

OCCURRENCE OF ALKALINE WATERS IN THE SOUTHERN APUSENI MOUNTAINS (ROMANIA) – RESULTS OF A PRELIMINARY SURVEY

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ABSTRACT. Consumption of alkaline water by the general population has increased over the past two decades, as certain customers value this type of water for its presumed ability to promote health. In spite of the commercial interest for natural alkaline water sources suitable for drinking purposes, relatively few scientific publications related to the occurrence of these waters are available. This article presents the results of a preliminary survey for alkaline water in the Southern Apuseni Mountains. This region has been selected as study area due to the presence of limestones and ophiolitic rocks, very often in contact with each other, both having the potential to bring the pH of natural waters to the alkaline range. A total of 78 sampling points, represented by streams, lakes, springs and dug wells have been investigated, and the physico-chemical common parameters were measured in the field. Alkaline water with pH above 8.0 has been found in almost 29 sampling points, out of which 7 points had a pH above 8.5. Most of the points were represented by surface running water. The prospective areas, as identified by this survey, correspond to Trascau Mts., and to the western (predominantly ophiolitic) part of the Metaliferi Mts. The data included in this paper may represent the starting point for a systematic survey and for a detailed study of the potential alkaline water resources in the study area.

Key words: *alkaline water, ophiolites, limestones, Apuseni Mountains.*



INTRODUCTION

Natural alkaline water, generally with pH in the range 7.5 – 9.5, represents a field of growing interest for the water bottling industry, as part of the consumers consider they may provide health benefits. Although there is commercial interest in this type of water, there are relatively few published papers dealing with alkaline waters for human consumption. The chemical features of groundwater, including the pH, are strongly influenced by the type of rocks the water is travelling through, being the result of complex water-rock interactions occurring along the water pathway. Ophiolites and limestones are rocks that are recognized for their ability to confer an alkaline character to waters with which they come into contact (Etiopie et al., 2017; Papp et al., 2017; Giampouras et al., 2019). The chemical composition of the alkaline waters in these cases is dominated by the bicarbonate and calcium cations (related to limestones) or magnesium (related to ophiolites). Under particular conditions, the pH may even be higher, exceeding 10.0 or even 11.0, and in this case the water becomes hyperalkaline, the ionic composition is dominated by calcium and hydroxyl, and it is not suitable for human consumption.

High pH may also occur in endorheic lakes in arid climates, which are prone to the accumulations of salts. Waters with a certain content of dissolved salts continuously or temporarily recharge such lakes, and the salt concentration is increasing as a result of the evaporation. Such particular lacustrine environments may show remarkably high values of the pH, sometimes exceeding 11.0. As an example, the Eras Lake, located in Central Spain, is a brackish to saline, highly alkaline lake, with pH up to 11.3 (Cabestrero et al., 2018). In SE Romania, Movila Miresii endorheic lake has pH values above 9.0 (Voicu et al., 2017; IBF, 1961-1973). Such alkaline lakes are suitable for bathing, and some therapeutic effects are recognized.

Taking into account the massive occurrence of ophiolites and limestones in the Southern Apuseni Mountains the geological premises for the genesis of alkaline waters are met, as shown by Nicula & Baciu (2019). Geothermal manifestations are also known in the study area (Orășeanu, 2020; Nicula et al. 2021), an aspect that could intensify the processes of water-rock interaction and increase the level of alkalinity in the water (Xia et al., 2020).

The current study intends to identify water sources with high pH, to identify the distribution and variability of the pH values in the concerned area, and to assess the prospective zones for more detailed studies.

STUDY AREA

Geologically, the Southern Apuseni Mountains represent a distinct portion, with particular features, of the Apuseni Mountains. The North Apuseni Mountains correspond to the outcropping area of the Tisia block, and mainly consist of medium or low-grade metamorphic rocks, with some granitic intrusions. This basement is covered by Permian-Mesozoic sedimentary formations (Săndulescu, 1984). By contrast, the Southern Apuseni correspond to the eastern Vardar mobile area (Schmid et al., 2020). They include ophiolitic units represented by tholeiites (Middle Jurassic) and calc-alkaline magmatic rocks (Late Jurassic to Early Cretaceous) (Mutihac, 1990). The tholeiitic series are present in the western part of the study area, and are dominated by basalts, intruded by gabbros and gabbro-peridotite bodies. The calc-alkaline series occur in the central and eastern part, and include basalts, basaltic andesites, and some acid rocks as dacites and rhyolites. The ophiolites are locally intruded by granitoids (Cioflica et al., 2001). The clockwise rotation of the Apuseni Mountains during the Middle Miocene led to the opening of graben-like basins on the western side of the mountains, that are filled with Miocene sediments. As a result of the extension, calc-alkaline extrusive magmatism has occurred contemporaneously (Seghedi, 2004).

All the sampling points are located in the Southern Apuseni Mountains (figure 1), predominantly along valleys, in depressionary areas. Two distinct zones were investigated. The north-eastern zone overlaps the following geomorphological units: Culmea Hășdate (P1 – P4 and P18 – P20), Colții Trascăului (P13 – P16), Trascău Depression (P5, P6 and P11, P12), Culmea Bedeleu P7, Sălcia Depression (P9), Ocoliș-Poșaga Depression (P8), Aiudului Hills (P17 and P10), Vlaha-Hășdate Depression at the boundary with Feleac Hill (P22 – P27). Most of the points (51 points in total) were tested within the southern area, north of the Mureș Valley. The geographical distribution of the investigated points, by geomorphological units, in the southern zone is the following: the Husului Mountains (P28 – P52), the Măgurea Mountains (P53 – P59, P73 – P75 and P77, P78), the Brad Depression (P67 – P70 and P76), Găina Mountain (P71, P72), Săcărâmb Mountains (P60 – P63 and P65), and three other points (P64 – P66) towards the eastern part of the study area, in the Almaș-Bălașa Depression.

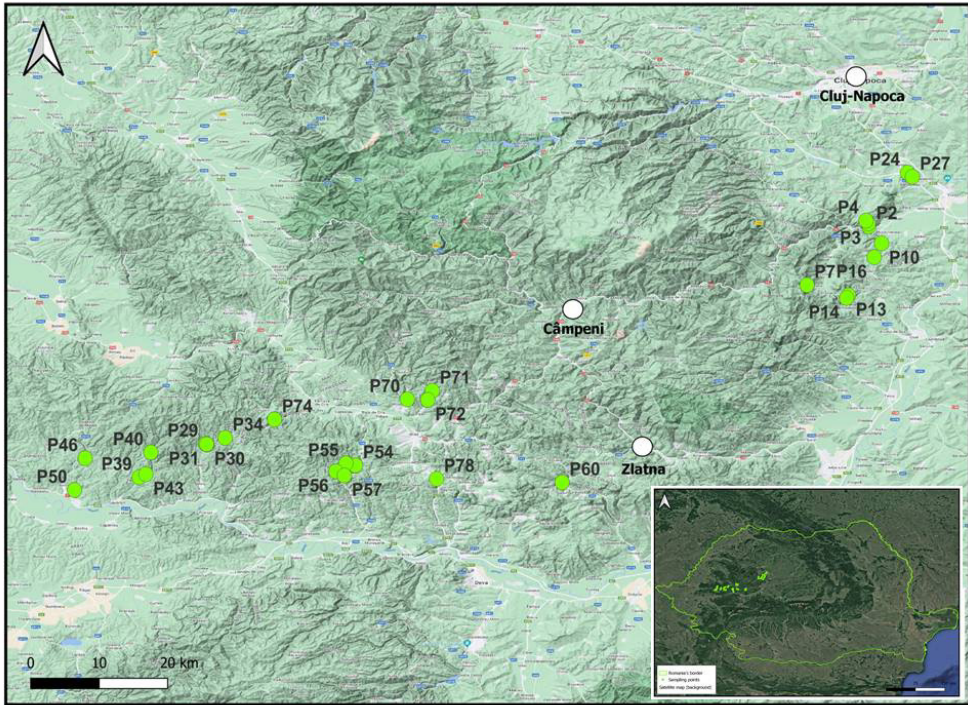


Fig. 1. Geographical distribution of the sampling points

Table 1 lists the sampling points, including their coordinates, the water source type (spring, stream, or well), and the measured pH.

Table 1. Distribution and features of the sampling points.

Sample ID	Site	Type	pH	Coordinates	
				N	E
P1	Spring near road to Buru	spring	7.31	46.51614	23.59192
P2	The lower waterfalls	stream	8.33	46.50842	23.64048
P3	Middle Borzești Gorge	stream	8.40	46.51356	23.63948
P4	The upper waterfalls	stream	8.14	46.51871	23.63517
P5	Spring in centre Rimetea	spring	7.43	46.45319	23.56738
P6	Well in the centre of Izvoarele village	well	7.08	46.40006	23.54016
P7	Point upstream basins (Izvoarele village)	stream	8.21	46.40272	23.52422
P8	Spring near road Sălciua	spring	7.33	46.45518	23.46761
P9	Șipote waterfalls	waterfall	7.77	46.40571	23.45998
P10	Upstream Moldovenеști	stream	8.23	46.478016	23.664321

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Sample ID	Site	Type	pH	Coordinates	
				N	E
P11	Big spring to Găvane	spring	7.83	46.37378215	23.60265164
P12	Small spring to Găvane	spring	7.80	46.37378225	23.60266812
P13	Stream after pine section	stream	8.50	46.3842286	23.6021629
P14	At Gavane	stream	8.51	46.37943	23.598975
P15	Spring in Podeni	spring	7.47	46.43079	23.63027
P16	Stream between Podeni and Pietroasa	stream	8.02	46.452699	23.650518
P17	Spring between Pietroasa and Moldovenesti	spring	7.58	46.477684	23.66272
P18	Hășdate stream Cheile Turzii 1	stream	7.8	46.56505778	23.6768071
P19	Hășdate Stream Cheile Turzii 2	stream	7.82	46.5643716	23.6842254
P20	Hășdate affluent (left)	stream	7.89	46.56232521	23.69103606
P21	Affluent Racilor stream	stream	7.24	46.60997647	23.70441082
P22	SpringTureni	spring	6.7	46.61597606	23.70649234
P23	Spring Cheile Turenilor	spring	6.96	46.60591395	23.71153263
P24	Racilor stream	stream	8.08	46.60547319	23.71282127
P25	Shallow spring	spring	7.37	46.60064863	23.71702568
P26	Affluent Racilor stream (right)	stream	7.65	46.5969597	23.7191388
P27	Affluent Racilor stream (stone quarry)	stream	8.12	46.5978715	23.7221041
P28	Spring Roșia Nouă	spring	7.31	46.1166526	22.3980453
P29	Stream after spring (P28)	stream	8.56	46.1165346	22.3987048
P30	Pond Roșia Nouă	pond	8.24	46.1152165	22.4011229
P31	Petriș stream in Roșia Nouă	stream	8.46	46.1156634	22.4006482
P32	Well Roșia Nouă	well	7.42	46.1167275	22.4021612
P33	Petriș stream downstream Obârsia	stream	7.76	46.1274422	22.4349795
P34	Affluent Petriș stream	stream	8.55	46.127221	22.4352019
P35	Roșia Noua spring	spring	6.83	46.11386988	22.40136358
P36	Well in Corbești	well	7.10	46.0866038	22.3888061
P37	Affluent Petriș stream (Corbești)	stream	7.55	46.078117	22.384998
P38	Petriș stream	stream	7.65	46.0493681	22.3882655
P39	Spring in Temeșești	spring	8.10	46.0560954	22.2742753
P40	Upstream Troas affluent	stream	8.3	46.1009959	22.2962234
P41	Troaş stream	stream	7.62	46.1013846	22.2961787
P42	Troaş affluent downstream	stream	7.60	46.0805159	22.3003221
P43	Troaş stream downstream Săvârșin	stream	8.10	46.0615179	22.2868142
P44	Julița stream downstream Slatina de Mureș 1	stream	7.88	46.1560409	22.1825789
P45	Julița stream downstream Slatina de Mureș 2	stream	7.71	46.1308698	22.1751594
P46	Affluent Julița stream	stream	8.24	46.090331	22.173169
P47	Spring downstream Julița	spring	7.36	46.0653764	22.1451813
P48	Well in Julița	well	6.9	46.0545446	22.133562

Sample ID	Site	Type	pH	Coordinates	
				N	E
P49	Bălcescu stream	stream	7.67	46.035404	22.106122
P50	Stejar stream	stream	8.06	46.033025	22.153194
P51	Cerbia stream	stream	7.05	46.0385959	22.4476029
P52	Spring	spring	6.82	46.0379853	22.4479596
P53	Spring on the roadside	spring	7.23	46.0743243	22.6765123
P54	Șarpe stream	stream	8.66	46.07753423	22.67930534
P55	Sârbi stream	stream	8.73	46.081039	22.661577
P56	Sârbi stream downstream Valea Poienii	stream	8.68	46.066849	22.642652
P57	Vișa spring	spring	8.36	46.05927768	22.65841995
P58	Sârbi stream upstream of Vorța	stream	7.86	46.030896	22.667898
P59	Sârbi stream in Valea Lungă	stream	7.83	45.984276	22.683951
P60	Geoagiu stream downstream Almașu	stream	8.52	46.04686	23.066191
P61	Spring in the forest	spring	7.53	46.046919	23.064608
P62	Voia downstream spring	spring	7.72	46.040195	23.055581
P63	Spring in Voia	spring	7.42	46.035768	23.04588
P64	Almășel stream	stream	7.32	46.0535626	23.0760686
P65	Bălașa stream	stream	7.56	46.0790215	23.0666046
P66	Ribișoara spring 1	spring	7.46	46.041913	23.072566
P67	Ribișoara spring 2	spring	7.07	46.1998411	22.7758753
P68	Well in Ribišoara	well	7.10	46.2164464	22.7745376
P69	Ribița stream base of the gorge	stream	7.55	46.228845	22.770022
P70	Ribița stream	stream	8.41	46.1966692	22.776397
P71	Junc stream downstream Dumbrava	stream	8.09	46.212113	22.823147
P72	Junc stream downstream Crișan	stream	8.45	46.195795	22.814543
P73	Vața stream upstream	stream	7.62	46.128577	22.507714
P74	Vața stream downstream	stream	8.49	46.1603619	22.5276124
P75	Spring in Căzânești	spring	7.60	46.1631897	22.5339477
P76	Luncoiu stream	stream	7.61	46.068456	22.7903386
P77	Vălișoara spring	spring	7.25	46.0531961	22.830805
P78	Căian stream downstream Vălișoara	stream	8.07	46.0531348	22.8310603

MATERIALS AND METHODS

The background information was obtained from the literature and from the available geological and hydrogeological maps. These data were used to produce the workplan and to establish the potential transects. The transects were outlined by using specific software as Quantum GIS and

Google Earth. The field investigations consisted of four campaigns that mainly targeted the ophiolitic areas defined in the background analysis stage. The north-eastern zone was investigated during three field campaigns focusing on the areas Hășdate-Tureni, Bedeleu, and Trascău. The southern zone was investigated during one campaign, that targeted the whole ophiolitic region located north of the Mureș valley. Field campaigns were carried out during the period 31.10.2022 – 14.05.2023.

During the field stage, the transects were tracked, and in-situ measurements of the collected water samples were carried out using the multiparameter portable meter WTW 350i. The following parameters were measured in-situ: temperature, pH, redox potential and electrical-conductivity; the salinity and TDS were derived from the latter. Water samples were taken from selected points of interest in order to carry out further analyses in the laboratory. Geographical coordinates were recorded for each sampling point. The Geo Tracker application was used to mark sampling points and other field data. In the final stage, the obtained data were systematized and interpreted in order to obtain an overview of the alkaline waters' distribution in the study area.

RESULTS AND DISCUSSIONS

The total number of points investigated in this study is 78. All types of water sources that could have an alkaline character, or can provide information on the genesis and distribution of alkaline waters were considered. Depending on the source type, the sampling points consist of 5 wells, 23 springs and 50 collection points are represented by surface running waters (streams).

The electrical conductivity of the water samples is generally low, varying in the range of 119 to 631 $\mu\text{S}/\text{cm}$, and reflecting the low dissolved solids content. The temperature of the springs and wells is relatively constant, being around 10°C in the case of springs, and around 12°C for dug wells. Of course, the temperature was variable in the case of surface waters, fluctuating between 2.8°C and 15.1°C, in accordance with the air temperature.

The pH was measured in all the 78 investigated points, out of which the pH exceeded the value of 8.5 in 7 points, all of them representing groundwater, it was in the range of 8.0 to 8.5 in 22 points (2 groundwater and 20 surface water), between 7.5 and 8.0 in 25 points (5 groundwater and 20

surface water), and below 7.5 in 24 points (20 groundwater and 4 surface water). Figure 2 shows the statistical distribution of the measured pH values for the investigated water sources.

The spatial distribution of the sampling points in relation with the geological background is represented in figures 3 and 4. As shown in figure 3 and 4, the distribution of points where waters with high pH were measured, extends over the ophiolitic complex. The hypothesis of the current research, inferring that the ophiolitic areas are potential generators of alkaline waters, was confirmed. The number of springs that were identified in the ophiolitic areas is low, as these rocks exhibit low permeability, and therefore, scarce conditions for the accumulation of groundwater. However, in the north-eastern zone, the ophiolites are in contact with Jurassic limestones, that are able to accumulate important amounts of water. Additionally, the limestones are prone to yield neutral-alkaline waters, usually with pH in the range 7.0 to 8.0.

Values of the pH above 8.5 were measured in 7 locations, all of them corresponding to surface running water. Their parameters measured in the field are presented in Table 2. The pH values measured in running waters in the ophiolitic areas allow us to presume that groundwater in the same areas would be even more alkaline.

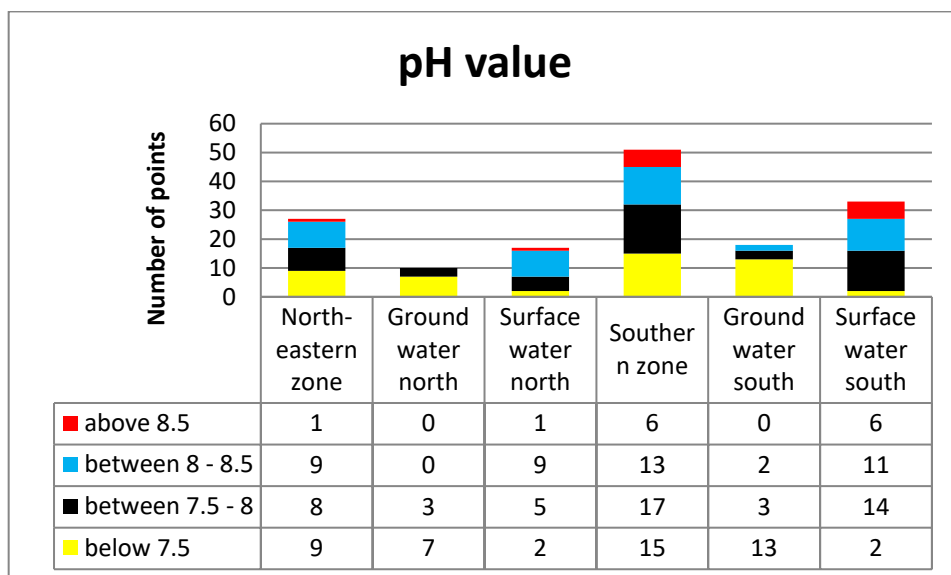


Fig. 2. Statistical distribution of the measured pH values.

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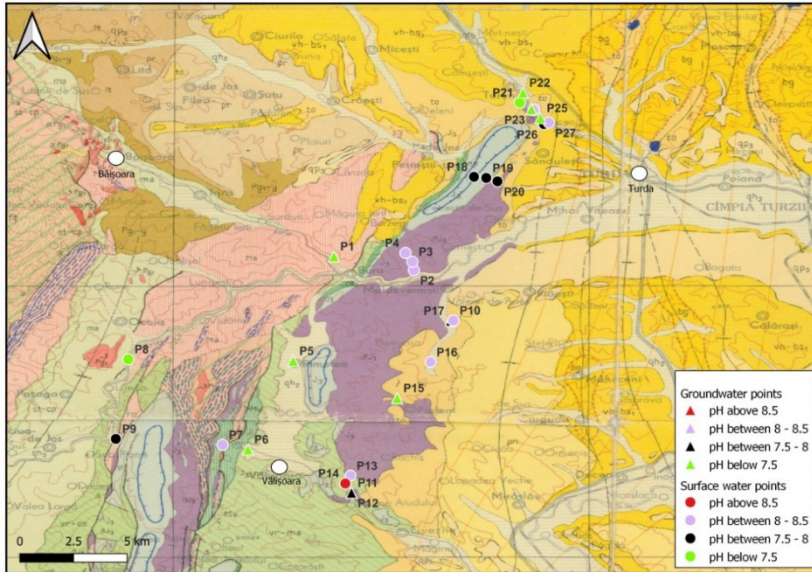


Fig. 3. The pH values of the investigated water sources in the southern zone. The ophiolitic complex in magenta on the geological map. Background: The geological map of Romania 1: 200,000 (Geological Institute, 1967)

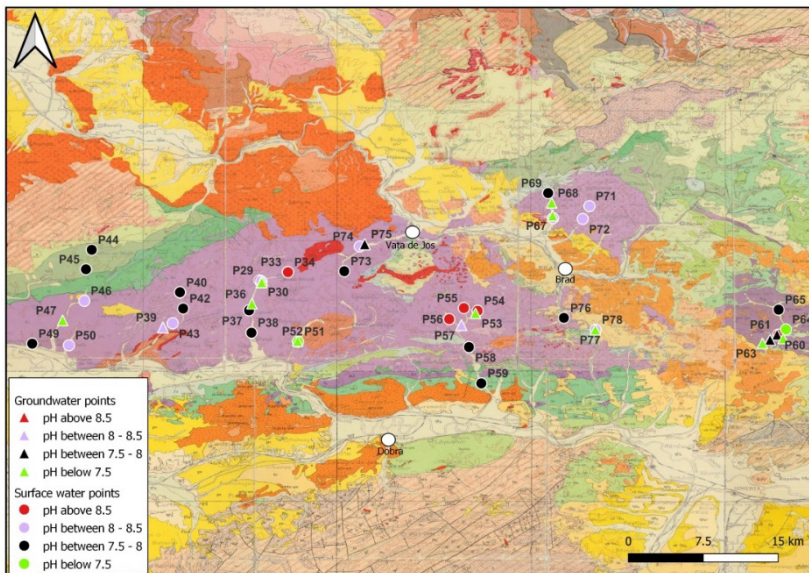


Fig. 4. The pH values of the investigated water sources in the north-eastern zone. The ophiolitic complex in magenta, and Jurassic limestones in light blue on the geological map. Background: The geological map of Romania 1: 200,000 (Geological Institute, 1967)

Table 2. *Physico-chemical in-situ measurement results for the most alkaline water sources*

Sample ID	Site	pH	Temperature (°C)	Salinity (‰)	Conductivity μS/cm	TDS (mg/l)	Redox potential (mV)
P14	At Gavane	8.51	3	0.1	314	200	-77.6
P29	Stream after spring (P28)	8.56	12.7	0.1	412	261	-83.3
P34	Affluent Petriș stream	8.55	11.7	0	293	187	-83.1
P54	Șarpe stream	8.66	11.8	0.1	299	192	-90
P55	Sârbi stream	8.73	14.1	0	278	177	-95.6
P56	Sârbi stream downstream Valea Poienii	8.68	13.3	0	266	172	-91.1
P60	Geoagiu stream downstream Almașu	8.52	12.1	0.1	312	201	-81.6

We include here a brief description of the water points where pH values above 8.5 were measured. Point P14 is located north of Poiana Aiudului. The water sample was collected from the stream that flows towards the locality, a stream that crosses an area with limestones and ophiolites. This is the only point in the north-eastern zone of the study area that shows a pH above 8.5. In the southern zone, a first point identified and placed in this category is P29. This point is located in the Roșia Nouă area on a tributary stream of the Petriș stream. The geological substrate is ophiolitic, but the springs and wells in the area do not have a pH above 8. It is noteworthy that the water sample taken from the Petriș stream (P31) had a pH of 8.46. Also in the same area, on a left tributary of the Petriș stream located between the Roșia Nouă and Obârsia, point P34 was sampled, with a pH of 8.55. Also, in the southern part of the study area within the Metaliferi Mountains near the village of Vișca, 3 points with alkaline waters were found, identified as P54, P55 and P56. All these samples were taken from streams that cross areas with ophiolitic substrate. This group of points had the highest pH values in the entire study. They are located on different streams, and are not influenced by each other. Similar to the situation previously presented on the parallel valley from Roșia Nouă, waters with a higher pH are found in

running water bodies and not in springs. However, it is worth noting that the most alkaline spring identified in the current research was measured in the town of Vișca (P57; pH=8.36).

A general remark on all points with high alkalinity concerns the low electric conductivity (266 – 412 $\mu\text{S}/\text{cm}$) and implicitly low TDS (172 – 261 mg/l). A general characteristic observed in the studied area is the compact texture of the rocks and the lack of deep fissures or fractures that would allow the circulation of fluids.

CONCLUSIONS

The data obtained in the present research confirm the potential of the Apuseni Mountains to generate alkaline waters, related to the ophiolitic substrate. About 30 points with waters with pH above 8 were identified in the field. Most points with alkaline waters were sampled in streams that flow through areas with basic rocks. Generally, ophiolitic areas generated waters with a higher pH than areas with a mix of limestone and ophiolite. The measured values of the pH in streams decrease when crossing lower areas, mainly consisting of detrital sedimentary rocks. The pH of waters from wells is around 7, they are dug in low areas with Quaternary alluvium, and likely do not interfere with the bedrock, mostly consisting of compact ophiolitic rocks.

The compact structure of the bedrock does not favour the accumulation of groundwater, thus the number of springs in the area is very limited. The pH of the identified springs is below 8.0. Very likely, the pathway of groundwater that generates the tested springs is shallow, being confined to the superficial deposits, without intercepting the ophiolites. No hyperalkaline waters (with pH above 9.0) have been identified until now in the Southern Apuseni Mountains. As the ultramafic rocks are only locally developed, detailed investigations in the target areas could identify also this kind of waters.

The contacts between the ophiolitic rocks and limestones could provide more favourable environments for the accumulation of alkaline groundwater. By continuing this research, other areas with alkaline water potential can be identified and more information can be provided about the areas preliminary investigated in the current study (identification of additional sources, detailed characterization of the chemical composition).

Following these preliminary investigations, it can be stated that the study area has the capacity to generate alkaline waters, potentially with economic value. The areas with higher potential seem to be the north-eastern

zone (Tureni – Buru – Trascău – Poiana Aiudului), and in the southern zone, Roșia Nouă – Vișca area. A detailed hydrogeological characterization of these areas may reveal exploitable alkaline water resources.

Acknowledgements

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