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# Spatio-temporal changes of water pollution, and its sources and consequences in the Bug River, Poland

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## ABSTRACT

An analysis of 17 physicochemical parameters of water of the Bug River in the period 2010–2019 was carried out at ten stations and throughout four seasons. A spatio-temporal analysis was performed on this database. Based on the cluster analysis, four clusters of stations were distinguished. There were statistically significant differences between the clusters and between the seasons (Kruskal–Wallis test). Average concentrations of parameters meet the standards of good ecological status. The spatial variability between the station was related to the content of nitrogen and phosphorus compounds and the amount of oxygen. The analysis of seasonal variability showed that the concentration of chlorides, sulfates and nitrates was the highest in winter. Hot spot analysis made it possible to detect the highest pollution in the head of the river and decreased along the flow path of the river. The periodic increase in water pollution is related to urbanization, wetland drainage and cropland management. Decreasing water quality reduces biodiversity and limits the possibilities of water use by people. The research results indicate that most of the physicochemical parameters of the Bug River waters require discernible consideration due to intense land-use changes and municipal wastewater discharges.

*Keywords:* Water quality; Pollution; Bug River; Cluster analysis; Principal components analysis; Hot spot analysis

## 1. Introduction

Due to their location in valleys, rivers are corridors for transporting pollutants. Surface waters are often used for various purposes, for example, in industry and agriculture. The increased understanding of the importance of water quality to public health and aquatic life translates into the great need to assess the quality of surface water. The quality of commercially used water is very often assessed using a set of physicochemical parameters. The state of surface water pollution is influenced by anthropogenic factors and natural processes [1–7]. Surface water contamination may be either related to point source or nonpoint source pollution. The main point sources of pollution include discharges from municipal and industrial wastewater treatment plants, landfills and septic tanks. Non-point sources of pollution are associated with the runoff of rainwater from agricultural and urban areas [8–11]. They render the water unfit for proper functioning in the ecosystem, which compromises the natural values by reducing biodiversity [12–18]. An effective water quality monitoring program is essential to protect freshwater resources. Physicochemical

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parameters are an important factor determining the quality and availability of water necessary for aquatic life [19,20]. The use of physicochemical parameters to the monitoring of river water quality is an excellent source of information. These data can be used to understand the temporal and spatial assessment of the ecological status of surface waters. This then forms the basis for the proper management of water resources. Monitoring and proper management of water quality are particularly important in the case of the Bug River. It is the last natural river in Europe and its catchment area is international [21,22].

We use multivariate methods for the statistical analysis of large sets of multi-annual data obtained in numerous stations and seasons. For the analysis of temporal and spatial variability of surface water quality, the following are commonly used: cluster analysis (CA), principal component analysis (PCA), and factor analysis (FA). Research water quality has been conducted in many countries, including: USA [23,24], Pakistan [25], Nigeria [7], Morocco [26], Malaysia [1], India [5], China [27], Korea [28], Brazil [12], Egypt [29]. Many researchers have shown that these statistical techniques can be used to group stations into clusters and identify important factors of pollution. These techniques also allow the determination of seasonal variability and identification of sources of water pollution [4,30–32]. CA, PCA and hot spot analysis are widely used by many researchers in various fields of science, for example, environmental science. PCA using sustainability evaluation for biomass supply chain synthesis [33]. Cluster analysis (CA) using effluent quality assessment of sewage treatment plant [34].

The problem of excessive pollution of surface waters was noticed in the second half of the 20th century. At that time, the Nitrates Directive [35] and the Water Framework Directive [36] were developed. The directives establish a framework for action aimed at better protection of waters (common water policy, limitation nitrates pollution from agricultural sources). In Poland, since the accession to the EU in 2004, the Environmental Monitoring System was introduced. Since then, research on the identification of pollutants has been conducted in a comprehensive manner. Numerous studies conducted in Poland indicate that the water quality has been constantly improving [37–46]. Surface water pollution has also been tested in the Bug River catchment area. Even though the Bug is an international river, the research conducted so far has been local. Recently, results of research conducted in Lviv Oblast, Volyn Oblast, and the Lublin Region have been published [47–51]. The significant problem in research coordination is the fact that the Bug River is the eastern border of the European Union.

The aim of this study is to analyze and interpret the dataset for the 10-y (2010–2019) period of base monitoring of the Bug River in Poland. To achieve this goal, statistical techniques were used to determine the temporal and spatial variability of surface water quality parameters. Using the cluster analysis, principal components analysis, box plots and hot spot analysis techniques, the following were determined: (1) similarities and differences between stations, (2) seasonal changes in surface water quality, (3) types of pollutants, and (4) potential sources of pollution. The presented results will enable spatial and temporal evaluation of the variability of physicochemical parameters of water quality in the Bug River.

## 2. Materials and methods

### 2.1. Study area

The catchment area of the Bug River is a transboundary area covering the area of three countries. 27.5% of the catchment area is located in Ukraine, 23.4% in Belarus, and 49.2% in Poland. The total catchment area is 39,420 km$^2$ and the river recharges the Zegrzyński Reservoir, flowing approximately 774 km from Lviv Oblast to the Narew River. This study was carried out in Poland to investigate the state of pollution of the Bug River. Water samples were collected from ten stations in the Mazovia and Lublin Regions (Fig. 1). Three stations are located on the Polish–Ukrainian border, four on the Polish–Belorussian border, and three in Poland. In the catchment area, there are vast wetlands developed as grasslands and forests. The border along the flow path of the river is protected as a Natura 2000 area. High natural values contribute to the emergence of dynamic tourism development [21,22,52,53].

### 2.2. Sample collection

Water quality data used in this study were collected from the Bug River as a part of the State Environmental Monitoring System. Water samples were collected from the Bug River during four different seasons (winter, spring, summer, autumn). The samples were collected from ten sites on the river in the multi-year period 2010–2019 (10-y). Four to twelve water samples were taken depending on the year of the research (in total 689 samples). The tests were performed both on-site and in the laboratory. The following parameters were measured in situ: dissolved oxygen (DO), electrical conductivity (EC), and pH using a Multi-Parameter Prober. For laboratory analyses, samples were taken in sealed 1 L bottles. The analysis of pollutant concentrations was performed using the following methods: total phosphorus (TP), phosphates ($PO_4$), total nitrogen (TN), nitrite–nitrogen ($NO_2$–N), ammonium nitrogen ($NH_4$–N), sulfates ($SO_4$), chloride (Cl), nitrate–nitrogen ($NO_3$–N), Kjeldahl nitrogen (N-K) – using the spectrophotometric method. Biochemical oxygen demand (BOD) was determined by the Winkler method, total suspension (TS), total dissolved solids (TDS) by the gravimetric method, total organic carbon (TOC) using a TOC 1200 analyzer, the total hardness (TH) was determined by the edetate method. Based on the sum of ammonium, nitrate and nitrite nitrogen concentrations, the dissolved inorganic nitrogen (DIN) was calculated. The laboratory determined the content of heavy metals and hazardous substances in water. The concentration of Cd, Pb, Hg, Ni, Cu, benzene, dichlorodiphenyltrichloroethane (DDT) was determined using the AAS method [54].

Point and non-point pollution sources were identified using the Google Earth Pro software. Using satellite and aerial photos, the use and topography, location of industrial plants and sewage treatment plants were determined. The information obtained from the application was verified during in situ tests.

Fig. 1. Location of sampling stations on Bug River.

### 2.3. Statistical analysis

In the preliminary stage of the research, the structure of the tested water quality characteristics was analyzed. In order to characterize the temporal and spatial variability of water quality parameters, multivariate analysis methods are most often used. With the help of statistical analyses, we can assess the temporal and spatial differences in the quality of river waters and identify potential sources of pollution. In order to detect the similarity of the measurement sites in terms of physicochemical parameters of water, the procedure of agglomerative hierarchical classification was used. The data were standardized prior to the analysis. Ward's algorithm of minimum variance with the Euclidean distance as a measure of similarity was used for clustering. Cluster analysis (CA) is a method that makes it possible to identify real groups of data [55].

In the next stage of the research, in order to deepen the analysis of the spatial-temporal structure of the tested physicochemical parameters in individual stations, the GIS tool was used, that is, optimized hot spot analysis. This tool is used to identify statistically significant clusters of hot and cold spots by calculating *z*-scores based on the Getis-Ord Gi* statistic [56,57]. The obtained results are automatically corrected on the basis of multiple tests and spatial dependence using the false discovery rate correction method. The essence of this method is the analysis of measuring points in the context of neighboring points. For a station to be considered statistically significant, the location must have a high value and additionally it must be surrounded by other objects with low values. The results of hot spot analyses for individual parameters and seasons were presented in the form of cold or hot spots where clusters of similar values were marked with a given confidence level. Hot spot analysis (Getis-Ord Gi*) is considered a helpful tool to recognize spatial clusters and has previously been applied to identify disease outbreaks [58,59].

Subsequently, the PCA was used to detect the interdependencies between the water quality parameters at the measuring stations and in the seasons. PCA allows the determination of a set of factors influencing water quality with the distinction of time and place of occurrence. PCA is used to reduce the number of variables describing phenomena, or to discover regularities between variables [60,61]. By means of this technique, we could eliminate redundant data without losing the reliability of the analyses. Then, the principal components analysis was completed by performing the procedure separately for each season. The results are presented as biplots.

In the last stage of the analyses, the basic characteristics of the distribution within the clusters distinguished on the basis of the classification analysis are presented in the box plot diagram. The charts were supplemented with raw observations, taking into account the seasonality factor. Then, the distributions of physicochemical parameters for the clusters and seasons under consideration were compared. Due to the rejection of the hypotheses about the normality of the distribution and the homogeneity of the variance, the analyses were based on non-parametric methods. The Kruskal–Wallis test was used for comparison with the post hoc analysis, assuming the significance level of 0.05.

Spatial analyses were performed in ArcGIS Pro [62]. All further data analysis was carried out using R software (version 4.0.3) [63] and Statistica 13 [64].

## 3. Results and discussion

Physicochemical parameters are one of the elements of ecological status assessment and form the basis of water quality classification [65]. They are also the basis for proper water management in the natural environment. For the average values of the parameters, the threshold of good ecological status was not exceeded (Table 1). However, in the case of the maximum values of TS, DO, BOD, TOC, EC, TDS, TN, DIN, N-K, TP, $PO_4$ concentrations, a few water samples did not meet the criterion of good ecological status. The results of the Cd, Pb, Hg, Ni, Cu, benzene and DDT tests were not used in further statistical analysis. These parameters were characterized by both concentrations and a coefficient of variation close to 0. The river flow after crossing various point and non-point pollution sources in Ukraine [49,66]. For this reason, excessive water pollution occurs at certain test dates.

### 3.1. Cluster and hot spot analysis

Based on CA, checkpoints were divided into four clusters (Fig. 2). The stations Zosin, Horodło and Kryłów are among the polluted G1 cluster. The following stations were included in the pure G3 cluster: Terespol and Krzyczew. The G2 cluster includes the following stations: Włodawa and Sławatycze. The following stations were included in the G4 cluster: Gnojno, Wyszków and Kózki. The G2 and G4 clusters were classified as moderately polluted waters. Box plots (Fig. 3) were prepared for the isolated clusters and the non-parametric Kruskal–Wallis test was performed. The statistical analysis confirmed the existence of significant differences in water quality between the clusters for most parameters (Table 2).

The average multiyear TS value was 21.36 ± 13.74 mg $L^{-1}$, and the extreme values range from 4 to 76 mg $L^{-1}$. This parameter was characterized by the highest coefficient of variation amounting to 64% (Table 1). For the clusters separated on the basis of CA, TS ranges from 18.2 to 23.9 mg $L^{-1}$, for G4 and G2, respectively (Fig. 3). Statistically significant differences were found between G4 and clusters G1 and G2 (Table 2). In spring, TS concentration was significantly higher (hot spot) in Włodawa, Sławatycze and Terespol, and significantly lower (cold spot) in Kózki and Gnojno (Appendix). In summer, the TS hot spot was in Zosin, Horodło and Kryłów, and the cold spot was in Wyszków and Kózki. In autumn, the cold spot was in Kózki. There are no significant differences in winter ($p = 0.677$, Appendix). Commonly used activities such as sewage treatment, bathing and cleaning are responsible for the increase in TS value [67]. In the case of Bug River, the electrical conductivity and total suspended should be monitored as indicators reflecting the effects of soil erosion and surface runoff. Suspensions carried by the river are retained in reservoirs, contributing to the formation of bottom sediments and shallowing of reservoirs [7,12,68–71].

The oxygen conditions were characterized by DO and BOD. The average multiyear content of DO was 9.25 ± 2.04 mg $O_2$ $L^{-1}$, and the extreme range was between 4.5 and 14.9 mg $O_2$ $L^{-1}$ (Table 1). For the selected groups, the mean DO content ranged from 8.5 to 9.8 mg $O_2$ $L^{-1}$ for G1 and G2 clusters, respectively (Fig. 3). Statistically significant differences were found between all clusters, except

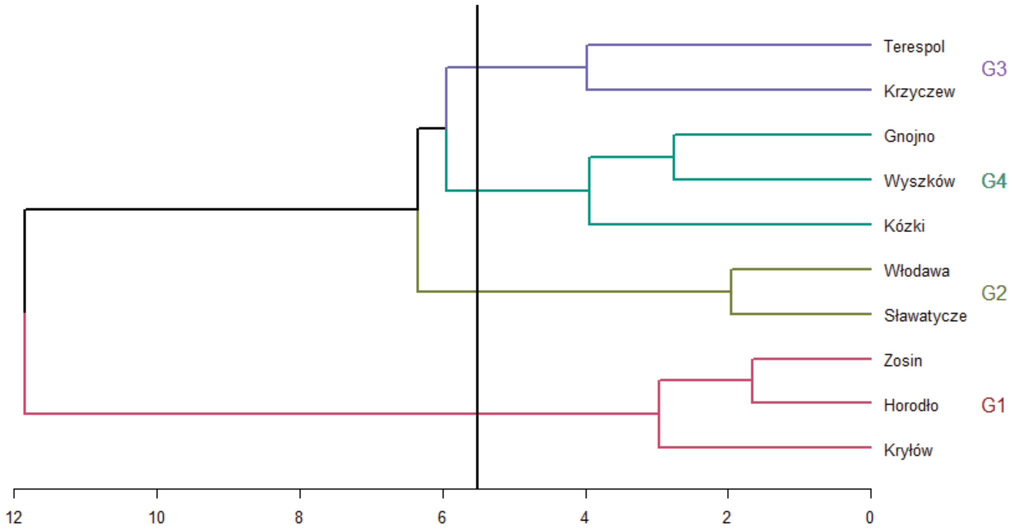


Fig. 2. The dendrogram shows the clustering of sampling stations.

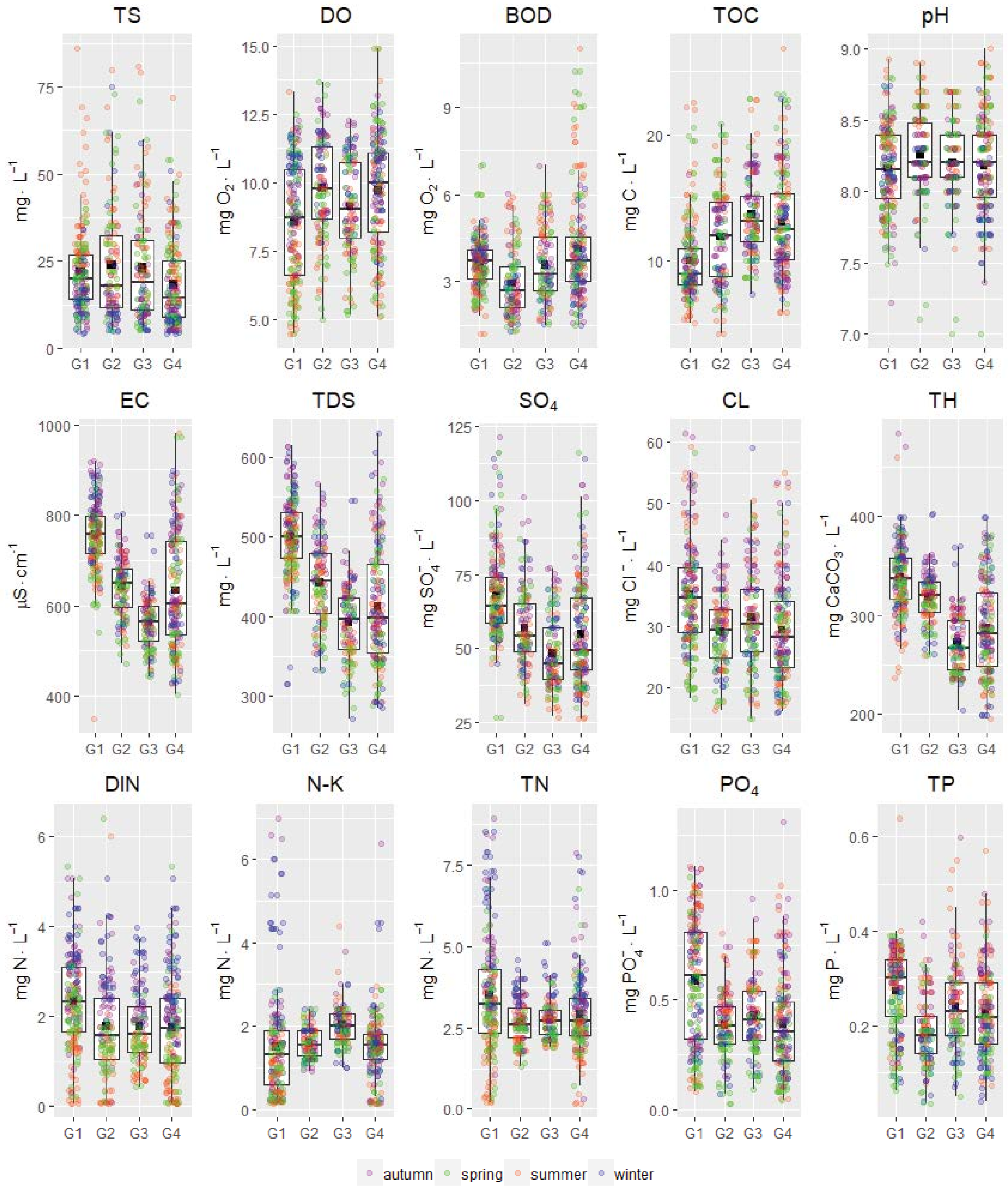


Fig. 3. Box plots of water quality parameters result considering the groupings formed by cluster analysis.

G2 and G4 (Table 2). Regardless of the season, the cold spot of dissolved oxygen content was in G1 rather than in the other clusters (Appendix). At Terespol and Krzyczew stations, the hot spot of DO content was in winter and spring. In turn, in spring and summer, the DO content hot spot was in Włodawa and Sławatycze. The mean BOD content ranged from 2.9 to 4.1 mg $O_2$ $L^{-1}$ for the G2 and G4 clusters. In the case of the G4 cluster, these contents reached a maximum of 11.0 mg $O_2$ $L^{-1}$. The mean BOD content was 3.62 ± 1.41 mg $O_2$ $L^{-1}$. Regardless of the season, the BOD was significantly lower in the G2 cluster. The hot spot of this value in the G1 cluster was in autumn and winter and in G4 in summer. Low BOD is closely related to high DO and vice versa. The oxygen content and temperature are the parameters for life in the aquatic environment. They are also related: the solubility of oxygen in water depends on the temperature and decreases with increasing temperature [50]. DO is inversely correlated to EC and to

Table 1
Characteristic values of physicochemical parameters of water

| Parameter | Data | Minimum | Maximum | Mean | Median | Standard deviation | Coefficient of variation |
|---|---|---|---|---|---|---|---|
| Total suspension, mg $L^{-1}$ | 689 | 4.00 | 86.00 | 21.36 | 18.00 | 13.74 | 64.35 |
| Dissolved oxygen, mg $O_2$ $L^{-1}$ | 689 | 4.46 | 14.90 | 9.25 | 9.40 | 2.04 | 22.08 |
| Biochemical oxygen demand, mg $O_2$ $L^{-1}$ | 689 | 1.20 | 11.00 | 3.62 | 3.50 | 1.41 | 38.91 |
| Total organic carbon, mg C $L^{-1}$ | 689 | 4.18 | 26.80 | 12.00 | 11.50 | 3.83 | 31.91 |
| pH | 689 | 7.00 | 9.00 | 8.20 | 8.20 | 0.31 | 3.73 |
| Electrical conductivity, µS $cm^{-1}$ | 689 | 403.00 | 981.00 | 659.14 | 656.00 | 114.37 | 17.35 |
| Total dissolved solids, mg $L^{-1}$ | 689 | 272.00 | 630.00 | 441.87 | 442.00 | 71.01 | 16.07 |
| $SO_4$, mg $SO_4^-$ $L^{-1}$ | 689 | 26.20 | 121.00 | 58.00 | 56.90 | 16.30 | 28.10 |
| Cl, mg $Cl^-$ $L^{-1}$ | 689 | 15.00 | 61.40 | 31.55 | 30.70 | 8.40 | 26.64 |
| Total hardness, mg $CaCO_3$ $L^{-1}$ | 689 | 195.00 | 484.00 | 306.27 | 309.00 | 44.74 | 14.61 |
| Dissolved inorganic nitrogen, mg N $L^{-1}$ | 689 | 0.06 | 6.42 | 1.95 | 1.89 | 1.09 | 55.95 |
| Total nitrogen, mg N $L^{-1}$ | 689 | 0.16 | 8.96 | 3.01 | 2.80 | 1.31 | 43.54 |
| Kjeldahl nitrogen, mg N $L^{-1}$ | 689 | 0.13 | 7.00 | 1.62 | 1.60 | 0.89 | 55.23 |
| Total phosphorus, mg P $L^{-1}$ | 689 | 0.03 | 0.64 | 0.24 | 0.23 | 0.09 | 39.04 |
| $PO_4$, mg $PO_4^-$ $L^{-1}$ | 689 | 0.03 | 1.31 | 0.46 | 0.42 | 0.24 | 52.59 |
| Cd, µg $L^{-1}$ | 689 | <0.02 | <0.02 | <0.02 | <0.02 | 0 | 0 |
| Pb, µg $L^{-1}$ | 689 | <2 | <2 | <2 | <2 | 0 | 0 |
| Hg, µg $L^{-1}$ | 689 | <0.02 | <0.02 | <0.02 | <0.02 | 0 | 0 |
| Ni, µg $L^{-1}$ | 689 | <2 | <2 | <2 | <2 | 0 | 0 |
| Cu, mg $L^{-1}$ | 689 | <0.01 | <0.01 | <0.01 | <0.01 | 0 | 0 |
| Benzene, µg $L^{-1}$ | 689 | <0.01 | <0.01 | <0.01 | <0.01 | 0 | 0 |
| DDT, µg $L^{-1}$ | 689 | <0.01 | <0.01 | <0.01 | <0.01 | 0 | 0 |

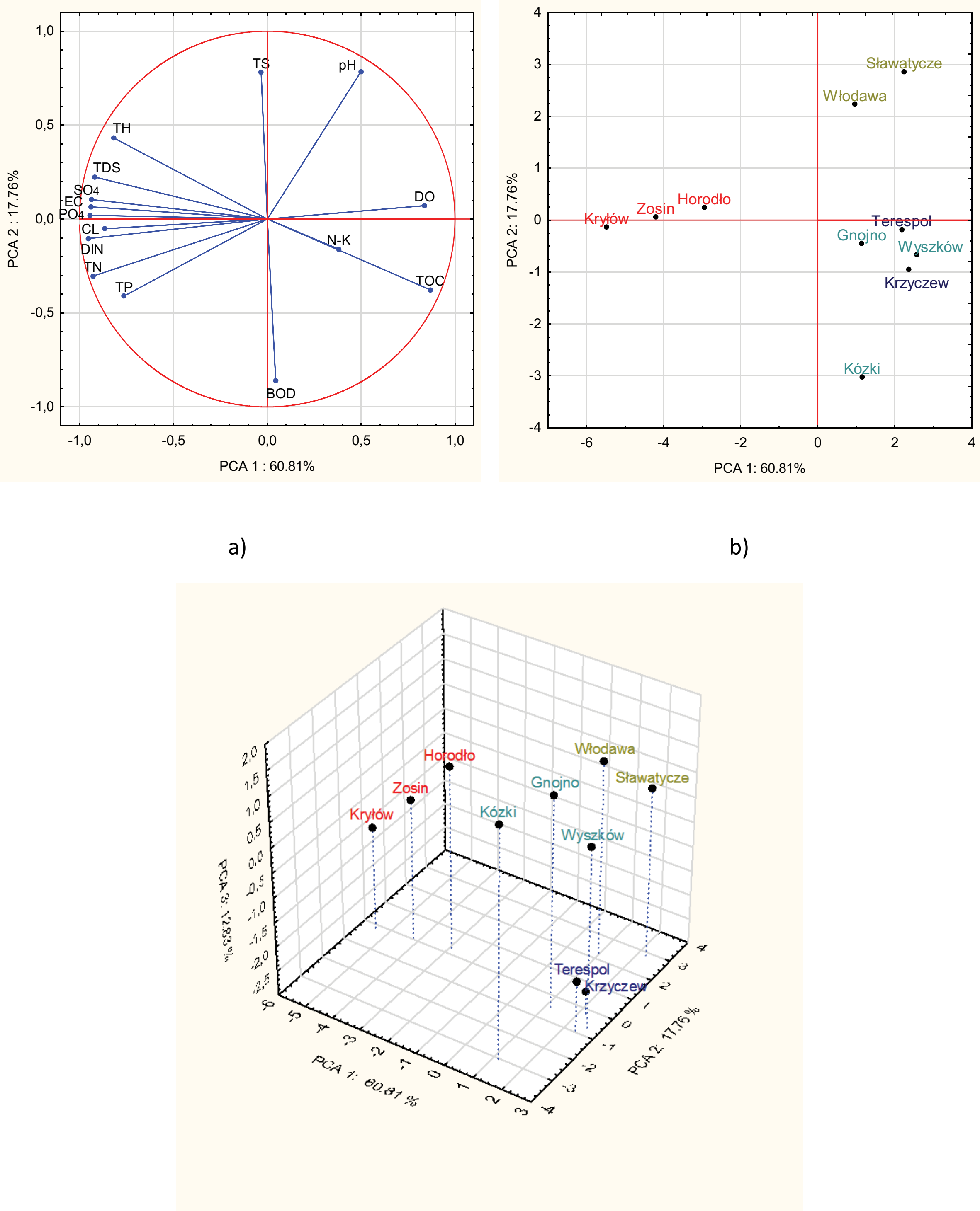
Table 2
Values of Kruskal–Wallis test statistics, *p*-values, and multiple comparison results for the parameter values at the cluster

| Parameter/factor | Kruskal–Wallis $\chi^2$ statistics | *p*-value | Multiple comparison test after Kruskal–Wallis | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | G1-G2 | G1-G3 | G1-G4 | G2-G3 | G2-G4 | G3-G4 |
| Total suspension | 17.78 | 0.0005 | | | > | | > | |
| Dissolved oxygen | 41.27 | 0.0000 | < | < | < | > | | < |
| Biochemical oxygen demand | 59.76 | 0.0000 | > | | | < | < | |
| Total organic carbon | 124.52 | 0.0000 | < | < | < | < | | |
| pH | 10.23 | 0.0167 | < | | | | | |
| Electrical conductivity | 294.70 | 0.0000 | > | > | > | < | | < |
| Total dissolved solids | 254.26 | 0.0000 | > | > | > | > | > | < |
| $SO_4$ | 155.50 | 0.0000 | > | > | > | > | | < |
| Cl | 62.31 | 0.0000 | > | > | > | | | |
| Total hardness | 251.15 | 0.0000 | > | > | > | > | > | < |
| Dissolved inorganic nitrogen | 132.02 | 0.0000 | > | > | | < | | < |
| Kjeldahl nitrogen | 100.71 | 0.0000 | < | < | | < | | > |
| Total nitrogen | 31.87 | 0.0000 | > | > | > | | | |
| $PO_4$ | 68.07 | 0.0000 | > | > | > | | | |
| Total phosphorus | 86.02 | 0.0000 | > | > | > | < | < | |

Groups where significant differences were found at a significance level of 0.05 are marked in color; the sign (>, <) defines the relationship between the medians for the groups indicated in the column header.

nutrient content (Fig. 4). Reducing the dissolved oxygen level in the water can have a negative impact on aquatic ecosystems. Low oxygen concentration often reduces biodiversity by increasing mortality in fish and benthic fauna [1,72,73]. Hypoxia conditions (<2 mg $O_2$ $L^{-1}$) were most commonly observed in coastal areas of the Gulf of Mexico and Chesapeake [74–76]. Oxygen deficiency also occurred in the estuary of the Chengjiang and Pearl Rivers [31,77,78].

The content of organic pollutants averaged 12.0 ± 3.83 mg C $L^{-1}$ and ranged from 4.18 to 26.8 mg C $L^{-1}$ (Table 1 and



a)

b)

c)

Fig. 4. Results of principal component analysis for (a) physicochemical parameters of water, (b) sites, and (c) sites – 3D.

Fig. 3). TOC concentration was significantly lower in the G1 cluster, regardless of the season (Table 2, Appendix). Hot spots of TOC were recorded in G3 in all seasons except spring, and in the spring in G4. Organic pollutants may result from the use of plant protection products in agriculture, the production of plastics, coal mining and wood preservation. The removal of organic pollutants is difficult using water and wastewater treatment technologies [39,79,80].

The mean pH value was 8.2 and ranged from 7.0 to 9.0 (Table 1). Only in the case of this parameter, no significant differences were found between almost all clusters (Table 2). The diversity of this parameter was found only in winter (Appendix). Significantly higher pH values were then noted in G1, and significantly lower in the G4 cluster. Alkaline water does not significantly affect the life of organisms. The very much larger problem is caused by acidic water [30,81,82].

Salinity was characterized by parameters such as EC, TDS, SO, Cl, TH. In the case of EC, the mean value was 659 μS $cm^{-1}$ ranging from 403 to 981 μS $cm^{-1}$ (Table 1). For the TDS parameter, the concentration was 442 mg $L^{-1}$ reaching a maximum of 630 mg $L^{-1}$ in the G4 group. In the case of TH, the average concentration was 306 mg $CaCO_3$ $L^{-1}$ ranging from 272 to 339 mg $CaCO_3$ $L^{-1}$ for G3 and G1, respectively. TH reaches a maximum value of 484 mg $CaCO_3$ $L^{-1}$ in the G1 cluster. For the $SO_4$ parameter, the maximum content was 121 mg $SO_4^-$ $L^{-1}$ in the G1 cluster with an average for the cluster of 48 to 68 mg $SO_4^-$ $L^{-1}$. In the case of Cl, the mean content was 31.55 mg $Cl^-$ $L^{-1}$, and the cluster average was 29 to 35 mg $Cl^-$ $L^{-1}$. The maximum content of Cl is 61.4 mg $Cl^-$ $L^{-1}$ in G1 (Fig. 3). In the case of water salinity, regardless of the season, significantly higher values and hot spots were found for cluster G1. On the other hand, significantly lower values and cold spots were most often recorded for the G3 cluster (Table 2, Appendix). This relationship did not apply to Cl, where the least differentiation was observed. In many regions of the world, the salinity of water resources threatens the biodiversity of aquatic life and causes economic losses. Salinity influences ecosystem processes such as biomass production and nutrient cycling [11,24,28,83]. In Poland, high water salinity in rivers is most often observed in urbanized areas in winter. This is due to the use of salt for de-icing roads and the low water level in rivers [41,84]. The low water level in the river is an element of climate change, that is, the lack of snow in winter [6,84–89].

Contamination with nutrients was characterized by parameters such as DIN, N-K, TN, $PO_4$, and TP. The average DIN concentration was 1.95 ± 1.09 mg N $L^{-1}$, and it reaches the maximum of 6.42 mg N $L^{-1}$ in the G2 cluster. For the N-K parameter, the mean content was 1.62 ± 0.89 mg N $L^{-1}$ and reaches a maximum of 7.0 mg N $L^{-1}$ in the G1 cluster (Fig. 3). Significant differences were found for the G3 group for the DIN and N-K parameters (Tables 1 and 2). In the case of DIN, hot spot pollutants (significantly higher) were observed in spring, summer and autumn for cluster G1 (Appendix). Cold spot pollutants (significantly lower) were observed in the G2 and G3 clusters in the spring. In the case of N-K, hot spots were found in winter for the G1 cluster and cold spots for the G3 cluster. For the remaining seasons, the situation was completely the opposite, that is, the hot spots were in the G3 cluster. The mean concentration of TN was 3.01 ± 1.31 mg N $L^{-1}$, and the maximum concentration was 8.96 mg N $L^{-1}$. For the $PO_4$ parameter, the concentration was 0.46 ± 0.24 mg $PO_4^-$ $L^{-1}$ on average and its maximum was 1.31 mg $PO_4^-$ $L^{-1}$. Regardless of the season, hot spots of N-K and $PO_4$ were observed in the G1 cluster. Cold spot pollutants were observed for clusters G2 and G3 for $PO_4$ in spring, and for N-K in all seasons except summer. The maximum concentration of TP was 0.64 mg P $L^{-1}$ with an average of 0.23 ± 0.09 mg P $L^{-1}$. Statistically significant differences were found between all clusters (Table 2). Regardless of the season, in the case of TP, hot spot pollutants were found for the G1 cluster (Appendix). On the other hand, cold spots were found for G2 and in winter for the G3 cluster. The main cause of point pollution with nutrients is the sewage discharged from industrial and municipal sewage systems [39,90]. They are highly concentrated and are discharged in an organized manner from the sewage treatment plant. Point pollution also includes water used in households, chalets areas and work places [9,27,81,91]. Another group consists of diffuse pollutants washed from agricultural and urban areas. In the case of arable lands, these include fertilizers and pesticides, which are extremely dangerous due to the high concentration of chemicals and the lack of control mechanisms [92]. In urbanized areas, these are runoffs of rainwater and snowmelt and runoffs from municipal landfills [93,94]. The literature shows that nitrogen concentration in the surface water is subject to seasonal changes [4,26,29]. In the summer season, due to nitrification and intensive plant development, the content of ammonia nitrogen decreases, while the increase in the decomposition of organic matter causes a decrease in nitrate nitrogen. The decrease in the concentration of phosphorus compounds in spring may be due to the dilution of the wastewater due to more intensive flows [51]. Large amounts of phosphorus get into the aquatic environment with sewage from households and farm buildings [41,95–97]. There is a significant growth of phytoplankton organisms in water bodies [29,98,99]. The number of cyanobacteria that produce toxins increases, thus damaging the fauna in the water [100,101]. The strong growth of plants near the shore limits the access of light to plants in the deeper layers of the water, which reduces their growth. Aquatic life is also exposed to limited access to oxygen, which in turn leads to a reduction in the number of individuals, often especially important for the preservation of biodiversity [7,43,46,91,102].

### *3.2. Principal component analysis*

On the basis of the PCA, 3 main components were distinguished, which explain 91.4% of the overall variability of the data set (Fig. 4). The first component (PCA 1) with the highest eigenvalue (9.12) explains 60.81% of the total variation. The second component (PCA 2) corresponding to the second eigenvalue (2.66) explains 17.76% of the total variation. On the other hand, the third component (PCA 3) was responsible for explaining about 12.83% of the variation with the eigenvalue equal to 1.93. The analysis of factor loadings showed that the main parameters influencing the water quality of the Bug River were TN, DIN, TP, $PO_4$, $SO_4$, Cl, EC, TH, DO, TOC and TDS (Fig. 4a). Let us note that variables such as DO and TOC are correlated with the positive part of the first component (PCA 1), while the other variables: TN, DIN, TP, $PO_4$, $SO_4$, Cl, EC, TH and TDS are strongly correlated with the negative part of this component. Numerous studies have shown that the concentrations of nitrogen and phosphorus species belonged to the first group of factors, while the content of dissolved oxygen and organic carbon belonged to the second group of factors [3,4,14,103]. Thus, our research confirms the dominant influence of nutrients on changes in water quality. The increase in the inflow of nutrients to water bodies increases the production of biomass, which in turn leads to an increase in oxygen demand. Increasing hypoxia and reducing water transparency contribute to increasing the development of cyanobacteria and limiting the development of benthic fauna [1,75,76,91]. For the second component (PCA 2), BOD, TS and pH have the highest factor loading value, with a strong negative correlation between BOD and TS variables. The third component (PCA 3) is most strongly correlated with only one variable, which is N-K. Considering the distribution of stations in the main component spaces (Fig. 4b), it is possible to indicate groups that are characterized by similar physicochemical properties. In particular, stations are clearly visible in the 3D (Fig. 4c), which corresponds to the division that was obtained by the cluster analysis. Note that the G1 cluster is strongly correlated with the negative part of the PCA 1 axis of the component, which means that the objects of this cluster are characterized by increased nutrient values and a decreased DO value. Mutual multivariate dependencies showed that in the stands with higher nutrient content, apart from lower DO content, increased salinity was also found. The Włodawa and Sławatycze (G2) stations are characterized by the highest pH level. On the other hand, the other two clusters, G3 and G4, are characterized by an increased value of the TOC parameter and decreased values of the TH, TDS, $SO_4$ and EC parameters.

PCA for all seasons showed that the variation was influenced by most parameters related to the first main component explaining 42.32% of the variability. These parameters include, in particular, $SO_4$, EC, TH, TDS, and TOC (Fig. 5a). The second component explaining 25.02% of the variability are the parameters TP, TS and DO. A clear seasonal grouping is visible, in particular, a difference between winter and summer can be observed (Fig. 5b). There is less marked differentiation between spring and autumn. Seasonal variability of water physical and chemical parameters was demonstrated in other rivers, for example, Akaki [103], Oum Er-Rbia [26], Nil [29], Jakara [7], Duliujian [15], and Pearl [31]. Water quality in summer is especially influenced by TS and TP, and in winter by nitrogen compounds and DO. The cause of the high concentration of suspended solids and phosphor in the summer season are mainly surface run-offs from agricultural areas. In Poland, in July there is intense rain, which causes erosion processes and washes away fertilizers and pesticides at cropland. In turn, in spring the main factor is TOC, and in autumn it is salinity (EC, TDS, $SO_4$, Cl, TH). The increase in salinity in autumn results from the end of the growing season (harvesting) and the beginning of plant rotting processes.

Box plots (Fig. 6) were prepared for the seasons and the non-parametric Kruskal–Wallis test was performed. The statistical analysis confirmed the existence of significant differences in water quality between the seasons (Table 3). In the case of TS, BOD, TOC and pH, the highest values were observed in the summer season, and the lowest in the winter season. In the case of DO, it was the opposite occurred. High TS concentrations in spring and summer occur due to water erosion. Erosion most often occurs in spring as a result of runoff of meltwater and in summer as a result of runoff of rainwater. Erosion contributes to soil degradation and crop yield reduction [104]. High BOD and low DO in summer are caused by the increased oxygen demand of aquatic plants and animals. Excessive increase in oxygen demand causes hypoxia and overall fish abundance [105]. In the case of salinity, the highest concentrations of EC, TDS, $SO_4$, Cl and TH occur in autumn, and the lowest in summer. In agricultural areas, the increase in salinity in autumn results from the use of phosphorus fertilizers and manure and decaying plant debris [106]. The observed phenomenon is short-lived and does not pose a threat to water quality. All parameters of salinity, that is, EC, TDS, $SO_4$, Cl, and TH meet the quality standards of drinking water [107]. In the case of nitrogen and its forms, the highest concentrations of pollutants were found in winter, and the lowest in summer. Changes in plant development directly affect the nitrogen content in the environment. In the summer season, there is an intensive development of plants that take up nitrogen for their growth. In the winter season, there is no vegetation at cropland [11]. In the case of phosphorus and phosphates, statistically higher concentrations were found in summer and autumn. Higher phosphorus and phosphate pollution in the summer season is due to the use of pesticides on croplands and the discharge of sewage from chalets area. In turn, the increase in pollution in the autumn season is due to the use of manure on cropland.

## 4. Conclusions

The water of adequate quality is essential for public health and animal life and the proper functioning of the ecosystem. The values of physical and chemical parameters of the water in the Bug River are influenced by natural and anthropogenic processes. The values of physical and chemical parameters of the water in the Bug River are influenced by natural and anthropogenic processes. The performed statistical analysis allowed us to determine the temporal and spatial variability of water pollution parameters. Based on the research carried out on the Bug River, four clusters of similarity were distinguished. This division has been confirmed by both CA and PCA. Detailed hot spot analysis allowed the detection of point sources of pollution. The average content of the physicochemical parameters of water for the multiyear period corresponded to a good ecological status. The greatest variability of physicochemical parameters of water was observed in the G1 cluster. Clear seasonal differentiation was observed especially between winter and summer. Temporary exceedances of the threshold occurred at all stations. The highest concentrations of pollutants were found at Kryłów, Horodło and Zosin stations (G1 cluster) located in the head section of the river. High concentrations of pollutants were probably related to the inflow of pollutants from Ukraine. The quality of the water in the Bug River within the borders of Poland

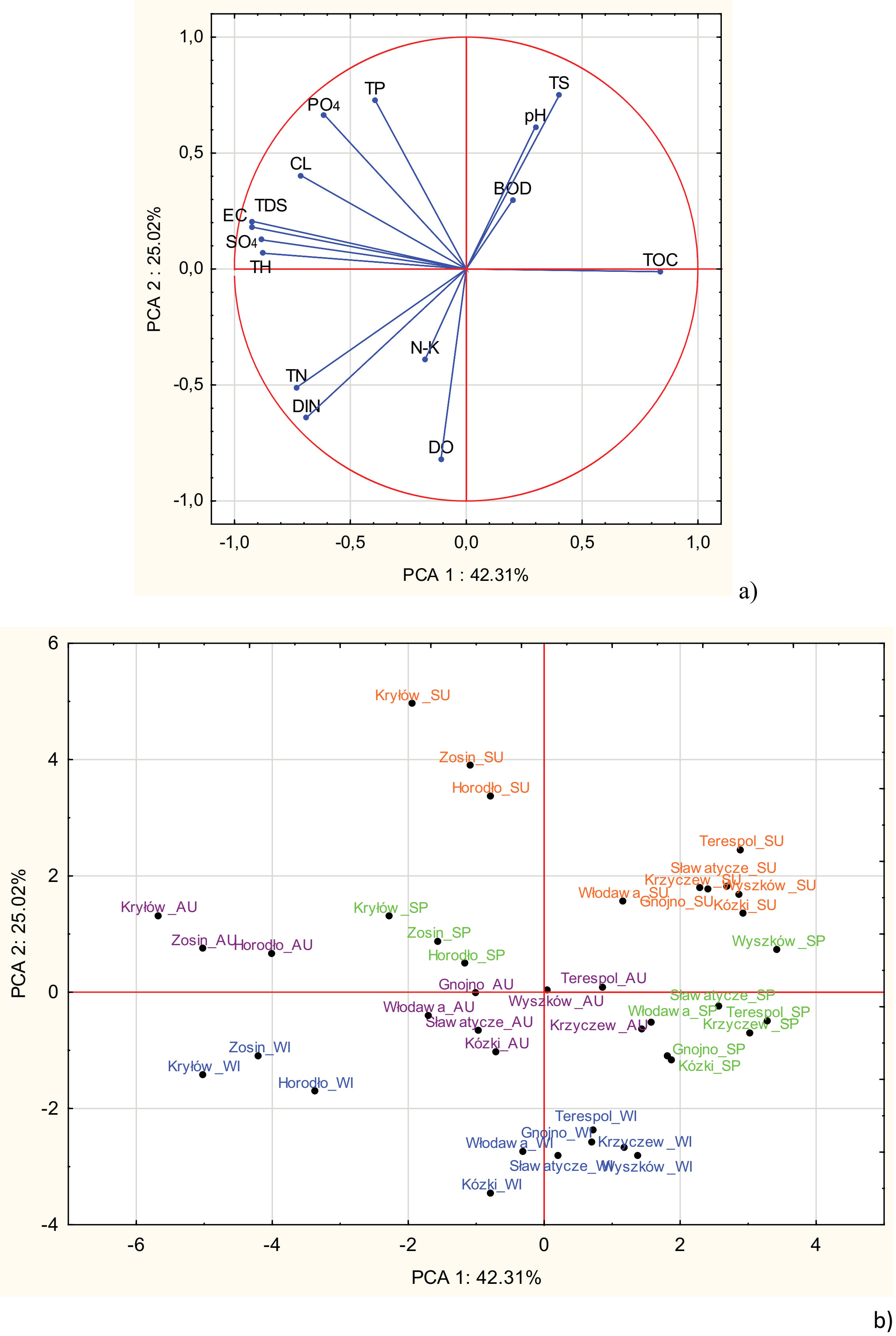


Fig. 5. Results of principal component analysis for (a) physicochemical parameters of water and (b) sites, in the seasons.

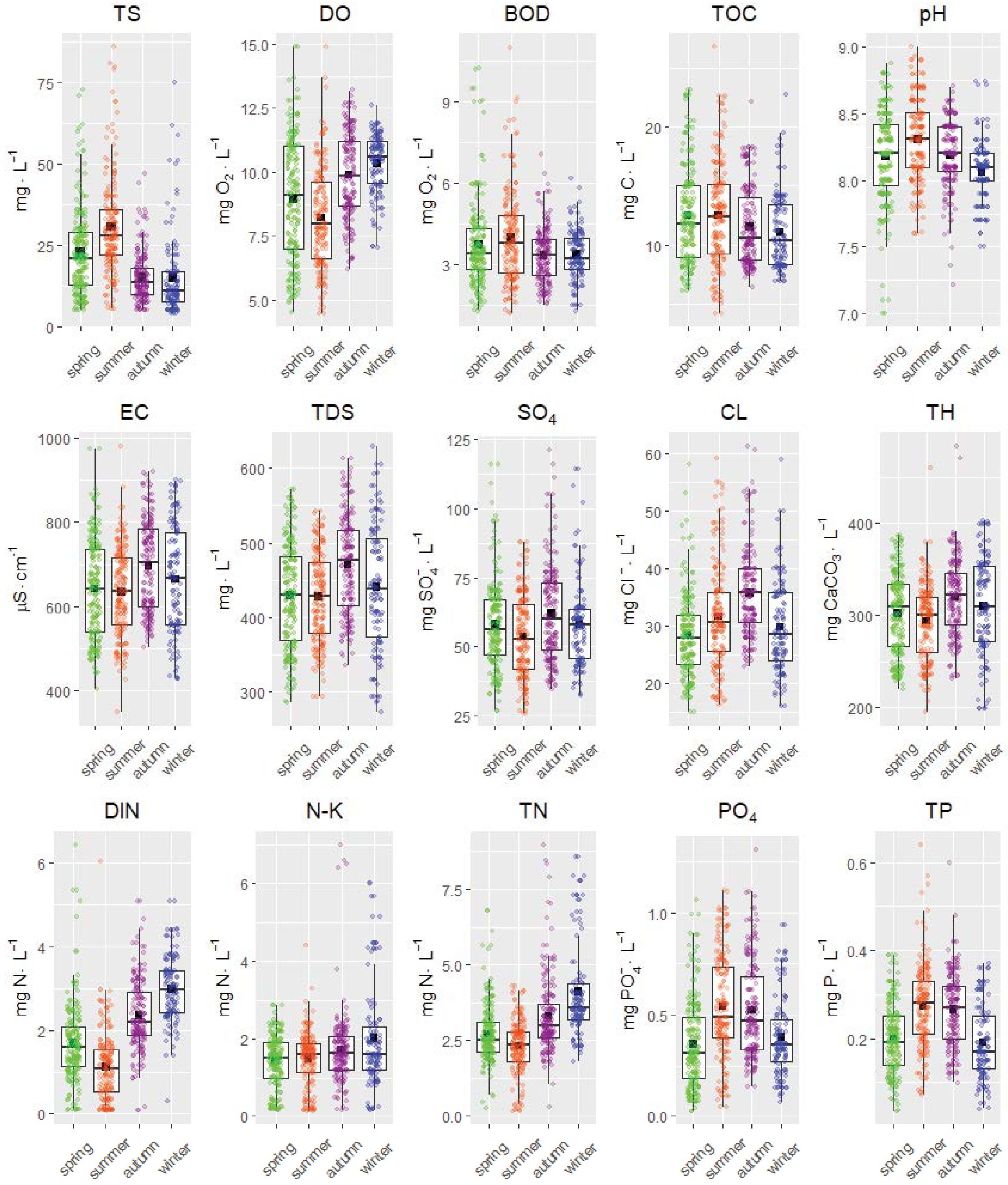


Fig. 6. Box plots of water quality parameters in the seasons.

improved along the flow path of the river. However, in Poland, the mouth there has been an increase in water pollution. Based on the presented research, we conclude that the water of the Bug River in Poland requires treatment to minimize pollution. High pollution levels compromise the ecological status, which has an impact on the provision of ecosystem services. In order to minimize water pollution in the river, it is necessary to modernize the municipal sewage treatment plant and take measures to eliminate discharges of untreated sewage from the Bug River basin. The research shows that the main cause of deterioration of water quality in the Bug River was anthropogenic activities. The main threats to water quality are the growing chalets area, the lack of active management of grassland areas and the drainage of wetlands. To protect water quality, all measures need to be coordinated at an international level.

Table 3
Values of Kruskal–Wallis test statistics, *p*-values, and multiple comparison results for the parameter values at seasons

| Parameter/factor | Kruskal–Wallis statistics | *p*-value | Multiple comparison test after Kruskal–Wallis | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | spring–summer | spring–autumn | spring–winter | summer–autumn | summer–winter | autumn–winter |
| Total suspension | 178.55 | 0.0000 | < | > | < | > | > | |
| Dissolved oxygen | 110.45 | 0.0000 | > | < | < | < | < | |
| Biochemical oxygen demand | 16.04 | 0.0011 | | | | > | > | |
| Total organic carbon | 14.51 | 0.0019 | | | > | | > | |
| pH | 47.71 | 0.0000 | < | | > | > | > | > |
| Electrical conductivity | 30.2 | 0.0000 | | < | | < | | |
| Total dissolved solids | 40.27 | 0.0000 | | < | | < | | > |
| $SO_4$ | 21.09 | 0.0001 | | | | < | | |
| Cl | 90.27 | 0.0000 | < | < | | < | | > |
| Total hardness | 33.85 | 0.0000 | | < | | < | < | |
| Dissolved inorganic nitrogen | 295.91 | 0.0000 | > | < | < | < | < | < |
| Kjeldahl nitrogen | 14.41 | 0.0024 | | < | < | | | |
| Total nitrogen | 167.27 | 0.0000 | > | < | < | < | < | < |
| $PO_4$ | 85.68 | 0.0000 | < | < | | | > | > |
| Total phosphorus | 110.39 | 0.0000 | < | < | | | > | > |

Groups where significant differences were found at a significance level of 0.05 are marked in color; the sign (>, <) defines the relationship between the medians for the groups indicated in the column header.

As the Bug River basin covers three countries (Ukraine, Belarus, Poland), further international research is necessary. This will allow a more extensive analysis and provide arguments when making decisions on the improvement of water quality.

## Author contributions

Conceptualization, Data curation: AG; Formal analysis: UB-M; Investigation: AG, UB-M; Methodology, Resources: AG; Software: UB-M; Supervision: AG; Visualization: UB-M; Writing - original draft, review & editing: KP.

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## Conflicts of interest

The authors declare no conflict of interest.

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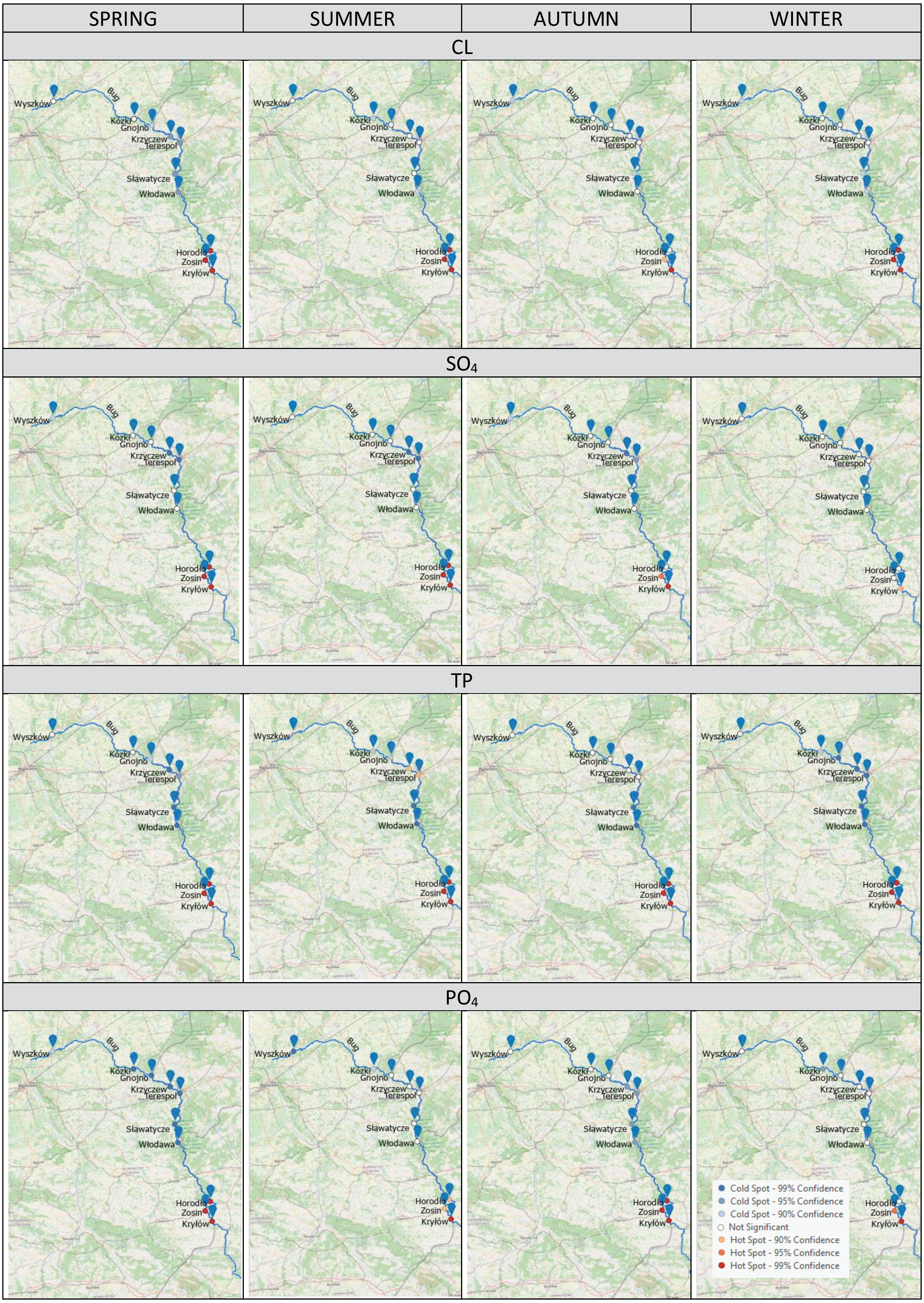
## Appendix

This Appendix presents the results of spatial analyses in the form of hot spot maps created for the analyzed parameters in seasons.

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Horodło
Zosin
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Cold Spot - 99% Confidence
Cold Spot - 95% Confidence
Cold Spot - 90% Confidence
Not Significant
Hot Spot - 90% Confidence
Hot Spot - 95% Confidence
Hot Spot - 99% Confidence


SPRING
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Kryłów
Cold Spot - 99% Confidence
Cold Spot - 95% Confidence
Cold Spot - 90% Confidence
Not Significant
Hot Spot - 90% Confidence
Hot Spot - 95% Confidence
Hot Spot - 99% Confidence


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