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IMPACT OF DEFORESTATION ON CHANGES OF ION SHARE IN CHEMICAL COMPOSITION OF WATERS OF THE MALINOWSKI STREAM ALONG LONGITUDINAL HYDROCHEMICAL PROFILES

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ABSTRACT

Aim of the study
The aim of the study was to determine the changes of ion share in chemical composition of water with the catchment area increase along longitudinal hydrochemical profiles in an area affected by an ecological disaster.

Material and methods
The research was conducted in the Malinowski stream catchment in the Skrzyczne massif in the Silesian Beskid mountain range from 2013 to 2014. The catchment was divided into smaller sub-catchments (dependent and independent) and 6 longitudinal profiles were separated along the catchment with the increase in the catchment area surface. Water samples were collected in catchments with a different deforestation level on a monthly basis and its physical and chemical features (pH, $EC_{25°C}$, Tw) were measured. The chemical composition of water was determined with the ion chromatography method (DIONEX 2000) in the range 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^-).

Results and conclusions
The conducted research showed the impact of deforestation on the ion share in the chemical composition of water. In the deforested catchments, an increase in the share of SO_4^{2-}, and a decrease in the share of HCO_3^- were observed. The share of SO_4^{2-} in the waters that were draining the deforested catchment was so high that it occured in the first position in the water's hydrochemical type, while the concentration of HCO_3^- was so low that its share was minimal. The analysis of hydrochemical types changes along longitudinal profiles showed the difference in chemical composition of waters draining the upper, deforested zone in comparison to the lower, forested zone. As the catchment area increases, the importance of NO_3^- decreases and the importance of HCO_3^- increases. If the research was conducted exclusively in the profile that closes the Malinowski stream catchment it would show that the catchment is a typical Carpathian catchment in hydrochemical terms, where bicarbonates are in the first place in water chemical composition. The analysis of water chemical composition conducted in the longitudinal profiles enables the identification of hydrochemical effects of the degradation of forest stand in mountain catchment.

Keywords: stream water chemistry, deforestation, acidic atmospheric deposition, concentration of NO_3^- and SO_4^{2-}

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INTRODUCTION

The chemical composition of stream waters in catchment according to Macioszczyk (1987), Pazdro and Kozerski (1990), Chełmicki (2012) is determined by an array of environmental factors. National factors such as geological structure, susceptibility to weathering and leaching, total precipitation play a dominant role. Also, it is strongly influenced by vegetation and plant root systems that, on one hand, collect water from the system, and on the other, change physicochemical conditions of the soil layer (or ground and residual soil layers), and promote the passage of chemical ingredients into soil solution. Even minor surface changes in terms of land use conditions (e.g. deforestation) in seepage spring area can strongly influence water's chemical composition (Czop et al., 2008). Today, in the period of a growing anthropopressure, human economic activity plays increasingly important role (Chełmicki, 2012). Atmospheric pollution has a negative impact on forest ecosystems as it is a direct cause of acid rainfalls (Bytnerowicz et al., 2002; Małek et al., 2005), it disturbs the natural chemistry of precipitation, surface and underground waters as well as soil (Małek and Gawęda, 2006a, 2006b; Małek, 2010; Borg and Sundbom, 2014). In the Silesian Beskid range it was shown that strong anthropopressure led to dying of forest stand in mountain areas (Małek and Krakowian, 2012; Kosmowska et al., 2016), and aggradation of sulphur and nitrogen compounds may cause disturbances in proper functioning of water and land ecosystems (Moldan and Schnoor, 1992; Borg and Sundbom, 2014).

The aim of the study was to determine the changes of ion share in chemical composition of water with the catchment area increase along longitudinal hydrochemical profiles in an area affected by an ecological disaster of dying of spruce.

RESEARCH SITE

The research on changes in a chemical composition of waters was conducted in the Malinowski stream catchment . The catchment is located in the Skrzyczne massif, the highest peak (1257 m a.s.l.) in the Silesian Beskid range. It is designated by the side ridge of the Skrzyczne massif, which stretches southwest through Małe Skrzyczne (1211 m a.s.l.), Kopa Skrzyczańska (1189 m a.s.l.) up to Malinowska Skała (1152 m a.s.l.) (see: Fig. 1). In terms of physical and geographical regionalisation, the area belongs to the Western Carpathians province, the Outer Carpathians sub–province, the Western Beskid macroregion and the Silesian Beskid mesoregion (Balon and Jodłowski, 2014).

These mountains were uplifted during the Alpine orogeny in the late Paleogene and the Miocene (Oszczypko, 1995). The glaciation that occurred in the Quaternary had a great impact on the relief of the area. As a result of intensive periglacial processes, characteristic gentle slopes and peaks formed that are intersected by deep valleys. The current landform of the Silesian Beskid is formed mainly as a result of water erosion. Landslides on slopes and valleys, which are the result of undercutting slopes by water erosion, play a major role in the evolution of the landform (Małek and Gawęda, 2004). Mountain ranges of the Silesian Beskid are formed of the Godula sandstone with a low content slates (Alexandrowicz, 1999; Geologiczna Mapa Polski 1:50000 1966a, 1966b).

This area is covered with a forest stand characterised by a high share of the Istebna spruce that grows mainly in monocultures (Barszcz and Małek, 2015). This spruce, however, is not a native species in the Silesian Beskid, hence its share in natural forest stands was low in the past. In the 18th century, along with the increase in the development of industry and agriculture, robbery of wood resources (beech and sycamore) increased. Natural lower subalpine forests were destroyed and replaced with monocultures of spruce of foreign origin, which with time began to disintegrate (Małek, 2015). The main reason for the dying out of forest stands in the research site was the bad condition of forest caused by the immission of industrial pollution from the Czech Republic and the Silesian–Cracow agglomeration. The dying out concerned mainly forests located in the ridge parts of the highest hills, most exposed to weather conditions (Capecki, 1994; Kosmowska et al., 2016; Małek et al., 2012a, 2012b).

The Malinowski stream catchment is limited by a stream gauge of the Polish Institute of Meteorology and Water Management (IMGW) in Lipowa, and it was monitored by the IMGW until 1983. In the 1974 to 1983 hydrological decade, the average discharge of the

Malinowski stream was 0.64 $m^3 \cdot s^{-1}$ and ranged from Q_{min} = 0.04 $m^3 \cdot s^{-1}$ 11.11.1983 r. to Q_{max} = 12.4 $m^3 \cdot s^{-1}$ 20.01.1974 r. (Hydrologiczny rocznik wód powierzchniowych, 1974–1983). Average annual rainfall in the Silesian Beskid is 1400 mm and average annual air temperature in the lower subalpine forest is 5.6°C. The average duration of the growing season is 192 days (Durło, 2012).

The Malinowski stream catchment has an area of 21.39 km^2. Sub-catchments located in the upper, ridge forest zone are independent and are characterised by a small area not exceeding 0.1 km^2. These catchments

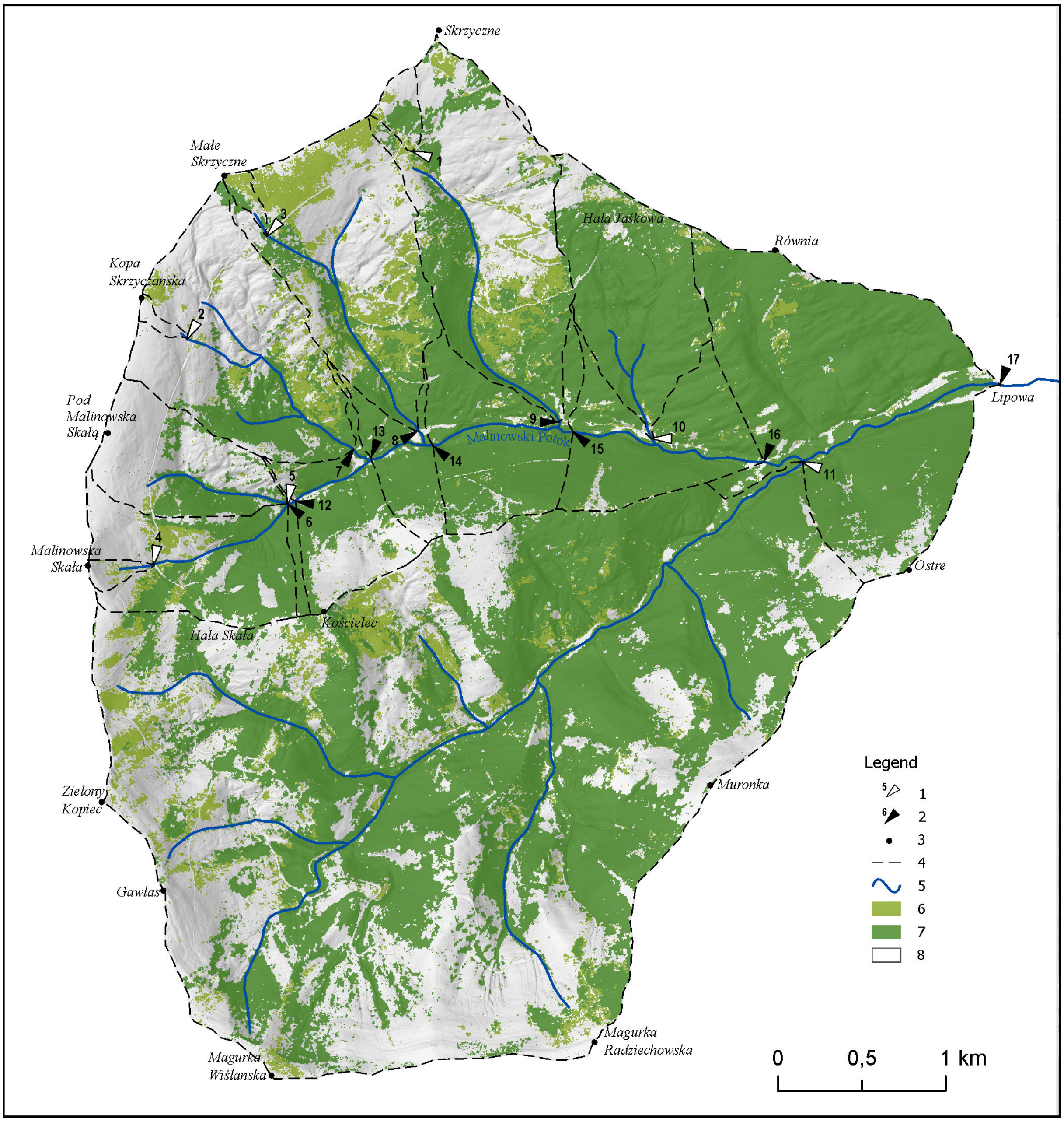

Fig. 1. Study area – Malinowski stream catchment 1 – independent catchments closing profiles, 2 – dependent catchments closing profiles, 3 – peaks, 4 – catchment boundaries, 5 – streams, 6 – young forest, 7 – high forest, 8 – deforested area

are the most deforested, from 1.3% of the forest cover in catchment no. 2 to 52.0% in catchment no. 1. Catchment no. 4 is deforested in 85.3% and is currently covered by young forest. Catchments (dependent and independent) located in the middle forest zone are characterised by a larger area ranging from 0.34 km^2 to 1.62 km^2 and much greater afforestation ranging from 44.2% to 85.9%. Catchments located in the lower forest zone are mostly dependent and they limit hydrochemical systems. They cover area ranging from 1.63 km^2 to 21.9 km^2, and their ranges from 57.1% to 69.9% (see: Table 1).

Table 1. Characteristics of sub-catchments of the Malinowski stream

Forest zones	ID	Type of catchment	Area	Forest cover			Average slope
				Young forest	High forest	Total	
			[km^2]	[%]	[%]	[%]	[°]
Upper	1	I	0.09	13.9	38.1	52.0	15.9
	2	I	0.03	1.2	0.1	1.3	15.4
	3	I	0.04	27.1	22.9	50.0	12.9
	4	I	0.05	12.8	1.9	14.7	24.2
Middle	5	I	0.34	3.7	40.5	44.2	9.9
	6	D	1.00	7.1	41.0	48.1	7.6
	7	D	1.39	22.5	47.1	69.6	9.2
	8	D	1.13	37.8	32.8	70.6	7.8
	9	D	1.62	19.2	48.3	67.5	8.2
	10	I	1.00	2.1	83.8	85.9	7.3
Lower	11	I	10.60	7.1	50.0	57.1	21.0
	12	D	1.63	8.5	61.4	69.9	20.7
	13	D	3.31	11.1	49.9	61.0	20.5
	14	D	4.79	16.8	44.2	61.0	19.7
	15	D	7.12	15.3	49.5	64.8	19.9
	16	D	8.36	12.2	56.3	68.5	18.6
Malinowski Potok	17	D	21.39	8.2	54.6	62.8	15.1

Data source: own research – completed table (Kosmowska et at. 2016).

RESEARCH METHODS: FIELD, LABORATORY AND DATA ANALYSIS

Field methods

In order to determine the impact of deforestation on changes of ion share in chemical composition of waters in the Malinowski stream catchment, research was conducted from November 2013 to October 2014. The research was conducted in 17 sub-catchments of the Malinowski stream. In 7 independent catchments (I) (spring or divergent ones) and 10 dependent (D) (catchments partially covering areas of other catchments) (Ozga-Zielińska and Brzeziński, 1994). In each catchment, the physical and chemical properties of the water were measured monthly with the Professional YSI PLUS multi–parameter meter (YSI Inc., USA): water temperature, conductivity ($EC_{25°C}$) and pH, and a water sample was taken to determine the chemical composition (n = 204).

Laboratory methods

Physical properties and chemical composition of water were analysed in the Hydrological and Chemical Laboratory of the Institute of Geography and Spatial Management of the Jagiellonian University (IGiGP UJ). In order to verify the values of EC and pH obtained with YSI meter in the field, they were analysed again in the laboratory. Subsequently, water samples were filtered through a syringe filter with a PTFE membrane (0.45 μm) to prepare them for the chromatography analysis. Chemical composition analysis of water samples was conducted with the ion chromatography method with the DIONEX ICS 2000 system (Dionex Corporation, USA). 14 ions were determined in the range of:

1) main ions of: calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), bicarbonate ions (HCO_3^-), sulphate (VI) (SO_4^{2-}), chloride (Cl^-);
2) biogenic compounds of: ammonium ions (NH_4^+), nitrate (III) (NO_2^-), nitrate (V) (NO_3^-), orthophosphate (V) (PO_4^{3-});
3) microelements of: lithium ions (Li^+), bromide (Br^-), fluoride (F^-).

The correctness of chemical analyses was verified based on the analysis of certified reference materials (Trios–94 [batch number 306]) and with the ion balance method (PN–89/C–04638/02). A detailed description of the progress of the laboratory procedure and methodology is presented in the monograph by Żelazny (Czasowo–przestrzenna zmienność cech fizykochemicznych wód Tatrzańskiego Parku Narodowego, 2012).

For interpretation, the main ions and NO_3^- were selected, and other ions (Li^+, NH_4^+, Br^- PO_4^{3-}, NO_2^-, F^-) were ignored in table comparisons due to their low concentration (often below detection limit) (see: Table 2).

Table 2. Ion detection limits [LOD]

Cation	LOD [mg · dm^{-3}]	Anion	LOD [mg · dm^{-3}]
Ca^{2+}	0.005	HCO_3^-	0.025
Mg^{2+}	0.005	SO_4^{2-}	0.01
Na^+	0.01	NO_3^-	0.0025
K^+	0.005	NO_2^-	0.0025
NH_4^+	0.005	Cl^-	0.0025
Li^+	0.005	F^-	0.001
		Br^-	0.005
		PO_4^{3-}	0.01

Data analysis

In order to determine the impact of deforestation on changes of ion share in chemical composition of water along longitudinal hydrochemical profiles:

– 6 longitudinal profiles (I, II, III, IV, V, VI) were designated along the catchment area (1–17) with the area increase. Profile I: 1–9–16–15–17, profile II: 2–7–13–14–15–16–17, profile III: 3–8–14–15–16––17, profile IV: 4–6–12–13–14–15–16–17, profile V: 5–12–13–14–15–16–17, profile VI: 10–16–17;
– for each sub-catchment, the degree of forest coverage, including young forest, and deforestation were calculated on the basis of aerial photographs taken in 2014;
– the average slope and catchment area were calculated for each sub-catchment;
– the chemical composition of waters was interpreted due to the share of ions in the chemical composition of water, expressed in (% mval · dm^{-3}). The share of ions was calculated assuming that the marked cations and anions constitute 100% of the chemical composition of water. It was assumed that anions and cations constitute 50% mval · dm^{-3} each so the total of anions = the total of cations. For the above assumption to be met, the spread of balance error was used (Ratajczak and Witczak, 1983 after: Witczak et al., 2013). The general mineralisation of waters was assumed as the total of determined ions;
– in order to present the synthetic chemical composition of waters the commonly used in hydrochemistry Szczukariew–Prikłoński classification was used (after: Macioszczyk, 1987). It assumes that the chemical features of natural waters are decided by 6 main ions (HCO_3^-, SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, Na^+) share of which is not lower than 10% mval · dm^{-3}, and the name of a type starts with an anionic part in order from largest to smallest share. Due to the fact that the share of NO_3^- in chemical composition of water sometimes exceeded 10% mval · dm^{-3}, NO_3^- was included in the classification and it was written in the short name of the hydrochemical type in square brackets;
– the share of ions in the chemical compositions was expressed with hydrochemical types;
– the seasonal change of chemical composition of waters was defined based on two criteria:

- time and volume of the share of NO_3^- in the structure of the chemical composition, expressed by the graph of the monthly coefficient of variation of the share of NO_3^- in the structure of the chemical composition of water. It is the quotient of the monthly concentration of NO_3^- (% mval · dm^{-3}) to the average annual concentration ($C_{month}/C_{annual\ avg.}$),
- the variability of the NO_3^- share marked with the coefficient of variation (Cv) that expresses the ratio of the standard deviation to the average, expressed as a percentage. The following criterion was adopted: Cv < 10% – equalised type, 10 < Cv < 20 – moderate type, Cv > 20 – non–equalised type;

– the chemical composition of stream waters was characterised with the following statistical measures: arithmetic mean, minimum and maximum value.

RESULTS OF THE STUDY

General characteristics

Water courses draining the forested catchments of the Malinowski stream are characterised by a weakly alkaline reaction, while the water courses draining catchments located higher, closer to ridges, and that are more deforested, are characterised by higher acidification (lower pH) and belong to medium acid waters [according to the division Pazdro and Kozerski (1990)]. In terms of mineralisation, these waters are low–mineralised and belong to so–called ultra–fresh waters (see: Table 3). Chemical composition analysis of waters draining forested and deforested catchments, show particularly large diversity within anions. SO_4^{2-} share in the chemical composition of waters draining independent, deforested catchments in the upper, ridge zone of the Skrzyczne massif is very large and that is

Table 3. Values of pH, electrical conductivity ($EC_{25°C}$), mineral content (M_t) and coefficient of variation (Cv) in stream water (n = 12)

Forest zones	ID	pH				$EC_{25°C}$				M_t			
		Min.	Avg.	Max.	Cv	Min.	Avg.	Max.	Cv	Min.	Avg.	Max.	Cv
		(pH)			[%]	[μS · cm^{-1}]			[%]	[mg · dm^{-3}]			[%]
Upper	1	6.33	6.49	6.57	1.0	43.8	47.3	51.1	5.1	27.67	31.45	35.25	6.8
	2	5.71	5.81	5.98	1.5	38.3	40.0	41.8	3.0	21.86	23.91	25.83	5.7
	3	6.28	6.45	6.55	1.5	44.2	49.3	52.8	5.1	29.38	35.16	41.04	9.7
	4	7.04	7.14	7.37	1.4	59.2	74.3	82.8	8.6	46.93	53.69	58.04	6.1
Average value		6.34	6.47	6.62	1.4	46.4	52.7	57.1	5.5	31.46	36.05	40.04	7.1
Middle	5	7.14	7.37	7.59	1.7	73.1	83.6	91.8	7.3	56.29	61.22	67.65	6.3
	6	7.05	7.25	7.38	1.2	62.1	74.2	91.2	10.3	47.21	53.92	65.85	9.4
	7	7.28	7.38	7.54	0.9	74.2	83.5	88.8	5.2	56.13	61.29	68.00	7.0
	8	7.09	7.23	7.33	1.0	59.0	64.8	71.5	5.2	42.75	47.06	56.72	8.4
	9	7.09	7.22	7.34	1.1	65.5	73.1	78.0	5.4	46.41	52.22	57.50	6.7
	10	7.15	7.32	7.56	1.6	59.3	69.8	81.2	9.5	39.95	51.44	61.99	11.9
Average value		7.13	7.30	7.46	1.3	65.5	74.8	83.8	7.2	48.12	54.53	62.95	8.3
Lower	11	7.06	7.37	7.56	1.9	64.6	76.2	82.2	6.3	51.78	56.75	65.41	7.4
	12	7.17	7.26	7.36	0.9	66.3	78.1	85.3	7.2	50.20	57.41	64.03	6.9
	13	6.89	7.30	7.49	2.3	48.4	77.2	85.3	15.0	40.98	56.86	65.66	13.3
	14	6.93	7.26	7.52	2.4	47.6	74.5	93.4	14.7	41.76	55.06	63.03	11.4
	15	6.65	7.25	7.49	3.2	41.4	73.8	90.0	15.9	34.34	53.27	60.00	12.9
	16	7.11	7.31	7.54	1.6	66.9	76.2	88.3	7.5	49.77	55.11	61.06	7.0
Malinowski stream	17	7.18	7.35	7.55	1.3	67.0	76.5	81.5	6.0	50.62	56.19	62.99	7.3
Average value		7.00	7.30	7.50	1.9	57.5	76.1	86.6	10.4	45.64	55.81	63.17	9.5
Average total		6.89	7.10	7.28	1.6	57.7	70.1	78.7	8.1	43.18	50.71	57.65	8.5

20.72% mval · dm^{-3} on average, and in catchment no. 2 (almost totally deforested) is up to 31.58% mval · dm^{-3}, while in forested catchments in the middle and lower zone of the Skrzyczne massif it is much lower (avg. = 14.30% mval · dm^{-3} and avg. = 14.38% mval · dm^{-3}). Average share of NO_3^- in waters from ridge zone is twice as high (avg. = 10.19% mval · dm^{-3}) as in forested catchments in the middle and lower zones (avg. = 5.42% mval · dm^{-3} and avg. = 4.62% mval · dm^{-3}). However, the average share of HCO_3^- in the chemical composition of waters is almost twice as high in forested catchments (avg. = 28.32% mval · dm^{-3} and avg. = 29.20% mval · dm^{-3}) than in deforested catchments (avg. = 16.59% mval · dm^{-3}) (see: Table 4).

Hydrochemical types

In terms of hydrochemistry, three–ion waters dominate in each of dependent and independent catchments, and they are described with the HCO_3–SO_4–Ca type (n = 166; 81%). In the ridge zone, the hydrochemical types of waters are more varied (n = 48). Four–ion waters of the HCO_3–SO_4–[NO_3]–Ca type dominate (n = 23; 48%), next are three–ion waters of the HCO_3–SO_4–Ca type (n = 13; 27%) and some waters of the following types: SO_4–[NO_3]–Ca–Mg (n = 6; 13%), SO_4–Ca–Mg (n = 3; 6%), SO_4–[NO_3]–Ca (n = 1; 2%), and two–ion waters of the SO_4–Ca type (n = 2; 4%). In the middle and lower catchment, waters of the HCO_3–SO_4–Ca type dominate (n = 153; 98%). The HCO_3–SO_4–[NO_3]–Ca type (n = 1; 0,6%) was observed only once in the middle zone, and in the lower the HCO_3–Ca type (n = 2; 1,4%) was observed twice (see: Table 5). The occurrence of this different hydrochemical type of water in the lower zone is probably related to the rapid, one–hour rainfall that occurred during the field research and water sampling.

Longitudinal profiles

Analysis of changes in the share of ions in the chemical composition of water shows that along the longitudinal hydrochemical profiles two different phenomena can be observed: enrichment and depletion of water into single ions, which results in an increase or decrease in the share of some ions expressed in % mval · dm^{-3} in the chemical composition of water in sub-catchments of the Malinowski stream. In the case of NO_3^-, a decrease of their share in the chemical composition of water usually occurs, in the direction away from ridge catchments toward stream mouths (profiles: I, II, IV, V). HCO_3^- act differently as with an increase of catchment area, their share in chemical composition of water increases (profile II). SO_4^{2-} act irregularly as both their increase and decrease in the chemical composition of water can be observed (see: Fig. 2).

Seasonal changes in the structure of the chemical composition of waters

Analysis of seasonal changes in the share of ions in the chemical composition of water shows no changes expressed in hydrochemical types of water for most catchments (n = 12). In four catchments, one change of hydrochemical type of water was observed in a year and several changes in catchment no. 2 – the most deforested one. In catchment no. 2, chemical composition of water is more complex in winter and spring – four–ion waters SO_4–[NO_3]–Ca–Mg, while in summer and autumn more diverse hydrochemical types of water can be observed: two–ion waters SO_4–Ca and three–ion waters: SO_4–[NO_3]–Ca, SO_4–Ca–Mg (see: Table 5).

Analysing changes in the share of NO_3^- in the chemical composition of water during the year, the changes observed were in line with expectations and opposite to expected. In most catchments (1, 2, 5, 6, 7, 8, 12, 13, 14, 17), a bigger share of NO_3^- in the chemical composition of water was observed in winter, while a smaller one in summer (see: Fig. 3). It is associated with the accumulation of nitrogen by plants during the growing season. At the time, the concentration of NO_3^- in waters decreases and their share in the chemical composition of water also decreases. A different phenomenon was observed in some heavily forested catchments (3, 9, 10) – in summer there was more NO_3^- in the chemical composition of water, while in winter there was less (see: Fig. 3). This may indicate a continuous breakdown of the forest stand in the catchment of the Malinowski stream. In some catchments (4, 11, 15, 16), no clearly oriented changes can be observed.

Analysing the variability of NO_3^- expressed with the variability coefficient, it was observed that it is mostly moderate (in nine catchments). The remaining, extreme types – equalised and non–equalised – occur each of four. Diversity of types shows that the forest

Table 4. The share of ions in the chemical composition of water [% mval · dm^{-3}] and coefficient of variation (Cv) in stream water (n = 12)

Forest zones	ID	Ca^{2+}				Mg^{2+}				Na^{+}				K^{+}				HCO_3^-				SO_4^{2-}				NO_3^-				Cl^-			
		Min.	Avg.	Max.	Cv	Min.	Avg.	Max.	Cv	Min.	Avg.	Max.	Cv	Min.	Avg.	Max.	Cv	Min.	Avg.	Max.	Cv	Min.	Avg.	Max.	Cv	Min.	Avg.	Max.	Cv	Min.	Avg.	Max.	Cv
		[% mval · dm^{-3}]			[%]	[% mval · dm^{-3}]			[%]	[% mval · dm^{-3}]			[%]	[% mval · dm^{-3}]			[%]	[% mval · dm^{-3}]			[%]	[% mval · dm^{-3}]			[%]	[% mval · dm^{-3}]			[%]	[% mval · dm^{-3}]			[%]
Upper	1	34.96	36.09	37.30	2.0	6.18	6.55	6.94	3.0	5.33	5.87	7.15	7.6	0.40	1.40	2.78	49.6	10.99	14.52	17.08	11.3	17.99	20.06	21.96	6.2	10.43	12.34	14.70	9.4	1.79	2.89	3.66	18.7
	2	27.44	28.76	29.43	1.9	9.76	10.14	10.68	2.3	7.86	8.38	8.66	3.0	1.92	2.43	4.38	26.3	2.54	5.16	9.38	43.9	28.0	31.58	34.2	6.4	8.87	10.54	12.92	13.3	1.65	2.56	3.04	16.9
	3	34.05	35.32	36.16	1.8	6.85	7.18	7.57	2.5	5.44	5.72	6.10	3.3	0.95	1.61	2.75	34.6	18.94	23.05	27.74	11.1	15.39	18.58	21.09	8.9	4.55	5.68	6.98	14.0	1.57	2.48	2.98	17.9
	4	33.81	34.36	34.82	0.9	9.12	9.42	9.86	2.5	4.80	4.96	5.23	2.8	1.06	1.23	1.53	9.1	21.53	23.62	26.86	7.0	11.84	12.67	13.31	3.1	9.59	12.18	14.12	10.5	0.83	1.38	1.68	20.1
Average value		32.57	33.63	34.43	1.7	7.98	8.32	8.76	2.6	5.86	6.23	6.79	4.2	1.08	1.67	2.86	20.9	13.50	16.59	20.27	18.3	18.31	20.72	22.64	6.2	8.36	10.19	12.20	11.8	1.46	2.33	2.84	18.4
Middle	5	34.79	37.08	37.80	2.4	7.25	7.49	8.24	3.5	3.88	4.29	5.75	11.9	0.93	1.10	1.81	23.1	24.80	27.67	32.00	7.1	11.31	12.92	13.75	6.0	5.69	7.89	10.22	16.7	0.84	1.38	2.22	25.9
	6	33.75	35.13	37.35	2.4	7.49	8.09	8.40	2.8	4.13	5.54	6.32	9.3	1.01	1.18	1.58	13.0	26.69	28.36	31.99	6.1	12.07	13.67	15.11	7.3	4.49	6.03	9.44	20.1	1.12	1.80	2.45	19.4
	7	35.71	36.41	36.79	0.9	7.59	7.73	7.96	1.4	4.53	4.74	5.13	3.9	1.01	1.09	1.20	4.6	27.63	29.56	32.13	4.4	12.54	14.12	15.37	5.6	4.02	4.82	5.35	7.8	0.80	1.34	1.80	20.9
	8	34.77	35.36	36.71	1.6	7.62	8.10	8.44	2.7	4.56	5.15	5.51	5.8	1.08	1.35	1.82	12.8	26.03	28.66	31.98	6.4	13.64	16.09	17.73	8.3	2.84	3.50	4.74	17.8	0.98	1.57	2.02	21.4
	9	34.18	34.82	35.60	1.2	8.05	8.37	8.72	2.3	5.02	5.42	5.74	3.9	1.25	1.35	1.60	6.4	23.05	24.51	26.59	4.6	13.71	14.98	16.50	5.9	6.88	8.25	9.49	11.9	1.84	2.07	2.31	6.4
	10	34.01	34.61	35.38	1.2	8.07	8.27	8.58	2.2	5.01	5.49	5.98	4.6	1.48	1.60	1.80	5.1	28.06	31.16	34.12	5.7	11.52	14.00	16.20	10.8	1.44	2.00	3.05	20.9	2.09	2.68	3.37	13.2
Average value		34.54	35.57	36.61	1.6	7.68	8.01	8.39	2.5	4.52	5.11	5.74	6.6	1.13	1.28	1.64	10.8	26.04	28.32	31.47	5.7	12.47	14.30	15.78	7.3	4.23	5.42	7.05	15.9	1.28	1.81	2.36	17.9
Lower	11	32.91	33.67	34.62	1.5	8.65	8.92	9.20	1.7	5.33	6.02	6.72	7.7	1.11	1.35	1.50	9.7	26.62	29.38	32.71	6.5	12.97	15.60	18.01	8.4	2.28	3.08	4.72	20.1	0.96	1.78	2.52	27.4
	12	34.91	36.05	36.74	1.3	7.58	7.79	8.05	1.7	4.63	4.97	5.60	5.4	0.99	1.12	1.56	13.6	26.08	28.19	31.90	6.3	11.71	13.37	14.65	6.5	5.22	6.75	7.85	10.7	0.99	1.55	2.26	22.2
	13	35.08	36.01	36.66	1.4	7.63	7.78	7.93	1.3	3.97	4.80	5.11	6.1	1.02	1.32	2.53	33.5	26.63	29.58	35.89	8.3	9.72	13.89	16.05	12.0	2.64	4.94	6.21	23.1	0.92	1.44	1.73	15.8
	14	32.85	35.49	36.42	2.9	7.39	7.90	8.56	3.6	3.95	5.04	6.28	10.6	1.08	1.39	2.53	35.9	26.42	29.84	36.25	8.4	9.75	14.14	16.59	12.1	2.60	4.22	4.92	14.8	0.92	1.57	2.48	24.8
	15	31.96	35.40	36.20	3.2	6.95	7.93	8.85	5.3	4.78	5.07	5.46	3.9	1.09	1.46	3.12	39.3	26.29	28.79	31.67	5.4	12.97	14.47	16.14	7.3	3.48	4.89	5.58	11.9	1.09	1.70	2.15	15.6
	16	35.00	35.54	36.12	0.9	7.74	7.98	8.26	1.9	4.86	5.17	5.40	3.0	1.16	1.28	1.62	11.5	27.27	29.13	31.49	5.0	12.70	14.33	15.71	7.0	4.02	4.67	5.22	8.5	1.07	1.73	2.25	18.5
Mali-nowski	17	34.05	34.55	35.34	1.1	8.20	8.45	8.71	1.7	5.16	5.65	6.05	4.4	1.19	1.32	1.41	4.7	26.95	29.46	32.42	6.3	12.36	14.86	16.77	8.5	3.15	3.76	4.64	10.9	1.06	1.77	2.39	21.2
Average value		33.82	35.24	36.01	1.8	7.73	8.11	8.51	2.5	4.67	5.25	5.80	5.9	1.09	1.32	2.04	21.2	26.61	29.20	33.19	6.6	11.74	14.38	16.27	8.8	3.34	4.62	5.59	14.3	1.00	1.65	2.25	20.8

Table 5. Hydrochemical types of water in the Malinowski stream catchment

Seasons		Winter			Spring			Summer			Autumn			Hydrochemical type						
Forest zones	ID	XI	XII	I	II	III	IV	V	VI	VII	VIII	IX	X	HCO_3–SO_4–Ca	HCO_3–Ca	HCO_3–SO_4–[NO_3]–Ca	SO_4–[NO_3]–Ca–Mg	SO_4–[NO_3]–Ca	SO_4–Ca–Mg	SO_4–Ca
Upper	1															12				
	2																6	1	3	2
	3													12						
	4													1		11				
Middle	5													11		1				
	6													12						
	7													12						
	8													12						
	9													12						
	10													12						
Lower	11													12						
	12													12						
	13													11	1					
	14													11	1					
	15													12						
	16													12						
	17													12						
Hydrochemical type	HCO_3–SO_4–Ca	9	8	9	9	9	9	9	9	8	9	9	9							
	HCO_3–Ca									2										
	HCO_3–SO_4–[NO_3]–Ca	2	3	2	2	2	2	2	2	1	2	2	2							
	SO_4–[NO_3]–Ca–Mg	1	1	1	1	1	1													
	SO_4–[NO_3]–Ca							1												
	SO_4–Ca–Mg								1	1		1								
	SO_4–Ca										1		1							

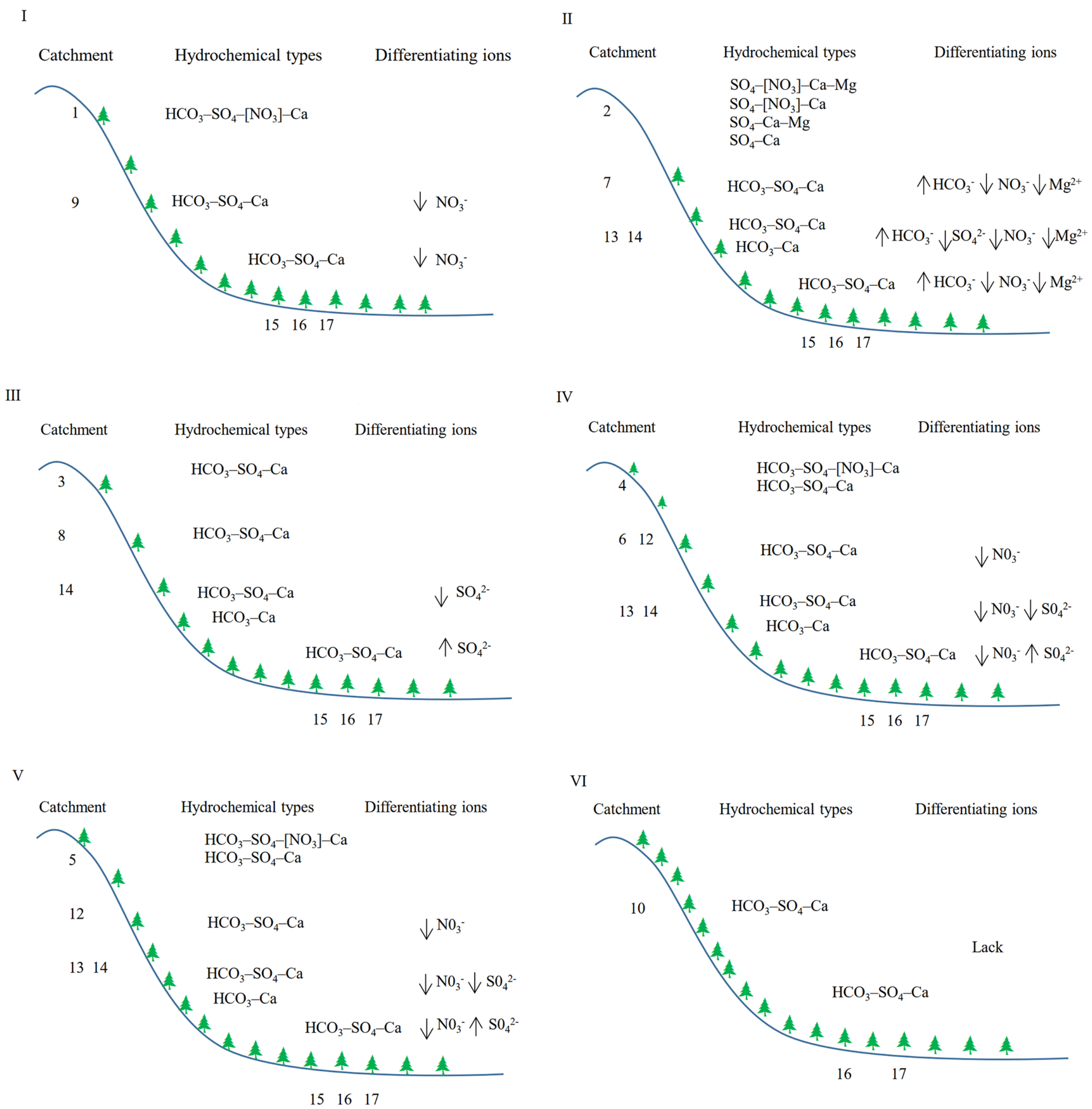

Fig. 2. Longitudinal hydrochemical profiles (I, II, III, IV, V, VI) in the Malinowski stream catchment (1–17 numbers of sub-catchments)

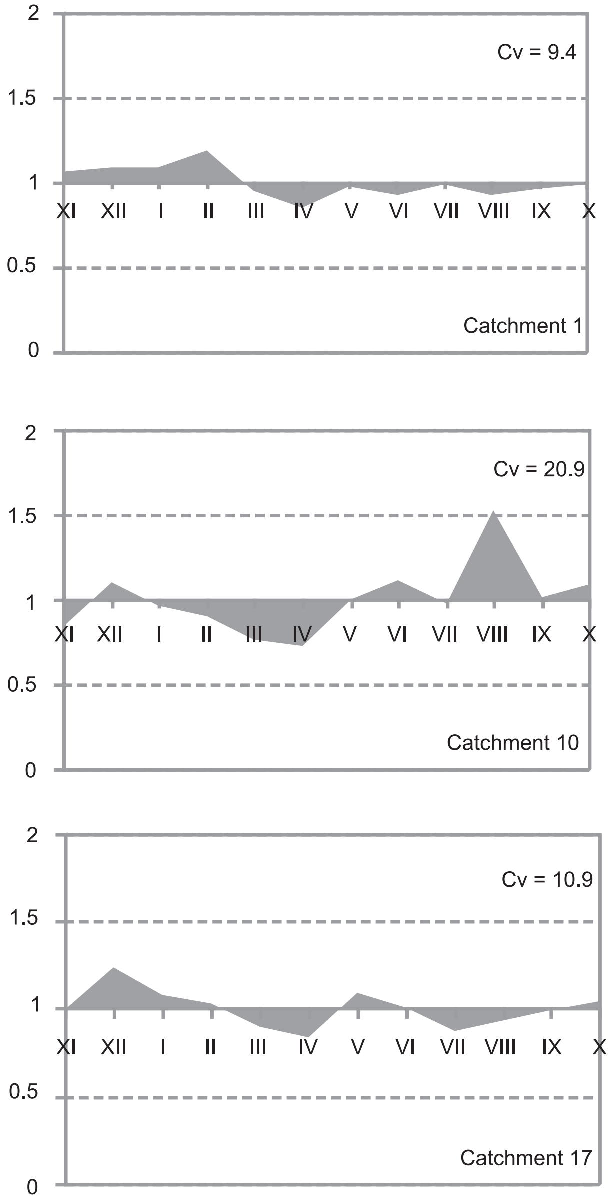

Fig. 3. The course of NO_3^- regime [% mval · dm^{-3}] in catchments: 1, 10, 17

stand in the Malinowski stream catchment continuously breaks down. It is worth noticing that in deforested catchments, the variability of NO_3^- in a year is higher (Cv = 13.3%; catchment no. 2) than in forested catchments (Cv = 9.4%; catchment no. 1) (see: Table 4). Deforested catchments are characterised mostly by moderate type, while forested ones: moderate and equalised. The most significant changes occur in catchments in which degradation of the forest stand (3, 9, 10) or its reconstruction (no. 4 – covered by young forest) can be observed.

SUMMARY AND DISCUSSION

The consequence of deforestation of the slopes in the Silesian Beskid range is a change of the sequence of anions in the chemical composition of water, which is reflected in the hydrochemical types of waters, which are their synthetic image. Share of SO_4^{2-} ions in the chemical composition of water in a stream that drains a catchment that is almost totally deforested (no. 2) was so significant that it was in the first place in this water's hydrochemical type: SO_4–[NO_3]–Ca–Mg, SO_4–Ca–Mg, SO_4–Ca, and SO_4–[NO_3]–Ca. Meanwhile, the concentration of HCO_3^- ions was so low that their share in the chemical composition of water was minimal. Analogous hydrochemical environments in which SO_4^{2-} dominated over HCO_3^- were described by Michalik (2008) and Michalik et al. (2012) in waters draining quartzite sandstones in the Świętokrzyskie Mountains, and by Kosmowska et al. (2015) and (2018) in the Malinowski stream catchment in the Silesian Beskid range. In the above catchments, the occurrence of SO_4^{2-} in the first place in the hydrochemical type of water is extremely rare for natural waters, especially since the Godula sandstones, that are the geological base of the above catchments, cannot be their source and the origin of SO_4^{2-} must be anthropogenic. In the Tatras, Wolanin et al. (2017) described an unusual chemical composition of a spring, that was dominated by SO_4^{2-} (28.12% mval · dm^{-3}) but it was probably genetically connected to gypsum or anhydrite rocks. A significant, and sometimes dominant, share of SO_4^{2-} in the chemical composition of water is associated with atmospheric supply of pollutants in the second half of the 20th century. It resulted in SO_4^{2-} accumulation in the residual soil, and now they are leached from the soil, which was discussed by Jasik and Małek (2013), Kosmowska et al. (2016) and (2018). In the waters draining the lower zone of the Skrzyczne massif and at the closing profile of the Malinowski stream catchment in Lipowa, a sequence of anions can be observed in the chemical composition of water that is typical for waters draining sedimentary rocks in the temperate climate, which is dominated by

HCO_3^-, with a smaller share of SO_4^{2-}, Cl^- and NO_3^-. It can be observed in the hydrochemical type of water in which HCO_3^- are in the first place: HCO_3–SO_4–Ca. This kind of ion sequence, in which HCO_3^- dominate and are in the first place, was obtained by Drużkowski and Szczepanowicz (1988) in a small catchment called Wierzbanówka in the Carpathian Foothills, Maultz (1972) in big catchments of the upper Wisła (Soła, Skawa), Welc (1985) in the catchment of the Bystrzanka stream, Żelazny (1995) and (2005) in catchments in the Wiśnicz Foothills, Siwek (2012) in small catchments at Carpatian Foothills (catchments of Stara Rzeka, Kubaleniec and Leśny Potok), Żelazny et al. (2017a) and (2017b) in the Kościeliski stream catchment in the Tatras. Also, research conducted in the Kościeliska valley in the Western Tatras confirm it (Żelazny et al., 2013; Kosmowska et al., 2018), as well as several years of observations of 23 streams in the Polish Tatras where Żelazny (2012) showed that HCO_3^- dominates among anions in the chemical composition of water regardless of hydrometeorological and lithological conditions. It is worth mentioning that in the Tatra catchments the mineralisation of water was strongly differentiated depending on the lithological structure. In the waters of streams draining catchments built up low–soluble granites, mineralisation was very low (avg. = 17.70 $mg \cdot dm^{-3}$ in the Roztoka catchment), while in catchments built up sedimentary rocks it was much higher (avg. = 301.45 $mg \cdot dm^{-3}$ in the Wielkie Koryciska catchment) (Żelazny, 2012).

Multidimensional PCA analysis carried out for waters that drain the Malinowski stream catchment did not show the expected seasonal variability of biogenes concentration, e.g. NO_3^-, i.e. higher in winter, and lower in summer (Kosmowska, 2016). However, the analysis of seasonal variability in the course of NO_3^- concentration in waters from individual sub-catchments (% $mval \cdot dm^{-3}$) showed typical variability. It is worth noting that among these catchments, also an unusual phenomenon was observed – in summer there is a higher concentration of NO_3^- than in winter (catchments no. 3, 9, 10). This should be explained by the intensive degradation of the forest stand in these catchments. This applies to catchments heavily transformed due to anthropopressure. According to Vitousek and Reiners (1975), Murdoch and Stoddard (1992), Swank and Vose (1997) this indicates a progressive degradation of the damaged forest stand, which behaves similarly to an aging forest stand and with time loses the ability to actively absorb NO_3^- in the growing season. Vitousek and Reiners (1975) showed a multiple difference between NO_3^- concentration in streams draining successional forest catchments (about Avg. = 5 $\mu EQ \cdot dm^{-3}{}_{July\ 1973}$) and oldeged forest catchments (about Arg. = 55 $\mu EQ \cdot dm^{-3}{}_{July\ 1973}$). For most catchments located in the middle and lower zones of the Skrzyczne massif, a typical course of NO_3^- concentration was observed – higher concentration in winter, and lower in summer. Similar results – NO_3^- concentration increase in non–growing period, and decrease in growing period – were obtained in the Tatras by Żelazny (2012), Wolanin (2013), Gromadzka et al. (2015), Sajdak et al. (2018), in the Babia Góra National Park by Malata (2015), in the Gorce range by Jasik et al. (2017), in the Silesian Beskid and the Żywiec Beskid by Astel et al. (2008), as well as in small agricultural catchments in the Lower Silesia by Pulikowski et al. (2005) and (2011). Similar seasonal variation in NO_3^- was observed in a small urbanised catchment in England by Worrall and Burt (1998) and in the UK by Jarvie et al. (2010).

Analysing the changes in the hydrochemical types of waters along the longitudinal profiles in the Malinowski stream catchment, attention should be paid to the differences expressed in hydrochemical types in the chemical composition of the water draining the deforested upper zone of the Skrzyczne massif in comparison to the lower zone. As the catchment area increases, the share of NO_3^- in the chemical composition of water decreases, and the share of HCO_3^- increases. Unique hydrochemical types of waters that drain the upper zone of the Skrzyczne massif (catchment no. 2) – SO_4–[NO_3]–Ca–Mg, SO_4–Ca–Mg, SO_4–Ca, and SO_4–[NO_3]–Ca – are the result of the forest stand degradation. Also, the methodological aspect related to the analysis of longitudinal hydrochemical profiles is important. The analysis of the ion share in the chemical composition of water that was carried out in the longitudinal hydrochemical profiles allows the identification of the hydrochemical effects of the degradation of the forest stand in the mountain catchment. It is worth noting that if the tests were carried out exclusively in the closing profile of the Malinowski stream catchment in Lipowa, then this catchment would be a typical Carpathian catchment in terms of hydrochemistry, where HCO_3^- is in the first place in the anionic part of the chemical composition. This would "mask" the impact of anthropogenic influence on the hydrochemical functioning of the catchment.

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WPŁYW WYLESIENIA NA ZMIANY UDZIAŁU JONÓW W SKŁADZIE CHEMICZNYM WÓD MALINOWSKIEGO POTOKU WZDŁUŻ PODŁUŻNYCH PROFILI HYDROCHEMICZNYCH

ABSTRAKT

Cel pracy

Celem badań było określenie zmian udziału jonów w składzie chemicznym wody wraz z przyrostem powierzchni zlewni wzdłuż podłużnych profili hydrochemicznych na obszarze dotkniętym klęską ekologiczną.

Materiał i metody

Badania prowadzono w zlewni Malinowskiego Potoku w Masywie Skrzyczne w Beskidzie Śląskim, w latach 2013–2014. Zlewnię Malinowskiego Potoku podzielono na mniejsze zlewnie cząstkowe: zależne i niezależne oraz wyodrębniono 6 profili podłużnych wzdłuż zlewni wraz z przyrostem powierzchni zlewni. W terenie pobierano co miesiąc próbki wody w zlewniach o różnym stopniu wylesienia oraz mierzono cechy fizyczno-chemiczne wody (pH, $EC_{25°C}$, Tw). 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^-).

Wyniki i wnioski

Przeprowadzone badania wykazały wpływ wylesienia na udział jonów w składzie chemicznym wody. W zlewniach wylesionych zaobserwowano wzrost udziału SO_4^{2-} i spadek HCO_3^-. Udział SO_4^{2-} w wodach odwadniających zlewnię wylesioną był tak duży, że pojawił się na pierwszym miejscu w typie hydrochemicznym tych wód, zaś HCO_3^- miały tak niewielkie stężenie, że ich udział był znikomy. Analizując zmiany typów hydrochemicznych wzdłuż profili podłużnych, zauważono odmienność składu chemicznego wód odwadniających górną, wylesioną strefę, w porównaniu do dolnej. Wraz z przyrostem powierzchni zlewni, następuje spadek znaczenia NO_3^- i wzrost znaczenia HCO_3^-. Gdyby badania prowadzono jedynie w profilu zamykającym zlewnią Malinowskiego Potoku, wówczas zlewnia ta byłaby typową zlewnią karpacką pod względem hydrochemicznym, gdzie na pierwszym miejscu w składzie chemicznym wody występują wodorowęglany. Analiza składu chemicznego wód przeprowadzona w podłużnych profilach pozwala zidentyfikować hydrochemiczne skutki rozpadu drzewostanu w zlewni górskiej.

Słowa kluczowe: chemizm wód, wylesienie, kwaśne opady, stężenie NO_3^- i SO_4^{2-}