

# Chemical composition of carbonate waters in Pădurea Craiului, Romania

by

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Water samples collected from the karstic area of Pădurea Craiului Mountains have been analysed to detect their main chemical characteristics. Most of them were found to be carbonate water samples, and only the Mişid Basin presented sulphate waters. The molar ratio  $Ca^{++}/Mg^{++}$  of carbonate waters has different values for those originating in Cretaceous and Jurassic limestones as compared to those from Triassic rocks. Most waters are undersaturated with respect to calcite and dolomite. The degree of saturation, as well as other chemical parameters are different for recharge, cave stream and spring waters.

## 1. Introduction

The Pădurea Craiului Mountains shelter one of the most important and interesting Romanian karstic zone. Suffice it to say that there is the biggest cave in the country, Peştera Vintului, whose length is over 28 km. Besides it there are many other caves as well as a large range of exo-karstic forms. Still little is known about the chemism of the waters of this area and the informations has been fragmentarily published. Rusu (1979) presents a series of analytical results obtained on samples collected in February—March 1972 (data partly published also by Bleahu, 1974). The author furnishes data about surface and ground waters, but enters into no detail. Other authors inform, in different contexts, about the analytical results they had obtained but, as a rule, they rely on few samples from restricted areals. In this respect mention shall be made of Iosof et al. (1974) and Pleşa et al. (1964).

The present work attempts the chemical characterization of natural waters from the karstic areal of the Pădurea Craiului Mountains. With this end in view, more than a hundred samples have been taken from 60 representative places. Thus the relationship between the nature of the rocks crossed by waters and the chemism has been evidenced. The saturation degree of natural waters with respect to calcite and dolomite was determined by a more rigorous procedure than that offered by equilibrium diagrams. We have also tried to establish the effect of draining conditions on chemical parameters of analysed waters.

## 2. Summary description of the study area

Placed in the north-west of the Apuseni Mountains, Pădurea Craiului is bounded on the north by the Crişul Repede Valley, on the east by Valea Iadului, on the south by the Crişul Negru Valley and on the west by Getic Piedmont. Between these limits stretches an area of more

than 700 km<sup>2</sup>, of which 425 km<sup>2</sup> are covered by sedimentary mesozoic karstifiable rocks. The carbonate rocks from this area belong to three distinctive cyclothemes: Triassic, Jurassic and Cretaceous. They form a relatively unitary zone in the eastern half of Pădurea Craiului. The Triassic covers 32.3% of the karstic zone area (Rusu, 1973a), and is more evident in the eastern part. It is represented both by limestones and dolomites. The Jurassic covers 25.1% of the karstifiable area. It is characterized by limestones disposed in heavy patches in the middle of the karstic zone. The cretaceous limestones appear in the western part of the zone and cover 42.6% of the area. The persistence of carbonate rocks is discontinued in many places by the cropping out of unkarstifiable formations, some of them imprinting unusual chemical characteristics to ground waters, for instance in the Mișid Basin.

The stream system draining the karstifiable area is tributary on one hand to the Crișul Repede in the north and on the other hand to the Crișul Negru in the south. The watershed crosses the massif from the north-west to the south-east being closer to the Crișul Repede Valley and almost faithfully following its course. Within the two main hydrographic basins other secondary basins were individualised. This was not an easy task as the surface stream system is disorganised as a result of the frequent undergrounding of rivers. After many artificial tracer markings, Rusu (1973 b) establishes the stream system map, as represented in Fig. 1. The author identifies 62 recharge waters and 52 emergences and at the same time points out 40 hydrokarstic penetrations.

There are two types of recharge waters: quick recharges through swallow holes (seldom through caves) and diffuse infiltrations in the valley lowermost bed. Most of the recharge waters are active from time to time. 24 of the emergences gush out through caves accessible on tens or hundreds meters distance, while the rest are karstic springs. Emergence waters discharge shows great fluctuations, depending on the season, but more than half of them are permanent. The most important emergences (with yearly average discharge of more than 100 l s<sup>-1</sup>) are situated on the periphery of the karstic zone.

### 3. Method

Most of the 105 samples of analysed waters were collected in May and July 1980. Some samples had been previously taken, that is in May 1979 and in March 1980. Sampling sites are mentioned on the map in Fig. 1. The water temperature was measured in the site by using a mercury thermometer with an accuracy of  $\pm 0.5^\circ\text{C}$ . For each analysed point we have used three sampling bottles; the first for Ca<sup>++</sup> and Mg<sup>++</sup> determination in which water was acidified immediately after the bottle was filled to prevent the respective carbonate precipitation, the second for SO<sub>4</sub><sup>--</sup> and Cl<sup>-</sup> analysis and the third for the pH and carbonate species measurements. Samples were taken to the laboratory and analysed as soon as possible.

The calcium and the total hardness were determined by complexometric micro titrations with photometric end-point determination. The

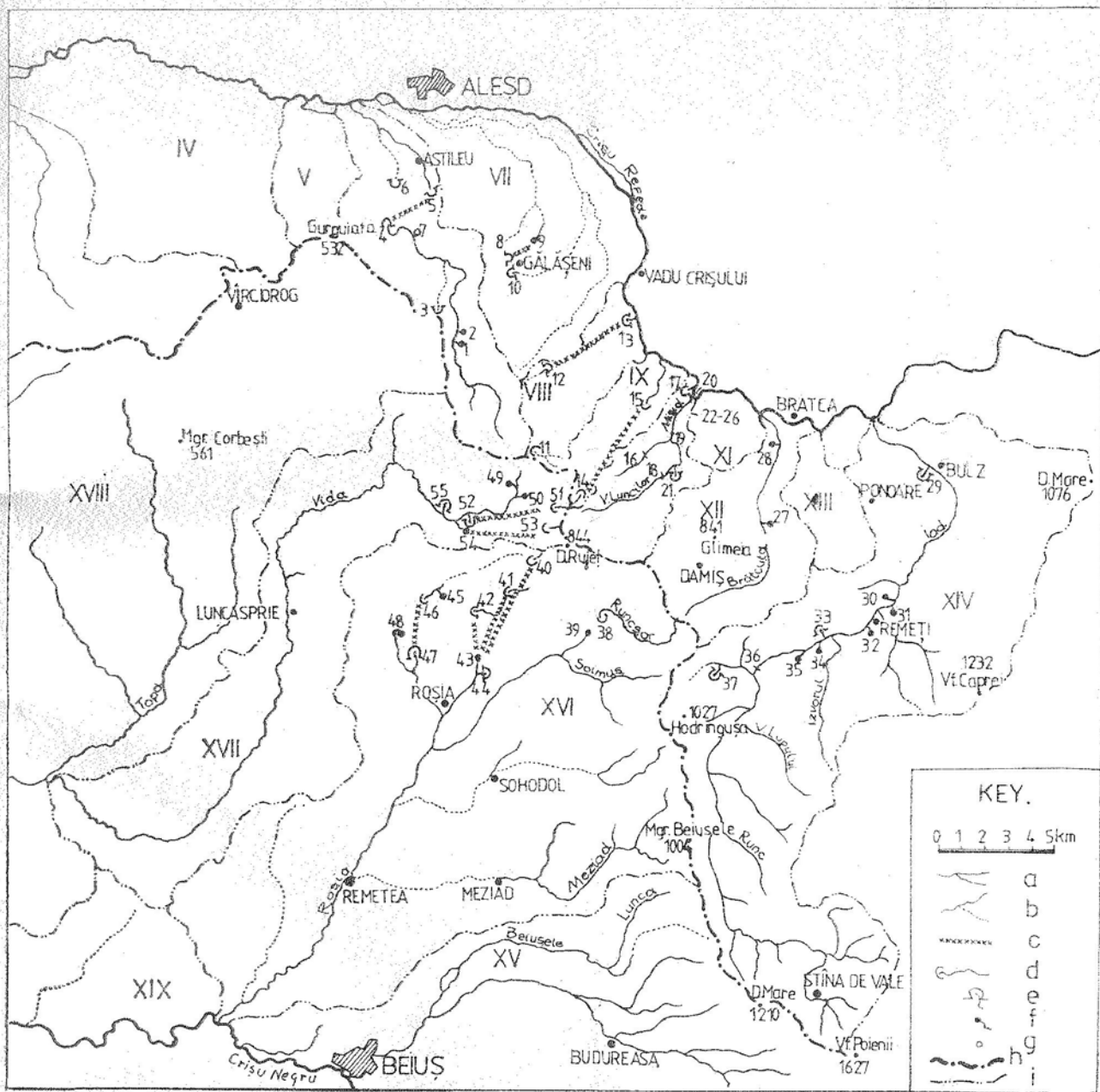


Fig. 1 — The stream system map of the Piatra Craiului karstic zone (after Rusu, 1973 b) and the disposition of sampling sites.

Key: a) stream waters; b) temporary flow valley; c) hydrokarstic penetrations determined by artificial tracers markings, mentioned in this work; d) recharge waters; e) emergence cave; f) spring; g) well; h) parting line of major hydrographic basins; i) parting line of secondary hydrographic basins. Sampling sites: 1 and 2. The emergences "La Moară"; 3. Cioroaietele Țircului; 4. Peștera lui Potrița; 5. Peștera Aștileu; 6. Peștera Pișița; 7. Well in Pustea Călătea; 8. Peștera Gălășeni; 9. Izbulul din Groapa Mofului; 10. Peștera de la Moara Jurjii; 11. Ponorul Tomii; 12. Peștera Bătrînului; 13. Peștera de la Vadul Crisului; 14. Ponorul Brezului; 15. Izbulul Izbindis; 16. Șesii Valley; 17. Peștera Vintului; 18—20. Mișid Valley; 21. Peștera Moanei; 22. Emergence on Mișid Valley; 23. Peștera de la Izvor; 24. Pîrîul Ungurului;

25. Peștera Ungurului; 26. Peștera Napiștileu; 27. Izbulul cu Travertin; 28. Izbulul Brătcănilor; 29. Peștera cu Apă de la Bulz; 30. Izvorul Captat; 31. Tăul fără Fund; 32. Izvorul Pancului; 33. Peștera de la Fața Apei; 34. Izvorul lui Davele; 35. Resurgența Strivinoasei; 36. Iad Valley; 37. Peștera cu Apă din Valea Leșului; 38. Ponorul Rucșor; 39. Izbulul Bulbuci; 40. Ponorul Sohodol; 41. Ponorul din Stanul Focșii; 42. Peștera din Valea Fiului; 43. Izbulul Roșiei; 44. Peștera Gruiețului; 45. Izvorul Albastru; 46. Ponorul din Cheile Albioarei; 47. Peștera Toplița; 48. Izvorul Captat; 49. Izvorul din Valea Letea; 50. Apa de Sub Stan; 51. Ponorul Păștioasa; 52. Peștera cu Apă din Valea Letea; 53. Ponorul Prislop; 54. Izbulul Groieșului; 55. Peștera cu Apă din Valea Vida.

Mg<sup>++</sup> concentrations were obtained by making the difference between the results of the two analyses. The method presents a very high accuracy for calcium (0.2%) and total hardness (0.35%) determinations, but is less accurate for magnesium (2.5%). The error in Mg<sup>++</sup> determination becomes more evident for a higher Ca<sup>++</sup>/Mg<sup>++</sup> ratio. Sulphate was determined by a turbidimetric procedure, with errors ranging between 5 and 10%. Chloride was analysed by mercurimetric photometric titration with a 2% error at most.

For pH determination and carbonate species analysis we have used sampling bottles similar to Winkler with determined volume. In the laboratory the analysis was carried on right in the sampling bottle, and the analysis was developed in a closed system to prevent the carbon dioxide loss from water. Total alkalinity, total carbonate content and free CO<sub>2</sub> acidity were determined by Gran titration (Mackereth et al., 1978). Working on 5 samples taken from the same site, the following relative errors were found: 0.2% for total alkalinity, 0.3% for total carbonate content and 2.3% for dissolved CO<sub>2</sub>.

For all samples where Gran titration procedure was applied, were calculated the saturation index with respect to calcite (SI<sub>c</sub>) and to dolomite (SI<sub>d</sub>) as well as partial CO<sub>2</sub> pressures. The following equations were used:  $SI_c = \log(aCa^{++}aCO_3^{--}/K_c)$ ,  $SI_d = \log[[aCa^{++}aMg^{++}(aCO_3^{--})^2]/K_d]^{1/2}$  and  $P_{CO_2} = aH^+aHCO_3^-/K_1 K_{CO_2}$ , where aX stands for activities. The activities of the implied ions were calculated by making the product between the analytically determined concentrations and the corresponding activity coefficients. In the case of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>--</sup> ions, the concentrations were deduced from total carbonate values. The Debye-Hückel relation was used to established the activity coefficients, by using ionic strength based on the determined molar concentrations. The equilibrium constants were calculated for each sample temperature separately, according to Jacobson and Langmuir (1974) values for K<sub>c</sub>, Langmuir (1971) values for K<sub>d</sub>, Harned and Davis (1943) values for K<sub>1</sub> and K<sub>CO<sub>2</sub></sub>. To a ±0.1 units uncertainty in pH determination corresponds an error of ±14% for SI<sub>c</sub> and ±9% for SI<sub>d</sub>.

Ek (1973) determines on 135 measurements simultaneously taken in site and in the laboratory a root-mean square error of 0.14 pH units (the maximum registered error being of 0.3 units pH). He also points out the fact the biggest errors are registered for waters with a low content of dissolved salts, such as recharge waters, while for emergences errors are smaller. On the other hand, Thrailkill (1971) alleges that, as a rule, pH measurements taken in the laboratory show more errors than that taken in site. Consequently, although we took a special care in water sampling and samples transport, pH measurements are probably accurate to within 0.2 pH units, and SI and P<sub>CO<sub>2</sub></sub> values are rather overestimated.

Estimations were also limited by overlooking ionic association in ion pairs. For instance, by applying the estimation procedure described before (Marin, 1979) to a water sample (26) we found that 3.2% of total calcium, 2.4% of total magnesium and 10.1% of total sulphate is associated in ion pairs. Although ion pairs formations was overlooked in the



determination of ionic activities, the resulting error is substantially smaller than the error due to uncertainty in pH measurement.

#### 4. Results

Table I records the analytical results for most of the analysed samples.

By examining the diagrams of Fig. 2 it will soon be noticed that carbonate waters are predominant, while sulphate waters appear only in some points. The latter belong to a single zone, with a limited area, situated in the north of the Mişid Valley Basin. There crops out the lias complex including quartzite sandstones, refractory sandstones, shales as well as refractory limestones, belonging to the Triassic. Because of the oxidation of pyrites associated to these formations, ground waters become highly acid and show high  $\text{SO}_4^-$  concentrations. Iosof et al. (1974) point out the presence of allophane in Peştera Vintului. It appears in the zone where sulphate waters mix with carbonate waters. The saturation degree determination for these waters, by the described procedure, is senseless. Their mineral acidity exceeds by far free  $\text{CO}_2$  acidity. Therefore samples from the north of Mişid Basin were omitted from further discussion.

#### 5. Data interpretation

The total dissolved solids content of carbonate waters from Pădurea Craiului is small, without exceeding  $500 \text{ mg l}^{-1}$ . In Figs. 3 and 4, the  $\text{HCO}_3^-$ ,  $\text{SO}_4^-$  and  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$  concentrations were represented as against TDS (total dissolved solids). One can notice that  $\text{HCO}_3^-$  and  $\text{Ca}^{++}$  are predominant and determine the mineralization of these waters.  $\text{SO}_4^-$  has, as a rule, low concentrations, while  $\text{Cl}^-$  appears in insignificant quantities. In Fig. 2 the chemical composition is presented in equivalent percentage concentrations. It is evident that  $\text{SO}_4^-$ ,  $\text{Cl}^-$  and probably  $\text{Na}^+$  and  $\text{K}^+$  weights are big for sink water, while for emergences they hardly reach 10% of ion total. In Table 2 are summarized the characteristics of analysed waters and the differences between sink waters and emergences chemism are easily noticed.

The  $\text{Mg}^{++}$  concentrations of waters are highly dependent upon the type of the rocks with which these come into touch. Waters deposited in Jurassic and especially in Cretaceous limestones are low in  $\text{Mg}^{++}$ , whereas waters in Triassic rocks are richer. Consequently, the  $\text{Ca}^{++}/\text{Mg}^{++}$  molar ratio values are great for the former and small for the latter. By representing this ratio as TDS function, we obtain regression lines with different slopes for both cases (Fig. 5). This is the result of the fact that the Triassic is represented both by limestones and dolomites. However, the smallest values of the ratio are about 2, that means that either Triassic flow waters come into a short-time touch with dolomites or that dolomite formations have a small share of limestone. To draw a parallel, for a series of emergences from Bihor (Padiş zone) were determined values of the  $\text{Ca}^{++}/\text{Mg}^{++}$

Table 1  
Chemistry of water samples

Sampling site	Type and estimated discharge	Geology	Date of collection	Temp. (°C)	pH	CO <sub>3</sub>	Ca <sup>++</sup>	Mg <sup>++</sup>	mg l <sup>-1</sup>						TDS	Al <sup>+</sup> meq l <sup>-1</sup>	Log P <sub>CO<sub>2</sub></sub>	SI <sup>a</sup> <sub>17</sub>	SI <sup>a</sup> <sub>18</sub>
									CO <sub>3</sub>	HCO <sub>3</sub>	CO <sub>3</sub>	SO <sub>4</sub>	Cl	TDS					
1																			
1	spr./D	C <sub>1</sub>	05.80	9.8	7.40	19.5	84.1	1.2	243.5	0.2	6.5	2.5	338	4.000	-2.10	0.00	-0.80		
2	spr./D	C <sub>1</sub>	05.80	10.2	7.60	8.0	81.2	1.3	236.2	0.4	4.5	2.4	326	3.877	-2.35	+0.20	-0.55		
3	c.w./C	C <sub>1</sub>	05.80	10.0	7.70	4.8	104.2	0.1	303.2	0.6	7.8	3.6	420	4.980	-2.30	+0.50	-0.90		
4	rch./A	C <sub>1</sub>	05.80	15.2	7.55	6.3	57.6	1.5	175.0	0.3	8.8	2.9	249	2.872	-2.35	-0.05	-0.70		
4		C <sub>1</sub>	07.80	20.4	7.55	6.0	60.6	1.8	188.5	0.3	5.0	2.1	261	3.096	-2.30	+0.10	-0.50		
5	c.w./A	C <sub>1</sub>	05.80	10.8	7.55	8.8	95.2	1.2	282.3	0.4	7.2	2.6	389	4.634	-2.20	+0.30	-0.55		
5		C <sub>1</sub>	07.80	13.7	7.60	8.5	90.5	1.9	276.9	0.5	8.1	1.9	382	4.547	-2.25	+0.35	-0.35		
6	c.w./B	C <sub>1</sub>	05.80	10.1	7.30	17.4	109.2	0.6	335.7	0.3	12.7	1.2	468	5.507	-2.00	+0.15	-0.55		
6		C <sub>1</sub>	07.80	10.5	7.40	13.9	92.6	2.0	321.5	0.3	13.1	0.8	448	5.274	-2.00	+0.10	-0.50		
7	well/-	C <sub>1</sub>	07.80	9.8	7.15	29.6	104.2	9.8	322.6	0.2	54.8	51.3	586	5.290	-1.70	-0.10	-0.50		
8	rch./C	J <sub>3</sub>	07.80	22.4	7.25	13.2	66.5	4.3	200.1	0.2	13.3	9.5	297	3.283	-2.00	-0.10	-0.55		
9	spr./B	J <sub>3</sub>	07.80	11.3	7.50	9.9	97.7	3.1	297.8	0.4	10.2	4.2	416	4.887	-2.15	+0.30	-0.35		
9		J <sub>3</sub>	05.80	10.3	7.55	10.8	106.0	0.3	315.7	0.4	7.2	1.6	433	5.181	-2.15	+0.30	-0.80		
10	c.w./A	J <sub>3</sub>	07.80	10.3	7.60	7.9	103.6	0.8	310.1	0.5	6.7	1.9	425	5.090	-2.20	+0.40	-0.55		
11	rch./C	J <sub>3</sub>	05.80	14.6	6.45	7.5	7.5	0.7	15.8	3.0 <sup>-3</sup>	5.5	0.6	30	0.258	-2.30	-2.75	-3.15		
12	rch./C	J <sub>3</sub>	05.80	15.2	7.05	3.8	9.8	0.8	30.5	2.0 <sup>-2</sup>	3.7	0.4	46	0.500	-2.60	-1.85	-2.30		
12		J <sub>3</sub>	07.80	13.4	6.95	4.3	8.6	0.8	30.5	1.0 <sup>-2</sup>	1.0	0.2	42	0.501	-2.50	-2.10	-2.50		
13	c.w./A	C <sub>1</sub>	05.80	10.3	7.50	13.2	95.7	1.0	286.3	0.4	6.6	1.5	392	4.689	-2.10	+0.20	-0.65		
13		C <sub>1</sub>	07.80	10.6	7.55	7.4	93.8	1.4	285.2	0.4	3.8	0.9	385	4.681	-2.15	+0.25	-0.55		
14	rch./C	T <sub>2</sub>	05.80	9.7	6.95	4.5	8.7	2.3	34.3	1.0 <sup>-2</sup>	4.0	2.1	53	0.563	-2.50	-1.15	-1.80		
15	spr./A	T <sub>2</sub>	05.80	9.8	7.60	7.0	74.5	4.4	238.0	0.4	6.3	1.3	325	3.906	-2.30	+0.15	-0.35		
15		T <sub>2</sub>	07.80	10.2	7.65	5.9	71.7	5.6	241.4	0.4	6.8	1.2	330	3.964	-2.35	+0.20	-0.40		
16	str./B	T <sub>2</sub>	03.80	4.9	8.05	-	11.5	1.6	-	-	17.2	2.9	57	0.361*	-	-	-		
17	c.w./B	T <sub>2</sub>	05.79	10.0	7.30	-	48.3	8.3	-	-	-	-	-	1.741*	-	-	-		
17		T <sub>2</sub>	05.79	10.0	7.45	-	55.4	10.6	-	-	74.0	5.3	306	2.442*	-	-	-		
17		T <sub>2</sub>	03.80	7.9	7.30	-	32.4	7.4	-	-	33.7	10.1	166	1.314*	-	-	-		
17		T <sub>2</sub>	05.80	10.0	7.60	2.4	55.2	9.4	108.6	0.2	95.5	6.6	285	1.783	-2.65	-0.35	-0.60		
17		T <sub>2</sub>	07.80	10.2	7.50	3.9	57.4	11.1	130.9	0.2	76.4	5.3	281	2.148	-2.50	-0.30	-0.55		
18	str./A	J <sub>3</sub>	05.80	15.6	7.20	9.1	25.5	1.1	77.7	5.0 <sup>-2</sup>	4.6	1.1	111	1.271	-2.35	-1.05	-1.60		

Table 1 (continued)

Sampling site	Type and estimated discharge	Geology	Date of collection	Temp. (°C)	pH	mg l <sup>-1</sup>							TDS	A <sub>p</sub> meq l <sup>-1</sup>	Log P <sub>CO<sub>2</sub></sub>	SI <sub>1</sub>	SI <sub>2</sub>	SI <sub>3</sub>
						CO <sub>2</sub>	Ca <sup>++</sup>	Mg <sup>++</sup>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>	Cl <sup>-</sup>						
19	str./A	T <sub>2</sub>	03.80	5.4	7.05	—	18.6	2.1	—	—	—	17.5	1.7	91	0.799*	—	—	—
20	str./A	T <sub>2</sub>	05.79	11.2	6.95	—	27.4	3.5	—	—	68.0	—	—	—	1.131*	—	—	—
20			05.79	15.2	7.15	—	34.2	2.4	—	—	17.2	1.4	189	1.116*	—	—	—	—
20			03.80	5.0	7.35	—	20.2	3.8	—	—	7.0	1.6	90	0.773*	—	—	—	—
21	c.w./C	J <sub>3</sub>	05.80	8.4	7.60	5.2	81.3	0.7	244.0	0.4	—	—	—	—	4.005	—	—	—
22	spr./C	T <sub>2</sub>	07.80	10.0	7.65	5.2	75.7	1.4	227.5	0.4	—	—	—	—	3.735	-2.35	+0.20	-0.75
23	c.w./C	T <sub>2</sub>	03.80	8.0	7.10	—	43.9	6.3	—	—	36.1	1.7	207	1.938*	—	-2.40	+0.20	-0.55
23			03.80	7.5	7.60	—	57.1	11.2	—	—	—	—	—	—	1.501*	—	—	—
23			07.80	9.1	7.05	3.5	58.7	12.3	—	—	145.0	15.1	303	0.990*	—	—	—	—
24	str./B	T <sub>2</sub>	05.79	11.1	3.30	—	116.0	25.7	29.2	10 <sup>-2</sup>	412.6	8.1	624	0.478	—	-2.70	-0.15	-1.55
25	c.w./B	T <sub>2</sub>	03.80	5.4	3.55	—	109.2	47.5	—	—	—	—	—	—	0.000*	—	—	—
25			05.79	7.2	4.40	—	76.6	32.6	—	—	426.8	4.1	599	0.000*	—	—	—	—
26	c.w./D	T <sub>2</sub>	03.80	5.5	4.50	—	57.4	33.9	—	—	—	—	—	—	0.000*	—	—	—
26			03.80	5.5	4.50	—	53.6	20.2	—	—	—	—	—	—	0.000*	—	—	—
27	spr./C	T <sub>2</sub>	03.80	8.2	7.30	—	44.3	3.3	—	—	—	—	—	—	0.003*	—	—	—
27			07.80	10.3	7.65	5.2	75.1	9.8	264.5	0.5	—	—	—	—	2.154*	—	—	—
28	spr./B	T <sub>2</sub>	07.80	10.6	7.40	8.9	51.9	4.4	179.5	0.2	—	—	—	—	4.343	-2.30	+0.25	-0.10
28			05.80	10.0	7.60	6.1	60.9	15.0	243.2	0.4	—	—	—	—	2.945	-2.20	-0.30	-0.70
29	c.w./A	T <sub>2</sub>	07.80	10.6	7.80	3.9	63.6	14.7	266.5	0.7	—	—	—	—	3.992	-2.30	-0.30	+0.10
29			07.80	10.0	7.55	6.8	58.7	6.1	207.0	0.3	—	—	—	—	4.379	-2.45	+0.35	+0.10
30	spr./C	T <sub>2</sub>	07.80	10.0	7.50	5.4	34.6	6.4	126.7	0.1	—	—	—	—	3.397	-2.35	-0.05	-0.40
31	spr./A	T <sub>2</sub>	05.80	7.9	7.50	4.3	38.0	8.2	151.4	0.2	—	—	—	—	2.079	-2.45	-0.50	-0.70
32	spr./B	T <sub>2</sub>	07.80	9.3	7.60	5.1	47.2	14.9	202.6	0.3	—	—	—	—	2.484	-2.40	-0.40	-0.60
32			07.80	9.9	7.60	5.9	49.4	15.4	221.6	0.3	—	—	—	—	3.325	-2.40	-0.10	-0.25
33	c.w./C	J <sub>3</sub>	05.80	8.4	7.65	4.7	50.2	3.4	164.0	0.3	—	—	—	—	3.637	-2.30	-0.10	-0.25
33			07.80	9.3	7.60	3.9	47.1	3.3	159.0	0.2	—	—	—	—	2.693	-2.50	-0.10	-0.60
34	spr./B	J <sub>3</sub>	05.80	7.5	7.35	6.3	29.2	0.8	79.1	0.1	—	—	—	—	2.609	-2.45	-0.20	-0.65
34			07.80	8.6	7.30	6.3	32.0	1.0	97.8	0.1	—	—	—	—	1.298	-2.55	-0.90	-1.60
35	spr./B	J <sub>3</sub>	05.80	7.8	7.45	2.6	27.7	2.6	91.6	0.1	—	—	—	—	1.604	-2.40	-0.85	-1.50
35			07.80	9.6	7.25	5.6	26.1	0.9	84.1	0.1	—	—	—	—	1.502	-2.55	-0.80	-1.25
36	str./A	J <sub>3</sub>	05.80	10.3	7.00	4.3	9.6	1.4	27.3	10 <sup>-2</sup>	—	—	—	—	1.379	-2.40	-1.00	-1.65
							9.6	1.4	27.3	10 <sup>-2</sup>	—	—	—	—	0.447	-2.65	-2.10	-2.40

37	c.w./A	J <sub>3</sub>	11.75	8.0	7.60	46.7	4.2	120.3	0.1	4.5	0.7	166	2.444*	-2.25	-0.75	-1.20		
37	rch./B	T <sub>3</sub>	05.80	8.0	7.25	37.9	2.6	177.5	4.10 <sup>-2</sup>	4.2	1.1	109	1.972	-2.20	-1.40	-1.55		
38			05.80	16.6	7.05	14.1	3.9	43.2	1.0 <sup>-2</sup>	4.7	1.1	64	0.708	-2.10	-2.35	-2.50		
38			07.80	13.8	6.70	9.9	2.8	142.3	0.1	5.8	1.2	197	2.334	-2.30	-0.50	-0.90		
39	spr./A	T <sub>3</sub>	05.80	9.5	7.40	43.4	4.1	140.7	0.1	4.2	1.1	189	2.309	-2.30	-0.60	-0.80		
39			07.80	10.5	7.35	33.5	8.6	40.2	1.0 <sup>-2</sup>	4.9	0.9	61	0.659	-2.20	-2.30	-2.70		
40	rch./C	J <sub>3</sub>	07.80	8.9	6.75	9.3	12.5	7.6	1.0 <sup>-6</sup>	3.9	0.7	17	0.125	-2.60	-3.40	-3.70		
41	rch./C	T <sub>2</sub>	05.80	11.3	6.45	10.7	4.1	6.2	16.10 <sup>-7</sup>	3.6	0.6	14	0.102	-2.40	-4.00	-4.25		
42	rch./C	T <sub>2</sub>	05.80	12.6	6.15	6.4	1.9	0.4	6.2	3.9	0.7	17	0.125	-2.40	-4.00	-4.25		
43	spr./A	J <sub>3</sub>	05.80	9.9	7.40	45.4	3.8	149.0	0.1	4.7	1.0	204	2.444	-2.30	-0.40	-0.85		
43			07.80	10.1	7.10	43.6	4.4	152.8	0.1	2.6	1.0	205	2.506	-2.00	-0.70	-1.10		
44	c.w./C	J <sub>3</sub>	07.80	10.3	7.45	8.5	1.7	207.3	0.2	1.9	1.9	281	3.400	-2.20	-0.10	-0.80		
45	spr./D	J <sub>3</sub>	07.80	9.8	7.70	5.7	70.6	1.2	216.8	0.4	1.3	0.4	291	3.560	-2.45	+0.20	-0.60	
46	rch./C	J <sub>3</sub>	05.80	16.0	7.40	8.4	63.7	0.9	190.0	0.2	9.7	0.9	267	3.116	-2.15	-0.10	-0.90	
46			07.80	18.3	7.55	9.1	55.1	1.5	174.3	0.3	8.9	0.4	245	2.861	-2.35	-0.05	-0.65	
47	spr./A	J <sub>3</sub>	05.80	10.0	7.45	8.7	64.8	0.3	192.1	0.2	6.2	1.4	266	3.152	-2.25	-0.15	-1.15	
47			07.80	10.7	7.40	10.1	63.7	1.4	199.4	0.2	6.1	1.1	275	3.271	-2.20	-0.15	-0.85	
48	spr./C	J <sub>3</sub>	05.80	11.8	7.55	7.6	78.2	0.9	226.6	0.3	5.2	1.3	310	3.717	-2.30	+0.15	-0.70	
48			07.80	11.7	7.60	7.1	78.2	1.5	242.8	0.4	5.3	0.9	331	3.986	-2.30	+0.20	-0.55	
49	spr./C	J <sub>3</sub>	05.80	7.8	7.40	7.9	48.0	1.0	138.7	0.1	5.6	1.4	195	2.275	-2.35	-0.45	-1.20	
50	spr./B	J <sub>3</sub>	05.80	9.2	7.55	6.7	69.0	1.2	204.0	0.3	6.9	1.5	282	3.349	-2.35	+0.05	-0.75	
50			07.80	9.3	7.50	8.6	69.0	1.7	213.7	0.3	7.0	1.0	295	3.507	-2.25	0.00	-0.70	
51	rch./C	J <sub>3</sub>	05.80	8.4	6.75	5.0	6.9	0.5	20.9	10 <sup>-3</sup>	3.7	0.3	33	0.343	-2.50	-2.50	-2.95	
52	c.w./C	J <sub>3</sub>	05.80	8.4	7.45	7.7	61.7	1.0	180.1	0.2	7.2	1.0	251	2.954	-2.30	-0.20	-1.00	
52			07.80	9.5	7.30	12.2	62.6	1.3	192.9	0.1	7.2	0.9	268	3.164	-2.10	-0.40	-1.10	
53	rch./C	J <sub>3</sub>	05.80	11.3	6.50	6.7	4.1	0.9	12.1	1.3	10 <sup>-3</sup>	3.3	0.2	21	0.198	-2.50	-3.00	-3.25
54	spr./B	J <sub>3</sub>	05.80	9.0	7.45	8.3	69.1	0.9	204.3	0.2	5.6	0.8	281	3.352	-2.25	-0.10	-0.95	
54			07.80	9.1	7.55	1.7	67.5	1.4	205.9	0.3	6.1	0.4	283	3.379	-2.35	0.00	-0.70	
55	c.w./C	J <sub>3</sub>	05.80	8.6	7.55	10.1	84.1	1.5	244.0	0.3	7.9	0.9	339	4.004	-2.25	+0.15	-0.65	
55			07.80	9.2	7.55	9.3	83.7	1.3	257.1	0.4	8.1	0.7	354	4.220	-2.25	+0.20	-0.60	

1) Type: spr. = spring water; c.w. = cave stream water; rch. = recharge water; str = surface stream water.

2) Estimated discharge:  $A > 100 \text{ l s}^{-1}$ ;  $100 \text{ l s}^{-1} > B > 10 \text{ l s}^{-1}$ ;  $10 \text{ l s}^{-1} > C > 1 \text{ l s}^{-1}$ ;  $D < 1 \text{ l s}^{-1}$

3) Geology, after Rusu (1979): T<sub>2</sub> = Middle Triassic; T<sub>3</sub> = Upper Triassic; J<sub>3</sub> = Upper Jurassic; C<sub>1</sub> = Lower Cretaceous

4) CO<sub>2</sub>: free CO<sub>2</sub> acidity determined by Gran titration procedure.

5) HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>: values calculated from total carbonate, determined in its turn by Gran titration procedure

6) TDS: calculated total dissolved solids.

7) A<sub>f</sub>: total alkalinity determined by Gran titration procedure, except samples marked with (\*) which were analysed by potentiometric titration with the alkalinity end-point fixed at pH 4.45.



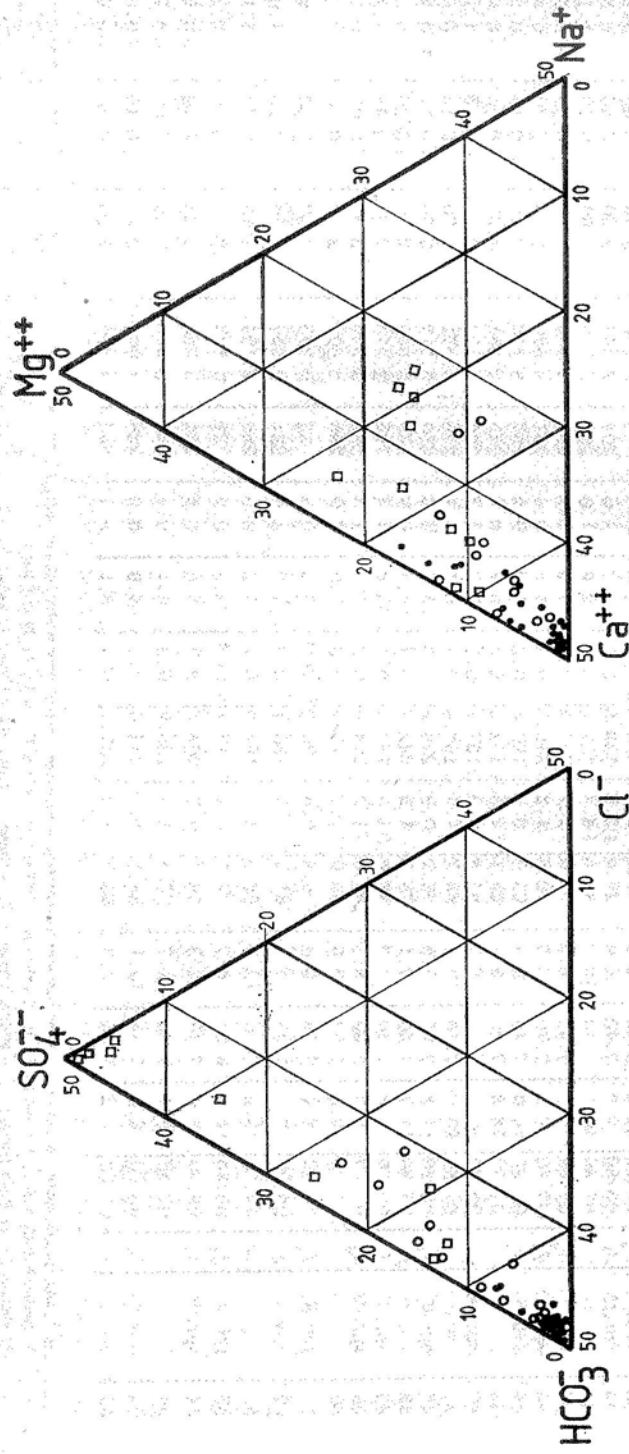


Fig. 2 — Graphical representation of the chemical composition (anions and cations) of analysed samples (March-May 1980), where emergences have been designated by (O); recharge waters by (O); samples from Mişid Valley Basin by (□).

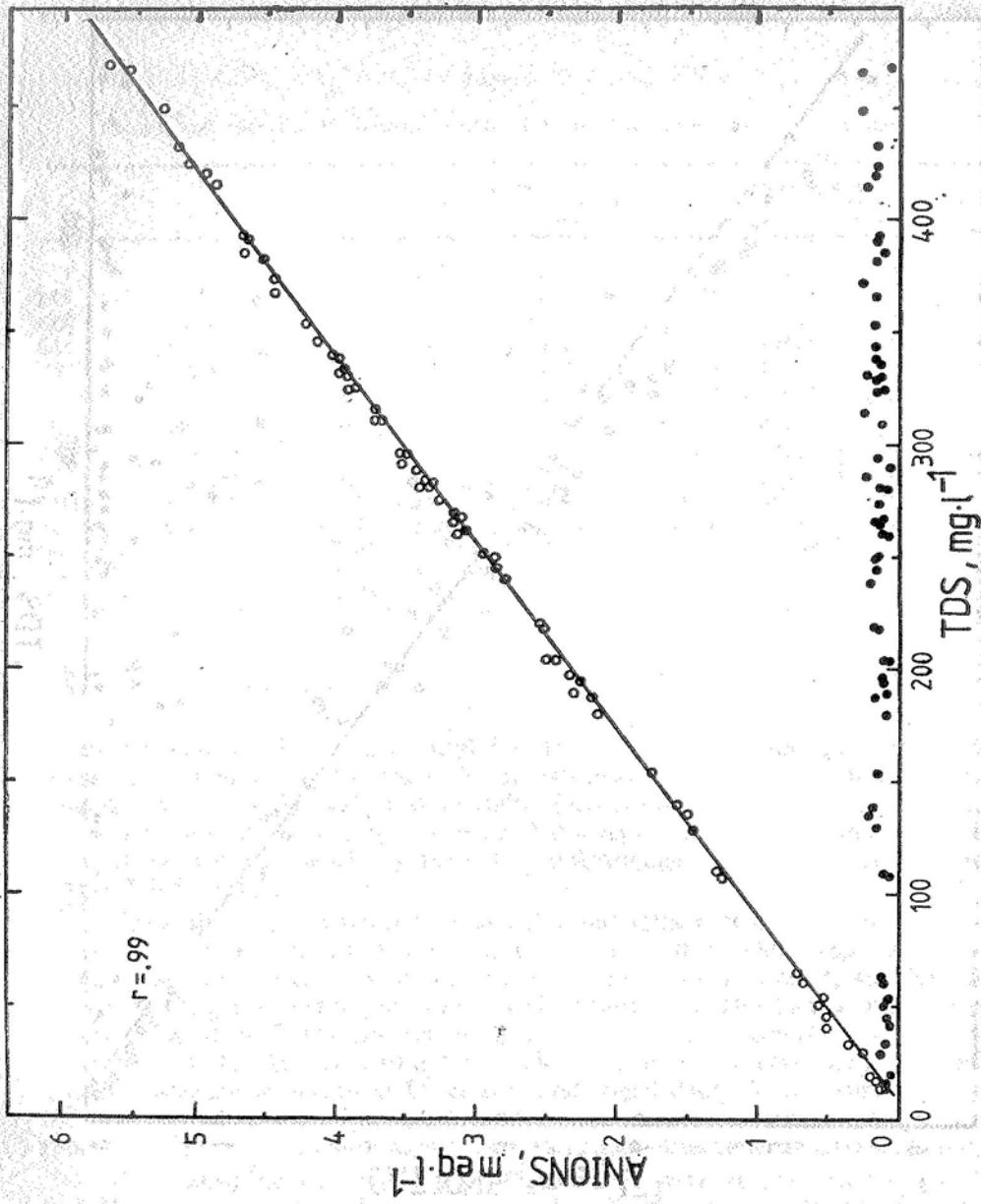


Fig. 3. - Change of HCO<sub>3</sub><sup>-</sup> (○) and SO<sub>4</sub><sup>2-</sup> (●) content in carbonate waters versus the total dissolved solids.

Fig. 4. — Change of  $\text{Ca}^{++}$  (○) and  $\text{Mg}^{++}$  (●) content in carbonate waters versus the total dissolved solids.

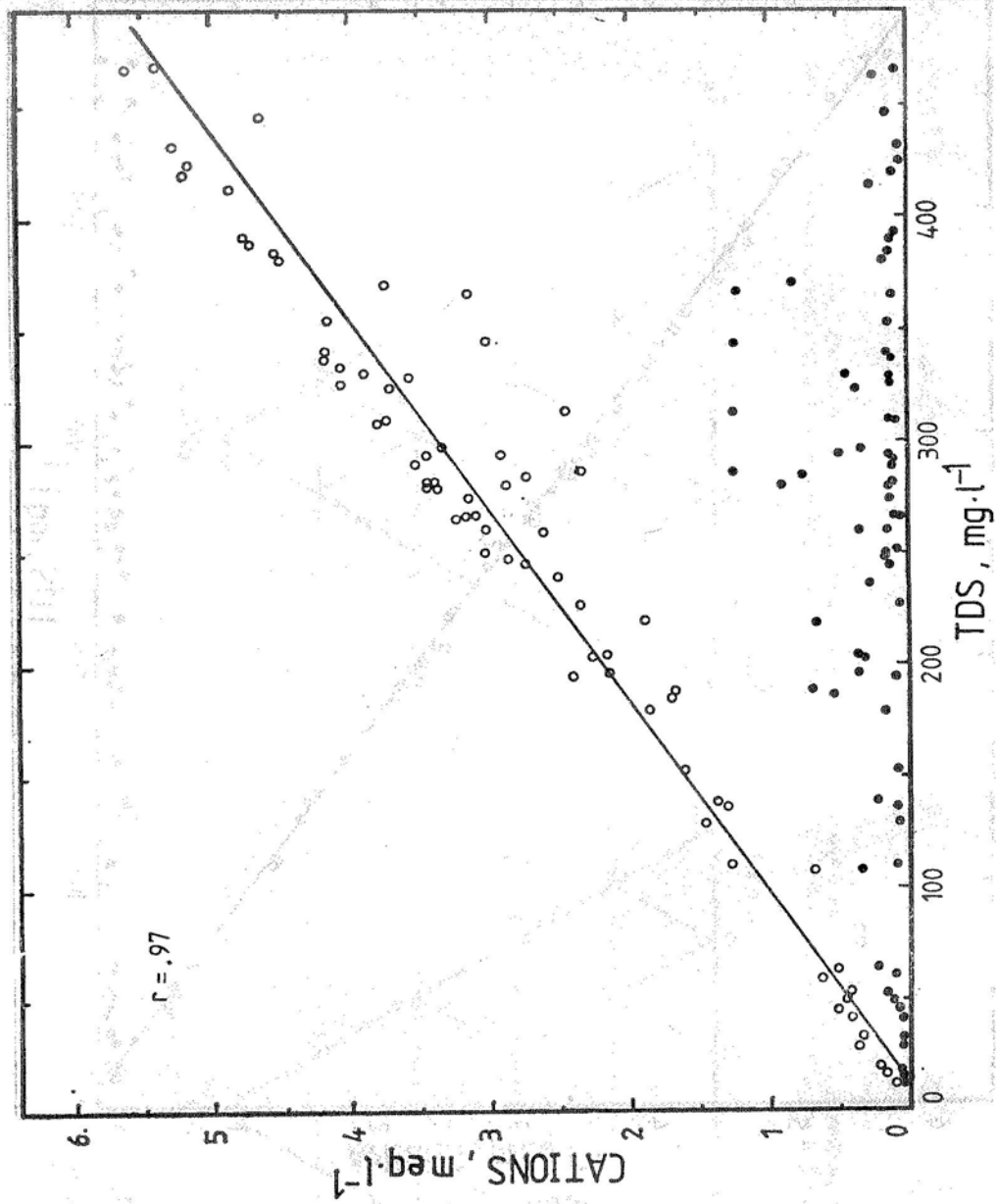


Table 2

Ranges and averages of chemical composition for the carbonate waters sampled

	Surface waters		Emergence waters	
	Range	Average	Range	Average
T (°C)	8.4 — 22.7	13.7	7.5 — 13.7	9.7
pH	6.15 — 7.55	6.95	7.10 — 7.80	7.52
CO <sub>2</sub> <sup>0</sup>	3.8 — 13.2	7.1	1.7 — 19.5	7.8
Ca <sup>++</sup> mg l <sup>-1</sup>	1.9 — 66.5	32.1	26.1 — 109.2	66.4
Mg <sup>++</sup> mg l <sup>-1</sup>	0.4 — 4.3	1.8	0.1 — 15.4	3.5
HCO <sub>3</sub> <sup>-</sup> mg l <sup>-1</sup>	6.2 — 200.1	75.1	79.1 — 335.7	210.1
CO <sub>3</sub> <sup>--</sup> mg l <sup>-1</sup>	6.10 <sup>-7</sup> — 0.3	0.07	0.1 — 0.7	0.3
SO <sub>4</sub> <sup>--</sup> mg l <sup>-1</sup>	1.0 — 13.3	5.4	1.3 — 12.7	7.1
Cl <sup>-</sup> mg l <sup>-1</sup>	0.2 — 9.5	1.4	0.1 — 4.2	1.3
TDS mg l <sup>-1</sup>	14 — 297	109	119 — 468	292
A <sub>t</sub> meq l <sup>-1</sup>	0.125 — 3.283	1.191	1.298 — 5.507	3.475
Log P <sub>CO<sub>2</sub></sub>	-2.55 — -1.85	-2.36	-2.63 — -2.00	-2.28
SI <sub>c</sub>	-4.00 — +0.1	-1.67	-1.00 — +0.50	-0.09
SI <sub>d</sub>	-4.25 — -0.5	-2.11	-1.65 — +0.10	-0.72
n	20		55	

n is the number of observations.

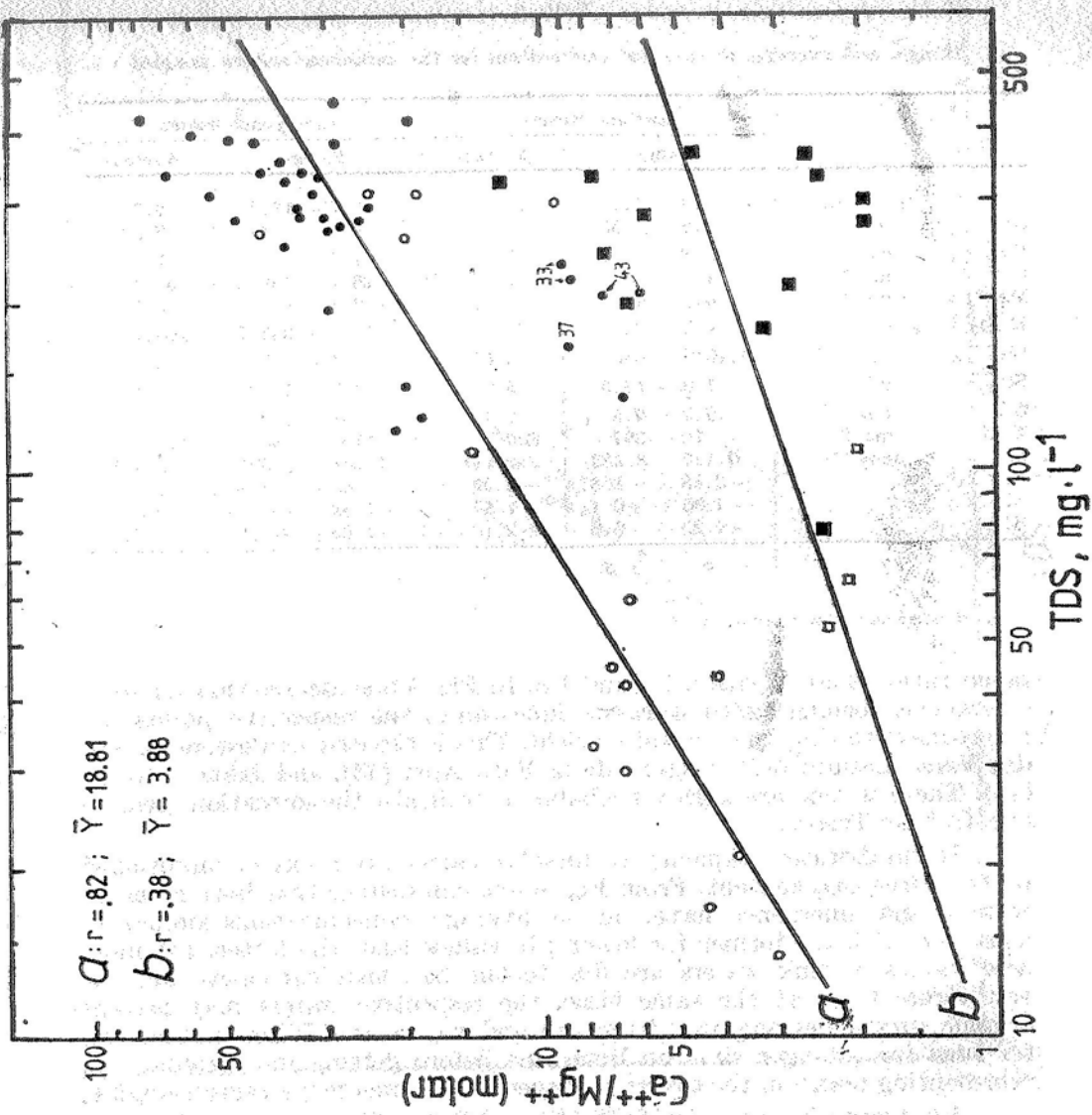
molar ratio situated within 1.2 and 1.8. In Fig. 5 one can see that for some emergences belonging to Jurassic limestones, the respective points are placed next to the Triassic waters field. This is the case of Peștera cu Apă din Valea Leșului (37), Peștera de la Fața Apei (33), and Izbucul Roșiei (43). These waters are highly probable to drain also the formations belonging to the Triassic.

Natural waters capacity to dissolve carbonate rocks is conditioned by their free CO<sub>2</sub> content. From Fig. 6 one can deduce that both recharge waters and emergence have, on an average, concentrations similar to dissolved CO<sub>2</sub>, the former for lower pH values than the latter. pH more acid values of sink waters are due to the fact that carbonates do not equilibrate CO<sub>2</sub>. At the same time, the respective waters may present organic substances acquired from soil and vegetation. When surface water runs for a longer time on limestone before getting into ground, the representing point on the diagram ranges in the emergence regression line.

By examining the dissolved CO<sub>2</sub> content with respect to the Ca<sup>++</sup> and Mg<sup>++</sup> content of analysed waters (Fig. 7) we find the difference between spring waters and cave stream waters. According to theoretical premises (Picknett et al., 1976), the dissolution of carbonate rocks is slowed down when water flows in a closed system, without benefiting from any CO<sub>2</sub> supply. On the contrary, water may dissolve the rock more quickly, when it has a permanent CO<sub>2</sub> source, as it happens when it runs through wide galleries. From Fig. 7 one can see that for the same dissolved CO<sub>2</sub> concentration, spring waters present smaller Ca<sup>++</sup> and Mg<sup>++</sup> concentrations than cave stream waters, although carbonate precipitation was included for the latter.



Fig. 5. — Relationship between molar ratio  $\text{Ca}^{++}/\text{Mg}^{++}$  and TDS in carbonate waters from Pădurea Craiului. Circles represent sites on Cretaceous and Jurassic limestones; the open ones — shallow holes, and the filled ones — emergences. Squares stand for sites on Triassic rocks.



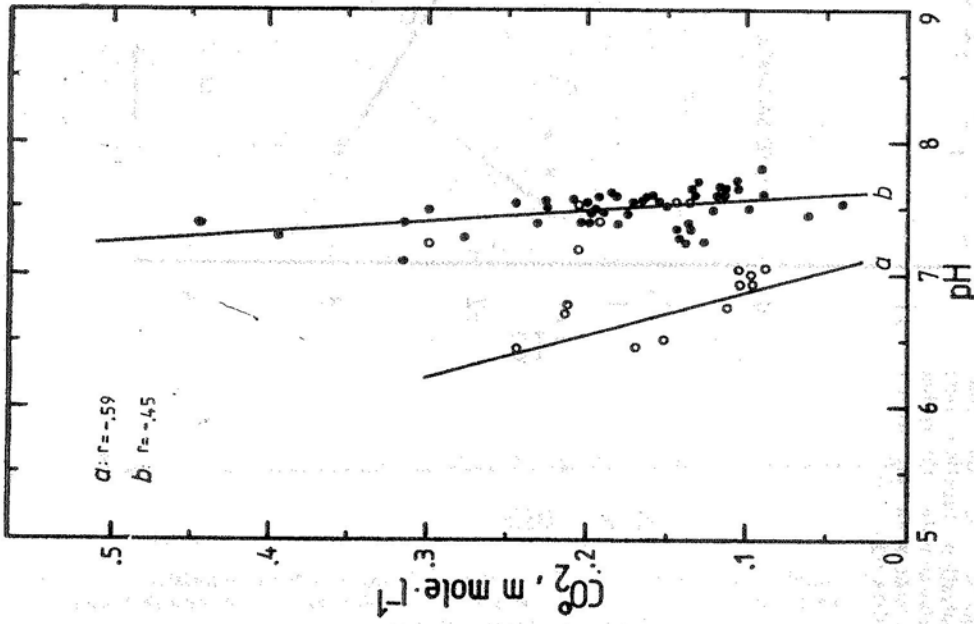


Fig. 6. — Relationship between the dissolved CO<sub>2</sub> content and the pH for : a) sinkhole waters (O) and b) emergence waters (●).

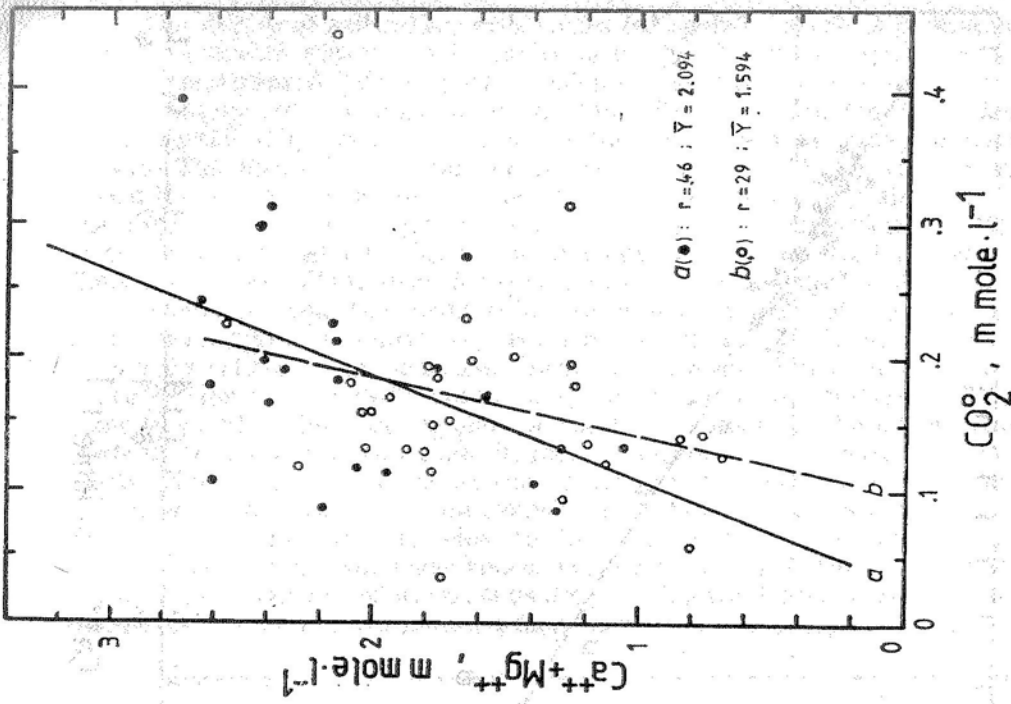
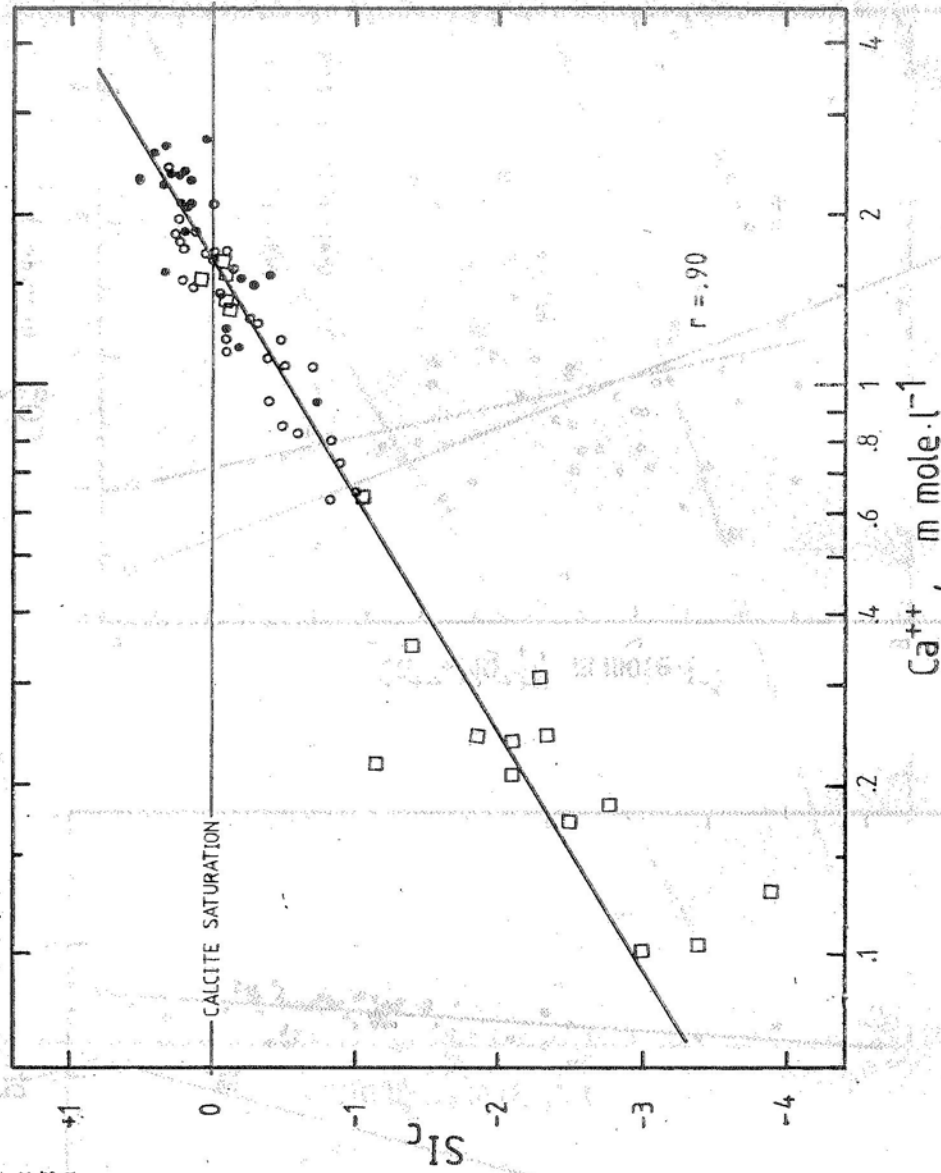


Fig. 7. — Ca<sup>++</sup> + Mg<sup>++</sup> content change versus dissolved CO<sub>2</sub> for : a) cave stream waters (●) and b) spring waters (O).

Fig. 8. —  $Si_0 - Ca^{++}$  concentration function for: recharge waters ( $\square$ ), spring waters ( $\bullet$ ) and cave stream waters ( $\circ$ ).



The degree of saturation also varies for spring waters as compared with cave stream waters. As it results from Fig. 8 cave waters are generally supersaturated with respect to calcite (medium  $SI_c = +0.1$ ), while spring waters are undersaturated (medium  $SI_c = -0.2$ ). On the other hand, partial  $CO_2$  pressures are lower for spring waters than for cave waters. The mean for the former is  $10^{-2.32}$ , and  $10^{-2.24}$  for the latter. The difference between these values is small and practically situated in the range of determination uncertainty. The same situation appears in the case of dissolved  $CO_2$ , whose analysis is less submitted to errors. Thus the dissolved  $CO_2$  mean for spring waters is 0.166 and 0.192 m mole  $l^{-1}$  for cave waters. The mean values obtained for  $SI_c$  and  $P_{CO_2}$  are different from those presented by Harmon et al. (1972) or Christopher (1978). For instance, Harmon finds mean partial pressures of  $10^{-2.36}$  for cave stream waters, and  $10^{-2.14}$  for spring waters. At the same time,  $SI_c$  values are smaller for the former than for the latter. This leads us to the conclusion that, in fact, most springs analysed from Pădurea Craiului karst area are not discharges of the deeper phreatic storage waters. For most of underground courses, the respective waters run through wide galleries and only when close to discharge fill the whole pipe section. In the case of caves, the large spaces run by waters near the cavemouths allow  $CO_2$  to come out of water, thus determining the high supersaturation degree. As expected, allogenic surface waters, before going underground

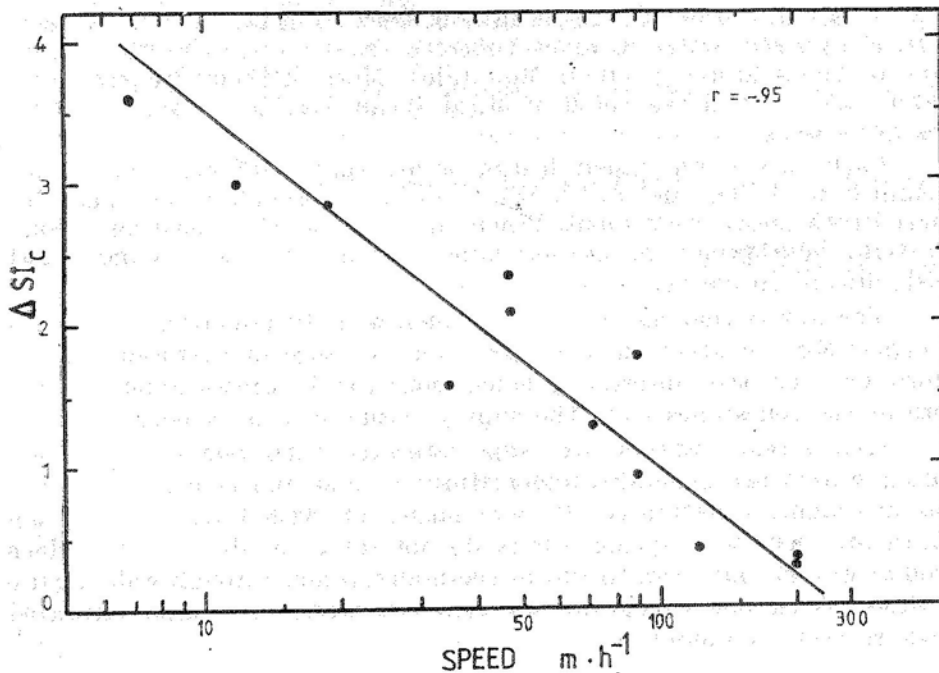


Fig. 9. — Relationship between the difference of saturation indexes with respect to calcite for swallow hole and the corresponding emergence waters ( $\Delta SI_c$ ) and the speed with which water covers the respective distance.



have very low saturation indexes (medium  $SI_c = 2.41$ ) and the  $P_{CO_2}$  mean is  $10^{-2.42}$ .

For a series of hydrokarstic penetrations, Rusu (1979) has determined the speed with which water runs underground courses. Representing a speed function, the difference between  $SI_c$  sink and  $SI_c$  emergence, the exponential relation in Fig. 9 was found.

Except the emergence of Peștera cu Apă de la Bulz, all analysed waters are undersaturated with respect to dolomite. No clear correlation could be established between  $Mg^{++}$  water content and  $SI_d$ . There are cases when undersaturation degree versus dolomite is smaller than expected, for reduced  $Mg^{++}$  concentrations. This happens every time when calcium concentrations are extremely high.

Although the time interval between the two main series of measurements was short, one could however notice that in July, the unsaturation degree of waters with respect to calcite and dolomite was lower than in May. This probably is the consequence of flow decrease and water mineralization increase.

## 6. Conclusions

This study presents the results obtained from the analysis of more than a hundred water samples collected from 60 sites in the karstic zone of the Pădurea Craiului Mountains. Most of them are carbonate waters and only in the north of Mișid Basin were found sulphate type ground waters.

Carbonate water mineralization is low (under  $0.5 \text{ g l}^{-1}$ ) and is determined by  $HCO_3^-$  and  $Ca^{++}$ .  $SO_4^{--}$ ,  $Cl^-$  and probably  $Na^+$  and  $K^+$  concentrations are very small. When compared to the whole ionic composition, these species appear more important in surface waters and almost insignificant in emergence waters.

The waters that had come into touch with Triassic formations have a higher  $Mg^{++}$  content than waters from Jurassic or Cretaceous limestones. On this basis interesting conclusions can be drawn about the nature of the limestones from the supply basins of some emergences.

Cave stream waters are supersaturated with respect to calcite, spring waters are generally undersaturated, and allogenic recharge waters are highly unsaturated. By correlating  $SI_c$  with  $P_{CO_2}$ , we could demonstrate that most spring waters do not represent discharges of deep ground waters, but seem to run in the underground through wide karstic cavities. With one exception, all analysed waters are undersaturated with respect to dolomite.

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