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Natural and anthropogenic factors controlling spring water quality in the southern part of the Małopolska Upland (southern Poland)

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Abstract A combination of mapping and principle components analysis were used to evaluate the factors controlling the hydrochemical composition of springs. From April to June 1999, 103 springs were sampled. Twenty to thirty springs were located in each of four farmland catchments (140–560 km^2) that represent a change in bedrock geology across the study area in southern Poland. The base cations and bicarbonate concentrations, products of weathering, increase towards the northeast consistent with a change in the underlying bedrock geology from Triassic dolomites to Jurassic limestones and Cretaceous marls. In contrast, the spatial distributions of NO_3 and PO_4 concentrations are more random with respect to the bedrock geology and are more closely associated with the distribution of farmland.

Key words groundwater quality; nitrate contamination; southern Poland; springs

INTRODUCTION

Groundwater contamination in farming areas originates from many different sources. Karst and densely fissured aquifers are particularly vulnerable to contamination caused by fertilizer application, animal-feeding operations, leaching of solid wastes at sanitary landfills, and leakage from household waste-disposal systems.

The objectives of this paper are to explain differences in the chemical composition of spring water in four catchments having similar land use (farm land) and characterized by different geology (Triassic dolomites, Jurassic limestones and Cretaceous marls), and to determine the spatial extent of the sources of contamination, i.e. widespread (connected with farming and fertilizing), or local (connected with waste disposal and poorly operated septic tanks). The catchments are in the southern part of the Małopolska Upland. They are drained by the north bank tributaries of the Rudawa (RU), and the Prądnik (PR), Dłubnia (DL), and Szreniawa (SZ). Each of these streams is a tributary to the River Vistula (Fig. 1 and Table 1).

There are several reasons for interest in the groundwater quality in the region. Recent extensive economic transformation of the area may result in a substantial change in farming practices including increased fertilizer use that may cause groundwater degradation. Because the landscape in the region is attractive, tourism and associated development has increased, e.g. the increasing number of country cottages and summerhouses. Concurrently, domestic and community-based sewage disposal systems are not regulated and many are in disrepair resulting in leaking septic tanks and leakage from animal waste disposal sites.

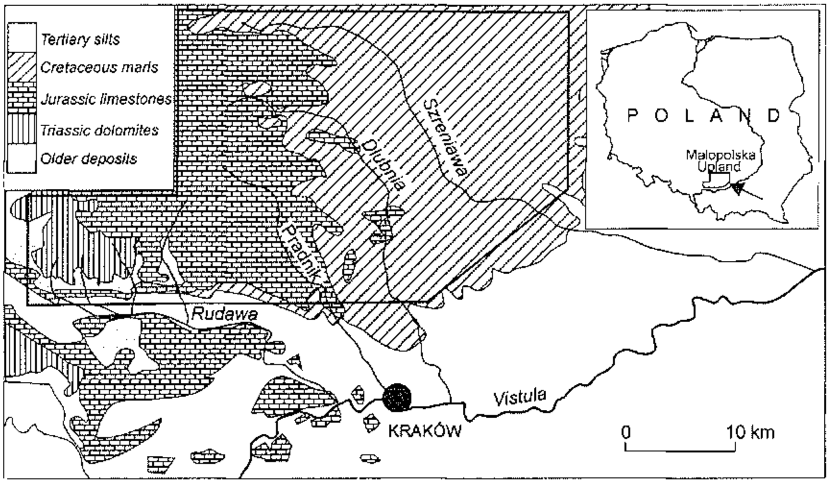

Fig. 1 Location and geology of the study area.

Table 1 Catchment characteristics.

Catchment name	Rudawa	Prądnik	Dłubnia	Szreniawa
Area under research (km^2)	247	140	190	564
Dominant bedrock	1 & 2	2	2 & 3	3
Forests (%)	13	16	9	7
Number of springs examined	30	21	27	25

1 Triassic dolomites; 2 Jurassic limestones; 3 Cretaceous marls.

Farming areas dominate the region (70–80% of the area) with arable lands dominating (80–90%) the farmland. Fertilizer application has decreased since the 1970s, from about 190 kg NPK ha^{-1} in 1970–1980, to 90 kg NPK ha^{-1} in 1999. Dispersed and small patches of forests cover only 7–16% of the total area. The largest forest complex, a National Park, covers part of the valley of the Prądnik stream.

GEOLOGY, GROUNDWATER AND SPRINGS

The area is underlain by Triassic dolomites, Jurassic limestones, and Cretaceous marls. The bedrock has a monoclinal structure gently sloping toward the northeast. Triassic strata outcrop only on the western edge of the area, Jurassic in the central part, and Cretaceous in the northeastern part (see Fig. 1). The area is faulted, which in part controls the karst (Jurassic limestones). The dense fissures and cracks (Cretaceous marls) facilitate local contacts between water-bearing units. The carbonate rocks are locally covered with loess deposits of variable thickness: thinner in the southeast (Rudawa) and thicker in the northeast (Szreniawa). Tertiary silts occur in the southern part of the area and fill tectonic depressions. The Tertiary silts and older Permian deposits do not form important water-bearing units.

The maximum elevations of the upland, flattened hilltop areas are 400–500 m a.s.l. The valleys, parts of which are typical karst gorges up to 100 m deep, dissect the area.

The depth to the groundwater table is more than 100 m at upland sites, and less in the valley bottom as evidenced by the presence of numerous springs.

Groundwater moves generally towards the northeast, but locally groundwater flow direction is modified by the drainage network and springs. In the southwestern part of the region near Rudawa and Prądnik, many small springs dominate with discharges rarely exceeding 10 l s^{-1}, whereas in the northeastern part near Dłubnia and Szreniawa, the springs have higher discharges, which in several cases exceed 100 l s^{-1}.

In the 1960s and 1970s the springs in the region were investigated by Dynowska (1964, 1983) and Dynowski & Zbadyńska (1974). The main characteristics of the spring water chemistry were described (TDS (total dissolved solids), hardness, electrical conductance and major ion concentrations). In these earlier studies, concentrations of NO_3^- and PO_4^{3-}, which typically reflect contamination by agricultural sources, were not examined. In the 1990s, Różkowski (1993, 1996) reported elevated groundwater NO_3^- concentrations at some locations in the area. From 1986 to 1996, Tyc & Opołka (1999) reported increasing NO_3^- concentrations in the springs situated northwest of Rudawa.

METHODS

From April to June 1999, 103 springs were sampled, of which between 20 and 30 were sampled from each of four catchments. The samples were analysed for TDS, HCO_3^-, NO_3^-, PO_4^{3-}, Cl^-, SO_4^{2-}, K^+, Ca^{2+}, Na^+ and Mg^{2+}. Spring water composition was summarized for each of the catchments (mean, minimum, maximum and standard deviation). The concentrations were positively skewed for most constituents and were subsequently log transformed and normalized. A principal component analysis (PCA) was used to identify independent factors explaining ion concentration for each of the four catchments. The principal components with eigen values greater than one were retained. To recognize the degree of similarity of particular water chemistry variables, Ward's method based on Euclidean distances was applied (Ward, 1963).

RESULTS

The TDS of spring water ranged from 220 to 625 mg l^{-1} with generally lower concentrations in the Triassic dolomites and Jurassic limestones (mean: 324 mg l^{-1}) and higher concentrations in the Cretaceous marls (mean: 398 mg l^{-1}). The higher TDS concentrations in the marls reflect the change in geology. The less monolithic, thin-bedded, densely fissured and cracked marls are more easily weathered than the limestones. A gradual change in the bedrock from the southwest (Rudawa), across the middle (Prądnik and Dłubnia) to the northeast (Szreniawa), is reflected by a general increase in HCO_3^-, Cl^-, Ca^{2+}, Na^+, and K^+ concentrations attributed to bedrock weathering (Fig. 2). In contrast, NO_3^- and PO_4^{3-} concentrations vary spatially reflecting transmission of ions of anthropogenic origin.

Concentrations of NO_3^- are usually considered one of the best indicators of pollution in farming areas. Typical background NO_3^- concentrations are less than 4 mg l^{-1}. NO_3^- concentrations exceeding the drinking water-quality standard of 50 mg NO_3^- l^{-1} were

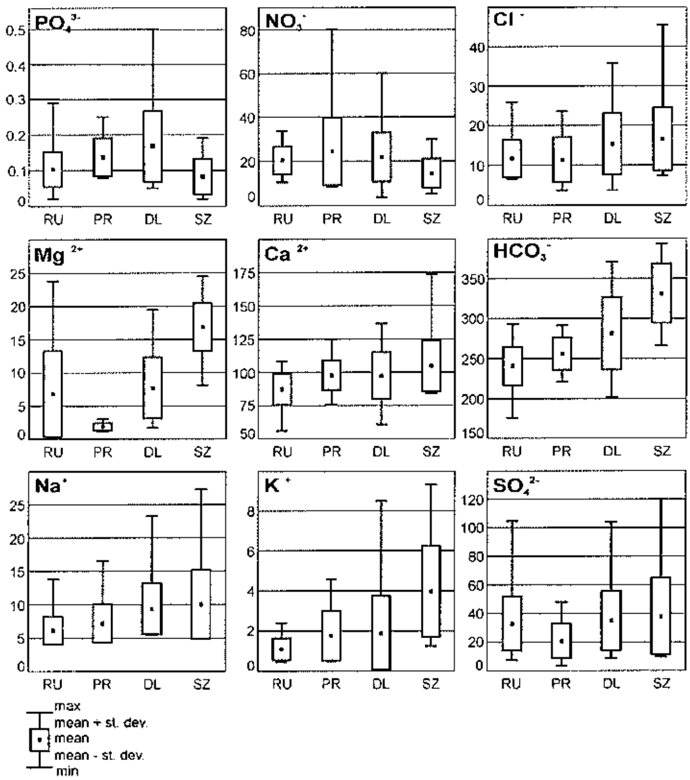

Fig. 2 Box plots of hydrochemical variables (mg l^{-1}) for the Rudawa (RU), Prądnik (PR), Dłubnia (DL), and Szreniawa (SZ) catchments.

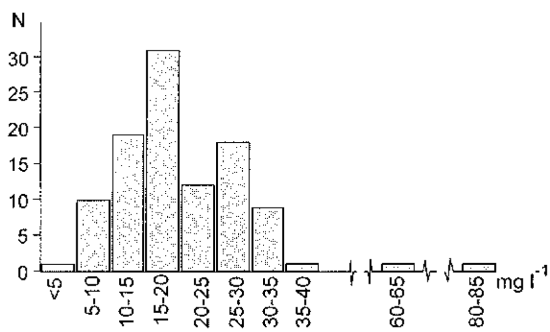

Fig. 3 Frequency distribution of NO_3^- concentrations in the spring water of four catchments in southern Poland.

found only in two springs (Fig. 3): in Prądnik (80.1 mg l^{-1}), and in Dłubnia (60.1 mg l^{-1}), both draining Jurassic limestone.

The results of the PCA are listed in Table 2. In Rudawa, three factors explain 81.4% of the variance in the hydrochemical data. Factor 1 (F1), explaining 45.3%, indicates a strong positive inter-correlation among Na^+, Cl^-, K^+ and Ca^{2+}. F2, explaining 21.7%, indicates a strong positive inter-correlation between Mg^{2+} and PO_4^{3-}. In

Table 2 Results summary of a principle component analysis of the chemical composition of spring water of four catchments.

Variables	Rudawa Matrix of factor loadings:			Prądnik			Dłubnia			Szreniawa		
	F1	F2	F3	F1	F2	F3	F1	F2	F3	F1	F2	F3
PO_4^{3-}	−0.16	**−0.72**	−0.08	0.53	0.65	0.05	−0.07	−0.45	**−0.87**	−0.21	−0.23	**0.90**
NO_3^-	0.59	−0.49	−0.40	**0.89**	−0.25	0.03	**−0.80**	−0.49	−0.02	0.29	**−0.80**	0.15
Cl^-	**0.87**	−0.35	−0.15	**0.92**	−0.25	0.08	**−0.92**	−0.23	−0.04	−0.46	**−0.75**	−0.11
Mg^{2+}	0.09	**0.85**	−0.43	0.60	0.11	**−0.77**	−0.30	**0.71**	−0.43	−0.39	0.67	0.36
Ca^{2+}	**0.78**	−0.10	0.51	**0.91**	0.10	0.26	**−0.89**	0.05	0.24	**−0.73**	−0.57	−0.05
HCO_3^-	0.57	0.48	0.60	0.45	**0.79**	0.11	−0.61	**0.71**	−0.09	**−0.81**	0.18	0.07
Na^+	**0.93**	−0.01	−0.09	**0.95**	0.02	−0.09	**−0.89**	0.03	0.05	**−0.92**	0.24	−0.02
K^+	**0.86**	0.02	0.08	**0.88**	−0.28	−0.31	**−0.80**	0.17	−0.07	**−0.86**	0.18	−0.23
SO_4^{2-}	0.63	0.33	−0.54	**0.80**	−0.22	0.51	**−0.81**	−0.29	0.14	**−0.93**	−0.22	−0.06
Eigen value	4.08	1.96	1.29	5.63	1.32	1.04	4.86	1.62	1.03	4.13	2.19	1.03
% variation explained	45.3	21.7	14.4	62.5	14.6	11.6	53.9	18.0	11.4	45.9	24.3	11.5
Cumulative %	45.3	67.0	81.4	62.5	77.1	87.7	53.9	71.9	83.3	45.9	70.2	81.7

Bold type indicates factor loadings with an absolute value greater than 0.7.

Prądnik and Dłubnia, three factors control 87.7% and 83.3% of the variance, respectively. F1 explains 62.5% and 53.9% of the variance, respectively, and is associated with a strong inter-correlation among the same constituents, including Na^+, Cl^-, Ca^{2+}, NO_3^-, K^+, and SO_4^{2-}. In Prądnik and Dłubnia, F2 is associated with HCO_3^- and is also associated with Mg^{2+} in Dłubnia. In Prądnik, Mg^{2+} is associated with a separate factor (F3), whereas in Dłubnia and Szreniawa, F3 is associated with PO_4^{3-}, a more local source. In Szreniawa, F1 explains 45.9% of the variance and is strongly associated with SO_4^{2-}, Na^+, K^+, and Ca^{2+}.

For springs in the Szreniawa river catchment, F2 is associated with NO_3^- and Cl^-. In this case, F1 is associated with ions derived from natural sources, whereas F2 is probably associated with farming practices. Clearly the higher and more variable NO_3^- and PO_4^{3-} concentrations in Prądnik and Dłubnia indicate that anthropogenic influences play a more essential role in controlling the hydrochemistry of spring water. However, PCA does not provide a distinct separation of an anthropogenic-related influence on the spring-water chemical composition for these two catchments.

Diagrams based on Ward's method show a certain similarity among particular constituents within four drainage areas (Fig. 4). Generally, the degree of similarity is the best for spring water in the Prądnik catchment, which with respect to geology, is the most uniform of the catchments. The similarity index in Prądnik, indicates that the correlation among chemical constituents are affected less by local contaminants than in the other catchments. The results for the Dłubnia catchment are similar but the Euclidean distances are larger. For the Szreniawa and Rudawa catchments, the similarity patterns are the most differentiated, which probably reflects spatially variable local sources of groundwater contamination. The dominance of a single factor from the PCA for the spring water chemistry of the Prądnik and Dłubnia catchments suggests more hydrochemical uniformity compared with the Rudawa and Szreniawa catchments.

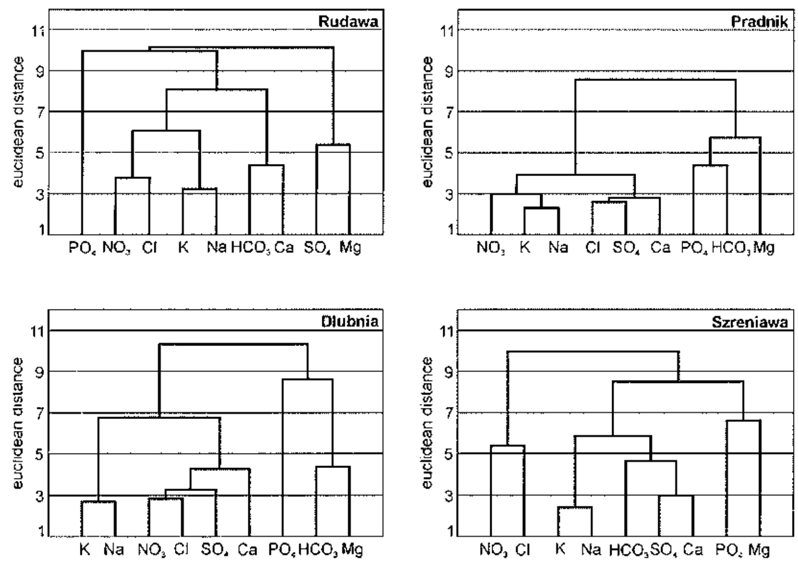

Fig. 4 Dendritic representation of similarity among spring water chemical constituents (based on Ward's method of Euclidean distances).

In general, it is difficult to separate and assess the magnitude of anthropogenic effects on the chemical composition of spring water in the Małopolska Upland. However, given the techniques described here, it is possible to identify hydrochemical differences and associations among the catchments with respect to anthropogenic and natural sources.

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