MIDDLE POMERANIAN SCIENTIFIC SOCIETY OF THE ENVIRONMENT PROTECTION

Rocznik Ochrona Środowiska

Volume 21. Year 2019 ISSN 1506-218X 672-690

Statistical Evaluation of Variation of the River Bug Water Chemical Contamination

*Katarzyna Rymuza**, *Elżbieta Radzka*

Siedlce University of Natural Sciences and Humanities, Poland

**corresponding author's e-mail: katarzyna.rymuza@uph.edu.pl*

1. Introduction and work's aim

Surface water contamination results from natural processes (atmospheric precipitation, rock weathering, erosion) and anthropogenic ones (industrial processes and agricultural activities) (Al-Shami et al. 2011, Brankov et al. 2012, Getirana et al. 2011, Kowalik et al. 2015, Mouri 2012, Sultan 2011, Piekutin 2011, Policht-Latawiec et al. 2014). In agricultural areas, water contamination with biogenic compounds has a marked influence on the condition of biological and physio-chemical elements (Kanclerz et al. 2008). Surface water contamination may be either point source pollution or nonpoint source pollution (Gałczyńska et al. 2011, Kowalik et al. 2015, Policht-Latawiec et al. 2013). In 2014, there were operating 88 entities, including 75 municipal and 13 industrial ones, disposing of their wastewater into the environment, in the area of the River Bug catchment. Nonpoint source pollution in particular includes surface runoff from agricultural areas, runoff of rainfall from road, yard and other paved surfaces (Raport… 2015). In catchments, whose total area includes a large share of agriculturally suitable land, the surface water quality is predominantly affected by nonpoint source pollutants (Bogdał & Ostrowski 2007, Kiryluk & Rauba 2009). They pose a threat to the functioning of water ecosystems, and influence water quality, which in turn affects the attractiveness of rivers and adjoining areas (Jaskuła et al. 2015, Pytka et al. 2013). Water quality status is of special importance as far as the Rive Bug is concerned as the river, due to its marked naturalness, is called the last wild river in Europe (Kuśmierczyk 1999). The results of water monitoring provide much data which is difficult to analyse and interpret (Przybyła et al. 2015). To this end, statistical analysis methods are used, mainly descriptive statistics procedures with visualisation in the form of box plots, non-parametric tests and multidimensional analyses (Brahman et al. 2013, Grzywna et al. 2017, Kowalik et al. 2015). It was attempted in the present work to conduct a complex statistical analysis of variation in chemical parameters of the River Bug as affected by locality and season (month).

2. Materials and methods

The international catchment of the River Bug covers an area of 39.4 th km^2 and is part of the Baltic Sea basin. Almost half (49.2%) of the catchment area is located in Poland, 23.4% in Belarus and 27.4% in Ukraine. Total nitrogen and phosphorus loads from the Ukrainian stretch of the Bug as well as the Belarusian rivers Muchawca and Leśna account for around 50% of the cross-border pollution recorded in the Polish Baltic catchment area. Of the overall 10.5 th tonnes per year of cross-border nitrogen and phosphorus pollution entering the River Bug, 72% (7.6 th tonnes) originated in Ukraine, and 28% (2.9 th tonnes) in Belarus (Raport …, 2015). The Polish part of the Bug catchment is located in the following voivodeships: Lubelskie, Podlaskie and Mazowieckie. The River Bug is 772 km long. About 14% of the Bug catchment area is protected by the international, national or regional law. In the catchment area, there is located the Polish-Ukrainian International West Polesie Biosphere Reserve as well as 18 areas of the European Ecological network Nature 2000. The area is primarily devoted to agriculture. In the present work, contamination analysis of the River Bug water in Lubelskie Voivodeship was undertaken. The Bug water quality examination is performed by the Voivodeship Inspectorate for Environmental Protection in Lublin (WIOŚ). Hydrothermal conditions are presented in figure 1.

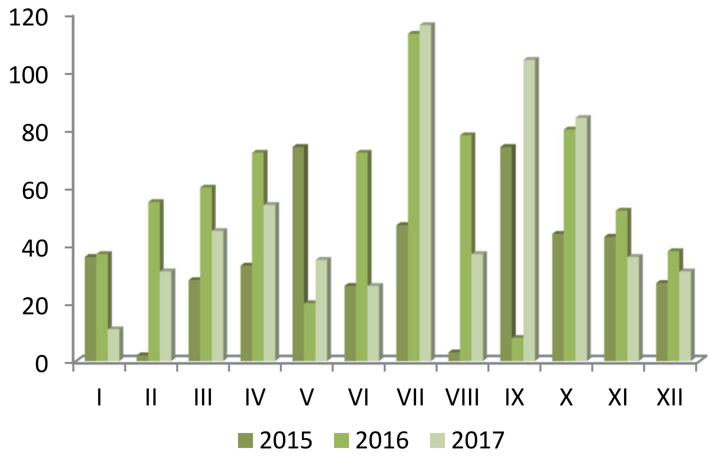

Fig. 1. Precipitation at the Włodawa station in 2015-2017

Analysis was based on the data of monitoring carried out in 2015-2017 at eight measurement points: Kryłów, Zosin, Horodło, Dorohusk, Włodawa, Kuzawka, Kukuryki and Krzyszew (Fig. 2) in February, April, June, August, October and December. The distances between the measurement points were 40, 10, 39, 59, 19, 43, 9.6 km, respectively. Throughout these months, readings were taken at all the localities during three years. As a result, data analysis was conducted for each locality based on eighteen measurements.

Fig. 2. Location of measurement points

The following chemical parameters were analysed: X_1 − dissolved oxygen (mg O_2/l), X_2 – BOD (mg O_2/l), X_3 – sulphates (mg SO_4/l), X_4 – chlorides (mg Cl/l), X_5 – total phosphorus (mgP/l). X_6 – ammonium nitrogen (mg N-NH_4/l), X_7 – nitrate nitrogen (mgN-NO_3/l) and X_8 – nitrite nitrogen (mg N-NO_2/l). Experimental factors were localities and months when measurements were taken. The first stage of statistical analysis involved checking whether the localities and months had an influence on variation in chemical parameters. To that end, a two-way analysis of variance and the Kruskal-Walis test were applied.

Two-way analysis of variance was applied for normally distributed variables (X_1-X_5). It followed the linear model for a completely randomised design:

$$y_{ijl} = m + a_i + b_j + ab_{ij} + e_{ijl} \quad (1)$$

where:
y_{ijl} – value of the examined characteristic,
m − population mean,

a_i – effect of the i-th level of factor A (localities),
b_j – effect of the j-th level of factor B (month of measurement),
ab_{ij} – effect of interaction A x B, e_{ijl} – random error.
Means were separated using Tukey test at $p \leq 0.05$.

For traits X_6-X_8, which were not normally distributed, transformations were used (Bliss, log and arc sin transformation) but they were not effective so Kruskal-Wallis test was applied. Differences between groups were checked by means of multiple comparisons test.

Principal component analysis and cluster analysis were used in order to assess the complex variation in localities in individual months in terms of all the analysed characteristics (chemical parameters). Principal component analysis is a technique of dimension reduction. It transforms original variables into new, non-correlated variables called principal components. They explain to the greatest degree the total variance of a sample of *p* primary variables $x_1, \ldots, x_p$, that is the value:

$$\sum_{j=1}^{p} s_j^2 = tr(S), \tag{2}$$

where:
S – sample covariance matrix,
tr – trace of the matrix,
s_j^2 – variance of the variable x_j, j = 1, …, p (Krzyśko 2009).

The first principal component reduces the greatest amount of this variation, the second one reduces the second greatest part of the variation which has not been reduced by the first component, etc.

Analysed and interpreted were the components whose eigenvalue, according to the Kaiser's criterion, was higher than 1 (Kaiser 1958).

Cluster analysis was performed on the basis of the principal components. The analysis is a tool used for grouping *n* objects described by means of a vector of *p* characteristics. It involves grouping of objects which are similar in terms of many characteristics. The groups are determined by means of measures of distance, the Euclidean distance being used in the analysis reported here:

$$d(x_r, x_s) = \sqrt{\sum_{i=1}^{p} (x_{ri} - x_{si})^2}, \tag{3}$$

where:
x_r and x_s – p-dimensional vectors of observation of r-th and s-th object (r, s = 1, 2, …, n) (Marek 1989; Krzyśko 2009).

Ward method, in which sums of squares of deviations within clusters are kept to a minimum, was used in order to estimate the distance between clusters. Mojena rule was applied to determine the cut-off point of the dendrogram (cluster similarity level). The cut-off point is the bond distance for which the following inequality is true:

$$d_{i+1} > \bar{d} + ks_d; \quad (4)$$

where:
$\bar{d}$ and s_d – respectively, mean and standard deviation of d_i,
k – a value within the range 2.75 to 3.50 (Mojena 1977). The value k was selected to be 1.25 as recommended by Milligan and Cooper (1985).
All the calculation were performed in STATISTICA 12.0.

3. Results and discussion

Variance analysis demonstrated significant differences between dissolved oxygen contents in the water of the River Bug stretching from Zosin to Krzyszew. The highest average value of this parameter was observed in Włodawa (10.91 mg O_2/l), Kuzawka (10.77 mg O_2/l) and Dorohusk (10.16 mg O_2/l), and it was significantly higher than in the stretch between Zosin and Kryłów. The amount of dissolved oxygen in Krzyszewo and Kukuryki did not differ significantly from values at the remaining measurement points (tab. 1). Statistical analysis confirmed there were differences in dissolved oxygen content between seasons of the year. Regardless of the measurement point, in the winter months (December and February) dissolved oxygen content was higher than in the summer months (August and June) (Tab. 2). Oxygen content and temperature are the parameters which condition life in the water environment. Also, they are interrelated: oxygen solubility in water is temperature-related and it declines as temperature increases (Kowalik et al. 2015).

Total phosphorus content in water changed along the river course, it being the highest from Kiryłów to Zosin and from Kururyki to Krzyszewo. Phosphorus content in the analysed three-year period was the lowest from Dorohusk to Kuzawka. Phosphorus content in water was significantly affected by season of the year, it being the highest in October and the lowest in April. The concentration of this element in December did not differ from the content in October and February. Statistical analysis demonstrated a significant interaction between localities and month of measurement, which means that phosphorus content for localities dvaried in individual months (Fig. 3). The average phosphorus content in Kryłów, Horodło and Zosin was statistically the same and ranged from 0.207 to 0.363 mg P/l. In Dorohusk, Włodawa and Kuzawka, phosphorus content, averaged across the three study years, was the highest in October and the lowest in April. The respective values were 0.303, 0.347, and 0.327 mg/l in October, and 0.220, 0.110, and 0,113mg/l in April. Phosphorus content in water between Kukuryki to Krzyszew was the lowest in April as well (0.173 and 0.143 mg/l, respectively). Changes in river water chemical composition are caused by surface run-offs from fields fertilised with organic manures and mineral fertilisers which contain high amounts of substances applied seasonally. A higher water content of phosphorus in autumn was reported by Igras & Jadczyszyn (2011) whereas Jaskuła et al. (2015) claimed that a decline in the concentration of phosphorus compounds from January to April may be due to dilution of wastewater caused by more intense flows. High amounts of phosphorus enter the water environment with sewage from households and farm buildings (Dąbkowski & Pawłat-Zawrzykraj 2003, Kiryluk & Ruba 2011, Krasowska 2017).

Sulphate content was related to localities and months of measurement. No significant interaction between the aforementioned factors was observed, which is indicative of the fact that at all the measurement points, the distribution of sulphate content in months was similar. The highest and comparable concentration of sulphates was recorded in Kryłów (89.02 mg SO_4/l), Zosin (81.34 mg SO_4/l) and Horodło (76.67 mg SO_4/l). Sulphates were significantly lower in water from Dorohusk (68.11 mg SO_4/l) through Włodawa (70.39 mg SO_4/l) to Kuzawka (66.00 mg SO_4/l), it being the lowest in Kukuryki (54.44 mg SO_4/l) and Krzyszew (52.89 mg SO_4/l) (tab. 1). The lowest sulphate content was recorded in August (58.41 mg SO_4/l), and the highest in December (86.62 mg SO_4/l). Also Krasowska (2017) recorded the highest concentration of sulphates in December, which according to the author, was due to a low water level. In the period February-June, sulphate content remained at a similar level (Tab. 2).

Chloride content was significantly affected by localities and months. No statistically significant location x month interaction was confirmed. The highest chloride content was determined in the river stretch from Kryłów to Zosin, it being the lowest in Kuzawka and Krzyszew. The amount of this substance in Kukuryki was similar to the quantity determined in Włodawa.

Analysis of variance revealed that, in the three-year study period, BOD values at the measurement points were similar, them being affected by the study months only. An interaction between months and measurement points for this characteristic was insignificant. The lowest BOD value was found in October (3.14 mg O_2/l) and December (3.54 mg O_2/l), it being the highest in June (4,21 mg O_2/l) and August (4,35 mg O_2/l). BOD values in February and April differed insignificantly from values determined for the remaining months.

Table 1. Average dissolved oxygen content, total phosphorus content, sulphates, chlorides and BOD by locality

Locality	Dissolved oxygen	Total phosphorus	Sulphates	Chlorides	BOD
Dorohusk	10.16^{a}	0.24^{b}	68.11^{b}	36.94^{cd}	3.89^{a}
Horodło	9.70^{b}	0.28^{a}	76.67^{ab}	39.82^{bc}	3.94^{a}
Kryłów	9.40^{b}	0.31^{a}	89.02^{a}	46.39^{a}	3.78^{a}
Krzyszew	9.82^{ab}	0.26^{ab}	52.89^{c}	31.61^{de}	3.83^{a}
Kukuryki	9.88^{ab}	0.30^{a}	54.44^{c}	34.13^{de}	4.05^{a}
Kuzawka	10.77^{a}	0.22^{b}	66.00^{bc}	31.50^{e}	3.62^{a}
Włodawa	10.91^{a}	0.24^{b}	70.39^{b}	32.94^{de}	3.42^{a}
Zosin	9.41^{b}	0.28a	81.34^{a}	43.14^{ab}	3.76^{a}

Means followed by the same letters (in columns) differ insignificantly at $p \leq 0.05$.

Table 2. Average dissolved oxygen content, total phosphorus content, sulphates, chlorides and BOD by month

Month	Dissolved oxygen	Total phosphorus	Sulphates	Chlorides	BOD
February	10.64^{ab}	0.25^{b}	72.67^{b}	34.15^{b}	3.81^{ab}
April	9.87^{bc}	0.18^{c}	71.12^{b}	31.85^{b}	3.67^{ab}
June	9.39^{cd}	0.29^{ab}	64.00^{bc}	32.68^{b}	4.21^{a}
August	8.71^{d}	0.26^{b}	58.41^{bc}	40.67^{a}	4.35^{a}
October	9.79^{bcd}	0.33^{a}	66.32^{bc}	43.63^{a}	3.14^{b}
December	11.64^{a}	0.29^{ab}	86.62^{a}	39.40^{a}	3.54^{b}

Means followed by the same letters (in columns) differ insignificantly at $p \leq 0.05$.

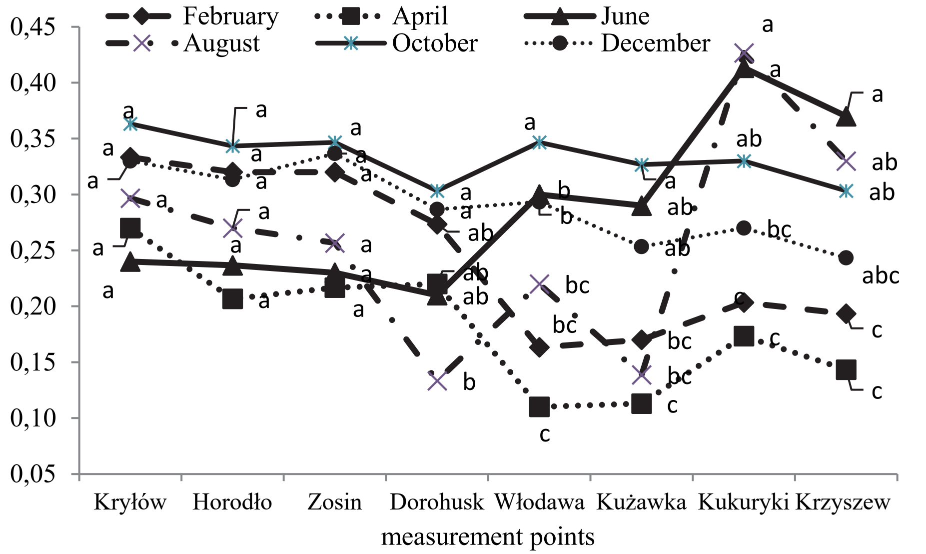

Fig. 3. Total phosphorus content by locality and month
Means accompanied by the same letters (between measurement points) differ insignificantly at $p \leq 0.05$

Ammonium nitrogen content differed at localities, it being the highest in Kukuryki (0.65 mg $N\text{-}NH_4$/l) and Krzyszew (0.56 mg $N\text{-}NH_4$/l). The amount of $N\text{-}NO_4$ in Kukuryki differed significantly from values determined at the remaining measurement points. Moreover, the concentration of this parameter in Krzyszew differed significantly from the content in Dorohusk, Włodawa and Kuzawka. Ammonium nitrogen content was also affected by months, it being higher in December and February than in the remaining months (Fig. 4). In months with higher temperatures, the concentration of ammonium ions is lower due to nitrification and utilisation of ammonium nitrogen by plants (Ligocka 2018). In contrast, in the period when temperatures are lower the concentration of ammonium ions increases (Gałczyńska et al. 2009).

The concentration of nitrate nitrogen in Kryłów, Zosin and Horodło was the highest, as indicated by the maximum values and medians. The highest variation in this characteristic was recorded in Dorohusk, Włodawa and Kuzawka. Nitrate nitrogen content was the lowest and the least variable in August, and the highest in February and December (Fig. 5).

Nitrite nitrogen content in Włodawa, Kuzawka and Kukuryki was lower than in Zosin and Horodło. The Kruskal-Walis test revealed that this parameter was affected by months, whereas the test of multiple comparisons demonstrated that nitrite nitrogen content in October differed from values for the remaining months. The concentration of this substance had the highest median and the greatest variation (Fig. 6). According to Sullivan and Drever (2001) as well as Clark et al. (2004), changes in the concentration of biogenes, nitrates in particular, are associated with the season. A decline in the substances in the spring-summer period may be due to increased decomposition of organic matter.

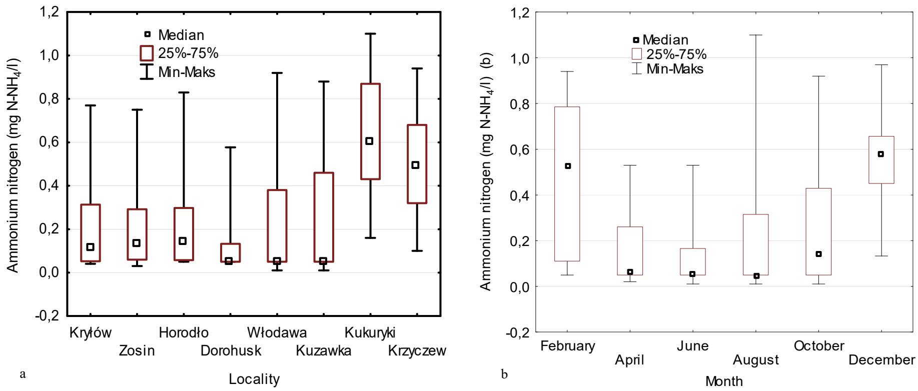

Fig. 4. Total ammonium nitrogen by locality (a) and month (b)

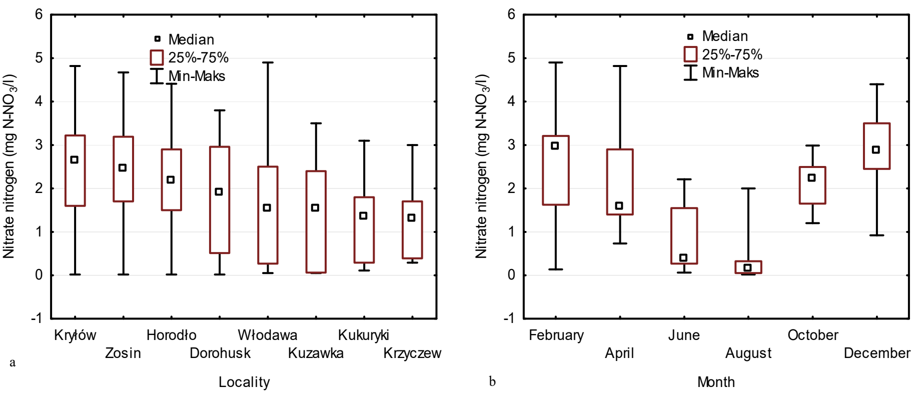

Fig. 5. Total nitrate nitrogen by locality (a) and month (b)

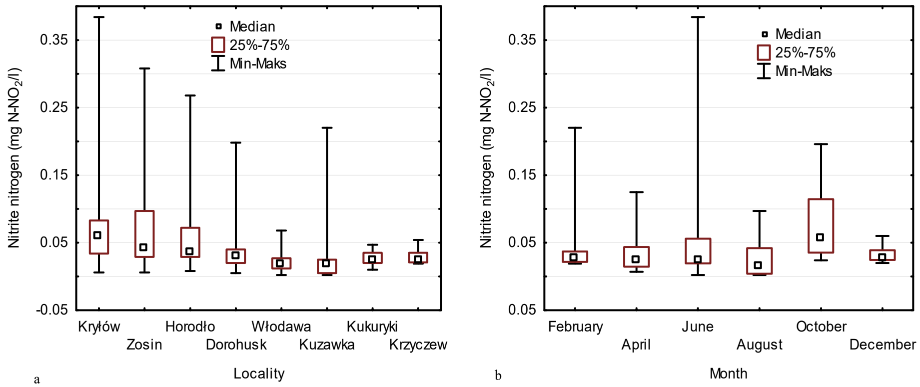

Fig. 6. Total nitrite nitrogen by locality (a) and month (b)

Table 3. Values of Kruskal-Wallis test (H) checking significance of differences between localities and months

	Ammonium nitrogen	Nitrate nitrogen	Nitrite nitrogen
Locality			
Value of the test H	48.61(p = 0.000)	14.96 (p = 0.031)	39.95 (p = 0.000)
Month			
Value of the test H	42.37 (p = 0.000)	78.54 (p = 0.000)	24.68 (p = 0.000)

The applied methods made it possible to compare both localities and months, viewed separately, in terms of the concentration of many chemical parameters. Assessment of variation of objects and their simultaneous grouping according to many characteristics may be achieved by means of multidimensional analyses (Mądry 2007). Multi-trait variation between localities in individual months was assessed using principal component analysis. In February, three principal components accounted for over 91% of variation between localities, the first components explaining over 50% of this variation (Tab. 4). The following characteristics were the most strongly associated with PC1: total phosphorus content, ammonium nitrogen content, sulphates, BOD and chlorides. Mutual multidimensional relationships showed that at localities where phosphorus content was higher, higher concentrations of sulphates, chlorides and BOD where determined in addition to a lower ammonium nitrogen content. Negative associations between ammonium nitrogen content and phosphorus content were reported by Ligocka (2018).

Table. 4. Eigenvalues, share of principal components in the overall variation and correlation coefficients between the components and water chemical parameters

Item	February			April	
	PC1	PC2	PC3	PC1	PC2
X_1 – Dissolved oxygen	0.537	-0.801	-0.096	0.769	0.405
X_2 – BOD	0.827	0.102	-0.442	-0.474	-0.618
X_3 – Sulphates	0.872	0.176	0.424	-0.753	0.504
X_4 – Chlorides	0.785	0.564	0.087	-0.957	0.183
X_5 – Ammonium nitrogen	-0.911	0.348	-0.044	-0.025	-0.859
X_6 – Nitrate nitrogen	0.257	-0.751	0.491	-0.959	0.124
X_7 – Nitrite nitrogen	-0.061	0.331	0.821	-0.997	0.062
X_8 – Total phosphorus	0.932	0.300	-0.147	-0.932	-0.118
Eigenvalue	4.115	1.885	1.330	5.08	1.60
Cumulative variance (%)	51.45	75.01	91.64	63.5	83.56

	June		August		
	PC1	PC2	PC1	PC2	PC3
X_1 – Dissolved oxygen	0.665	0.693	0.905	0.257	0.113
X_2 – BOD	0.978	0.055	-0.648	-0.040	0.734
X_3 – Sulphates	-0.906	0.277	0.924	-0.345	0.144
X_4 – Chlorides	-0.943	-0.142	0.433	-0.749	0.491
X_5 – Ammonium nitrogen	0.542	-0.830	-0.806	-0.351	-0.302
X_6 – Nitrate nitrogen	-0.975	-0.207	0.699	-0.648	-0.261
X_7 – Nitrite nitrogen	-0.955	-0.217	-0.084	-0.961	-0.207
X_8 – Total phosphorus	0.871	-0.410	-0.646	-0.733	0.078
Eigenvalue	6.02	1.52	3.84	2.75	1.02
Cumulative variance (%)	75.28	94.40	48.04	82.44	95.22

	October			December	
	PC1	PC2	PC3	PC1	PC2
X_1 – Dissolved oxygen	0.821	0.496	0.141	0.816	-0.546
X_2 – BOD	-0.688	-0.599	-0.374	-0.869	0.394
X_3 – Sulphates	-0.956	0.203	-0.071	-0.886	-0.425
X_4 – Chlorides	-0.694	-0.501	0.515	-0.991	0.035
X_5 – Ammonium nitrogen	0.585	-0.723	-0.316	0.812	0.324
X_6 – Nitrate nitrogen	-0.930	0.269	-0.061	-0.830	-0.452
X_7 – Nitrite nitrogen	0.359	-0.774	-0.070	-0.951	0.228
X_8 – Total phosphorus	0.073	-0.303	0.949	-0.923	-0.025
Eigenvalue	3.88	2.18	1.44	6.20	1.02
Cumulative variance (%)	48.57	75.85	93.83	78.64	91.11

The second principal component was the most strongly associated with dissolved oxygen content and nitrate nitrogen. At localities where dissolved oxygen content was higher, there was more nitrate nitrogen in water. The third principal component was most strongly correlated with nitrite nitrogen. In April, variation between localities was to the greatest extent affected by nitrogen content (nitrite nitrogen and nitrate nitrogen associated with PC1, and ammonium nitrogen associated with PC2), phosphorus content and chlorides. In June, the first two principal components accounted for over 90% of variation between localities, the parameters with the greatest influence being BOD, nitrate and nitrite nitrogen contents, chlorides, sulphates and phosphorus content. In August, multi-variable differences between river stretches were associated with dissolved oxygen content, nitrite and ammonium nitrogen contents as well as total phosphorus content. The characteristics which affected the multi-trait variation between the measurement points in October included: nitrate nitrogen, sulphates and dissolved oxygen content, all of them being associated with the first principal component which accounted for 48.57% of variation. The second principal component carried information on chlorides whereas the third component was associated with phosphates. PCA demonstrated that in December variation between localities was affected by most of the parameters associated with the first principal component accounting for 78.64% of variation, in particular nitrite nitrogen, total phosphorus and chlorides. Similar associations resulting from principal component analysis were reported by Przybyła et al. (2015) who demonstrated that for river waters the following parameters were positively correlated with the first principal component: dissolved oxygen content, calcium content, magnesium content and water hardiness whereas chlorides, phosphates and conductivity were associated with the second component. Similarly to research by Krasowska (2017), PCA made it possible to analyse season-related variation in the concentration of chemical substances in rivers.

Cluster analysis conducted based on principal components enabled classification of measurement points into two or three groups characterised by different chemical parameters according to month in which measurements were taken. Three groups were formed in August only. The first group was made up of Horodło, Kryłów and Zosin, the second one included Krzyszew and Kukuryki whereas the third one consisted of Włodawa, Kuzawka and Dorohusk. In the remaining months, two clusters were formed. The first cluster of localities with similar chemical parameters was formed by Krzyszew, Kukuryki, Włodawa as well as Kuzawka, and the second one by Zosin, Horodło, Kryłów and Dorohusk (Fig. 7).

Table 5. Average values of characteristics for groups of localities formed based on cluster analysis

Group	Dissolved oxygen	BOD	Sulphates	Chlorides	Ammonium nitrogen	Nitrate nitrogen	Nitrite nitrogen	Total phosphorus
February								
1	10.40	3.24	64.92	29.83	0.69	2.49	0.04	0.18
2	10.88	4.38	81.02	38.48	0.24	2.58	0.04	0.31
April								
1	10.27	3.58	63.50	27.08	0.19	1.28	0.02	0.13
2	9.49	3.77	78.76	36.62	0.13	2.95	0.06	0.23
June								
1	10.39	5.36	54.33	28.33	0.16	0.27	0.02	0.34
2	8.39	3.06	73.68	37.03	0.07	1.28	0.12	0.23
August								
1	9.22	4.28	76.29	45.11	0.15	1.03	0.04	0.26
2	7.78	4.43	42.17	37.50	0.60	0.23	0.04	0.34
3	9.17	4.34	57.49	37.63	0.13	0.11	0.01	0.20
October								
1	10.23	3.57	69.28	34.10	0.64	2.26	0.05	0.23
2	11.05	4.06	76.66	34.21	0.28	2.81	0.03	0.27
December								
1	12.08	3.09	76.75	34.75	0.66	2.58	0.02	0.27
2	11.20	3.98	96.50	44.06	0.43	3.28	0.04	0.32
3	9.22	4.28	76.29	45.11	0.15	1.03	0.04	0.26

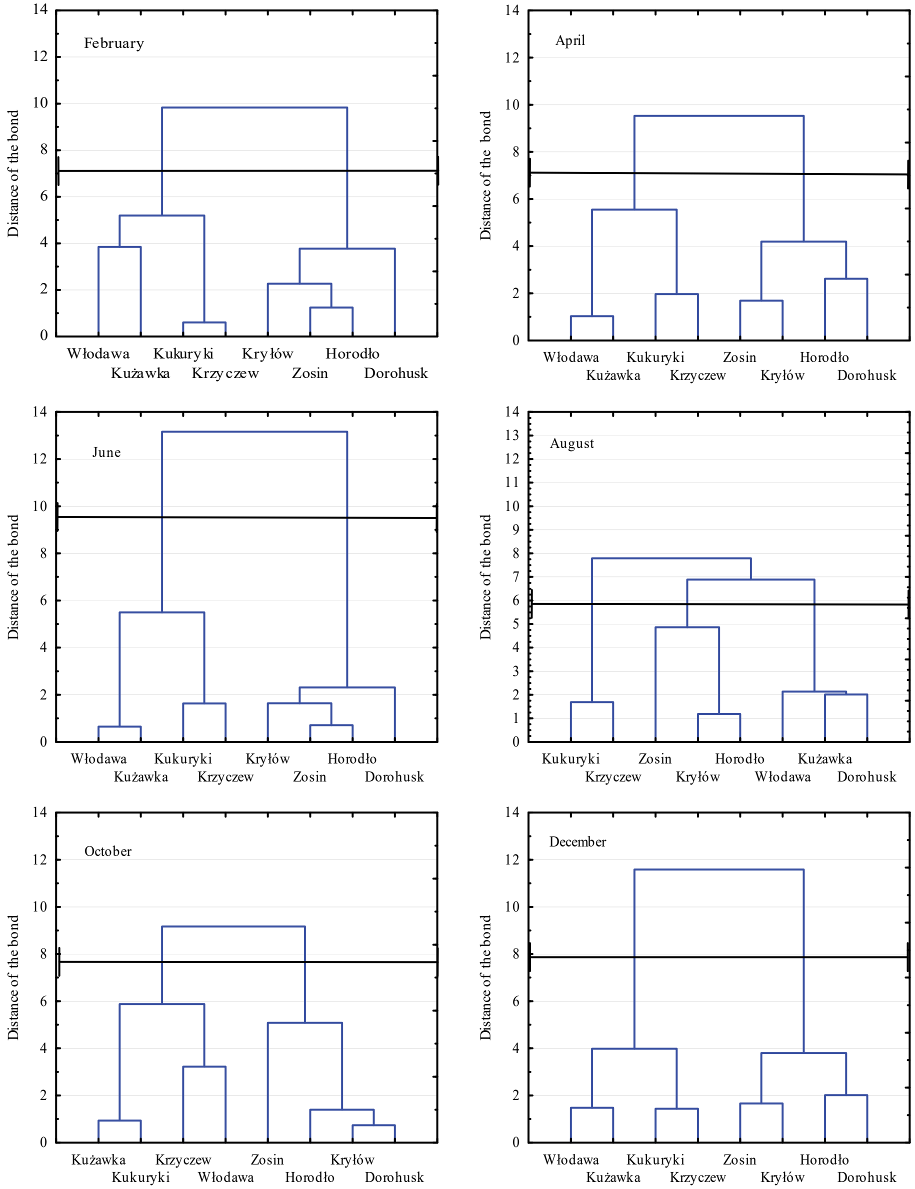

Fig. 7. Dendrogram of division of measurement points

The average ammonium nitrogen content was higher in localities forming the first cluster (ranging from 0.19 to 0.69 mg/l depending on the month). Moreover, at these measurement points, there were recorded higher dissolved oxygen contents in April (10.27 mg/l), June (10.39 mg/l) and December (12.08 mg/l), as well as phosphorus in June (0.34 mg/l). In August, the lowest average sulphate content (42.17 mg/l) and dissolved oxygen content (7.78 mg/l) were determined in Krzyszew and Kukuryki (group 2) in addition to the highest ammonium nitrogen content (0.60 mg/l), phosphorus content (0.34 mg/l) and BOD (4.43). The average dissolved oxygen content (9.22 mg/l), sulphates (76.29 mg/l) and nitrate nitrogen content (1.03 mg/l) were the highest in Horodło, Kryłów and Zosin (group 1). Localities which formed group 3 (Włodawa, Kuzawka and Dorohusk) had a relatively high average dissolved oxygen content (9.17 mg/l), and the lowest amount of nitrite nitrogen (0.01 mg/l) and total phosphorus (90.20 mg/l) (Tab. 5).

4. Conclusions

The concentration of chemical substances and compounds in the River Bug differed at individual measurement points (localities) and in study months.

Phosphorus content, sulphates and chlorides declined along the course of the river. BOD did not differ at individual localities. Dissolved oxygen content was the highest in the stretch from Dorohusk to Włodawa. Ammonium nitrogen content was the highest in Kukuryki and Kuzawka whereas nitrate and nitrite nitrogen contents were the highest from Zosin to Horodło.

In winter months, there was an increase in the concentration of ammonium ions, dissolved oxygen content, sulphates and chlorides. In the summer, BOD and phosphorus content were on the increase whereas sulphates and nitrate nitrogen content declined.

Principal component analysis demonstrated that differences in the chemical sta tus of the River Bug water between the measurement points resulted mainly from the concentration of nitrogen compounds, total phosphorus content and chlorides.

Cluster analysis made it possible to divide the analysed stretch of the River Bug into two parts with different chemical status in February, April, June, October and December. The first part included the following measurement points: Krzyszew, Kukuryki, Włodawa and Kuzawka, all of which had higher average concentrations of ammonium nitrogen, dissolved oxygen and total phosphorus. The second part, consisting of Kryłów, Zosin and Horodło, was characterised by increased average concentrations of BOD, sulphates and chlorides.

In August, the examined river stretch was divided into three clusters. The first cluster was made up of Horodło, Kryłów and Zosin which had the highest dissolved oxygen content, sulphates and nitrate nitrogen. The second cluster, characterised by the highest average dissolved oxygen content and sulphates, consisted of Krzyszew and Kukuryki whereas the third cluster (Włodawa, Kuzawka and Dorohusk) included localities with the lowest amount of nitrite nitrogen and total phosphorus.

References

Al-Shami, S.A., Rawi, Ch.S.M., Ahmad A.H., Hamid, S.A., Nor, S.A.M. (2011). Influence of agricultural, industrial, and anthropogenic stresses on the distribution and diversity of macroinvertebrates in Juru River Basin, Penang, Malaysia. *Ecotoxicology and Environmental Safety*, *74*, 1195-1202.

Bogdał, A., & Ostrowski, K. (2007).Wpływ rolniczego użytkowania zlewni podgórskiej i opadów atmosferycznych na jakość wód odpływających z jej obszaru. *Woda − Środowisko − Obszary Wiejskie, 7. Z. 2a (20),* 59-69.

Brahman, K. D., Kazi, T. G., Afridi, H. I., Naseem, S., Arain, S. S., Wadhwa, S. K., Shah, F. (2013). Simultaneously evaluate the toxic levels of fluoride and arsenic species in underground water of Tharparkar and possible contaminant sources. A multivariate study. *Ecotoxicology and Environmental Safety*, *89*, 95-107.

Brankov, J., Milijasević, D., Milanović, A. (2012). The assessment of the surface water quality using the water pollution index: a case study of the Timok River (the Danube River Basin), Serbia. *Archives of Environmental Protection*, *38(2)*, 49-61.

Clark, M.J., Cresser, M.S., Smart, R., Chapman, P.J., Edwards, A.C. (2004). The influence of catchment characteristics on the seasonality of carbon and nitrogen species concentrations in upland rivers of Northern Scotland, *Biogeochemistry*, *68*, 1-19.

Dąbkowski, S.L. & Pawłat-Zawrzykraj, A. (2003). Jakość wód Raszynki i jej dopływów. *Woda – Środowisko – Obszary Wiejskie*, *3 z specj. (6),* 111-123.

Dąbrowska, A., A Bawiec, A., Pawęska, K., Kamińska, J., Stodolak, R. (2017). Assessing the impact of wastewater effluent diversion on water quality. *Pol. J. Environ. Stud., 26(1),* 9-16.

Gałczyńska, M., Gamrat, R., Pacewicz, K. (2011). Influence of different uses of the environment on chemical and physical features of small water ponds. *Pol. J. Environ. Stud*, *20(4),* 885-894.

Gałczyńska, M., Burczyk, P., Gamrat, R. (2009). Próba określenia wpływu rodzaju uprawy na stężenie związków azotu i fosforu w wodach wybranych śródpolnych oczek wodnych na Pomorzu Zachodnim. *Woda − Środowisko − Obszary Wiejskie*, *9, 4(28),* 47-57.

Getirana, A.C.V., Espinoza, J.C.V., Ronchail J., Rotunno Filho, O.C. (2011). Assessment of different precipitation datasets and their impacts on the water balance of the Negro River basin. *Journal of Hydrology*, 404, 304-322.

Grzywna, A., Sender, J., Bronowicka-Mielniczuk, U. (2017). Analysis of the ecological status of surface waters in the Region of the Lublin Conurbation. *Rocznik Ochrona Środowiska, 19*, 439-450.

Igras, J., Jadczyszyn, T. (2011). Zawartość azotanów i fosforanów w płytkich wodach gruntowych w Polsce. *Problemy Inżynierii Rolniczej*, *5*, 91-101.

Jaskuła J., Sojka M., Wicher-Dysarz, J. (2015). Analiza tendencji zmian stanu fizyko-chemicznego wód rzeki głównej. *Inżynieria Ekologiczna* , *44*, 154-161.
Kaiser, H.F., (1958). The varimax criterion for analytic rotation in factor analysis. *Psychometrica, 23*, 187-200.
Kanclerz, J., Murat-Błażejewska, S., Sojka, M., Przybyła ,A. (2008). Zmiany jakości wody i struktury ichtiofauny rzeki nizinnej w latach 2000-2009. *Infrastruktura i Ekologia Terenów Wiejskich*, *9*, 145-155.
Kiryluk, A., & Rauba, M. (2009). Zmienność stężenia związków azotu w różnie użytkowanej zlewni rolniczej rzeki Ślina. *Woda − Środowisko − Obszary Wiejskie*, *9, 4 (28),* 71-86.
Kiryluk, A., & Ruba, M. (2011). Wpływ rolnictwa na stężenie fosforu ogólnego w wodach powierzchniowych zlewni rzeki Śliny. *Inżynieria Ekologiczna*, 26, 122-132.
Kowalik, T., Kanownik, W., Bogdał, A., Policht-Latawiec, A. (2015). Wpływ zmian użytkowania zlewni wyżynnej na kształtowanie jakości wody powierzchniowej. *Rocznik Ochrona Środowiska*, *16(1),* 223-238.
Krasowska, M. (2017). Sezonowe zmiany składu chemicznego wód rzecznych w zlewni rolniczej *Inżynieria Ekologiczna Ecological Engineering, 18(3),* 175-183.
Krzyśko, M., (2009). *Podstawy wielowymiarowego wnioskowania statystycznego*. Poznań: Wyd. Nauk. UAM Poznań.
Kuśmierczyk, J. (1999). *Zagrożenia ekologiczne dotyczące doliny Bugu i możliwości ich minimalizowania,* [w:] Kozłowski S.(red.), Bug – europejski korytarz ekologiczny, Ekologiczny Klub UNESCO, Pracownia Na Rzecz Bioróżnorodności, Piaski, 103-114.
Ligocka, K. (2018). Monitoring stężeń biogenów w wodzie powierzchniowej małego śródpolnego zbiornika wodnego położonego w zlewni rolniczej. *Inżynieria Ekologiczna Ecological Engineering, 19(2)*, 9-14
Marek, T., 1989. *Analiza skupień w badaniach empirycznych. Metody SAHN*. Warszawa: PWN.
Mądry, W., (2007). Metody statystyczne do oceny różnorodności fenotypowej dla cech ilościowych w kolekcjach roślinnych zasobów genowych. *Zesz. Probl. Post. Nauk Rol. 517*, 21-41.
Milligan, G.W., & Cooper, M., 1985. An examination of procedures for determining the number of clusters in a data set. *Psychometrica, 50(2),* 159-179.
Mojena, R., (1977) . Hierarchical grouping methods and stopping rule: an evaluation. *The Computer J., 20*, 359-363.
Mouri, G., Shinoda, S., Oki, T. (2012). Assessing environmental improvement options from a water quality perspective for an urban-rural catchment. *Environmental Modelling & Software, 32*, 16-26.
Piekutin, J. (2011). Zanieczyszczenie wód produktami naftowymi. *Rocznik Ochrona Środowiska, 13*, 1905-1914.
Policht-Latawiec, A., Bogdał, A., Kanownik, W., Kowalik, T., Ostrowski, K., Gryboś P. (2014). Jakość i walory użytkowe wody małej rzeki fliszowej. *Rocznik Ochrona Środowiska, 16*, 546-556.

Policht-Latawiec, A., Kanownik, W., Łukasik,, D. (2013). Wpływ zanieczyszczeń punktowych na jakość wody rzeki San. *Infrastruktura i Ekologia Terenów Wiejskich, 1(4),* 253-269.

Przybyła, Cz., Kozdrój, P., Sojka, M. (2015).Wykorzystanie wielowymiarowych metod statystycznych w analizie stanu fizykochemicznego wód w systemie rzeka – zbiornik retencyjny na przykładzie zbiorników retencyjnych Pakosław i Jutrosin położonych w zlewni rzeki Orli. *Rocznik Ochrona Środowiska* , *17*, 1125-1141.

Pytka, A., Jóźwiakowsk, K., Marzec, M., Gizińska, M., Sosnowska, B. (2013*).* Ocena wpływu zanieczyszczeń antropogenicznych na jakość wód rzeki Bochotniczanki. *Infrastruktura i Ekologia Terenów Wiejskich, 3*, 15-29.

Raport o jakości wód rzeki Bug i jej dopływów w latach 2005-2014. (2015). Inspekcja Ochrony Środowiska Wojewódzki Inspektorat Ochrony Środowiska w Lublinie, Lublin 2015, 20.

Sullivan, A.B., & Drever, J.I. (2001). Spatiotemporal variability in stream chemistry in a high-elevation catchment affected by mine drainage*, J. Hydrol., 252*, 240-253.

Sultan, K., Shazili N.A., Peiffer, S. (2011). Distribution of Pb, As, Cd, Sn and Hg in soil, sediment and surface water of the tropical river watershed, Terengganu (Malaysia). *Journal of Hydroenvironment Research*, *5*, 169-176.

Abstract

The work presents analysis of chemical condition of the water of the River Bug stretch extending from Kiryłowo to Krzyszew. The analysis was preformed based on data of monitoring of surface water quality available on the website of Voivodeship Inspectorate of Environmental Protection in Lublin (WIOŚ) spanning the years 2015-2017. Eight measurement points and the following months were considered: February, April, June, August, October and December. Analysis of variance and Kruskal-Wallis test were used to analyse the effect of localities and months on selected chemical indicators. The concentrations of nearly all the parameters (excluding BOD) were found to be influenced by the localities. Phosphorus content, sulphates and chlorides increased along the course of the river. Also, the analysis revealed that the concentration of ammonium ions, dissolved oxygen, sulphates and chlorides increased in winter. Multidimensional analysis demonstrated that differences in chemical conditions between the localities were predominantly due to nitrogen compound content, total phosphorus content and chlorides. Cluster analysis showed that in nearly all the months (excluding August) the tested stretch of the River Bug could be divided into two parts with different chemical composition parameters. The first part, characterised by higher average values of ammonium nitrogen content, dissolved oxygen content and total phosphorus content, included the following measurement points: Krzyszew, Kukuryki, Włodawa and Kuzawka. The second part was formed by the following localities: Kryłów, Zosin and Horodło, all with higher average BOD values, sulphates and chlorides.

Keywords:
the River Bug, chemical contaminants, principal component analysis, cluster analysis, analysis of variance.

Statystyczna ocena zmienności zanieczyszczenia chemicznego wód rzeki Bug

Streszczenie

W pracy przedstawiano analizę chemicznego stanu wód rzeki Bug na odcinku od Kryłowa do Krzyszewa. Analizy tej dokonano na podstawie danych pochodzących z monitoringu jakości wód powierzchniowych zamieszczonych na stronie Wojewódzkiego Inspektoratu Ochrony Środowiska w Lublinie (WIOŚ) z lat 2015-2017. Pod uwagę wzięto dane z lutego, kwietnia, czerwca, sierpnia, października i grudnia z 8 punktów pomiarowych. Przy pomocy analizy wariancji oraz testu Kruskala-Wallisa przeanalizowano wpływ miejscowości oraz miesięcy na zawartość wybranych wskaźników chemicznych. Stwierdzono, że zawartość prawie wszystkich parametrów (poza BZT5) różnicowana była przez miejscowości. Wraz z biegiem rzeki zmniejszała się zawartość fosforu, siarczanów i chlorków. Analiza wykazała ponadto, że zimą rosło stężenie jonów amonowych, zawartość tlenu rozpuszczonego, siarczanów i chlorków. Wielowymiarowa analiza natomiast dowiodła, że różnice stanu chemicznego pomiędzy miejscowościami związane były głównie z zawartością związków azotu, fosforu ogólnego oraz chlorków. Na podstawie analizy skupień prawie we wszystkich miesiącach (poza sierpniem) odcinek rzeki Bug pod względem stanu chemicznego można podzielić na dwie części. Pierwszą grupę stanowi odcinek rzeki z punktami pomiarowymi w Krzyszewie, Kukurykach, Włodawie i Kuzawce o większych średnich zawartościach azotu amonowego, tlenu rozpuszczalnego i fosforu ogólnego. Drugą grupę utworzyły miejscowości: Kryłów, Zosin i Horodło o wyższych średnich stężeniach BTZ_5, siarczanów i chlorków.

Słowa kluczowe:
rzeka Bug, zanieczyszczenia chemiczne analiza składowych głównych, analiza skupień, analiza wariancji.