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Changes in the quality of shallow groundwater in agriculturally used catchment in the Wiśnickie Foothills (Southern Poland)

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Abstract: The aim of this study was to examine the changes in the chemical composition of shallow groundwater and its quality that have occurred in the last decade in an agriculturally used, heavily populated and characterized by a complex geological structure, catchment of the Stara Rzeka river, located in the flysch part of the Outer Carpathians. Water samples were collected during 2013 from 19 still operating wells. Analyses of pH, electrolytic conductivity and chemical composition by ion chromatography were conducted. The obtained results were compared with the results of studies conducted in 2003 for the same wells. The quality of groundwater and its suitability for consumption was assessed based on the regulations currently existing in Poland. 21% of the wells still do not meet the requirements for drinking water in terms of at least one component. However, there was a decrease in the concentration of mineral forms of nitrogen and phosphorus in most of the wells and their mean concentration as compared to 2003 was reduced. In terms of physical and chemical characteristics groundwater of this region is typical of the hypergenic zone of the temperate climate. The highest concentrations were observed for Ca^{2+} and HCO_3^- ions, while K^+ and Cl^- were characterized by the largest variability. Principal Component Analysis (PCA) demonstrated that the factors determining the quality and chemical composition of the analyzed waters include the composition of bedrock (mineralogy of the rock environment) and human economic activity, and that they have not been significantly changed over the past decade.

Introduction

Groundwater accounts for 97% of freshwater in the world and is used, among others, in agriculture, industry, recreation and – primarily – as the main source of drinking water in many regions of the world (Schmoll et al. 2006). The quality of drinking water has impact on human health and life. The quality of groundwater is affected mainly by natural factors. However, the contamination of groundwater is increasingly caused by human activity. There is abundant literature describing cases of groundwater pollution resulting from anthropogenic activity (Spalding and Exner 1993, Ongley 1996, Jeong 2001, Hancock 2002, Elhatip et al. 2003, Mahavi et al. 2005, Balderacchi et al. 2013). Contamination of groundwater is much more common in agricultural, industrial and heavily built-up areas (Vrba 2003). In the cases of such contamination, groundwater contains increased concentrations of, among others, nitrogen, phosphorus, sulfur, heavy metals and pesticides.

In the Wiśnickie Foothills groundwater is an important resource. Often, groundwater constitutes the main source of drinking water and in many cases it is not being purified before consumption. Increasing pressure on the quality of groundwater by intensified land use, as well as pollutions from agricultural activity that enter groundwater, negatively affect the quality of drinking water supplies in this area (Słowik 2003, Żelazny 2005). At the same time, progressing construction of municipal infrastructure (water supply and sewerage systems) should have positive effect on the quality of groundwater.

The aim of this study is to determine the changes in the chemical composition and the quality of shallow groundwater that have occurred in the last decade in a typical catchment, located in the flysch Outer Carpathians on an agriculturally used, heavily populated area with complex geological structure. This study also includes the examination of factors affecting the quality of groundwater 10 years ago and at present.

Study area

The studied area is situated in Outer Carpathians, in the northern part of the Wiśnickie Foothills (Starkel 1988, German 1992, Kondracki 1994) in the Stara Rzeka catchment (Fig. 1) and is characterized by a complex geological structure (Fig. 1). The Carpathian Foothills here is of clearly two-stage character (Kaszowski and Święchowicz 1995). The upper layer is built of resistant Carpathian flysch composed of sandstones, shales and clays. The lower layer is built of less resistant flysch rocks, Tortonian sandstones and clays located thereon (Grabowiec beds), and salt layer deposits (Bochnia salt series, Chodenice beds) (Olewicz 1968, 1973 a,b, Siwek 2012) (Fig. 1).

The entire area is covered with a thick layer of dust loess--like deposits, with thickness reaching up to several meters (Kaszowski and Święchowicz 1995). Together with flysch weathering they constitute the soil bedrock. Large genetic homogeneity of these deposits is demonstrated by only slight diversity of soil cover and the prevalence of luvisols and pseudogley soils, covering 80% of the catchment area (Skiba 1992, Skiba and Drewnik 1995, Skiba et al. 1995).

The study area is situated within warm temperate climate zone (Hess 1965). Mean annual temperature of this area is 8.2–8.3ºC, total annual precipitation is about 665 mm and the period of snow cover is on average 70 days per year (Obrębska--Starkel 1988).

The Stara Rzeka catchment is characterized by large share of forests (41.9%) in the total land area. Arable land is characterized by high fragmentation and represents 36.2% of the area. Meadows and pastures, located mainly in the bottom of the valley, occupy 14.9% (Święchowicz and Michno 2005).

Currently, the study area is entirely covered with water supply system. Wells are still being used as an additional source of water supply only in some households. However, as compared to 2003, their number decreased by two-thirds (Słowik 2003). Until now the construction of a sewerage network over an entire area has not been completed, therefore sewage is discharged to septic tanks, which are not always tight and systematically emptied. Sewage is also poured directly on agricultural land, to drainage ditches and into forests (Pietrzak 2005). Manure pits and piles of manure are also a potential threat to the quality of groundwater.

Material and methods

Field studies were conducted in 2003 and 2013 and involved the collection of water samples from 19 operating wells. In both sampling campaigns the samples were collected in winter from the same wells being in continuous use. Also in both

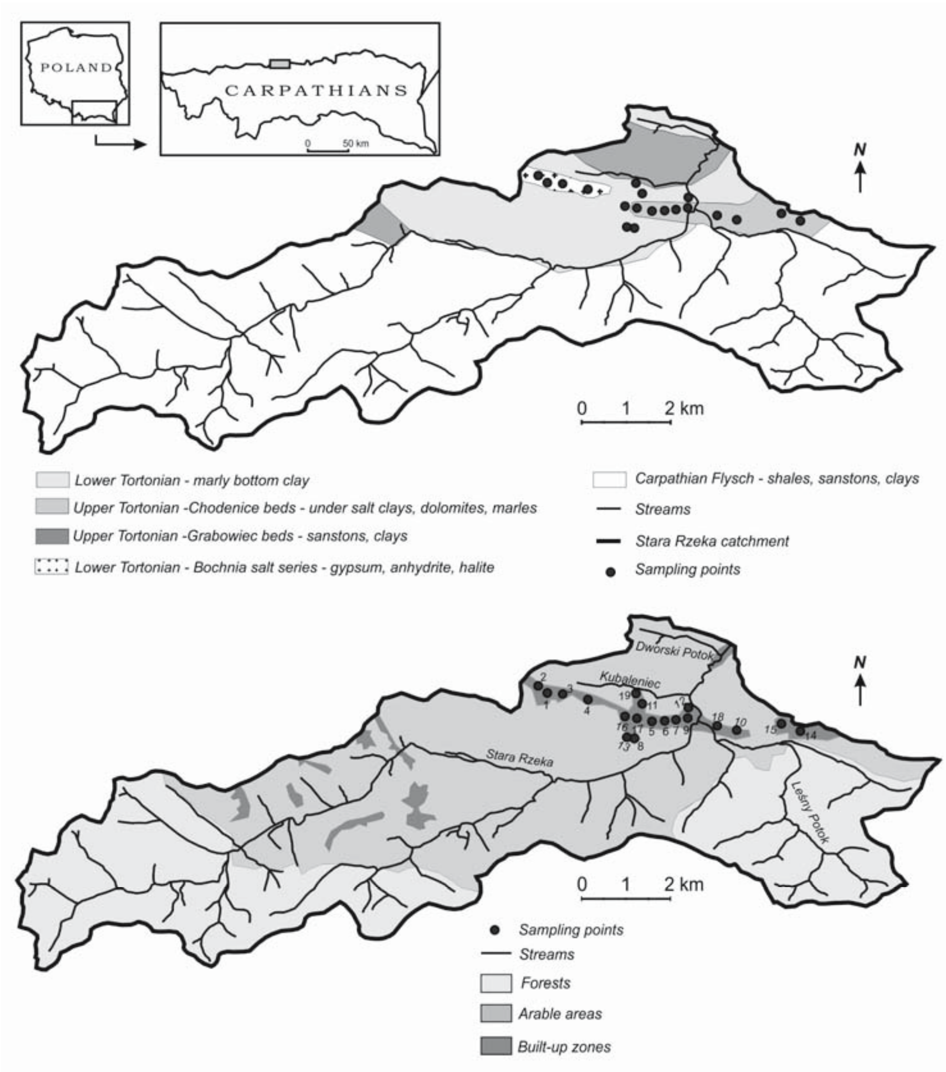

Fig. 1. Location, land use and geological structure of the study area

campaigns the method of collection remained the same – the samples were taken directly from wells using a sampler, which was washed several times with the analyzed water prior to the collection. Electrolytic conductivity (EC) and pH of water were measured onsite.

Analyses of chemical composition in 2013 were performed by ion chromatography. The applied DIONEX chromatographic system consisted of two simultaneously operating ICS-2000 chromatographs and an AS-40 autosampler, and was equipped with AS-18 and CS-16 columns. This allowed for the determination of 14 ions in the collected water samples (main ions: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^-, SO_4^{2-}, Cl^-, nutrients: NH_4^+, NO_3^-, NO_2^-, PO_4^{3-} and microelements: F^-, Br^-, Li^+). Water mineralization (TDS) was calculated as a sum of determined ions, while total hardness of water – as a sum of Ca^{2+} and Mg^{2+} expressed as milliequivalents. Each time the ion chromatography system was calibrated on the basis of 12 anionic and 10 cationic standards, prepared by mixing appropriate proportions of Merck single-element standards at 1000 mg/l. The proper operation of the system was controlled using certified reference materials such as: MAURI-09, SANGAMON-03, AES-02, TROIS-94, LETHBRIDG-03. Each time, the relative error of analysis was calculated for each sample using the ion balance method. For the examined samples it ranged from -4.2% to 1.9%.

The chemical composition of the samples collected in 2003 was determined by titrimetric methods (HCO_3^-, Cl^-, total hardness), flame photometry (Ca^{2+}, Na^+, K^+), Mg^{2+} by spectrophotometric determination of magnesium by titan yellow, SO_4^{2-} by turbidimetry. NH_4^+, NO_3^-, NO_2^-, PO_4^{3-} ions were determined using Merck Spectroquant spectrophotometric tests. The chromatographic method used in 2013 and methods used in 2003 gave comparable results, which were verified in the course of previous works. The total hardness of water in 2013 was calculated as the sum of Ca^{2+} and Mg^{2+} concentrations in mval/l. In 2003 Li^+, Br^-, F^- ions were not determined, while in 2013 the concentrations of Li^+ and Br^- were below the limits of quantification.

Multivariate statistical analysis has been successfully applied in a number of hydrogeochemical studies (Seyhan et al. 1985, Voundouris et al. 2000, Voza et al. 2015). Thyne et al. (2004) state that this method can be used in order to extract key information from complex systems of hydrochemical data sets. In this study, Principal Component Analysis (PCA) was used to identify the factors affecting the quality of groundwater. The factors were selected based on the Kaiser criterion (eigenvalue >1) and when the value of explained variance was greater than 10%.

The changes in water quality were assessed based on the Polish regulations on the quality of water for human consumption (Journal of Laws No. 61, Item 417, Journal of Laws No. 72, Item 466, Council Directive 98/83/EC, 1998), which sets the limits of maximum values for the ion concentrations in drinking water.

Results and discussion

Table 1 shows the general characteristics of physical and chemical properties of the analyzed groundwater. The average pH of groundwater was ~7 pH and ranged from 6.2 to 7.9. Such pH fits within the range given by Hem (1985) for the majority of groundwater. The Polish regulations recommend a pH range between 6.5 and 9.5 in waters used for public supply (Journal of Laws No. 61, Item 417, Journal of Laws No. 72, Item 466, Council Directive 98/83/EC, 1998). Mean conductivity of water was ~972 μS·cm^{-1}. Given the water mineralization (TDS), the examined samples can be classified as fresh water, only some of them can be regarded as slightly saline (Dawis and DeWiest 1970). On the other hand, in terms of hardness, these are usually very hard waters (Hem 1985).

When assessing the chemical composition of the analyzed groundwater, the greatest concentrations were recorded for

Table 1. Characteristic values of physical and chemical characteristics of groundwater

Parameter	Unit	Mean	Median	Min	Max	Q25%	Q75%	Cv	LOD
TDS	mg/L	697.6	697.0	255.2	1325.0	551.0	815.8	35.8	n/a
pH		7.0	7.0	6.2	7.9	6.7	7.2	5.2	n/a
EC	μS/cm	971.9	951.8	350.0	1830.2	713.0	1189.0	38.3	n/a
Ca^{2+}	mg/L	102.5	100.1	43.4	228.8	70.6	136.5	40.4	0.04
Mg^{2+}		18.8	19.2	6.7	39.6	11.5	23.7	45.0	0.002
Na^+		45.8	32.8	7.9	157.2	21.9	70.9	74.1	0.012
K^+		30.4	3.2	0.4	181.6	1.7	26.7	168.1	0.004
NH_4^+		0.29	0.03	0.01	3.24	0.01	0.09	254.3	0.002
HCO_3^-		265.5	230.0	78.1	606.3	191.5	351.4	46.0	0.05
SO_4^{2-}		115.3	102.3	47.7	209.8	79.3	150.7	43.2	0.012
Cl^-		80.3	45.3	8.6	402.3	23.4	93.6	108.8	0.02
NO_3^-		38.2	26.8	1.7	130.3	16.5	50.1	83.5	0.008
NO_2^-		0.11	0.02	0.01	3.09	0.01	0.02	454.3	0.01
PO_4^{3-}		0.25	0.16	0.01	1.99	0.06	0.28	151.3	0.04
F^-		0.19	0.14	0.004	1.88	0.02	0.22	169.8	0.004
Hardness	mval/L	6.7	6.5	3.1	14.7	4.8	7.7	39.1	n/a

Ca^{2+} among cations. Slightly lower concentrations were recorded for Na^+ and K^+. The remaining cations were usually characterized by multiple times lower concentrations. Among anions, the greatest concentrations were observed for HCO_3^-. The lowest concentrations were recorded for SO_4^{2-} and Cl^-. The widest range of main ion concentrations, expressed as a coefficient of variation (Cv) was observed for K^+ among cations and among anions – for Cl^-. The order of main cations in terms of their concentrations in the analyzed groundwaters was usually as follows: $Ca^{2+}>Na^+>K^+>Mg^+$, while for main ions it was: $HCO_3^->SO_4^{2-}>Cl^-$. The highest concentrations among nutrients were recorded for NO_3^-, and considerably lower for NH_4^+ and PO_4^{3-}. Concentrations of NO_2^- were usually below the limit of detection.

The high content of K^+, NO_3^- as well as the presence of NH_4^+ and PO_4^{3-} in groundwaters may indicate the pollution of water in the considered region, since these compounds are generally associated with anthropogenic activity (Singh et al. 2005). Br^- and Li^+ ions were at concentrations below the limit of quantification.

The trilinear Piper diagrams of the major cations and anions in the groundwater of the study region are shown in Fig. 2. These diagrams show that among cations, Ca^{2+} dominated the aquifer in this region. On the other hand, bicarbonates were the predominant anions. There were also a few samples with high concentrations of Cl^-, Na^+ and K^+. Therefore, the majority of groundwater samples belonged to the Ca-HCO_3 type, whereas some of them were also the type with Na^+, K^+ and Cl^-. Furthermore, it was found that the concentrations of main ions: Ca^{2+}, Na^+, HCO_3^-, SO_4^{2-} and Cl^- changed in the last decade. The largest changes concerned particularly water in wells No. 2, 3, 12, 15 and 19.

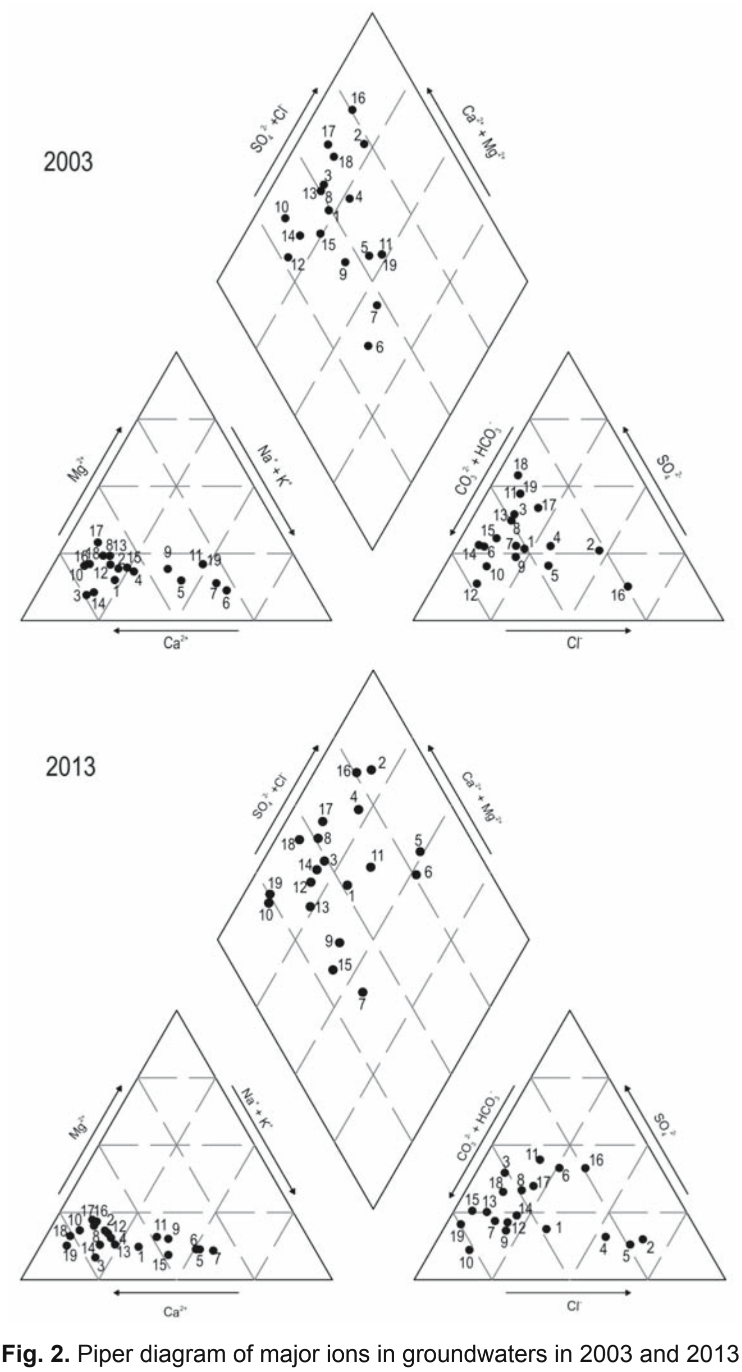

Fig. 2. Piper diagram of major ions in groundwaters in 2003 and 2013

Based on the electrolytic conductivity (EC), mineralization (TDS) and pH of water, as well as the concentration of main ions and nutrients in the analyzed groundwaters, the Principal Component Analysis (PCA) allowed to determine two main factors (Fig. 3) affecting the quality of water both in 2003 and 2013. They explain in total 62% of variance in 2003 and 60% in 2013. For the samples collected in 2003, the factor 1 explains 44% of variance, factor 2 – approx. 18%. In addition, in 2013 the factor 1 explains 41%, while factor 2 – 19%.

For samples collected in 2003 as well as in 2013, factor 1 is strongly correlated with TDS, EC and main ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and Cl^{-}). This factor can be explained by the influence of bedrock and sediments in which the analyzed groundwaters circulate. Caissie et al. (1996) confirmed that the strong correlation between main ions (Ca^{2+}, Mg^{2+}, Na^{+}, HCO_3^{-}) indicates their origin from weathering of rocks. Factor 2 is correlated with K^{+}, NH_4^{+}, PO_4^{3-} and NO_2^{-}. The presence of potassium and nutrients in this factor may evidence that the chemical composition of groundwater is affected by the anthropogenic pressure. High levels of potassium may be also due to the geological structure of the considered area. The previously observed concentrations of potassium in the waters of lower Bochnia unit were even 10-times higher than in the remaining areas of the Stara Rzeka catchment (Żelazny 2005). Within this unit there are deposits of halite, mined since the medieval times in the salt mines of Wieliczka and Bochnia. The results of Principal Component Analysis conducted for water samples in 2003 and 2013 show that their chemical composition and quality are determined by the same factors. This is evidenced by both similar values of explained variance in factors 1 and 2 and by the relationships occurring between the physicochemical characteristics and the chemical composition of the analyzed groundwaters.

Based on both Polish regulations and the European Union provisions concerning the quality of drinking water, it was verified whether the consumption of analyzed waters is safe for human health. The limit value for NO_3^{-} is 50 mg/L, for NO_2^{-} – 0.5 mg/L, Cl^{-} – 250 mg/L, SO_4^{2-} – 250 mg/L (Journal of Laws No. 61, Item 417, Journal of Laws No. 72, Item 466, Council Directive 98/83/EC, 1998). In accordance with the presented regulations, samples collected from 21% of the examined (19) wells exceed the given values in the case of at least one of those parameters both in 2003 and 2013. The limit values are most frequently exceeded for NO_3^{-}. Although, as compared to 2003, the concentration of these ions decreased in most wells (Fig. 4), they still do not meet the mentioned requirements. A decrease in the concentration of most nutrients – NO_2^{-}, NH_4^{+}, PO_4^{3-} (Fig. 4) was observed in wells in the last

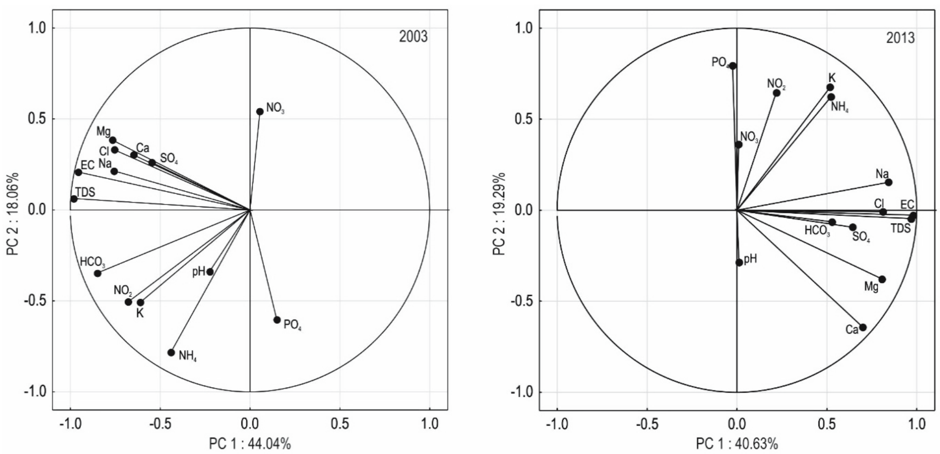

Fig. 3. PCA analysis of physico-chemical characteristics of groundwater samples in 2003 and 2013

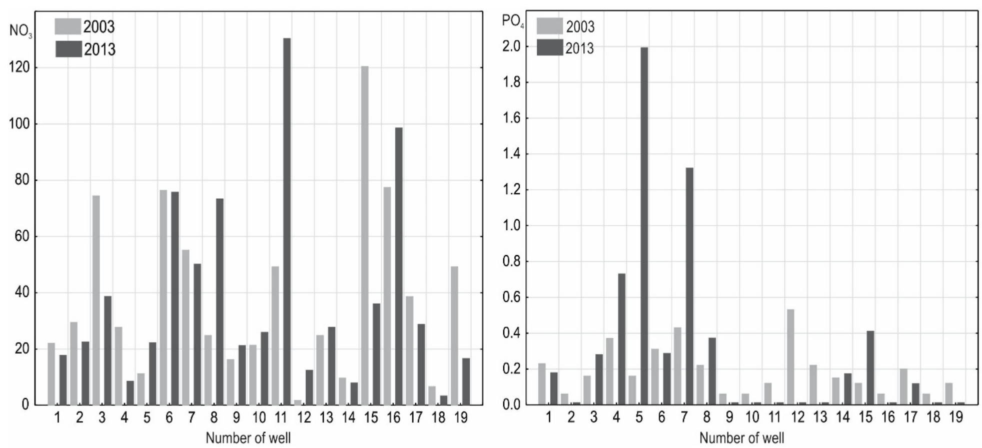

Fig. 4. Changes in the concentration (mg/L) of NO_3^{-} and PO_4^{3-} in last decade (2003–2013)

decade. The consumption of water with such composition may constitute a potential hazard for human health. Groundwater contamination, resulting from anthropogenic activity, is observed also in other parts of Poland. For example, spring waters of the Lesser Poland Upland have the concentrations of NO_3^- exceeding 60 mg/L (Siwek and Chełmicki 2004).

Conclusions

In terms of physical and chemical characteristics, groundwater of the analyzed region is typical of the hypergene zone of the temperate climate, where anions are mostly dominated by bicarbonates, while cations – by calcium. The impact of the geological structure on the chemical composition of groundwaters is also evident. This primarily concerns the occurrence of halite and gypsum in the ground, which in some waters results in high concentrations of Na^+, Cl^- and SO_4^{2-}.

The examined waters are contaminated, which is manifested by the content of nutrients. The observed contamination results mainly from the anthropogenic activity and is associated with the discharge of municipal sewage and organic-mineral fertilization of agricultural land.

In the last decade the concentration of nutrients in groundwater decreased, however this did not result in improved quality of drinking water, because their concentrations still exceed the permissible levels. The Principal Component Analysis also showed that the factors affecting the chemical composition of groundwater did not change in the last decade.

The applied statistical methods are useful in assessing the quality and processes that shape the chemical composition of groundwater. The PCA confirmed that the chemical composition of groundwater is significantly affected by both mineralogy of the rock environment and the economic activity of people in this region.

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Zmiany jakości płytkich wód poziemnych w użytkowanej rolniczo zlewni na Pogórzu Wiśnickim (Południowa Polska)

Streszczenie: Celem opracowania jest zbadanie zmian składu chemicznego płytkich wód podziemnych i ich jakości jakie zaszły w ostatnim dziesięcioleciu w użytkowanej rolniczo, silnie zaludnionej, cechującej się skomplikowaną budową geologiczną zlewni Starej Rzeki, położonej we fliszowych Karpatach Zewnętrznych. W 2013 roku z 19 nadal użytkowanych studni pobrano próbki wody i poddano je analizie pH, przewodnictwa elektrolitycznego właściwego oraz składu chemicznego metodą chromatografii jonowej. Uzyskane wyniki porównano z wynikami badań z 2003 roku dla tych samych studni. Jakość wody podziemnej i jej przydatność do spożycia przez ludzi oceniono na podstawie obowiązujących w Polsce przepisów. 21% studni nadal nie spełnia wymogów stawianych wodzie do picia w zakresie przynajmniej jednego składnika, jednakże zaobserwowano spadek stężenia mineralnych form azotu i fosforu w większości studni oraz zmniejszenie się ich stężenia średniego w stosunku do 2003 r. Pod względem cech fizycznych i chemicznych wody podziemne tego regionu są typowe dla strefy hipergenicznej klimatu umiarkowanego. Najwyższe stężenia miały jony Ca^{2+} i HCO_3^-, a najwyższą zmiennością cechowały się natomiast jony K^+ i Cl^-. Analiza składowych głównych (PCA) dowiodła, że czynnikami decydującymi o jakości i składzie chemicznym wód są skład podłoża skalnego oraz gospodarcza działalność człowieka i nie uległy one znaczącym zmianom w minionym dziesięcioleciu.