

Urban stream Osówka in Szczecin – how efficiently as possible should the variability of the stream water quality be studied along the road of runoff in time?

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Abstract The water quality of the stream Osówka in the NW part of the Szczecin city was studied. Water samples were collected in four seasons of 2014 – January, April, July and October in 6 sampling stations, from station near the source of the stream – to inflow of Osówka stream water to the lake Rusalka. 20 selected water chemistry indices were measured. The aim of discernment variability of water quality along stream runoff path during studied period chemometric procedures were conducted: cluster analysis (CA), calculations of linear regression equation $y_i = \bar{y}_i + \sum_{j=1}^6 \alpha_j S_j + \sum_{k=1}^4 \beta_k T_k + SEE$ for selected water quality indices (y_i), where S_j and T_k – are sampling stations and sampling terms numbers – respectively, and factor analysis (FA). It has been shown significant variability of Osówka water quality along the runoff path and established what parameters characterizing the variability of stream water chemistry should be examined in the places of indicated sampling stations – the same as in the studies – the quantities of terms of sampling in 4 consecutive seasons.

Strumień Osówka w Szczecin – jak najefektywniej badać regularnie w czasie zmienność jakości wód tego strumienia wzdłuż drogi ich spływu?

Słowa kluczowe ciek wodny w mieście, ciek Osówka, analiza chemometryczna, regresja liniowa, analiza czynnikowa, analiza skupień, jakość wody

Streszczenie Badano jakość wód strumienia Osówka w NW części miasta Szczecina. Próbkę wody do badań pobierano w czterech terminach – styczeń, kwiecień, lipiec i październik 2014 roku w miejscu 6 stacji, począwszy od ujęcia w pobliżu źródła strumienia – aż do dopływu wód Osówki do jeziora Rusalka. Oznaczano 20 wybranych wskaźników jakości wód. Celem rozoznania zmienności jakości wód wzdłuż drogi spływu w okresie badawczym przeprowadzono studia chemometryczne posługując się procedurami: CA, obliczano równania regresji $y_i = \bar{y}_i + \sum_{j=1}^6 \alpha_j S_j + \sum_{k=1}^4 \beta_k T_k + SEE$ dla poszczególnych wskaźników jakości wód (y_i), gdzie S_j i T_k – to numery stacji i terminów poboru próbek – odpowiednio, a także FA. Wykazano znaczną zmienność jakości wód Osówki wzdłuż drogi spływu i ustalono, jakie parametry charakteryzujące zmienność chemizmu wód strumienia powinny być badane w miejscach

wskazanych stacji pomiarowych – przy identycznej jak w przeprowadzonych badaniach – ilościach terminów poboru próbek w następujących po sobie 4 porach roku.

Introduction

Examination of streams and rivers water flowing through urban areas, which is associated with very significant changes in the quality of waters – contaminated with sewage during flows through city areas, becoming an increasingly important issue in relation to their progressive degradation (Liu et al. 2014; Wilkins et al. 2015; Huang et al. 2016). In many papers this problem is known as „urban stream syndrome” (Liu et al. 2014; Wilkins et al. 2015; Huang et al. 2016).

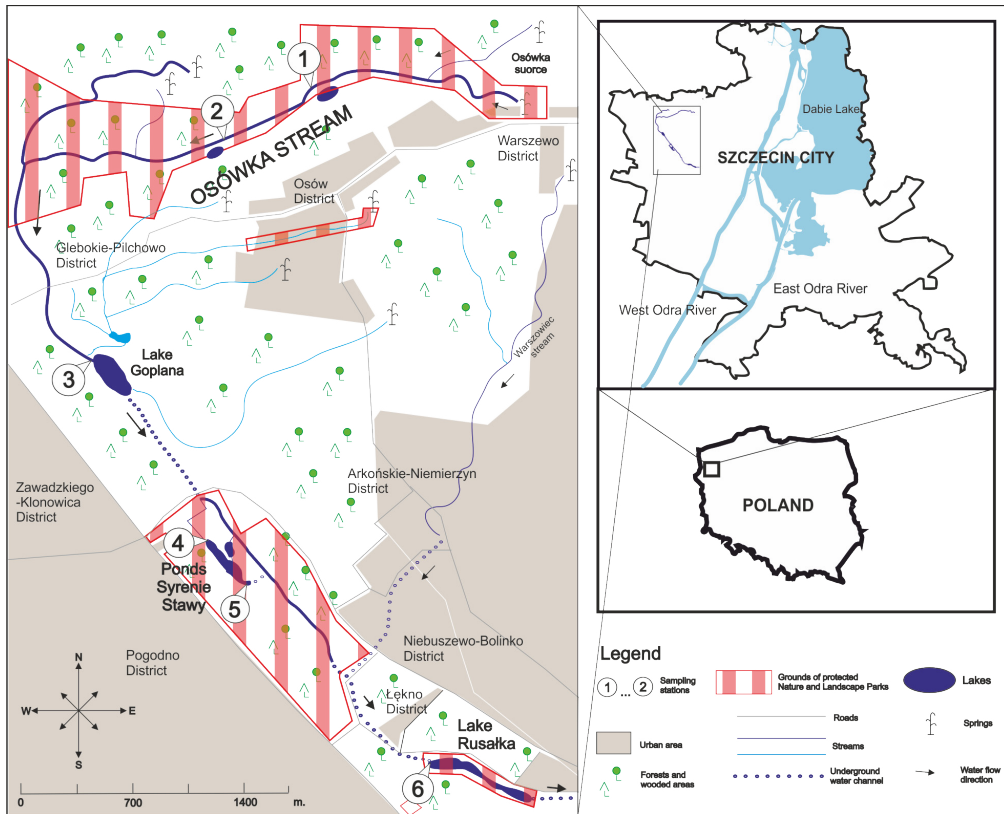


Figure 1. Osówka stream in Szczecin city (NW-Poland)

Osówka stream located in the north-west part the Szczecin city (Fig. 1) is a stream around which are located areas of nature conservation and recreation. Two nature and landscape protection complexes were established here: "Dolina Siedmiu Młynów i źródło strumienia Osówka" and "Zespół Parków Kasprowicza-Arkoński" (Uchwała 1994, Stan 2004). At the same time stream Osówka is included in the municipal rain sewer system and receives rainwater and sewage,

unfortunately, which gradually run down with natural watercourse and by open concrete channels or underground concrete channels to Western Odra. Studies having the character of random studies of Osówka stream waters and inflow water to Osówka have been published – so far – in a relatively small number of publications, eg. Raczńska (2012a & b), Miller et al. (2014 a & b).

Characteristics of Osówka stream

The total length of the Osówka stream in the north-west part of Szczecin is about 13 km. Sources of the stream are located in the Warszewkie hills on the southern slope of Lisia Mountain (108 m asl). From the source – through the Valley of the Seven Mills waters of Osówka flow down as a rapid stream to Lake Goplana (5.15 km). Above Goplana lake to Osówka inflow waters of two relatively small streams: Bystry Potok (0.75 km) and Jasmudzka Struga (3.73 km). Near the Osówka water outflow from the Goplana lake – is an underground inflow the Arkonka stream. Osówka water flows out of the Lake Goplana (5.52 km) with an underground channel with a length of approx. 700 m. After that stream bed separates into two – already on the surface – above the Syrenie Stawy Ponds (6.72 km). From the Ponds Syrenie Stawy the Osówka waters outflows with an open channel and when combined with the "relief" channel (bypassing Syrenie Stawy) flow down further with underground channel to the Rusalka lake. Along the way, (7.60 km) into an underground channel, falls water of the Warszawiec stream. At 8.63 km underground channel ends in the Rusalka lake. Osówka stream water after passing the Rusalka lake outflows from the reservoir (km 9.34) and falls further with underground channel to Western Odra (Report 2004).

Material

Water samples of Osówka stream were collected at six sampling stations located respectively at 1.57; 2.27; 5.52; 6.72; 7.00 and 8.64 km from the source – recognized as the beginning of the stream. Water samples were collected from the stream according to the rules specified in PN-ISO 5667-6: 2003, and from the water reservoirs through which waters of Osówka flowed – using a model Bucket – from the surface waters from a depth of about 25 cm below the water – according to PN-ISO 5667-4: 2003. Water sampling was conducted during the four seasons, ie. during the period of winter – on 15.01.2014, the period of spring – 16.04.2014, summer – 15.07.2014, and autumn – 15.10.2014. Examination of urban streams in different seasons is recommended in a number of publications (Sun et al. 2016; Ledford, Lautz 2016; Pratt, Chang 2012).

In studies of water streams and rivers flowing through the cities chemometric procedures are a fundamental tool, eg. Muangthong, Shrestha (2015), Haque et al. (2016), Hamid et al. (2016). In our work measurement data were analyzed using cluster analysis (CA), linear regression equation was calculated: $y_i = \bar{y}_i + \sum_{j=1}^6 \alpha_j S_j + \sum_{k=1}^4 \beta_k T_k + SEE$ showing the relationship of the following investigated water quality indices from the average values of all measurements \bar{y}_i from the sampling station and terms of samples collection – where in equation the next values of S_j take a value 1 for j-th sampling station and value 0 for next station numbers, similarly – T_k take a value 1 for k-th term and 0 – for next terms. Regression equations were calculated using the method of stepwise deletion and addition *a priori* (Forward) (Stanisz 2007). Subsequent equations were calculated using the sequence Fisher-Snedecor test using as a criterion for rejection of the variables test values – $F = 4$. Last chemometric method conducted was factor analysis (FA) – using PCA as an

extraction method, and after PCA – normalized varimax rotation – for all the data collected during the research. Before factor analysis was conducted Kaiser-Meyer-Olkin (KMO) and Bartlett's sphericity tests were performed to confirm adequacy of the collected data to FA. These procedures made it possible to determine which parameters have changed with the statistically significant way and identify which indices should be studied regularly in order to comprehensively examine changes in water quality over time along the path of runoff. All calculations were performed using the Statistica 12.0 PL and Statgraphics Centurion XVII.

Analysis of selected physical and chemical indices of water quality of Osówka stream were performed with the methods recommended by the APHA (2012) according to the analytical procedures contained in the Polish Standards (Polskie Normy). At the sampling stations the temperature of water by mercury thermometers and pH – potentiometrically were determined, as well as total alkalinity (Alk), converted to the concentration of HCO_3^- – by acidimetry titration. Separate water samples were taken for assessment of the concentration of dissolved oxygen (DO) and 5 day biochemical oxygen demand (BOD_5). Designation of dissolved oxygen in water was performed in the laboratory by Winkler method. Collected Additional samples of water for analysis other selected water quality indices were collected to determine: without filtration – COD-Cr, COD-Mn and total concentration of nitrogen (TN) and phosphorus (TN) and also total concentrations of iron (Fe_{tot}) and manganese (Mn_{tot}); with filtration through filters having a diameter of micropores $0,45 \cdot 10^{-9}\text{m}$ – NO_3^- , NO_2^- and NH_4^+ , PO_4^{3-} (SRP), Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} .

All analyzes performed in the laboratory within 24 hours after sampling. Waster saturation by O_2 (WS) was calculated according to Nemerow (1985). COD-Cr i COD-Mn – were performed by titration method. Concentrations of NO_3^- , NO_2^- , NH_4^+ and SRP (soluble reactive orthophosphates (V)) – by colorimetric methods as well as total concentrations of TN and TP – after samples mineralization. By titration method with EDTA – total concentration of calcium and magnesium was measured. Concentration of chlorides by argentometric Mohr method. Gravimetric method was used to define concentration of sulfates (VI). Total concentrations of iron and manganese were indicated by colorimetric method. Similar water quality indices in urban streams were examined, eg. at work Chang (2008).

Results and discussion

The test results of water samples taken in sampling stations S_1 – S_6 located respectively at km1.43; 2.27; 5.52; 6.72; 7.00 and 8.64 of the stream are shown in Tab. 1–4. Fig. 2 and 3.

Table 1. The values of selected water quality indices for the subsequent water sampling stations (S_j) on the Osówka stream in January of 2014. Sampling date: 15.01.2014

L.p.	Water quality indices	Units	Stacja (S_j)					
			S_1	S_2	S_3	S_4	S_5	S_6
1	2	3	4	5	6	7	8	9
1	Temperature	°C	4.3	1.5	0.6	0.6	0.4	5.3
2	pH	pH units	7.80	8.29	7.66	7.20	7.26	8.70
3	COD-Mn	$\text{mg O}_2 \cdot \text{dm}^{-3}$	7.4	7.7	8.9	9.5	7.2	8.8
4	COD-Cr	$\text{mg O}_2 \cdot \text{dm}^{-3}$	13.4	20.2	87.6	215.0	67.4	303.0

1	2	3	4	5	6	7	8	9
5	BOD ₅	mg O ₂ · dm ⁻³	2.6	2.0	8.0	2.0	2.6	4.0
6	DO	mg O ₂ · dm ⁻³	8.6	10.8	10.4	2.0	2.6	5.0
7	WS	%	66.0	86.4	83.1	16.0	20.8	39.1
8	NO ₃ ⁻	mg NO ₃ ⁻ · dm ⁻³	0.30	0.24	0.42	0.77	1.00	0.99
9	NO ₂ ⁻	mg NO ₂ ⁻ · dm ⁻³	0.088	0.013	0.005	0.314	0.127	0.030
10	NH ₄ ⁺	mg NH ₄ ⁺ · dm ⁻³	0.31	0.21	0.28	0.32	0.39	0.34
11	TN	mg N · dm ⁻³	0.65	0.52	0.83	1.51	1.52	1.91
12	SRP	mg P-PO ₄ ³⁻ · dm ⁻³	0.07	0.02	0.04	0.35	0.15	0.18
13	TP	mg P-PO ₄ ³⁻ · dm ⁻³	0.13	0.07	0.10	0.44	0.92	0.41
14	Ca ²⁺	mg Ca · dm ⁻³	74	58	51	67	105	136
15	Mg ²⁺	mg Mg · dm ⁻³	5	6	<5	6	19	16
16	Cl ⁻	mg Cl · dm ⁻³	27	22	21	34	31	32
17	SO ₄ ²⁻	mg SO ₄ ²⁻ · dm ⁻³	13	10	14	81	77	69
18	HCO ₃ ⁻	mg HCO ₃ ⁻ · dm ⁻³	225	225	175	150	225	275
19	Fe _{tot}	mg Fe · dm ⁻³	0.09	0.08	0.01	1.33	1.33	0.16
20	Mn _{tot}	mg Mn · dm ⁻³	0.01	0.10	0.01	0.01	0.01	0.01

Table 2. The values of selected water quality indices for the subsequent water sampling stations (*S_j*) on the Osówka stream in April of 2014. Sampling date: 16.04.2014

L.p.	Water quality indices	Units	Stacja (<i>S_j</i>)					
			<i>S₁</i>	<i>S₂</i>	<i>S₃</i>	<i>S₄</i>	<i>S₅</i>	<i>S₆</i>
1	2	3	4	5	6	7	8	9
1	Temperature	°C	4.8	5.0	4.6	5.1	5.2	3.8
2	pH	pH units	8.16	8.67	8.02	7.54	8.05	7.95
3	COD-Mn	mg O ₂ · dm ⁻³	9.4	10.0	9.1	10.1	10.0	11.3
4	COD-Cr	mg O ₂ · dm ⁻³	66.3	70.2	63.9	213.0	119.0	142.0
5	BOD ₅	mg O ₂ · dm ⁻³	2.2	2.3	5.4	3.5	3.2	3.8
6	DO	mg O ₂ · dm ⁻³	12.4	13.5	12.8	3.5	4.2	8.0
7	WS	%	99.1	108.0	102.3	28.0	33.6	60.6
8	NO ₃ ⁻	mg NO ₃ ⁻ · dm ⁻³	0.40	0.42	0.38	0.64	0.81	0.72
9	NO ₂ ⁻	mg NO ₂ ⁻ · dm ⁻³	0.144	0.152	0.139	0.231	0.118	0.025
10	NH ₄ ⁺	mg NH ₄ ⁺ · dm ⁻³	0.51	0.54	0.49	0.82	1.02	0.85
11	TN	mg N · dm ⁻³	2.06	2.18	1.99	3.32	3.11	2.60
12	SRP	mg P-PO ₄ ³⁻ · dm ⁻³	0.17	0.18	0.17	0.28	0.21	0.20
13	TP	mg P-PO ₄ ³⁻ · dm ⁻³	0.64	0.68	0.62	1.04	1.15	0.65
14	Ca ²⁺	mg Ca · dm ⁻³	57	60	55	91	103	123

1	2	3	4	5	6	7	8	9
15	Mg ²⁺	mg Mg · dm ⁻³	<5	<5	<5	5	10	8
16	Cl ⁻	mg Cl · dm ⁻³	19	20	19	31	27	32
17	SO ₄ ²⁻	mg SO ₄ · dm ⁻³	33	35	32	53	49	41
18	HCO ₃ ⁻	mg HCO ₃ · dm ⁻³	200	225	175	200	225	250
19	Fe _{tot}	mg Fe · dm ⁻³	0.43	0.45	0.41	0.69	0.60	0.40
20	Mn _{tot}	mg Mn · dm ⁻³	0.09	0.09	0.08	0.14	0.07	0.03

Table 3. The values of selected water quality indices for the subsequent water sampling stations (*S*_{*j*}) on the Osówka stream in July of 2014. Sampling date: 15.07.2014

L.p.	Water quality indices	Units	Stacja (<i>S</i> _{<i>j</i>})					
			<i>S</i> ₁	<i>S</i> ₂	<i>S</i> ₃	<i>S</i> ₄	<i>S</i> ₅	<i>S</i> ₆
1	Temperature	°C	12.5	13.2	12.1	13.4	13.5	12.1
2	pH	pH units	8.03	8.53	7.89	7.89	8.40	8.30
3	COD-Mn	mg O ₂ · dm ⁻³	8.8	9.3	8.5	9.4	9.3	10.6
4	COD-Cr	mg O ₂ · dm ⁻³	56.4	59.7	54.3	181.0	87.0	110.0
5	BOD ₅	mg O ₂ · dm ⁻³	0.3	0.3	7.7	0.5	0.5	4.3
6	DO	mg O ₂ · dm ⁻³	12.3	8.6	8.0	0.5	0.5	4.3
7	WS	%	98.3	68.4	63.9	4.0	4.0	39.7
8	NO ₃ ⁻	mg NO ₃ ⁻ · dm ⁻³	0.52	0.55	0.50	0.84	1.01	0.92
9	NO ₂ ⁻	mg NO ₂ ⁻ · dm ⁻³	0.147	0.156	0.068	0.236	0.123	0.030
10	NH ₄ ⁺	mg NH ₄ ⁺ · dm ⁻³	0.50	0.53	0.48	0.80	1.00	0.83
11	TN	mg N · dm ⁻³	2.18	2.31	2.10	3.50	3.29	2.78
12	SRP	mg P-PO ₄ ³⁻ · dm ⁻³	0.31	0.39	0.30	0.50	0.57	0.56
13	TP	mg P-PO ₄ ³⁻ · dm ⁻³	1.15	1.22	1.11	1.85	2.06	1.56
14	Ca ²⁺	mg Ca · dm ⁻³	49	51	47	78	90	110
15	Mg ²⁺	mg Mg · dm ⁻³	<5	<5	<5	<5	7	5
16	Cl ⁻	mg Cl · dm ⁻³	18	19	17	29	25	30
17	SO ₄ ²⁻	mg SO ₄ · dm ⁻³	31	33	30	50	46	38
18	HCO ₃ ⁻	mg HCO ₃ · dm ⁻³	200	225	150	175	225	250
19	Fe _{tot}	mg Fe · dm ⁻³	0.34	0.36	0.33	0.55	0.46	0.26
20	Mn _{tot}	mg Mn · dm ⁻³	0.07	0.08	0.07	0.12	0.05	0.01

Table 4. The values of selected water quality indices for the subsequent water sampling stations (S_j) on the Osówka stream in October of 2014. Sampling date: 15.10.2014

L.p.	Water quality indices	Units	Stacja (S_j)					
			S_1	S_2	S_3	S_4	S_5	S_6
1	Temperature	°C	13.7	14.5	13.2	14.7	14.8	13.4
2	pH	pH units	7.65	8.03	7.43	7.62	8.13	8.03
3	COD-Mn	mg O ₂ · dm ⁻³	9.4	10.0	9.1	10.1	10.0	11.3
4	COD-Cr	mg O ₂ · dm ⁻³	60.7	64.3	58.5	195.0	101.0	124.0
5	BOD ₅	mg O ₂ · dm ⁻³	0.7	0.8	4.5	1.2	1.9	5.1
6	DO	mg O ₂ · dm ⁻³	14.3	8.4	7.8	1.2	1.9	5.7
7	WS	%	114.3	67.1	62.4	9.6	15.2	54.4
8	NO ₃ ⁻	mg NO ₃ ⁻ · dm ⁻³	0.17	0.18	0.42	1.27	0.44	0.35
9	NO ₂ ⁻	mg NO ₂ ⁻ · dm ⁻³	0.164	0.174	0.158	0.264	0.151	0.058
10	NH ₄ ⁺	mg NH ₄ ⁺ · dm ⁻³	0.06	0.07	0.20	0.63	0.30	0.13
11	TN	mg N · dm ⁻³	1.49	1.58	1.43	2.39	2.18	1.67
12	SRP	mg P-PO ₄ ³⁻ · dm ⁻³	0.10	0.11	0.10	0.16	0.17	0.16
13	TP	mg P-PO ₄ ³⁻ · dm ⁻³	0.38	0.40	0.36	0.60	0.67	0.17
14	Ca ²⁺	mg Ca · dm ⁻³	49	52	47	79	91	111
15	Mg ²⁺	mg Mg · dm ⁻³	<5	<5	<5	6	7	8
16	Cl ⁻	mg Cl · dm ⁻³	17	18	16	27	23	28
17	SO ₄ ²⁻	mg SO ₄ ²⁻ · dm ⁻³	24	25	23	38	34	26
18	HCO ₃ ⁻	mg HCO ₃ ⁻ · dm ⁻³	150	175	125	175	250	275
19	Fe _{tot}	mg Fe · dm ⁻³	0.43	0.45	0.41	0.69	0.60	0.40
20	Mn _{tot}	mg Mn · dm ⁻³	0.08	0.09	0.08	0.13	0.06	0.02

Demonstrated dendrograms showing further gradual variation (Fig. 2) of water quality along the runoff path from S_1 to S_6 , wherein can be seen clearly that between stations S_4 – S_6 was always a distinct change of Osówka water quality. Tab. 1–4 shows that there has been a significant deterioration in the quality of the examined water irrespective of the date of measurement. Fig. 3 presented dendrogram showing the variation of the quality of the examined waters in terms from T_1 to T_4 . It revealed that the examined waters in winter (T_1) and summer (T_3), when water temperatures were relatively stable – this variation was similar, whereas in terms T_2 and T_4 (spring and autumn) when significant changes occur in water temperatures in our climate zone – variability of examined indices was also – though different – similar. All collected data were used to calculate the next dendrogram on Fig. 4, which shows the variability of selected water chemistry indices. The dendrogram shows that there were certain groups of water quality indices, which changed in a similar way. These indices are very clearly grouped in several clusters which correspond to gradually changes in organic matter, oxygen conditions, pH and mineralization of the tested waters, and even show a correlation between changes in the concentrations of total

iron and sulphates (VI), which might indicate that the Osówka waters were contaminated with pollutants containing FeSO_4 . In turn, the linear regression equation showing effect of station number and date of the sampling on the variability of the examined indicators clearly show that the variability of Osówka water chemistry changing very substantially over time and along the path of the water runoff, because the in equations are virtually all stations from S_1 to S_6 and all sampling terms T_1 – T_4 . Thus, at each station, water quality is clearly different from the stations nearer or more distant from the station.

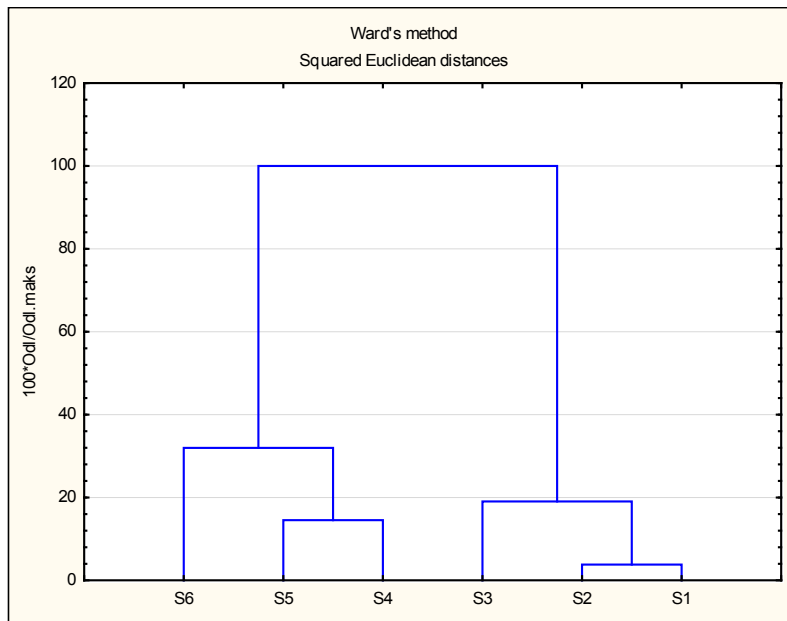


Figure 2. Dendrogram showing clustering of sampling stations in April and October

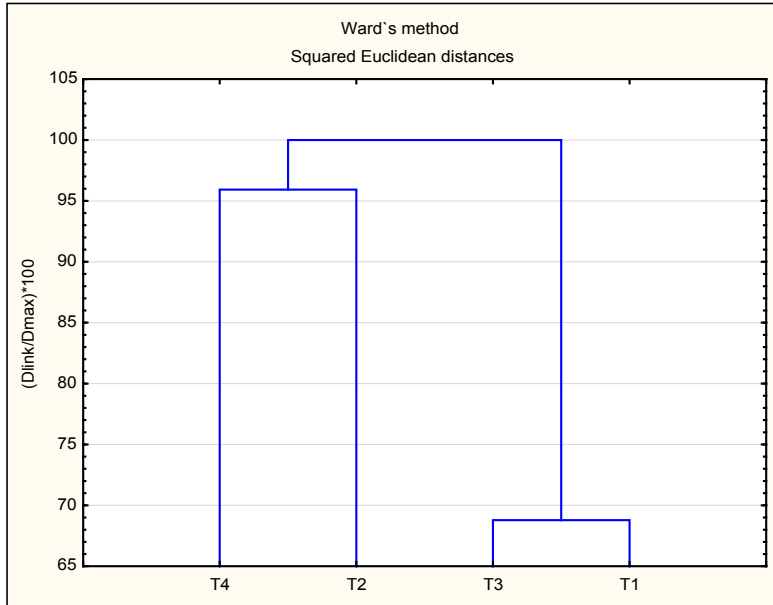


Figure 3. Dendrogram showing clustering of terms of sampling

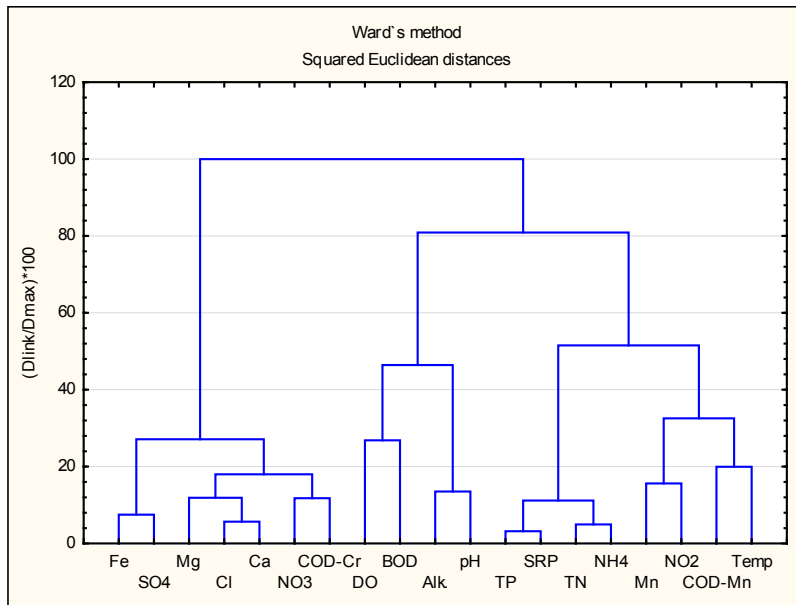


Figure 4. Relationship between selected water quality indices of Osówka stream in 2014

Table 5. Linear regression equations showing the relationship between selected water quality indices (y_i) from their mean values (\bar{y}_i), sampling station location (S_j) and term of sampling (T_k)

No.	Water quality indices (y_i)	$y_i = \bar{y}_i + \sum_{j=1}^6 \alpha_j S_j + \sum_{k=1}^4 \beta_k T_k + SEE$	Significance level of coefficients in calculated equation		SEE	R ²
1	2	3	4		5	6
1	Temperature	$y = 8.43 + (11.94 \pm 0.96)T_1 + (-9.31 \pm 0.69)T_2$	$\alpha_0 = 0.0000$ $\beta_{T1} = 0.0000$	$\beta_{T2} = 0.0000$	0.69	0.95
2	pH	$y = 7.97 + (0.44 \pm 0.17)S_2 + (-0.37 \pm 0.17)S_4 + (0.31 \pm 0.17)S_6 + (0.36 \pm 0.17)T_3$	$\alpha_0 = 0.0000$ $\alpha_{S4} = 0.0184$ $\alpha_{S6} = 0.0436$	$\beta_{T1} = 0.0487$ $\beta_{T3} = 0.0201$	0.17	0.64
3	COD-Mn	$y = 9.38 + (0.69 \pm 0.29)S_4 + (1.14 \pm 0.29)S_6 + (-1.73 \pm 0.29)T_1 + (-0.67 \pm 0.29)T_3$	$\alpha_0 = 0.0000$ $\alpha_{S4} = 0.0000$ $\alpha_{S6} = 0.0001$	$\beta_{T1} = 0.0287$ $\beta_{T3} = 0.0147$	0.29	0.82
4	COD-Cr	$y = 106.00 + (144.71 \pm 22.70)S_4 + (113.46 \pm 22.70)S_6$	$\alpha_0 = 0.0001$ $\alpha_{S4} = 0.0000$	$\alpha_{S6} = 0.0000$	22.70	0.74
5	BOD	$y = 2.89 + (4.73 \pm 0.55)S_3 + (2.63 \pm 0.55)S_6 + (1.21 \pm 0.49)T_1 + (1.07 \pm 0.49)T_2$	$\alpha_0 = 0.0000$ $\alpha_{S3} = 0.0000$ $\alpha_{S6} = 0.0001$	$\beta_{T1} = 0.0024$ $\beta_{T2} = 0.0423$	0.99	0.82
6	DO	$y = 6.97 + (1.86 \pm 0.85)S_1 + (-8.23 \pm 0.85)S_4 + (-7.73 \pm 0.85)S_5 + (-4.28 \pm 0.85)S_6 + (2.50 \pm 0.69)T_2$	$\alpha_0 = 0.0002$ $\alpha_{S1} = 0.0433$ $\alpha_{S4} = 0.0000$	$\alpha_{S5} = 0.0000$ $\alpha_{S6} = 0.0000$ $\beta_{T2} = 0.0001$	1.39	0.92
7	WS	$y = 56.00 + (-65.82 \pm 7.23)S_4 + (-61.82 \pm 7.23)S_5 + (-31.78 \pm 7.23)S_6 + (19.06 \pm 5.90)T_2$	$\alpha_0 = 0.0004$ $\alpha_{S4} = 0.0000$ $\alpha_{S5} = 0.0000$	$\alpha_{S6} = 0.0003$ $\beta_{T2} = 0.0004$	11.81	0.92
8	NO ₃ ⁻	$y = 0.59 + (0.50 \pm 0.11)S_4 + (0.44 \pm 0.11)S_5 + (0.39 \pm 0.11)S_6$	$\alpha_0 = 0.0000$ $\alpha_{S4} = 0.0002$	$\alpha_{S5} = 0.0009$ $\alpha_{S6} = 0.0039$	0.19	0.67
9	NO ₂ ⁻	$y = 0.130 + (0.131 \pm 0.022)S_4 + (-0.094 \pm 0.022)S_6$	$\alpha_0 = 0.0000$ $\alpha_{S4} = 0.0000$	$\alpha_{S6} = 0.0006$	0.03	0.82
10	NH ₄ ⁺	$y = 0.48 + (0.29 \pm 0.07)S_4 + (0.44 \pm 0.07)S_5 + (0.39 \pm 0.07)S_6 + (-0.38 \pm 0.06)T_1 + (-0.46 \pm 0.06)T_4$	$\alpha_0 = 0.0074$ $\alpha_{S4} = 0.0000$ $\alpha_{S5} = 0.0000$	$\alpha_{S6} = 0.0001$ $\beta_{T1} = 0.0003$ $\beta_{T4} = 0.0114$	0.12	0.87
11	TN	$y = 2.05 + (1.06 \pm 0.13)S_4 + (0.91 \pm 0.13)S_5 + (0.62 \pm 0.13)S_6 + (-1.53 \pm 0.13)T_1 + (-0.90 \pm 0.13)T_4$	$\alpha_0 = 0.0466$ $\alpha_{S4} = 0.0000$ $\alpha_{S5} = 0.0000$	$\alpha_{S6} = 0.0000$ $\beta_{T1} = 0.0000$ $\beta_{T4} = 0.0001$	0.22	0.95
12	SRP	$y = 0.23 + (0.31 \pm 0.03)S_4 + (0.16 \pm 0.03)S_5 + (0.11 \pm 0.03)S_6 + (0.11 \pm 0.03)T_2 + (0.07 \pm 0.03)T_3$	$\alpha_0 = 0.0000$ $\alpha_{S4} = 0.0000$ $\alpha_{S5} = 0.0001$	$\alpha_{S6} = 0.0039$ $\beta_{T2} = 0.0041$ $\beta_{T3} = 0.0259$	0.06	0.89
13	TP	$y = 0.77 + (0.41 \pm 0.08)S_4 + (0.62 \pm 0.08)S_5 + (0.12 \pm 0.08)S_6 + (0.45 \pm 0.08)T_2 + (1.15 \pm 0.08)T_3$	$\alpha_0 = 0.0000$ $\alpha_{S4} = 0.0000$ $\alpha_{S5} = 0.0000$	$\alpha_{S6} = 0.0000$ $\beta_{T2} = 0.0001$ $\beta_{T3} = 0.0141$	0.14	0.95

1	2	3	4	5	6	
14	Ca ²⁺	$y = 76.00 + (22.47 \pm 4.17)S_4 + (40.97 \pm 4.17)S_5 + (63.72 \pm 4.17)S_6 + (-10.30 \pm 3.41)T_3 + (-10.80 \pm 3.41)T_4$	$\alpha_0 = 0.0000$ $\alpha_{S_4} = 0.0005$ $\alpha_{S_5} = 0.0000$	$\alpha_{S_6} = 0.0000$ $\beta_{T_3} = 0.0005$ $\beta_{T_4} = 0.0000$	6.81	0.95
15	Mg ²⁺	$y = 17.00 + (6.81 \pm 3.23)S_4 + (13.81 \pm 3.23)S_5 + (11.56 \pm 3.23)S_6 + (48.78 \pm 2.74)T_4$	$\alpha_0 = 0.0000$ $\alpha_{S_4} = 0.0493$ $\alpha_{S_5} = 0.0000$	$\alpha_{S_6} = 0.0004$ $\beta_{T_4} = 0.0021$	5.59	0.95
16	Cl ⁻	$y = 24.00 + (-1.76 \pm 0.77)S_3 + (10.19 \pm 0.77)S_4 + (6.44 \pm 0.77)S_5 + (10.44 \pm 0.77)S_6 + (6.27 \pm 0.73)T_2 + (3.16 \pm 0.73)T_3$	$\alpha_0 = 0.0000$ $\alpha_{S_3} = 0.0367$ $\alpha_{S_4} = 0.0000$ $\alpha_{S_5} = 0.0000$	$\alpha_{S_6} = 0.0000$ $\beta_{T_2} = 0.0005$ $\beta_{T_3} = 0.0000$	1.26	0.97
17	SO ₄ ²⁻	$y = 37.00 + (30.29 \pm 7.37)S_4 + (26.29 \pm 7.37)S_5 + (18.29 \pm 7.37)S_6 + (-12.62 \pm 6.02)T_4$	$\alpha_0 = 0.0000$ $\alpha_{S_4} = 0.0005$ $\alpha_{S_5} = 0.0020$	$\alpha_{S_6} = 0.0226$ $\beta_{T_4} = 0.0497$	12.76	0.61
18	Alkalinity	$y = 205.00 + (-45.00 \pm 11.91)S_3 + (-16.25 \pm 11.91)S_4 + (35.00 \pm 11.91)S_5 + (67.50 \pm 11.91)S_6 + (-20.27 \pm 9.17)T_3$	$\alpha_0 = 0.0000$ $\alpha_{S_3} = 0.0319$ $\alpha_{S_4} = 0.0001$	$\alpha_{S_5} = 0.0008$ $\alpha_{S_6} = 0.0005$ $\beta_{T_3} = 0.0402$	16.46	0.83
19	Fe _{tot}	$y = 0.47 + (0.50 \pm 0.13)S_4 + (0.43 \pm 0.13)S_5 + (-0.11 \pm 0.11)T_3$	$\alpha_0 = 0.0000$ $\alpha_{S_4} = 0.0011$	$\alpha_{S_5} = 0.0036$ $\beta_{T_3} = 0.0065$	0.24	0.53
20	Mn _{tot}	$y = 0.06 + (0.04 \pm 0.01)S_4 + (-0.04 \pm 0.01)S_6 + (-0.05 \pm 0.01)T_1$	$\alpha_0 = 0.0000$ $\alpha_{S_4} = 0.0146$	$\alpha_{S_6} = 0.0052$ $\beta_{T_1} = 0.0000$	0.02	0.77

Notation: Values of y_i are received after substitution for the appropriate S_j and T_k – the value 1

To determine which water quality indices should be examined in order to record the variability of water quality of Osówka stream, and also to verify that the parameters S_j and T_k also prejudice that water should be tested in all selected measuring stations – factor analysis were conducted. The analysis results are shown in Tab. 6. for all the stations and terms of sampling. It was assumed that the important parameters for which the coefficients in Tab. 6 are ≥ 0.70 . It was established – in such way – that the parameters characterizing the variability of the examined waters are: among the general parameters – temperature, pH, DO, COD-Cr and COD-Mn, WS, BOD₅, from indices characterizing the content of biogenic substances – all test indices, i.e., NO₃⁻, NO₂⁻, NH₄⁺, TN, SPR, TP, from the indices characterizing the mineralization – concentrations: Ca²⁺, Mg²⁺, Cl⁻ and HCO₃⁻. At the same time FA showed importance of station number (S_j) and sampling date (T_k) – which confirms our earlier findings made with Tab. 5. Of course the value of assumed classification criterion as eg. recommended by Liu et al. 2003 can be increased to value 0.75 and the important parameters would be: temperature, pH, BOD₅, NO₃⁻, NO₂⁻, NH₄⁺, TN, SRP, TP, Ca²⁺, Mg²⁺, S_j and T_k . While such changes would prevent the conduction of studies on the biogeochemical processes taking place in examined waters eg. equilibria of processes of organic matter mineralization (Yu et al. 2015), or balance processes between the forms of nitrogen (Lusk, Toor 2016), as well as studies on the concentrations of ion macronutrients in water (Halstead 2014). The case determines the value of classification criterion as above may also be a matter of judgment.

Table 6. Factor analysis after varimax rotation for Osówka Stream in four seasons of 2014 year

	FV1	FV2	FV3	FV4	FV5
Temperature	-0.18	0.15	0.06	0.86	0.28
pH	-0.07	0.25	0.83	0.10	0.20
COD-Mn	0.25	0.21	0.03	0.72	-0.28
COD-Cr	0.70	0.22	-0.25	0.11	-0.11
BOD ₅	0.04	-0.17	0.09	-0.13	-0.90
DO	-0.71	-0.35	0.28	-0.17	-0.12
WS	0.66	0.55	-0.17	-0.07	0.08
NO ₃ ⁻	-0.05	0.21	-0.81	0.19	0.41
NO ₂ ⁻	0.21	0.91	0.06	-0.06	-0.11
NH ₄ ⁺	0.23	0.87	-0.06	0.33	0.04
TN	0.16	0.84	0.02	0.18	0.14
SRP	0.06	0.91	0.03	0.12	0.21
TP	0.91	0.14	0.30	0.03	-0.08
Ca ²⁺	0.82	-0.22	0.06	-0.30	0.15
Mg ²⁺	0.87	0.20	-0.10	-0.19	-0.07
Cl ⁻	0.71	0.33	-0.39	-0.26	0.19
SO ₄ ²⁻	0.64	0.10	0.69	-0.01	0.14
HCO ₃ ⁻	0.43	0.09	-0.73	-0.11	0.29
Fe _{tot}	-0.48	0.30	-0.30	0.29	0.22
Station	0.87	0.22	0.10	0.20	-0.28
Term of sampling	-0.16	0.06	-0.03	0.94	0.13
Expl.Var	6.02	4.18	2.89	2.74	1.62
Prp.Totl	0.29	0.20	0.14	0.13	0.08
Eigenvalue	7.18	4.27	2.98	1.75	1.25
% Total	34.21	20.32	14.20	8.33	5.97
Cumulative Eigenvalue	7.18	11.45	14.43	16.18	17.44
Cumulative %	34.21	54.54	68.73	77.07	83.04

Conclusion

1. The study showed that the Osówka stream waters are characterized by high variability along the road runoff. from the station near to Osówka source to stream inflow to the Rusalka lake. The biggest changes of quality occurred between the station 3 and 4 – ie. between the Goplana lake ponds Syrenie Stawy.

2. When examining the variability of water quality Osówka – if such monitoring would be carried out – should be mean. among the general indices – temperature. pH. DO. COD-Cr. COD-Mn. WS. BOD₅ and as regards the biogenic substances : NO₃⁻. NO₂⁻. NH₄⁺. TN. SPR. TP; and in terms of mineral substances: Ca²⁺. Mg²⁺. Cl⁻ and HCO₃⁻. All the above data seem to be necessary for a thorough determination of the water quality variability and to collect data to indicate what biogeochemical processes occurred in examined waters in the Osówka ecosystem. Among the 20 designated water quality indices of Osówka stream – should be examine – by our findings – 16 indices when the water sampling would be made. as it was done at 6 measuring stations located along the runoff path in terms for 4 seasons. In our opinion. sampling of water in more sampling stations and more than 4 times a year would be advisable.

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