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Dedicated to prof. dr. I. C. Popescu
on the occasion of his 70th anniversary

GROUNDWATER QUALITY IN SHALLOW WELLS FROM FELEACU VILLAGE, CLUJ COUNTY, ROMANIA

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ABSTRACT. This study includes monitoring of the most important physico-chemical parameters in ten shallow wells from Feleacu village, Cluj County, Romania, in order to establish if the water sources can be used as drinking water. dH_t, dH_T, COD, TDS, conductivity, pH, NO_2^-, NH_4^+, Mn^{2+} and Fe_{total} were determined using appropriate standard methods and compared with allowable values for drinking water, according to Romanian legislation. Based on the determined parameter values, most of the samples were characterized by high mineralization and some of them are contaminated with nitrite ions. Thus in order to ensure that the water consumed as drinking water will not create health problems to the population, periodically monitoring of physico-chemical parameters should be compulsory performed.

Keywords: *groundwater, shallow wells, drinking water, quality parameters, monitoring*

INTRODUCTION

On planet Earth, on large areas, drinking water supply is represented by the groundwater, particularly from wells, without the usage of electrical equipment [1]. According to statistics, in Romania, about 45% of the population lives in rural areas and more than 2500 villages benefit from centralized water supply system, the rest using their local water sources (wells, springs). Generally, wells in Romania are built at smaller depth, 20 meters, and there are not suitably covered [2, 3].

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The groundwater quality parameters variation depend on the geological structure of the area, the activities that take place close to the points of sampling, the climatic conditions, the alternation of rainy and dry periods, etc. [4, 5].

Groundwater may contain natural impurities or contaminants, which can originate from watershed or soil. Water moving through underground rocks and soils may pick up magnesium, calcium, iron, manganese and chlorides. Some groundwater naturally contains dissolved elements such as selenium, boron, arsenic or radon – a gas formed by the natural breakdown of radioactive uranium in soil. These natural contaminants can produce various health problems depending on their amount [6, 8].

Also, groundwater is often polluted due to human activities, such as: fertilizers usage, animal manures, pesticides, improperly built and located septic systems for household wastewater, storm-water drains that discharge chemicals to groundwater, improper disposal or storage of wastes, chemical spills at local industrial sites [9-11].

Between groundwater pollutants, a special problem is generated by the presence of high nitrate/nitrite ions quantities. Naturally existent quantities are increased by various human activities (septic tanks, animal manures, fertilizers, etc.). Nitrogen compounds from soil are transformed and the nitrate ions are picked up by flowing water and transferred in groundwater. Therefore shallow wells drinking water in our country could reach many times higher levels that the allowable values according to Romanian legislation [12]. The actual toxicity is given by nitrite ions which are formed from nitrates ions in organisms or abiotic environment (water pipelines and storage tanks). The susceptibility to nitrite ions of new-born children and animals is due to the fetal hemoglobin, which has more affinity for oxygen, therefore forms methemoglobin quicker than in adults [12-18].

Water from wells can be consumed directly without previous treatments if groundwater is not in a contaminated area and if the well is properly built and maintained. Wells should be placed away from latrines or barns, and if possible, above or at the same level. Water quality must be regularly checked and periodically disinfected, while the well walls are cleaned and disinfected [18-20].

This paper includes a case study regarding groundwater quality in shallow wells from Feleacu village, Cluj County, Romania. The area was chosen taking into consideration the fact that this village is not connected to the centralized water supply even if is very close to Cluj-Napoca city.

RESULTS AND DISCUSSION

Based on water hardness, expressed in German degree, water can be classified as very soft (0-4 °d), soft (4-8 °dH), moderately hard (12-18 dH),

hard (18-30 °dH) and very hard (>30 °dH) [21]. Temporary hardness values determined in the collected water samples (W1-W10) are listed in Table 1, all values are above 5 °dH, value specified by the Romanian legislation. It can be seen that some values are quite high, as water collected in October 2013 from W4, W5, W7 wells. This indicates the presence of bicarbonates of calcium and magnesium, resulting from dissolution of minerals by meteoric waters. Small amounts of temporary hardness for W1, W3, W9 water samples are due to the fact that cleaning and disinfection was realized just a few days before sampling. Total hardness values, Table 1, showed that all water samples have high hardness and can be included in the category of very hard water (W1, W2, W4-W8, W10), hard (W9) and moderately hard (W3). Values showed in Table 1 and Figure 1 suggest that the total hardness is slightly higher for each well for samples collected in October and May, by comparison with those collected in March. This fact can be attributed to the higher temperatures registered in those months, when higher amounts of minerals are dissolved before they reach the groundwater level. Groundwater from these wells can be used as drinking water after preliminary boiling and cooling or storage in suitable containers for several hours when calcium and magnesium salts dissolved in water is deposited.

Table 1. Total and temporary hardness values of W1-W10 samples.

Well	October		March		May		Water type*
	dH_t	dH_T	dH_t	dH_T	dH_t	dH_T	
	(°dH)						
W1	16.24	37.52	10.92	32.20	16.24	33.04	Very hard
W2	16.80	40.32	13.44	42.28	14.00	39.20	Very hard
W3	13.44	16.24	8.40	21.28	11.76	22.96	Moderately hard
W4	20.44	44.52	13.44	39.76	16.24	33.04	Very hard
W5	21.00	38.36	12.32	35.00	15.68	32.48	Very hard
W6	17.92	47.88	15.12	43.12	16.80	47.60	Very hard
W7	23.52	45.92	14.00	30.52	16.24	35.28	Very hard
W8	17.36	31.36	10.08	29.96	14.56	34.72	Very hard
W9	5.60	33.60	3.92	25.48	3.36	24.08	Hard
W10	15.69	34.44	15.12	33.68	15.12	36.40	Very hard

* Based on dH_T values

Chemical oxygen demand (COD) values determined in the collected water samples are generally under the maximum allowable value (MAV) specified by the Romanian legislation (5 mg O_2/L or 12 mg $KMnO_4$/L) with exception of W1 and W3 samples collected in October and W7 collected in

March, which are close to MAV (Figure 2). Therefore, taking in account the diversity of factors that affect COD values, in the cases where high values were recorded, closer monitoring, identification of the exact cause and remediation of the identified problem are required.

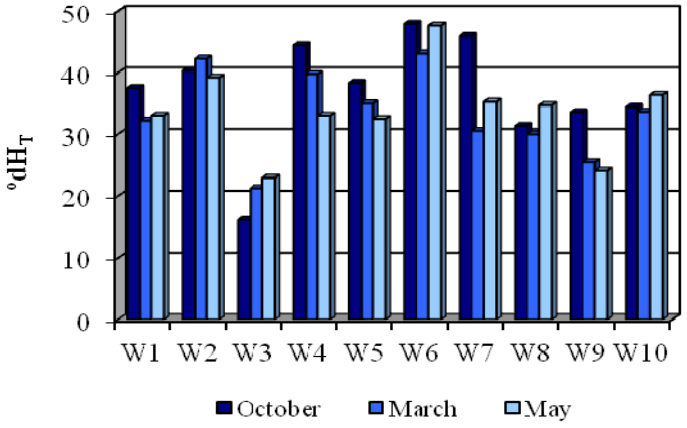

Figure 1. Evolution of total hardness values of W1-W10 samples over the monitoring time intervals.

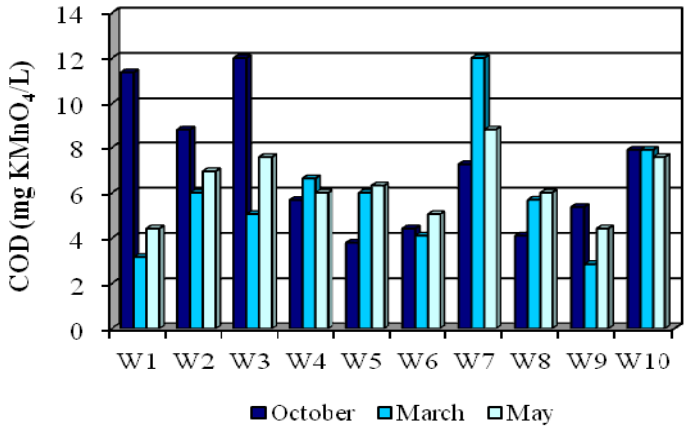

Figure 2. Chemical oxygen demand values of W1-W10 samples over the monitoring time intervals.

For total dissolved solids (TDS), in all water samples were registered values lower than the MAV specified by the Romanian legislation (1200 mg/L), Table 2. Also in case of most of the samples collected in March, TDS values are smaller than for those collected in October and

May. These values are correlated with COD and dH_T values for the same well. pH values determined for W1-W10 samples are all in the pH range specified by Romanian legislation (6.5-9.5), Table 2. Lower values were recorded for W9 (pH 6.50 – 6.80), while higher values were recorded for W1, W6, W7, Table 2.

Table 2. Solid residue and pH values of W1-W10 samples.

Well	TDS (mg/L)				pH			
	October 2013	March 2014	May 2014	MAV*	October 2013	March 2014	May 2014	MAV**
W1	560	240	680	1200	7.54	8.43	7.65	6.5-9.5
W2	800	680	920		6.98	7.86	7.81	
W3	720	200	360		6,78	7.80	8.06	
W4	640	160	600		7.03	8.33	7.91	
W5	880	560	400		7.29	7.94	7.75	
W6	840	760	480		7.30	8.20	7.52	
W7	1120	800	560		7.19	8.26	7.76	
W8	280	320	240		7.12	7.77	7.23	
W9	520	520	320		6.80	6.74	6.50	
W10	240	400	480		6.89	8.18	7.57	

* Acording to Romanian STAS 3638/76
** Acording to Romanian Laws 458/2002 and 311/2004

The electrical conductivity of water samples collected is relatively high, compared with water from Cluj-Napoca drinking water network (60-80 µS/cm), with values between 671 µS/cm for W3 in October 2013 and 1792 µS/cm for W7 in October 2013. All values are under the MAV value according to Romanian legislation (2500 µS/cm).

The concentration of nitrite ions in W1-W10 samples (Figure 3) have in general values under the MAV according to Romanian legislation (0.50 mg/L). In few cases, W1 and W10, were recorded very high values 1.094 and 1.606 mg/L, respectively. Relatively high values but below the maximum were recorded for samples W2, W7 and W9. These wells are located downstream of the house and household annexes, therefore groundwater can easily seep nitrogen. Taking in account the high toxicity of nitrite ions, this parameter has to be periodically checked and the consumption as drinking water stopped until treatment and removal of the pollution sources was realized.

Ammonium concentrations in all samples collected, as can be seen from Figure 4, have values below the MAV according to Romanian legislation (0.50 mg/L) the highest value recorded in a sample was 0.226 mg/L for W1 in March.

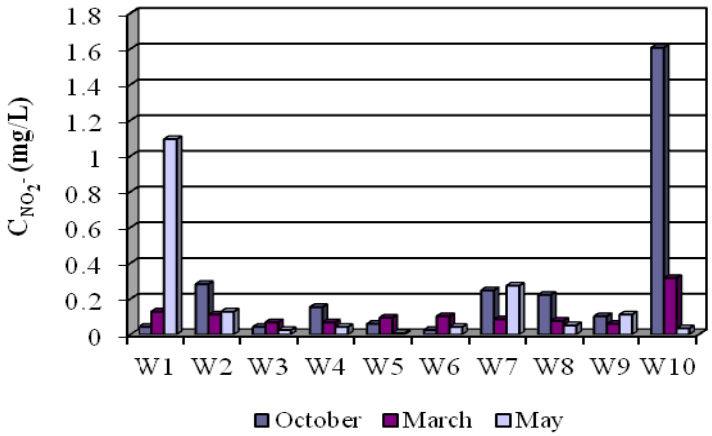

Figure 3. Nitrite ions concentration values in W1-W10 samples over the monitoring time intervals.

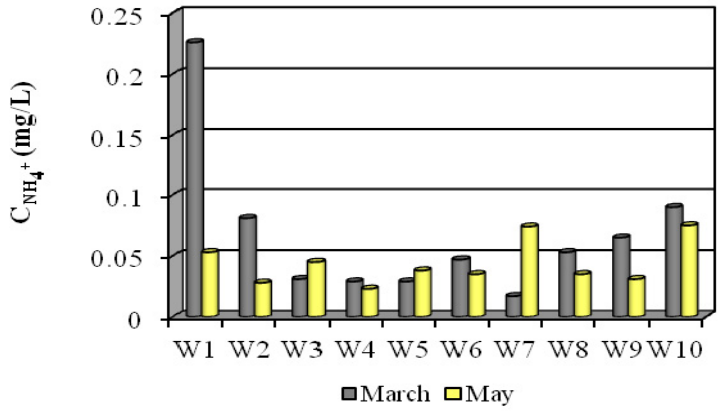

Figure 4. Ammonium concentration values in W1-W10 samples in March and May 2014.

Concentrations of manganese and iron ions are very small for all samples. Concentration values were below the MAV values imposed by the Romanian legislation, 50 µg Mn^{2+}/L and 200 µg Fe_{total}/L. In addition, iron ions are not toxic to the body, on the contrary, is considered a vital trace element, essential for the synthesis of heme from red blood cells and of myoglobin.

CONCLUSIONS

Based on the physico-chemical monitoring carried out (dH_t, dH_T, COD, TDS, conductivity, pH, NO_2^-, NH_4^+, Mn^{2+} and Fe_{total}) on 10 shallow well

waters from Feleacu village, Cluj County, Romania, it was found that in generally, groundwater is characterized by high mineralization (they are hard or very hard water) and often, due to human activity are contaminated with nitrite ions. Groundwater from these wells can be used as drinking water after preliminary boiling and cooling or storage in suitable containers for several hours, when calcium and magnesium salts dissolved in water are deposited. According with the results presented in this study, some of the considered wells present high concentrations of COD and NO_2^-, therefore closer monitoring, identification of the exact cause and remediation of the identified problems are required.

EXPERIMENTAL SECTION

Collection site and water sampling

Water samples were collected from 10 wells (W1-W10, Figure 5) located in Feleacu village, Cluj County, Romania, in October 2013, March and May 2014. This village is situated on Feleacu Massif, located on Someş River Plateau, Transylvania region. The Massif is oriented on the east-west direction over a length of 20 km, along which two other peaks are present, Peana (832 m), Măgura Sălicii (824 m) [20]. An important feature of this Massif is the presence of Sarmatians deposits, also known "Feleacu concretions". These deposits were created by gradual and long-time precipitation of $CaCO_3$ in the soil. $CaCO_3$ was initially trapped in the waters that soaked sandy layers, after that precipitation took place around limestone rock fragments or shells debris. Thus, these processes have led to the formation of concentric deposits of $CaCO_3$ around grains of sand [21, 22].

Climatic conditions in the area are moderate with not very cold winter and not excessively hot summers. The transition from winter to spring takes place usually in mid-March and from autumn to winter in November. Thus, average annual temperatures are between 8-9°C, and mean annual precipitation ranges from 600 to 700 mm [22].

In terms of hydrography, Feleacu village area has no running water or lake, however, geological substrate in this region has allowed the emergence and development of aquifer, which is the main water source for villagers in discussion. Sarmatian deposits allow accumulation of water with the formation of aquifers, fed directly by water infiltration. These accumulations have thus the character of an aquifer with fresh water [22-24]. Due to the special bedrock, these waters are characterized by a high degree of mineralization.

Water samples were collected in plastic containers, previously rinsed 2-3 times with the water sample, completely filled, and then closed

so that no air bubbles remain inside the bottle. On wells equipped with pumps, water sample was collected after a minimum of 10 minutes run, while from wells with extraction bucket collection was made introducing the bucket at 10-30 cm below the water mirror. After collection, bottles were placed in dark boxes. Until the analyses were run, water samples were kept at temperatures below 5°C and processed within 6 h from collection.

Water samples analysis

Wells water samples were characterized using the physico-chemical methods according to Romanian legislation (Laws 458/2002, 311/2004). The following water quality parameters were determined: temporary hardness (dH_t) and total hardness (dH_t) in degrees German (°dH), pH, chemical oxygen demand (COD-Mn) in mg $KMnO_4$ mg/L, solid residue (mg/L), electrical conductivity (μS/cm), Mn, Fe_{total}, NO_2^-, NH_4^+ (mg/L). pH and electrical conductivity were determined using a Consort C863 pH meter (SR ISO 10523/96, SR ISO 7887/97). Total dissolved solids (TDS) were determined using gravimetric method (Romanian STAS 3638/76). Temporary and total hardness and chemical oxygen demand were determined by volumetric method (Romanian STAS 7313-82, STAS 3326-76, STAS 3002-85). Concentration of Mn^{2+}, Fe_{total}, NO_2^- and NH_4^+ were determined using molecular absorption (SR 8662-1, 2/96, SR 13315/96, STAS 3048/2-96, STAS 6328/85) using an UV VIS Spectrometer Jenway 6305. Each sample was measured three times, the averaged values were presented.

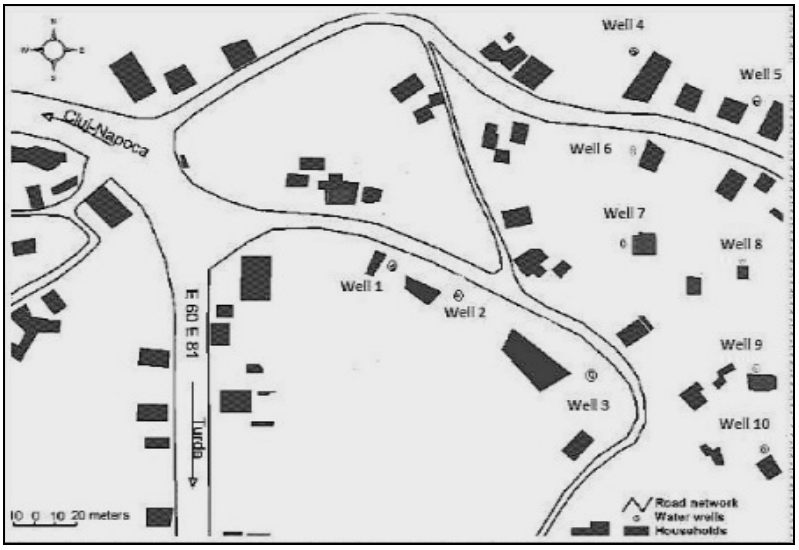

Figure 5. Location of the water wells, Feleacu village, Cluj County.

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