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Applicability of Chemometric Methods for Estimating the Influence of Environmental Factors on the Water Quality on the Example of Some Lakes in Wolin National Park

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1. Introduction

Water, the one of the main elements of the natural environment, mainly surface water, is exposed to numerous contaminating. These pollution has become a growing threat to human society and natural ecosystems in the recent decades (Garizi et al. 2011, Dray & Josse 2015). Frequently, although not the most important, source of pollution of natural waters are thermal inflows and precipitations (e.g. Kulikowska-Karpińska and Kłusewicz 2009, Poleszczuk et al. 2012, Sorokovikova et al. 2015). Also occurring climate changes have certain effects and interactions. Therefore, vulnerability assessment is one of the key tools used to gain knowledge about the degree of impact of threats on aquatic ecosystems and how aquatic ecosystems deal with this threat (e.g. Zurovec et al 2017).

Understanding the phenomena (e.g. Bailey 2012) occurring in natural waters is based on the correct interpretation of analytical data obtained during the experiments. Therefore, ecologists (e.g. Dray & Josse 2015) usually collected and stored various data from multiple sampling sites. Additional information can be recorded to investigate their impact on the observed ecosystems (Dray & Josse 2015).

Multivariete stastistical analysis methods are part of chemometric procedures are methods of extracting information from chemical and biological systems by data-driven means (Wold 1995). They can summarize the main structures of a data containing the measurements of several quantitative variables. Newly detected structures can provide information previously hidden and invisible that can used to assess the quality of water through the standard procedure of prediction methodology such as neural network or fuzzy logic tool boxes (e.g. Sahooa et al. 2015).

This paper attempts to use chemometric methods (PCA, DA, CA) on data collected from the lakes Czajcze and Domysłowskie (Wolin National Park, NW Poland) in vegetation season in 2000-2013 and an attempt was made to assess the impact of selected environmental factors (water level of lakes and monthly sum of precipitation) on some hydrochemical parameters of the lakes.

2. Characteristic of investigated area

Czajcze and Domysłowskie Lake (Fig. 1) are located on the Wolin island, in the territory of Wolin National Park (WNP) in the Warnowo Protection Zone.

Both lakes belong to the type of flow lakes - they are directly fed by the waters of the Lewinska Struga stream. Along the runoff of the stream through the WNP territories, waters go by lakes: Rabiąż, Czajcze, and Domysłowskie. After passing through WPN protected areas runoff goes by further through other lakes of the Warnowsko-Kołczewski district to the Kamieński Lagoon (Wawrzyniak et al. 2012). Basic morphometry of studied lakes are presented in Table 1 after Jańczak (Jańczak 1997).

Table 1. Morphometric characteristic of studied lakes in Wolin National Park, after Jańczak (1997)

Lake Parameters	Lake	
	Czajcze	Domysłowskie
Latitude	$53^0 56.5'$	$53^0 56.4'$
Longitude	$14^0 34.0'$	$14^0 34.6'$
Surface (ha)	71.5	43.5
Max. Length (m)	1630	1140
Max. Width (m)	640	550
Length of shore-line (m)	4970	3000
Development of shore-line (m above sea leavel)	1.66	1.28
Altitude	1.3	1.3
Average depth (m)	2.9	2.1
Max. Depth (m)	4.6	3.1
Volume (thousand m3)	2073.5	913.5
Uncover factor	24.7	20.7

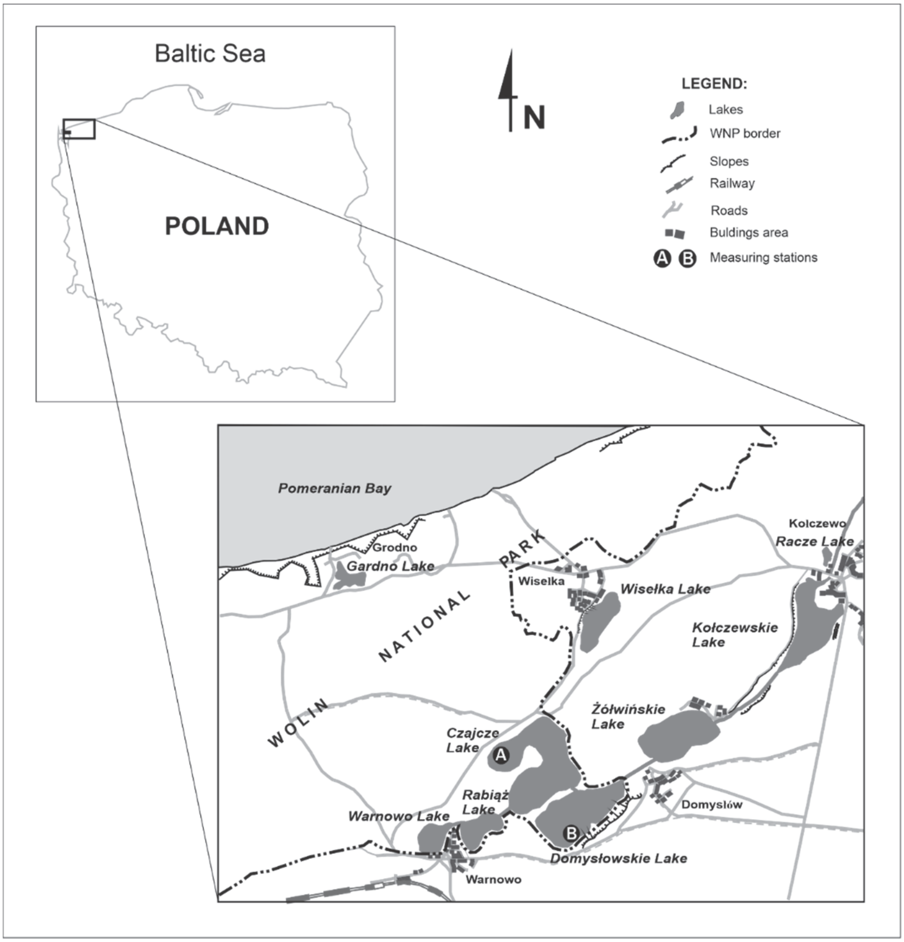


Fig. 1. Czajcze and Domysłowskie Lakes in Wolin National Park

3. Material and methods

In the period of March to October in years 2000-2013 water samples were collected from the surface layer (ca. 25 cm below the water surface) of Lakes Czajcze and Domysłowskie (Fig. 2) (APHA 1998) a frequency of once a month.

Nine selected physicochemical water quality indices were determined i.e. water temperature, pH, concentration of dissolved oxygen (DO), water saturation (WS), five day biochemical oxygen demand (BOD), chemical oxygen demand (COD), concentrations of calcium ions (Ca^{2+}), chloride ions (Cl^-) and total alkalinity (HCO_3^-). Sampling, sample processing and analytical methods were compatible with APHA (APHA 1998, 2005).

Table 2. Descriptive statistics of environmental factors and selected water quality indices of Czajcze and Domysłowskie Lakes in years 2000-2013

No	Water quality indices (units)	Descriptive statistics									
		Czajcze Lake					Domysłowskie Lake				
		min	$\bar{x}$	max	SD	CV [%]	min	$\bar{x}$	max	SD	CV [%]
Czajcze Lake											
1	Precipitation (mm)	10.70	57.26	259.00	47.19	82	10.70	57.26	259.00	47.19	82
2	Water level (cm)	73.00	100.03	123.00	13.93	14	40.00	60.53	85.00	12.68	21
3	Water temperature (°C)	2.00	13.04	23.60	6.88	53	1.00	12.42	23.10	6.87	55
4	pH (pH units)	6.86	7.68	8.64	0.39	5	5.25	7.65	8.69	0.60	8
5	DO (mg $O_2 \cdot dm^{-3}$)	1.80	7.78	26.70	3.93	50	1.50	8.19	19.80	3.98	49
6	Water saturation (%)	20.98	70.69	273.50	40.02	57	15.90	73.86	188.50	37.94	51
7	BOD_5 (mg $O_2 \cdot dm^{-3}$)	5.60	8.57	13.80	1.54	18	6.60	9.83	17.20	2.14	22
8	COD-Mn (mg $O_2 \cdot dm^{-3}$)	0.10	2.92	7.40	2.02	69	0.00	2.89	7.90	1.89	65
9	Ca^{2+} (mg $Ca \cdot dm^{-3}$)	38.00	57.06	84.00	9.52	17	22.00	50.87	72.00	13.04	26
10	HCO_3^- (mg $HCO_3 \cdot dm^{-3}$)	105.0	162.93	300.00	46.65	29	128.10	193.30	366.00	55.10	29

Obtained results were subjected to the statistical analysis – basic statistics (descriptive methods, Pearson correlations), time series analysis (Mann-Kendall trend test) and chemometric methods: principal component analysis (PCA), cluster analysis (CA) and discriminant analysis (DA). Before chemometric analyses normal distribution test were performed using Kolmogorov-Smirnov test (Kumarasamy et al. 2014, Thomas et al. 2015). To avoid misclassification due to wide differences in data units and dimensionality – standardization of experimental data to PCA and CA was performed. For DA raw data were used (Basilevsky 2009, Einax 1995). All statistical analyses were done using STATISTICA 13.1PL.

Water level in lakes and precipitation (as month sum) has been obtained from the Management of Wolin National Park and internet sources (http://www.wolinpn.pl/).

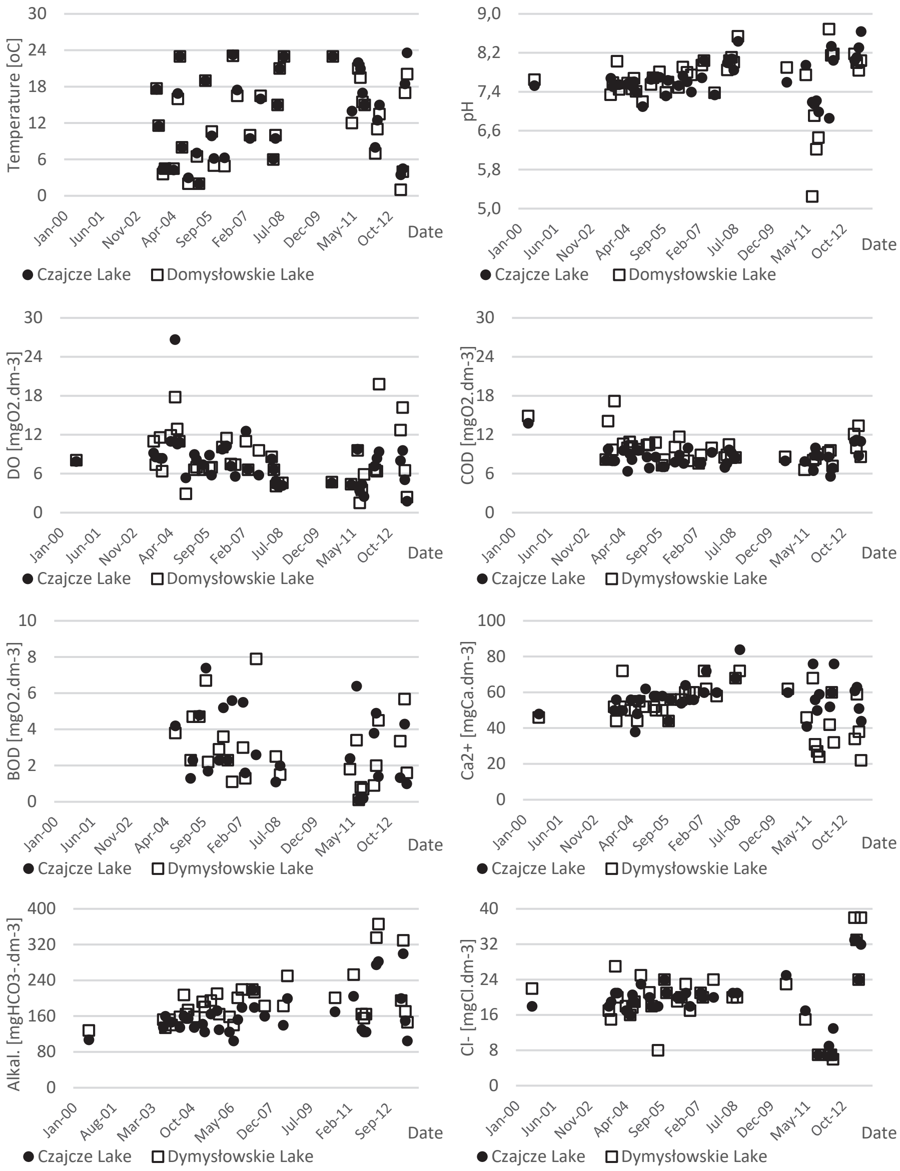


Fig. 2. Changes in concentrations of selected water quality indices for Czajcze and Domysłowskie Lakes

5. Results and discussion

Based on the analysis of collected data, a clear picture of the water quality of investigated lakes and changes of these water quality in period investigated was obtained (Fig. 2). The variability of the studied water quality indices was typical for these lakes, which is indicated by the research carried out so far (e.g. Grzegorczyk et al. 2008, Bucior & Poleszczuk 2013). Attention is drawn to the large variability of the pH parameter in Domysłowkie Lake, observed in particular in the period August-October 2011 (Fig. 2, Table 2). It could be associated with increased processes of decomposition of organic matter of an allochtonic nature, probability of origin from municipal sewage (Pitter 1999). For a more complete description of the experimental data the description statistics were determined (Table 3). The changes of water level in Czajcze Lake and Domysłowskie Lake and precipitation sum in month in period 2000-2013 was presented on Fig. 3.

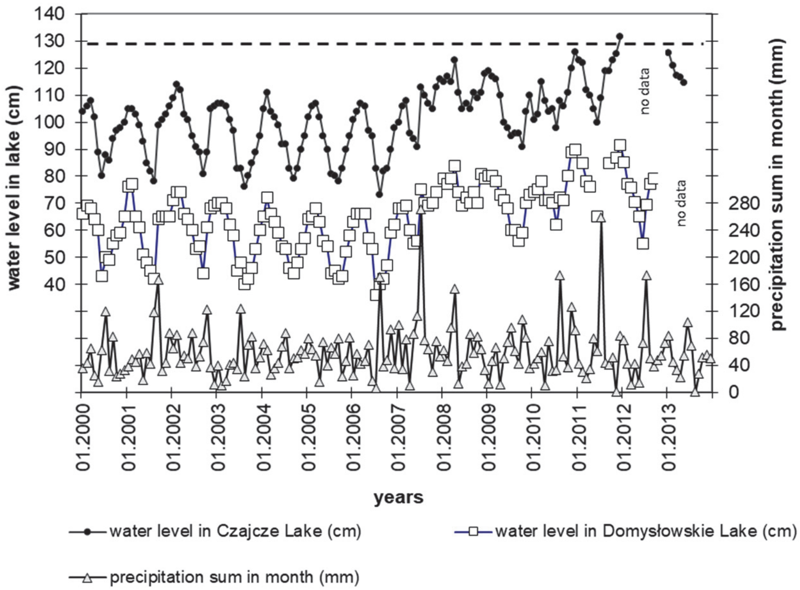


Fig. 3. Changes of water level in Czajcze and Domysłowskie Lakes on background precipitation in years 2000-2013

On the basis of experimental data – time series of selected water quality indices and environmental factor were obtained. This enabled to perform Mann-Kendall trend test to detect whether or not trends are present (Tab. 3).

Table 3. Mann-Kendall trend test for environmental factors and selected water quality indices of Czajcze and Domysłowskie Lake

Examined factor	Domysłowskie Lake			Czajcze Lake		
	Kendall's tau	p	S	Kendall's tau	p	S
Precipitation	-0.019	0.870	-0.001	-0.019	0.870	-0.001
Water level	0.312	**0.005**	**0.015**	0.427	**0.000**	**0.017**
temp.	0.106	0.345	0.001	0.105	0.351	0.001
pH	0.297	**0.007**	**0.000**	0.261	**0.019**	**0.000**
DO	-0.236	**0.035**	**-0.011**	-0.349	**0.002**	**-0.011**
Water saturation	-0.078	0.484	-0.003	-0.220	**0.048**	**-0.017**
COD	-0.211	0.059	0.000	0.018	0.879	0.000
BOD	-0.239	**0.031**	0.000	-0.165	0.139	0.000
Ca	-0.073	0.521	-0.002	0.258	**0.023**	**0.012**
Alkal.	0.330	**0.003**	**0.017**	0.188	0.093	0.001
Cl^-	0.003	0.991	0.000	0.106	0.355	0.001

For Czajcze Lake water level and alkalinity had statistically significant increasing trend when concentration of dissolved oxygen had decreasing trend. Trend for pH and BOD were also detected.

Pearson correlations (Tab. 4), shows the dependence between each investigated water quality indices in the matrix correlation (e.g. Little and Rubin 2014).

The analysis of Pearson's correlation was carried out in order to detect whether the variability of the tested water quality indices is individual or whether it depends on the runoff of the Lewińska Struga stream through the examined lakes. As Table 3 shows only BOD and COD have not shown correlation effect thus, this may indicate the effect of impurities other than by the stream, as well as another composition of microorganisms carrying out the decomposition of organic matter (Mostofa et al. 2013).

On the based the principal components analysis (PCA) eigenvalues of the matrix correlation were appointed (Table 4), which are a measure of the variability of the primary (original) data in the coordinates of the main components. On this basis, a graph was obtained (Fig. 4.) to illustrate which variables (water quality indices) show a similar pattern of changes, and which are clearly distinguished on the background of effect water level in lakes and monthly sum of precipitation.

PCA was performed on the basis of normalized results of hydro-chemical analyses. A similar approach to hydrochemical interpretation of water was presented by Siwek (Siwek et al. 2013).

Table 4. Pearson correlation of selected water quality indices between Czajcze and Domysłowkie Lakes

Water quality indices		Czajcze Lake							
		pH	DO	WS	BOD	COD	Ca^{2+}	Cl^-	HCO_3^-
Domysłowskie Lake	pH	**0.469** *	-0.001	0.046	0.080	0.093	0.278	0.182	**0.452** *
	DO	-0.357	**0.691** ***	**0.469** *	0.140	0.050	0.051	0.144	0.051
	Water saturation	-0.369	**0.575** **	**0.590** **	0.230	0.076	0.099	0.063	0.044
	BOD	-0.086	0.318	0.345	0.417	-0.062	-0.200	0.301	-0.202
	COD	0.154	0.299	0.216	-0.029	0.205	0.115	0.193	-0.077
	Ca^{2+}	0.056	0.292	0.440	0.135	-0.408	**0.601** **	-0.163	0.197
	Cl^-	**0.586** **	-0.105	-0.186	-0.253	**0.545** *	-0.097	**0.944** ***	-0.411
	HCO_3^-	0.014	0.147	0.219	0.365	-0.394	0.097	**-0.576** **	**0.956** ***

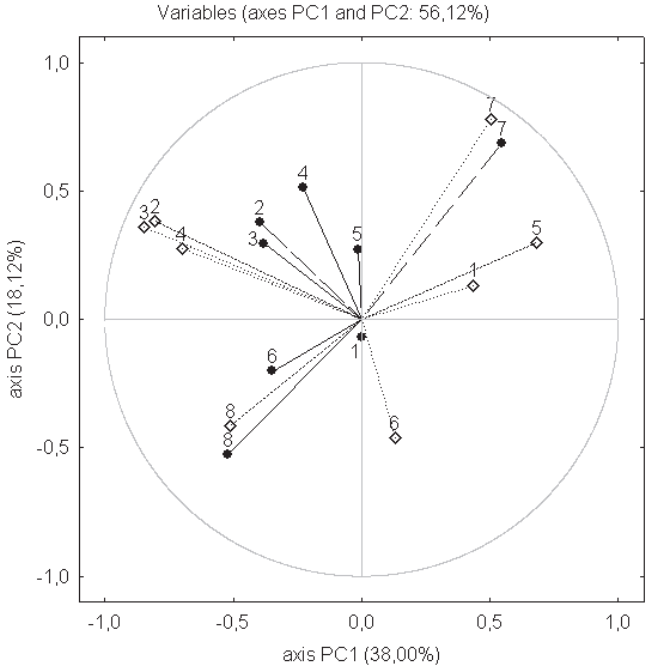
Significant level: *** $\alpha \leq 0{,}001$, ** $0{,}001 < \alpha \leq 0{,}01$, * $0{,}01 < \alpha \leq 0{,}05$

It is clearly shown in Fig. 4, which of the investigated water quality indices have a similar nature of change and which are clearly different from each other. Those of the water quality indices that had higher intrinsic values had the corresponding self-correlated vector values less correlated with the other parameters (Smoliński et al. 2016).

The analysis of the eigenvalues main components > 1 PCA shows that the plane of first and second principal component describes 56.12% of the variance of the primary (original) data (Fig. 4).

According to the above criteria, only principal components (PCs) with values higher than the values of the principal components were considered (Kowalkowski et al. 2006, Kannel et al. 2007). In literature it is assumed that if the percentage explained by the first two dimensions is 64% (e.g. Howaniec & Smoliński 2014) than it is significant statistically.

Those of the investigated parameters-water quality indices that had a higher eigenvalues, had the corresponding to that value eigenvector less correlated with other parameters (Smoliński et al. 2016). Then, using the cluster analysis, hierarchical dendrograms of the surface water quality indices of Lake Czajcze and Lake Domysłowskie were presented in Fig. 5. Water quality indices were grouped into indicators that provide the most and least information about the interactions between the examined indices and environmental factors (e.g. Vega et al. 1998, Singh et al. 2004).



Legend: ◊ Czajcze Lake; • Domysłowskie Lake
1 – pH (pH units); 2 – DO (mg O_2/dm^3); 3 – water saturation by O_2 (mg O_2/dm^3);
4 – BOD_5 (mg O_2/dm^3); 5 – COD-Mn (mg O_2/dm^3); 6 – Ca^{2+} (mg Ca/dm^3);
7 – Cl^- (mg Cl/dm^3); 8 – HCO_3^- (mg HCO_3/dm^3)

Fig. 4. PCA ordination diagrams of investigated water quality indices

Dendrograms based on CA analysis had emerged 3 groups of factors for both examined Lakes (Fig. 5). For the Czajcze Lake the first group with DO, water saturation, BOD and alkalinity as showed oxygen dependent group, second – water temperature and sum of precipitation – and third group with COD, Cl, pH, water level and Ca – as environmental dependent groups.

For Domysłowskie Lake the first group which included Ca, water level, pH and alkalinity was environmental dependent group. Second – as oxygen conduction related group with DO and WS. The third – including precipitation, temperature, Cl, COD, BOD – as environmental group with external contamination risk.

Similarities in variability in precipitation and water temperature may be related to their variability and seasonal dependence. The variability of the water level with respect to the variability of pH and Ca concentrations may provide information on the inflow of alkaline waters with a high content of bicarbonates.

Similarities in the variability of COD and Cl concentrations may indicate organic pollutants of natural origin, but in combination with BOD they reveal the effect of anthropogenic pollution (Miller et al 2016).

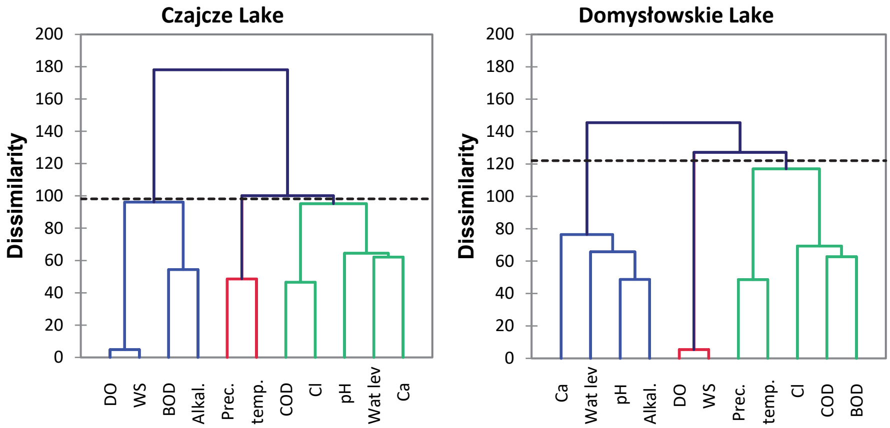


Fig. 5. Dendrograms showing variation in the variability of studied water quality indices for lakes Czajcze and Domysłowskie

The results of the CA confirms and complement the results obtained by using the PCA method (Fig. 4, Tab. 5 and Tab. 2). Similar results have been reported by Zhang et al. (2017) in his research on surface waters of the Ganjiang River (China), who used identical statistical methods for the interpretation of experimental data.

The discriminant analysis results are shown in Table 6 and in Figure 6 (Tab. 6, Fig. 6). In this report, the discriminant analysis was carried out to assess which of the variables (selected water quality indices, environmental factors) discriminated between the subjected lakes. The assumed criterion was belonging to the lake and the season of the year. The analysis showed the correctness of the assumption - the assumed grouping criteria perfectly reflect the differences between the studied seasons and lakes (Fig. 5). Analysis based on seasons shown that most discriminant power among analyzed factors had water level, water temperature, pH, DO, alkalinity and lake from which water were sampled. In the other hand analysis based on the lake criterion shown that only water level, COD and alkalinity had any discriminant power (Tab. 6). As a practical dimension of the analysis, it may be assumed to reduce the number of tests required to distinguish significant differences between the studied reservoirs in different research seasons.

Table 5. PCA results

No.	Water quality indices (units)	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8
Czajcze Lake									
1	pH (jedn. pH)	0,435	0,133	0,697	0,398	-0,349	0,052	-0,152	0,039
2	DO (mg O_2/dm^3)	-0,805	0,383	0,206	-0,305	0,075	0,191	0,008	0,167
3	Water saturation (%)	-0,846	0,360	0,254	-0,192	0,081	0,034	-0,140	-0,162
4	BOD_5 (mg O_2/dm^3)	-0,700	0,276	-0,091	0,480	0,067	-0,433	0,002	0,045
5	COD-Mn (mg O_2/dm^3)	0,682	0,300	-0,138	0,107	0,621	0,035	-0,165	0,031
6	Ca^{2+} (mg Ca/dm^{-3})	0,129	-0,461	0,689	-0,372	0,291	-0,267	0,039	0,012
7	Cl^- (mg Cl/dm^3)	0,504	0,777	0,285	0,040	0,068	0,004	0,228	-0,048
8	HCO_3^- (mg HCO_3/dm^3)	-0,512	-0,415	0,243	0,566	0,325	0,264	0,103	-0,025
Domysłowskie Lake									
1	pH (jedn. pH)	0.000	-0.070	0.570	0.467	0.260	0.203	0.147	-0.055
2	DO (mg O_2/dm^3)	-0.398	0.377	0.088	-0.378	0.424	0.202	0.084	0.131
3	Water saturation (%)	-0.379	0.295	0.050	-0.308	0.452	-0.038	-0.091	-0.261
4	BOD_5 (mg O_2/dm^3)	-0.227	0.512	-0.030	-0.032	-0.044	-0.306	0.136	-0.020
5	COD-Mn (mg O_2/dm^3)	-0.015	0.273	0.254	-0.143	0.186	0.114	-0.332	0.322
6	Ca^{2+} (mg Ca/dm^{-3})	-0.349	-0.202	0.543	-0.251	0.031	-0.293	0.046	-0.279
7	Cl^- (mg Cl/dm^3)	0.546	0.686	0.240	0.026	0.060	0.128	0.266	-0.007
8	HCO_3^- (mg HCO_3/dm^3)	-0.521	-0.527	0.205	0.539	0.145	0.237	0.046	-0.032
	Eigenvalue	3.040	1.449	1.235	0.991	0.718	0.370	0.134	0.062
	Cumulative eigenvalue	3.040	4.490	5.725	6.716	7.434	7.804	7.938	8.000
	Cumulative (%)	38.00	56.12	71.56	83.94	92.92	97.55	99.23	100.00

The cause of a completely different qualitative composition of investigated lakes waters since 2006 than in earlier years was detected in the first place, in climatic conditions. There was an attempt to link them with an increased amount of precipitation.

It has been observed, that since the second half of 2006, the amount of atmospheric precipitation on the territory of the Warnowskie lakes increased slightly. Unfortunately, it was not large enough growth of atmospheric precipitation (with a few exceptions) to give a clear explanation for this state of affairs.

Table 6. Results of discriminant analysis based on different grouping factors

Grouing factor: season				Grouing factor: lake			
Variable	Lambda	F	p-value	Variable	Lambda	F	p-value
water level	**0.932**	**3.695**	**0.049**	**water level**	**0.314**	**146.342**	**< 0.0001**
temp.	**0.602**	**21.804**	**< 0.0001**	season	0.999	0.054	0.818
pH	**0.708**	**13.609**	**< 0.0001**	temp.	0.996	0.238	0.627
DO	**0.907**	**3.369**	**0.040**	pH	0.988	0.802	0.374
WS	0.938	2.191	0.120	DO	0.998	0.148	0.702
COD	0.977	0.775	0.465	WS	0.998	0.122	0.728
BOD	0.993	0.223	0.800	**COD**	**0.919**	**5.917**	**0.018**
Ca	0.967	1.128	0.330	BOD	1.000	0.018	0.895
Alkal.	**0.903**	**3.550**	**0.034**	Ca	0.964	2.495	0.119
Cl	0.975	0.850	0.432	**Alkal.**	**0.860**	**10.894**	**0.002**
Lake	**0.998**	**3.369**	**0.039**	Cl	0.960	2.822	0.098

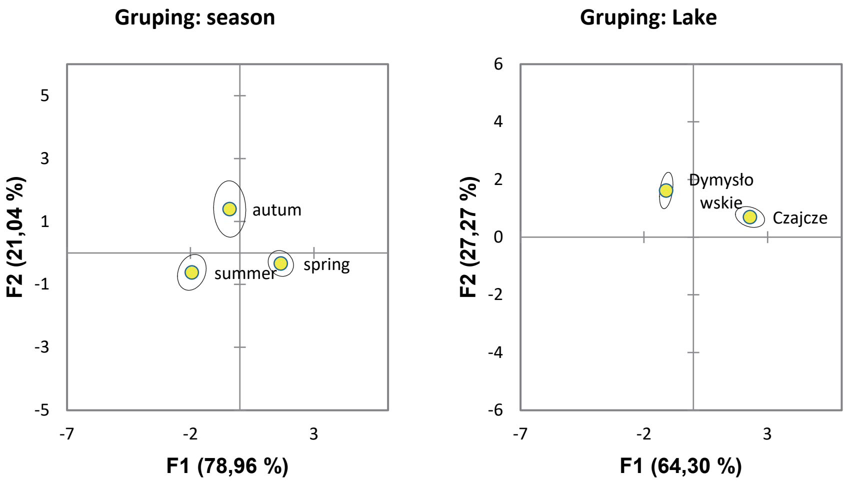


Fig. 6. Relationship between seasons and lakes based on discriminant analysis

Consider, in turn, tributary of the waters from Lake Rabiąż (Eastern Warnowo) which is connected to Lake Czajcze by clearly shore narrow channel-watercourse did not make sense, because at present the channel-watercourse connecting the two lakes is completely overgrown (Dąbrowski 2005) and has bottom sediments. So any water flow from Lake Rabiąż to Lake Czajcze is impossible. So it can be concluded that maybe the insignificant growth of atmospheric

precipitation together with other, unknown to the author of this work, factors influenced to the persistent growth of water level and the new quality composition of water in Lake Czajcze. The Domysłowskie Lake is the last from the WNP lakes, which the waters of Lewińska Stream flow down. Thus water from Czajcze Lake flows down to Domysłowskie Lake. The water of Czajcze Lake to Domysłowskie Lake "the new composition" quantitative the quality of waters. Probably only the rafting of waters from Czajcze Lake is the general cause of new quality and quantity composition of waters in Domysłowske Lake.
Those results confirms presented earlier the analytical results of experimental data analyzed by chemometric and classical statistical methods.

Methods presented in this work are well-developed and often used by researchers as statistical techniques to identify and pre-characterize the different groups of elements in water that exhibit similar seasonal variability and correlations (e.g. Giri & Singh 2014; Krishna & Mohan 2014; Bu et al. 2015, Mao et al. 2017). In addition, this study demonstrates the usefulness of chemometric techniques for a better understanding of seasonal variations (changes) in water quality (Garizi et al. 2011, Arslan 2013, Aksever & Büyükşahin 2017).

The seasonal variability of water quality indices in the surface waters of both investigated lakes undoubtedly depended on many factors (e.g. Siwek et al. 2013). Chemometric analysis indicated have shown statistically significant correlations between selected water chemistry indices and environmental factors i.e. meteorological (e.g. Rafałowska 2008) and hydrological conditions (Krajewska & Fac-Beneda 2016, Lopata et al. 2016) of studied lakes.

6. Conclusions

As is known, chemometric methods have become widely used methods for analysis and inference in the natural sciences. As classification methods, they allow getting better information about relations within dataset (Einax 1995, Kumarasamy et al. 2014). They enable the detection of specific relationships between samples and studied water quality indices, as well as their direct impact on aquatic ecosystems. They enable the determination of naturally occurring groups of factors within large dataset (Einax 1995, Kumarasamy et al. 2014, Thomas et al. 2015). At the same time, the use of these methods allows to reduce the amount of data that is needed to define environmental changes, determining the most important factors shaping its variability over the period considered (Einax 1995, Thomas et al. 2015). Based on the performed chemometric analyzes, it was shown that environmental factors can have a major impact on the shaping of lake water quality on the example of flowable reservoirs, covered by special legal protection and not under strong anthropopressure. It was shown that among the studied water quality indices only the variability of BOD and COD were not dependent on runoff between lakes, which may indicate a different nature of biodegradation of organic matter or illegal discharges of pollutants into lakes. In addition, it was noted that the variability of water quality between the studied reservoirs in long time range was mainly classified by the water level, COD and alkalinity, while analyzing the seasonal variation indices with the highest discriminant power were water level, temperature, pH, and alkalinity. That can be considered as a suggestion to reduce the number of analyzed water quality indices when it comes to show significant differences in the formation of the variability between lakes.

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Abstract

Selected water quality indices collected form Czajcze and Domysłowsie Lakes in Wolin National Park in years 2000-2013 were studied. With the chemometric procedures an attempt was made to assess the impact of selected environmental factors in particular water level of lakes and monthly sum of precipitation on hydrochemistry of the lakes. It has been demonstrated that the level of lake waters can significantly shape the quality of the examined waters on the runoff of a river through lakes.

Keywords:
PCA, DA, CA, Wolin National Park, water quality

Możliwość zastosowania metod chemometrycznych do oceny wpływu czynników środowiskowych na jakość wody na przykładzie jezior w Wolińskim Parku Narodowym

Streszczenie

Oznaczano wybrane wskaźniki jakości wody zebrane z jezior Czajcze i Domysłowskie w Wolińskim Parku Narodowym w latach 2000-2013. Przy użyciu procedur chemometrycznych podjęto próbę oceny wpływu wybranych czynników środowiskowych, w szczególności poziomu wody w jeziorach, jak i miesięcznej sumy opadów, na hydrochemię jezior. Wykazano, że poziom wód jeziornych może znacząco wpłynąć na jakość badanych wód podczas spływu rzeki przez jeziora.

Słowa kluczowe:
PCA, DA, CA, Woliński Park Narodowy, jakość wody