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The Role of the Catchment Area in Shaping Water Quality in the Lowland Springs of the Knyszyn Forest (NE Poland)

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Abstract: The Puszcza Knyszyńska springs are an important element of the environment, conditioning the high geo- and biodiversity in the region. These springs are layered outflows that drain the waters of the Quaternary level. More than 200 outflows have been cataloged, and 80 of them have measured/estimated yields and analyses of their water qualities. During periods of low water levels, the discharge efficiency most often fluctuated within a range of 0.5–2.0 $dm^3 \cdot s^{-1}$. In light of the applicable legal standards, the tested waters were of excellent quality. They belonged to the two hydrochemical types HCO_3-Ca and HCO_3-Ca-Mg, indicating the Quaternary aquifer's homogeneity in the post-glacial areas. Small concentrations of most of the chemical parameters of water were found in the forest springs. Larger transformations in the chemical composition of water occurred in the outflows located in agricultural land and rural areas. A characteristic feature of the chemical composition of the water in the region's lowland springs was an increased concentration of biogenic compounds (nitrogen, phosphorus, and carbon compounds), both organic and inorganic. The average concentration of dissolved organic carbon in the water of the lowland springs in summer exceeded 4 $mg \cdot dm^{-3}$. In some outflows, most often of a swamp nature or located in peat areas, the concentration of dissolved organic carbon even exceeded a dozen or so $mg \cdot dm^{-3}$.

Keywords: lowland springs; water quality; land use

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1. Introduction

Springs are unique ecosystems at the interface between groundwater and surface water [1,2] and between the terrestrial and the aquatic habitats [3]. It is a complex environment encompassing immense biodiversity for soil and water microorganisms that are the primary agents responsible for key ecosystem processes [4–7]. Springs occur more frequently in mountains and upland areas, and there are fewer reports on the biology and ecology of typical springs in lowlands of Central Europe [8,9]. Springs are mostly low-trophic ecosystems, except for those located in areas subject to strong human pressure, where groundwater may contain many nutrients or even be oxygen-deficient [10,11]. A water quality analysis in Bialystok indicated the lowest water trophy in the springs compared with other water types [11–13]. Unique wetland ecosystems may develop around springs, e.g., soligenous bogs or spring marshes. Sometimes, as a result of erosion in the outflow zone, concave landforms form—spring niches [14]. In lowland areas, these are shallow, but they contribute to the diversification of the old-glacial landscape, determining its geodiversity and providing a habitat for valuable flora and fauna species, often of a relict nature [15]. Significant differences in the number of bacteria in the springs from this area were also found, which reflected how the direct catchment was managed [4]. It influences the area's high biodiversity, improving local water relations [3,5–7].

Although springs have been recognized as important, rare, and globally threatened ecosystems, there is, as of yet, no consistent and comprehensive classification or common lexicon for springs, especially for those in lowland areas [16]. In lowland areas, the most useful is the hydrobiological classification of springs reflecting the habitat's quality features [10].

The scientific, educational, and landscape values of natural groundwater outflows and their natural, economic, and cultural significance in lowland areas are increasingly recognized [12]. Springs usually drain the first aquifer. In lowlands, the waters of the first aquifer are shallow and, therefore, are exposed to anthropogenic pollution. The use of the surface catchment is a good indicator of the degree of transformation of the water quality of the first aquifer. Current research on the springs in the Knyszyn Forest makes this possible. The crenological studies in the Knyszyn Forest (PK) were aimed at:

- Drawing attention to the presence and importance of natural groundwater outflows in the lowlands;
- The assessment of the physical and chemical compositions of the waters showing the specificity of the water quality of lowland springs (a significant concentration of biogenic elements that determine their fertility);
- The impact of land use as a factor differentiating the quality of shallow groundwaters flowing onto the surface in the form of springs.

2. Study Area

The research area was located in Poland (Central Europe). The crenological studies were carried out in the Puszcza Knyszyńska located in the North Podlasie Lowland, which is part of the Podlasie-Belarusian Wysoczyzna sub-provinces, extending into the western part of the West Russian Lowland [17,18]. The Puszcza Knyszyńska is the second largest (after the Puszcza Białowieska) forest complex in the Podlaskie Voivodeship. It occupies over 126 thousand ha. In 1988, the Professor Witold Sławiński Puszcza Knyszyńska Landscape Park was created on its territory (PKLP). The Puszcza Knyszyńska has also been included in the Natura 2000 network. The special bird protection area "Puszcza Knyszyńska" (PLB200003) covers the entire Puszcza Knyszyńska and the Gródecko-Michałowska Basin. There are at least 38 species of birds from Annex 1 of the Birds Directive and 14 species from the Polish Red Book of Animals. The area of special protection of habitats "Ostoja Knyszyńska" (PLH200006) covers the entire forest complex of the Puszcza Knyszyńska. The forest areas are cut by agricultural valleys of small rivers and clearings. In the description of "Ostoja Knyszyńska", attention was drawn to the varied topography and the mosaic of habitats which determine the great landscape value of this area. Numerous springs were considered peculiarities.

From a hydrological point of view, the area in question lies in the Baltic catchment, almost entirely in the Supraśl catchment belonging to the Upper Narew catchment (Figure 1), and extends along the main watershed between the Vistula and Neman catchments [19,20]. The natural drainage axis is the Supraśl river with its right-bank tributaries—Czarna, Sokołda, and Słoja, and left-bank tributaries—Płoska, Pilnica, and Biała.

In the North Podlasie Lowland, the Precambrian crystalline rocks of the Mazurian-Belarusian Anteclysis occur quite shallowly below the surface. This ascent is part of the great Eastern European Platform [21]. The series of sedimentary rocks older than the Quaternary is not very thick, with numerous stratigraphic gaps. The pieces of the Jurassic and Cretaceous appear directly on the crystalline foundation. The tertiary sediments occur in the forms of islands, e.g., in the Gródecko-Michałowska Basin. The quaternary sediments were formed during the Pleistocene glaciations, and their thicknesses range from 130 to 220 m [18,22,23]. They are represented by boulder clays, gravel-sand deposits, dammed lake silts, and varved clays (Figure 2a–c). The bottoms of the river valleys and the excavation depressions are filled with Holocene formations: silt, sand, gravel, gyttja, and peat [21].

The Upper Narew catchment, especially the Supraśl catchment, is richly carved for an old-glacial area [24,25]. Among the convex forms in the landscape, the Gródek-Czarna Białostocka field embankment, recognized as an esker, stands out [24]. Other convex landforms are latitudinal hills made of layered sand and gravel. These forms are considered to be melted-out glacier depression hills. The most common convex forms in the Upper Narew catchment are kames. The concave forms include melting basins, valleys, and shallower bowls and basins. The melting forms in the discussed area occur in groups, creating a complex polygenetic system of depressions connecting the Supraśl valley with an erosion base. The numerous springs are the consequence of the diversified relief of the area.

The main and most important groundwater environment of North-Eastern Poland is the Quaternary formations. The porous nature of the groundwater in the region is a common feature. They occur mainly in the infiltration equilibrium, and the shallowest aquifer occurs in the sands and gravels lying on the clays of the Warta glaciation [26]. The distribution of the springs in the Puszcza Knyszyńska is uneven (Figure 3). The largest number of springs occur in the valleys of the rivers: Krzemianka, Czarna, Jałówka, and Świniobródka. These are valley outflows (39 objects). There are slightly more outflows located at the feet of slopes and flanks (41 objects). From the hydrobiological point of view, rheocrenes dominate—55 springs (Figure 4), whilst there are fewer helocrenes—21 springs and limnocrenes—4 springs (Table 1). Among the limnocrenes, two artificially created ones were distinguished: No. 11 is a timbered spring in the countryside (Figure 5), and No. 57 is a limnocrene created by blocking the outflow of water with a beaver dam (Figure 6).

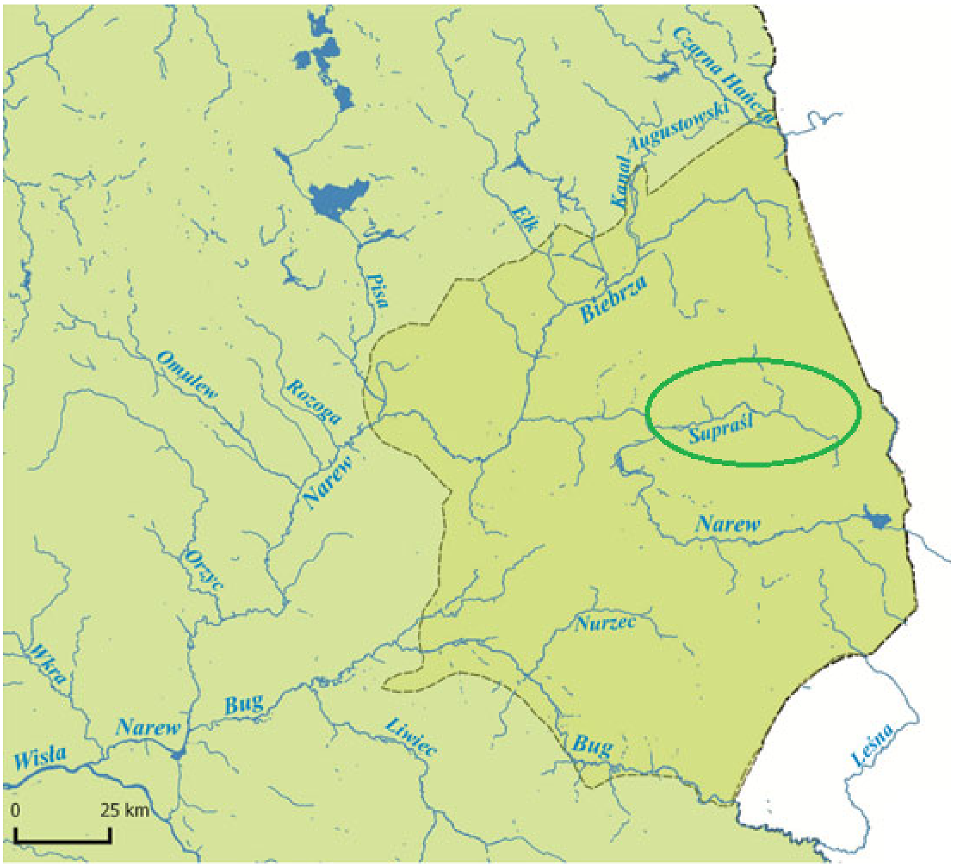

Figure 1. Hydrological location of the study area.

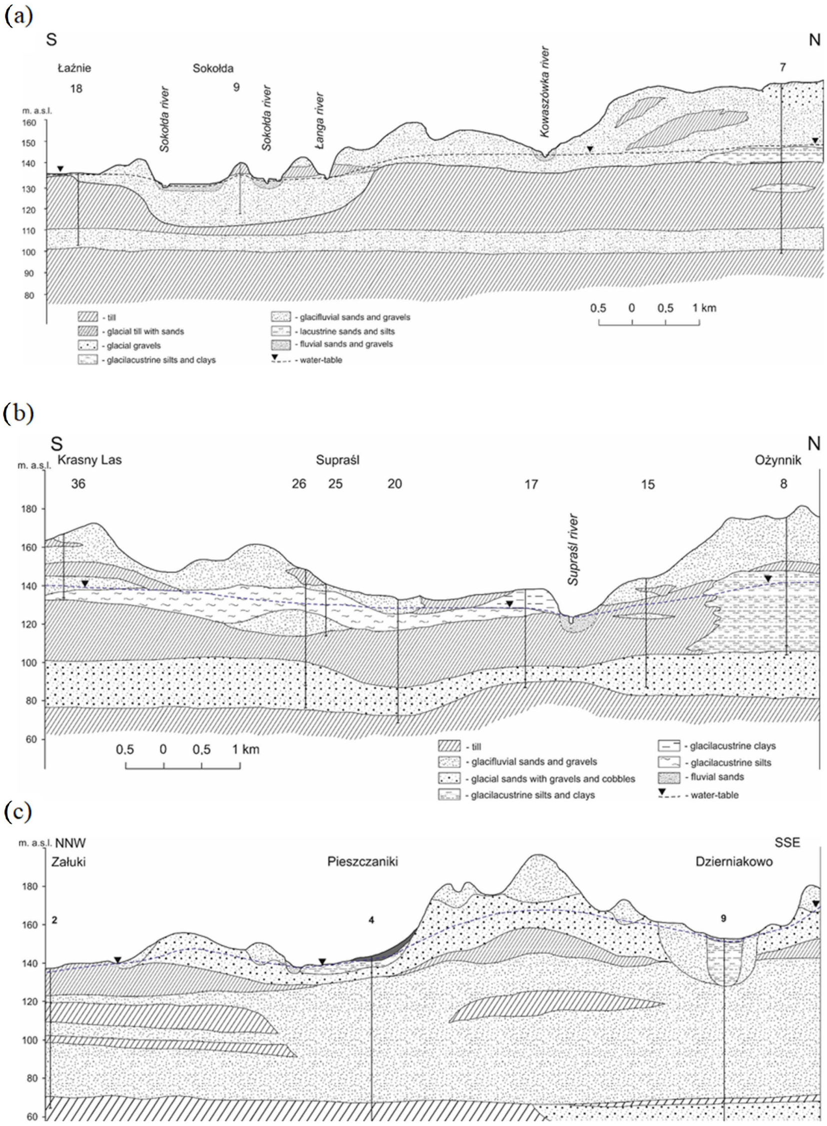

Figure 2. Hydrogeological cross-section through the Knyszyn Forest: the central part of Łaźnie-Kowalewszczyzna (**a**), the central part of Krasny-Las Ożynnik (**b**), and the eastern part of Załuki-Dzierniakowo (**c**).

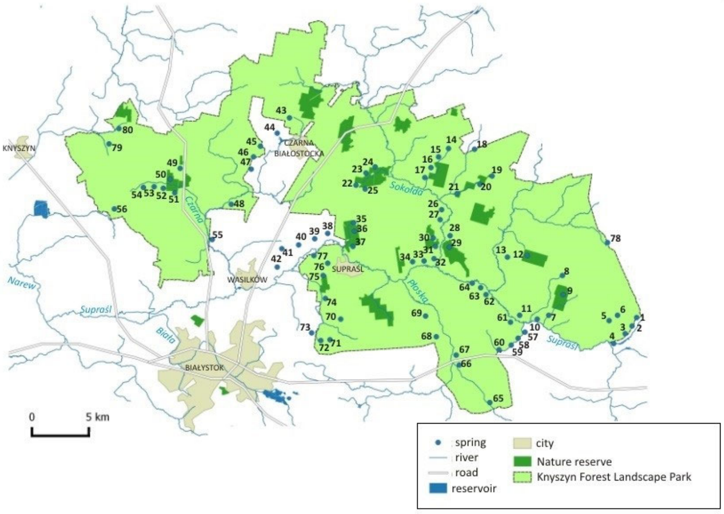

Figure 3. Locations of the studied springs in the Knyszyn Forest.

Figure 4. Rheocrene in the Migówka valley (Pstrągownia, spring No. 22).

Figure 5. Artificial limnocrene created as a result of the outflow being captured by lining (spring No. 11).

Figure 6. Artificial limnocrene created as a result of the construction of a beaver dam (spring No. 57).

Table 1. Characteristics of the springs in the Knyszyńska Forest.

No	Geographical Coordinates	Hydrological Location	Geomorphological Type of Spring	Hydrobiological Type of Spring	Hydrochemical Type of Water	Land Use
1	N: 53°8′58.19″ E: 23°42′56..39″	right-side direct tributary of the Supraśl river → Breszczeczka catchment	hillslope	rheocrene	HCO_3-Ca	forest
2	N: 53°8′17.31″ E: 23°41′41.48″	right-side direct tributary of the Supraśl river → Breszczeczka catchment	hillslope	rheocrene	HCO_3-Ca-Mg	grassland
3	N: 53°8′7.23″ E: 23°41′24.34″	right-side direct tributary of the Supraśl river → Breszczeczka catchment	hillslope	helocrene	HCO_3-Ca-Mg	grassland
4	N: 53°8′7.52″ E: 23°40′52.87″	right-side direct tributary of the Supraśl river → Breszczeczka catchment	hillslope	rheocrene	HCO_3-Ca-Mg	rural area
5	N: 53°8′47.39″ E: 23°40′39.82″	right-side direct tributary of the Supraśl river → Breszczeczka catchment	hillslope	rheocrene	HCO_3-Ca-Mg	forest
6	N: 53°8′47.03″ E: 23°40′58.74″	right-side direct tributary of the Supraśl river → Breszczeczka catchment	hillslope	rheocrene	HCO_3-Ca-Mg	forest
7	N: 53°10′25.56″ E: 23°38′7.25″	right-side direct tributary of the Supraśl river → Średnica catchment	valley	helocrene	HCO_3-Ca	grassland
8	N: 53°11′22.72″ E: 23°36′56.28″	right-side direct tributary of the Supraśl river → Radulinka catchment	valley	rheocrene	HCO_3-Ca-Mg	forest
9	N: 53°10′19.79″ E: 23°36′18.84″	right-side direct tributary of the Supraśl river → Radulinka catchment	valley	rheocrene	HCO_3-Ca	grassland
10	N: 53°9′38.68″ E: 23°34′29.02″	right-side direct tributary of the Supraśl river → Radulinka catchment	valley	helocrene	HCO_3-Ca-Mg	grassland
11	N: 53°9′29.32″ E: 23°34′16.04″	right-side direct tributary of the Supraśl river → Radulinka catchment	valley	artificial limnocrene	HCO_3-Ca-Mg	rural area
12	N: 53°12′46.19″ E: 23°34′14.97″	Słoja catchment → Skrobacianka catchment	hillslope	helocrene	HCO_3-Ca	forest
13	N: 53°12′30.63″ E: 23°32′11.91″	direct tributary of the Słoja river → Słoja catchment	hillslope	rheocrene	HCO_3-Ca-Mg	forest
14	N: 53°18′28.05″ E: 23°26′57.28″	Sokołda catchment → Karnicha catchment	hillslope	rheocrene	HCO_3-Ca-Mg	forest/grassland
15	N: 53°17′42.44″ E: 23°25′37.06″	Sokołda catchment → Karnicha catchment	valley	rheocrene	HCO_3-Ca-Mg	forest
16	N: 53°16′41.53″ E: 23°25′4.8″	Sokołda catchment → Karnicha catchment	valley	rheocrene	HCO_3-Ca-Mg	forest
17	N: 53°17′35.3″ E: 23°28′44.07″	Sokołda catchment → Kowszówka catchment	valley	helocrene	HCO_3-Ca-Mg	forest
18	N: 53°17′43.72″ E: 23°30′21.1″	Sokołda catchment → Łanga catchment	valley	rheocrene	HCO_3-Ca-Mg	rural area
19	N: 53°15′23.85″ E: 23°30′3.88″	Sokołda catchment → Łanga catchment	valley	rheocrene	HCO_3-Ca-Mg	rural area
20	N: 53°16′52.31″ E: 23°30′51.01″	Sokołda catchment → Łanga catchment	valley	rheocrene	HCO_3-Ca	rural area
21	N: 53°16′5.05″ E: 23°31′1.89″	Sokołda catchment → Łanga catchment	hillslope	rheocrene	HCO_3-Ca-Mg	rural area
22	N: 53°16′53.67″ E: 23°22′15.75″	Sokołda catchment → Migówka catchment	hillslope	rheocrene	HCO_3-Ca	forest
23	N: 53°16′54.62″ E: 23°22′27.36″	Sokołda catchment → Migówka catchment	hillslope	rheocrene	CO_3-Ca-Mg	forest
24	N: 53°16′49.47″ E: 23°22′44.93″	Sokołda catchment → Migówka catchment	valley	rheocrene	HCO_3-Ca-Mg	forest
25	N: 53°16′26.7″ E: 23°21′24.73″	Sokołda catchment → Migówka catchment	valley	rheocrene	CO_3-Ca-Mg	forest
26	N: 53°14′4.31″ E: 23°29′43.08″	direct tributary of the Sokołda river → Sokołda catchment	valley	rheocrene	HCO_3-Ca	grassland
27	N: 53°14′35.73″ E: 23°27′38.92″	direct tributary of the Sokołda river → Sokołda catchment	valley	helocrene	HCO_3-Ca	grassland
28	N: 53°14′53.01″ E: 23°28′59.46″	direct tributary of the Sokołda river → Sokołda catchment	hillslope	limnocrene	HCO_3-Ca-Mg	forest
29	N: 53°14′38.13″ E: 23°29′28.2″	direct tributary of the Sokołda river → Sokołda catchment	hillslope	rheocrene	HCO_3-Ca-Mg	forest
30	N: 53°12′44.98″ E: 23°27′28.53″	direct tributary of the Sokołda river → Sokołda catchment	hillslope	helocrene	HCO_3-Ca-Mg	grassland

Table 1. *Cont.*

No	Geographical Coordinates	Hydrological Location	Geomorphological Type of Spring	Hydrobiological Type of Spring	Hydrochemical Type of Water	Land Use
31	N: 53°12′37.01″ E: 23°27′29.49″	direct tributary of the Sokołda river → Sokołda catchment	hillslope	helocrene	HCO_3-Ca	forest/grassland
32	N: 53°12′24.64″ E: 23°27′16.42″	direct tributary of the Sokołda river → Sokołda catchment	hillslope	helocrene	HCO_3-Ca-Mg	forest/grassland
33	N: 53°12′19.2″ E: 23°27′7.29″	direct tributary of the Sokołda river → Sokołda catchment	hillslope	helocrene	HCO_3-Ca	forest/grassland
34	N: 53°12′23.77″ E: 23°26′2.44″	direct tributary of the Sokołda river → Sokołda catchment	hillslope	helocrene	HCO_3-Ca-Mg	rural area
35	N: 53°13′40.52″ E: 23°20′26.84″	Sokołda catchment → Jałówka catchment	valley	rheocrene	HCO_3-Ca-Mg	forest/grassland
36	N: 53°14′30.49″ E: 23°20′50.34″	Sokołda catchment → Jałówka catchment	valley	rheocrene	HCO_3-Ca	forest/grassland
37	N: 53°14′4.58″ E: 23°20′41.57″	Sokołda catchment → Jałówka catchment	valley	rheocrene	HCO_3-Ca-Mg	forest
38	N: 53°14′28.01″ E: 23°18′7.49″	right-side direct tributary of the Supraśl river → Supraśl catchment	hillslope	rheocrene	HCO_3-Ca-Mg	forest/grassland
39	N: 53°13′34.82″ E: 23°15′45.74″	right-side direct tributary of the Supraśl river → Supraśl catchment	hillslope	rheocrene	HCO_3-Ca	forest/grassland
40	N: 53°14′31.25″ E: 23°19′12.46″	right-side direct tributary of the Supraśl river → Supraśl catchment	hillslope	rheocrene	HCO_3-Ca	grassland
41	N: 53°14′31.38″ E: 23°17′15.09″	right-side direct tributary of the Supraśl river → Supraśl catchment	hillslope	rheocrene	HCO_3-Ca	grassland
42	N: 53°12′39.65″ E: 23°13′42.02″	right-side direct tributary of the Supraśl river → Supraśl catchment	hillslope	helocrene	HCO_3-Ca	grassland
43	N: 53°19′13.31″ E: 23°15′18.6″	Czarna catchment → Czapielówka catchment	valley	rheocrene	HCO_3-Ca	rural area
44	N: 53°18′7.34″ E: 23°13′13.77″	Czarna catchment → Jurczycha catchment	valley	helocrene	HCO_3-Ca	rural area
45	N: 53°17′24.1″ E: 23°12′25.18″	Czarna catchment → Czarna Rzeczka catchment	valley	helocrene	HCO_3-Ca-Mg	forest
46	N: 53°16′50.22″ E: 23°11′31.01″	direct tributary of the Czarna river → Czarna catchment	valley	rheocrene	HCO_3-Ca-Mg	forest
47	N: 53°16′3.72″ E: 23°12′56.16″	Czarna catchment → Czarna Rzeczka catchment	valley	rheocrene	HCO_3-Ca-Mg	forest
48	N: 53°15′35.27″ E: 23°10′0.62″	direct tributary of the Czarna river → Czarna catchment	valley	helocrene	HCO_3-Ca	grassland
49	N: 53°17′12.6″ E: 23°8′2.38″	Czarna catchment → Czarna Rzeczka catchment	hillslope	helocrene	HCO_3-Ca-Mg	forest
50	N: 53°16′55.79″ E: 23°7′5.98″	Czarna catchment → Krzemianka catchment	valley	rheocrene	HCO_3-Ca-Mg	forest
51	N: 53°16′38.56″ E: 23°3′30.18″	Czarna catchment → Krzemianka catchment	valley	rheocrene	HCO_3-Ca-Mg	forest/FV
52	N: 53°16′27.53″ E: 23°5′28.25″	Czarna catchment → Krzemianka catchment	valley	rheocrene	HCO_3-Ca-Mg	forest
53	N: 53°15′5.65″ E: 23°8′40.17″	Czarna catchment → Krzemianka catchment	valley	rheocrene	HCO_3-Ca	forest
54	N: 53°14′46.25″ E: 23°8′10.17″	Czarna catchment → Krzemianka catchment	valley	helocrene	HCO_3-Ca-Mg	forest
55	N: 53°13′39.73″ E: 23°10′4.77″	direct tributary of the Czarna river → Czarna catchment	hillslope	rheocrene	HCO_3-Ca-Mg	grassland
56	N: 53°13′9.44″ E: 23°1′24.03″	right-side direct tributary of the Supraśl river → Supraśl catchment	hillslope	helocrene	HCO_3-Ca	rural area
57	N: 53°8′19.35″ E: 23°33′17.86″	left-side direct tributary of the Supraśl river → stream from Sofipol catchment	hillslope	artificial limnocrene	HCO_3-Ca	grassland
58	N: 53°8′17.93″ E: 23°33′12.44″	left-side direct tributary of the Supraśl river → stream from Sofipol catchment	hillslope	rheocrene	HCO_3-Ca	grassland
59	N: 53°8′20.26″ E: 23°33′5.42″	left-side direct tributary of the Supraśl river → stream from Sofipol catchment	hillslope	rheocrene	HCO_3-Ca-Mg	grassland
60	N: 53°8′21.2″ E: 23°33′7.51″	left-side direct tributary of the Supraśl river → stream from Sofipol catchment	hillslope	rheocrene	HCO_3-Ca-Mg	grassland/FV

Table 1. *Cont.*

No	Geographical Coordinates	Hydrological Location	Geomorphological Type of Spring	Hydrobiological Type of Spring	Hydrochemical Type of Water	Land Use
61	N: 53°9′26.11″ E: 23°31′44.04″	left-side direct tributary of the Supraśl river → stream from Sofipol catchment	valley	rheocrene	HCO_3-Ca	grassland
62	N: 53°9′52.42″ E: 23°31′30.91″	left-side direct tributary of the Supraśl river → Supraśl catchment	valley	rheocrene	HCO_3-Ca	rural area
63	N: 53°10′21.9″ E: 23°31′2.85″	left-side direct tributary of the Supraśl river → Supraśl catchment	hillslope	rheocrene	HCO_3-Ca-Mg	forest
64	N: 53°10′35.29″ E: 23°30′3.76″	left-side direct tributary of the Supraśl river → Supraśl catchment	valley	rheocrene	HCO_3-Ca-Mg	forest
65	N: 53°6′20.46″ E: 23°29′48.26″	Płoska catchment → Świniobródka catchment	valley	rheocrene	HCO_3-Ca	forest
66	N: 53°6′53.57″ E: 23°29′43.86″	Płoska catchment → Świniobródka catchment	valley	rheocrene	HCO_3-Ca-Mg	forest/grassland
67	N: 53°7′13.04″ E: 23°30′34.1″	Płoska catchment → Świniobródka catchment	valley	rheocrene	HCO_3-Mg-Ca	forest/grassland
68	N: 53°6′12.95″ E: 23°24′31.8″	direct tributary of the Płoska river → Płoska catchment	hillslope	helocrene	HCO_3-Ca-Mg	forest/grassland
69	N: 53°9′42.33″ E: 23°27′18.34″	direct tributary of the Płoska river → Płoska catchment	hillslope	rheocrene	HCO_3-Ca-Mg	forest
70	N: 53°9′52.69″ E: 23°21′41.36″	left-side direct tributary of the Supraśl river → Starzynka catchment	valley	rheocrene	HCO_3-Ca-Mg	forest
71	N: 53°9′5.69″ E: 23°18′25.66″	Supraśl catchment → Krasna Rzeczka catchment	hillslope	helocrene	HCO_3-Ca-Mg	forest
72	N: 53°9′13.86″ E: 23°17′26.2″	Supraśl catchment → Krasna Rzeczka catchment	hillslope	rheocrene	HCO_3-Ca-Mg	forest
73	N: 53°9′12.1″ E: 23°17′24.11″	Supraśl catchment → Krasna Rzeczka catchment	hillslope	limnocrene	HCO_3-Ca	forest/FV
74	N: 53°9′29.54″ E: 23°17′42.11″	left-side direct tributary of the Supraśl river → Supraśl catchment	valley	rheocrene	HCO_3-Ca	forest
75	N: 53°9′43.62″ E: 23°17′47.22″	left-side direct tributary of the Supraśl river → Supraśl catchment	hillslope	rheocrene	HCO_3-Ca-Mg	forest
76	N: 53°13′17.37″ E: 23°18′1.96″	left-side direct tributary of the Supraśl river → Supraśl catchment	valley	rheocrene	HCO_3-Ca	forest
77	N: 53°13′13.9″ E: 23°18′5.54″	left-side direct tributary of the Supraśl river → Supraśl catchment	valley	rheocrene	HCO_3-Ca-Mg	forest/grassland
78	N: 53°11′37.9″ E: 23°42′17.62″	Niemen catchment → Nietupa catchment	hillslope	rheocrene	HCO_3-Ca-Mg	forest/grassland/FV
79	N: 53°18′19.94″ E: 23°1′55.69″	Narew catchment → Jaskranka catchment	hillslope	helocrene	HCO_3-Ca-Mg	rural area
80	N: 53°19′12.49″ E: 23°3′23.81″	Narew catchment → Jaskranka catchment	hillslope	rheocrene	HCO_3-Ca	rural area

3. Material and Methods

3.1. Map Analysis and Field Research

The springs in the Puszcza Knyszyńska were researched. More than 200 outflows were cataloged. Outflows from which there was an outflow throughout the year (80 springs) were selected for the research (Figure 3). Water samples were collected in the summer (July/August) at the places of concentrated water outflow from the spring niches. In the field, the yield was measured with gauging weirs. Often, the yield was estimated. The geographic coordinates of the spring niches and the development of the direct catchment in the area were determined. In the fall period of the analysis of the thematic maps, the hydrological and geomorphological locations of the springs, the use of the catchment area, and the hydrobiological types were determined. Based on the land use of the Knyszyn Forest, four types of land use were selected: forest, rural, grassland, and fine-textured vegetation (FV).

3.2. Water Quality Assessment

In the field, using a HQ40D multiparameter probe, the following were examined: water temperature, reaction, electrolytic conductivity of water (EC), oxygen concentration, oxygen saturation (OS), and oxidation reduction potential (ORP). The water samples were collected in polyethylene liter containers for further analysis.

Detailed chemical analyses of the water samples in accordance with ISO standards were carried out in the laboratory of the Department of Environmental Protection in the University of Bialystok. Calcium ions (Ca^{2+}) were determined via titration with disodium EDTA against calcite methods. HCO_3^- ions were determined via titration with hydrochloric acid (HCl) in the presence of an indicator, methyl orange [27]. The remaining water chemical parameters were determined using the spectrophotometric method with a SpectraMax M2, with the application of procedures and reagents by Riedel-de Haen. Sodium (Na^+) and potassium (K^+) ions were determined via flame photometry. The color of water on the Pt scale, concentration of phenols (method with Folin–Ciocalteu's reagent), forms of phosphorus (molybdate method), and forms of iron (method with ortho-phenanthroline) were determined using spectrophotometric methods [27]. Sulfate (SO_4^{2-}) ions were determined using the nephelometric method with barium chloride and chloride (Cl^-)ions using a method with mercury thiocyanate.

Water was filtered through a filter GF/F with a pore diameter of 0.45 µm. Five fractions of phosphorus and iron were analyzed:

- Total (TP, TFe) samples of unfiltered and mineralized water;
- Dissolved (DP, DFe) samples of filtered and mineralized water;
- Reactive (SRP, SRFe) samples of unfiltered and non-mineralized water;
- Particle fractions (PP, PFe) were calculated using the following formulas: PP = TP − DP PFe = TFe − Dfe;
- Dissolved organic fractions (ODP, ODFe) were calculated using the following formulas: ODP = DP − SRP ODFe = DFe − SRFe.

Nitrate nitrogen (NO_3^--N) was determined using the reduction method with N-(1-naphthyl) ethylenediamine, nitrite nitrogen (NO_2^--N) with sulphanilic acid using the chromotropic acid method, and ammonium nitrogen (NH_4^+-N) using the indophenol method. Kjeldahl nitrogen was analyzed with a Tecator 2300 (Kjeldahl analyzer). Mineral nitrogen (TIN) was calculated as the sum of NH_4^+-N, NO_3^--N, and NO_2^--N. Total nitrogen (TN) was calculated as the sum of Kjeldahl nitrogen, nitrites, and nitrates. Dissolved organic carbon concentration (DOC) was determined using a Shimadzu TOC-5050A analyzer with an IR detector [28]. Aromaticity of organic matter (SUVA) was calculated according to the formula: $SUVA = Abs_{\lambda 260} \times 1000/DOC$ [abs 1 cm·1gC^{-1}].

3.3. Statistical Analyses

The statistical calculations were performed with Statgraphics 5.0 for Windows and XLSTAT version 2017.6. The tested waters were classified according to the Alekin and Szczukariew–Prikłoński classifications [29]. These classifications were developed with all-natural waters in mind: atmospheric, surface, and underground. The Alekin classification considers one dominant anion, based on which the water class is determined, and one dominant cation, which determines the group of water distinguished within each class. Individual groups are also divided into types marked with Roman numerals, depending on the ions' relations. Due to the prevalence, the hydrochemical types of water are presented according to the Szczukariew–Prikłoński classification. The class name is made up of the principal ions, with the anion name being given first [29].

Using PHREEQC Interactive 2.15 software, the water analyses results' correctness, the calculations of the ionic compositions of the waters, and the saturation indexes (SI) were assessed. The correctness of a water analysis can be assessed based on the water ion balance. The analysis is correct when the following condition is met:

$$\frac{Kt - An}{Kt + An} \times 100\% \leq 10\%$$

where:

$\mathrm{Kt} = \sum \mathrm{m_i}^{\mathrm{Kt}} \cdot \mathrm{z_i}^{\mathrm{Kt}}$;
$\mathrm{An} = \sum \mathrm{m_j}^{\mathrm{An}} \cdot \mathrm{z_j}^{\mathrm{An}}$;
$\mathrm{m_i}^{\mathrm{Kt}}$—cation concentration [$\mathrm{mol \cdot dm^{-3}}$];
$\mathrm{m_j}^{\mathrm{An}}$—anion concentration [$\mathrm{mol \cdot dm^{-3}}$];
$\mathrm{z_i}^{\mathrm{Kt}}$—valence of cations;
$\mathrm{z_j}^{\mathrm{An}}$—valence of anions.

If the analysis error exceeds 10%, the analysis cannot be used to calculate the ionic composition of the water [30]. Based on the described method of statistical verification, all hydrochemical analyses were performed correctly in the conducted tests. Additionally, the migrations of macronutrients dissolved in the spring waters were determined [31,32]. The spatial analysis of the hydrochemical data was performed with the Surfer computer program.

Several statistical models were used to describe the relationship between the water quality and land use of the catchment area. First, the Kolmogorov–Smirnov test of the normality of the distribution was performed. Most of the variables did not distribute normally, so non-parametric statistical tests were conducted. The Spearman's rank correlation and a redundancy analysis (RDA) were used to describe the water-quality–landscape interactions. A log transformation of exploratory and response variables was used prior to the regression analysis to reduce deviation from normality [33]. A partial RDA was employed to estimate the total variation in water quality data, which can be explained by the four groups of environmental variables, and to partition the influence of each group. The resulting graph of an RDA can express a water sample's physical and chemical compositions and explanatory variables in the same coordinate plane. The length of the arrowhead of the explanatory variable indicates the influence degree of the explanatory variable on the water quality. A longer arrowhead indicates a larger influence. The angle between the explanatory-variable arrow and the water sample's physical-and-chemical-compositions line indicates the correlation between them. When the angle is acute, they are positively correlated, and when it is equal to 90 degrees, there is no correlation.

4. Results

During periods of low water levels in the summer, the efficiencies of the natural groundwater outflows in the Puszcza Knyszyńska most often fluctuated within a range of 0.5–2.0 $\mathrm{dm^3 \cdot s^{-1}}$.

The tested waters, according to the Alekin classification, belonged to the bicarbonate class C and the Ca group of the second type ($\mathrm{r\,HCO_3^- < r\,Ca^{2+} + Mg^{2+} < r\,HCO_3^- + r\,SO_4^{2-}}$) ($\mathrm{C_{II}^{Ca}}$). Most of them were three-ion waters and, less often, double-ion waters. According to the Szczukariew–Prikłoński classification, they were $\mathrm{HCO_3}$-Ca and $\mathrm{HCO_3}$-Ca-Mg types (Table 1). The Piper diagram is a graphic representation of the hydrochemical types of spring water showing the waters' similarities (Figure 7).

The average water temperature in the studied springs in the summer period in 2014–2015 was 14.2 °C. In the complex of the most efficient springs (springs in Pieszczaniki, No. 57–61), the water temperature in the summer was around 9 °C. The springs' water was characterized by a neutral pH (7.81 ± 0.44 pH), good oxygenation (OS 74 ± 74%), and a moderate concentration of dissolved mineral compounds (EC 399 ± 90 $\mathrm{\mu S\ cm^{-1}}$). The redox potential was within wide limits and slightly above 70 mV (Table 2), on average. A clear spatial variation in the water's physical characteristics was noted in the springs of the Puszcza Knyszyńska (Figure 8a–d).

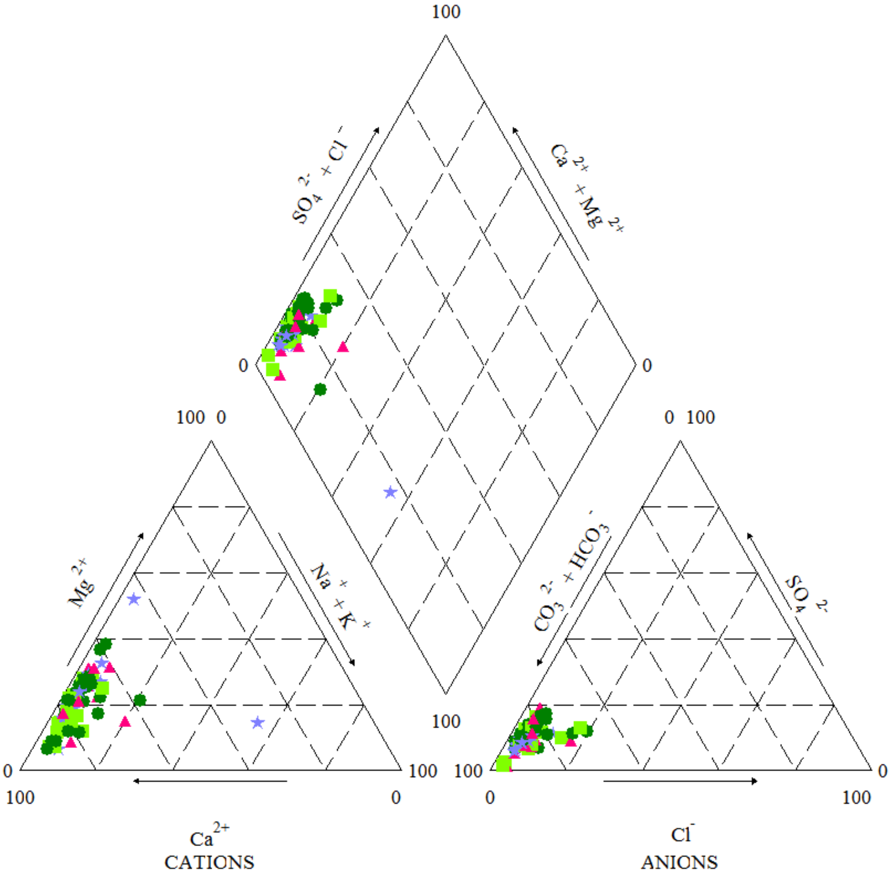

Figure 7. Hydrochemical types of water in springs in the Knyszyn Forest.

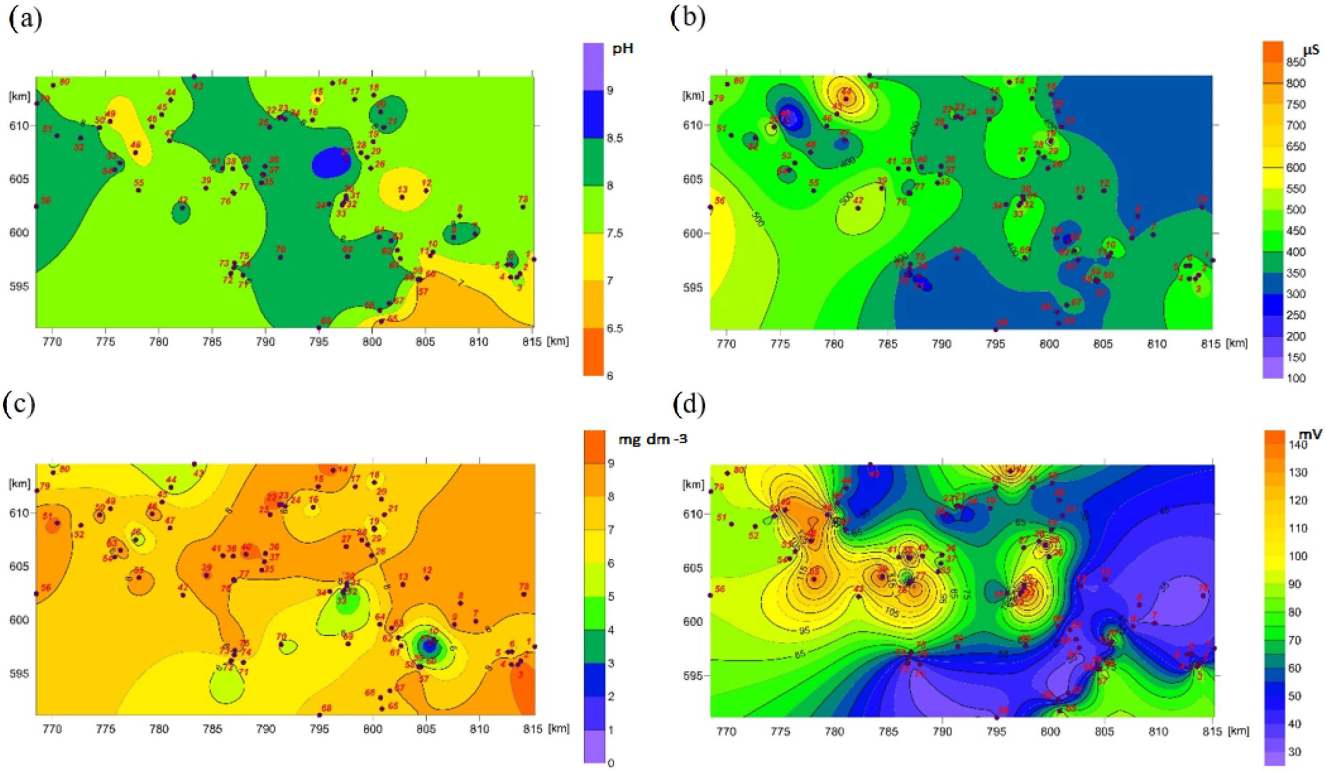

Figure 8. Spatial variability of water's physical properties: (**a**) electrolytic conductivity, (**b**) water reaction, (**c**) dissolved oxygen, and (**d**) oxidation-reduction potential.

Table 2. Statistical summary of the physical and chemical parameters of the Knyszyn Forest springs water.

Parameter		**Mean**	**Min.**	**Max.**	**SD**	**CV**
Water temperature	°C	14.2	9.4	21.2	3.13	22
Reaction	pH	7.81	6.22	9.02	0.44	6
Electrolytic conductivity	$\mu S\ cm^{-1}$	399	153	846	90	23
ORP	mV	73.0	28.3	145.0	34.1	47
Oxygen	$mg\ dm^{-3}$	7.42	1.12	9.74	1.66	22
Oxygen saturation	%	74	10	96	74	23
Water color (Pt)	$mg\ Pt\ dm^{-3}$	14.7	0.1	64.2	14.7	82
Ca^{2+}	$mg\ dm^{-3}$	78.4	43.1	122.6	13.9	18
Mg^{2+}	$mg\ dm^{-3}$	14.4	3.6	35.1	6.2	43
Na^{+}	$mg\ dm^{-3}$	5.2	0.01	31.62	4.36	84
K^{+}	$mg\ dm^{-3}$	1.6	0.01	37.14	4.58	289
HCO_3^{-} (C)	$mg\ dm^{-3}$	53.8	28.7	82.3	9.0	17
SO_4^{2-}	$mg\ dm^{-3}$	27.7	1.6	50.0	8	28
Cl^{-}	$mg\ dm^{-3}$	11.5	5.3	52.6	8.7	76
SiO_3^{2-}	$mg\ dm^{-3}$	2.24	0.5	5.3	1.05	47
TFe	$mg\ dm^{-3}$	1.24	0.09	5.20	1.24	54
DFe	$mg\ dm^{-3}$	0.82	0.04	1.59	0.82	61
PFe	$mg\ dm^{-3}$	0.42	0.002	4.13	0.42	124
SRFe	$mg\ dm^{-3}$	0.15	0.009	0.85	0.16	98
ODFe	$mg\ dm^{-3}$	0.67	0.012	1.53	0.67	74
TN	$mg\ dm^{-3}$	1.86	0.40	18.16	21.6	116
$N\text{-}NH_4^{+}$	$mg\ dm^{-3}$	0.24	0.049	0.939	0.244	55
$N\text{-}NO_3^{-}$	$mg\ dm^{-3}$	0.66	0.052	4.576	0.916	139
$N\text{-}NO_2^{-}$	$mg\ dm^{-3}$	0.002	0.0001	0.009	0.001	71
TP	$mg\ dm^{-3}$	0.17	0.028	1.311	0.16	96
DP	$mg\ dm^{-3}$	0.121	0.017	1.174	0.144	119
PP	$mg\ dm^{-3}$	0.049	0	0.253	0.050	103
SRP	$mg\ dm^{-3}$	0.066	0.013	0.717	0.086	130
DOP	$mg\ dm^{-3}$	0.056	0	0.457	0.056	134
DOC	$mg\ dm^{-3}$	4.16	1.09	16.27	3.32	80
SUVA	$mg\ dm^{-3}$	17.03	1.6	32.8	9.0	53
Phenols	$mg\ dm^{-3}$	0.46	0.13	1.19	0.22	48

Note(s): (ORP–oxidation reduction potential, TFetotal iron, DFedissolved iron, PFeparticle iron, SRFesoluble reactive iron, ODFedissolved organic iron, TN–total nitrogen, TP–total phosphorus, DPdissolved phosphorus, PPparticle phosphorus, SRP–soluble reactive phosphorus, ODPdissolved organic phosphorus, DOCdissolved organic carbon, SUVAaromaticity of organic matter, and CVcoefficient of variation).

The analyses of the chemical compositions of the waters carried out with PHREEQC Interactive 2.15 software showed that in the Puszcza Knyszyńska springs, ionic forms were the basic form of occurrence of dissolved mineral compounds (HCO_3^{-}, Cl^{-}, SO_4^{2-}, NO_3^{-}, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, and Fe^{2+}).

Alkaline earth elements, calcium and magnesium, were also present at small concentrations in the forms of hydrated molecules of sulfates, carbonates, and hydrogen phosphates ($CaHCO_3$, $CaCO_3$, $CaSO_4$, $CaHPO_4$, $MgHCO_3$, $MgCO_3$, $MgSO_4$, and $MgHPO_4$). Sodium and potassium cations were present practically completely in the ionic form. Trace amounts of the hydrated neutral sodium bicarbonate molecule were recorded, but its content in the solutions did not exceed 1%. The mean concentration of calcium slightly exceeded 75 $mg \cdot dm^{-3}$, magnesium 14 $mg \cdot dm^{-3}$, sodium 5 $mg \cdot dm^{-3}$, and potassium 1.5 $mg \cdot dm^{-3}$ (Table 2).

The main forms of bicarbonates in the waters of the Puszcza Knyszyńska springs were the bicarbonate ion and carbon dioxide (HCO_3, CO_2). The average concentration of HCO_3^{-} oscillated around 290 $mg \cdot dm^{-3}$. The average CO_2 concentration in the water, calculated with PHREEQC, was about 400 $\mu mol \cdot dm^{-3}$. Chloride ions appeared only in the anionic form (11.5 ± 8.7 mg·dm^{-3}) and sulfate ions mainly in the anionic form and neutral aqueous complexes of calcium and magnesium sulfates ($CaSO_4$ and $MgSO_4$) (27.7 ± 8.0 mg·dm^{-3}).

The total iron content in the outflow waters ranged on average between 0.09 and 5.20 mg·dm^{-3}. Most iron compounds (65%) were dissolved, with the reactive iron form accounting for 13% and the molecular form accounting for about 30% TFe. The main forms of iron in the waters of the Puszcza Knyszyńska springs were the Fe^{2+}, $FeHCO_3$, and $FeCO_{3.}$

The average values of the saturation indexes (SI) in relation to the minerals in the waters of the Knyszyn Primeval Forest springs are shown in Table 3. Its values range from8.81 to 16.43.

Table 3. Average values of the saturation indexes (SI) in relation to minerals in the waters of the springs of the Knyszyn Forest.

Minerals		**Saturation Index**
Halite	$NaCl$	−8.81
Iron (III) hydroxide, hydrated	$Fe(OH)_3$	1.97
Goethite	$FeOOH$	7.25
Hematite	Fe_2O_3	16.43
Calcite	$CaCO_3$	0.28
Aragonite	$CaCO_3$	0.12
Dolomite	$CaMg(CO_3)_2$	−0.29
Siderite	$Fe\ CO_3$	−0.47
Gypsum	$CaSO_4\ 2H_2O$	−2.01
Anhydrite	$CaSO_4$	−2.27
Jarosite K	$KFe_3(SO_4)_2(OH)_6$	−6.65
Melanterite	$Fe\ SO_4\ 7\ H_2O$	−7.31
Hydroxyapatite	$Ca_5(PO_4)\ 3OH$	−0.07
Vivianite	$Fe_3(PO_4)_2\ 8\ H_2O$	−3.84
Quartz	SiO_2	0.07
Chalcedony	SiO_2	−0.41
Chrysolite	$Mg_3Si_2O_5(OH)_4$	−7.61
Sepiolite	$Mg_2Si_3O_7\ 5OH\ 3\ H_2O$	−5.34
Talc	$Mg_3Si_4O_{10}(OH)_2$	−4.96

Relatively high concentrations of nitrogen and phosphorus compounds were also recorded in the spring waters (Table 2). Nitrogen compounds were practically limited in their occurrence to ionic forms (NO_3^- and NH_4^+). Phosphorus compounds appeared in the form of two ionic forms: mono and dihydrogen phosphates (H_2PO_4, $CaHPO_4$, and $MgHPO_4$). The monohydrogen phosphate ion predominated in the analyzed environment. The statistical analyses showed that in 70% of the samples, the concentrations of mineral and organic forms of these elements exceeded the average values, determining the exceptionally high fertility of the environment. Spatial changes in the concentrations of nitrogen and phosphorus compounds in the Puszcza Knyszyńska were significant (Figure 9a–d).

The average concentration of DOC in the spring waters exceeded 4 mg·dm^{-3}. In some outflows, most often of a marsh nature or located in peat areas, DOC concentrations exceeded several mg·dm^{-3}. The different quality of dissolved organic matter in these outflows is evidenced by the aromaticity of organic matter (SUVA), on average reaching 17 abs.1 cm·1gC^{-1}. Nevertheless, this parameter's variability range is wide: from 1 to 32 abs.1 cm·1gC^{-1}. A large spatial variation in DOC and SUVA was noted (Figure 9e,f). The water color was also highly variable, on average reaching a value of almost 15 mgPt·dm^{-3} (Table 2).

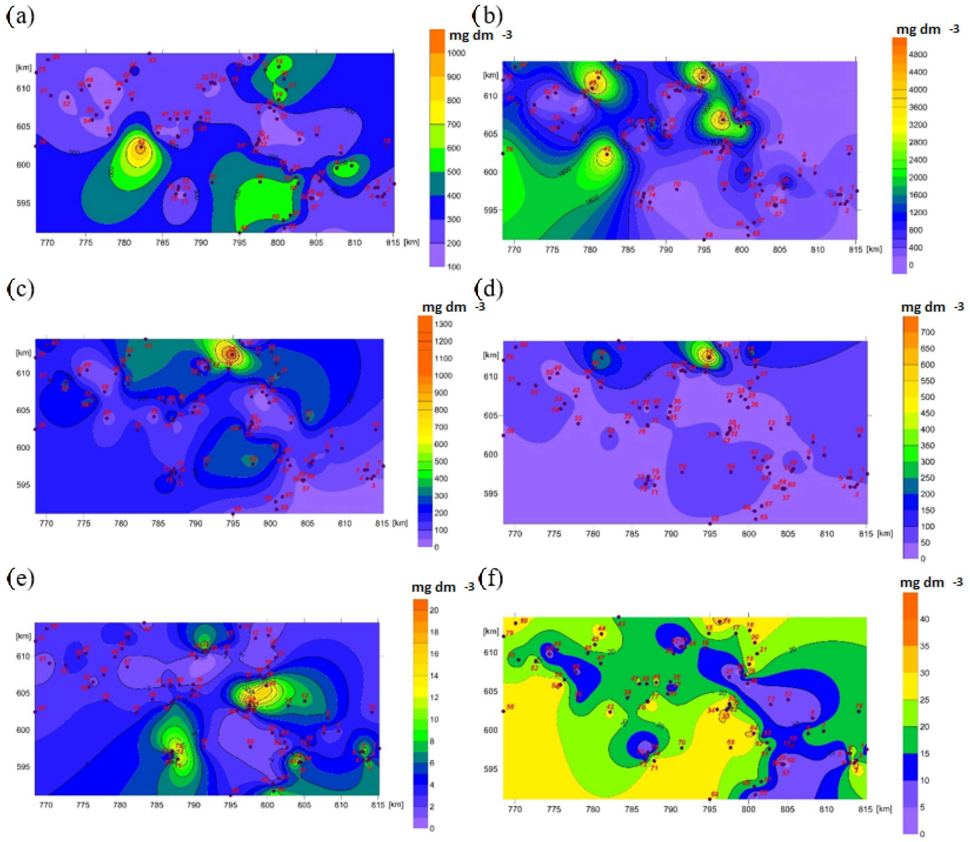

Figure 9. Spatial variability of water chemistry: (**a**) NH_4^+, (**b**) NO_3^-, (**c**) TP, (**d**) SRP, (**e**) DOC, and (**f**) SUVA.

5. Discussion

Springs are a unique resource from an ecological, economic, and cultural perspective [13,34]. Springs occur at the interface between groundwater, surface water, and terrestrial ecosystems, and, as such, they constitute a unique threeway ecotone [13]. Ecotones possess specific physical and chemical attributes, biotic values, and energy and matter exchange processes. They are unique in their interactions with adjacent ecosystems [35,36].

Ecotones often contain significant biodiversity values, including a diverse mixture of cosmopolitan and endemic flora and fauna and a range of ecosystem functions specific to the ecotone [12,26,37]. For this reason, they are often protected [6,35,38]. In many regions of the world, spring water is used as drinking water. It requires monitoring of its quality in terms of hydrochemical and biological features [39–45]. Additionally, in the era of climate change, natural groundwater outflows will serve as hydrological refugia [46–48].

The shallow groundwaters of the Quaternary level and the waters of the North Podlasie Lowland's deeper aquifers and, thus, also those of the Puszcza Knyszyńska, are poorly mineralized waters. They occur under the overburden of glacial tills that are numerous in the lowlands of Poland. All the Polish Lowland's aquifers are dominated by HCO_3Ca twoion or HCO_3CaMg threeion waters [23]. HCO_3CaMg threeion waters dominated in the springs of the Puszcza Knyszyńska—50 springs (Table 1, Figure 4). One of the outflows located in the southern part of the study area (Świniobródka catchment) was characterized by HCO_3MgCa water. The other outflows were HCO_3Ca twoion waters—29 springs. More than half of the threeion waters occurred in anthropogenically transformed areas (28 springs) or their vicinity. This is typical in NorthEastern Poland [4,13,49].

The water of the lowland springs was characterized by oxidative environmental conditions (Eh > 0.15 V).The iron was at higher degrees of oxidation, and was formed as sparingly soluble compounds, observed in the niches as rusty sediment (iron hydroxide), on the sediments lining them and sometimes on the leaves of plants growing on niches.

The range of total iron concentration in the waters of the Puszcza Knyszyńska springs was significant (0.09–5.20 mg dm^{-3}), and the average content of this parameter was even higher than in the water of spring draining formations containing iron ores [50]. The concentration of total iron in the Quaternary layer's waters is often abovenormative [4,13,39,51].

The saturation index shows that minerals containing chlorides, sulphates, and phosphates can dissolve. Compounds of silicates and carbonates are stable in terms of dissolution (Table 3). Iron compounds are precipitated, mainly in their hydrated forms. Their presence is visible in spring niches in the form of a ginger coating on sediments and plants [28].

Springs are sites of sharp environmental gradients, with rapid changes in water chemistry occurring over small spatial scales [12]. For example, the low pH of groundwater is associated with the dissolution of CO_2. As soon as the water rises to the surface, the pH increases as CO_2 is lost into the atmosphere. Oxygenation of reduced groundwaters also occurs rapidly at springheads [52]. The recorded oxygen concentrations in the majority of the natural groundwater outflows in the Puszcza Knyszyńska confirm this thesis. It is also evidenced by the significant positive Spearman's correlation coefficient in the forest areas and negative in the green and rural areas (Table 4).

Table 4. Results of the Spearman's rank correlation analyses of water quality parameters and niche land use type of the Knyszyn Forest.

	Niche Land Use Type			
Parameter	**Forest**	**Grassland**	**Rural Area**	**FV**
Water temperature	0.003	−0.135	**0.255**	−0.009
Reaction	0.125	−0.145	0.042	−0.010
Electrolytic conductivity	**−0.301**	0.081	0.040	**0.276**
Eh	−0.079	0.030	−0.143	**0.161**
Oxygen	**0.272**	**−0.194**	**−0.266**	0.070
Oxygen saturation	**0.212**	**−0.220**	**−0.161**	0.120
Water color	0.030	−0.013	0.070	−0.088
Ca^{2+}	−0.090	−0.019	−0.034	**0.164**
Mg^{2+}	0.003	−0.086	−0.046	0.124
Na^{+}	**−0.306**	0.082	**0.185**	**0.182**
K^{+}	−0.115	0.145	0.082	−0.071
HCO_3^{-}	**−0.188**	−0.101	0.149	**0.255**
SO_4^{2-}	**0.215**	−0.091	−0.068	−0.142
Cl^{-}	**−0.187**	**0.176**	−0.046	0.091
SiO_3^{2-}	−0.090	−0.073	**0.267**	0.015
TFe	−0.145	−0.029	**0.212**	0.053
DFe	−0.133	0.009	**0.227**	0.024
PFe	−0.126	−0.013	0.067	0.065
SRFe	**−0.256**	0.146	**0.216**	0.011
ODFe	−0.068	−0.026	**0.205**	0.005
SRMn	−0.046	−0.125	−0.021	**0.211**
TN	0.016	0.126	−0.051	−0.136
NNH_4^{+}	−0.037	−0.060	**0.286**	−0.070
NNO^{3-}	−0.095	0.081	0.116	−0.011
NNO^{2-}	−0.033	0.056	0.060	−0.049
TP	0.120	**−0.222**	**0.255**	−0.115
DP	0.128	**−0.190**	**0.238**	−0.153
PP	0.039	−0.096	0.130	−0.054
SRP	0.099	−0.046	**0.217**	**−0.264**
DOP	0.086	**−0.279**	**0.157**	0.065
DOC	0.028	**0.184**	**−0.227**	−0.085
SUVA	−0.044	**−0.177**	**0.200**	0.120
Fenols	0.006	0.022	0.013	−0.037

Values in bold are different from 0 with the significance level alpha = 0.05.

Redox conditions induce nitrification and denitrification processes in spring niches [53]. The mineralization of organic debris leads to the release of nitrogen from proteins. The ammonia nitrogen source in the waters is the ammonification process carried out by putrefactive bacteria and fungi, which lasts all year round. The released NH_4^+ ions under aerobic conditions are oxidized into their nitrate form in the nitrification process [54]. The importance of these processes involving bacteria in shaping nitrogen compounds in water was confirmed in the studies by Zieliński et al. [4]. The mean concentration of ammonium nitrogen in the waters varied and the mean content did not exceed 0.24 $mg \cdot dm^{-3}$. Nitrate ions are the most important source of nitrogen for green plants for many reasons. The preferential uptake of nitrate also has a metabolic basis: it is nitrate, not ammonia, that regulates the activity of assimilation enzymes. Plants cannot react to an increased concentration of NH_4^+ with respectively higher enzyme activity and faster nitrogen assimilation [55]. Studies on the distribution of vegetation in spring niches confirm this thesis [12,26]. Relatively high concentrations of total nitrogen were also recorded in the waters of the lowland springs. The statistical analysis showed that in 70% of the samples, its concentration did not exceed 2 $mg \cdot dm^{-3}$. Nevertheless, there were also outflows where the total nitrogen content was much higher, conditioning the environment's exceptionally high fertility. These were mainly outflows located in rural building areas (Figure 8a,b, Figure 10). Natural nitrate levels in groundwater are generally very low, but nitrate concentrations grow due to human activities, such as agriculture, industry, domestic effluents, and emissions from combustion engines [39].

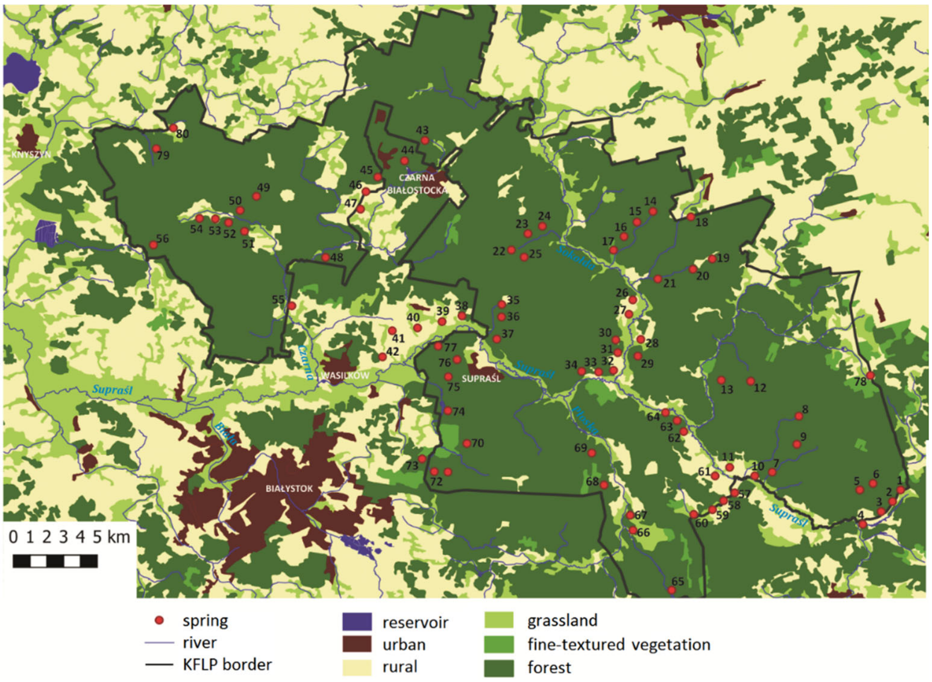

Figure 10. Land use in the Knyszyńska Forest in comparison with the distribution of springs.

When assessing the habitat conditions in spring niches, one should also pay attention to phosphorus compounds in the water. The concentration of SRP in water is largely influenced by plant organisms' uptake, which may lower their concentration in water, mainly in the summer periods. The complexation of this ion by organic substances or iron hydroxides also affects the reduction of SRP content [56]. On the other hand, the enrichment of water with orthophosphoric ions occurs due to the mineralization process of organic matter (which is more intensive in the warm season) and the leaching of this compound from an aquifer. The conversion of trivalent to divalent iron releases considerable amounts of phosphorus previously adsorbed by iron hydroxides. The decrease in the concentration of orthophosphates in the water is favored by humic substances, which bind phosphorus into mineral–organic complexes and sorption on trivalent iron hydroxides. The described processes were very clearly observed in the niches of the wells located in the areas characterized by the catchment area of forest and meadow spots (Tables 4 and 5). In the springs located in rural areas, the concentrations of phosphorus forms were significantly influenced by anthropopressure (Table 4, Figure 8c,d).

Table 5. Percentage of variance accounted for by land use, partitioned by a partial redundancy analysis.

	Variance Component	Explanation [%]
Land Use	Forest	46.5
	Finetextured vegetation (FV)	16.9
	Grassland	25.7
	Rural	10.7
Total explained		68.9
Unexplained		31.1

The location of springs at the interface between groundwater and surface water drives many of their key physicochemical characteristics, including their relative physicochemical constancy. Indeed, the hydrogeological context of a spring strongly influences the flow stability, thermal constancy, and water chemistry [52], and can be seen as the overarching determinant of spring structure and function [35]. In our study, the investigated springs could not be differentiated into distinct classes. Due to the geological and geographical homogeneity of the area investigated in this study, the chemical conditions of the springs were very similar. Only largescale investigations of springs with different geological settings or investigations of acidified springs [48,57,58] show distinct differences in spring water chemistry. Such relationships also occur in mountain areas [59,60].

This study clearly showed the complexity of spring ecosystems in the Puszcza Knyszyńska. In the Puszcza Knyszyńska, there are rheocrenes, helocrenes, and limnocrenes (Table 1). The latter type of springs is extremely rare here, but the accumulation of spring waters by beavers or the housing of outflows causes artificial limnocrenes (Figures 5 and 6). Natural groundwater outflows in the analyzed area are very rarely used for economic purposes, and therefore transformations of the groundwater outflow site to the surface are sporadic here. Helocrene springs usually emerge in a diffuse fashion in cienega (marshy, wet meadow) settings [16]. Rheocrenes usually accompany areas with increased ground leveling [16]. In the Puszcza Knyszyńska, these areas are mainly related to river valleys. The variable rate of water circulation between the types of springs and the impact of the type of outflow on organisms occurring in niches were the reasons for the search for a relationship between the type of outflow and the physical and chemical characteristics in the springs of the Puszcza Knyszyńska [3,61]. The prevailing number of rheocrenes in this area, the small number of helocrenes studied, and the minimal number of limnocrenes (including artificial ones) do not allow for drawing correct regularities between the biological type of outflow and water quality characteristics. Preliminary analyses show the significant fertility of the outflows of helocrenes, expressed by a higher concentration of nutrients. It does not always go together with the presence of different organisms. A correlation between abiotic and macrozoobenthos data showed that physicochemical parameters had little impact on macrozoobenthic composition, whereas specific substrate parameters strongly influenced macrofauna composition [62].

It is not easy to assess the influence of one factor on the quality of spring waters, even in areas where the fissure circulation of groundwater dominates [63]. In NE Poland, a region with a very wellpreserved natural environment, the important determinant of spring water quality is human activity. Most of the analyzed springs were located in forested areas. There were fewer spring niches associated with rural areas and grasslands (Table 1). The analysis of the spatial variability of water physicochemical characteristics shows that values deviating from the mean value were observed mainly in rural areas (Figures 8–11). This is confirmed by the RDA analysis, where natural elements of land use are presented on the left side of the chart, while rural areas occupy the right side (Figure 11). The forest variable is positively correlated with the oxygen content of the water. Meanwhile, the rural variable is positively correlated with higher concentrations of iron forms and ammonia. The results of the partial redundancy analysis show that natural forests and seminatural grasslands have the greatest impact on water chemistry; in total, they explain more than 70% of the variability in water quality characteristics (Table 5).

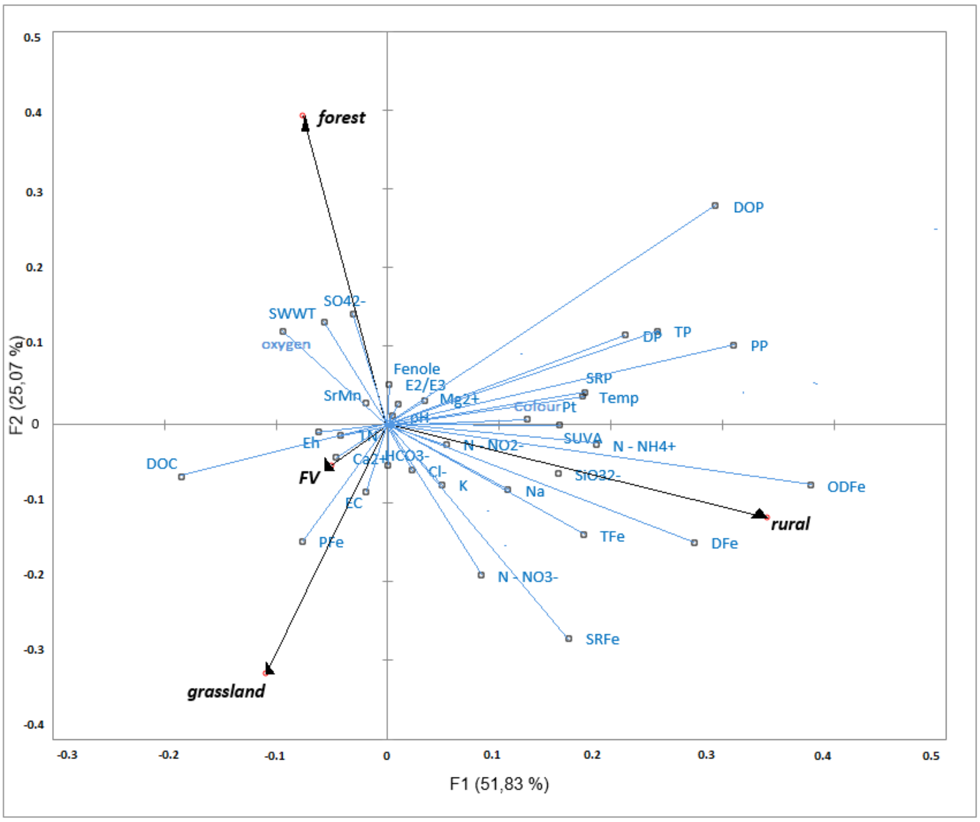

Figure 11. Redundancy analysis (RDA) of water quality parameters and influence factors.

In many forest systems, the near stream, or riparian zone, has control of both the quantity and quality of water DOC [64]. The DOC concentration increases toward the soil surface and results in an increased DOC level in the surface waters [65]. Landscape diversity has a negative impact on water quality, whereas forests and grasslands have a positive impact. Forest complexes promote the "sink" effect on nutrients and control the nutrients' inflow from agricultural sources [66]. Human activity significantly increases water temperature and decreases oxygen concentration [49,67]. Rural areas significantly affect the increased concentrations of sodium, ammonium ions, and iron and phosphorous compounds in spring waters (Table 5). The impact of land use on the quality of shallow groundwater is often observed in the shallow groundwater environment [68–70].

6. Summary

In the Puszcza Knyszyńska (Supraśl catchment) located in the Polish Lowland (North Podlasie Lowland), springs are quite common. In terms of hydrobiology, rheocrenes—55 springs—dominate, and there are fewer helocrenes—21 springs and limnocrenes—4 springs (including two artificially created). The predominant share of rheocrenes results from the varied topography of the Knyszyn Forest (ground level differences reach several dozen meters). During periods of low water levels in the summers of 2014 and 2015, the outflow yields most often fluctuated within a range of 0.5–2.0 $dm^3 \cdot s^{-1}$.

Despite the low efficiencies of the springs, they increase the biodiversity and geodiversity of the area. They also testify to large resources of groundwater.

The studied waters, according to the Alekin classification, belonged to the bicarbonate class C and Ca group, the second type (r HCO_3^- < r Ca^{2+} + Mg^{2+} < r HCO_3^- + r SO_4^{2-}) (C_{II}^{Ca}). They were two or threeion waters (HCO_3Ca and HCO_3CaMg). The hydrochemical types of the spring waters in the Knyszyn Forest were typical for lowland areas. A specific feature of the spring waters was their significant nutrient content (mean value: TN = 1.86 mg dm^{-3}, TP = 0.17 mg dm^{-3}, and DOC = 4.16 mg dm^{-3}). In the spring waters, a high content of total iron (TFe) was also found (average value 1.24 mg dm^{-3}).

The nature of the catchment use exerted the greatest influence on the quality of the spring waters in the Supraśl catchment. The lowest concentrations of chemical parameters of water were found in the forest springs. Larger changes in the chemical composition of water occurred in the outflows located in agricultural land, and the largest in the rural development zone. In springs with a significantly transformed surface catchment, an increase in the concentrations of chlorides, sulfates, sodium, potassium, and nitrate nitrogen and a decrease in the concentration of oxygen dissolved in water were noted. Forest complexes are efficient filters and promote the "sink" effect on nutrients. Anthropogenic activities generally raise water temperature and decrease oxygen concentration. Rural areas may have significantly higher concentrations of sodium, ammonium ions, and iron and phosphorous compounds in spring waters.

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