The effect of environmental conditions on surface water quality in the Zimnik and Czyrna catchments of the Beskid Śląski

Stanisław MAŁEK, Katarzyna KRAKOWIAN

Agricultural University in Cracow, Department of Forest Ecology, Forest Faculty, al. 29 Listopada 46, 31–425 Cracow, Poland, e-mail: rlmalek@cyf-kr.edu.pl, krakowian.k@gmail.com

Abstract: The study was carried out in the year 2004 in the Zimnik and Czyrna catchments situated on opposite slopes of Skrzyczne in the Beskid Ślaski Mts. Water samples collected from streams during three sampling sessions were analysed. The first session was carried out during snowmelt (April/May), the second during intensive rainfall in the vegetation season (June) and the third – during low water level (October). A data set consisting of conductivity, water pH, concentrations of major anions (Cl⁻, NO₃⁻, SO₄²⁻) and cations (NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺) was produced and waters were then classified according to Polish standards (years 2002 and 2004). Chemical composition of stream waters depended on physical and geological properties of drainage areas and on seasonal changes of water level in the catchment. Water class depended also on precipitation and on forest type. It was found that water from most sampling points in streams was unfit for drinking - 66 out of collected 89 samples were beyond the first A1 category and the main reason for that was too low pH and high concentrations of NH₄⁺ and NO₃⁻. During intensive rainfall in the vegetation season higher washing out of cations was observed from beech and multispecies forest stands than from spruce stands, which partly neutralized water pH and in consequence improved water quality. This phenomenon should be considered while afforesting streams neighborhoods where water is or will be used as a source of drinking water.

Key words: Beskid Śląski Mts., forest type, geology, species composition, surface water, water quality

INTRODUCTION

Numerous publications describe the impact of environmental conditions on chemical properties of waters in different regions (DYNOWSKA, 1986; CHEŁMICKI et al., 2001; KOSTARKIEWICZ, 2001; MICHALCZYK, 2001; SIWEK, 2004). According to ZDANOWICZ (1994) and ŻMUDA (1994) the process of water self-purification runs best in mountain streams, where fast current ensures permanent oxidation. Moreover, in mountain regions the sources of rivers are often located within the

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borders of forests, which affects water quality and increases its retention as it is the case in the Beskid Śląski. Structure of geological profile, type of rocks and forest influence the chemical composition of outflow waters. It was found, that in mountain areas the release of minerals weathering from the rock substratum may be a dominant factor responsible for chemical composition of outflowing waters (MUNK and FAURE, 2004; TRUDGILL et al., 2004). Moreover, biological processes in the soil layer or in stream water may play significant role (WRÓBEL, 1998). Chemical composition of spring water depends strongly on the type of soil and geological profile and on plant cover, surface configuration and even on slope exposition (MAŁEK and GAWĘDA, 2004; 2006a; 2006b; MAŁEK and KRAKOWIAN, 2007). One of the factors which determine the content of inorganic compounds in surface waters is seasonal variability of water level in the catchment (SZCZĘSNY and ZIĘBA, 2001). Quantitative and qualitative analyses of surface waters were done in order to find the effect of long lasting spruce monoculture on physical and chemical water properties. The paper is part of the hydro-chemical description of waters in the Beskid Śląski systematically monitored within the scope of activity of the Department of Forest Ecology at the Agricultural University in Cracow (MAŁEK and GAWEDA, 2004; 2006a; 2006b; MAŁEK and KRAKOWIAN, 2007). Unfortunately, the chemical composition of surface water was not evaluated in a complex way that would consider: geological conditions of the catchment area, prevailing forest stands, seasonal variability of water level and other environmental factors in particular catchments. This is the reason why we decided to apply multivariate environmetric techniques to surface waters in order to verify the hypothesis whether the chemical composition and drinking water quality class of streams located in the Zimnik and Czyrna catchments depend on physico-geological structure of drainage areas.

STUDY SITE

The study was carried out in part of the Zimnik and Czyrna catchment located on slopes of Skrzyczne (1257 m a.s.l) – 49°34'N, 18°50'E – above the level of building development. Waters in the Czyrna catchment flow into the Żylica that has an outlet in Lake Żywieckie – a dam reservoir on the Soła River. Waters from the Zimnik catchment flow to the Leśnianka River which is the left side tributary to the Soła. Those two rivers belong to the Wisła drainage basin. Point no. 46 "Lipowa" of the Regional Monitoring of Underground Waters is located in the study area. Waters of the region are of calcium-bicarbonate-sulphate type (PACHOLEWSKI et al., 2004). According to the administration division of State Forests, Skrzyczne is located within the borders of the Regional Directorate of National Forest in Katowice, Forest Division Węgierska Górka, Forest Circle Lipowa, Forest District – Skrzyczne, and Forest Division Bielsko, Forest Circle Szczyrk, and Forest District

– Skalite and Czyrna. These areas are situated within the Forest Promotion Complex "Beskid Śląski Forest" and in the natural reservoir of Beskid Śląski (Plan..., 1998–2001; Plan..., 2004–2013).

The area is classified into the Interior Western Europe, Carpathians subarea, Sub-Carpathians, and Valleys, the Carpathians and Sub-Carpathians province, Exterior Wester Carpathians subprovince, Beskidy Zachodnie macro-region, Beskid Śląski mesoregion according to physical and geographical regional divisions by KONDRACKI (2000) (internal code: 513.45).

Present topographic profile of the Beskid is mainly a result of erosive activity of running waters. Large falls create energetic erosion deepening the valleys; whereas, at the outlet of streams there are plains of intermountain valleys. An important role in structuring the profile have slopes and valley landslips that occur due to undercutting of slopes by water erosion or to slipping of sandstones on waterlogged slates (MAŁEK and GAWĘDA, 2004; 2006a; 2006b; MAŁEK and KRAKOWIAN, 2007; www.wsa.bielsko.pl). Skrzyczne (1257 m a.s.l.) is the highest summit of the Beskid Śląski; Barania Góra also belongs to this range (KONDRACKI, 2000).

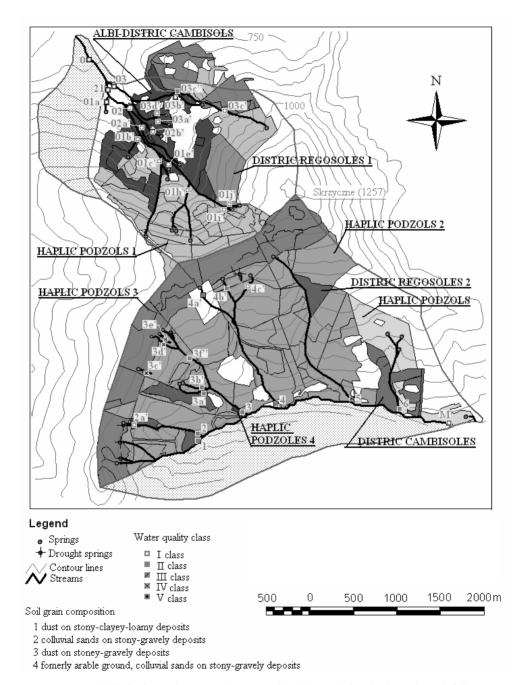
Podzols, cambiosols and regosols dominate in the geological formations. Soils in the Czyrna catchment are more fine-grained than those in the Zimnik catchment (map 1). The podzolization process of soils was probably, like in other regions of the Beskid, intensified by improper activities, in particular due to "spruce-mania" (MACIASZEK *et al.*, 2000).

Location of habitat types of forests in the two catchments reflects their connection with the climate, elevation and exposure (map 2). In the Czyrna catchment due to north or north-west slope exposition we have mixed mountain forests (LMG) and mixed mountain coniferous forests (BMG) (for explanation see map 2). Those forest types reach lower parts of the catchment. Moreover, there is also spruce monoculture forest type not present in the Zimnik catchment. In the latter, forest habitats are composed of fir and beech, which are lacking in Czyrna.

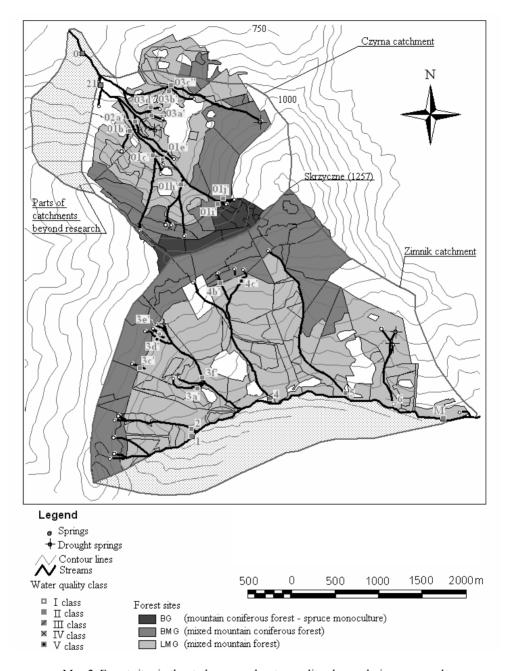
The majority of spruce communities surveyed by WILCZEK (1995) was assigned to fir-spruce forest of lower subalpine forest, which indicates habitat disturbance or even degradation (over 40% of disturbed habitats in the Czyrna and Zimnik catchments are mixed mountain forests). Moreover, there is still a tendency of diminishing water resources on mountain slopes and deteriorating of water quality in streams (DORDA, 2004). As a result of "spruce-mania" foresters are currently dealing with the problem of spruce dying out, which is also present in the study area.

METHODS

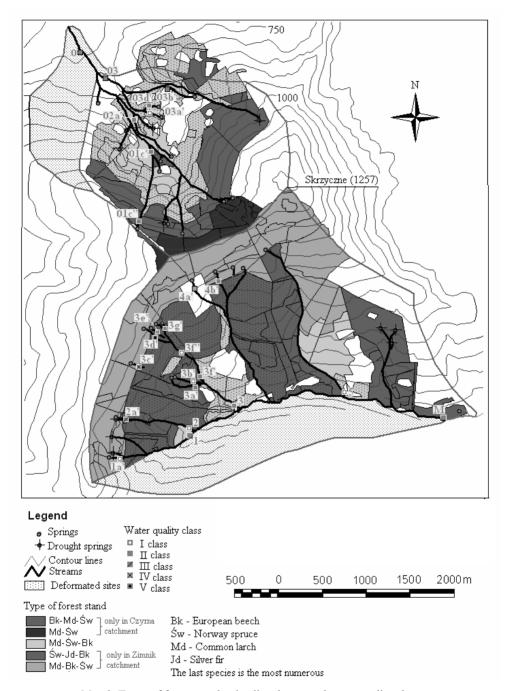
Sampling sites were selected in each stream from spring till the outflow to the other stream. In the Zimnik catchment 20 points and in the Czyrna catchment 18 points were selected (maps 1, 2, 3). Sampling was performed in three sessions: I –



Map 1. Soils in the study area and water quality classes during the intensive rainfall



Map 2. Forest sites in the study area and water quality classes during snow melt



Map 3. Types of forest stands, site disturbance and water quality classes in the study area during low water flow

during snowmelt (13.04.2004 and 2–4.05.2004), II – during heavy precipitation (18–20.06.2004) and III – during low water flow (15–17.10.2004).

Water samples were analysed in the chemical laboratory of the Department of Forest Ecology. pH of samples (pH-meter Eijkelkamp 18.37) and electrolytic conductivity – EC (conductivity meter Eijkelkamp EC 18.34) were measured before filtering the samples. Then the concentrations of: Li⁺, Na⁺, NH₄⁺, K⁺, Ca²⁺, Mg²⁺, F⁻, Cl⁻, NO₃⁻, SO₄²⁻, PO₄³⁻, HCO₃⁻ were analysed with the ion chromatograph Dionex –320.

Results were elaborated in the following stages:

- a) selection of samples for further analysis based on ionic balance;
- b) classification of water quality acc. to the Directive of the Minister of Environment as of 11 February 2004, and Directive of the Minister of Environment as of 27 November 2002 due to examined characteristics;
- c) removal from further analyses: 3d' in the first and third session, 4c', 02a', 03d', and 03b' in the third session (principle of three signs) and chemical species of too low content (Li⁺, F⁻, NH₄⁺, PO₄³⁻);
- d) reduction of analysed chemical species correlations between concentrations of specific ions and EC were calculated. Pearson's coefficient of linear correlation (significance level 0.05) was used. From among significantly correlated variables, strongly correlated variables (p > 0.7) were selected. The feature of the highest coefficient of variability was left for further analysis, i.e. in the Zimnik Catchment Na was left from the group of Na⁺, Mg²⁺, K⁺ and Ca²⁺ from Ca²⁺ HCO₃⁻, in the Czyrna catchment: Mg²⁺ from Na⁺, Mg²⁺ and HCO₃⁻ from Ca²⁺, HCO₃ group;
- e) analysis of correlation between the dependent variables and environmental conditions: age of the main stand density, height above sea level, soil and geological foundation, inclination and exposition of the slope, forest site, site moisture and site deformation, forest type, session;
- f) in the case of correlation with continuous variables a regression analysis was performed; the remaining features were divided into groups according to assigned ranks, and in such groups the averages were compared according to the scheme in Figure 1.

RESULTS AND DISCUSSION

The layout of mountain streams in the examined basins represents two variants. The network of mountain streams in the Czyrna catchment may be described as oval, concentric with mountain streams running close to each other to the main outflow, creating a hydrological node. The network of mountain streams in the Zimnik catchment has feather-like form and is extended (map 2). Comparison of the

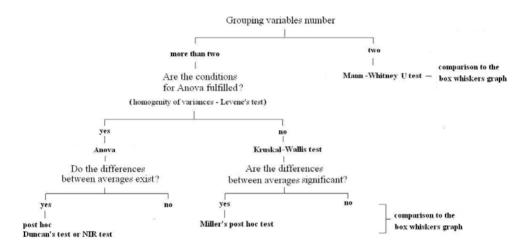


Fig. 1. Procedure concerning statistics of the grouping variables

surface and length of the two basins and the density of river network reflects described layouts (Tab. 1).

During the study we noticed periodical changes in the occurrence and location of the mountain streams (map 1–3). This is a natural phenomenon associated with general water circulation resulting from the dynamics of underground and ground water reservoirs. This dynamics may be also noticed throughout one year (MAŁEK and GAWĘDA, 2004; 2006a; 2006b). There is one hydro-isobath locating the groundwater table at a depth of two meters in the study area (hydrographic maps 2002). One of the examined plots (01a') is within its range. Water reservoir in the upper part of Skrzyczne depends on atmospheric precipitations. During June precipitations, even with a disappearance of some mountain streams, the density of river network was biggest, and the springs were at higher altitudes than in other sampling sessions (Tab. 1).

The majority of analysed chemical species fulfilled the norms for the I class water quality and for A1 category. High concentration of ammonium ions and nitrates and too low pH were the limiting factors (Tab. 2–4).

Snow melt was followed by nitrate input to streams. pH of examined waters was low so that most of them fell into the II class (mean pH of water in the Zimnik catchment on that sampling occasion was 5.85, and in Czyrna -6.19; see map 2).

During intensive precipitation the water quality improved in Czyrna (average pH -6.68; map 1), whereas in Zimnik the number of parameters with waters below the II class increased (average pH -6.10) probably as a result of acidifying effect of spruce stand and outwashing of acid substances from the rock subsoil and humic acids from the surface soil layers (MACIASZEK *et al.*, 2000).

Table 1. Selected physiographic parameters of studied catchments

	Zimnik catchment	Czyrna catchment
Mean elevation, m a.s.l.	916.24	930.11
Area of catchment, km ²	7.52	4.14
Catchment's length, km	4.73	2.32
Terrain configuration index	0.32	0.36
Ordinate of the highest spring, m a.s.l.		
– on hydrographical maps 2002	1130 (4a)	1210 (01h)
– in the study	1130 (4a)	1125 (01h)
River network density according to Neuman, km·km ⁻²		
– on hydrographical maps 2002	1,99	2.91
- study maximum (June 2004)	2.07	2.57
- study minimum (October 2004)	1.85	2.08
Springs density index, amount·km ⁻²		
on hydrographical maps 2002	1.73	3.87
– in the study – all springs	2.79	4.11
– in the study – springs present in all sessions	1.86	3.14

Table 2. Mean concentrations of chemical species in sessions

Session	Catch-	Na	NH ₄	K	Ca	Mg	Cl	NO ₃	SO_4	HCO ₃	nII.	EC
Session	ment]	mg·dm ⁻	3				рп	EC mS·cm ⁻¹
ī	Zimnik	1.00	0.20	0.44	5.83	0.73	0.88	4.26	11.60	5.84	5.85	66.29
1	Czyrna	1.08	0.29	0.61	8.13	1.09	1.01	6.38	12.96	10.52	6.19	82.00
П	Zimnik	1.56	0.25	0.53	8.88	1.02	1.85	1.79	13.76	16.50	6.10	70.23
11	Czyrna	1.37	0.23	0.59	8.40	1.05	1.94	2.90	10.76	15.65	6.68	108.58
Ш	Zimnik	1.54	0.56	0.58	6.39	1.27	1.62	3.14	15.17	10.98	5.98	66.56
111	Czyrna	2.94	0.68	1.05	3.65	2.37	2.04	4.11	17.34	5.39	6.80	88.43

Low water stage was still the only factor responsible for qualification of waters to the IV and V class due to low reaction (mean pH in the basin of Zimnik – 5.98, in Czyrna – 6.80 – averages covering sites excluded from further analysis). In the Zimnik catchment the lowest pH was 4.91 in site 3d'. Moreover, there were remarkably high concentrations of ammonium ions not observed in previous sessions. Their presence in the third session was connected with autumn decomposition of organic matter (Tab. 3, 4, map 3).

A substantial improvement of water pH in the Czyrna catchment, during intensive precipitations and at low water flow proves that low pH in that catchment is influenced mainly by snowmelt. The points that preserved low pH during all sampling sessions in the Zimnik catchment evidence that the reaction of waters did not depend exclusively on precipitation but also on permanent factors like geology and soils (ASTEL *et al.*, 2008a; 2008b; 2009).

Table 3. The number of samples in water quality classes during three sampling sessions with specified limiting factors

		Λ			-			
		IV			7			
on.	class	III	1					
III session		П	9	1	3	7	-	
]		I		9			-	
	total number	of samples		17			8	
		IV			4			
nc	class	Π			10			_
II session		I		κ			17	
	total number	of samples		17			18	
		^			7			
n	class	II		9	7		12	13
l session		I		_			0	
	total number	of samples		14			13	
	Limiting	19001	NH ₄ ⁺	NO_3^-	Hd	$\mathrm{NH_4}^+$	NO_3^-	Hd
	Catchment			Zimnik			Czyrna	

Table 4. The number of samples in drinking water quality categories during three sampling sessions with specified limiting factors

	beyond A3	1	
ion	cat. A2	17	∞
III session	cat. A1	0	0
	cat. A1 cat. A2 total number cat. A1 cat. A2	17	∞
	cat. A2	1 14	7 1
II session	cat. A1	3	15
Π	cat. A1 cat. A2 beyond total number A3 of samples	17	18
	beyond A3	2	
on	cat. A2	5	4 13
I session	cat. A1	3	0
	total number of samples	14	13
Limiting	ment factor	$\mathrm{NH_4}^+$	NH4 ⁺
Cotob	ment	Zimnik	Czyrna

Classification of waters according to the Directive of 2002 is considerably stricter for ammonium ions whereas the allowable nitrate concentrations are higher (waters from all points fell into A1 category due to nitrogen concentration) (Tab. 3, 4).

Results of correlation analysis are presented in Tables 5 and 6 with statistically significant coefficients given in bold (data generated in Statistica software).

In the Zimnik catchment we found statistically significant relationship between: SO_4^{2-} and geological sediments and session. Electrolytic conductivity was correlated with soil type and elevation above sea level, Cl^- with session and age of forest stand and Na^+ Mg^{2+} , K^+ with geological sediments. In the Czyrna catchment we found statistical significance of correlation between: SO_4^{2-} and geological sediments, EC and elevation above sea level, Cl^- and slope and session; Na^+ Mg^{2+} and forest moisture, site degradation and forest type, Ca^{2+} , HCO_3^- and age of the forest type, H^+ and session (Tab. 5, 6).

Correlation analysis and comparisons of averages in the groups demonstrated (Tab. 7, 8) that precipitation exerted the strongest influence on the chemistry of waters in mountain streams. During snow melt the reaction of waters was lowest in the Czyrna catchment – this was the consequence of snow cover acidity (MAŁEK and ASTEL 2008). The snow cover remaining in higher parts of Skrzyczne in spruce overgrown areas supplied substantial amounts of NO_3^- . The average concentration of NO_3^- ions was higher in Czyrna (6.38 mg·dm⁻³) than in Zimnik (4.09 mg·dm⁻³). This difference indicates a great significance of the slope exposition which affected precipitations and their supply to streams (Fig. 2, 3, Tab. 2).

Spatial distribution of precipitation is markedly diversified in the area of the Beskid Śląski and depends on the elevation above sea level, on topographic profile and exposition. Annual average precipitation varies from 900 mm in the lower part of the site to 1400 mm in the summit areas. Mean long term (1961–2000) annual precipitation estimated in the Institute of Meteorology and Water Management (IMGW) in Szczyrk was 1325 mm. The precipitation ranged from 947 mm in the driest year (1969) to 1816 mm in the most humid period (hydrographical map 2002). The dominance of westerly winds is the reason why the Czyrna catchment receives more rainfalls than the Zimnik catchment situated in the precipitation shadow. Low concentration of chlorides during snow melt, in comparison with other sampling seasons, suggests that the continental air mass dominated in winter 2004.

The highest electrolytic conductivity (mean $EC-108.6~\mu S\cdot cm^{-1}$) was estimated during intensive precipitations in the Czyrna catchment. However, no increase of examined ions was noted that could increase the value of EC. Therefore, the outwashing of small molecules from plants' surfaces and humus layer (humus and humic acid) rather than the release of ions from the rock subsoil was responsible for high conductivity. The lowest concentrations of NO_3^- in the Zimnik catchment are another argument in favour of the fact that reaction in that catchment is

Table 5. Analysis of correlation – Zimnik Catchment

				Spearman	bearman correlation				Pearson c	correlation
Parameter	geological sediments	lios	ədols	exposition	forest mois- ture	site distur- bance	type of for- est stand	session	elevation	age of for- est stand
EC	0.061	0.378	0.026	0.169	0.193	-0.289	-0.304	0.160	-0.49	0.11
$\mathrm{H}^{\!+}$	-0.127	-0.225	-0.206	-0.020	-0.189	0.056	0.268	-0.259	0.13	80.0
$Na^{+}, Mg^{2+}, K^{+},$	0.336	0.303	-0.187	-0.099	0.074	-0.289	-0.116	0.261	-0.23	80.0
CI	0.067	0.146	-0.007	-0.033	-0.074	-0.077	0.052	0.547	-0.09	0.34
NO ₃ -	0.169	-0.039	-0.169	0.133	-0.052	0.047	-0.090	-0.270	-0.16	0.04
SO_4^{2} -	0.327	0.048	0.154	-0.035	0.111	0.153	-0.187	0.704	-0.01	0.47
Ca^{2+}, HCO_3^{-}	0.245	0.195	-0.155	-0.194	0.044	-0.277	-0.142	0.135	-0.23	0.13

Table 6. Analysis of correlation - Czyrna Catchment

				Spearman	Spearman correlation				Pearson c	Pearson correlation
Parameter	geological sediments	lios	slope	exposition	forest mois- ture	site distur- bance	type of for- est stand	session	elevation	age of for- est stand
EC	-0.281	0.347	-0.462	0.262	-0.377	-0.016	0.308	0.357	-0.43	0.07
$\mathrm{H}^{\!+}$	0.254	-0.320	0.204	0.123	0.195	-0.180	-0.182	-0.088	0.20	60.0
$\mathrm{Na}^{+},\mathrm{Mg}^{2+}$	0.166	0.136	-0.270	-0.049	0.063	0.080	0.122	0.245	-0.09	0.16
CI	-0.094	0.289	-0.199	-0.090	-0.250	0.407	0.352	0.367	-0.33	0.10
NO_3^-	-0,161	0.129	-0.372	0.257	-0.089	-0.080	0.167	0.201	-0.15	0.11
$\mathrm{SO_4}^{2-}$	0.278	-0.183	-0.005	0.233	0.275	-0.224	-0.256	0.060	0.24	0.13
Ca^{2+}, HCO_{3}^{-}	-0.375	0.313	-0.167	0.227	-0.216	0.112	0.226	0.310	-0.12	-0.27

Table 7. Results of averages in groups comparison in Zimnik catchment

	Grouping variables	EC	H^{+}	$\begin{array}{c} \mathrm{Na}^{+}, \\ \mathrm{Mg}^{2+}, \\ \mathrm{K}^{+} \end{array}$	Ca ²⁺ , HCO ₃ -	Cl-	$\mathrm{NO_{3}^{-}}$	$\mathrm{SO_4}^{2-}$
Geological	thick-bedded glauconity sandstone and green shales	ľ	r	Ţ	Ţ	Ţ	r	r
sediments	thin-bedded flinty sandstone with green and dark shales	ы	г	ı	T	Т	ı	'n
	polygenetic conglomerates	L L	Т	ы	T	ı	ы	ı
Soil	haplic podzols, colluvial sands on stony-gravely deposits	ı	Т	ы	T	Т	ч	ı
	haplic podzols, dust on stony-gravely deposits	ı	Т	ы	T	Т	ч	ı
	haplic podzols	ч	ī	ы	Ţ	ī	ы	ı
	dystric cambisols	ы	r	ы	T	r	ı	ı
	dystric regosoles, colluvial sands on stony-gravely deposits	ы	r	ı	T	r	ı	L
Slope	8–12%	max	Т	ы	T	ı	ы	ı
	13–17%		Г	ы	Т	Г	ı	L
	18–30%		ı	u	п	ı	'n	ı
Exposition	П	ı	r	u	r	r	ı	L
	S-E	ы	Т	ы	T	ı	ы	ı
	田	ı	ı	'n	ı	ı	'n	ı
Forest site	LMG							
Site moisture ¹⁾	strongly fresh	ы	Т	ы	T	T	ı	L
	fresh	u	ı	'n	r	ı	'n	ı
Site deforma-	natural	ı	r	u	r	r	ı	L
tion	disturbed	ı	ı	L	ı	ı	'n	ı
Type of forest	Md-Św-Bk	u	ı	L	ı	ı	'n	ı
stand	Św-Jd-Bk	ы	Г	ы	Т	Г	ı	L
Session	snow melt	ı	Т	ы	T	min	max	min
	intensive rainfall	ı	>3	u	T		min	
	low water level (3)	ч		u	п			max
	HAX FO TE E TE TE TO THE	1.:4 II 4	4					

r - group averages are equal (Anova) or samples belong to the same population (Mann-Whitney U test). Max, min etc. - result of post hoc tests and their comparison to box whiskers graphs.

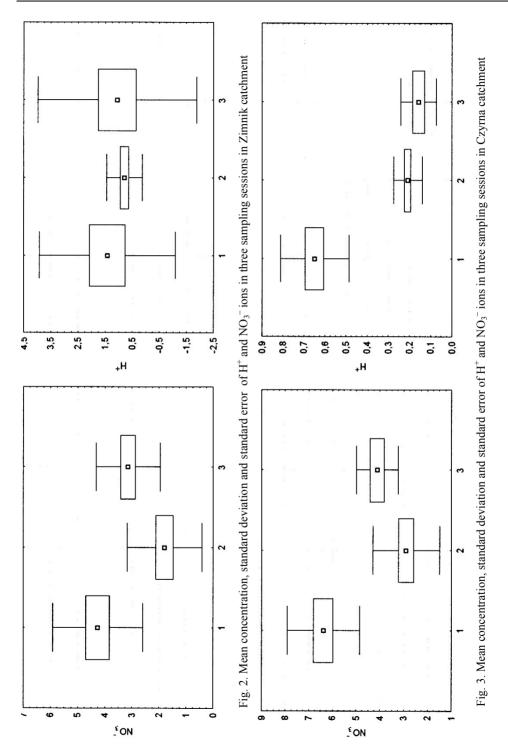
¹⁾ Fresh – restrained moisture with good water proportion without permanent influence of ground water, strongly fresh – as above, but stagnation of water below one month per year is permissible and ground water during spring may be present at shallower level (1.8 m).

Table 8. Results of averages in groups comparison in Czyrna catchment

	Grouping variables	EC	$^{+}\mathrm{H}$	Na, Mg+	$\mathbf{K}^{_{+}}$	Ca^{2+} , HCO ₃ -	Cl ⁻	NO_3^-	SO_4^{2-}
Geological	thin-bedded flinty sandstone and green shales	I	Ţ	ľ	I	I	ľ	I	ľ
sediments	thick-bedded glauconity sandstone and green shales	ч	ч	u	ч	ы	u	.	ı
	thin-bedded flinty sandstone with green and dark shales	ч	ı	'n	ı	ы	ı	ч	ı
Soil	haplic podzols, dust on stony-clayey-loamy deposits (11)	ч	ч	ı	r	ы	ı	ч	г
	haplic podzols, dust on stony – gravely deposits	ы	ч	<u>></u>	п	ь	ы	ы	ı
	albi distric cambisols	ы	ч	ı	r	ы	ı	ч	r
	no data (area beyond PGL LP)	ч	ı	'n	ı	L	ı	ı	ı
Slope	8–12%	<u>\</u>	ı	'n	ı	L	ı	ı	ı
	13–17%	ı	-	۱	ı	L	'n	u	r
	18–30% (kod 4)		-	۱	ı	L	'n	u	r
Exposition	Z	ч	ı	ı	r	ы	ı	ı	r
	N-E	ы	ч	ı	r	ы	ı	ч	r
	S-W	ч	п	ı	r	ы	ı	ч	ľ
	N-W	ч	ч	u	ч	ы	u	.	ı
Forest site	BG	max	ı	ч	ч	L	u	ч	ī
;	BMG	ы	ı	ч	ч	L	u	ч	ī
Site moisture ¹⁾ strongly fresh	strongly fresh	ı	ī	ı	r	L	ı	ı	Ţ
	fresh	ı	¥	u	ı	L.	u	ı	ı
Forest site	natural	ı	¥	u	ı	L.	u	ı	ı
	disturbed	ч	ы	u	ı	u	u	L	ı
Type of forest Bk-Md-Św	Bk-Md-Św	ч	ч	ı	r	ы	ı	ч	г
stand	Md-Św-Bk	ы	ч	ı	r	ы	ı	ч	r
	meadow or ski trail	ы	ч	ı	r	ы	ı	ч	r
Session	snow melt	ı	max	u	ı	u	min	max	ī
	intensive rainfall	max	ı	L	ч	L	u	ı	П
	low water level	ľ	r	max	ľ	min	ľ	r	max
	COLL CELL SC C. T. T. T. C. C. T. T. C. C. C. T. T. C. C. C. T. C.								

r - group averages are equal (Anova) or samples belong to the same population (Mann-Whitney U test). Max, min - result of post hoc tests and their comparison to box whiskers graphs.

¹⁾ Fresh - restrained moisture with good water proportion without permanent influence of ground water, strongly fresh - as above, but stagnation of water below one month per year is permissible and ground water during spring may be present at shallower level (1.8 m).



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determined by the characteristics of soil and rock foundation. Low concentration of NO_3^- may be caused by a smaller input of waters from spruce stands (MAŁEK and ASTEL, 2008; ASTEL *et al.*, 2009).

During a low water stages the highest concentration of $\mathrm{Na^{+}}$ and $\mathrm{Mg^{2^{+}}}$ ions was found in the Czyrna and of $\mathrm{SO_4^{2^{-}}}$ in both catchments. These results indicate a substantial outwashing of ions from the rock foundation (ASTEL *et al.*, 2008a; 2008b; 2009).

Moreover, the lowest concentration of bicarbonates and calcium ions was noted in the Czyrna catchment.

The remaining variables affected water chemistry in Czyrna in various ways. The highest *EC* was noted in points at the slopes of the smallest inclination, which may be explained by accumulation of ions where the water flow diminishes. Lower concentrations of Mg²⁺ and Na⁺ were noted in disturbed than in natural sites. Probably, this resulted from a higher content of these ions in deciduous trees (beech, sycamore) than in stand dominated by spruce (MACIASZEK *et al.*, 2000; ASTEL *et al.*, 2008a; 2008b; 2009). No statistically significant differences in chemical characteristics of environment features connected with flora (forest site, its deformation, type of forest stand) were noted in the Zimnik catchment.

It is worth looking closer on the protruding points that were not qualified for further measurements but no error was found in the measurement of their features (items fulfilling ions balance conditions). In the Zimnik catchment, we found point 3d' during the first and third session and 4c' in the first session. Water from these sites had a very low pH of 5.14, 4.91, and 5.13, respectively. Following previously mentioned line of evidence, a low reaction of these waters may be a result of washing out of acid substances from the rock foundation and humus and humic acids from decaying spruce litter, and in the first session – also from inflow of nitrogen from the snow melt. A slightly higher pH in site 3d' during precipitation (5.51) may result from dilution of these substances by rain water. Undoubtedly, in this place there were specific local conditions; also other points located in similar environment, not indicating such deviations, underwent the examination.

In the Czyrna catchment, the protruding points had a slightly opposite character. 02a', 03d', and 03b' were characterised in the third session by high concentration of Mg^{2+} , and 03b' also by high Na^+ . These ions may come from two sources. The first is the release of cations form the rock foundation (all sites are in the range of substantially fertile brown podzoil soils). Higher concentration of magnesium and sodium could indirectly result from the decay of leaf litter (beech, sycamore) in tree stands neighbouring the described sites and affecting stream waters. The decay of litter has an important influence on chemical characteristics of water, which may be demonstrated by an increase of NH_4^+ concentration during the October session.

SUMMARY AND CONCLUSIONS

Chemical composition of stream waters located in the Zimnik and Czyrna catchments depends on physico-geological constitution of drainage areas and on seasonal changes of water stage in the catchment. The dying out of spruce in the Beskid Śląski influenced the quality of waters in streams running along the slopes of Skrzyczne. Most important for water chemistry is the air pollution supplied to stand with precipitations and species composition of tree stands. A crucial moment is the snowmelt period when contamination is delivered to forest ecosystems in a concentrated form.

The main factor that makes waters at Skrzyczne unsuitable for drinking purposes is low reaction of waters and a high concentration of nitrate and ammonium ions. A regular consumer of these waters does not have the possibility to evaluate water quality in streams that one might get across. Water quality depends not only on easily visible reasons of its possible deterioration (spruce stand composition, snowmelt period) but also on local conditions. Water quality differed during intensive rainfalls when in the Czyrna catchment 15 out of 18 samples reached the highest A1 category (suitable for drinking) while in the Zimnik catchment such category was achieved by only 3 out of 17 samples.

Chemical features of water may to some degree be modified through structuring the composition of tree stand, which was confirmed by higher concentration of magnesium and sodium ions in waters from sites neighbouring multi-species deciduous tree stands (beech, sycamore). Therefore, it is necessary to elaborate rules and principles of managing spring areas, particularly in the regions from where water is intended to be taken for drinking purposes.

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STRESZCZENIE

Wpływ warunków środowiskowych na jakość wód powierzchniowych w zlewni Zimnika i Czyrnej w Beskidzie Śląskim

Słowa kluczowe: Beskid Śląski, budowa geologiczna, jakość wód, skład gatunkowy, typ siedliskowy lasu, wody powierzchniowe

Badania zostały przeprowadzone w 2004 roku w zlewniach Zimnika i Czyrnej leżących na przeciwległych stokach Skrzycznego w Beskidzie Śląskim. Analizie poddano wody pobrane z potoków podczas trzech sesji pomiarowych. Pierwsza odbyła się podczas roztopów śniegu (kwiecień/maj), druga sesja w trakcie intensywnych opadów deszczu w okresie wegetacji (czerwiec), trzecia przy niskim stanie wód (październik). Analizowano odczyn i przewodność elektrolityczną, oraz stężenie anionów (Cl⁻, NO₃⁻, SO₄²⁻) i kationów (NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺). Wyniki poddano klasyfikacji wód pitnych wg polskich norm (z 2002 i 2004 r.). Skład chemiczny wód powierzchniowych zależy od fizycznych i geologicznych właściwości utworów budujących zlewnie. Przynależność wód do klasy zależy również od wystąpienia i rodzaju opadów atmosferycznych oraz składu gatunkowego. Stwierdzono niezdatność dużej części badanych wód do picia – 66 z 89 pobranych prób znajdowało się poza klasa A1, głównie ze względu na niski ich odczyn oraz wysokie stężenie NH₄⁺ i NO₃⁻. W drzewostanach bukowych i wielogatunkowych zaobserwowano znacząco większe niż w świerkowych wymywanie kationów podczas intensywnych opadów deszczu, co w pewnym stopniu neutralizowało odczyn wód a tym samym podnosiło jakość wód. Ten fakt powinien być brany pod uwagę przy zalesianiu terenów źródliskowych i sąsiadujących z potokami w obszarach, gdzie wody te wykorzystywane są lub będą w przyszłości, jako dodatkowe ujęcia wód pitnych.

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Prof. Nicolas Clarke Prof. Stanisław Niemtur