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Capacity of River Valleys to Retain Nutrients from Surface Runoff in Urban and Rural Areas (Southern Poland)

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Abstract: Studies on water quality are necessary, as catchments of small watercourses are exposed to anthropogenic influences associated with agricultural activities, settlement, transport and other undertakings, leading to water pollution. There has been insufficient research performed on the valley's ability to retain nutrients during floods, contributing to water accumulation. The main object of the study was to identify the retention capacity of river valleys under various aspects of human urbanization. To represent soil water retention, the Soil Conservation Service Curve Number (SCS-CN) method was used. Spatiotemporal autoregressive models were exploited to investigate the relationship between pollutants in precipitation and surface water in rivers. In contrast, multivariate analysis was used to identify and reveal patterns of land use for specific chemical compounds in the headwaters. The canonical-correlation analysis (CCA) showed that Mg^{+2} and Ca^{+2} cations in rainwater and surface waters play the main roles in the geochemical cycle in urban and rural areas. In the urban catchment area, the strongest relations were found for NO_3^-, K^+ and Na^+. The average NO_3^- concentration in urban headwater was 8.3 mg·dm^{-3}, the highest in the study area. The relationship between NO_3^- concentration in headwater and rainwater was found for all study catchments using spatial autoregression (SAR). High concentrations of SO_4^{2-} in surface water have been identified in urban areas. Severe water erosion raises the risk of nutrient leaching in soils prone to surface runoff. As a consequence of low soil permeability and urbanization, retention capacity is significantly reduced in areas with low soil permeability. Land development plans should take spatial retention capacity into consideration. To ensure that large reservoirs can retain water in the face of climate change, riparian buffer zones (protective zones in valleys for small water bodies as well as Nature-based Solution) are important.

Keywords: catchment retention; Nature-based Solution; rainfall-runoff model; water circulation

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1. Introduction

Recently, the interest in the retention capacity of catchments has grown significantly [1]. This results from the increasing frequency of floods and their negative consequences, resulting in economic and social losses [2]. Thus, it is important to note the retention capacity of a catchment [3]. The soil and its filtration capacities, i.e., the permeability of the soil or the surface layer of the soil, represent one of the most important factors in this respect. The type of soil may significantly influence the retention potential, as its ability to absorb water plays a particularly important role [4,5]. The role of spatial planning in catchment retention capacity has gained increasing recognition. It is emphasised in various programme documents and legal acts, both at the national and European levels [6]. This issue is gaining in importance, especially in the context of the transformation of arable lands into built-up and urban areas, and this significantly influences the increase in surface runoff and reduces water absorption by the ground [7].

An improvement in the soil structure improves the soil retention capacity. Appropriate agricultural practises, the use of organic fertilisers and other activities increase the soil water resources [8]. Agromelioration practises are also important, as they improve the soil structure and eliminate layers of poor permeability when performed correctly. The agromelioration practises have the following double role: they increase the soil retention capacity and facilitate water penetration into the aquifer [9]. The water parameters of the soil significantly influence the retention parameters of the substrate. Rainwater may move within the soil; however, this depends on many factors. Porosity is influenced by various factors, such as moisture content, precipitation, methods of use and farming practises [10]. Absorption of rainwater means mainly vertical water movement [11]. The initial phase of water absorption involves soil wetting [12].

Researchers all over the world study issues associated with water quality in large and small areas. The management of water resources is decisive for sustainable development [13,14]. One of the methods to retain water in an urban catchment is through activities termed 'small retention measures', which are mainly associated with the construction of dams on local watercourses and the creation of water reservoirs [15]. The aim of measures supporting small retention is to increase the water volume in the soil through technical (agricultural, agromelioration and phytomelioration) activities and water retention by plants [16]. Apart from storage of water for direct use, small retention aims at regulating and controlling water circulation in the environment [17]. It facilitates better protection and renewal of water resources. It also enables reliable water management without disrupting the balance in nature and develops urban resilience [18]. Reservoirs of dams play a very important role in water management because they help to reduce flood waves in urbanised areas [19], while they can be used to supply water to a river during a drought [20]. Furthermore, small water reservoirs are very popular in bare, arid areas where water for drinking, household use and irrigation in agriculture is particularly scarce [21,22]. In many countries, small retention tanks are very useful in rural areas because they gather water that is later used in agriculture, mainly to irrigate crop areas [23].

Surface waters in micro and small catchments are studied by research centres, which determine the effect of human activities on the quality of water resources in previously unmonitored catchments [24]. On a global scale, changes that took place in land cover and use are named as the cause of poor quality of water [25]. An increase in the area of arable land and pastures, as well as an increasing number of paved non-permeable surfaces, with a simultaneous decrease in the area of green lands and forests, resulting in a global reduction in evapotranspiration [26], with a simultaneous increase in the surface runoff [27,28]. This had a significant influence on the quality of surface waters, as their salinity increased and parameters deteriorated [29,30] due to fertilisers used in agriculture and contaminations flowing from urbanised areas [31].

One of the methods to solve complicated problems of water management may be various environmental, technical and organisational actions supporting water accumulation, delaying runoff and increasing its availability to the economy, including agricultural production and land development, such as the fashionable 'Sponge City' concept [32]. Recently, nature-based solutions have been particularly popular [33,34]. In this respect, geographic information systems and remote sensing procedures are helpful [35], enabling the description of catchment characteristics and integrating data within one system [36]. Various programmes are proposed to improve the quality of water through correct development and management of river catchments [37]. Therefore, the paper verified the physical and chemical parameters of a surface watercourse in urban and rural areas, and of rainwater. It is very important to ensure that the supply of a sufficient quantity of water is combined with its appropriate quality, as polluted water may cause the degradation of a water reservoir within a short time [38]. An analysis of the spatial retention capacity of three small catchments used in different ways is very important in terms of current policies related to climate change [39]. Cost-effective engineering solutions can reduce flood risk by optimising drainage and detention [40]. In response to climate change, it has become necessary to improve the water retention capacity of catchments and protect valleys [41].

Areas with varying degrees of anthropogenization were calculated based on catchment characteristics and soil type. Nutrient leaching into small catchments needs to be quantified to ensure the forest environment's productivity. For drained forest catchments, it can be implemented, for instance, through improved water runoff measures. A rural area's social interests should be managed and protected in the most effective way. Insufficient research has been conducted on the valley's ability to retain water during floods, contributing to water accumulation overall. A vegetative buffer zone should be established around local water supply networks to prevent valley retention. Consequently, the following research objectives were established: (i) measuring the effect of anthropopressure on water quality in a catchment area; (ii) identifying soil retention rates in urban, suburban and rural areas; (iii) calculating the optimal balance between retention capacity and drainage of river valleys; (iv) conducting spatial analysis of rainfall and surface water quality.

2. Materials and Methods

2.1. Research Area

The studied catchments are located in three different regions of the Małopolskie Voivodeship, the Western Carpathians province, and the Outer Western Carpathians subprovince [42]. A catchment of the urban watercourse (6.69 km^2) is located in the direct vicinity of the northern border of the city of Kraków in the Wyżyny Polskie province. A suburban catchment (of 7.21 km^2) is located to the southeast of Tarnów. A rural area catchment (4.92 km^2) is in the southwest part of Małopolska, away from large urban complexes (Figure 1).

Sub-urban catchment is located in the Central Beskidian Piedmont (Pogórze Środkowobeskidzkie) macroregion, the Ciężkowice Piedmont (Pogórze Ciężkowickie) mesoregion, which stretches between valleys of two rivers. The Cretaceous-Ciężkowice sandstones and conglomerates are distinguished by their resistance amongst rock series of the Silesian nappe, forming west-east folds [42].

The urban catchment is located in the south-western part of the Nida Basin (Niecka Nidziańska) macroregion and the Proszowicki Plateau (Płaskowyż Proszowicki) mesoregion. Its catchment is a low-raised upland (up to 250 m a.s.l.) of Miocene rocks (clays and sands) covered with a relatively thick layer of loess. This area, with numerous flat hills, is divided by lower sections of Nidzica, Szreniawa and Dłubnia valleys. Appropriate black soils and advantageous morphological conditions make the Proszowicki Plateau one of the most fertile regions of Poland, with very good conditions for farming and agricultural production. [42]. The geological substrate in the study area of the rural catchment is formed by sedimentary rocks. The highest parts of this catchment are formed by flysch rocks of the Magura nappe, of which the southern part, similar to this entire region, is made of undulating, alternating and resistant to denudation layers of sandstones and conglomerates, with interbeddings of less resistant argillaceous schists and, occasionally, marly slates. Hollows in the land are scoured in siltstones and argillaceous schists, more susceptible to erosion [43].

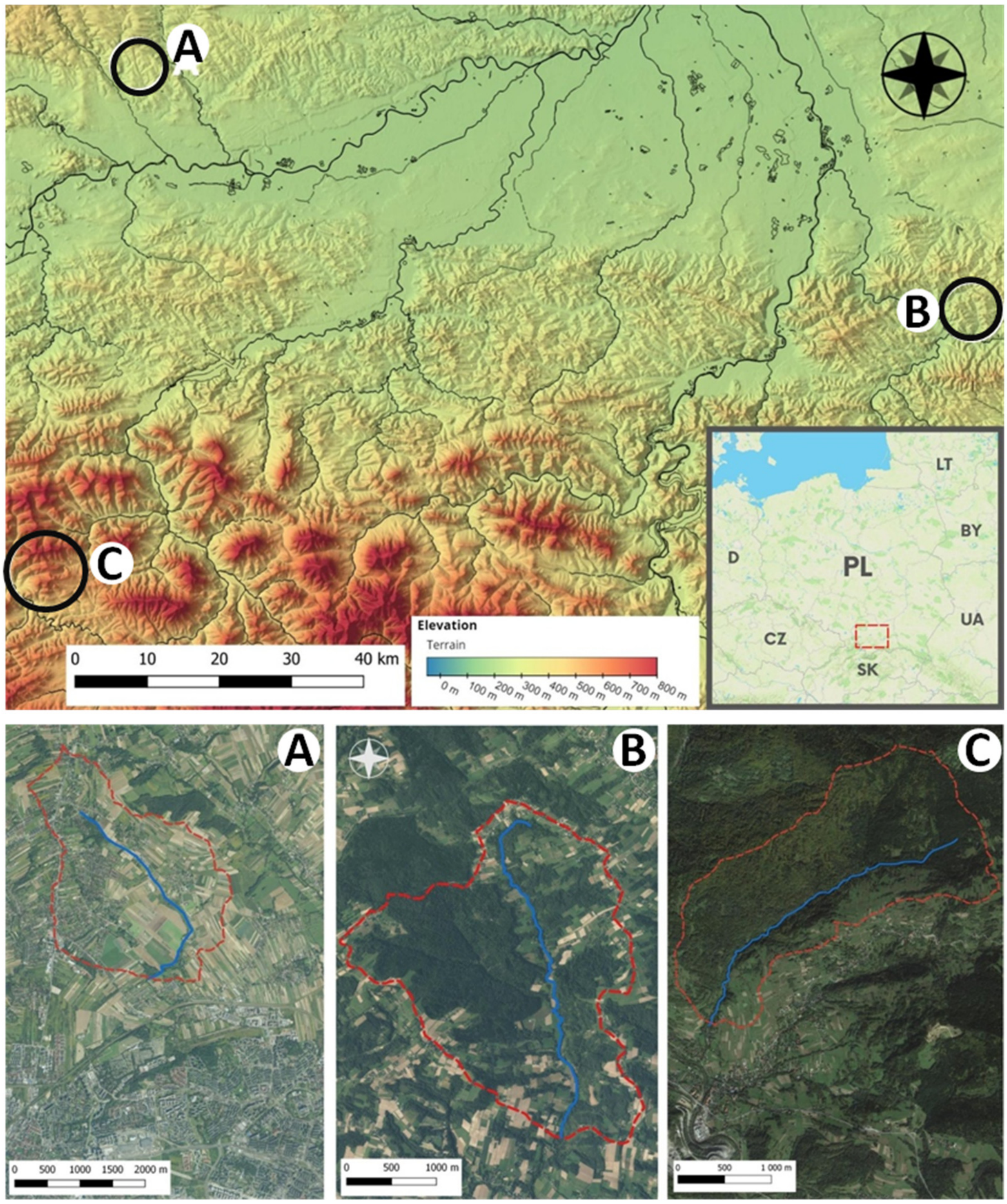

Figure 1. Location of the research area and boundaries of the examined catchments (**A**—urban; **B**—suburban; **C**—rural).

2.2. Examined Indices of Surface Water and Rainwater Quality

In the selected catchments, regular monthly analyses of water quality indicators were conducted over a four-year period. In the studied brooks, in the terrain directly in the cross-section of dams and in planned reservoirs, water temperature, specific conductivity, pH, dissolved oxygen and oxygen saturation were determined on a randomly selected day of the month. The majority of indices were determined once a month, and only heavy metals ($Cr_{Tot.}$, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}) once a quarter, according to the Polish departmental regulation. Rainwater samples were taken once a month on the same day as surface water samples. A trap container near the planned water reservoir was used to collect this water. Rainwater collection traps use a tray with a hole in the bottom were joined by a hopper.

2.3. Apparatus and Methods for Determination of Studied Indices

Water temperature, dissolved oxygen and water saturation with oxygen were measured directly in field using the apparatus of CO-411 type. Its pH was measured with a pH-meter CP-104, and specific conductivity with an electrical conductivity meter CC-102.

Parameters determined in the laboratory included total suspended solids by the oven test; dissolved substances by evaporation; SO_4^{2-} level by precipitation; BOD_5 by the Winkler method; COD by the permanganate method [44] and levels of Ca^{2+}, Na^+, K^+, Mg^+, Mn^{2+}, $Cr_{Tot.}$, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Fe_{Tot} by the atomic absorption spectrometry method using the spectrometer UNICAM SOLAR 969. Biogenic indicators such as ammoniacal ($N–NH_4^+$), nitrite ($N–NO_2^-$) and nitrate ($N–NO_3^-$) nitrogen, PO_4^{3-} and Cl^- were determined by the flow colourimetric assay using FIAstar 5000. The results of $N–NH_4^+$, $N–NO_2^-$ and $N–NO_3^-$ determinations were used to calculate levels of NH_4^+, NO_2^- and NO_3^-. Coliform and faecal coliform counts were determined on media containing lactose, following incubation at 37 and 44 °C, to within ± 0.5 °C.

2.4. Land Use and Development

Maps of land cover were drawn on a basis of 1:2000 scale cadastral maps and 1:13,000 scale ortho-photos purchased at the Provincial Centre for Geodetic and Cartographic Documentation, which were then verified during onsite visits. Hypsometric and slope maps were drawn on the basis of a digital terrain model (DTM). Obtained DTM data, in form of triangulated irregular networks (TIN) created with a spatial precision corresponding to a 1:10,000 scale map, were transformed to a raster file in the form of a regular square GRID, of a resolution of 20 m/pixel. The study was divided into stages, of which the first includes the literature review, describing soil retention capacity, modelling of surface runoff and a rainfall-runoff model. Then the following three studied areas: Rygliczanka brook, Osielczyk and Sudół Dominikański catchments were characterised. The characteristics of the study area include descriptions of the catchment's administrative and geographical locations, geology and geomorphology, climate and weather conditions, catchment hydrography, soil map and land cover and use. The final stage presents test results. The study used the SCS-CN method [45], for which map studies were prepared using QGIS 3.8. During development of features at the study sites, spatial analyses and creation of maps, the GIS software: ArcGIS 10, MapInfo Professional 8.0, Surfer 8, Erdas Image 8.7 and Corel Draw Graphics Suite X3 were used.

2.5. Hydromorphological Evaluation of Fresh Waters for Nature-Based Solution

A hydromorphological evaluation of running waters was performed according to the River Habitat Survey (RHS) method adapted from the Frame Water Directive (FWD) [46]. The illustrative picture shows the hydrological processes studied, including catchment retention, detention and drainage of soil water in the valley and nutrient flux to surface headwater and river (Figure 2).

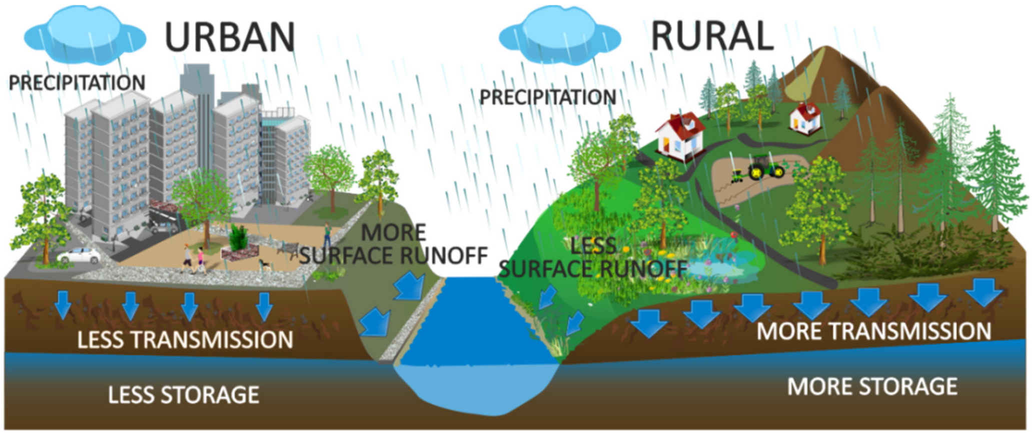

Figure 2. Illustration representing hydrological processes examined in urban and rural catchments.

The studies performed according to the RHS system allowed for the collection of ca. 400 parameters determining hydromorphological riverbed conditions were collected in 10 control profiles located every 50 m, and in a synthetic description of elements not registered in profiles. The evaluation took place at the location of the planned dam, and a five-hundred-meter-long section was examined upstream along the brook bed. The qualitative parameters describing morphological features were analysed and then used as a basis for the calculation of the following two synthetic watercourse quality indices for all studied sections:

(1) The Habitat Quality Score (HQS), based on a presence and diversity of natural elements of the course and the river valley;
(2) The Habitat Modification Score (HMS) determining the range of modifications in the watercourse morphology [47].

Values of the Habitat Quality Score, HQS, for a given section are calculated on a basis of a sum of partial values for the following categories listed below:

- Flow type (waterfall, spill, boil, torrential, chaotic, rapid, rising, smooth, invisible, or dry bed);
- Bed bottom material (rock outcrop, boulders, stones, small stones/gravel, sand, mud, clay/loess, peat/muck, concrete, mesh and stone gabions, claddings and pavings, riprap, or synthetic covering);
- Natural morphological elements of the bed (rock outcrop, exposed boulders, rock outcrops/boulders covered with vegetation, a central bar not stabilised by vegetation, a central bar stabilised by vegetation, an island, a natural dam);
- Natural morphological elements of banks (lateral erosion, stable bank erosion, a meander fluvial bar not stabilised by vegetation, a meander fluvial bar stabilised by vegetation, a point bar not stabilised by vegetation, a point bar stabilised by vegetation and natural embankment);
- Structure of bank vegetation (none, uniform, simple, or complex);
- Meander fluvial bars (stabilised and not stabilised by vegetation);
- Groups of water plants (liverworts and mosses, emergent broad-leaf plants, emergent narrow-leaf plants, submerged plants with floating leaves, free-floating plants and plants rooted on the bank with stems floating on the water, submerged broad-leaf plants and submerged plants with narrow and with strongly lobed leaves),
- The use of the land within a belt of 50 m from the bank top (deciduous/mixed forests, coniferous forests, wetlands);
- Tree stands and elements morphologically accompanying them (isolated/dispersed, regularly distributed, continuous and semi-continuous);

- Valuable elements of the river environment (waterfall, side channel, leaf heaps, natural reservoir, reed bed, peat bog, or bog).
- The value of the Habitat Modification Score, HMS, is based on a sum of partial values for the following categories listed below:
- Modifications observed in control points (bank stabilisation; bed stabilisation; bank or bed profiling; braided channel; an embankment on a river bank slope; a culvert; a damming structure; a crossing; a bank trampled by livestock);
- Structures not observed in control profiles (a pedestrian crossing; a road or railway bridge; a groyne; a damming structure; a crossing; a culvert);
- Modifications observed during a synthetic evaluation not registered in the control profiles (bed bottom material of anthropogenic origin; a stabilised entire bank profile; a profiled bank; a sectional bank profile; an embankment on a river bank slope; an embankment outside a river bank slope; plants removed from the bed; bank mowing) [48].

2.6. Statistical Analyses

Statistical analyses were performed in STATISTICA 9 [49]. An arithmetic mean and a median, as well as minimum and maximum values were calculated for all indices studied in surface and rain waters, and the sample sizes were specified. Three tests: Student's *t*-test, Cochran-Cox test and non-parametric U Mann–Whitney (Wilcoxon) test were used for analyses of the seasonal variability in structures in surface and rain waters.

When at least one data set (sample) of a given indicator from the summer or the winter half of the year was not characterised by a normal distribution, the U Mann–Whitney test was used for analyses, as it is considered a non-parametric equivalent of the Student's *t*-test. When both samples were characterised by the normal distribution, the hypothesis about homogeneity of variance of relevant populations was verified. As in all cases the size of the studied sample was always ≤50, the z-test was not used. When variances were equal, the Student's *t*-test was used; otherwise, the Cochran-Cox test was selected. The level of significance $\alpha = 0.05$ was assumed for all statistical analyses.

In all cases, also in the case of inter-object analyses, the normality of distribution of studied samples was evaluated through analyses of histograms and the Kolmogorov–Smirnov test, which was the least powerful test verifying normality, versus the Shapiro–Wilk and Lilliefors tests. The Kolmogorov–Smirnov test was selected as a specific compromise between a will to examine the significance of differences with parametric tests (more powerful than non-parametric ones), and requirements of these tests assuming a normal distribution of the analysed parameter.

In all cases, the homogeneity of variance was verified with the Brown–Forsythe test, which conducts an analysis of variance (ANOVA) for each variable on a basis of the absolute deviation of a value from its individual median. The Brown–Forsythe test determined the homogeneity of variance. In multiple comparisons, a one-way ANOVA was used. When it established that there was a significant difference between the analysed objects, Tukey's post-hoc test was performed, which precisely indicated the objects between which that significant difference existed. When at least one of conditions for normality of the distribution in a given sample or for the homogeneity of variance was not met, then the Kruskal–Wallis Nonparametric ANOVA on Ranks was performed, which indicated significance of differences and led to multiple comparison of mean ranks for all samples. The PCA (Principal component analysis) was also used to demonstrate the most important physical and chemical variables in surface waters using software PQ stat ver. 1.6.8. The canonical correspondence analysis (CCA) was applied to compare physical and chemical parameters in rainwater and surface waters for each catchment, separately and independently in Cancoco for Windows ver. 4.51. Spatial relations between studied catchments and physical and chemical parameters of surface and rain waters were demonstrated on a basis of the simultaneous autoregressive model (SAR), using the Spatial Analysis in Macroecology (SAM; version 4.0) software [50].

3. Results

3.1. Physical and Chemical Properties of Surface Waters

The highest values for levels of the studied indices were noted in rainwater from the urban area. The inter-object analysis of the significance of differences in surface water quality indices showed that the highest differences were found between the waters of the mountains and the urban areas. No significant differences between objects were found for water temperature, total suspended solids and heavy metal levels (Table 1). The temperature of the water running off in the winter half of the year was significantly lower than that in the summer half of the year, and this results from climate conditions. This led to significantly higher levels of dissolved oxygen during the winter. Nitrite, phosphate, dissolved substances, magnesium and potassium levels and specific conductivity values were significantly higher in the summer, while nitrate levels were significantly higher in the winter. Seasonal differences in the group of metals were statistically significant only in a very few cases. In most cases, the object and seasonal variability were consistent with the results of inter-object comparisons. Significant differences were noted for pH, dissolved oxygen, COD-Mn, PO_4^{3-}, Pb^{2+} and microbiological indices. The inter-object analysis of differences in values of indices in rainwater shows that the majority of them are statistically significantly higher in the urban area versus the suburban and rural areas (Table 2). PCA demonstrated the importance of physical and chemical parameters in each studied catchment. On the basis of PCA, the most important physical and chemical parameters of surface waters were selected for the spatial model. For selected parameters, the SAR model demonstrated that NO_3^- played a large role in the studied catchments, while in the urban catchment, the SO_4^{2-} level was also an important factor (Table 3).

Table 1. Average concentrations of physical and chemical indices for surface water in the entire studied area.

Parameter		Urban Area	Suburban Area	Rural Area
pH	-	7.90	8.10	8.17
EC	$\mu S \cdot cm^{-1}$	811	454	236
DO	$mg \cdot dm^{-3}$	8.38	10.47	11.40
PO_4^{3-}	$mg \cdot dm^{-3}$	0.84	0.03	0.04
NH_4^+	$mg \cdot dm^{-3}$	6.85	0.01	<0.001
NO_2^-	$mg \cdot dm^{-3}$	0.20	0.04	0.01
NO_3^-	$mg \cdot dm^{-3}$	8.3	1.9	1.8
SO_4^{2-}	$mg \cdot dm^{-3}$	70.4	40.9	17.9
Cl^-	$mg \cdot dm^{-3}$	54.2	9.5	2.1
Ca^{2+}	$mg \cdot dm^{-3}$	107.0	65.0	44.0
Mg^{2+}	$mg \cdot dm^{-3}$	20.8	18.2	5.42
Na^+	$mg \cdot dm^{-3}$	28.3	9.8	5.2
K^+	$mg \cdot dm^{-3}$	9.9	2.1	1.5
Fe_{Tot}	$mg \cdot dm^{-3}$	0.43	0.55	0.13
Mn^{2+}	$mg \cdot dm^{-3}$	0.14	0.09	0.02
TDS	$mg \cdot dm^{-3}$	605	324	166
TSS	$mg \cdot dm^{-3}$	18.2	6.2	4.5

Table 2. Average levels of physical and chemical indices for rainwater in studied catchments.

Parameter		Urban Area	Suburban Area	Rural Area
pH	-	5.5	5.0	4.9
EC	$\mu S \cdot cm^{-1}$	33.0	19.0	19.0
DO	$mg \cdot dm^{-3}$	-	-	-
PO_4^{3-}	$mg \cdot dm^{-3}$	0.43	0.19	0.15
NH_4^+	$mg \cdot dm^{-3}$	1.77	1.04	0.95
NO_2^-	$mg \cdot dm^{-3}$	0.10	0.04	0.03
NO_3^-	$mg \cdot dm^{-3}$	3.20	2.10	2.60

SO_4^{2-}	mg·dm^{-3}	3.30	5.00	2.60
Cl^-	mg·dm^{-3}	1.70	0.80	0.70
Ca^{2+}	mg·dm^{-3}	2.10	0.80	1.00
Mg^{2+}	mg·dm^{-3}	0.30	0.10	0.10
Na^+	mg·dm^{-3}	0.30	0.20	0.20
K^+	mg·dm^{-3}	0.50	0.60	0.20
Fe_{Tot}	mg·dm^{-3}	0.40	0.20	0.10
Mn^{2+}	mg·dm^{-3}	0.05	0.03	0.02
TDS	mg·dm^{-3}	26.0	21.0	21.0
TSS	mg·dm^{-3}	2.90	3.10	3.40

Table 3. Results for spatial autoregressive models. A level of the studied element in rainwater was chosen as a dependent variable, while levels of elements in the surface watercourse were used as independent variables. Only significant results were presented.

Variable	OLS Coefficient	SAR Coefficient	Standard Coefficient	Standard Error	*t*	*p*
Urban area						
Constant	12.532	−23.082	2.452	0.241	0.923	0.834
NO_3^-	23.792	7.862	1.313	0.271	6.722	0.013
SO_4^{2-}	4.552	16.972	0.883	1.341	2.562	0.045
PO_4^-	11.432	5.252	0.123	1.893	1.003	0.039
Cl^-	0.342	0.762	0.021	0.631	0.232	0.032
Suburban area						
Constant	53.382	−85.981	0.831	-	-	0.643
NO_3^-	1.723	1.252	1.311	0.273	6.721	<0.001
Mg^{2+}	24.933	−02.973	−0.741	-	-	0.041
Ca^{2+}	−32.553	22.891	0.883	-	-	0.021
PO_4^-	0.073	0.0253	<0.001	5.162	0.005	0.009
Cl^-	<0.001	<0.001	−0.042	<0.001	−0.24	0.079
Rural area						
Constant	12.942	56.342	0.132	0.042	1.092	0.028
NO_3^-	11.052	2.752	0.092	0.272	6.642	0.002
Mg^{2+}	14.683	−1.083	−0.972	0.033	3.973	0.007
Ca^{2+}	−2.542	1.893	−0.782	0.363	2.673	0.043

Note: Result for predictor variables using OLS is $R^2 = 0.98$; Result for predictor + space is $R^2 = 0.89$.

The hydrochemical analysis of running waters—RHS—adapted to the Polish conditions demonstrated that the suburban and the rural catchments can be classified as unmodified watercourses, while the urban catchment, with the HMS score of 28 points, can be called a partly modified course.

3.2. Catchment Retention Capacity

In the urban catchment area (Figure 3), the curve number (CN) ranged from 55 (forests on soils of permeability above average) to 98 (non-permeable areas). In the suburban catchment area, the calculated CN (Figure 4) ranged from 55 (forests on soils of permeability above average) to 98 (non-permeable areas). In the rural catchment area, the CN (Figure 5) assumed values from 77 (forests on soils of low permeability) to 98 (non-permeable areas).

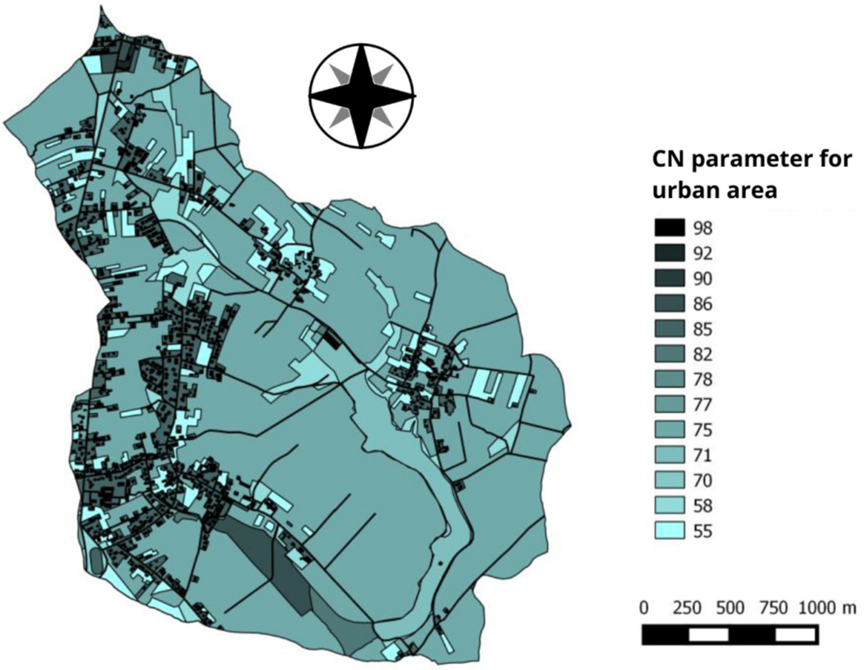

Figure 3. Curve number for urban area.

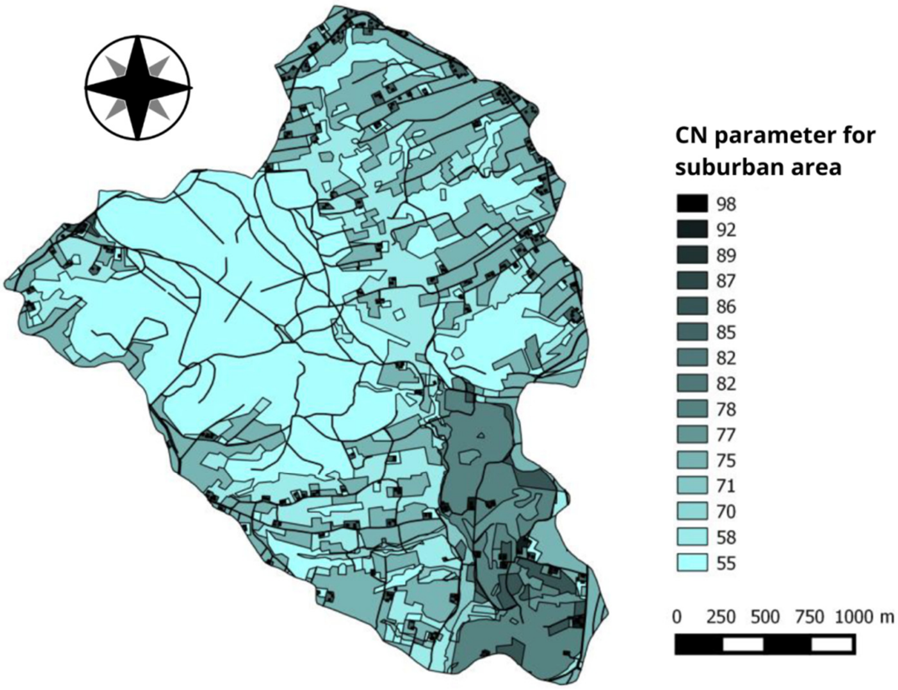

Figure 4. Curve number for suburban area.

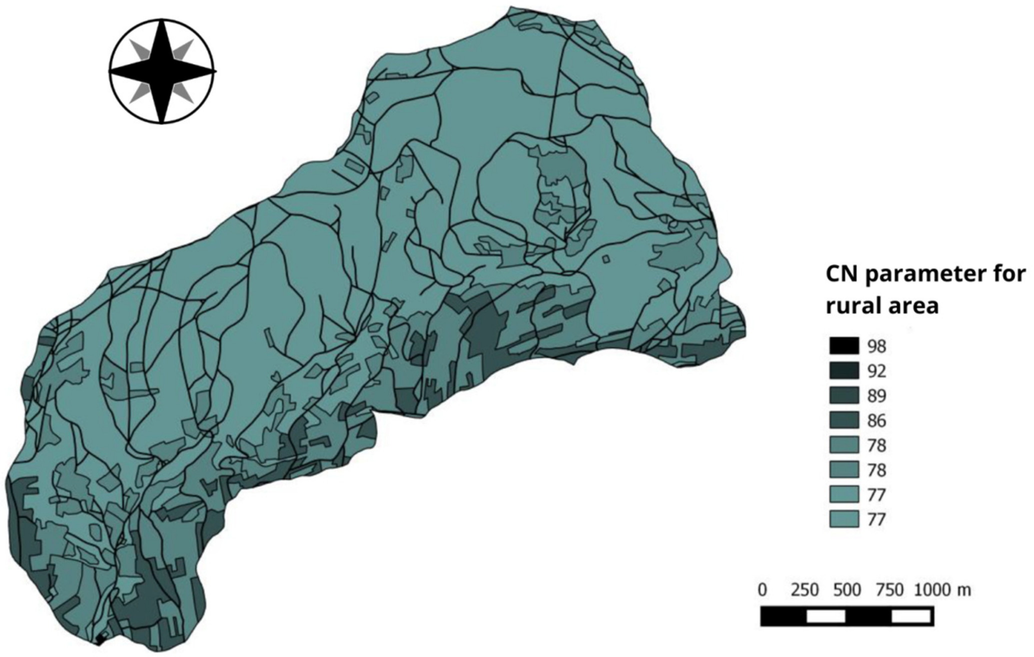

Figure 5. Curve number for rural area.

The highest potential retention in the urban area was noted in the study points in forests (207.82 mm) and meadows (183.93 mm) growing on soils of permeability above average (Figure 6). The lowest potential retention was found in areas with non-permeable cover (5.18 mm). The areas of the lowest possible retention are located mainly in the western part of the catchment. The eastern and central parts of the catchment, except for small clusters, are characterised by much higher potential retention.

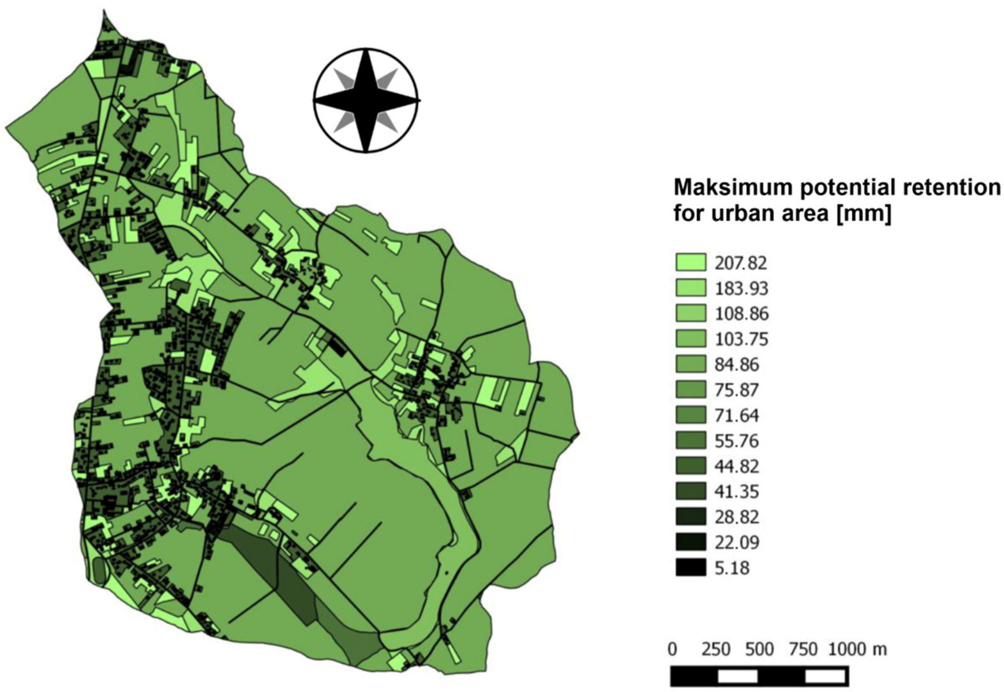

Figure 6. Maximum potential retention for urban area.

The highest potential retention in the suburban area was characterised by areas with forests (207.82 mm) and meadows (183.93 mm) growing on soils with a permeability above average (Figure 7). The lowest potential retention was found in areas with non-permeable cover (5.18 mm). The highest potential retention in the rural area (Figure 8) was observed in areas with forests (75.87 mm) and meadows (71.64 mm). The lowest potential retention was found in areas with non-permeable cover (5.18 mm).

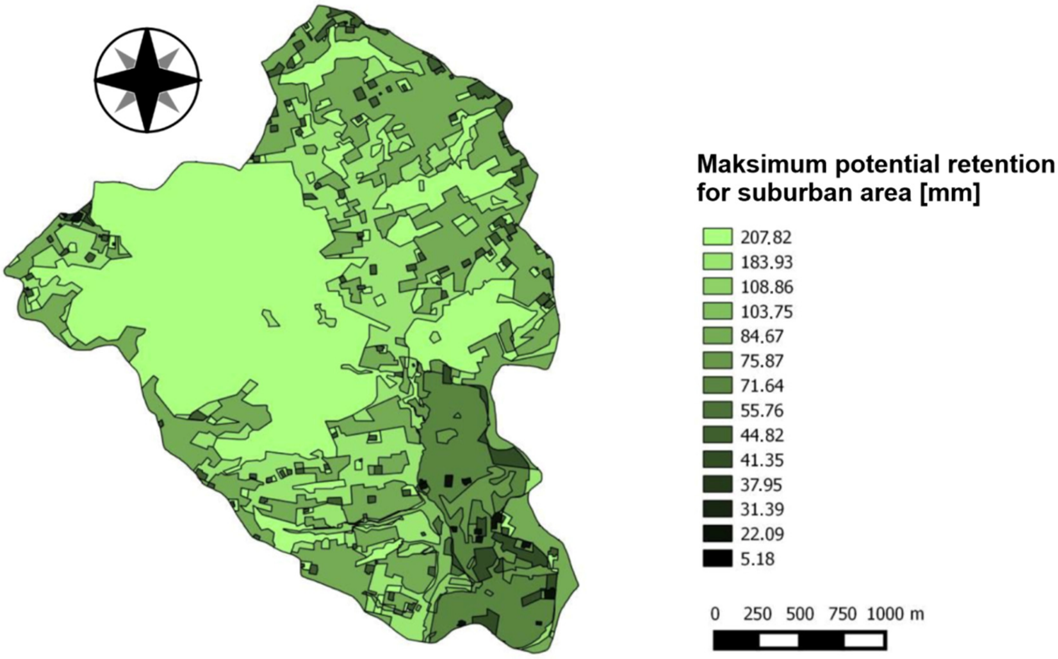

Figure 7. Maximum potential retention for suburban area.

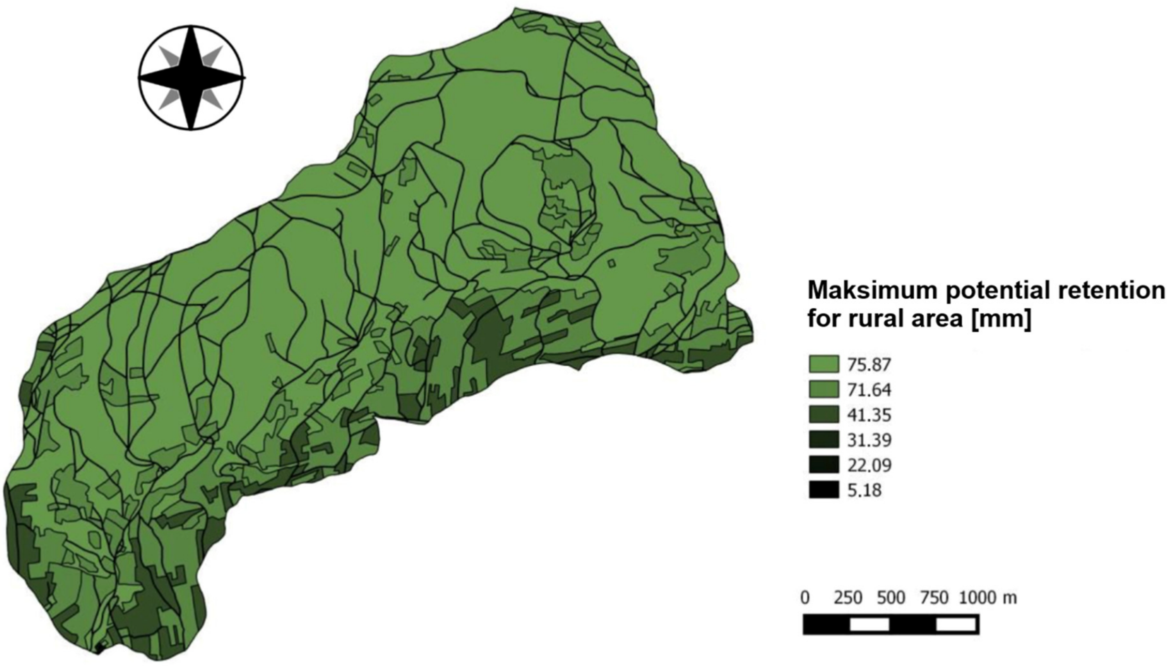

Figure 8. Maximum potential retention for rural area.

In the urban area, surfaces with a moderate retention capacity (Figure 9) predominate (69.33%). The areas with very high, low, very low and high retention capacity have a much lower share (11.83%, 9.19%, 5.65% and 4%, respectively). In the suburban catchment, areas with very high retention capacity (Figure 10) have the highest share (55.24%). The areas qualified as characterised by high and very low retention capacity have the lowest share of the total surface area (1.43% and 1.55%, respectively). In the rural area, surfaces with a moderate retention capacity (Figure 11) strongly predominate (88.30%). The areas with low and very low retention capacity were also noted (8.51% and 3.19%, respectively). The areas of very high and high retention capacity were not confirmed.

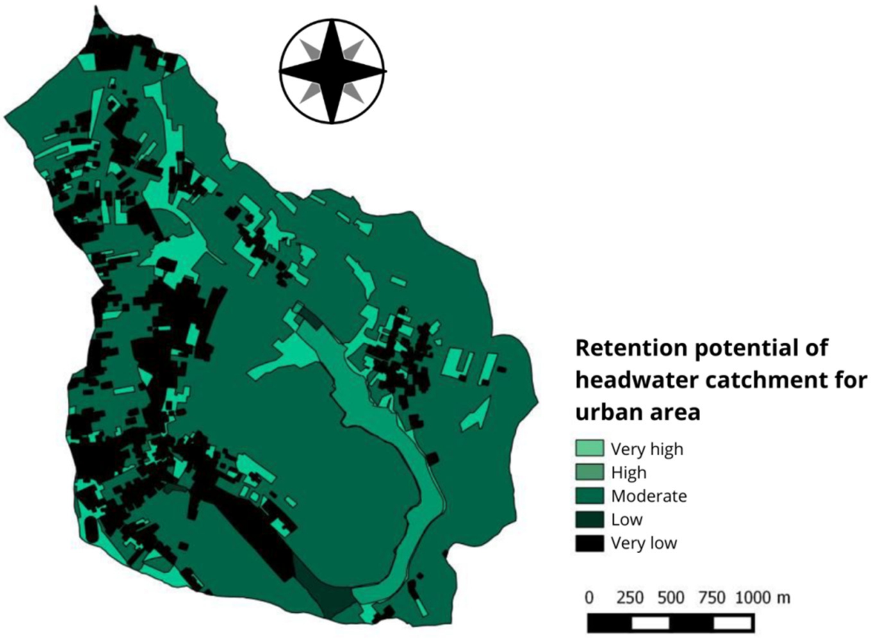

Figure 9. Retention potential of headwater catchment for urban area.

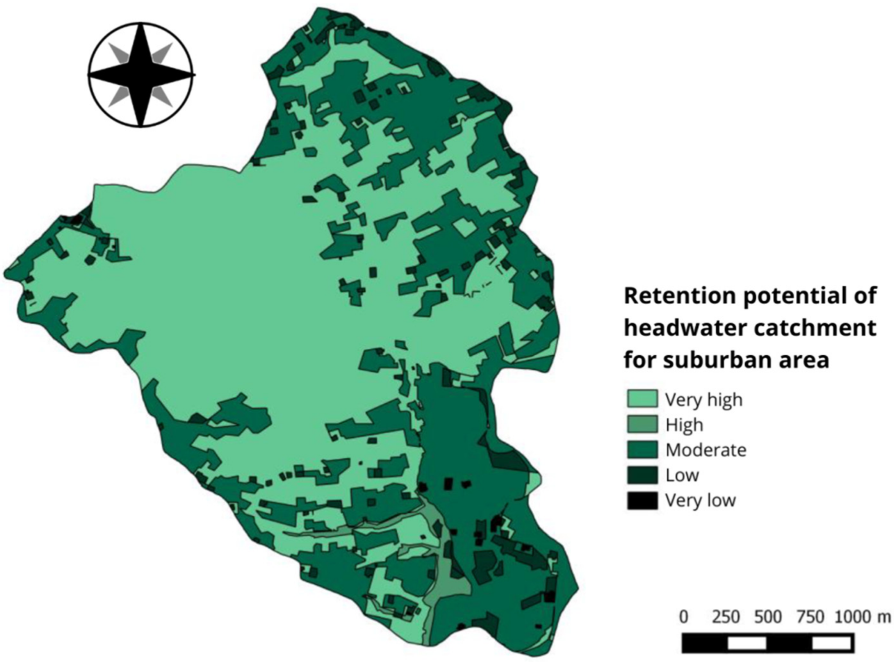

Figure 10. Retention potential of headwater catchment for suburban area.

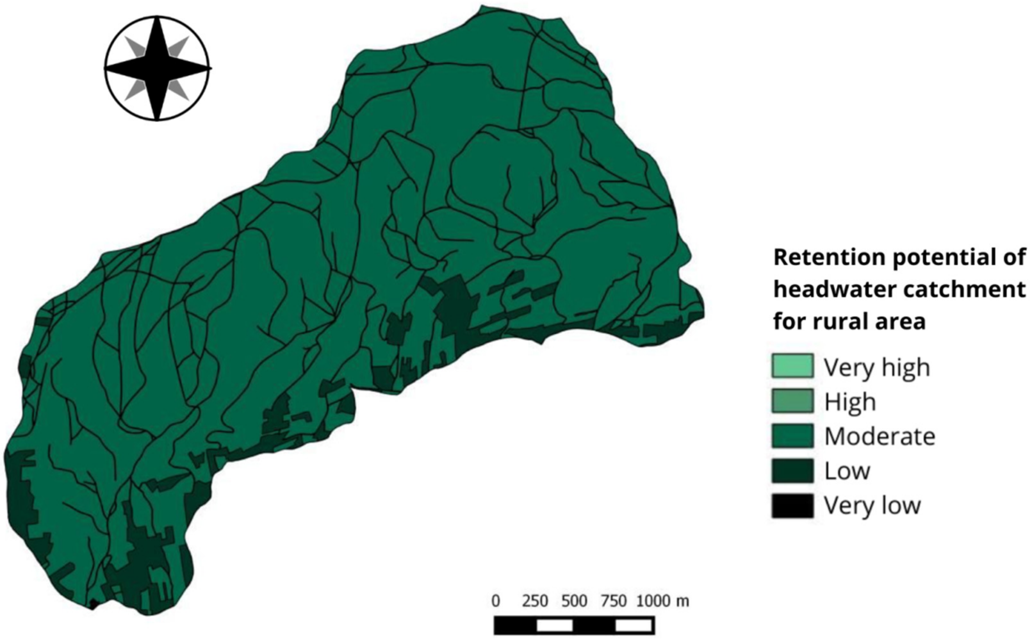

Figure 11. Retention potential of headwater catchment for rural area.

4. Discussion

4.1. Relationship between a Land Use and Physical and Chemical Quality of Running Waters

As has already been mentioned, the excessive content of physical and chemical components in surface waters of small catchments also depends on the soil type, its pH, plant cultivation methods [51] and the intensity of erosion processes. This last factor is determined not only by the soil type and the way of land use but also by morphological characteristics of the catchment, such as land slopes, exposure, or slope length [52]. It also depends on the climate, especially the rainfall amount and intensity, and the temperature, with its low values causing freezing of the soil [53]. Water analyses at characteristic points along the entire length of the watercourse in the urban catchment between July and February were conducted by Kanownik and Rajda [54]. When analysing the indices (temperature, specific conductivity, dissolved substances, dissolved oxygen, NH_4+, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, Fe_{Tot}, Mn^{2+}, Ca^{2+}, Mg^{2+} and Cl^-), they noted an increase in twelve out of sixteen analysed parameters in the section where a wastewater discharge from a local treatment plant was located. The poor quality of water discharged from the sewage treatment plant was confirmed by own tests, as during their performance the sewage treatment plant in Węgrzce was closed because the local sewage system was connected to the Kraków-Płaszów treatment plant, so the values of the indices before and after closing of the treatment plant could be compared. It was found that the levels of the majority of the indices improved significantly, but levels of oxygen, NO_3^-, $Mg^{2+,}$ Zn^{2+} and Ni^{2+} deteriorated (Table 1).

The worst quality of rainwater in the town located in the urban catchment can be associated within a close vicinity of the city of Kraków, and in particular, of its industrial district, Nowa Huta, with the operating large steelworks. The studies conducted in areas of northern France, also subjected to the influence of a similar plant manufacturing steel, conducted before and after its closure, demonstrated that the quality of rainwater significantly improved after the closing of the steelworks [55]. When compared to rainwater studied in large global agglomerations, the rainwater from our facilities was not acidic as, e.g., in China [56], Japan [57] or the United States [58].

Studies on the quality of water in a lowland river on the Szczecin sea coast, whose catchment was used mainly for agricultural purposes (no forests and a very small share of grasslands), showed that the nitrate (NO_3^-) levels ranged from 0.9 to 42.0, with a mean level of 6.8 mg·dm$^{-3,}$ ammonia (NH_4^+) levels ranged from 0.06 to 1.80 with a mean level of 0.32 mg·dm^{-3}, and phosphates ranged from 0.01 to 1.60 with a mean level of 0.35 mg·dm^{-3}. The mean potassium level was 13.4 mg·dm^{-3} (ranging from 6.5 to 28.6) [59]. Comparing our results to those shown above, it can be said that only K^+ levels in lowland rivers were higher than in all three sites; in all remaining cases, the values of biogenic indices (PO_4^{3-}, NH_4^+, NO_3^-) in a lowland river on the Szczecin sea coast were similar to levels noted in Węgrzce, yet they were always lower by at least 5%.

When our results are compared to studies of Olszewska and Krzemińska conducted in an agricultural catchment of the Jeziorka river, a right-bank tributary of the river Odra in the Malczyce region, it can be said that mean values of PO_4^{3-}, NH_4^+, NO_3^-, Ca^{2+} and Mg^{2+} levels were between mean values calculated for the catchments in the rural and urban areas, while the mean values of Mn^{2+}, Fe_{Tot}, SO_4^{2-} and Cl^- levels in the Jeziorka river were much higher than levels noted in our monitoring (Table 1) [60]. The mean NO_3^- level was the highest in Rumia; in the remaining cases, it ranged from 0.9 to 3.2. The specific conductivity in all sites was not high and ranged from 19 to 52 μS·cm^{-1}; similarly, the following remaining indices: SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, Na^+ and K^+ were characterised by very low levels.

PCA demonstrated that TDS had the greatest influence on the studied variables (Figure 12). The total suspended solids (TSS) could enter the surface watercourse together with Na+ (Figure 13). In the catchment of the suburban watercourse, Na+ also had a high influence, but it did not necessarily enter the water together with suspended solids (TSS) as in the urban catchment described above. In the rural area, TSS played the main role in the surface watercourse. The remaining studied indices, especially Ca^{2+} and SO_4^{-2}, were characterised by significant correlations (Figure 14).

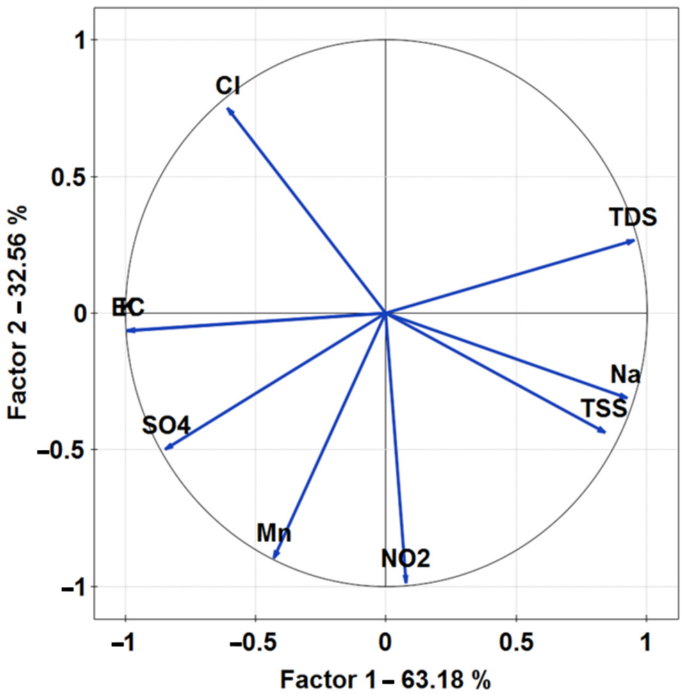

Figure 12. Projected data for physicochemical properties of stream in studied urban area using PCA.

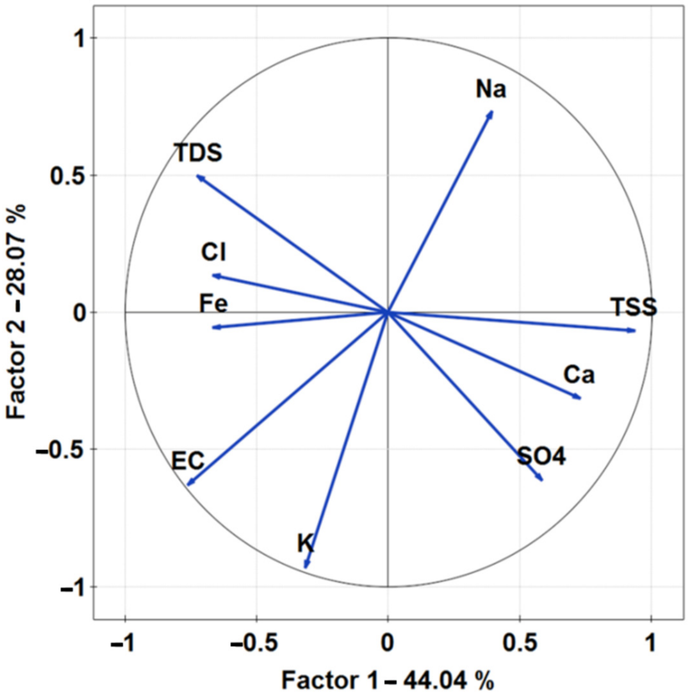

Figure 13. Projected data for physicochemical properties of stream in studied suburban area using PCA.

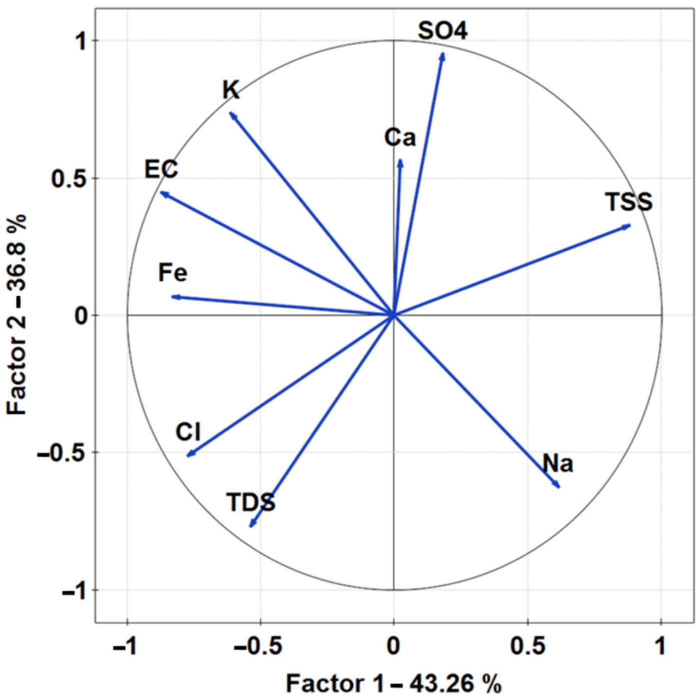

Figure 14. Projected data for physicochemical properties of stream in studied rural area using PCA.

A hydrochemical evaluation of running waters, RHS adapted to the Polish conditions, was used as an assay supporting evaluation of water quality. Szoszkiewicz and Gebler (2011) conducted a statistical analysis on 950 sites all over Poland, analysed using the said method [61]. On the basis of the HMS indicator, they classified the rivers as modified (HMS > 45) and unmodified (HMS—from 0 to 2). The studies concerning the quality of water in small catchments using the same measurement methods and determination of physical and chemical indices, as in our study, were also conducted by [62]. They conducted their observations on watercourses flowing through variously used areas for two hydrological years. In those studies, pH, dissolved oxygen, NH4+, NO3-, NO2-, PO43-, SO42-, Cl-, Ca2+, Mg2+ and specific conductivity were determined in the surface water every month. The studies were conducted in microcatchments of the following: forest (75% forest, 13% arable land, 7% grasslands, 3% orchards, a few houses); agricultural (81% arable land, 7% grasslands, 5% orchards, 4% forests and tree stands, scarce dispersed houses), and settlement and agricultural (59% arable land, 19% forest, 8% grassland, 4% orchards, numerous dispersed houses) character. The CCA shows that Mg^{+2} and Ca^{+2} cations in rainwater and surface watercourses play the main roles both in urban and suburban areas (Figure 15). No large dependencies were noted in the rural areas. Additionally, NO_3^- influences rural areas. In the urban catchment area, the strongest relations were found for NO_3^-, K^+ and Na^+. It has been shown that rainfall can have an effect on the biogeochemical cycle of NO_3^- (Figure 16). Overall, higher amounts of NO_3^- flow into the watercourse statistically significantly (Table 3). Watercourses in rural areas retain significant concentrations of NO_3^- as well as K^+ (Figure 15).

Spatial autoregressive parameter (rho): 0.43

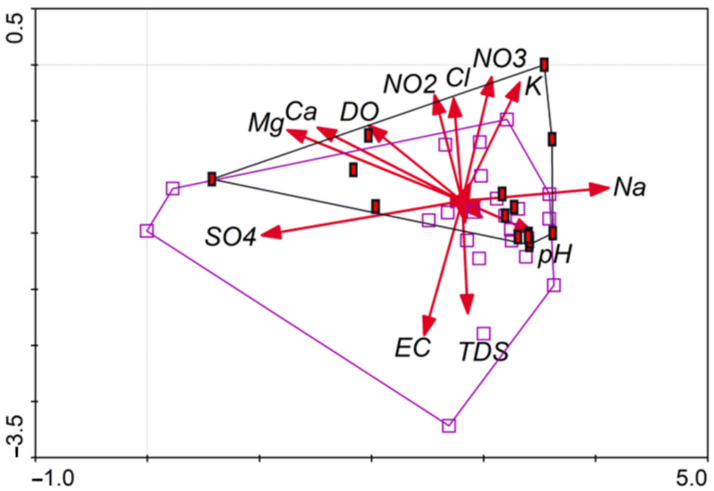

Figure 15. CCA plot with eigenvectors designated factors affecting physicochemical parameters in rainwater. Open squares show urban area. Red squares represent rural area.

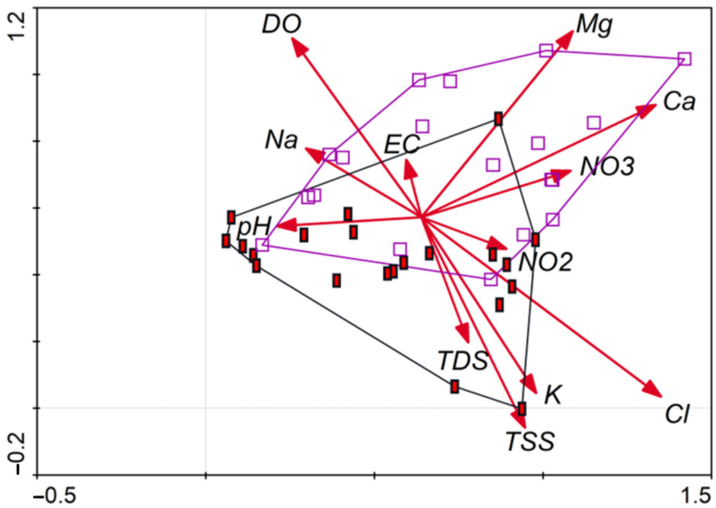

Figure 16. CCA plot with eigenvectors designated factors affecting physicochemical parameters in river. Open squares show urban area. Red squares represent suburban area.

The land use and cover are of fundamental importance for the quality of water resources in the catchment. Long-term studies of water temperature, pH, BOD_5, COD, dissolved substances, total phosphorus and total nitrogen, determined in water samples collected from 118 points in the Han River catchment (South Korea), showed that there is a correlation between the urban development of the land and water pollution [63]. In the catchment of the Little Miami River (USA), it was also found, using geographic information systems (GIS), that agricultural areas and paved non-permeable surfaces in urbanised areas cause much higher water pollution when compared to other ways of land use and cover [64]. Physical and chemical indices of surface water are correlated with farming activities [65]. This group consists of phosphates related to phosphate fertilisers, chlorides associated with potassium salt fertilisers, as well as nitrogen in its various forms of NH_4^+, NO_2^- and NO_3^- caused by the use of nitrogen fertilisers [66,67]. The partial influence of agriculture is emphasised by indices such as BOD_5, COD and sulphates [68,69]. Studies in Slovakia have shown that with a decrease in field fertilisation with nitrogen compounds, its levels in brooks flowing through the studied areas decreased [70]. Swedish researchers studying 35 small (2–35 km^2) agricultural catchments for five years noted a strong correlation between inorganic nitrogen levels and the way of land use [71].

4.2. Hydrochemical Evaluation of Rainwater

CCA has shown that there are relationships between the chemical composition of rainwater and surface waters. In the mountain catchment, the content of Mg^{2+}, Ca^{2+} and NO_3^- should be noted (Figure 16). In the rural catchment, additionally, Na and Cl^- levels are of importance, while in the urban catchment, NO_3^-, K^+ and Na^+ should also be noted. Many factors contribute to the quality of surface waters [72,73], and their influence on excessive levels of physical and chemical components in those waters is different and varies over time [74]. In small catchments, the anthropogenic influence on the quality of surface waters is partly combined with the effect of natural components such as rocks, soil humus substances [75], and, to some extent, precipitation [76]. The main source of pollution is of anthropogenic origin [77]. A deterioration in the quality of water in the urban catchment is associated with human existence and economic activities [78], including incorrect water and wastewater management, excessive use of artificial and organic fertilisers, and air pollution [79].

When compared to our study, a two-year study by Rajda et al. (2001) on selected physical and chemical components of rainwaters in a region of a small forest catchment of the Jagódka brook located in an eastern part of the Little Beskids, as well as the study by Ostrowski et al. (2000) in three microcatchments located near the city of Andrychów, also in the Little Beskid, demonstrated that only in two cases mean values of the indices were higher in the urban catchment than mean levels noted in the Little Beskid, while the lowest mean values predominated in the urban catchment waters, and this confirms that rainwaters of the best quality were found in the area located the furthest from large agglomerations [80,81].

The SAR model has shown that NO_3^- in the urban and suburban areas and SO_4^{2-} in the urban area may be of significance when determining the influence of rain on the physical and chemical quality of water in the catchment (Table 3). Even partial settlement development of land in small catchments causes greater water pollution than is the case in typical agricultural catchments [82]. Factors associated with settlements such as the number of inhabitants, the build-up area share, the arable land share, the number of livestock and quantities of mineral and organic fertilisers used within the catchment area have a significant influence on levels of certain indices of surface water quality [75,83].

It is difficult to compare the results of physical and chemical determinations conducted by different authors in other sites, as methods used for measurements and analyses of the results vary. Furthermore, complete information on studied sites is not available, and it is difficult to establish precisely which factors significantly influence many simultaneous processes decisive for water quality [84].

4.3. Modelling of Surface Runoff

Surface runoff is one of the processes associated with water circulation in the environment. It is that part of rainwater that flows on the surface of the ground. It occurs after intensive rainfalls or is the result of snow melting in spring [85]. The surface runoff speed depends on the land slope and coverage [86]. The integration models are of importance for the evaluation of thermal cooling in river revitalisation processes [87]. During intense rainfalls and a small resistance to water flow, the runoff intensifies and floods develop [88]. The results showed that issues associated with hydrological modelling mainly concern the transformation of the effective precipitation in the surface runoff. Land development must be planned to take into account soil permeability so that any excess rainwater can be removed. In areas covered by soils of low permeability, the share of non-permeable surfaces should be limited [89]. This can be achieved, for example, by using open slabs, using the greatest possible areas such as green belts, parks and green squares, and maintaining the existing natural plant coverage to the greatest extent possible. The CN parameter showed that, in terms of the rainwater-runoff relationship, urban soils (Figure 3) are haracterized by low permeability at the same low level as suburban (Figure 4) or rural (Figure 5) areas.

Soil permeability is a significant element influencing surface runoff. Soil permeability influences the absorption of rainwater and depends on the physical properties of a substrate [90]. On permeable soils, rainwater is absorbed by the soil, reducing surface runoff. In areas where non-permeable soils are found, water evaporates [91].

A very important problem that needs to be solved is how to prevent the pollution of running water. One of the ways to protect water is the natural structure of bank vegetation, which helps to maintain biological diversity and improve the condition of the natural, especially aquatic, environment [92]. The creation of buffer zones with forest tree stands has a positive effect, as they provide conditions for the development of flora and fauna, improving the ecological state of a watercourse [93]. Grasses also have a positive influence on the reduction of non-point pollution of agricultural origin. It is recommended to plan grasslands in the vicinity of watercourses and reservoirs to form a natural buffer to protect against an excessive supply of nutrients leading to water eutrophication as a nature-based solution [94]. Moreover, waters in courses with forests, grasslands and organic soils located along them were characterised by good quality, as they captured a significant part of non-point pollution running off from fields [95,96]. Rainwaters, reaching the soil surface, partly infiltrate it depends on the ground permeability, supplying groundwaters [97]. The maximum retention capacity of a catchment can depend on the way it is used and the distribution of trees and shrubs in the valley (Figure 6). The results of the study showed that areas with large groups of trees located on the borders of cities increase the retention capacity of the catchment. Rainwater accumulation and runoff were similar to agricultural catchment areas in rural areas (Figure 8). The slope is also an important factor, and the steeper the slope, the greater the water runoff [98]. When rain falls on nonurbanised areas covered with vegetation, the water soaks into the soil and slowly infiltrates into the surface and groundwater. In urbanised areas, where paved surfaces predominate, much of the rainwater ends up in canals and watercourses [99].

4.4. Catchment Retention Capacity

The majority of urban catchment areas are located on soils with above-average permeability. The soils in the suburban brook catchment were characterised by above-average permeability. Forests grew on low-permeable soils in the rural brook catchment, resulting in a moderately retained catchment area that was not affected by the drought. Catchment retention capacity is significantly influenced by the type of soil that is used. As non-permeable surfaces (buildings, roads, etc.) increase, catchment retention capacity declines.

The conducted studies showed that the way of the catchment area's development significantly influences its retention capacity. The highest retention capacity was observed in forests and meadows, i.e., non-urbanised areas covered with natural vegetation (Figure 9). The more urbanised the catchment area is, the lower its maximum retention capacity. Additionally, the type of soil found in a given area is very important, as the low soil permeability significantly reduces the retention capacity (Figure 10).

Built-up, urbanised areas found on soils of low permeability have a very low retention capacity, and this intensifies the water runoff [100]. Urbanisation resulted in a reduction of the soil infiltration capacity in the catchment, as described by the CN parameter (Figure 3). This study contains observations indicating that the retention capacity may be a very important factor, which should be considered in the spatial planning process. The soil permeability study enables correct decisions concerning land cover, so the risk of disruptions in water runoff leading to floods in urban [101] and rural [102] areas is reduced.

The small retention (natural water retention measures), particularly in rural areas, aim at increasing water resources. One of the actions included in natural water retention measures may include procedures aiming at catching water running off from slopes of significant incline, as was the case in the Spanish mountains Sierra de Gador, where water flowing from slopes was harvested and directed to cisterns through a system of canals [103,104]. In the presented maps, areas where values of the CN parameters changed significantly due to water erosion and a reduction in water retention, as well as those related to urbanisation and the development of road infrastructure in recent years (Figure 4) and in rural areas (Figure 5) were identified.

Ponds, i.e., small hollows in the land where water accumulates, play an important role in natural water retention, as they support its circulation [105]. Apart from their landscape and environmental values contributing to areas where they can be found, they also increase water resources in their vicinity through a network of blue and green infrastructure [106]. In cities, urban wetland parks and specific natural areas should be created by using the ecohydrological approach or development of wetlands [107]. Variability in the catchment retention capacity plays an important role in the shaping of the surface runoff (Figure 6). The maximum retention capacity can be used to estimate the direct runoff level in catchments characterised by soils of low permeability (Figure 3). Due to deviations in the runoff size calculated according to NRCS, CN requires an adjustment to be taken into account, e.g., a correction for initial losses or water content conditions. In urban conditions (Figure 3), the variability in the formation of the surface runoff should take into account the local characteristics of the catchment.

Construction of reservoirs for limited retention should be preceded by analyses of water quality, as actions to improve water parameters should be initiated in catchments with water of poor or unsuitable quality. Taking this aspect of water quality into account when making decisions about the construction of water reservoirs will contribute to their multifunctional and optimal use. Maintaining good quality water in planned reservoirs for low retention will require proper operation, control over water and wastewater management, and the elimination of unlicensed waste landfills in the catchment areas. The analysis of water quality and functional parameters in the context of its long-term retention in reservoirs will enable us to specify how to use it for local purposes. Enhancing the catchment retention capacity of urbanised watercourses could be achieved by limiting the construction of entirely sealed surfaces and by increasing biologically active surfaces. The results of this study may also contribute to the development of guidelines for establishing new nature conservation sites in urban riverside parks. supporting a process of planning blue and green infrastructure in the cities and designing water reservoirs for small retentions in rural areas.

5. Conclusions

Soil drainage affects nutrient leaching in all studied catchments. A variety of land-use practises have also contributed to the retention of nutrients in the river valley. Urbanised areas and valley drainage were associated with NO_3^- concentrations in surface water based on the spatial analysis of the autoregressive SAR model. Results of CCA indicated that rainwater and surface watercourses accumulating Mg^{2+} and Ca^{2+}tend to be found in urban, suburban and rural areas. A rural area's land use may also influence NO_3^- concentrations in surface water. The strongest correlations were revealed in the urban catchment for NO_3^-, K^+ and Na^+ concentrations in surface waters. The quality of nutrients in the catchment was affected by varying levels of anthropogenic pressure due to land use and development. It was found that there was no statistically significant difference in most of the rainwater indicators tested across all catchments. At each catchment, significant differences were displayed only for pH, Na^+ and Fe_{Tot}. The pH values were lower, and Na^{2+} and Fe_{Tot} values were higher in the summer half of the year. Further, periodic soil and valley susceptibility research is needed to address climatic change's effects on catchments' capacity to retain nutrients.

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