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THE IMPACT OF SEASONAL VARIABILITY ON PHYSICAL-CHEMICAL AND BACTERIAL INDICATORS OF DRINKING WATER OF GARI VILLAGE, DIBRA, NORTH MACEDONIA

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Abstract

The main goal of this research is to present a useful assessment to understand the level of physicochemical and microbiological parameters at different seasons in drinking water from the village of Gari in the region of Dibra. A special focus is on the study of physicochemical parameters (pH, ammonia, nitrates, nitrites, etc.) and the study of microbial pathogens and total coliforms in the four seasons of the year mainly from the summer season of 2018 to the spring season of 2019. Therefore, for the first time in the village of Gari of this previously unexplored source, these parameters have been analyzed to get acquainted with this important and useful knowledge for our society in general. From the physicochemical analysis, as well as the microbiological analysis of all water samples collected from the source of Stogova mountain, Gari village of Dibra there was significantly changes ($P < 0.05$) related to climatic influences, but their balance in the ratio of mineral composition was acceptable which makes the water of a good quality to drink.
Keyword: pH, ammonia, nitrates, nitrites

1. Introduction

About 2% of the territory of the Republic of North Macedonia is below the water surface. There are about 35 rivers and 53 natural and artificial lakes. According to the number of water resources, Macedonia is part of the area with sufficient water resources. According to the hydrographic division, in the Territory of the Republic of North Macedonia, there are four basins: Vardar, Drini i Zi, Strumica and South Morava. The large population growth in the world and the development of industry and other fields have made the needs for drinking water great, all this comes as a result of the great pollution of the environment, which is making people's lives more difficult day by day in many respects. When it comes to environmental pollution, there is no doubt that drinking water pollution is a serious problem, and this is mainly due to the great carelessness of people, whether in different settlements with urban or industrial wastewater. So based on this it is seen that the supply of drinking water is a big problem and requires a special interest. The change in water quality may be due to atmospheric changes, seasons of the year, biological composition, etc (Krasniqi, 2019).

It is estimated that about 37% of the population, or about 770,000 people, in the Republic of North Macedonia live in 1,420 rural settlements. About 27% of the rural population is connected to urban water supply systems, professionally managed by 56 municipal public enterprises. About 62% of rural residents are

supplied with water from small water systems in rural neighbourhoods depending on local water supply facilities (wells, pumps, village taps). Common problems that affect the quality of drinking water in small water systems are the lack of protected areas and fences, outdated and damaged water network, irregular chlorination of drinking water and improper water purification. In ecological terms of particular interest is the study of the quality of groundwater resources, which are used by the majority of the population for beverages (Hamzai, 2016.).

In the Republic of North Macedonia, all water supply systems built so far have a local or central character, while the regional ones are: Studençica (Kichevo, Brod, Krushevo, Prilep and the largest number of villages); Llukare (supplies Kavadarci, Negotin and 13 villages) and Dibra (Dibra and more settlements of the village). In the following period, the local systems will be grouped and expanded in the regions, with now water received from springs and underground, and will also include waters from rivers, respectively accumulation (Hristovska et al., 2013).

The influence of climatic elements (temperature, humidity, insulation, flooding, precipitation, winds, etc.) and climatic factors are related to the development and existence of living life, complete human activity and certain processes in nature, as important elements in the average annual temperature is 14.2 °C, the absolute minimum temperature is -17.2 °C, and the absolute maximum is 36.5 °C. Precipitation in this region is conditioned by the Mediterranean pluviometric regime. Most of the annual rainfall falls in the cold part of the year with a maximum in late autumn and the minimum in the summer months. The average annual rainfall is 708.3 mm, in November rainfall is strongest with 98.4 mm and the lowest rainfall is on July 24 mm and August 29.6 mm. Relative air humidity increases in December-January to an average of 79% and the lowest in June- August with 60% or average humidity which is 71% (Arsovski, 1997).

In contrast to surface water, groundwater is usually characterized by low concentrations of organic substances, but with significant concentrations of mineral salts, sometimes dissolved gases (H_2S, CO_2). If surface water communicates with groundwater, then it becomes oxidizable. It has been experimentally proven that there is a direct burial between the volume of the groundwater collector and the degree of their mineralization. Frequent groundwater has high hardness and increased concentration of iron and manganese. (Arsovski, 1997).

Based on the genesis of groundwater in the village of Gari and the concentrates of some elements of groundwater and surface water, in the coming period during the processing of chemical analysis of groundwater from the source area, special attention should be paid to the presence of manganese (Mn) in groundwater. This element (Mn) in groundwater is encountered as Fe in the type of bicarbonate Mn (HCO3) 2. In outdoor waters with active hydraulic connection to surface waters manganese can enter the composition of complex components with humic acid. The presence of Mn can also occur as a result of the presence of microorganisms of organic origin. Manganese compounds are almost always present in waters where they are usually found in the form of bicarbonates, near-surface streams, near which water bodies are located. Problems with large amounts of rare metals in natural waters are not new, but their presence as a result of documented damaging effects on the human body is under the lens of rigorous legal restrictions in all parts of the world. Due to this, the maximum concentrations of these harmful constituents are constantly decreasing (Arsovski, 1997).

Although groundwater is of better quality, its rational use is necessary. This is especially due to the fact that the excessive exploitation of groundwater leads to a reduction in soil capacity as well as possible pollution of

resources and disruption of the hydrogeological characteristics of the external area in the groundwater collector and a reduction in the outflow of the same.

2. Materials and Methods

1.1.*Materials*

The study was conducted to assess the physicochemical and bacteriological qualities of drinking water. The safety and availability of drinking water is an important concern and goal for people from all over the world. Harmful health effects associated with drinking water come from the use of contaminated water with infectious agents, toxic and radioactive substances. Outdoor water contains various ingredients that determine water quality and suitability for a certain use. To determine the quality of water or the degree of water pollution, different components must be determined, respectively the different physical, chemical and microbiological parameters. It is a complex analysis, a dynamic system, in which a large number of components are present, which differ in space and time, but also affect each other (Janevska, 2014). Modernizing the approach to providing clean and hygienic drinking water is a contribution to improving people's health.

The place, respectively the source of water that is studied or analyzed, is the source from Gari Village which is located near the city of Dibra, next to the village there are water sources known as Garska or Small River which flows down and flows into the big River or Radika. These water sources of this village fall on the shoulders of the highest peak of Mount Stogovo (Pavlovski, 2006).

During the research, the seasonal monitoring of drinking water was carried out during the 4 seasons of the year, starting from the summer season of 2018 until the spring season of 2019.

Chemical analysis of water refers to the determination of several substances found in drinking water and may affect its hygienic suitability. The abbreviated chemical analysis of water known as routine analysis involves the determination of the fortification of drinking water, iron, fecal indicators, oxygen, and biological oxygen consumption. Complete chemical analysis is performed only occasionally and includes the determination of iodine and fluoride, as well as toxic substances (lead, mercury, and cyanide), detergents, pesticides and radioactive materials. A bacteriological analysis is performed to determine the number of non-pathogenic and pathogenic bacteria in the water, as well as other pathogenic data and is the most important factor in the hygienic quality of water. That is why it is important to first compile a program according to which will be analyzed, respectively assessed for water quality (Petrusevska & Ivanovska, 2015).The analysis is performed to determine whether the water meets the quality requirements for a specific purpose (beverages, industrial needs, sports and recreation, etc.), where in the case of this research the main goal is the purpose of drinking water (Janevska,2014).

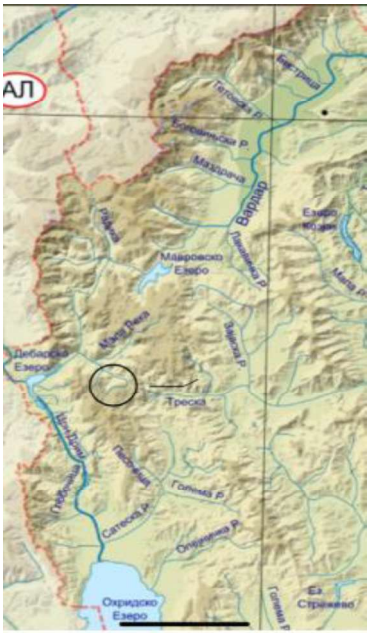

Figure 1. Map of Gari village near Stogovo, Mountain and river Garska

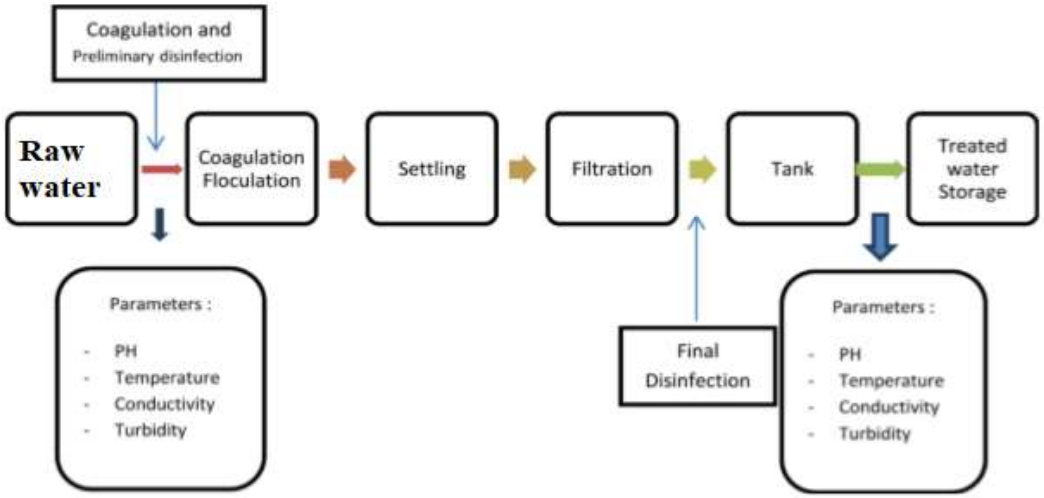

Figure 2. Diagram of the water treatment processes

2.2.Methods

Spectrophotometric methods were used to determine nitrates, nitrites and other minerals: SQ Pharo 300 1 unit 190-1100nm and Thermoreactor TR 420 Spectroquant. The determination of water turbidity is performed through Turbiquant 1100 IR Turbidimeter portable. For the measurement of pH value, electrical conductivity and oxygen content, multifunctional device were used: Phenomenal MU 6100L set, Multiparameter, pH meter / Conductivity / Oxygen meter.

Statistical analysis

Duncan's multiple comparison tests were used as a guide for paired comparisons of treatment means. The significance of differences between treatments was considered at $P < 0.05$ using SPSS version 9.0 for Windows (SPSS Inc., Chicago, IL, USA).

3. Results and Discussion

Water temperature is one of the most important ecological and physical factors that have a profound impact on both living and non-living components of the environment, thus affecting organisms and the functioning of an ecosystem, including one of the most important factors. Important to consider when assessing water quality, temperature also affects other parameters that can change some of the important physical and chemical properties of water. Based on this, water temperature should be calculated by determining metabolic rates and photosynthesis production, toxicity complex, dissolved oxygen and other gas-dissolved concentrations, conductivity and salinity, reduction of potential oxidation, the density of water and pH.

Although temperature generally affects the overall water quality (physicochemical and biological characteristics), there are no recommended guidelines for drinking water. Therefore, analyzing the temperature for water samples collected throughout the year (four seasons) from the village of Gari, had different temperatures whereas we see from the final results the lowest temperature is 4.5˚C displayed in the winter season, while the highest is 15.6˚C in the summer season. Comparing and based on the results we notice that from the two values such as the maximum in the summer season and the minimum in the winter season, although they are not out of the regulation, we can still say that the most suitable season in terms of temperature is water is the spring and autumn season where the temperature is 10.8 -11˚C.

Compared to the results of the Shkumbin River water the season with the lowest water temperature was the winter season (January) with 7.10˚C in the village of Brodec while the highest with 26.20˚C in the season of summer (August) in the village of Saraqinë (Durmishi, 2005). Based on these results and our water results from the village of Gari we conclude that the water temperature in the village of Gari is lower both in the winter season by 2.6 ˚C and in the summer season by 10.6˚C.

Water pH is important because many biological activities can only occur within a narrow range, so any change beyond an acceptable limit can be fatal to a particular organism. Water with a pH of less than 6.5 can be mildly acidic and corrosive. Acidic water can contain metal ions such as iron, manganese, lead and zinc. In other words, acidic water contains high levels of toxic metals where it can cause premature damage and these waters have a dry taste. From the samples analyzed in Gari village (Table 1) different pH values appear in different seasons and periods and all water samples collected during the four seasons had pH values within the recommended standard intervals. The lowest pH was presented in the samples analyzed in the summer season, (7.6) measured at 25˚C and the highest (8.3) measured at 25˚C in the autumn season. Thus this water indicates that in all seasons it can be classified as suitable for drinking purposes. Comparing and based on all the results for all seasons we notice that although with close results the autumn season in terms of PH pH of water is more suitable for consumption.

Compared to the results of the waters of the Shkumbin River (Durmishi, 2005) we note that the lowest pH was in March with 7.38 in the village Brodec while the highest was in the autumn season 8.36 in the village Saraqinë. Based on these results and our water results from Gari village we conclude that there was a very close pH where the season with the lowest pH is higher in Gari village by 0.22 and that of the highest season is lower by 0.06 in the village of Gari.

Nitrates are accurate and important indicators for assessing the quality of drinking water. Nitrates in groundwater depend very much on the type of soil and the geological condition of the area, at natural levels do not exceed 5.0mg/l. Oxidation of the ammonia form of nitrogen from animal and human waste to nitrite is a possible way for nitrates to enter groundwater. At higher concentrations of nitrates, can also be related to cancerous disease. From the analyzed samples as seen in the results given, the level of nitrate content is adjusted and is within the intervals allowed by the standards of our country of drinking water; the results have reached from 3.7 to 4.6 mg/l. The lowest value of nitrates was observed in the spring season, which was 3.7 mg/l, while the highest value was reached in the summer season, which was 4.6 mg/l.

Comparing and based on all the results for all seasons we notice that although with close test results the spring season in terms of nitrate content in water with 3.7mg / l is more suitable for consumption as that this value is lower than all other seasons and the lower the value the better the water. Nitrites also present clear and important indicators for assessing the quality of drinking water. Nitrite in groundwater does not exceed values of 0.50 mg / l. From the analyzed samples as seen in the given results, the level of nitrite content has reached from 0.03 to 0.05 mg/l. The lowest value of nitrites was observed in the winter season which was 0.03 mg/l, while the highest value was reached in the spring season which was 0.05 mg/l. Comparing and based on all the results for all seasons we notice that although with very close analysis results again the winter season in terms of nitrite content in the water with 0.03mg/l is more suitable for consumption as this value is lower than all other seasons and the lower the value the better the water.

The ammonia content is also an important parameter for evaluating the quality of drinking water. The value of ammonia in all analyzes was in the limits allowed from 0.03 to 0.08 mg/l. From the analyzed samples as can be seen in the results given, the lowest value of ammonia was observed in the spring season which was 0.03mg/l, while the highest value was reached in the summer season which was 0.08 mg/l. Comparing and based on the results for all seasons we notice that although with very close results of the analysis the spring season in terms of ammonia content in water with 0.03mg / l is more suitable for consumption since and this value is lower than all other seasons and the lower the value the better the water.

Chlorides are determined among the most common pollutants of drinking water where according to the allowed standards the level of chlorides in drinking water should not exceed 250mg/l. The results from the analyzes performed from the water samples from the village of Gari in the given tables it is seen that the maximum value of chlorine has not been more than 0.75mg / l, this also includes the spring season although with very similar results to other seasons. The lowest value obtained from the sample analyzes is 0.64mg / l in the summer and autumn season, which means the 2 seasons with the best drinking water and the safest.Based on the standards given by the World Health Organization and the European Union of Drinking Water (Directive 98/83 / EC) on the allowable values of nitrates (up to 50 mg / l), nitrites (up to 0.50 mg/l) , ammonia (up to 0.50mg/l) and Chlorides (up to 250mg/l) we conclude that drinking water from the source of Gari village significantly includes values below the allowable level in all seasons which means that the water is of high quality for drinks.

Table 1. Physicochemical paramteters of watter from Gari Vilage during four seasons

	Season							
Parameters	**Spring**	**Summer**	**Autumn**	**Winter**	**Unit**	**Max,V**	**Methods**	***ANOVA***
Colour	0	0	0	0	mg/l, Pt/Co	20		/
Temperature	10,8	15,6	11	4,5	˚C	25		0,000
Turbidity	1,5	0,8	1,9	1	NTU	1,5		0,000
pH (25^0C)	8,2	7,6	8,3	7,9	/	6,5-9,5	ISO 10523:1994	0,002
$KMnO_4$ consumption	7	5,61	6,5	5,3	mg/l	8	ISO 8467	0,000
Electrical conductivity	215	238	263	264	μScm^{-1}/ 20˚C	1500	ISO 7888:1985	0,000
Total hardness	6,7	8,3	7,5	6,8	dH ˚	/	ISO 6059:1984	0,000
NH_3	0,03	0,08	0,07	0,04	mg/l	0,5	ISO 7150-1	0,004
$NO\text{-}_2$	0,05	0,04	0,05	0,03	mg/l	0,5	EPA 354,1	0,381
$NO\text{-}_3$	3,7	4,6	3,9	4	mg/l	50	DIN 38405-9	0,000
Cl	0,75	0,64	0,64	0,72	mg/l	250	EPA 325,1	0,001
SO_4^{2-}	4	2,8	3,1	3	mg/l	250	EPA 375,4	0,000
Fe	0,03	0,1	0,1	0,01	mg/l	0,2	ISO 9297:1989	0,000
Mn	0,04	0,04	0,03	0,01	mg/l	0,5	ISO 6333:1986	0,053
Ca	41,4	49,2	45,4	43,5	mg/l	/	ISO 7980:1986	0,000
Mg	7,1	5,1	6,1	5,3	mg/l	/	ISO 7980:1986	0,000

K	<5	<3,0	<3,0	<3,0	mg/l	/	ISO 9964-3:1993	0,000
Cu	<0,05	<0,02	<0,03	0,01	mg/l	2	ISO 8288:1986	0,053
Pl	0	0	<0,01	0	mg/l	0,01	ISO 8288:1986	/
Ca	0	0	0	0	mg/l	0,5	ISO 8288:1986	/
Ni	0	0	0	0	mg/l	0,2	ISO 8288:1986	/

The content of iron in drinking water is not very tolerable, this is also shown by the maximum allowable value that must not be more than 0.2mg / l (Directive 98/83 / EC). From the analyzed samples which are presented in tabular form, we see that in the winter season the concentration of iron was lower 0.01 mg / l and during the analysis of samples in the summer and autumn season, the concentration of the amount of iron was at higher levels 0.1mg / l but again at a lower concentration than the allowable value. By making the comparison and based on the results we conclude that all the samples analyzed in all seasons the result is at the allowed levels and the most suitable one is in the Winter season as it presents a lower value of 0.01mg / l. The main element found on a smaller scale such as manganese, which is found in groundwater, does not pose a health risk to humans or the environment, but it does cause organoleptic concerns.From the results presented in the Table 1 from the analysis of samples in different periods of the year, it is seen that the consumption of potassium permanganate ranges from 5.3 to 7.0 mg / l. The lowest value, which is 5.3 mg / l, appeared in the winter season and the highest value was presented during the analysis in the spring season, where the level of KmNO4 reached 7.0 mg / l.Comparing and based on the results for all seasons it is noticed that water in the winter is more suitable for consumption as this value is lower from all other seasons.The total number of coliform bacteria is indicative of water pollution by faecal microorganisms which are pathogenic and can cause serious health problems in humans. The general bacterial count in the waters analyzed by samples taken in the village of Gari showed that all seasons of the year are without bacteria of this type.The enumeration of bacteria at 22°C and 36°C is a standard microbiological method for counting all anaerobic mesophilic bacteria found in drinking water. The number itself is an indicator of the microbiological purity of the water, as well as its quality where the number itself indirectly indicates water pollution by pathogenic microorganisms of various natures, but mainly by faecal contamination. The above notes regarding this microbiological method determine the maximum allowable limits for the total number of living microorganisms in drinking water according to international standards and they should not exceed the limits to maintain water quality.

Table 2. Microbial parameters of the watter from the Gari Village

Seasons	***Pseudomonas aeruginosa***	***E.Coli***	***Total bacteria 22^0C***	***Total bacteria 36^0C***
Spring	0	0	34	20
Summer	0	0	15	7
Autumn	0	0	10	0
Winter	0	0	5	2
Unit	cfu/250ml	cfu/250ml	cfu/ml	cfu/ml
MaxDK	/	/	100	20
Methods	Chromogenig agar – BRD 07/21-04/12	Chromogenig agar – BRD 07/21-03/11	EN ISO 6222 (07/1999)	EN ISO 6222 (07/1999)

In the technological processes of microbiological purification of water, ie its disinfection, this method is widely used in the monitoring of the process itself. According to the results in Table 2, the largest number of bacteria were founded in the spring season (34 CFU) in 22 °C and 20 colonies in 36 °C, while no number of bacteria at 22 °C were found in the winter season(10 CFU) and in the Autumn season(0 colonies).

2. Conclusion

From the physicochemical analysis, as well as the microbiological analysis of all water samples collected from the source of Stogova mountain, Gari village of Dibra region there are changes related to climatic influences, but their balance in the ratio of mineral composition is very good which makes the water of a good quality to drink.

During the spring period, when the rainfall is higher, the water shows a greater amount of organic matter, which significantly increases the consumption of potassium components. This confirms the fact that the source is located in a mountainous region, a region filled with lush vegetation that it contributes to the growth of organic matter, and variations can be seen in the microbiological analysis of samples. While important is the fact that in none of the analyzes were found pathogenic microorganisms isolated. Even in the geochemical composition of the soil, as well as the genesis of surface waters in this area proves the fact that the massif is rich in metamorphic deposits of manganese and iron that the same in water can be found in the form of bicarbonate. Quite interesting is the fact that manganese can enter the composition of complex compounds with humus acid, one of the characteristic features of spring water sources also manganese can appear in the presence of microorganisms of organic origin.It is concluded that the summer season is safer for drinking, but the changes that occur in physicochemical and microbiological parameters in different seasons and especially in the autumn and spring season itis necessary adequate technological treatment before use for drinks.

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References

[1]. Arsovksi.M. (1997) “Elaborate on the results of detailed geological exploration of mineral resources - groundwater locality Gari” ,Dibra.
[2]. Janevska,S. (2014)."Food Analysis" pp.28 , Skopje
[3]. KrasniqiA. (2019) “Ecological factors” pp.18,
[4]. Water sector - http://www.moepp.gov.mk/?page_id=3967&lang=AL
[5]. Petrusevska-Tozi L.& T.P.Ivanovska, (2015).”Practical exercises after water testing and control” Skopje
[6]. HamzaiE. (2016) “Telegraph, Macedonia today marks World Water Day”.
[7]. HristovskaN.& B.Ilievska-Hristova & I.Muhaxheri,(2013) “Hydrotechnical facilities“pp.33
[8]. Pavlovska, J. (2006). Mi-Anova Encyclopedia: M-P. Skopje: MI-AN Book Publishing House.
[9]. Macedonia Regulator - Food and Veterinary Agency. (2018). Regulation on drinking water safety and quality requirements.
[10]. Law on Mineral Resources. ("Official Gazette of the Republic of Macedonia"No..24/07,88/08,52/09,6/10,158/10 и 53/11.).
[11]. Durmishi,B.H. (2005). “Determination of the degree of pollution of Shkumbin River waters (PENA) with heavy metals and other effluents with spectrometric method and "Striping" voltammetry”, Pristina
[12]. Council Directive 98/83/EC on the quality of water intented for human consumption. Adopted by the Council, on 3 November 1998
[13]. WHO's Guidelines for Drinking water Quality, the international reference point for standard setting and drinking-water safety. Geneva, 199