

KARST HYDROGEOLOGY OF ROMANIA

Iancu ORĂȘEANU & Adrian IURKIEWICZ Editors



ORADEA 2010

KARST HYDROGEOLOGY OF ROMANIA

Edited by:
Iancu ORĂȘEANU
Romanian Association of Hydrogeologists

Adrian IURKIEWICZ
DCGGA, University of Bucharest



Copyright © 2010 Belvedere Publishing House. All rights reserved.

No part of this publication may be reproduced stored in a retrieval system or transmitted in any form or by any means electronic mechanical photocopying, recording or otherwise, without prior written permission of the publisher or the editors.

Permissions may be sought directly from:

BELVEDERE Publishing Houses

str. M. Kogalniceanu, nr. 66

410094 Oradea, Romania

Phone: +40(0)359 410557

Phone/fax: +40(0)259 431069

E-mail: belvedere@camptechnical.ro

This volume has been published with the financial support from S.C. SPELEMAT S.R.L., the Romanian Federation of Speleology and the Romanian Chapter of the IAH (International Association of Hydrogeologists)

The information contained in this volume has been compiled from various authors believed to be reliable and represent the best opinion on the subject as of 2008. Reasonable efforts have been made to publish reliable data and information, but the authors and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. However no warranty, guarantee or representation, express or implied is made by the Publishing House as to the correctness or sufficiency of this information or to the results to be obtained from the use thereof. The publisher and authors disclaim any liability, in whole or in part, arising from information contained in this publication. The reader is advised to consult with any appropriate licensed professional prior to taking any action or making any interpretation that is a routine of a licensed professional practice.

The contents of the articles making up (composing) this volume are the exclusive responsibility of the authors and do not necessarily conform to the opinions of the editors or organization to which they belong.

Printed in Romania.

Cover photo: Corcoaia Gorges, Cerna Valley, photo Andrei Posmoșanu

Layout: Andrei Posmoșanu

Descrierea CIP a Bibliotecii Naționale a României
ORĂȘEANU, IANCU

Karst hydrogeology of Romania / Iancu Orășeanu, Adrian

Iurkiewicz. - Oradea : Belvedere, 2010

ISBN 978-606-92444-0-1

I. Iurkiewicz, Adrian

556(498)

4.2. GEOCHEMISTRY OF THE SULFIDE MESO-THERMAL GROUNDWATER COMPLEX AT MANGALIA

by **Constantin MARIN**

"Emil Racoviță" Institute of Speleology of the Romanian Academy, constmarin@gmail.com

1. Introduction

From the point of view of groundwater hydrology, Southern Dobroudja represents, beyond doubt, one of the most interesting and most thoroughly investigated areas in our country. That circumstance is to a large extent the result of investigations associated to the Danube - Black Sea channel project completion, and which on the other hand have been also required by the severe disturbances induced by excessive irrigation having been conducted during the '60-'80 decades of the previous century in that area. Additionally, ensuing to the discovery in 1986 of Movile cave (Constantinescu, 1989), which harbors an exceptional fauna community, strong incentives have been provided for the development of several complex research programs. Remarkable syntheses concerning the hydrogeological data available by the early 1980-s have been provided by Pascu (1983), those authors outlining the mixing process of the different waters that occurred in that setting. Groundwater flow has been investigated both by means of environmental isotopes methods (Tenu et al., 1975; Tenu et al. 1987; Davidescu et al., 1991), and by means of artificial tracers (Gâstescu & Hîncu, 1971; Gașpar & Orășeanu, 1987).

A multitude of chemical analyses addressing both surface water and groundwater have been conducted since a very long time, essentially in order to take advantage of the involved water therapeutic characteristics, or for outlining the local hydrogeological setting. Unfortunately, most part of that information has not been published, being included in internal professional reports only. A remarkable synthesis of hydrochemical data obtained during the 1969-1980 period has been devised by Capotă (1980). Those data have been further used as a support for a series of hypotheses concerning the groundwater genesis and flow (Feru & Capotă,

1991; Feru, 1993), without yet being considered the correlations between chemical composition and hydrological parameters, and even less correlations with the geochemical processes that occurred within that aquifer. In spite of the multitude of investigations having been conducted, there haven't been yet elucidated a series of issues concerning the cause of the water heating, while the H_2S source is still controversial.

The present paper opens with a concise review of the main issues related to the sulfur speciation in natural aqueous systems. Geochemistry has traditionally considered, as far as sulfur components are concerned, mainly the behavior of the hydrogen sulfide (H_2S) and of the sulfate (SO_4^{2-}) anion. That circumstance is to a large extent also the result of the analytical accessibility of those two components. As it is well known, the transfer of 8 electrons is required in order to achieve the inter-conversion between H_2S to SO_4^{2-} . That process cannot advance in a single stage, and it actually involves compulsory partial stages developments, during which only one, or at most two electrons are transferred at a time, a process by which more or less stable chemical species result. The importance of meta-stable species, which include sulfur that in terms of oxidation occupies intermediate positions, undergoes nowadays increasing recognition in relationship with the appropriate interpretation of a multitude of processes.

2. Sulfur speciation in natural aqueous systems

Sulfur is probably the chemical element subject to the richest natural speciation known so far, being able to develop in natural environments an impressive number of both inorganic and organic species, which are the result of not only a-biotic, but also biotic reactions. Compounds occurring

within a certain oxidation stage take part in the equilibria by means of protons exchange, of precipitation or of complex combinations, many among the latter concentrations being liable to be subject to the micro-organisms, especially bacteria, control.

The analysis of sulfur speciation in natural environments is probably one of the most difficult fields of the present-day analytical chemistry. Because of their large number and of their elevated instability, many of those species cannot be detected by the currently known techniques. In principle, thermodynamic modeling is able to establish the sulfur species distribution along the course of the bio- or geochemical processes. However, the thermodynamic properties knowledge still remains highly inaccurate for most species, a circumstance which prevents the development of models able to substitute the quantitative analysis methods convincingly.

Within nature, there occurs also a large variety of sulfur-based organic compounds, many of which display a not yet well understood behavior. The most representative classes are: tiols ($R-SH$), organic sulfides ($R-S-R$), organic disulfides ($R-S-S-R$), polysulfides (RS_x^{2-}), sulfonates (RSO_3^-) and sulfoxides (R_2SO), where R may be an alchilic group, or either humic or fulvic compounds that include sulfur in their molecule (Luther III & George, 1992). Tiols are outstandingly important since they are major transitional forms in the sulfur microbial cycle, and since as a result of their high reactivity they play in geochemical processes a fundamental part. Additionally, they contribute to the preservation of macromolecules, to the bounding of the metals to the enzymes active centers, and they may also serve as co-enzymes (Mopper & Taylor, 1986).

The micro-organisms involvement in the processes of converting species from one another is a broad research field, that topic benefiting of excellent review works (Luther III & George, 1992; Bloechl, 1992; Wilkin & Barnes, 1996). By oxidizing sulfides, via elementary sulfur, to sulfate, sulfur-oxidizing bacteria, as for instance *Beggiatoa*, acquire the energy required for their chemo-autotrophic development. Some species of sulfate-reducing bacteria display, besides their well-known ability of reducing sulfate to sulfides, also the ability of disproportioning the thiosulfate ($S_2O_3^{2-}$) or

sulfite (SO_3^{2-}) anions to SO_4^{2-} and sulfide (S^{2-}) (Joergensen, 1990; Vairavamurthy et al., 1993).

3. Geo-hydrologic setting

The investigated area is bounded to the east by the Black Sea shore, to the south by the lake Mangalia, to the north it is bounded by the lake Tatlageac, while to the east it extends for about 2-3 km². That area belongs to the Southern Dobroudja Platform, which in terms of landforms has reached the peneplain stage, with a poorly developed streams network (Ujvári, 1972), and displaying a specific type of surface karst (Constantinescu, 1995).

The geological structure of that area is rather well known, to its understanding contributing also data provided by a large number of boreholes drilled by several institutions for various purposes. Since the groundwater chemistry characteristics are controlled by the petrographic nature of the substratum, the latter shall be described in the following in accordance with the specifications existing in the dedicated studies (Chiriac, 1960; Mutihac & Ioneși, 1974; Feru & Capotă, 1991; Koleva-Rekalova, 1994). The crystalline basement, consisting of crystalline schists and of green schists ascribed to the Proterozoic, is overlain by an unfolded sedimentary cover which in Mangalia region extends for a depth of more than 2500 m. The first sedimentation cycle has occurred during the Paleozoic, specifically in the Silurian and the Devonian, and it has been followed by a sea retreat period, a circumstance which resulted in the absence of the Late Paleozoic, Triassic and Early Jurassic age deposits from the sedimentary stack. The second sedimentation cycle has belonged to the Mesozoic (Jurassic and Cretaceous), being also continued during the Neozoic (Eocene, Sarmatian and Quaternary).

Paleozoic age deposits intercepted by wellbores drilled in Mangalia area consist of shales with limestone insertions, of quartzites, argillites, quartzite sandstones, marls and fossiliferous marly limestone. They occur at depths in excess of 550 m. Boreholes have intercepted between 200 and 550 m depth Jurassic deposits, that are about 350 m thick and include at their bottom arenitic, conglomeratic, sometimes marly limestone, overlain by a thin layer of marly limestone which pro-

gressively turns into limestone, that as a general rule is compact, with sparse sandstone insertions. The Late Jurassic includes a thick stack of dolomitic limestone that is fractured and only to a poor extent subject to karst processes.

Below 100 m depth, wellbores have intercepted Cretaceous deposits which are 60-80 m thick and display a carbonate facies including limestone, marly limestone, carbonate sandstones and friable limestone. The Eocene deposits are 25-100 m thick and they occur at depths of less than 180 m. Their bottom section includes green glauconitic sandstones, overlain by organogenic limestone with nummulites, and by shell rock limestone with nummulites. South of Mangalia, in the region of Vama Veche, a formations stack has been identified which consisted of clays and of disordilic bituminous shales. The latter have been ascribed to the Oligocene and have been assumed by Mutihac and Ionesi (1974) to be responsible for the H_2S content of the springs in that area. On the other hand, structures with hydrocarbon content become increasingly significant farther to the south, in the Bulgarian zone of Dobroudja (Dimitrov et al, 1991; Dimitrov et al., 1994).

In a few sites within that area there outcrop Sarmatian deposits, which are 120 m thick in the southern part of the town of Mangalia to become progressively thinner farther to the north. Their bottom section includes a clays and clayey marls stack that is about 25 m thick (in the southern part of Mangalia) and which becomes increasingly thinner to the north, to completely vanish in the Mangalia Swamp area. Subsequent Sarmatian deposits include white or white-yellowish, cavernous, slightly friable shell rock limestone (of Bessarabian age), with scarce insertions of marls, friable sandstones and sands of prevalently carbonate constitution. Still of Sarmatian (specifically Kersonian) age are the oolitic limestone deposits which are subject to fractures along which various size dissolution pockets have developed (Dumitrescu et al., 1965). Sarmatian deposits are overlain by a Quaternary sedimentary cover which may be up to 30 m thick and which consists of aleuritic clays, of sandy clays and of sands. In swamp areas Quaternary deposits consists of peat accumulations as well.

Since no continuous impervious layers exist between the Jurassic, Cretaceous and Eocene age carbonate deposits, they are globally addressed as

a single aquifer complex, whose hydrometric properties vary as a function of depth (Feru & Capotă, 1991). Alternatively, Sarmatian deposits are considered as a distinct aquifer, subject to a remarkably high discharge capacity.

The hydrologic regime of that area is influenced to a significant extent by its tectonic setting, that circumstance being first outlined by Nicolescu (Nicolescu, 1965), while subsequent studies of Zamfirescu et al. (1994) addressed it in more detail and further elaborated on that issue. There is conjectured that the supply of the "obane" in the neighborhood of Mangalia, Kara Oban included, occurs along underground pathways that follow a fault (Gâstescu & Hîncu, 1971) which is assumed to reach large depths, at least down to the Silurian age deposits (Feru, 1993). That fracture strikes roughly NW-SE, along a lineament connecting Kara Oban with Mangalia Swamp, and it further extends for several kilometers beneath the sea, being associated to several abundant submarine vents occurrences (Lascu et al., 1994).

In the framework of the South-Eastern Dobroudja major hydrogeological unit, the aquifer complex at Mangalia is considered to be a distinct sub-unit not because of some specific structural-tectonic setting, but because of the physical-chemical properties of its water, namely: the thermal character and the dissolved H_2S content. The entire hydrogeological unit that includes it has to be taken into account when its recharge is considered, since no hydrodynamical separation from the adjoining sub-units occurs. The two major aquifers inferred to assume local characters, namely the Sarmatian and the Eocene-Jurassic aquifers, are in fact embedding the characteristics of the overall hydrogeological unit (Țenu et al., 1987; Pascu, 1983).

Groundwater flow across Sarmatian formations starts within the closed drainage areas located in the western part of the groundwater structure, specifically at Amzacea, Plopeni, Negru-Vodă, being directed mainly toward Techirghiol, and in subsidiary toward Mangalia (Davidescu et al., 1991; Țenu et al., 1994). Significant disturbances started being induced in the groundwater regime of that area after the commissioning of the irrigation systems, in the first years of the 1970 decade. There has been demonstrated that this significant inflow of low mineralized water is responsible for the alteration of the Techirghiol Lake chemical

characteristics and for the accelerated decline of its therapeutic quality (Tenu & Davidescu, 1993). The same process can be assumed to be the cause of new, never before mentioned spring occurrences in the area of the "obane" at Mangalia.

4. Investigation approach

There have been analyzed water samples collected from both wellbores and natural sources located within the investigated area. Natural sources mainly included springs, different water collecting sites in Movile cave, and a single surface water, namely the lake Kara Oban. The sampling has been carried out during several investigation trips.

The sources repertory, together with the wellbores specifications and the sampling dates are indicated in Fig. 1 and Table 1.

Because some physical-chemical and compositional parameters are quite unstable, a series of *in situ* determinations have been carried out simultaneously with the collecting of the samples for laboratory analyses. Specifically, temperature, pH, Eh, total alkalinity and total dissolved H₂S content have been measured in the field. Samples which were to be subsequently analyzed in the laboratory have been subject to various stabilizing procedures, as a function of the specific component which had to be quantitatively analyzed.

Map No.	Sample	Name	Water Yielding Unit	Interval Sampled (m)
1	DS01-9312	Well F6 ISLGS (Paradise Bar)	Sarmatian	24.5-28.5
2	DS02-9311	Well F7 ISLGS (Trident Bar)	Jurassic	200-302.5
3	DS03-9310	Well F1 ISLGS (Carpathians Trust)	Paleozoic, Lower Jurassic	300-530
4	DS04-9730	Spring Cap Aurora		
6	DS06-9731	Well 8 SAFAR (Topaz Hotel)	Eocene, Cretaceous	94-190
7	DS07-9735	Spring Venus		
8	DS08-9710	Well F9 SAFAR (Venus beach)	Eocen, Cretaceous	76-188
9	DS09-9728	Well F2 ISLGS (Venus station)	Eocen, Cretaceous, Jurassic	50.5-200
10	DS10-9729	Well 4074 (Venus – Mangalia Swamp)	Sarmatian	8-49
11	DS11-9721	Well 4076 (Saturn beach)	Sarmatian	38.5-39.5
12	DS12-9726	Well 4075 (Saturn - Mangalia Swamp)	Sarmatian, Eocene	21-99
13	DS13-9718	Well 4073 (Mangalia Swamp)	Sarmatian, Eocene	19-83
14	DS14-9706	Spring in Mangalia Swamp (Stud)		
15	DS15-9725	Radu's Spring		
16	DS16-9708	Kara Oban Lake		
18	DS18-9724	Sulfurous runlet (right)		
19	DS19-9723	Sulfurous runlet (left)		
21	DS21-9717	Movile Cave		
22	DS22-9301	Well Oban	Sarmatian	70
23	DS23-9732	Well F4 I.B.F. (Mangalia, Hercule Hotel)	Cretaceous, Lower Jurassic	201-220
26	DS26-9733	Well F2 I.B.F. (Mangalia, Callatis Hotel)	Eocene, Cretaceous	125-175
27	DS27-9716	Well F5 SAFAR (Mangalia Harbour)	Eocene, Cretaceous	120-241
28	DS28-9734	Well 5082 (Mangalia)	Paleozoic, Lower Jurassic	350-410
32	DS32-9701	Hagieni Spring		
33	DS33-9714	Spring in Hagieni Forest		

Table 1. Description of sampling sites from the studied area.

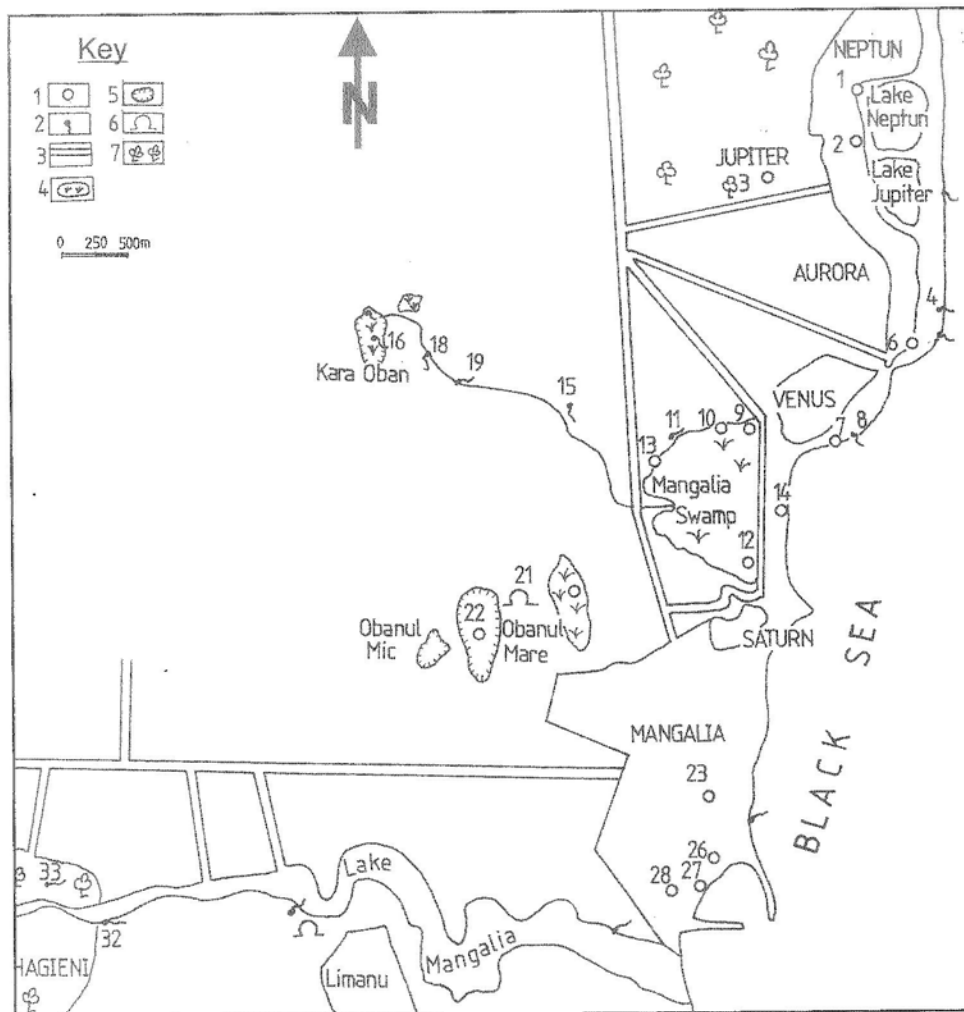


Figure 1. Location of the sampling sites used in this study.

Significance of the numbers is presented in Table 1. Key:

- 1 - well;
- 2 - spring;
- 3 - road;
- 4 - swamp;
- 5 - karstic depression;
- 6 - cave;
- 7 - forest.

5. Results and discussion

Figure 2 illustrates the groundwater mineralization range of variation, as a function of the sampling point type and of the age of the deposits within which the corresponding supply occurs. Figures 3 and 4 comparatively illustrate, by maintaining the same criteria of categorization for the sampling points, the distributions of the temperatures and of the total dissolved H_2S contents. The computed ionic strength is obviously correlated with the water mineralization (Fig. 5), the latter being mainly controlled by the dissolved chlorides (Fig. 6). In the following, there shall be provided a brief review concerning the specificities of the investigated groundwater species distribution.

The particular character of the Mangalia hydrogeological complex groundwater chemistry derives from chemical facies and mineralization values on the one hand, and from the elevated temperature and the hydrogen sulfide occurrence on the other (Marin & Nicolescu 1993). As far as the first issue is considered, there has to be speci-

fied that for any karst area outside Dobroudja, when a surface stream enters a carbonate rocks substratum, its water type will very quickly acquire a $Ca/Mg-HCO_3$ character which is maintained along the entire evolution across the karst realm, irrespective of the mineral load that is accumulated, and only slight variations in the components ratios may be correspondingly recorded. In contrast, in the case of the Sarmatian aquifer at Mangalia the water chemical character is $Na-HCO_3$, and occasionally even $Na-Cl$, in spite of the persistent contact with the limestone reservoir.

For the investigated aquifer, the total dissolved H_2S contents appear to be somehow correlated with the corresponding sources temperatures (Fig. 7). As normally expected, high H_2S concentrations are associated to low SO_4^{2-} concentrations (Fig. 8). Moreover, the sulfate anion is frequently absent. Besides these analytical observations concerning the sulfur speciation, additional features are outlined by the thermodynamic modeling. The largest percentage among the total dissolved H_2S species is occupied by the HS^- anion, while the H_2S^0 molecules

assume a less significant weight, the ratio between the two species being controlled by the pH values of the water (Fig. 9). Also the dissolved polysulfides distribution is controlled by the pH values, polysulfides with 4, 5 and 6 atoms of sulfur being more abundant than lower grade polysulfides.

Equilibrium computations indicate that the S^{2-} anion content amounts to less than 0.004% of the total concentrations of dissolved H_2S . The HSO_4^- or $H_2SO_4^0$ abundances are, similarly, insignificant. Such evidence contradicts previous claims issued by certain investigators, according to which carbonate rocks dissolution in that area is achieved by sulfuric acid generated as a result of H_2S oxida-

tion. When considered as an independent entity, the $H_2SO_4^0$ species occurs in the Mangalia region groundwater as 10^{-20} m concentrations. H_2S oxidation undoubtedly occurs, yet no significant advance toward sulfate can be achieved within a closed natural system. An illustrative example in this respect is provided by the Balck Sea basin, where thiosulfate can be considered to be the final product of the dissolved H_2S oxidation.

As far as alkaline and calc-alkaline metals derived species are concerned, there is recorded a net prevalence of the free cations (Fig. 10). Among the ion pairs in which the latter are involved, those with the carbonate anions are more significant. In contrast, transitional metals, which in the Mangalia region groundwater occur as trace concentrations, exhibit a completely different behavior (Fig 11). Some of them occur practically entirely complexed with the bisulfide anion. Metals like Ni^{II} and Mn^{II} , that do not easily form soluble sulfides, exhibit a more diverse speciation, in which complexes having CO_3^{2-} as a ligand are prevalent. The tendency toward aqueous solution hydrolysis exhibited by certain elements is consistent with the results of species distribution computations. In this respect, a typical example is the aluminum speciation, with hydrocomplexes exhibiting the largest occurrence weights.

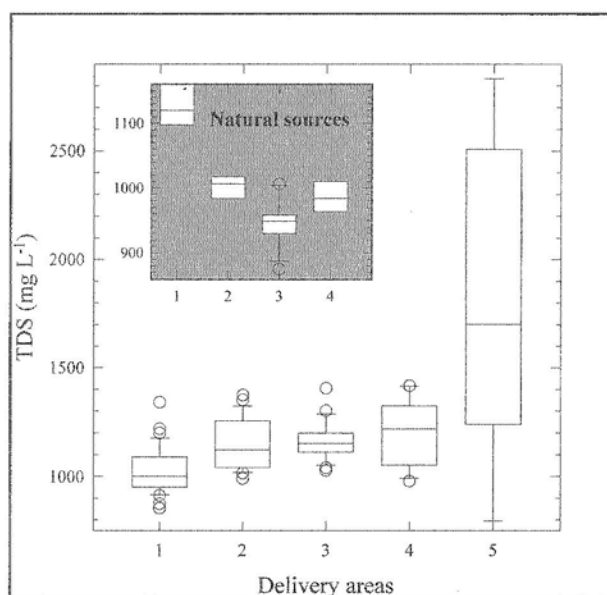


Figure 2. Distribution of the Mangalia hydrogeologic complex groundwater total mineralization as a function of the sampling point type and of the age of the deposits within which the corresponding supply occurs.

Numbers in the abscissa represent: 1 - natural sources (37 observations); 2 - wellbores discharging from Sarmatian deposits (25 obs.); 3 - wellbores discharging from Eocene and Cretaceous formations (24 obs.); 4 - wellbores discharging from Cretaceous and Jurassic deposits (19 obs.); 5 - wellbores discharging from Jurassic and Paleozoic formations (9 obs.). The inset provides additional details concerning the natural sources, with the numbers in the abscissa indicating: 1 - seashore springs in Cap Aurora and Venus resorts (6 obs.); 2 - Radu spring (4 obs.); 3 - outlets at the Sulfur River (12 obs.) and 4 - Movile cave (7 obs.). In this type of representation of a data set, the box space outlines the region where most values occur, the horizontal bar within the box indicates the average value, the vertical bars indicate the highest probability distribution domain for the considered determinations, while circles represent values exceeding that domain, hence illustrating the maximum field of variation for all the observations.

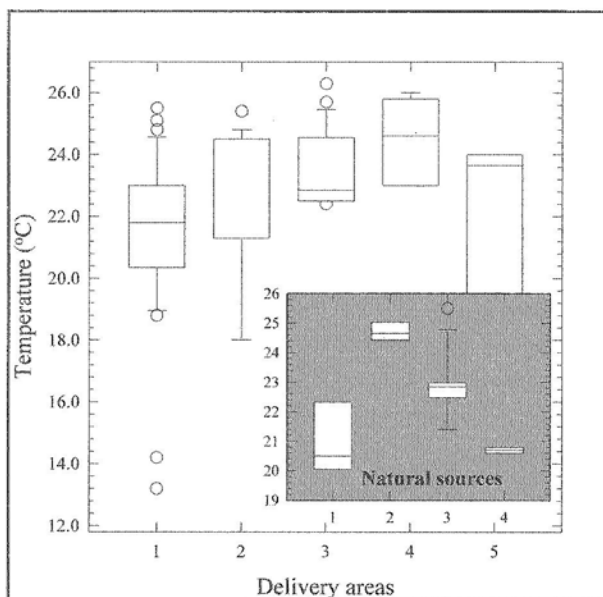


Figure 3. Distribution of the Mangalia hydrogeologic complex groundwater temperature as a function of the sampling point type and of the age of the deposits within which the corresponding supply occurs.

Numbers in the abscissa have the same meaning as in Fig. 1.

Chemical analyses by themselves (Table 2) reveal little about processes that change the chemical character of groundwater as it moves through the aquifer systems. One of the principal method of interpreting natural groundwater geochemistry is to assume that all dissolved species are at equilibrium. This assumption permits the use of thermodynamic models of aqueous solutions to calculate the distribution of dissolved species, a technique adopted for this study. A wide variety of computer-based models is available to calculate distributions and activities of dissolved species.

Once the species activities are calculated, the saturation state of the groundwater with respect to mineral and gases can be tested. Additional computations can also be made that quantitatively predict the evolution of an initial solution into a final solution by mixing and reaction with other solutions, gases, or solids. The aqueous model used during this study is contained in the PHREEQC 2.15.0 computer program (U.S. Geological Survey).

PHREEQC calculates both activities of aqueous species and departure from equilibrium (saturation index, SI) for many solid phase (minerals) and gases that might be in contact with the aqueous phase. The SI is expressed as:

$$SI = \log \frac{IAP}{K_T}$$

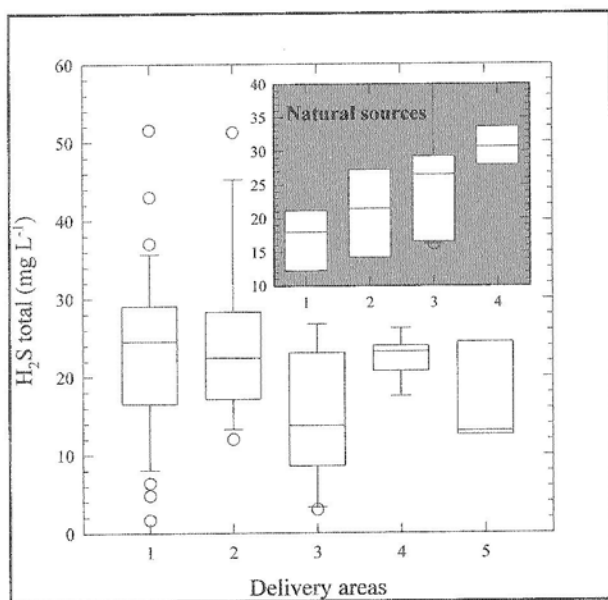


Figure 4. Distribution of the of total dissolved H_2S content of the Mangalia hydrogeologic complex groundwater as a function of the sampling point type and of the age of the deposits within which the corresponding supply occurs.

Numbers in the abscissa have the same meaning as in Fig. 1.

where IAP is ion activity product of the components of the solid or gaseous phase, and K_T is solid or gaseous phase solubility equilibrium product at the specified temperature.

When SI is equal to 0, the solid or gaseous phase is in equilibrium with the aqueous phase. When SI is less than 0, the solid or gaseous phase is undersaturated, that is, the phase has thermodynamic potential to dissolve. When SI is greater than 0 the solid or gaseous phase is supersaturated, and the phase has the potential to exsolve by precipitation or volatilization.

If present in the aquifer system, minerals probably are dissolving when negative saturation indices are calculated, although the dissolution rates may be exceedingly slow. However, a potential to precipitate when SI is greater than 0 does not by itself cause minerals to form in the aquifer; there are other factors such as mineral surface topography, surface poisoning, and nucleation energy that may inhibit the formation and growth of a mineral.

The physical-chemical setting of the aquifer prevents the elemental sulfur precipitation, in spite of the hydrogen sulfide occurrence. In contrast, the water displays an obvious tendency for metal-

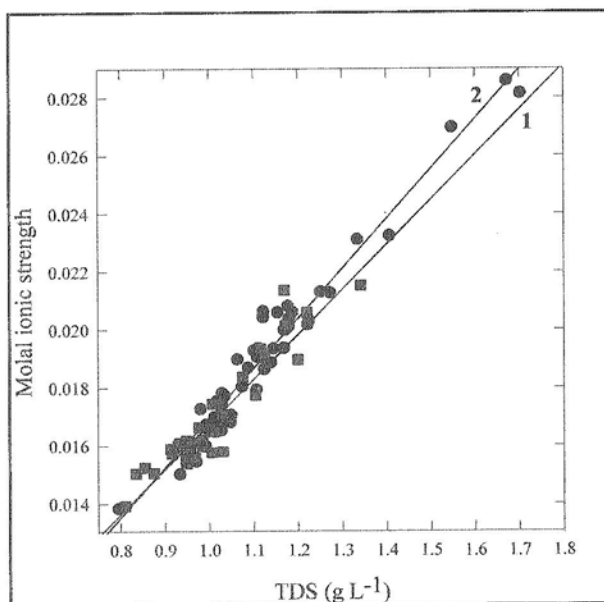


Figure 5. Correlations between the total mineralization and the molal ionic strength computed by means of the speciation model for the Mangalia hydrogeologic complex groundwater.

Regression line 1 and symbol (■) refer to natural sources, while regression 2 and (●) refer to all the wellbores. Regressions are linear, the regression coefficients and the slopes being: 1 - 0.8745, and 0.0155 respectively; 2 - 0.9565, and 0.0172 respectively.

lic sulfides precipitation. Saturation indexes for pyrite (FeS_2), greigite ($\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{S}_4$) or mackinawite (FeS) are strongly positive.

As far as carbonates are concerned, only the normal anhydrous ones [calcite (CaCO_3), aragonite (CaCO_3), magnesite (MgCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$)] evolve close to a state of saturation (Table 3). Water discharged by wellbores supplied by Paleozoic deposits is super-saturated with respect to those minerals and equilibrated with respect to huntite [$\text{CaMg}_3(\text{CO}_3)_4$]. Alternatively, a state of strong under-saturation is recorded with respect to acid and non-hydrated carbonates, that circumstance being due to at least two reasons. Some carbonates of this category [hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) and natron ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$)] are characteristic to low temperature hydrothermal mineralizations, a setting which is totally different from that of the Mangalia aquifer complex. Other mineral species, such as artinite [$\text{Mg}_2\text{CO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$], nahcolite (NaHCO_3), trona ($\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$) or thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), are characteristic to saline deposits generated by water evaporation, and they are therefore usually associated with halite (NaCl) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Additionally,

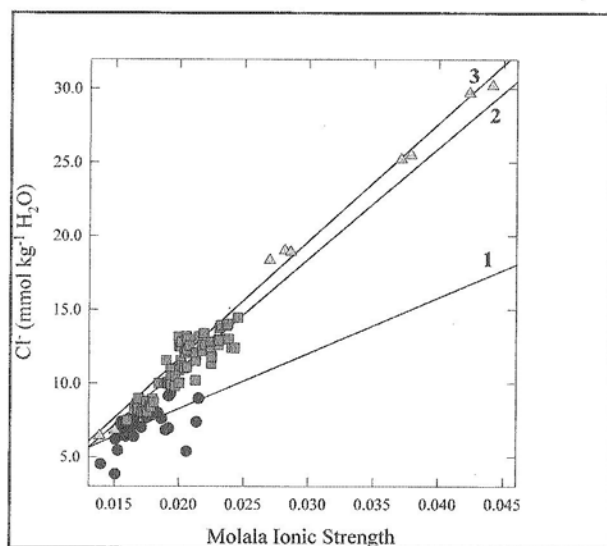


Figure 6. Chlorides concentration variation as a function of the molal ionic strength, for certain groundwater categories of the Mangalia hydrogeologic complex.

All regressions are linear. The numbers and the symbols have the following meanings: 1 (●) – natural sources ($r^2 = 0.3236$, $x_{\text{coef}} = 376.39$); 2 (■) – wellbores discharging from deposits whose ages range from Jurassic to Sarmatian ($r^2 = 0.7712$, $x_{\text{coef}} = 752.60$) și 3 (▲) – wellbores discharging from Jurassic and Paleozoic formations ($r^2 = 0.9940$, $x_{\text{coef}} = 799.65$).

strongly negative saturation index values with respect to minerals induces a state of under-saturation with respect to sulfate minerals, both the anhydrous ones [anhydrite (CaSO_4) and thenardite (Na_2SO_4)] and especially the hydrated ones, like epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), gypsum, melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) or mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$).

As far as oxides and hydroxides are concerned, the Mangalia region groundwater appears to be saturated with respect to hematite (Fe_2O_3) and magnetite (Fe_3O_4), being alternatively aggressive toward ferric hydroxide [$\text{Fe}(\text{OH})_3$], goethite (FeOOH), maghemite (Fe_2O_3), brucite [$\text{Mg}(\text{OH})_2$], or toward mineral species which are not present within the system. A similar setting is recorded as far as silicates are concerned. There occurs, as a general rule, a state of super-saturation with respect to the SiO_2 group minerals (chalcedony, cristobalite, quartz), the water resulting to be, alternatively, strongly under-saturated with respect to pyroxens [clinoenstatite (MgSiO_3), diopside ($\text{CaMgSi}_2\text{O}_6$)] or nezosilicates [forsterite

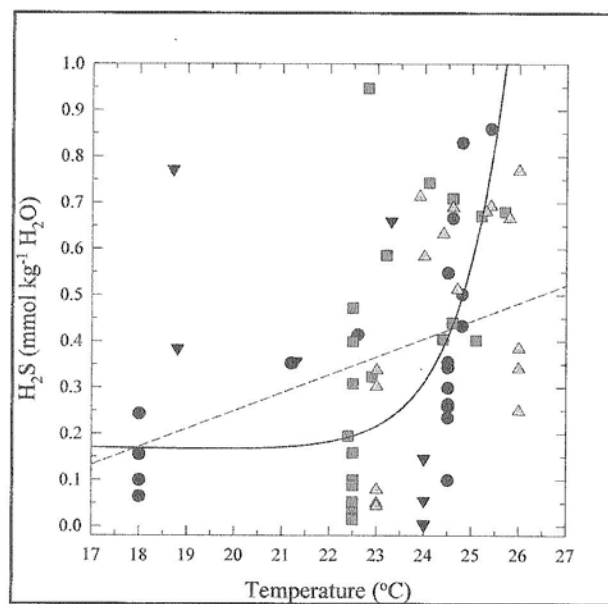


Figure 7. Plot of total dissolved H_2S concentrations against temperature, for groundwater discharged by wellbores from the Mangalia hydrogeologic complex.

Symbols indicate wellbores discharging from formations whose age is: ● Sarmatian, ■ Eocene–Cretaceous, ▲ Cretaceous–Jurassic, ▼ Jurassic–Paleozoic. Only for samples originating in Sarmatian deposits could be a regression satisfactorily fitted: it is indicated by the continuous line, whose equation is $y = a + be^x + cx^{0.5}$, with the parameters $a = 0.10084$, $b = 5.741e^{-12}$, $c = 0.28733$ and the correlation coefficient 0.6967. The dashed line indicates the overall correlation trend for all the experimental points.

Sample	Temp. (°C)	pH	Eh (mV)	H ₂ S (mg/L)	TDS (mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Fe (mg/L)	HCO ₃ (mg/L)	Si (mg/L)	NH ₄ (mg/L)	NO ₂ (mg/L)	NO ₃ (mg/L)	SO ₄ (mg/L)	Cl (mg/L)
DS01-9312	24.8	7.40	-300	28.3	991	185.6	22.8	30.6	48.7	0	376.1	4.6	1.83	0	0.8	2.1	265.3
DS02-9311	21.3	7.90	-217	12.2	795	151.4	3.5	33.8	41.7	0	306.5	4.5	0.87	0.001	0.4	5.5	228.2
DS03-9310	23.3	7.36	-	22.5	933	178.9	16.7	40.1	24.4	0	370.5	4.6	4.07	0	0.4	2.7	241.6
DS04-9730	19.9	7.07	-297	20.7	1124	168.3	13.2	45.9	75.8	0.01	457.5	11.5	0	0.664	0	5.6	269.7
DS06-9731	24.1	7.05	-312	25.3	1272	257.1	14.1	40.0	67.2	0.09	388.4	7.9	0	0	0	14.4	408.5
DS07-9735	23.0	7.46	-276	12.6	1115	206.2	12.7	43.0	67.5	0.10	414.4	7.9	0	0.815	0	5.6	329.3
DS08-9710	25.1	7.46	-306	13.7	1028	187.7	12.0	37.2	66.4	0.44	384.8	16.0	0	0.062	0	7.3	297.4
DS09-9728	24.6	7.35	-310	23.5	1026	183.1	14.6	38.1	62.4	0.11	376.0	10.1	0	0.002	0	10.0	291.3
DS10-9729	22.5	7.34	-323	22.4	1020	179.0	13.8	37.8	65.0	0.07	373.1	11.0	0	0	0	12.4	287.9
DS11-9721	24.6	7.26	-289	22.7	1108	206.0	19.4	39.7	66.4	0.17	362.8	11.5	0	0	0	2.6	355.7
DS12-9726	25.0	7.33	-330	25.6	1119	217.0	12.1	37.0	66.4	0.07	377.5	11.0	0	0.005	0	13.6	341.5
DS13-9718	24.8	7.41	-320	14.8	1034	191.3	13.4	35.6	65.9	0.40	382.0	15.8	0	0.006	0	5.6	301.5
DS14-9706	20.3	7.26	-313	6.4	913	136.2	7.1	38.3	71.3	1.46	385.6	15.6	0	0.004	0	4.6	226.9
DS15-9725	24.5	7.22	-345	26.1	976	161.2	15.7	40.0	60.5	0.16	358.9	10.3	0	0.002	0	2.1	276.4
DS16-9708	22.3	7.49	-295	6.9	825	123.7	10.2	37.0	62.8	0.19	347.2	15.8	0	1.960	0	5.0	213.4
DS18-9724	22.7	7.38	-349	23.7	875	125.4	17.5	38.3	62.3	0.11	359.3	11.0	0	0.005	0	4.1	219.5
DS19-9723	22.7	7.51	-361	25.3	916	148.9	12.7	35.9	63.2	0.10	364.6	11.7	0	0.009	0	2.6	243.9
DS21-9717	20.8	7.25	-305	27.6	1010	164.0	8.3	38.9	61.9	0.32	436.6	14.8	0	0.005	0	4.5	226.3
DS22-9301	21.4	7.58	-324	51.3	1073	175.9	27.6	43.8	58.1	0	382.2	4.8	2.52	0.019	1.2	0.0	309.0
DS23-9732	24.0	7.40	-296	19.9	1179	236.4	16.0	39.2	68.6	0.08	379.5	9.5	0	0	0	2.5	392.3
DS26-9733	22.4	7.57	-248	6.6	1121	226.8	17.5	45.9	65.5	0.09	306.9	10.1	0	0	0	4.8	433.6
DS27-9716	24.6	7.72	-290	15.0	1100	218.1	12.3	39.7	64.6	0.19	382.5	16.8	0	0.054	0	4.0	352.3
DS28-9734	18.8	8.06	-305	13.1	1547	406.1	26.1	47.0	40.8	0.07	355.1	9.7	0	0.002	0	2.5	651.1
DS32-9701	13.2	7.49	81	0	1172	262.0	8.7	35.9	57.8	0	388.6	0	0	0	0	6.2	388.6
DS33-9714	13.6	7.00	166	0	834	50.5	1.7	49.0	95.5	0	422.9	0	0	0	0	13.5	135.6

Table 2. Representative hydrochemical data for groundwater and surface waters in the study area

Sample	P _{CO₂} (atm)	Calcite	Chalcedony	Chrysotile	Cristobalite	Diopside	Dolomite	Gypsum	Huntite	Magnesite	Nahcolite	Nesquehonite	Quartz	Sepiolite	Talc	Tremolite
DS01-9312	1.25E-02	0.08	0.17	-3.97	0.20	-3.35	0.31	-3.52	-3.57	-0.35	-3.92	-2.76	0.60	-2.57	0.06	-2.02
DS02-9311	3.18E-03	0.40	0.20	-1.26	0.24	-1.65	1.02	-3.15	-2.11	0.05	-4.04	-2.36	0.64	-0.58	2.79	4.23
DS03-9310	1.36E-02	-0.27	0.19	-4.02	0.23	-3.80	0.01	-3.71	-3.78	-0.30	-3.91	-2.71	0.63	-2.51	0.04	-2.88
DS04-9730	3.19E-02	-0.04	0.63	-5.28	0.68	-3.92	-0.00	-2.96	-4.30	-0.53	-3.81	-2.94	1.08	-2.49	-0.39	-3.43
DS06-9731	2.92E-02	-0.14	0.42	-5.41	0.45	-4.13	-0.17	-2.62	-4.57	-0.61	-3.76	-3.01	0.85	-3.10	-0.90	-4.51
DS07-9735	1.23E-02	0.30	0.43	-2.98	0.47	-2.53	0.73	-3.01	-2.75	-0.14	-3.80	-2.55	0.86	-1.41	1.55	1.17
DS08-9710	1.17E-02	0.30	0.71	-2.26	0.75	-1.80	0.70	-2.89	-2.86	-0.18	-3.89	-2.59	1.14	-0.54	2.86	3.86
DS09-9728	1.42E-02	0.14	0.52	-3.32	0.55	-2.68	0.42	-2.76	-3.38	-0.30	-4.04	-2.71	0.95	-1.55	1.41	0.69
DS10-9729	1.41E-02	0.11	0.58	-3.60	0.62	-2.81	0.31	-2.66	-5.66	-0.38	-3.91	-2.79	1.02	-1.55	1.22	0.31
DS11-9721	1.68E-02	0.05	0.57	-3.73	0.61	-2.90	0.22	-3.34	-3.77	-0.41	-3.89	-2.82	1.01	-1.73	1.11	-0.06
DS12-9726	1.48E-02	0.13	0.55	-3.40	0.59	-2.67	0.36	-2.63	-3.52	-0.35	-3.86	-2.76	0.98	-1.56	1.40	0.68
DS13-9718	1.30E-02	0.24	0.71	-2.67	0.74	-2.06	0.56	-3.00	-3.14	-0.26	-3.88	-2.67	1.14	-0.80	2.45	2.95
DS14-9706	1.82E-02	0.09	0.76	-4.01	0.80	-2.94	0.20	-3.03	-3.93	-0.46	-3.96	-2.86	1.20	-1.45	1.13	0.03
DS15-9725	1.82E-02	-0.03	0.53	-4.03	0.57	-3.18	0.11	-3.46	-3.95	-0.44	-3.99	-2.85	0.96	-2.00	0.71	-1.01
DS16-9708	1.98E-02	0.25	0.77	-2.40	0.78	-1.91	0.59	-3.04	-3.08	-0.23	-4.07	-2.64	1.17	-0.48	2.74	3.63
DS18-9724	1.23E-02	0.13	0.58	-3.28	0.62	-2.62	0.37	-3.13	3.49	-0.33	-4.08	-2.74	1.01	-1.35	1.55	1.01
DS19-9723	9.12E-03	0.26	0.60	-2.55	0.64	-2.08	0.60	-3.32	-3.07	-0.23	-4.01	-2.64	1.04	-0.82	2.32	2.86
DS21-9717	1.99E-02	0.05	0.73	-4.05	0.77	-3.05	0.20	-3.11	-3.87	-0.42	-3.86	-2.83	1.17	-1.54	1.05	-0.29
DS22-9301	7.09E-03	0.24	0.23	-2.83	0.27	-2.65	0.66	-5.80	-2.86	-0.15	-3.96	-2.56	0.67	-1.59	1.28	0.72
DS23-9732	1.27E-02	0.21	0.50	-3.17	0.53	-2.56	0.51	-3.36	-3.22	-0.27	-3.80	-2.68	0.93	-1.46	1.50	1.02
DS26-9733	7.02E-03	0.26	0.54	-2.09	0.58	-1.91	0.69	-3.10	-2.82	-0.15	-3.88	-2.55	0.98	-0.60	2.66	3.56
DS27-9716	6.19E-03	0.52	0.74	-0.66	0.77	-0.76	1.17	-3.17	-1.86	0.08	-3.84	-2.33	1.17	0.59	4.50	7.61
DS28-9734	2.37E-03	0.50	0.56	0.31	0.61	-0.53	1.34	-3.62	-1.36	0.27	-3.56	-2.13	1.01	1.16	5.05	8.81

Table 3. Partial pressure of CO₂ and values of mineral saturation index (SI) obtained by speciation modeling.

(Mg_2SiO_4), while as far as amphiboles [tremolite ($\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$) and phyllosilicates [talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$), chrysotile ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$), sepiolite ($\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$)] are concerned, an erratic behavior is recorded.

6. Conclusions

Hydrogen sulfide occurrences in carbonate karst environments are normally related either to thermo-mineral water flows, or to influences due to neighboring hydrocarbon accumulations. Both circumstances are present in the case of the Mangalia hydrogeological complex, and there is an obvious involvement of the H_2S in the karst processes that take place within the carbonate structures of that area.

Conclusions derived from the data provided by the present study can be summarized as follows. Features which make the Mangalia region groundwater distinct from that of other karst aquifers in Romania are its hydrochemical facies, its total mineralization, its temperature and its significant content of dissolved hydrogen sulfide. Although the aquifer occupies carbonate rocks, the groundwater chemical character within the deeper hori-

zons is definitely Na-Cl, being still Na-Cl, or at least Na- HCO_3 , also within the upper horizons, where Sarmatian deposits prevail. Associated to that specific facies there are recorded also unusual total mineralization amounts, which exceed mineralization values recorded in carbonate-karst areas outside Dobroudja by a factor of three to four.

Chemical reactions taking place within that groundwater structure consist primarily of carbonates precipitation and of sulfates dissolution. Mineral species that frequently precipitate from that solution are aragonite, calcite, and in many instances even dolomite or magnesite. In contrast, groundwater is always under-saturated with respect to anhydrite, gypsum, mirabilite, thenardite, etc.

Bibliography

- Bloechl, E., Keller, M., Waechtershaeuser, G. & Stetter, K. O. (1992). Reactions depending of iron sulfide and linking geochemistry with biogeochemistry. *Proc. Natl. Acad. Sci. USA*, **89**, pp. 8117-8120.
- Capotă, A. (1980). Studiu geologic, hidrogeologic și chimic complex privind apele mezotermale sulfuroase din zona Mangalia-Nord, județul Constanța. Technical Report Proiect 998/H, Institutul de Studii și Proiectări pentru Gospodărire Comunală.

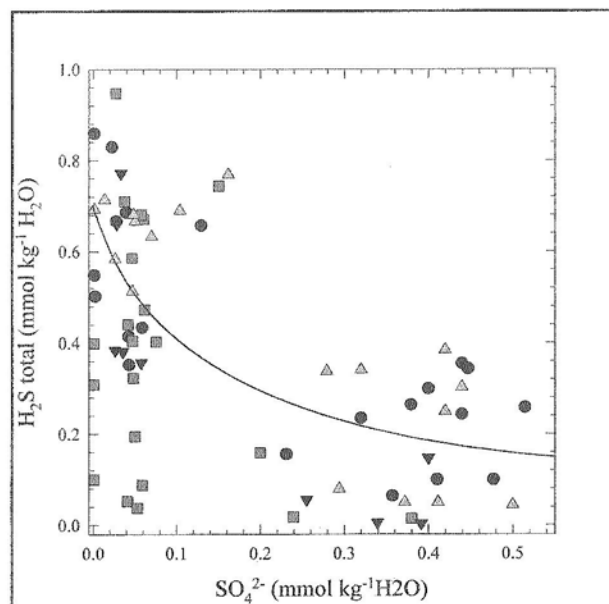


Fig. 8. Plot of the ratio between total dissolved H_2S concentrations and concentrations of the SO_4^{2-} free ion in the Mangalia region wellbores.

The meaning of the symbols is indicated in the legend of the diagram in fig. 6. The regression line fits all the plotted values and its equation is: $y = a + bx + cx^{0.5} + dx^{-1} + e \ln x \cdot x^{-2}$, with the parameters: $a = 0.81429$, $b = 0.8927$, $c = -1.55838$, $d = -0.00021417$ and the correlation coefficient 0.4918.

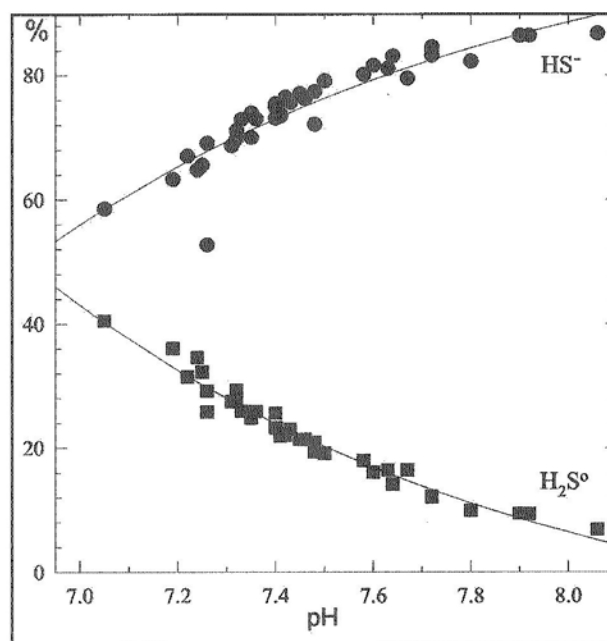


Fig. 9. HS^- and H_2S^0 species concentrations distribution (percents) as a function of pH, computed for the samples originating in the Mangalia mesothermal water accumulation.

- Chiriac, M. (1960). Notă asupra depozitelor sarmațiene din Dobrogea. *Comunicările Academiei R.P.R.*, **10** (7), pp. 613-623.
- Constantinescu, T. (1989). Considerations sur la zone karstique de "La Movile" (Mangalia, Dobrogea du Sud, Roumanie). *Misc. Speol. Rom.*, **1**, pp. 7-12.
- Constantinescu, T. (1995). Le karst de type Movile (Mangalia, Dobrogea de Sud, Roumanie). *Theor. Appl. Karstol.*, **8**, pp. 91-96.
- Davidescu, F. D., Țenu, A. & Slăvescu, A. (1991). Environmental isotopes in karst hydrology. A lay-out of problems with exemplifications in Romania. *Theor. Appl. Karstol.*, **4**, pp. 77-86.
- Dimitrov, D., Machkova, M. & Velikov, B. (1991). Hydrochemical classification of ground waters in northeast Bulgaria. *Geol. Balcanica*, **21**(5), pp. 77-85.
- Dimitrov, D., Velikov, B. & Machkova, M. (1994). Processing of ground water hydrochemical data by means of cluster and discriminant analyses. In: *Impact of Industrial Activities on Groundwater*. Bucharest University Press, pp. 123-138.
- Dumitrescu, M., Orghidan, T., Tanasachi, J., Georgescu, M. (1965). Contribuții la studiul monografic al Peșterii de la Limanu. *Lucr. Inst. Speol. "Emil Racoviță"*, **4**, pp. 21-58.

- Feru, M. U. (1993). Considérations sur la genèse et la circulation des eaux thermominérales karstiques de la zone de Mangalia (Roumanie). *Theor. Appl. Karstol.*, **6**, pp. 189-198.
- Feru, M. U. & Capotă, A. (1991). Les eaux thermominérales karstiques de la zone de Mangalia (Roumanie). *Theor. Appl. Karstol.*, **4**, pp. 143-157.
- Gaşpar, E. & Orășeanu, I. (1987). Natural and artificial tracers in the study of the hydrodynamics of karst. *Theor. Appl. Karstol.*, **3**, pp. 31-107.
- Gâstescu, G. & Hîncu, I. (1971). *Lacurile din România. Limnologie Regională*. Editura Academiei R.S.R., București.
- Joergensen, B. B. (1990). The sulfur cycle of freshwater sediments: Role of thiosulfate. *Limnol. Oceanogr.*, **35** (6), pp. 1329-1342.
- Koleva-Rekalova, E. (1994). Sarmatian aragonite sediments in north-eastern Bulgaria - Origin and diagenesis. *Geol. Balcanica*, **21** (5), pp. 47-64.
- Lascu, C., Popa, R. & Sârbu, Ș. (1994). Le karst de Movile (Dobrogea de Sud). (I). *Rev. Roum. Géograph.*, **38**, pp. 85-94.
- Luther III, G. W. & Church, T. M. (1992). An overview of the environmental chemistry of sulphur in Wetland systems. In: S. J. W. B.

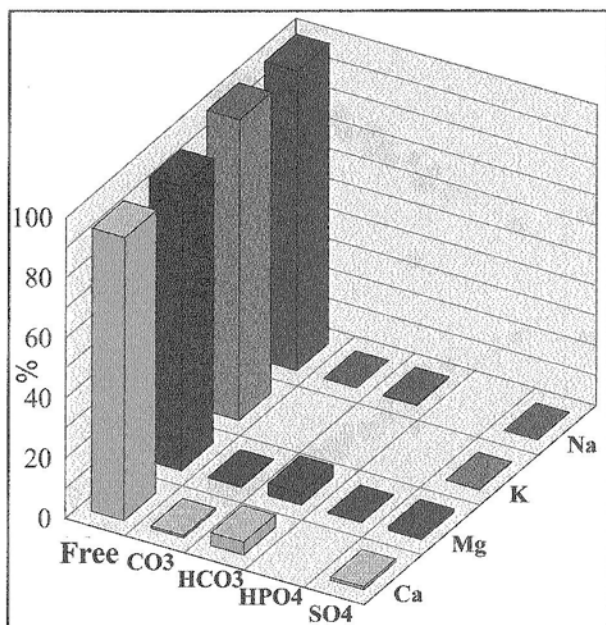


Fig. 10. Major cations speciation in the Mangalia region groundwater – free ions and ionic associations with inorganic ligands. The ordinate represents percentages of the considered cationic compounds total concentration.

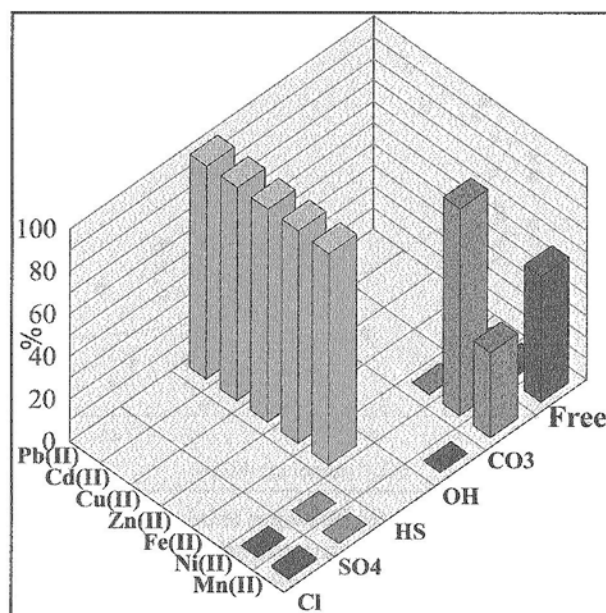


Fig. 11. Speciation of certain trace elements computed for sources in Mangalia area – free ions and complexes with inorganic ligands. For the species formed with the same ligand, the weights have been cumulated.

- Howarth, R. W. and M. V. Ivanov (eds.): *Sulfur Cycling on the Continents*. John Wiley and Sons Ltd., New York, Chapt. 6, pp. 125-142.
- Marin, C., Nicolescu, T. (1993). The geochemistry of groundwater from southeastern Dobrogea, Romania. *Trav. Inst. Spéol. "Emile Racovitza"*, **32**, pp. 229-247.
- Mopper, K. & Taylor, B. F. (1986). Biogeochemical cycling of sulfur. Thiols in coastal marine sediments. In: M. L. Sohn (ed.): *Organic Marine Geochemistry*, No. 305 in ACS Symposium Series. American Chemical Society, Washington, DC, Chapt. 19, pp. 324-339.
- Mutihac, V. & Ioneși, L. (1974). *Geologia României*. Editura Tehnică, București.
- Nicolescu, M. (1965). Rolul tectonicii în circulația și găsirea apei în carstul din Dobrogea. *Hidro-tehnica, Gospodărirea Apelor, Meteorologia*, **10** (1), pp. 40-46.
- Pascu, M. R. (1983). *Apele Subterane Din România*. Editura Tehnică, București.
- Țenu, A. & Davidescu, F. (1993). Relations entre le lac Techirghiol (Dobroudja du sud, Roumanie) et les aquifères adjacents. *Theor. Appl. Karstol.* **6**, pp. 163-174.
- Țenu, A., Davidescu, F., Simionăș, S., Eichinger, L., Bertleff, B., Michel, W., Secară, E., Caradima, Z. & Pițu, N. (1994). Assessment of the pollution impact of the groundwater quality in south Dobrogea. In: *Impact of Industrial Activities on Groundwater*. Bucharest University Press, pp. 557-571.
- Țenu, A., Davidescu, F. D. & Slăvescu, A. (1987). Recherches isotopiques sur les eaux souterraines des formations calcaires dans le Dobroudja meridionale (Roumanie). In: *Isotope Techniques in Water Resources Development*. International Atomic Energy Agency, pp. 439-453.
- Țenu, A., Noto, P., Cortecchi, G. & Nuti, S. (1975). Environmental isotopic study of the barremian-jurassic aquifer in south Dobrogea (Romania). *J. Hydrol.* **26**, pp. 185-198.
- Ujvári, I. (1972). *Geografia Apelor României*. Editura Științifică, București.
- Vairavamurthy, A., Manowitz, B., Luther III, G. W. & Jeon, Y. (1993). Oxidation state of sulfur in thiosulfate and implications for anaerobic energy metabolism. *Geochim. Cosmochim. Acta*, **57** (7), pp. 1619-1623.
- Wilkin, R. T. & Barnes, H. L. (1996). Pyrite formation by reaction of iron monosulfides with dissolved inorganic and organic sulfur species. *Geochim. Cosmochim. Acta*, **60** (21), pp. 4167-4179.
- Zamfirescu, F., Moldoveanu, V., Dinu, C., Pițu, N., Albu, M., Danchiv, A. & Nash, H. (1994). Vulnerability to pollution of karst aquifer system in southern Dobrogea. In: *Impact of Industrial Activities on Groundwater*. Bucharest University Press, pp. 591-602.