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Effect of deforestation on water chemistry in the Kościeliska Valley in the Western Tatras in southern Poland

MIROSŁAW ŻELAZNY[1], AMANDA KOSMOWSKA[1], TOMASZ STAŃCZYK[2], MARIA MICKIEWICZ[1]
[1] Institute of Geography and Spatial Management, Jagiellonian University
[2] Faculty of Civil and Environmental Engineering, Warsaw University of Life Sciences – SGGW

Abstract: *Effect of deforestation on water chemistry in the Kościeliska Valley in the Western Tatras in southern Poland.* Bark beetle infestation is a leading source of local tree stand damage in Tatra National Park. In addition, hurricane-force winds also cause damage to tree stands, as in the case of the 2013 wind event in the Kopki Kościeliskie area of the Kościeliska Valley. The purpose of the study was to determine the effect of deforestation on seasonal changes in water chemistry, especially in the case of nitrate. The research was performed in the years 2015 and 2016 in seven catchments. The total number of monthly water samples was 175. Three forested catchments were selected along with two catchments deforested by high winds, one catchment deforested due to the action of the bark beetle, and one catchment affected by several different forms of deforestation. The following four types of measurements were performed in the field: pH, electrolytic conductance ($EC_{25°C}$), total mineralization (*Mt*). The following analyses were performed in the laboratory using DIONEX 2000 ion chromatography equipment – concentration of 14 ions in water samples: Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, Li^+, HCO_3^-, SO_4^{2-}, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, Br^-, F^-. The concentration of NO_3^- was many times higher in samples collected in deforested areas ($\bar{x}$ = = 16.53 mg·L^{-1}) versus forested areas ($\bar{x}$ = 3.06 mg·L^{-1}). The share of NO_3^- in overall water chemistry in catchments deforested by high wind events is more than three times higher (3.25% mval·L^{-1}) than in forested catchments (1.07% mval·L^{-1}), and almost twice as high as that for a catchment affected by the bark beetle (1.8% mval·L^{-1}). In fact, it is high enough that the position of the nitrate ion in the sequence of anions in the deforested catchment shifts from HCO_3 > > SO_4 > NO_3 > Cl (natural sequence occurring in forested carbonate-type catchments) to HCO_3 > > NO_3 > SO_4 > Cl. In addition, the concentration of nitrate in stream water was found to be lower during the vegetation season, which is associated with the nitrogen intake of plant root systems in the summer season.

Key words: streamwater chemistry, deforestation, nitrate concentration

INTRODUCTION

Water chemistry is affected by abiotic factors such as catchment geology, slope water residence, and atmospheric pollutant influx as well as biotic factors such as microorganism activity in weathering material and soils along with plant cover type. Catchment land use also remains an important factor. According to Czop et al. (2008), even small changes in regional land use near springs in the Poprad Valley as well as changes in spring recharge areas may strongly affect mineral water chemistry and carbonated spa water chemistry. The higher rate of spruce forest decline observed in recent years in mountain areas in Poland and Slovakia suggests that more research is needed due to the special role played by forests in the natural environment.

Forested areas in the Tatra Mountains today are facing a large number of threats, which are often called catastrophic threats. Woodland management in this part of Europe has been difficult over the years due to the occurrence of foehn winds known as halny, which cause the felling of trees across large swaths of mountain land. The most recent catastrophic wind event in Tatra National Park occurred in 2013 when hurricane-force winds reaching 200 km/h felled more than 100,000 trees in the area. The second largest threat to spruce stands in the Tatra Mountains is the work of the spruce bark beetle (*Ips typographus*) and the European bark beetle (*Pityogenes chalcographus*). Damaged trees serve as ideal feeding grounds for the small insects, which make their home in their midst (Grodzki and Guzik 2009). Winds events described as extreme also occur in Slovakia and damage tree stands as well. One of the largest of such events was that on 19 November 2004 when more than 10,000 ha of woodland became deforested rather abruptly (Balon and Maciejowski 2005).

This event served as a rare opportunity to perform fieldwork designed to help determine changes in water chemistry in catchment waters. Similar research work was done in the United States in the Coweeta catchment in the 1930s and the Hubbard Brook catchment in the 1960s. Each research team proceeded by cutting down trees using a variety of methods followed by an observation of changes in water chemistry in surface water and groundwater (Swank et al. 1988). Similar research was conducted in the western Sudety Mountains and the Silesian Beskid Range in southern Poland in catchments with tree stands decaying due to the effects of industrial pollution generated in Germany, Poland, and the Czech Republic (Černy and Pačes 1995, Pierzgalski et al. 2007, 2009, Kosmowska et al. 2015).

The purpose of the study was to determine the effect of deforestation on seasonal changes in water chemistry with a special focus on nitrate. The effects of abrupt deforestation were assessed in cases caused by high winds as well as slow deforestation caused by the bark beetle (lasting 10 to 15 years).

STUDY AREA

The research was conducted in the Kościeliska Valley in southern Poland. In the classification system by Balon and Jodłowski (2005), the studied valley is found in the meso-region of the Western Tatras – and Tatra Chain macro-region and Central Western Carpathian sub-province. The study area lies amidst Jurassic and Triassic rock formations (Lower Tatra series) including limestone, dolomite, marl, as well as Podhale flysch consisting of dolomite sandstone (Bac-Moszaszwili et al. 1979). The area is characterized by fluvial denudation-type relief featuring narrow V-shaped valleys (Klimaszewski 1988). The climate of the study area is moderately cool and cool, while the annual precipitation total ranges from 1,200 to 2,000 mm (Hess 1974).

The study area (Fig. 1) is located in the woodland zone (sub-tatric-subalpine), which generally does not exceed 1,500 m of elevation (Balon et al. 2015). However, this zone has become deforested to a substantial degree in recent years. The cause of the deforestation

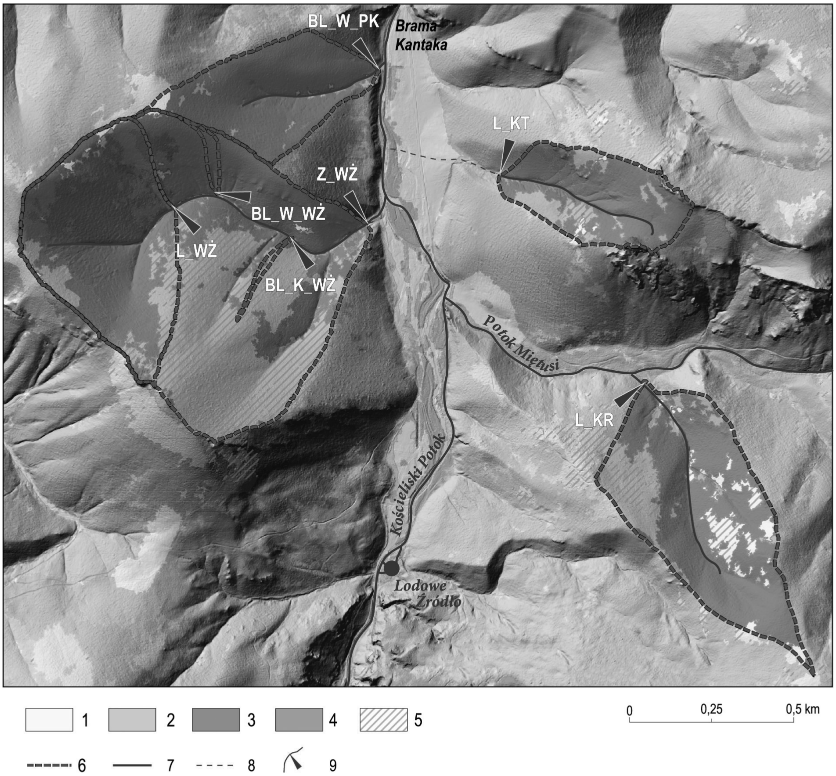

FIGURE 1. Land cover of study area: 1 – meadows/area deforested before, 2 – area deforested because of the bark beetle, 3 – area deforested by 2013 windthrow, 4 – forested area, 5 – succession on deforested areas, 6 – catchment boundaries, 7 – permament streams, 8 – periodical streams, 9 – catchments closing sections, water sampling

was high winds blowing in the area on the night between 24 and 25 December 2013. The wooded downstream part of the Kościeliski Stream catchment was substantially deforested in an area called the Kopki Kościeliskie. The eastern-facing slopes (Fig. 2) experienced the greatest loss of forest: Przednia Kopka (1,113 m of elevation), Pośrednia Kopka (1,305 m), Zadnia Kopka (1,333 m). One factor contributing to this degree of deforestation in the Kościeliska Valley was the degree of tree stand decline caused by the years of strong activity of the bark beetle.

METHODS

Seven partial catchments in the Kościeliski Stream catchment were selected for research purposes. The aim of the study was to analyze effect of deforestation on water chemistry and seasonal changes in water chemistry. The study area was covered by forest to varying degrees. Water samples from the following three forested catchments were studied herein: Kończysta Turnia (L_KT), Krowi Żleb (L_KR), one partial catchment within Wściekły Żleb (L_WŻ). In addition, three deforested catchments

FIGURE 2. View of the deforested slopes in study area

were studied: Wściekły Żleb (BL_K_ WŻ) – deforested by the bark beetle, one partial catchment within Wściekły Żleb (BL_W_ WŻ) and Pośrednia Kopka (BL_W_PK) – deforested by high winds. For the purpose of comparison, a mixed--type catchment was also examined – the Wściekły Żleb (Z_ WŻ) catchment. Fieldwork was conducted on a monthly basis from July 2015 to December 2016. The measurements that were produced as part of fieldwork were temperature, electrolytic conductance ($EC_{25°C}$), pH and then a 1 L of water was taken to the bottle.

Ion chromatography (DIONEX 2000) was used to determine water chemistry in terms of the following ions: Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, Li^+, F^- i Br^-. The work was done at the Hydrochemical Laboratory at the Institute of Geography and Spatial Management at Jagiellonian University in Kraków. In the Żelazny's monograph (2012) on the chemistry of Tatra waters there is a detailed description of the laboratory methods used. Main ions and nitrate were chosen for advanced analysis. The concentrations of the remaining ions were very low, often below the detection limit, and the results are not published in the tables available in the paper. Total mineralization (*Mt*) was calculated as the sum of all ion concentrations in the study. Water chemistry was determined using the arithmetic mean ($\bar{x}$) of ion concentrations and the share of ion concentrations in overall water chemistry. Seasonal differences were estimated using the coefficient of variation (*Cv*), which expresses the quotient of the standard deviation and the average value.

The significance of the difference in average NO_3^- concentration between water groups was determined by the variance analysis (ANOVA) and the Scheffe post hoc test. The level of significance was assumed $p = 0.05$.

RESULTS

According to the Pazdro and Kozerski (1990) classification system, water produced by both wooded and deforested catchments may be termed weakly alkaline, and classified as freshwater of medium hardness (Table 1). The studied waters are dominated by the calcium cation whose average concentration is 57.30 mg·L^{-1} (Table 2). Less concentrated anions included Mg^{2+} (5.78

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

Land cover	Catchment	ID	pH		$EC_{25°C}$		M_t	
			$\bar{x}$	Cv	$\bar{x}$	Cv	$\bar{x}$	Cv
			pH	%	$\mu S \cdot cm^{-1}$	%	$mg \cdot L^{-1}$	%
Forested (L)	Krowi Żleb (KR)	L_KR	8.07	3.5	321.7	1.2	274.6	1.2
	Kończysta Turnia (KT)	L_KT	7.92	3.1	310.9	9.1	267.7	8.9
	Wściekły Żleb (WŻ)	L_WŻ	7.65	3.0	304.9	7.6	259.8	7.5
	Average value			3.2	312.5	6.0	267.4	5.9
Deforested – windfall (W)	Pośrednia Kopka (PK)	BL_W_PK	7.92	3.4	336.6	9.7	288.6	10.2
	Wściekły Żleb (WŻ)	BL_W_WŻ	7.97	4.1	310.5	4.9	265.1	6.9
	Average value		7.86	3.4	316.1	7.0	270.2	7.6
Deforested by beetle (K)	Wściekły Żleb (WŻ)	BL_K_WŻ	7.91	3.8	278.5	7.0	239.9	6.1
Mixed: deforested/forested	Wściekły Żleb (WŻ)	Z_WŻ	7.94	4.0	292.7	5.9	250.8	5.9
Total average			7.91	3.6	308.0	6.5	263.8	6.7

$mg \cdot L^{-1}$) as well as sodium and potassium. The sequence of average cation concentrations is as follows: Ca > > Mg >> Na > K. This is regardless of forest coverage. The anion with the highest concentration was bicarbonate – with an average of 183.3 $mg \cdot L^{-1}$. Nitrate (7.95 $mg \cdot L^{-1}$) and sulfate (7.46 $mg \cdot L^{-1}$) concentrations were much lower and similar to one another. However, research has shown that the concentration of nitrate does depend on forest coverage. Waters obtained from areas deforested by high winds had an average nitrate concentration of 13.80 $mg \cdot L^{-1}$), while waters obtained from non-deforested areas had a concentration of 4.39 $mg \cdot L^{-1}$.

Hence, deforestation yields a shift in the sequence of average water ion concentrations: $HCO_3 > SO_4 > NO_3 > Cl$ (forested catchments), $HCO_3 > NO_3 > > SO_4 > Cl$ (deforested catchments).

Average nitrate concentrations in forested catchments were determined to range from 3.06 to 5.44 $mg \cdot L^{-1}$ (Table 2). Concentrations in deforested catchments are different to a substantial extent. The average concentration of nitrate in water is about twice as high (13.80 $mg \cdot L^{-1}$) in catchments deforested by high wind events versus catchments deforested by the bark beetle (6.69 $mg \cdot L^{-1}$).

TABLE 2. Average concentration ($\overline{x}$) and coefficient of variation (Cv) of ions in stream water

Land cover	Catchment	ID	Ca^{2+}		Mg^{2+}		Na^{+}		K^{+}		HCO_3^{-}		SO_4^{2-}		NO_3^{-}		Cl^{-}	
			$\overline{x}$	Cv	$\overline{x}$	Cv	$\overline{x}$	Cv	$\overline{x}$	Cv	$\overline{x}$	Cv	$\overline{x}$	Cv	$\overline{x}$	Cv	$\overline{x}$	Cv
			$mg \cdot L^{-1}$	%	$mg \cdot L^{-1}$	%	$mg \cdot L^{-1}$	%	$mg \cdot L^{-1}$	%	$mg \cdot L^{-1}$	%	$mg \cdot L^{-1}$	%	$mg \cdot L^{-1}$	%	$mg \cdot L^{-1}$	%
Forested (L)	Krowi Żleb (KR)	L_KR	42.26	3.6	18.32	4.8	0.25	8.6	0.36	6.3	203.0	1.5	6.82	11.0	3.06	7.9	0.50	8.3
	Kończysta Turnia (KT)	L_KT	58.45	10.4	5.78	48.2	0.71	26.5	0.56	14.4	190.5	9.2	6.34	23.6	4.66	20.5	0.59	32.4
	Wściekły Żleb (WŻ)	L_WŻ	60.40	7.7	3.11	26.0	0.87	31.1	0.44	12.9	181.0	8.1	7.93	23.7	5.44	36.2	0.56	36.6
	Average value		53.70	7.2	9.07	26.3	0.61	22.1	0.45	11.2	191.5	6.3	7.0	19.4	4.39	21.5	0.55	25.8
Deforested – windfall (W)	Pośrednia Kopka (PK)	BL_W_PK	66.03	8.6	3.74	28.4	1.17	37.6	0.59	21.1	196.7	11.4	8.47	30.0	11.06	38.7	0.79	31.1
	Wściekły Żleb (WŻ)	BL_W_WŻ	61.24	6.4	3.16	19.1	0.71	30.6	0.51	13.1	174.1	8.2	7.98	23.3	16.53	33.4	0.86	27.5
	Average value		63.64	7.5	3.45	23.8	0.94	34.1	0.55	17.1	185.4	9.8	8.23	26.6	13.80	36.0	0.83	29.3
Deforested by beetle (K)	Wściekły Żleb (WŻ)	BL_K_WŻ	54.88	7.3	3.16	17.9	0.79	27.1	0.41	25.3	166.1	5.3	7.21	22.6	6.69	32.6	0.62	13.2
Mixed: deforested/ /forested	Wściekły Żleb (WŻ)	Z_WŻ	57.86	6.7	3.19	20.3	0.85	22.5	0.53	29.7	172.0	5.9	7.47	19.9	8.18	31.5	0.65	28.7
Total average			57.30	7.2	5.78	23.5	0.76	26.3	0.49	17.5	183.3	7.1	7.46	22.0	7.95	28.7	0.65	25.4

Differences between average NO_3^- concentrations in the separated water groups are significant, which is confirmed by the analysis of variance (ANOVA) and they are illustrated in Figure 3.

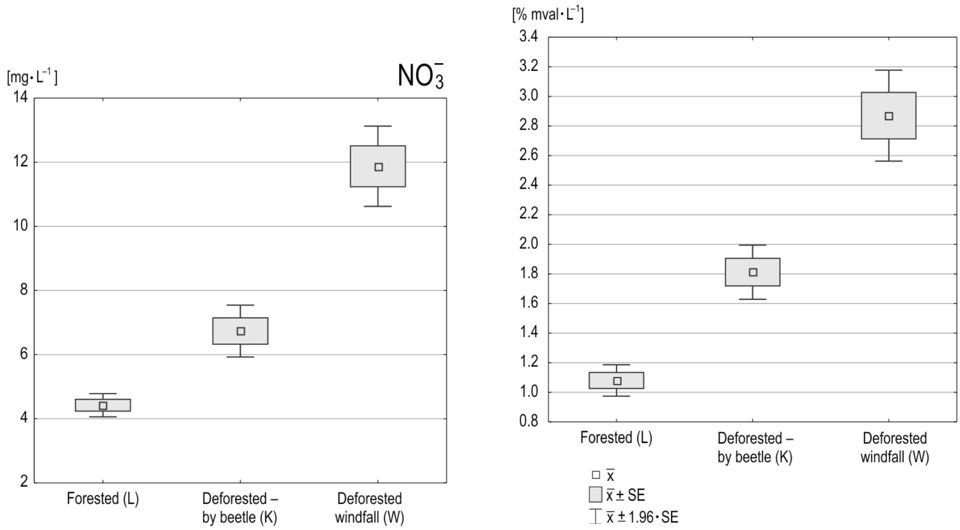

FIGURE 3. Concentration NO_3^- [mg·L^{-1}; % mval·L^{-1}] and for distinguished groups of water samples

The water concentration of nitrate is lower during the vegetation season (Fig. 4) versus all other seasons due to the absorption of nitrogen compounds by plant root systems (Johnson et al. 1969, Johnson et al. 1976, Drever 1997, Żelazny 2012). Research has shown that ions with the highest concentrations tend to not vary substantially in concentration Ca^{2+} (*Cv* = 7.24%) and HCO_3^- (*Cv* = 7.09%). On the other hand, the highest variance values were noted for Na^+ (*Cv* = 26.29%) and NO_3^- (*Cv* = = 28.69%). Finally, the largest difference in concentration variance is that for the nitrate ion in water samples collected from deforested catchments (*Cv* = 21.53%) and forested catchments (*Cv* = 36.05%).

Analysis of water chemistry in streams draining both forested and deforested catchment areas has shown large differences in the two catchment types, especially in terms of the anion concentration (Fig. 5). The share of nitrate in the water chemistry of catchments deforested by a high wind event was 3.25% mval·L^{-1} on average, which was more than three times higher relative to values for forested catchments: 1.07% mval·L^{-1} (on average). It was also almost twice as high as the value for a catchment affected by the bark beetle: 1.8% mval·L^{-1} on average (Table 3). The share of the nitrate ion in water chemistry in the deforested catchments was high enough that the anion sequence for the study area experienced a shift from $HCO_3 > SO_4 > > NO_3 > Cl$ (sequence natural to the study area) to $HCO_3 > NO_3 > SO_4 > Cl$. The most likely cause of the increase in the nitrate concentration in waters obtained

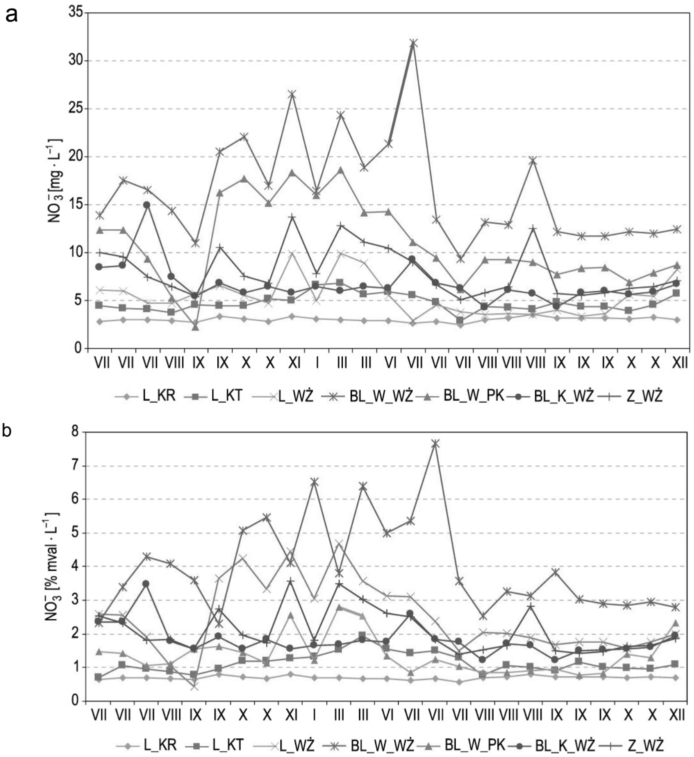

FIGURE 4. Seasonal changes in nitrate concentration (a) and seasonal changes in nitrate content (b) in stream water collected in forested and deforested catchments

from deforested catchments is reduced intake due to a decline in tree stands or their complete destruction, as shown by Burns and Murdoch (2005) as well as Wang et al. (2006). At the same time, nitrate in such areas is also produced by the slow decay of organic matter (Dahlgren 1998).

Damaged tree stands behave in a manner similar to that of aging stands – their ability to actively absorb nitrate becomes reduced (Vitousek and Reiners 1975, Murdoch and Stoddard 1992, Swank and Vose 1997). The increase in nitrate concentration in water illustrates well the process of nitrogen leaching from catchments, which undoubtedly impacts a catchment's hydrochemical regime (Rothe and Mellert 2004). The results produced in this study are also confirmed by the work of Houlton et al. (2003) performed over many years in the Hubbard Brook catchment in the United States. The said study showed that nitrate concentrations were several times higher in water obtained from a catchment deforested by a hailstorm. The result was similar in work by Martin et al. (1986) who studied the White Mountains in the state of New Hampshire in the United States. In this case, the increase in the nitrate concentration was also quite substantial for water from streams in a forest where the trees had been cut down.

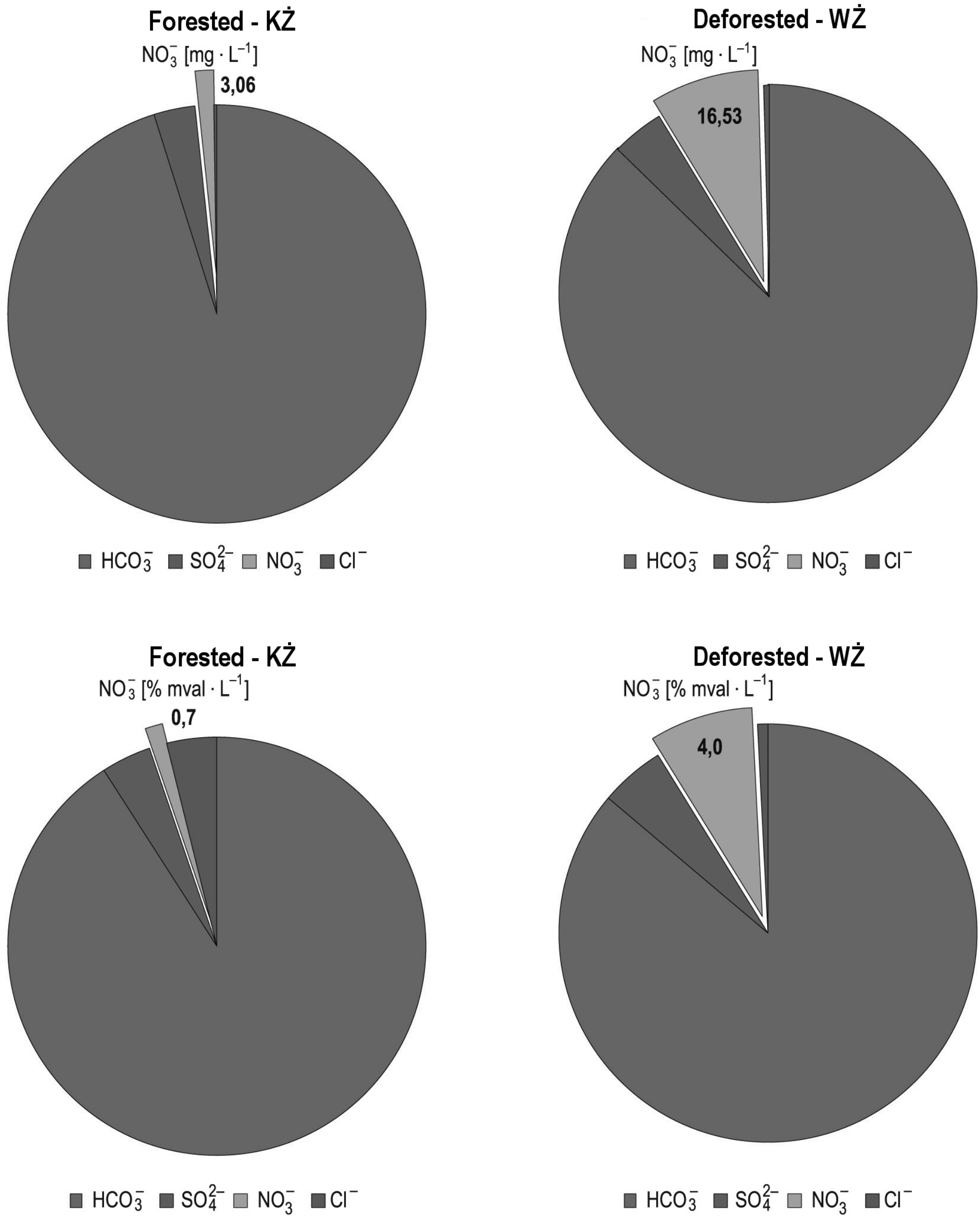

FIGURE 5. Share of nitrate in total anion content in a forested catchment (left) and a catchment deforested by high winds (right)

TABLE 3. Average concentration and coefficient of variation (*Cv*) of content ions in stream water

Land cover	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*
			% $mval \cdot L^{-1}$	%	% $mval \cdot L^{-1}$	%	% $mval \cdot L^{-1}$	%	% $mval \cdot L^{-1}$	%	% $mval \cdot L^{-1}$	%	% $mval \cdot L^{-1}$	%	% $mval \cdot L^{-1}$	%	% $mval \cdot L^{-1}$	%
Forested (L)	Krowi Żleb (KR)	L_KR	29.0	2.8	20.7	4.0	0.2	8.8	0.1	6.2	47.0	0.5	2.0	10.7	0.7	7.8	0.2	8.1
	Kończysta Turnia (KT)	L_KT	42.5	6.8	6.8	43.1	0.4	19.3	0.2	11.6	46.6	1.2	2.0	17.4	1.1	25.4	0.2	38.3
	Wściekły Żleb (WŻ)	L_WŻ	45.4	2.2	3.8	23.0	0.6	26.7	0.2	13.2	45.8	1.6	2.5	19.6	1.4	42.1	0.2	42.6
	Average value		38.97	3.9	10.4	23.4	0.4	18.3	0.2	10.3	46.5	1.1	2.2	15.9	1.1	25.1	0.2	29.7
Deforested – windfall (W)	Pośrednia Kopka (PK)	BL_W_PK	45.0	2.4	4.1	21.1	0.7	30.5	0.2	26.8	44.7	2.6	2.4	22.1	2.5	43.0	0.3	31.5
	Wściekły Żleb (WŻ)	BL_W_WŻ	45.5	1.6	3.9	16.8	0.5	25.7	0.2	11.0	43.0	3.5	2.5	18.2	4.0	34.1	0.4	28.4
	Average value		45.2	3.4	4.0	25.5	0.6	24.1	0.2	14.6	44.3	2.0	2.5	18.6	2.9	33.9	0.3	34.1
Deforested by beetle (K)	Wściekły Żleb (WŻ)	BL_K_WŻ	45.0	1.8	4.3	15.9	0.6	24.3	0.2	22.6	45.4	1.6	2.5	19.2	1.8	26.3	0.3	12.6
Mixed: deforested/ forested	Wściekły Żleb (WŻ)	Z_WŻ	45.1	2.0	4.1	19.7	0.6	23.3	0.2	26.1	45.1	1.7	2.5	18.1	2.1	31.0	0.3	29.2
Total average			42.50	2.8	6.81	20.5	0.51	22.7	0.19	16.8	45.37	1.8	2.34	17.9	1.94	30.0	0.27	27.2

CONCLUSIONS

Deforestation in the Kościeliska Valley in the Tatra Mountains caused by slow tree stand decline triggered by the work of the bark beetle as well as the effects of hurricane-force winds caused changes in local water chemistry. The concentration of nitrate increased several times in stream water obtained from deforested catchments. The increase was higher in a catchment deforested by high winds versus a catchment deforested by the bark beetle.

A significant increase in the share of nitrate in the water anion total caused a shift in the anion sequence. The nitrate ion is now found before the sulfate ion and after the bicarbonate ion in water obtained from catchments deforested by high winds. Finally, nitrate concentrations were found to be many times higher outside of the vegetation season compared with those for the vegetation season.

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Streszczenie: W*pływ wylesienia na zmiany składu chemicznego wód w Dolinie Kościeliskiej w Tatrach Zachodnich.* Współcześnie wskutek gradacji kornika lokalnie ulegają zniszczeniu lasy Tatrzańskiego Parku Narodowego. W 2013 r. przejście huraganowego wiatru spowodowało masowe wylesienie stoków Kopek Kościeliskich w Dolinie Kościeliskiej. Celem badań było określenie wpływu wylesienia na skład chemiczny wód i ich sezonowe zmiany, w szczególności azotanów. Badania przeprowadzono w latach 2015–2016 w 7 zlewniach, w których w rytmie miesięcznym pobrano 175 prób wody. Wybrano trzy zlewnie porośniete lasem, dwie wylesione przez wiatrołom, jedną wylesioną wskutek gradacji kornika oraz zlewnię, gdzie wylesienia miały różną genezę. W terenie zmierzono stan wody, cechy fizykochemiczne (pH, *EC*, *Mt*), a w Laboratorium Hydrologiczno-Chemicznym IGiGP UJ 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^{-}). W zlewniach wylesionych zaobserwowano wielokrotnie wyższe ($\bar{x}$ =16,53 mg·L^{-1}) stężenia NO_3^{-} niż w wodach odwadniających zlewnie porośnięte lasem ($\bar{x}$ =3,06 mg·L^{-1}). Udział NO_3^{-} w strukturze składu chemicznego wód odwadniających zlewnie wylesione wskutek wiatrołomu ponad trzy razy wyższy (3,25% mval·L^{-1}) niż w zlewniach zalesionych (1,07% mval·L^{-1}) i prawie dwukrotnie większy niż w zlewni dotkniętej gradacją kornika (1,8% mval·L^{-1}). Udział NO_3^{-} w strukturze składu chemicznego wód odwadniających zlewnie wylesione przez wiatrołomy był na tle duży, że uległa zmianie pozycja azotanów w sekwencji anionów w kolejności malejącej z: HCO_3 > > SO_4 > NO_3 > Cl, która naturalnie występuje w wodach odwadniających węglanowe stoki porośnięte lasem, na sekwencję HCO_3 > NO_3 > SO_4 > > Cl. Dodatkowo w wodach potoków w okresie wegetacyjnym zaobserwowano niższe stężenia azotanów niż w okresie poza wegetacyjnym, co jest związane z pochłanianiem związków azotu przez systemy korzeniowe roślin w czasie półrocza letniego.

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Authors' adress:
Mirosław Żelazny
Zakład Hydrologii
Instytut Geografii i Gospodarki Przestrzennej
Uniwersytet Jagielloński w Krakowie
ul. Gronostajowa 7, 30-387 Kraków
Poland
e-mail: miroslaw.zelazny@uj.edu.pl