Journal homepage: www.fia.usv.ro/fiajournal
Journal of Faculty of Food Engineering,
Ştefan cel Mare University of Suceava, Romania
Volume XV, Issue 1- 2016, pag. 29 - 35

CHEMICAL ANALYSIS OF FRESH WATER FROM A KARST AREA IN UKRAINE

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Received January 26th 2016, accepted March 24th 2016

Abstract: *The chemical composition analysis was performed for fresh water samples taken from a karst area located in the region of Chernivtsi, Ukraine. Water samples were taken from private wells, springs and open ponds near Verenchanka. Total water hardness exceeded the sanitary limits for all the well samples and ranged from 11 to 29 mmol-eq/l (respective sanitary limit is 7 mmol-eq/l). This can be caused by the close-to-surface karst formations located under the village which release massive amounts of water hardness ions in the well water as a result of karst ablation. However, the heavy metals content (Fe, Zn, Cu, Mn) was within the sanitary limits excepting two samples which slightly exceeded zinc content.*
Total hardness of the surface spring and pond waters ranged from 6.2 to 11 mmol-eq/l and the heavy metals ions contents were comparatively low.

Keywords: *fresh water, total hardness, heavy metals content, karst area, trilonometry, atom-absorption spectrometry.*

1. Introduction

Availability of fresh water is a key issue for any inhabitant of municipal or rural areas and it is an indicative parameter of the life quality and safety, keeping the public health and improvement of the life conditions. This problem has gained the primary importance for many countries and regions all over the world.
It is known that quality of approximately 10 % of the drinking water in Ukraine remains below sanitary standards and requirements set for its chemical composition and bacterial parameters [1]. Moreover, a lot of inhabitants of rural areas of Ukraine traditionally consume the untreated water, which is often contaminated by chemical and/or germ agents, which results in worsening of the total organism resistance and immune status [2].
It seems interesting to investigate possible effects of the karst formation and development processes on the drinking water quality in the nearby areas.
Karst is an integral watercycling rock geosystem enriched with numerous pores and channels formed as a result of dissolution/sedimentation of the primary rock materials by circulating natural waters. The near-surface subterranean karst formation causes numerous specific phenomena in the local relief and hydrology related to significant voidage and channels penetrability of the rock. All these factors result in formation of some specific karst land-

scapes. Changes in the hydrology regime of the area can lead to dynamic changes in the karst character, which causes changes in the water cycling followed by possible changes in the local natural waters composition [3].

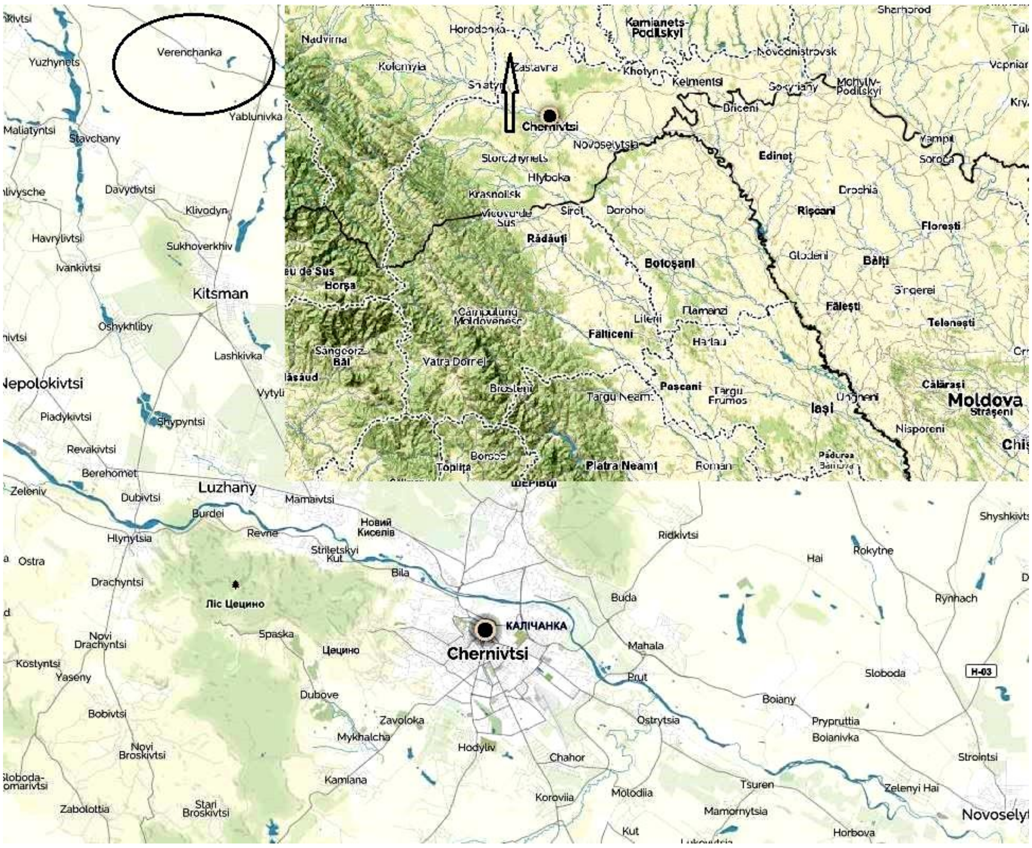

Fig. 1. Approximate location of vil. Verenchanka in Chernivtsi region (encircled) and the same in bigger scale (arrowed) in the map of the West of Ukraine (embedded).

The karst rocks can perform a strong adsorption action since they are formed by quite porous materials capable to extract various heavy metals while water is infiltrating through karst. On the other hand, the karst rocks is represented mainly by a comparatively easy-soluble limestone and gypsum, which results in releasing of significant amounts of calcium and magnesium (hydro)carbonates, sulfates and other salts into water.

As a result, the overall influence of the karst rocks on the drinking water quality and composition depends on numerous local specifics and should be investigated thoroughly for each locality of interest.

The village of Verenchanka is located in Zastavna district of Chernivtsi region, Ukraine (see Fig. 1) at the well-known subsurface gypsum karst formation. Numerous occurrences of karst phenomena have been continuously reported in the nearby area and within the village. Besides, there is a gypsum opencast mine near Verenchanka.

The 20-30 meters thick sub-surface karst formations are mostly responsible for the active karst manifestations in the middle part of Pruth-Dnister interfluve. Local karst manifestations in the area of Verenchaka are related to the block tectonic structure of the local rock and different karst opening depth by the draining rivers incuts [4].

Therefore, it is expected that karst phenomena can provide quite a tangible influence on the well-water quality in the village. Basing on this assumption we planned and carried out a systematic investigation of some physico-chemical parameters of the water samples taken from various sources inside and around the village. Water quality parameters have been determined using the following methods: organoleptic evaluation (taste, odor and color), trilonometric determination of the total water hardness and atom-absorption spectrometry (AAS) measurement of some heavy metals contents.

2. Materials and methods

Water sampling has been performed according to [5, 6] using the 0.5 liter polyethylene containers washed preliminary with nitric acid and then distilled water. 5 ml of the highly purified nitric acid have been added to each water sample for the purpose of conservation. Total series involved 32 samples taken from the wells, springs and ponds inside and nearby the vil. Verenchanka.

Total water hardness has been determined using the well-known method of trilonometry based on formation of stable complexes of ethylenediamine tetraacetic acid (EDTA) with Ca^{2+} and Mg^{2+} ions. pH of the solution was kept at 9–10 by the ammonia buffer solution (NH_4Cl + NH_4OH) and Eriochrome Black-T was used as an indicator.

Then the heavy metals content has been measured by AAS. It should be noted that this method has proved its superior sensitivity, high accuracy and requires comparatively short time. On the other hand, it requires preliminary chemical decomposition of the samples. The 'matrix' composition should also be taken into consideration.

Qualitative determination of Fe, Zn, Mn and Cu in all the samples has been done according to the method [7, 8] using the air-acetylene flame and standard solutions approach. Details of the determination regimes for different elements are available from Table 1.

Table 1.

Determination regimes for Fe, Zn, Mn and Cu

Element	Wavelength, nm	Determination limit, mg/l
Fe	248.3	0.08
Zn	213.9	0.012
Mn	279.5	0.025
Cu	324.8	0.04

3. Results and discussion

As seen from a map (see Fig. 2), the wells are scattered practically all around the village area. They are located both in valleys and uplands. The valley wells are relatively shallow (7, 8, 20, 21 and 28) and their depth is limited by 9 meters while the upland wells (1, 13÷19, 22÷27, 29÷32) are much deeper and their depth can reach 25 m (see Table 2). An average well depth in the area is 12.9 m.

As seen from Table 2, the water quality parameters are ranged within quite wide limits. However, no reliable dependence between well locations and the water quality parameters has been found. In our opinion, this can be caused by different geological conditions and water feeding regimes for each of the wells. Our results are in good agreement with a concept of geological structure of the region. Therefore, high total hardness can be caused by an intense circulation of the well-feeding waters inside the Miocene gypsum rocks forming karst structures in the area. The total water hardness was found very high for all the wells and it exceeds substantially the sanitary value. More detailed results of the water quality investigation and explanation of the sampling points location are given in Table 3.

Table 2.

Well parameters in the area of vil. Verenchanka

№	Parameter	Averaged value	Minimal value	Maximum value	Permissible sanitary values
1	Total hardness, mmol-eq/l	18.52	11	29	7
2	Fe content, mg/l	< 0.08	< 0.08	0.09	0.3
3	Zn content, mg/l	0.38	0.082	1.887	1.0
4	Cu content, mg/l	0.031	0	0.265	1.0
5	Mn content, mg/l	< 0.02	< 0.02	< 0.02	0.1
6	Well depth, m	12.875	7	25	–

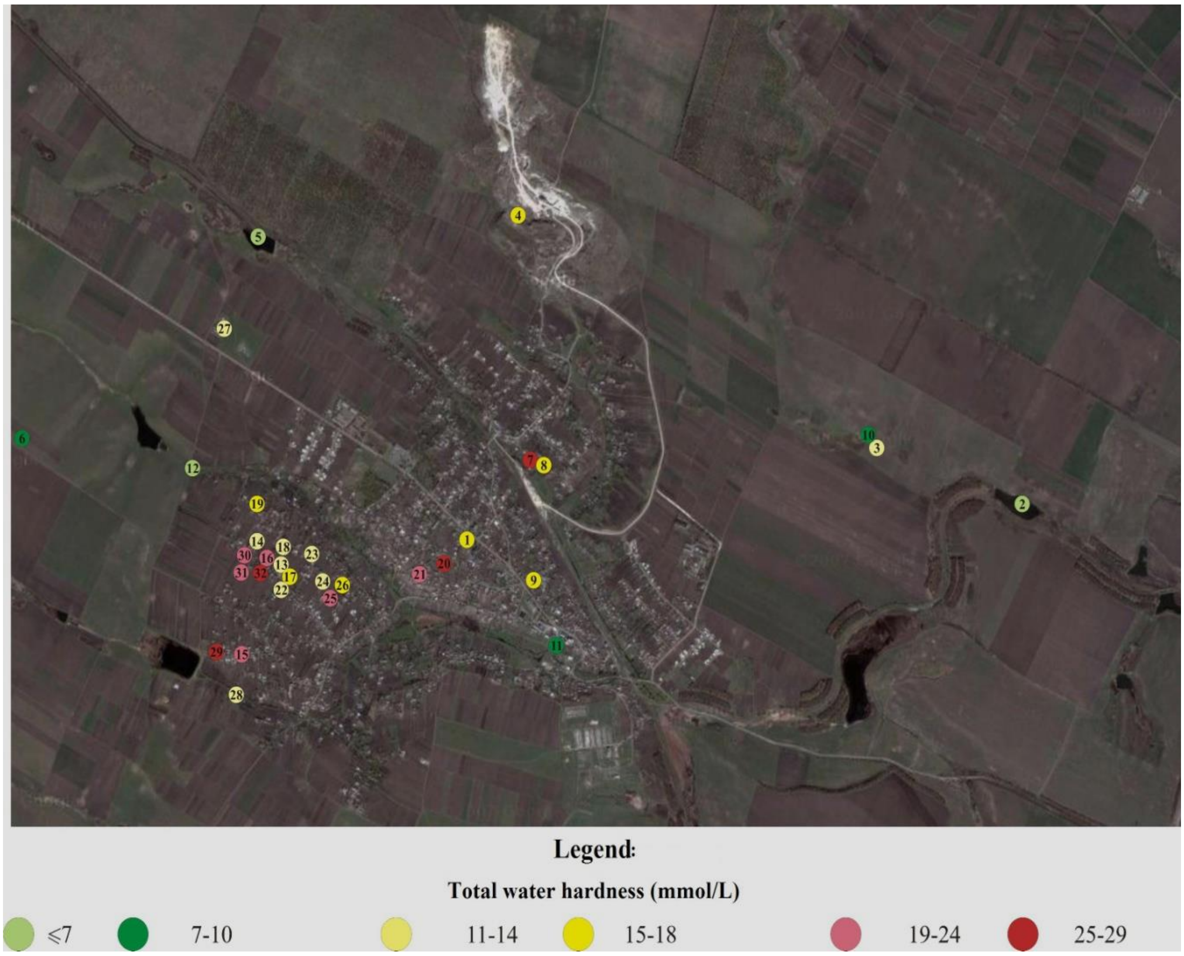

Fig. 2. Locations and total hardness of the water sampling points

It is known that calcium and magnesium sulfates, chlorides, carbonates, bicarbonates and other soluble forms are responsible for the natural water hardness. Soft water is conditionally limited by the total hardness 3.5 mmol-eq/l; moderately hard – by 7; hard – by 10, and very hard water is over 10 mmol-eq/l. It should be understood, that this classification is based mostly on the organoleptic characteristics since water tastes bitter if it is excessively hard. Therefore, it is desirable to have drinking water of the soft or moderately hard category.

It was found that the 10 well (7, 15, 16, 20, 21, 25, 29÷32) water samples had water hardness higher than the averaged value (18.52 mmol-eq/l). They are scattered all over the village but part of them are located as a group (16, 25, 30, 31, 32).

Table 3.

Complete results of analysis of the water samples

Sample	Content, mg/l				Total hardness, mmol-eq/l	Organoleptic parameters			Well depth	Type of the sampling point
	Fe	Mn	Zn	Cu		Smell, points	Taste, points and character	Colour		
1	–	–	0.11	0.065	18	1	1, bitter-sour	no	15	well
2	–	–	0.016	–	6.2	2	–	yellowish	–	pond
3	–	–	0	–	11.4	1	0	no	–	spring
4	–	–	0.021	0.025	15.6	1	1, bitter-sour	no	25	well
5	–	–	0.02	–	6.2	2	1	yellowish	–	pond
6	–	–	0.031	0.035	9	1	1	no	–	spring
7	–	–	0.082	–	26	1	2 bitter-sour	no	7	well
8	–	–	0.143	0.015	17	1	0	no	8	well
9	–	–	0.094	0.02	16.4	1	1, bitter-sour	no	20	well
10	–	–	0.032	0.025	10	1	–	no	–	spring
11	0.16	–	0.064	0.015	10	1	–	yellowish	–	pond
12	0.08	–	0.055	0.015	7	1	–	no	–	spring
13	0.08	–	0.106	–	11	1	0	no	12	well
14	–	–	0.134	–	11	1	0	no	15	well
15	–	–	0.196	–	22	1	1, bitter-sour	no	15	well
16	–	–	0.137	–	22	1	1, bitter-sour	no	20	well
17	–	–	0.746	0.015	18	1	1, bitter-sour	no	15	well
18	–	–	0.097	0.01	14	1	0	no	12	well
19	–	–	0.111	0.04	15	1	1, bitter-sour	no	12	well
20	0.09	–	0.941	0.265	26	1	2 bitter-sour	no	9	well
21	0.08	–	0.143	0.02	24	1	2 bitter-sour	no	8	well
22	–	–	0.144	0.045	14	1	0	no	12	well
23	0	–	0.805	–	14	1	1	no	12	well
24	0.08	–	0.281	0.035	14	1	1	no	15	well
25	–	–	0.159	0.02	21	1	2 bitter-sour	no	15	well
26	–	–	0.179	0.035	16	1	1, bitter-sour	no	12	well
27	–	–	1.887	–	13	1	1	no	15	well
28	–	–	1.379	0.01	12	1	1	no	7	well
29	–	–	0.3	0.045	29	1	2 bitter-sour	no	12	well
30	–	–	0.214	0.025	20	1	1, bitter-sour	no	12	well
31	–	–	0.263	0.025	23	1	1, bitter-sour	no	14	well
32	0.08	–	0.48	0.065	28	1	2 bitter-sour	no	15	well

Concentration of Zn is another particular local feature, which even exceeded the sanitary value in some wells. The highest Zn contents have been found in the samples number 17 (0.745 mg/l), 20 (0.941 mg/l), 23 (0.805 mg/l), 27 (1.887 mg/l – exceeding) and 28 (1.379 mg/l – exceeding). In the contrary, the concentration of Cu is within the sanitary values for all the samples. The concentration of Fe was also far below its sanitary limits. No correlation between the total hardness and concentrations of the heavy metals ions has been established for all the wells except the well 20. This sample has showed both high total hardness (26 mmol-eq/l) and quite high contents of Fe, Zn and Cu (0.09, 0.941 and 0.265 mg/l respectively). This well is located quite close to the area of the former spirits production factory that has been closed because of the karst activation in the nearby area years ago. In our opinion, former and continuous spills and discharges of the factory's technological liquids and wastewaters could be accumulated in the local soil and caused high contents of the salts in this sample.

Spring and pond waters analysis results

There are some springs and ponds within the village and the organoleptic and physico-chemical parameters of their waters have also been analyzed in the same manner as for the wells in order to enhance our survey of natural water quality in the area.

As seen from comparison of the analysis results, the spring and pond water composition is quite different from that of the well water (see Fig. 3). For instance, the total hardness of the spring and pond water sample is ranged within 6.2-11 mmol-eq/l while this parameter for the well water samples is significantly higher – its minimal value for the well waters is 11 mmol-eq/l.

This is an evidence of difference in water feeding sources of local wells and springs/ponds. The wells are fed mostly from the underground water sources, which seem to be enriched with Ca and Mg salts. It is quite obvious since the region is located on the thick and comparatively high (6-22 m from the surface) bed of gypsum [9-11]. This is the most probable source of the water hardness ions released to the well waters. Alternatively, the surface springs and ponds are fed mostly by the rain and snowmelt waters, which are much softer.

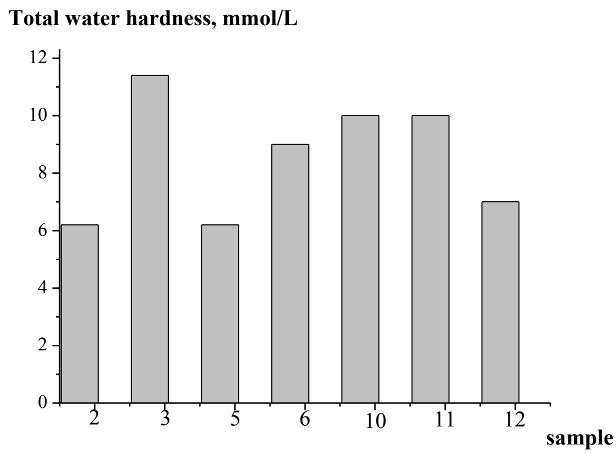

Fig. 3. Total hardness of the spring and pond water samples

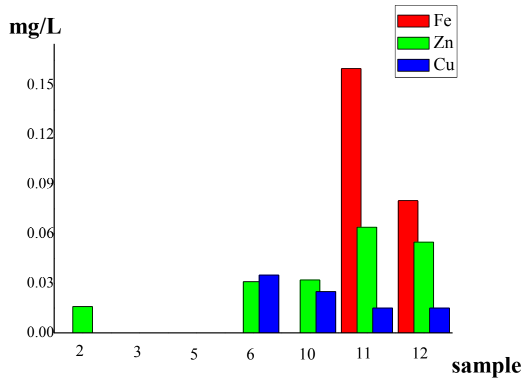

Fig. 4. Contents of the heavy metals ions (Fe, Zn, Cu) in the spring and well waters.

More detailed results of investigation of the heavy metals ions in the spring and pond waters are represented in Fig. 4. As seen from this Figure, the samples 11 and 12 have the highest Fe (0.16 and 0.08 mg/l respectively) and Zn (0.064 and 0.055 mg/l) contents. However, even these values are far below their sanitary levels.

4. Conclusion

The well water of village Verenchanka has shown comparatively high total hardness (11-29 mmol-eq/l), which exceeds significantly the sanitary limits. This problem can be originated from the thick and close-to-surface karst formations in the village area. According to the AAS results, the sub-threshold or exceeding contents of Zn have been registered in the samples 17, 23, 27 and 28 (0.746, 0.941, 0.805 and 1.887 mg/l respectively). The highest Zn content in the sample 28 that exceeds the sanitary limits can be resulted by the influence of the old spirit production factory spills and wastewater discharges that took place in the nearby area. Concentrations of Fe, Mn and Cu in all the samples were far below the sanitary limits. On the other hand, the total hardness of the surface water objects (springs and ponds) in the area of investigation was found much lower than that of the well water. This hardness was ranged within 6.2-11 mmol-eq/l and, in our opinion, this is an evidence of different water feeding sources for the surface water objects and the wells. The former are fed preliminary by the softer rain and snowmelt water while the latter are fed by the karst-originated hard ground water. Concentrations of Fe, Zn, Mn and Cu in all the surface samples were also much lower than the sanitary limits. Taking into account the character of the well water feeding in the area of investigation, no solution can be proposed to bring the total water hardness back to its sanitary limits except intense utilization of water softener agents whenever this parameter seems critical (cooking, washing, using water in the home heating systems network). Karst area is much wider than the area of the village and finding a spot to establish a soft water source near the village does not seem realistic. On the other hand, the surface water springs can provide water with appropriate hardness but they cannot cover required water output while soft water from the local ponds can hardly meet other sanitary requirements (mostly bacteriological).

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