

## RADIOCARBON DATING IN A KARSTIFIED COASTAL AQUIFER IN CUBA

D. M. ARELLANO<sup>1</sup>, I. R. FAGUNDO<sup>2</sup>, PAVEL HLEK<sup>3</sup>, JAN ŠILAR<sup>3</sup>

<sup>1</sup> Instituto de Recursos Hidráulicos, La Habana, Cuba

<sup>2</sup> Centro Nacional de Investigaciones Científicas, La Habana, Cuba

<sup>3</sup> Faculty of Science, Charles University, Praha, Czechoslovakia

*Abstract:* The intrusion of marine water into a coastal karstified aquifer in western Cuba results in oversaturation of the solution in respect to calcite, in low  $^{14}\text{C}$  activity, and, consequently, in apparent high radiocarbon ages of ground water. The  $^{14}\text{C}$  activity of ground water in limestones is affected by diffusivity in the fissured medium with a porous matrix.

### INTRODUCTION

During the study of groundwater in the Pinar del Río Southern Coastal Plain, Cuba, radiocarbon dating was used together with measurements of tritium in wells and with determination of stable isotopes concentration ( $^{13}\text{C}$ ,  $^{18}\text{O}$ ,  $^2\text{H}$ ) in rainfall, springs and wells. The area investigated is characterized by a karstified aquifer of Miocene age and by a sea water intrusion to the aquifer; it is an open groundwater basin.

The purpose of the present investigation has been to explain how radiocarbon dating may be influenced by the kinetics of the water-rock system. This is the first work of this kind which has been done in the Republic of Cuba.

### REVIEW OF THE NATURAL CONDITIONS OF THE AREA STUDIED

The investigated area is located in the Pinar del Río province southwest of Havana. Its southeastern part belongs to the Southern Coastal Plain; in the northwest it extends into a mountainous area. Its eastern boundary is the San Juan River, its northern limit is located within the Cordillera de Guaniguanico mountain range, its western boundary is the Guama River, and the southern limit the coast of the Caribbean sea. The surface area is approximately 4 600 km<sup>2</sup> (see fig 1).

The prevailing relief is plain-shaped and vertically little dissected. It covers the whole southern part of the investigated area.

The Cordillera de Guaniguanico consists of the Sierra de los Organos to the west and of the Sierra del Rosario in the east. The Sierra de los Organos consists of two parallel mountain ranges (Alturas de Pizarras del Norte and Alturas de Pizarras del Sur) with a karstified zone, the Planja de los Mogotes, in between. The latter is formed of cupola shaped karst hills (mogotes) or mountains the surface area of which is up to 8 km<sup>2</sup>. Their slopes are steep, even vertical. Between the karst hills and mountains there are karst valleys (poljes) the surface of which is composed of unconsolidated rocks. They form aquifers with groundwater originating in the karstified limestone. The altitude of the highest hills is between 400 m and 700 m above sea level.

The rainfall in the mountain range is subject to fluctuations depending on the physical and geographical conditions. Although two seasons are distinguished, namely the wet season (from May to October) and dry season (from November to April), two maximum rainfalls in June and September and one minimum rainfall in December are observed in a long observation period (more than 20 years).

TRUSOV, IZQUIERDO, DIAZ [1983] have pointed out that the rainfall

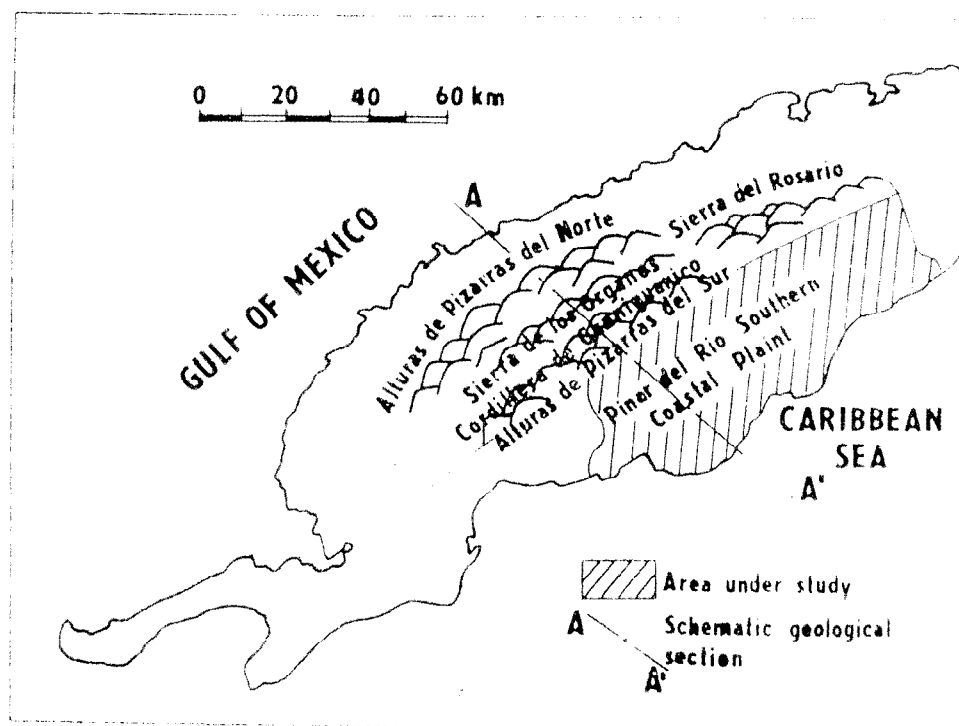


Fig. 1 Location of Pinar del Rio Southern Coastal Plain

amount to 25 % of probability reaches 1600 mm to 1800 mm in the mountain range and 1000 to 1500 mm in the plain. 17.7 percent of the rainfall is falling during the dry season and 82.3 percent in the wet season (BATISTA 1973). In the depressions and valleys, rainfall is less frequent. Its amount increases with altitude (100 mm/100 m of altitude on the average). Higher vertical gradients (122 mm/100 m) are observed in the lower part of the mountains to 400 m of altitude. Over 400 m (400--525 m), the mean gradient is 39 mm/100 m. In general, the rainfall distribution is different during the year. Extreme rainfalls may occur during a tropical cyclone (3--5 days).

The air temperature in the Southern Coastal Plain is typical for tropical zones. The average daily air temperature in the coldest month (January) is 20°C and in the hottest month, August, and in some days of July it reaches 30°C. In the Pinar del Río Southern Coastal Plain there is no evidence of groundwater of deep origin. At least it has not been found in wells and hydrogeological investigation boreholes which go 300 to 400 m deep.

#### KARST PROCESSES : TROPICAL KARST

According to LEHMANN (1960), tropical karst is a particular karst evolution caused by the tropical climate. Organic components forming  $\text{CO}_2$  and organic acids apparently play an important role under tropical conditions. In Cuba, karst is developed in surface and subsurface forms. In a relatively small and quasi homogeneous area, from the climatological point of view, there is a set of different types and subtypes of karst.

According to NÚÑEZ JIMENEZ *et al.* (1963), the following types and subtypes occur:

1. Coastal plain karst:

- coastal plain karst below the sea level;
- coastal plain karst recently emerged;
- coastal plain karst with overburden of swamps in which saline and fresh waters are present;
- coastal plain karst with overburden of continuous and thick alluvial, deltaic or mixed sediments (Pinar del Río Southern Plain).

2. Highland karst.

3. Diapiric-structure karst.

4. Coastal karst of the so-called "seboruco" type which is due to biochemical, chemical and mechanical processes which are typical in tropical seas.

All types and subtypes mentioned ad 1 and ad 2 occur in the area studied

## GEOLOGICAL CONDITIONS

A schematic geological section (A—A') of the Pinar del Río province is shown in fig. 2. From the geological point of view the mountainous zone consists of Jurassic limestones which are highly karstified. Fractures, grikes, sinkholes, labyrinths, underground rivers and mogotes occur frequently. In the mountainous zone (Sierra del Rosario, Sierra de los Organos and Alturas de Pizarras) abandoned dry riverbeds and long large caves occur in karstified limestone massifs.

In the front-range zone the San Cayetano formation (the oldest geological formation in Cuba) extends. It is composed of an aleurolitic terrigenous shale — carbonate sequence of Lower Jurassic to Upper Jurassic age.

Metamorphic rocks (of the Faja Cangre series) are represented by quartzose shales and terrigenous rocks of the Lower Jurassic to Eocene. These rocks occur along the Pinar Fault. The Pinar Fault is one of the

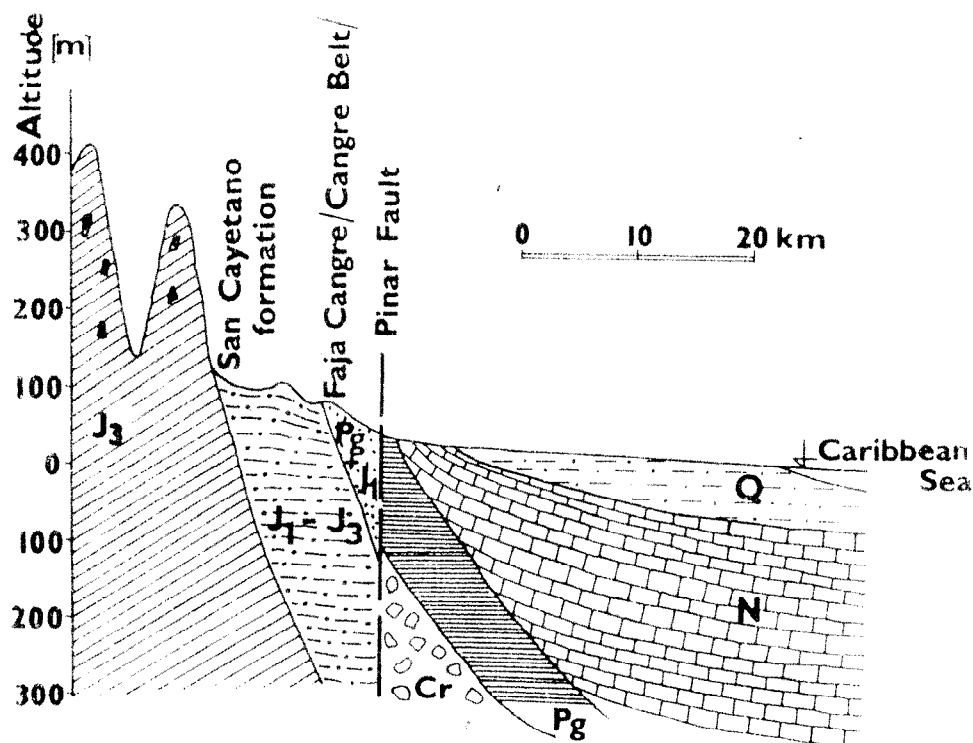


Fig. 2 Schematic geological section of the Pinar del Río Province (A—A' in the map, fig. 1)

deepest structures in Cuba. It is of Jurassic age and it strikes NE forming a long arc bending a little towards E. The Pinar Fault has a length of 160 km. The plane of the fault is steeply inclined towards SE. The vertical amplitude of the fault is considered to be about 3000 m. The width of the fault zone is 4 km and it constitutes a foredeep fault forming a fan-shaped fold. In the Paleogene deposits which crop out in the front-range zone, parallel to the Pinar Fault, various groundwater outflows occur. These deposits are composed of terrigenous carbonate facies with a low permeability.

The Pinar del Río Southern Coastal Plain is of Miocene age. It is composed of carbonate and terrigenous-carbonate layers. In the Lower and Middle Miocene limestone deposits occur which are very karstified. Their maximum thickness is 160 m. According to the data collected during drilling operations, the thickness of these terrigenous-carbonate deposits is higher than 600 m.

Quaternary and contemporary lake and swamp deposits are composed of alluvial and proluvial deposits (sandstone, sandy clay, gravel). Their thickness can reach up to 80 m in isolated areas (e.g. in the eastern part of the Southern Coastal Plain).

#### HYDROGEOLOGICAL AND HYDROCHEMICAL DATA

The Pinar del Río Southern Coastal Plain has been studied during the last years (KALASNIK *et al.* 1981; ARELLANO 1986 and others).

The piezometric levels of groundwater depend on the lithological composition of the sedimentary rocks which form the aquifer. According to the position of the piezometric level, this coastal plain has been divided into three hydrogeological zones (western, central, eastern). Table No. 1 shows the main hydrogeological parameters which give a rough characterization of each hydrogeological zone. The average value of the infiltration coefficient is 0.09 and the mean yearly recharge is 120 mm year<sup>-1</sup>; the coefficient of storage has a wide range from  $1 \cdot 10^{-3}$  to  $1 \cdot 10^{-2}$ . The hydraulic gradients of the groundwater flow are low, in the order of  $1 \cdot 10^{-3}$  to  $1 \cdot 10^{-1}$ , although in the zone near the sea they may reach  $4 \cdot 10^{-4}$ .

Table No. 1 Main parameters of the hydrogeological zones

Zone	Discharge of wells [l.s <sup>-1</sup> ]	Transmissivity [m <sup>2</sup> .d <sup>-1</sup> ]
Eastern	275—300	$10 \cdot 10^3$ — $20 \cdot 10^3$
Central	200—250	$2 \cdot 10^3$ — $10 \cdot 10^3$
Western	200—250	$2 \cdot 10^3$ — $20 \cdot 10^3$

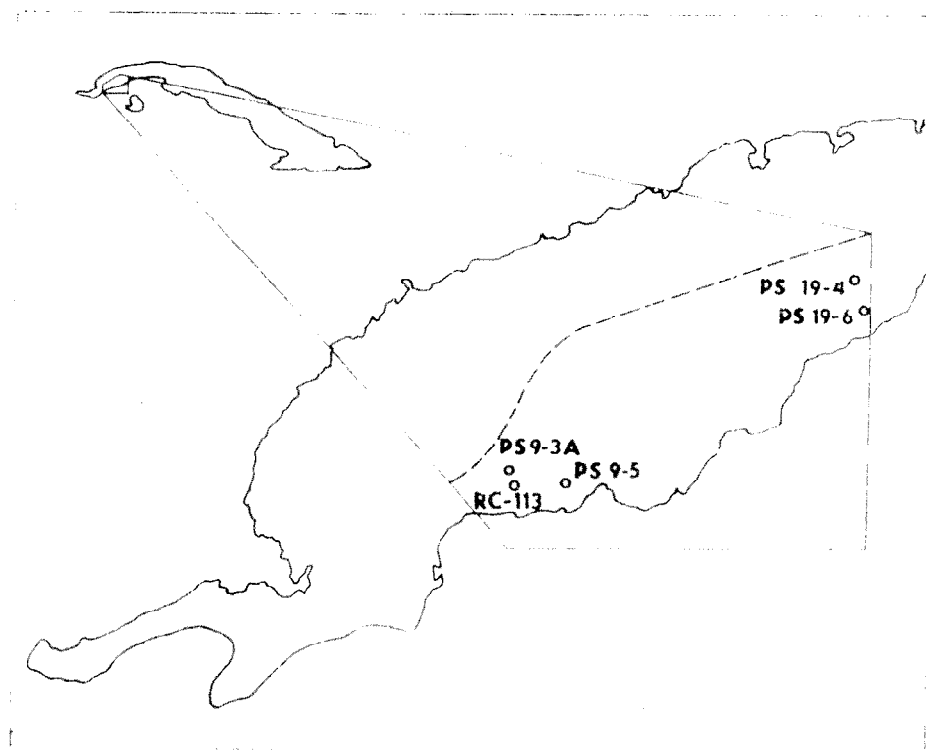


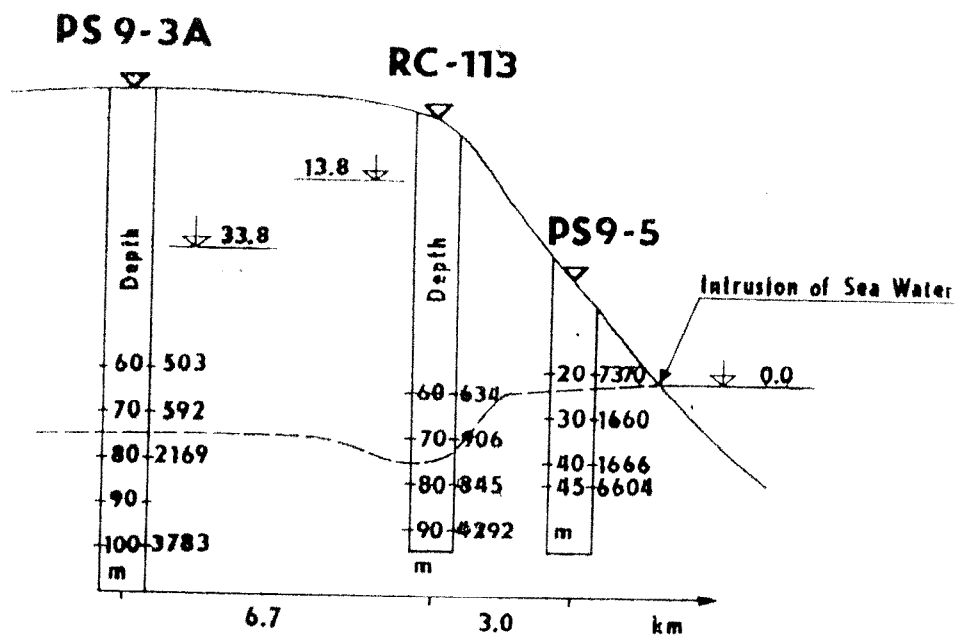
Fig. 3 Location of the wells where hydrochemical analyses were made

Besides the geological and hydrogeological data, hydrochemical data are very significant for the interpretation of radiocarbon dating. Fig. 3 shows the location of wells where hydrochemical analyses were made. Fig. 4 shows a representative hydrochemical profile in the eastern hydrogeological zone. The sea water intrusion is evident. In the eastern zone the situation is similar.

During the geochemical zoning of the whole area (ARELLANO, FAGUNDO 1985), geochemical parameters such as the total dissolved solids (TDS, ppm),  $p\text{CO}_2$  (atm), calcite saturation ratio (CSR), specific conductivity (SPC,  $\mu\text{mhos} \cdot \text{cm}^{-1}$  at  $25^\circ\text{C}$ ), dolomite saturation ratio (DSR), and hardness (as ppm of  $\text{CaCO}_3$ ) were calculated in sixteen wells distributed within the three hydrogeological zones. The ionic concentration [ $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ] values were determined in each well in two to five depths.

In addition to the above mentioned parameters, pH values were reported. The ionic concentrations, SPC, TDS and pH were measured

NW



The groups of four numbers in the Table correspond to four sampling depths, respectively indicated in the figure

TDS	339.00		
(ppm)	372.00	384.00	447.00
	1305.00	550.00	1088.00
	—	516.00	1102.00
	2146.00	2308.00	3416.00
pH	7.30	7.40	7.40
	7.60	7.60	7.40
	7.70	7.70	7.50
	7.70	7.70	7.50
Mg Ca	0.18	0.30	0.49
	0.28	0.36	0.53
	0.80	0.36	0.52
	1.01	1.12	1.28
	0.52	1.01	1.62
Na Ca	0.78	1.34	1.89
	2.88	1.29	1.91
	4.14	4.62	3.82
HCO <sub>3</sub> /Ca	1.03	1.06	1.34
	0.97	0.87	0.73
	0.75	0.93	0.75
	0.62	0.65	0.28
Cl/HCO <sub>3</sub>	0.65	1.17	1.32
	1.08	2.05	3.51
	5.00	1.79	3.44
	9.09	9.07	19.60

Fig. 4 Hydrochemical profile in the western zone. piezometric level  
 Upper part: wells with indicated specific conductivity (SPC) and total dissolved solids (TDS)  
 Lower part: TDS, pH and ionic ratios at different depths

Table No. 2. Chemical composition of sea water near the area studied

Locality: "La Coloma" [Date of sampling: 29 Jan. 1984]

Distance from the seashore (km)	Ionic concentrations (ppm)									
	pH	SPC	TDS	CO <sub>3</sub> H	Cl	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K
0.2	7.3	29820.0	31303.0	134.0	17750.0	1800.0	380.0	1008.0	9890.0	341.0
0.6	7.2	32508.0	32611.0	120.0	17750.0	3256.0	380.0	1456.0	10350.0	403.0

The analyses were made in the water-chemistry and biological laboratory of the Instituto de Hidroeconomía, Republic of Cuba (A. Santos, 1984; *personal communication*).

in the sea, in two distances from the seashore. Table No. 2 shows the chemical composition of these waters. It should be noted that in both points the Mg/Ca ratio is 2.6 and 3.8, i. e. higher than one, as could be expected. Figs. 5 and 6 show the dependency between the CSR and DSR with depth, respectively. In both cases oversaturation occurs in the zone of fresh water — sea water mixing. This oversaturation was

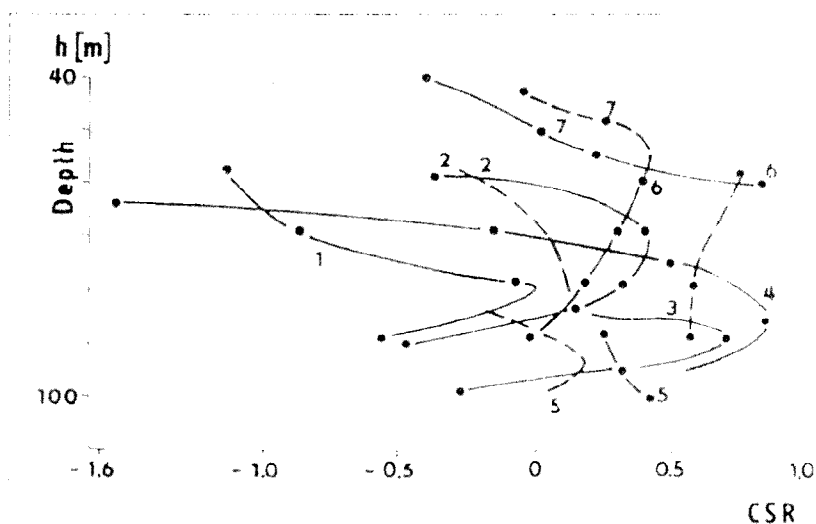


Fig. 5. Calcium Saturation Ratio (CSR) with depth in seven selected wells.

Well studied:

- |              |              |
|--------------|--------------|
| 1. — PS 9—3A | 5. — PS 18—3 |
| 2. — RC—113  | 6. — PS 19—4 |
| 3. — PS 9—5  | 7. — PS 19—6 |
| 4. — PS 11—2 |              |

Dashed line = Date of sampling May 1981

Solid line = Date of sampling Dec. 1984



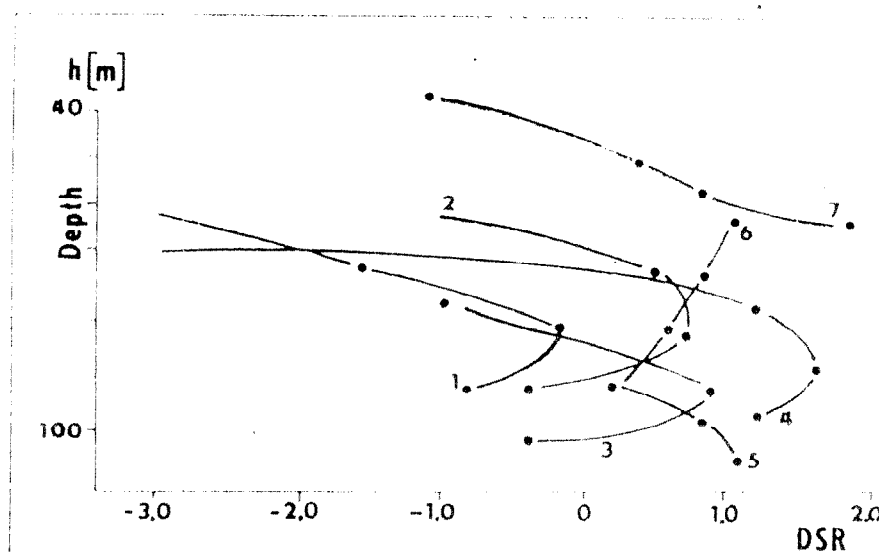


Fig. 6 Dolomite Saturation (DSR) with depth in seven selected wells  
Well studied:

- |              |              |
|--------------|--------------|
| 1. — PS 9-3A | 5. — PS 18-3 |
| 2. — RC-113  | 6. — PS 19-4 |
| 3. — PS 9-5  | 7. — PS 19-6 |
| 4. — PS 11-4 |              |

also found by HANSHAW, BACK and DEIKE (1971) during their investigations in the Tertiary limestone aquifers of the Florida and Yucatán Peninsulas. Such saturation with respect to the two carbonates increases in the direction of the flow until the solution apparently becomes over saturated.

#### ISOTOPIC INFORMATION ANALYZED

The Pinar del Río Southern Coastal Plain has been studied using isotopic techniques. The aim of this investigation is to clear up the local conditions of groundwater circulation. Measurements of  $^{18}\text{O}$ ,  $^2\text{H}$  and  $^3\text{H}$  in rainfall, springs and wells were made for this purpose at selected sampling points and intervals.

The preliminary results indicate that:

1. There is a stratification of groundwater.
2. The area studied consists of three hydrogeological zones. The main particular facts which distinguish each of these zones, besides the lithological factors and tectonics, are:
  - a) in the eastern zone possible contribution of rivers to the groundwater circulation

- b) in the central zone the contribution of water from the neighbouring zones and from the mountainous zone in the NW
  - c) in the western zone the local infiltration of rainfall.
3. The component of groundwater due to the recent rainfall has a residence time close to 18 years, according to the  $^3\text{H}$  units found. In 22 wells the values of  $^3\text{H}$  concentration measured in two different depths range from 9.2 to 0.9 T. U. In all cases if  $\text{TU} < 3$  the groundwater is affected by intrusion of sea water. This fact has been proved by means of chemical analysis of these waters.
4. According to the results of the isotopic composition of water measured in springs, rainfall and wells (ARELLANO, SEILER *in preparation*), there is a connection between the groundwater in plain and the water in mountainous and premountainous zones.

#### FACTORS AFFECTING GROUNDWATER DATING IN THE NATURAL CONDITIONS OF THE AREA UNDER STUDY

In the karstified aquifers in tropical climatic conditions where, moreover, sea water intrusion is present, complex physico-chemical and mechanical processes have developed which influence the radiocarbon dating, among them:

##### 1. Saturation of water with respect to calcite

If fresh water is not saturated with calcite, it will dissolve calcite until equilibrium between calcite and the dissolved species is achieved.

According to VERNON (1969), the karstification along the coast may be caused by dissolving of limestone due to mixing of fresh and saline water. That is, mixing of saline and fresh water in the interface zone

Table No. 3 Hydrogeochemical and hydrogeological parameters of water in the wells studied

Well No	Depth (m)	Static level (m)	CSR	DSR	$p\text{CO}_2$ (atm)	Hardness (ppm)
CUB-5	57.0	18.2	0.37	0.71	10 <sup>-2.51</sup>	313.4
CUB-6	80.0	33.0	-0.03	-0.94	10 <sup>-2.05</sup>	216.2
CUB-7	10.0	1.0	-1.01	-2.47	10 <sup>-1.68</sup>	206.9
CUB-8	43.0	29.5	0.27	-0.08	10 <sup>-2.00</sup>	658.3
CUB-9	40.0	23.5	0.20	0.06	10 <sup>-2.01</sup>	409.6
CUB-10	34.0	14.4	0.29	0.50	10 <sup>-2.13</sup>	408.1
CUB-11	90.0	40.4	0.19	0.24	10 <sup>-1.71</sup>	501.9

The pH values were measured in the field. The CSR, DSR and  $p\text{CO}_2$  values were calculated by means of a computer program (AGMAR Program, FAGUNDO, VALDES, 1983).

Table No. 4 Results of the chemical analysis of water in the wells studied

Well	T [°C]	pH	TDS ppm	SPC	Ionic concentrations (ppm)						
				$\mu\text{mhos cm}^{-1}$ at 25 °C	HCO <sub>3</sub> <sup>-</sup> (ppm)	(mol.l <sup>-1</sup> )	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>
CUB-5	26.5	7.8	895	1376.0	204	$3 \times 10^{-3}$	354	41	81	27	171
CUB-6	27.0	7.3	398	568.0	211	$3 \times 10^{-3}$	68	7	80	4	23
CUB-7	24.0	6.7	461	666.0	158	$2 \times 10^{-3}$	107	54	68	9	61
CUB-8	25.0	7.3	1431	2000.0	270	$4 \times 10^{-3}$	405	276	229	21	230
CUB-9	25.0	7.5	552	752.0	228	$4 \times 10^{-3}$	122	36	94	16	0
CUB-10	25.0	7.5	803	1000.0	281	$5 \times 10^{-3}$	187	87	109	33	0
CUB-11	25.0	7.2	774	936.0	368	$6 \times 10^{-3}$	116	68	140	37	45

may cause limestone dissolution. In this process the concentration of both  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  would increase in the solution phase which could cause oversaturation.

It seems that the indication of NORDSTRÖM *et al.* [1985] concerning the  $\text{pCO}_2$  and pH values may be applied to the karstified limestone with saline intrusion: in groundwater which has pH values near 6 and  $\text{pCO}_2$  about 10 bars ( $10^{-2}$  atm, approx.), calcite is unstable and tends to dissolve under partially closed conditions until water reaches pH values of about 8 at saturation. Then if calcite begins to be precipitated, pH should be maintained close to 8 [see fig. 7]. According to the table No. 3, this fact may be considered.

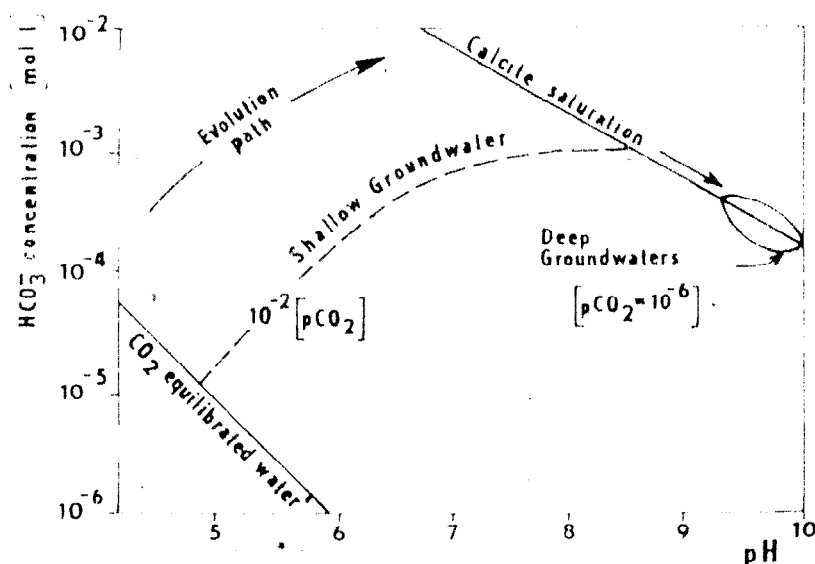


Fig. 7 Schematic evolutionary diagram of bicarbonate, pH and  $\text{pCO}_2$  during calcite dissolution [after NORDSTRÖM *et al.* 1985]

## 2. Ion exchange reactions

Regardless that saturation with respect to calcite is reached, ion exchange reactions may be expected:



## 3. Salting out effect

Another mechanism through which the  $^{14}\text{C}$  activity may decrease is the "salting out effect". In this case the quantity of non biogenic carbon from  $\text{CO}_3^{2-}$  may increase as a result of a higher solubility when alkaline ions occur.

That is:

$$K_c = (\text{Ca}^{2+}) (\text{CO}_3^{2-})$$

where  $K_c$  is the calcite solubility product.

## 4. Diffusive loss of radiocarbon into the rocks

The diffusive loss of radiocarbon into the cavernous zone may become very significant, depending on spacing, width, and communication between the conducts. The residence time of the individual carbonate ions is longer than the residence time of water flowing through narrow fissures because of their larger size compared to the molecules of water. Both residence times depend on the porosity values.

All these physico-mechanical processes in rocks have a great influence on the  $^{14}\text{C}$  activity. The geochemical models formulated to estimate the "initial" activity of the total dissolved carbon do not seem to be sufficient to explain the values obtained.

## MATERIAL AND METHODS

Fig. 8 shows the wells where samples for determining  $^{14}\text{C}$  and  $^{13}\text{C}$  were taken. The samples were collected in the field following the method reported by the IAEA (1983).  $^{14}\text{C}$  activity of the samples was measured in the  $^{14}\text{C}$  laboratory at the Charles University in Prague. The  $\delta^{13}\text{C}$  values of carbonates in the water samples were determined in the laboratory of the Central Geological Survey in Prague by BUZEK and HLADÍKOVÁ (*personal communication* 1985).

All the samples were taken from water-supply wells. The water comes directly from the aquifer by continuous pumping, with the exception of CUB—7 which is a shallow farm well ("criollo well").

For this reason the  $^{14}\text{C}$  values obtained in the latter were used only as additional and qualitative information. The samples from the wells CUB-1 and CUB-2 were taken in 1981 (ARELLANO, SANTOS 1984). The well CUB-1 is located in the recharge area. The  $^{14}\text{C}$  activity values are in table No 5. In all the samples the initial  $^{14}\text{C}$  activity was estimated to 70 % of 0.95 NBS activity.

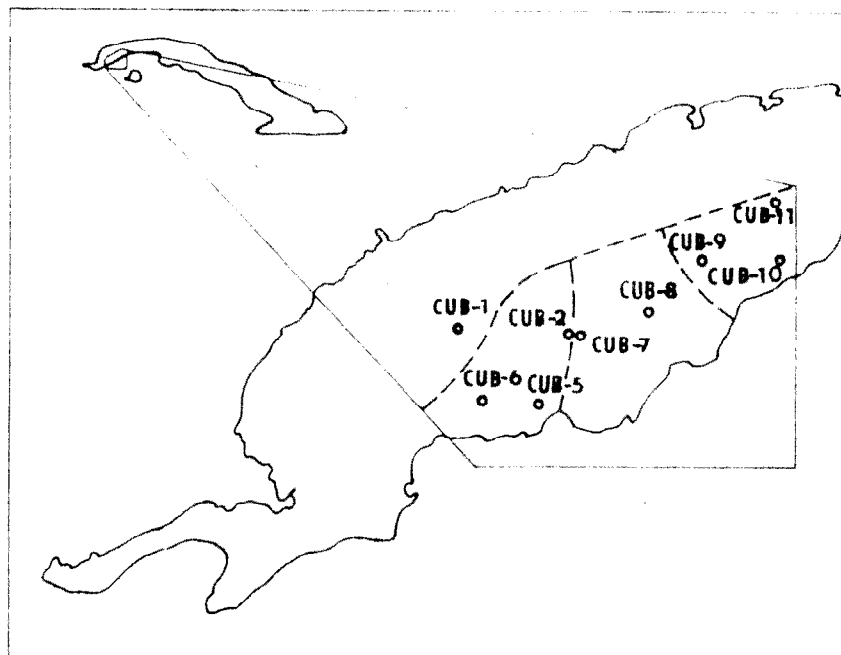


Fig. 8 Location of points in which  $^{14}\text{C}$  activity and  $^{13}\text{C}/^{12}\text{C}$  ratio were measured

Table No. 4 shows the results of the chemical analyses of water in the wells where  $^{14}\text{C}$  activity and  $\delta^{13}\text{C}$  were determined. Additional hydrogeochemical and hydrogeological parameters are shown in table No. 3.

The  $p\text{CO}_2$  values (atm) were determined in the recharge zone. They are indicated in table No. 6.

Table No. 5  $^{14}\text{C}$  activities in wells

Well	Activity with respect to 0.95 act. of NBS [‰]	$^{14}\text{C}$ age [years BP]
CUB-1	$72.22 \pm 1.89$	contemporary
CUB-2	$59.42 \pm 1.96$	1300      160

Table No. 6  $p\text{CO}_2$  values in the recharge zone

Place of measurement	Locality	$p\text{CO}_2$ (atm)	pH	Other SPC (ppm)	parameters (1) (2)	
Surface water	A. Pizarras	$10^{-2.9}$	7.56	170	0.91	0.8
Streambed in the cave	La Viuda	$10^{-2.5}$	7.84	370	2.8	0.7
Cave spring	La Castaña	$10^{-2.4}$	7.68	360	7.3	0.9
Spring	Las Yaguas	$10^{-2.0}$	7.32	450	4.9	4.2
Dropping water	Sierra Resolladero	$10^{-2.9}$	7.90	210	1.0	0.7
Well (h=10 m)	Caiguanabo	$10^{-1.7}$	7.10	437	7.6	1.0
Well (h=10 m)	La Guira	$10^{-1.8}$	7.65	803	6.2	2.7

parameters:

(1) — Ca/Mg ratio; (2) — Ca/HCO<sub>3</sub>— ratioTable No. 7  $\delta^{13}\text{C}$  values in plants

Plant	$\delta^{13}\text{C}$ (‰ PDB)	Photosynthetic cycle
Sugar cane	-11.42	Hatch-Slack
Rice	-28.94	Calvin-Benson
Coffee	-28.68	Calvin-Benson

The determination of  $\delta^{13}\text{C}$  values in typical vegetation (sugar cane, coffee, rice) was carried out. The measurements were made in the Isotopic Hydrology and Geochemistry Laboratories, University South Paris, France, by FONTES (1983, personal communication). The values obtained are in table No. 7.

The samples of carbonates extracted from water in the field as  $\text{BaCO}_3$  were processed in the radiocarbon laboratory of the Charles University in Prague in the following way: They were converted to  $\text{CO}_2$  by acidification and purified to a high degree by repeated freezing in a vacuum line with liquid nitrogen traps and by adsorption in sodium hydroxide. During the processing a small amount of the  $\text{CO}_2$  sample was separated by freezing in an ampoule for measuring  $\delta^{13}\text{C}$ .

The purified carbon dioxide was filled into a proportional counter with an effective volume of 723 ml to a pressure of about 0.25 MPa. The background of the counter is decreased by using a vacuum-silver-plated tube of pure quartz as a cathode in a copper tube purchased from an old brewery pipeline. A molybdenum wire 0.03 mm in diameter is used as an anode. The proportional counter is shielded by a plastic-scintillator

mantle with two large-diameter photomultipliers, each at one front, and is closed in a light-tight case. The whole counter with the anticoincidence shielding is in a passive mechanical shielding box consisting of a double layer of old lead (150 mm thick in total) with a neutron shielding in between (boric acid dispersed in polymers) and a layer of soft steel.

The background in this arrangement is about 2.1 cpm, depending on the barometric pressure. The samples are measured for about 1200 minutes. The measurements are registered automatically and calculated to radiocarbon ages on a computer. Corrections for barometric pressure as well as for room temperature,  $\delta^{13}\text{C}$  and dilution of the sample by inactive carbon dioxide (if necessary) have been incorporated into the programme for evaluating the measurements. The radiocarbon ages are rounded up only to whole years to facilitate statistical evaluation and comparisons. The results are in table No. 9.

## RESULTS OBTAINED AND THEIR DISCUSSION

### 1. Partial pressure of $\text{CO}_2$ and its relation to the radiocarbon dating in the area, $\delta^{13}\text{C}$ values.

The geological and morphological complexity of the recharge zone (development of karst, caves, underground streams, surface streams, springs) results in different flow patterns and different behaviour of  $\text{CO}_2$  in water.

The  $\text{CO}_2$  content in karst surface water and in the water from caves is small, the escaping of  $\text{CO}_2$  in these waters is high. The values of hardness, mineralization and specific conductivity are generally low. In confined aquifers these values develop towards a higher  $\text{CO}_2$  content, hardness, mineralization, specific conductivity, Ca/Mg ratio, and towards a lower pH (FAGUNDO, PAJON and SPASOV *in press*). The southern coastal plain may be considered a closed system with regard to  $\text{CO}_2$ .

In all the hydrogeological zones the  $p_{\text{CO}_2}$  values are in the order from  $10^{-4}$  to  $10^{-2}$  atm. This means that the dissolution of the rock occurs. Therefore a contribution of  $\text{CO}_2$  of inorganic origin should be expected. This is a hydrogeochemical point of view of the problem. Besides that, the difference between the  $p_{\text{CO}_2}$  values depends on whether the ground-water flows through fissured or porous media. This is a hydrodynamic point of view of the problem.

The contribution of carbonates of inorganic origin has been tested by the CSR values which, with the exception of the well CUB—7 (CSR = -1.01), indicate oversaturation with respect to calcite.

In the well CUB—7 there is a major contribution of carbonates of bio-

genic origin, if we take into account that  $\delta^{13}\text{C} = -12.9\text{‰}$  is a highly negative value among the values examined. It should be remarked that this well is a shallow farm well 3 m deep, in Quaternary sediments.

The values found in the well CUB-5 ( $\delta^{13}\text{C} = -7.2\text{‰}$ ) and in the well CUB-8 ( $\delta^{13}\text{C} = -8.7\text{‰}$ ) are due to the dissolution effect of calcite. In both wells the groundwater is oversaturated with respect to calcite due to the effect of sea water intrusion. In these wells the total dissolved solids (TDS) at the sampling point are 895.0 and 1431.0 ppm, respectively, with a corresponding specific conductivity of  $1376\text{ }\mu\text{mhos}\cdot\text{cm}^{-1}$  and  $2000\text{ }\mu\text{mhos}\cdot\text{cm}^{-1}$  at  $25^\circ\text{C}$ .

The  $\delta^{13}\text{C}$  values obtained in the wells CUB-9, CUB-10 and CUB-11 indicate the contribution of carbonates of inorganic origin. The extreme value found in the well CUB-6 ( $\delta^{13}\text{C} = -15.2\text{‰}$ ) is a particular case. This well is located in a part of the basin ( $25\text{ km}^2$ , approx.) where the unconfined aquifer conditions are evident. Thus, a major contribution of  $\text{CO}_2$  of biogenic origin can be expected.

## 2. Possibility of deeper origin of groundwater

Table No. 8 shows the available information on the  $^3\text{H}$  concentration (RAUERT, *personal communication*, [1985]) measured in wells located near those where  $^{14}\text{C}$  activity was determined. The distances between the wells vary between 1 and 10 km, approximately.

Table No. 8  $^3\text{H}$  concentration values measured in wells located near those where  $^{14}\text{C}$  was determined

Well	Depth (m)	Corresponding $^3\text{H}$ well	Depth (m)	$^3\text{H}$ concentration (TU)
CUB-5	22	PS9-5	20-30	1.8-1.6
CUB-6	36	PS9-3A	40-70	3.4-4.4
CUB-7	3	PS11-2A	60-90	5.3-5.1
CUB-8	33	PS13-5A	25-35	2.6-1.8
CUB-9	27	PS17-3	60-80	7.0-3.5
CUB-10	18	PS19-6	40-50	5.0-9.0
CUB-11	37	PS18-1A	80	3.7

The two different  $^3\text{H}$  concentrations in the last column correspond to the respective depths in the previous column. According to the  $^3\text{H}$  concentration values in these wells, the occurrence of old groundwater of deep origin does not seem to be realistic.

It should be remarked that in wells where tritium-concentration values are lower than 3 TU, the sea water intrusion is present and these values are caused by its effect.



An important fact is that the mean oxygen 18 content ( $\delta^{18}\text{O}$ ) measured in these wells, where  $^3\text{H}$  concentration was determined, is in the same range as it is in the mountainous recharge zone. The variations found are due to the local infiltration of rainfall in zones where the aquifer is unconfined or where the infiltration from rivers into the aquifer occurs.

### 3 Interpretation of the $^{14}\text{C}$ activity measurements

For calculating the  $^{14}\text{C}$  activities to groundwater  $^{14}\text{C}$  ages ( $t$ ) the conventional Libby half life of  $^{14}\text{C}$   $T_{1/2} = 5568 \pm 30$  years was used according to

$$t = \frac{T_{1/2}}{\ln 2} \ln (A_0/A)$$

where  $A$  is the measured  $^{14}\text{C}$  activity of the sample and  $A_0$  is its assumed initial  $^{14}\text{C}$  activity.

For comparison three different empirically found values of the initial  $^{14}\text{C}$  activity  $A_0$  were used for the calculation as found in sedimentary rocks [MÜNNICH and VOGEL, 1959; VOGEL, 1970; GEYH, 1972], i.e. 60 %, 70 % and 85 % of modern standard activity (0.95 activity of NBS oxalic acid). The fourth value of  $A_0$  was calculated according to Gonfiantini's model (as reported by SALEM *et al.* 1980) according to the following equation:

$$A_0 = \frac{100(\delta - \delta_c)}{\delta_g + \delta_c + \varepsilon} (1 + 2\varepsilon/1000)$$

The values adopted for the calculation were

- $\delta_c$  .....  $\delta^{13}\text{C}$  value in the solid carbonate, equal zero
- $\delta$  .....  $\delta^{13}\text{C}$  value in the bicarbonate of the water sample
- $\delta_g$  .....  $\delta^{13}\text{C}$  value in the soil  $\text{CO}_2$ , equal  $-25\text{‰} + 1\text{‰}$  (PDB)
- $\varepsilon$  ..... fractionation factor between bicarbonate of the water sample and soil  $\text{CO}_2$ , equal  $-8\text{‰}$

The indicated value of  $\delta_g$  is generally found for dicotyledonous plants [FONTES 1983]. This type of vegetation is very common in the area where the investigated wells are located. The resulting  $^{14}\text{C}$  groundwater ages are given in table No. 9.

### CONCLUSIONS

The  $^{14}\text{C}$  activity values of 11.51 %, 42.42 %, 43.79 %, 49.32 % obtained in the wells CUB—5, CUB—6, CUB—9 and CUB—10, respectively, sug-

Table No. 9 Calculation of groundwater age on the basis of  $^{14}\text{C}$  activity

Well	Number of sample	Number of measur.	$^{14}\text{C}$ activity [‰ 0.95 NBS]	$^{14}\text{C}$ age $\pm 1\sigma$ for initial activity			Ratio for Confidence model [‰ PDB]	$\delta^{13}\text{C}$
				60 ‰	70 ‰	85 ‰		
CUB—5	201	CU—562	11.51 $\pm$ 6.31	13261 $\pm$ 507	14500 $\pm$ 507	16359 $\pm$ 507	10592 $\pm$ 507	-7.2
CUB—6	202	CU—563	42.42 $\pm$ 2.83	2785 $\pm$ 227	423 $\pm$ 227	5583 $\pm$ 227	6117 $\pm$ 227	-15.2
CUB—7	203	CU—564	104.52 $\pm$ 1.61	Contemporary	Contemporary	Contemporary	Contemporary	-12.9
CUB—8	204	CU—565	114.10 $\pm$ 1.57	Contemporary	Contemporary	Contemporary	Contemporary	-8.7
CUB—9	205	CU—569	43.79 $\pm$ 2.35	2531 $\pm$ 169	3769 $\pm$ 169	5329 $\pm$ 169	4480 $\pm$ 169	-12.8
CUB—10	206	CU—560	49.32 $\pm$ 2.19	1575 $\pm$ 176	2513 $\pm$ 176	3333 $\pm$ 176	2545 $\pm$ 176	-11.4
CUB—11	207	CU—567	68.16 $\pm$ 1.89	Contemporary	Contemporary	1772 $\pm$ 152	Contemporary	-11.9

gested the presence of "old" groundwaters in the karst area, where the existence of such waters had not been evidenced. However, the following conclusions should be considered:

1. In karst conditions with intrusion of sea water the low  $^{14}\text{C}$  activity values seem to be due to chemical processes, which are similar to those explained by NORDSTROM *et al.* [1985], i. e. due to the increased dissolution of calcite. The intrusion of water from the sea promotes the oversaturation of groundwater; the dissolution of calcite decreases the  $^{14}\text{C}$  activity and it affects the calculation of the  $^{14}\text{C}$  age. Moreover, in this case the salting out effect should be expected, too.
2. In karst conditions the diffusive loss of radiocarbon into the rock seems to have a great influence on the radiocarbon concentration. This loss is a physico-mechanical process which has not been considered in the existing geochemical models, but it is significant.
3. The first investigations using isotopic techniques in Cuba should continue in future on a larger scale. It is desirable to perform comparative measurements in other laboratories.

Both the physico-chemical and geochemical processes which occur in the karstified medium where the  $^{14}\text{C}$  activity is measured should be taken into account during the detailed interpretation of the results.

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#### RADIOUHLÍKOVÉ DATOVÁNÍ VODY V KRASOVÝCH HYDROGEOLOGICKÝCH KOLEKTORECH V TROPICKÝCH KLIMATICKÝCH PODMÍNKÁCH

D. M. ARELLANO ACOSTA, J. R. FAGUNDO, F. JILEK, J. ŠILAF

V sedmi vrtech v provincii Pinar del Rio na západní Kubě v podzemní vodě pobřežního krasového hydrogeologického kolektoru byly měřeny: nasycení vzhledem ke kalcitu,  $\mu\text{CO}_2$  a radiouhlíková aktivita, z níž bylo s použitím různých modelů vypočteno radiouhlíkové stáří podzemní vody.

Pomocí měření specifické vodivosti, celkové mineralizace a iontových poměrů [ $\text{Mg}^{2+}/\text{Ca}^{2+}$ ,  $\text{Cl}^-/\text{HCO}_3^-$ ,  $\text{Na}^+/\text{Ca}^{2+}$  a dalších] byla zkoumána intruze mořské vody do pobřežního kolektoru. Tato intruze určuje kinetické faktory hydrogeologického systému.

Intruze mořské vody do vápenců má za následek přesycení roztoku a nízkou radio-

uhlíkovou aktivitu, z čehož vyplývají radiouhlíková stáří vody od 1 000 do 16 000 roků. Tato stáří nejsou v souladu s dostupnými předběžnými údaji o koncentraci stálých izotopů ( $\delta^{18}\text{O}$  a  $\delta^2\text{H}$ ) měřených ve sračkách, pramenech a vrtech, a s měření tritia, které nasvědčuje přítomnosti současné vody.

Krasové dutiny a pukliny ovlivňují nízkou radiouhlíkovou aktivitu. Difusivita v horninách ovlivňuje měřenou aktivitu, jak plyne z teoretických předpokladů i z pokusů v rozpukném pórovitém prostředí.

V humidním tropickém klimatu je biologická aktivita velmi intenzivní a vypočtené hodnoty  $p\text{CO}_2$  jsou  $10^{-3}$  až  $10^{-2}$  MPa.

V napjatém krasovém hydrogeologickém kolektoru jsou hodnoty průtočnosti v rozmezí 5 000 až 20 000  $\text{m}^2/\text{den}$  ( $0,06 \text{ m}^2/\text{s}^{-1}$  až  $0,23 \text{ m}^2/\text{s}^{-1}$ ) a vydatnost studní dosahuje během čerpacích zkoušek až 390  $\text{l} \cdot \text{s}^{-1}$ .

## DATAACION POR RADIOCARBONO DEL AGUA SUBTERRANEA EN ACUIFEROS KARSTICOS COSTEROS EN CUBA

D. M. ARELLANO ACOSTA, J. R. FAGUNDO, P. JLEK, J. ŠILAR

En siete pozos de la provincia de Pinar del Río, en Cuba, en un acuífero kárstico costero, se midió la saturación a calcita,  $p\text{CO}_2$ , y la actividad de radiocarbono y a partir de ésta por medio de varios modelos, se calculó la edad del agua subterránea.

A través de la medición de la conductividad específica, de la mineralización total y de proporciones iónicas ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  y otros) se investigó la intrusión de agua marina en el acuífero costero. Esta intrusión determina los factores cinéticos del sistema hidrogeológico.

La intrusión de agua marina provoca la sobresaturación de la solución, disminución de la actividad de radiocarbono y por ello la edad del agua desde 1 000 hasta 16 000 años. Estas edades no corresponden con datos preliminares disponibles sobre las concentraciones de isótopos estables ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ) medidas en precipitaciones, manantiales y pozos y con las mediciones de tritio que indican la presencia del agua contemporánea moderna.

Las cavidades kársticas y fracturas influyen en la baja actividad de radiocarbono. La difusividad en las rocas afecta la actividad medida como se deriva de consideraciones teóricas y de experimentos en ambiente poroso fracturado.

En climas húmedos tropicales la actividad biológica es muy intensa y los valores calculados de  $p\text{CO}_2$  son de  $10^{-3}$  hasta  $10^{-2}$  MPa.

En acuíferos kársticos confinados los valores de trasmisividad son entre 5 000 hasta 20 000  $\text{m}^2/\text{d}$  ( $0,06 \text{ m}^2/\text{s}^{-1}$  hasta  $0,23 \text{ m}^2/\text{s}^{-1}$ ) y el gasto de los pozos alcanza durante aforos hasta 390  $\text{l} \cdot \text{s}^{-1}$ .

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