleb	DB_WŻ	45.4	1.4	3.9	15.0	0.5	13.4	0.2	9.4	45.7	1.1	2.3 1	15.9	1.7 1	18.3	0.3	15.6
(a) t	(')		Kopa Skrzyczańska	DA_KS	28.8	1.9	10.1	2.3	8.4	3.0	2.43	26.3	5.2	43.9 3	31.6	6.4 1	10.5 1	13.3 2	2.56	16.9
orestec	A) əzns		Małe Skrzyczne	DA_MS	35.3	1.8	7.2	2.5	5.7	3.4	1.61	34.6	23.1	11.1	18.6	6.8	5.7 1	14.0	2.48	17.9
Det	esenic pres	Beskid Śląski	Pod Malinowską Skałą	DA_PMS	37.1	4.2	7.5	3.5	5.0	11.9	1:1	23.1	27.7	7.1	12.9	0.9	7.9 1	16.7	4.	25.9
	лоро	I	Average value	alue	33.7	2.0	8.3	2.8	6.4	6.1	1.7	28.0	18.7	27.0 2	21.0	7.1	8.0 1	14.7	2.1	20.2
	Anti Young forest (YF)		Malinowska Skała	DA_YF_ MS	34.4	6.0	9.4	2.5	5.0	2.8	1.23	0.1	23.6	7.0 1	12.2	3.1 1	12.2	10.5	1.37	20.1

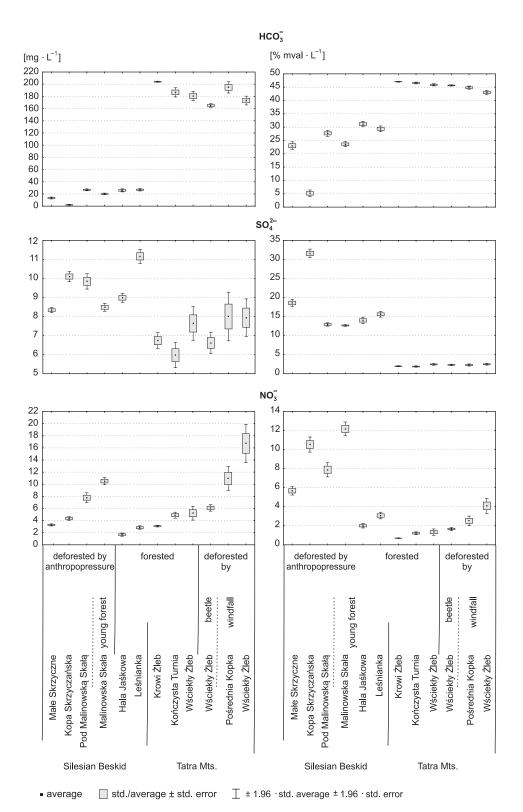


Fig. 2. Diversification of anions in the chemical composition of water

due to the low mineralization of water in the Beskidy Mountain area.

It is worth noting the role played by nitrates in shaping the structure of the chemical composition of streams. The reason for the increase in nitrate concentration in the waters draining deforested catchments in the Tatras is their reduced abstraction due to the damage or destruction of the tree stand, as documented by: Burns, Murdoch (2005), Wang et al. (2006); therefore, an increase in the supply of nitrates to the soil from dead organic matter is observed (Dahlgren 1998), and consequently, their concentration in water is much higher.

The damaged tree stand behaves similarly to the aging tree stand, which loses the active absorption of NO₃ ions with age (Vitousek, Reiners 1975; Murdoch, Stoddard 1992; Swank, Vose 1997). The decrease in NO₃ concentration in the waters from the deforested catchments in the Beskid Śląski is most probably connected with plant succession in these catchments. We do not observe intensive leaching of nitrogen from the catchment, as in the Tatra Mountains, because instead it gets assimilated by the newly growing plants and the young forest in these catchments. Similar results were obtained by Houlton et al. (2003) who conducted multi-year studies in the Hubbard Brook catchment. They showed a repeated increase in NO₂ concentration in waters from the catchment deforested as a result of hailstorm, which proves the rapid reaction of the natural environment associated with the destruction of the biotic catchment fragment. While conducting research in the USA in the White Mountains in watercourses draining the catchments in which the forest was cut down, Martin et al. (1986) also obtained a multiple increase in NO₃ concentration. It is also worth noting that in the studied deforested catchments, the variability of nitrates and bicarbonates is high, which is confirmed by the coefficient of variation, showing the highest variability (Cv = 49.8%, DA KS catchment) for bicarbonates in the deforested catchment of the Beskid Śląski, and high variability in other deforested catchments (see: Table 3).

CONCLUSIONS

Deforestation of slopes in the Kościeliska Valley in the Tatras due to the windfall and to slow gradation of bark beetles; and slopes deforestation in the Skrzyczne massif of the Beskid Ślaski due to immission of anthropogenic pollution, caused changes in the chemical composition of waters, especially in the proportions od anions. In the Tatras, the multiple increase in NO₃ ions concentration, and a very substantial increase in their proportion (% mval · dm⁻³) in the anionic element within the chemical composition of water led to their increased role in shaping the chemical composition of water, as demonstrated by their position in the sequence of anions. In the watercourses, which drain the Tatra basins deforested as a result of windfall, NO₃ ions precede SO₄²- ions, giving way only to HCO₃ ions. In the Beskid Śląski, deforestation of anthropogenic nature resulted in a multiple increase in the share of SO_4^{2-} (% mval·dm⁻³) and at the same time, a decrease in the HCO₃ share in the anionic element within the chemical composition of waters. In the watercourses draining deforested catchments, SO₄²⁻ ions play a dominant role in shaping the chemical composition of water. The role of bicarbonates in shaping the chemical composition of waters in the deforested area of slopes near the ridge is sometimes even smaller, because they are also preceded by NO₃ in the sequence.

The observed deforestation in the Beskid Śląski, especially in the parts of the slope located near the ridge, results in the disturbance of the natural sequence of anions. In the spatial aspect, there is an unusual phenomenon of hydrochemical mosaicism of waters draining the deforested areas near the ridge. In these areas, the importance of individual anions in shaping the chemical composition of waters is variable, and even bicarbonates, which are usually perceived as the most important anions in the temperate zone, sometimes can play a negligible, tertiary role.

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WPŁYW WYLESIEŃ NA SKŁAD CHEMICZNY WÓD W KARPATACH POLSKICH NA PRZYKŁADZIE TATR ZACHODNICH I BESKIDU ŚLĄSKIEGO

ABSTRAKT

W artykule opisano badania wpływu wylesień na wartości cech fizyczno-chemicznych i skład chemiczny wód odwadniających zlewnie pokryte lasem i wylesione w zachodnich Karpatach Polskich. Badania przeprowadzono w niezależnych zlewniach w masywie Skrzycznego w Beskidzie Śląskim w latach 2013–2014 i w Dolinie Kościeliskiej w Tatrach Zachodnich w latach 2015–2016.

W terenie pobierano co miesiąc próbki wody w zlewniach o różnym stopniu wylesienia oraz mierzono cechy fizyczno-chemiczne wody (pH, EC, T_w). W laboratorium metodą chromatografii jonowej (DIONEX 2000) oznaczono skład chemiczny wód w zakresie 14 jonów (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , Li^+ , HCO_3^- , SO_4^{2-} , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} Br $^-$, F^-). Przeprowadzone badania wykazały wpływ wylesień na wartości cech fizyczno-chemicznych i skład chemiczny wód.

Wylesienie stoków spowodowało zmiany w strukturze składu chemicznego wód szczególnie w zakresie relacji między anionami. W Tatrach, w zlewniach wylesionych wskutek wiatrołomu zaobserwowano zgodnie z oczekiwaniem znaczny wzrost udziału NO₃⁻ (% mval · dm⁻³) w członie anionowym składu chemicznego wody, a w Beskidzie Śląskim w wylesionych zlewniach wskutek rozpadu drzewostanu związanego z imisją zanieczyszczeń zaobserwowano znaczny wzrost udziału SO₄²⁻ (% mval · dm⁻³) i znaczny spadek HCO₃⁻ (% mval · dm⁻³) w anionowym członie struktury składu chemicznego wód. Te przykłady dokumentują niezwykle ważną rolę, jaką odgrywają lasy pokrywające stoki górskie w hydrochemicznym funkcjonowaniu zlewni. W aspekcie przestrzennym występuje nietypowe zjawisko mozaikowości hydrochemicznej, polegające na występowaniu różnych relacji między anionami, szczególnie wodorowęglanami, siarczanami i azotanami.

Słowa kluczowe: chemizm wód, wylesienie, stężenie azotanów, siarczanów