

Article

Assessment of the Impact of Forestry and Settlement-Forest Use of the Catchments on the Parameters of Surface Water Quality: Case Studies for Chechło Reservoir Catchment, Southern Poland

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Abstract: The aim of the study was to determine the impact of natural and anthropogenic factors on the values of 22 quality indicators of surface waters flowing out of two small catchments differing in physiographic parameters and land use, in particular forest cover and urbanization of the area. The research was carried out in the years 2012–2014 at four measurement-control points located on the Chechło river and the Młoszówka stream (Poland), which are the main tributaries of the retention reservoir. Basic descriptive statistics, statistical tests, as well as cluster analysis and factor analysis were used to interpret the research results. The water that outflowed from the forestry-settlement catchment of the Młoszówka stream contained higher concentrations of total phosphorus, phosphates, nitrite, and nitrate nitrogen and salinity indicators than outflow from the Chechło river. Water from the Młoszówka stream was characterized by more favourable oxygen conditions. Higher oxygen concentration in the catchment influenced a large slope of the watercourse and thus higher water velocity, which is promoted by the mixed process. In the case of the forest catchment of the Chechło river, the water quality was generally better than in the Młoszówka stream, mainly in cases of total suspended solids TSS, total phosphorus TP, phosphates PO_4^{3-} , total nitrogen TN, nitrite N-NO_2^- , nitrate N-NO_3^- , and salinity parameters. Despite it being a short section of the river taken into the study, favourable self-purification processes like mixed, nitrification, and denitrification were observed in its water. The research shows that forest areas have a positive effect on the balance of most substances dissolved in water, and natural factors in many cases shape the quality and utility values of surface waters on an equal footing with anthropogenic factors. In the case of a large number of examined parameters and complex processes occurring in water, the interpretation of the results makes it much easier by applying multivariate statistical methods.

Keywords: forest catchment; eutrophication; water quality; multivariate statistics

1. Introduction

Anthropogenic activities most often have a negative impact on the environment, including the aquatic environment. As a result of these activities, changes in the relief and soil cover take place, land is drained or flooded, soil, forests, natural ecosystems, and surface and groundwater are degraded. All these changes, resulting from direct or indirect human influence on the environment, are called anthropogenic changes, and the actions causing them are called anthropogenic factors [1,2].

The content of chemical components in surface water depends on natural and anthropogenic factors. Substances of natural origin, the sources of which are rocks, uncultivated soils, humus substances, organic matter decomposition, and clean precipitation, form a natural quality of water. Anthropogenic substances most often cause water pollution, thus changing its original natural composition [3,4]. Due to the way they are discharged into water, they can be divided into area, spot, and linear anthropogenic substances [5].

Pollution means any adverse change in the physical, chemical, or biological properties of surface waters. Pollution occurs as a result of the introduction of substances into water in quantities exceeding the harmless or natural values possible to assimilate, which reduce the utility values and the ability of water to self-purify [6–9]. In rural areas, anthropogenic changes in surface water quality are related to plant and animal production [10,11]. In addition, there are pollutants from urbanized areas, which come from the discharge of untreated or insufficiently treated wastewater [12–14], from rainwater flushing of various substances from properties, impervious areas and waste dumps [15,16], and are the result of emission of pollutants to the atmosphere, returning in the form of precipitation on the surface of the catchment [11].

Heavy rainfall triggers water erosion, as a result of which significant amounts of various substances are transferred from the soil to surface waters [17], including nutrient elements [18]. The amount of constituents introduced into the surface waters with suspended solids depends on the intensity of erosion, which is strictly dependent on the type of soil and vegetation cover and the intensity of land use [19,20]. Grassland is much better protected against erosion than arable land, thus improving the hydrological conditions of the catchment and reducing water pollution [21–23]. Forest areas play an even better protective role than grassland ecosystems, as they retain significant amounts of water in litter and soil, thus significantly reducing surface runoff and preventing erosive leaching of matter [24]. For these reasons, the use and development of the catchment area is considered to have the greatest impact on surface water quality [21,25,26].

Deterioration of water quality is mainly influenced by settlement areas and arable land, while woodland areas usually show negative correlations with most surface water quality indicators [10,27]. Forest catchments with no aggressive forms of use or catchments with high forest cover and low share of agricultural and/or settlement areas are currently treated as objects with environmental conditions similar to natural ones. In most cases, they constitute a reference point for comparison for waters flowing out of catchments subjected to stronger anthropogenic activities resulting from agricultural uses of different intensities, or caused by a significant share of settlement areas, or even urbanized catchments [28,29].

The aim of this study is to assess the influence of land cover on the quality of surface waters outflow into the Chechło retention reservoir. This objective was attempted to be reached on the basis of comparative and statistical analysis of hydrochemical data from a three-year study carried out in two small river catchments, differing in physiographic parameters and land use. A research hypothesis was assumed that due to a smaller share of urban areas and greater forest cover of the catchment, the water of Chechło river is of much better quality than the Młoszówka stream.

Our research has an important cognitive and practical significance, as it concerns river catchments located in the region of Poland that has been subject to the influence of the mining industry for many centuries, which has led to a significant degradation of the environment. Forests in this area improve not only landscape values, but can also influence the shaping of surface water properties. This is important since the basic factor for the utility function of the Chechło retention reservoir, as well as for the proper functioning of aquatic and water-dependent ecosystems, is the good quality of water, which was evaluated on the basis of the analysis of physicochemical parameters of water.

2. Materials and Methods

2.1. Description of the Study Catchments

The study included surface waters outflows out of two catchments—the Młoszówka stream and the Chechło river, both of which discharge to Chechło retention reservoir (Figure 1). The reservoir was established in 1944–1945 mainly for water retention for industrial plants and fire-fighting purposes. In addition, it is used to equalize outflow in the Chechło river bed, reduces the effects of flooding in the valley below impounding level, and serves as a recreational area. With a normal level of impounding, the floodplain has an area of 38.50 ha and the amount of retained water reaches 587.5 thousand m³.

The catchment area of the Chechło reservoir is located (Latitude 50°8.29′ N, Longitude 19°30.24′ E) in the north-western part of the Małopolskie Voivodeship (Poland)—in the districts of Chrzanów and Krakow (Figure 1). Several important communication routes run parallel through the catchment area, such as the A4 motorway, national road No. 79 on the Krakow-Katowice route, and the railway line connecting the Krakow and Silesian agglomerations. According to the Kondracki's [30] division of Poland into physio-geographical regions, the catchment area of the Chechło reservoir is located in province 34 (Polish Upland), in the south-eastern part of the Silesian-Krakow Upland—subprovince 341. In geological terms, the catchment of the Chechło reservoir belongs to the Silesian-Krakow monocline, which is a large plate gently inclined towards the northeast. In its geological structure there are Tertiary, Mesozoic, and Paleozoic formations. The southern part of the plate forming the ground is intersected with leaps running from NW to SE, between which the lowered rock strata form the Krzeszowicki rift fault and Dulowska Basin.

The Chechło river originates from ponds, wetlands, and peat bogs of the Dulowska Forest. It is a right-bank tributary of the Vistula River. About halfway along the Chechło river, i.e., at the 16 + 000 km, there is a front dam of the Chechło water reservoir. In abiotic terms, it is a type 6 watercourse, i.e., it belongs to the group of upland carbonate streams with fine-grained substrate on loess and loess-like soils [31]. The route of the upper running of Chechło river, from its sources to the reservoir, is not very winding and runs from the south-east to the north-west (Figure 1). From the reservoir to the intersection with the highway, the few-meters wide riverbed of the Chechło river was strongly transformed by man by straightening its route and securing the base of the slopes with a fascine fence and as a result of the construction of a damming structure which enables the supply of fish ponds with water. Clearly more watercourses drain the right-hand side of the catchment (Figure 1). The average levelled slope of the Chechło river is 0.5% and the density of the river network is 3.11 km·km⁻² (Table 1). From the hydrological point of view and in terms of protection of quantitative and qualitative resources of the Chechło river, attention should be paid to the presence of marshy areas and small water reservoirs in its catchment area. The Młoszówka stream currently discharges to the water reservoir, but originally it was one of the largest right-bank tributaries of the Chechło river. The water in it flows in a bed that shows little winding; in the upper part it has been paved or protected with prefabricated openwork slabs and concrete walls, while in the lower part it is turfed and locally protected with fascine fences. In the catchment of the Młoszówka stream, the river network is much less developed than in the case of the Chechło river, as its density is only 1.97 km·km⁻². Clearly more watercourses are located in the lower part of the catchment, while in the upper part there is only the Młoszówka stream with a rather long dry valley. The average levelled slope of the bottom of Młoszówka is 2.5 times greater than the Chechło river and amounts to 1.2% (Table 1, Figure 1).

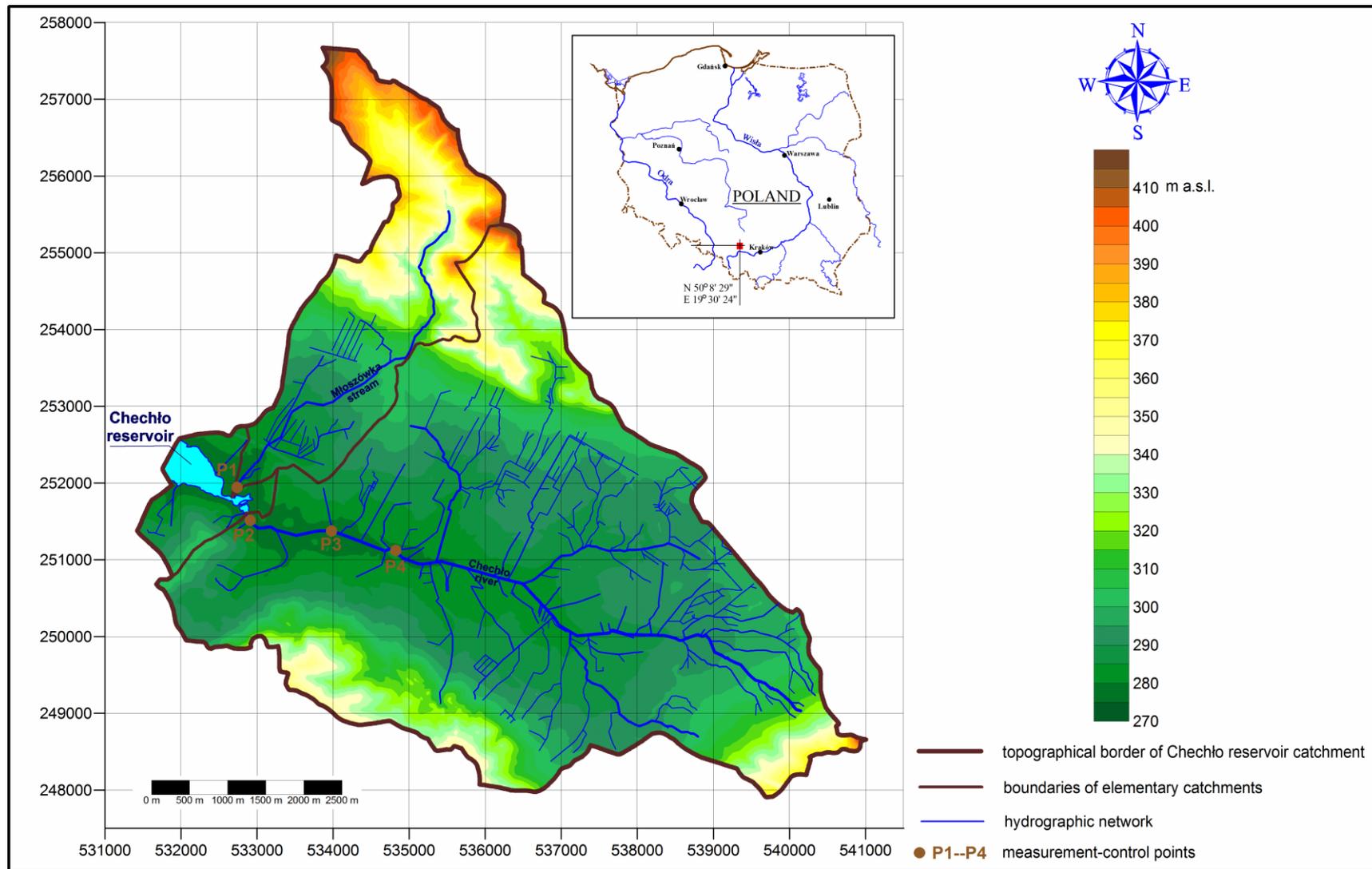


Figure 1. Hydrographic map of research catchments.

Table 1. The basic physiographic and hydrographic parameters of the study catchments.

| Parameter | Unit | Catchment of | |
|--|---------------------------------|---------------|------------------|
| | | Chechło River | Młoszówka Stream |
| Area | km ² | 32.32 | 8.35 |
| Average length | km | 8.67 | 6.05 |
| Maximum length | km | 9.04 | 7.96 |
| Average width | km | 3.58 | 1.05 |
| Circumference | km | 29.85 | 18.06 |
| Form index | – | 0.40 | 0.13 |
| Elongation index | – | 0.71 | 0.41 |
| Circularity index | – | 0.46 | 0.32 |
| Gravelius index | – | 1.48 | 1.76 |
| Minimum elevation | m a.s.l. | 275.0 | 275.0 |
| Weighted average elevation | m a.s.l. | 300.9 | 347.4 |
| Maximum elevation | m a.s.l. | 418.4 | 419.2 |
| Weighted average land slope | % | 3.5 | 7.5 |
| Average precipitation (1971–2010) | mm | | 739 |
| Average temperature (1971–2010) | °C | | 8.3 |
| Land use | | | |
| forest and tree planting | % | 66.7 | 40.2 |
| arable lands | % | 8.5 | 14.8 |
| grassy ecosystems | % | 14.9 | 24.3 |
| Orchards | % | 0.6 | 3.1 |
| areas under standing waters | % | 0.3 | 0.0 |
| built-up areas | % | 6.3 | 15.1 |
| communication areas | % | 2.7 | 2.5 |
| Length of main watercourse | km | 8.330 | 5.398 |
| Length of tributaries | km | 92.068 | 11.064 |
| Total length | km | 100.398 | 16.462 |
| Water network density | km·km ⁻² | 3.11 | 1.97 |
| Average slope of the main watercourse | % | 0.5 | 1.2 |
| Lakeity index | % | 0.3 | 0.0 |
| Fragility index | % | 5.1 | 2.4 |
| Flow | | | |
| Average annual | m ³ ·s ⁻¹ | 0.272 | 0.071 |
| Average low | m ³ ·s ⁻¹ | 0.079 | 0.019 |
| Maximum with average return period (1/year) | | | |
| 200 | m ³ ·s ⁻¹ | 38.61 | 10.10 |
| 100 | m ³ ·s ⁻¹ | 33.00 | 8.63 |
| 50 | m ³ ·s ⁻¹ | 27.55 | 7.21 |
| 25 | m ³ ·s ⁻¹ | 20.53 | 5.37 |
| 10 | m ³ ·s ⁻¹ | 15.31 | 4.00 |
| 5 | m ³ ·s ⁻¹ | 10.30 | 2.69 |
| 2 | m ³ ·s ⁻¹ | 4.22 | 1.11 |

The Chechło reservoir catchment at the site of the dam is 42.46 km², of which 76% of the area belongs to the catchment of the Chechło river, 20% is the basin of the Młoszówka stream, and the remaining 4% of the area is the littoral (Figure 1). The Chechło river catchment covers an area of 32.32 km² and has an average and maximum length of 8.67 and 9.04 km. The shape indicator values allow considering the catchment as firm, medium-elongated, and strongly close to the wheel. The catchment area of the Młoszówka stream equals 8.35 km² and is almost four times smaller than the catchment area of the Chechło river. For these reasons, other geometrical parameters are also much smaller (Table 1). The value of the elongation index (0.41) indicates the lanceolate shape of the catchment, which may theoretically influence the extension of the runoff path and thus the smoother formation of freshets.

The catchments of both of the analyzed watercourses are upland in character, with the area of the Chechło river catchment being less sculpted, and the northern part of the Młoszówka stream catchment being the most sculpted (Figure 1). The highest point in the Chechło river catchment is located on the watershed in the northern part of the catchment—Kowalikowa Mountain of height 418.4 m above sea level. The height difference is 143.4 m above sea level, the weighted average altitude is 300.9 m above sea level and the weighted average slope is 3.5%. The highest and at the same time the northernmost point on the watershed of the Młoszówka stream catchment is a hill without a name (419.2 m above sea level), situated at the foot of Ostra Mountain. The height difference of this catchment is similar, while the average weighted height is 46.5 m above sea level higher, and the weighted average slope is more than twice as high, compared to the Chechło river catchment (Table 1, Figure 1).

The soils of the Chechło reservoir catchment area are characterized by great diversity, both typologically and in terms of species. There are mineral soils of temperate (brown, lessive, and limestone soils) and dry (e.g., podzolic soils) habitats; there are marshy soils as well as organic soils at different stages of moorshification. On more than half of the area of the Chechło river catchment, mainly under the Dulowska Forest (Figure 2), poorly drained clayey sands developed into podzolic soils. In the valleys of watercourses, there are constantly or periodically over-wetted soils. These are mineral formations with grain size of medium clays, from which gley soils and fen soils were formed, organic-mineral formations in the form of muck-mineral, mucky, and peat-muddy soils, as well as organic formations in the form of shallow low peats. These soils, irrespective of their origin, belong to the medium grassland complex. In the central-southern part of the catchment, there are also lessive soils, brown leached soils and brown specific soils, black degraded soils, grey soils, and limestone soils. Depending on the moisture content and terrain, these soils belong to the wheat faulty or rye very good and good arable land complexes or form weak and very weak grassland complexes. The catchment area of the Młoszówka stream is dominated by brown specific and brown leached soils, which were formed mainly from strong and light clayey sands or loess formations. In the northern and southern part of the catchment, under large and dense forest complexes (Figure 2), podzolic soils were formed from poorly drained clayey and light clayey sands. In the lower part of the Młoszówka stream catchment there are shallow low peats and muck-mineral and mucky soils. Organic formations form marshy forest habitats or middle class grassland.

Land use and development have a significant influence on the balance and hydrologic and biogeochemical cycling in the catchment area. In this respect, it can be stated that the Chechło river catchment is forest dominated, as forests and areas of afforestation occurring mostly in a concentrated form in the central and eastern part (Dulowska Forest) occupy almost 67% of the catchment area. The second largest form of land use is grassy ecosystem occupying about 15% of the catchment area. These are both natural and anthropogenic habitats, which in some places are periodically too dry or over-wetted. Arable land occupies only 8.5% of the catchment area, with the largest area thereof in the northern, south-western, and source south-eastern part of the catchment. The built-up areas occupy 6.3% of the catchment area and are located mainly in the vicinity of asphalt roads (Table 1, Figure 2).

The catchment of the Młoszówka stream is also dominated by forests, but the forest cover of over 40% is much smaller than that of the Chechło river catchment. The forest areas are partially scattered, with the largest share in the northern and southern part of the catchment area. Grass ecosystems and arable land covering 24.3 and 14.8% of the total area respectively, are situated mainly in the central and northern part of the catchment. The built-up areas, mostly in the middle part, cover 15.1% of the area and together with the areas under the paved roads form 17.6% of the sealed catchment area (Table 1, Figure 2). In terms of land use, the catchment area of the Młoszówka stream can be considered as a mixture of forestry and settlement areas.

Compared to the Młoszówka stream, the maximum flows likely in all variants in the Chechło river are about 3.8 times higher (Table 1). Moreover, on the basis of the calculated maximum flows with a probability of 1%, it was found that the corresponding unit outflows calculated for the Chechło river catchment and the Młoszówka stream are at a very similar level and amount to about $1.02 \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{km}^{-2}$.

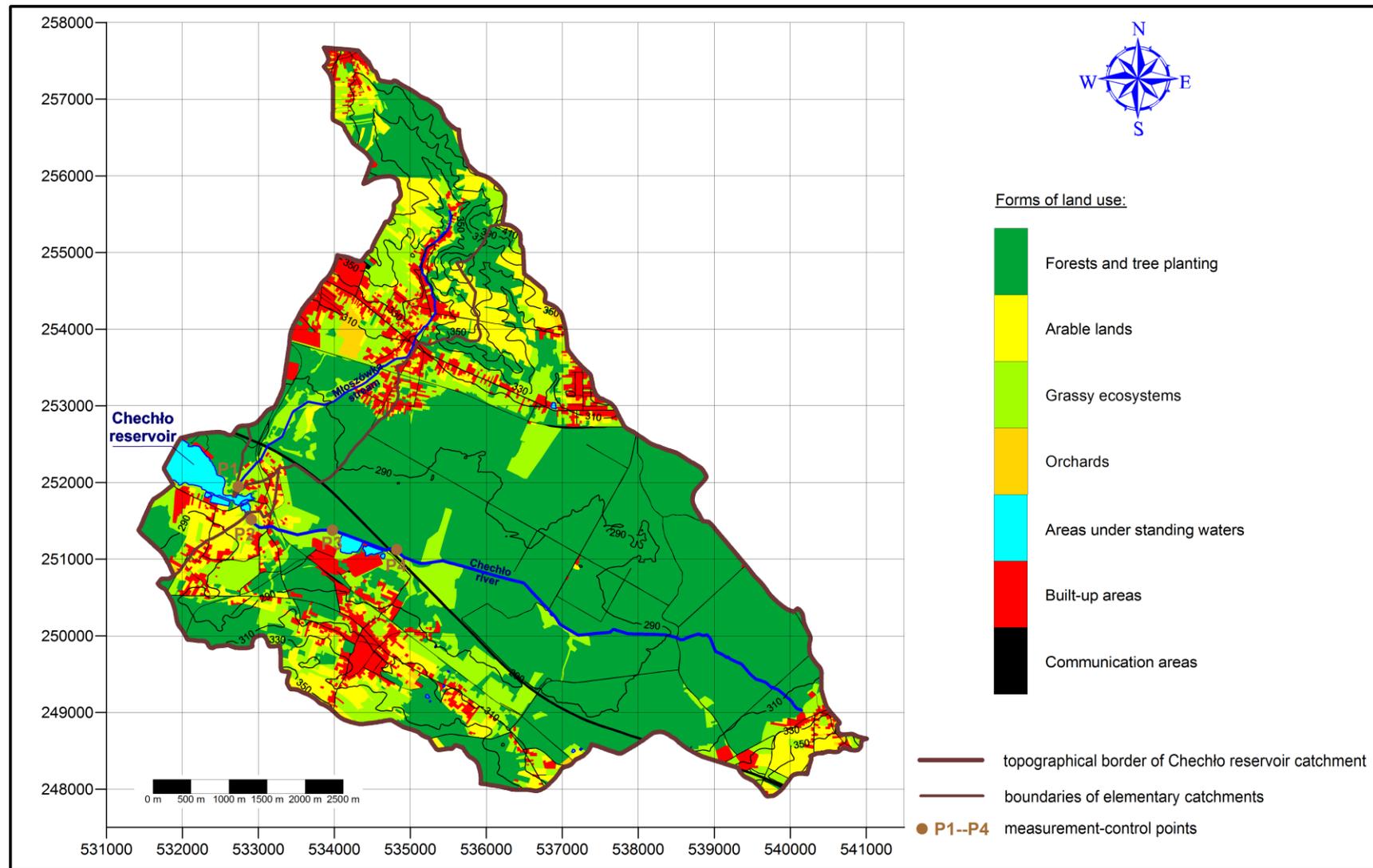


Figure 2. Land-use map of research catchments.

2.2. Sampling and Analytical Methods

Monthly water samplings were conducted in years 2012–2014 at four measurement and control points, for which the following coding was applied (Figures 1 and 2): P1–A point located on the Młoszówka stream, 150 m above the mouth of the Chechło reservoir (km 0 + 150); P2–A point located on the Chechło river, 10 m above the mouth of the reservoir (km 17 + 710); P3–A point located on the Chechło river, 820 m above the mouth of the Chechło reservoir and 200 m below a small post-mining reservoir (km 18 + 520); P4–A point located on the Chechło river, 1750 m above the mouth of the reservoir and 50 m below a bridge on the A4 highway (km 19 + 450).

During the sampling for analysis, the following parameters were measured in situ: pH with the CP-104 pH meter and water temperature, dissolved oxygen concentration (DO) and water saturation (DO_{sat}) using a CO-411 oxygen meter. Also, in situ measurements of velocity of flow were conducted using current meter type HeGa. The following parameters were determined in the laboratory: with the gravimetric method for total suspended solids (TSS) and dissolved substances (DS); ion concentration of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), and chlorophyll “a” (Chl a) were determined by absorption atomic spectrometry on UNICAM SOLAR 969 spectrometer; concentration of nitrogen in ammonium ($N-NH_4^+$), nitrite ($N-NO_2^-$), and nitrate form ($N-NO_3^-$) as well as total phosphorus, phosphates (PO_4^{3-}), and chlorides (Cl^-) were determined using colorimetric method using the FIAstar 5000 apparatus; concentration of sulphates (SO_4^{2-}) was determined using the precipitation gravimetric method; the five-day biochemical oxygen demand (BOD_5) was determined using the Winkler titration method, and the chemical oxygen demand (COD_{Cr}) and organic nitrogen (Org-N) using the titration method. The total nitrogen (TN) concentration was calculated by summing up the results of $N-NH_4^+$, $N-NO_2^-$, $N-NO_3^-$, and Org-N concentrations. All analytical tests were carried out in three replicates using a certified equipment.

2.3. Data Analysis

2.3.1. Basic Data Analysis

For all the analyzed water quality indicators, measured separately at each gauging location, basic descriptive statistics were determined: minimum and maximum values (ranges), arithmetic mean values, and standard deviations. The coefficient of variation (CV) values were calculated from the ratio of standard deviation and mean value. On the basis of the CV, the assessment of variation of data in the data sets was made, with four classes of variation used: small variation (0–20%), medium variation (21–40%), large variation (41–60%), and very large variation (>60%). In order to test whether the values of surface water quality parameters examined at individual locations differ significantly, a statistical test was carried out. Since most of the compared empirical data groups were found to possess no normal distributions (W Shapiro-Wilk test) or homogeneity of variance (Brown-Forsythe test), non-parametric Mann-Whitney U test designed for independent samples was used assuming a significance level $\alpha = 0.05$. Using the Vollenweider and Organisation for Economic Co-operation and Development OECD classification [32], the trophic condition of the examined waters was assessed.

A detailed analysis of physiographic characteristics of the researched catchments were performed with the use of GIS geoinformatics software tools and probable flows were calculated using regional formulas.

2.3.2. Cluster Analysis

With a large number of physicochemical indicators sampled in many locations, an accurate interpretation of water quality assessment results is quite difficult. In such a case, multivariate statistics can be used. One of the most frequently used is the hierarchical method of cluster analysis, in which single clusters are gradually combined by adding up smaller clusters into larger ones. The formation of clusters is a process in which the vectors of parameters are combined into cluster groups so that in each cluster the vectors are as similar as possible, and—in relation to other groups—as different

as possible [33]. Cluster analysis was performed on empirical data standardized according to the following formula [34,35]:

$$Z_{ij} = \frac{x_{ij} - \bar{x}_i}{s_i} \quad (1)$$

$$\bar{X}_i = \frac{\sum_{j=1}^t X_{ij}}{t} \quad (2)$$

$$s_i = \frac{\sum_j (x_{ij} - \bar{x}_i)^2}{t - 1} \quad (3)$$

where: x_{ij} —value for the i -th object and j -th feature; \bar{x}_i — arithmetic mean relative to the i -th feature; s_i —standard deviation relative to the i -th feature.

A square Euclidean measure (metric) of the distance between the objects described by their respective features was used as a measure of similarity for calculations. This metric is often used to classify objects due to its convenient graphical interpretation and simple mathematical properties [36]. It is a geometric distance in a multivariate space, calculated on the basis of the formula:

$$\text{distance}(x, y) = \sum_i (x_i - y_i)^2 \quad (4)$$

Euclidean distances were calculated on the basis of raw data and not standardized data. To estimate the distance between clusters, the Ward method [37] was used, which is based on the analysis of variance. This method seeks to minimize the sum of the squares of deviations of any two clusters that can be formed at each stage. This method is deemed as very effective, although it aims at creating small clusters. It is a commonly used technique for regionalization in hydrology, meteorology, and hydrochemistry [37,38].

Cluster analysis was performed for six variants and presented graphically in the form of dendrograms, for the following groups of indicators:

1. all examined physicochemical indicators (mentioned below),
2. physical and acidification indicators (temperature, TSS, pH),
3. oxygen indicators (DO, BOD₅, COD_{Cr}),
4. phosphorus indicators (TP, PO₄³⁻),
5. nitrogen indicators (Org-N, N-NH₄⁺, N-NO₂⁻, N-NO₃⁻),
6. salinity indicators (SO₄²⁻, Cl⁻, Ca²⁺, Mg²⁺, Na⁺, K⁺).

As a result of the cluster analysis, a cluster hierarchy was obtained, which was presented in the form of dendrograms. The interpretation of the results obtained was based on diagrams of the trend of agglomeration of data, which, due to the limitation of volume, were not included in this study.

2.3.3. Factor Analysis

The purpose of factor analysis was, among others, to detect the structure and general regularities in relationships between the examined physicochemical parameters of water, to reduce the number of variables, and to describe and classify the examined variables in the separated spaces described by the new factors [35]. This analysis uses mathematical models in the form of a system of linear equations. In general, in factor analysis, variables are transformed in order to replace them by a smaller number of factors on which the tested variables are linearly dependent and can explain the correlations between them in the best possible way. Factor analysis attempts to explain the correlations between the observations in terms of the underlying factors, which are not directly observable [39]. The analysis was performed for the following water pollution parameters: water temperature, pH, dissolved oxygen, BOD₅, COD_{Cr}, PO₄³⁻, TP, Org-N, N-NH₄⁺, N-NO₂⁻, N-NO₃⁻, SO₄²⁻, Cl⁻, Ca²⁺, Mg²⁺, Na⁺, and K⁺. Interdependent parameters, such as TSS, O_{sat}, TN, and DS, were omitted. In the group of pollution parameters, physical, aerobic, biogenic, and mineral parameters influencing water salinity

may be included. The question arises whether there are any connections and regularities between these parameters in the sampled water and whether it is possible to replace these parameters with new factors that will represent the quality of the sampled surface water.

In the first stage of the analysis, a correlation matrix between all the variables was performed, which allowed to draw preliminary conclusions as to the regularities occurring in the sample. Then, to assess the significance of the correlation matrix, Bartlett's sphericity test [40] was used to verify the null hypothesis that the correlation matrix is a unitary matrix ($H_0: R = I$), all correlation coefficients of which are equal to zero. When assuming a null hypothesis, there is no point in performing factor analysis. However, the hypothesis can be tested using chi-square distribution statistics with $p(p - 1)/2$ degrees of freedom:

$$U = -\left(n - 1 - \frac{2p + 5}{6}\right) \sum_{i=1}^p \ln \lambda_i \quad (5)$$

where: p —number of variables; n —number of cases; λ_i — i -th eigenvalue.

In the present case, the value of U statistics was -233.113 , which corresponded to a test probability below 0.0000001 , meaning the assumption of a null hypothesis was rejected. Thus, it was confirmed that the analyzed correlation matrix is not a unitary matrix. In the next step, the eigenvalues informing about the hierarchy of significance of the respective factors in explaining the overall variance were determined. Based on the recommendations given by Pekey et al. [40], only those factors whose eigenvalues exceeded 1 were selected for further analysis. For a selected number of new factors (variables), factor loadings, interpreted as correlation coefficients of the individual parameters, and their corresponding new factors (variables) were calculated. Also a communality expressed as part of the variance of the variable explained by common factors was calculated. The results of the calculations are presented in graphical form, taking into account the process of rotation of the coordinate system made using the Varimax method [41].

3. Results and Discussion

The catchment areas of the Chechło river and the Młoszówka stream are characterized by high retention capacities. This is mainly due to the relatively small land gradient, the dominant northern exposure of the slopes which caused lower evaporation losses and, above all, the dominated forest land cover of the area. Taking into account the last factor, it can be concluded that both catchments have high retention capacity, as they are dominated by forests with areas of afforestation with 66.7% and 40.2% of the respective catchment area, respectively. Such a large share of forest area and their mostly concentrated distribution in the Chechło river catchment (Dulowska Forest) will, by retaining a significant amount of water, influence the levelling of outflow [42,43] and the circulation of mineral and organic components. However, it should be taken into account that in the case of long-term rain-free periods and high air temperatures, such a high forest cover may reduce groundwater resources through an increase in evapotranspiration [44]. This, in turn, may cause the occurrence of deepened and long-lasting low groundwater levels which, by transforming over time into hydrological droughts, may threaten the proper functioning of the Chechło water reservoir. From the point of view of quantitative and qualitative resources, attention should be paid to a few percent of wetlands, which may mitigate the effects of climate change [45] and reduce the amount of nutrients and sediments washed out of the catchment [46]. On the other hand, arable land located mainly in the upper part of the Młoszówka stream catchment, with relatively large slopes of the land, may contribute to the formation of erosion processes and influence the increased leaching of substances from the soils.

Assessing the impact of anthropogenic activities on hydrological regime and habitat condition, the Chechło river catchment can be considered as not at risk, as the share of urbanized areas does not exceed 10% of the catchment area [47]. Thus, the hydrological regime and geomorphological and habitat conditions may be similar to natural catchments. The Młoszówka catchment, on the other hand, can be considered at risk (with 17.6% of the impervious areas), with clear signs of degradation

caused by anthropogenic activities, such as larger and more frequent runoffs changing the geometry of watercourses, unstable banks of watercourses, and deterioration of habitat quality. The catchment is also much more likely to undergo rapid freshets and deepened low waters. Unfortunately, the presence of forest areas in it is not very beneficial from the point of view of the retention role, as these areas are scattered and their largest share occurs in the lower part of the catchment area. This situation may potentially result in the largest runoffs, which occur in the headwaters of the catchment, not being sufficiently slowed down by vegetation [48]. This, in turn, can lead to larger and more violent freshets in the lower part of the catchment. The distribution of grasslands in the central part of the catchment should slightly alleviate the unfavourable conditions for the formation of freshets. In the case of the Chechło river catchment, the greatest potential for the formation of significant surface runoffs is in the northern part of the catchment. The shape of the catchment also plays a significant role in the formation of the outflow. The value of the elongation index at the level of 0.71 indicates that the shape of the Chechło river catchment is similar to a circle, which may theoretically influence the more rapid formation of freshets. In the case of the catchment of the Młoszówka stream, on the other hand, the value of the elongation factor of 0.41 proves its lanceolate shape. Theoretically, this may have an effect on the extension of the water run-off route and thus on the alleviation of freshets. However, with this catchment, a somewhat faster reaction to rainfall compared to the catchment of the Chechło river is possible. This is due to the fact that the average slope of the Młoszówka catchment area is more than twice as high, and its area and forest cover are smaller. Undoubtedly, this is also influenced by the greater share of impervious areas in the catchment of the Młoszówka stream, which results in a faster surface runoff and a more rapid outflow of water from the catchment.

Understanding the sources of supply, concentration, and circulation of matter components is essential for the assessment of pollution loads that can lead to deterioration of water quality [49]. Therefore, a detailed analysis of changes in the values of physicochemical indicators of waters outflow of the two catchments differing in physiographic parameters, including land use, was undertaken. Table 2 presents basic descriptive statistics of the examined water quality parameters, and Table 3 presents the results of statistical test carried out with the use of Mann-Whitney U test.

The sampled water in the Chechło river was warmer than in the Młoszówka stream, as shown in Table 2. The largest amount of TSS flowed out of the catchment of the Młoszówka stream, and the smallest amount thereof in the waters of the Chechło river (Table 2). The reason for this are likely to be higher slopes, lower forest cover, and higher share of soils more susceptible to erosion in the catchment of the Młoszówka stream. Similar observations were noted by Halecki et al. [18], based on research conducted in small Carpathian catchments.

Due to the enrichment of water with alkaline substances, the pH values increased systematically along the length of the examined section of Chechło river. Throughout the research period, the reaction of river waters varied from slightly acidic to slightly alkaline. A similar reaction was also found in the water of the Młoszówka stream; however, in this case, the pH values were significantly higher on $\alpha = 0.05$ (Tables 2 and 3), at some dates indicating it as strongly alkaline. This state of affairs was definitely influenced by the humus substances contained in the water that are washed away from poor and acidic forest soils located in the bed of the Chechło river catchment. Similar relationships were described in the studies of Muwamba et al. [50] in the catchment WS79, at Santee Experimental Forest in coastal South Carolina in the US.

The most favourable oxygen conditions prevailed in the Młoszówka stream; DO and DO_{sat} (Tables 2 and 3), whose average slope of the riverbed bottom is over twice as high as in the Chechło river, which results in a higher speed of flowing water and intensity of aeration. The biggest problem with the quality of the Chechło river waters are the organic substances contained in them, which were determined on the basis of the values of indicators indirectly informing about the level of organic pollution—BOD₅ and COD_{Cr}. The basic source of organic substances is the Dulowska Forest with its organic soils, swamps, and a large amount of decomposing plant matter. It can, therefore, be concluded that in the case of the waters of the river investigated here we are dealing with a natural source of

pollution by organic substances, which contain mainly humus substances, as indicated by the brown color of the water. Analyzing the values of the four oxygen parameters and organic pollution at the individual measuring-control points, it was observed that the higher the values of BOD₅ and COD_{Cr}, the lower the concentrations and saturation of water with dissolved oxygen—and vice versa. Such relationships between these parameters are related to oxygen consumption in the processes of biochemical and chemical mineralization of organic substances contained in water, as confirmed by studies by Singh et al. [51] and Sotomayor et al. [52].

Forest vegetation can function as a natural filter against pollutants dumped in watersheds; hence, vegetation cover, diversity, and structure are key drivers of water quality [53,54]. Taking into account the above, the concentrations of all analyzed nutrients were generally at a medium level, while at some study dates only trace values of phosphates and nitrite nitrogen were recorded in the water of the main tributaries of the Chechło reservoir. The highest concentrations of phosphates, which usually occurred at a relatively low level either way, were found in the outflow from the catchment of the Młoszówka stream. Also in the waters of the same watercourse the highest concentrations of TP were recorded, with the difference, however, that their concentrations were quite visible, but did not differ significantly between the examined watercourses for $\alpha = 0.05$ (Tables 2 and 3). The reason for the higher content of these two biogenic parameters of pollution in the water of the Młoszówka stream should be sought in the high urbanization of the central part of its catchment and the presence of arable land. Zhao et al. [55] and Wan et al. [56] state that the settlement and agricultural land use is positively correlated with the content of nutrients in waters, in particular with phosphorus compounds. Undoubtedly, the water quality of the Chechło river is influenced by the buffer role of woodland source areas of the catchment in minimizing phosphorus pollution [57].

The waters outflow from the Młoszówka stream catchment contained significantly higher concentrations of N-NO₂⁻ and N-NO₃⁻ and lower values of N-NH₄⁺ in comparison to the values recorded at the other measurement locations. Poorly visible decreasing tendency of concentration of most nitrogen indicators indicates slow self-purification processes of water along the Chechło river (Tables 2 and 3). The slow rate of this process is evidenced by the low nitrate nitrogen content, which appears as a result of nitrification of organic forms of nitrogen. The situation is different in the case of the waters of the Młoszówka stream, in which higher concentrations of N-NO₂⁻ and lower concentrations of N-NH₄⁺ were found. This indicates temporal and spatial distribution of pollution of the Młoszówka stream waters, in which the self-purification process resulted in a significant increase in the concentration of N-NO₃⁻ at the expense of a decrease in the content of N-NH₄⁺ (Tables 2 and 3). The higher intensity of these favourable processes taking place in Młoszówka is related to the large amount of oxygen dissolved in water, which was also confirmed by the studies of Kowalik et al. [29], and to the reservoir located in the lower part of the catchment, which is heavily overgrown with wetland vegetation and acts as a wetland sewage treatment plant.

Table 2. Descriptive statistics of studied water quality parameters ¹ at the monitoring sites during the research period.

| Parameters | Units | Sampling Location | | | | | | | | | | | |
|--------------------------------|-------------------------------------|-----------------------|---------------|--------|-----------|---------------|--------|------------|---------------|--------|------------|---------------|--------|
| | | P1 | | | P2 | | | P3 | | | P4 | | |
| | | Range | Mean ± SD | CV (%) | Range | Mean ± SD | CV (%) | Range | Mean ± SD | CV (%) | Range | Mean ± SD | CV (%) |
| Chla | µg·dm ⁻³ | LD ² –11.8 | 5.0 ± 5.8 | 117 | LD–16.2 | 5.1 ± 7.4 | 145 | LD–16.6 | 7.9 ± 7.5 | 95 | LD–4.7 | 1.7 ± 2.3 | 139 |
| Temperature | °C | 0.3–22.5 | 11.4 ± 6.4 | 56 | 0.0–22.6 | 12.3 ± 7.1 | 58 | 0.0–21.3 | 12.1 ± 6.8 | 56 | 0.0–20.9 | 11.6 ± 6.8 | 59 |
| TSS | mg·dm ⁻³ | 0.1–8.7 | 3.7 ± 2.0 | 56 | 0.3–5.3 | 2.7 ± 1.7 | 62 | 0.9–10.7 | 2.8 ± 2.4 | 85 | 0.1–4.2 | 1.6 ± 1.2 | 75 |
| pH | pH unit | 7.1–8.1 | 7.7 ± 0.3 | 4 | 6.6–7.7 | 7.3 ± 0.3 | 4 | 6.6–7.7 | 7.2 ± 0.3 | 5 | 6.4–7.6 | 7.1 ± 0.4 | 5 |
| DO | mg O ₂ ·dm ⁻³ | 7.3–13.5 | 9.7 ± 1.6 | 17 | 5.4–12.3 | 8.3 ± 1.9 | 23 | 2.4–12.0 | 7.8 ± 2.7 | 34 | 2.0–12.8 | 7.9 ± 2.6 | 34 |
| DO _{sat} | % | 73–110 | 89 ± 1 | 13 | 30–115 | 79 ± 115 | 19 | 28–99 | 70 ± 19 | 27 | 23–111 | 73 ± 211 | 29 |
| BOD ₅ | mg O ₂ ·dm ⁻³ | 1.0–10.0 | 3.9 ± 2.8 | 73 | 1.0–10.0 | 4.2 ± 3.0 | 71 | 1.0–15.0 | 4.2 ± 3.4 | 80 | 1.2–10.0 | 4.7 ± 2.6 | 55 |
| COD _{Cr} | mg O ₂ ·dm ⁻³ | 1.8–33.1 | 16.4 ± 8.0 | 49 | 25.2–80.0 | 40.6 ± 17.0 | 42 | 16.1–125.2 | 51.1 ± 30.6 | 60 | 25.8–118.0 | 60.4 ± 29.7 | 49 |
| TP | mg·dm ⁻³ | 0.10–0.93 | 0.26 ± 0.27 | 105 | 0.04–0.93 | 0.20 ± 0.24 | 117 | 0.03–0.59 | 0.17 ± 0.17 | 97 | 0.04–0.82 | 0.16 ± 0.19 | 123 |
| PO ₄ ³⁻ | mg·dm ⁻³ | LD–0.095 | 0.038 ± 0.027 | 71 | LD–0.080 | 0.020 ± 0.027 | 134 | LD–0.062 | 0.018 ± 0.023 | 124 | LD–0.089 | 0.022 ± 0.028 | 128 |
| TN | mg·dm ⁻³ | 1.06–3.82 | 2.42 ± 0.61 | 25 | 0.97–4.92 | 1.97 ± 0.91 | 46 | 1.02–3.76 | 1.80 ± 0.63 | 35 | 1.23–3.74 | 1.93 ± 0.62 | 32 |
| Org-N | mg·dm ⁻³ | 0.38–1.74 | 1.06 ± 0.38 | 36 | 0.27–4.11 | 1.10 ± 0.89 | 81 | 0.16–2.97 | 0.82 ± 0.64 | 78 | 0.49–2.95 | 1.05 ± 0.60 | 57 |
| N-NH ₄ ⁺ | mg·dm ⁻³ | 0.03–0.40 | 0.19 ± 0.10 | 53 | 0.16–0.90 | 0.48 ± 0.22 | 46 | 0.21–0.95 | 0.48 ± 0.20 | 42 | 0.24–1.33 | 0.60 ± 0.31 | 51 |
| N-NO ₂ ⁻ | mg·dm ⁻³ | LD–0.029 | 0.014 ± 0.009 | 66 | LD–0.019 | 0.005 ± 0.007 | 142 | LD–0.060 | 0.009 ± 0.016 | 177 | LD–0.065 | 0.008 ± 0.017 | 205 |
| N-NO ₃ ⁻ | mg·dm ⁻³ | 0.28–2.10 | 1.16 ± 0.46 | 40 | 0.06–1.23 | 0.39 ± 0.36 | 91 | 0.09–1.23 | 0.49 ± 0.38 | 79 | 0.01–1.38 | 0.27 ± 0.34 | 124 |
| DS | mg·dm ⁻³ | 360–628 | 432 ± 68 | 16 | 180–296 | 254 ± 35 | 14 | 148–284 | 242 ± 32 | 13 | 142–314 | 251 ± 47 | 19 |
| SO ₄ ²⁻ | mg·dm ⁻³ | 34.8–101.0 | 81.0 ± 18.6 | 23 | 14.8–71.5 | 40.0 ± 15.1 | 38 | 18.1–74.9 | 41.6 ± 17.7 | 42 | 11.9–77.8 | 40.4 ± 19.1 | 47 |
| Cl ⁻ | mg·dm ⁻³ | 36.0–95.3 | 64.7 ± 13.3 | 21 | 28.6–54.5 | 44.8 ± 7.77 | 17 | 29.6–60.4 | 45.4 ± 8.8 | 19 | 27.7–46.4 | 38.1 ± 5.5 | 15 |
| Ca ²⁺ | mg·dm ⁻³ | 54.9–87.4 | 73.4 ± 10.0 | 14 | 19.7–51.2 | 36.8 ± 7.4 | 20 | 17.4–41.4 | 34.0 ± 5.9 | 17 | 16.1–66.9 | 39.0 ± 11.7 | 30 |
| Mg ²⁺ | mg·dm ⁻³ | 6.5–10.6 | 8.1 ± 1.0 | 13 | 2.4–5.3 | 4.3 ± 0.7 | 17 | 2.0–5.2 | 4.2 ± 0.8 | 19 | 1.9–5.7 | 4.1 ± 0.9 | 22 |
| Na ⁺ | mg·dm ⁻³ | 26.3–45.9 | 32.5 ± 5.6 | 17 | 11.3–25.3 | 20.3 ± 4.0 | 20 | 11.4–28.7 | 20.9 ± 4.4 | 21 | 10.6–20.8 | 15.6 ± 2.8 | 18 |
| K ⁺ | mg·dm ⁻³ | 3.2–8.0 | 4.9 ± 1.2 | 25 | 1.2–3.6 | 2.2 ± 0.6 | 27 | 1.1–3.7 | 2.2 ± 0.6 | 28 | 0.6–3.1 | 1.6 ± 0.7 | 41 |

¹ number of samples, for each P1, P2, P3 and P4, taking during the research period was 36, ² LD—below the limit of detection.

Table 3. Comparison of water quality parameters values between measurement-control points using non-parametrical Mann-Whitney U test.

| Parameter | Test Probability Values (p) in Variants | | | | | |
|--------------------------------|---|-------|-------------------|-------|-------|-------|
| | P1–P2 | P1–P3 | P1–P4 | P2–P3 | P2–P4 | P3–P4 |
| Chla | 0.84 | 0.69 | 0.54 | 0.55 | 0.69 | 0.31 |
| Temperature | 0.68 | 0.71 | 0.84 | 0.87 | 0.81 | 0.87 |
| TSS | 0.35 | 0.06 | 0.05 ¹ | 0.87 | 0.04 | 0.02 |
| pH | 0.00 | 0.00 | 0.00 | 0.35 | 0.41 | 1.00 |
| DO | 0.09 | 0.10 | 0.07 | 0.84 | 0.57 | 0.94 |
| DO _{sat} | 0.02 | 0.00 | 0.01 | 0.37 | 0.46 | 0.74 |
| BOD ₅ | 0.81 | 0.68 | 0.20 | 1.00 | 0.46 | 0.46 |
| COD _{Cr} | 0.00 | 0.00 | 0.00 | 0.31 | 0.08 | 0.41 |
| TP | 0.12 | 0.12 | 0.01 | 0.84 | 0.54 | 0.84 |
| PO ₄ ³⁻ | 0.05 | 0.05 | 0.05 | 0.84 | 0.90 | 0.81 |
| TN | 0.00 | 0.00 | 0.01 | 0.41 | 0.90 | 0.39 |
| Org–N | 0.37 | 0.02 | 0.49 | 0.11 | 0.84 | 0.05 |
| N–NH ₄ ⁺ | 0.00 | 0.00 | 0.00 | 0.90 | 0.41 | 0.31 |
| N–NO ₂ ⁻ | 0.01 | 0.07 | 0.04 | 0.74 | 1.00 | 0.87 |
| N–NO ₃ ⁻ | 0.00 | 0.00 | 0.00 | 0.51 | 0.09 | 0.02 |
| DS | 0.00 | 0.00 | 0.00 | 0.27 | 0.94 | 0.49 |
| SO ₄ ²⁻ | 0.00 | 0.00 | 0.00 | 0.84 | 0.94 | 0.71 |
| Cl ⁻ | 0.00 | 0.00 | 0.00 | 1.00 | 0.01 | 0.02 |
| Ca ²⁺ | 0.00 | 0.00 | 0.00 | 0.24 | 0.71 | 0.23 |
| Mg ²⁺ | 0.00 | 0.00 | 0.00 | 0.94 | 0.31 | 0.39 |
| Na ⁺ | 0.00 | 0.00 | 0.00 | 0.71 | 0.00 | 0.00 |
| K ⁺ | 0.00 | 0.00 | 0.00 | 0.94 | 0.00 | 0.01 |

¹ The statistically significant values are marked in red, for $p \leq \alpha = 0.05$.

The most saline water flowed out of the Młoszówka stream catchment, as the values of all salinity indicators (DS, SO₄²⁻, Cl⁻, Ca²⁺, Mg²⁺, Na⁺ and K⁺) were statistically significantly for $\alpha = 0.05$, higher than in the Chechło river (Tables 2 and 3). For these reasons, the water flowing through Młoszówka was mostly medium-hard, while the water in the Chechło river was soft. This fact mainly stems from land use and build-up of the area, i.e., greater urbanization of the catchment of the Młoszówka stream, much greater forest cover of the Chechło river catchment and quite significant differences in soil types occurring in both catchments. This is consistent with the studies described by Zhang et al. [58], in which it was found that the greatest impact on the deterioration of water quality in watercourses are in urban areas, followed by arable land, while grassland ecosystems and forest areas usually have a beneficial effect on water chemistry. Similar observations were presented in the works of Kosmowska et al. [59], De Mello et al. [60,61], Namugize et al. [62], and Wijesiri et al. [63]. For these reasons, we can speculate on greater anthropogenic activities in the Młoszówka catchment, the central part of which is heavily built-up and the concrete and paved bed of the stream runs in many places parallel to asphalt roads. In addition, above the main road between Trzebinia and Krakow there are several interceptors that drain rainwater directly running off asphalt surfaces into the Młoszówka stream, which undoubtedly results in higher salinity and, consequently, in a deterioration of water quality.

Differentiation of the measured pH values during the study period was small at all water sampling locations, which is confirmed by the coefficient of variation values within the range of 4–5%, as shown in Table 2. Low or average random variation occurred for DO, DO_{sat}, and TP, as well as for most salinity indicators. Large differences in empirical data were recorded for temperature, COD_{Cr} and N–NH₄⁺, and very large for the other water quality parameters. In general, the physicochemical parameters of water flowing out of the Młoszówka stream were characterized by lower random variation compared to the outflow from the Chechło river catchment (Table 2).

On the basis of hydrological measurements mean velocity between the profiles P4 and P2 was equal to 0.39 m·s⁻¹ and distance between profiles was equal 1740 m. Thus the approximated travel time

is about 1.23 h. For the reason that water samples were collected from the Chechło river in a few-minute interval, in the order of point P4, P3, and P2, it can be concluded that the quality parameters were measured in the same water. The description of the test results presented in Table 2 are based on average values, but the relationships related to the decrease in the length of the Chechło river were also recorded in each field measurement dates. In a distance of 1740 m of the Chechło river the values of organic pollution indicators decreased: in the case of BOD₅ by 11%, and COD_{Cr} by 33% of the initial value recorded in point P4. The concentration of TN and Org-N slightly increased on the tested section of the river, but this state was probably affected by biodegradation of organic compounds occurring in the self-purification process, as a result of which nitrogen-containing compounds are also formed.

There are only a few small tributaries on the examined part of the Chechło river, in which water flows periodically. Therefore, it can be concluded slightly diluting effect on the decline in the value of some pollution indicators (dilution is also an element of the water self-purification process). On the other hand, the rapid flow of water in the river causing its oxygenation increases and oxygen is used in the process of biodegradation of organic substances, and thus affects the water self-purification.

According to the trophicity criteria proposed by Vollenweider [32], average TP concentrations at all measurement gauging locations allowed the water to be classified as hypertrophic, and—due to mineral nitrogen content—as mesotrophic waters. The assessment based on TP concentrations carried out in accordance with OECD criteria [32] confirmed that the sampled waters are hypertrophic. Chlorophyll “a” concentrations indicate mesotrophy of waters flowing out of the catchments of Chechło river and the Młoszówka stream.

On the basis of the cluster analysis carried out with the Ward method for a total of 18 physicochemical parameters and separately for physical parameters and acidification, aerobic, phosphorus, nitrogen, and salinity parameters, six dendrograms were obtained showing similarity or differences in the quality of the water tested at individual measurement and gauging locations (Figure 3).

Taking into account all the examined indicators, the similarity of water quality between the locations was less noticeable than in the other analyzed variants, because the whole data aggregation process ended at an intra-cluster distance of 89, and at a distance of 12 two clusters developed (Figure 3a): the first consisting of three points located on the Chechło river (P2–P4) and the second comprising only point P1 located at the mouth of the Młoszówka stream into the water reservoir. This proves that there are large differences in the quality of water flowing in both of the sampled watercourses. In order to analyze the data in detail, a cluster analysis was carried out separately for each group of the examined physicochemical indicators.

The arrangement of clusters in the dendrogram for physical parameters and acidification (temperature, TSS and pH) indicates a very high similarity in the water quality of the Chechło river in points 2 and 3. Smaller values of the three analyzed parameters of water flowing out of the Dulowska Forest resulted in the formation of a single cluster in point P4. One-element cluster also occurred in the case of point P1 located on the Młoszówka stream, which was influenced by the highest values of all analyzed physical parameters and acidification (Figure 3b).

In the case of oxygen parameters (O₂, BOD₅, COD_{Cr}) at the level 2 cut-off point, three clusters were formed, including two single clusters at points P1 and P4, and one double cluster consisting of points P2 and P3 (Figure 3c). This arrangement of clusters was influenced by the highest concentrations of dissolved oxygen and the lowest COD_{Cr} values in the water of the Młoszówka stream. On the other hand, the formation of a separate cluster in point P4 is related to the self-purification processes in the Chechło river water, which led to the decomposition of organic substances and contributed to the reduction of BOD₅ and COD_{Cr} values at the measurement and control points along the river—P3 and P2.

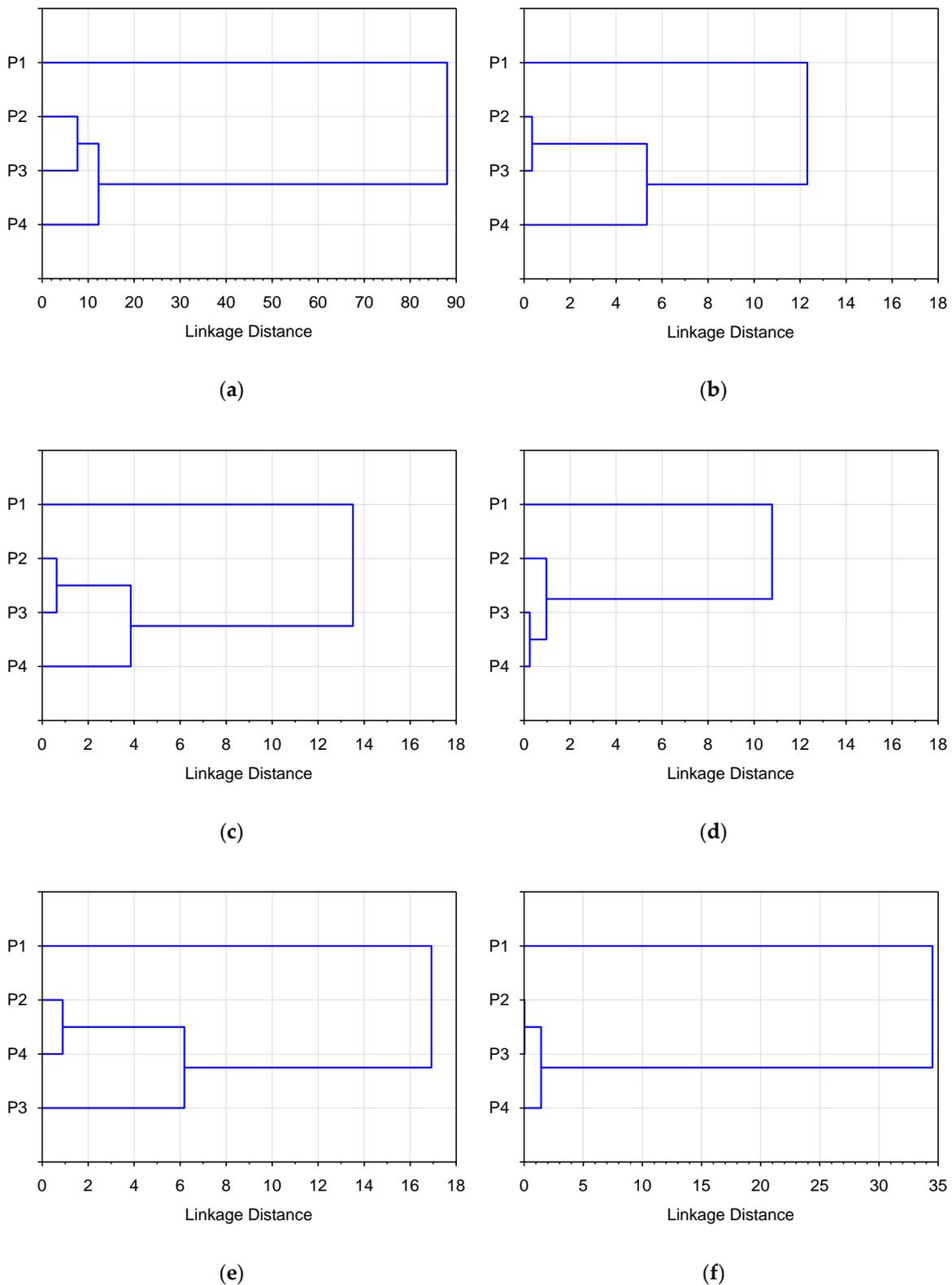


Figure 3. Dendrograms (Ward’s Method—Square of Eukclidean Distance) showing similarity of surface water quality examined in individual measurement-control points, taking into account the values of (a) all examined physicochemical indicators, (b) physical and acidification indicators, (c) oxygen indicators, (d) phosphorus indicators, (e) nitrogen indicators, (f) salinity indicators.

Two clusters (cut-off level 2), including one three-element cluster consisting of P2–P4 points located on the Chechło river and one-element cluster on the Młoszówka stream (Figure 3d), were formed on the dendrogram made for phosphorus indicators (TP and PO_4^{3-}). Such arrangement of data aggregation is mainly caused by much higher phosphate concentrations in point P1, which is undoubtedly influenced by a large share of built-up areas in the catchment of the Młoszówka stream.

In the case of nitrogen indicators (Org-N, N-NH_4^+ , N-NO_2^- and N-NO_3^-), at the level 2 cut-off point, three clusters were formed, including two single clusters at points P1 and P3, and one double cluster consisting of points P2 and P4 (Figure 3e). This cluster arrangement resulted from the highest concentrations of N-NO_2^- and N-NO_3^- and the lowest concentrations of N-NH_4^+ recorded in the water of the Młoszówka stream. The separate cluster on the Chechło river at point P3 results from lower concentrations of Org-N and higher values of N-NO_3^- , which is the result of the decomposition of organic substances in the small post-mining reservoir located upstream the measurement and control point.

The dendrogram generated on the basis of concentrations of SO_4^{2-} , Cl^- , Ca^{2+} , Mg^{2+} , Na^+ , and K^+ ions shows that the water flowing out of the Młoszówka stream catchment is much more saline than the water flowing down the Chechło river (Figure 3f). Such a cluster system is characteristic for river catchments with significantly different anthropogenic pressure, which is the case with the two tributaries of the Chechło reservoir under examination.

From the presented correlation matrix (Table 4) it is evident that there is a group of interrelated variables. It can be seen that the pH is strongly positively correlated with all salinity ions and PO_4^{3-} and negatively correlated with the chemical oxygen demand (COD_{Cr}). Dissolved oxygen (DO) concentrations are strongly negatively correlated with COD_{Cr} , N-NH_4^+ and water temperature. COD_{Cr} values correlate strongly positively with N-NH_4^+ and negatively with N-NO_3^- as well as all salinity ions. Phosphates correlate strongly positively with Cl^- and Mg^{2+} ions, while N-NH_4^+ concentrations with all salinity ions and negatively with N-NO_3^- . Nitrate nitrogen is strongly positively correlated with saline ions, which are also correlated with each other. No strong correlation was found for BOD_5 , Org-N, and N-NO_2^- .

Based on the analysis of eigenvalues, four factors were identified which together explain almost 71% of the total variation of the analyzed water quality indicators. The highest variation of parameters observed in the analyzed sample is explained by the first factor –45% of variation. Another three factors explained over 32% of the variation. In subsequent analyses, the variables were further reduced and eventually three factors were adopted, for which the minimum value is 1.31 and which explain 71% of the total variation (Table 5).

On the basis of a detailed analysis of the results presented in Table 5, it can be concluded that concentrations of SO_4^{2-} , Cl^- , Ca^{2+} , Mg^{2+} , Na^+ , and K^+ have high factor loadings with the first factor, water temperature and DO with the second factor, and BOD_5 and Org-N with the third factor. Three new variables can therefore be created, which will represent water salinity (factor 1), oxygen conditions (factor 2) and water pollution by organic substances (factor 3). Factors selected in this way determine to the greatest extent the quality of water flowing into the Chechło reservoir. The conducted factor analysis largely coincides with the results obtained from the cluster analysis in which it was shown that well oxygenated waters with high salinity (mineralization) flow through the Młoszówka stream, and the waters of the Chechło river contain significant amounts of organic substances.

A graphical summary of factor loadings for the analyzed water quality indicators is presented in Figure 4. Figure 4a shows that the highest factor loadings for Factor 1 occur in the case of mineral compounds. For Factor 2 a large share was found in case of water temperature, DO N-NH_4^+ , N-NO_2^- , and COD_{Cr} .

Table 4. The correlation matrix of the analyzed variables.

| Parameters | Temperature | pH | DO | BOD ₅ | COD _{Cr} | PO ₄ ³⁻ | Org-N | N-NH ₄ ⁺ | N-NO ₂ ⁻ | N-NO ₃ ⁻ | SO ₄ ²⁻ | Cl ⁻ | Ca ²⁺ | Mg ²⁺ | Na ⁺ | K ⁺ |
|--------------------------------|-------------|--------|---------------------|------------------|-------------------|-------------------------------|--------|--------------------------------|--------------------------------|--------------------------------|-------------------------------|-----------------|------------------|------------------|-----------------|----------------|
| Temperature | 1.000 | 0.142 | -0.564 ¹ | -0.272 | 0.355 | 0.149 | 0.182 | 0.321 | 0.324 | -0.384 | -0.252 | 0.192 | 0.195 | -0.078 | 0.157 | -0.225 |
| pH | 0.142 | 1.000 | 0.114 | 0.108 | -0.465 | 0.465 | 0.105 | -0.311 | 0.142 | 0.260 | 0.574 | 0.425 | 0.611 | 0.661 | 0.510 | 0.479 |
| DO | -0.564 | 0.114 | 1.000 | -0.101 | -0.530 | -0.291 | -0.003 | -0.420 | -0.192 | 0.348 | 0.370 | 0.095 | 0.155 | 0.262 | 0.193 | 0.364 |
| BOD ₅ | -0.272 | 0.108 | -0.101 | 1.000 | -0.017 | 0.096 | -0.264 | -0.025 | -0.136 | 0.124 | 0.107 | -0.204 | -0.146 | 0.046 | -0.207 | -0.011 |
| COD _{Cr} | 0.355 | -0.465 | -0.530 | -0.017 | 1.000 | -0.166 | 0.140 | 0.688 | 0.258 | -0.554 | -0.700 | -0.456 | -0.429 | -0.605 | -0.545 | -0.667 |
| PO ₄ ³⁻ | 0.149 | 0.465 | -0.291 | 0.096 | -0.166 | 1.000 | -0.098 | -0.017 | 0.258 | 0.152 | 0.253 | 0.404 | 0.346 | 0.414 | 0.348 | 0.190 |
| Org-N | 0.182 | 0.105 | -0.003 | -0.264 | 0.140 | -0.098 | 1.000 | -0.039 | 0.049 | -0.068 | -0.144 | -0.007 | 0.149 | 0.001 | 0.045 | -0.022 |
| N-NH ₄ ⁺ | 0.321 | -0.311 | -0.420 | -0.025 | 0.688 | -0.017 | -0.039 | 1.000 | 0.303 | -0.616 | -0.524 | -0.374 | -0.521 | -0.602 | -0.446 | -0.740 |
| N-NO ₂ ⁻ | 0.324 | 0.142 | -0.192 | -0.136 | 0.258 | 0.258 | 0.049 | 0.303 | 1.000 | 0.036 | 0.058 | 0.300 | 0.264 | 0.179 | 0.309 | 0.047 |
| N-NO ₃ ⁻ | -0.384 | 0.260 | 0.348 | 0.124 | -0.554 | 0.152 | -0.068 | -0.616 | 0.036 | 1.000 | 0.658 | 0.516 | 0.520 | 0.590 | 0.537 | 0.748 |
| SO ₄ ²⁻ | -0.252 | 0.574 | 0.370 | 0.107 | -0.700 | 0.253 | -0.144 | -0.524 | 0.058 | 0.658 | 1.000 | 0.617 | 0.686 | 0.733 | 0.664 | 0.736 |
| Cl ⁻ | 0.192 | 0.425 | 0.095 | -0.204 | -0.456 | 0.404 | -0.007 | -0.374 | 0.300 | 0.516 | 0.617 | 1.000 | 0.764 | 0.690 | 0.949 | 0.641 |
| Ca ²⁺ | 0.195 | 0.611 | 0.155 | -0.146 | -0.429 | 0.346 | 0.149 | -0.521 | 0.264 | 0.520 | 0.686 | 0.764 | 1.000 | 0.857 | 0.781 | 0.734 |
| Mg ²⁺ | -0.078 | 0.661 | 0.262 | 0.046 | -0.605 | 0.414 | 0.001 | -0.602 | 0.179 | 0.590 | 0.733 | 0.690 | 0.857 | 1.000 | 0.762 | 0.815 |
| Na ⁺ | 0.157 | 0.510 | 0.193 | -0.207 | -0.545 | 0.348 | 0.045 | -0.446 | 0.309 | 0.537 | 0.664 | 0.949 | 0.781 | 0.762 | 1.000 | 0.712 |
| K ⁺ | -0.225 | 0.479 | 0.364 | -0.011 | -0.667 | 0.190 | -0.022 | -0.740 | 0.047 | 0.748 | 0.736 | 0.641 | 0.734 | 0.815 | 0.712 | 1.000 |

¹ The statistically significant values are marked in red.

Table 5. The factor loadings for three selected factors.

| Parameter | Factor 1 | Factor 2 | Factor 3 |
|--------------------------------|----------|--------------------|----------|
| Temperature | 0.097 | 0.798 ¹ | 0.299 |
| pH | 0.687 | 0.065 | -0.094 |
| DO | 0.188 | -0.750 | 0.163 |
| BOD ₅ | -0.060 | -0.066 | -0.834 |
| COD _{Cr} | -0.605 | 0.610 | 0.072 |
| Org-N | 0.010 | 0.042 | 0.703 |
| N-NH ₄ ⁺ | -0.556 | 0.629 | -0.058 |
| N-NO ₂ ⁻ | 0.312 | 0.630 | 0.030 |
| N-NO ₃ ⁻ | 0.648 | -0.434 | -0.169 |
| SO ₄ ²⁻ | 0.804 | -0.303 | -0.221 |
| Cl ⁻ | 0.872 | 0.120 | 0.129 |
| Ca ²⁺ | 0.910 | 0.053 | 0.155 |
| Mg ²⁺ | 0.906 | -0.142 | -0.071 |
| Na ⁺ | 0.914 | 0.047 | 0.160 |
| K ⁺ | 0.833 | -0.372 | -0.024 |

¹ The statistically significant values are marked in red.

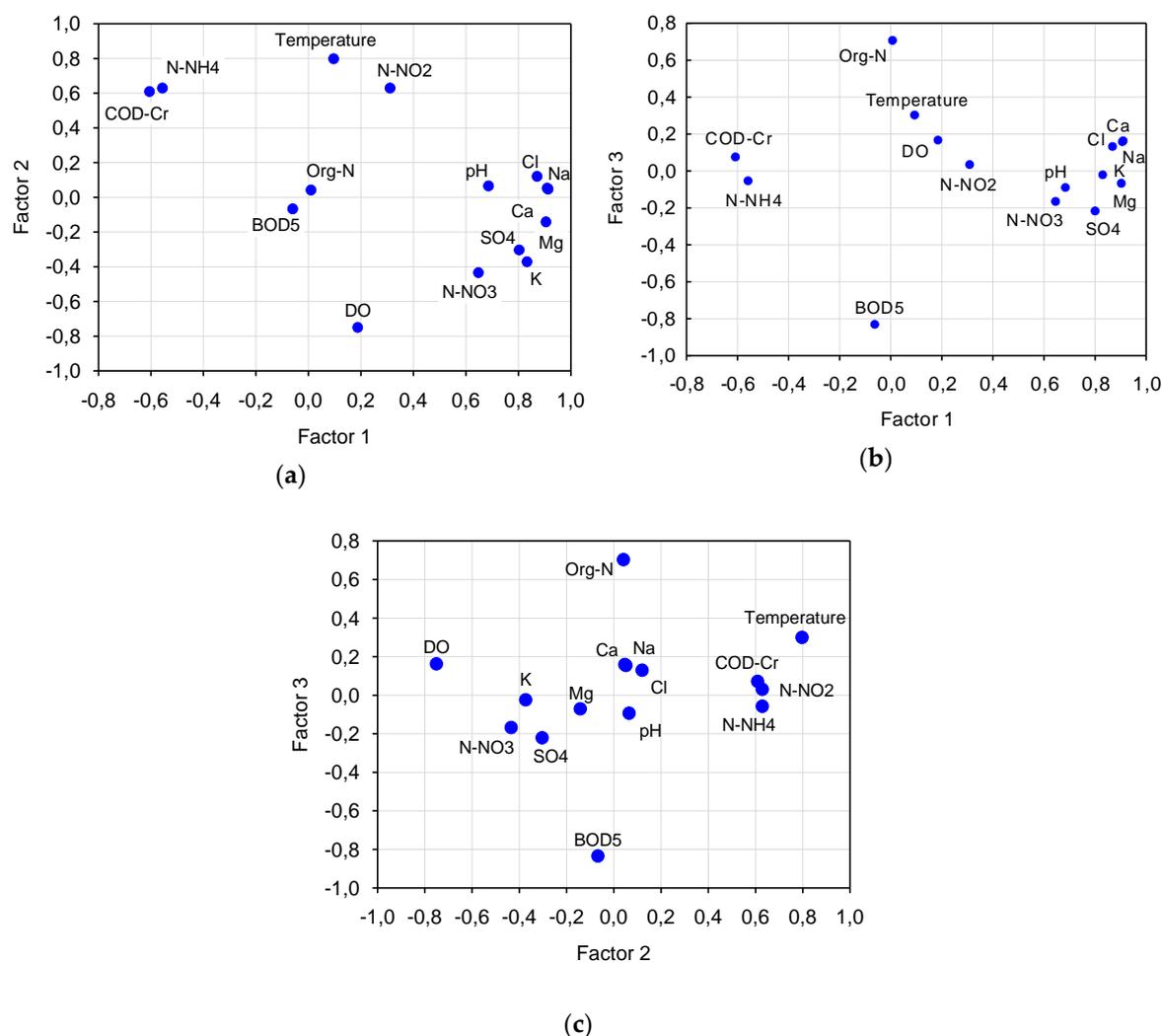


Figure 4. Factor load charts between: (a) factor 1 and 2, (b) factor 1 and 3, (c) factor 2 and 3.

All these parameters represent aerobic conditions or are associated with the conversion of pollutants under aerobic conditions (N-NH₄⁺ and N-NO₂⁻). The opposite position of temperature

and DO indicates their inversely proportional relationship. In the case of factor 3 we can observe a large share of Org–N and BOD₅ factor loadings (Figure 4a,b). This can be explained by the fact that BOD₅ is a parameter specifying the amount of oxygen needed for the decomposition of readily decomposable organic compounds contained in water, which is closely related to the mineralization process. Since organic nitrogen compounds decompose relatively slowly, they generally do not cause an increase in BOD₅ in the initial period.

4. Conclusions

The interactions between different forms of land use and water quality are difficult to estimate due to the huge number of parameters and complexity of the processes occurring in the catchment and streamwater [64,65]. In addition to these factors, there are physiographic parameters of the catchment that can positively or negatively influence the properties of surface water. These hypotheses are confirmed by the results of our research. Water outflow from the forest and settlement mixed catchment, which is characterized by higher land slopes and a high share of mineral soils, contained higher concentrations of phosphorus, phosphates, nitrite, and nitrate nitrogen as well as salinity indicators compared to the nearby forest catchment. In spite of a larger share of urbanized areas and roads, the water was characterized by more favourable oxygen conditions, which was a result of a large gradient of the bottom of the investigated watercourse and a smaller amount of organic substances subject to the process of decomposition. In terms of land cover, generally better water quality was found in the forest catchment, which confirmed the assumed research hypothesis about the beneficial effect of this type of land use on surface water quality. It should be noted, however, that water outflow from this catchment is also polluted, but, in this case, with organic substances of natural origin, i.e., from organic soils and from the decomposition of plant matter occurring in the Dulowska Forest. Despite the short section of the river under study, beneficial self-purification processes were observed in the water. The research shows that forest areas have a positive effect on the balance of most substances dissolved in water, and natural factors, in many cases, shape the quality and utility values of surface waters on an equal footing with anthropogenic factors.

The results of this study also allowed to state that in case of a large number of examined physicochemical parameters of water, the interpretation of the results for their relationships and interactions is rather difficult, justifying the use of multivariate statistical methods. Cluster analysis allows, among others, for objective determination of similarities of the examined groups of water parameters between the individual measurement and control points, while factor analysis allows to reduce the number of variables to those actually having greatest impact on the quality of surface waters [66,67].

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