Research Article

Monitoring of drinking water from the karst springs of the Ljuberadja-Niš water supply system (Serbia)

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Abstract

The Ljuberadja-Niš water supply system is one of the main components of the Niš water supply system. This system consists of a series of natural, karst springs of groundwater (Krupac, Mokra, Divljana, Ljuberadja), with the capacity of 800–1450 L/s. The most important factors in a healthy drinking water supply are the proper choice and protection of water springs. Considering that water composition may sometimes have an adverse effect on consumer health, production processes in some industries and also on facilities and water company equipment, the aim of this paper was to examine water composition and to monitor its quality by analyzing the physical, chemical, and microbiological indicators. Water quality is tested in accordance with the corresponding directives and regulations of national and international authorities. The analysis of drinking water encompassed the appointment of the following parameters (quality indicators): physical parameters: temperature, turbidity, pH value and electrical conductivity of water; chemical parameters: chloride, ammonia, nitrite, nitrate, sulfate, calcium, magnesium, iron, manganese, aluminum and chromium in the form of Cr^{6+} and Cr^{3+} ions; microbiological parameters: culturable organisms, total and fecal coliform bacteria, intestinal enterococci, sulfite reducing clostridia, *Pseudomonas aeruginosa* and *Proteus* strain. Monitoring has confirmed the hygienic and health adequacy of the water distributed to cosumers.

Keywords Drinking water · Monitoring · Quality indicators

1 Introduction

The most important factors in a healthy drinking water supply are the proper choice and protection of water springs [39]. Groundwater is the most reliable source of drinking water because of the minimized anthropogenic influence like the widespread use of chemical fertilizers and rapid urbanization of populated areas extending beyond the protected sanitary catchment zones [3].

In northern Europe, groundwater exploitation has substantially increased in the past two centuries. Nowadays, a significant part of western and central Europe obtains drinking water from groundwater springs. For citizens of Italy, Iceland, Austria, Denmark, and Lithuania groundwater accounts for nearly 90% of the total water consumption. With the citizens of France, Sweden, and Finland that percentage is around 50% and it is similar in Germany and the Netherlands (50–79%). In England, 30–35% of drinking water is groundwater, whereas in Norway, the percentage is the lowest—about 15% [25]. It is estimated that groundwater satisfies about 70% of the water demand in Serbia [4].

Natural phenomena may affect water quality at spring sites:

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– Air, water and ground and precipitation temperature changes;
– Drainage via the surface of the ground, dipping, physical, chemical, biological and biochemical changes of water composition on the surface and in the ground;
– Contamination by organisms in nature.

Fecal contamination of water springs is still a global issue, particularly in countries with low and medium income. The latest study performed in Indonesia estimates that the greatest risks of intestinal infections appear as a result of fecal contamination in spring and well water [14]. Agricultural activities such as the application of manure to arable land and grazing cattle in pastures offer economic and ecological advantages, but on the other hand, they pose a risk of microbiological contamination in water springs [32]. *Escherichia coli* (*E. coli*), which is an indicator of fecal contamination, is part of the microbiological flora of human and animal feces, and it can be found in wastewaters, all natural waters and in the ground. *E. coli* and intestinal enterococci are marked by the World Health Organization as the general indicators of fecal contamination of water [42, 45].

The Ljuberadja-Niš water supply system is one of the main components of the Niš water supply system. It supplies about 250,000 residents of the city of Niš and the local economy. This system consists of a series of natural, karst springs of groundwater (Krupac, Mokra, Divljana, Ljuberadja), with the capacity of 800–1450 L/s.

Ljuberadja Spring is a sprawling karst spring consisting of a series of separate springs in the valley of the Lužnica upstream from the village of Ljuberadja at a length of 500 m. Between 1981 and 1984, five springs were tapped and incorporated into the water supply system of Niš. Good-quality groundwater flows out of karstified limestone from the Lower Cretaceous with the capacity ranging between 450 and 5500 L/s (Fig. 1).

Divljana Spring is located on the left bank of the Koritnica, opposite the village of Divljana in close proximity to the Bela Palanka-Babušnica road. It has been in the city's water supply system since 1984. The main reservoirs of groundwater are carbonate deposits (limestone) from the Lower Cretaceous with the flow capacity ranging from the minimum 45–60 L/s to the maximum 1500 L/s (Fig. 2).

Mokra Spring in the vicinity of the village of Mokra and at the foot of Suva Planina is essentially the source of the Mokranjska river, which is the left tributary to the Koritnica. It has been in the city's water supply since 1984. From a lithological perspective, almost the entire drainage basin of the spring is built of carbonate rocks—limestone and dolomite from the Lower Cretaceous. The average perennial yield is 310 L/s (Fig. 3).

Krupac Spring penetrates the rocky mass at the village of Krupac where the sides of the mountains around

Fig. 2 Divljana Spring

Fig. 1 Ljuberadja Spring

Fig. 3 Mokra Spring

Svrljig steeply descend into the basin of Bela Palanka. Between 1981 and 1984, the spring was tapped and introduced into the water supply system of Niš. It is a common karst spring and Cretaceous limestone predominates in its collecting area. It is categorized as the highest yield spring but simultaneously one of its characteristics is large yield fluctuations ranging from the minimum of 35 L/s to the maximum of 10,000 L/s (Fig. 4).

The area has a moderate continental climate with prevailing mountainous climate, with average annual precipitation of 602 mm and the average annual air temperature of 11.3 °C (Fig. 5).

After chlorination (with gas chlorine) the water from these springs is directed to the Vinik reservoir and is thereafter distributed to consumers.

Water analysis is conducted with adherence to set rules pertaining to sampling and it involves ascertaining the physical, chemical and microbiological indicators of water quality.

Considering that water composition may sometimes have an adverse effect on consumer health, production processes in some industries and also on facilities and water company equipment, the aim of this paper was to examine water composition and to monitor its quality by analyzing the physical, chemical and microbiological indicators.

Bacteria concentrations may be used for mathematical modeling with the view of predicting bacteriological contamination of natural water [19]. However, modeling cannot anticipate low concentrations of fecal contamination whereby water quality monitoring remains a priority in assessing intestinal infection health risks and waterborne disease risks [36].
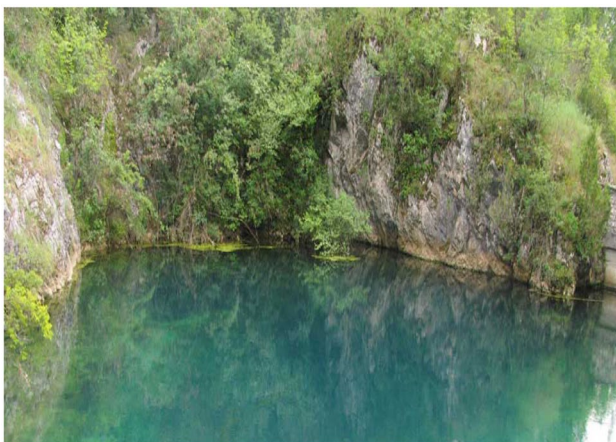

Fig. 4 Krupac Spring

2 Materials and methods

2.1 Water quality monitoring

Water quality is tested in accordance with the corresponding directives and regulations of national and international authorities. In the Republic of Serbia, drinking water quality is determined by the Ordinance on the hygienic adequacy of drinking water in the Republic of Serbia [35] which is aligned with the Europian Union Council Directive 98/83/EC [7], US EPA, Edition of the Drinking Water Standards and Health Advisories, EPA 822-S-12-001 [38] and the WHO, Guidelines for Drinking-water Quality [44]. Drinking water quality is regulated by the stipulation of maximum permitted levels of certain parameters.

Physicochemical and microbiological drinking water quality monitoring is accomplished by performing basic and periodic sample examinations of natural spring water (before disinfection with gas chlorine) and chlorinated water from the Vinik reservoir (after disinfection with gas chlorine and before discharge into the distribution system).

Sample testing was performed in an accredited laboratory, JKP "Naissus" Niš (SRPS ISO/IEC 17025: 2006). Water samples for physicochemical and microbiological examinations were taken by experts in accordance with the standards: SRPS EN ISO 5667-1:2008, SRPS EN ISO 5667-3:2017, SRPS EN ISO 5667-5:2008 and SRPS EN ISO 19458:2009.

2.2 Quality indicators (parameters) and methods

The analysis of drinking water encompassed the appointment of the following parameters:

Physical parameters (methods): temperature (SRPSH. Z1.106:1970), turbidity (EN ISO 7027: 1999), pH (EN ISO 10523:2008) value and electrical conductivity (SRPS EN 27888:2009) of water.

Chemical parameters (methods): chloride (SRPS ISO 9297/1:2007 revision 1), ammonia (SRPS.H.Z1.184:1974), nitrite (SRPS ISO 26777:2009), nitrate (spectrophotometric-Manual P–V-31/C (Standard methods for testing hygienic correctness "Drinking water" [33])), sulfate (USEPA 375.4:1978), calcium and magnesium (USEPA 215.2:1978-Ca, Mg- by calculation from calcium), iron (SRPS ISO 6332:2003), manganese (spectrophotometric-Manual P–V-26A (Standard methods for testing hygienic correctness "Drinking water" [33])), aluminum (ISO 10566:1994) and chromium in the form of Cr^{6+} and Cr^{3+} ions (ISO 11083:1994(E)).

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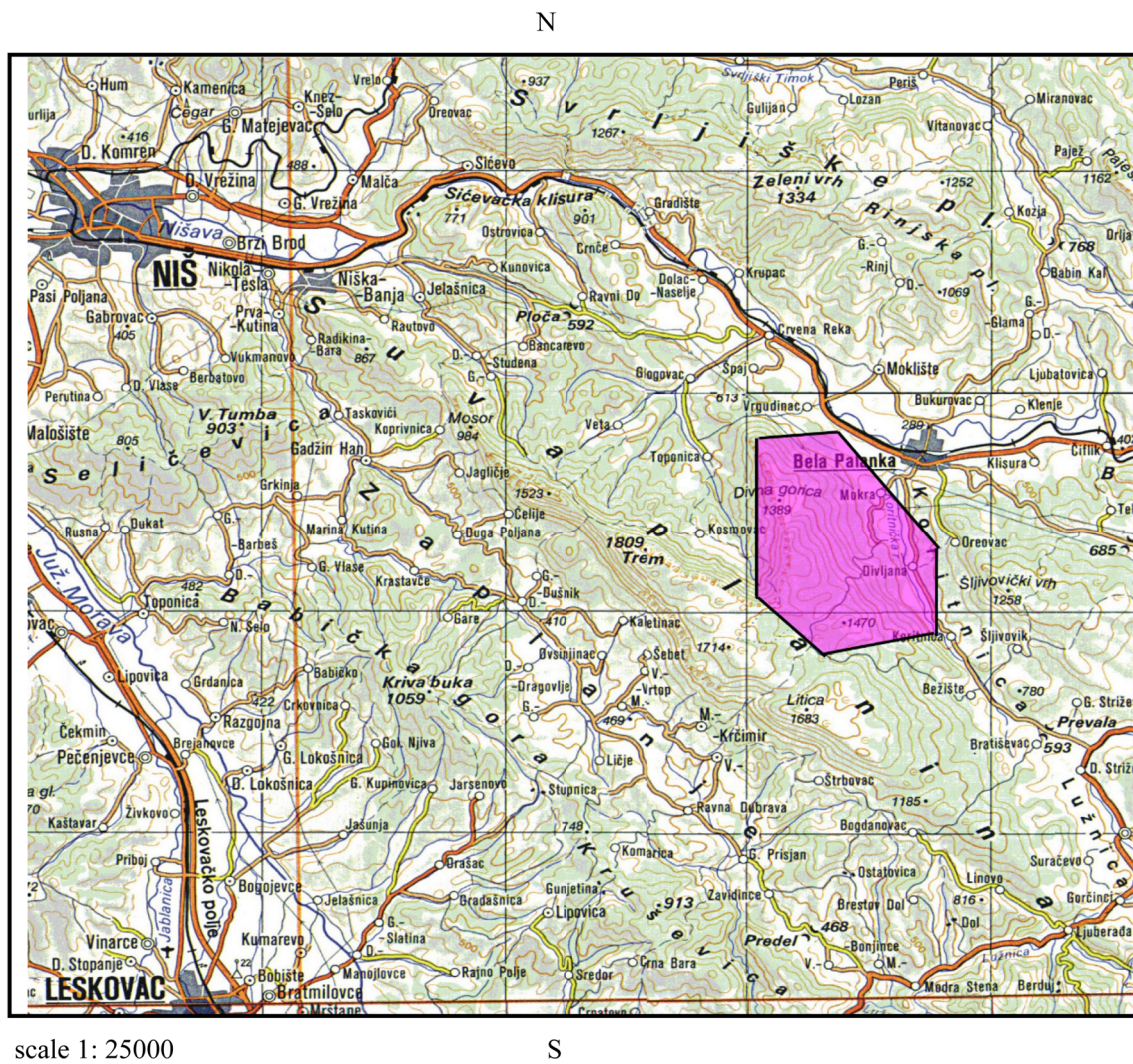
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Research area (about 52 km^2)

Fig. 5 Map of the research area

Microbiological parameters (methods): culturable organisms (SRPS EN ISO 6222: 2010); total and fecal coliform bacteria (SRPS EN ISO 9308-1:2010); Intestinal enterococci (SRPS EN ISO 7899-2:2010); sulfite reducing clostridia, *Pseudomonas aeruginosa* and *Proteus* strain (methods in the Manual (Standard methods for testing hygienic correctness "Drinking water" [33])).

The water from the water system Ljuberadja-Niš was examined in the period between January 2018 and December 2018 with the sampling frequency of once a month for determining the physical parameters of water,

chloride, ammonia, nitrite, nitrate, Fe, Mn and microbiological parameters. The sampling frequency for Cr^{6+}, Cr^{3+} and Al was four times a year.

3 Results and discussion

3.1 Physical–chemical water quality monitoring

Physical parameters are important indicators of water quality. Temperature measurements, turbidity, pH value

and electrical conductivity results for the springs Divljana, Mokra, Krupac, Ljuberadja, and the Vinik reservoir are presented in Table 1.

Water temperature is not standardized by national and international standards because it does not affect health directly, but it does influence the chemical and microbiological processes in water. In the northern parts of Serbia (where, according to the official data, is the worst water quality in Serbia), in Bačka, the groundwater temperature ranges from 14 to 24 °C [23], while in the Ljuberadja-Niš system water is colder (7.9–18.4 °C).

The chloride concentration in all water samples from the springs and the reservoir is below the method's detection threshold (<5.0 mg/L), and they meet the recommended value and the maximum allowed content. In natural waters, chloride appears in low concentrations, but chloride content increases with mineral content growth. High chloride concentrations raises the electrical conductivity and increase the tendency of water to cause corrosion in distribution systems [34]. Chlorides of themselves are not toxic to humans. For this reason, WHO [44] did not issue chloride directives. According to US EPA [38], chloride concentration in drinking water poses no risk to human health which is why a secondary maximum contaminant level (MCL) of 250 mg/L was issued (same as the Ordinance on the hygienic adequacy of drinking water in the Republic of Serbia [35]). At higher concentrations, chlorides give water a salty taste. According to the EU Directive [7], the maximum allowed content for chlorides is 200 mg/L. In Serbia, Banat, groundwater has low chloride content ranging from 5 to 50 mg/L [22].

The ammonium-nitrogen concentration (NH_4^+–N) in all water samples from the springs and the reservoir is below the method's detection threshold (<0.04 mg NH_4^+–N/L) and they meet the recommended value and the maximum allowed content. The natural level of ammonia in groundwater is generally lower than 0.2 mg/L. High concentrations may be expected in layers rich in humic acid or iron. The presence of ammonia in concentrations higher than the geological level is an important factor for fecal contamination. Research indicates that monitoring low levels of free ammonia in chloraminated water is important for effectively managing potable water disinfection [12]. Ammonia is not of direct relevance to human health in concentrations expected in drinking water so WHO [44] and US EPA [38] did not set guidelines for this parameter. According the Ordinance on the hygienic adequacy of drinking water in the Republic of Serbia [35], the maximum allowed concentration for ammonium ion is 0.5 mg/L. In Serbia, southern Banat, groundwater has low ammonium ion content from 0.72 to 2.75 mg/L [22].

Nitrates and nitrites may occur in water naturally, but anthropogenic processes are the most common causes:

excessive use of inorganic nitrogen fertilizers, wastewater, cesspools, runoff from farms, industrial wastewater, etc. Nitrite is an unstable nitrogen form and bacteria relatively quickly convert it into nitrate which is why nitrite concentration in an ecological environment such as water is very low even when nitrate concentration is high. Nitrate concentrations at the exit of the waterworks are highly correlated with nitrate concentrations within the distribution net or at the consumers' taps, while nitrite and ammonium concentrations are generally lower within the net compared with the exit of the waterworks due to nitrification [30]. According to WHO [44], the border limit for nitrates in drinking water is 50 mg/L (or 11 mg NO^{3-}–N/L). It is based on the epidemiological evidence of methemoglobinemia in children appearing after brief exposure. The limit for nitrite is 3 mg/L (or 0.9 mg NO^{2-}–N/L). Due to the possibility of a simultaneous nitrite and nitrate presence in water, the sum of the concentration ratio of each component and its limit value cannot exceed 1. US EPA [38] set the maximum allowed concentration for nitrates (measured as N) and nitrites (measured as N) of 10 mgNO^{3-}–N/L and 1 mgNO^{2-}–N/L, respectively. An infant under six months consuming water with nitrates and nitrites in concentrations higher than the maximum contamination level may get sick or even die. Symptoms include shortness of breath and blue baby syndrome. According to the EU Directive [7] the upper limit for nitrate and nitrite presence in drinking water is 50.0 mg/L and 0.5 mg/L respectively, under the condition that {[nitrates]/50 + [nitrites]/3} ≤ 1. According to the Ordinance on the hygienic adequacy of drinking water in the Republic of Serbia [35] the maximum allowed concentration for nitrates is 50.0 mg/L and 0.03 mg/L for nitrites. The nitrate-nitrogen concentration NO^{3-}-N/L in all water samples from the springs and the reservoir with the highest measured value of 3.9 mg/L are far below the recommended values and the maximum allowed content. (Table 1). The nitric nitrogen concentration (NO^{2-}–N) in all water samples from the springs and the reservoir are below the method's detection threshold (0.005 mgNO^{2-}–N/L) and therefore meet the recommended values and the maximum allowed content. In the USA, Texas, a region that aside from oil and natural gas production also engages in agriculture, the groundwater nitrate concentration varies from <0.44 to 149 mg/L whereby in 3 out of 40 water samples nitrate concentration exceeds the national standard of 44 mg/L [13]. Statistics show that nitrate concentration drops with well depth [13].

The greatest sulfate concentration was measured in the Vinik reservoir 16.8 mg/L in March whereas the lowest concentration was measured at Divljana Spring 6.20 mg/L in September (Table 1). Sulfates are the least toxic anions. Available literature does not indicate a sulfate concentration in water that may be detrimental to health.

Table 1 An annual basis representation of temperature, color, turbidity, pH value, electrical conductivity, nitrate, Ca, Mg and sulfate of raw water from the springs Divljana (D), Mokra (M), Krupac (K) and Ljuberadja (Lj), and chlorinated water from the Vinik (V) rezervoir

Month	January	February	March	April	May	June	July	August	September	October	November	December
Temperature (°C)												
D	11.9	12.9	11.4	11.3	10.7	13.0	13.4	14.5	14.4	14.8	12.2	10.4
M	14.0	17.1	11.4	13.4	11.6	12.6	18.0	14.8	15.3	18.4	17.3	14.0
K	12.1	11.4	10.9	10.7	10.9	12.9	13.1	14.8	14.8	11.3	11.3	7.9
Lj	8.7	13.0	10.4	11.1	11.1	13.9	12.1	14.4	14.1	13.2	10.6	8.3
V	11.4	11.0	11.0	11.7	11.2	12.4	13.9	16.7	16.1	13.9	14.4	11.7
Turbidity (NTU)												
D	<0.20	<0.20	0.30	0.36	0.21	0.67	0.38	0.25	0.80	<0.20	0.28	*1.30*
M	<0.20	0.25	0.33	0.33	0.33	0.60	0.30	0.25	0.20	0.24	0.25	*1.55*
K	0.48	*5.70*	0.37	0.30	0.22	0.36	0.74	0.29	0.60	0.22	0.31	*5.40*
Lj	0.81	0.60	0.52	0.54	0.71	0.67	0.48	0.45	0.57	0.24	0.60	*1.70*
V	0.29	0.28	0.34	0.24	0.2	0.4	0.55	0.48	0.37	0.3	0.24	<0.20
pH value												
D	7.36	7.32	7.35	7.36	7.36	7.42	7.52	7.50	7.52	7.47	7.36	7.37
M	7.30	7.23	7.32	7.41	7.33	7.40	7.42	7.47	7.37	7.45	7.38	7.36
K	7.40	7.34	7.35	7.40	7.46	7.40	7.40	7.45	7.29	7.36	7.51	7.28
Lj	7.40	7.45	7.40	7.39	7.45	7.46	7.55	7.56	7.52	7.48	7.40	7.49
V	7.40	7.31	7.26	7.39	7.35	7.48	7.39	7.39	7.39	7.40	7.40	7.43
Electrical conductivity (µS/cm)												
D	454	451	467	450	458	460	454	450	454	460	460	474
M	465	467	469	450	465	460	463	460	474	466	460	477
K	497	494	487	480	483	492	510	503	511	503	498	501
Lj	436	435	450	456	454	456	448	444	448	455	459	451
V	465	478	466	457	460	457	487	463	468	493	464	462
NO^{3-} (mg/L)												
D	3.5	2.7	1.9	2.7	2.3	2.3	2.5	2.6	3.0	3.1	3.0	2.4
M	4.1	3.2	3.4	3.7	3.2	2.8	3.1	3.4	3.4	3.3	3.6	2.4
K	3.7	3.5	2.5	2.7	2.6	3.2	2.8	3.3	3.5	3.6	3.7	3.3
Lj	3.2	2.7	3.1	2.7	3.5	2.6	2.7	2.9	3.1	3.0	2.9	2.9
V	3.5	3.5	2.9	3.0	2.5	2.8	3.1	3.4	3.2	3.8	3.9	3.5
Ca (mg/L)												
D	89.3	87.2	88.2	88.4	89.23	89.5	90.1	95.5	88.3	97.1	94.2	99.9
M	83.5	87.7	85.2	86.5	88.1	92.4	84.6	82.6	83.4	90.5	97.3	103.1
K	101.7	99.8	102.9	98.6	96.6	90.2	93.4	97.7	97.4	99.2	92.5	103.9
Lj	86.2	88.7	89.6	82.2	90.2	81.8	83.9	84.1	85.2	88.2	90.2	90.3
V	85.7	83.6	82.8	84.4	86.1	90.9	89.2	87.6	89.9	84.3	89.5	88.7
Mg (mg/L)												
D	9.2	8.7	10.3	6.8	8.7	8.6	9.2	10.4	10.7	7.6	8.5	5.3
M	12.1	10.4	11.5	8.2	13.9	8.1	11.9	13.0	13.3	8.9	6.4	2.2
K	9.4	7.9	7.6	7.8	8.7	10.4	9.1	10.2	9.2	9.3	8.6	7.8
Lj	7.3	9.1	9.6	5.4	8.4	10.9	9.3	7.9	7.5	7.4	9.2	6.5
V	10.7	7.8	14.1	8.6	8.4	7.2	10.8	12.8	12.9	9.2	7.9	6.4
$SO4^{2-}$ (mg/L)												
D	14.8	12.4	14.3	9.3	8.1	8.1	8.8	16.4	6.2	10.2	13.5	7.8
M	13.3	11.9	13.2	7.6	10.5	8.1	7.8	14.5	7.1	9.5	8.7	8.0
K	12.6	8.8	9.4	12.1	6.9	13.0	7.4	13.2	6.8	11.6	9.6	8.8
Lj	10.6	7.9	10.6	8.4	9.7	11.2	9.1	7.9	7.7	9.0	10.6	8.9
V	13.5	9.2	16.8	8.7	10.6	15.8	8.9	9.3	11.8	10.2	11.4	7.8

Studies suggest that in concentrations between 1000 and 1200 mg/L sulfates have a laxative effect but without diarrhea, dehydration and weight loss [47]. US EPA [38] categorized sulfates into the secondary group of contaminants and placed a secondary MCL of 250 mg/L. According to the EU Directive [7] under the condition that water is not aggressive and in accordance with the Ordinance on the hygienic adequacy of drinking water in the Republic of Serbia [35], the maximum allowed content for sulfates is 250 mg/L. Sulfate presence in drinking water may affect taste. The lowest threshold for the sulfate taste perception is about 250 mg/L (sodium salt). Also, sulfates may contribute to corrosion in distribution systems [47]. The sulfate concentrations with the greatest measured value of 16.8 mg/L in all water samples from the springs and the reservoir meet the recommended values and the maximum allowed concentration. In Serbia, Banat, groundwater with high arsenic content up to 217 µg/L has a low sulfate concentration ranging from 3 to 90 mg/L [22].

The content of magnesium and calcium in groundwater of Serbia varies in a very wide range depending on the observed area and is a consequence of the highly complex geological structure of Serbia [17]. Due to a greater diffusion in nature, calcium concentration in natural waters is higher than magnesium concentration. Together with magnesium, most commonly in the form of carbonates and bicarbonates calcium makes water hard. Magnesium in groundwater goes up to 50 mg/L and rarely exceeds 100 mg/L wherefore the main component of hardness is calcium [46]. Hard water leads to the sedimentation of limescale in water pipes, taps, and heaters which decreases their working efficiency. On the other hand, in the last five decades, ecological, epidemiological and analytical (anamnestic) data have been accumulated on the protective effect of high values of hardness and Ca and Mg from drinking water on morbidity and mortality from cardiovascular disease [11, 28, 31]. Even though many studies shave favored Mg as the main protective element of hard water for IHD [6, 26], Rylander in his most recent study has concluded that Mg and Ca have to be taken into account together, as the analysis of many epidemiological and experimental studies has shown that the risk of death from cardiovascular disease was associated with both the content of Mg and the content of Ca [29]. It is proven that soft water substantially reduces the content of various essential elements (including Ca and Mg) in food if used for cooking vegetables, meat, and grain. Reductions go up to 60% for Mg and Ca or even more for some microelements (Ex. Cu 66%, Mn 70%, Co 86%). As opposed to that if hard water is used in cooking there is a lesser reduction of elements (Haring and Van Dleft 1980). WHO [44] in the drinking water quality guide estimated calcium and magnesium from the perspective of water hardness. But,

it did not set any minimum or maximum recommended values. The EU Directive [7] and US EPA [38] did not standardize calcium and magnesium either. The Ordinance on the hygienic adequacy of drinking water in the Republic of Serbia [35] set the maximum allowed content of calcium to 200 mg/L and magnesium to 50 mg/L. The calcium concentration, with the highest measured value of 103.9 mg/L and the magnesium concentration, with the greatest measured value of 14.1 mg/L, in all water samples from the springs and the reservoir meets the recommended values and the maximum allowed concentration (Table 1).

The iron concentrations in all water samples from the springs and the reservoir are below the method's detection threshold (<0.01 mg/L) and thus meet the recommended values and the maximum allowed concentration. Iron does not pose health risks at concentrations which occur in natural water which is why WHO [44] didn't recommend guidelines. However, at concentrations higher than 0.3 mg/L water may acquire turbidity and color and as a result of iron-oxidizing bacteria, pipes may be lined with mucous layers. The results of some research discover that occluded water in the scales of the pipes has an acidic environment and high concentration of iron, manganese, chloride, sulfate and nitrate, which aggravates many pipeline leakage accidents [37]. US EPA [38] categorized iron as a secondary contaminant and set a secondary MCL of 0.3 mg/L. The reason for that is its influence on the organoleptic water characteristics: the color of rust in water, metal taste, reddish or orange coloration. Iron also promotes the growth of iron-oxidizing bacteria. These bacteria obtain their energy precisely from the oxidation process of Fe^{2+} into Fe^{3+} ions which leads to the formation of a slimy layer in pipes. This problem appears with iron concentrations above 0.3 mg/L. The EU Directive [7] set the maximum allowed content for iron in water to 0.2 mg/L. In accordance with the Ordinance on the hygienic adequacy of drinking water in the Republic of Serbia [35] the maximum allowed concentration of iron in water is 0.3 mg/L. In northern Serbia, in Subotica, the iron concentration in groundwater samples varies from 0.04 to 0.96 mg/L [22].

The manganese concentrations in all water samples from the springs and the reservoir are below the method's detection threshold (<0.025 mg/L) thereby meeting the recommended values and the maximum allowed content. Manganese belongs to the elements whose presence in groundwater is considered natural [44]. Certainly, it can occur there as a result of anthropogenic actions. The behavior of manganese in water is similar to that of iron. Manganese also promotes the development of manganese-oxidizing bacteria. These bacteria obtain energy for growth precisely from the oxidation process of Mn^{2+} into Mn^{3+}, which leads to the formation of a slimy layer in pipes. This problem occurs at manganese concentrations

above 0.1 mg/L [44]. These bacteria are not detrimental to health; however, they may cause clogging in the water system [8]. At manganese concentrations above 0.1 mg/L water taste becomes bad and stains appear in water pipes and on laundry [44]. WHO [44] did not set guidelines for manganese as the concentrations at which it appears in drinking water do not affect health. However, at concentrations higher than 0.1 mg/L, it causes an unpleasant taste and it colors pipes and laundry. Like iron, it may lead to the accumulation of sediment in the distribution system. Concentrations below 0.1 mg/L are acceptable for consumers. US EPA [38] categorized manganese as a secondary contaminant and set a secondary MCL of 0.05 mg/L. According to the EU Directive [7] and the Ordinance on the hygienic adequacy of drinking water in the Republic of Serbia [35] the maximum allowed content for manganese is 0.05 mg/L. In the groundwater of the Pannonian Basin (eastern Hungary and western Romania), manganese concentrations vary from <0.001 to 0.336 mg/L [27].

The Cr^{3+} and Cr^{6+} concentrations in all water samples from the springs and the reservoir are below the method's detection threshold (<0.01 mg/L) and therefore meet the recommended values and the maximum allowed concentration. The distribution of compounds containing Cr^{3+} and Cr^{6+} depends on the reduction potential, pH value, oxidizing and reducing compounds presence, kinetics of reduction reactions, formation of Cr^{3+} complexes or insoluble Cr^{3+} salts and the total chromium concentration. When chromium concentration is low, Cr^{3+} is present as a monovalent $HCrO_4^-$ below the pH value of 6.5 and divalent CrO_4^{2-} at the pH value between 6.5 and 10 [24]. In water without oxygen or with a very low concentration of it, Cr^{3+} is a dominant particle which occurs in the cationic (Cr^{3+}, $CrOH^{2+}$ or $Cr(OH)$) or the neutral ($Cr(OH)_3$) form depending on the pH value. Cr^{3+} is insoluble (<20 μg/L) within the pH range of 7 to 10, with the minimum solubility at the pH value of 8 (1 μg/L) [24]. In natural minerals, chromium mostly appears in the form of Cr^{3+}. Since the effect on health depends on the state of chromium's oxidation, WHO [44] considers that separate guidelines for Cr^{3+} and Cr^{6+} should be set. However, the current analytic methods and the variable chromium speciation in water favor guidelines for total chromium. WHO [44] set a temporary guideline for total chromium of 50 μg/L. Because it can cause allergic dermatitis US EPA [38] set MCL and MCLG (Maximum Contaminant Level Goal) for total chromium at 100 μg/L. According to the EU Directive [7] and the Ordinance on the hygienic adequacy of drinking water in the Republic of Serbia [35], the total chromium content in drinking water must not exceed 50 μg/L. The results of Croatia's studies have shown that contaminated groundwater (Fe, Pb, Ni and Cr) becomes a large hygienic and toxicological problem, since it considerably impedes groundwater

utilization [9]. Even though, all of these contaminants have not yet reached toxic levels, they still represent long-term risk for health of the population [9].

Aluminum presence points to the assumption that the water system is supplied from artesian wells located in the industrial zone. Aluminum poses a risk to human health, primarily in mines but also factory workers may have lung problems due to aluminum dust. Elevated aluminum concentrations may lead to significant health problems, primarily nervous system problems, dementia, memory loss, and diarrhea. It is suspected that drinking water containing fluoride and aluminum results in negative health effects especially on brain, liver, and kidney [41]. But, it was demonstrated that the treated drinking water containing F and Al with par with WHO or moderately above the WHO levels or AlFx in low level (0.07–15 mg/L) does not lead to CKD in mice [41]. In kidney patients, it may cause problems when it gets inside the organism through kidney dialysis. There is a suspicion that it might have an effect on the appearance of Alzheimer's disease (WHO, Guidelines for drinking water quality [43]). According to WHO [44] the limit for aluminum in drinking water is 200.0 μg/L. According to the Ordinance on the hygienic adequacy of drinking water in the Republic of Serbia [35], the maximum allowed concentration of aluminum is also 200.0 μg/L. The aluminum content in all water samples from the springs and the reservoir is below the method's detection threshold (<0.020 mg/L) thus meeting the recommended values and the maximum allowed content.

3.2 Microbiological water quality monitoring

The numbers of culturable organisms (TCV) in natural water samples from the springs are given in Table 2.

Even though this parameter is not an indicator of fecal contamination in water, it is useful for the estimation of general bacteria content in water. From the results we can observe that the measured values of these bacteria went up to 212 cfu/mL (one sample from Krupac Spring) and that only one more sample from that spring had a value above the maximum allowed concentration (107 cfu/mL) according to the ordinance (100 cfu) for natural water from enclosed springs. By comparing the results with the values from the physicochemical analysis, it can be inferred that in the periods of elevated turbidity at this spring (5.4–5.7 NTU), the bacterial load is the greatest. This is understandable considering that bacteria are suspended particles which, among other things, may affect the increased turbidity values. All the other values of this parameter were far below the maximum allowed concentration, ranging from 1–11 cfu/mL (Divljana, July).

Total coliform bacteria (TC) which are not of fecal origin may exist in natural water and their presence can be

Table 2 An annual basis representation of the number (n) of culturable organisms (TCV), total coliform bacteria (TC), fecal coliform bacteria (FC), intestinal enterococci (SF), sulfite-reducing clostridia (SSA), Pseudomonas aeruginosa (PA), and Proteus strain (Pv) in the raw water from the springs Divljana (D), Mokra (M), Krupac (K) Ljuberadja (Lj) and and the Vinik (V) reservoir

Month	January	February	March	April	May	June	July	August	September	October	November	December
TCV at 37 °C, cfu/1 mL												
D	<1	1	<1	<1	<1	<1	11	<1	<1	<1	<1	<1
M	1	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	5
K	<1	5	*212*	<1	4	1	<1	47	1	<1	11	*107*
Lj	<1	2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
V	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
TC n/100 mL												
D	1	Ɵ	Ɵ	Ɵ	1	5	13	2	Ɵ	Ɵ	24	1
M	1	*17*	Ɵ	2	Ɵ	7	*24*	Ɵ	3	10	8	Ɵ
K	24	1	*31*	1	8	54	24	24	Ɵ	1	92	*>161*
Lj	1	Ɵ	*>161*	Ɵ	Ɵ	1	Ɵ	1	Ɵ	Ɵ	Ɵ	Ɵ
V	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ
FC n/100 mL												
D	*1*	Ɵ	Ɵ	Ɵ	*1*	5	3	Ɵ	Ɵ	Ɵ	24	*1*
M	Ɵ	Ɵ	Ɵ	*1*	Ɵ	7	24	Ɵ	Ɵ	10	3	Ɵ
K	24	*1*	31	*1*	8	24	24	24	Ɵ	*1*	17	*>161*
Lj	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	*1*	Ɵ	*1*	Ɵ	Ɵ	Ɵ	Ɵ
V	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ
SF n/100 mL												
D	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	*1*	*1*	Ɵ	*1*	*1*
M	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	*1*	Ɵ	Ɵ	4	*1*	3
K	*1*	Ɵ	13	Ɵ	3	24	24	Ɵ	Ɵ	Ɵ	92	*>161*
Lj	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ
V	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ
SSA n/100 mL												
D	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	2	Ɵ
M	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	1	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ
K	2	3	1	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	3
Lj	Ɵ	Ɵ	2	Ɵ	Ɵ	Ɵ	Ɵ	1	Ɵ	Ɵ	Ɵ	Ɵ
V	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ
PA n/100 mL												
D	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ
M	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ
K	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	*1*	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ
Lj	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ
V	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ
Pv n/100 mL												
D	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ
M	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ
K	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ
Lj	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ
V	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ	Ɵ

cfu- the number of formed colonies

Ɵ—no bacteria

tolerated to a degree, so the Ordinance on the hygienic adequacy of drinking water [35], allows up to 10 TC bacteria in 100 mL of natural water samples from enclosed springs. An annual basis representation of these bacteria in our research (Table 2) indicates that the values in examined water samples range from 1 to 24/100 mL and that Krupac Spring, in the second half of the year, has values from 54 to 161/100 mL. Ljuberadja Spring, which is predominantly without TC bacteria findings, had elevated values of total coliform bacteria in March only in one sample (>161/100 mL). Research in the world has shown that the total coliform bacteria in a high percentage (55.3%) can be found in tap water samples [21].

A more suitable name for fecal coliform bacteria (FC) is thermostable coliform bacteria and aside from *E.coli* water samples mostly contain *Klebsiella*, *Enterobacter* and *Citrobacter*. The discovery of these bacteria suggests a recent fecal contamination and an epidemiological hazard from a potential finding of pathogenic microorganisms. Most drinking water sources were found to have coliform counts above the recommended national and international guidelines [2]. Research in Jakarta shows that bouts of diarrhea, reported in one-third of households were closely related to water contaminated with more than 100 fecal coliform bacteria in 100 mL of water samples [40]. In the USA, up to 14% of the population depend on private wells as their primary drinking water source and *E. coli*, arsenic and nitrate concentrations exceeded their respective regulatory levels [20].

When it comes to *E. coli* and other indicators of fecal contamination, primarily intestinal *Enterococci* (SF), but also *Proteus* strains (Pv) and *Pseudomonas aeruginosa* (PA), the Ordinance on the hygienic adequacy of drinking water [35], and the EU Directive [7] do not permit the finding of these bacteria in drinking water (neither natural nor disinfected). Microbiological research results for fecal contamination indicating bacteria are given in Table 2 where it can be observed that the bacteriological load in natural water with FC and SF bacteria is the greatest in summer months as well as at the end of the year, especially when springs are turbid (Krupac Spring). Analyses around the world suggest that routine inspection of drinking water's bacteriological quality for the presence of coliform bacteria is very important in relation to the viral assessment of the presence of enteric viruses, especially hepatitis A in water [16].

Proteus strains, as indicators of fecal contamination and organic matter decomposition, were not isolated in any of the samples from the springs belonging to the Ljuberadja-Niš system (Table 2).

Pseudomonas aeruginosa, which are considered to be highly resistant in nature and resistant to disinfectants, was not isolated in the water of this system except one

sample from Krupac Spring (July) (Table 2). In contrast to public believe, bottled waters are not free of *Pseudomonas aeruginosa*, and it is suggested that authorities should provide stricter monitoring and control plan for water resources and plants [18].

Sulfite reducing sporogenic anaerobic bacteria (*Clostridia*) (SSA) are indicators of old fecal contamination and the Ordinance on the hygienic adequacy of drinking water [35] allows one SSA bacteria in a natural water sample of 100 mL from an enclosed spring whereas they are not permitted in chlorinated water. In our analysis (Table 2), these bacteria were isolated in a lesser number (2–3/100 mL) in several samples from Krupac Spring while the rest of the springs (Divljana, Mokra, and Ljuberadja) are commonly without SSA bacteria or may have sporadic occurrences in small quantities (1–2/100 mL).

The microbiological testing of chlorinated water quality from the Vinik reservoir shows (Table 2) that none of the samples contain the mentioned bacteria. This confirms the hygienic adequacy of the water distributed to consumers. It is necessary to emphasize that besides chlorination proper maintenance of the distributive network is very significant in terms of preserving drinking water safety. Research from around the world suggests that bacteriological contamination in water may deteriorate when sanitary protection zones are poorly managed, when water is treated inadequately and when the distribution system is not maintained [5, 15]. A high degree of microbiological contamination in drinking water for households certainly is a hazard for consumers' health [1], which is definitely not the case with the drinking water from the Ljuberadja-Niš system considering that the microbiological examination of water quality shows that consumers receive 100% microbiologically safe tap water.

4 Conclusions

Quality monitoring has shown that groundwater is the most reliable source of drinking water.

Except occasional increases in turbidity only in natural water samples, physical, and chemical parameters in tested water system Ljuberadja-Niš are below the values of the maximum allowed concentration prescribed by national and international authorities.

Despite the fact that microbiological analysis detects sporadic microbiological contamination in natural water, primarily with coliform (total and fecal) bacteria, after gas chlorine disinfection the health and hygienic adequacy is achieved. By comparing the results with the values from the physicochemical analysis it can be inferred that in the periods of elevated turbidity at this spring the bacterial

load is the greatest (primarily the increased number of culturable organisms).

The microbiological testing of chlorinated water quality from the Vinik reservoir shows that none of the samples contain the tested bacteria.

Monitoring has confirmed the hygienic and health adequacy of the water distributed to consumers.

In order to maintain the health safety of drinking water, it is necessary to continue quality monitoring by examining the physical, chemical, and microbiological parameters at the same time.

Compliance with ethical standards

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