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MONITORING OF SPRING WATER QUALITY

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Abstract. Water is a strategic resource for every country. In recent years, the level of pollution in many water bodies has increased significantly. Military operations on the territory of Ukraine have caused great damage to natural resources. To identify possible sources of water supply, it is necessary to monitor the water quality of natural water bodies. Water samples from six forest springs located a short distance from the city of Przemyslany were taken at different times of the year. The water in all samples is clear, without turbidity or color, and odorless at 20 °C and 60 °C. The total water mineralization, pH, and nitrate content were measured. The water hardness, calcium and magnesium content were determined by the complexometric titration method. The study of physical and chemical indicators of water quality of forest springs shows small changes in the studied parameters during the year in five out of six forest springs. The obtained values do not exceed the standards established for drinking water. In the water samples of source No. 6, the nitrate content and total water hardness are high, although they do not exceed the permissible standard values. Significant fluctuations in the nitrate content of water samples from source No. 6 were found throughout the year. The use of such water for drinking and production needs may have a potentially harmful effect. The water of the studied springs requires further research and can be considered as an alternative source of water supply.

Keywords: water quality, chemical parameters, water resources, water quality assessment.

1. Introduction

Water is a strategic resource, the national wealth of each country, which not only ensures the quality of life and health of people, but also the opportunities for economic development of the entire society. The importance of efficient use of water resources and monitoring of pollution of natural water bodies is evidenced by the fact that this issue is one of the main goals of sustainable development. In 2023, the UN Conference adopted the Water Agenda for Action, which focuses on the problems and solutions to the water crisis and provides for sustainable water management (Historic UN conference, 2023). Water resources are unevenly distributed on the planet. Ukraine belongs to the group of countries with limited water resources and is one of the least water-scarce countries in Europe per capita (Derzhvodahentstvo, 2021). Over the past decades, there has been a decrease in clean water reserves and significant pollution due to use for industry, agriculture, and domestic needs. Global warming and climate change (Liuta et al., 2023; Kravets et al., 2023) are causing an increase in water evaporation. This leads to a decrease in surface water levels, shallowing of natural reservoirs, dehydration and even drying up of springs and rivers.

Monitoring the quality of natural water allows us to systematize and analyze data on the state of water sources, to predict possible changes, which is the basis for justifying optimization measures. A new report published recently by the European Commission indicates that most surface waters in Europe are contaminated with chemicals (Europe's state of water, 2024). Only 39.5 % of surface waters of rivers and lakes can be classified as "good". The situation with groundwater in Europe is better – 86 % has a

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good ecological status, although in most EU countries nitrates from agriculture are present in groundwater. "With most countries expected to miss the EU target for all surface water to be in "good" status by 2027, failure to act could result in legal action" (Europe's state of water, 2024). In order to prevent the situation with water pollution from worsening, urgent decisions need to be made regarding the treatment of water supply and continuous monitoring of water bodies. Among the main priorities of the EU's drinking water policy is to ensure adequate purity of drinking water to protect human health, to ensure quality control of drinking water and effective monitoring. The Drinking Water Directive (Drinking Water Directive, 2020), which is the main EU document on drinking water, has strengthened water quality standards. In some positions, they are stricter than the recommendations of the World Health Organization (Guidelines for drinking-water-quality, 2017). Attention is also focused on new pollutants, such as microplastics, per- and poly-fluoroalkyl substances (PFAS), endocrine disruptors (European Commission, 2024).

To characterize water quality, the maximum permissible values of physical, chemical, and biological indicators are regulated by the normative standards (DSanPiN 2.2.4-171-10, 2010). There is no single indicator for a comprehensive assessment of water quality. To determine the suitability of water for industrial or domestic use, it is necessary to determine the physical, chemical, and biological indicators of water quality. The analysis of water from a particular source establishes the composition and concentration of impurities, the degree and nature of water pollution, and the degree of its epidemiological and toxicological safety. Based on the results obtained, the necessary water treatment methods are selected.

The quality of drinking water should be controlled by standards based on modern scientific research. To assess the environmental safety of water supply, it is advisable to conduct a comprehensive assessment of the water source. Systematic sampling and determination of water quality benchmarks should be combined with their analysis and assessment of the likelihood of possible negative impact, primarily on the human body. The authors S. L. Vasylenko and V. Y. Kobyliansky (Vasylenko & Kobylianskyi, 2015) consider a method of comprehensive assessment of water quality in municipal water supply systems, which considers the indicators of harmfulness, their maximum permissible concentrations in drinking water and spatial and temporal features of water supply systems. This comprehensive assessment of drinking water quality is based on the use of a ranking of quality indicators and control points of a significantly branched water supply network. Quality indicators are differentiated by the hazardousness and hazard classes of pollutants (properties) using cumulative coefficients and normalization against the normative values of indicators − as a rule, maximum permissible concentrations. The final comprehensive assessment is reduced to a specific parameter in the form of a numerical value.

Considering the cumulative impact of chemical harmlessness indicators on human health allows to calculate an integral indicator of drinking tap water quality (Romanchuc & Bashinska, 2019). The use of probable estimates of the development of adverse effects in the human body allows for an integrated assessment of water quality by chemical harmlessness indicators using the thresholdless model method. This approach involves assessing the potential risk to human health, considering the negative long-term impact of hazardous toxic compounds contained in drinking tap water on the human body, which, in turn, is manifested in the increase in the incidence of the population that constantly consumes water of substandard quality.

In article (Krysinska & Klymenko, 2021), it is proposed to use methods for calculating environmental risk to assess environmental safety. The authors found that even if individual indicators of the content of harmful substances in drinking water did not exceed the maximum permissible concentrations, their combined effect showed a potential environmental risk.

Military operations on the territory of Ukraine have a negative impact on the state of water systems and water purity. A huge amount of pollutants, including oil products, fuels and lubricants, and aggressive chemicals, are entering the soil and water bodies. The aggressor's destruction of the infrastructure of settlements, water treatment plants and wastewater treatment facilities significantly worsen the quality of our country's water resources. Since up to 80 % of drinking water is obtained from surface water bodies, the quality of water in natural reservoirs is an important issue that affects human health (Vodna stratehiia Ukrainy do 2050, 2022). The growing use of fresh surface and groundwater requires systematic studies of the state of water bodies, implementation of innovative strategies and technologies for water purification of surface water bodies (Malovanyy et al., 2021; Grechanik et al., 2023). According to (DSanPiN 2.2.4-171-10, 2010), it is recommended to give preference to groundwater as a source of drinking water supply. At the same time, water from surface natural sources is used for drinking purposes in a large part of our country. The aim of this work is to monitor the quality of water from forest springs by physical and chemical indicators and evaluate the results. This will allow us to determine the possibility of using water as an alternative source of water supply for domestic and industrial needs.

2. Materials and methods

The water of six forest springs in the Peremyshlyanska territorial community was chosen as the object of study (Fig. 1). The springs are located within a radius of 10 kilometers. This water is consumed by the local population as an alternative to tap water. Water samples were collected during 2024 at different times of the year. Three water samples were collected from each source four times, in particular on January 29; April 15; June 10; and October 17.

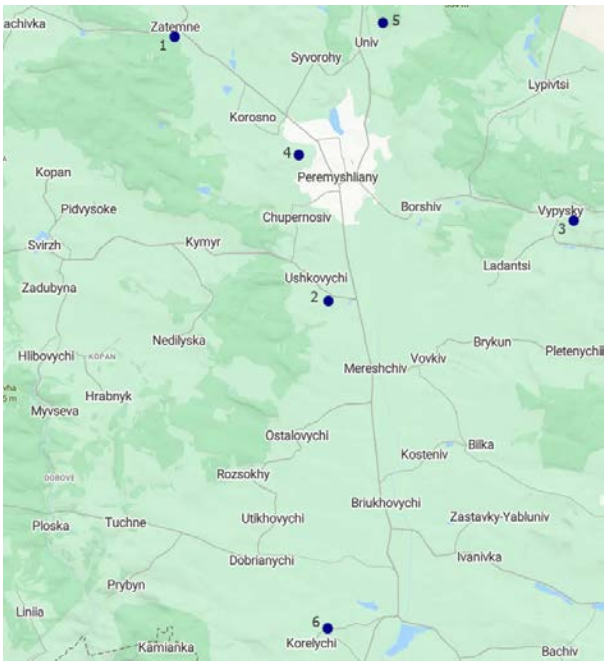

Fig. 1. Localization of the studied sourcesin the Peremyshlyany region: 1 – village Zatemne; 2 – village Ushkovychi; 3 – village Vypysky; 4 – district “Synii Kamin” (town Peremyshliany); 5 – village Univ; 6 – village Korelychi

Sampling was carried out in accordance with DSTU ISO 5667-6:2009 (DSTU ISO 5667-6:2009, 2009). For surface water sampling, special containers were used, the design of which ensures complete tightness to prevent leakage or ingress of foreign substances into the sample. The material used to make such containers must be chemically inert, i. e., not react with the components of the sample, not change its chemical composition, and not cause any physical or chemical changes during storage. Water samples were collected in clean glass containers. The volume of one water sample was at least 1 dm^3.

Water quality indicators were determined no later than 24 hours after sampling. Chemical parameters of water were determined in accordance with current standards (DSTU ISO 6059:2003, 2003). The quality of drinking water was assessed by comparing the results with the standards (DSanPiN 2.2.4-171-10, 2010). To measure acidity, mineralization, and electrical conductivity, the EZ-9908 device (China) was used, and the nitrate concentration was determined using the Nitratometer H-405 (Ukraine).

3. Results and discussion

Visual examination showed water transparency, no turbidity or coloration in all samples, and no odor at 20 °C and 60 °C.

At the first stage, we determined the hydrogen index, total mineralization and conductivity (Table 1).

The hydrogen index reflects the concentration of hydrogen ions in water. It is determined by the pH value, which is the negative logarithm of the concentration of hydrogen ions: pH = –lg[H+]. In a neutral environment, pH is 7, in an acidic environment, pH is less than 7, and in an alkaline environment, pH is greater than 7. It is one of the key indicators of water quality that determines the nature of chemical and biological processes in it. Usually, the pH value is in the range where it does not directly affect the consumer properties of water. At the same time, it is known that at low pH, water exhibits high corrosive activity, and at high values (pH > 11) it acquires an unpleasant odor and can cause eye and skin irritation. Therefore, for drinking and household water, the optimal pH level is between 6.5 and 8.5, according to Sanitary and Epidemiological Norms 2.2.4-171-10 (DSanPiN 2.2.4-171-10, 2010).

Table 1

Physical and chemical indicators of water quality in the Peremyshlyany region

Indicator	*Valid indicator	Sample 1, Zatemne	Sample 2, Ushkovychi	Sample 3, Vypysky	Sample 4, "Synii Kamin"	Sample 5, Univ	Sample 6, Korelychi	Water samplingtime, month
Hydrogen index, pH	6.5–8.5	7.21	7.45	6.70	7.27	7.06	7.21	01
		7.28	7.55	6.76	7.30	7.16	7.31	04
		7.31	7.75	7.46	7.50	7.53	7.52	06
		7.30	7.72	7.40	7.51	7.54	7.48	10
Total mineralization, mg/dm^3	≤1000	221	98	275	152	276	179	01
		231	115	294	175	169	175	04
		248	126	230	186	220	170	06
		243	131	225	185	276	158	10
Nitrate content, mg/dm^3	≤50	10.4	7.6	21.7	11.5	10.2	16.6	01
		13.0	7.7	47.2	13.6	8.6	11.6	04
		11.2	7.5	31.2	12.4	7.8	15.8	06
		10.5	9.9	28.2	12.0	8.2	14.2	10

** Due to (DSanPiN 2.2.4-171-10, 2010).*

As can be seen from the data in Table 1, the pH values in the studied samples of spring water are within the normal range. Slight fluctuations in the hydrogen index during the year in the water samples are explained by the higher intensity of oxidative processes at higher temperatures in the warm seasons. In the water samples from the source of the village of Vypylyky, the pH value varies significantly throughout the year (Fig. 2).

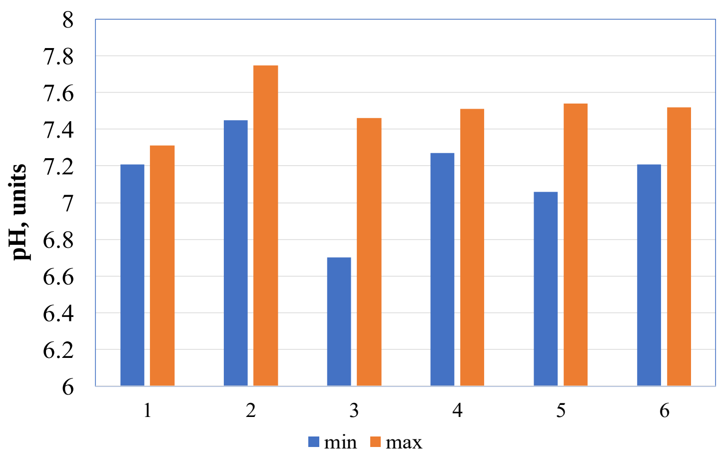

Fig. 2. Changing of Hydrogen index of spring water: 1 – village Zatemne; 2 – village Ushkovychi; 3 – village Vypysky; 4 – district "Synii Kamin" (town Peremyshliany); 5 – village Univ; 6 – village Korelychi

Water salinity is determined by the total content of dissolved salts. The most common salts are inorganic salts, including bicarbonates, chlorides and sulfates of calcium, magnesium, potassium and sodium, as well as a small amount of organic matter. The level of mineralization of drinking water characterizes the quality of natural sources. In addition to natural factors, the overall mineralization is significantly affected by the possibility of contaminants from agricultural and industrial activitiesentering the soil and surface water layers. In general, water with a salt content of up to 600 mg/dm^3 is considered to have a pleasant taste. According to organoleptic indicators, the recommended upper limit of mineralization is 1000 mg/dm^3. According to the standards for drinking water approved by the World Health Organization, there are no clear requirements for the salt content of water. In natural waters, the salt content is allowed up to 1500 mg/dm^3 (DSanPiN 2.2.4-171-10, 2010). In the studied water samples, the lowest value of total mineralization was in sample 2 (Ushkovychi spring) – 98 mg/dm^3, and the highest in sample 3 (Vypysky spring) – 294 mg/dm^3. The total water salinity slightly increases in spring and summer (Fig. 3) and is within the normal range for drinking water.

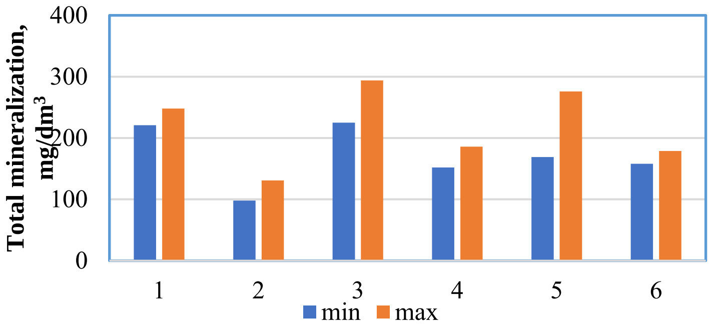

Fig. 3. Change in total mineralization of spring water: 1 – village Zatemne; 2 – village Ushkovychi; 3 – village Vypysky; 4 – district “Synii Kamin” (town Peremyshliany); 5 – village Univ; 6 – village Korelychi

Nitrates in water are a common pollutant in surface water sources. The main reason for nitrates in water is the often excessive use of mineral fertilizers and pesticides in agriculture. Nitric acid salts are highly soluble in water, so after entering the soil, they easily pass into the surface water. As a result, nitrates contaminate large areas of soil and rivers, lakes, reservoirs, as well as wells and shallow boreholes. Water contaminated with nitrates is clear in appearance, without turbidity, has a pleasant taste, and no aftertaste. The use of nitrate-contaminated water for drinking purposes can be harmful to human health, causing severe disorders of the nervous system and gastrointestinal tract. According to national standards, the concentration of nitrates in drinking water should not exceed 50.0 mg/dm^3 for tap and well water and 10.0 mg/dm^3 for packaged water.

The results of determining the concentration of nitrate ions in the source water samples (Table 1) show a relatively high nitrate content – up to 47.2 mg/dm^3 in sample 3 (source of the village of Vypysky). This may be due to seasonal runoff from agricultural land located higher up the landscape. Although this figure does not exceed the norm, the systematic use of such water poses a potential environmental risk. Our studies of the nitrate content in the water of forest springs showed a slight fluctuation of the determined indicators depending on the season of the year (Fig. 4).

Water samples from five other sources showed low levels of nitrate, ranging from 7.6 mg/dm^3 to 16.6 mg/dm^3. This is likely due to the considerable distance from agricultural lands. The presence of nitrates in the water of forest springs is due to natural processes of nitrogen cycling in nature, in particular, during the decomposition of microorganisms, animal and plant proteins. In general, the nitrate content in the spring water does not exceed the regulatory values.

The water hardness is determined by the presence of dissolved calcium and magnesium salts. High hardness worsens the organoleptic properties of water, as it adds a bitter taste. Consumption of such water has a negative impact on the digestive system. It is optimal to use water with a total hardness of 3–4 mmol/dm^3 for drinking purposes. Water hardness is divided into temporary (carbonate) and permanent (non-carbonate).

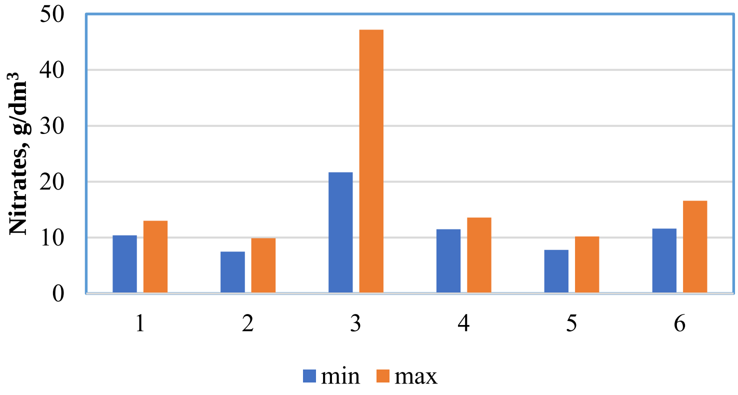

Fig. 4. Change in nitrate content of spring water: 1 – village Zatemne; 2 – village Ushkovychi; 3 – village Vypysky; 4 – district "Synii Kamin" (town Peremyshliany); 5 – village Univ; 6 – village Korelychi

The total water hardness, which is the sum of carbonate and non-carbonate hardness, is determined by the titrimetric method of analysis (titration with Trilon B solution in the presence of ammonium buffer and chromogen black indicator). We found that samples from sources 1 and 3 are characterized by the highest total hardness (Table 2). Water with a hardness of less than 2 mmol/dm^3 is called soft, from 2 to 10 – medium, and more than 10 – hard, so according to the results of the analysis of water samples from all studied sources, the samples are classified as water with medium hardness in terms of total hardness.

Temporary water hardness is caused by calcium and magnesium bicarbonates dissolved in water. The value of temporary water hardness was determined by titration with hydrochloric acid in the presence of methyl orange. For all water samples, the value of temporary hardness is in the range of 4.70–5.85 mmol/dm^3.

Table 2

Indicators of spring water hardness

Indicator	*Valid indicator	Sample 1, Zatemne	Sample 2, Ushkovychi	Sample 3, Vypysky	Sample 4, "Synii Kamin"	Sample 5, Univ	Sample 6, Korelychi	Water samplingtime, month
Total hardness, mmol/dm^3	≤7.0–10.0	7.10	4.90	6.50	5.80	5.90	5.76	01
		7.20	5.18	7.82	5.82	6.10	5.80	04
		7.16	5.10	7.20	5.80	6.10	5.80	06
		7.19	5.10	7.10	5.80	6.00	5.75	10
Carbonate hardness, mmol/dm^3	–	5.85	4.70	5.85	4.80	5.72	5.00	01
		5.63	4.65	5.90	4.75	5.70	5.00	04
		5.85	4.68	5.90	4.80	5.80	5.10	06
		5.85	4.65	5.80	4.80	5.75	5.10	10
Calcium content, mg/dm^3	25–75	122.20	78.1	114.3	90.2	100.2	96.20	01
		121.04	86.17	127.45	94.19	110.22	96.99	04
		122.12	82.10	120.50	92.60	107.12	96.00	06
		122.10	80.50	118.2	93.00	102.30	95.40	10
Magnesium content, mg/dm^3	10–50	12.15	12.15	9.72	15.80	10.94	11.66	01
		14.09	10.69	17.74	13.61	7.29	11.66	04
		12.15	11.22	14.72	14.3	9.24	11.65	06
		12.11	13.15	14.60	14.08	10.87	12.02	10

* *Due to (DSanPiN 2.2.4-171-10, 2010).*

The determination of physical and chemical water quality indicators allows for an initial assessment of the water's suitability for use. According to the Sanitary and Epidemiological Norms and Regulations 2.2.4-171-10 "Hygienic Requirements for Drinking Water Intended for Human Consumption", the total hardness should be less than 10 mmol/dm^3, and as an indicator of physiological adequacy, it should be in the range of 1.5–7 mmol/dm^3. Indicators of the physiological adequacy of drinking water quality characterize the extent to which its mineral composition meets the biological needs of the human body. According to Fig. 4, the experimentally determined values of total water hardness of all s ources meet the requirements of regulatory indicators for spring and tap water, as well as, except for sources 1 and 3, indicators of physiological adequacy. In the studied water samples, carbonate hardness prevails (Table 2). The content of the chemical elements Magnesium and Calcium in all the studied samples is within the optimal limits.

Despite the results that indicate that the source water meets the requirements, the obtained results should be processed in terms of a comprehensive assessment and obtaining an integral indicator of source water quality. Accordingly, the next stage of our research will be to obtain an integral indicator using fuzzy logic tools.

4. Conclusions

The conducted studies of physical and chemical indicators of water quality show a slight change in their values during the year. For water samples from five springs, the values of the main chemical indicators of water quality do not exceed the normalized values of total mineralization, pH, nitrate content, water hardness, calcium and magnesium content. Water from the source of the village of Vypysky has a rather high content of nitrates, total hardness, and these indicators change significantly during the year, indicating a significant impact on the component composition of the source of surface water subjected to anthropogenic impact. Seasonal factors such as precipitation, agricultural activities on nearby land, and biological processes at different temperatures can have a significant impact on the composition of surface water sources. The use of such water requires preliminary treatment. The water from the Peremyshlyanshchyna springs can be recommended as an alternative source of water supply for industrial needs. Further study is required to determine biological indicators, new pollutants such as microplastics and obtain an integral indicator of spring water quality.

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