

# HYDROLOGIC AND HYDROCHEMICAL CHARACTERIZATION OF THE PUNTA ALEGRE GYPSUM KARST (CUBA)

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## ABSTRACT

A hydrologic and hydrochemical characterization of the gypsum area of Punta Alegre, Ciego de Avila province, Cuba was carried out during the joint Italo-Cuban expedition in 1991. Water circulation dynamics, water chemical evolution, and gypsum concentration and their relationships with chloride, which comes from the marine intrusion into the aquifer, and perhaps also from the underlying halite deposits have been investigated. A chemical laboratory simulation, using gypsum-saturated waters with different NaCl content, was taken as reference. Subsequently the Punta Alegre gypsum area was subdivided into 4 geochemical zones according to water chloride concentration.

## INTRODUCTION

Papers concerning geomorphology, hydrogeology, and hydrochemistry of gypsum karst are scarce in the international literature with respect to those devoted to calcareous terrains, even in the countries of Spain, ex-USSR, USA, and Italy in where there is more field research in (CALAFORRA & BOSCH, 1989). In Cuba only a few geological reports (LUKAC, 1969; ITURRALDE-VINENT, et al., 1982) exists but none concerning hydrological or hydrochemical research where made where such karst involves a negligible area.

It is well known that dissolution of evaporitic minerals (gypsum and anhydrite) occurs through a process of physical dissolution in which only the molecules of the mineral and the water are involved. According to the thermodynamical laws, the dissolution of 2.41 g/l of gypsum is possible at 25 °C and its solubility decreases at higher temperatures.

In many gypsum karsts water reaches concentrations higher than 2.0 g/l, while in carbonate karst calcium carbonate concentrations higher than 0.35 g/l are due to the influence of sulphides and chlorides (FORD & WILLIAMS, 1989). Usually, natural water shows a sulfate content, which depends on the rock type and /or the presence of some pollutants. PERCHORKIN (1986) reported calcium sulfate concentrations ranging from 0.06 g/l, up to 2.4 g/l in a Permian gypsum-anhydrite aquifer, while FORTI (1988) found contents between 2.58 and 2.7 g/l in the waters of Poiano spring, in the Triassic gypsum-anhydrite of Reggio Emilia: according to historic data, NaCl contents of this spring decreased from 15 g/l in 1862 to 3.1 g/l in 1984.

The results of the hydrologic and hydrochemical characterization carried out during the joint Italo-Cuban Expedition to the gypsum area of Punta Alegre, Ciego de Avila province, Cuba (July 1991) is here presented. Our aim is to contribute to improve the knowledge about the dynamics of such hydrochemical processes, as well as to compare them, in the future, with the data coming from similar environment in other climates.

## THE GYPSUM DIAPIR OF PUNTA ALEGRE

The gypsum outcrop of Punta Alegre is the cap rock of a larger diapiric structure present underground. It shows the classical concentric structure with the Miocene gypsum in the center and, along the border, the Holocenic colluvial cover, which has been pierced by the uplifting diapir (CHIESI et al., 1992).

The gypsum outcrop has an extension of about 20 square kms and consists mainly of detritic aggregates of crystals of different sizes: the rock is not pure but often includes several limestone, sandstone or marl clasts and gravels.

Small relicts of the limestone cover (up to 5-10 m thick) often overlie the gypsum, thus locally hindering its dissolution.

Only scarce news in this karst area was available before the Cuban-Italian expedition of 1991 (JIMENEZ et al., 1988).

The whole gypsum area is characterized by well-developed karst forms (dolines, sinkholes, karren etc.) and the deep karst consists of small vertical and horizontal caves, which often reach the groundwater level (CHIESI et al. 1992).

## MATERIALS AND METHODS

During the period within July 5th and 9th, 1991, many samples of waters from wells, caves, springs, and lagoons located in and around the gypsum outcrop were collected (Fig.1), also the water of the aqueduct supplying two small towns (Máximo Gómez and Punta Alegre) were analyzed.

Some measurements (temperature, pH, electric conductivity and dissolved carbon dioxide) were made in the field (table 1). Moreover in Máximo Gomez settlement a laboratory was set up to determine the concentration of the bicarbonate, carbonate, sulfate, calcium and magnesium ions. The analytic techniques used were those recommended by MARKOWICZ & PULINA (1979) for field conditions. Na<sup>+</sup> and K<sup>+</sup> were determined by flame photometry.

Waters polluted by sugar cane wastes were analyzed (see table 2) using special techniques (AA.VV., 1985).

The artificial gypsum waters, with different NaCl concentrations, were obtained by mixing solutions of natural gypsum from Punta Alegre and sea waters: the final NaCl content ranging from 25.9 g/l up to 1548 g/l (table 3).

The aggressivity of the natural samples with respect to calcite (CSR), dolomite (DSR) and gypsum (GSR) were determined by a computer algorithm (FAGUNDO et al., 1985) based on the method proposed by BACK et al., (1966).

## RESULTS AND DISCUSSION

### 1. HYDROLOGIC AND HYDROGEOLOGIC CHARACTERIZATION

The whole massif has an underground drainage: only one superficial small stream exists in its northeastern part and it is presently used for dumping the sugar cane mill wastes.

Relicts of an ancient superficial water network are evident on the upper part of the massif. Due to the fragmentation and partial demolition of the carbonate cover, the gypsum outcrops almost the whole area, thus, an accelerated dissolution process has occurred, as testified by widespread macro- and microforms. Therefore rainwaters rapidly percolate to the groundwater through many karst depressions, ponors and sinkholes. Cavities originated by this process are small and their vertical development is controlled by the piezometric level.

Several superficial streams, such as the Esteron and Chambas rivers, seem to have springs originating at least partially from the gypsum area discharge.

*Table 1 Hydrochemical parameters of the waters sampled during the Italo-Cuban Expedition 1991.*

*Samples: 1. Sugar cane froth polluted cave; 2. Fresh water well; 3. Rivero Well 1; 4. Rivero Well 2; 5. Los Moya Well; 6. Heradio Ochoa Well; 7. Punta Alegresalt minewell; 8. Well close to the cementery; 9. Correa Well; 10. Brackish lagoon; 11. Rock Salt Cave; 12. Cueva del Agua Well 1; 13. Cueva del Agua Well 2; 14. Cueva del Agua; 15. Los Corrales Well; 16. Santiago Ferrer Well; 17. Isidro Fajardo Well; 18. Salin spring 19. Lylaboa Well; 20. Aqueduct intake.*

NO	T(°C)	pH	CE (m s/cm)	CO <sub>2</sub>	HCO <sub>3</sub> <sup>-</sup> (mg/l)	Cl <sup>-</sup> (mg/l)	SO <sub>4</sub> <sup>2-</sup> (mg/l)	Ca <sup>2+</sup> (mg/l)	Mg <sup>2+</sup> (mg/l)	Na <sup>+</sup> (mg/l)	K <sup>+</sup> (mg/l)	CaSO <sub>4</sub> (mg/l)	TSS (mg/l)
1	29.0	6.40	4780	184.4	167.8	869.8	1668.0	580.0	156.0	460.0	1.2	2248	3902
2	29.0	7.20	5000	110.0	441.0	584.0	1739.5	661.6	124.2	378.8	1.2	2401	3930
3	28.0	7.70	3020	15.8	319.0	115.7	1525.4	684.0	54.0	32.7	5.9	2263	2737
4	29.0	7.40	4030	19.4	239.7	324.8	1733.8	680.0	72.0	210.5	2.0	2209	3263
5	30.5	7.10	3330	64.7	328.2	147.0	1573.9	668.0	72.0	64.4	4.3	2242	2858
6			1209			77.7							
7	31.8	7.25	3560	51.9	328.2	332.3	1586.4	676.0	102.0	120.0	9.4	2262	3155
8	30.5	7.40	3250	30.1	329.4	212.3	1603.2	646.2	106.2	77.1	10.5	2249	3945
9	28.0	7.00	4560	122.1	444.1	488.5	1766.9	758.0	118.8	271.6	23.0	2525	3817
10	28.0	7.40	21000	8.8	273.3	4260.0	3360.0	1296.0	88.8	2786.2	44.5	4656	12109
11	25.0	7.00	3480	6.6	105.0	70.3	1545.6	652.8	25.2	25.5	2.3	2199	2427
12	29.0	7.60	1538	16.7	194.0	60.4	587.5	238.0	42.0	39.3	0.4	826	1162
13	27.0	7.70	3870	22.0	256.0	232.9	1792.8	608.0	115.2	186.1	0.8	2401	3 192
14	26.0	7.90	2670	22.0	314.2	98.0	1419.8	600.0	64.8	44.4	5.1	2020	2546
15	26.0	7.20	3710	94.6	314.2	356.8	1596.0	650.0	111.6	151.8	2.0	2246	3182
16	26.0	7.35	3150	22.0	331.2	214.8	1675.2	596.0	115.2	159.2	2.3	2271	3094
17	26.5	7.40	36600	73.0	350.8	13951.5	1008.0	490.0	114.0	8842.9	51.5	1498	24809
18	29.0	7.00	26900	26.8	274.5	9052.5	1300.8	1160.0	210.0	4832.3	39.0	2461	16869
19	28.5	6.90	3260	120.8	396.5	294.7	1386.7	660.0	78.0	90.4	10.1	2047	2916
20	28.0	7.70	550	-	237.9	62.1	48.0	42.2	21.6	36.5	2.0	7	417

Anyway most of the karst discharge is seaward, mainly through springs below the sea, the largest of which, northward to the area, may be easily detected in the aerial photography and it is well known by the local fishermen. There are also several seasonal springs about 10 m a.s.l., which are active during the rain periods, but their waters result

normally brackish, probably due to the sea water intrusion into the aquifer (see sample B). In fact the groundwater is in dynamic contact with the sea which floods the gypsum aquifer probably through karst galleries.

Another source for the chlorides may be the halite dispersed into the gypsum formation (as it was proved for the Poiano spring in Italy (FORTI et al., 1988)) : in fact during the geological studies carried out on this area within the periods 1957-1958 and 1963-1965 (LUKAC, 1959; ITURRALDE-VINENT et al., 1982), the existence of halite beds at depths from 150 and 450 m was proven.

## 2. HYDROCHEMICAL CHARACTERIZATION

The physico-chemical parameters of the collected samples are listed in Tab.1 . Sample 1 corresponds to a sugar cane froth polluted cave, which was flooded due to an accidental overflow of the pipeline bringing the wastes from the sugar cane mill to an oxidizing pond in the cave surroundings. In Tab.2 a more detailed characterization of this sample is given.

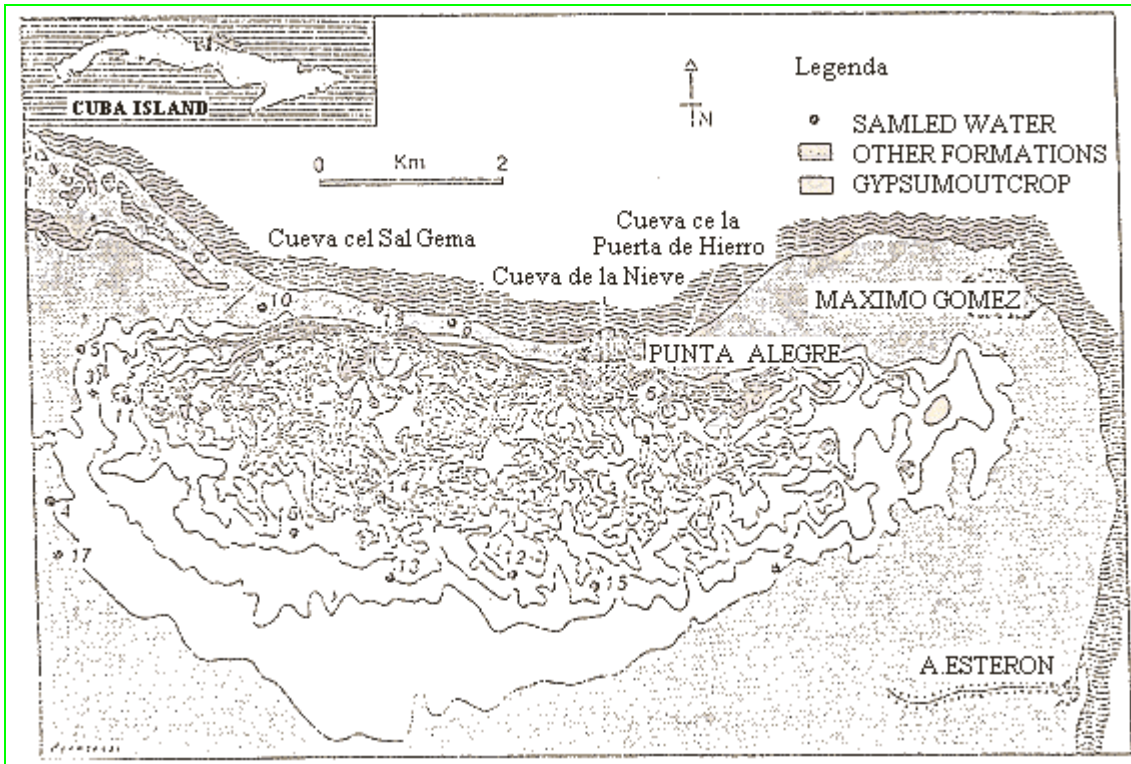


Fig.1 Index map for the collected samples

Table 2 Physico-chemical parameters (mg/l) of the sample 1 (polluted with sugar cane froth) obtained by using waste characterization techniques

Alkalinity	1225
Acidity	320
DQO	2383
ST	5025
STF	3680
STV	1345
SST	1395
SSF	305
SSV	90
Porto	27
Ptot	44
Ninorg	15
Norg	21

ST- Total solids; STF- total fixed solids; STV- total volatile solids; SST- total suspended solids; SSF- fixed suspended solids; SSV- Volatile suspended solids.

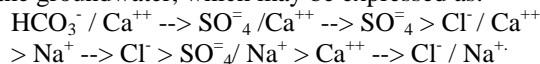
All the samples were collected in the Punta Alegre gypsum area, except sample 20, which comes from the aqueduct supplying the region's settlements, whose intake is directly in the Chambas River.

According to the Table 1, the presence of six different hydrochemical facies may be established as follow:

$\text{HCO}_3^- / \text{Ca}^{++}$ :	0 samples	
$\text{SO}_4^{--} / \text{Ca}^{++}$	13	samples(1,3,5,7,8,9,11,12,13,14,15,16, 19)
$\text{SO}_4^{--} > \text{Cl}^- / \text{Ca}^{++} > \text{Na}^+$	2 samples (1, 2)	
$\text{Cl}^- > \text{SO}_4^{--} / \text{Na}^+ > \text{Ca}^{++}$	1 samples (10)	
$\text{Cl}^- / \text{Na}^+$		2 samples (17,18)
$\text{HCO}_3^- > \text{Cl}^- / \text{Ca}^{++} > \text{Na}^+ > \text{Mg}^{++}$	1 sample s (20)	

STIFF (1951) graphic diagrams for some of the samples are reported in Fig. 2, where they are listed on the basis of the increase of their chlorine content (in meq/l). The chemical composition of sample 20 (the drinking water) is also reported.

The achieved data show the existence of a vertical hydrochemical evolution inside the gypsum karst, from the surface down to the groundwater, which may be expressed as:



The first (calcium-hydrocarbonate) facies corresponds to waters associated with the seepage of meteoric waters in the aerate zone of the limestones overlying the diapire: they are present mainly in the eastern part of the massif, but also, as relicts, in small areas of the central and western zones. This facies, unfortunately, could not be identified during the expedition because the dry season avoided the presence of water inside the small limestone caves.

The second facies correspond to waters of calcium-calcium type. One sample of this type (n.12) is quite interesting having a very low mineralization: its salts content (TSS) was 1.16 g/l,  $\text{CaSO}_4$  being only 0.83 g/l. The origin of this water may be referred to the interaction of carbonate waters associated to a transit zone with a soil reach in calcium carbonate with some gypsum: probably the well, from which this sample has been taken, is only drilled in the cover sediments formed by mixed carbonates and gypsum in which the first largely prevail.

Waters of the calcium sulfate faces are, of course, the more abundant. In many cases, these are originated by direct infiltration in the gypsum outcrop, as it was the case for the samples 11 and 12 collected inside gypsum caves: both are characterized by low chloride concentration (0.06 and 0.10 g/l respectively), medium to high gypsum content (2.20 and 2.02 g/l) and low total mineralization (2.25 g/l TSS).

Owing to the marine intrusion and perhaps also to a possible interaction with the underlying halite beds, the meteoric seeping water mixes in a different ratio with waters of higher NaCl content when reaching deeper zones of the diapir.

As a result of the ionic strength effect, the gypsum saturated waters in the karst aquifer, mixing with the chlorine ones increase their  $\text{CaSO}_4$  content: in fact the waters of sulfate-calcic type have  $\text{Cl}^-$ ,  $\text{CaSO}_4$ , and TSS values of 0.49, 2.53 and 3.82 g/l respectively.

Waters of the sodium-chloride-calcium-sodium facies are represented by only two samples, one of which was polluted with sugar froth. Their chloride contents ranges between 0.58 and 0.87 g/l; calcium sulfate between 2.40 and 2.55 g/l and TSS of 3.90.

The chloride-calcium-sodium-calcium type sample has 4.26 g/l of Chloride, 4.66 g/l of calcium sulfate and 12.22 g/l of TSS.

Laboratory experiments shown that distilled water is able to dissolve about 2.0 g/l of pure gypsum, but this quantity increases progressively reaching 7.5 g /l with the addition of 100 g/l of NaCl (FORD & WILLIAMS, 1989). Then, the solubility decreases if more NaCl is added: this is largely consistent with our laboratory results obtained when pure gypsum from Punta Alegre deposits were dissolved until saturation using waters with different NaCl content (see Tab.3).

In the Fig. 3 the diagrams of dissolved gypsum with respect to chloride concentration for collected samples (N.2 and 12 were excluded due to their anomalous behavior) and those prepared in the laboratory are presented. Both show the same trend: the higher the chloride concentration, the greater the calcium sulfate contents for the interval in which anionic facies  $\text{SO}_4^-$ ,  $\text{SO}_4^- > \text{Cl}^-$  and  $\text{Cl}^- > \text{SO}_4^-$  are prevailing, while in the interval where chloride facies largely prevails the trend for the gypsum dissolution is either to decrease or to maintain its ratio constant.

Figure 4 provides a scheme for the chloride content in the collected waters : the studied area may be subdivided into four geochemical zones controlled by their altitude: 1) a low Cl content (50-110 mg/l) zone associated to areas located, in general, over 50 m a.s.l.; 2) a middle Cl content (111-360 mg/l) zone, mainly related to an altitude between 50-20 m a.s.l.; 3) a high Cl content (361-1000 mg/l) zone between 20-10 m a.s.l.; and 4) a highest Cl content zone located beneath the 10 m a.s.l.

The anomalous high chloride concentration in sample 1 must be due to pollution. The samples 3 and 11 also showed a relatively high chloride contents in relation to their altitude, but presently we have no explanation for their behavior.

In the carbonate karst the calcite dissolution process is controlled by the carbon dioxide - water - calcium carbonate equilibrium, therefore a constant ratio exists between the partial pressure of  $\text{CO}_2$ , the pH and the dissolved  $\text{CaCO}_3$ . Although the above equilibrium do not act directly over the gypsum dissolution process, a sufficient constant ratio between the carbon dioxide and the pH have been experimentally proved for the Punta Alegre waters: the data of Tab.1, in fact, shows that samples with higher  $\text{CO}_2$  content (52-184 mg/l) present lower pH (6.4- 7.4). While the lower  $\text{CO}_2$  (6.7-7.7) corresponds to the higher pH (7.0-7.7). Anyway these two parameters are shown to have no control over the dissolved gypsum.

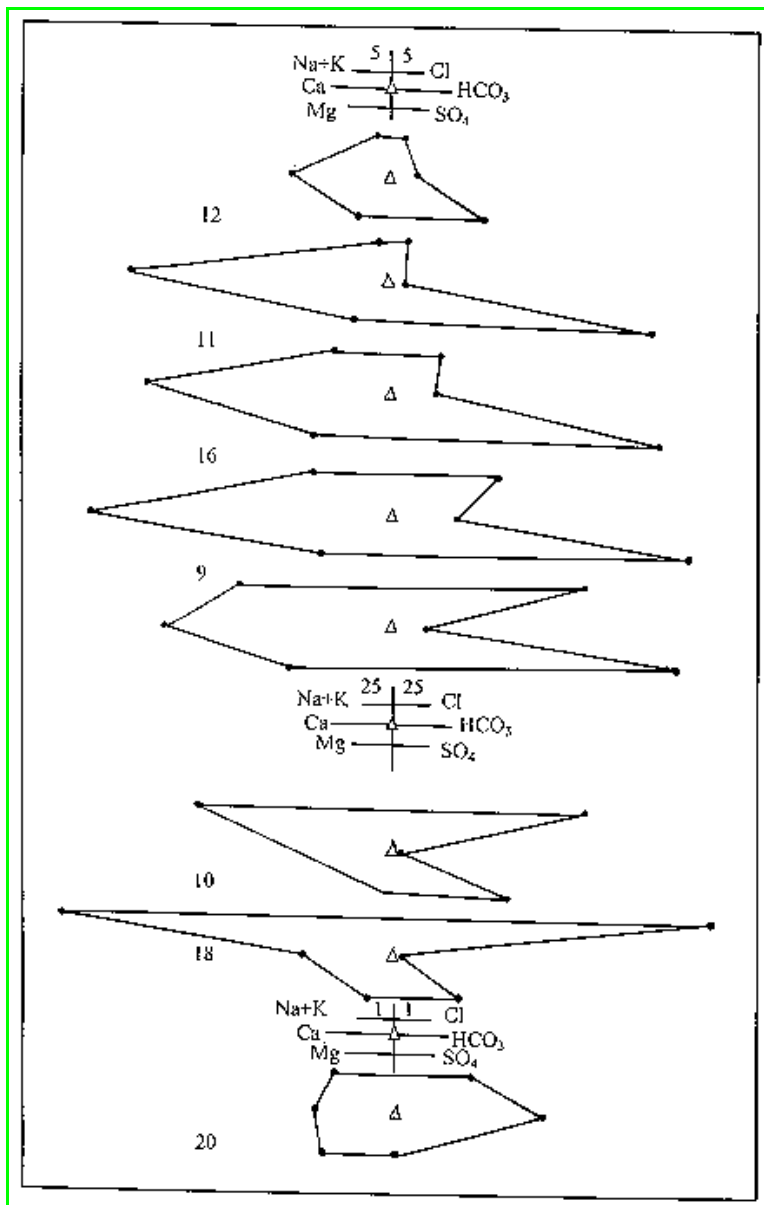


Fig.2 Stiff diagrams for some of the waters collected in Punta Alegre area

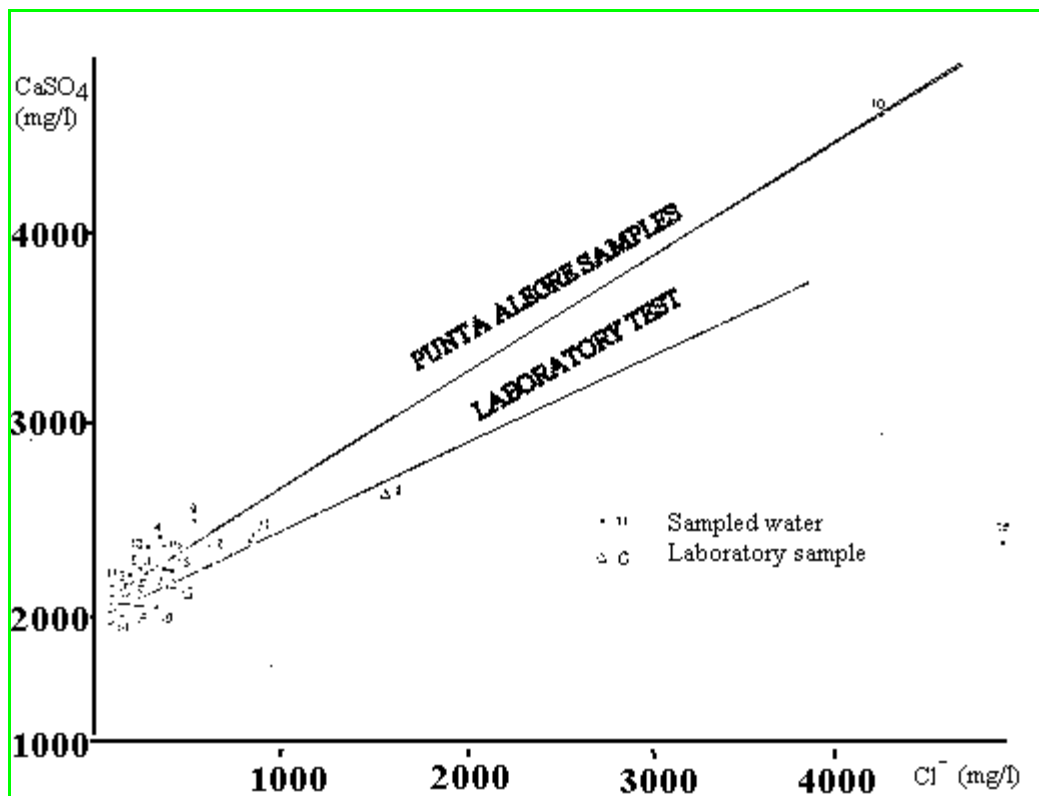
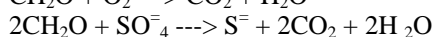
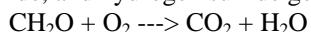


Fig.3 Dissolved gypsum and chloride content in the Punta Alegre sampled waters and in those prepared in the laboratory tests

Table 3 Chemical composition of the gypsum (from Punta Alegre) saturated waters prepared in the laboratory at different NaCl concentrations

Sample	EC(uS/cm)	pH	Ionic concentration(mg/l)							
			HCO <sub>3</sub>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>=</sup>	Ca	Mg	Na+K	CaSO <sub>4</sub>	TSS
A	2070	6.9	45.8	25.9	1440	620	0	34	2040	2146
B	2090	7.15	45.8	34.0	1448	620	0	39.3	2108	2230
C	2160	7.2	45.8	44	1448	620	0	45.8	2108	2244
D	2160	7.2	45.8	60.7	1448	620	0	56.6	2108	2271
E	2260	7.2	45.8	96.9	1448	620	12	57.0	2108	2320
F	2280	7.4	45.8	203.8	1448	620	31	82.6	2108	2471
G	3210	7.5	45.8	376.3	1536	640	36	192.1	2176	2826
H	4550	7.5	45.8	816.5	1728	720	72	408.3	2448	3791
I	6820	7.7	152.5	1547.8						
J				5000						
K				10000						
A-M	47900	8.1	161.7	19205.5	2928	1220	1248	10112	4148	34875

Finally, the very high CO<sub>2</sub> concentration and very low pH values of the sample 1 are due to the additional carbon dioxide, and hydrogen sulfide generated by the decomposition of the organic matter coming from the sugar cane mill:



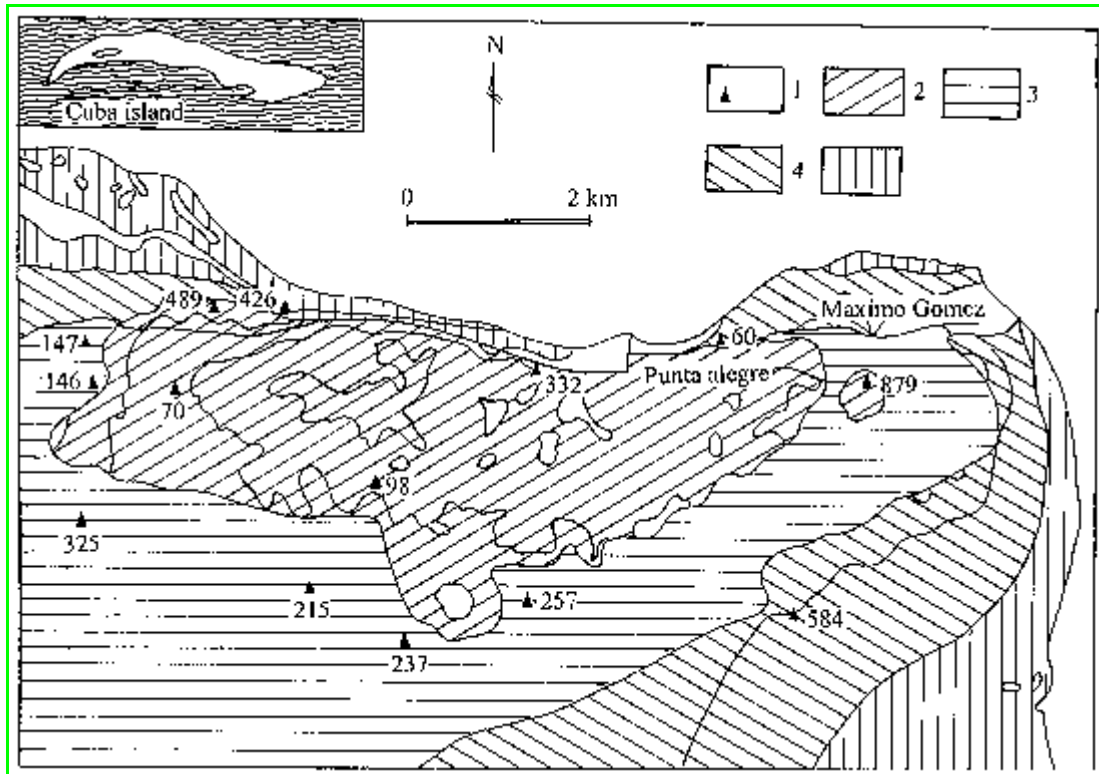
It is important to point out that these man-induced processes accelerate the dissolution of gypsum firstly increasing the ionic strength and secondly lowering the sulfate ion concentration and, therefore, this kind of pollution of the karst area must be avoided.

### FINAL REMARKS

Generally speaking, the waters of this region are prone to supersaturation regarding calcite and dolomite and nearby the saturation with respect to gypsum. Only sample 1 (polluted with sugar cane froth) and sample 11 (obtained from direct seepage inside the gypsum outcrop) proved to be aggressive toward calcite and dolomite. Sample 20 (aqueduct water) has a gypsum concentration relatively low. The samples 12 and 17 are those, which present the lower calcium sulfate content. Finally sample 10 (brackish lagoon) shows a relatively high supersaturation value with respect to gypsum and a high NaCl content.

In conclusion all the available data confirms that in the tropical climate of Punta Alegre, the hydrochemical equilibrium controlling the karst process are quickly reached and therefore the karst evolution of the area is very rapid.

It would be interesting to compare these data, which are only referred to a dry period, with other taken in the rainy season, in order to have more complete information on the hydrogeochemistry of such a karst region.



*Fig.4 Zonation of the Punta Alegre area with respect to the chlorine content of its waters*



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