ASSESSMENT OF WATER SUITABILITY FOR DRINKING IN THE SPRING IN LEŚNIÓW (SOUTHERN POLAND)

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ABSTRACT

Natural springs are one of the potential sources of water supply. Increasing anthropogenic activity, inadequate sanitary conditions and intense rainfall are important factors that threaten the maintenance of adequate water quality in springs. Physicochemical and microbiological tests were performed in two measurement series for water from the spring in Leśniów (southern Poland). The test results were compared with the permissible limits for drinking water and the Nemerow Pollution Index (NPI) value was calculated for these parameters. The average conductivity of water in this spring is approximately 390 μS/cm, pH is about 7 and due to its alkalinity, water can be classified as hard. The NPI values varied, i.e. from about 33 to about 3, which was due to the high mercury content measured in the first sample. Additionally, the number of coliform bacteria reached 35 cfu/100 ml, and the total number of microorganisms at 22±2°C reached 27 cfu/ml in the first measurement series. Such values indicate water contamination, which may pose a significant threat to human health when consuming such water. The second series of measurements showed lower pollution values, but the previously obtained results suggest that it is necessary to control the water quality in the springs and control nearby pollutant emitters.
Keywords: spring, Nemerow Pollution Index, microbiology, drinking water, Kraków-Częstochowa Upland.

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INTRODUCTION

Springs are natural, spontaneous outflows of groundwater onto the land surface. The physicochemical properties of water in springs are determined primarily by geological conditions, climatic conditions as well as land development, climate and land use [1,2,3]. Water in springs also appears on the surface due to tectonic conditions, i.e. a network of faults, cracks or contact with rocks. Springs are an element of the surface water and groundwater system [4,5], therefore, they are very vulnerable to pollution and anthropogenic impacts [6,7,8]. The topography of the land as well as the method of spatial development are the main factors that may affect the amount of pollution [9]. It should be noted that the pollutant load may also increase with increasing precipitation, migration of leachate from landfills, sewage treatment plants or sewage pipes [10,11,12]. Water from springs has different quality also due to the content of microorganisms and changes in chemical composition due to, for example, weathering or leaching processes [13].

It should also be borne in mind that springs can support economic activity and also affect the aesthetic and recreational values of the landscape. The hydrology and ecology of springs are often closely linked to variations in surface water and groundwater interactions. Globally, approximately 30% of freshwater is groundwater, which is influenced by changes in climate change and anthropogenic activities [14]. Spring waters should also be protected due to their frequent use as a source of drinking water [15]. Springs reflect the mineral rock composition in surrounding geological processes, and the presence of minerals in spring water is considered beneficial to health [16]; [17]. While water in springs can have a positive impact on human health, pollution and poor sanitary conditions can negatively impact health, causing gastrointestinal diseases and liver diseases [18].

Springs can be described in terms of hydrological, hydrogeological, bacteriological, as well as biological aspects of the fauna and flora occurring in their area [19]; [20]. The hydrogeological and geochemical properties of spring influence the water quality, velocity and the discharge [21]. Natural and anthropogenic factors can change properties of spring water and lead to water contamination.

In this article, attention is focused on the hydrological and hydrogeological aspects and the bacteriological composition. Emerging organic pollutants are an important indicator of anthropogenic micropollution, which is difficult to assess in aquatic environments due to their low concentrations. However, this is one of the most important topics in recent years, which can help conduct water quality monitoring and purification activities [22,23]. Similarly, determining the content of microorganisms in spring waters and their importance for the proper functioning of aquatic ecosystems plays an important role [24]. Microorganisms - including pathogens and potential pathogens - which may pose a serious threat to human health and well-being are often observed in spring waters. Monitoring fecal coliforms, enterococci, P. aeruginosa and C. perfringens provides the most information.

The aim of the article is to present the results of testing the quality of spring water in the spring in Leśniów (southern Poland). This spring was selected for research due to the fact that it is constantly used by residents, tourists and pilgrims, and due to the geological and hydrogeological conditions that increase the vulnerability of these waters to pollution. The results of chemical analyses, bacteriological composition and hydrometric measurements were taken into account.

STUDY AREA

The research covered the Leśniów spring, which is located in the Żarki commune (southern Poland) at an altitude of 345 m above sea level. In terms of physical and geographical regionalization, according to Kondracki (2000), it is located in the Kraków-Częstochowa Upland macroregion and in the Częstochowa Upland mesoregion. The spring is completely enclosed, and taps are installed at the outlet to facilitate water consumption. Due to the fact that the spring is located in the area of the Sanctuary of Our Lady of Leśniowska, the water is taken by pilgrims and tourists. The water flows out through a stone trough.

The average annual air temperature here is 7.5 - 8.0°C. Atmospheric precipitation recharges aquifers. Precipitation dominates in the summer half of the year (the maximum falls in July). The average annual rainfall is approximately 750 mm. The highest relative humidity occurs in November and December. Hydrographically, the source in Leśniów lies in the Leśniówka catchment, which is a right-bank tributary of the third-order catchment - the Warta (Fig. 1). The spring in Leśniów is classified as a hillside, fissure and descending type of spring.

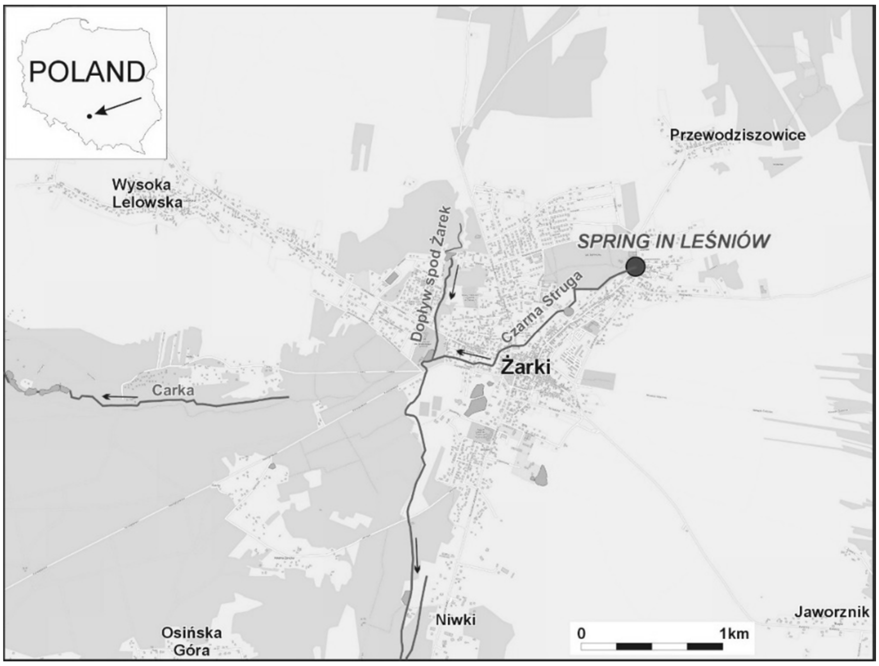

Fig. 1 Study area.

In the geological profile in the vicinity of the spring in Leśniów there are three structural levels - the Variscan fold level, the Alpine cover level and Cenozoic formations. Paleozoic formations, cut by erosion, are covered with Triassic and Jurassic epicontinental formations, forming a fragment of the Silesian-Kraków monocline. The thickness of Mesozoic deposits in this region is approximately 700 m [25,26].

The Upper Jurassic formations are represented by rocky limestones, shoal limestones and plate limestones with marl inserts belonging to the upper part of the Middle Oxfordian and Upper Oxfordian [27]. The shoal limestones in this area are associated with tuberolite limestones. The thickness of the shoals ranges from 30 to 100 cm. Marly inserts in this area do not exceed 5 cm. Rocky limestones are massive, hard and compact, ranging in color from white to light cream. Plate limestones are thin-bedded marly limestones with a bed thickness of approximately 10 cm. Quaternary deposits are river sands and gravels with a thickness of up to 50–70 m [28]. In this area, there are also sandy and sandy-silty sediments filling the valley depressions. The thickness of these sediments ranges from 2 to 20 m. Sands, fluvioglacial sands and gravels from the Oder glaciation can be observed on the surface (Fig. 2).

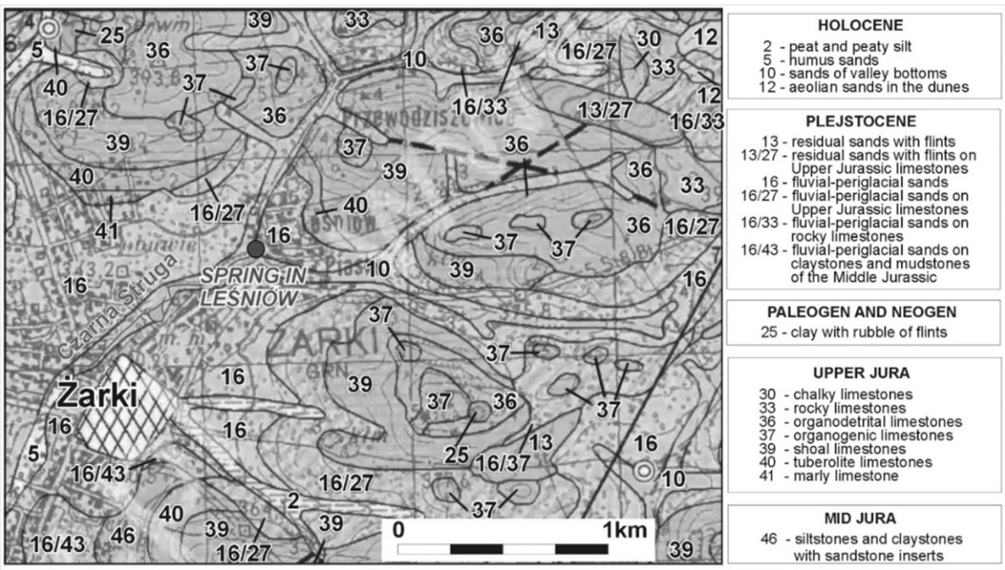

Fig. 2 Geological map of the study area.

The described source is located in the area of the main groundwater reservoir - Krzeszowice-Pilica. It is a fractured-karst-porous reservoir associated with the Upper Jurassic formations. The porosity of Jurassic rocks is on average 9.3%. The system of cracks, fissures and karst voids plays a fundamental role in water conduction.

The Quaternary aquifer is characterized by lack of continuity and low resources. In the area of the described source, this aquifer is of little importance. The thickness of the aquifer does not exceed 5 meters. Due to the direct supply of the Quaternary zone and the small thickness of the aeration zone, the waters therein are highly exposed to pollution. The main aquifer in the analyzed research area is the Jurassic aquifer. It consists of two aquifer levels. The described source is located within the aquifer associated with the sands and sandstones of the Kościelisko strata (Middle Jurassic). The thickness of the aquifer ranges from 12 to 43 meters, while the hydraulic conductivity ranges from 0.27 to 5.79 m/d. The highest values are obtained on outcrops under Quaternary formations. Jurassic formations are poorly conductive [29]. The regional outflow in this aquifer is towards the north-east. The depth to the first aquifer in this area ranges from 2 to 5 meters. The hydrodynamic field throughout the Kraków-Częstochowa Upland indicates the existence of a number of groundwater divisions. Springs are the basis of drainage. The water is classified as quality class II, i.e. water requiring simple treatment. The assessment of the vulnerability [30,31,32] of groundwater to pollution was determined by factors such as the soil layer, hydrogeological properties (the type of rock medium in both the aeration and saturation zones), the hydrodynamic system and the types of pollutants. The groundwater included is located in an area with a very high degree of vulnerability to pollution, for which the arrival time of the pollution has been determined to be less than 5 years [33].

METHODOLOGY

Spring research included two measurement series conducted in November 2023 and February 2024. During field trips, discharge measurements were made and water samples were taken for physicochemical and bacteriological analyzes. Physicochemical and bacteriological analyzes were performed in an accredited laboratory. The results of both series were double-checked by the laboratory to reduce the risk of measurement error. In terms of physicochemical parameters, the values of electrical conductivity, pH, Ca, Na, K, Mg, Fe, Al, Mn, Ni, Cu, Sr, S, Cl, SO_4, HCO_3, NO_3, NO_2, NH_4, PO_4, N, K, TOC were examined Pb, Cd, Cr, Hg, Zn, acidity and alkalinity. The potential presence of pathogens in environmental waters can be inferred by monitoring coliforms, enterococci, P. aeruginosa and C. perfringens. Additionally, the determination of coliform E. coli is recommended as an indicator of the degree of recent fecal contamination [34].

The flow rate was obtained by dividing the container volume by the filling time. In order to improve the reliability of the measurement, three different measurements were made and the average value was recorded. The bucket method was used to measure discharge [35].

The values of main ions in the source water were related to the values of the natural hydrogeochemical background determined in the work of Siwek and Baścik [36], for the waters of the Jurassic aquifer in this area. The hydrogeochemical background was defined as the value of the 90th percentile in the empirical distribution of concentrations of a given ion within the population [37]. The upper background limit values were determined to be 137.9 mg/l for calcium, 17.3 mg/l for magnesium, 9.8 for sodium, 6.2 mg/l for potassium, 400.4 mg/l for bicarbonate, 63.1 for sulfate, 26.9 mg/l for chloride, 32.2 mg/l for nitrates. Additionally, the obtained results of physical and Minister of Health of December 7, 2017 on the quality of water intended for human consumption (Journal of Laws chemical analyzes and bacteriological composition were compared to the values contained in the Regulation of the of 2017, item 2294).

Additionally, for all parameters mentioned in the regulation, the Nemerow index was calculated [38]. The Nemerow Pollution Index (NPI) is one of the most popular methods which can be used to evaluate the status of water quality [39]. It is calculated on the basis of the following formula:

$$NPI = \frac{C_i}{L_i}$$

where:

C_i - is the measured value of the i^{th} parameter

L_i - is the allowable limit of the i^{th} parameter

An index value < 1 suggests low pollution, a value from 1 to 3 equals to moderate pollution, a value from 3 to 6 and the remaining values indicate very high pollution. Data from the regulation were used as the permissible value for individual parameters.

The NPI index was calculated for the following parameters: EC, Na, Mg, Fe, Al, Mn, Ni, Cl, SO_4, nitrogen compounds, Pb, Cd, Cr and Hg.

RESULTS AND DISCUSSION

The discharge spring measurement results were 0.22 l/h in November 2023 and 0.31 l/h in February 2024. The obtained biological and physicochemical values were compared to the quality standards of water intended for human consumption and NPI values were calculated for these parameters. Except for the biological parameters - coliform count, Escherichia coli count, which exceeded the recommended limits (0 CFU/100 ml) for drinking water and mercury content, all other physiochemical parameters were within the standard permissible limit. The value of specific electrolytic conductivity was 384 μS/cm in the first measurement series, and 399 μS/cm in the second series. The values of most parameters were in most cases a dozen or so percent of the norm for drinking water (Table 1).

Tab. 1

Results of physicochemical and bacteriological analyzes in both measurement series

Parameter	Unit	November 2023	February 2024	Limits for drinking water
EC	µS/cm	384	399	2500
Ca	mg/l	90	89	
Na	mg/l	5.5	5.8	200
K	mg/l	0.5	1.5	
Mg	mg/l	1.5	3.4	125
Fe	mg/l	0.002	0.058	0.2
Al	mg/l	0.005	0.005	0.2
Mn	mg/l	0.0005	0.006	0.05
Ni	mg/l	0.002	0.002	0.002
Cu	mg/l	0.002	0.006	
Sr	mg/l	0.066	0.088	
S	mg/l	9.5	11	
Cl	mg/l	13	13	250
SO_4	mg/l	36	40	250
HCO_3	mg/l	202	208	
NO_3	mg/l	26	24	50
NO_2	mg/l	0.033	0.033	0.5
NH_4	mg/l	0.065	0.065	0.5
PO_4	mg/l	0.13	0.11	
N_K	mg/l	2.5	2.5	
TOC	mg/l	1	1	
Pb	mg/l	0.002	0.002	0.01
Cd	mg/l	0.00025	0.00025	0.005
Cr	mg/l	0.0015	0.0015	0.05
Hg	mg/l	0.031	0.00012	0.001
Zn	mg/l	0.0025	0.022	
Acidity	mmol/l	0.6	0.47	
Alkalinity	mg/l $CaCO_3$	166	171	
The number of coliform bacteria	cfu/100ml	35	7	0
Number of Escherichia coli	cfu/100ml	13	3	0
Number of Enterococci	cfu/100ml	0	0	0
Number of Clostridium perfringens	cfu/100ml	0	0	0
Total number of microorganisms at 22±2°C	cfu/ml	27	0	100
Number of Pseudomonas aeruginosa	cfu/100ml	0	0	0
Total number of microorganisms at 36±2°C	cfu/ml	0	0	20

The nitrate content was approximately half of the permissible standard, while the nickel content was exactly in line with the permissible standard. The total value of the NPI index for the analyzed waters was 33.43 for the November sample and 2.66 for the February sample. In the first measurement series, the final index result was influenced by the mercury content. The mercury content was 31 times higher than the permissible standard for drinking water. This represents almost 93% of the total NPI value. About 3% is nickel content and 1.5% nitrate content. Magnesium, manganese and iron had the smallest share in the total NPI value in this measurement series. (Fig. 3).

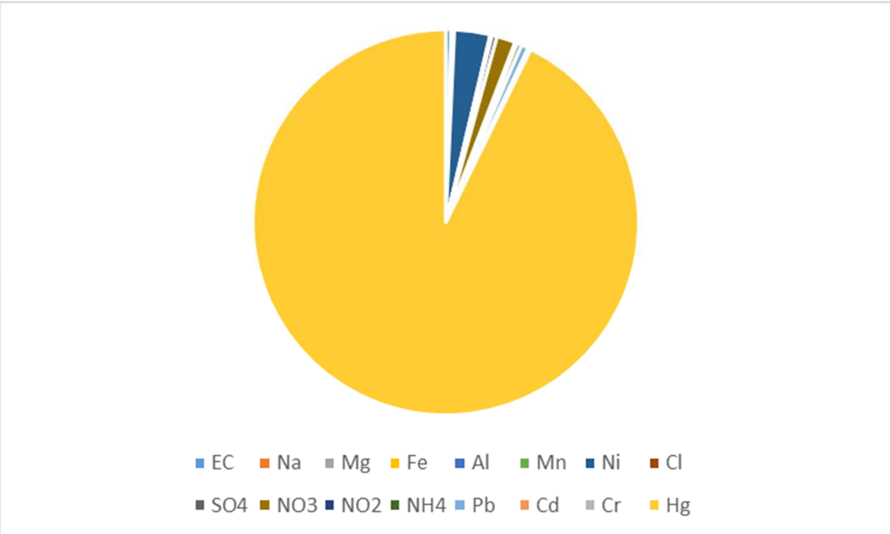

Fig. 3 The share of individual components in the NPI index value in the first measurement series.

In the case of the second measurement series, the permissible mercury content in water was not exceeded. An increase in the content of magnesium, sulfur, sulfates and bicarbonates was observed. The magnesium content has more than doubled, but the content is still small. However, the nitrate content decreased. This resulted in a significant decrease in the value of the NPI index and the share of individual components in the total index value (Fig. 4). The dominant share in the index value for this measurement series is the content of nickel, sulphates and lead. Although in the case of the latter, the content is below the limit of quantification.

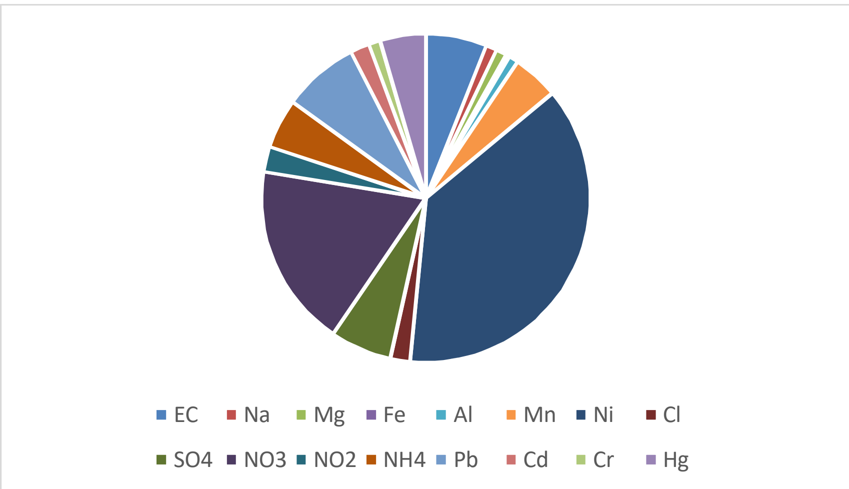

Fig. 4. The share of individual components in the NPI index value in the second measurement series.

The mercury identified in the first measurement series is certainly not related to the geological conditions in a given area, but is a consequence of anthropogenic activity. It should be borne in mind that in the area of the source there are also single-family houses and roads that pose a potential threat to water. On the one hand, this may be a consequence of the release of mercury accumulated as a result of deposition in the atmosphere during increased rainfall, which in this area was higher in November than in February (IMGW) on the other hand, it may be a consequence of the migration of pollutants from leaky nearby cesspools. Pollution issues have been raised before [40].

Despite the fact that high mercury concentrations were found only in one measurement, it should be borne in mind that heavy metals naturally occurring in the aquatic environment at higher concentrations may be toxic due to accumulation in organisms [41]. Elements like mercury, cadmium, lead and arsenic are non-essential micronutrients for plants, animals, and humans and they are considered as the most harmful elements [42]. It is estimated that the level of mercury in the atmosphere is currently five times higher than the natural level [43] and therefore mercury has been included on the list of priority pollutants [44]. The main sources of mercury in the atmosphere are fossil fuels and the smelting and burning of solid waste. Mercury migrates from the atmosphere to soils and waters, hence the content of this element may be increased in drinking water. Mercury compounds can interfere with most enzymatic reactions [45]. Research related to determining negative health effects after consuming food or water containing high concentrations of mercury indicates affecting the central human nervous system [46,47,48,49]. Health effects associated with consuming water containing mercury vary depending on the dose and the frequency and duration of consumption [50]. In order to determine both non-cancer and cancer risks for children and adults caused by the consumption of water with increased mercury concentration, it would be necessary to assess the amount of this water consumed by local residents or other people and calculate the chronic daily intake (CDI). The variation in mercury content may be dictated by episodic inflow of pollutants from the local environment or the effect of the content of this element in the atmosphere and migration with precipitation.

Surface water is potentially dangerous as a carrier of pathogenic microorganisms wherever it comes into contact with human waste. Microbiologically contaminated water becomes extremely dangerous to drink. Negative anthropogenic impacts can lead to oxygen disruption in water.. Escherichia coli serves as an excellent indicator of fecal water contamination. The microbiological analyzes showed that the number of heterotrophic bacteria was equal 13 cfu/100ml in the first sample and 3 in the second sample (the number of Escherichia coli). The number of coliform bacteria was 5 times higher in the first sample. Mesophilic bacteria occurring naturally in the human body and along with faecal matter cause water pollution. Increased precipitation may also lead to the migration of these pollutants to sources, e.g. from rivers [51]. It is worth mentioning that the survival of these bacteria in water is higher in alkaline and neutral environments, which is confirmed by measuring the pH of the water in the spring. Taking into account the results of both bacteriological analyses, the seasonal occurrence of fecal bacteria can be noticed. The number of bacteria found in a sample taken in winter confirms lower activity of microorganisms at lower temperatures.

SUMMARY AND CONCLUSIONS

Water plays an important role in the development of various economic sectors around the world. The demand for drinking water is constantly increasing, therefore maintaining good chemical condition of water is crucial. Due to negative anthropogenic impact, water quality may deteriorate. To maintain the quality and quantity of water resources, monitoring and protection of natural resources are the basis for rational water management. This also applies to springs.

The results of water analyzes from the spring in Leśniów showed that, apart from the high mercury content in the first measurement series, the physicochemical properties of the tested water sources correspond to the values adopted by the national guidelines on the quality of drinking water. The Nemerow index, which was approximately 33 in the first measurement series, decreased by more than 10 times in the second measurement. This involves a significant change in mercury concentration.

Of all the pathogenic bacteria tested, the number of coliform bacteria (number of Escherichia coli) was the most numerous at the sampling sites. The presence of bacteria in the water makes it impossible to consume. In the winter series, microbial activity decreased due to lower temperatures.

Due to the way the area in the immediate vicinity is developed, the quality of the spring's water should be monitored to prevent people from taking in unfit for drinking water, which may lead to diseases of the digestive or nervous system. Further measurements are planned to determine the seasonality of water quality changes in this source. Additionally, it is planned to conduct research in other sources located in karst areas in this part of the country.

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