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Water Quality in a Small Lowland River in Different Land Use

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Abstract: The paper describes water quality in the Raszynka River based on selected chemical parameters dependent on different land use. The research was carried out in the Raszynka River catchment, characterized by a small surface area (75.9 km^2) and length (17.14 km). The river is a right tributary of the Utrata River. It is located in the Piaseczno and Pruszkow districts in the Mazowieckie voivodship. The dominant type of land use in the basin is agricultural land. Water samples were collected from 2017 to 2019 from previously designated research points at similar distances along the river. Selected physicochemical indicators examined in the samples include total alkalinity, electrolytic conductivity (EC), pH, and chemical oxygen demand (COD). Moreover, the concentration of selected substances was determined, including nitrogen compounds: NO_3^- (nitrates) and NH_4^+ (ammonium), TP (total phosphorus), and Cl^- (chlorides). The results showed that the values of some of the examined indicators do not meet the standards set for first-class surface water quality. Indicators significantly exceeding the limit included ammonium, chlorides, and pH. The highest concentration of chlorides, ammonium, and nitrate was found in urbanized areas. The highest concentrations of total phosphorus and COD were determined in agricultural areas and total alkalinity in meadows.

Keywords: land use; river; water quality; physicochemical indicators

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1. Introduction

Water quality in small lowland rivers should have a considerable impact on the condition of the entire Polish fluvial system, as well as all lakes and water reservoirs those rivers flow through. Research shows that the state of large Polish rivers (such as Vistula, Oder, or Warta) is, to a lesser extent, affected by sources of pollution in their direct vicinity, and to a greater extent by pollutants supplied with small tributaries [1–4]. It is, therefore, necessary to conduct a comprehensive investigation of entire river catchments. Rivers flowing out of Poland constitute the main source of phosphorus and nitrogen in the Baltic Sea, leading to its degradation, development of the eutrophication process, more frequent cyanobacterial blooms, development of oxygen deserts, etc. [5–9].

Sources of river pollution can be divided into point sources (e.g., discharge of municipal waste) and diffuse sources (e.g., agriculture). A decrease in the effect of point sources on water quality in rivers has been observed in recent years [5–7]. It is related to the modernization of obsolete wastewater treatment plants, introduction of the third degree of wastewater treatment—intensified nutrient removal, and construction of a substantial number of wastewater treatment plants (also resulting in a decrease in illegal sewage discharges directly to rivers) [10–13]. An increasing effect of agriculture as a source of river pollution has also been observed due to the application of a greater quantity of natural and mineral fertilizers, application of pesticides, clearing of field tree stands, and removal of buffer zones at river banks, leading to intensified leaching of pollutants from the soil into rivers [14–20].

Lowland rivers flow through ponds, lakes, and retention reservoirs, considerably affecting their quality. River waters flowing through such a reservoir slow down their flow rate, allowing for the deposition of sediments on the bottom, and reducing the concentration of pollutants behind the reservoir. Retention reservoirs are a very important element of water management, as well as a source of drinking water. They contribute to the improvement of water relations during drought and reduce flood flows by retaining water. The construction of many new small retention objects is currently observed. Their basic task is to increase the amount of retained water available during droughts, as well as to reduce the pollution of water flowing through them [21–24].

The water environment is closely related to human activities. The quality of water in rivers, lakes, and catchments changes depending on catchment use. Research shows that the strongest impact on the quality of water is agricultural and industrial activities, including cities. Human activities can have a beneficial effect on water quality, e.g., through the afforestation of land and maintenance of forest communities [25]. The quality of water in the river depends on the way of using the catchment area [25–28]. Understanding how land use can affect surface water quality is an extremely important issue. This is especially important in small catchments that supply large rivers where the pollution load from a given area accumulates [29]. Agricultural land management with intensive agricultural production creates a risk of nitrogen and phosphorus compounds entering the waters. These compounds usually enter rivers as a result of surface runoff or flooding [26,30,31]. These are large-scale pollutants that usually affect the entire catchment area. Surface runoff, as well as the development of vegetation, usually increases the content of soluble carbon compounds in the river [32]. All these pollutants contribute to the increase in the eutrophication of water reservoirs and, in extreme conditions, even to the disappearance of biological life [33]. Therefore, it is extremely important to know the size of the pollutant load that we find in small catchments, which can be used in policy to improve the quality of water in rivers. The aim of the study was to examine both the influence of the use of the catchment area and the variability of the concentration of individual water quality parameters over the research period.

2. Materials and Methods

2.1. Characteristics of the Raszynka River Catchment

The Raszynka River is a right tributary of the Utrata River. Its total length is 16.84 km. The river begins its course in the Lesznowola commune and flows into the Utrata River at 48.92 km of its course in Pęcice.

The surface area of the Raszynka catchment is 75.9 km^2. It can be therefore classified as a small catchment. Pursuant to the system of physic geographic regionalization adopted by Kondracki [21], the area of the designated catchment is located at the boundary of two mesoregions: the Łowicko-Błońska Plain (western part of the catchment) and the Warsaw Plain (eastern part of the catchment).

The Raszynka catchment is located in the region of the Mazovian-Podlasie climate [34]. The number of days in a year with a temperature above 5 °C ranges from 107 to 117. The mean annual temperature reaches 6.5 °C. Precipitation is at the following levels: in the winter half-year (X–III)—209 mm, in the summer half-year (IV–IX)—380 mm. The mean annual precipitation is 589 mm. The driest month in the year is January, with mean precipitation of 24 mm. The highest precipitation is recorded in July, averaging 75 mm [35].

The catchment area is characterized by snow and rain type supply. The highest water stages occur in the Spring months. In winter, the river sometimes periodically freezes. Moreover, the waters of the Raszynka River are supplied with treated wastewater from the Commune Wastewater Treatment Plant in Raszyn and periodically with water from the fish ponds of the Experimental Facility in Falenty. The land use structure of the Raszynka catchment is dominated by arable land (63%), urbanized land (23%), and forests 11%. The river's catchment is therefore classified as an agricultural catchment [36].

2.2. Sampling

Basic physicochemical water properties were measured in the years from 2017 to 2019. The study covered nine measurement sites representative of the entire length of the river (Table 1, Figures 1 and 2).

Table 1. Description of the location of the sampling sites on the Raszynka River.

Sampling Locality			
Number of Samples	**Geographical Coordinates**	**Km River**	**Land Use**
P1	52.160563 N 20.845211 E	2.20	Agricultural land
P2	52.158987 N 20.859988 E	3.50	Agricultural land
P3	52.157642 N 20.876194 E	4.50	Meadow
P4	52.156924 N 20.891203 E	6.00	Urbanized areas
P5	52.153720 N 20.908024 E	7.20	Urbanized areas
P6	52.150380 N 20.919491 E	8.50	Urbanized areas
P7	52.145495 N 20.933610 E	10.20	Agricultural land
P8	52.141619 N 20.948051 E	13.90	Meadow
P9	52.137210 N 20.963244 E	16.30	Meadow

Characteristics landscape of sampling sites are shown in Figure 2. Water samples for analysis were collected from nine sampling locations located along the entire river course. The sampling points were located in areas of different land use. Samples 3, 8, and 9 came from grasslands, 4, 5, and 6 from urbanized areas, and 1, 2, and 7 from agricultural areas. In each year, samples were taken from each measuring point four times (once per quarter—in February, May, August, and November). At each date, four partial samples were collected, which constituted a collective sample. A total of 108 water samples were tested. The measurement results were compared with the Polish Regulation of the Minister of Maritime Economy and Inland Navigation on 11 October 2019 on the classification of ecological condition, ecological potential, chemical condition, and the method of classification of the state of surface water bodies, as well as environmental quality standards for priority substances.

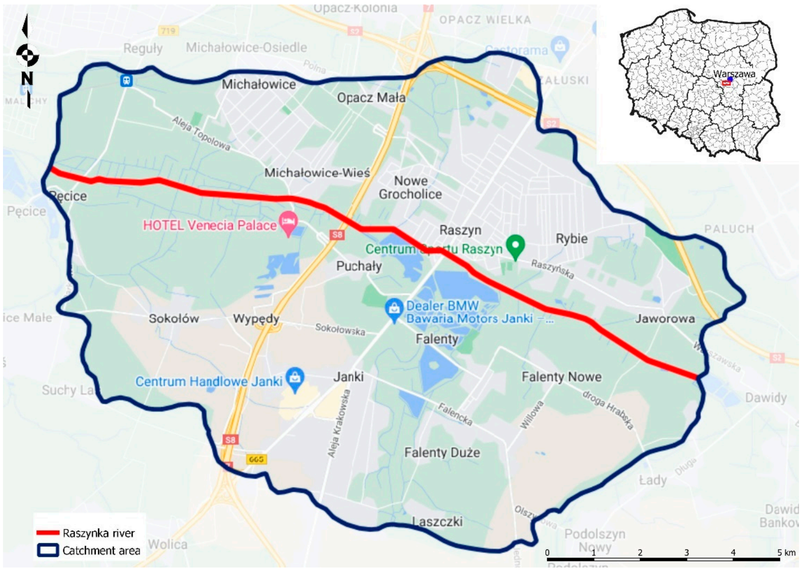

Figure 1. Localization of Raszynka river and its catchment in the framework of Poland.

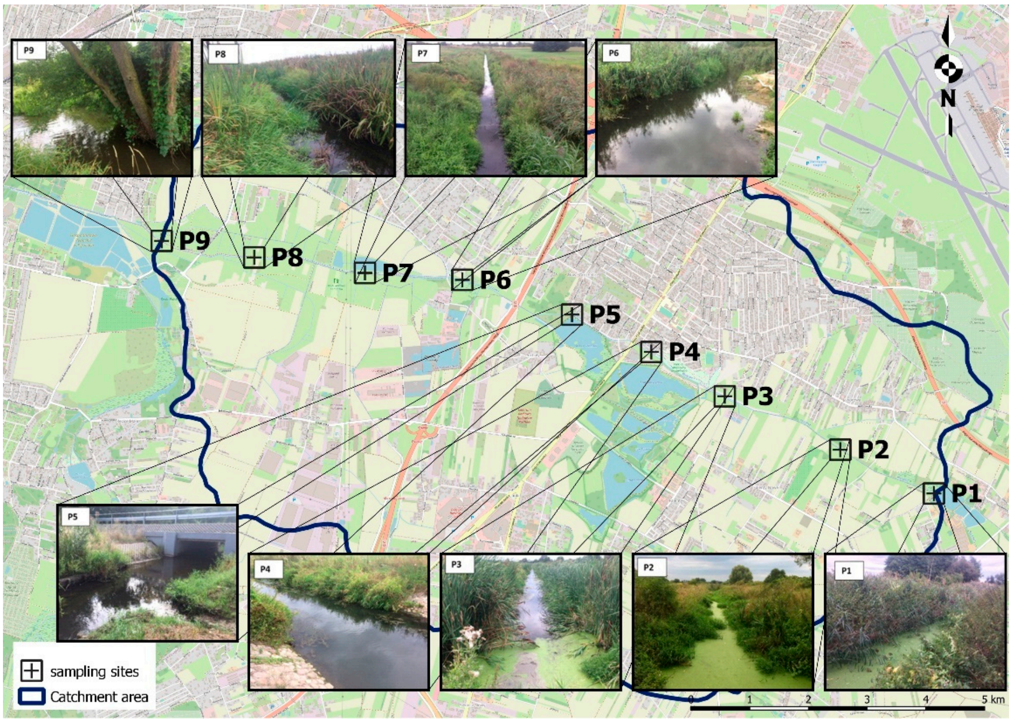

Figure 2. Water sampling scheme (google.maps.com, accessed date on 8 October 2022) in Raszynka river catchment.

2.3. Methodology of Determination of Selected Physicochemical Indices

The research was limited to those indicators of the physicochemical assessment of water quality, which are obligatorily required by the Minister of Maritime Economy and Inland Navigation [37]. The following was determined in the water samples:

- Ammonium (NH_4^+) was determined by means of the flow injection analysis method (FIA) with spectrophotometric detection [38].
- Nitrates (NO_3^-) were determined by means of the flow injection analysis (FIA) with spectrophotometric detection [39].
- Total phosphorus (TP) was determined by means of the method with the application of ascorbic acid [40].
- Chlorides (Cl^-) were determined by means of the titration method with the application of silver nitrate (Mohr method) [41].
- Chemical oxygen demand (COD) was determined by means of the titration method with the application of potassium permanganate [42].
- EC was determined conductometrically [43].
- pH was determined by means of the potentiometric method [44].
- Total alkalinity was determined by means of the titration method against phenolphthalein and methyl orange [45].

2.4. Statistical Analysis of Results

In this research, we examine the influence of the use of the catchment area and the variability of the concentration of individual water quality parameters over the research period.

Statistical comparisons of averages were conducted by means of a two-way analysis of variance (ANOVA) and a Tukey's HSD test at a probability level of 0.05 (Table 2) [46].

Table 2. Two-way analysis of variance.

Effect	**SS**	**df**	**MS**	**F**	***p***
			$N\text{-}NH_4{}^+$		
Intercept	51.51406	1	51.51406	1949.577	0.000000
Year	0.32950	2	0.16475	6.235	0.003030
Point	17.85419	8	2.23177	84.463	0.000000
Yearxpoint	2.46053	16	0.15378	5.820	0.000000
Error	2.14028	81	0.02642		
			$N\text{-}NO_3{}^-$		
Intercept	134.5807	1	134.5807	2890.525	0.000000
Year	4.1392	2	2.0696	44.451	0.000000
Point	8.1390	8	1.0174	21.851	0.000000
Yearxpoint	6.6174	16	0.4136	8.883	0.000000
Error	3.7713	81	0.0466		
			P		
Intercept	2.418015	1	2.418015	1106.549	0.000000
Year	0.014735	2	0.007368	3.372	0.039219
Point	0.128169	8	0.016021	7.332	0.000000
Yearxpoint	0.045881	16	0.002868	1.312	0.210273
Error	0.177000	81	0.002185		
			Cl^-		
Intercept	75,176.67	1	75,176.67	12,318.19	0.000000
Year	357.12	2	178.56	29.26	0.000000
Point	2579.05	8	322.38	52.82	0.000000
Yearxpoint	347.54	16	21.72	3.56	0.000078
Error	494.33	81	6.10		
			COD		
Intercept	8916.746	1	8916.746	2235.176	0.000000
Year	84.848	2	42.424	10.634	0.000079
Point	642.888	8	80.361	20.144	0.000000
Yearxpoint	39.479	16	2.467	0.619	0.860166
Error	323.132	81	3.989		
			EC		
Intercept	15,931,393	1	15,931,393	65,094.98	0.000000
Year	52	2	26	0.11	0.899610
Point	524,679	8	65,585	267.98	0.000000
Yearxpoint	3412	16	213	0.87	0.603027
Error	19824	81	245		
			pH		
Intercept	5720.333	1	5720.333	373,666.9	0.000000
Year	0.107	2	0.054	3.5	0.034777
Point	0.318	8	0.040	2.6	0.013953
Yearxpoint	0.341	16	0.021	1.4	0.166464
Error	1.240	81	0.015		
			alkalinity		
Intercept	3,078,136	1	3,078,136	27,355.67	0.000000
Year	509	2	254	2.26	0.110897
Point	56,971	8	7121	63.29	0.000000
Yearxpoint	3412	16	213	1.90	0.032603
Error	9114	81	113		

3. Results

The examined parameters were more diversified depending on the measuring point than for a year (Table 2). The concentration of NH_4^+ in different sections of the river showed high variability (Table 3). In the upper (P1, P2, P3) and lower courses (P7, P8, P9), NH_4^+ concentration was considerably lower than in the middle course of the river (P4, P5, P6). Pursuant to norms binding in Poland, the concentration of NH_4^+ always exceeded the acceptable value for class I of water quality at $\leq$0.170 mg NH_4^+ dm^{-3}. In P4, P5, and P6, the concentration of ammonium ions exceeded the limit value for quality class II (0.553 mg NH_4^+ dm^{-3}).

Table 3. Changes in the concentration of nitrogen and phosphorus forms and COD average in 2017–2019.

Year	P1	P2	P3	P4	P5	P6	P7	P8	P9
NH_4^+ (mg dm^{-3})									
2017	0.24 a	0.22 a	0.27 a	1.51 f	0.92 e	1.55 g	0.28 a	0.98 e	0.60 c
2018	0.47 b	0.41 b	0.48 c	0.69 d	0.97 e	1.30 f	0.21 a	0.48 c	0.50 c
2019	0.41 b	0.41 b	0.48 c	1.42 f	0.96 e	1.60 g	0.21 a	0.54 c	0.55 c
NO_3^- (mg dm^{-3})									
2017	0.97 d	0.74 c	0.22 a	1.02 de	0.84 cd	1.38 f	0.93 d	0.76 c	0.79 c
2018	1.31 f	1.04 e	1.53 g	1.41 f	1.84 h	1.13 e	1.02 d	0.85 d	0.55 b
2019	1.26 f	1.22 e	1.46 g	1.13 e	1.91 h	2.13 i	1.21 e	0.85 d	0.65 bc
TP (mg dm^{-3})									
2017	0.12 b	0.14 b	0.13 b	0.12 b	0.16 bc	0.16 bc	0.11 a	0.19 c	0.19 c
2018	0.14 b	0.15 b	0.18 c	0.12 b	0.18 c	0.16 bc	0.15 b	0.21 c	0.21 c
2019	0.06 a	0.11 a	0.08	0.12 b	0.13 b	0.15 b	0.14 b	0.21 c	0.26 d
COD (mg O_2 dm^{-3})									
2017	9.14 c	9.41 c	9.51 c	9.43 c	9.22 c	9.50 c	15.22 e	10.51 d	9.71 c
2018	8.11 b	9.49 c	8.11 b	7.85 b	7.31 b	7.66 b	16.39 f	8.35 b	8.33 b
2019	7.17 b	6.45 a	7.16 b	7.67 b	6.43 b	5.84 a	16.13 f	7.38 b	7.88 b

Letters a–i—homogeneous groups—groups in which the mean values of the examined parameters do not differ significantly.

The analysis of spatial management showed that the increased presence of ammonium in the middle course of the river is a result of the direct vicinity of fish ponds. The "Stawy Raszyńskie" reserve is the main emitter of ammonium due to the fish farming function of the ponds. The results show that the chemical oxygen, ammonia, phosphate requirements, and microbiological parameters of the river water increase significantly with discharges from fish farming [47,48].

Like in the case of NH_4^+, NO_3^- was the significantly highest for measurement site P6 (Tables 2 and 3). In this section of the river, the level of the ion varied depending on the month from 1.13 to 2.13 mg NO_3^- dm^{-3}. Both the threshold value of $\leq$1.6 mg NO_3^- dm^{-3} for class I and $\leq$2.5 mg NO_3^- dm^{-3} for class II of water quality were considerably exceeded, classifying the waters to class II and below class II of water quality. Probably the causes of high NO_3^- concentration in the middle course of the river are also associated with the presence of the Commune Wastewater Treatment Plant in Raszyn municipality. At the remaining sites, NO_3^- concentration was at a similar level and did not exceed the acceptable norms. In the lower and upper course of the river, pollution was even several times lower. This was caused by limited extensive agricultural use. Sites P7, P8, and P9 were characterized by the significantly lowest concentrations of NO_3^-. A factor determining this situation is the direct vicinity of meadows and bushy areas not subject to agricultural use.

Depending on the years of study, total phosphorus concentration in the Raszynka River varied from 0.06 to 0.26 mg P dm^{-3} (Table 3). In points P8 and P9 in 2018 and 2019, the limit value for class 1 water quality (0.2 mg P dm^{-3}) was exceeded. In any of the tested points, the permissible standards for class II (0.3 mg P dm^{-3}) were not exceeded. An increase in phosphorus concentration in the river waters with its course is evident. The significantly highest phosphorus concentration was observed at sampling sites P8 and P9. The dominant land use categories in the Raszynka River catchment in its lower course are meadows and arable land. Higher than average phosphorus values in the water suggest the supply of these compounds to water with surface runoff from arable fields.

Chemical oxygen demand in the waters of the Raszynka River pointed to variability between particular measurement sites (Table 3). The lowest chemical oxygen demand was recorded for a water sample collected in 2019 from site P6 (5.84 mg O_2 dm^{-3}). It is worth paying attention to sampling site P7, where the index value was considerably higher than at the remaining sites in all years. This could have been caused by the abundant occurrence of water vegetation in that place. 55% of samples met the criteria for classifying them as class I of water quality ($\leq$8.4 mg O_2 dm^{-3}), and 37% of water samples were classified as class II of water quality ($\leq$10.1 mg O2 dm^{-3}). COD values for samples from sites P7 and P8 exceeded the acceptable norms.

Chloride concentration in the analyzed water samples ranged from 13.3 to 37.1 mg Cl^- dm^{-3} (Table 3). The significantly lowest concentration of chlorides was observed in the lower course of the Raszynka River. A site particularly standing out among other sites is site P7, with the lowest concentration of chlorides. The site is located within the municipality of Falenty, and the area directly adjacent to the sampling site is under agricultural use.

The highest chloride concentration was determined for water samples collected from sites in the upper course of the river (P1, P2, P3). The threshold value for class I of water quality in the case of chlorides is $\leq$14.0 mg Cl^- dm^{-3} and $\leq$34.5 mg Cl^- dm^{-3} for the second class of water quality. This means that the analyzed water was excessively polluted with chlorides.

Electrical conductivity values of the analyzed water were within a range of 179–439 µS cm^{-1}. The significantly lowest values were recorded for site P7. Water sampled for the study from sites P1, P2, P3, P4, P5, P6, P8, and P9 showed low variability of EC. Like in the case of analysis of other physicochemical indices, water samples collected from site P7 stand out among others. The value of EC at that site is lower by more than 50% in comparison to water sampled from the neighboring site P8. Probably this situation could have been determined by limited water flow between these sites. Measurement site P7 was characterized by the occurrence of a high abundance of water vegetation. Pursuant to norms binding in Poland, surface water of quality class I should contain no more than 411 µS cm^{-1}, and class II, not more than 553 µS cm^{-1}. More than half, i.e., 55% of the analyzed water samples, were classified as good quality (class I). The remaining water samples were within the norms of the regulation, classifying them as waters of class II.

The lowest pH was recorded at measurement site P1 at the source of the river and the highest at site P3. According to Polish law, the permissible pH values for class I are 7.4–8.0, and for the second class, 6.7–8.1.

Total water alkalinity analyzed in the waters of the Raszynka River showed considerable variability in particular sections of the river (Table 4). Threshold values throughout the river section varied from 139.2 to 220.4 mg $CaCO_3$ dm^{-3}. According to Polish law, the water alkalinity for class I are $\leq$185, and for the second class, $\leq$205. The lowest value was recorded for water sampled from site P7 and the highest for site P9 at the mouth of Raszynka to the Utrata River. Results presented in Table 4 suggest that total water alkalinity at sampling points in the upper and middle course of the river was maintained at an approximate level.

Table 4. Changes in chloride concentration, EC, pH, and total alkalinity in the Raszynka River average 2017–2019.

Year	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**	**P9**
					Cl^- (mg dm^{-3})				
2017	28.8 e	30.1 e	26.8 d	27.2 d	27.9 d	29.5 e	13.3 a	22.9 c	21.6 b
2018	29.4 e	26.3 d	28.3 e	26.2 d	25.9 d	29.9 e	15.7 a	21.7 b	20.6 b
2019	27.1 d	36.7 g	37.1 g	32.6 f	31.1 e	30.8 e	18.2 b	23.6 c	23.4 c
					EC (µS cm^{-1})				
2017	401 d	401 d	414 d	432 e	384 c	389 c	195 a	427 e	422 e
2018	410 d	400 d	426 e	430 e	373 b	392 c	179 a	439 e	401 d
2019	401 d	401 d	417 d	425 e	373 b	393 c	204 ab	432 e	409 d
					pH				
2017	7.1	7.4	7.3	7.3	7.3	7.2	7.1	7.2	7.3
2018	7.2	7.2	7.3	7.3	7.2	7.2	7.3	7.2	7.3
2019	7.4	7.4	7.4	7.3	7.3	7.2	7.2	7.2	7.3
					total alkalinity (mg $CaCO_3$ dm^{-3})				
2017	166.4 b	153.6 a	150.8 a	147.2 a	158.4 a	194.6 c	139.2 a	215.2 e	220.4 e
2018	156.8 a	149.2 a	152.5 a	160.4 a	155.2 a	174.4 b	148.8 a	197.6 d	204.4 d
2019	152.8 a	154.4 a	148.8 a	150.8 a	156.4 a	190.8 c	156.8 a	195.6 d	207.2 d

Letters a–g—homogeneous groups—groups in which the mean values of the examined parameters do not differ significantly.

Table 5 shows the average measured values of monitored parameters for the years 2017–2019 according to land use.

Table 5. Relation between water quality and land use.

	Cl^-	**NH_4^+**	**NO_3^-**	**P**	**COD**	**EC**	**pH**	**Total Alkalinity**
Agricultural land	25.06 a	0.32 a	1.08 b	0.18 b	10.83 b	332.4 b	7.27 a	153.1 a
Meadow	25.08 a	0.54 b	0.85 a	0.12 a	8.55 a	420.8 a	7.29 a	188.0 c
Urbanized areas	29.00 b	1.21 c	1.42 c	0.14 a	7.88 a	399.0 a	7.28 a	165.4 b

Letters a–c—homogeneous groups—groups in which the mean values of the examined parameters do not differ significantly.

As shown in Table 5, land use had an impact on the values of the studied indicators in the RaszynkIt is OKa River. The highest concentration of chlorides, ammonium, and nitrate was found in urbanized areas. The highest concentrations of total phosphorus and COD were determined in agricultural areas and total alkalinity in meadows. The pH of the water was not dependent on land use.

4. Discussion

The analysis of results of measurements of surface waters in the Raszynka River showed variability between particular sampling sites, as well as between years. Samples with quality exceeding threshold values of class I or II of water quality constituted 47% of all collected samples. The most frequently exceeded threshold values of physicochemical properties included pH and NH_4^+, and Cl^- (Tables 3 and 4).

Water quality in small Polish rivers directly translates into the state of cleanliness of large rivers and, eventually, marine waters—in the case of Poland in the Baltic Sea. Polluted rivers are responsible for 100% of phosphorus present in the Baltic and approximately 20–30% of nitrogen [49]. The majority of studies regarding the pollution and eutrophication of freshwaters primarily concern lakes and retention reservoirs. The quality of flowing waters should therefore become the subject of a greater number of studies. Rivers constitute the main resources of inland waters for household, industrial, and irrigation use. Rivers provide the habitat for many ecosystems and are necessary for hydrological and biochemical cycles [50,51]. Changes in the dynamics of pollution of surface waters resulting from global warming have also been observed in recent years. They result in frequent droughts and floods, leading to changes in the condition of river waters and in the concentration of pollutants [52]. The progressing urbanization, intensive agricultural activity, deforestation, and climate warming result in irreversible transformations of the natural environment and ecosystems. The primary pollutants include organic matter and nutrients related to the agricultural activity or presence of wastewater treatment plants, as well as toxic substances such as heavy metals and hydrocarbons related to the progressing urbanization and industrial development [53,54].

The highest concentration of ammonium and nitrate ions was found in the middle course of the river in urbanized areas. Probably the causes of high NO_3^- concentration in the middle course of the river are also associated with the presence of the Commune Wastewater Treatment Plant in Raszyn. Burzyńska [36] observed similar dependencies in her research. Waters on agricultural land show high concentrations of nutrients such as total phosphorus, NO_3^-, and NH_4^+ from organic and mineral fertilizers [55,56]. High local phosphorus concentrations can also result from municipal pollution [57]. Phosphorus concentration in rivers is also largely determined by spring snowmelt, intensive rainfall, and particularly storms washing phosphorus from agricultural land, municipal sewage, and surface runoff from urbanized areas [58]. These results correlate with our results. The increase in the concentration of biogenic elements was observed in urbanized areas. The negative relationships between water quality and urban land cover and in lowland catchments suggest that lowland river water-quality state is strongly influenced by agricultural and urban land use. This association between water-quality degradation and intensive agricultural and urban land use in lowland catchments has been reported in many other regions [59,60]. An increase in the concentration of nitrates can be caused by agriculture, particularly in areas under intensive use, where the nitrification process occurs, favoring the leaching of nitrates [61]. Urbanized lands dominate the structure of land use in the lower part of the river. The way land was used probably had an effect on the partial reduction of $N\text{-}NO_3$ concentration in river waters. Similar changes in lower water pollution in the lower part of the Raszynka River were also observed by Pawłat-Zawrzykraj [62].

Higher than average COD values in flowing waters may be caused by both considerable pollution with organic substances subject to biodegradation and inorganic substances. Increased values of the indicator are often related to the occurrence of high concentrations of total phosphorus and NH_4^+. Such an effect is particularly evident in summer months when the intensified supply of agricultural pollutants occurs [63,64]. High concentration of chemical oxygen demand may also be related to the occurrence of a high abundance of microorganisms in the river [65,66]. Just like in our research, studies have shown that the small rivers contain high concentrations of nitrates and phosphates, which led to the quick growth as well as death of plants and algae. The result is accumulation and decomposition of organic wastes leading to high DOC and BOD values [67,68].

Own research found high variability of chloride concentrations. Chloride concentrations were higher in the upper course of the river than in the lower ones. In the upper course of the river, there are areas with intensive plant production. Points P1 and P2 are areas used for agriculture. Research by other authors clearly shows that land use affects the concentration of chlorides in the water. At the same time, land use change reduces the leaching of this ion from the soil [69].

The highest concentrations occurred at measurement sites on urbanized land. Research by [70] points to an increase in chloride concentrations in the waters of rivers neighboring agricultural and residential areas. Our research also corresponds to German research in which similar relationships were obtained [71].

High concentrations of total phosphorus, NH_4^+, NO_3^-, and chemical oxygen demand with simultaneous low dissolved oxygen concentration in rivers may lead to eutrophication. Human activity is often identified as the cause of eutrophication, particularly agriculture and improper waste management [72,73]. According to research by some authors, draughts have a considerable effect on temperature and dissolved oxygen concentration but do not affect the concentration of nutrients [74].

The conducted research showed considerable changes in EC (179 vs. 439 µS cm^{-1}). More than 50% of the analyzed samples were qualified as class I water quality. The remaining samples were qualified as class II water quality. Water samples collected from site P7 stand out among others. The value of EC at that site is lower by more than 50% in comparison to water sampled from the neighboring site P8. Probably this situation could have been determined by limited water flow between these sites. Other research suggests that groundwater may be a large source of nutrients in the river [75]. According to research by Wysocka-Czubaszek and Wojno [76], an increase in EC suggests the low self-cleaning capacity of a river. In the case of the Raszynka River, an increase in EC occurred in water from sites with restricted water flow related to strong overgrowing of the areas with water vegetation. Other studies also indicate that in agricultural settings, the EC of surface waters was found to be significantly higher than that of surface waters with natural vegetation or urban land surrounding them [77]. The influence of land use disappears during prolonged rainfall and snowmelt-induced floods when the water circulation pattern in catchments is similar [78].

The quality of the water flowing out of the catchment area of a river depends primarily on the form of land development. Research conducted by Cavalcante et al. (2017) [53] and Rodrigues et al. (2018) [79] demonstrates that the link between the quality of water in rivers and the type of catchment used (urbanized and agricultural land) varies, depending on the terrain, region, weather, and climatic conditions. The waters in agricultural areas contain high concentrations of biogenic substances such as total phosphorus, nitrate nitrogen, and ammonium nitrogen, the sources of which are organic and mineral fertilizers [55]. High local concentrations of phosphorus may also be the result of municipal pollution [80]. The main sources of ammonium nitrogen in rivers are point sources, e.g., sewage treatment plants and surface sources—surface runoffs from farmlands [81].

5. Conclusions

The Raszynka River waters were of low quality due to the high concentration of nitrogen, chloride, and COD. The most polluted surface waters of the lower section of the river are located in the vicinity of the urbanized area, and the least polluted water is from agricultural land and natural meadows.

Regarding legal regulations in terms of quality, the Raszynka river water did not meet the standards in terms of concentration of NH_4^+ ions in urbanized areas and COD in agricultural areas. The concentration of ammonium in river water was four times higher in the urbanized area compared to agricultural land use (1.21 and 0.32 mg dm^{-3}, respectively). On the other hand, the concentration of phosphorus was almost 30% higher in agricultural land use compared to urbanized area (0.18 and 0.14 mg dm^{-3} respectively). In terms of nitrate concentration in the water, the highest one was measured in the middle course of the river (sampling points P5 and P6). The nitrate concentration was up to twice to three times higher than in the other sampling points (1.91–2.13 and 0.65–1.22 mg dm^{-3}, respectively). This was associated with the presence of the Commune Wastewater Treatment Plant in Raszyn municipality. Water pH in the Raszynka River varied from 7.1 to 7.4 and did not depend on land use. The highest chemical oxygen demand in the waters of the Raszynka River was measured on the sampling points P7 and P8, which could have been caused by the abundant occurrence of water vegetation in that location.

In order to limit the effects of the uncontrolled spreading of nutrients to the environment, periodic monitoring of the surface water in river valleys in agricultural areas should be carried out. It is also recommended to increase buffer zones between arable land and the river.

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