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HYDROCHEMICAL CONSIDERATIONS IN THE LOWER CERNA RIVER BASIN

BY

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The paper deals with a series of data concerning the chemism of Cerna, karstic waters and main thermomineral sources from the area of Băile Herculane. The karstic springs are compared withe limestone surface streams. It is ponted out their more alkaline pH values as compared to those from the other karstic areas. Regarding the thermomineral sources from karstic aquifers, the salt effect is rendered evident a determinant of limestone dissolution. This situation is exemplified at Hercule spring.

1. INTRODUCTION

The area drained by Cerna in the region of Băile Herculane presents one of the most interesting hydrogeological cases. Here there are three categories of waters in a close proximity : karstic sources and streams, thermomineral sources and Cerna river. Their interferences cause important changes of primay chemical properties. The area is of major economic interest from hydroenergetic and balneoterapuetics point of view. For this reason numerous studies have been already made about the water chemism, especially of Cerna and thermomineral sources. The karstic waters have been less analysed in spite of their influence both on Cerna *(Trufaş and Marin,* 1980), and on the thermomineral deposit from Băile Herculane spa *(Povară and Lascu,* 1978 ; *Povară,* 1980). It is worth mentioning the data presented by *Alexandru et al.* (1981) as well as the attempt to find the limestone saturation degree. This paper point out the peculiarities of karstic waters chemism in the lower basin of Cerna River, as well as a series of factors determining them. It is also made an attempt to get a general view on the hydrochemistry of the region.

2. SAMPLING SITES AND METHOD

The analysed Karstic area belongs to the Mehedinţi Mountains, on which there already are detailed geographic studies *(Sencu,* 1975 ; *Alexandru* et al., 1981). The samples have been taken from both the karstic springs and the limestone surface waters which are Cerna left side affluents. The northernmost affluent is Arşasca while the southernmost point being reached is Topleţ spring. The sampling stations of the Cerna have been located too between these limits. At the same time, sampling from the main thermomineral sources belonging to Băile Herculane spa have been carried on.

The samples from karstic waters and Cerna have been collected in two series in May and July 1978 while thermomineral water samples have been taken in March 1981 and April 1982. A special attention has been paid to Hercule spring, where the mixture of thermal and karstic waters is obvious (*Povară*, 1973 ; *Bulgăr and Povară*, 1978). There two series of sampling have been performed, each of about a hundred samples, first of them during March and April 1981 with sampling intervals between 6 and 12 hours, and the second, during March-June 1982, whith daily samplings.

On each site, temperature has been measured with a mercury thermometer calibrated to 0.02°C, while the pH values and alkalinity have been electrometrically determinated either in the laboratory maximum 2 hours after the sampling, or on site, in the case of Hercule spring. The calcium and magnesium have been measured by complexometric microtitration with photometric end-point determination. Sulphate has been founded by a turbidimetric procedure. Chloride has been analysed by means of mercurimetric photometric titration for karstic waters and by argentometric titration in case of thermomineral waters. The sulphuretted hydrogen has been iodometrically measured after being chemically fixed with cadmium acetate.

3. RESULTS AND INTERPRETATION

As a result af these analysis, it may be ascertained that the waters from the searched area belong to two main hydrochemical classes. Cerna river and karstic waters are carbonate waters while the termomineral sources are chloride-sodic waters as regards their ionic structure. They are also assumed as sulphureous waters due to their high content of dissolved H_2S. Table 1 records the analytical results for some of the tested samples.

In the frame of the main categories of classification there are important difference. Thus, among the carbonate waters, the emergences and the karstic streams have higher mineralisations than Cerna, due to their more intimate contact with the karstifiable rock. For these waters there is an excellent correlation between the carbonate alkalinity expressed in HCO_3^-, and Ca^{++} concentrations (Fig. 1). In their turn, karstic waters present differentiated chemical properties depending on the draining manner. From Table 2, summarizing the variation range of concentrations as well as the average concentrations of the dosed compounds for the carbonate water samples, it is to be observed that the emergence waters present usually higher concentrations than surface waters.

The draining conditions also determine the higher alkaline pH of the analysed karstic waters. pH-values higher than 8.0 (Fig. 2) are very frequent for surface wates, which indicate a short contact between water and limestone. On one hand, this is due to the relative scanty surface of the karstifiable rock areas, being run accrosby the water, and, on the

Table 1

Some chemical data on water samples collected from lower Cerna river basin

No.	Type	Sampling site	T (°C)	pH	H_2S	Ca^{++}	Mg^{++}	$Na^{+}+K^{+*}$	HCO_3^-	SO_4^{--}	Cl^-	TDS*
					mg/l							
1	Karstic waters	Arşasca	10.0	7.75	—	9.8	1.4	4.8	37.0	8.3	1.4	63
2		Ogaşul cu Bolovani	9.5	8.10	—	39.9	1.3	3.9	126.5	8.4	0.6	181
3		Pişetori	9.8	8.00	—	52.7	1.6	4.7	170.4	7.3	0.7	237
4		Tîmna	9.6	8.40	—	59.3	1.7	2.1	180.4	10.1	0.8	254
5		Izvorul lui Birău	9.8	8.30	—	49.5	1.2	3.1	155.6	6.3	1.0	217
6		Prisacina	11.6	8.60	—	60.1	2.6	8.6	195.7	17.1	0.8	285
7		Ţesna	11.3	8.10	—	43.0	1.6	0.9	126.8	9.8	1.2	183
8		Şapte Izvoare Reci (North)	9.8	7.65	—	49.7	2.0	1.4	155.3	5.2	1.8	215
9		Şapte Izvoare Reci (South)	9.3	7.55	—	69.0	2.0	8.2	227.8	9.5	1.0	318
10		Ogaşul Cociului	10.5	8.25	—	47.5	2.0	1.0	141.2	11.0	1.3	204
11		Izvorul Alb	9.0	7.80	—	46.4	1.3	2.1	140.3	8.8	1.3	200
12		Faţa Izvorului	8.5	8.25	—	43.6	0.8	5.2	133.5	11.8	1.2	196
13		Bîrza spring	10.5	7.85	—	33.7	3.5	5.3	113.2	14.9	1.0	172
14		Pecinişca, right outlet	10.3	7.35	—	42.1	2.5	3.8	125.9	17.4	1.8	194
15		Toplet spring	18.0	7.25	—	52.6	5.2	7.2	187.8	7.5	4.8	265
16	Cerna river	Bobot falls	8.5	6.95	—	8.7	1.2	0.2	24.8	4.0	1.8	41
17		Şapte Izvoare Reci	9.3	8.10	—	11.7	1.2	2.7	39.6	6.0	1.0	62
18		Pecinişca	—	—	—	28.0	4.8	5.0	85.7	15.7	15.2	148
19		Toplet	—	—	—	30.0	1.3	12.5	84.4	17.8	13.9	160
20	Thermomineral sources	Crucea Ghizelei, drillhole	34.0	7.50	—	49.1	10.1	3.5	201.5	4.7	1.1	270
21		Şapte Izvoare Calde, spring	36.0	7.85	—	16.0	0.7	195	61.3	130	200	603
22		Scorilo, drillhole	51.0	7.25	—	24.8	2.7	249	47.3	142	303	769
23		Hercule, spring	37.5	7.25	1.8	275	5	449	95.3	89	1069	1980
24		Apollo II, drillhole	48.0	6.70	67	318	4	639	42	108	1455	2566
25		Neptun I + IV, drillholes	48.0	6.40	99	850	3	1535	22	121	3776	6306
26		Traian, drillhole	58.0	6.50	107	1010	2	1765	21	116	4414	7327
27		Sonda 4578, drillhole	41.5	6.15	79	1092	3	1884	26	48	4793	7850

* = calculated values

Table 2

Variation ranges and averages of chemical composition for the carbonate waters sampled in the lower Cerna riven basin

	Karstic waters					
	Emergence waters			Surface waters		
	n	Range	Average	n	Range	Average
T (^0C)	25	7.0 — 18.0	10.0	34	7.4 — 14.0	10.9
pH	32	7.25 — 8.25	7.77	34	7.60 — 8.60	8.23
Ca^{++} (mg/l)	32	14.8 — 75.0	48.9	34	9.8 — 65.1	46.8
Mg^{++} (mg/l)	32	0.7 — 5.2	1.9	34	0.9 — 4.9	2.1
$Na^+ + K^+$ (mg/l) *	20	1.4 — 8.2	4.2	22	0.9 — 8.6	3.8
HCO_3^- (mg/l)	32	52.0 — 240.5	160.0	34	37.0 — 213.6	149.1
SO_4^{--} (mg/l)	20	5.1 — 18.7	9.1	22	6.3 — 34.4	11.6
Cl^- (mg/l)	32	0.6 — 4.8	1.4	34	0.6 — 4.7	1.3
TDS (mg/l) *	20	85 — 338	225	22	63 — 302	215

	Cerna river					
	upstream Băile Herculane			dowstream Băile Herculane		
	n	Range	Average	n	Range	Average
T (^0C)	13	8.5 — 15.0	11.7	—	—	—
pH	13	6.95 — 8.15	7.89	—	—	—
Ca^{++} (mg/l)	14	8.7 — 22.0	14.5	36	13.4 — 53.2	30.5
Mg^{++} (mg/l)	14	0.9 — 1.9	1.3	36	0.9 — 8.5	3.0
$Na^+ + K^+$ (mg/l) *	8	0.1 — 3.8	1.8	36	1.5 — 49.0	14.5
HCO_3^- (mg/l)	14	24.3 — 77.8	50.2	36	61.0 — 117.9	87.7
SO_4^{--} (mg/l)	8	4.0 — 9.0	6.1	36	1.6 — 65.6	15.7
Cl^- (mg/l)	14	0.5 — 1.8	1.2	36	5.8 — 73.8	20.7
TDS (mg/l) *	8	42 — 113	76	36	121 — 302	174

* = calculated values

n = number of observations

other hand, to their great velocity of running. Most of the surface waters are side flows. On the contrary, emegence waters exhibit some lower pH values owing to a prolonged contact beteen water and limestone, the carbonate solution tending to equilibrium. However, on the whole, the carbonate waters from the examined area, are much more alkaline than the same kind of water belonging to regions with a higher degree of karstification, as for instance Pădurea Craiului (*Marin*, 1981) and Anina Mountains (*Sencu*, 1982).

The saturation degree of the waters vs. calcite is directly related to pH values. The equilibrium diagram shown in Fig. 3 indicates that surface waters have a higher supersaturated degree than the emergence waters. The equilibrium curves are calculated according to *Langmuir* (1971) for the aveage values of temperature and ionic streagth of the presented types of water. True to the diagram, the underground waters circulate especially in „closed" system.

Cerna river having a water discharge of some cubic meters per second, presents very low mineralizatons (as seem in Table 2). Its total

Fig. 1 — Relationship between HCO_3^- and Ca^{++} contents for karstic waters from the lover Cerna river basin.

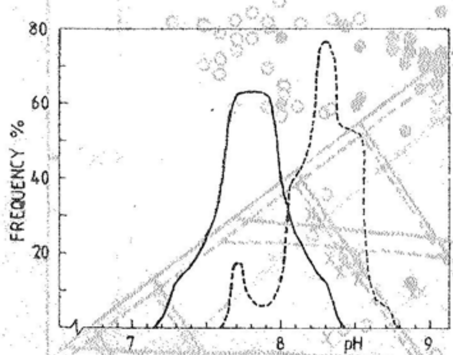
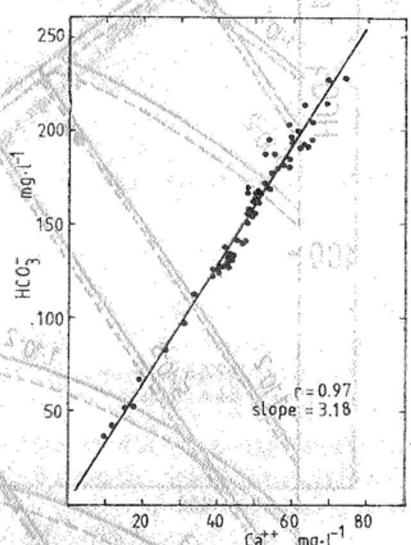


Fig. 2 — Frequncy of the pH values for carbonate waters: emergence waters (solid curve) and surface waters (dotted curve).



percentual of dissolved solids is increased especially in Na^+, K^+, Cl^- and SO_4^{--} by the discharge of thermomineral sources from Băile Herculane, with a high mineralization. Cerna waters is understurated versus calcite on all its length.

The considered thermonineral sources include both natural springs and hydrogeological drillholes. All the drilled wells show artesianheads, increasing along the Nourth to South direction, the maximum value, +45 m was recorded at Sonda (well) 4578. They do not present an uniform chemism. Crucea Ghizelei, the northmost of them is in fact a mesothermal source and its chemical properties are very similar to those of karstic waters. The mineralizations are gradually increasing downstream, attaining maximal values at the southernmost sources. From all the thermomineral sources, Hercule spring is the most strongly affected by cold karstic waters. During the sampling periods there were recoded here temperature fluctuations between 17.4 and 43.0°C and discharge variations between 18.2 and 93.6 l/sec. (*Povară and Marin*, 1984). These parameters are quasi-constants for the majority of the thermomineral sources.

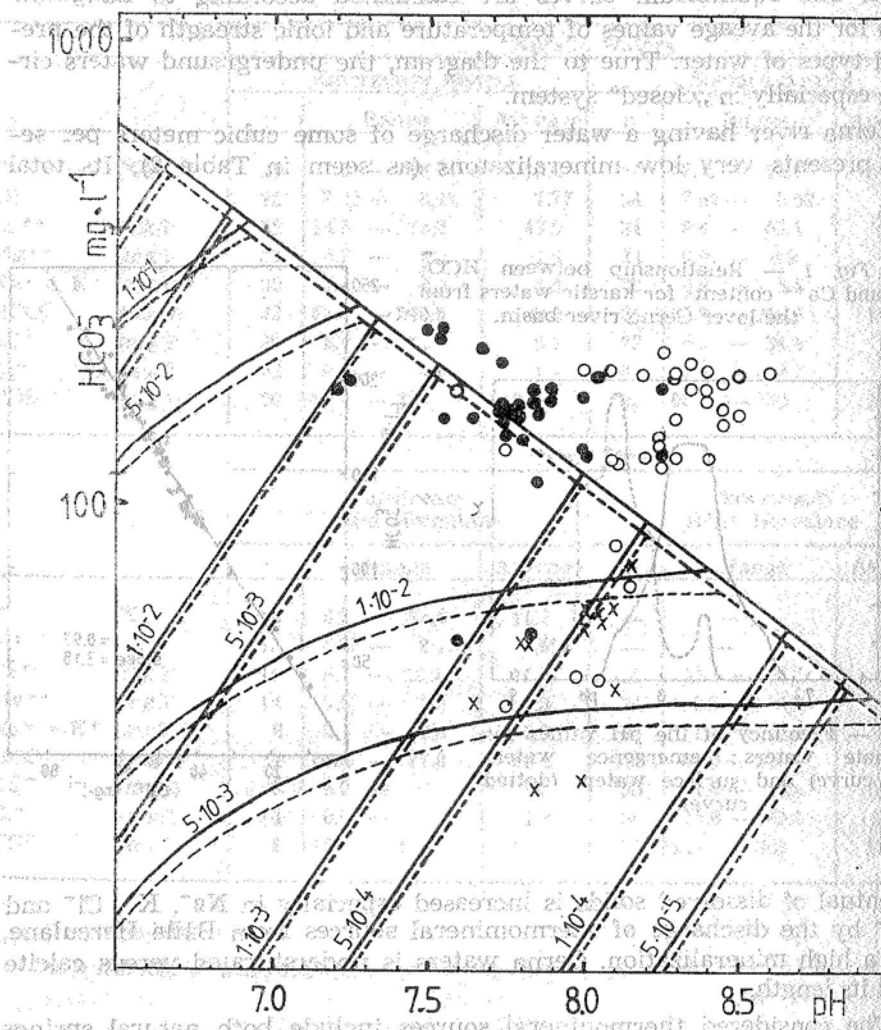


Fig. 3 — Possible approaches to carbonate waters equilibrium with calcite: emergence waters (●), surface waters (o) and Cerna river (x). The lines falling from left to right represent saturation curves. These lines divide the diagram into a zone on the upper right — supersaturation zone, and one on the lower left — under saturation zone. The lines rising from left to right represent the attainment of saturation by water in "open" system for different P_{CO_2} values. The curved lines represent the attainment of saturation by water in "closed" system (no CO_2 added). Solid lines were calculated for 10.5°C and 4.13 10^{-3} moles l^{-1} ionic strength (average values for tested karstic waters). Dotted lines were calculated for 13.2°C and 2.91 10^{-3} moles l^{-1} ionic strength (average values for Cerna river).

Hercule spring is in fact the resurgence of a cave which is to be explored on some tenth meters (*Povară*, 1973). In spite of the karstic component preponderence at this spring, the limestone dissolution is due an a vrey small extent to the common mechanism of attack by means of the

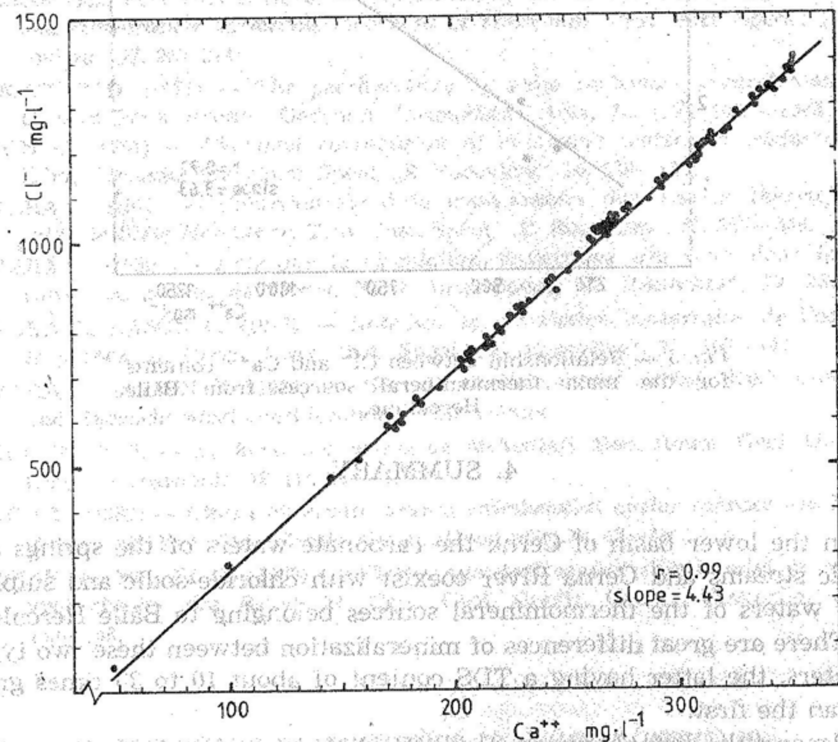


Fig. 4 — Relationship between Cl^- and Ca^{++} contents for Hercule spring (9th Mar.-26th June, 1982).

dissolved CO_2, but essentially to the salt effect. This is proved by the very close correlation between Cl^- and Ca^{++} concentrations (Fig. 4). Here the major anion is chloride which ussually forms, together with sodium and potassium, more than 70% of the total dissolved solids (TDS). These ions give to the water a very high ionic strength as compared with the ordinary karstic waters, modifying calcite solubility. HCO_3^- and Ca^{++} concentrations can not be correlated (correlation index 0,005). Some similar behaviour is also obvious in the case of other thermomineral sources (Fig. 5). These elements support the inflow North of Crucea Ghizelei of poor mineralized waters, at depth, across the limestone body, which subsequently are directed along Cerna Graben, to the thermomineral deposit.

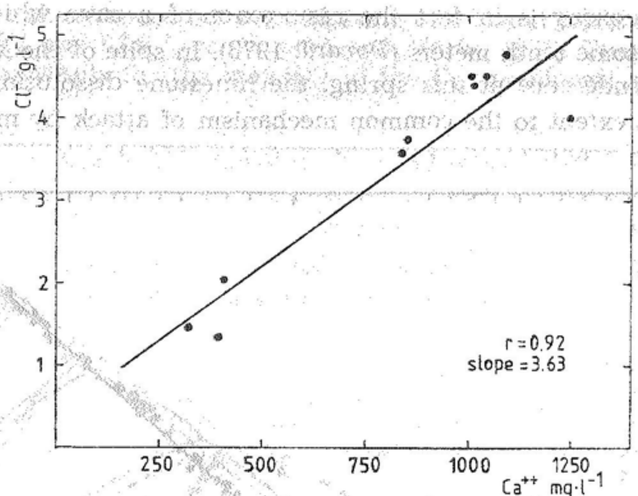


Fig. 5 — Relationship between Cl^- and Ca^{++} contents for the main thermomineral sources from Băile Herculane.

4. SUMMARY

In the lower basin of Cerna the carbonate waters of the springs and karstic streams and Cerna River coexist with chloride-sodic and sulphureous waters of the thermomineral sources belonging to Băile Herculane spa. There are great differences of mineralization between these two types of waters, the latter having a TDS content of about 10 to 30 times greater than the first.

Among the karstic waters then are differences between the surface waters and the springs, which are obvious both for the ionic concentrations and especially for pH-values. Surface waters generally have lower mineralizations than emergence waters, as well as a much more alkaline pH values. As a result of a qualitative estimation it has been determined on one hand a high degree of supersaturation in calcite for both categories of karstic waters, and on the other hand, a „closed" system circulation for the underground waters.

Cerna exhibits the lowest mineralization in the area as well as the greates discharges. Upstream from Băile Herculane its chemism undergoes considerarable alterations, due to the thermomineral waters discharge.

Among the mineral sources Hercule spring raises the most interesting questions, the karstic component being more emphasized. Here, the salt effect determines the limestone dissolution disguising the part of the dissolved carbon dioxide.

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OBSERVAȚII HIDROCHIMICE ÎN BAZINUL INFERIOR AL RÎULUI CERNA

Rezumat

În bazinul inferior al Cernei coexistă atît apele carbonatice ale emergențelor și cursurilor carstice de suprafață, precum și ale Cernei, cît și apele cloro-sodice și sulfuroase ale surselor termominerale din cuprinsul stațiunii Băile Herculane. Diferențele de mineralizare dintre aceste două tipuri de ape sînt substanțiale, ultimele avînd o mineralizare de cca. 10—30 de ori mai mare față de primele.

În cadrul apelor carstice există deosebiri între cele de suprafață și izvoare. Deosebirile sînt evidente în ceea ce privește concentrațiile ionice, dar mai ales la valorile de pH. Apele de suprafață au, în general, mineralizări mai reduse față de emergențe și pH-uri mult mai alcaline. În urma evaluării calitative, se constată un grad ridicat de suprasaturare față de calcit pentru ambele categorii de ape carstice, iar pe de altă parte, este probabilă o circulație a apelor carstice subterane preponderent cu nivel înecat.

Cerna prezintă mineralizările cele mai scăzute din zonă, dar și debitele cele mai mari. Aval de Băile Herculane chimismul ei suferă mutații importante datorită deversărilor de ape termale puternic mineralizate.

Alineate în lungul Cernei, sursele termominerale nu prezintă un chimism unitar. Sursa cea mai nordică, forajul Crucea Ghizelei, este de fapt o sursă mezotermală ce prezintă caracteristici chimice foarte apropiate de ale apelor carstice. Mineralizările cresc progresiv spre aval, atingînd valori maxime la sursele cele mai sudice: Sondele 4579 şi 4578

Dintre toate ivirile de ape termominerale, izvorul Hercule resimte în modul cel mai drastic influenţele apelor carstice reci. În ciuda preponderenţei componenţei carstice de la acest izvor, punerea în soluţie a calcarelor se datorează în foarte mică măsură mecanismului obişnuit de atac prin intermediul dioxidului de carbon dizolvat. Dizolvarea lor trebuie pusă pe seama efectului de sare (sau al ionilor străini), fapt ilustrat de corelaţia deosebit de strînsă care există între concentraţiile de Cl^- şi Ca^{++}. O comportare similară este evidentă şi în cazul celorlalte surse termominerale. Acest element confirmă faptul că la nord de Crucea Ghizelei are loc pătrunderea în profunzime, prin corpul calcarului a unor ape slab mineralizate, ape care sînt antrenate în lungul grabenului Cernei spre zăcămîntul termomineral.

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