

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 Beskidy 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, PEW, T_w). In the laboratory, the chemical composition of water, specifically the content of 14 ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , Li^+ , HCO_3^- , SO_4^{2-} , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} , 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 NO_3^- ($\% \text{ mval} \cdot \text{dm}^{-3}$) 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 SO_4^{2-} ($\% \text{ mval} \cdot \text{dm}^{-3}$) and a significant decrease in HCO_3^- ($\% \text{ mval} \cdot \text{dm}^{-3}$) 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 intensive 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 absorbed 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 present 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 Beskidy range).

In order to determine the impact of deforestation on the chemical composition of water, for research purposes, twelve independent catchments were selected (see: Figure 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_WŻ), and two catchments deforested as a result of windfall – Wściekły Żleb (DW_WŻ) and Pośrednia Kopka (DW_PK). In the Beskid Śląski – two catchments covered with forest were selected: Hala Jaśkowa (F_HJ) and Leśnianka (F_L), as well as four deforested catchments: Pod Malinowska Skałą (DA_PMS), Kopa Skrzycznańska (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 ($PEW_{25^{\circ}C}$), 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: Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , HCO_3^{-} , SO_4^{2-} , Cl^{-} , nutrients: NO_3^{-} , NO_2^{-} , NH_4^{+} , PO_4^{3-} and micronutrients: Li^{+} , F^{-} i Br^{-} . The main ions and NO_3^{-} 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_t) 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.

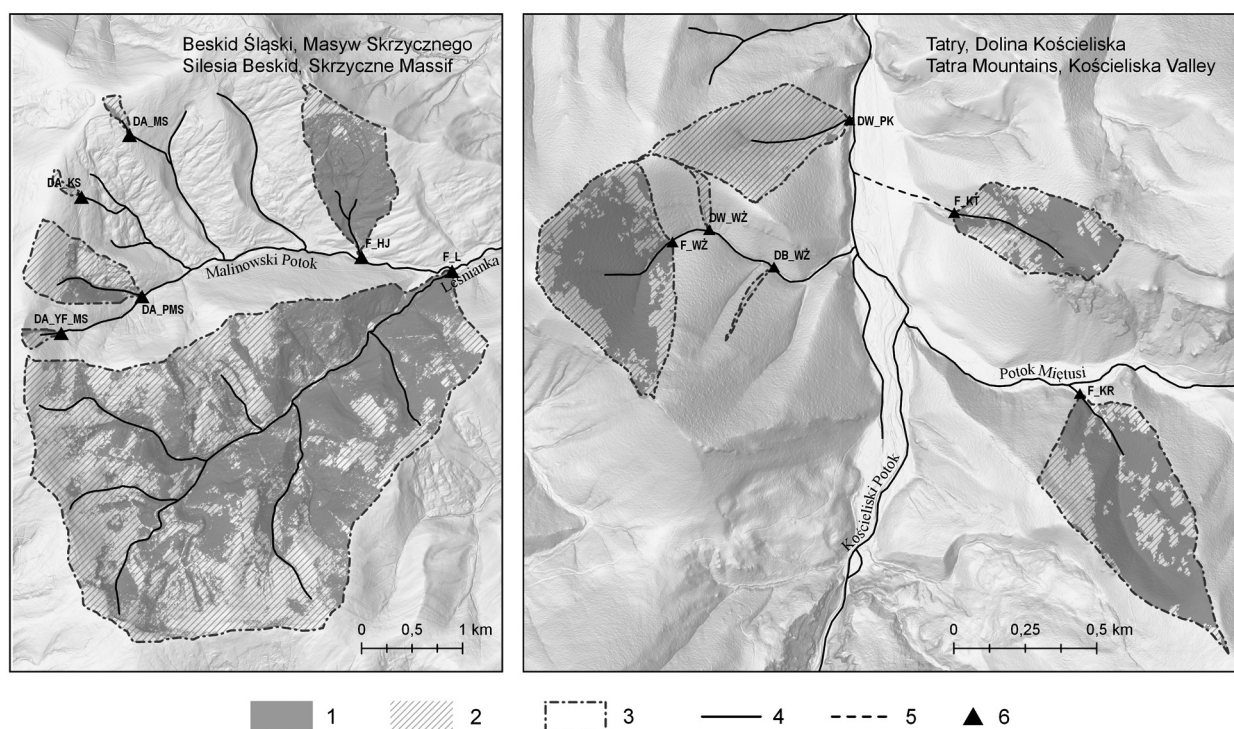


Fig. 1. Study area: 1 – forested areas, 2 – deforested areas, 3 – catchment boundaries, 4 – permanent streams, 5 – periodical streams, 6 – catchment-closing sections, water sampling locations

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 Śląski, 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 Śląski 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 Mg^{2+} , 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 Ca^{2+} 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, $PEW_{25^{\circ}C}$ and M_t values in stream water

Land cover	Region	Catchment	ID	pH		$PEW_{25^{\circ}C}$		M_t		
				\bar{x}	Cv	\bar{x}	Cv	\bar{x}	Cv	
				(pH)	[%]	$[\mu S \cdot cm^{-1}]$	[%]	$[mg \cdot dm^{-3}]$	[%]	
Forested (F)	Tatry	Krowi Żleb	F_KR	8.20	2.6	321.7	1.3	275.4	1.1	
		Kończysta Turnia	F_KT	8.01	2.6	304.1	8.2	262.4	8.0	
		Wściekły Żleb	F_WŻ	7.72	2.4	302.3	8.1	258.6	8.0	
	Average value				7.98	2.5	309.4	5.9	265.5	5.7
	Beskid Śląski	Hala Jaškowa	F_HJ	7.32	1.6	69.8	9.5	51.4	11.9	
		Leśnianka	F_L	7.37	1.9	76.2	6.3	56.7	7.4	
Average value				7.34	1.7	73.0	7.9	54.0	9.6	
Windfall (W)	Tatry	Pośrednia Kopka	DW_PK	8.03	3.0	331.2	8.7	285.4	9.1	
		Wściekły Żleb	DW_WŻ	8.09	3.5	307.3	5.2	264.0	7.5	
		Average value				8.06	3.2	319.2	6.9	274.7
	Bark beetle (B)	Wściekły Żleb	DB_WŻ	8.07	3.2	273.2	4.0	237.2	3.7	
Deforested (D)	Anthropogenic pressure (A)	Beskid Śląski	Kopa Skrzyczańska	DA_KS	5.81	1.5	40.0	3.0	23.9	5.7
			Małe Skrzyczne	DA_MS	6.45	1.5	49.3	5.1	35.2	9.7
		Pod Malinowską Skałą	DA_PMS	7.37	1.7	83.6	7.3	61.2	6.3	
		Average value				6.54	1.6	57.6	5.1	40.1
	Young forest (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 SO_4^{2-} 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 = $14.2 \text{ mg} \cdot \text{dm}^{-3}$) 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 = $4.40 \text{ mg} \cdot \text{dm}^{-3}$). 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 ($6.09 \text{ mg} \cdot \text{dm}^{-3}$) (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 $HCO_3 > SO_4 > NO_3 > Cl$, in the deforested catchments it is $HCO_3 > NO_3 > SO_4 > Cl$ whereas in more diversified waters in the Skrzyczne massif it is $SO_4 > NO_3 > HCO_3 > Cl$ or $HCO_3 > NO_3 > SO_4 > Cl$.

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

Land cover	Region	Catchment	ID	Ca ²⁺		Mg ²⁺		Na ⁺		K ⁺		HCO ₃ ⁻		SO ₄ ²⁻		NO ₃ ⁻		Cl ⁻			
				\bar{x} [$\text{mg} \cdot \text{dm}^{-3}$]	Cv [%]	\bar{x} [$\text{mg} \cdot \text{dm}^{-3}$]	Cv [%]	\bar{x} [$\text{mg} \cdot \text{dm}^{-3}$]	Cv [%]	\bar{x} [$\text{mg} \cdot \text{dm}^{-3}$]	Cv [%]	\bar{x} [$\text{mg} \cdot \text{dm}^{-3}$]	Cv [%]	\bar{x} [$\text{mg} \cdot \text{dm}^{-3}$]	Cv [%]	\bar{x} [$\text{mg} \cdot \text{dm}^{-3}$]	Cv [%]	\bar{x} [$\text{mg} \cdot \text{dm}^{-3}$]	Cv [%]	\bar{x} [$\text{mg} \cdot \text{dm}^{-3}$]	Cv [%]
Forested (F)	Tatry	Krowi Żleb	F_KR	41.64	3.1	18.74	3.9	0.23	4.8	0.36	5.4	204.0	1.0	6.74	12.6	3.08	8.6	0.51	8.6	8.6	
			F_KT	58.02	8.5	5.07	13.7	0.67	16.9	0.54	8.3	186.6	8.2	5.98	22.5	4.89	20.9	0.60	38.6	38.6	
	Beskid Śląski	Wściekły Żleb	F_WŻ	60.18	7.8	2.99	25.2	0.84	27.3	0.43	9.9	180.7	8.7	7.64	23.7	5.22	44.4	0.56	41.9	41.9	
			Average value	53.28	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	29.7	29.7	
	Beskid Śląski	Hala Jaskowa	F_HJ	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	4.0	4.0	
			F_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	2.84	18.0	0.93	24.1	24.1	
	Windfall (W)	Tatry	Pośrednia Kopka	DW_PK	65.69	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	38.1	38.1
				Average value	63.33	7.5	3.24	20.5	0.88	26.4	0.52	12.4	184.0	9.1	7.97	28.9	13.84	37.6	0.79	35.6	35.6
	Bark beetle (B)	Tatry	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	6.09	17.8	0.59	14.9	14.9
				Average value	63.33	7.5	3.24	20.5	0.88	26.4	0.52	12.4	184.0	9.1	7.97	28.9	13.84	37.6	0.79	35.6	35.6
Deforested (D)	Anthropogenic pressure (A)	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	16.8	
			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	20.0	20.0	
	Beskid Śląski	Małe 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	17.5	17.5	
			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	20.0	20.0	
	Young forest (YF)	Beskid Śląski	Malinowską Skatą	DA_YF_MS	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	22.6	22.6
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	20.0	20.0	

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 NO_3^- in the structure of chemical composition of water draining the catchments deforested as a result of wind-fall is on average $3.3\% \text{ mval} \cdot \text{dm}^{-3}$; it is over three times higher than in the forested catchments, with the average of $1.1\% \text{ mval} \cdot \text{dm}^{-3}$, and almost twice as large as in the catchments affected by the bark beetle with the average of $1.7\% \text{ mval} \cdot \text{dm}^{-3}$ (see: Table 3, Figure 2). In the Beskid Śląski, the share of SO_4^{2-} ions in the structure of chemical composition of water draining the catchments deforested as a result of pollution is on average $21.0\% \text{ mval} \cdot \text{dm}^{-3}$ which makes it twice as high as in forested catchments, where the average is $14.8\% \text{ mval} \cdot \text{dm}^{-3}$ (see: Figure 2). The average share of NO_3^- is almost three times higher in the water from the deforested catchment (average = $8.0\% \text{ mval} \cdot \text{dm}^{-3}$) compared to forested areas (average = $2.5\% \text{ mval} \cdot \text{dm}^{-3}$). In turn, the average share of HCO_3^- ions in the chemical composition of waters is almost twice as high in forested catchments (with the average of $30.3\% \text{ mval} \cdot \text{dm}^{-3}$), than in the deforested catchments (with the average of $18.7\% \text{ mval} \cdot \text{dm}^{-3}$). It is worth noting that in the basin of deforested, but almost entirely overgrown young forest, the share of HCO_3^- in the structure of chemical composition of water increases significantly (with the average of $23.6\% \text{ mval} \cdot \text{dm}^{-3}$), whereas the share of SO_4^{2-} decreases (with the average of $12, 2\% \text{ mval} \cdot \text{dm}^{-3}$). (see: Table 3).

The consequence of deforestation in both the Tatras and in the Beskid Sądecki range is the change of the anion sequence within the structure of the chemical composition of waters in these areas. The proportion of NO_3^- 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 $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}$ occurring in the waters in this area changed to the sequence $\text{HCO}_3^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}$. In the Beskid Śląski, a large proportion of SO_4^{2-} ions in the structure of the chemical composition of waters draining deforested catchments has changed the sequence of anions from $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}$, which dominates in waters from forested catchments, to $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^- > \text{Cl}$, dominant in waters from the deforested catchment, or

$\text{HCO}_3^- > \text{SO}_4^{2-} = \text{NO}_3^- > \text{Cl}$ 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 $\text{SO}_4^{2-} > \text{NO}_3^- > \text{HCO}_3^- > \text{Cl}$. 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

Land cover	Region	Catchment	ID	Ca ²⁺		Mg ²⁺		Na ⁺		K ⁺		HCO ₃ ⁻		SO ₄ ²⁻		NO ₃ ⁻		Cl ⁻			
				\bar{x}	Cv	\bar{x}	Cv	\bar{x}	Cv	\bar{x}	Cv	\bar{x}	Cv	\bar{x}	Cv	\bar{x}	Cv	\bar{x}	Cv	\bar{x}	Cv
Forested (F)	Tatry	Krowi Żleb	F_KR	28.5	1.5	21.2	2.1	0.1	5.4	0.1	5.8	0.1	47.1	0.6	2.0	12.1	0.7	8.3	0.2	8.7	
			Kończysta Turmia	F_KT	43.2	1.0	6.2	6.6	0.4	11.0	0.2	9.3	0.2	46.6	1.4	1.9	18.8	1.2	25.3	0.3	43.6
				F_WŻ	45.6	1.8	3.7	19.8	0.6	20.2	0.2	12.8	0.2	45.9	1.8	2.4	18.6	1.3	50.7	0.2	48.0
			Average value	39.1	1.4	10.4	9.5	0.4	12.2	0.2	9.3	0.2	46.5	1.3	2.1	16.5	1.1	28.1	0.2	33.4	
			Beskid Śląski	Hala Jaskowa	F_HJ	34.6	1.1	8.3	2.2	5.5	4.6	1.6	5.1	31.2	5.7	14.0	10.8	2.0	20.9	2.7	13.2
	Leśnianka	F_L		33.7	1.5	8.9	1.7	6.0	7.7	1.3	9.6	29.4	6.5	15.6	8.4	3.1	20.1	1.8	27.4		
	Average value	34.1	1.3	8.6	1.9	5.7	6.1	1.4	7.3	30.3	6.1	14.8	9.6	2.5	20.5	2.2	20.3				
	Wiatrołom Windfall (W)	Tatry	Pośrednia Kópka	DW_PK	45.3	1.8	3.9	17.2	0.6	27.4	0.2	23.8	44.8	2.7	2.3	24.5	2.5	40.7	0.3	40.4	
				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	17.8	4.1	38.9	0.4	33.6
					Average value	45.4	1.5	3.8	16.0	0.5	23.0	0.2	15.2	43.9	3.3	2.4	21.1	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	15.9	1.7	18.3	0.3	15.6
					Average value	45.4	1.4	3.9	15.0	0.5	13.4	0.2	9.4	45.7	1.1	2.3	15.9	1.7	18.3	0.3	15.6
Anthropogenic pressure (A)	Beskid Śląski	Kopa Skrzyżańska	DA_KS	28.8	1.9	10.1	2.3	8.4	3.0	2.43	26.3	5.2	43.9	31.6	6.4	10.5	13.3	2.56	16.9		
			Małe Skrzyżne	DA_MS	35.3	1.8	7.2	2.5	5.7	3.4	1.61	34.6	23.1	11.1	18.6	8.9	5.7	14.0	2.48	17.9	
				Average value	33.7	2.0	8.3	2.8	6.4	6.1	1.7	28.0	18.7	27.0	21.0	7.1	8.0	14.7	2.1	20.2	
			Young forest (YF)	Malinowska Skala	DA_YF_MS	34.4	0.9	9.4	2.5	5.0	2.8	1.23	0.1	23.6	7.0	12.2	3.1	12.2	10.5	1.37	20.1
					Average value	34.4	0.9	9.4	2.5	5.0	2.8	1.23	0.1	23.6	7.0	12.2	3.1	12.2	10.5	1.37	20.1

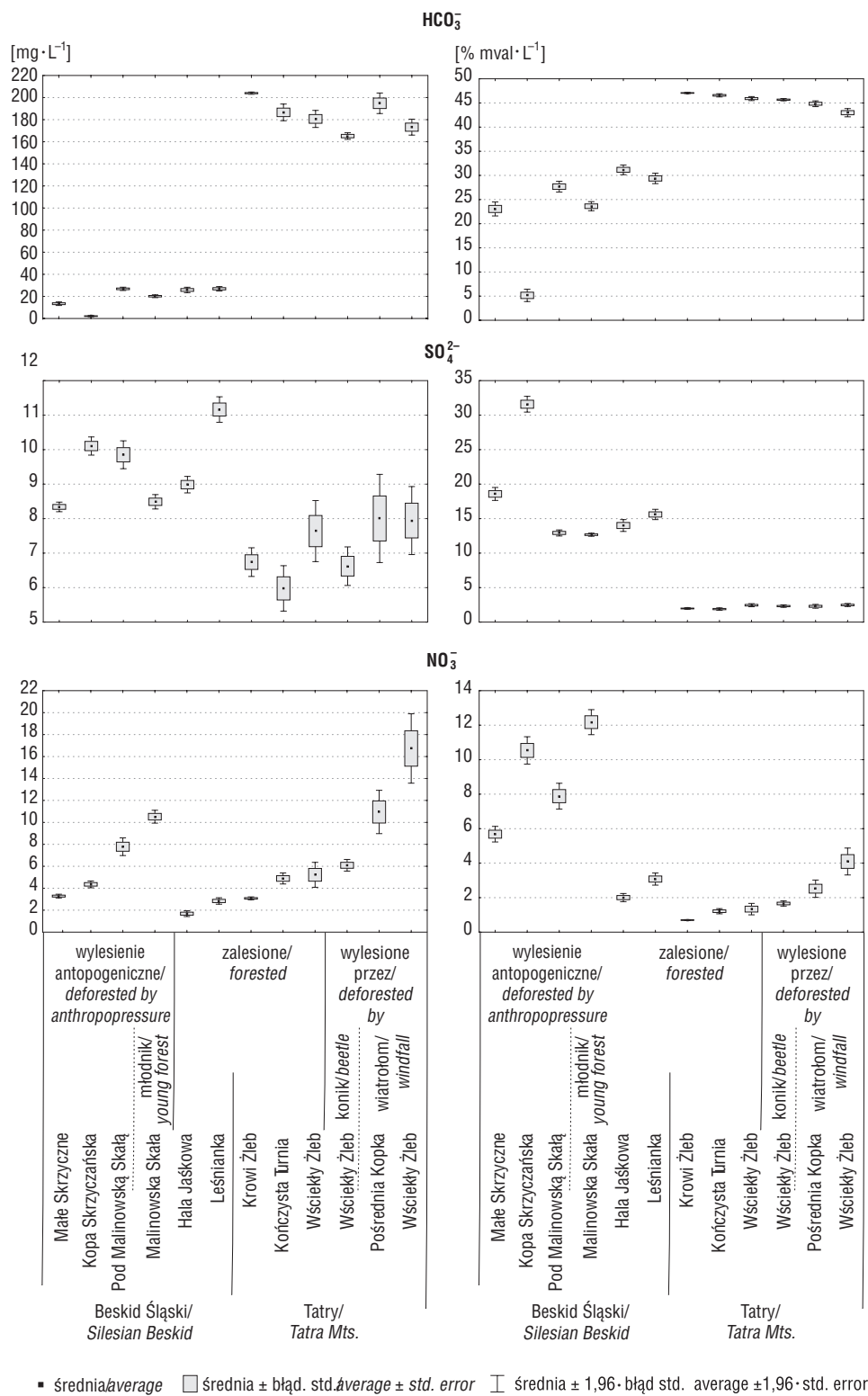


Fig. 2. Diversification of anions in the chemical composition of water

due to the low mineralization of water in the Beskid 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 NO_3^- ions with age (Vitousek, Reiners 1975; Murdoch, Stoddard 1992; Swank, Vose 1997). The decrease in NO_3^- 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 NO_3^- 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 NO_3^- 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 ($C_v = 49.8\%$, 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 Śląski due to immission of anthropogenic pollution, caused changes in the chemical composition of waters, especially in the proportions of anions. In the Tatras, the multiple increase in NO_3^- ions concentration, and a very substantial increase in their proportion ($\% \text{ mval} \cdot \text{dm}^{-3}$) 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, NO_3^- ions precede SO_4^{2-} ions, giving way only to HCO_3^- ions. In the Beskid Śląski, deforestation of anthropogenic nature resulted in a multiple increase in the share of SO_4^{2-} ($\% \text{ mval} \cdot \text{dm}^{-3}$) and at the same time, a decrease in the HCO_3^- share in the anionic element within the chemical composition of waters. In the watercourses draining deforested catchments, SO_4^{2-} 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 NO_3^- 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

STRESZCZENIE

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, PEW, 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 NO_3^- ($\% mval \cdot dm^{-3}$) w członie anionowym składu chemicznego wody, a w Beskidzie Śląskim w wylesionych zlewniach wskutek rozpadu drzewostanu związanego z emisją zanieczyszczeń zaobserwowano znaczny wzrost udziału SO_4^{2-} ($\% mval \cdot dm^{-3}$) i znaczny spadek HCO_3^- ($\% mval \cdot dm^{-3}$) 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