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Original Scientific Article

AMMONIUM, NITRATE AND NITRITE CONCENTRATIONS IN DRINKING WATER OF THE SOUTH BAČKA DISTRICT OF VOJVODINA

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Abstract. *Safe drinking water is one of the basic conditions for life on our planet, necessary for all vital processes in the biosphere. Pollution of water sources, largely from wide-scale agricultural fertilizer use, has resulted in nitrate and nitrite contamination of drinking water. Aim: To determine the concentrations of ammonium, nitrate, and nitrite in drinking water as potential hazards in the settlements of the South Bačka administrative district of Autonomous Province of Vojvodina (northern part of Serbia). A cross-sectional study was conducted during 2019. We analysed 8434 drinking water samples (7319 purified chlorinated, 386 untreated but chlorinated, and 729 untreated). For assessing the concentration of ammonium, nitrate, and nitrite in drinking water, samples were analyzed by a certified laboratory at the Institute of Public Health of Vojvodina using spectrophotometric method. After analyzing samples of purified chlorinated, untreated chlorinated, and untreated water, the exceedance of the prescribed values of ammonium were found in 0.45%, 64.77% and 68.45%, and for nitrites in 0.04%, 5.96% and 0.82% of the samples, respectively. The concentration of nitrate in drinking water concerning the degree of water purification (purified chlorinated and untreated water) exceeded the prescribed value in 0.01% and 5% of the samples, respectively. Determined exceedances of the prescribed limit values for nitrite concentrations recorded in purified chlorinated, untreated chlorinated, and untreated drinking water as well as for nitrate mainly in untreated drinking water, could be considered as potential hazards for human health, especially for the sensitive population group.*

Key words: *drinking water, ammonium, nitrates, nitrites.*

Introduction

Ammonium, nitrates, and nitrites occur naturally as part of the nitrogen cycle — the nitrogen cycle circles nitrogen through the atmosphere, water, soil and living beings. Nitrogen is present in the atmosphere as an inert gas, and most organisms cannot use it [1]. The chemical characteristics of natural waters are a reflection of the soils and rocks with which the water has been in contact. Contaminants may include inorganic and organic substances. Some inorganic minerals dissolve quickly and change the composition of water rapidly, while other minerals, such as silicates, dissolve slower and have less conspicuous effects on the water composition [1, 2]. Groundwater contamination occurs due to excessive use of mineral and natural fertilizers, construction of permeable septic tanks, conversion of old wells into septic tanks, and uncontrolled disposal of previously untreated solid and liquid waste [2]. According to the World Health Organization (WHO), nitrate (NO3−) is the stable form of nitrogen, while nitrite (NO2−) is relatively unstable in oxic groundwater and oxygenated water systems. Elevated concentrations of ammonium in groundwater samples may indicate faecal pollution [3].

The main source of nitrate for humans is food, namely: vegetables, certain processed foods (meat) additives and drinking water. The European Food Safety Authority has confirmed an acceptable daily intake (ADI) of 0 to 3.7 mg/kg/TM for nitrates and 0 to 0.07 mg/kg/TM for nitrites [4]. The most critical place for nitrate reduction in nitrites is the base of the tongue, where a stable nitrate-reducing microflora is present. After transport to the stomach, nitric to nitric acid is rapidly transformed under acidic conditions, decomposing spontaneously to nitrogen oxides, including nitrogen monoxide. Low pH in an empty stomach (pH 1-2) is considered too low for the growth of microorganisms and thus bacterial reduction of nitrates [5]. Most absorbed nitrates are excreted in the urine as nitrate, ammonia or urea [6].

Nitrates have low toxicity, and the adverse health effects are due to the action of nitrites caused by the metabolic conversion of nitrates [5]. Nitrite toxicity is manifested by methemoglobinemia, the so-called. "blue baby syndrome" [1]. Due to the role of nitrate and nitrite as precursors of genotoxic N-nitroso compounds in endogenous nitrosation, nitrate and nitrite in drinking water potentially can cause cancer in the gastrointestinal and urinary tract as well as at other site [7].The International

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Agency for Research on Cancer (IARC) classified nitrate and nitrite as probably carcinogenic to humans (Group 2A) [8]. Despite this classification as "probably carcinogenic", there are some of evidence that nitrate in drinking water is associated with cancer, in particular colorectal cancer and bladder cancer. There is also evidence that nitrate in drinking water may be associated with an increased risk of birth defects and other adverse reproductive outcomes [9-12]. In addition, according to the WHO guidelines, nitrate and nitrite in drinking water can have negative human health impacts, while ammonium is not of direct importance for human health [13].

WHO guidelines set the limit value for nitrates of 50 mg/l as ammonium ion NO3-1 or 11.3 mg/L as nitrogen N - while for nitrites of 3 mg/L [13]. According to US Environmental Protection Agency (EPA) guidelines, the limit value for nitrates is 10 mg/L as N, while for nitrites, it is 1 mg/L as N [14]. According to EU Directive 98/83/EC, the limit value for nitrates is 50 mg/L and for nitrites is 0.1 mg/L [15]. In the Republic of Serbia, nitrate and nitrite concentrations are defined by national regulations, setting the limit value for nitrates at 50 mg/L and at 0.03 mg/L for nitrites [16].

The water supply in the South Bačka district relies solely on groundwater from wells, while in the city of Novi Sad and its surrounding settlements, a regional water supply system is in place. Groundwater accumulates in the upper parts of the terrain, reaching depths of up to 250 meters, and the most common method of groundwater abstraction is through well extraction [1]. A number of springs are also found in the inundation zone. For example, in the City of Novi Sad, river wells (wells with horizontal drains) are primarily supplied with river water through natural infiltration, and the quality of surface water directly impacts the quality of drinking water [1]. Water supply facilities are constructed to make natural water sources accessible to consumers. The choice of water supply facility depends on the origin and quality of water at the catchment or springs, as well as their capacity and the number of consumers [17-19].

There are two categories of water supply: central and local [16]. We have classified water sources into purified water, purified chlorinated water, untreated water, public wells, and eco fountains to facilitate more precise monitoring of critical points. The annual report of the Institute of Public Health of Vojvodina (IPHV) provides data based on types of water sampling and districts included in the analysis [20]. Those data enables us to identify potential hazards associated with different water sources and take appropriate measures. The absence of waterborne epidemics serves as evidence that the drinking water was safe.

Central water supply is an organized method for providing water to a settlement or a region that has a regulated and protected water source, catchment, reservoir, and water supply network. In water treatment plants, raw water undergoes purification through a series of stages including aeration, sedimentation, filtration, ozonation, and disinfection, resulting in purified chlorinated water. Local water supply facilities serve as sources from which water is mechanically or pump-supplied, catering to a smaller population. Unfortunately, water treatment processes, except for chlorination, are often omitted. This means that water is distributed to the population as either untreated chlorinated water or simply untreated water. Chlorination is not feasible when there is a significant presence of organic matter or elevated concentrations of potassium permanganate [1-4].

Aim

This paper aims to determine the concentrations of ammonium, nitrates and nitrites in drinking water on the territory of the South Bačka district of Autonomous Province of Vojvodina (northern part of Serbia) as potential hazards and to assess whether the nitrite concentration in drinking water could present a hazard to human health on the territory of the South Bačka District (SBD) of the Autonomous Province of Vojvodina (APV), the northern part of the Republic of Serbia.

Materials and Methods

A cross-sectional study was conducted during 2019. Regarding the treatment, we separately included 7319, 386 and 729 of purified chlorinated, untreated chlorinated, and untreated samples drinking water, respectively retrieved from central and local waterworks and public wells. All samples were coded based on their sampling location, either at the exit of waterworks, within the distribution system, or at the consumers' taps. The samples were analysed by a certified laboratory at IPHV following accredited national standards (standardize semi quantitative analyses defined in ISO standard EN 15975-2:2013), i.e. using standard – spectrophotometric method.

Planning, sampling, transport, and field analysis of drinking water, as well as the laboratory analysis of drinking water samples, were carried out by a multidisciplinary team from the certified and accredited laboratory of IPHV. The selection of measurement points was made based on expert assessments in consultation with service users, considering public health interests and ensuring representation from all parts of the water supply network. Sampling was not carried out in private facilities, unless an agreement with the user is reached, serving the public interest.

The selection of measurement points, preparation of packaging for sampling, actual sampling, transport, and field analysis of drinking water were conducted following standard methods outlined in SRPS H.Z1. 106, SRPS EN ISO 5667-1:2022, SRPS EN ISO 5667-3:2018, and SRPS ISO 5667-5:2008 standards for packaging preparation, specifically SRPS EN ISO 5667-3. International guidelines were also adhered to for the determination of residual chlorine concentration in the field and the measurement of ambient air temperature during the fieldwork [3, 13, 14].

The determination of ammonium, nitrate, and nitrite concentrations in drinking water was conducted in compliance with accredited spectrophotometry methods.

These methods included the verified method by the IPHV for spectrophotometry (ammonium content determination), as well as the Standard Methods For the Examination of Water and Wastewater (SMEW) W20th 4500-NO3 (nitrate concentration determination) and SMEW W20th 4500-NO2 (nitrite concentration determination) methods [20].

The assessment of drinking water safety was interpreted in accordance with the applicable legal and regulatory framework of the country [16].

Data regarding water quality, as published in the state of health report by IPHV [19], are categorized by district and type of water sampling. These data allow us to identify potential hazards associated with various water sources and propose appropriate measures to mitigate them.

Data analysis

Standard parametric and non - parametric methods were used for data processing. Numerical data are presented through arithmetic mean, minimum, and maximum values, standard deviation, and coefficient of variation. The data are presented in tables and a map. The SPSS statistical package (version 17), Microsoft Office Excel, and Microsoft Visual Fox Pro were used for all statistical analyses.

Results

Regarding purified chlorinated drinking water, we found an exceedance of the limit value of nitrate concentration in one sample (2.0%) from Gardinovci (municipality of Titel), and nitrite concentration in three samples (1.46%) from Bačka Palanka, respectively. Exceeding the limit value of ammonium was found in 33 (0.45%) of analyzed samples, and majority of them were detected from Titel (60.0%) (Table 1, Figure 1).

When we analyzed samples of untreated chlorinated drinking water, there were no samples above the limit values regarding nitrates. However, in total, samples above the detection limits were detected particularly for nitrite (5.96%, 23/386) and ammonium (64.77%, 250/386). The majority (10.0%, 7/70) of nitrite concentrations above the limit values were found in tested samples from Nadalj (municipality of Srbobran), as well as in Bačka Palanka (9.65%, 11/114). The exceedance of the limit value of ammonium was found in all observed municipalities, with the majority of positive samples in the following municipalities: Bečej (92.05%, 81/88), Bački Petrovac (63.33%, 19/30), and Srbobran (61.43%, 43/70), (Table 2, Figure 1).

To assess the concentrations of ammonium, nitrates and nitrites within untreated drinking water, a total of 729 samples were tested, and we found that (in total) all observed parameters exceeded the limited values. In total, 68.45%, 4.94%, and 0.82% of tested samples were above limited values for ammonium, nitrates and nitrites, respectively. The exceedance values for nitrites were found

Table 1 The concentrations of ammonium, nitrate, and nitrite in purified chlorinated water in 2019 by municipalities in South Bačka District

Municipality	The total number of samples	Purified chlorinated water																				
		Ammonium							Nitrate							Nitrite						
		X	MIN	MAX	SD	CV	Exceedance n	Exceedance %	X	MIN	MAX	SD	CV	Exceedance n	Exceedance %	X	MIN	MAX	SD	CV	Exceedance n	Exceedance %
Bačka Palanka	206	0.04	0.02	1.10	0.06	150.25	3	1.46	7.52	1.60	9.30	1.60	21.21	0	0.00	0.006	0.005	0.15	0.011	183.31	3	1.46
Beočin*	45	0.02	0.02	0.10	0.06	300.15	0	0.00	4.46	1.70	6.80	1.60	35.81	0	0.00	0.005	0.005	0.005	0.010	200.01	0	0.00
Bečej	206	0.02	0.02	0.10	0.06	300.16	0	0.00	6.95	5.70	9.00	1.26	18.12	0	0.00	0.005	0.005	0.005	0.007	140.02	0	0.00
Vrbas	223	0.02	0.02	0.03	0.06	300.54	0	0.00	2.81	0.40	9.70	1.59	56.53	0	0.00	0.005	0.005	0.007	0.006	120.01	0	0.00
Novi Sad**	6466	0.03	0.02	0.12	0.06	200.61	0	0.00	2.55	1.20	6.80	1.56	61.14	0	0.00	0.005	0.005	0.005	0.002	40.01	0	0.00
Titel***	50	0.56	0.02	1.10	0.36	64.16	30	60.00	1.94	0.10	83.40	1.63	84.02	1	2.00	0.007	0.005	0.092	0.002	28.60	0	0.00
Sremski Karlovci	123	0.03	0.02	0.10	0.06	200.51	0	0.00	2.40	1.50	3.50	1.59	66.21	0	0.00	0.005	0.005	0.005	0.002	40.00	0	0.00
Total	7319	0.10	0.02	0.38	0.10	216.62	33	0.45	4.09	1.74	18.36	1.55	48.00	1	0.01	0.011	0.013	0.04	0.010	107.42	3	0.04

*Municipality of Beočin: Čerević, Rakovac; **Municipality of Novi Sad: Budisava, Bukovac, Čenej, Futog, Kać, Kisač, Kovilj, Ledinci, Stari Ledinci, Petrovaradin, Rumenka, Sremska Kamenica, Stepanovićevo, Veternik; ***Municipality of Titel: Gardinovci, Lok

X- arithmetic average; MIN- minimum value; MAX- maximum value; SD- standard deviation; CV- coefficient of variation

Table 2 The concentrations of ammonium, nitrate and nitrite concentrations in unpurified chlorinated water in 2019 by municipalities in South Bačka District

		Purified chlorinated water																				
		Ammonium							Nitrate							Nitrite						
							Exceedance							Exceedance							Exceedance	
Municipality	The total number of samples	X	MIN	MAX	SD	CV	n	%	X	MIN	MAX	SD	CV	n	%	X	MIN	MAX	SD	CV	n	%
Bačka Palanka*	114	0.62	0.02	4.81	0.59	95.11	59	51.75	0.68	0.010	9.61	1.68	247.06	0	0.00	0.023	0.005	0.670	0.09	391.01	11	9.65
Bački Petrovac**	30	0.69	0.02	1.55	0.58	84.02	19	63.33	0.22	0.101	0.82	1.65	750.00	0	0.00	0.005	0.005	0.005	0.09	1800.12	0	0.00
Bečej***	88	1.14	0.02	2.53	0.28	24.51	81	92.05	0.28	0.101	1.64	1.65	589.29	0	0.00	0.008	0.005	0.039	0.09	1125.32	2	2.27
Vrbas~	72	0.62	0.02	1.94	0.62	96.71	42	58.33	1.08	0.101	10.11	1.74	161.11	0	0.00	0.030	0.005	1.502	0.09	300.21	3	4.17
Žabalj^	12	0.55	0.13	0.91	0.62	109.01	6	50.00	0.25	0.101	0.85	1.67	668.00	0	0.00	0.005	0.005	0.005	0.09	1800.41	0	0.00
Srbobran^^	70	0.92	0.02	1.92	0.61	65.21	43	61.43	0.54	0.101	20.31	1.64	303.70	0	0.00	0.010	0.005	0.072	0.09	900.12	7	10.00
Total	386	0.79	0.04	2.27	0.54	79.09	250	64.77	0.50	0.085	7.22	1.67	453.19	0	0.00	0.013	0.005	0.382	0.09	1052.86	23	5.96

* Municipality of Bačka Palanka: Pivnice, Obrovac, Mladenovo, Tovariševo, Silbaš, Despotovo, Parage, Karađorđevo; ** Municipality of Bački Petrovac: Kulpin, Bački Maglić; *** Municipality of Bečej: Bačko Gradište, Bačko Petrovo Selo, Mileševo, Radičević, Poljanice; ~ Municipality of Vrbas: Bačko Dobro Polje, Kucura, Ravnoselo, Savino selo, Zmajevo; ^ Municipality of Žabalj: Đurđevo; ^^ Municipality of Srbobran: Turija, Nadalj

X- arithmetic average; MIN- minimum value; MAX- maximum value; SD- standard deviation; CV- coefficient of variation

Table 3 The concentrations of ammonium, nitrate and nitrite concentrations in unpurified water in 2019 by municipalities in South Bačka District

		Purified chlorinated water																				
		Ammonium							Nitrate							Nitrite						
							Exceedance							Exceedance							Exceedance	
Municipality	The total number of samples	X	MIN	MAX	SD	CV	n	%	X	MIN	MAX	SD	CV	n	%	X	MIN	MAX	SD	CV	n	%
Bačka Palanka*	307	3.86	0.02	9.12	3.89	100.71	288	93.81	2.08	0.10	23.12	19.41	932.21	0	0.00	0.009	0.005	1.000	0.005	55.51	5	1.63
Bač**	3	1.88	0.03	4.91	2.64	140.41	2	66.67	0.23	0.02	0.34	0.11	24.81	0	0.00	0.005	0.005	0.005	0.000	0.01	0	0.00
Beočin***	11	0.8	0.02	2.82	4.15	518.72	5	45.45	3.48	0.20	7.54	19.30	555.52	0	0.00	0.005	0.005	0.005	0.005	100.02	0	0.00
Bečej~	49	3.27	0.66	53.42	3.89	118.90	49	100.00	1.00	0.09	16.05	19.22	1915.01	0	0.00	0.005	0.005	0.020	0.005	100.01	0	0.00
Vrbas^	89	1.59	0.02	8.91	3.88	244.01	82	92.13	0.72	0.10	8.51	18.60	2577.80	0	0.00	0.006	0.005	0.044	0.005	83.30	1	1.12
Žabalj^^	36	2.37	0.09	9.75	3.85	162.42	29	80.56	0.40	0.10	3.43	18.01	4510.00	0	0.00	0.005	0.005	0.005	0.004	90.01	0	0.00
Novi Sad^^^	200	0.36	0.02	72.63	3.72	1033.31	29	14.50	21.47	0.10	118.87	18.10	84.41	35	17.50	0.006	0.005	0.023	0.004	68.32	0	0.00
Temerin§	16	11.8	0.48	20.17	4.00	33.91	15	93.75	3.67	0.10	12.42	17.24	468.41	0	0.00	0.005	0.005	0.005	0.004	76.01	0	0.00
Sremski Karlovci	18	0.04	0.02	0.13	4.03	1007.51	0	0.00	26.73	17.7	51.85	17.42	65.22	1	5.56	0.005	0.005	0.005	0.004	80.01	0	0.00
Total	729	2.88	0.15	20.20	3.78	373.32	499	68.45	6.64	2.05	26.90	14.44	1237.01	36	4.94	0.006	0.005	0.123	0.004	72.52	6	0.82

* Municipality of Bačka Palanka: Pivnice, Obrovac, Mladenovno, Tovariševo, Gajdobra, Nova Gajdobra, Silbaš, Despotovo, Parage, Neštin, Karađorđevo, Vizić; ** Municipality of Bač: Bačko Novo Selo; *** Municipality of Beočin: Banoštor, Susek; ~ Municipality of Bečej: Bačko Gradište, Bačko Petrovo selo, Radičević, Poljanice; ^ Municipality of Vrbas: Bačko Dobro Polje, Vrbas, Zmajevo, Kucur, Ravno selo, Savino selo; ^^ Municipality of Žabalj: Čurug, Đurđevo, Gospođinci, Žabalj; ^^^ Municipality of Novi Sad: Bukovac, Ledinci, Sremska Kamenica, Stari Ledinci; § Temerin, Sirig

X- arithmetic average; MIN- minimum value; MAX- maximum value; SD- standard deviation; CV- coefficient of variation

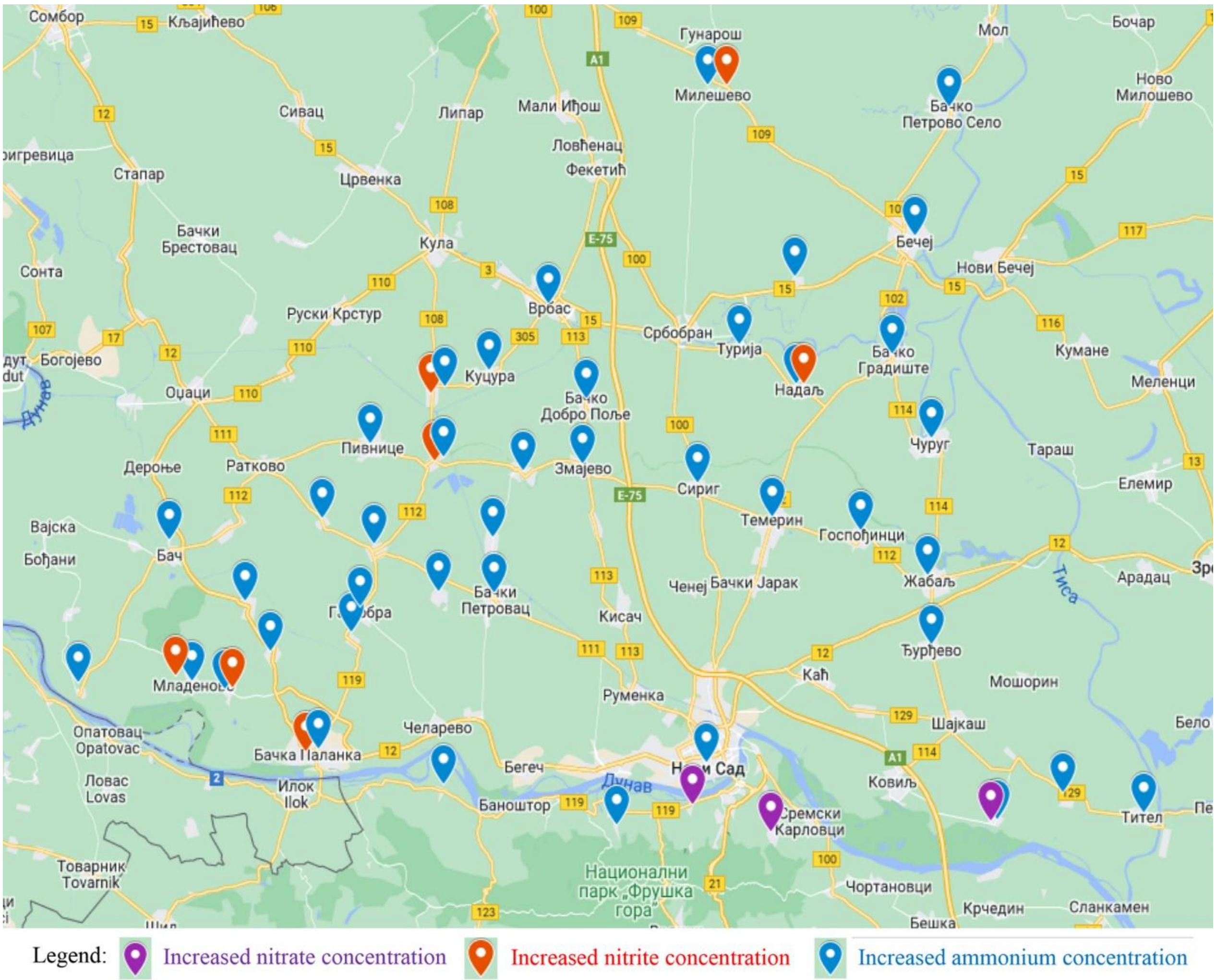

Fig. 1 Map of exceeding the values of ammonium, nitrate and nitrite concentration in purified chlorinated, untreated chlorinated and untreated drinking water by municipalities of the South Bačka administrative district from 01. 01. 2019 to 31. 12. 2019

in two municipalities (Bačka Palanka and Vrbas), for nitrates also in two municipalities (Novi Sad and Sremski Karlovci), but for ammonium in all eight observed municipalities, with 100% above limited value of ammonium in tested samples from municipality of Bečej, and no detection of ammonium above limit value from samples in Sremski Karlovci (Table 3, Figure 1).

Discussion

According to the WHO, 57 million of people do not have safe drinking water and 26 million of people do not have elementary sanitary conditions [13]. The chemicals are the important health concern in some natural waters, mainly due to excessive amounts of natural nitrates/nitrites [3]. For routine analysis of drinking water in the Republic of Serbia regarding the biological and chemical hazards are represented as the thermotolerant coliforms, especially *Escherichia coli* (E. coli), *Enterococci* (genus Streptococcus), *Pseudomonas aeruginosa*, *Proteus species* and excessive concentrations of nitrates/nitrites. The significant health concern in some natural waters lies in the presence of chemical hazards, particularly excessive amounts of natural nitrates/nitrites. Nitrates and nitrites are often found in drinking water due to sewage contamination or agricultural runoff, making them reliable chemical indicators of fecal pollution. High concentrations of nitrates are typically observed in untreated and non-disinfected underground waters, whereas the more toxic nitrites are present in non-treated but disinfected waters [17]. Results of our study showed that ammonium, nitrates and nitrites exceeded the limited values regrading different treatments (purified chlorinated, untreated chlorinated and untreated) of drinking water. There were not excessive amounts of nitrates only in samples of untreated chlorinated water. Although we cannot be certain that the determined concentration of observed chemicals has direct negative effects on human health, we presume that future investigations can provide confirmation for this association. In line with this, it must be taken into account that water supplies often include mixtures of chemical contaminants that vary in time and space. Accurate exposure assessment in human observational studies is essential to obtain valid results and constitutes a main methodological challenge. On the other hand, difficulties in identifying and measuring contaminants in water supplies at very low concentrations and substances occurring in mixtures, hinder the evaluation of human exposure, thus requiring new methods in health risk analysis [7].

The results of studies performed in 2009 in the United States, including about 2.100 private wells, showed that nitrates were the most common inorganic contaminant that was found at concentrations higher than the Federal Drinking Water Standard for Public Water Supplies (45 mg/L) in USA [18]. The seriousness of the problem of groundwater treatment with nitrates was also pointed out by the European Environment Agency (EEA). Northern Europe countries (Norway, Sweden, Estonia, Latvia, and Lithuania) present good quality of groundwater in terms of nitrates presence. However, in general, regions of central Europe (France, Germany, Poland among others) have a remarkable percentage of areas with a risk of up to 10% of groundwater with poor chemical status due to nitrates. Moreover, some areas in the Czech Republic, Slovenia, Netherlands, and Spain present a percentage between 70% and 90% classified as bad quality, which is considered a concerning problem to be solved in the near future [19].

During 2019, nitrites in drinking water from public wells in the APV exceeded guideline values in 3.05% of untreated drinking water samples, presenting a hazard mainly in the SBD [20]. Depending on whether we tested purified chlorinated, untreated chlorinated, or untreated water samples, 0.04%, 5.96%, and 0.82% of the samples exceeded the limit values for nitrites, respectively. In the territory of the City of Novi Sad and surrounding settlements that use purified drinking water (city water supply), there were no significant deviations from the limit values of nitrate and nitrite concentrations. However, significant deviations between the mentioned concentrations were observed in settlements that use untreated chlorinated (Nadalj, Despotovo, Savino Selo) and untreated (Bukovac, Ledinci) water. This could be explained due to the absence of organized supply of drinking water to the population of certain settlements and the use of water from insufficiently controlled private wells. In the eastern and western parts of Serbia, out of 182 individually controlled water supplies, 21% had nitrate levels above the guideline levels [21]. The results of a study conducted in suburban Belgrade, which included 200 local water supply systems, showed that 7% of the samples exhibited elevated nitrite levels. Additionally, out of the 38 water samples collected at 25 sites, 39.5% did not comply with the limit values for one or more of the tested elements (ammonium, nitrites, nitrates, and iron) [22], as the limited values were exceeded.

It is a well-known fact that the most effective means of ensuring the water safety in drinking water supply is through a comprehensive risk assessment and risk management approach. A previous comprehensive investigation, which evaluated the likelihood of hazards in 45 settlements of APV, demonstrated a low risk in purified and disinfected samples, but a medium and high risk in settlements with non-purified, but disinfected, and non-purified and non-disinfected water samples. The main hazards in the non-purified, but disinfected and non-purified and non-disinfected water samples included arsenic, nitrites, nitrates, coliforms, and *Escherichia coli* [17]. Ammonium is not of direct relevance to human health in concentrations expected in drinking water, so WHO [3] and US EPA [14] did not set guidelines for this parameter. According to the Ordinance on the hygienic adequacy of drinking water in the Republic of Serbia, the maximum allowed concentration for ammonium ion is 0.5 mg/L [16]. High concentrations may be expected in layers rich in humic acid or iron. It is a known fact that presence of ammonium in concentrations higher than the geological level is an important factor for fecal contamination [23, 24]. Untreated drinking water in the SBD is characterized by increased concentration of ammonium, which although are not dangerous to human health, but justifiably cause rejection of water by consumers and represent a problem for technical-technological processes of water purification [19].

As mentioned above, nitrate in drinking water is associated with cancer. It is known that epidemiological studies are limited in their ability to estimate long-term exposure on a detailed individual level. However, a large Danish study, which included 1.7 million individuals aged 35 years and above, with the highest exposure to drinking water between 1978 and 2011, showed that persons exposed to the highest level of drinking water nitrate had a hazard ratio of 1.16 (95% CI: 1.08-1.25) for colorectal cancer compared to persons exposed to the lowest level [25]. These results were also confirmed by a meta-analysis [26]. Furthermore, a systematic review and meta-analyses covering the period between 1990 and 2021 identified a positive association of nitrate exposure with gastric cancer (OR = 1.91, 95%CI = 1.09-3.33) per 10 mg/L increment in nitrate ion [27]. Another meta-analysis determined a correlation between median dosage of nitrate from drinking water and gastric cancer, as well as brain cancer & glioma (OR = 1.15, 95% CI: 1.06-1.24) [28]. There is also strong evidence that average drinking water nitrate concentration above the 95th percentile (>2.07 mg/L) is associated with bladder cancer [29]. Additionally, considering that nitrate may pass the placental barrier, there is some evidence that exposure to nitrate is associated with the risk of pregnancy loss in the first trimester [30]. Nitrites exert acute toxicity through methemoglobinemia or cardiovascular effects, and chronic toxicity is associated with endocrine, reproductive, and developmental effects. Nitrites have also been classified as probable gastric carcinogens [31]. These facts have been confirmed by several other studies conducted in different regions [32-34].

In assessing the concentrations of ammonium, nitrates, and nitrites in untreated drinking water, we discovered that (in total) observed parameters exceeded the acceptable limits. This finding strongly indicates the continuous need for drinking water treatment.

To our knowledge, this is the first systematic investigation of chemical hazards in drinking water observed across all municipalities of the SBD in the APV. Notifying certain municipalities about the exceeding values of observed chemical hazards (ammonium, nitrates, and nitrites) can encourage public, policy makers and all stakeholders to prioritize risk assessment of these hazards in drinking water. Lastly, our results contribute to the existing evidence suggesting increased concentrations of chemical hazards in drinking water samples within the SBD. A discussion on the adequacy of the drinking water standards concerning chronic effects is warranted.

Our study had some limitations. First, we did not observe seasonal variability in concentrations of ammonium, nitrates, and nitrites. Second, we did not perform a risk assessment for these hazards when explaining the results. Third, we tested all water samples collected throughout the year without specifying the sampling frequency for the collected samples. Fourth, due to the short duration of the study, we were unable to establish a follow-up association between exposure to drinking water with excessive values of chemical hazards and negative effects on the health of consumers. Further research could explore the association between long-term nitrate exposure in drinking water and colorectal and/or bladder cancer in our country. Despite the aforementioned limitations, we presume that they did not significantly compromise the main results of our study.

Conclusion

The results of our study showed the presence of chemical hazards in the tested samples of drinking water. The observed exceedances of prescribed limit values for nitrite concentrations in purified chlorinated, untreated chlorinated, and untreated drinking water, as well as for nitrate primarily in untreated drinking water, could be regarded as potential hazards to human health, particularly for the sensitive population groups such as infants, young children, chronically ill and immunocompromised individuals, and the elderly. In light of these findings, further comprehensive studies are needed. Moreover, prioritizing continuous risk assessment in managing the safety of drinking water in the SBD is necessary, taking into account all adverse effects of chemical hazards on human health as described in the aforementioned studies.

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