CHEMICAL CHARACTERIZATION AND GELOGICAL CONTROL OF SPRING WATER IN SIERRA DEL ROSARIO, PINAR DEL RÍO, CUBA

Fagundo Castillo, J. Reynerio.[1]; Carrillo-Rivera, J. Joel[2]; Antigüedad Auzmendi, Iñaki[3]; González Hernández, Patricia[1]; Peláez Díaz, Roberto[4]; Hernández Díaz, Rebeca [5]; Cáceres Govea, Dámaso[5]; Hernández-Santana; J. R.[2] Suárez Muñoz, Margaret[1]; Melián Rodríguez, Clara[1]; Rodríguez-Piña, Mónica[6].

1. Centro Nacional de Medicina Natural y Tradicional (Cuba): _juanrfag@infomed.sld.cu_; 2. Instituto de Geografía UNAM (México): _cigaihsud@mx.inter.net_; 3. Universidad del País Vasco (España): _gopanaui@lg.ehu.es_; 4. Empresa GEOMINERA, Pinar del Río (Cuba): _rpelaez@geo.upr.edu.cu_; 5. Universidad de Pinar del Río (Cuba): _rebeca@geo.upr.edu.cu_; 6. Centro de Estudios del Medio Ambiente (Cuba): _mrp@rect.uh.cu_.

ABSTRACT

Flows of different hierarchy, which travel through limestone, schist, sandstone and ultra-basic rocks, with ages from the Paleocene to the Jurassic, at Sierra del Rosario, Pinar del Río, Cuba, were characterized. The waters were sampled from 1984 until 2004 and the data were statistically processed by means of chemical equilibrium and physico-chemical models. Results demonstrate that the physico-chemical properties of the water are controlled by water-rock interaction resulting from the residence time since rainwater infiltrate the discharge area is reached, and the type of aquifer material. Geochemical indices allow the definition of the different types of flow (local, intermediate, regional) to be characterized, permitting a further definition of the different flow systems and rock type involved, as well as its use for water supply and medical use. The main geochemical processes which control the chemical composition acquisitions mode are: congruent dissolution of calcite, dolomite, and halite; incongruent dissolution of plagioclase and microcline minerals; pyrite oxidation, sulphate reduction, and SiO_2 dissolution at the surface or SiO_2 precipitation at deep saturation and circulation zones.

Keywords: groundwater flow systems, hydrogeochemical characterization, hydrogeochemical modeling, geochemical process, carbonate aquifer, chemical composition origin, Pinar del Río, Cuba.

INTRODUCTION

During the last forty years several important contributions have been made to gain knowledge on the hydrogeology of Sierra del Rosario (mountain range) in the Pinar del Río Province, Cuba. However, most results in terms of geology and water chemistry have been treated somehow separately, failing to obtain an agreeable integration. Generally, groundwater studies have been related to the karstic chemical denudation (Pulina and Fagundo, 1984; 1992; Fagundo and Rodríguez, 1995; Fagundo et al., 1997) or have pursued SPA-medical objectives (Fagundo et al., 2001), and results have been published in local journals and books, making them unavailable for professionals elsewhere interested in groundwater resources in karstic terrains and in regional flow systems.

The abrupt topography of the mountain ranges of the study area had undergone little environmental changes; it is barely inhabited, as most of the development has been confined to low topographic and flat areas by the foothills of the mountain ranges. The indigenous flora and

fauna has been subject to little human influence. Further, UNESCO declared Sierra del Rosario a Biosphere Reserve in 1985.

From a geological perspective the study area is heterogeneous, including ophiolites, Cretaceous siliciclastic, calcareous and volcanic rocks, as well as Paleocene to Eocene rocks constituted by sandstone, schist and limestone. Drilling procedures were made early in the 1990's to acquire sub-surface geological data as an effort to gain further hydrogeological understanding of the geological controls on the water resources of the area (Peláez et al., 1990). The hydrogeology of Sierra del Rosario is highly inhomogeneous with springs discharging water with contrasting chemistry. Information on water chemistry of springs has been collected since 1984 and reported by Fagundo et al. (1997). The presence of most springs is supposed to be a response of the karstic nature of the terrain; however, restricted interest was given to the springs origin in relation to their geological setting. The main objectives of this paper are the following: a) to order available water chemistry information of spring data according to each particular geological setting and flow hierarchy, b) postulate prevailing water-rock interactions based on major ions and field measurements through hydrogeochemical modeling, c) and to explain the origin of the chemical composition of the ground water of the region according with the local environmental geology.

SITE DESCRIPTION

The center of the study area is located in the Pinar del Río Province, approximately 100 km to the southwest of the city of Havana, in the main island of the Cuban archipelago (Figure 1). The Sierra has a surface area of about 1,125 km^2. The highest summit of Sierra del Rosario and also of the western Cuba is Pan de Guajaibón with an altitude of 669 m.

The mean yearly environmental temperature in the higher elevations, and by the seashore, in this part of the island, is 23 ºC and 25 ºC, respectively. The warmest months are July and August, and the coldest are December and January. The yearly registered precipitation on Sierra del Rosario is 2,000 mm, out of which some 1,600 mm falls during summer (May to October) and about 400 mm during the winter months (November to April). Precipitation achieves its minimum values towards the lowest topographic territory to the north (about 1,050 mm/year).

GEOLOGICAL FRAMEWORK

The history of the geology of the area under investigation has been subject to considerable arguments beyond the objectives of this paper. However, the present geological setting is that it is an anticlinorium formed, mainly, by calcareous rocks that may be observed in mountain ranges that belong to the Cordillera Guanigüanico (Figure 2). Two main structural features limit the Sierra del Rosario, the Pinar Fault to the south and the Bahía Honda Fault to the north (Academia de Ciencias de Cuba, 1989).
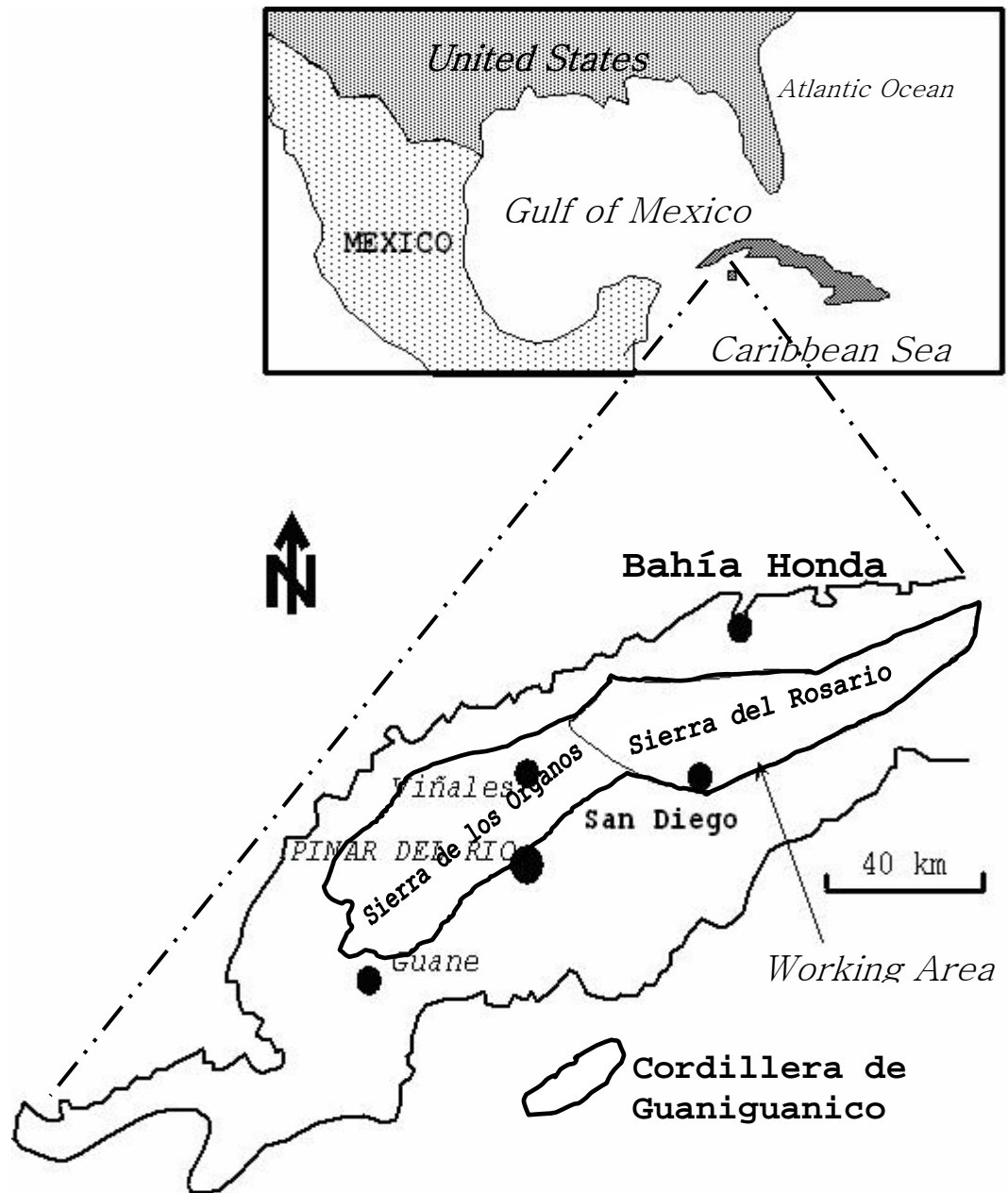
Figure 1. Schematic map with the Sierra del Rosario location.

The pre-Late Eocene geology of Cuba principally consists of a series of folded accreted terrains of continental and oceanic affinity that strike approximately parallel to the axis of the island. In the study area the basement consists in the allochthonous terrain Guanigüanico which consist of

Jurassic-Cretaceous sediments of continental margin type, some ophiolites and Cretaceous volcanic rocks as well as Paleocene to Lower Eocene foreland sediments. It is strongly deformed and display varying degrees of metamorphism. Its emplacement below the Cretaceous volcanic rocks appears to have been completed in Middle Eocene (Somin and Millán, 1981). The Guanigüanico terrain structure consists of a stack of several northwestward-trending thrust belts (Iturralde-Vinent, 1996). The structurally lower units are named, from bottom to top, Los Órganos and Rosario belts (subdivided into Rosario South, Rosario North and Quiñones) and chiefly consist of sedimentary rocks of possible Early Jurassic to Late Cretaceous age (Pszczolkowski, 1978). The structurally higher belts consist of serpentinites, gabbros and Cretaceous igneous and sedimentary rocks of the Felicidades belt.

The lithology of the main units that outcrop in the study area (Figure 2) are described from the oldest to the most recent. A general characterization of the more relevant units is presented followed by a mineralogical description resulting from an analysis of core samples obtained locally through standard drilling procedures.

The **San Cayetano Formation** (J_1-J_3 ox) is the oldest unit outcropping in the Sierra del Rosario. It is of Late Jurassic (Oxfordian) age. It consists of quartz sandstone, shale lutite, argillite, phillitoid schist and carbonaceous material. Its thickness could reach an excess of 3,000 m. The main minerals of the sandstone are: quartz (60-75%), plagioclase (2-5%), muscovite (1-2%), tourmaline and chlorite (1 %). Occasionally the sandstone is cemented by iron oxides clayey material, limestone strata are rarely found. Locally this unit is about 1,000 m thick and reported to contain dispersed pyrite, titanium minerals (<1%), apatite (<1%), zirconium (<1%), tourmaline (<1%) and carbon substances (<1%).

The **Artemisa Formation** (J_3-K_1 b) is the most widespread unit in the study area (Figure 2). It belongs to Upper Jurassic-Lower Cretaceous age and is represented by limestone strata inter-bedded, in its upper part, with siliciclastic rocks. Its total thickness is of approximately 800 m (Pszczolkowski, 1987). Locally it is represented by inter-bedded limestone (80-95%) with crystalline and micro-crystalline calcite with a fractured structure, and about 5-15% of carbonaceous material. It contains some quartz (<1%), titanium mineral (<1%), and other minerals. Occasionally chert layers (1-5 cm thick) are found as well as impurities of clayey-ferruginous matter (Peláez et al., 1990). Artemisa Formation has economic importance because it can be the Caribbean-Antilles basin oil reserve.

The **Encrucijada Formation** (K_1 a-al) belongs to the Lower Cretaceous age (Aptian-Albian), is represented by andesite-basalts, siliciclastic rocks, limestone, argillite and aleurolite.

The **Quiñones Formation** (K_2 cm-t), of Upper Cretaceous age (Cenomanian-Turonian), consists of pedernals, sandstone aleurolite, argillite, volcanic-sedimentary rocks and limestone.

The **Sierra Azul Formation** (K_{1-2}) belongs to the Lower-Upper Cretaceous age and is represented by carbonaceous terrigenous material as well as by limestone, marlstone, argillites, and siliciclastic rocks. Its reported thickness (Pszczolkowski, 1987) is of 600 m (locally has 280 m).
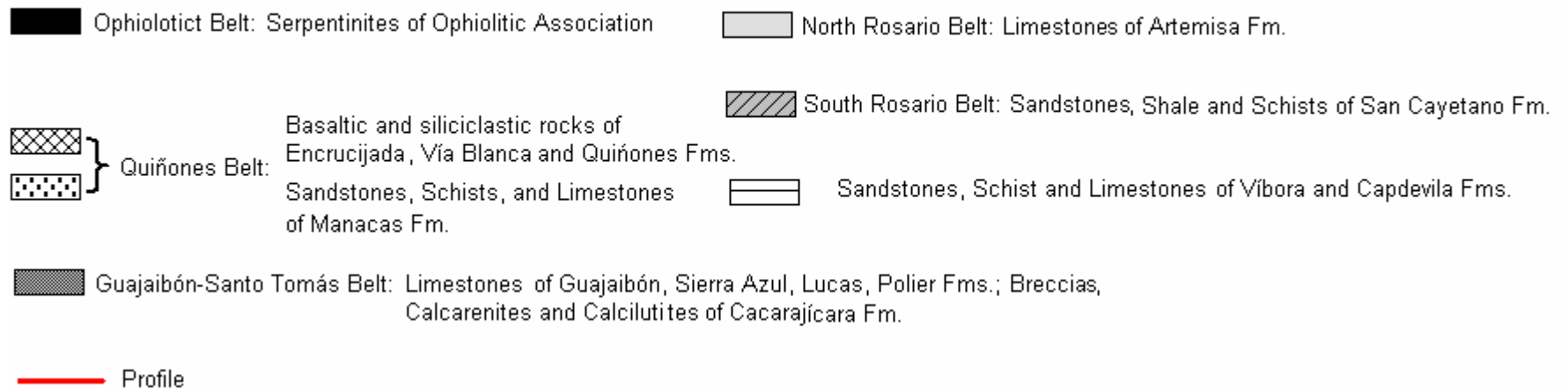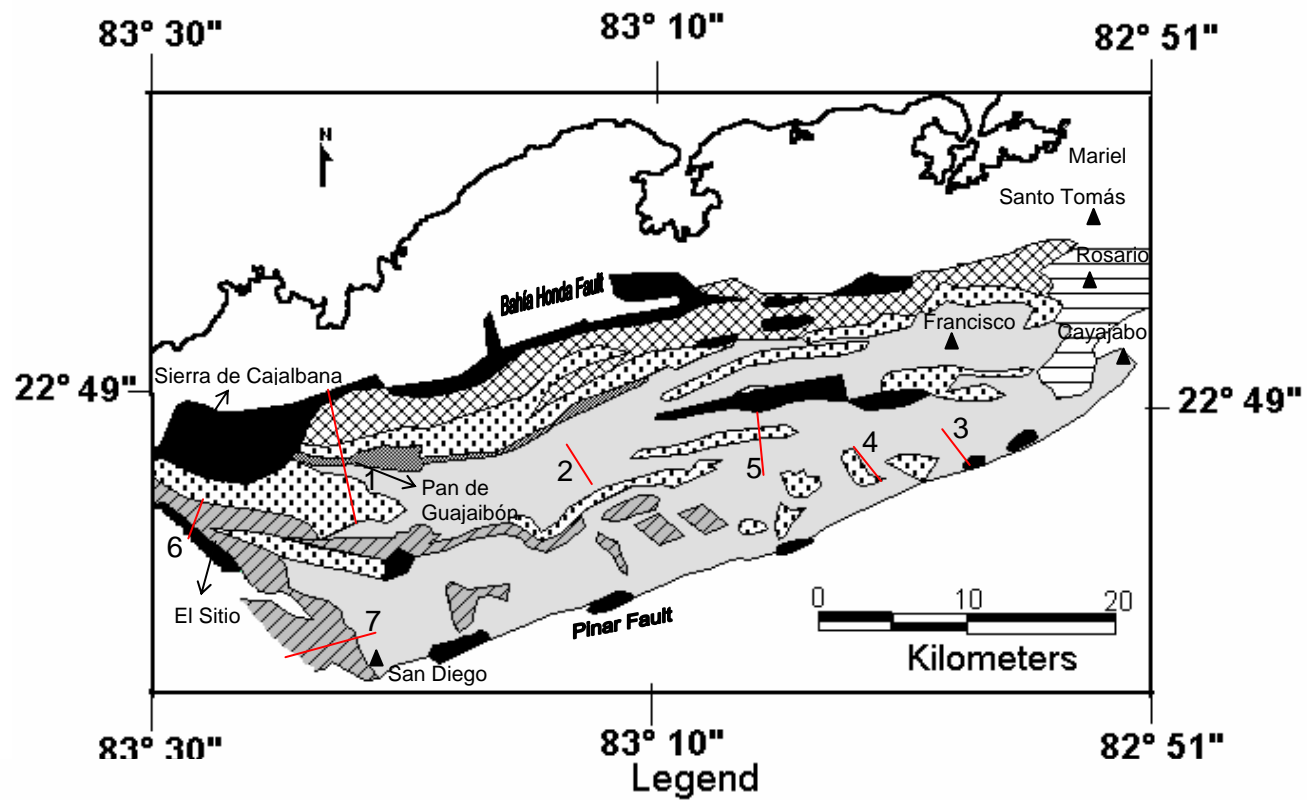
Legend

Ophiolotict Belt: Serpentinites of Ophiolitic Association

North Rosario Belt: Limestones of Artemisa Fm.

Quiñones Belt:
Basaltic and siliciclastic rocks of Encrucijada, Vía Blanca and Quiñones Fms.

Sandstones, Schists, and Limestones of Manacas Fm.

South Rosario Belt: Sandstones, Shale and Schists of San Cayetano Fm.

Sandstones, Schist and Limestones of Víbora and Capdevila Fms.

Guajaibón-Santo Tomás Belt: Limestones of Guajaibón, Sierra Azul, Lucas, Polier Fms.; Breccias, Calcarenites and Calcilutites of Cacarajícara Fm.

Profile

Figure 2. Schematic geological map of the Sierra del Rosario with the selected cross - section.

The **Guajaibón Formation** (K_{1-2} al-cm) is allocated an Upper Cretaceous age (Albian-Cenomanian), it consists of massive limestone, and calcareous sandstone (Pszczolkowski, 1987). Its maximum estimated thickness is of 600 m (locally is represented by 500 m at the Pan de Guajaibón massif).

The **Cacarajicara Formation** (K_2 m) is Upper Cretaceous of Maastrichtian age and consists of breccias, calcarenites and calcilutites. The breccia is composed mainly by fragment of limestone, chert and volcanic rocks (trachytic composition) while metamorphic and alkaline rock fragments are reported to appear less frequently. Its maximum thickness is of about 450 m, however, locally only 50 m of this formation is reported.

The **Vívora Formation** (P_1) belongs to Paleocene age, is composed of sandstone, conglomerates, clays, marls and limestone.

The **Manacas Formation** (P_{1-2}) is assigned an indifferently Paleocene-Eocene age. It consists of an estimated maximum of 200 m sandstone, schist, limestone and olistostromes (Pszczolkowski, 1987). Locally this unit is represented by 20 m of limestone and sandstone strata. The later is made up of fragments of plagioclase (30%), limestone (25%), quartz (10%), basaltic rocks (1%) and calcareous sandstone (34%). Impurities are found of clayey ferruginous material, volcanic devitrified glass and apatite.

The **Capdevila Formation** (P_2^1) belongs to Lower Eocene age, and is made up of sandstone, aleurolite, conglomerate and marls.

The morphology of the study area reflects its geological characteristics and tectonics. For instance, the main conspicuous morphological feature, the Pan de Guajaibón ridge, constitutes a broken fold of Cretaceous rocks (Artemisa Formation) that is divided into blocks and often brecciated by an Eocene orogeny. These rocks are covered in depressions, by fluvial or lateritic deposits, including thick covers of terra rossa. The area is surrounded by non-karstifiable sandy-clay sedimentary unit (Manacas FORMATION), a terrigenous shale and sandstone unit (Jurassic, San Cayetano Formation) and volcanic rocks (Cretaceous, of basic composition).

The Cordillera de Guaniguanico was formed at Middle Eocene. Its tectonic style (more studied in Sierra de los Organos than in Sierra del Rosario) is of alpine type, and can be characterized by differential displacement of rocks masses forming nappes, subsequent structural inversion of tectonic units and zonation of tectonic deformation (Piotrowska, 1978). In Sierra del Rosario, this feature is represented by the occurrence of fault of vertical and horizontal displacement, and orogenic overthrust.

The Northern Ophiolitic melange is an allochtonous body that has been thrust north and northwestward onto the foreland basins of the Guanaiguanico terrene. Usually they are strongly deformed, partially metamorphosed and occur amalgamated both with nappes of the foreland basement and with segments of the overlying Cretaceous arc rocks. The melange is composed of deformed serpentinite and Mesozoic gabbros (Iturralde-Vinent et al, 1996) intruded by isolated ultramafic and mafic dikes. These mafic igneous and sedimentary sections have been interpreted as sequences formed within marginal sea-back arc environment (Iturralde-Vinent, 1994) or within a subduction forearc setting (Fonseca et al., 1990). These rocks are composed maily of serpentinits, harzburgits, lherzolits and wherlits.

HYDROGEOLOGICAL FRAMEWORK

The information related with the hydrogeological properties of the units that constitute the Sierra del Rosario is scarce, except for those places where prospecting works have been carried out for mining and the search of mineral medicinal waters (Peláez et al., 1990) or specific studies to measure the intensity of the karstic denudation (Pulina and Fagundo, 1992; Rodríguez et al., 1985; 1995).

As it has already been pointed out, the Sierra del Rosario is characterized by the presence of belts of different lithological constitution, ranged from north to south (Figure 2), which are in tectonic contact according to overturned surfaces, additionally deformed in nappe groups, crossed by transverse faults to the main faults (Pinar and Bahía Honda), originating blocks of smaller proportions (Rodríguez et al., 1985). These belts are:

1. Ophiolitic Belt. It extends from the Sierra of Cajalbana almost to the Mariel. It is constituted by ultramafic rocks of the Ophiolitic Association. Quiñones Band (Felicidades) extends from the north of the Pan de Guajaibón to the Rosario's village. It is composed by effusive - sedimentary rocks of the Cretaceous (Encrucijada, Vía Blanca and Quiñones Formations) and schist, sandstone and limestone of the Paleogene (Manacas Formation).

2. Guajaibón-Santo Tomás Belt. It extends from the Pan de Guajaibón to the town of Santo Tomás. This formation is constituted by limestone, calcarenite, dolomite and siliciclastic limestone of the Guajaibón, Sierra Azul, Cacarajícara, Polier and Lucas Formations.

3. North Rosario Belt. It extends from the town El Sitio to Francisco's town. Its is made up of stratified limestone of the Artemisa Formation, schist, sandstone and limestone of the Paleogene (Manacas Formation) and ultramafic rocks.

4. South Rosario Belt. It extends approximately from the riverbank of San Diego river to Cayajabo town. It is constituted by calcareous and siliciclastic rocks of Artemisa Formation, schist and sandstone of San Cayetano Formation and basalts.

The deposits that compose the Ophiolitic Belt originate fissured type aquifers. In spite of the lack of information with regard to these aquifers of the Sierra del Rosario, it is known that the flows of the wells perforated in these materials, in other places of the country, are in the order from 0,2 to 0,3 l/s (Ergorov and Luege, 1967). However, in areas of tectonic dislocations the flows can reach up to 20 l/s. Flows in these materials belong to local and intermediate flow systems. Associated to this region, in this work were studied some waters in Sierra de Cajalbana. In the Quiñones Belt, the constituent materials of the formations (Cretaceous and Paleogene) present a very low permeability. Nevertheless, in some places where fissured limestone exist, appreciable flows are obtained. In the Sierra del Rosario, these deposits originate local and intermediate flows. Of these materials, samples were taken from springs, wells and streams in the proximities of Pan de Guajaibón.

The Guajaibón-Santo Tomás Belt is characterized by the prevalence of carbonated formations. Consequently, a karstic relief is developed in the region. The infiltration of rainfall is instantaneous and with gravitational character. The hydrogeological areas in the karstic region have been defined by the relative position of the piezometric level and the movement of the water. Caves reach a depth of up to 100 m and less frequently depths of the order of 300-350 m. The caves constitute underground conduits originated by chemical dissolution and the position of the piezometric level has been established by field observations and well perforations. Recent speleological investigations have confirmed the existence of extensive cavernous systems in the area. In this belt it was studied a great number of waters, corresponding to local or intermediate

flows. Among these studied places were: infiltration waters from caves; karstic exsurgences and springs (associated to Guajaibón, Sierra Azul and Cacarajícara Formations), as well as one thermal spring (Cacarajícara sulfuroso spring) associated to the Cacarajícara Formation.

The North and South Rosario Belts possess very similar hydrogeological characteristics, due to the great distribution of the limestone of Artemisa Formation. Both belts also present not carbonated rocks of similar composition and a similar tectonic style. Fissured and karstic aquifers formation is favored, originated by local, intermediate or regional flows, some of them with high sulfur contents. The thermal waters of more interest by its therapeutic properties are Mil Cumbres sulfuroso, Pozo Azul, Soroa, La Pastora, Pedernales, Brocal, San Juan sulfuroso, Cueva Portales, M-1 springs; El Sitio, P-4, wells; and El Tigre, El Templado, La Gallina springs and P-1 well at the thermal site of San Diego de los Baños (Spa).

The specific discharge determined in the wells perforated in the constituent materials (schist, shale and quartz sandstone) of the San Cayetano Formation (South Rosario Belt) was low, in the order of 0.7 to 4.6 l/s/m in the wells P-1, P-2 and P-3 near San Diego de los Baños (Peláez et al,. 1990). The flows of the karstic springs (Artemisa Formation) in this area are similar to those of the Pan de Guajaibón region (local flows). The waters coming from the deep drainage (regional flows) possess a smaller flow. The flows of the mineral medicinal springs are in the order of less than 1 l/s in Bermejales, near 1 l/s in Soroa and of 10 l/s in San Diego de los Baños.

MATERIALS AND METHODS

Standard hydrogeochemical procedures were used to further validate previous hydrogeological model of groundwater flow. Under the prevailing hydrogeological setting two main questions were examined from chemical data obtained in spring water: (a) establish a theoretical hierarchy for the various flows in terms of their local, intermediate and regional length of path and (b) define a possible geological structure control.

Chemical constituents in groundwater provide valuable information on the history of flow path in the surrounding environment. Consequently, analyses of groundwater collected from springs and boreholes were assessed to outline a flow description. Sampling techniques included detailed field measurements of temperature, pH, Eh, electrical conductivity and dissolved O_2 using an in-line flow-cell to ensure the exclusion of atmospheric contamination and to improve measurement stability. Alkalinity was determined through standard volumetric titration method using green-methyl red indicator; H_2S and CO_2 were analyzed using iodimetric and orange-methyl procedures, respectively. All used equipment was calibrated in situ. Determinations for major ions were performed in laboratory or field using standard APHA-AWWA-WPCF techniques (1992). These techniques have been adapted for field conditions by Markowicz and Pulina (1979) and Krawczyk (1992).

With the aim to study the physico-chemical behavior of the waters that drain the different lithologies of Sierra del Rosario, the samples were distributed to groups and sub-groups (Table 1).

All water samples, including rain waters, were analyzed in the field or laboratory during the following 24 hours after their collection. All chemical solutions used during field determinations were subject to quality control at the National Center for Scientific Research using the above methods. All reported values have ionic balance error within 5 %, except some samples of mineral waters, which show less than 10% error. In this study advanced hydrogeochemical modeling (PHREEQC; Parkhurst and Appelo, 1999; MODELAGUA; Fagundo-Sierra et al., 2001) was used to evaluate the water-mineral equilibrium. The main geochemical processes which originate the chemical compositions of the waters at Sierra del Rosario are listed in Table 2.

RESULTS AND DISCUSSION

Table 3 contains the chemical composition of water samples from Sierra del Rosario, indicating field data (T, pH, Eh, O_2), major ions as well as CO_2 and H_2S. This table includes available historical data distributed in 9 groups according to their hydrogeochemical characteristics and geological settings. The number of analyses available by group (N) since 1984 is also indicated. The spatial distribution of these sampling points is shown in Figure 3. The nature of the flow path length in terms of local, intermediate or regional flow is proposed based on results of Table 3 as suggested by the flow-system theory (Tóth, 1999). Figure 4 shows several schematic cross-sections where representative flows which drain different lithology and structures of Sierra del Rosario are located.
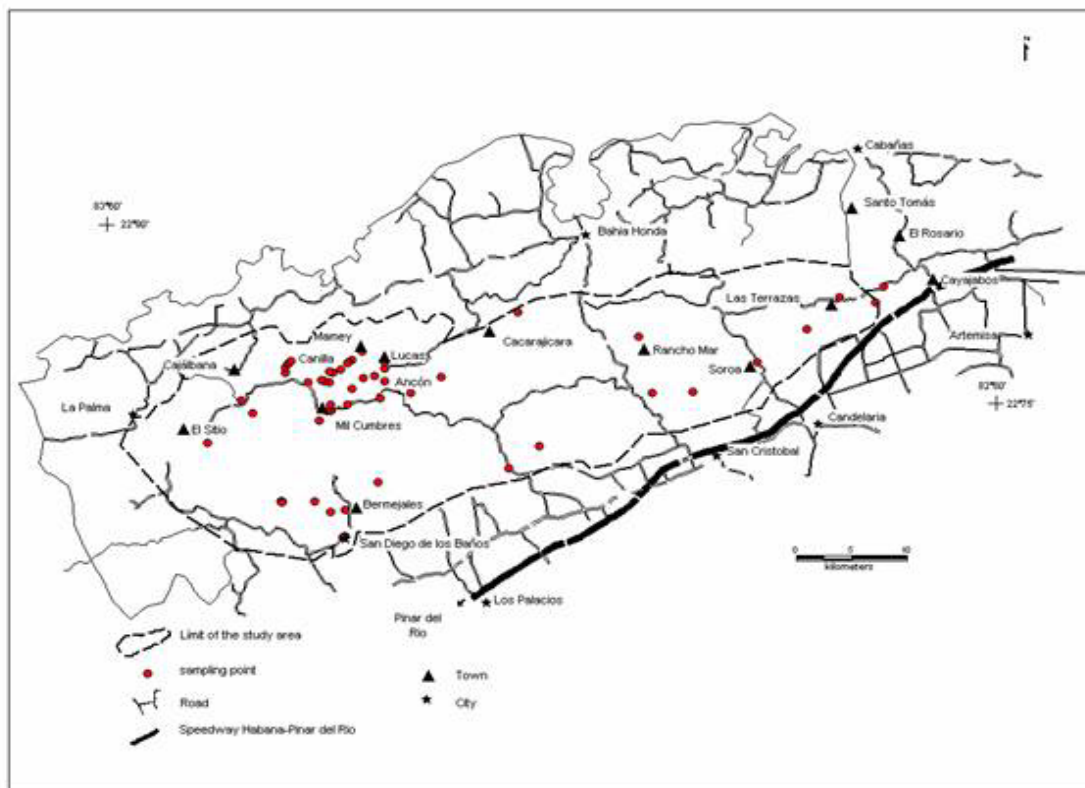

Figure 3. Location of the sampling points at Sierra del Rosario

Table 1. Groundwater flow groups and sub groups of Sierra del Rosario

Group	Geologic Formation	Lithology	Sub group	Flow	Travel	Source	No	N	TSS
1	Manacas Fm.	Schist, sandstone and limestone	1	LF	Short	Streams and wells	1-2	5	134
			2	LF	Medium	Streams and springs	3-4	31	412
2	Ofiolític Association	Serpentinite	1	LF	Short	Streams	5-9	17	329
3	Guajaibón Fm.	Massive limestone	1	LF	Short	Caves	10-13	21	240
			2	LF	Short	Springs	14-18	14	366
			3	LF	Short	Karstic springs	19-23	94	298
4	Sierra Azul, Lucas and Cacarajícara Fms.	Stratified limestone, clacilutit and calcarenit	1	LF	Short	Karstic springs	24-27	6	454
			2	IF	Medium	Springs	28	1	696
5	Artemisa Fm.	Stratified limestone	1	LF	Short	Karstic springs and wells	29-40, 30A	37	479
			2	LF	Short	Resurgences	41-42	6	306
6	Artemisa Fm.	Stratified limestone	1	IF	Medium	Springs and wells	43-47	25	622
7	Artemisa Fm.	Limestone and mix with other litholoy	1	IF	Medium	Springs and wells	48-52	9	743
8	San Cayetano Fm.	Schist and sandstone	1	LF	Short	Wells	53	1	345
			2	IF	Medium	Springs and wells	54-56	11	1284
9	Artemisa Fm. (deep drainage with longer residence timet)	Limestone, schist and sandstone, ultramafic rocks	1	RF	Large and deep	Springs and wells	57-72	75	2237

LF: Local flow; IF: Intermediate flow; RF: Regional flow.

With the aim to study the physico-chemical behavior of the waters that drain the different lithologies of Sierra del Rosario, the samples were distributed to groups and sub-groups as follow:

Group 1. Springs and wells which drain sediments of Manacas Fm.

Sub-group 1: Local flows with short flow path.

Sub-group 2: Local flows with longer flow path.

Group 2. Springs and streams which drain ultramafic rocks of the Ophiolitic Association (local flows).

Group 3. Waters which drain carbonate rocks of Guajaibón Fm.

Sub-group 1: Infiltration waters at the caves (local flows).

Sub-group 2: Karstic springs from the recharge zone Sierra del Pan de Guajaibón (local flows).

Sub-group 3: Karstic springs (surgences, resurgences and springs) from the discharge zone of Sierra del Pan de Guajaibón (local flows).

Group 4. Karstic springs which drain carbonate rocks of Sierra Azul and Cacarajícara Fms.

Sub-group 1: Local flows which drain limestone of Sierra Azul Fm.

Sub-group 2: Intermediate flows which drain limestone of Sierra Azul and Cacarajícara Fms.

Group 5. Springs and streams which drain limestone of Artemisa Fm (local flows).

Sub-group 1: Springs.

Sub-group 2: Streams sampled near karstic resurgences.

Group 6. Springs which drain limestone of Artemisa Fm (intermediate flows).

Group 7. Springs which drain different lithologies (intermediate flows): limestone (Artemisa Fm), schist and sandstone (San Cayetano Fm), and ultrabasic rocks (Ophiolitic Association).

Group 8. Local and intermediate flows which drain schist and sandstone of San Cayetano Fm.

Sub-group 1. Borehole in the shallow drainage (local flows).

Sub-group 2. Springs and wells (intermediate flows).

Group 9. Regional flow from the deep drainage of Artemisa Fm, which drains limestone and interacts with schist and sandstone (San Cayetano Fm) and ultrabasic rocks (Ophiolitic Association).

The general hydrogeochemical features of the depicted groups are the following:

Group 1, is represented by local flow draining unconfined aquifers constituted by schist and sandstone of the Manacas Formation (Table 3, No 2 and 3). These waters are characterised by low temperature (23.8±3.3 oC), are slightly alkaline (pH, 7.72±0.40), have relatively low CO_2 (2.3±2.0 mg/l), low chloride (19.8±5.1 mg/l), low sulfate (7.7±9.0 mg/l) and moderate total dissolved solids (TDS) contents (373±137 mg/l). The defined hydrochemical facies is Ca>Na-HCO3 (Figure 5, sample 2). The ionic relationships are homogeneous, showing the presence of two well differentiated subgroups: the flows of the sub-group 1 are subsaturated with regard to the calcite (CSR) and the dolomite (DSR) while the flows of the sub-group 2 tend to the saturation with regard to both minerals (Figure 6.1). With regard to gypsum both flows are unsaturated.

Table 2. Main geochemical process which explain the origin of the waters chemical composition at Sierra del Rosario

Geochemical processes and formulation
1. Halite dissoluiión – precipitation $\underline{NaCl}$ (s) = Na^+ (ac) + Cl^- (ac) Halite
2. Calcite dissoluiión – precipitation CO_2 (g) + H_2O (l) + $\underline{CaCO_3}$ (s) = Ca^{2+} (ac) + 2 HCO_3^{2-} (ac) Calcite
3. Dolomite dissoluiión – precipitation 2 CO_2 (g) + 2 H_2O (l) $\underline{+ CaMg(CO_3)_2}$ (s) = Ca^{2+} (ac) + Mg^{2+} (ac) + 4 HCO_3^{2-} (ac) Dolomite
4. Serpentinite weathering 12 CO_2 (g) + 10 H_2O (l) + $\underline{Mg_6Si_4O_{10}(OH)_8}$ (s) = 6 Mg^{2+} (ac) + 4 H_4SiO_4 (ac) + 12 HCO_3^{2-} (ac) Serpentinite

5. Plagioclase weathering: (x $NaAlSi_3O_8$ + y $CaAl_2Si_2O_8$) = $Na_ACa_BAl_CSi_DO_8$
 	
                Albite   Anorthite   Plagioclase
(x+y) $\underline{Na_xCa_yAl_{x+2y}Si_{3x+2y}O_8}$ (ac) + (x+2y) CO_2 (g) + (11/2x+3y) H_2O (l) = x Na^+ + y Ca^{2+} (ac) + (x+2y) HCO_3^- (l) + 2x H_4SiO_4 (ac)
Plagioclase
                                      + (x/2 + y) $\underline{Al_2Si_2O_5(OH)_4}$ (s) (x = moles de Na^+; y = moles de Ca^{2+})
                                         Kaolinite

6. K-Feldspar weathering 2 $\underline{KAlSi_3O_8}$ (s) + 2 CO_2 (g) + 11 H_2O (l) = 2 K^+ (ac) + 2 HCO_3^- (ac) + 4 H_4SiO_4 (l) + $\underline{Al_2Si_2O_5(OH)_4}$ (s)   K-Feldspar (microcline)   Kaolinite
7. Pyrite oxidation and   8. Sulphate reduction by the action of bacteria 2 $\underline{FeS_2}$ (s)+ 7 O_2 (g) + 8 HCO_3^- (ac) = 2 $\underline{Fe(OH)_2}$ (s) + 4 SO_4^{2-} (ac) +8 CO_2 (g) + 2 H_2O (l);   2 CH_2O (ac) + SO_4^{2-} (ac) = H_2S (g) + 2 HCO_3^- (ac) Pyrite   Hematite   Organic material

9. Quartz dissolution – precipitation
  SiO_2 (s) + 2 H_2O (l) = H_4SiO_4 (ac)
  Quartz

Table 3. Mean chemical composition of water samples from Sierra del Rosario

No	N	Group	Sub Group	T °C	Eh mv	O$_2$ mg/l	pH	CO$_2$ mg/l	SiO$_2$ mg/l	H$_2$S mg/l	HCO$_3^-$+CO$_3^{2-}$ mg/l	Cl$^-$ mg/l	SO$_4^{2-}$ mg/l	Ca^{2+} mg/l	Mg^{2+} mg/l	Na$^+$ mg/l	K$^+$ mg/l	TDS mg/l	Ref
1	4	RW		22.2			7.04	2.2	0	0	12.2	5.7	0.0	0.8	4.5	4.8	0.5	24	1
2	5	1	1	24.5			7.39	4.7	8.6	0	84.6	12.1	2.9	15.5	3.8	15.0	0.5	133	1
3	31		2	23.1			7.78	1.9	14.7	0	277.6	21.0	8.4	54.4	10.7	37.4	1.3	412	1
4	17	2		23.3	156	8.4	8.35	2.3	18.8	0	236.2	16.6	8.9	5.2	44.7	15.4	0.4	329	1
5	21	3	1	21.7			8.17	1.4	7.4	0	156.4	16.8	5.4	47.0	4.2	10.2	0.2	240	1
6	14		2	22.1			7.62	9.7	4.6	0	256.7	15.0	2.6	68.8	6.9	15.5	0.2	366	1
7	94		3	22.7			7.54	8.2	4.5	0	197.2	15.2	10.1	55.9	5.4	14.0	0.4	298	1
8	6	4	1	23.1			7.11	41.5	5.9	0	280.1	20.0	16.7	79.4	8.5	18.6	0.6	424	1
9	2		2	25.8	-174	5.5	7.02	50.3	12.1	8.1	364.6	30.3	67.0	101.4	12.3	48.3	1.5	625	1
10	35	5	1	23.3	-238	1.6	7.32	24.5	5.1	0	309.5	17.9	34.1	92.8	6.6	22.9	0.7	486	1,2
11	4		2	19.2	91.7	5.7	8.52	0.0	4.1	0	174.7	14.6	20.2	65.3	6.2	9.3	0.0	306	1
12	28	6		24.6	-228	1.2	7.18	61.0	11.3	9.2	395.7	37.8	30.5	110.9	13.9	32.5	1.1	622	1
13	9	7		26.3	-327	1.8	7.35	40.1	34.6	56.2	493.5	25.7	22.8	83.6	31.2	56.5	1.7	715	1,2
14	1	8	1	25.0			8.00	0.0	12.0	0	192.6	17.0	34.6	8.0	3.7	86.0	2.7	345	2
15	12		2	27.8	-317	1.2	8.04	20.0	26.6	67.7	742.4	125.3	86.5	36.9	17.3	317.5	9.8	1336	1,2
16	93	9		38.9	-300	2.5	7.25	42.7	22.0	26.0	245.2	37.5	1300	456.6	50.9	119.2	5.6	2209	1,2,3

1): Rain water, RW; **2)**: Springs and wells which drain Manacas Fm (local flows with short flow path): Arroyo La Sed spring; Minero well; **3)** Springs and streams which drain Manacas Fm (local flows with longer flow path): Mamey ponor; Fluoresceina spring; **4)** Springs and streams which drain rocks of the Ophiolitic Association (local flows): Cajalbana 1 spring; Cajalbana 2 spring; Cajalbana 3 spring; Cajalbana 4 spring; Cajalbana 5 spring; **5)** Infiltration waters at the caves of Guajaibón Fm: Lechuza cave; Mamey cave; Ancón cave; Canilla cave; **6)** Karstic springs from the recharge zone of the Guajaibón Fm (local flows): Macagua spring; Cuchillas de Sagua spring; Mamey spring; Mineros spring; Conuco de la Bija spring; **7)** Karstic springs from the discharge zone of Guajaibón Fm (local flows): Canilla resurgence; Ancón surgence; Ancón 2 resurgence; Fernado spring; La Curra spring; **8)** Springs which drain limestone of Sierra Azul Fm. (local flows): Lucas 1 sprimg; Lucas 2 spring; Lucas 3 spring; Cacarajícara no Sulfuroso spring; **9)** Springs which drain Sierra Azul and Cacarajícara Fms (intermediate flows): Cacarajícara sulfuroso spring; **10)** Shallow springs which drain limestone of Artemisa Fm (local flows): Caimito spring; Mil Cumbres no sulfuroso spring; El Perdido (El Sitio) spring; Kíquere spring; Recogedor spring; Batea spring; San Marcos spring; Cuatro Caminos spring; Julio Carmona spring; Majagua spring; San Juan no Sulfuroso spring; P-2 (90 m) well; P-3 (173 m) well; **11)** Streams which drain Artemisa Fm (local flows): Taco Taco resurgence; Bacunagua resurgence; **12)** Springs from the deep drainage of the Artemisa Fm (intermediate flows): La Pastora spring; Pedernales spring; Pedernales well; El Brocal well; San Juan Sulfuroso spring; **13)** Springs which drain different lithologies (intermediate flows): P-13 well; Pozo Azul spring; Martín Mesa spring; Soroa spring; El Sitio well; **14)** Borehole in the shallow drainage of San Cayetano Fm (local flows): P-3 (40 m) well; **15)** Springs which drain San Cayetano Fm (intermediate flows): Mil Cumbres sulfuroso spring; P-4 well; Rancho Mar spring; **16)** Springs from the deep drainage of the Artemisa Fm intercepting sandstone and ultramafic rocks (regional flows): Azufre (Sal y Cruz) spring; El Tigre spring; El Templado spring; La Gallina spring; M-1 Bermejales spring; Cueva Portales spring; P-1 spring; P-12 spring; P-17 well; P-19 well; P-4 (145-195 m) well; P1 (0-23 m) well; P1 (0-122 m) well; P1 (120-200 m) well; P1 (120-281 m) well; P1 (237-320 m) well. **Ref**: Bibliographic references 1) Fagundo et al., 1997; 2) Peláez et al., 1990; 3) González et al., 2000.

The local flows of group 1, possess hydrochemical facies of the sodium calcium hydro carbonate hydrocarbonate type. (No 1 and 2, table 4). The more typical ionic relationships are: $r\dfrac{Ca^{2+}}{Mg^{2+}}$, $r\dfrac{Na^{+}}{Ca^{2+}}$ and $r\dfrac{Na^{+}}{Mg^{+}}$. The chemical composition of the waters of this group, can be originated by the geochemical processes of calcite and dolomite or plagioclase (anorthite, albite, microcline) and serpentinite dissolution using biogenic CO_2. Although the first two minerals are more soluble at low temperatures and they are usually very distributed in the covering sediments, the sandstone of the referred formations are rich in aluminium-silicates. Other processes, such as pyrite oxidation, quartz dissolution and ionic exchange also contribute in the process of acquisition of the chemical composition of this water (Table 5).

Group 2, local flow draining unconfined ultra-basic rocks of the Ophiolitic Association (Table 3, No 4). It is distinguished by a low temperature (23.3±1.2 ^{o}C), high pH (8.35±0.44); low CO_2 (2.3 ±3.4 mg/l), low chloride (16.6±2.5 mg/l), low sulfate (8.9±12.8 mg/l) and moderate TDS concentrations (307±50 mg/l). This water is oxidizing (Eh, 156 mV and 8.4 mg/l of dissolved O_2 content) and has a Mg-HCO_3 hydrochemical facies (Figure 5). These waters reach the chemical equilibrium in the course of their journey (Figure 6.2) with regard to the serpentine (expressed in dolomite terms, DSR), but not with regard to the calcite (CSR) and the gypsum given the little availability of these minerals in the rocks.

These waters that drain the ultramafic massifs, form an homogeneous group of magnesium hydrocarbonate composition (No 2, table 4). Typical ionic relationships are: $r\dfrac{Mg^{2+}}{HCO_3^{-}}$ and $r\dfrac{Na^{+}}{Ca^{2+}}$. The origin of its chemical composition is explained by means of processes of serpentine dissolution, pyrite oxidation and consumption of biogenic CO_2 and SiO_2 dissolution (No 1, table 5). Like the rest of the flows of local character, these waters present oxidizing conditions and they possess relatively high contents of dissolved oxygen.

Group 3, is represented by local flow, which drain unconfined aquifer materials (upper-vadose and discharge karst zones) constituted by limestone of the Guajaibón Formation. This group includes water collected in caves (sub-group 1) resulting from percolation through limestone (Table 3, No 5) and karstic springs (sub-group 2, No 6, and sub-group 3, No 7). The cave waters have low temperature (21.7±1.2 ^{o}C), high pH (8.17±0.16) and low CO_2 content (1.4±1.7 mg/l), but spring waters have lower pH (7.62±0.35 - 7.54±0.34) and higher CO_2 content (4.7±6.9 - 8.2±6.5 mg/l). The chloride concentration is low in these waters (sub-group 1: 16.8±3.8 mg/l; sub-group 2: 15.0±3.0 mg/l; sub-group 3: 15.2±3.9 mg/l), as well as sulfate contents (sub group 1: 5.4±4.9 mg/l; sub group 2: 2.6±3.4 mg/l; sub group 3: 10.3±9.1 mg/l). Consequently TDS concentration is low (240±44 mg/l, 366±81, 298±47 respectively). The hydrochemical facies is Ca-HCO3 (Figure 5). The cave waters tend to be closer to chemical equilibrium with regard to the calcite (CSR) and the dolomite (DSR) than the karstic spring waters (Figure 6.3). With regard to the gypsum (GSR) all the waters are unsaturated.
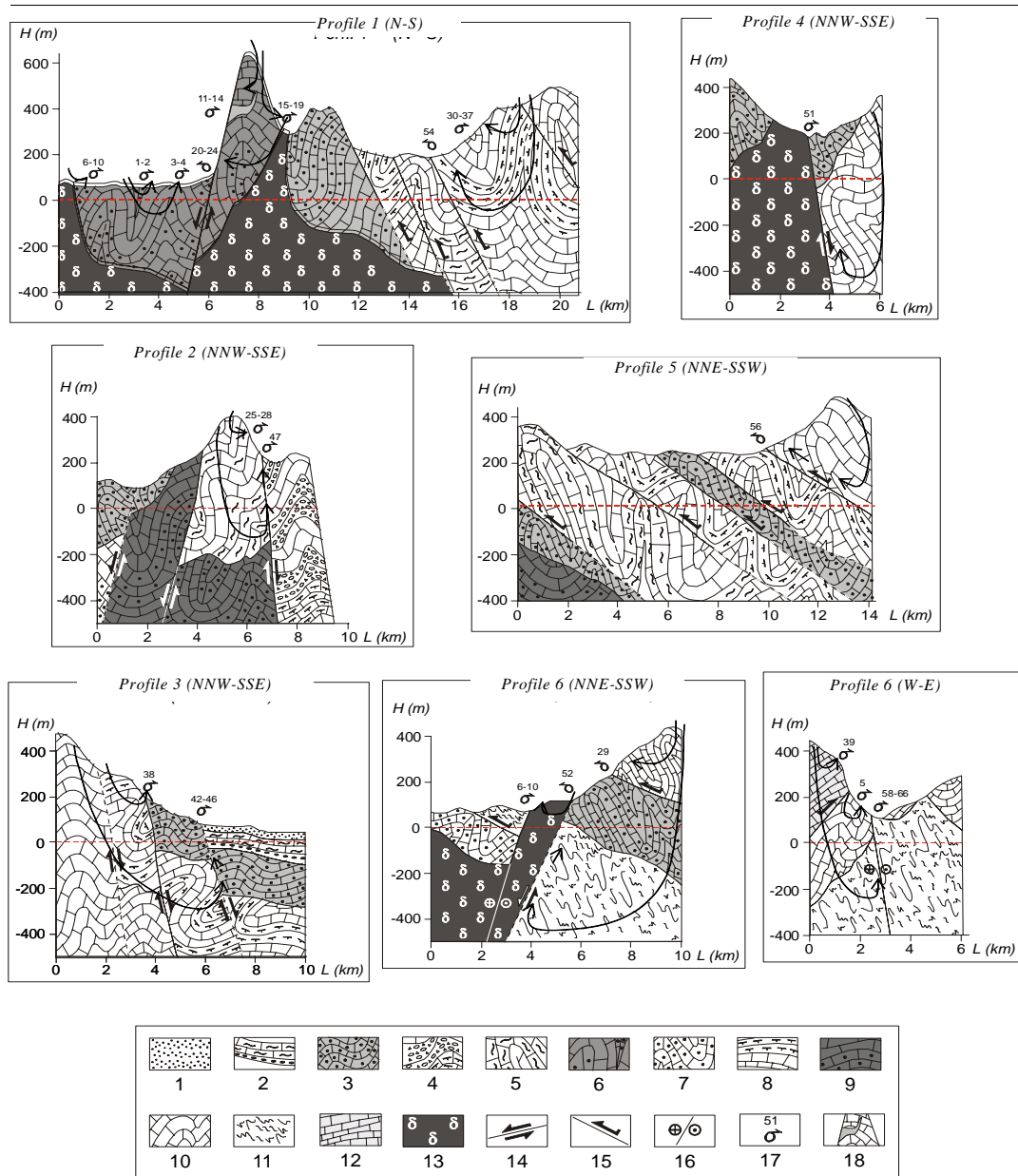
Legend: 1. Quaternary deposits constituted by sands, clays and gravels (Q); 2. Marls, conglomerates and sandstone from Lower and Middle Miocene (N_1^{1-2}); 3. Limestone and sandstone from Paleocene - Eocene (P_{1-2}); 4. Calcareous breccia and argillites from Upper Cretaceous (K_2); 5. Marls and limestone from Upper Cretaceous (Maastrichtian) (K_2 m); 6. Sandstone and limestone from Upper Cretaceous (Cenomanian - Turonian) (K_2 cm-t); 7. Sandstone from Lower - Upper (Albian - Cenomanian) (K_{1-2} al-cm); 8. Limestone and argillites from Lower Cretaceous (Aptian - Albian) (K_1 a-al); 9. Limestone and sandstone from Lower Cretaceous (Berriasian - Barremian) (k_1 b-bm); 10. Limestone from Upper Jurassic - Lower Cretaceous (J_3-K_1); 11. Schist, quartzite and sandstone from Lower - Upper Jurassic (Oxfordian) (J_1-J_3 ox); 12. Limestone from Upper Jurassic (Oxfordian - Thitonian) (J_3 ox-t); 13. Serpentinites, pyroxenes, peridotites and serpentinized dunites of the northern ophiolític complex; 14. Neotectonic fault of vertical displacement. 15. Orogenic and pre-oceanic overthrust; 16. Fault of horizontal displacement. 17. Sampling points. 18. Cavernary system.

Figure 4. Stratigraphic columns of the selected geological cross - sections at Sierra del Rosario (See Figure 2).
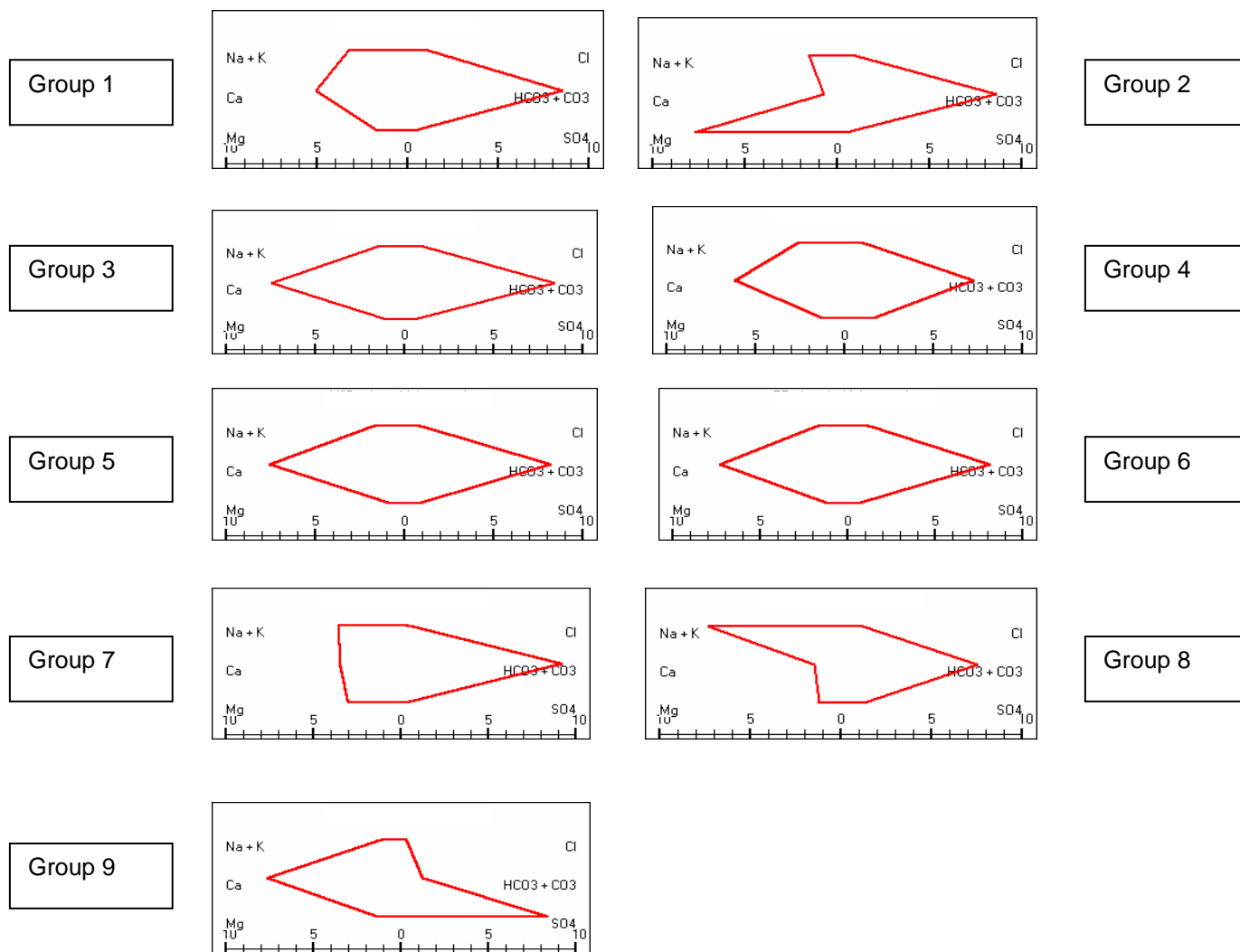
Figure 5. Hydrogeochemical patterns of some representative samples: Group 1, LF: Mamey stream (Ca>Na-HCO$_3$); Group 2, LF: Cajalbana 1 stream. (Mg-HCO$_3$); Group 3, LF: Ancon spring (Ca-HCO$_3$); Group 4, IF: Cacarajicara sulfuroso spring (Ca>Na-HCO$_3$, H$_2$S); Group 5, LF: Mil Cumbres (Ca-HCO$_3$); Group 6, IF: Pedernales well (Ca-HCO$_3$, H$_2$S); Group 7, IF: El Sitio well (Na>Ca>Mg-HCO$_3$); Group 8, IF: Mil Cumbres sulfuroso spring (Na>Ca>Mg-HCO$_3$, H$_2$S); Group 9, RF: la Gallina spring (Ca-SO4, H$_2$S).

The local flows that drain the limestone massive of the Guajaibón Formation present Ca-HCO$_3$ hydrochemical facies whose ionic relationships are homogeneous between them (Table 4). The more typical ionic relationships are: $r\dfrac{Ca^{2+}}{Mg^{2+}}$ and $r\dfrac{Ca^{2+}}{HCO_3^{-}}$.

The chemical composition of this water is explained by means of processes of calcite and dolomite dissolution, pyrite oxidation, consumption of CO_2 in ground, SiO_2 dissolution and ion exchange (Table 5).

These characteristics are similar for all carbonate aquifers (Groups 3, 4, 5, 6)

Group 4, is mainly local flow, which drain unconfined aquifer materials constituted by limestone of Sierra Azul Formation and by breccias and calcareous sandstone of the Cacarajícara Formation. The shallower waters (Table 1, No 8) have low temperature (23.1±0.8 ^{o}C), the pH is near to neutral (7.11±0.42), but the CO_2 content is high (41.5±12.0 mg/l). This flow has low chloride content (20.0±5.8 mg/l), low sulfate content (24.7±24.0) and moderate TDS concentration (492±143 mg/l). These waters have negative redox potential (Eh between -63 to -80 mV and high dissolved O2 content (5.3-7.7 mg/l). The deeper waters (No 9), which interact with the Cacarajícara Formation, intermediate flow, have higher values of all the physical and chemical parameters (Table 3) and contain H2S. The hydrochemical facies is Ca-HCO3 at the higher and Ca>Na-HCO3 (Figure 4) at the lower part of the aquifer. The behavior of the values of CSR, DSR and GSR (Figure 6.4) is similar to that of the subgroup of the karstic springs of the Guajaibón Formation (Group 3).

These waters that drain shallowly the massive limestone of the Sierra Azul Formation (Table 1), they constitute a homogeneous group of Ca-HCO3 hydrochemical facies with ionic relationships in the same order of the Guajaibón Formation (Table 4). They are distinguished from the previous ones for presenting a relatively high content of CO2 and a lower pH. The processes that explain their chemical composition are also similar (Table 5).

Group 5, is local flow, which drain unconfined aquifer materials constituted by limestone of the Artemisa Formation (Table 3, No 10 and 11). Its water processes similar properties to that of the Groups 3 and 4 (draining also carbonated rocks). Spring waters (No 10) have low temperature (23.3±1.3 ^{o}C), slightly neutral pH (7.32±0.40), moderate CO_2 content (24.5±17.8 mg/l), low chloride content (17.9±4.2 mg/l), low sulfate content (34.1±17.4 mg/l) and moderate to relatively high TDS concentration (486±78 mg/l), and the similar ionic relationships. The Eh of these waters is from -91.7 to -238.9 mV and have a high dissolved O_2 content of 1.6 to5.7 mg/l. The hydrochemical facies is Ca-HCO$_3$ (Figure 5). Stream waters sampled near karstic resurgences (No 11) posses similar characteristic but the pH is higher (8.52±0.20) and the TDS lower (306±22 mg/l). In general, the waters coming from springs (sub-group 1) tend to reach the chemical equilibrium with regard to the calcite (CSR) and dolomite (DSR), while those that emerge through big conduits (resurgence, sub-group 2) are usually oversaturated with respect to calcite (Figure 6.5). This different behavior is related with biggest the escape of the CO_2 dissolved in the water in the second sub-group. With regard to the gypsum all the waters are unsaturated.

The local flows that drain the stratified limestone of the Artemisa Formation (Table 3) possess similar properties to the groups 3 and 4, those that drain also carbonated rocks. This is manifested in the hydrochemical type (calcium hydrocarbonate) and the similar ionic relationships to the group 3 (table 4). The hydrogeochemical processes that originate the chemical composition of these waters are similar to those above explained for calcium hydrocarbonate waters (Table 5).
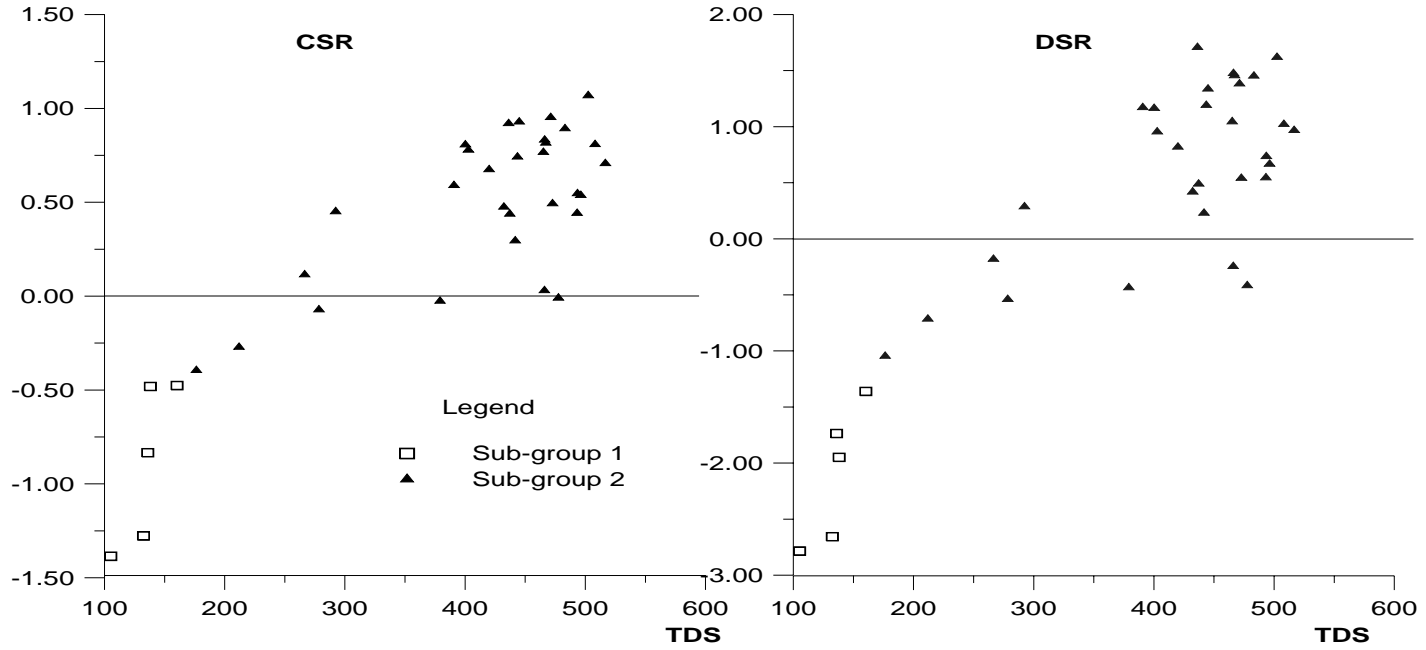
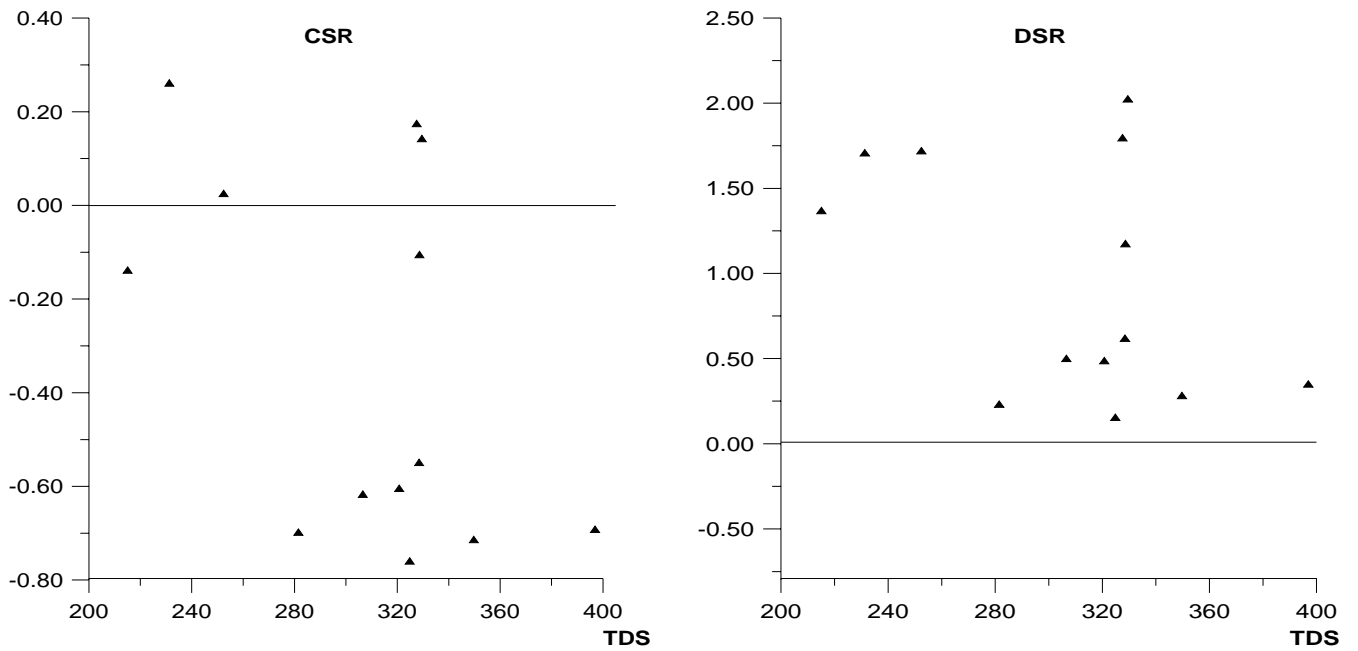Figure 6-1. CSR - TDS and DSR - TDS relationships (Group 1).

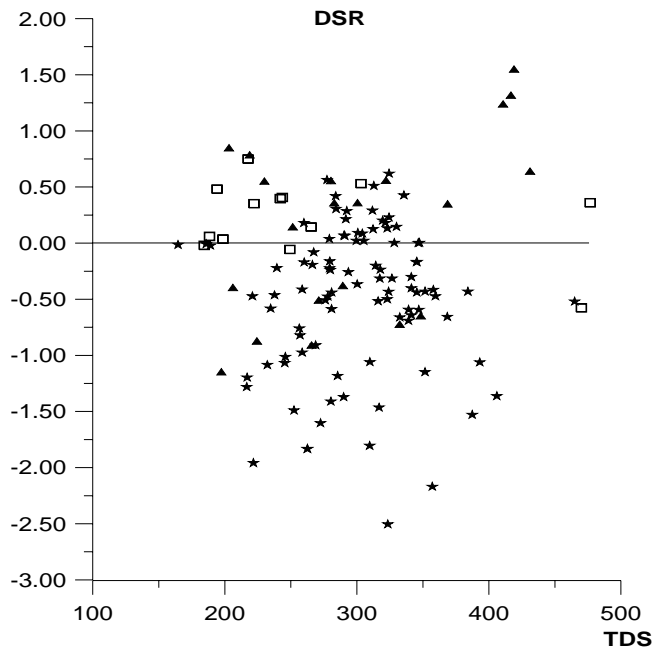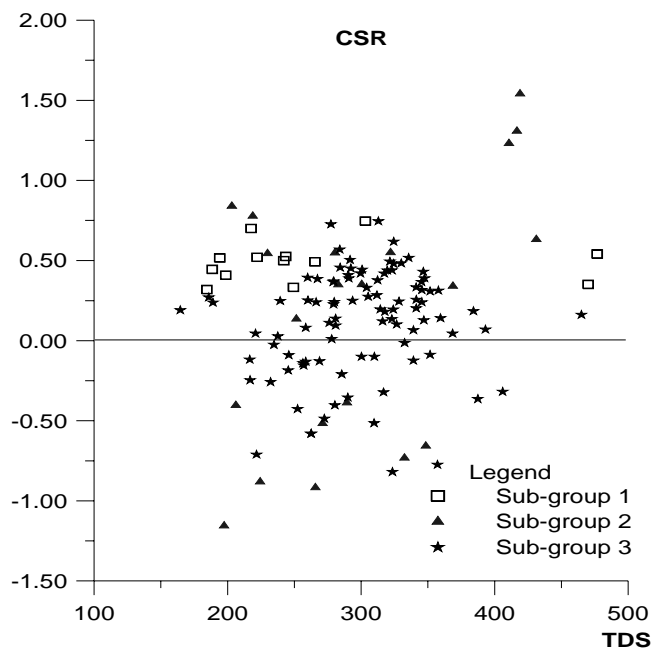Figure 6-2. CSR -TDS and DSR - TDS relationships (Group 2).

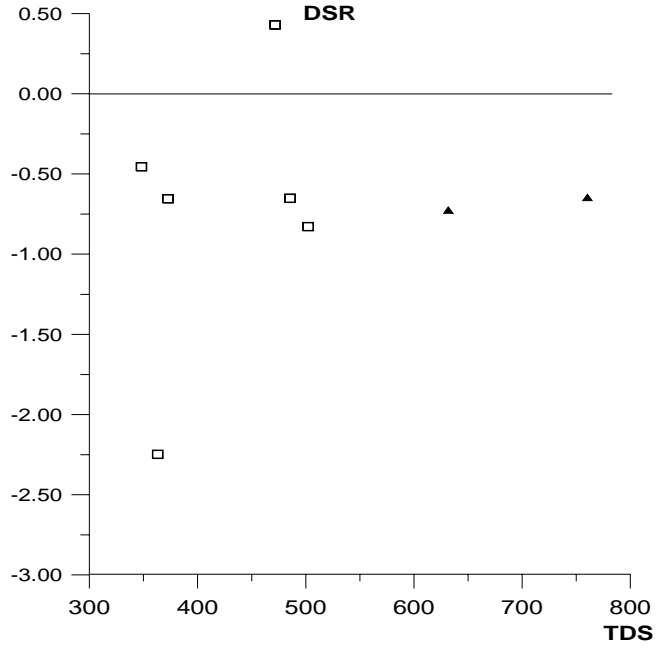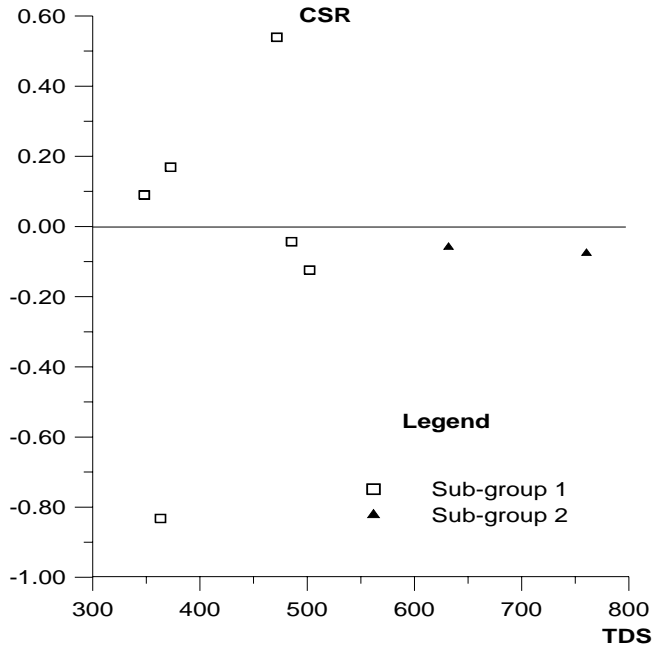Figure 6-3. CSR - TDS and DSR - TDS relationships (Group 3).

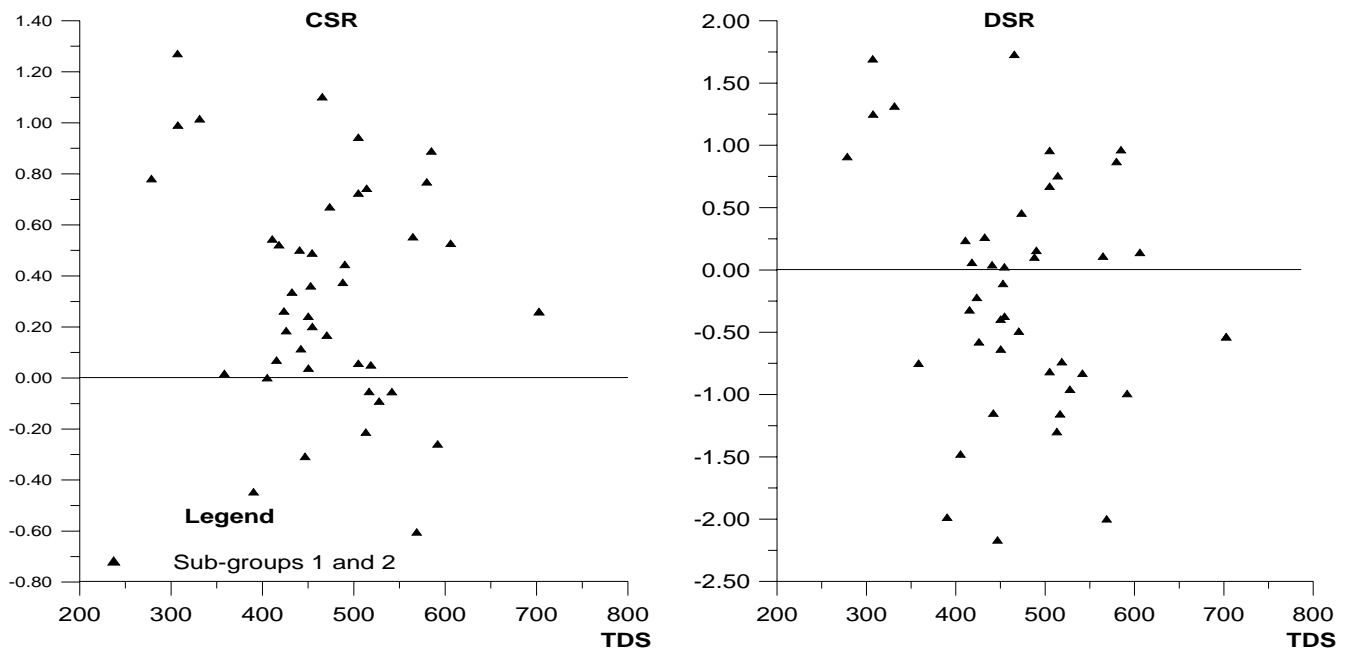Figure 6-4. CSR - TDS and DSR - TDS relationships (Group 4).

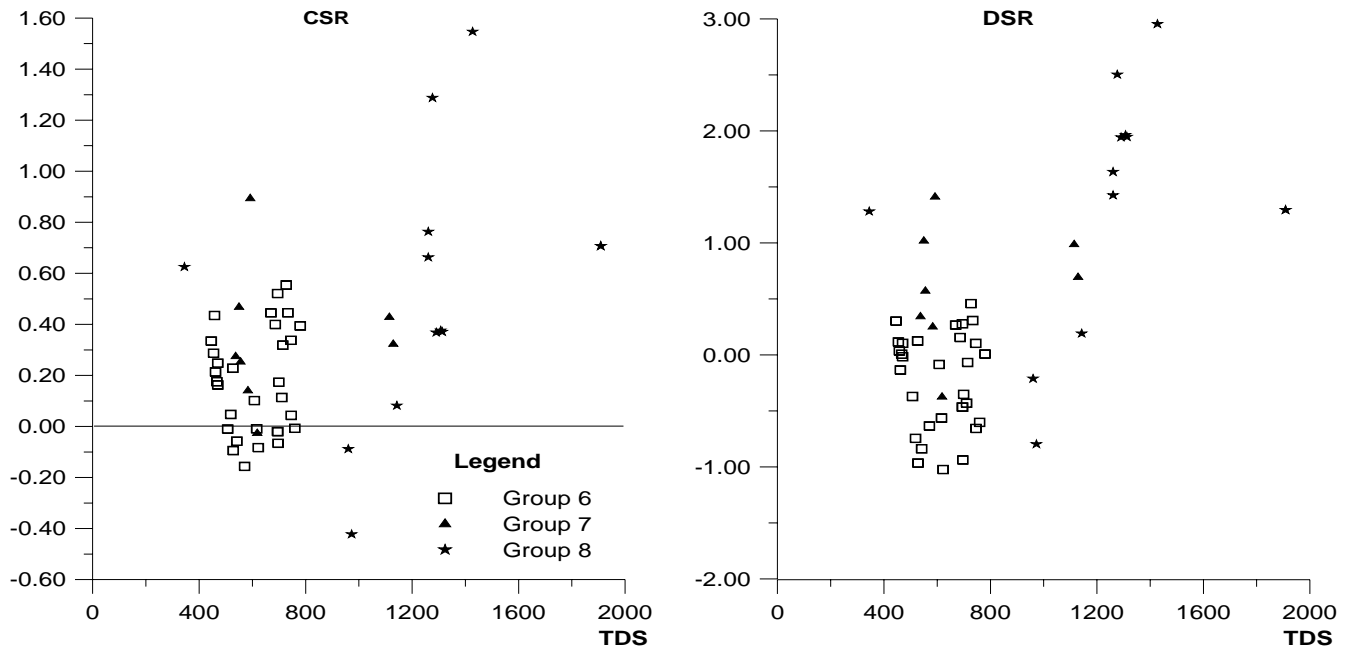Figure 6-5. CSR - TDS and DSR - TDS relationships (Group 5).

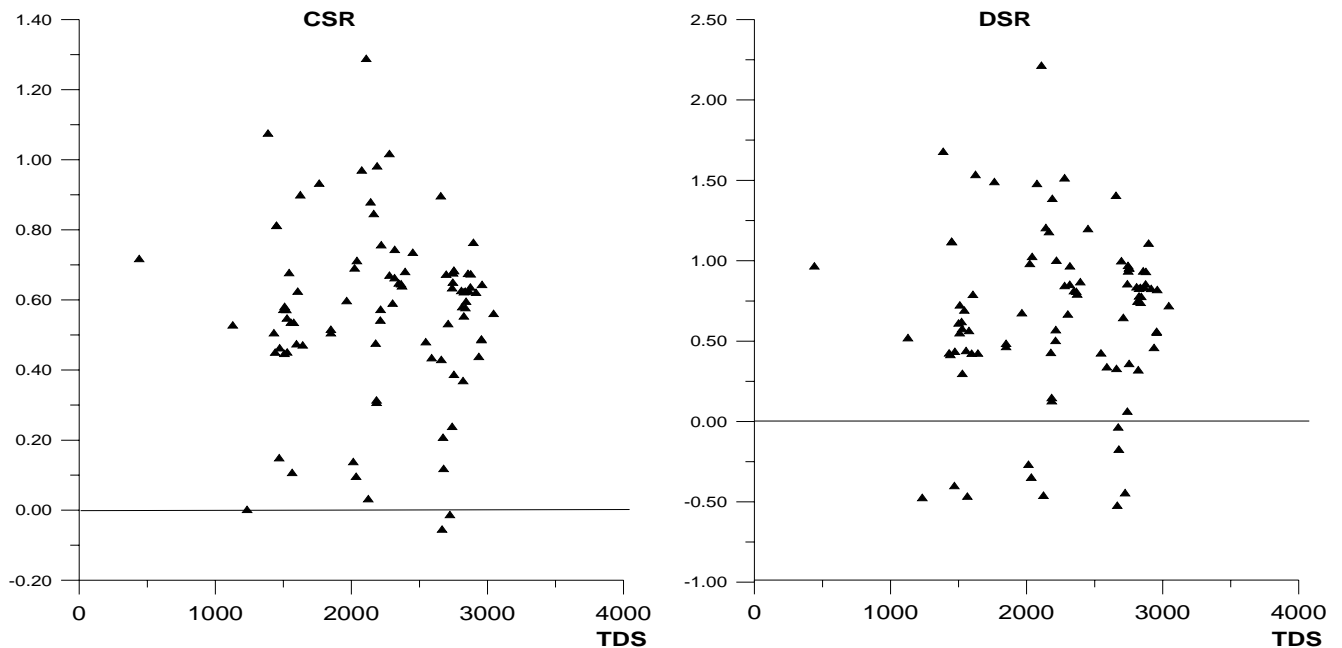Figure 6-6. CSR - TDS and DSR - TDS relationships (Groups 6, 7 and 8).

Figure 6-7. CSR - TDS and DSR - TDS relationships (Group 9).

Group 6, includes intermediate flows, which drain unconfined aquifer materials constituted by limestone of the Artemisa Formation (Table 3, No 12). These waters are associated to fractures originated by the Pinar fault and related transversal fractures and faults. The temperature of this groundwater is occasionally higher than the above study waters (24.6±1.6 ^{o}C), the pH is near neutrality (7.18±0.21), has a relatively high CO_2 content (61.0±30.2 mg/l), higher chloride (37.8±13.2 mg/l), sulfate (30.5±29.1 mg/l) and TDS concentration (622±115 mg/l) than the above. These waters have negative redox potential (-235 to -280 mv), low dissolved O_2 content (1.2-1.9 mg/l) and have a relatively high H_2S content (5.4-10.0 mg/l). The hydrochemical facies is Ca-HCO_3. This group is similar in its ionic relationships and hydrochemical type to the waters of the Group 5, although the magnitude of Ca/Mg is lightly smaller (indicative of a bigger presence of dolomite dissolution). It differs of Group 5 in the present of a larger content of chloride, the total of dissolved ions (TDS), as well as for the presence of H_2S. They tend to reach the equilibrium with regard to the calcite (CSR) and dolomite (DSR) (Figure 6.6), but they are unsaturated with regard to the gypsum.

This group corresponding to intermediate flows that drain limestone of the Artemisa Formation (Table 4). It is similar in their ionic relationships and hydrochemical type (Ca-HCO_3) to the waters of the group 3.

In the above studied waters the content of mean chloride is in the order of 16.3 mg/l, and for the mass balance, was assumed as conservative ion so to calculate the quantities of acquired masses for the water for each ion during weathering of the massif, the product of the concentration factor (for evapotranspiration) is multiplied by the mean composition of the water. In the case of the waters of the group 6, because this water possess a content of chloride higher than water of meteoric type, this ion is not taken as conservative, and the concentration factor is

the calculated as a mean of the composition of all the meteoric waters (Fc = 2.88). Applying this procedure, it was found that the ions in excess extracted by the water may be tied, in this case, to the processes of halite, calcite and dolomite dissolution, pyrite oxidation with partial reduction of sulphate, as well as to the processes of silica dissolution and consumption of CO_2 (Table 5). As the process of pyrite oxidation goes accompanied by the generation of CO_2, a part of the dissolved calcite could be formed for consumption of CO_2 of non-biogenic type.

The absence of gypsum in the silts of the carbonated and not carbonated Formations of the Rosario's Sierra, at least up to where the waters reach, suggests that the source of sulphate is pyrite that originates (after a reduction process) the H_2S. The relatively high content of this gas in the waters could be due to flows reaching the Pinar fault where they interact with the schist and sandstone of the San Cayetano Formation before arising for the springs. As referenced in the literature, the schist are rich in pyrite (Appelo and Potma, 1993). However, the limestone of the Artemisa Formation are fetid (they smell like sulfhydric acid when they are crushed) and they can have occluded H_2S, as it was demonstrated by Embil (1947).

Group 7, represents intermediate flows, which drain mainly limestone of Artemisa Formation, and also sandstone and ultramafic rocks of the Ophiolitic Association (Table 3, No 13). These waters have a relatively high temperature (26.3±2.1 ^{o}C), pH from neutral to alkaline (7.35±0.18), generally high CO_2 (40.1±14.4 mg/l) and H_2S contents (26.1-196.9 mg/l). The chloride (25.7±14.0 mg/l) and TDS (715±241 mg/l) of these waters are relatively high and the sulfate is moderate (22.8±14.8 mg/l). The waters show very high negative redox potential (-238 to -325 mV) and the dissolved O_2 content is low (1.2-2.7 mg/l). The hydrochemical facies (Figure 5) are of Mixed-HCO_3 type (Ca > Na-HCO_3, Ca>Mg-HCO_3 and Ca>Mg>Na-HCO_3). Their main cation composition is in proportion with the differentiated contribution of the sands, calcite and serpentine respectively. In the emergence they tend to be saturated with respect to the calcite (CSR) and the dolomite (DSR) (Figure 6.6) and unsaturated with respect to the gypsum.

The group 7 it is constituted by waters corresponding to intermediate flows that in their underground flow path interact with different lithologies: limestone, sandstone, serpentinite (Table 3). Their composition is of Mixed- HCO3 type (Table 4).

The origin of the chemical composition of these waters is shown in the Table 5. The processes that originate the composition are: halite, calcite and dolomite or serpentine dissolution (both minerals contribute equals proportions of HCO_3^- and Mg^{2+}) in the weathering of the rocks constituted by the corresponding minerals. Processes of pyrite oxidation also take place with partial reduction of sulphate.

Group 8, represents local and intermediate flows, which drain schist and sandstone of the San Cayetano Formation (Table 3, No 14 and 15). The local flow has relatively low temperature, high pH, low CO_2 content and low minerals dissolved. The waters of intermediate flow have a relatively high temperature (27.8±2.9 ^{o}C), alkaline pH (8.04±0.7), generally low CO_2 (20.0±19.8 mg/l) and high H_2S contents (21.6-87.0 mg/l). The chloride (125±67.1 mg/l), sulfate (86.5±49.4 mg/l) and TDS (1336±300 mg/l) of these waters are higher than the above. The waters show very high negative redox potential (-238 to -325 mV) and the dissolved O_2 is low (1.2-2.7 mg/l). The hydrochemical facies are Na-HCO_3 and Na>Cl-HCO_3 (Figure 5). Waters of the intermediate flow fundamentally come from larger depths, where the water extracts the sodium from the aluminosilicate minerals due to the relatively high temperatures reached in its descent (Figure 4, cross-sections 6 and 7). In similar form they also acquire high contents of SiO2 (Table 3). As in the previous case, the waters tend to the saturation or oversaturation with respect to the calcite (CSR) and the dolomite (DSR) (Figure 6.6) and to the unsaturation with respect to the gypsum, that is indicative of a not very accented effect of the hydrological cycle on these waters.

This group it is integrated by waters of the type Na-HCO3 or Na>Cl-HCO3, which fundamentally drain the schist and sandstone (San Cayetano Formation) up to larger depths, where the water extracts the Na^+ from the aluminosilicate minerals due to the relatively high temperatures reached in its descent (Table 3). In similar form they also acquire high contents of SiO_2. The more typical ionic relationships are: $r\dfrac{Na^+}{Ca^{2+}}$, $r\dfrac{Na^+}{Mg^+}$, $r\dfrac{Na^+}{HCO_3^-}$, $r\dfrac{Ca^{2+}}{Mg^{2+}}$ and $r\dfrac{SO_4^{2-}}{Ca^{2+}}$ (Table 4).

The origin of these waters is related with the processes of incongruous dissolution of plagioclases (albite, anorthite), microcline and silica, accompanied by the processes of pyrite oxidation with partial reduction of sulphate (Table 5). The plagioclase is $Na_{0.9}Ca_{0.1}Al_{1.1}Si_{2.9}O_8$.

Group 9, represents intermediate and regional flows, which drain confined aquifer materials whose waters interact with limestone of the Artemisa Formation and schist and sandstone of the San Cayetano Formation (Table 3, No 16). These flows are associated to the Pinar and San Diego faults. These waters have relatively high temperature (38.9±6.3 ^{o}C) and their pH is near to neutrality (7.25±0.28). Their gas content is relatively high (CO_2, 42.7±13.0 mg/l; and H_2S, 7.9-38.5 mg/l). Their chloride content is high (37.5±11.3 mg/l), and the sulfate (1300.2±449.4 mg/l) and TDS (2209 ±607 mg/l) contents are the highest found at the Sierra del Rosario. The Eh value is highly negative (-254 to -325 mV) and the O_2 dissolved contents is low (2.1-2.7 mg/l). The hydrochemical facies are $Ca-SO_4$ and $Ca-SO_4>HCO_3$ (Figure 5). these waters tend to the saturation or oversaturation with respect to the calcite (CSR) and the dolomite (DSR) (Figure 6.7) and are near the saturation with respect to the gypsum. The thermal waters which emerge near the Pinar fault possess relatively appreciable contents of chloride, fluoride, lithium, strontium and these contents are larger in San Diego de los Baños springs (SPA) than in Bermejales springs, suggesting that the latter correspond to long and deeper flow path of the Sierra del Rosario. This appreciation is coherent with the obtained results using chemical geothermometers

This group is quite homogeneous; it is constituted by intermediate and regional flows that drain the limestone of the Artemisa Formation, in occasions under confined conditions, also contacting the sandstone and ultramafic rocks (Figure 2).

In their underground flow path these flows reach large depths with relatively high temperatures, and acquire high contents of chloride, sulphate, magnesium, sodium and potassium.

The springs that emerge in this place also possess relatively appreciable contents of Cl, F, Li, Sr and Rn, suggesting that they correspond to flows of long and deeper underground flow path, with larger contents in the waters that emerge at San Diego de los Baños than in those emerging at Los Bermejales. This appreciation is coherent with the obtained results using chemical geothermometers (Fagundo et al., 2001). The hydrochemical facies present are: $Ca-SO_4$, $Ca-SO_4>HCO_3$ and $Ca>Na-SO_4$. Their ionic relationships correspond with this composition (Table 3):

$r\dfrac{SO_4^{2-}}{HCO_3-}$, $r\dfrac{Ca^{2+}}{Mg^{2+}}$ and $r\dfrac{Ca^{2+}}{HCO_3^-}$.

Table 4. Ionic relationships and hydrochemical facies of waters at Sierra del Rosario.

No.	N	Ca/Mg	Na/Ca	Na/Mg	SO$_4$/Ca	Cl/Na	Cl/HCO$_3$	SO$_4$/HCO$_3$	Ca/HCO$_3$	Mg/HCO$_3$	Na/HCO$_3$	Tipo de agua
1	5	4.0	1.0	3.4	0.1	0.5	0.3	0.1	0.6	0.2	0.5	Ca>Na-HCO3
2	31	3.3	0.7	2.1	0.1	0.4	0.1	0.0	0.6	0.2	0.4	Ca>Na-HCO3
3	17	0.1	4.5	0.2	0.9	0.4	0.1	0.0	0.0	1.0	0.2	Mg-HCO$_3$
4	21	8.1	0.2	1.8	0.1	0.4	0.2	0.1	0.9	0.1	0.2	Ca-HCO3
5	14	8.6	0.2	1.5	0.0	0.4	0.1	0.0	0.8	0.1	0.2	Ca-HCO3
6	94	7.1	0.2	1.6	0.1	0.4	0.1	0.1	0.9	0.1	0.2	Ca-HCO3
7	6	6.4	0.2	1.3	0.1	0.6	0.1	0.1	0.9	0.2	0.2	Ca-HCO3
8	2	5.1	0.4	2.2	0.3	0.4	0.1	0.2	0.9	0.2	0.4	Ca>Na-HCO3
9	37	11.3	0.2	2.5	0.2	0.5	0.1	0.1	0.9	0.1	0.2	Ca-HCO3
10	6	6.5	0.1	0.8	0.1	0.2	0.1	0.1	1.0	0.2	0.1	Ca-HCO3
11	25	5.2	0.3	1.4	0.1	0.7	0.2	0.1	0.9	0.2	0.2	Ca-HCO3
12	9	1.8	0.7	1.1	0.1	0.3	0.1	0.1	0.5	0.3	0.3	Ca>Mg>Na-HCO3
13	1	1.3	9.7	12.9	1.8	0.7	0.1	0.2	0.1	0.1	1.2	Na-HCO3
14	11	1.2	40.2	10.9	6.1	0.2	0.3	0.2	0.1	0.1	1.2	Na-HCO3
15	70	5.6	0.2	1.3	1.2	0.3	0.3	7.2	6.0	1.0	1.4	Ca-SO$_4$
16	5	5.1	0.1	0.5	1.0	0.4	0.0	8.2	7.2	1.4	0.7	Ca-SO$_4$

1): Springs and wells which drain Manacas Fm (local flows with short flow path): Arroyo La Sed spring; Minero well; **2)** Springs and streams which drain Manacas Fm (local flows with longer flow path): Mamey ponor; Fluoresceina spring; **3)** Springs and streams which drain rocks of the Ophiolitic Association (local flows): Cajalbana 1 spring; Cajalbana 2 spring; Cajalbana 3 spring; Cajalbana 4 spring; Cajalbana 5 spring; **4)** Infiltration waters at the caves of Guajaibón Fm: Lechuza cave; Mamey cave; Ancón cave; Canilla cave; **5)** Karstic springs from the recharge zone of the Guajaibón Fm (local flows): Macagua spring; Cuchillas de Sagua spring; Mamey spring; Mineros spring; Conuco de la Bija spring; **6)** Karstic springs from the discharge zone of Guajaibón Fm (local flows): Canilla resurgence; Ancón surgence; Ancón 2 resurgence; Fernado spring; La Curra spring; **7)** Springs which drain limestone of Sierra Azul Fm. (local flows): Lucas 1 sprimg; Lucas 2 spring; Lucas 3 spring; Cacarajícara no Sulfuroso spring; **8)** Springs which drain Sierra Azul and Cacarajícara Fms (intermediate flows): Cacarajícara sulfuroso spring; **9)** Shallow springs which drain limestone of Artemisa Fm (local flows): Caimito spring; Mil Cumbres no sulfuroso spring; El Perdido (El Sitio) spring; Kíquere spring; Recogedor spring; Batea spring; San Marcos spring; Cuatro Caminos spring; Julio Carmona spring; Majagua spring; San Juan no Sulfuroso spring; P-2 (90 m) well; P-3 (173 m) well; **10)** Streams which drain Artemisa Fm (local flows): Taco Taco resurgence; Bacunagua resurgence; **11)** Springs from the deep drainage of the Artemisa Fm (intermediate flows): La Pastora spring; Pedernales spring; Pedernales well; El Brocal well; San Juan Sulfuroso spring; **12)** Springs which drain different lithologies (intermediate flows): P-13 well; Pozo Azul spring; Martín Mesa spring; Soroa spring; El Sitio well; **13)** Borehole in the shallow drainage of San Cayetano Fm (local flows): P-3 (40 m) well; **14)** Springs which drain San Cayetano Fm (intermediate flows): Mil Cumbres sulfuroso spring; P-4 well; Rancho Mar spring; **15)** Springs from the deep drainage of the Artemisa Fm intercepting sandstone and ultramafic rocks (regional flows): Azufre (Sal y Cruz) spring; El Tigre spring; El Templado spring; La Gallina spring; M-1 Bermejales spring; Cueva Portales spring; P-1 spring; P-12 spring; P-17 well; P-19 well; P-4 (145-195 m) well; **16)**: P1 (0-23 m) well; P1 (0-122 m) well; P1 (120-200 m) well; P1 (120-281 m) well; P1 (237-320 m) well. **Ref**: Bibliographic references 1) Fagundo et al., 1997; 2) Peláez et al., 1990; 3) González et al., 2000.

Table 5. Mass Transfer (mg/)l originated by dissolution or chemical reaction (+) or by precipitation or consumption (-) in the geochemical process take in account by means of the rain – rock interaction process at Sierra del Rosario.

Geochemical process	1	3	5	10	14	20	24	28	30	41	43	51	52	53	54	59	60	69
Halite	12.4	25.9	20.0	16.7	8.8	16.0	14.0	40.6	18.5	13.5	35.1	27.4	31.6	18.7	85.9	47.2	50.0	46.2
Calcite	15.0	85.2	15.3	76.3	103.3	125.6	137.0	200.5	191.6	134.8	264.0	148.3	191.3	0.0	0.0	868.8	1054.1	1371.5
Dolomite	29.0	75.7	0.0	25.1	27.4	32.0	52.0	88.8	35.9	42.0	116.4	33.7	43.5	0.0	0.0	151.9	239.5	311.6
Serpentinite	0.0	0.0	200.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	95.6	173.2	11.9	72.7	49.5	74.6	116.8
Plagioclase	32.2	149.8	32.9	6.7	3.7	14.7	2.1	296.7	55.4	0.0	265.4	126.0	659.9	460.9	1191.4	377.6	314.9	862.0
Microcline	0.8	6.0	0.1	0.1	0.0	0.1	0.0	13.5	0.8	0.0	3.8	9.7	43.5	19.4	55.1	32.8	29.1	69.6
Pyrite	1.5	4.8	7.0	3.3	0.5	6.3	3.0	58.2	23.1	14.0	36.5	56.9	379.8	21.6	87.7	505.3	836.2	1301.3
H_2S	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.1	0.0	0.0	10.0	26.1	169.6	0.0	21.6	18.1	17.3	39.7

1) La Sed stream; 3) Mamey ponor; 5) Cajalbana 1 spring; 10) Lechuza cave; 14). Macagua spring; 20) Ancón karstic spring; 24). Lucas 1 karstic sprig; 28) Cacarajícara sulfuroso spring; 30) Mil Cumbres karstic spring; 41) Taco Taco karstic resurgence; 43) La Pastora spring; 51) Soroa spring; 52) El Sitio well; 53) P3 (40 m) well; 54) Mil Cumbres Sulfuroso spring; 59) El Templado spring; 60) La Gallina spring; 69) P1 (237-320 m) spring.

The chemical composition of the waters of the calcium sulphated type with high mineralization can be explain by means of processes of halite, calcite, dolomite (or serpentine) and silica dissolution, incongruous dissolution of plagioclases (albite, anorthite, microcline), as well as pyrite oxidation and reduction of sulphate (Table 5). The chemical composition of the waters of the $Ca-SO_4>HCO_3$ type, and those of the $Ca-SO_4$ type, with lower contents of dissolved minerals can be explained, applying models of mass balance and of mixes of waters (Fagundo et al., 2004), by means of similar processes previous mixture of extreme members of the types $Ca-HCO_3$ and $Na-HCO_3$ in different proportions (Figure 7).

The solubility relationships among serpentinite and some minerals in the system MgO-SiO2-H2O at 25 oC are shown in Figure 8. Local flows (P3 well 40 m. and Cajalbana stream) are located on the stability field of serpentinite while intermediate flows (P4 and El Sitio wells) are located near the chemical equilibrium, according with the weathering process (Table 2).

The microbiologic processes that produce CO_2 in soil, reduction of sulphate and pyrite oxidation (Appelo and Postma, 1993) are more intense in the intermediate and regional flows, originating an additional dissolution of carbonated minerals. The position that occupies the different types of waters in the Eh-pH stability diagram is shown in Figure 9. While the local flows appear distributed in the field of stability of the SO_4^{2-}, the intermediate and regional flows appear in the fields of Fe_2S, H_2S and HS^-.
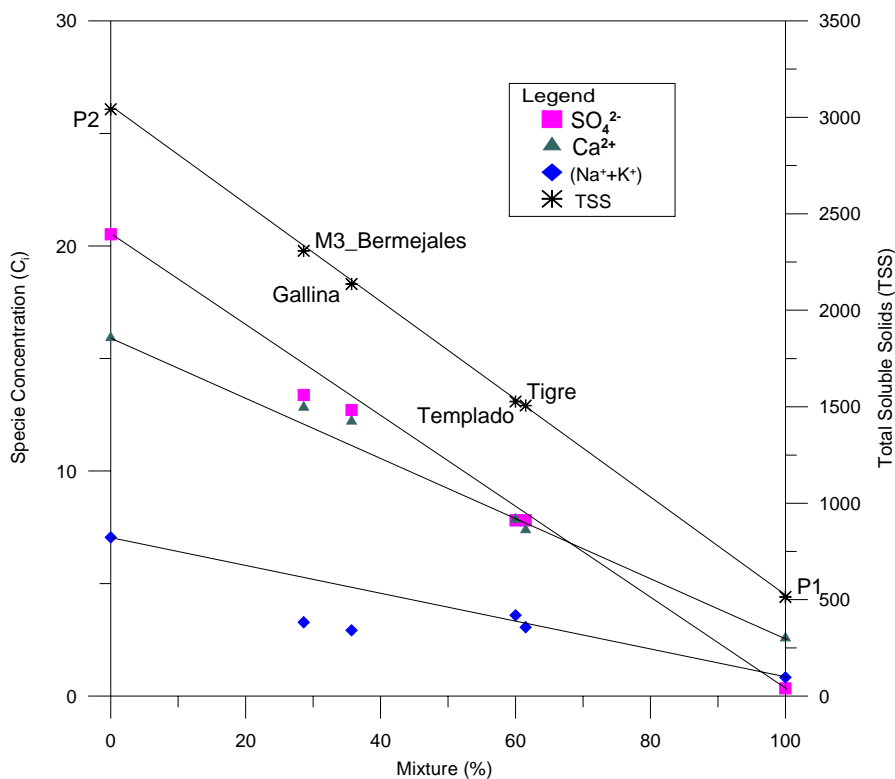

Figure 7. Mixture between P1 and P2 wells which explain the chemical composition of some water spring at San Diego de Los Baños and Bermejales, Sierra del Rosario, Cuba.
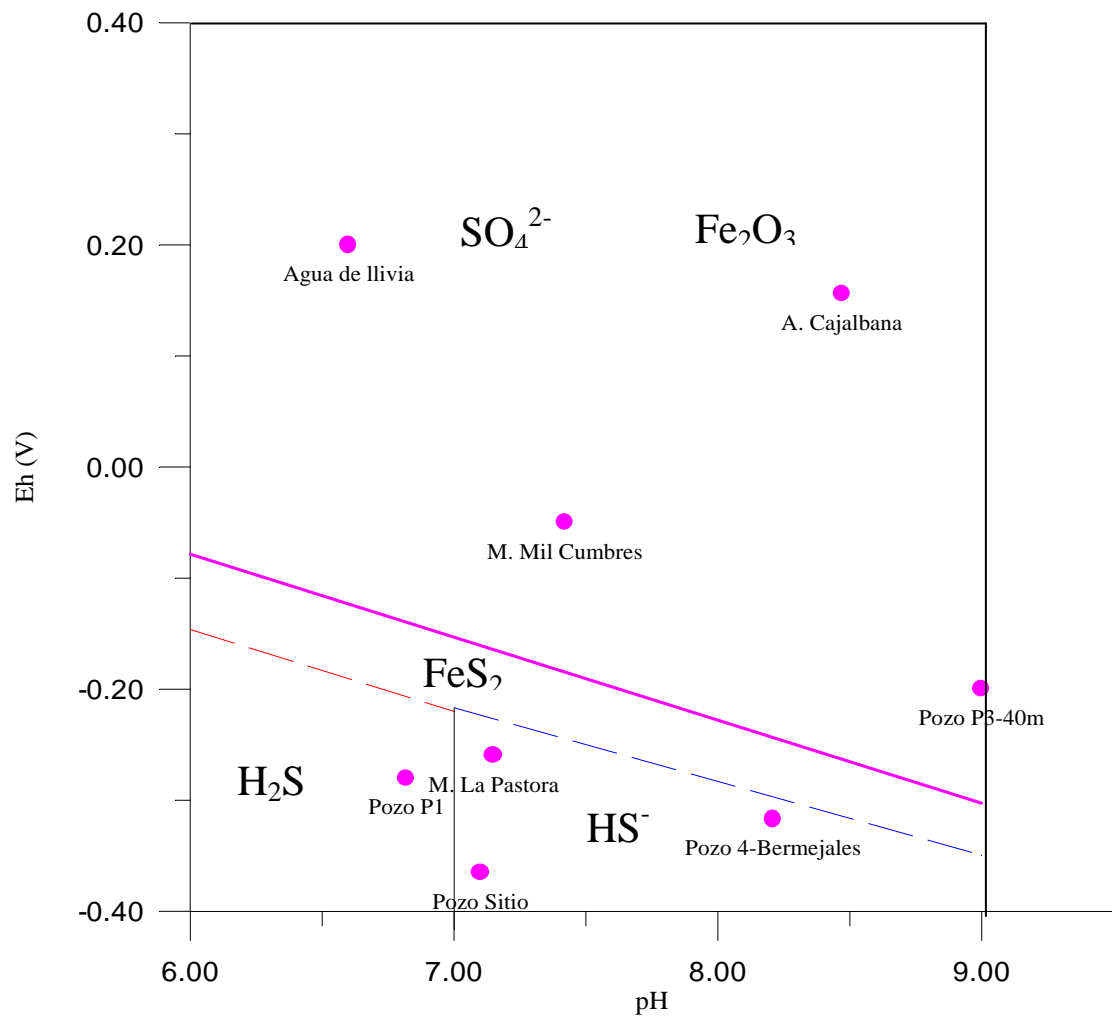
Figure 8. Stability diagram for the system $MgO-SiO_2-H_2O$ at 25 $^{\circ}C$.
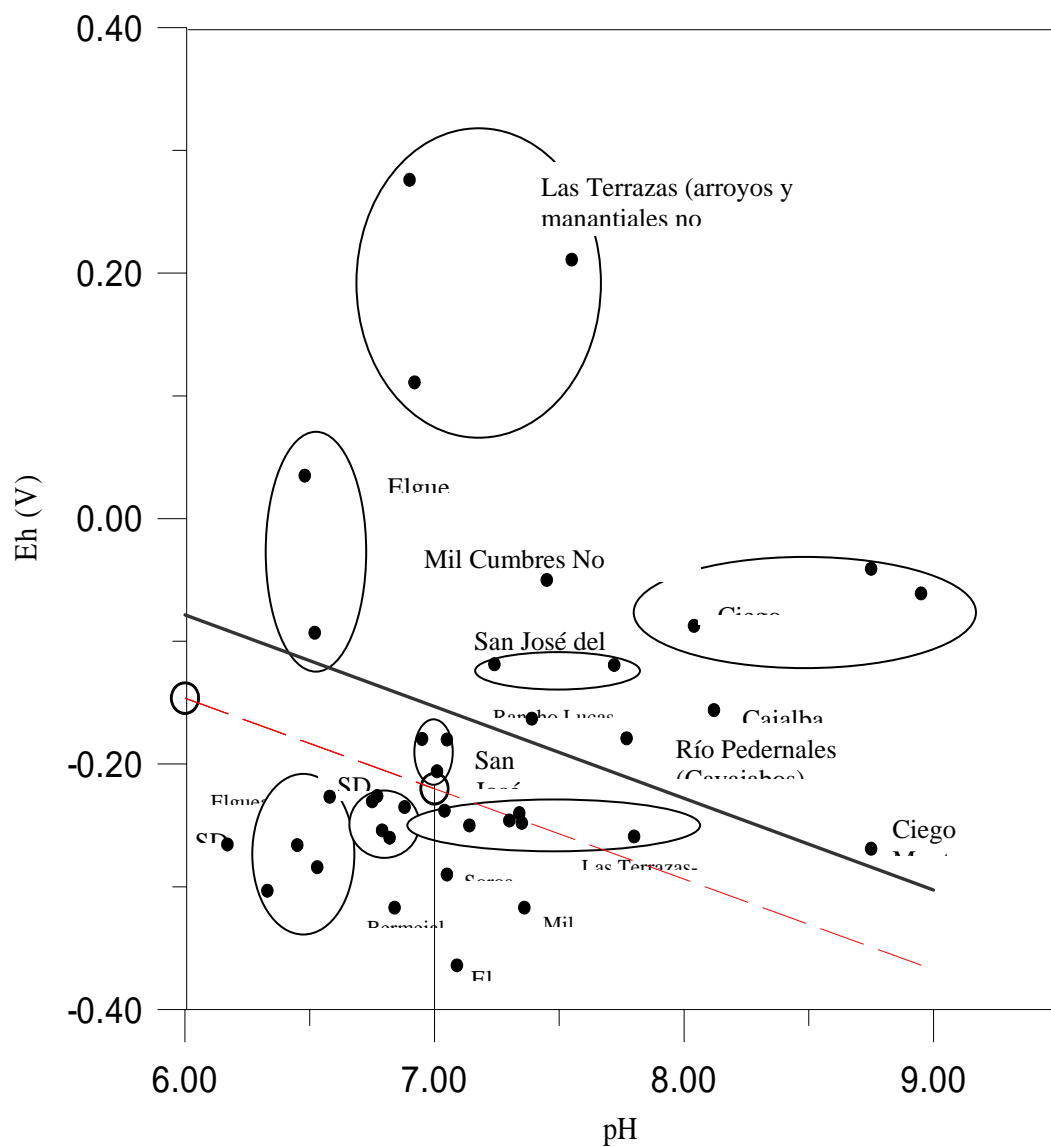
Figure 9. Eh-pH stability diagram.

Temperature and mineralization variation

Analytical results of the analyzed water samples when related to their geological setting suggest a control of the lithology as well as of the geological structure on observed chemical and physical groundwater composition. Groundwater temperature has been used as an indicator of the type of flow (Tóth, 1999; Carrillo-Rivera et al., 1996) permitting to associate groundwater with an abnormal high temperature to regional flow, and lower temperature readings to flows of more local nature.

The groundwater temperature depends on climatic and geothermal conditions, but also on flow patterns due to the capacity of water flow to transport heat. Table 6 shows the seasonal variation of temperature and total dissolved solids (TDS) in some waters from Sierra del Rosario. From a groundwater movement perspective, the karstic systems in Cuba are very dynamic in terms of the travel time, which implies a rapid flow and low storage capacity. This is reflected locally by the seasonal temperature changes in the shallow groundwater, resulting in the observed 18.0 to 24.2 ⁰C for the winter and summer months, respectively, in the waters from Guajaibón Formation (Group 3). This difference in temperature is more dramatic in the Manacas Formation (Group 1), where values of 17.8 to 28.4 ⁰C are reported, suggesting both lower residence time and storage capacity than the Guajaibón Formation. These waters are considered to belong to flows of local nature; this appears to be confirmed by their topographic position and geological setting. A similar behaviour is observed in the waters that drain the ultrabasic sediments (Group 2) and the rest of the calcareous formations (Groups 4 and 5), all of them belonging mainly to local flow systems.

In the waters from intermediate flows (Groups 6, 7 and 8), a marked difference in the period of summer is not noticeable. In order to understand the effect of the rain over the response of the aquifers in Sierra del Rosario, is more useful to use the average temperature of the coldest months (November-March) than the absolute temperature (Fagundo et al., 1997). Another complementary method consists on taking the value of the temperature variation coefficient (table 6), which is smaller in those waters that reach larger depths and therefore they are less subjected to the hydrological cycle action. The shallowest waters on the contrary, possess larger seasonal fluctuation of their temperature, which is reflected in a larger value of the temperature variation coefficient.

Table 6. Seasonal fluctuation indicators of the temperature and the total dissolved solids (TDS) in some waters of the Sierra del Rosario.

No	Group	N	T	VC_T	TDS	VC_{TDS}
1	2	28	23.3	9.0	407	26.4
2	3	39	22.6	1.9	271	14.0
3	3	38	22.7	1.1	305	13.1
4	5	18	22.7	0.9	438	7.7
5	9	30	45.8	0.5	2811	3.2

1) Mamey ponor (No 3 in Table 1); 2) Ancón spring (No 7); 3) Canilla spring (No 7); 4) Mil Cumbres spring (No 10); 5) P 1 well (No 16). N: Number of samples; T: Annual mean temperature (^{o}C); TDS: Mean value of the total dissolved solids (mg/l); VC: variation coefficient (%).

The mineralization of the waters in the outlet depends on the drained lithology residence time, the depth that reaches the water, the content of available CO_2 in the ground and the conditions in which that CO_2 is taken by the waters coming from the rain during its infiltration (conditions of closed, opened or mixed system). The shallowest waters present a seasonal variation of the mineralization (total of soluble solids, dry residual, hardness, and electric conductivity). Where the

water has a longer groundwater flow path or drain deeper lithologies, the temperature, ionic, gas and mineral dissolved contents increase, as shown in Tables 1 and 7.

Table 7. Variation of the some physical and chemical characteristics of the P1 well waters (San Diego de los Baños) with the deep (Peláez et al., 1990).

Depth interval (m)	T (^{o}C)	CO_2 (mg/l)	H_2S (mg/l)	SiO_2 (mg/l)	SO_4^{2-} (mg/l)	TDS (mg/l)
0 - 87	26.0	10.0	0.0	14.0	440.0	354
80 - 120	31.0	22.0	9.0	18.1	732.5	1376
120 - 200	36.2	22.0	9.0	20.0	1058.1	1870
240 - 280	44.0	27.0	28.5	24.0	1731.0	2955
237 - 320	46.0	38.0	39.7	26.7	1972.0	3331

However, a value of variation coefficient of TDS relatively high can be observed in deep waters that have mixed with superficial waters in its ascent or when arriving to the surface have suffered changes.

In the table 7, it is shown the variation of the temperature and some ionic contents in P 1 well located near San Diego de los Baños SPA. The deeper water (237-320 m) changes its temperature (46.0 ^{o}C), carbon dioxide (38.0 mg/l), sulphide (39.7 mg/l), silica (39.7 mg/l), sulphate (1972.0 mg/l) and TDS (3331 mg/l) contents with respect to the shallower one to 26.0 ^{o}C and 10.0, 0.0, 14.0, 440.0, 354 respectively.

In general, the thermal waters of San Diego de los Baños in the outlet loose part of the dissolved gases they possess and they experience pH and redox potential changes, for what the ionic recombination processes are possible originating mineral precipitation and decrease of the dissolved ion contents.

Flow Systems and chemical composition of the waters

Starting on the chemical composition of the local rains and previously taking in consideration the defined groups on the bases of their chemical-physical properties and their relationship with the lithological and structural features of the drain ground, seven flow lines can be defined:

1. Rain-local and intermediate flows that drain sandstone of the Manacas Formation.

2. Rain-local and intermediate flows that drain ultra basic sediments of the Ophiolitic Association.

3. Rain-local and intermediate flows that drain limestone of the Guajaibón Formation.

4. Rain-local and intermediate flows that drain carbonated rocks of the Sierra Azul Formation and interaction with sediments of the Cacarajícara Formation.

5. Rain-local and intermediate flows that drain sediments of different constitution (mixed): limestone, schist, sandstone and ultra basic rocks.

6. Rain-local and intermediate flows that drain schist and sandstone of the San Cayetano Formation.

7. Rain-local, intermediate and regional flows that drain limestone of the Artemisa Formation and in their trajectory final interact with ultra basic rocks (Ophiolitic Association) and schist and sandstone (San Cayetano Formation).

The first flow line originates cold waters of the sodium calcium hydrocarbonate type with medium to moderate mineralization according to the flow nature. The relationship between its ions and the TDS can be evaluated starting from the correlation matrix of the combined data of the group 1 and the rain. The most significant correlation (r > 0.84, N = 39) are obtained between HCO_3^-, Ca^{2+}, Mg^{2+}, Na^+ and TDS, and the less significant ones are obtained with the temperature (T).

The second flow line originates cold waters of the magnesium hydrocarbonate type. The most significant correlation (r > 0.89, N = 17) are observed in this case between HCO_3^-, Cl^-, Mg^{2+} and TDS, but good correlation are not obtained with temperature (T).

The third flow line originates cold waters of the calcium hydrocarbonate type. The data correlation matrix, shows that HCO_3^-, Ca^{2+} and TDS correlate very well (r > 0.90, N = 133), while, as in the previous cases, is not as good with respect to T.

The fourth flow line that also originates waters of the $Ca-HCO_3$ type, is characterized with the corresponding data correlation matrix. The most significant correlation (r > 0.90, N = 10) are obtained among HCO_3^-, Ca^{2+}, Mg^{2+}, Na^+, TDS and SO_4^{2-} and Na+ and Cl^-. Although the correlation with T in not significant, good correlation are obtained if only the temperatures of the coldest months (from November to March) are used. In this case the significantly correlation with the temperature (r = 0.93, N = 7) is obtained with: Cl^-, Ca^{2+}, Mg^{2+} and TDS. These results indicate that the waters that emerge from the springs related with the Cacarajícara Formation, corresponds to the deepest drainage in Sierra Azul karstic system. If the temperature of the coldest month is related also with the waters of the group 3 in a correlation matrix, a similar result is obtained to the one with the group 4, so it could be inferred that waters that drain the massif of Pan de Guajaibón also contributes to the deep drainage of the Sierra Azul system.

The fifth flow line originates lightly temperate waters of the mixed hydrocarbonate type ($Ca>Na–HCO_3$; $Ca>Na–HCO_3$; $Ca>Mg>Na–HCO_3$), characterized by data correlation matrix. The most significant correlation (r > 0.90, N = 11) is obtained among HCO_3^-, Ca^{2+}, Mg^{2+}, Na^+ and TDS. With regards to the temperature, it correlates in highly significant form (r > 0.67, N = 11) with the ion HCO_3^- and in a significant way (r > 0.60, N = 11), with the ions Cl^-, Na^+, Ca^{2+}, Mg^{2+} and the TDS, which is indicative of the controller character of the depth in this type of water.

The sixth line of flow originates waters of the sodium hydrocarbonate type. The most significant correlation (r > 0.90, N = 14) are obtained between HCO_3^-, Cl^-, Mg^{2+}, Na^+ and TDS. With regards to the temperature thelargest correlation (r>0.76, N = 14) is obtained with the Na^+, although if only the temperatures of the coldest months are considered, good correlation are obtained (N > 0.84, N = 7) also with Cl^-, HCO_3^-, SO_4^{2-} and TDS. These waters reach relatively high temperatures with the depth, where dissolved bigger proportions Cl^-, Na^+ and SiO_2 are larger.

The seventh line of flow originate, in its underground flow path, waters of the types Ca-HCO3, sulphide Ca-HCO3, as well as $Ca-SO_4>HCO_3$, $Ca–SO_4$ and $Ca>Na-SO_4$ also with H_2S. The corresponding data correlation matrix shows that the largest correlation (r > 0.90, N = 155) are obtained between SO_4^{2-}, Ca^{2+}, Mg^{2+} and TDS, although good correlation are also obtained (r > 0.80, N = 155) between SO_4^{2-}, Na^+ and TDS. The correlation with the temperature are highly significant (r > 0.80, N = 155) with SO_4^{2-}, Ca^{2+}, Mg^{2+} and TDS. There is a poor correlation between HCO_3^- and the SO_4^{2-} and the corresponding correlation coefficient has negative sign, indicating that while the second ion is increased the first one is decreasing. Of this behavior it is inferred that, in this flow line, the waters evolve from calcium hydrocarbonate to calcium sulphate type with the depth.

From the global analysis of the results it can be said that the relationship among the Ca^{2+} ion and the TDS can be used as indicator of the evolution of the studied waters through the different flow

lines, from the most superficial parts in different types of aquifers the deepest parts (where they have higher temperature, gas content and dissolved ions). In Figure 10 the corresponding tendencies are shown. As it can be appreciated, the biggest contribution of the calcium ion to the total mineralization of the water is shown in the flow line 7 (Artemisa-San Cayetano Formations) and this contribution decrease in the following order: flows lines 3 (Guajaibón Formation), 4 (Sierra Azul-Cacarajícara), 1 (Manacas), 5 (Mixed waters), 6 (San Cayetano) and 2 (Ophiolitic Association).

With these results, the chemical evolution model can be assessed as is shown in Figure 11. As it can be observed in this figure, in all the cases, a progressive increase of the chemical-physical parameters is appreciated (T, H_2S, Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+} and Na^+), from the rain water to the final members of each rocky formation, through the lines that connect the corresponding local, intermediate and regional flows.
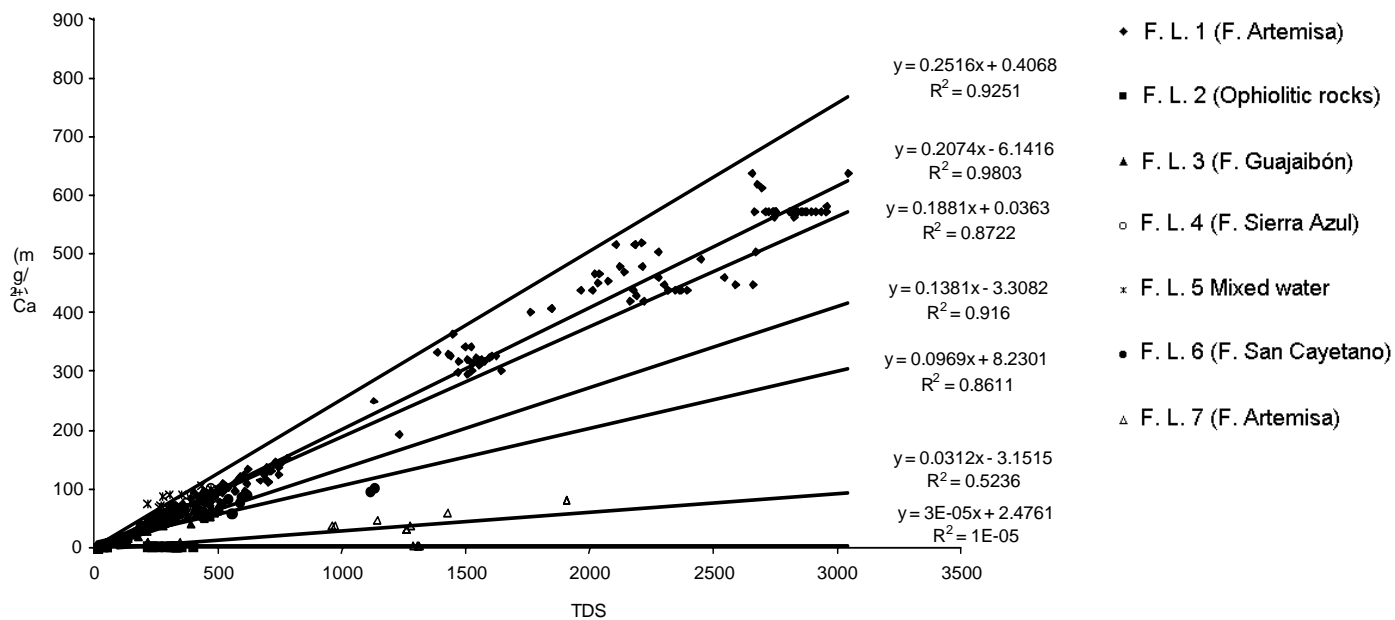

Figure 10. Relationships between the calcium contents and TDS. Water flow lines at Sierra del Rosario.
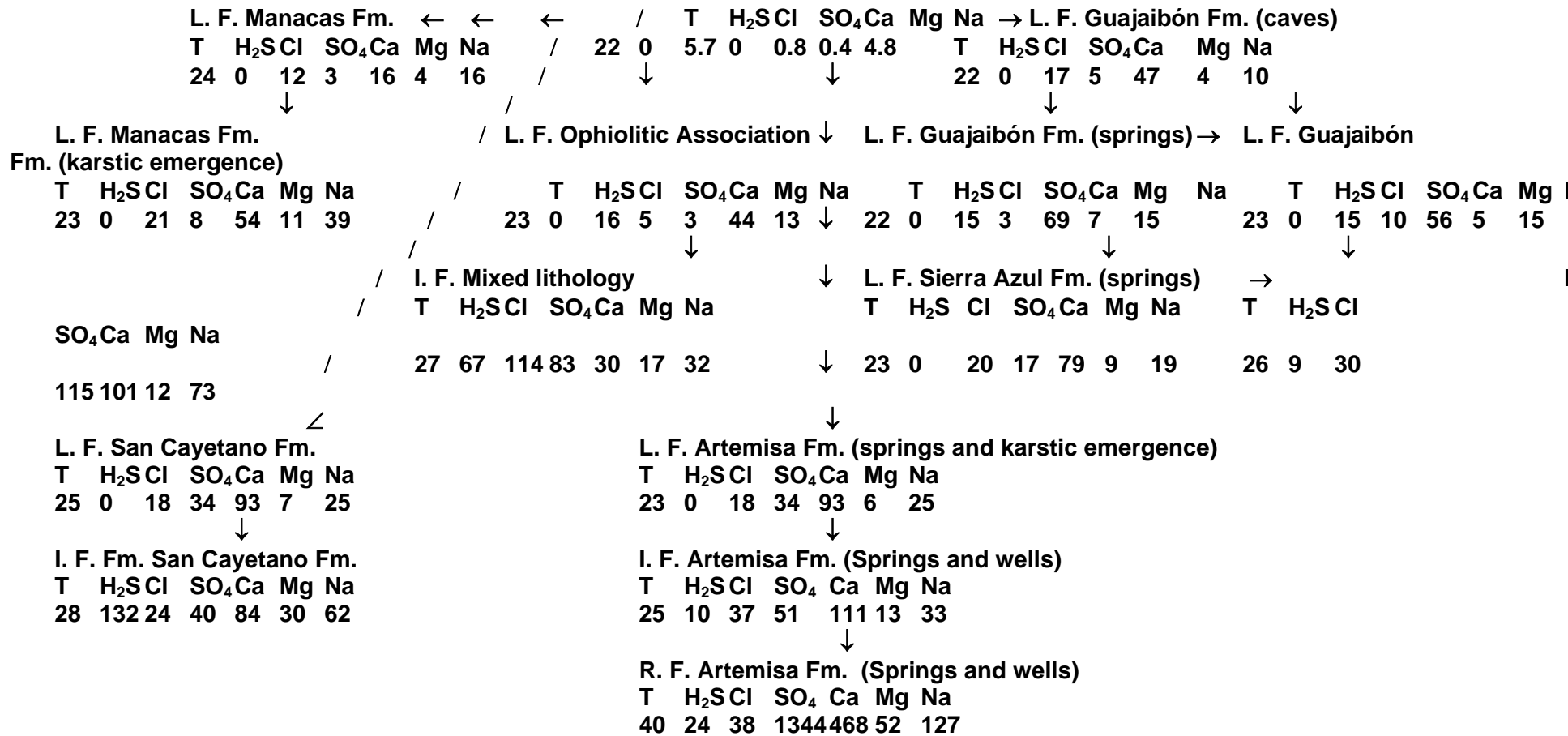
Rainwater

L. F. Manacas Fm. ← ←   ←   /   T   H₂S Cl SO₄ Ca Mg Na → L. F. Guajaibón Fm. (caves)
T   H₂S Cl SO₄ Ca Mg Na   /   22 0   5.7 0   0.8 0.4 4.8   T   H₂S Cl SO₄ Ca   Mg Na
24 0   12 3   16 4   16   /   ↓   ↓   22 0   17 5   47   4   10
            ↓   /   ↓   ↓

L. F. Manacas Fm.   / L. F. Ophiolitic Association ↓   L. F. Guajaibón Fm. (springs)→ L. F. Guajaibón
Fm. (karstic emergence)
T   H₂S Cl SO₄ Ca Mg Na   /   T   H₂S Cl SO₄ Ca Mg Na   T   H₂S Cl SO₄ Ca Mg   Na   T   H₂S Cl SO₄ Ca Mg
23 0   21 8   54 11 39   /   23 0   16 5   3   44 13 ↓ 22 0   15 3   69 7   15   23 0   15 10 56 5   15
                       /   ↓   ↓   ↓
                 / I. F. Mixed lithology   ↓   L. F. Sierra Azul Fm. (springs)   →
                 / T   H₂S Cl SO₄ Ca Mg Na   T   H₂S Cl SO₄ Ca Mg Na   T   H₂S Cl
SO₄ Ca Mg Na
                 /   27 67 114 83 30 17 32   ↓   23 0   20 17 79 9   19   26 9   30
115 101 12 73
            ∠   ↓
L. F. San Cayetano Fm.   L. F. Artemisa Fm. (springs and karstic emergence)
T   H₂S Cl SO₄ Ca Mg Na   T   H₂S Cl SO₄ Ca Mg Na
25 0   18 34 93 7   25   23 0   18 34 93 6   25
            ↓   ↓
I. F. Fm. San Cayetano Fm.   I. F. Artemisa Fm. (Springs and wells)
T   H₂S Cl SO₄ Ca Mg Na   T   H₂S Cl SO₄ Ca Mg Na
28 132 24 40 84 30 62   25 10 37 51   111 13 33
                                                                 ↓
                                                    R. F. Artemisa Fm. (Springs and wells)
                                                    T   H₂S Cl SO₄ Ca Mg Na
                                                    40 24 38 1344 468 52 127

Figure 11. Geochemical evolution of the different flows which drain the Sierra del Rosario massiff.

CONCLUSIONS

The study of a 376 chemical analysis set of waters sampled in the Sierra del Rosario between 1984 and 2004, allowed to establish the geochemical behavior of 9 groups of waters, selected on the base of the different geological drained medium. The characteristics of the different flows (local, intermediate and regional) and their interactions with the aquifer materials (limestone, ultrabasic rocks, schist and sandstone) were interpreted by means of geochemical indices related with the water equilibrium in contact with the calcite, dolomite and gypsum minerals.

In general, it was found that the waters of short flow path (local flows) possess in their emergences cold temperatures, an oxidizer medium (high values of Eh and dissolved O_2), neutral (limestone) or alkaline pH (ultrabasic rocks, schist and sandstone), low levels of CO_2 and dissolved minerals, as well as absence of H_2S. The variation coefficients of the temperature and the TDS are high and during the rainy periods the waters were sometimes unsaturated regarding to the calcite and the dolomite, while in dry periods they are saturated regarding to these minerals.

The groundwater that have a longer and deeper flow path (regional flows), on the contrary, possess in their emergences relatively high temperatures, a reducer medium (low values of Eh and dissolved O_2), the pH is acid or neutral, high content of dissolved gases (CO_2, H_2S), as well as of macro constituents (Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, SiO_2) and mineralization (TDS), whose reciprocal proportions vary in dependence of the aquifer material and of the less permeable layers they interact with. Low values of the variation coefficients of the temperature and the TDS are present and they tend to be saturated or oversaturated with respect to calcite and the dolomite and near the saturation regarding to the gypsum.

The waters corresponding to the intermediate flows possess chemical-physical parameters and geochemical indexes whose magnitudes are intermediate between the both water types above mentioned.

In the superficial flows (not saturated or vadose zone) and of short groundwater flow path (local flows), constituted by carbonates of the Guajaibón, Sierra Azul and Artemisa Formations, the main geochemical processes that explain the origin of the chemical composition of the waters (of the Ca-HCO$_3$ type) are the calcite and dolomite dissolution; in the aquifers constituted by ultrabasic rocks (Ophiolitic Association), the environment originates Mg-HCO$_3$ waters whose origin is explained by means of the serpentine dissolution, while those aquifers developed in schist and sandstone produce (from weathering), water of the type: Ca>Na-HCO$_3$ (Manacas Formation), Na-HCO$_3$ and Na-HCO$_3$>Cl. (San Cayetano Formation) whose composition is explained by means of processes of incongruous dissolution of plagioclases. In all the cases the content of SO_4^{2-} in the waters is due to the pyrite oxidation and the content of SiO_2 is the due to the silica dissolution, which is bigger in the schist and sandstone.

In the medium depth flow (saturated area) and medium flow path (intermediate flows), the waters possess a similar composition to the above described in the respective lithologies, although locally there are waters of mixed character with regard to the anions or cations. The geochemical processes that originate this water are also similar, but in larger proportions in term of mass transference.

In the deepest flow (saturation and deep circulation area) and of extensive flow path (regional flows), the chemical composition of the waters of high mineralization (Ca-SO$_4$), is explained by means of processes of appropriate dissolution of halite, calcite, dolomite and silica, incongruous dissolution of plagioclase, pyrite oxidation with sulphate reduction, while in other waters of smaller mineralization (Ca-SO$_4$, Ca-SO$_4$>HCO$_3$ and Ca>Na–SO$_4$), the composition is originated by

means of water mixture of extreme members Ca-SO$_4$, Na-HCO$_3$ and Ca-HCO$_3$, with geochemical processes similar to those exposed above.

By means of the used methodology it was demonstrated that in the Sierra del Rosario, the lithology and local structure control the way in that the waters acquire their chemical composition.

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