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Geology and land-use related pattern of spring water quality. Case study from the catchments of the Małopolska Upland (S. Poland)

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ABSTRACT

Spring water chemical composition was investigated in three catchments (i.e. Prądnik, Dłubnia and Szreniawa) located within a monocline made up by the Upper Jurassic and Cretaceous carbonate rocks that constitute voluminous aquifers. The total spring water dissolved solids (TDS) displayed a concentration increase between 1974 and 1999. Using principal component analysis (PCA), the authors identified factors determining spring water chemistry. The research focused on making a distinction between the regional (large-area) and the local factors, the latter being related to the land-use in the direct vicinity of the springs. PCA yielded evidence that local sources of pollution can significantly contribute to the differentiation of spring-water chemical composition.

KEYWORDS | **Hydrogeology. Springs. Groundwater quality. Groundwater pollution. Nitrates.**

INTRODUCTION

Spring water itself and specifically its chemical composition and physical properties reflect the processes going on in the relevant geological environment. Rather than drawn mechanically from water-wells, spring water runs to the surface naturally, thus maintaining its properties developed in the process of the natural circulation in the bedrock environment. Understanding spring water chemistry and physics is particularly important in monitoring research aimed at assessing environmental impact. As a result of human activity the quality of spring water has been undergoing increasing change. Such change can take place on a large, regional scale or on local scale, limited to just the nearest vicinity of the effluent. It is scientifically and practically important to understand the extent of the change to the spring water quality over a period of time (in terms of years) and to identify what has been causing the change (local or regional factors).

This paper aims to identify the role of the local and regional factors having impact onto the chemical composition of spring water at the Małopolska Upland using as case studies catchments of three rivers, i.e. the Prądnik, Dłubnia and the Szreniawa, all running in the southern part of the upland (Fig. 1). This project was triggered by information whereby spring water dissolved solid (TDS) increased in the area over the last 25 years. Thus, the research had to answer the following questions:

- What caused the increased TDS in spring water?; and
- Were these causes of regional or just local nature related to merely local pollution sources?

To assess the rise of spring water concentration, the comparison was made between the TDS values in 1974 and 1999. Principal Component Analysis (PCA) was

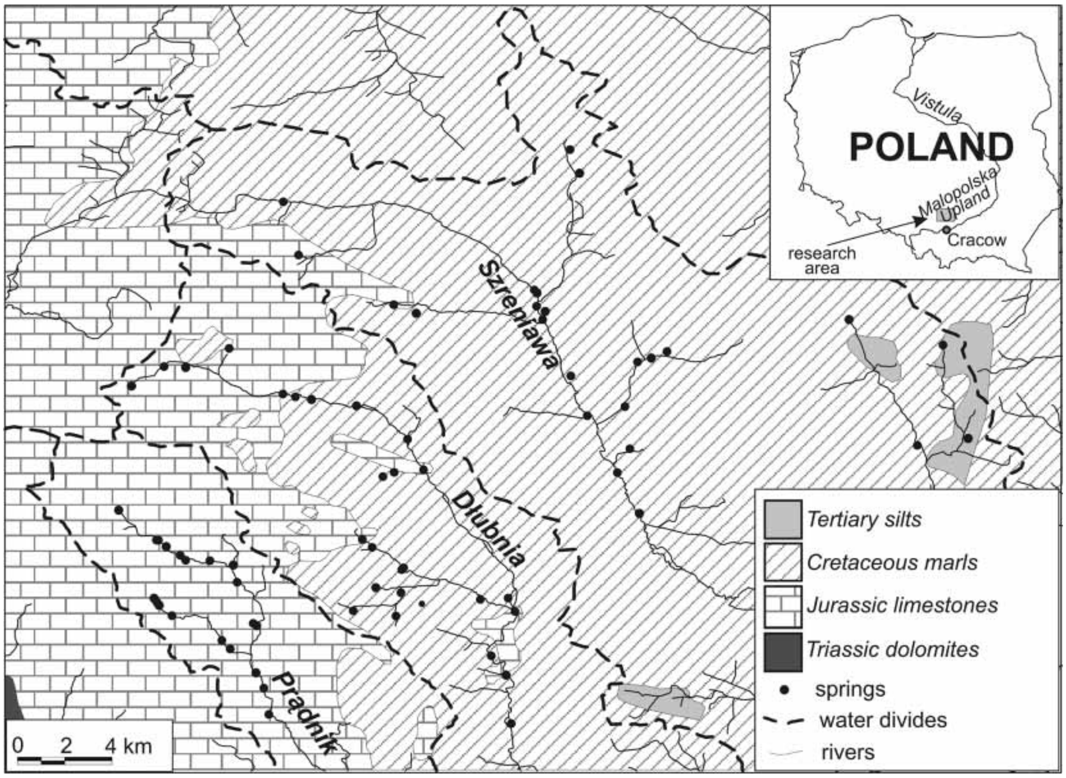

FIGURE 1 | **Geology of the study area.**

applied to identify factors crucial for the spatial pattern in spring water chemistry. Similar approach to spring water hydrochemical interpretations was presented for 243 springs of Reunion by Join et al. (1997). In our study particular attention was paid to the identification of the human influence, whether on a regional or local scale. Chemical composition was compared both between and within the catchment basins. Additionally, the land-use in the immediate vicinity was probed for any relationship with the chemical composition of the spring water.

AREA DESCRIPTION

The Małopolska Upland constitutes a portion of an upland belt in southern Poland. The southern part of the Małopolska Upland consists of a vast monocline dipping towards ENE. In the W and SW, the monocline is built of Triassic dolomites; as the structure continues in the direction of NE, the dolomites are overlaid, in the upland's middle part, by Jurassic limestone and, farther on, the limestone is overlaid by Cretaceous marl and limestone (Fig. 1). The bedrock structures are partly covered by Quaternary loess formations of varied thickness. The Triassic, Jurassic and Cretaceous formations constitute large aquifers.

The Jurassic aquifer consists mainly of Upper Jurassic limestone formed in massive limestone and bedded limestone, up to 230 m in thickness. The rocky outcropping watershed ridges are as high as 400-500 m above sea level and the valleys cut down to 250-300 m. At certain locations, the limestone structure is highly cracked and subject to karst processes. At the watershed ridges, the ground water table may be as deep as 100 m. There are numerous springs of various discharge in the beds of the valleys, typically of the karst gorge type. Most of the springs yield between 1 and 5 litres per second; larger sources are few and far between.

The Cretaceous aquifer is built chiefly of Upper Cretaceous marl, limestone and gaize, gradually growing in thickness from a few dozen metres in the west to 800-1000 m (for the entire Cretaceous formation) in the east. The much-cracked and surface-weathered marls are exposed to rainwater infiltration. At the watershed ridges that reach 350-400 m, the ground water table can be as deep as in excess of 100 m. Just as in the Jurassic aquifer, springs occur in the valleys, but the proportion of springs with discharge of greater than 5 litres per second is higher. Clusters of several high-discharge springs, some exceeding 100 litres per second, are found at fault zones.

The rivers, Prądnik (catchment area: 141 km^2), Dłubnia (286 km^2) and Szreniawa (595 km^2) are all left-side tributaries of the Vistula river. The southwesternmost of the researched rivers, the Prądnik, drains the Upper Jurassic aquifer, while the Szreniawa river at the opposite side of the research area drains the Upper Cretaceous aquifer. The middle catchment of the Dłubnia river is located at the contact of the two aquifers where the Upper Jurassic sediments dip towards the NE under the Cretaceous sediments (Fig. 1).

The area is dominated by farmland (70-80%) and the only continuous forest, the Ojcowski National Park, is found in the Prądnik catchment. However, the mostly small-sized farms (typically a few hectares) are engaged in a rather low-intensity activity with little fertiliser use (90 kg NPK/ha in 2000). Over the last 30 years, the development of rural water supply systems was not matched by the same rate in the development of sewage systems. Hence, the underground waters have been exposed to potential pollution from inadequately insulated individual sewage tanks and wildcat sewage dumping directly into rivers. Other threats include general air pollution from the neighbouring heavy industry located in the Upper Silesia region (coal mining and steel industry), the town of Olkusz (zinc and led mining) and in the city of Cracow (steel sector).

DISSOLVED SOLIDS IN SPRING WATER IN 1974 AND 1999

In 1974, across the Małopolska Upland major features of springs were measured, including springs located within the catchments of the Prądnik, Dłubnia and Szreniawa (Dynowska, 1983). The research was repeated in 1999 (Chełmicki, 2001; Chełmicki and Siwek, 2001). When compared, the total dissolved solids measured in 1999 were always higher than in 1974, whenever values for both years were available (Fig. 2). While the comparison was admittedly based on just a single sample taken in each of the measured source, making the result not entirely representative, the consistently higher value of the dissolved solids in all cases clearly indicated an upward trend. As the measurements taken in 1974 did not include the ion content, the actual components contributing to the increase could not be identified. However, based on the chemical analysis of the spring water performed in 1999 and on systematic studies conducted during 2000-2001 (Siwek, 2002), an attempt can be made at identifying the human-contribution to the development of spring water chemical pattern.

GENERAL CHEMICAL PATTERN OF SPRING WATER

During 2000-2001, a focused research project covered 74 springs in the three river catchments (the Prądnik, Dłubnia and Szreniawa). The chemical composition was sampled in either one-month intervals (22 springs) or three-month intervals (52 springs).

During the period, the spring water TDS typically fell within the range of 200-500 mg/dm^3 (90% of samples), with the maximum-recorded value of 677 mg/dm^3. The highest TDS and macro-element concentrations were measured in the springs fed by the Upper Cretaceous aquifer (the Szreniawa catchment), while the lowest values came from the Jurassic aquifer (the Prądnik catchment) (Table 1). Typically, the samples revealed two-ion-type water of the HCO_3-Ca type (Fig. 3). Only some of the springs in the Szreniawa and Dłubnia catchments periodically changed their hydro-chemical type into the HCO_3-Ca-Mg or SO_4-HCO_3-Ca types.

The dissolved nitrogen occurred in the spring water practically only in the form of nitrates. Nitrate concentration ranged from 1.7 to 60.6 mg NO_3^-/dm^3. As a result of good oxygen saturation of the karst water and water in

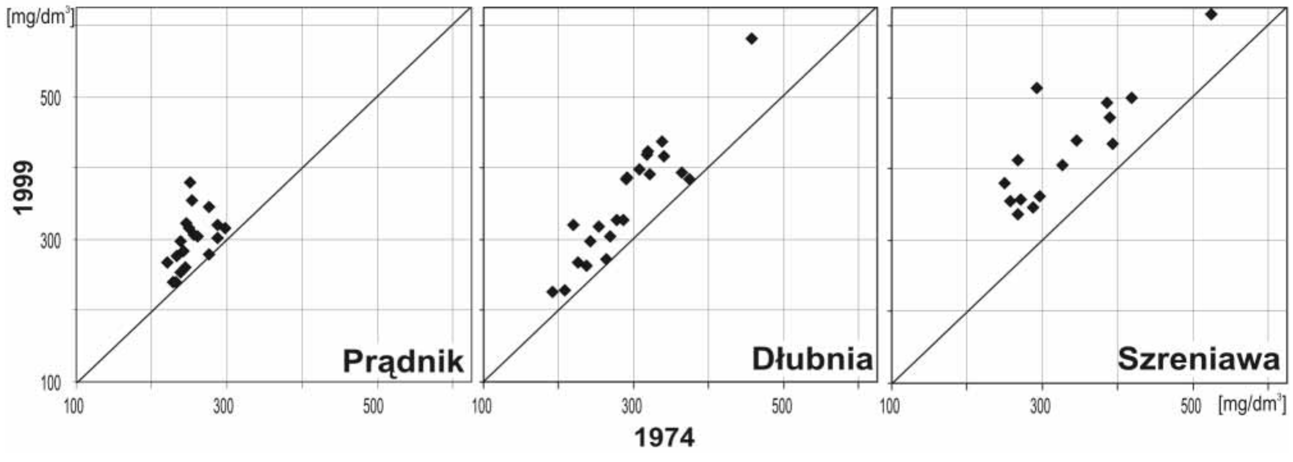

FIGURE 2 **Comparison of spring water TDS in 1974 and 1999. Each diamond represents one spring.**

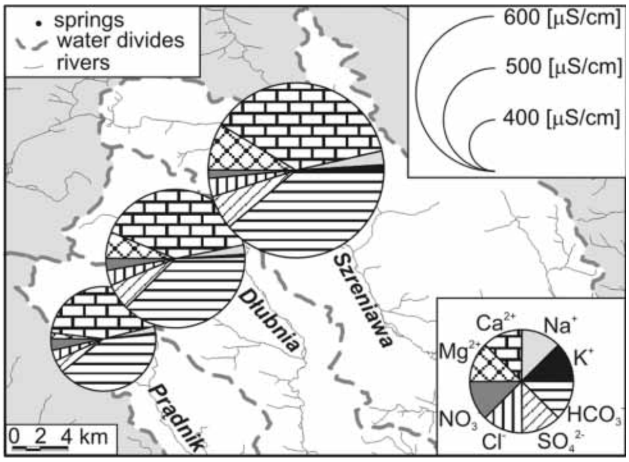

FIGURE 3 **The mean chemical composition of spring water in the catchments of Prądnik, Dłubnia and Szreniawa.**

cracks, the NH_4-N and NO_2-N forms of nitrogen only occurred in trace quantities. In contrary to major ions, the highest contents of nitrates featured in the springs located in the Prądnik catchment and the lowest in the Szreniawa catchment (Fig. 4A and Table 1). Compared to the Cretaceous aquifer, almost all springs fed from the Jurassic aquifer featured higher nitrate contents. This would indicate that the quality of the Jurassic spring water had deteriorated as a result of the aquifer-wide pollution. In the Prądnik catchment basin, the highest concentrations of nitrates were measured in its upper reaches where the population density was at its highest. This provides evidence that not just the large-area regional pollution, but also local factors cause spring water quality deterioration.

Orthophosphate concentration ranged typically from 0.1 to 0.2 mg/dm^3. Just as with the nitrates, the lowest concentrations of PO_4^{3-} were measured in the springs of the Szreniawa catchment (Fig. 4B and Table 1). The highest concentrations (up to 0.52 mg/dm^3) were found in the Dłubnia catchment springs. Little variation in the phosphate concentration from one spring to another was found in the Prądnik and the Szreniawa catchments. In contrast, the Dłubnia catchment featured springs with either high or low phosphate contents, often close together. In comparison to nitrates, the spatial pattern of phosphate contents displayed less regularity.

LOCAL AND REGIONAL SOURCES OF POLLUTION IN THE LIGHT OF A STATISTICAL ANALYSIS

The method of Principal Component Analysis (PCA) was applied to identify the key factors deciding the variation of chemical composition in spring water. PCA involving 11 physical and chemical parameters was conducted on all springs under research leading to the identification of three main factors together explaining 84% of the population variance (Table 2).

TABLE 1 **The mean values of spring water chemical composition in the catchments of Prądnik (PR), Dłubnia (DL) and Szreniawa (SZ).**

Variable		PR	DL	SZ
Number of observations		156	189	185
SEC	[µS/cm]	503	569	639
TDS	[mg/dm^3]	292	361	421
Mg^{2+}	[mg/dm^3]	2.1	8.9	14.3
Ca^{2+}	[mg/dm^3]	86.4	97.4	103.8
Na^+	[mg/dm^3]	4.7	5.9	8.1
K^+	[mg/dm^3]	2.0	2.5	5.3
HCO_3^-	[mg/dm^3]	239.8	275.4	322.3
SO_4^{2-}	[mg/dm^3]	17.8	35.1	40.8
Cl^-	[mg/dm^3]	11.4	15.1	16.7
NO_3^-	[mg/dm^3]	21.8	20.6	13.2
PO_4^{3-}	[mg/dm^3]	0.17	0.15	0.08

The main factor (F1) involved specific electrical conductance (SEC), TDS and all major ions, as evidenced by the highest absolute values of the factor loads. This explained 57% of variance and reflected the diversity of the investigated set so far, as the concentration of the principal major components. The variation was caused by the hydrogeological diversity of the research area. The second of the factors (F2) explained 17% of the variance and was related to NO_3^- and PO_4^{3-} and, to a lesser extent, to Cl^-. This means that the factor was strictly related to the human impact. Combined, the first and second factor split the investigated set of springs along the lines of hydrography into the catchment basins (Fig. 5A), and along the lines of hydrogeology into the main aquifers. In other words, the natural and human-induced factors shaping the chemical composition of spring water had a different degree of impact on each of the three catchments. The hydrogeological diversity of the area was crucial for the processes influencing the groundwater chemical composition and, because of the different susceptibility of the aquifers to pollution, the key to the effect of the human influence.

Local sources of pollution account for a considerable share of the Jurassic spring water pollutants in the Prądnik catchment. PCA identified two factors, together explaining 80% of the variance (Table 3). Factor $F_{PR}1$ was related to the human impact crucially important for the increase of each of SEC, TDS and concentrations of Na^+, K^+, SO_4^{2-}, Cl^-, NO_3^- and PO_4^{3-}. The factor clearly differentiated the springs according to the type of land-use in the near vicinity of the effluent (Fig. 5B), which would suggest a relationship between the diversity of spring-water

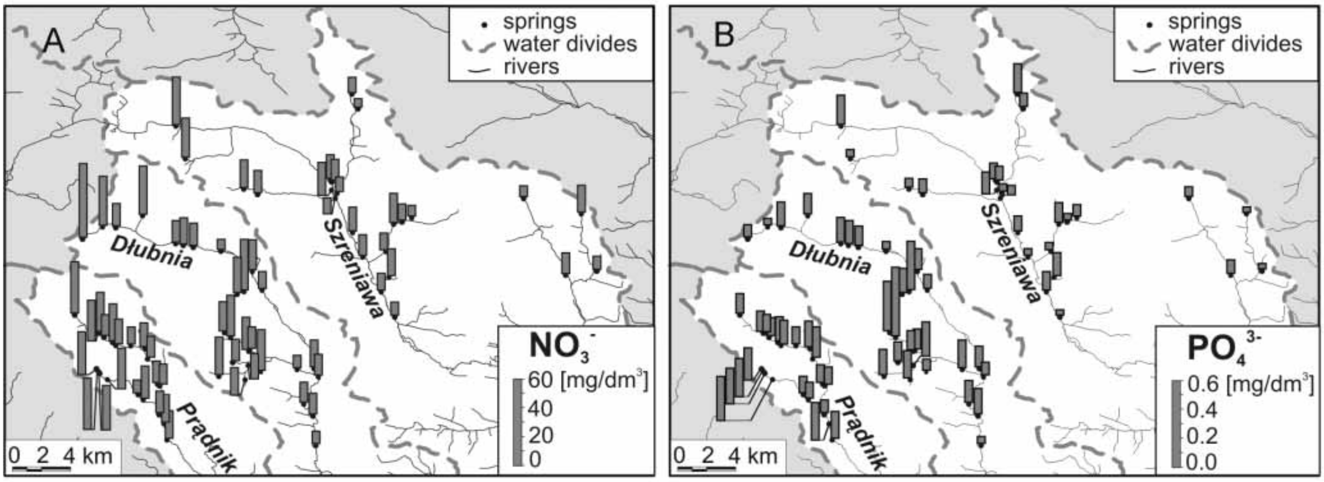

FIGURE 4 | **The mean values concentration in spring water. A) Nitrate. B) Phosphate.**

chemical composition in the Prądnik catchment and the local pollution sources. The second of the identified factors ($F_{PR}2$) explained 20% of the variance and displayed the strongest relationship with the ions of HCO_3^-, Ca_2^+ and with TDS, thus reflecting the natural processes influencing the Jurassic aquifer chemical composition. A weak relationship was also found between this factor and the seasonality, and specifically with the changing conditions of the water supply to the aquifer.

Three factors were identified for the population of springs in the Dłubnia catchment, together explaining 82% of the variation (Table 3). Just as in the Prądnik catchment, the main factor ($F_{DL}1$) was linked both with those ions, which originated as a result of natural processes, and with those whose presence was normally regarded as evidence of a human influence. The large negative values of the factor were typical for the springs located near farm buildings (Fig. 6A), indicating that the variation of chemical composition in the investigated springs was largely a result of pollution from local sources. The factor, however, did not differentiate springs between forest and farmland sites. Mainly linked to Mg^{2+} and HCO_3^-, factor $F_{DL}2$ reflected a split between the feeding aquifer. Indeed, the highest concentration of magnesium and carbonates featured in the springs fed from the Cretaceous aquifer, which in turn was typified by lower nitrate content than the Jurassic aquifer. The third identified factor ($F_{DL}3$), with low eigenvalue (see Table 3), characterised the variation of the set by the phosphate content. While this variation was not linked to the land-use in the near vicinity of the spring, all springs with littered niches featured large (negative) values of the factor.

TABLE 2 | **Factor loadings matrix of PCA of the chemical composition of spring water.**

Variable	**F_1**	**F_2**	**F_3**
SEC	**-0.93**	0.11	0.06
TDS	**-0.94**	0.00	-0.12
Mg^{2+}	**-0.72**	-0.43	0.12
Ca^{2+}	**-0.74**	-0.05	**-0.64**
Na^+	**-0.87**	0.14	0.31
K^+	**-0.71**	-0.39	**-0.55**
HCO_3^-	**-0.71**	-0.39	**-0.55**
SO_4^{2-}	**-0.85**	0.20	0.15
Cl^-	**-0.81**	0.45	0.11
NO_3^-	-0.08	**0.89**	0.14
PO_4^{3-}	0.34	**0.69**	0.29
% variation explained	57	17	10

(Factor loadings with value greater than 0.5 are marked out)

No impact of immediate-vicinity land-use on spring-water chemical composition was confirmed in the Szreniawa catchment. PCA identified three factors, which between themselves explained 79% of the variation (Table 3) in the spring-water chemical composition. The main factor ($F_{SZ}1$) explained 51% of the variation and was linked with the physical and chemical features shaped mainly under the influence of natural processes. It reflected the variation of the chemical contents in spring water related to the local lithology of the Cretaceous formations and to the supply from various ground water depths. The second factor ($F_{SZ}2$) reflected the variation of the set by the concentration of NO_3^-, Cl^- and PO_4^{3-} and, in reverse relationship of Mg^{2+}. While the positive values of the factor could account for the human impact, no relationship to the local pollution sources was found (Fig. 6B). This fac-

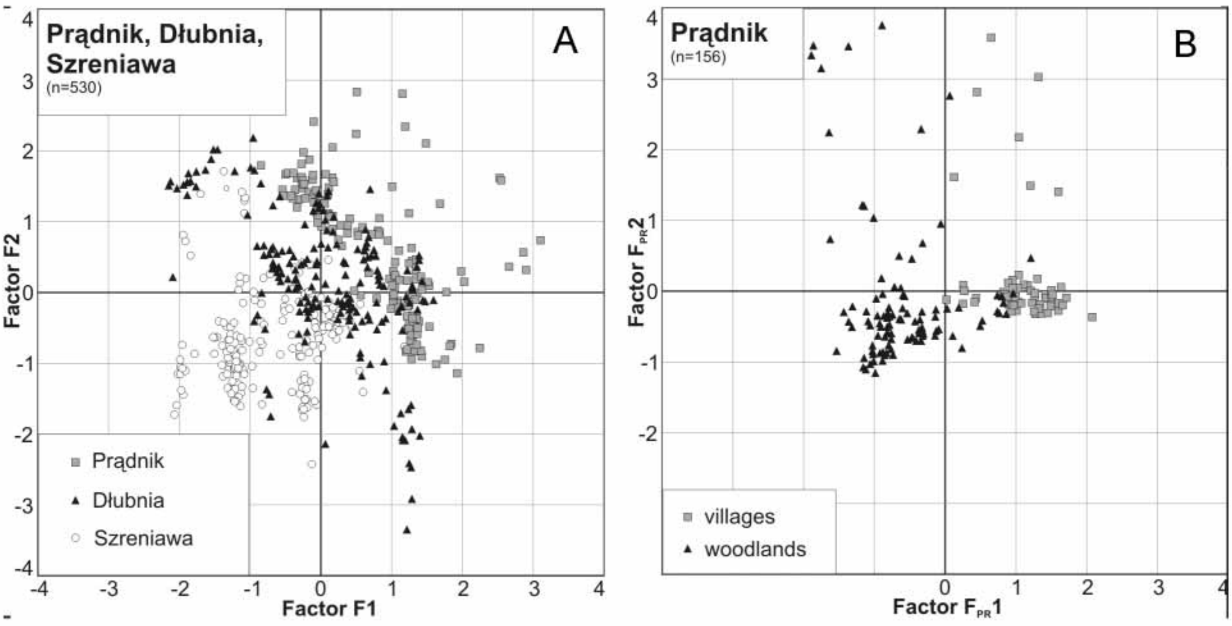

FIGURE 5 | **Factor scores of PCA. A) In relation to division into catchments. B) In relation to land-use in the spring vicinity in the catchment of Prądnik.**

tor played its greatest role in springs fed from the Jurassic limestone and marl rocks in the Jurassic western area of the catchment. In turn, springs fed from marl showed higher contents of magnesium and lesser impact of the factor causing increased concentrations of NO_3^-, Cl^- and PO_4^{3-}.

The PCA results were confirmed by a comparative analysis of the average values of physical and chemical parameters depending on the land-use in the near vicinity of the spring (Fig. 7). In the Prądnik catchment, springs located within villages featured higher concentrations of PO_4^{3-} and NO^{3-} than springs located in forests. This relationship was also recorded in relation to other major elements, except for Ca^{2+} and HCO_3^-. There was less immediate land-use related variation in the ground water chemical composition in farmland and near farm buildings.

TABLE 3 | **Factor loadings matrixes of PCA of the chemical composition of spring water in the catchments of Prądnik, Dłubnia and Szreniawa.**

Variables	**Prądnik**		**Dłubnia**			**Szreniawa**		
	F$_{PR}$1	**F$_{PR}$2**	**F$_{DL}$1**	**F$_{DL}$2**	**F$_{DL}$3**	**F$_{SZ}$1**	**F$_{SZ}$2**	**F$_{SZ}$3**
SEC	**0.92**	0.15	**-0.97**	-0.12	0.06	**-0.92**	0.22	-0.02
TDS	**0.73**	**-0.57**	**-0.95**	0.00	0.07	**-0.92**	0.16	0.02
Mg^{2+}	**0.67**	0.05	-0.46	**-0.74**	-0.02	**-0.51**	**-0.52**	-0.09
Ca^{2+}	0.44	**-0.88**	**-0.81**	-0.10	-0.25	**-0.70**	0.46	-0.49
Na^+	**0.95**	0.13	**-0.87**	0.12	0.17	**-0.85**	-0.34	0.20
K^+	**0.92**	0.13	**-0.79**	-0.06	0.01	**-0.80**	-0.31	0.23
HCO_3^-	0.26	**-0.95**	**-0.62**	**-0.64**	-0.36	**-0.67**	0.14	**-0.68**
SO_4^{2-}	**0.85**	0.08	**-0.81**	0.29	0.30	**-0.86**	0.10	0.24
Cl^-	**0.93**	0.17	**-0.90**	0.28	0.01	**-0.61**	**0.50**	0.43
NO_3^-	**0.84**	0.25	**-0.72**	**0.50**	-0.04	0.18	**0.76**	0.34
PO_4^{3-}	**0.71**	0.26	-0.08	0.42	**-0.84**	0.45	0.49	-0.18
% variation explained	60	20	59	14	9	51	17	11

(Factor loadings with value equal or greater than 0.5 are marked out)

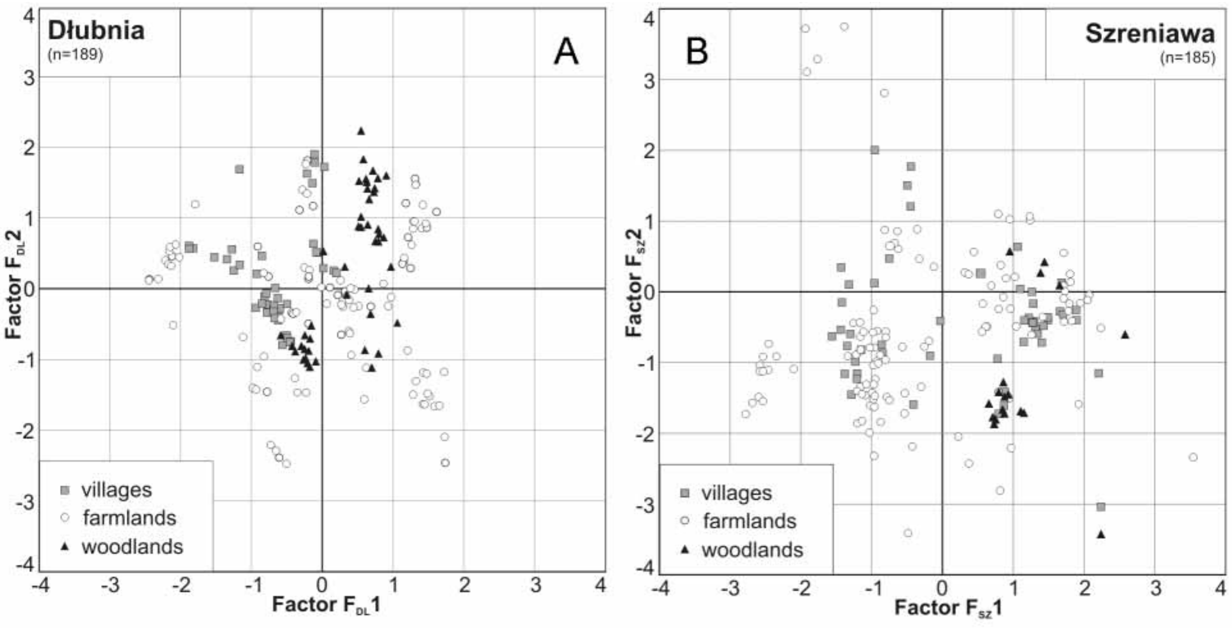

FIGURE 6 **Factor scores of PCA in relation to land-use. A) In the spring vicinity in the catchment of Dlubnia. B) In the spring vicinity in the catchment of Szreniawa.**

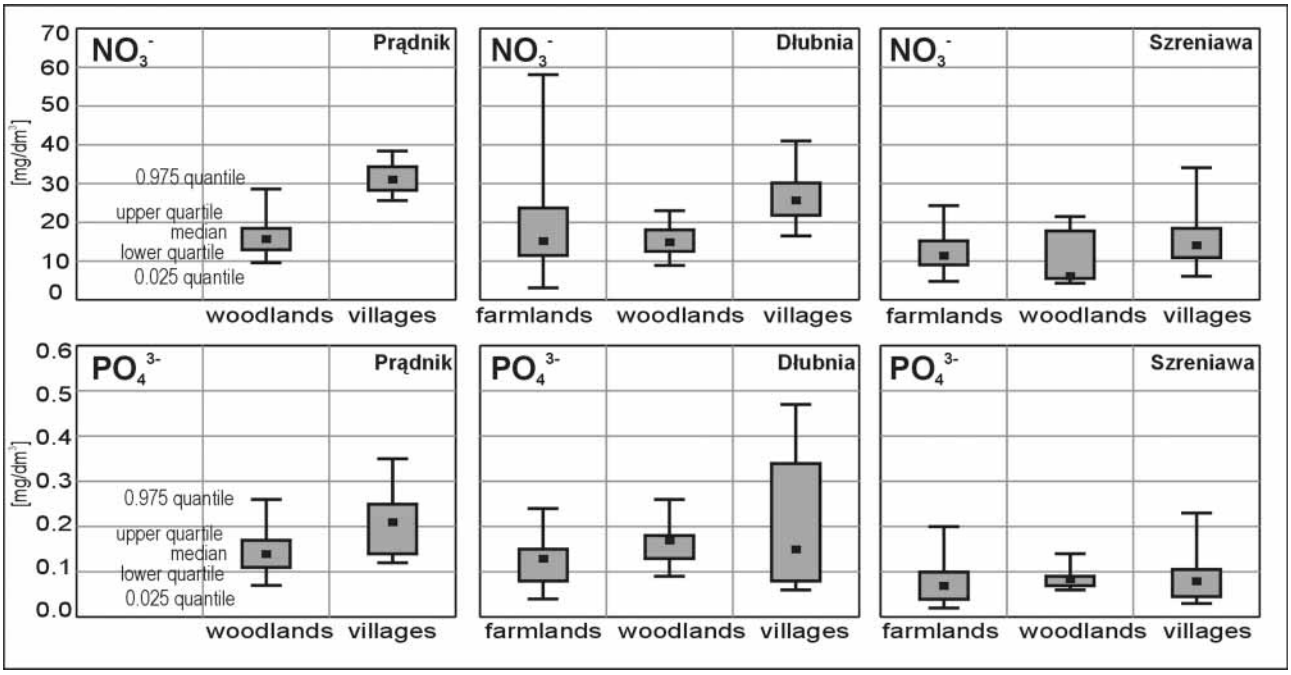

FIGURE 7 **Nitrate and phosphate concentrations in relation to land-use in the spring vicinity.**

CONCLUSIONS

The comparative research into spring water quality at the Małopolska Upland taking into account data from 1974 and 1999 indicated a considerable increase in dissolved solids (average by ca. 30%) as a result of human activity, i.e. the supply of pollutants from large-area sources. The Jurassic aquifer characterised by karst processes displayed a particular susceptibility to water pollution. Springs fed from this aquifer were characterised by higher nitrate contents, with concentrations up to 60 mg NO_3/dm^3, as compared to the standard border value for potable water of 50 mg NO_3/dm^3. Springs fed from the Cretaceous aquifer featured lower nitrate contents, thanks to its lower vulnerability.

Results of the PCA indicated that the local pollution sources tended to play a considerable role in the spatial variation of spring water chemical composition. In the Jurassic part of the area, springs located within villages were particularly exposed to this stream of pollution. Local pollution was caused by the faster rates of development of rural water supply systems than those of the sewage systems. In relevant areas, household sewage tends to be collected in individual sewage tanks often leaking the content into the ground water. In the Cretaceous part of the research area, the impact of the settlement on spring-water quality is much less pronounced. The lower vulnerability of the Cretaceous aquifer and the supply of springs from deeper water circulation levels through systems of cracks and crevices contribute to the sustained high quality of spring water fed from this aquifer.

In view of the low rates of fertiliser application, the agricultural use of the immediate spring vicinity has not shown any clear impact on the quality of spring water. This, however, is not to suggest that a considerable role in the supply of pollutants to the ground water by farming should be excluded, but such pollution would be of a rather dispersed and large-area type having impact on the ground water chemical composition across the entire recharge area.

While the research has confirmed a material influence of human activity on spring-water quality, most of the springs in the research area still supply high quality water and continue to be precious objects of nature that deserve protection.

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