

## GROUNDWATER QUALITY IN A RURAL AREA FROM BUZĂU COUNTY, ROMANIA

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### Abstract

*The underground water is the only source of drinking water in Buzău County. As a consequence the investigation of the underground water has a major importance. In the present study, a number of seven groundwater sources, located in Bisoca commune, NE of Buzău County, were selected in order to investigate the underground water quality. Several physico-chemical (temperature, pH, total dissolved solids, electrical conductivity, oxidation-reduction potential, salinity and turbidity) and chemical ( $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $NH_4^+$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$ ,  $Cu$ ,  $Cd$ ,  $Cr$ ,  $Zn$ ,  $Fe$ ,  $Ni$  and  $Pb$ ) parameters were analyzed. The waters proved to have low salinity values (0.1- 0.8‰) and electrical conductivity (89.5 – 1993.0  $\mu S/cm$ ). The dissolved ions distribution is dominated by the presence of sodium (3.6 – 232.9 mg/l), calcium (6.8 – 365.43 mg/l), sulphates (10.9 – 1301.4 mg/l), bicarbonates (427 – 793 mg/l) and chloride (5.1 – 166.1 mg/l). In the case of iron and lead there were registered exceeding's of maximum permissible limits for drinking water.*

**Key words:** Buzău County, groundwater, water quality parameters

### INTRODUCTION

Accessibility and availability of fresh clean water represents a key factor for a sustainable development, being an essential element in the human health, food production and poverty reduction [10]. In many rural areas from Romania, the underground water represents the primary source of drinking water, which is usually considered a safe source of drinking water.

In Buzău County, the underground water is the only source of drinking water in the area. Buzău Land is an isolated, mostly mountainous area, inhabited by approximately 40,000 people. It's located at the bending of the Carpathians, in the proximity of the Vrancea seismic zone, in a geodynamical active context that gives rise to slope failures, mud volcanoes, natural gas seepage and mineralized water springs [3], [5], [6],[7], [8]. The main goals of the present study were: to assess the water quality of seven ground water sources located in a rural area from Buzău

County (NE of Romania) and to find out the potential health risks for local people by using these sources as drinking water sources.

### MATERIALS AND METHODS

The investigated water sources are located in Bisoca commune in the north of Buzău County, Romania. Bisoca commune is composed of eight villages: Băltăgari, Bisoca, Lacurile, Lopătăreasa, Pleși, Recea, Sările and Șindrila. The commune area it has a surface of 73 km<sup>2</sup> and a population of 2,962 inhabitants. The investigated water sources consisted of five captured springs (S1-Bisoca village, S2-Sările village, S3-Recea village, S4-Lacurile village and S5-Băltăgari village), one well (W6) from Bisoca village and the public network from the Bisoca commune (PN7) (Fig. 1). The investigated ground waters are used for drinking, cooking, bathing, agricultural and therapeutically (sample S5 which is a sulphurous spring) purposes. The investigated water sources are located in the

future Geopark of Buzău Land. The water samples were collected during October 2014.



Fig. 1. Location of the investigated area

Source: Own determination.

The unstable physico-chemical parameters (temperature, pH, redox potential – ORP, electrical conductivity – EC, total dissolved solids – TDS, salinity, dissolved oxygen – DO and turbidity) were measured *in situ* using a portable multiparameter (WTW inolab 350i) and a portable turbidimeter (WTW pHotoFlex Turb). The water samples used for major dissolved ions analysis were collected in polyethylene bottles; the water samples were filtered *in situ* using 0.45 µm syringe filters. The water samples used for heavy metals analysis were acidified to a pH ≈ 2 (with HNO<sub>3</sub> 65%). The samples were then shipped to the laboratory, stored at dark and 4°C, and analyzed within 48 hours from sampling. The major dissolved ions (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>) were analyzed by ion chromatography (IC1500 Dionex), while CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> were determined titrimetrically. The heavy metals (Fe, Zn, Cu, Cd, Cr, Pb and Ni) were analyzed by using the flame atomic absorption spectrometry (FAAS) and graphite furnace (GAAS), depending on the concentration. For

the heavy metals analysis, an AAS system ZeeNIT 700, Analytik Jena was used. All the analyses were performed in the Environmental Laboratory from the Faculty of Environmental Science and Engineering (Babeş Bolyai University from Cluj-Napoca). The analyzed data were compared with the standard values recommended by the Romanian and international legislation.

## RESULTS AND DISCUSSIONS

The results of both *in situ* and instrumental analyses are summarized in Table 1.

Table 1. Synthesis of the physico-chemical and chemical parameters of the analyzed water samples

Parameter	Min.	Maxim	Average	Maximum Permissible Limit <sup>1</sup>
T(°C)	9	15	12	-
pH	5.6	7.5	6.6	6.5 – 9.5
ORP (mV)	-49.4	58.2	-3.13	-
EC (µS/cm)	89.5	1993.0	752.4	2500
TDS (mg/l)	57.1	1278.0	478.1	500 <sup>2</sup>
Salinity (‰)	ND <sup>3</sup>	0.8	0.2	-
DO (mg/l)	2.3	5.4	3.8	>5
Turbidity (NTU)	ND	27.6	7.16	≤5
Li <sup>+</sup> (mg/l)	ND	0.3	0.2	-
Na <sup>+</sup> (mg/l)	8.6	232.9	144.9	200
K <sup>+</sup> (mg/l)	2.6	19.3	8.3	10 <sup>2</sup>
Mg <sup>2+</sup> (mg/l)	1.6	46.5	15.3	50 <sup>2</sup>
Ca <sup>2+</sup> (mg/l)	6.8	365.4	99.8	200 <sup>2</sup>
NH <sub>4</sub> <sup>+</sup> (mg/l)	ND	0.4	0.3	0.5
F <sup>-</sup> (mg/l)	ND	2.2	0.9	1.2
Cl <sup>-</sup> (mg/l)	5.1	166.1	62.2	250
Br <sup>-</sup> (mg/l)	ND	3.9	-	-
NO <sub>2</sub> <sup>-</sup> (mg/l)	ND	4.1	-	0.5
NO <sub>3</sub> <sup>-</sup> (mg/l)	1.9	12.9	8.1	50
SO <sub>4</sub> <sup>2-</sup> (mg/l)	10.9	1301.4	235.7	250
HCO <sub>3</sub> <sup>-</sup> (mg/l)	427	793	610.9	-
Fe (µg/l)	76.2	405.4	172.9	200
Zn (µg/l)	9.9	1240.9	307.3	5000
Cu (µg/l)	18.5	83.6	42.8	100
Cd (µg/l)	0.01	0.31	0.14	5
Cr (µg/l)	4.5	31.8	12.6	50
Pb (µg/l)	27.4	571.9	127.4	10

<sup>1</sup>According to Romanian legislation for drinking water (Law 458 from 08.07.2002); <sup>2</sup>According to BC Health Act Safe Drinking Water Regulation–Canada [1] and World Health Organization [11], [12]; <sup>3</sup>ND = Not Detected  
Source: Own calculation.

As it can be seen in Table 1 and Fig. 2 the analyzed water samples were slightly acidic to neutral, having the pH between 5.6 and 7.5. In the water samples collected from two springs

(S3, S4) and from the well (W6) the pH level was lower than the permissible limit (6.5) set by the Romanian drinking water law (458/2002).

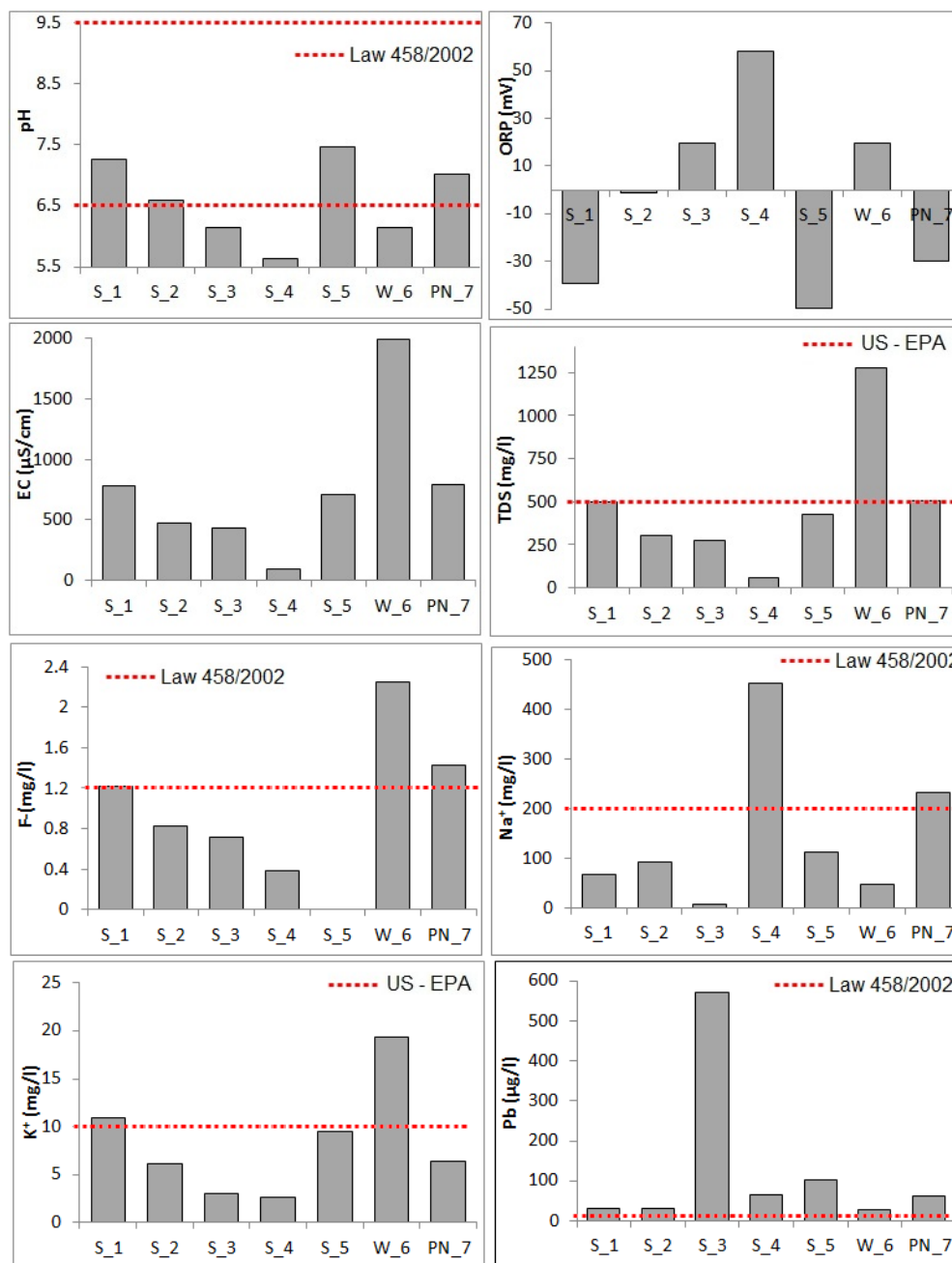


Fig. 2. The main physico-chemical and chemical parameters of the analyzed water samples (S1 – captured spring from Bisoca village; S2 – captured spring from Sărule village; S3– captured spring from Recea village; S4 – captured spring from Lacurile village; S5 – captured sulphurous spring from Băltăgari village; W6 – well from Bisoca village and PN7 – public network from Bisoca commune)  
Source: Own calculation.

The analyzed water samples had a redox potential between -49.5 and 58.2 mV. The highly negative value was recorded in samples taken from the sulphurous spring (S5), while the highly positive value was

recorded in the water sampled from the spring S4 (Fig. 2). Such high values of ORP, ensures chemical stability for some metal salts and hydroxides (Fe, Mn, etc.) and chemical instability of organic substances, increasing

their decomposition. A low ORP may indicate the presence of anaerobic redox potential and reducing conditions in the aquifer, while a positive redox potential indicate the presence oxidizing environments. All the analyzed water samples had the ORP between -100 and 100 mV, values recommended by the WHO (World Health Organization) and US-EPA (United States – Environmental Protection Agency) for drinking water [9], [11], [12].

With the exception of sample collected from well (W6), the analyzed waters had a relatively low electrical conductivity, between 89.5 and 790  $\mu\text{S}/\text{cm}$ , being lower than the limit (2500  $\mu\text{S}/\text{cm}$ ) imposed by national legislation. The water sampled from well from Bisoca village (W6) had a higher EC (1993  $\mu\text{S}/\text{cm}$ ), being however lower than the maximum limit imposed by legislation.

With the exception of sample W6, the analyzed waters proved to be oligomineral waters, having the total dissolved solids contend below 1 g/l [4]. Sample W5 can be classified as mineral water mineral with an average mineralization, having the TDS between 1 and 15 g/l. Because of the high TDS contents, it is not recommended to use the water from W6 sampling point for agriculture purposes. A TDS values between 1000 - 2000 mg/l present high risk for agricultural use [13], reducing the soil permeability and aerating.

As in the case of EC and TDS, with the exception of sample W6 (0.8‰), the analyzed waters proved to have a low salinity (0.1‰ for S1, S5 and PN7), being within the maximum limit (0.2‰) imposed by US-EPA. The high values of EC, TDS and salinity recorded for the well W6 from Bisoca village, reflect the high content of dissolved salts in water samples, which are correlated with the geological characteristics of the aquifer. High values of EC and TDS, reflect the presence of high concentrations of salt ( $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ) of calcium, magnesium, sodium and silica in the water samples. In addition an increased level of salts increases water turbidity and hardness, decreases dissolved oxygen level, causing different problems in the water treatment process.

With the exception of sample S5 (5.4 mg/l),

the investigated waters, had a low level of dissolved oxygen (2.3-4.6 mg/l), which is below the minimum limit of 5 mg/l imposed by national legislation (Law 458/2002).

With one exception (S4), the investigated water sources had a low turbidity, being lower than 1 NTU, which is the maximum permissible limit imposed by national legislation.

In the spring S4, a considerably higher level was registered (27.6 NTU), which can be associated with the presence of a large number of micro-organisms, such as viruses, parasites and certain bacteria.

The continuous consumption of drinking water from these sources may be associated with symptoms such as nausea, cramps, diarrhea and headaches.

As it is shown in the Piper Diagram (Fig. 3) the major dissolved ions distribution is dominated by the presence of sodium (3.6 – 232.9 mg/l), calcium (6.8 – 365.43 mg/l), sulphates (10.9 – 1301.4 mg/l), bicarbonates (427 – 793 mg/l) and chloride (5.1 – 166.1 mg/l).

The investigated water sources proved to have a relatively low level of calcium and magnesium. With the exception of sample W6, the both calcium (6.8 – 124.53 mg/l) and magnesium (1.6 – 19.38 mg/l) levels were within the maximum limits (200 mg/l and 50 mg/l) recommended by the World Health Organization. The investigated well from Bisoca (W6) proved to have higher calcium content (365.4 mg/l). Calcium and magnesium are among the macroelements essential for life. It is known the importance of Ca/Mg ratio in water. An optimal value for this ratio is 2:1, offering greater protection against cardiovascular disease. In the present study, the values of Ca/Mg ratio ranged between 3.1 and 10.3. In addition, a high content of calcium and magnesium increase the water hardness.

The water samples collected from spring S4 and from the public network (PN7) had considerably high sodium level, exceeding the maximum permissible limit (200 mg/l) imposed by national legislation (Fig. 2). The other samples had a low level of sodium, between 8.6 and 112.1 mg/l.

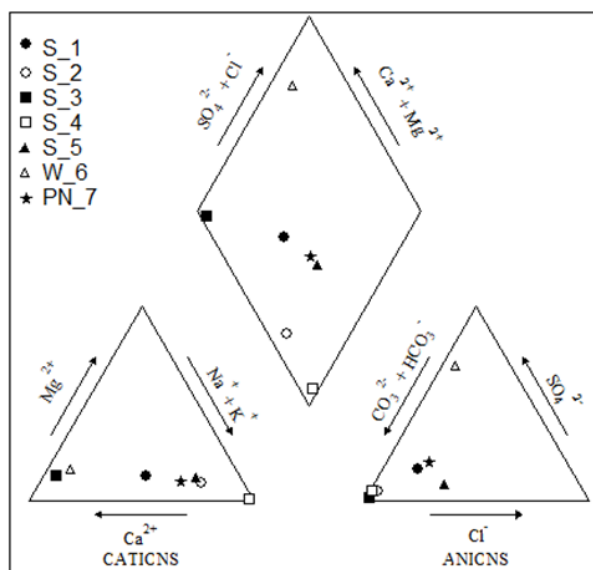


Fig. 3. Piper diagram for the investigated water sources  
Source: Own determination.

The spring S1 and the well W6 had the higher potassium level, exceeding 10 mg/l, value recommended by US-EPA and WHO for human health protection (Fig. 2). Recent studies [2] showed that high levels of sodium and potassium in the diet or drinking water can be associated with increased incidence of hypertension. The optimal Na/K ratio is 3:1. In the analyzed water samples, the Na/K ratio was relatively high, ranging between 2.5 and 174.9.

Lithium (0.03-0.33 mg/l) and ammonium (0.2 mg/l in S3 and 0.4 mg/l in PN7) had the lower levels among the analyzed cations, being within the maximum permissible limit for drinking water.

Laboratory analysis showed that three of the investigated water sources (S1, W6 and PN7) had a relatively high content of fluoride, this parameter exceeding the maximum permissible limit (1.2 mg/l) (Fig. 2), which coincides with the value recommended for dental caries prevention. This parameter was not detected in the sulphurous spring (S5), probably due to the high dilutions of samples prior analysis.

The chloride level was relatively low (5.1 – 166.1 mg/l), being lower than the maximum permissible limit (250 mg/l) in all the analyzed samples. Bromine and nitrites were detected only in sample S2 (3.9 mg/l and 4.1 mg/l). In case of nitrite, the maximum

permissible limit for drinking water (0.5 mg/l) was considerably exceeded. The continuous usage of this source as drinking water represents a real threat for local people health, because nitrites are classified as toxic to human body. The high content of nitrites indicates the presence of a recent pollution source.

Nitrate was detected in all the investigated water, the level of this chemical parameter ranged between 1.9 and 12.9 mg/l, being considerably lower than the maximum permissible limit (50 mg/l) imposed by national legislation.

With the exception of well from Bisoca village (W6), the analyzed water samples had a low level of sulphates (10.9 – 119.7 mg/l), being lower than the maximum permissible limit of 250 mg/l. Because of the high level of sulphates (1301.4 mg/l), the water from sampling point W6 can be used as sulphated waters (>1 g/l sulphates). Sulphated waters can be used for internal treatment in digestive diseases (intestinal, hepatobiliary), but only in strict doses and under the supervision of doctor.

Carbonate ion was not detected in the investigated waters, while the bicarbonate ion was detected in all analyzed samples, ranging between 427 and 793 mg/l. The highest values were recorded for well W6 which indicate that these waters are alkaline water, sodium bicarbonate being the dominant in these waters.

Distribution of heavy metals in water samples investigated is dominated by the presence of zinc (9.9 -1240.9  $\mu\text{g/l}$ ), iron (76.2 – 405.4  $\mu\text{g/l}$ ), copper (18.5 – 83.6  $\mu\text{g/l}$ ) and lead (27.4 – 571.9  $\mu\text{g/l}$ ). Cadmium (0.01 – 0.31  $\mu\text{g/l}$ ) and chromium (4.5- 31.8  $\mu\text{g/l}$ ) were present in lower concentrations (Table 1). The investigated water sources proved to have low levels of Zn, Cu, Cd and Cr, all this chemical parameters were within the maximum permissible limits imposed by national legislation for drinking water. Nickel was not detected in any of the analyzed samples. With the exception of well W6 from Bicoca, where the Fe level was 405.4  $\mu\text{g/l}$ , the other investigated drinking water sources had a lower Fe level (76.2 – 169.0  $\mu\text{g/l}$ ), being

within the maximum permissible limit of 200 µg/l.

The laboratory analysis proved the presence of high level of lead (27.4 – 571.9 µg/l). This element exceeded the maximum permissible limit (10 µg/l) in all the analyzed water samples (Fig. 2). The highest level was recorded in the spring S3 from Recea village. Lead is a toxic element, classified as "carcinogenic to humans". As such, the constant usage for a long time of these water sources as drinking waters can lead to severe health effects for residents. Target organs that may be affected are the kidneys, liver, spleen and lungs. These water sources must be carefully monitored in order to investigate the existence of an accidental pollution source, otherwise the water consumption from these sources should be stopped or significantly restricted.

## CONCLUSIONS

The results of the present study showed that in some of the investigated groundwater sources, some of the analyzed physico-chemical and chemical parameters exceeded the maximum permissible limit imposed by national and international legislation. The exceeding's were recorded in the case of: pH, TDS, DO, turbidity, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, F<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Fe and Pb. The continuous consumption of drinking water from these sources may be associated with symptoms such as nausea, cramps, diarrhea and headaches.

Because the high level of NO<sub>2</sub><sup>-</sup> (in sample S2) and Pb (in sample S3), the continuous usage of this springs as drinking water sources represents a real threat for local people health, because these elements are classified as toxic to human body. These water sources must be carefully monitored in order to investigate the existence of an accidental pollution source, otherwise the water consumption from these sources should be stopped or significantly restricted.

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