THE GEOCHEMISTRY OF GROUNDWATER FROM SOUTHEASTERN DOBROGEA, ROMANIA

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This paper is an approach to define the main characteristics and origin of sulphidic thermal waters from southeastern Dobrogea region, which included the cave „Peştera de la Movile". The model submitted is based on our water analyses achieved during the period 1986—1991, as well as on data reported by C a p o t a (1980). Computer programs were used to calculate real chemical compositions and mixing proportions of natural waters from the area. The results show that water from shallow aquifer mixes with water from the deep aquifers in the groundwater discharge area, yielding a range of intermediate compositions.

1. INTRODUCTION

The southeastern Dobrogea region was shown to be the site of some of the most interesting and complex Romanian hydrogeological features. The discovery of the cave „Peştera de la Movile" (C o n s t a n t i n e s c u, 1989), with its exceptional troglobitic community, has entailed again the attention of the specialists to this area.

On the ground of microbiological considerations (S a r b u, 1990) opinion that this cave contains the first known subterranean ecosystem based on chemoautotrophic production of the microbiota, which uses H_2S as a source of energy was postulate out (S a r b u et al. 1991; P o p a and S a r b u, 1991). This supposition is due to several paleogeographical and hydrogeological considerations (L a s c u, 1989), and comes to the conclusions that there is not obvious input of feeding from the surface and no local mixing between surface and subterranean water (S a r b u and P o p a, 1992).

Several institutions and some individual researchers have studied the hydrogeology of this area [for a description see, among others T e n u et al., (1987), D a v i d e s c u et al. (1991), F e r u and C a p o t a (1991)]. Despite these extensive studies there remain several unknown features of the carbonated aquifers of southeastern Dobrogea. Some authors furnish certain chemical data, in different contexts, about this underground waters, but enter into no detail.

The primary goal of our paper is to characterize and interpret the chemistry of groundwater from the studied area. Based on all available sources of information regarding the chemical composition, as well as on our own analytical determinations we make a preliminary attempt in this sense. The authors' purpose is not to determine fine-scale chemical variations, but to discern broad regional trends that might shed light on water migration and fundamental hydrochemical processes.

2. STUDY AREA

The South-Dobrogean platform, which embraced the examined territory, is from morphological point of view a region in the stage of peneplain with a very poor hydrographical network. The geological structure of

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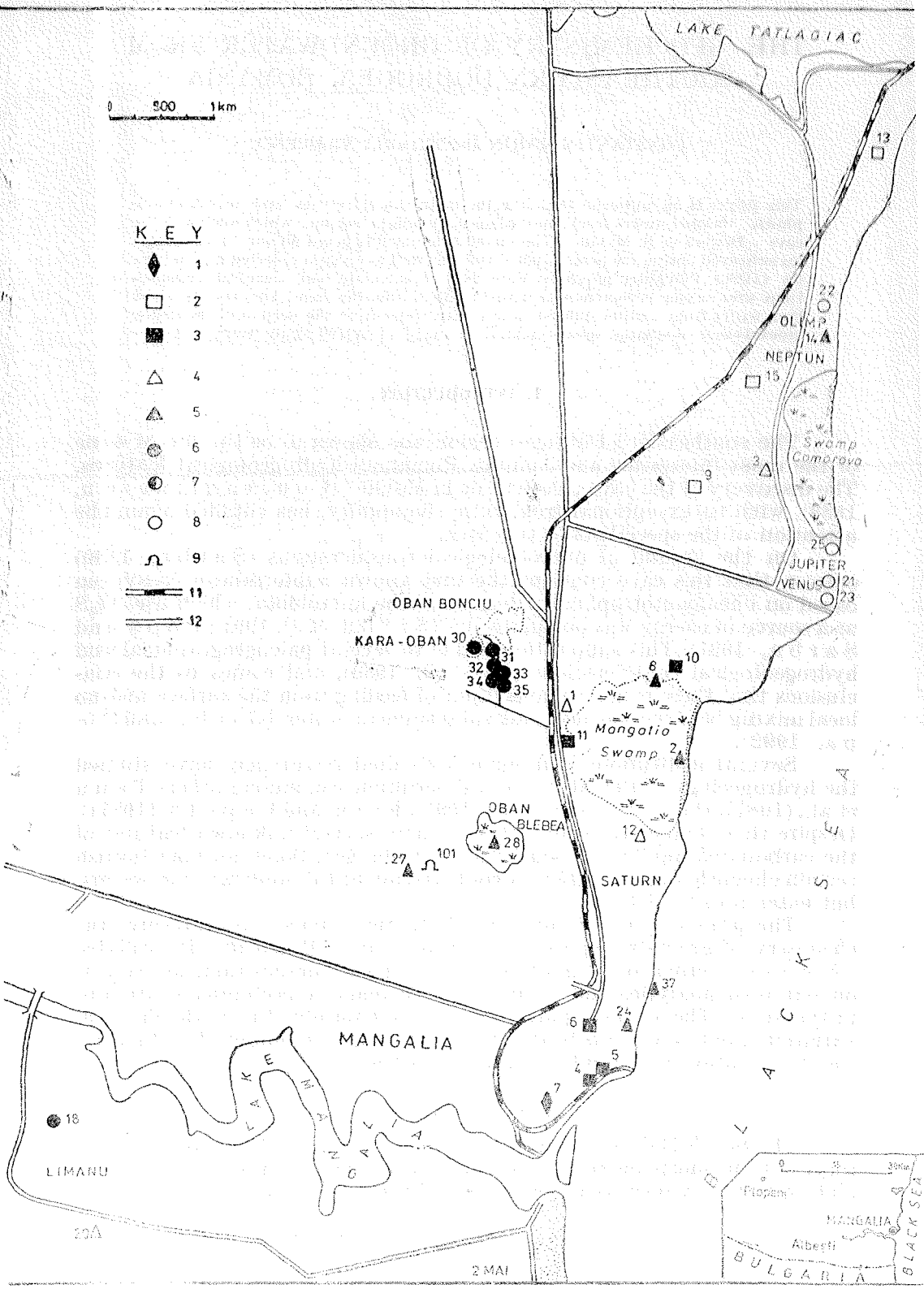
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this area is quite well known thanks to the numerous drilling which have been dug here beginning on 1962 down to 1979 (F e r u and C a p o t a, 1989). The crystalline basement, assigned as age to the Proterozoic, not reached in this region, is covered by sedimentary deposits.

From bottom to top the sedimentary formations consists of the following. (1) Sedimentary deposits of Paleozoic age intercepted by the profoundest well dug in Mangalia zone (Well No. 5082) between 559—1203 m depth. (2) Jurassic deposits of 350—450 m thick, consisting of limestones and compact dolomite. (3) Up to 100 m thick intermediate layers of Cretaceous age represented by marl limestones middle bands, clayey sands and calcareous sandstones. (4) Eocene deposits of about 100 m thickness consisting of sandstones, sands and limestones. (5) Sarmatian deposits developed between 0 and 120 m depth and represented by fossiliferous limestones with rare and thin marl bands. These sediments, with a thickness of about 26 m in the Mangalia city territory, gradually become thin and disappear in the sector of Mangalia swamp (Fig. 1). (6) Quaternary rocks with a thickness of 0—30 m and consisting of sandstones, clayey marl and clay soils.

It could be assumed (F e r u and C a p o t a, 1991) that sedimentary deposits of Jurassic, Cretaceous and Eocene age form a unified karstifiable complex, whereas sarmatian limestones another one. Between these two units there is a thicker layer of impermeable clays more striking in southward Mangalia locality. From the hydrological point of view these units are considered as two distinct aquifers.

By interpreting of a large number of experimental data consisting of environmental isotope analyses, T e n u et al. (1987) and D a v i d e s c u et al. (1991) delimited the recharge zones for both aquifers and established the main flow directions and drainage areas in the following way :

— For the Jurassic aquifer the recharge territory is determined in pre-Balkan Plateau (Bulgaria), having two flowing directions, a main path toward the area of major drainage in the NE of Constanța city, a secondary flowing direction towards Mangalia ;

— For the Sarmatian aquifer, which according to the above-mentioned authors is drastically influenced by precipitation waters, a recharge area with recent water in the Plopeni—Credința zone, where irrigation

Fig. 1. Location of samples utilized in study. *Key:* Well with open interval in the levels: 1. Paleozoic, 2. Jurassic, 3. Cretaceous, 4. Eocene + Sarmatian, 5. Sarmatian. Springs: 6. Sarmatian rocks, 7. Eocene + Sarmatian rocks, 8. without H_2S. 9. Cave. 10. Rail way. 11. Route. *Sampling sites*, in brackets final depth of the drilling, in meters: 1 — Well No. 4073, herghelie (83); 2 — Well No 4076, Mangalia beach (31); 3 — Well No. 1 IBF, Neptun (160); 4 — Well No. 2 IBF, Mangalia (Callatis) (182); 5 — Well No. 3 IBF, Mangalia (232); 6 — Well No. 4 IBF, Mangalia (Hercules) (220); 7 — Well No. 5082, Mangalia (1204); 8 — Well No. 4074, Venus (49); 9 — Well No. 1 ISLGC, Neptun (530); 10 — Well No. 2 ISLGC, Venus (200); 11 — Well No. 3 ISLGC, Mangalia swamp (200); 12 — Well No. 4 ISLGC, Mangalia swamp (100); 13 — Well No. 5 ISLGC, Olimp (301); 14 — Well No. 6 ISLGC, Neptun II (29); 15 — Well No. 7 ISLGC, Neptun (303); 18 — Spring in Limanu village; 20 — Well CAP Limanu (95); 21 — Venus spring; 22 — Olimp spring; 23 — Aurora spring; 24 — Sanatoriu Mangalia spring; 25 — Jupiter spring; 27 — Oban well (70); 28 — Topitoria de in well; 30 — Kara Oban underwater spring; 31 & 35 — Piriul sulfuros springs; 37 — Buncar well; 101 — "Peștera de la Movile" cave.

water penetrates down is mentioned, with flowing direction approximately NW—SE.

According to Feru and Capota (1991) all hydrogeological drilling from the studied area present artesian discharges range between 0.2 and 55 l/s, having hydrostatic levels between +0.5 and +16.8 m.

3. METHODS

Two series of data were utilized in this study. The first is represented by the analyses reported by Capota (1980). This author was compiled in her study more than one hundred of chemical data obtained under several research programs in several laboratories during the period 1969—1980. Unfortunately, the analytical methods used were not mentioned. From this paper we have selected 86 analyses of samples collected from 20 wells, 5 natural springs, and from the Black Sea.

The second series of data consists of our water analyses. On the whole, 53 samples of different types of waters have been collected during the period 1986—1987 (4 samples) and June-December 1991 (49 samples). For the geographical distribution of the sampling sites see Fig. 1.

In the field, at the time of the sampling, we have recorded the temperature (± 0.1°C), the pH (potentiometrically, ± 0.05 pH unit), total alkalinity and total sulphide. In the laboratory, we have analyzed the following contents: sodium, potassium, magnesium, calcium, total iron, total boron, dissolved silica, ammonia, nitrite, nitrate, total phosphorus, sulphate and chloride.

For *in situ* total sulphide ($H_2S + HS^- + S^{2-}$) determination the samples were added over known volumes of standard iodine solution and the residual iodine was titrated with standard thiosulfate solution in presence of starch indicator. Total alkalinity was analyzed by titration with a standard acid solution against of joint indicator formed of bromcresol green and methyl red. For both determination two or three replicates were necessary to record a good concordance.

For most samples the sodium and potassium were analyzed by standard flame photometric methods. For the other samples sodium was determined photometrically with uranyl acetate (Ghimcescu and Hincu, 1974) and potassium by a turbidimetric procedure with sodium tetraphenylboron (Costache, 1966). The calcium and the total hardness were determined by complexometric micro titration with photometric end-point determination. The magnesium concentration was obtained by making the difference between the results of the two analyses. Total iron was analyzed photometrically with 1.10-phenanthroline (Manescu et al., 1978).

To remove hydrogen sulphide interference in sulphate and ammonia determinations, the samples collected in separate bottles were immediately treated with cadmium acetate to precipitate dissolved sulfide species as cadmium sulfide. Subsequently, sulphate was determined turbidimetrically (Aminot, 1974) and ammonia ($NH_3 + NH_4^+$) by indophenol blue method (Mackereth et al., 1978). In order to measure total

phosphorus a digestion procedure followed by the photometric molybden blue method (Mackereth et al., 1978) was used. Nitrate was analyzed by chromotropic acid method (West and Ramachandran, 1966). The total boron was determined by carmine method (Bull et al., 1975) and dissolved silica was analyzed photometrically with molybdate (Pakalns and Flynn, 1967). The concentrations of nitrite, and chloride were determined by standard methods (Patroescu and Ganescu, 1980).

A computer program based on a model previously outlined (Marin and Patroescu, 1992) was used to calculate the elements speciation in aqueous solutions. The input required consists of total amounts of the chemical equilibria of species concerned with their equilibrium constants. By this procedure were determined not only the activities of the components involved but also the equilibrium partial pressure of dissolved gases. The model proposed by us yields results comparable to the programs used by other workers.

The computer model NETPATH (Plummer et al., 1991) was employed to calculate mixing proportions of groundwater from shallow aquifer with groundwater from profound aquifers. The various statistical calculations were conducted using the SYSTAT program.

4. RESULTS

Table 1 presents a statistical treatment of the data which has been carried both on our analytical results and on those reported by Capota (1980). It is very difficult to compare water analyses achieved by different laboratories, within a long period of time. On the whole, there are no major discrepancies between our results and those compiled by Capota, except H_2S and SO_4 determinations.

In the case of H_2S our results are broader than the others, which reveal the existence of systematic analytical errors. The method which is based upon the reaction of sulphide with iodine followed by back-titration with thiosulfate is much used by our laboratories. From this procedure we replaced the fixation of H_2S as a insoluble sulphide, by performing the determination in the field. In this way, we avoided a source of losses of dissolved H_2S but, in the same time, our analyses becomes probable much less specific.

As regards SO_4 determination, the values reported by Capota are obviously overestimated. The error is probably due to the fact that H_2S has not been from the samples, and a part of it was oxidized at the sulphate until analyses were achieved in the laboratories.

The wells were sorted into classes depending on age of the sedimentary formations existing in the open intervals. The characteristics of the drilling were taken off by Capota (1980) and Feru and Capota (1991).

Of course, most of the drilling capture water arisen from deposits with different ages. Because of this, the names assigned to the classes from Table 1 have only a generic meaning. Thus, the Well No. 5082, which

represents the *Paleozoic level* drains both deposits of Paleozoic age and Lower Jurassic. The *Jurassic level* is the only case when the respective wells are exclusively opened in formations of this age. The wells included in *Cretaceous level* are prioritarily supplied by Cretaceous age deposits, but there are frequent cases when the Upper Jurassic or the Lower Eocene is reached. In *Eocene + Sarmatian level* were introduced the drillings which have open intervals in both deposits. The *Sarmatian level* includes not only the wells which exclusively capture water arisen from this aquifer but also all the sulphidic natural springs being in zone. Although the „Peştera de la Movile" cave is dug in Sarmatian age rocks, it is separately presented in order to distinguish its aquifer chemical characteristics.

In spite of the fact that undergroundwater from southeastern Dobrogea is sheltered in carbonated rock, it plainly has different chemical features towards the other karstic areas groundwater. For instance, in the Pădurea Craiului Mountains, which shelter one of the most important Romanian karstic zone, also developed in Cretaceous and Jurassic limestones, the values of total dissolved solids (TDS) never exceed 0.5 g/l, while Ca and HCO_3 are the main components of these waters (M a r i n, 1981). Instead of this fact, in the studied area from Dobrogea, TDS contents are extended between 0.8—3 g/l having an average about 1.2 g/l, while sodium and chlorine are prevailed. At the same time, here, we can find in main concentrations unusual components of „classic" karst waters, such as hydrogen sulphide, ammonia, bromine, iodine, a.s.o..

Table 1

Chemical composition of groundwater, southeastern Dobrogea (Total concentration in solution expressed in mg/l)

	No. of cases	Mean	Minimum	Maximum	Standard Deviation
PALEOZOIC LEVEL					
Period: 1973—1991					
Temp. (°C)	6	22.3	18.7	24.0	2.71
pH	6	7.54	6.50	8.61	0.92
H_2S	6	5.0	0.1	13.7	5.48
TDS	6	2629	2318	2972	280.02
Na	5	821.2	694.0	942.3	114.37
K	5	24.3	21.0	27.0	2.33
Mg	6	22.8	6.1	37.4	12.43
Ca	6	24.3	12.5	48.1	12.62
Fe	6	0.325	0.012	0.900	0.345
B	5	4.98	3.01	6.00	1.16
HCO_3	6	635.5	561.2	744.3	70.91
SiO_2	6	16.8	4.9	25.9	7.58
NH_4	5	1.37	0.10	2.00	0.73
NO_2	5	0.017	0.000	0.070	0.028
NO_3	4	0.78	0.05	4.00	1.58
PO_4	2	0.051	0.046	0.055	0.007
SO_4	6	31.5	20.0	38.4	6.95
Cl	6	976.5	893.6	1070.9	82.21
Br	4	5.6	2.0	10.0	3.44
I	4	1.15	0.5	2.3	0.79

Table 1 (continued) [Pag. 2]

	No. of cases	Mean	Minimum	Maximum	Standard Deviation
JURASSIC LEVEL					
Period: 1976—1980					
Temp. (°C)	8	22.0	18.0	24.5	3.31
pH	8	7.38	6.30	8.00	0.57
H_2S	8	15.4	0.5	29.2	11.09
TDS	8	1100	822	1921	346.02
Na	8	210.8	77.7	499.7	130.64
K	7	7.5	5.0	9.3	1.68
Mg	8	42.2	27.5	70.0	15.71
Ca	8	63.8	33.6	100.0	24.26
Fe	6	0.39	0.1	0.8	0.30
B	4	0.51	0.15	0.79	0.27
HCO_3	8	367.7	305.0	439.2	48.60
SiO_2	8	13.3	8.6	26.2	5.77
NH_4	6	2.21	1.00	4.50	1.32
NO_2	5	0.036	0.005	0.060	0.023
NO_3	5	0.34	0.05	0.8	0.32
SO_4	8	16.59	1.2	42.2	13.56
Cl	8	338.2	234.0	819.7	196.5
Br	3	1.57	0.1	4.0	2.13
I	2	0.55	0.3	0.8	0.35
CRETACEOUS LEVEL					
Period: 1976—1991					
Temp. (°C)	35	23.6	21.0	26.3	1.31
pH	35	7.30	6.00	8.01	0.49
H_2S	35	11.3	0.5	32.3	8.09
TDS	35	1208	916	1440	116.47
Na	35	267.9	165.2	360.1	44.03
K	35	13.1	5.4	23.6	3.94
Mg	35	37.5	23.0	63.0	8.25
Ca	35	57.3	36.1	133.0	18.76
Fe	35	0.284	0.015	1.900	0.358
B	21	1.96	0.03	2.50	0.80
HCO_3	35	342.3	195.2	475.8	51.26
SiO_2	34	17.5	8.6	35.7	7.82
NH_4	26	2.14	0.22	5.00	1.06
NO_2	29	0.031	0.000	0.240	0.044
NO_3	29	0.33	0.003	2.20	0.50
PO_4	10	0.069	0.033	0.089	0.016
SO_4	35	24.2	1.0	51.0	16.2
Cl	35	420.3	314.0	512.5	52.08
Br	15	1.77	0.8	5.0	1.07
I	12	0.77	0.01	1.8	0.46
EOCENE + SARMATIAN LEVEL					
Period: 1969—1977					
Temp. (°C)	22	22.7	20.0	25.0	1.75
pH	22	7.11	6.5	8.00	0.47
H_2S	22	9.62	0.2	17.6	4.73
TDS	22	1206	903	2274	261.2
Na	22	263.7	177.5	691.6	102.84

Table 1 (continued) [Pag. 3]

	No of cases	Mean	Minimum	Maximum	Standard Deviation
K	14	11.9	3.7	15.5	2.80
Mg	22	35.6	25.2	48.6	5.46
Ca	22	57.4	44.1	80.2	9.96
Fe	22	0.624	0.10	5.90	1.237
B	10	3.44	0.99	12.39	4.04
HCO_3	22	376.4	317.2	488.1	35.77
SiO_2	22	17.5	9.2	41.6	6.51
NH_4	12	2.16	0.10	5.00	1.25
NO_2	14	0.031	0.001	0.080	0.022
NO_3	12	0.13	0.00	0.50	0.16
SO_4	22	42.1	3.3	93.4	22.41
Cl	22	373.5	212.9	1049.7	163.6
Br	14	1.19	0.1	3.3	0.92
I	9	0.92	0.7	1.2	0.19
		SARMATIAN LEVEL			
Period: 1969—1991					
Temp. (°C)	41	22.3	18.0	25.4	2.20
pH	41	7.49	6.50	8.20	0.32
H_2S	37	20.8	2.2	43.8	12.78
TDS	41	1148	830	2259	226.64
Na	41	242.6	160.0	690.6	85.13
K	30	13.5	9.2	16.6	2.17
Mg	41	33.6	19.0	47.2	6.42
Ca	41	53.1	30.5	72.1	9.76
Fe	41	0.398	0.001	0.695	1.050
B	25	1.89	0.34	10.0	1.76
HCO_3	41	374.6	244.0	488.0	47.02
SiO_2	40	23.2	9.4	33.4	23.2
NH_4	37	2.00	0.01	5.50	1.41
NO_2	40	0.028	0.000	0.170	0.034
NO_3	40	0.34	0.01	2.3	0.44
PO_4	21	0.108	0.052	0.184	0.036
SO_4	41	32.1	0.5	88.3	20.48
Cl	41	338.4	202.0	1007.0	135.30
Br	3	0.68	0.05	1.5	0.74
I	4	0.44	0.05	0.96	0.46
		MOVILE CAVE			
Period: 1986—1991					
Temp. (°C)	8	21.0	20.6	21.8	0.42
pH	8	7.58	7.36	8.15	0.29
H_2S	8	31.4	28.1	33.3	1.85
TDS	8	1001	939	1059	32.64
Na	8	189.6	160.0	212.3	15.16
K	7	11.9	7.0	15.3	2.95
Mg	8	31.6	20.5	48.6	7.84
Ca	8	45.8	34.5	55.3	5.64
Fe	7	0.240	0.010	0.485	0.210
B	6	1.30	1.20	1.60	0.15
HCO_3	8	398.3	376.5	414.8	13.37
SiO_2	7	26.8	9.9	33.2	8.65

Table 1 (continued) [Pag. 5]

	No. of cases	Mean	Minimum	Maximum	Standard Deviation
NH_4	7	1.73	1.00	2.60	0.51
NO_2	7	0.008	0.000	0.022	0.006
NO_3	7	0.83	0.05	4.3	1.42
PO_4	7	0.104	0.034	0.207	0.057
SO_4	8	9.8	4.4	32.0	9.48
Cl	8	239.5	216.0	251.7	11.72

5. DISCUSSIONS

5.1. CHEMICAL CHARACTERISTICS OF THE WATER OF THE AQUIFER

The groundwater of carbonated aquifer from southeastern Dobrogea is typically Na-chloride and its total dissolved solid (TDS) contents are quite homogenous. In the framework of this aquifer several sub-units, can be distinguished each of them individualized by specific hydrochemical peculiarities. Generally, each subdivision of the sedimentary deposits has the same age, but at the same time corresponds to certain depths. Of course, the various tectonic disturbances emphasized in the area, frequently place the formations of the same age at different depths. The diagram presented in Fig. 2 correlates TDS contents both with age of the deposits and with depth of the open intervals of the wells. It points out in a remarkable way the constant variation of these contents, in the sense of their diminish from Paleozoic to Sarmatian and from depth to the surface.

The water of Paleozoic level differentiates itself plainly from all the other horizons from above, not only by a higher TDS content, but also by the very reduced weight of calcium and magnesium contents comparative to sodium. The situation is explained by the lithology of these sedimentary deposits, consisting mainly by sandy clays and clay slates and to a smaller degree by carbonated rocks (Feru and Capota, 1991). From this point of view, the Sarmatian level is placed on the opposite side. Its chemical composition reflects influences generated by the meteoric water (Tenu et al., 1987 and Davidescu et al., 1991).

The parcel of rocks placed between the two opposite levels, considered as a unified karstifiable complex (Feru and Capota, 1991) and which shelters a unitary hydrogeological aquifer (Tenu et al., 1987), is, from a hydrochemical point of view, quite heterogeneous. The corresponding level of the Jurassic formations possesses the smallest TDS contents, and the Mg and Ca share is the highest in the area. The Cretaceous and Eocene levels appear with very similar hydrochemical properties. This fact may also be a consequence of the way the respective deposits are opened by drilling. Both levels have an excess of TDS contents, both in Jurassic and in Sarmatian levels.

5.2. TEMPERATURE AND HYDROGEN SULPHIDE CONTENT

The origin of the thermalism and of the high concentrations of H_2S in the groundwater from southern Dobrogea, is one of the problems argued,

for a long time in the specialized literature, but still not cleared up. Generally, is accredited the opinion that the water from a certain depth which ascend toward the surface are warmer and rich in H_2S (F e r u and C a-

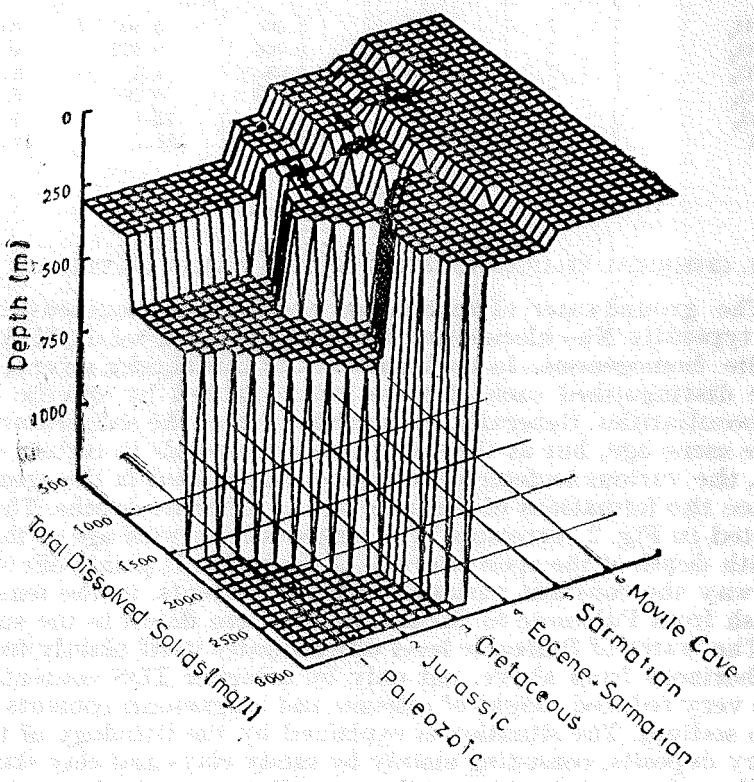

Fig. 2. — Evolution of the total dissolved solid content as a function of hydrogeologic subunits and the depth of the open intervals of the drilling.

p o t a, 1991; S a r b u et al., 1992). The statistic interpretation of the registered data in 12 years (C a p o t a, 1980) and of the proceedings carried out afterwards as well, own counter to this assertion.

The Cretaceous level appears to be the warmest and starting from it, the temperature decreases both towards the surface and in depth. If, in the first places the declension of the temperature can be caused by the contribution of cold waters from the surface, in the second one we cannot offer a satisfying explanation.

Total H_2S contents pursue quite vaguely the temperature distribution. The Jurassic level appears to be rich in such component, the concentrations decrease both towards Paleozoic and towards Eocene, but increase again in the Sarmatian level. As we have already shown, there existed an analytical incongruity between the results reported by Capota and those we have obtained. The representation of the concentrations of

aqueous H_2S calculated at equilibrium versus the depth from which these samples come from (Fig. 3), shows that using analytical method, the two series of measures gave results in good agreement.

Examining the correlation between total H_2S contents and total SO_4 (Fig. 4), it can be noticed that to small concentrations of H_2S from Cretaceous and Eocene correspond high concentrations of SO_4. Therefore, it is possible, that hydrogen sulphide coming from Jurassic deposits spreads to superior levels, but here it can be oxidized to sulphate. This oxidation can be generated by the infiltration at the respective level of important surface water quantities.

The fact that in the Sarmatian level total H_2S concentrations are higher comparative to inferior levels, suggests the existence of a local sulfides source, independent of that from the Jurassic level. In this direction it is worth mentioning the observation of Mutihac and Ionesi (1974), who assign to the Oligocene from the southern side of Mangalia-city a sequence of clays and bituminous slates. The authors assume that these are the H_2S sources existent in the natural springs of this territory.

The hydrogen sulphide of the groundwater is implied in a great variety of redox processes, which generate intermediary sulfur compounds (Morel, 1983), being largely under biological control (Boulegue and Michard, 1979). It is evident that only a quantitative evaluation of these processes can confirm the suppositions from above.

5.3. ORIGIN OF GROUNDWATER COMPOSITION

The Black Sea, being in the immediate neighborhood of the aquifer can be considered a major source of H_2S and high TDS content. This possibility is not yet confirmed by the values of the mole ratios from computed molality of free ions (Table 2). Also, the Cl/Na ratio for Paleozoic level is neither that of halite nor that of seawater (Fig. 5). The value of this ratio indicates, as in other cases (Land and Prezbindowski, 1982), that the common source for these two components are clays existent at this level.

Table 2

Mean mole ratios from computed molality

Ion Ratios	BLACK SEA	THE LEVELS OF THE AQUIFER				
		Paleozoic	Jurasic	Cretaceous	Eocene + Sarmat.	Sarmatian
Cl/Na	1.2	0.8	1.1	1.0	0.9	0.9
Cl/K	48.8	45.4	50.2	38.0	43.2	28.9
Cl/Mg	10.8	53.5	6.6	8.4	7.8	7.5
Cl/Ca	55.5	64.9	6.5	9.2	7.9	7.8
Cl/HCO_3	114.7	3.5	1.7	2.4	1.9	1.8
Cl/SO_4	36.8	61.9	179.5	1870.3	57.0	1278.0
Br/I	30.38	8.65	4.2	3.7	1.9	2.8
Na/K	39.3	57.2	45.1	36.6	44.4	31.9
Ca/Mg	0.2	1.2	1.0	0.9	1.0	1.0

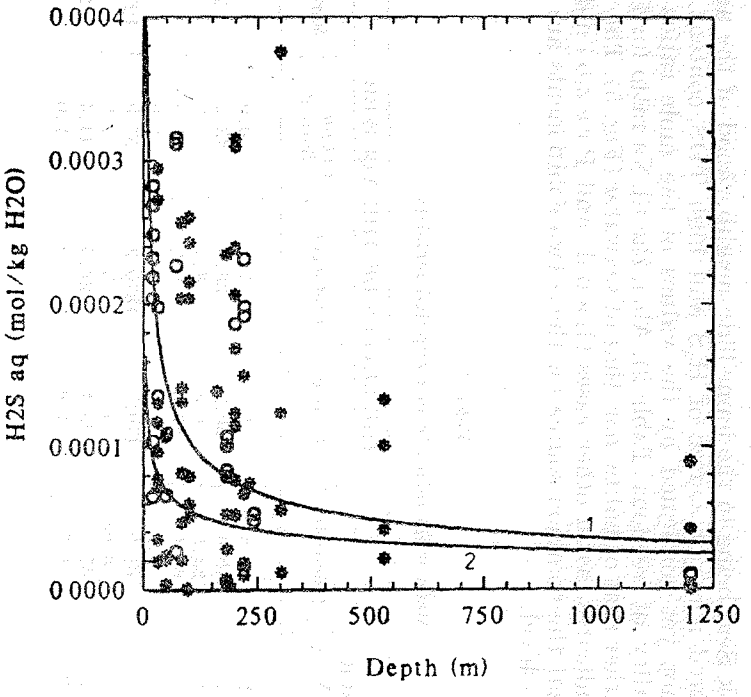

Fig. 3. — Dissolved H_2S vs. depth of the open interval of the wells. The regression curves are of power type calculated on the base of the analytical data: 1. (circles) — this study; 2 (stars) — reported by Capota (1980)

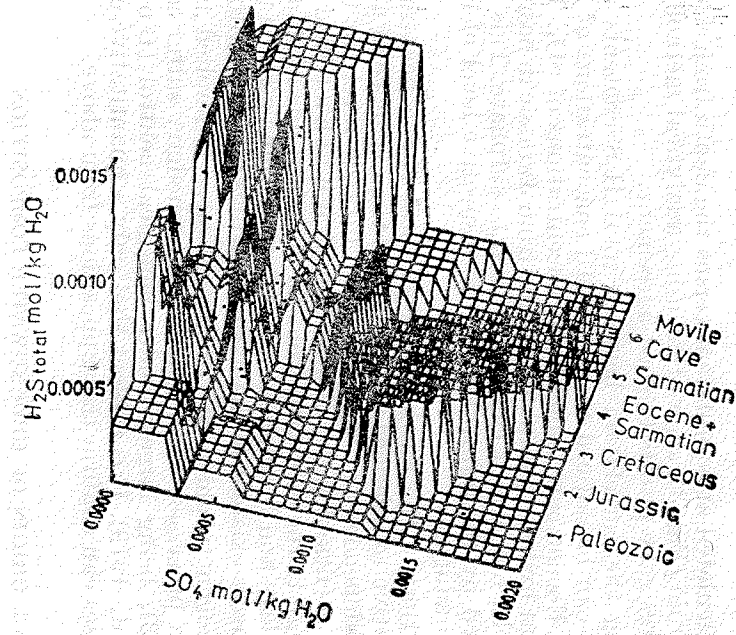

Fig. 4. — Correlation between total H_2S and total SO_4 as a function of the hydrogeologic subunits.

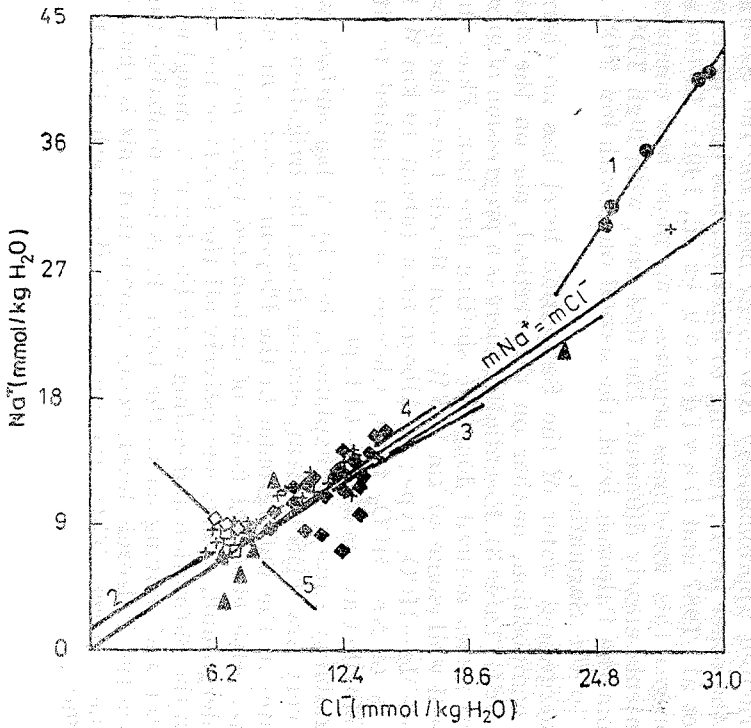

Fig. 5. — Scatter plot of molality of sodium vs. molality of chloride. 1 and *circles* depict samples from Paleozoic level (r = 0.995); 2 and *triangles* depict samples from Jurassic level (r = 0.940); 3 and *filled squares* depict samples from Cretaceous level (r = 0.629); 4 and *plus* depict samples from Eocene and Sarmatian levels (r = 0.979); 5 and *empty squares* depict samples from "Peştera de la Movile" cave.

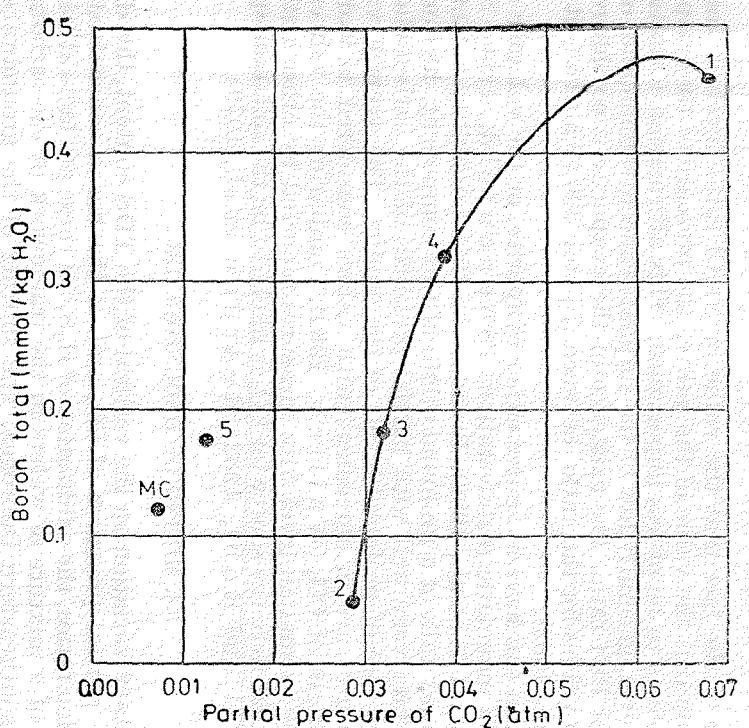

Fig. 6. — Plot of mean molality of total boron vs. partial mean partial pressures of carbon dioxide for: 1 — Paleozoic level, 2 — Jurassic level, 3 — Cretaceous level, 4 — Eocene + Sarmatian level, 5 — Sarmatian level, 6 — "Peştera de la Movile" cave.

In spite of the fact that the value or Na/Cl ratio develops for the other levels towards the value of the halite, the presence of the evaporite in this area seems to be of less importance. This affirmation is sustained both by the level, generally low of the sulphate concentrations, and of the small value of Br/I ratio. The existence of the evaporite is considered to correspond to values for this ratio between 75 and 300 (Sarrot-Reynauld et al., 1982).

The boron can have as source either evaporite, or the volcanic emanations or the magmatic manifestations (Sonnenfeld, 1984; Sarrot-Reynauld et al., 1982). Because the first possibility is not too probable we may talk of a profound origin of this component. Its concentrations correlate very well with partial pressures of the carbon dioxide (Fig. 6) in the case of profound levels of the aquifer. The average values of these pressures are in agreement with values considered to indicate a profound origin of CO_2 (Wallick, 1982). Comparing the values obtained for the Sarmatian level with measures reported by other authors, it is evident that here the source for CO_2 is likely to be the soil atmosphere (Thrailkill and Robl, 1982; Reardon et al., 1979).

5.4. MIXING OF GROUNDWATER

The unitary variation on the vertical of the TDS content, the distribution of the partial pressures of CO_2 and of the boron concentrations, the values of ion ratios, the oxidization of H_2S, all these are facts attaining the existence of a mixture of waters in the framework of the carbonated aquifer from southeastern Dobrogea. The shifting of the groundwater in a direction oriented approximately NW—SE, both for the Sarmatian level and for the other levels, reaching to Jurassic, has been demonstrated (Tenu et al., 1987 and Davidescu et al., 1991). In the southeastern Dobrogea this watermass acquires two more new components with TDS contents clearly different. The first one, with high TDS content comes from the Paleozoic level, the second one, with low TDS content, belongs to the Sarmatian.

The underground water of the Sarmatian level has no chemical homogeneous composition, neither on the vertical, nor on the shifting direction NW—SE (Table 3). Essentially, there is a progression of groundwater chemical facies noticed along the shifting direction. Thus, in the sector of Plopeni well (some 40 km WNW from Movile Cave) the groundwater is of Ca—Mg—HCO_3 type; in Albeşti area (about 10 km W from Movile Cave) is of Na—HCO_3 type, whereas in the studied territory, including the Movile Cave, is of Na—Cl type.

This variability cannot be explained, but by a big surface water amount with very low TDS content, coming from the irrigation system, which penetrates in the underground in the Plopeni region. On our opinion, this water with chemical facies of carbonated type, once penetrated in the underground, affects successively all the levels of the aquifer beginning with the Sarmatian and ending with the Jurassic, mingling with the groundwater and moving on to the East. It is less probable that it would influence the Paleozoic level, being known that this is characterized by a reduced permeability and an ascend flow path (Feru and Capota, 1991).

Table 3

Molal concentrations and saturation indexes of some Sarmatian groundwaters[+]

SPECIES	Plopeni Well*)	Albesti Well	Movile Cave	Oban Well	Kara Oban Spring**)
Temp. (°C)	16.8	14.8	21.4	21.2	23.0
pH	7.40*)	7.49	7.42	7.63	7.43
TDS (mg/l)	718	976	974	1058	1012
PCO_2 (atm)	1.374E−2	1.203E−2	1.218E−2	6.015E−3	1.095E−2
Na^+	1.543E−3	8.420E−3	9.215E−3	9.326E−3	8.430E−3
K^+	1.533E−5	2.731E−4	2.316E−4	4.147E−4	3.194E−4
Mg^{2+}	2.108E−3	9.318E−4	8.015E−4	1.185E−3	1.142E−3
Ca^{2+}	1.749E−3	1.020E−3	8.134E−4	1.180E−3	1.166E−3
Fe^{2+}	3.473E−7	1.709E−7	1.767E−7	2.400E−6	1.161E−4
H_3BO_3 aq	5.477E−5	4.553E−5	1.458E−4	1.534E−4	1.183E−4
HCO_3^-	6.565E−3	7.300E−3	5.738E−3	4.645E−3	5.198E−3
CO_3^{2-}	9.049E−6	1.934E−5	9.307E−6	1.245E−5	9.121E−6
H_4SIO_4 aq	2.144E−4	3.661E−4	5.365E−4	4.975E−4	4.284E−4
H_2S aq	8.421E−7	1.519E−6	2.249E−4	2.033E−4	1.603E−4
HS^-	2.094E−6	4.355E−6	6.856E−4	1.007E−3	5.300E−4
SO_4^{2-}	4.621E−4	8.083E−4	1.276E−4	8.788E−7	4.500E−4
Cl^-	1.601E−3	3.594E−3	6.099E−3	8.985E−3	7.187E−3
PHASE		Log IAP/K			
Anhidrite	−2.195	−2.226	−3.047	−5.076	−2.350
Calcite	0.243	0.103	−0.066	0.195	0.066
Dolomite	0.589	0.158	−0.049	0.478	0.233
Gypsum	−1.884	−1.890	−2.790	−4.816	−2.111
Hematite	0.596	0.094	−0.282	2.141	5.669
Magnesite	0.002	−0.281	−0.344	−0.076	−0.198
Magnetite	0.847	0.106	−0.060	3.892	8.794
Pyrite	8.024	8.433	11.669	12.491	14.299
Quartz	0.467	0.732	0.792	0.763	0.670

NOTES:* Analytical data supplied by I. Orășeanu; **) Underwater spring, sample collected by C. Lascu; +) Calculated value by AQ code (Marin and Patroescu, 1992).

With the computer program NETPATH (P l u m m e r et al., 1991) we achieved an evaluation of the mixing proportions of underground water. This code is used to interpret net geochemical mass-balance reactions between an initial and final water along a hydrologic flow path. The following constraints were considered : C, Ca, Mg, Cl, Si and S, and the following phase : calcite, dolomite, CO_2 gas, SiO_2, $MgSiO_3$ and gypsum. Chloride is significant as a „marker" component. Besides, its concentrations present an almost unitary distribution in the profoundness of the aquifer (Fig. 7), so no chloride phases were included, and the mixing ratio was automatically based on Cl.

For proposed set of phases, one model was found which satisfied the selected constraints. Some of the mixing fractions calculated from the chloride are presented in Table 4. Replacing the Plopeni well with the Albești well and repeating the calculation based on the same model, there can be noticed that this is not satisfying the constraints in the case of the Movile Cave, when the second initial source is the Oban well. Thus,

it is very probable that except the Plopeni area, where there are no other locations, great amounts of surface water would penetrate in the underground.

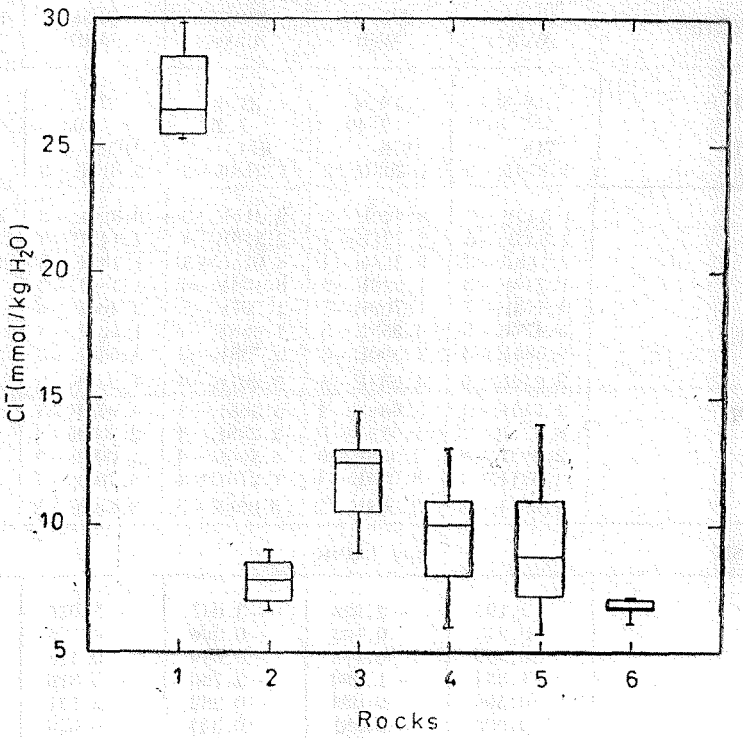

Fig. 7. — Box plot of chloride (free ion) for: 1 — Paleozoic level, 2 — Jurassic level, 3 — Cretaceous level, 4 — Eocene + Sarmatian level, 5 — Sarmatian level, 6 — "Peştera de la Movile" cave.

Table 4

Mixing proportions of groundwater in southeast of Dobrogea, calculated with NETPATH solution-mineral equilibrium model (Plummer et al., 1991)

INITIAL WELLS	FINAL WELLS				
	Albeşti Well	Movile Cave [101]	Oban Well [27]	Well 4073 [1]	Well 4 IBF [6]
Plopeni Oban Well [*Sarmatian*]	76.8 % 23.2 %	39.7 % 60.3 %			
Plopeni No 4073 [*Sarmatian+ Eocene*]	83.9 % 16.1 %	45.9 % 54.1 %	10.2 % 89.8 %		
Plopeni No. 4 IBF [*Eocene+ Cretaceous*]	83.9 % 16.1 %	62.5 % 37.5 %	37.7 % 62.3 %	30.7 % 69.3 %	
Plopeni No. 5082 [*Jurassic + Paleozoic*]	92.4 % 7.6 %	82.2 % 17.8 %	70.4 % 29.6 %	67.0 % 33.0 %	52.5 % 47.5 %

6. CONCLUSIONS

The chemical evolution of groundwater within the carbonated aquifer from southeastern Dobrogea was explained by considering : the geologic history of the region since the Paleozoic, the geochemical sources of dissolved constituents, and the processes of groundwater flow and mixing. The characterization from the hydrochemical point of view of this zone has been realized on the basis of two series of data, the first being a compiling of analytical results in the period 1969—1980 (C a p o t a, 1980), and the second series of data consists of our water analyses which have been achieved during the period 1986—1991. Most of the samples come from the wells dug of several research programs, achieved by various institutions in the area.

Although the southeastern Dobrogea aquifer is heterogeneous in its lithology and hydrogeological parameters it can be considered as a regionally continuous aquifer because its great thickness and extension facilitates hydrologic interconnection between the different layers. On account of this, the fact that many of the drilling attempts are opened in sedimentary deposits of different ages is a difficulty hard to overcome in order to precisely determine the hydrochemical properties of the stratigraphic horizons. In spite of this, based on the processing of the data both from the point of view of the chemical equilibrium and statistically we can put forth a series of conclusions about the drainage existent in the area.

The groundwater of this aquifer is typically Na-chloride, but weight of the Ca, Mg and HCO_3 can become important. We consider rock sources of major components to be for Na and Cl sandy clays and clay slates which appear abundantly at the Paleozoic level, and for Ca, Mg and HCO_3 limestones and dolomite which are the main constituents of sedimentary formations from the other levels of the aquifer.

The source of H_2S can't be precisely determined. The only certain aspect in this sense is the fact that it is not supplied by the Black Sea. The statistical interpretation of the data suggests the existence of two sources of hydrogen sulphide, the first placed at the Jurassic level, from where it spreads both towards the surface and depth, and the second placed at the Eocene and/or Sarmatian level. Any way, both the analytical results, reported by C a p o t a (1980), that have exposed the existent situation during and immediately afterwards the drilling, as well as the data we obtained, indicate the Sarmatian as being the richest level in H_2S, and the Paleozoic the poorest.

The unitary decrease of TDS contents from depth towards the surface, as well as the variation on the vertical of the concentrations of some components, indicates the achievements in the framework of this aquifer of a mixture of waters haven't different properties. Thus, the Jurassic, Cretaceous and Eocene levels are influenced by water with high TDS content belonging to Paleozoic level, and on the other side by the water with low TDS content coming from the Sarmatian level.

In its turn, the Sarmatian level does not present a homogeneous chemical composition, neither in depth, nor on the drainage direction NW—SE. We may assert therefore, that it suffers under the influences

of levels from the depth of the aquifer, but necessarily also from the part of a water contribution with very low TDS content. Probably, this component of the mixture is represented by the water come from the irrigation system, which penetrates in the underground in the Plopeni area (some 40 km WNW from Mangalia city).

A mixing-model approach using the computer program NETPATH was employed to estimate the mixing proportion of underground water. By applying this model to cave water from „Peştera de la Movile" cave it arises that here the mixture is formed of 17.8% water belonging to the Paleozoic level and 82.2% water of the Sarmatian level from Plopeni neighborhood.

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