

AGRICULTURAL USE AND WATER QUALITY AT KARSTIC CUBAN WESTERN PLAIN

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ABSTRACT

Some results about the study taken in account at the karstic aquifer developed on the western plain of Cuban territory are shown. The intensive overdraft that these aquifers are submitted for agricultural and population water supply induce an increase of the marine encroachment, water salinization and progressive increase of the chemical corrosion with a greater carbonate dissolution. In the study time (1983-1998) a trend to the water quality deterioration was observed by means of chronological series of hydrochloride contents.

INTRODUCTION

Carbonate aquifers are dynamic geochemical systems in which rock - water interactions occurs continuously (Hanshaw and Back, 1980). The dispersive mixing zone formed by sea - water encroachment and groundwater discharge is the chemically most active part of the system.

Groundwater intrusion from the sea causes a mixing process of two waters, which differ in their chemical and physical behaviors. Such mixture is present at the coastal karstic aquifers under certain equilibrium conditions, wastewater disposal, etc. Between the more significant changes which occur when two waters of different nature are mixed are the followings: incongruent dissolution of mineral by ion common effect, ferric mineral precipitation by formation of more oxidizing mixing, increase or decrease of the solubility by pH changes, increase of carbonate solubility by saline or ionic strength effect, carbonate chemical dissolution increase by mixing - corrosion effect, dolomitization or dedolomitization and ion exchange processes.

The kinetics and geochemical aspects of the fresh - salt water systems in sea water intrusion conditions have been studied, in the particular case of the karstic aquifers at different regions under different climatic conditions: Florida and Yucatan (Back and Hanshaw, 1981; Back Back et al., 1986; Plummer, 1975); Ampulia, Italy (Cotecchia; 1979); Mallorca and Menorca, Spain (Herman, Back and Pomar, 1986); Western Cuba (Arellano et al., 1989, Fagundo et al., 1993; 1996, 1998; Morell et al., 1997 and Gozález et al., 1996; 1998).

In all the above mentioned cases human impact affect both hydrostatic and calcite dissolution - precipitation processes. In the first case, a great volume of seawater pollutes the groundwater, in the second case, affectations in the hydrogeochemical processes are originated.

Although apparently slow processes in terms of time, these undesirable impacts on the karst coastal aquifers caused by overdraft, both in hydrodynamic and hydrogeochemical terms, have irreversible effects on the water quality used for the plant irrigation and population supply.

The aim of this paper is to show the changes along a short time of the water quality and the chemical corrosion process at the coastal karstic aquifers developed at the western part of Cuba submitted by the human impact for agriculture and population water supply purpose.

Geochemical process in coastal karstic aquifers

1. Carbonate dissolution - precipitation process

A detailed explanation of groundwater saturation, subsaturation and oversaturation conditions with respect to calcite, and the basis on the carbonate dissolution - precipitation equilibrium changes was given by Custodio (1986) as a function of the following effects:

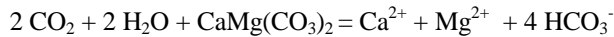
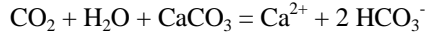
- a) Common ion effect: Ca^+ contributions to the carbonate dissolution allow a medium, previously saturated with calcite or dolomite, to exceed its solubility product, those giving rise to carbonate deposits.
- b) Ionic change effect: the Ca^+ and Mg^+ concentrations affected by clay exchanges originate Na^+ and other elements. This effect can only be appreciated in slow flow conditions.
- c) Ionic strength or saline effect: An increase of the ionic strength (μ) due the mineralization increase cause a decrease of the calcium ion activity coefficient (γ) and an increase of carbonate solubility

$$K_c = \gamma_{Ca} m_{Ca} \gamma_{CO_3} m_{CO_3}$$

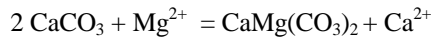
$$K_d = \gamma_{Ca} m_{Ca} \gamma_{Mg} m_{Mg} (\gamma_{CO_3} m_{CO_3})^2$$

- d) Temperature changes: Temperature affects the dissolution – precipitation equilibrium constants and activities.
- e) Mixture of waters with different composition: The mixture of two saturated waters with respect to calcite, both with a different chemical composition, produces a water that can be subsaturated or oversaturated.

The dissolution and precipitation of calcite and dolomite can be summarized in the following equilibrium:

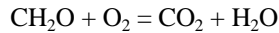


The dolomitization can be a common process in a coastal karstic aquifer by the higher Mg^{2+} contents of the seawater. This process can be writing as following:



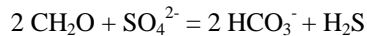
1. Redox process

There is much reduction - oxidation processes in nature. The oxygen consumption in a karstic aquifer may react with any reduced substance in the aquifer sediment, such as organic mater or Fe^{2+} bearing minerals like pirate. For the oxidation of organic matter can be writing:



The above process increases the dissolution of calcite in natural condition of the aquifer. By human impact (organic waste disposal) this effect is much more emphasized.

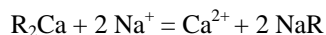
Another interesting redox process in coastal karstic aquifers is the sulfate reduction. Sulfate from the sea can be reduced by organic matter by means of biogeochemical process catalyzed by anaerobic bacteria of the genus *Desulfovibrio* (Bitton, 1994) according to the overall reaction:



Where: CH_2O represents the organic matter. The H_2S produced can be react with the Fe^{2+} - oxides in the sediment and form iron sulfate minerals (Appelo and Postma, 1993). This type of geochemical process is very common at the southern karstic plain of the western of Cuba where lagoons and swamps exist along the coastal line (González et. al., 1998).

2. Adsorption and ion exchange

Although this process is more common in detritic aquifers, the above was also reported in karstic aquifers (Custodio, 1986; Pulido-Bosch et. al., 1993). The reaction can be expressed as:



Fresh water in coastal terrain is dominated by the Ca^{2+} and HCO_3^- ions, as a result of dissolution of calcite and Ca^{2+} have mainly adsorbed on the surface (direct exchange), while in sea water, Na^+ and Cl^- are the dominant ions and sediment in contact with sea water will have adsorbed Na^+ for large part (inverse exchange).

Geographical, Geological and Hydrogeological framework

Western karstic plain (Fig. 1) is a result from the more widespread morphology throughout the territory. They are developed on Paleocene - Pliocene carbonate terrigenous and transgressive limestone packages. On such sequences there is a Pliocene - Quaternary developed karst, with great capacity and transmission aquifers, with open seaward discharge.

The transmissivity of the aquifers change from 5000 m^2/d to 50 000 m^2/d to account of the karstification degree of the limestone. The stored coefficients change from 0.03 to 0.2. Such high transmission capacity is due to the high primary porosity of the rocks, the increasing of the fracturing and the intense karstification, specially in terms of the speedily corrosion effect as a consequence of the fresh - sea mixed waters at the coastal. In such aquifers the marine intrusion usually reach long distance inland.

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According to Núñez Jiménez (1984) there are five plain karstic type in Cuba: 1) naked karst, 2) karst covered by soils, 3) littoral karst in marine terraces, 4) thick fluvial and laterital sediments and 5) coastal swamp karst (Fig. 1).

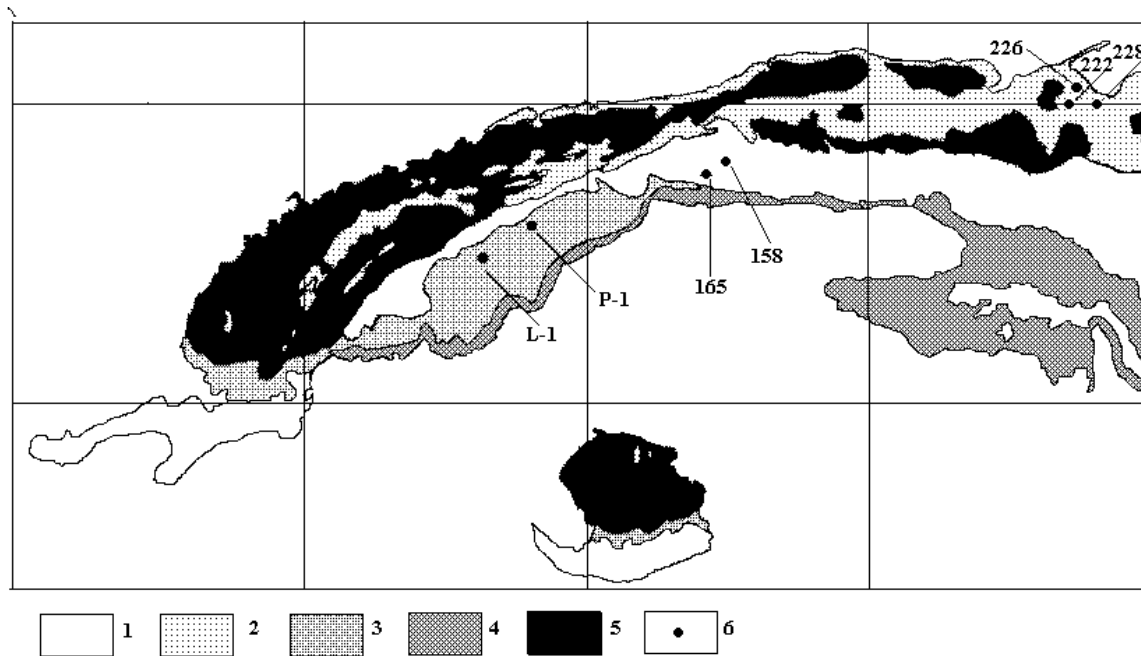


Fig. 1

The wells chosen for this study were: Lopez Peña (L-1) and Los Palacios (P-1), at the southern plain of Pinar del Río Province; P158 and P165 (South Basin of Havana Province), and P224, P225 and P226, at the Varadero-Cardenas hydrogeologic sector (Matanzas Province), all located at the western portion of the Cuban karstic plain.

Increase of the groundwater salinity in function of agriculture and population water supply demand

The groundwater extraction for agricultural purpose in some regions of the Cuban karstic plain is of the order of 3.5 m²/s while for population supply is of 3.2 m²/s (Jiménez et al., 1997).

Table 1 shows the exploitation in the period 1983 – 1995 at the Havana South basin. This territory reach the maximum values of exploitation in 1984 (188.8 Hm³) and 1991 (202.5 Hm³). The hyperyear rain for this place was of 1398 mm, lightly lower than the yearly mean (1375 mm), but in the period 1983-1995 occur a deficit with respect to this cipher, especially in the period 1984-1999.

Tab. 1. Precipitation (mm) and exploitation (Hm³) at the P165 well (Havana South basin).

Year	Precipitation (mm)	Exploitation (Hm ³)	Year	Precipitation (mm)	Exploitation (Hm ³)
1983	1961	151.8	1991	1614	202.5
1984	983	188.8	1992	1465	140.7
1985	1139	183.2	1993	1513	129.9
1986	1266	192.9	1994	1270	117.3
1987	1141	165.9	1995	1543	117.1
1988	1195	140.1	1996	1241	106.2
1989		156.2	1997	1466	107.8
1990	1269	164.1	1998	1064	

As a result of combined effect of the rain deficit and the increasing of exploitation the NaCl contents was increased in the groundwater (Fig. 2).

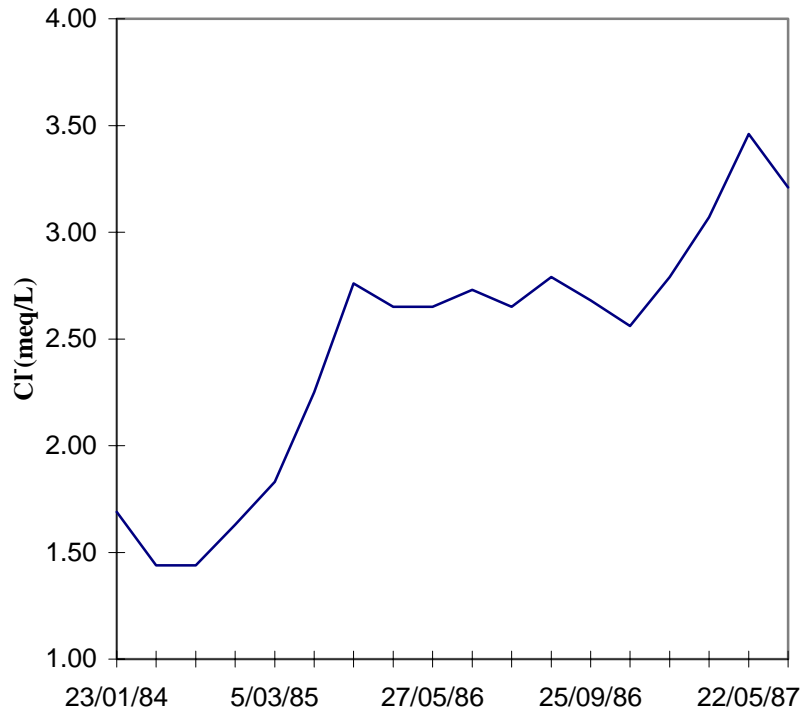


Fig. 2. Temporal variation of precipitation, exploitation and hydrochloride contents at P165 well (Havana South basin).

Similar overexploitation with poor precipitation was produced in other places of the plain (Pinar del Río, La Habana and Matanzas).

Chemical corrosion in the aquifer by mixing between fresh and saline waters

Mixing two waters with different CO_2 and ionic contents will result in subsaturation. The renewed aggressiveness in mixed waters may cause calcite dissolution, effect which has been called "mischungskorrosion" in German literature (Bögly, 1978).

With the aim to evaluate de effects of the mineralization and the ion strength (μ) on the decrease of the calcium ion activity coefficient (γ) and the increase of carbonate solubility (table 2), a fresh-sea mixture at different proportions (0-100%) was prepared in laboratory. The fresh water was from the Jaruco-Aguacate basin, located at great distance from the coast. The aquifer is developed on Miocene limestone. The seawater was sampled at the Atlantic Ocean.

Table 2. Ion concentrations, electric conductivity (EC), total soluble solids (TSS), ion activity coefficients and square root of the ion strength (μ) at a fresh water (Jaruco Aguacate basin) and at different proportions of seawater mixture (Atlantic Ocean).

Sea water (%)	0	1	2	3	4	5	6	7	8	9	10
Study ions											
HCO ₃ ⁻ (mg/L)	270	266	268	260	258	255	250	246	252	248	252
Cl ⁻ (mg/L)	17	200	389	568	761	938	1120	1314	1498	1680	1863
SO ₄ ²⁻ (mg/L)	12	34	66	83	111	140	159	196	214	246	262
Ca ²⁺ (mg/L)	60	66	69	72	74	79	84	86	89	92	96
Mg ²⁺ (mg/L)	15	32	41	52	66	73	89	101	115	123	139
Na ⁺ (mg/L)	13	118	220	320	426	525	632	728	835	938	1042
K ⁺ (mg/L)	1	5	8	12	16	21	24	28	31	35	39
EC (μ S/cm)	553	1230	1850	2596	3306	3850	4470	5080	5672	6270	6850
$\gamma_{Ca^{2+}}$	0.71	0.64	0.60	0.57	0.54	0.52	0.50	0.48	0.47	0.46	0.44
$\gamma_{HCO_3^-}$	0.92	0.89	0.87	0.86	0.85	0.84	0.83	0.82	0.81	0.81	0.80
TSS (mg/L)	388	721	1061	1367	1712	2031	2358	2699	3034	3362	3693
$\sqrt{\mu}$	0.08	0.12	0.14	0.16	0.18	0.20	0.21	0.23	0.24	0.25	0.27

As can be appreciate the ions contents (in terms of TSS and EC) increase with the percent of see water in the mixture, while decrease hydrocarbonate (γ_{HCO_3}) and calcium (γ_{Ca}) activity coefficients. The chemical corrosion ($[Ca^{2+}]_{chc}$) in terms of calcium (mg/l) removed from the aquifer by the waters was calculated by the following equation:

$$[Ca^{2+}]_{chc} = [Ca^{2+}]_s - [Ca^{2+}]_m \quad (1)$$

Where:

$[Ca^{2+}]_s$: Calcium contents determined with analytical methods

$[Ca^{2+}]_m$: Calcium contents calculated from the conservative mixture.

The above parameters were calculated using the relationships between the hydrochloride contents and the fresh water percent on the mixture of the mixture (P_m) as well as the calcium contents relationships. The resulting equation was the following:

$$P_m = 0.1812 [Cl]_s - 0.09 \quad (2)$$

Where $[Cl]_s$ is the hydrochloride concentration of the sample (mg/l). The slop represents the Cl⁻ concentration at the 0 percent of the mixture and the intercept is the Cl⁻ contents of the groundwater without salinization. Them, the calcium contents supplied for the mixture $[Ca^{2+}]_m$ is:

$$[Ca^{2+}]_m = 0.2 P_m + 3.0 \quad (3)$$

Which can be calculated as a function of the mixture percent from the corresponding relationships (table 1). Combined (1), (2) and (3) can be arrived to the equation:

$$[Ca^{2+}]_{chc} = [Ca^{2+}]_s - 0.03824 (Cl) + 2.982 \quad (4)$$

The $[Ca^{2+}]_{chc}$ values can be expressed in terms of CaCO₃ hardness (mg/l) as the following:

$$[CaCO_3]_{chc} = 50 [Ca^{2+}]_{chc} \quad (5)$$

This magnitude can be used for comparison the corrosion developed at the different sites of the basin or at the aquifers located at different places.

With the aim to estimate the above calculations two pairs of wells from different aquifers representative of waters with lower and higher salinity in the same basin at Pinar del Río, Havana and Matanzas Provinces were chosen. The different behavior of the wells are due to the local differences of the limestones composition, porosity and fisuration of the terrain, location with respect to the coastal line and the degree of water extraction for agricultural and population supply porpoise. In the mentioned tables (3-5), the mixture percent (P_m %) and the chemical corrosion ($[CaCO_3]_{chc}$, mg/l) are shown from the studied period in the karstic aquifer open to sea at Pinar del Río, Havana and Matanzas Provinces respectively.

Table 3. Mixture percent and chemical corrosion magnitude at the Pinar del Río southern karstic plain.

AÑO	L-1			P-1		
	N	P_m	$CaCO_3$ cq (mg/L)	N	P_m	$CaCO_3$ cq (mg/L)
1974	1	0.07	24			
1975	5	0.10	21			
1976	5	0.02	17	5	0.70	69
1977				11	0.69	53
1978				8	0.69	61
1979	1	0.03	40			
1980	1	0.01	47			
1982	3	0.03	41	9	0.85	71
1983	7	0.03	36	8	0.87	66
1984	7	0.04	33	2	1.04	57
1985	7	0.03	33	2	1.04	59
1986	4	0.03	41	2	1.02	86
1987	3	0.03	32	2	1.16	99
1988	1	0.03	28	2	1.16	90
Mean value		0.04	32		0.81	66

Table 4. Mixture percent and chemical corrosion magnitude at the Havana southern karstic plain.

AÑO	Pozo 158			Pozo 165		
	N	P _m	CaCO ₃ cq (mg/L)	N	P _m	CaCO ₃ cq (mg/L)
1984	6	0.06	78	4	0.21	67
1985	4	0.08	80	2	0.30	92
1986	10	0.11	88	9	0.43	85
1987				3	0.53	145
Mean value		0.09	83		0.38	92

Table 5. Mixture percent and chemical corrosion magnitude at the hydrogeologic sector of Varadero-Cardenas (Matanzas Province).

AÑO	Pozo 222		
	N	P _m	CaCO ₃ cq (mg/L)
1982	4	2.10	106
1983	2	1.21	53
1984			
1985			
1986			
1987	3	6.34	133
1988	1	7.79	82
1989	1	3.95	118
1990	4	5.26	215
Mean value		4.18	133

In general, the quantities of CaCO₃ removed from the limestones at the three studied places of the western Cuban karstic plain are locally different, and a major increase of the chemical corrosion can be appreciate at that aquifers which has larger percent of water see in the mixture.

The quantity of CaCO₃ removed from the limestone is similar in the Pinar del Río and Matanzas wells, but more of double of Havana, maybe due to the different lythologic and tectonic characteristics of the aquifers.

The CaCO₃ magnitude higher at the Havana aquifers than the Pinar del Río Province aquifers can be related with the different nature of its catchment areas. At the rather, the catchment is direct from precipitations, and the CaCO₃ are dissolved in CO₂ open system conditions, while at the Pinar del Río area, the aquifers are confined and the CaCO₃ are dissolved in closed system conditions with respect to CO₂. The low values obtained at Matanzas where the aquifers are also open to the precipitations as Havana can by explained by the different characteristics of the limestone. At the Cardenas –Varadero sector of Matanzas, the limestone's are more dolomitized. The dissolution of dolomite at the groundwater temperature of Cuba (25 °C) is lower than the pure limestone.

The additional role of the CO₂ contents on the chemical corrosion can be illustrated by the example of the P222 well (Fig. 3) at the Varadero-Cardenas hydrogeologic sector (table 6). In this place, a sugar cane factory spill its wastes directly throw a pond to the karst and high CO₂ contents are developed.

Table 6. Relation among the basic chemical corrosion removed from selected places at the Pinar del Río, Habana and Matanzas Provinces with a mixture percent on the order of 0.04-0.05 %.

	POZO	N	CaCO ₃ cq (mg/L)
Pinar del Río	L-1	15	30
Habana	158	7	69
Matanzas	226	7	30

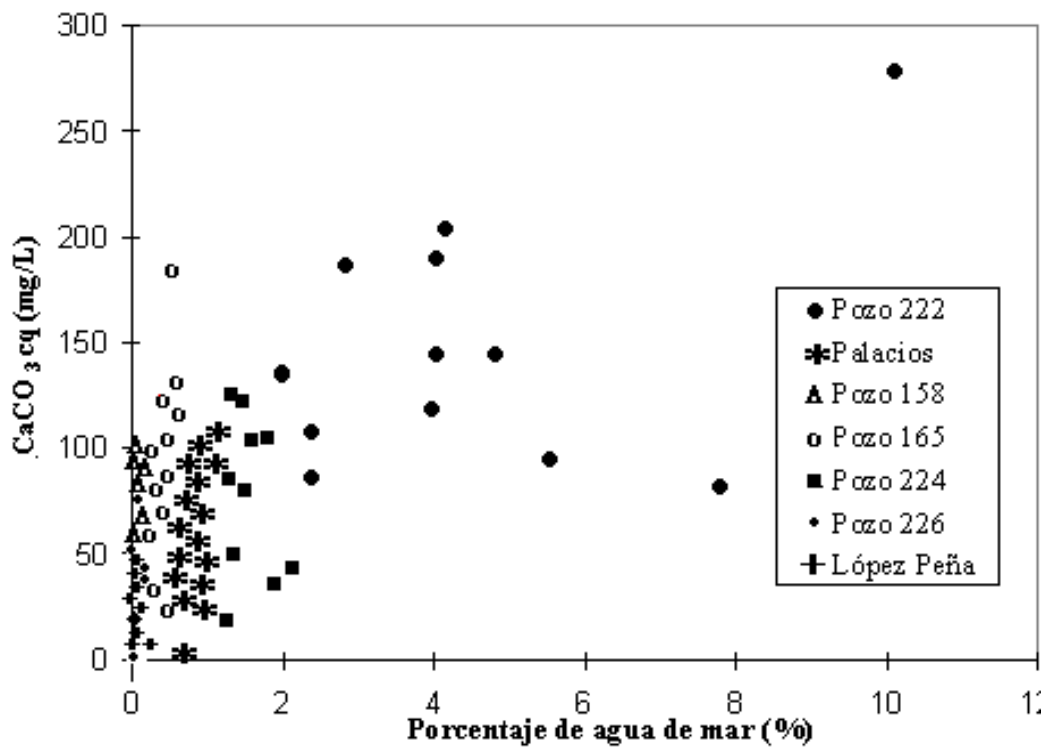


Figura 3. Chemical corrosion variation (as mg/l of CaCO₃) with respect the sea water percent in the mixture at the Cuban western littoral karstic aquifers.

The kinetics experiment carried out in laboratory (Table 7), are coherent with the water underground behavior.

Table 7. Variation of the chemical corrosion in a CO₂-H₂O-CaCO₃ interaction process with different percent of NaCl in the water.

0	0
2	144
6	269
10	344

The results discussed above allow the reflection about the drastic changes that the human impact can develop in karstic coastal areas in both, the water quality deterioration and the increase of secondary porosity of the carbonates, specially as the result of the aquifer overexploitation and the organic wastes spill.

CONCLUSIONS

By means of an hydrochloride contents chronological series studies, significant differences of the chemical corrosion magnitude at the karstic coastal aquifers developed on the Cuban western Miocene limestones were found. The aquifers show an intense chemical corrosion, which is function of the of the sea water percent in the mixture and the human impact. These aquifers are submitted to great exploitation for agricultural and water supply purpose, and occasionally are affected by the sugar cane waste spill.

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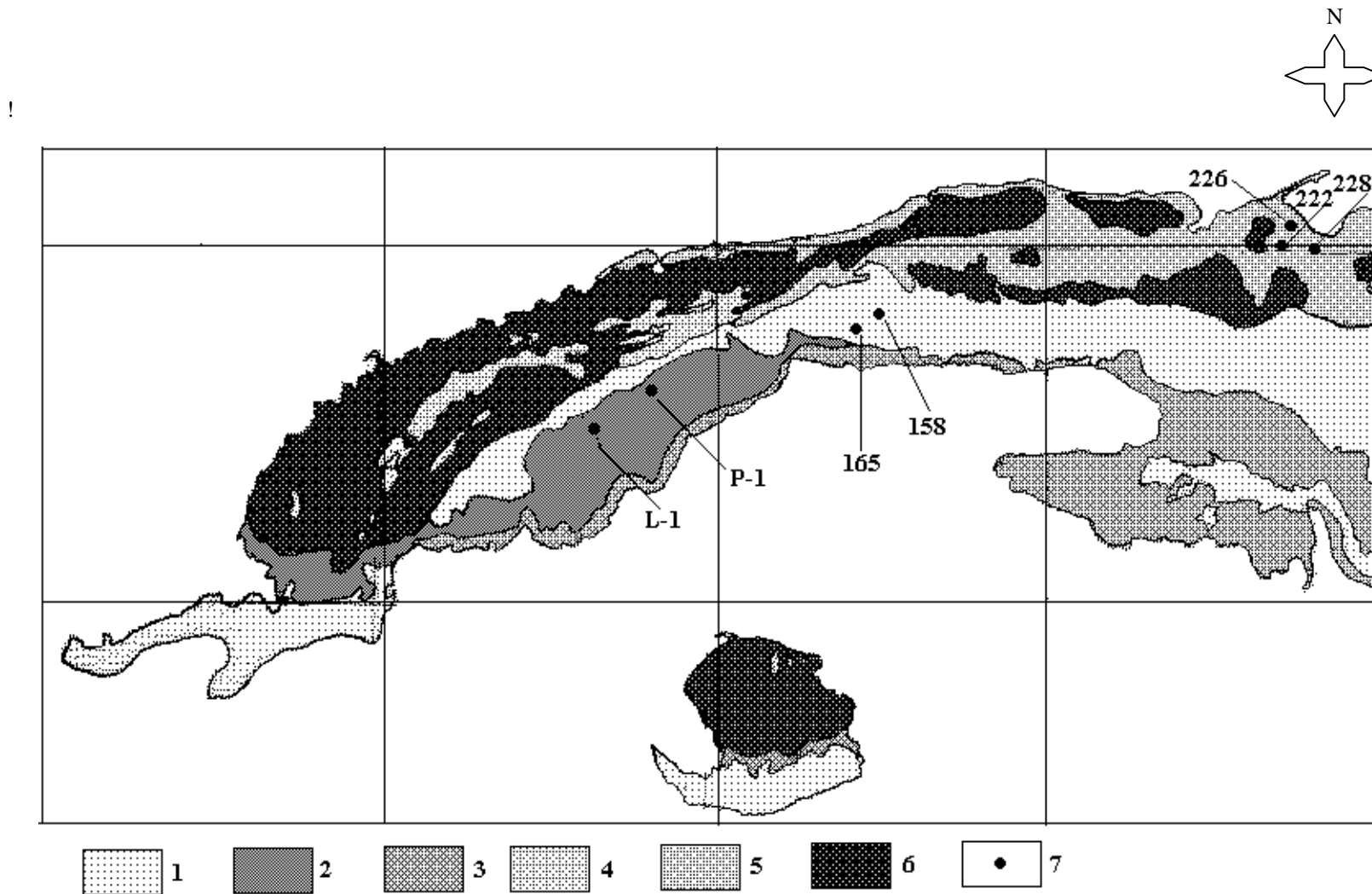
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Plain karst exposed limestone:

- 1 Naked karst
- 2 Karst covered by soil
- 3 Coastal swamp karst

Uplands and Mountains

- 4. One and towers karst
- 5 Karst in limestone and marbles

6. Non karstics areas

- 7 Sampling points

Fig. 1. Karts areas of Cuban after Nuñez Jiménez (1984)