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**STREAM OSÓWKA IN SZCZECIN – CHEMOMETRIC ANALYSIS
OF WATER QUALITY INDICES IN WINTER SEASON**

Abstract

In the period from december 2013 to march 2014 water quality of stream Osówka in Szczecin and in particular oxygenation of water, abundance of water in organic matter, concentrations of various forms of nitrogen and phosphorus, and some macro and microelements were investigated. Water samples were collected at five sampling station in the middle and lower course of the stream. For chemometric analysis 17 indicators of water quality were selected. It has been demonstrated using the procedures: cluster analysis (CA), principal component analysis (PCA) and factor analysis (FA) that organic matter and nitrogen compounds are most likely introduced into the Osówka stream water from the city rainwater drainage system, and phosphorus compounds – from deposits in the sediments in the Syrenie Stawy Ponds, through which water of Osówka flowed, and the mineral substances came down from upper course of the stream. On the basis of PCA/FA indicated which water quality indices should be measured for the purpose of water quality monitoring of the Osówka stream in winter. Thereby the usefulness of chemometric procedures used for the presentation of the collected data and its analysis were positively verified.

Keywords: water quality management, multivariate data analysis, cluster analysis, principal component analysis, factor analysis

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Introduction

Flowing through urban agglomerations rivers and streams are always contaminated by a variety of waste substances discharged into the water. This is a problem in all urban areas and has always been, and still is taken very seriously (e.g. Felipe-Sotelo et al. 2007; Kannel et al. 2007; Liu et al. 2014). Even at full urban sewage and built-effective wastewater treatment plants, rivers and streams in urban areas are always included in the network of drainage system and are collectors of rainwater polluted in various level flowing from the urban areas. It is even worse when the water flowing through the city are discharged industrial or municipal waste (Osmulska-Mróż 1992).

The problem of water pollution also applies to the Osówka stream in Szczecin City (Figure 1), this stream and ponds through which water of Osówka flows are incorporated into the municipal drainage and are significantly contaminated and the water quality of the Osówka is deteriorating especially just in the inflow zone of rainwater (Poleszczuk and Bucior 2009; Poleszczuk et al. 2013; Miller et al. 2014).

The aim of this paper was to conduct a study of selected water quality indices on the monitoring stations along the Osówka runoff in the Szczecin City in winter, i.e. when biological factors limited impact on water quality changes and to try to determine whether – and if so – in what place and to what extent change their quality for worse, which should be helpful in determining the locations of discharge of pollutants into the stream. In addition the possibility of use of the chemometric methods (Einax 1995) for the presentation and analysis of measurement data in the case of small number of independent water sample – were examined.

Characteristics of Osówka Stream

Water of the Osówka stream flowing from the source located at the Warszawskie Hills (maximum height – 131 m above sea level) in the northwestern part of the city of Szczecin by green areas and urban areas (about 13 km road longitude). Osówka from sources, through the Valley of the Seven Mills until the inflow into the lake Goplana – reminds a mountain stream. Next, water flows in underground channels to Syrenie Stawy Ponds, and then after passing through Syrenie Stawy – it flows again by underground channels to the Rusalka Lake at Kasprowicz Park. Waters of the stream leaves Rusalka by underground canal to the West Odra River.

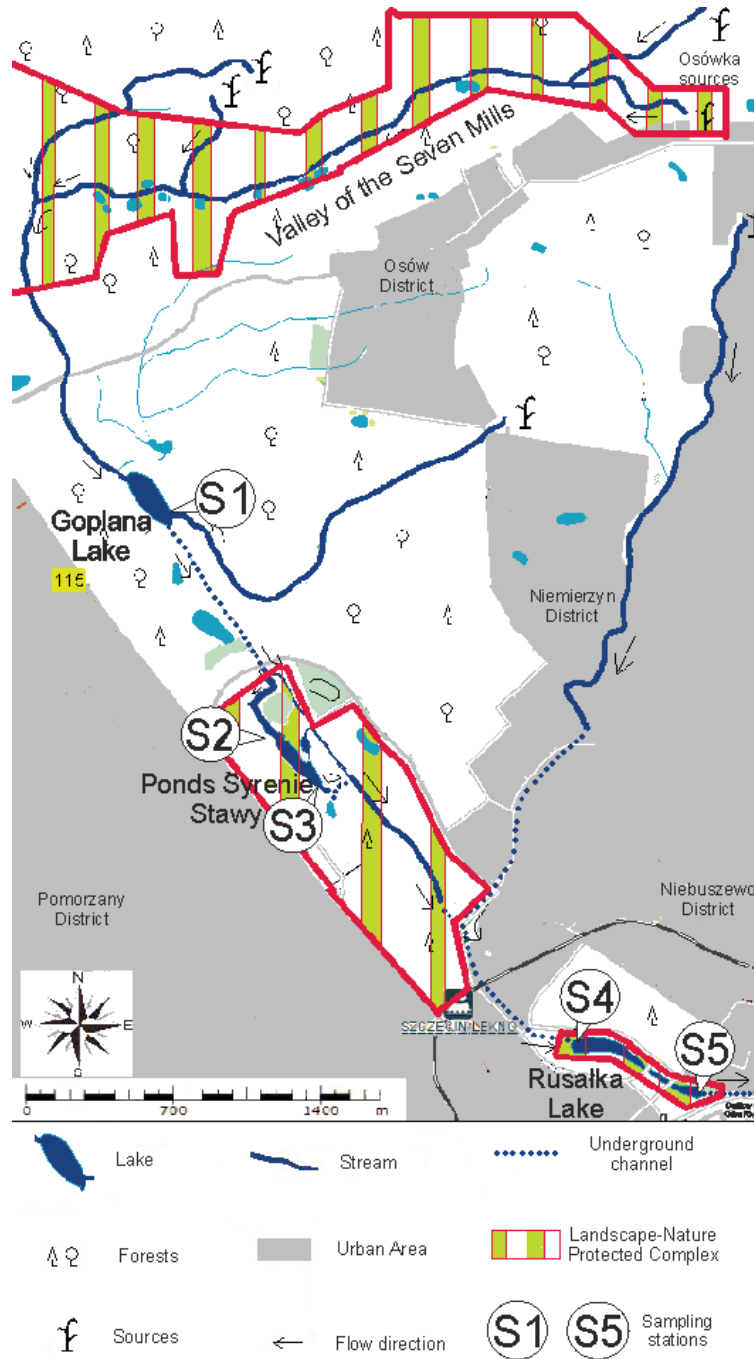


Figure 1. Osówka Stream in Szczecin (Miller et al. 2014)

Osówka in the upper and middle course of the stream flows through protected by law areas, namely two landscape-nature protected complexes: “Valley of the Seven Mills and sources of the Osówka stream” and “Complex of the Parks Kasprowicza-Arkoński”.

Osówka stream is incorporated into the municipal rain water system in which artificial reservoirs, i.e. Syrenie Stawy Ponds and lakes through which the water of Osówka stream flows act as reservoirs for rainwater, settling ponds and biological ponds. Reservoirs located along the Osówka watercourse subject to hydrotechnical works, in particular: in 1997 the Rusalka Lake and Syrenie Stawy Ponds in 2003 and in the period from 2010 to 2012 (Miller et al. 2014).

Material and methods

Water samples were collected at five sampling stations S1-S5 (Figure 1), i.e. along the Osówka stream runoff course from outflow area of the Goplana Lake (S1), and are the inflow and outflow to/from the Syrenie Stawy Ponds (S2 and S3) and in the zone of inflow and outflow to and from the Rusalka Lake (S4 and S5) on: 5.12.2013, 1.06.2014, 11.02.2014, 14.03.2014. Goplana Lake, Syrenie Stawy and Rusalka Lake in the period from 1.12.2013 to 23.02.2014 were covered with thin ice layer.

The water sampling, preservation, transportation and analysis of the water samples were performed according to APHA (1998). The selected parameters such as pH, dissolved oxygen (DO), temperature (TEMP), chemical oxygen demand (COD-Cr), five-day biochemical oxygen demand (BOD₅), nitrogen-ammonia (N-NH₄⁺), nitrogen-nitrate (N-NO₃⁻), nitrogen-nitrite (N-NO₂⁻), total nitrogen (TN), soluble reactive phosphates (SRP), total phosphorus (TP), calcium (Ca_{tot}), magnesium (Mg_{tot}), chloride (Cl), sulphate (SO_{4tot}), hydrocarbonate (HCO₃⁻) – determined as total alkalinity and total iron (Fe_{tot}). These data were used for the chemometric analysis. All water quality indices are expressed in mg·dm⁻³ except pH (pH units) and TEMP (°C).

The results were analyzed using selected chemometric procedures, in particular: cluster analysis (CA), principal component analysis (PCA) and factor analysis (FA), which are standard procedures used for the presentation and evaluation of the data used in recent publications such as Mustapha et al. (2013), Poudel et al. (2013), Kumarasamy et al. (2014).

The dataset contains data from 17 water quality indices (Table 1) of the stream Osówka on subsequent sampling stations has been standardized (z – standardization, the standardized values of the ratio x i.e.: $z_i = (x_i - \bar{x})/SD$ – for the i -th value of the parameter x , where \bar{x} – the average value of x , SD – standard deviation). Dataset was analyzed by multivariate statistical methods, in particular: cluster analysis (CA), principal component analysis (PCA) and factor analysis (FA). CA was performed in order to find similarities and differences between the water quality indices results at subsequent sampling stations, at a subsequent term of measurements and to determine the relationship between water quality indices. Ward method were used, assuming as a metric distances between clusters – squared Euclidean distance. In turn, the PCA and FA allowed the separation, based on eigenvalues greater or equal 1, principal components and factors determining the contribution of the water quality indices of the Osówka stream to the value of the variance in the study period. FA correlation matrix presented in the work were obtained after varimax rotation.

Table 1. Results of the water quality indices of Osówka Stream in winter period 2013/2014

No.	Sampling Station		S1	S2	S3	S4	S5
	Water quality indices (units)						
1	2	3	4	5	6	7	8
1	Temperature (°C)	Range	2.7–7.9	1.8–8.8	0.6–8.6	3.0–8.0	0.5–8.4
		Mean	4.5	5.3	3.9	5.7	3.1
		SD	2.4	2.9	3.5	2.1	3.7
2	pH (pH units)	Range	7.66–8.20	7.07–7.49	7.10–7.81	7.78–8.70	7.86–8.21
		Mean	7.99	7.25	7.44	8.09	7.96
		SD	0.26	0.18	0.32	0.42	0.17
3	COD-Cr (mg O ₂ · dm ⁻³)	Range	27–167	84–373	67–388	150–303	86–445
		Mean	92	255	186	232	242
		SD	57	133	67	66	155
4	BOD ₅ (mg O ₂ · dm ⁻³)	Range	1.3–4.0	2.0–4.0	2.6–5.0	4.0–5.8	0.8–6.6
		Mean	2.8	2.7	3.8	5.0	4.0
		SD	1.2	0.9	1.0	0.9	2.5
5	Dissolved Oxygen (mg O ₂ · dm ⁻³)	Range	4.0–12.0	2.0–5.0	2.6–6.9	5.0–11.0	3.5–11.2
		Mean	7.8	3.1	4.7	7.9	7.4
		SD	3.4	1.4	2.0	3.3	3.4
6	NO ₃ ⁻ (mg N-NO ₃ · dm ⁻³)	Range	0.21–1.10	0.64–1.45	0.43–1.75	0.45–1.50	0.56–0.90
		Mean	0.53	1.05	1.05	0.99	0.77
		SD	0.39	0.40	0.54	0.42	0.15

1	2	3	4	5	6	7	8
7	NO ₂ ⁻ (mg N-NO ₂ · dm ⁻³)	Range	0.005–0.028	0.029–0.055	0.013–0.029	0.013–0.033	0.020–0.031
		Mean	0.016	0.039	0.021	0.026	0.025
		SD	0.009	0.012	0.008	0.009	0.006
8	NH ₄ ⁺ (mg N-NH ₄ · dm ⁻³)	Range	0.28–0.35	0.31–0.51	0.31–0.63	0.31–0.51	0.29–0.41
		Mean	0.31	0.37	0.47	0.40	0.35
		SD	0.03	0.09	0.15	0.09	0.05
9	TN (mg N dm ⁻³)	Range	0.83–2.50	1.42–4.00	1.20–3.80	1.91–3.50	1.20–3.30
		Mean	1.54	2.73	2.53	2.45	2.07
		SD	0.78	1.46	1.36	0.72	0.92
10	SRP (mg PO ₄ · dm ⁻³)	Range	0.01–0.21	0.12–0.50	0.05–0.21	0.02–0.18	0.08–0.25
		Mean	0.09	0.28	0.13	0.12	0.14
		SD	0.09	0.18	0.07	0.07	0.08
11	TP (mg P dm ⁻³)	Range	0.06–0.56	0.36–0.90	0.31–0.92	0.18–0.45	0.15–0.50
		Mean	0.21	0.59	0.67	0.33	0.32
		SD	0.23	0.24	0.29	0.13	0.17
12	Ca _{tot} (mg Ca · dm ⁻³)	Range	42–103	56–132	49–131	73–253	48–136
		Mean	66	82	97	149	107
		SD	26	33	34	75	41
13	Mg _{tot} (mg Mg · dm ⁻³)	Range	5–40	6–12	7–85	7–40	5–21
		Mean	12	8	31	18	10
		SD	18	3	36	14	7
14	Cl ⁻ (mg Cl · dm ⁻³)	Range	18–25	32–102	27–105	32–63	33–72
		Mean	21	20	48	47	44
		SD	2	34	38	12	18
15	SO _{4 tot} (mg SO ₄ · dm ⁻³)	Range	28–58	88–276	96–256	104–318	66–128
		Mean	38	138	149	172	102
		SD	13	92	74	98	26
16	HCO ₃ ⁻ (mg HCO ₃ · dm ⁻³)	Range	160–195	105–295	160–265	260–345	225–305
		Mean	178	192	228	301	267
		SD	14	80	48	36	34
17	Fe _{tot} (mg Fe · dm ⁻³)	Range	0.01–0.33	0.73–1.33	0.74–1.33	0.16–0.72	0.09–0.36
		Mean	0.09	1.11	0.95	0.38	0.21
		SD	0.16	0.28	0.26	0.25	0.12

In this study, all the mathematical and statistical procedures were performed using the STATISTICA 10.0 and STATGRAPHICS Centurion XVI.

Results and discussion

The data presented in Table 1 and on dendrogram in Figure 2 shows that the waters of the Osówka stream during study period changed its quality along the

water course and the changes were irregular. The most different from other were waters in the station S2, i.e. in the Syrenie Stawy water inflow area – compared to water quality at water outflow area from the Goplana Lake, and in comparison with the waters on the other stations S3–S5, where the quality water was not very diverse. The data presented in Tab. 1 and on dendrogram in Figure 3 shows that the quality of the tested waters also changed depending on the term of samples collection, wherein the water quality of the Osówka in December (term T1) clearly differed in the other periods (T2–T4). This diversity demonstrates the significant effect of the amount of rainfall, the amount of acid deposits and most likely incidental discharges of pollutants into groundwater. The specific variation of the water chemistry indices examined at sampling stations could be linked also with the ongoing hydrotechnical works (including infilling) in Syrenie Stawy. At the same time total concentration of Mg (measured by method with EDTA) is calculated as the difference between total hardness and total concentrations of Ca. Result calculated in this way is essentially the sum of the concentrations of magnesium and total concentrations of metals with valences plus two or more. Thus, the presence of abnormally high concentrations of total Mg is associated with periodic discharges of compounds of different metals to Osówka stream waters, as pointed out in the work Hłyńczak et al. (2008), Poleszczuk et al. (2013). Osówka catchment area is exposed to a large “wet” and “dry” deposits of sulfur compounds from the atmosphere associated with the close proximity to the sulfuric acid factory in Police (approx. 13 km) and “Dolna Odra” Power Plant (approx. 30 km) which combust sulfurized coal (see Poleszczuk and Łysiak-Pastuszek 1998; Poleszczuk et al. 2014). The analysis of the dendrogram in Figure 4 shows that the tested water quality indices can be divided into several groups of indicators, which characterized a similar variability. In the first main group were the indices characterizing the abundance of water in organic matter, nitrogen and phosphorus compounds and some inorganic compounds, such as Cl and Fe_{tot} . This group can be divided into two subgroups, i.e. comprising a first COD-Cr, N-NO₃, TN, N-NH₄ and Cl, and N-NO₂, which may indicate that these substances were introduced into waters in parallel with waste waters-rich in organic matter and chlorine, so most likely the rainwater running off the city streets, or from municipal sewage. In contrast, a second subgroup of phosphorus substances were probably coming from the bottom sediments, as evidenced by membership in the group of total iron. The second main group were the indices characterizing the oxidative-reducing and acid-base balance, as well as determining the abundance

of water in mineral substances. In this case the two groups can be distinguished – a first characterized by aeration, the activity of the processes of biochemical oxidation and pH, and a second subgroup, which included macronutrient ions of the water such as Ca_{tot} , HCO_3^- (as the alkalinity), $\text{SO}_{4\text{tot}}$, and Mg_{tot} . The attention is drawn to the parallel changes in alkalinity and concentrations of Ca_{tot} , which indicates that the acidity of the tested water is stabilized by calcium carbonate contained in the suspension or lingering in the bottom sediments in the lakes.

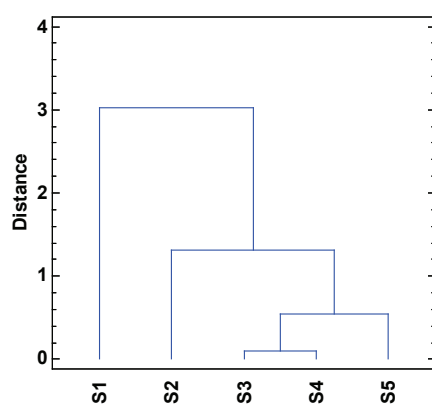


Figure 2. Dendrogram showing clustering of sampling stations

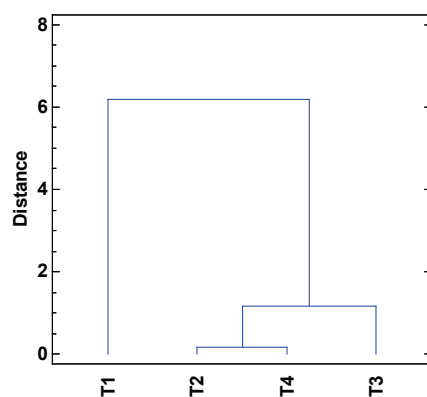


Figure 3. Dendrogram showing clustering of water quality indices

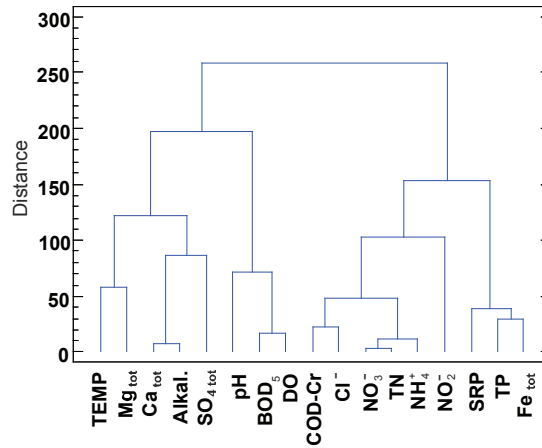


Figure 4. Dendrogram showing clustering of term of sampling

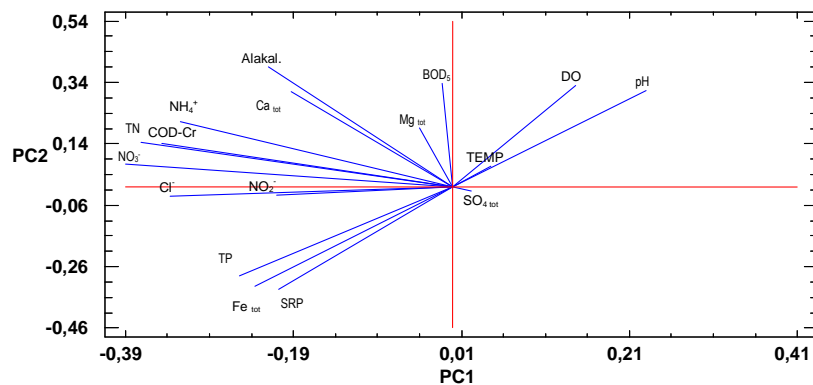


Figure 5. PCA of water quality indices

A principal component analysis (PCA) (Figure 5) of 17 analysed water quality indices emerge, based on eigenvalue higher than 1, from 20 calculated principal components – the 5 main principal components explaining about 83.25% of the total variance in the during the study period in winter (Table 2). It shows that no indicators of water quality have positive loading for PC1 (defines 31.80% of the total variance), and have negative loading on COD-Cr, N-NO₃, N-NH₄, TN and Cl⁻. PC2 – explaining 20.48% of the total variance was

positively correlated with the pH, BOD, DO and alkalinity, while SRP and Fe_{tot} were negatively correlated with PC2. The third main component (PC 3) which explained the 14.37% of total variance has a positive loading on temperature, Mg_{tot} , and negative one on DO. Recent principal components – PC4 and PC5 – explained 9.71% and 6.89% of the total variance and were correlated positively with BOD_5 , Mg_{tot} and $SO_{4\ tot}$; also with temperature, N- NO_2 , SRP, $SO_{4\ tot}$, and negatively only with Mg_{tot} – respectively.

Table 2 Loadings of water quality indices for first five significant principal components (PC) explaining 83.25% of total variance

Variable	PC1	PC2	PC3	PC4	PC5
TEMP	0.045	0.068	0.540	0.058	0.300
pH	0.230	0.313	-0.032	-0.223	0.168
COD-Cr	-0.346	0.143	-0.133	-0.157	0.234
BOD_5	-0.013	0.335	-0.287	0.438	0.121
DO	0.146	0.329	-0.365	0.131	0.094
NO_3^-	-0.390	0.072	-0.062	-0.106	-0.104
NO_2^-	-0.210	-0.027	0.262	-0.054	0.529
NH_4^+	-0.325	0.212	0.018	0.139	-0.318
TN	-0.372	0.143	0.005	0.010	0.070
SRP	-0.207	-0.333	-0.157	-0.132	0.314
TP	-0.254	-0.290	-0.103	0.110	-0.207
Ca_{tot}	-0.192	0.311	0.283	-0.156	-0.061
Mg_{tot}	-0.040	0.190	0.394	0.302	-0.361
Cl ⁻	-0.337	-0.029	-0.294	0.024	0.005
$SO_{4\ tot}$	0.022	-0.013	-0.017	0.658	0.354
Alkalinity	-0.220	0.389	0.067	-0.108	0.074
Fe_{tot}	-0.235	-0.323	0.200	0.299	-0.029
Eigenvalue	5.406	3.482	2.443	1.650	1.171
Variability (%)	31.801	20.481	14.369	9.708	6.887
Cumulative %	31.801	52.282	66.651	76.359	83.246

Table 3 shows the varimax rotated correlation matrix for the five first (out of 20 calculated varifactors). VF1–VF5 were chosen because they explain a total of 83.25% of the total variance, in particular, VF1 31.80%, VF2, VF3 14.37%, VF4 and VF 5 9.71%, 6.89% and have eigenvalue higher than 1. Using the classification criteria proposed by Liu et al. (2003), to characterize the

performance of the correlation matrix citeration between VF and water quality indices it was assumed that the correlation value within the range of 0.75–1.00 characterized by strong correlations, 0.50–0.75 average correlations, while in the range of 0.30–0.50 weak correlations.

Table 3. Loading of varimax rotated factors matrix for first five significant factors explaining 83.25% of total variance

Variable	VF1	VF2	VF3	VF4	VF5
TEMP	-0.128	-0.070	0.389	0.822	-0.020
pH	-0.121	-0.853	0.039	0.041	-0.025
COD-Cr	0.875	0.055	-0.300	0.091	0.021
BOD ₅	0.302	-0.349	0.110	-0.280	0.788
DO	0.052	-0.677	-0.060	-0.402	0.481
NO ₃ ⁻	0.868	0.324	-0.055	-0.064	-0.124
NO ₂ ⁻	0.367	0.194	-0.184	0.731	0.023
NH ₄ ⁺	0.801	0.232	0.387	-0.161	0.081
TN	0.866	0.230	0.004	0.125	0.076
SRP	0.166	0.536	-0.699	0.110	-0.090
TP	0.233	0.776	-0.177	-0.214	-0.049
Ca _{tot}	0.642	-0.194	0.429	0.318	-0.206
Mg _{tot}	0.118	0.094	0.871	0.172	0.084
Cl ⁻	0.689	0.380	-0.347	-0.267	0.127
SO _{4 tot}	-0.168	0.194	0.052	0.190	0.872
Alakalinity	0.801	-0.330	0.219	0.167	0.026
Fe _{tot}	0.081	0.911	0.052	0.249	0.089
Eigenvalue	5.406	3.482	2.443	1.650	1.171
Variability (%)	31.801	20.481	14.369	9.708	6.887
Cumulative %	31.801	52.282	66.651	76.359	83.246

Water quality indices identified as the most important and with the most positive impact on the Osówka stream water quality variance in the winter season were: COD-Cr, N-NO₃, N-NH₄, TN, alkalinity, Mg_{tot}, temperature, BOD₅ and SO_{4 tot}. The analysis showed that only the pH of the water investigated during the winter have negative charge of correlation on variation of Osówka water quality. Thus, these indicators should be considered as basic indicators to study changes in Osówka stream water quality.

Conclusions

1. It has been shown that the water of Osówka stream which flowed from Goplana Lake to outflow of Rusałka Lake changed its quality in most in the water inflow area to Syrenie Stawy Ponds, and the quality of water after outflow from the Ponds and then passing through the Rusałka Lake underwent minor changes, which indicates that the waters of Osówka stream were polluted primarily by waste water from rain drainage system of the Szczecin City to Syrenie Stawy Ponds and contaminated by substances released from bottom sediments deposited in Syrenie Stawy Ponds, which speaks well for the variability of the quality of the investigated water at a time, mostly due to the periodic occurrence of rainfall and incidental deposition of acidic substances compounds from the atmosphere.

2. It has been shown that the dissolved and suspended organic matter and nitrogen compounds have sewage origin, while phosphorus and iron deposits derived from lingering along the water course mainly in the water reservoir. The specific water “resistance” of Osówka stream to pH changes, is associated with the presence of CaCO_3 suspended in the water and brought together with other mineral components (macronutrients) with water flowing down from the catchment.

3. It has been shown, that water quality indices the most suitable for monitoring changes in Osówka stream water quality in the winter – to the respondents in this study – as is clear from the analysis of PCA/FA would be: pH, COD-Cr, N- NO_3 , N- NH_4 , TN, alkalinity, Fe_{tot} , Mg_{tot} , temperature, BOD_5 and SO_4_{tot} .

4. On the basis of research and study it was demonstrated that the application for the CA and PCA/FA procedures for the presentation and reasoning with a small number of independent test samples of water, as in the present work – was verified positively.

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STRUMIEŃ OSÓWKA W SZCZECINIE – ANALIZA CHEMOMETRYCZNA WSKAŹNIKÓW JAKOŚCI WODY W OKRESIE ZIMOWYM

Streszczenie

W okresie od grudnia 2013 roku do marca 2014 roku badano jakość wód strumienia Osówka w Szczecinie, oznaczając natlenienie wód, zasobność wód w materię organiczną, stężenia różnych form azotu i fosforu oraz niektóre makroskładniki i mikroskładniki mineralne. Próbkę wody pobierano w pięciu stacjach poboru próbek w środkowym i dolnym biegu strumienia. Do analizy chemometrycznej wybrano 16 wskaźników jakości wody. Wykazano przy użyciu procedur analizy klastrowej (CA), analizy głównych składowych (PCA) i analizy czynnikowej (FA), że materia organiczna i związki azotowe najprawdopodobniej wprowadzone są do wód strumienia Osówka z kanalizacji deszczowej miasta, zaś związki fosforu – z depozytów w osadach w Syrenich Stawach, przez które wody Osówki przepływały, zaś substancje mineralne spływały z górnego biegu ciek. Na podstawie PCA/FA wskazano, jakie wskaźniki należy oznaczać dla celów monitoringu jakości wód Osówki w zimie. Zweryfikowano tym samym pozytywnie przydatność stosowanych procedur chemometrycznych do prezentacji zebranych danych i ich analizy.

Słowa kluczowe: zarządzanie jakością wody, wieloczynnikowa analiza danych, analiza klastrowa, analiza głównych składowych, analiza czynnikowa

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