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Effect of Environmental Conditions on Chemical Profile of Stream Water in Sanctuary Forest Area

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Abstract This study reports the evaluation of chemical composition of a Black Vistula and White Vistula streams' waters taking into consideration both geological conditions of the stream's catchment area and different water' level related to seasonal variations in particular catchment ecosystem (high stage: beginning of the vegetation period; medium stage: vegetation period; low stage: final time of vegetation period). The complex data matrix (744 observations), obtained by the determination of major inorganic analytes (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}) in water samples by ion chromatography was treated by linear discriminant analysis and non-parametrical testing. In case of both streams obtained results indicate presence of two discriminant functions (DFs). The data variance explained by DFs is as follows: Black Vistula stream—first DF: 93.5%, second DF: 6.5%; White Vistula stream—first DF: 66.3%, second DF: 33.7%. In case of Black Vistula stream first DF allows distinction of medium, high and low water-stage related samples while second DF between high/low and medium water stage related samples. In case of White Vistula stream first DF allowed to distinguish between medium/high and low water stage related samples while second DF between medium and high water level samples. In case of both streams, the most informative DFs were related to geological conditions of investigated catchments (contents of Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}), while the second to nutrient biocycle (mainly NH_4^+ and NO_3^-) related to slope's exposition and inclination.

Keywords Barania Mountain · Black Vistula and White Vistula streams · Chemical profile · Discriminant analysis · Slope's exhibition and inclination · Surface water

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1 Introduction

Constitution of geological profile, type of rocks and a type of forest humus exert an influence on the chemical profile of forest area's outflow waters. An occurrence of variety of forest sites causes that unequivocal identification and explanation of an impact of a type of forest stand or geological constitution on the quality of outflow waters appears to be a problematic task. It was found, that in the mountain area, a dominant factor responsible for a chemical profile of outflow water may be related to washing out of minerals weathering from the rock foundation. Additionally, a significant role may be played by biological processes which proceed in the soil layer or in stream's waters (Wróbel 1998). A chemical constitution of forest catchment water's outflowing from shallow soil layer strongly depends on a type of soil and geological profile as well as on plants cover, surface configuration and even exhibition of slopes (Małek and Gawęda 2004, 2006a, b; Małek and Krakowian 2007). Among of factors which determine qualitatively and quantitatively the content of inorganic compounds in surface waters, high and low water stage of streams plays also a significant role (Szczęsny and Zięba 2001).

Since 1997 an intensive studies on the mountain forest ecosystem have been conducted by a team of research from the Forest Ecology Department, Agriculture University of Cracow in Bukowiec Forest Subdistrict (Wisła Forest District, Silesian Beskid Mountains; Małek and Gawęda 2004, 2006a, b). In most cases the objective of the studies was focused on assessment of environmental conditions of growth of the Istebna spruce ecotype and identification needs and threats from the point of view of forest sustainability. Quantitative and qualitative analysis of surface water was done so that the final effect of a long term water chemical and physical balance in this area was expected. In general, the waters of Black Vistula and White Vistula streams, which are the beginning of the main river in Poland—Vistula River, differ in their chemical composition from the waters of the Silesian Beskid Mts. (Pawlik-Dobrowolski 1965; Wróbel 1998) and surface waters from the Babia Góra Mt. (Szczęsny and Zięba 2001). Unfortunately, up to now, the chemical composition of stream waters was not evaluated in a complex way, taking into consideration both geological conditions of the stream catchment area and different water level related to seasonal variations in particular catchment ecosystem. This is why, the main hypothesis verified in the present work are:

- an identification and explanation of surface water parameters' fluctuation reasons taking into consideration seasonal changes of water stage is possible;
- the chemical composition of Black Vistula and White Vistula streams differs from each other because of differences related to physico-geological constitution of drainage areas and catchments considering seasonal changes of water stage in both streams.

2 Experimental

2.1 Site Description

The research presented was aimed at investigating the chemistry of surface waters in sections of the White Vistula and Black Vistula (WV and BV, respectively) streams within the "Barania Mt." nature reserve in the Silesian Beskid Mts. Due to the southern dip of the strike of beds of the istebna sandstone, there is a possibility of the outflow of water from the White Vistula catchment and its movement towards the southern part of the slope drained by the Black Vistula Stream. Analysis of stream's network maps as well as site inspection indicate differences in density of the corresponding stream networks and crenologic index value in case of Black Vistula and White Vistula catchments. In general, density of White Vistula stream network was higher in 1960s than in 2004, while opposite tendency was observed for Black Vistula's network density. Comparing to other mountain regions (Tatra Mts.: 5.4 (Pazdro and Kozierski 1990); Skrzyczne Mt. (Silesian Beskid): 3.9 (Małek and Krakowian 2007) the crenologic index for Black Vistula and White Vistula streams is quite high. A comparison of selected parameters for both catchments are depicted in Table 1, while descriptive distribution of the dominant soil types on the investigated catchments and geographical catchments location are presented on Figs. 1 and 2, respectively. Moreover, on Fig. 3 the percentage contribution of slope's exhibition and slope's inclination both for Black Vistula and White Vistula catchments are presented.

2.2 Sampling

Field work was carried out during the vegetation season of 2004. In the first stage the current course of the stream network was established and based on sampling sites were pointed along the main stream. Samples were collected during three measurement campaigns:

- during the high stream's stage: on May 12–13th on the Black Vistula and on May 14–15th on the White Vistula,

Table 1 A comparative juxtaposition of selected parameters of the White Vistula and Black Vistula catchments in 2004 and 1955–1957

Element of comparison		Unit	1955–1957	2004
White Vistula catchment	Length of stream network	km	5.2	4.5
	Density of stream network	km/km^2	5.7	4.9
	Crenologic index	Number of sources per square kilometer	15.3	14.2
Black Vistula catchment	Length of stream network	km	4.1	6.5
	Density of stream network	km/km^2	4.5	5.0
	Crenologic index	Number of sources per square kilometer	5.4	10.1

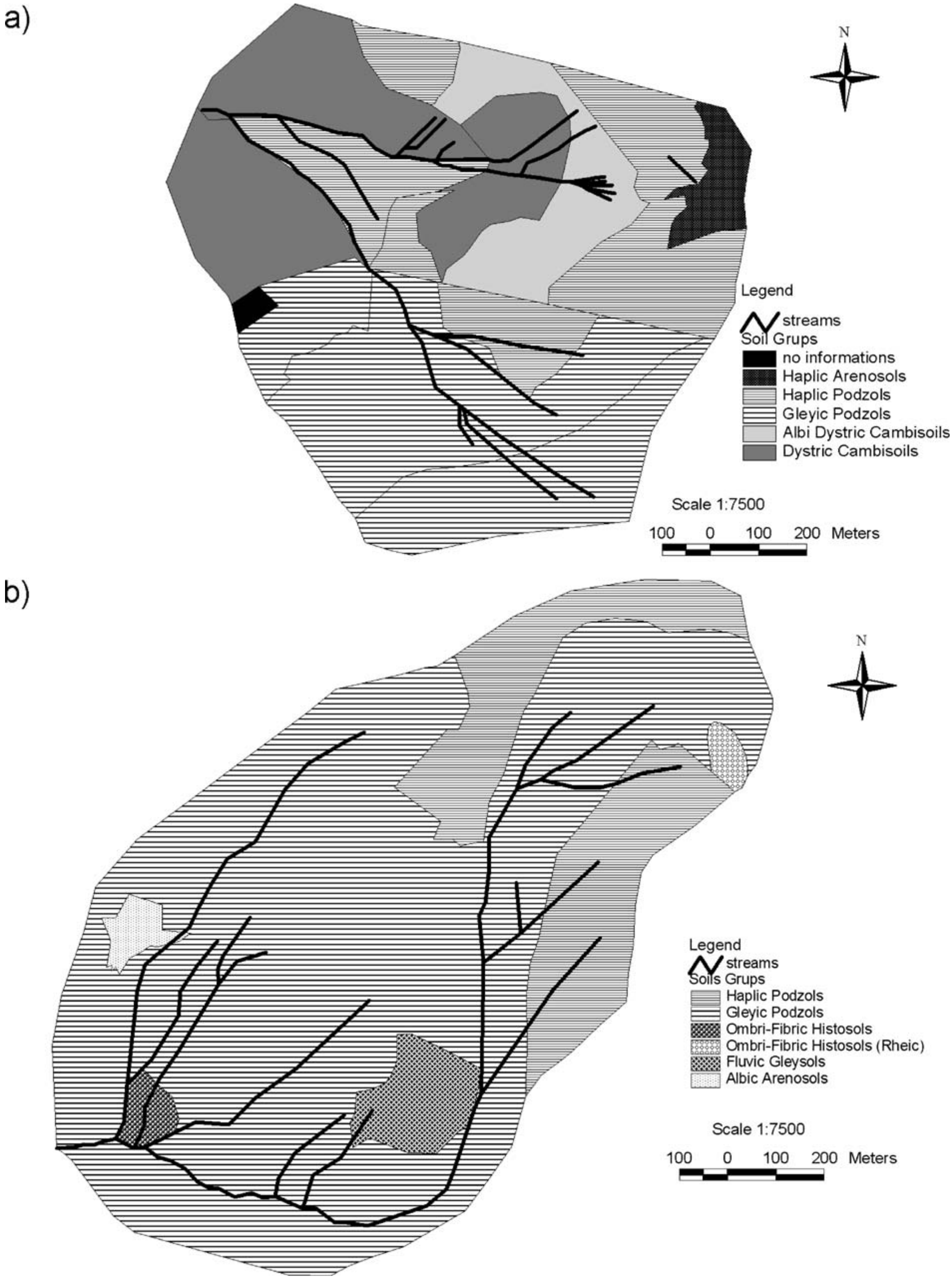
– medium stream's stage: on June 24th on the White Vistula and on June 25th on the Black Vistula,
– low stream's stage: on October 15–16th on the Black Vistula and on October 14–15th on the White Vistula.

2.3 Chemical Analyses

Water samples was analysed using ion chromatography (Dionex-320, Sunnyvale, CA, USA) to determine the concentration of: Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+} according to the current standards PN-ISO 10304-1:1998 and PN-ISO 14911-1:2001. The ion chromatograph was coupled with double piston GP40 IC Pump, CD20 IC Conductivity Detector and Dionex PeakNet (ver 5.11) software. In particular, the anions in the calibration solution and stream water samples were analyzed using analytical column Dionex IonPac AS17 Analytical Column (250×2.0 mm i.d.) with IonPac AS17 Guard Column (50×2.0 mm i.d.) and ASRS® ULTRA Anion Self-Regenerating Suppressor. The mobile phase was a mixture of 3.5 mmol l^{-1} Na_2CO_3 and 1.0 mmol l^{-1} $NaHCO_3$ under flow rate of 0.25 ml min^{-1}. The column temperature was 30°C and the pressure was 6.20 MPa. In both cases (anions and cations) an injection was accomplished by dose loop (15 µl) operating in room temperature. The analysis of cations was carried out using analytical column IonPac CS12A (250×2.0 mm i.d.) with IonPac CG12A Guard Column (50×2.0 mm i.d.) and CSRS® ULTRA Auto Suppressor working in recycle mode. The mobile phase was 18 mM methanosulphonic acid under flow rate of 1.0 ml min^{-1}. The column temperature was 30°C and the pressure was 11.37 MPa. A low-pH acid rain sample from southern Ontario (Canada), RAIN.97 and No 409 served as a certified reference material (CRM) were analyzed as well. A detailed description of the analytical technique, its calibration and validation based on a certified reference material can be found elsewhere (Małek and Astel 2007). The obtained results were consecutively evaluated statistically basing on samples which fulfill the criteria of ionic balance and similar salinity.

2.4 Statistical Analyses

Advanced multivariate statistical approaches contribute to better understanding of the data collected during monitoring episodes for a long period of observation. Careful specification of the objectives of the particular research should be done before selection of suitable data mining technique. In order to find a relatively small number of factors from a data set of many correlated variables or interpret hidden, complex and casually determined relationships between features and objects principal component analysis (PCA) is often applied (Einax et al. 1998, 1997; Simeonov et al. 2002, 2001). On the other hand, when statistical assessment of differences between features' mean values in *a priori* defined groups of objects is a crucial point, analysis of variance (ANOVA) offers many advantages. Keeping in mind what was mentioned above, and due to the specific PCA and ANOVA options discriminant function analysis (DFA) was chosen to identify and explain the reason for chemical indicators fluctuation in stream water samples taking into account the seasonal variability in water level. DFA enables determination of variables responsible for discrimination between two or more naturally occurring groups in the data set (Jordán et al. 1998; Singh et al. 2006). The DFA computed statistics include significance of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◀ **Fig. 1** Soil distribution of the soil on the White Vistula (**a**) and on the Black Vistula (**b**). (Soils according Classification of Polish Forest Soils (2000)

the contribution of each variable to the discrimination between groups whose contributions to the discrimination do not overlap. Moreover, a canonical correlation analysis is performed to determine the successive discriminant functions, while individual discriminate scores can be viewed and plotted. Usually, technique accuracy is assessed by classification matrix, which is a measure of the prediction accuracy of the discriminant function, and its classification scores are calculated with classification functions, determining to which group each most likely belongs. Concerning the contribution of the independent variables to the discrimination of groups, this can be appreciated either by the assay of the classes homogeneity using statistic F like in the case of ANOVA/MANOVA method, either by using Wilks' lambda for each variable. Wilks' lambda is the standard statistic used to express the significance of the overall discriminatory power of the variables in the model. The value 1.0 indicates no discriminatory power, whereas 0 indicates a perfect discriminatory power. The partial Wilks' lambda describes the unique contribution of each variable to the discriminatory power of the model. The closer the partial lambda to 0, the better the discriminatory force of the

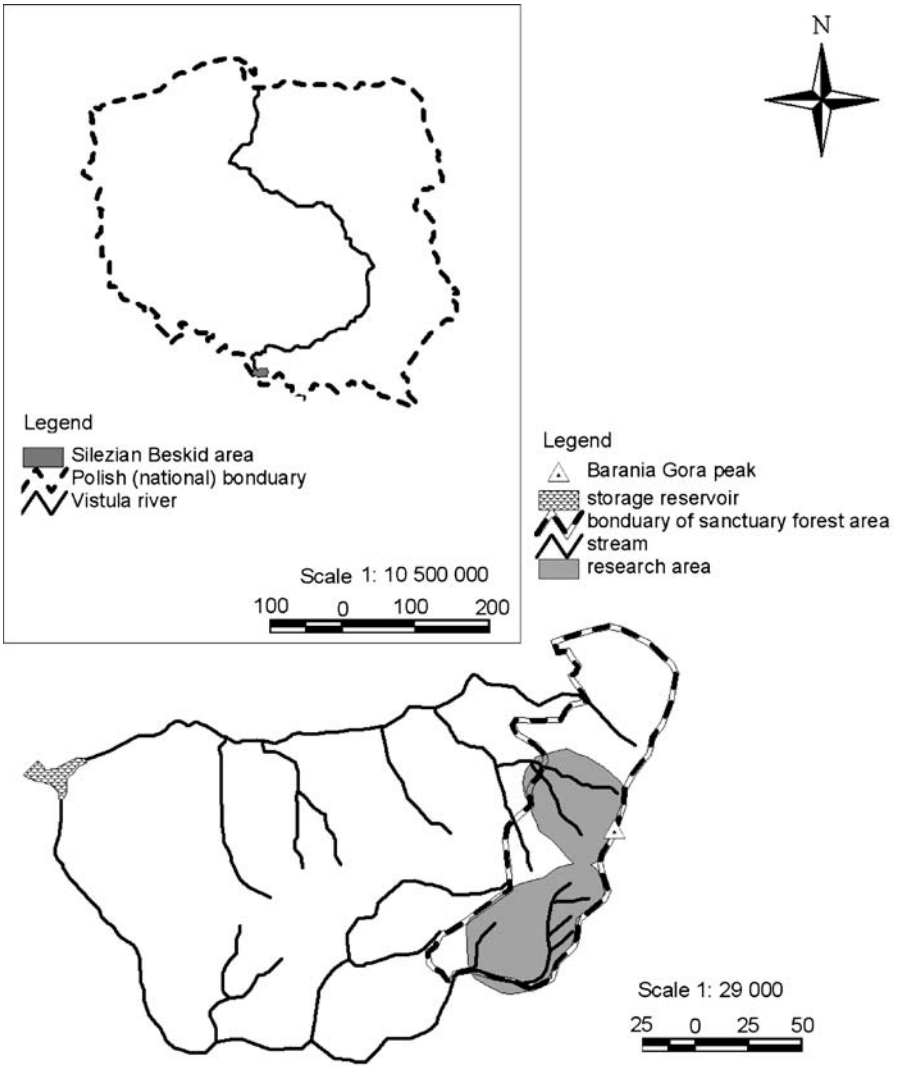

Fig. 2 Location of investigated Black Vistula and White Vistula research catchments

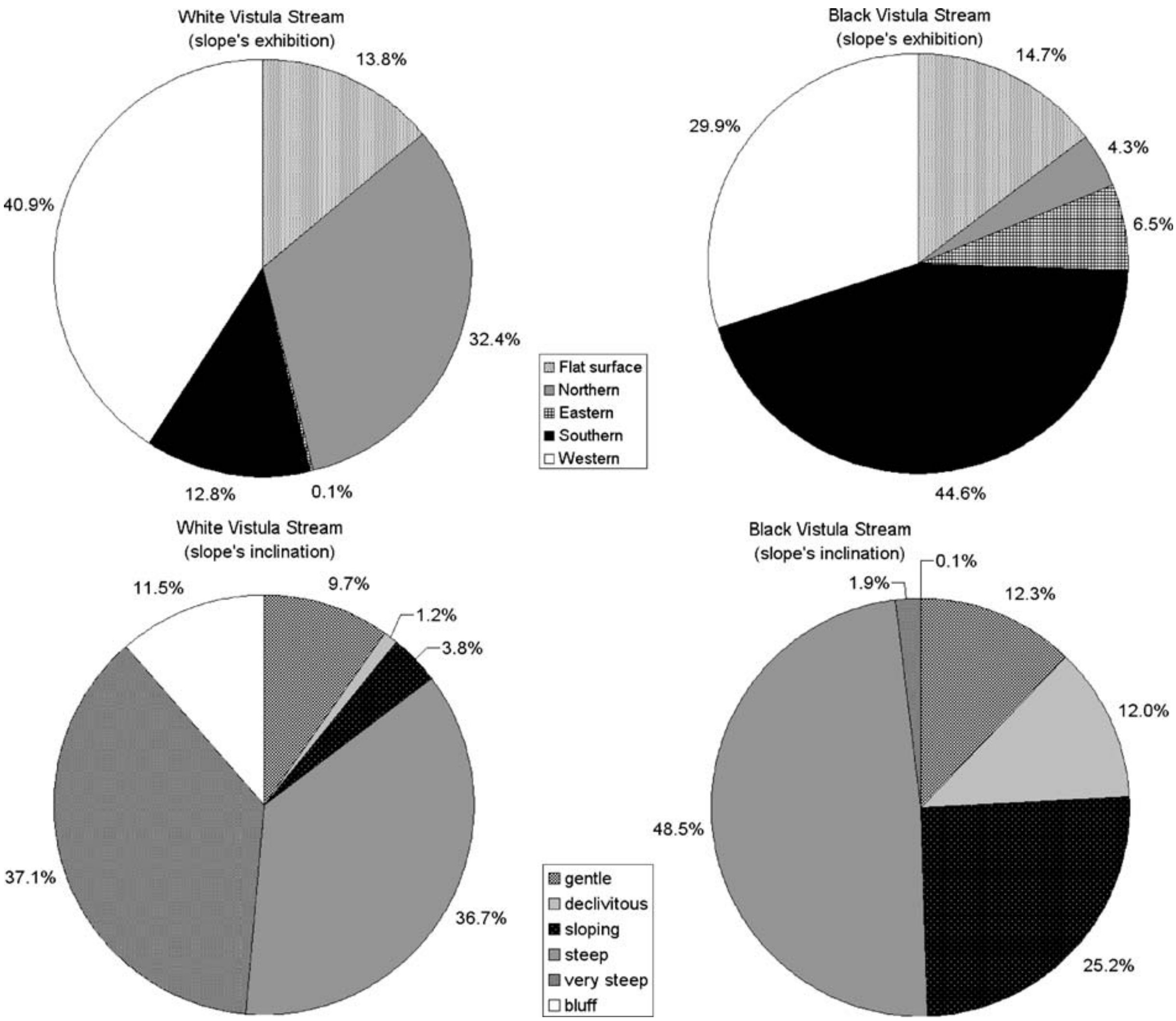

Fig. 3 Percentage contribution of slope's exhibition and inclination for Black Vistula and White Vistula catchments

variable. In addition, the tolerance value gives information to the redundancy of the respective variable in the model, and is computed as 1 minus R-squares of the respective variable, with all other variables included in the model. Put in other words, it is the proportion of the variance contributed by respective variable. If variable is completely redundant, the squared tolerance value approaches zero. This kind of information can be obtained from value of the discriminant coefficients associated to the descriptive variables x_i, and also from the correlation coefficients between each variable x_i and the vector score. The higher the discriminant coefficient (absolute value) and the closer the correlation coefficient to one respectively, the more the variable important for the samples separation in defined groups. Also, the standardized discriminant coefficients, like beta weights in regression, are used to asses the relative classifying importance of the independent variables. DFA was widely described before and this is why, the readers is referred to the referenced literature (Manly 1986; Massart et al. 1980; Brereton 1990; Einax et al. 1997; Scarponi et al. 1982; Diáz-Flores et al. 2004; Mikkonen et al. 2006). Keeping in mind this theoretical background, it could be concluded that DFA enables, comparable to PCA, compression of a data set dimensionality in the features space and attribution of scientific explanation to the identified

DFs. On the other hand, comparable to ANOVA, it enables statistical assessment of contribution of the independent variables to the discrimination of *a priori* defined groups. DFA partially covers advantages of the two independent techniques like PCA and ANOVA, and that is why, DFA was chosen as the most suitable interpretation tool.

Second major hypothesis, which assumes that Black Vistula and White Vistula stream waters differ because of various geological catchment condition, considering the seasonal changes in water's stage in both streams (high stage: beginning of the vegetation period; medium stage: vegetation period; low stage: final time of vegetation period) were tested by applying non-parametric *U* Mann–Whitney test.

Throughout the study the commercial statistics software packages SPSS 16.0 Evaluation and Statistica 8.0 (StatSoft, Inc.) running on Windows 2000/XP platform were used for calculation and visualization purposes.

3 Results and Discussion

Descriptive statistics (mean, minimum, maximum and standard deviation) based on contents of inorganic analytes in stream water samples collected at Black Vistula and White Vistula research catchments are depicted in Table 2.

Forward stepwise discriminant function analysis based on sequential Wilk's Lambda was performed on the raw data set. DFA was applied to determine variables, which allow to distinguish possible groups related to water stage in the stream (high, medium or low) individually for Black Vistula and White Vistula streams. For both of them, two sets of discriminant functions (DFs) were obtained. The summary of the stepwise analysis for Black Vistula (λ=0.1740, F=14.72, p<0.05) as well as for White Vistula (λ=0.11563, F=16.76, p<0.05) depicted in Table 3 shows the variables retained in the model. The statistics which are also depicted in Table 3 illustrate variable's contribution.

Table 2 Descriptive statistics of determination of Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-} (mg dm^{-3}) in stream water samples collected at Black Vistula and White Vistula research catchments divided in respect to water stage

Stream	Water stage	N	Statistics	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
Black Vistula	High	16	Mean	0.55	0.47	0.35	0.36	1.03	0.56	1.76	7.00
			Min	0.331	0.147	0.171	0.109	0.507	0.375	0.409	4.116
			Max	0.82	0.98	0.49	0.84	2.38	0.71	3.62	9.56
			SD	0.14	0.23	0.08	0.24	0.61	0.09	0.86	1.76
	Medium	15	Mean	1.00	0.29	0.37	0.57	2.22	1.27	0.58	8.11
			Min	0.440	0.002	0.220	0.227	0.862	0.907	0.158	5.410
			Max	2.03	1.31	0.66	1.69	5.44	1.56	1.21	11.04
			SD	0.43	0.44	0.13	0.44	1.19	0.20	0.38	1.86
	Low	14	Mean	2.12	0.56	0.55	1.35	3.55	1.92	0.67	9.20
			Min	1.144	0.002	0.220	0.353	1.572	1.652	0.198	4.981
			Max	4.01	2.04	1.13	2.94	6.70	2.40	1.45	12.37
			SD	0.71	0.72	0.25	0.66	1.30	0.21	0.42	2.25
White Vistula	High	17	Mean	0.87	0.47	0.52	1.17	6.05	1.83	1.91	11.12
			Min	0.322	0.183	0.218	0.376	0.929	1.299	0.563	6.846
			Max	1.33	0.98	0.85	1.81	11.35	2.40	3.22	16.42
			SD	0.30	0.25	0.17	0.45	3.49	0.26	0.83	2.23
	Medium	18	Mean	1.57	0.11	0.64	1.45	7.96	1.48	1.78	13.09
			Min	0.538	0.002	0.003	0.523	1.871	1.221	0.585	8.785
			Max	2.45	0.86	1.14	2.70	14.55	1.81	4.06	19.40
			SD	0.54	0.23	0.27	0.64	3.71	0.15	0.94	2.67
	Low	13	Mean	2.60	0.76	1.05	2.77	11.71	2.01	1.98	16.37
			Min	0.694	0.002	0.528	1.399	3.944	1.689	1.294	12.379
			Max	4.50	2.69	1.50	4.83	20.54	2.48	2.72	22.50
			SD	1.24	0.77	0.32	1.08	6.58	0.23	0.45	2.49

Table 3 Variables retained in the model (the most discriminant variables) for Black Vistula and White Vistula streams

	Wilk's Lambda	partial	*F*-remove	*p*-level	Tolerance (R^2)	$1-R^2$
Black Vistula stream						
Cl^-	0.074	0.235	58.671	0.0000	0.756	0.244
NO_3^-	0.025	0.692	8.021	0.0013	0.513	0.487
Na^+	0.025	0.694	7.925	0.0014	0.313	0.687
Ca^{2+}	0.029	0.601	11.934	0.0001	0.074	0.926
Mg^{2+}	0.029	0.607	11.637	0.0001	0.053	0.947
K^+	0.026	0.672	8.795	0.0008	0.226	0.774
SO_4^{2-}	0.020	0.850	3.165	0.0542	0.449	0.551
White Vistula stream						
Cl^-	0.181	0.638	10.799	0.00019	0.650	0.350
Na^+	0.144	0.802	4.680	0.01524	0.266	0.734
SO_4^{2-}	0.164	0.706	7.930	0.00132	0.464	0.536
Mg^{2+}	0.147	0.786	5.165	0.01037	0.165	0.835
NH_4^+	0.121	0.954	0.916	0.40883	0.552	0.448
Ca^{2+}	0.157	0.735	6.857	0.00287	0.230	0.770
NO_3^-	0.142	0.814	4.353	0.01986	0.465	0.535
K^+	0.124	0.929	1.449	0.24746	0.329	0.671

Decreasing variables contribution to the samples separation for Black Vistula stream is given by following sequence: $Cl^- > Ca^{2+} > Mg^{2+} > K^+ > Na^+ > SO_4^{2-}$. The value of tolerance (R^2) and $1-R^2$ respectively delivers information of the correlation of the respective variable with all other variables included in the model. One can observe that the most redundant variables appear to be Cl^-, NO_3^- and SO_4^{2-}, while the most informative variables seem to be Ca^{2+} and Mg^{2+}. Similarly to Black Vistula, for White Vistula stream the greatest variables contribution is presented by following sequence: $Cl^- > SO_4^{2-} > Ca^{2+} > Mg^{2+} > NO^{3-} > K^+ > NH_4^+$. To the group of the most redundant variables Cl^- (R^2=0.650), NH_4^+ (R^2=0.552) and SO_4^{2-} (R^2=0.464) and NO_3^- (R^2=0.465) were included.

The results concerning the standardized canonical discriminant functions (DFs) coefficients for investigated streams are depicted in Table 4, while the structure matrix is presented in Table 5 (variables ordered by absolute size of correlation within function).

For Black Vistula stream first DF is related to Cl^-, Na^+ and Ca^{2+}, characterized by eigenvalue 21.874, canonical correlation equal to 0.978 and variance explanation of 93.5%. Second DF is characterized by eigenvalue 1.513, canonical correlation equal to 0.776 and it explains 6.5% of the total variance being related to NO_3^-, Mg^{2+}, K^+ and NH_4^+. First DF allows distinction for medium, high and low water stage related samples

Table 4 The standardized canonical discriminant function coefficients for Black Vistula and White Vistula streams's discriminant analysis

	DF1	DF2
Black Vistula stream		
Cl^-	1.020	0.163
NO_3^-	−0.465	0.809
Na^+	0.821	0.742
Ca^{2+}	−0.858	−2.791
Mg^{2+}	1.331	3.097
K^+	−0.894	−1.070
SO_4^{2-}	−0.114	−0.730
Eigenvalue	21.874	1.513
Cumulative proportion	0.935	1.000
White Vistula stream		
Cl^-	0.361	−0.896
Na^+	0.501	0.988
SO_4^{2-}	0.454	0.918
Mg^{2+}	0.732	−1.256
NH_4^+	0.335	0.053
Ca^{2+}	−1.255	−0.122
NO_3^-	−0.732	0.136
K^+	0.476	0.296
Eigenvalue	2.667	1.358
Cumulative proportion	0.663	1.000

DF1 First discriminant function, *DF2* second discriminant function

Table 5 Structure matrix for Black Vistula and White Vistula streams

	Function	
	DF1	DF2
Black Vistula stream		
Cl^-	0.707[b]	−0.130
Na^+	0.298[b]	0.251
Ca^{2+}	0.215[b]	0.007
SO_4^{2-}	0.101[b]	−0.011
NO_3^-	−0.164	0.432[b]
Mg^{2+}	0.190	0.225[b]
K^+	0.111	0.186[b]
NH_4^+ [a]	−0.074	0.180[b]
White Vistula stream		
Mg^{2+}	0.559[b]	0.125
K^+	0.525[b]	0.160
Na^+	0.519[b]	0.338
SO_4^{2-}	0.485[b]	0.285
Ca^{2+}	0.289[b]	0.148
Cl^-	0.444	−0.622[b]
NH_4^+	0.292	−0.307[b]
NO_3^-	0.048	−0.065[b]

[a] This variable not used in the analysis.

[b] Largest absolute correlation between each variable and any discriminant function

while second DF between high/low and medium water stage-related samples.

For White Vistula stream first DF is related to Mg^{2+}, K^+, Na^+, SO_4^{2-} and Ca^{2+}, characterized by eigenvalue 2.667, canonical correlation equal to 0.853 and it explains 66.3% of the total variance. Second DF is characterized by eigenvalue 1.358, canonical correlation equal to 0.59 and it explains 33.7% of the total variance being related to Cl^-, NH_4^+ and NO_3^-. First DF allowed to distinguish between medium/high and low water level samples while second DF between medium and high water level samples.

In the final step of DFA the classification rules were tested basing on obtained DFs. In case of Black Vistula excellent separation of samples (subjects) in a good agreement with their origin and nature was obtained. A complete set of objects (100%) related to various water's stage were classified correctly. For White Vistula the classification correspondence was slightly less effective only in case of low water stage. For low water stage-related samples 84% (11) samples were classified correctly, while two samples were erroneously included to the group characterized by high water stage. In general, DFs indicate a high efficiency in classification process connected with investigation of statistical significantly variables responsible for differences in chemical profile of samples obtained for various water stages. The statement is well supported by the two-dimensional scatterplots using the discriminant functions of the samples along DF1 and DF2 as can be seen for Black Vistula and White Vistula streams on Figs. 4 and 5, respectively.

As was mentioned above, for Black Vistula catchment, first DF allows efficiently distinction water samples basing on contents of Cl^-, Na^+ and Ca^{2+} for medium, high and low water stage. Together with decreasing water stage, concentration of Cl^-, Na^+ and Ca^{2+} increases because these ions are easy leached from the lower istebna sandystone and soils formed on this bedrock (Maciaszek and Zwydak 1998). Dynamics of calcium elution processes from the Black Vistula research catchment is under high interest due to general, low content of Ca^{2+} in investigated part of the Western Carpathians (Wróbel 1998). Second DF allows distinction between medium stage-related samples (collected in the middle of vegetation period) and low/high stage-related samples basing on contents of NO_3^-, Mg^{2+}, K^+ and NH_4^+. In general, increased content of NO_3^-, Mg^{2+}, K^+ and NH_4^+ was determined during high and low water level conditions in Black Vistula stream. High water level corresponds to preliminary stage of the vegetation period, while low corresponds to final one. Such observation is in agreement with nitrogen changes cycle within the year in surface water (Dojlido 1995) and data published before by Szczęsny and Zięba (2001). They determined higher concentrations of nitrates in surface water samples during the spring-time thawing, while increasing concentration of magnesium and calcium in autumn. Not only those anions and cations are leached in the beginning and at the end of the vegetation period but also Cl^-, Na^+, K^+ and NH_4^+ which is the evidence of the effect of Norway spruce monoculture (Małek 2004; Małek et al. 2005; Małek and Astel 2007). Contrariwise, in middle of vegetation period the leaching of NO_3^- Mg^{2+}, K^+, and NH_4^+ can be limited due to increasing demand related to the photosynthesis activity of the forest ecosystems (Małek 2004; Małek and Astel 2007). Changes in dynamics of NO_3^-, Mg^{2+}, K^+ and NH_4^+ in surface waters of Black Vistula catchment may be also related to exhibition of slopes. In case of

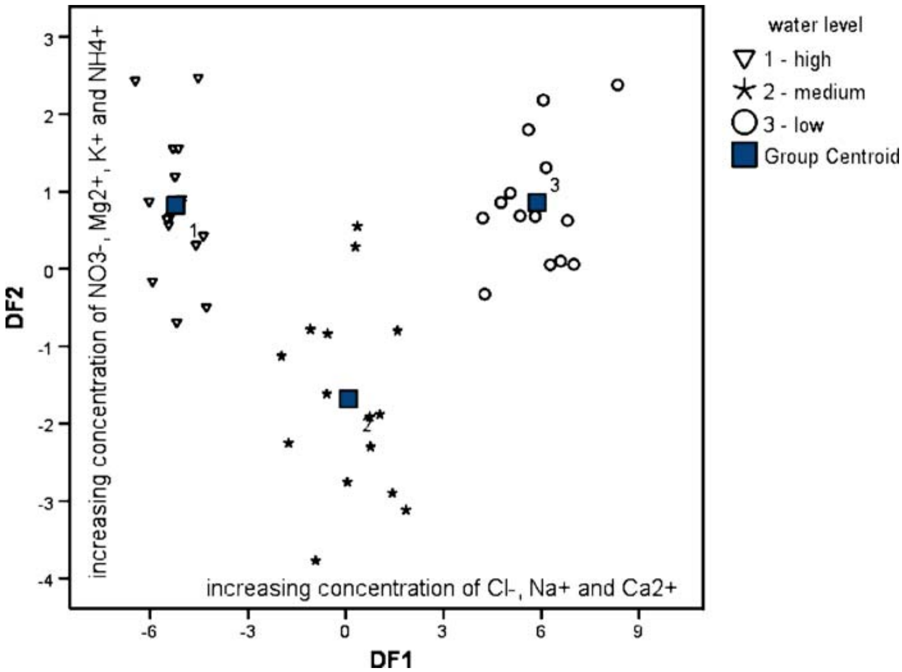

Fig. 4 Scatterplot of canonical scores on the plan described by DF1 and DF2 for Black Vistula stream

investigated catchment southern (44.6%) and western (29.9%) exhibition prevails. South-western exhibition may cause an accelerated snow cover decay as well as higher insolation and temperature's gradient during vegetation period. This is why the most intensive photosynthesis activity may occur in the middle of vegetation period and be also prolonged to the final one. Additionally, such conditions may intensify decomposition of organic matter and increase release of these analytes in the final stage of vegetation period.

For White Vistula catchment, DF1 allows distinction of water samples basing on the content of Mg^{2+}, K^{+}, Na^{+}, SO_4^{2-} and Ca^{2+} for low and medium/high water stage. Similar to Black Vistula, together with decreasing water stage, concentration of mineral

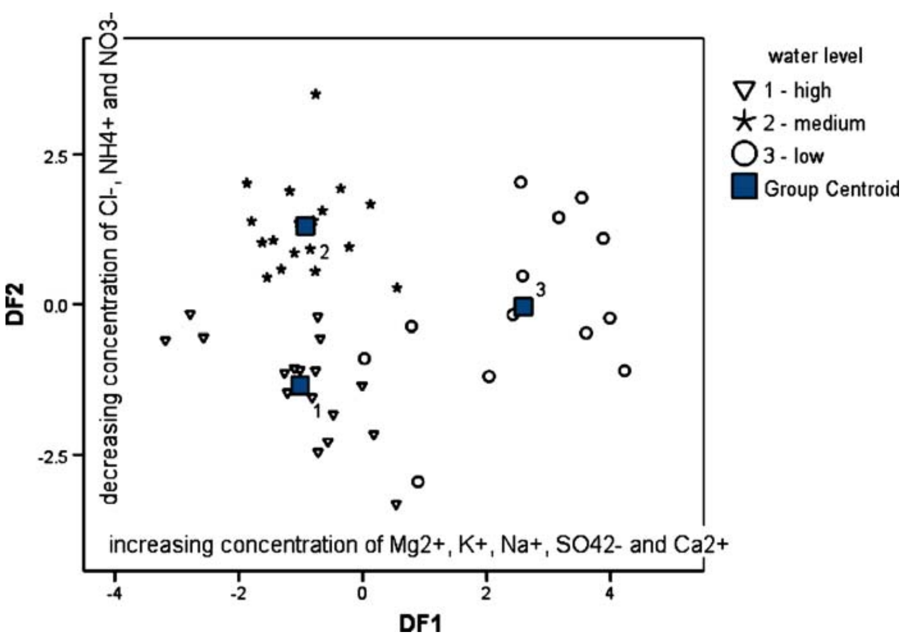

Fig. 5 Scatterplot of canonical scores on the plan described by DF1 and DF2 for White Vistula stream

analytes increases. However, due to more diversified kind of soils (Haplic Podzols, Gleyic Podzols, Dystric Cambisoils, Haplic Arenosols, Albi Dystric Cambisoils) leaching processes can be intensified (Fig. 2). Second DF allows distinction between medium stage-related samples and high stage-related samples (collected in the preliminary stage of the vegetation period). Decreased contents of NO_3^-, Cl^- and NH_4^+ was determined mainly during medium water's stage conditions in White Vistula stream. Limited leaching of nitrates and ammonium for middle vegetation period is in agreement with annual nitrogen changes cycle in surface water (Dojlido 1995), but can be related also in this case, to north-west exhibition of slopes. For White Vistula catchment western (40.9%) and northern (32.4%) exhibition prevails. Contrariwise to Black Vistula, north-western exhibition may cause delayed snow cover decay as well as lower insolation and temperature's gradient during vegetation period. This is why the most intensive photosynthetic activity may be limited to middle stage of vegetation period. Additionally, decomposition of organic matter may be inhibited because of mentioned above conditions and this can influence on nitrification and denitrification processes as well. It has to be mentioned that in both cases the first, most informative DFs, were related to geological conditions of investigated catchments, while the second ones to forest ecosystems needs.

In the consecutive step, the differences between chemical composition of Black Vistula and White Vistula streams, taking into consideration the seasonal changes in water stage at both streams (high stage: beginning of the vegetation period; medium stage: vegetation period; low stage: final time of vegetation period), were assessed by applying non-parametric *U* Mann–Whitney test. At a significance level $\alpha=0.05$ the difference between Black Vistula and White Vistula stream at high water stage was statistically significant for: Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}. The division related to the type of the catchment at high stage turned out to be insignificant for NH_4^+ and NO_3^-. At a significance level $\alpha=0.05$ the difference between Black Vistula and White Vistula stream at medium water stage was statistically significant for: Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-} and NO_3^- while at low water stage was statistically significant for: K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-} and NO_3^-. The division related to the type of the catchment at low water stage turned out to be insignificant for Na^+, NH_4^+ and Cl^-. On Fig. 6 the differences between chemical composition of Black Vistula and White Vistula streams, taking into consideration the

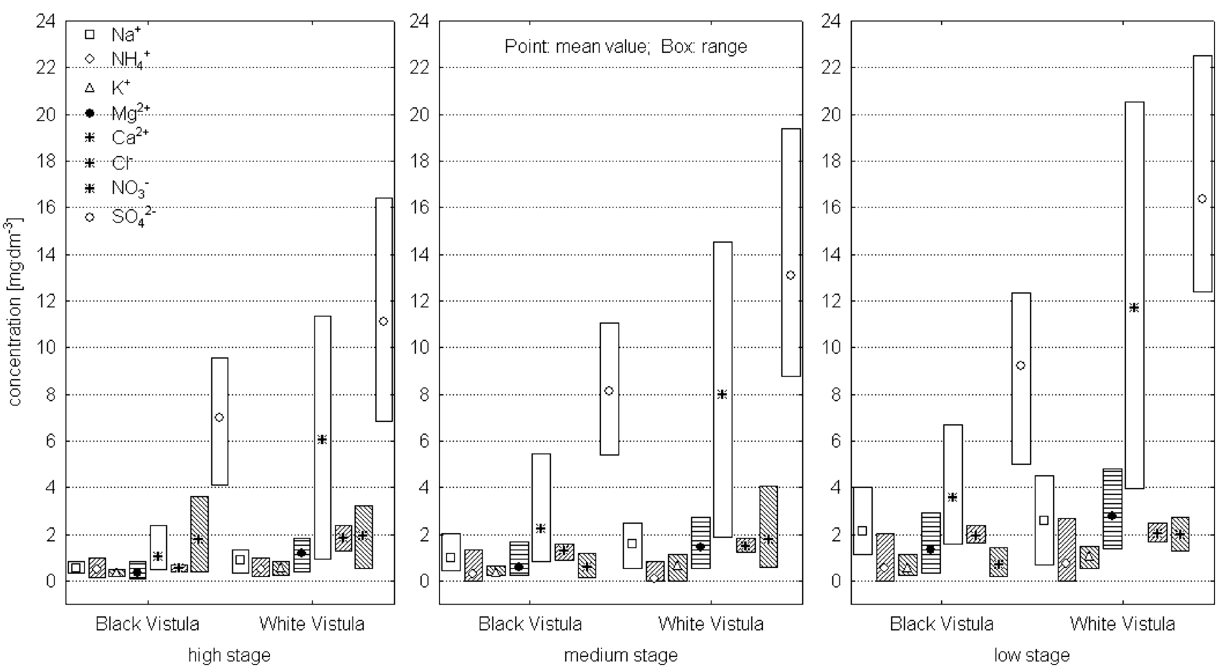

Fig. 6 Differences in Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-} ions concentration in Black Vistula and White Vistula streams, taking into consideration the seasonal changes in water's stage

seasonal changes in water stage at both streams are presented in the form of box diagram.

Mentioned above, the most significant differences in the chemical composition of stream water reflect to environmental conditions like: slope's exhibition and inclination, geology and soil composition in the catchment. White Vistula catchment is mainly composed of high godula sandystone and lower istebna sandystone with rich soils like Dystric Cambisoils and Albi Dystric Cambisoils (Fig. 1) with forest type Dentario-Glandulosae-Fagetum on them in lower part of the catchment. Therefore, water passing through this kind of soils and stands becomes enriched in macro-elements like Na^+, K^+, Ca^{2+} and Mg^{2+}. Whereas the Black Vistula catchment is composed mainly of lower istebna sandystone with silica conglomerates and soils like Haplic Podzols and Gleyic Podzols (Fig. 1) with forest type Abietii Piceetum-montanum and Plagiothecio-Picctum tatricum (Maciaszek and Zwydak 1998; Wróbel 1998). Among investigated ions the highest differences in the average concentration were observed for calcium, magnesium and sulphates. For Black Vistula stream, similar to results of investigations carried out in the Western Carpathians area presented before by Wróbel (1998), in each water stage relatively low concentration of Ca^{2+} was found. Determined Ca^{2+} concentration was even lower comparing to results presented by Małek and Gawęda (2006a, b) on Dupniański Stream catchment (Ca^{2+}=11.6 mg dm^{-3}). Contrariwise, in White Vistula stream Ca^{2+} concentration was in an average four times higher than in Black Vistula stream. It seems that calcium content is one of the major factors which discriminate both streams. White Vistula stream water is enriched with Mg^{2+} (two to three times) comparing to Black Vistula stream water. Determined Mg^{2+} concentration in Black Vistula stream was lower comparing to Mg^{2+} concentration determined in Dupniański Stream (Ca^{2+}=2.61 mg dm^{-3}; Małek and Gawęda 2006a, b). The content of SO_4^{2-} in Black Vistula stream varies in the range of 4.116 and 12.37 mg dm^{-3}, with average for high, medium and low water stage equal to: 7.0, 8.11 and 9.20 mg dm^{-3}, respectively. In general, SO_4^{2-} content in White Vistula stream was almost two times higher during corresponding water stages. For both streams during the high and medium water stage the concentration of SO_4^{2-} was lower than an average for polish surface waters (SO_4^{2-}=10.0−80.0 mg dm^{-3}; Dojlido 1995). The higher content of SO_4^{2-}, Na^+, K^+, Ca^{2+} and Mg^{2+} in the water of White Vistula stream can also be a consequence of constant inflow of inter-layer waters from steep and very steep slopes, which prevail on this catchment (Fig. 3). Intensified infiltration may be a reason of occurrence of bog-springs. Such phenomenon connected with favorable geological structure causes better trophic condition close to outflow of the White Vistula catchment.

Slope's exhibition applies mainly to nitrates concentration and seems to be a significant factor affecting the differences in the chemical composition of stream water related to forest stands needs. Statistically significant differences in NO_3^- concentration between Black Vistula and White Vistula streams water were noticed only for medium and low water stage. During medium and low water stage condition in Black Vistula stream, concentration of NO_3^- was around three times lower than in White Vistula stream. As was mentioned above such phenomenon may be related to slope's exhibition. South-western prevailed exhibition in Black Vistula catchment may cause an accelerated snow cover decay as well as higher insolation and temperature's gradient during vegetation period. Whereas, north-western prevailed exhibition in White Vistula catchment may cause delayed snow cover decay as well as lower insolation and temperature's gradient during vegetation period. In general, at first catchment the most intensive photosynthesis activity may occur in the middle of vegetation period and be also prolonged to the final one. The length of vegetation period can impact the nitrification and denitrification processes.

4 Conclusion

Basing on both chemical analysis of water streams and geological condition in investigated areas it is possible to identify and explain differences between two forest catchments (Black Vistula and White Vistula streams) by linear discriminant function analysis, taking into consideration the seasonal change of the stream water level. In case of both streams, the most impacting factor is related to geological conditions (contents of Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}), while the second one to nutrient biocycle (mainly NH_4^+ and NO_3^-) related to slope's exposition and inclination. Because of more diversified soil composition (high godula sandystone and lower istebna sandystone) in White Vistula stream leaching of macro-elements like Na^+, K^+, Ca^{2+} and Mg^{2+} is intensified especially in the beginning of the vegetation period. The details of nutrient biocycle at both catchments are limited by snow cover decay, insolation and temperature's gradient during vegetation period which directly arises from slope's exposition and inclination.

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