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Quality assessment of spring water from the area of the Łysogóry Mts. in Świętokrzyski National Park in 2010

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Abstract

The study was conducted in the year 2010 in the Łysogóry Mts. in Świętokrzyski National Park. Spring water samples were collected in three rounds. The first round was carried out after the period of snowmelt (March/April 2010), the second – after intensive rainfall (May 2010) and the third – when water levels were low (July 2010). The data set attained concerned conductivity, water pH, and also concentrations of the foremost anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}). Spring water quality was assessed in line with Polish policy on groundwater (Regulation of the Minister of Environment of 23 July 2008, The results confirmed that spring water quality strongly depended on wet acid deposition and the geological structure. Tree species (fir and beech), exposition and soil types within the alimentation area did not influence water chemistry. Spring water were found in low quality classes according to Polish standards due to low water pH as well as high NO_3^- and NH_4^+ concentration.

Key words

springs, Świętokrzyski National Park, water quality, water chemistry

Introduction

Springs are very important elements of the natural environment, especially in the areas that are under legal protection. In order to better understand protected areas, one should pay particular attention to identifying water conditions, both quantitative and qualitative. Springs being natural groundwater outflows respond well to any changes that occur in natural ecosystems (Wolanin and Żelazny 2010), and therefore can be classified as important hydrogeological indicators. Recent climate change has contributed to the occurrence of extreme events such as droughts and floods, causing fluctuations in groundwater levels. Forest ecosystems play a very important role in the protection of aquatic environment and in climate change mitigation. In mountainous areas, and especially in national parks where conducting hydrogeological drilling is restricted, springs are an important element of groundwater studies (Humnicki 2007). The evaluation of spring waters quality is a fundamental analysis to study their physico-chemical properties (Małek and Krakowian 2009). Within Poland's area, spring water chemistry has been afore studied, and among others in: the Tatra Mountains (Żelazny et al. 2011), the Silesian Beskid Mts. (Astel et al. 2009; Małek et al. 2009, 2010), Pomerania (Mazurek

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2006) and in the Świętokrzyskie Mts. (Michalik 2008). The aim of the present research was to verify the following hypothesis:

– chemical quality of spring water from the Łysogóry Mts. is determined by the geological structure of drainage areas modified by seasonal changes of catchment water, level;
– differences in chemistry of spring waters depend on a level of massif hydration with other environmental factors such as geological structure, soil and species composition of tree stands.

Material and methods

The study was conducted in the Łysogóry massif located in Świętokrzyski National Park, in the northern part of Świętokrzyskie Province (south-central Poland) (fig. 1). The geographical coordinates of the Łysogóry massif are: 50°50'–50°55'N and 20°52'–21°05'E. Altitude difference between the Łysica peak (612 m a.s.l.) and the lowest point- located in the Pokrzywianka valley (225 m a.s.l.) – is 387 m. The Łysogóry massif is built mainly of various types of hard quartzitic sandstones, quartz sandstones, siltstones and claystones – collectively quartzite of Łysogóry. The massif is approximately 300 m higher in position in relation to the area around and as a result affected by both local and distant sources of industrial pollution, especially those in the western and south-western directions (Kozłowski and Adwent 2011). Very high SiO_2 content in cambrian quartzites and quartzite sandstones (98–99%) and very low contents of Ca, Mg and P predetermine extremely acidic nature of the rocks and their weathering products (Kowalkowski et al. 2001). Quartz sandstones collapse monoclinally toward the north, resulting in shorter and steeper slopes in massif northern side in comparison to cradle-shaped slopes in the southern side. The area where water samples were collected is covered by fir and beech forests.

Water samples from springs were collected over the vegetation season in 2010 during three measurement rounds: after snowmelt (30 March–3 April), after intensive rainfall (27–31 May) and after rainless period (21–24 August). For chemical analyses and statistical tests there were taken into consideration only waters from the springs active in all three measurement

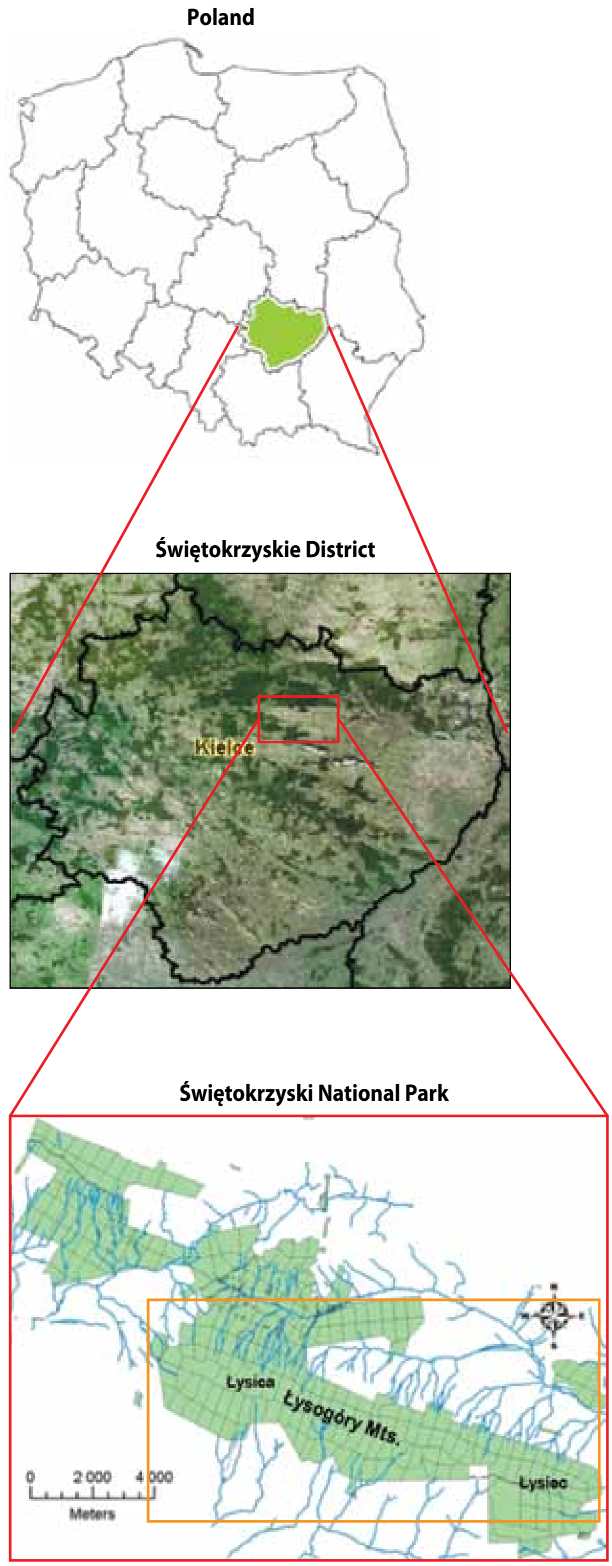

Fig. 1. Location of study area

rounds – 50 points (fig. 2). The water samples collected were analyzed in the chemical laboratory of the Forest Ecology Department, University of Agriculture in Kraków. Sample pH value (pH-meter Eijkelkamp 18.37) and electrolytic conductivity – EC (conductivity meter Eijkelkamp EC 18.34) were measured before filtering. The concentrations of: Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^- and SO_4^{2-} in filtered samples were analyzed with Dionex –320 ion chromatograph.

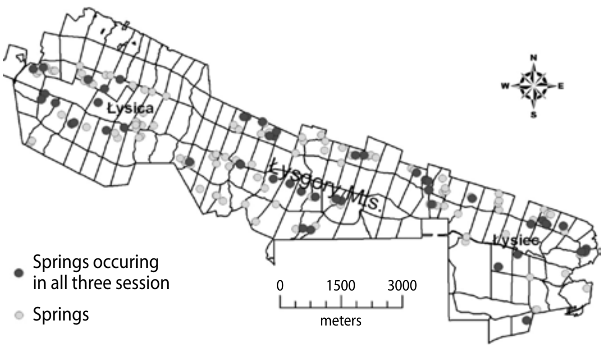

Fig. 2. Location of springs in the Łysogóry Mts. in Świętokrzyski National Park

Water quality was assessed in line with Polish law (Regulation of the Minister of Environment of 23 July 2008 on the criteria and method of assessment of the status of groundwater, Dz.U. 2008 No 143 art. 896).

The results were statistically analyzed using STATISTICA 9.1 software. The tests included calculations of means and standard deviations. Normal distribution of the data was tested with the Shapiro Wilk test. The distribution for each variable was not consistent with normal distribution, thus the Kruskal-Wallis test and Ward's method for hierarchical clustering were used in nonparametric comparisons.

Results and discussion

The classification of spring water quality in line with the Regulation of the Minister of Environment of 23 July 2008 is presented in tab. 1. The quality class I, was indicated only in 6 springs during the period of low water level. In the two other measurement rounds, there were not found springs with the quality equivalent to class I. The main factor causing quality drop was too low pH value in the waters observed. In the first measurement round only 3 springs indicated appropriate pH (pH 6.5–9.5 for I, II and III quality classes, respectively), however higher concentrations of NH_4^+ (max. 0.5 mg/dm^3 for class I, 1 mg/dm^3 for class II and 1.5 for class III) and NO_3^- (max 10 mg/dm^3 for class I and 25 for class II) decreased the quality of spring waters to class II. In the second measurement round carried out after intensive rainfalls, none of the samples indicated appropriate pH value, and additionally the concentration of NH_4^+ and NO_3^- allocated the springs investigated in class II. The best status of waters was observed in the period of low water level, when 6 springs were assigned to class I and 6 springs were assigned to class II. In this measurement round there were recorded higher pH values, however, 38 springs does not comply with these criteria.

The results of ion chromatography showed differences in chemical composition of water, depending on the sampling period. Waters collected from the springs in the third measurement round were characteristic of higher concentrations of Na^+, Mg^{2+}, Ca^{2+}, Cl^-, and definitely higher pH (tab. 2).

Ward's method (cluster analysis) grouped the springs in terms of water physico-chemical properties (fig. 3). However, except for the differences in chemical composition and pH, a group significantly different in terms of natural conditions (soil, trees, location) was not found. The reason for the lack of relationship between the species composition and quality of spring

Tab. 1. Number of the points classified to each water class in each studied session with the pointed out the limited factors in line with the Regulation of the Minister of Environment of 23 July 2008 – standards for groundwater (Dz.U. 2008 No 143 art. 896)

Limiting factor	Snowmelt					Rainfall					Dry period				
	I	II	III	IV	V	I	II	III	IV	V	I	II	III	IV	V
NH_4^+		41	4				48					31	6		
NO_3^-		20					14				6	15			
pH				47					50					38	

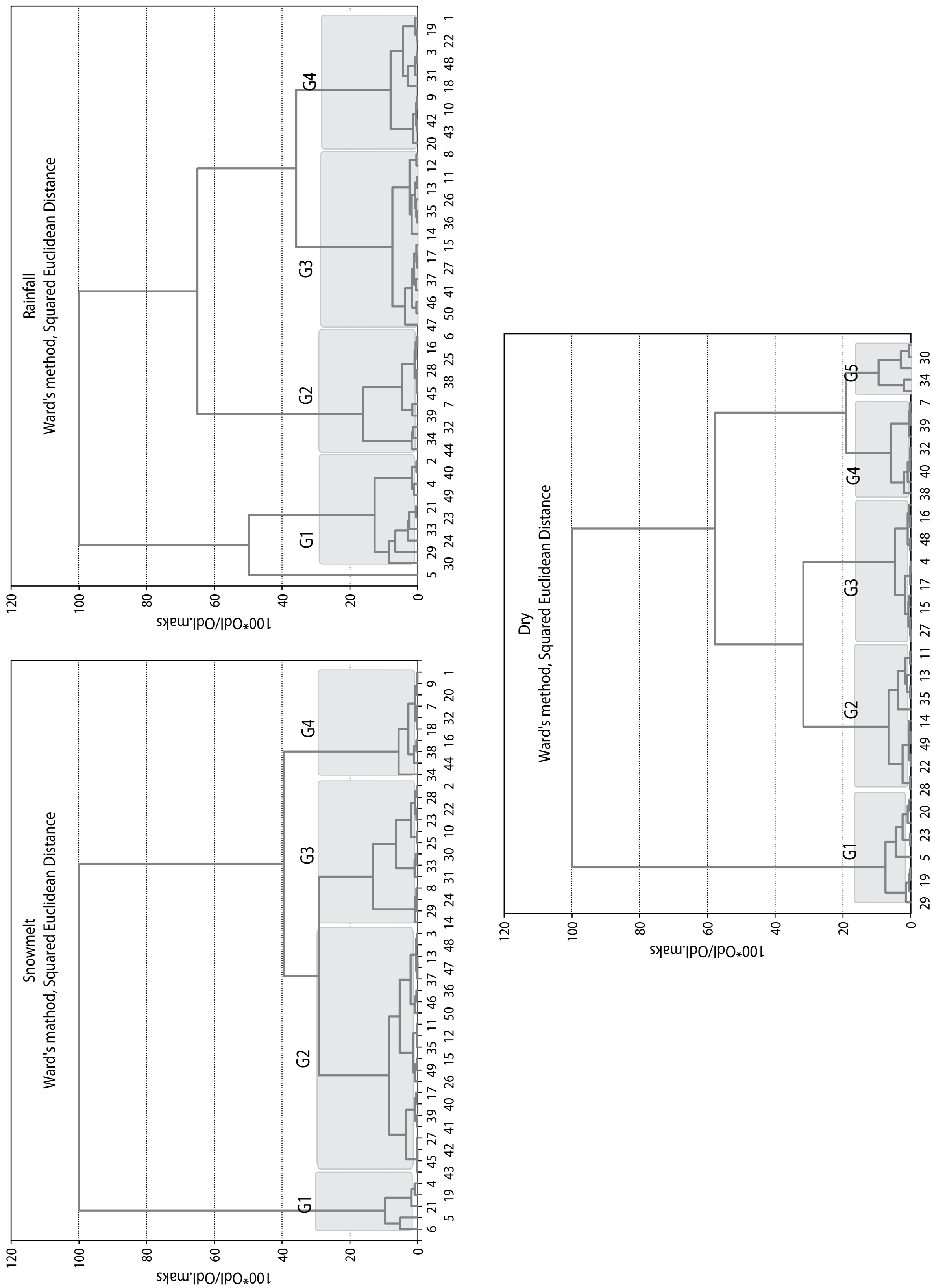

Fig. 3. Dendrograms showing clusters of springs according as chemical water properties in three measurement rounds

Tab. 2. Mean values and standard deviations of factors analyzed (mg/dm^3)

Session		Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	pH
Snowmelt	mean	1.45	0.79	0.72	2.05	7.30	4.62	8.61	33.90	5.03
	st. dev.	0.99	0.19	0.49	1.16	3.22	1.98	4.96	13.43	0.76
Rainfall	mean	1.52	0.69	0.74	2.00	7.08	4.48	7.64	34.99	4.88
	st. dev.	1.24	0.11	0.53	0.95	3.74	1.86	4.86	14.13	0.57
Dry	mean	2.82	0.76	0.98	2.43	8.02	5.58	7.99	24.20	5.67
	st. dev.	1.06	0.22	0.71	0.91	2.64	2.09	5.51	15.39	0.95

waters lies in the fact that the species of trees growing at the outflow of springs are not always representative for the whole area. A broader view on water collection area – the alimentation area (tank maintenance) brings one closer to knowledge on the impact of environmental conditions on the quality of springs.

The Świętokrzyskie Mts. is the area highly elevated over the surrounding region. This increases the intensity of imission and impacts on pedo- and lithosphere of the area even by long-range emitters (> 100 km) (Jóźwiak and Kowalkowski 2003). The latter include the Upper Silesian Industrial Region, Agglomeration of Kraków and Bełchatów Brown Coal Mine. Winds carry high levels of nitrate and sulphate ions which are deposited both in the form of dry deposition and wet acid deposition (Jóźwiak and Kozłowski 2004). The low pH value of precipitation in the Łysogóry Mts. together with further acidifying effects of tree crowns and forest litter affect soils (Kozłowski and Adwent 2011) as well as they impact mountain springs causing changes in water chemical properties.

Spring waters collected in the last round (rainless period) were characteristic of higher pH value as well as concentrations of Na^+, Mg^{2+}, Ca^{2+}, Cl^- (tab. 3). In the rainless period there were observed low water conditions and no effect of precipitation on the spring waters analyzed.. At this point, spring waters are mainly supplied by underground waters (not with rain), which may result in higher concentrations of the ions. The greater impact on chemistry of spring waters might have had local cambrian shale layers, since they are slightly richer in magnesium and sodium than basic rocks that build the main massif (Kowalkowski et al. 2001). Besides, research conducted in the Tatra Mts. (Tatra National Park) showed key effects of the geological structure on spring water chemistry, especially during the period of low water levels (Żelazny et al. 2011). Likewise, the impact of geology on spring water chemical composition was stressed by Michalik et al. (2008).

Tab. 3. Kruskal-Wallis test results for factors analyzed

Factor	Rang sum			p
	snowmelt a	rainfall b	dry period c	
Na^+	2733.5	2793.0	$5798.5^{a.b}$	$p < 0.001$
NH_4^+	$4504.5^{b.c}$	3255.5	3565.0	$p = 0.013$
K^+	3433.5	3487.5	4404.0	$p = 0.043$
Mg^{2+}	3444.0	3448.5	4432.5	$p = 0.032$
Ca^{2+}	3693.5	3347.5	4284.0	$p = 0.093$
Cl^-	3396.0	3146.0	$4783.0^{a.b}$	$p < 0.001$
NO_3^-	4050.5	3528.5	3746.0	$p = 0.483$
SO_4^{2-}	4222.5	4281.5	$2821.0^{a.b}$	$p < 0.001$
pH	3355.5	3078.0	$4891.5^{a.b}$	$p < 0.001$
EC	4180.0	4218.5	$2926.5^{a.b}$	$p < 0.003$

The values in grey cells indicate statistically significant differences.

According to Kowalkowski et al. (2001) in soil environment of the Łysogóry massif, there is no possibility of returning to balanced circulation of ions and even a small influx of acidic components will result in further increasing acidity of ground – and surface water.

Conclusions

1. Spring waters in the Łysogóry Mts. are of poor quality in keeping with Polish Minister of Environment regulations on groundwater. Only a few samples had pH values and the content of NO_3^- and NH_4 suitable for water of good quality.

2. The main impact on the quality of water has a pH value and high concentrations of ion NH_4^+ and NO_3^- due to the geological structure of the Łysogóry massif (mainly acidic quartzite and quartzitic sandstones) and the dry and wet deposition of acidic substances.
3. Higher quality of spring waters was recorded in the period of low water levels – with limited inflow of pollutants from precipitation.
4. Seasonal dynamics of electrolytic conductivity inversely proportional to the pH value was indicated. Minimum conductivities were noted during low massif hydration with maximum pH values observed.
5. Tree species (fir and beech), exposition and soil types within the alimentation area did not influence spring water chemistry.

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