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SOUTHERN ITALY

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Abstract

ISOTOPIC MEASUREMENTS IN RESEARCH ON SEAWATER INGRESSION IN THE CARBONATE AQUIFER OF THE SALENTINE PENINSULA, SOUTHERN ITALY.

Cretaceous calcareous and dolomitic rocks, bedded, jointed and karstified, and hence generally very permeable, form the basement of the Salentine Peninsula. These rocks constitute a huge aquifer with fresh and brackish groundwaters that float on groundwaters of marine origin. Sea level constitutes the base level of the groundwaters. A basic outline is first given of the hydrogeology and the paleohydrogeology, so as to provide the necessary background information on the seawater intrusion phenomenon and to permit comparison of the results of the isotope data with those obtained by the classical methods of hydrogeological investigation. This is followed by presentation of the results of the isotopic measurements on ^{18}O , D, ^{13}C and ^{14}C . The $\delta^{13}\text{C}$ contents indicate, in good agreement with the carbon dioxide and bicarbonate concentrations, that seawater ingression leads to the migration of carbon dioxide from the fresh and brackish waters towards the subjacent intrusive waters of marine origin. Along those stretches of coast where the seawaters are in direct communication with the groundwaters, all the isotope data point to very active renewal of groundwaters of marine origin by seawater. In the central parts of the peninsula and along those stretches of coast where direct communication between seawaters and groundwaters is impeded by impervious clays, the ^{14}C contents indicate that the seawater intrusion and consequently the migration of carbon dioxide are either very slow and continuous in time or that they occurred relatively rapidly in the past. Taking into consideration the paleohydrogeology of the peninsula, and the fact that the $\delta^{18}\text{O}$ and δD values are higher than those of the present seawaters, leads to the belief that seawater intrusion may well have occurred during major variations in the sea level in the past, when climatic conditions were different from those now prevailing.

1. INTRODUCTION

The problems stemming from seawater intrusion in a coastal aquifer are well known.

Intensive hydrogeological studies of the conventional type have clarified many aspects of the phenomenon in the Salentine Peninsula. The main purpose of the environmental isotope investigations was to introduce the time factor in the relations between seawater and groundwater.

An assessment of the renewal of the groundwater of marine origin along those stretches of coast where very permeable terrain outcrops, and

especially if marine estavelles are present, is of particular interest relating to the possibility that the groundwaters are polluted by the sea, in which all manner of wastes are nowadays dumped.

For a better understanding of the results obtained with the environmental isotope investigations, a brief outline is first given of the hydrogeology and paleohydrogeology of the area in question.

2. HYDROGEOLOGICAL OUTLINE

Cretaceous, calcareous and dolomitic rocks, bedded, fractured and karstified, and hence generally very permeable, form the base of the Salentine Peninsula. Here fresh and brackish groundwater continually floats on salt groundwater because of the intrusion of the sea into the peninsula. The sea level thus constitutes the base level of the fresh and brackish groundwaters. The gradient of the water table is always less than 1‰ and locally may be as low as 0.1‰.

Isotope investigations have been carried out in the central part of the Salentine Peninsula (Fig. 1), in a flat area generally 30-50 m above mean sea level.

Mean annual rainfall is 620 mm, 26.6% of which (165 mm) falls in the spring and summer (from April to September) and 73.4% (455 mm) in the autumn and winter (from October to March). As evapotranspiration is much more marked in the spring-summer period (when the mean air temperature is 21.6°C, against 11.9°C in the autumn-winter period), it ensues that the groundwaters are recharged almost exclusively during the months of October to March inclusive.

The temperature of the main coastal springs ranges between 17.5° and 18.5°C, seasonal variations being less than 0.3 degC. This shows that the springs are not fed directly by infiltrating waters but that they drain aquifer waters, as confirmed by the relatively constant discharges, notwithstanding the very considerable seasonal variations in rainfall.

The groundwaters are not recharged solely by the infiltration of rain on the outcrops of the permeable Cretaceous limestones and dolomites. Indeed, in the south-western part of the area shown in Fig. 1, recharge occurs also by concentrated infiltration in terrain that is not very permeable or which is practically impervious: run-off gathers in natural channels and reaches the aquifer via swallow holes.

In the north-eastern part of the area shown in Fig. 1, on the other hand, recharge is mainly by subsurface flows from the extensive outcrop of limestone and dolomite, which receives good rainfall, located to the north-west of Mesagne.

As regards the connection between the groundwaters and the sea, along the Adriatic coast a strip of silty clay, sandy silt and calcarenite, irregularly permeable or practically impervious, overlying permeable limestone and dolomites lying beneath sea level, impedes outflow of the groundwaters to the sea. Indeed, outflow occurs mainly through a number of springs, the largest of which is the Idume Spring (labelled ID. Spring in the figures; discharge 1000 litres/s [1]). The same situation is encountered along the Ionian coast starting from a point 5 km north-west of Porto Cesareo, where almost the whole seaward flow occurs through the Chidro (CH.) Spring (discharge 2500 litres/s [2]) and the Boraco (BR.) Spring (discharge

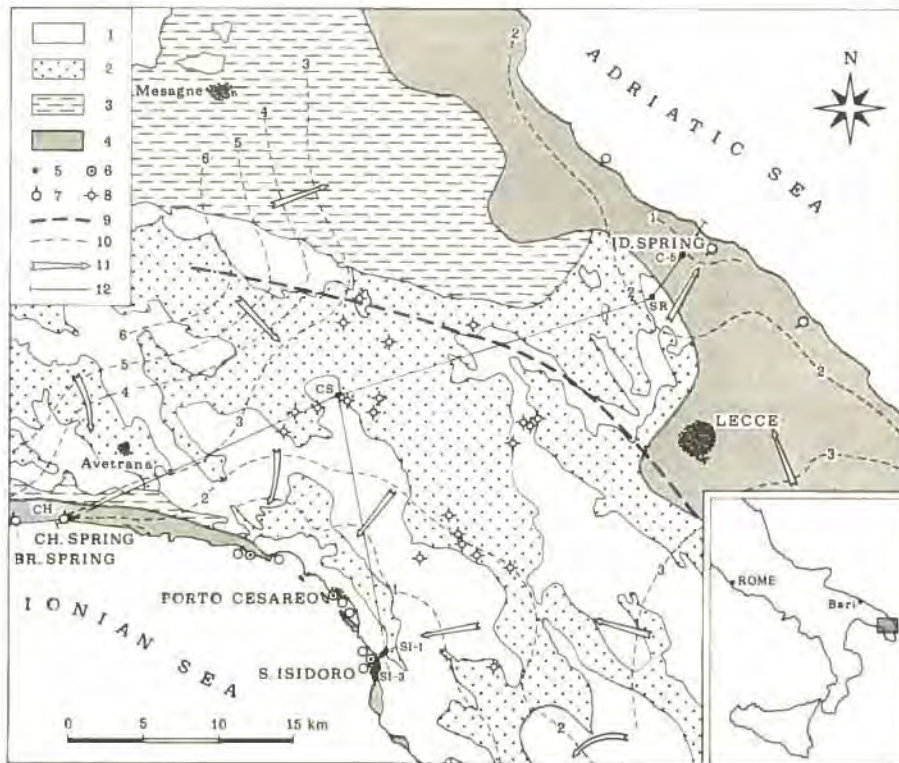


FIG.1. Schematic hydrogeological map of the central part of the Salentine Peninsula. 1: Cretaceous limestones and dolomites, permeable because of fissuring and karstification; 2: Mio-Plio-Quaternary formations with some primary permeability (calcarenites) or practically impervious (silts and clays), but permeable as far as recharge of the deep aquifer is concerned, since run-off is conveyed to the aquifer via swallow holes or via neighbouring outcrops of Cretaceous limestones and dolomites; 3: Mio-Plio-Quaternary formations with little primary permeability or practically impervious; Quaternary formations with little primary permeability or practically impervious, covering Cretaceous limestones and dolomites lying beneath sea level and hence impeding outflow to the sea; 4: Mio-Plio-Quaternary formations with little primary permeability or practically impervious, covering Cretaceous limestones and dolomites lying beneath sea level and hence impeding outflow to the sea; 5: Wells in which environmental isotope measurements have been made; 6: Marine estavelles or groups of marine estavelles; 7: Springs or groups of springs; 8: Swallow holes conveying surface run-off to the aquifer; 9: Underground watershed of the fresh and brackish groundwaters; 10: Trend of water-table contours (in metres above mean sea level); 11: Main directions of groundwater flow; 12: Lines followed by the sections in Fig.4.

200 litres/s). In the Porto Cesareo area, however, where the limestones and dolomites outcrop right down to the sea, outflow occurs in diffused form or through numerous springs.

The outflow of groundwater occurs more readily and more abundantly towards the Ionian Sea, as is shown by the fact that though the aquifer is recharged most heavily in the south-westerly part, the underground watershed lies decidedly closer to the Adriatic Sea. However, the combined action of outflows towards the Ionian and Adriatic Seas is such as to attract

underground flows both from the north-western and south-eastern areas of the peninsula, as shown by the trend of the water-table contours and hence the direction of groundwater flows (Fig. 1).

The waters of the coastal springs draining the aquifer, all brackish (rarely containing less than 2 g/litre of salts and sometimes over 8 g/litre), carry to the sea large quantities of water of marine origin, mixed with fresh groundwaters, because of the molecular diffusion and dispersion which occurs at the sea-groundwater/fresh-groundwater interface. A similar quantity of salt water, of course, then flows inland from the sea. In addition there is the seawater which moves to and from the land mass because of seasonal fluctuations of the interface. The phenomenon is clearly indicated by the existence of marine estavelles in the Porto Cesareo-San Isidoro area, where the limestones and dolomites outcrop down to the sea [3].

Examination of the temperatures of the groundwaters in relation to recharge and groundwater circulation shows that the thermal regime is stationary [4]; this fact indicates that at present the hydrological regime is stationary also. Therefore for the most part the same quantity of water flows seawards each year as infiltrates into the subsurface.

The chemical composition of the perched groundwaters, which have no connection with the sea or with the groundwaters of marine origin, is similar to that of the fresher waters floating on the groundwaters of marine origin

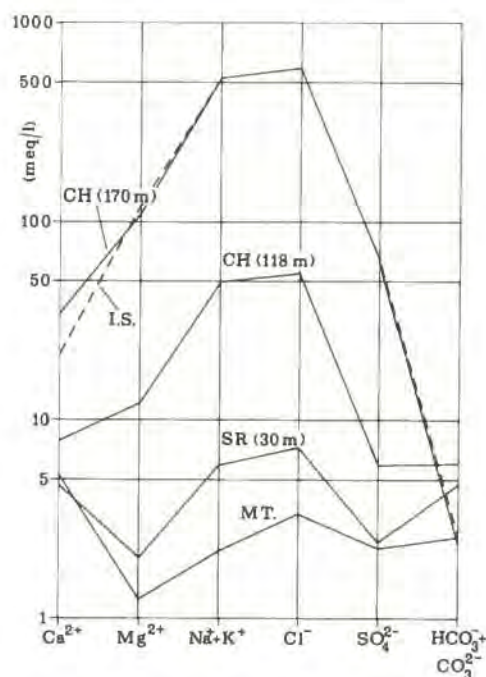


FIG. 2. Chemical composition of the Ionian Sea (I.S.), sea-groundwaters (CH Well at 170 m), brackish groundwaters (CH Well at 118 m) and fresh groundwaters (SR Well at 30 m), and also of spring MT, draining a perched aquifer.

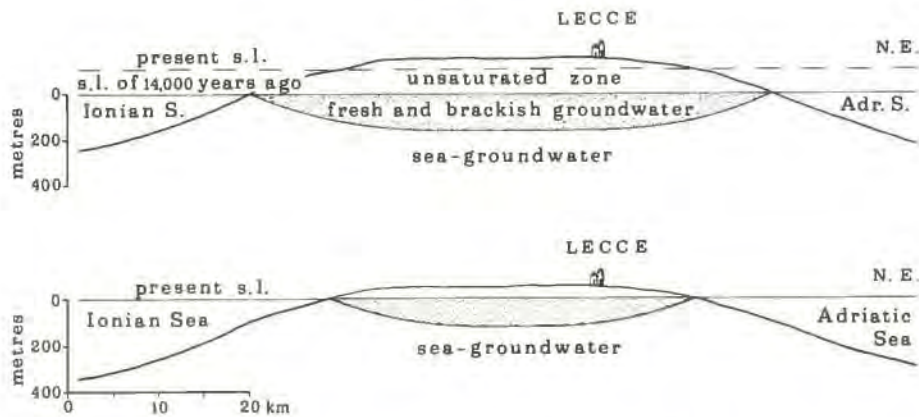


FIG. 3. Schematic sections through the Salentine Peninsula, showing thickness and extension of fresh and brackish groundwaters at present (bottom) and at the climax of the last marine regression (top).

(henceforth referred to simply as "sea-groundwaters"). Likewise, the chemical composition of the sea-groundwaters is more or less the same as that of the sea (Fig. 2).

As regards the paleohydrogeology, it is known that in the Late Pleistocene important variations occurred in the sea level through glacial eustasy, and locally through tectonic movement. A fair amount is known about relative movements between the sea and land in the Salentine Peninsula during the Tyrrhenian and Holocene periods [5 - 7]. In particular, during the time of the last maximum regression, some 14 000 years ago, the sea was about 100 m below its present level. The Flandrian transgression then began, which brought the sea to its present level. This rise in sea level reduced the distance between the Ionian and Adriatic Seas by about one third and hence also reduced by the same amount the thickness of the fresh and brackish groundwater lens, which is a direct function of the distance from the coast-line, naturally, for given values of discharge and permeability (Fig. 3). Therefore as the level of the sea rose during the Flandrian period, the volume of fresh and brackish groundwater was reduced to less than half. Consequently, whereas on the one hand the seaward outflow was generally greater than the corresponding recharge, on the other hand, to compensate for the big reduction in volume of fresh and brackish groundwaters, the level of the underlying sea-groundwater rose, and inflow of seawater occurred.

3. ENVIRONMENTAL ISOTOPE INVESTIGATIONS

Table I sets forth some chemical and isotope data, ^{18}O , D, ^{13}C and ^{14}C , of the waters sampled.

Isotope data on the Ionian Sea, Adriatic Sea and on water sampled at various depths in six wells which reached the sea-groundwaters, as well as

TABLE I. CHEMICAL AND ISOTOPE DATA

| No. | Location | Collection Date | t (°C) | pH | Cl ⁻ (meq/l) | HCO ₃ ⁻ (meq/l) | CO ₃ ²⁻ (meq/l) | TC (mM/l) | δ ¹⁸ O _{SMOW} (‰) | δD _{SMOW} (‰) | δ ¹³ C _{PDG,TC} (‰) | δ ¹³ C (‰Meq) |
|-----|---------------------|-----------------|-----------|------|----------------------------|--|--|--------------|--|---------------------------|--|-----------------------------|
| 1 | Borsco Spring (BR.) | 9. 2.1971 | 17.4 | 7.00 | 29.2 | 5.94 | - | 5.8 | -5.5 | -34.5 | -10.70 ± 0.5 | 41.1 ± 0.8 |
| 2 | Chidro Spring (CH.) | 3. 2.1971 | 18.4 | 7.40 | 59.8 | 6.15 | - | 5.6 | -5.3 | -33.5 | - 9.50 ± 0.5 | 34.3 ± 0.7 |
| 3 | Mume Spring (ID.) | 14. 7.1971 | 18.2 | 7.24 | 114.8 | 4.29 | - | 4.1 | -4.2 | -36.5 | - 9.54 ± 0.5 | 52.7 ± 0.8 |
| 4 | CH Well | | | | | | | | | | | |
| | m 40 | 2. 2.1971 | 17.4 | 7.07 | 39.5 | 6.23 | - | 5.8 | -5.9 | -33.5 | -10.80 ± 0.5 | 35.1 ± 0.7 |
| 5 | m 69 | 2. 2.1971 | 17.5 | 7.17 | 42.0 | 6.24 | - | 6.5 | -5.7 | -33.0 | -11.30 ± 0.5 | 49.3 ± 0.7 |
| 6 | m 86 | 3. 2.1971 | 17.5 | 7.08 | 54.9 | 6.20 | - | 5.5 | -5.7 | -32.0 | -10.70 ± 0.5 | 35.7 ± 0.7 |
| 7 | m 118 | 2. 2.1971 | 17.5 | 6.97 | 55.2 | 6.12 | - | 6.5 | -5.6 | -32.0 | -12.10 ± 0.5 | 30.4 ± 0.7 |
| 8 | m 147 | 30. 7.1971 | 17.9 | - | 594.9 | 2.40 | - | 2.3 | +1.6 | +10.0 | - 7.09 ± 0.5 | - |
| 9 | m 170 | 30. 7.1971 | 18.0 | 7.27 | 594.5 | 2.53 | - | 1.9 | +1.7 | +11.0 | - 5.17 ± 0.5 | 5.8 ± 0.2 |
| | SI-1 Well | | | | | | | | | | | |
| 10 | m 19 | 9. 7.1971 | 17.0 | 7.26 | 31.9 | 5.54 | - | 5.3 | -5.4 | -31.5 | -11.04 ± 0.5 | 64.0 ± 0.8 |
| 11 | m 30 | 9. 7.1971 | 17.0 | 7.06 | 44.0 | 5.63 | - | 5.8 | -5.3 | -31.0 | -12.40 ± 0.5 | 65.4 ± 0.8 |
| 12 | m 40 | 13. 7.1971 | 17.1 | 7.40 | 581.9 | 2.36 | - | 1.9 | +1.3 | + 8.5 | - 5.00 ± 0.05 | 40.7 ± 0.7 |
| | SI-2 Well | | | | | | | | | | | |
| 13 | m 9 | 13. 7.1971 | 17.2 | 7.17 | 55.4 | 5.48 | - | 5.1 | -6.1 | -29.5 | -13.92 ± 0.5 | 66.9 ± 0.8 |
| 14 | m 18 | 13. 7.1971 | 17.9 | 7.25 | 580.2 | 2.40 | - | 1.7 | +1.3 | + 8.5 | - 3.70 ± 0.5 | 92.6 ± 0.9 |

| | | | | | | | | | | | | | |
|----|---------------------------|------------|------|------|-------|------|------|-----|-------|-------|---------------|-------------|--|
| | CS Well | | | | | | | | | | | | |
| 15 | m 56 | 23. 2.1971 | 16.8 | - | 2.3 | 4.37 | - | 3.6 | -5.1 | -31.0 | -34.37 ± 0.5 | 77.2 ± 0.8 | |
| 16 | m 108 | 24. 2.1971 | 16.8 | - | 27.8 | 6.89 | - | 4.1 | -4.9 | -30.6 | -11.30 ± 0.5 | - | |
| 17 | m 175 | 26. 2.1971 | 17.1 | - | 562.3 | 2.68 | - | - | +1.0 | + 6.5 | - 8.87 ± 0.5 | 1.4 ± 1.4 | |
| 18 | m 164 | 6.12.1972 | 17.1 | - | 565.2 | - | - | 2.5 | +0.80 | + 6.1 | - 7.60 ± 0.05 | - | |
| | SR Well | | | | | | | | | | | | |
| 19 | m 30 | 17. 2.1971 | 17.2 | 7.00 | 7.3 | 4.93 | - | 5.1 | -6.10 | -36.1 | -14.40 ± 0.5 | 84.2 ± 2.4 | |
| 20 | m 70 | 18. 2.1971 | 17.5 | 7.00 | 12.3 | 4.79 | - | 4.6 | -6.9 | -34.0 | -13.32 ± 0.5 | 55.8 ± 2.0 | |
| 21 | m 146 | 19. 2.1971 | 19.4 | - | 587.3 | 2.65 | - | 2.3 | +1.2 | + 7.5 | - 5.61 ± 0.05 | 1.6 ± 0.6 | |
| 22 | m 164 | 5.12.1972 | 19.4 | - | 584.3 | - | - | 2.5 | +1.44 | + 3.2 | - 5.29 ± 0.05 | - | |
| | C-S Well | | | | | | | | | | | | |
| 23 | m 33 | 14. 7.1971 | 18.6 | 7.27 | 16.4 | 4.59 | - | 4.2 | -5.8 | -33.5 | -10.90 ± 0.5 | 51.4 ± 0.8 | |
| 24 | m 70 | 14. 7.1971 | 18.4 | 7.40 | 561.5 | 2.46 | - | 2.2 | +1.3 | + 9.0 | - 4.09 ± 0.05 | 31.7 ± 0.7 | |
| 25 | Plinio Spring (PL.) | 4. 1.1972 | 16.2 | 7.78 | 1.15 | 3.25 | - | 3.5 | -6.0 | -34.5 | -11.60 ± 0.1 | 97.0 ± 0.6 | |
| 26 | Tre Fontane Spring (TRF.) | 4. 1.1972 | 15.0 | 7.15 | 1.62 | 4.82 | - | 4.9 | -5.7 | -33.5 | -12.20 ± 0.1 | 82.8 ± 0.8 | |
| 27 | Mocattieri Spring (MT.) | 11. 1.1972 | 14.1 | 7.70 | 2.32 | 5.40 | - | 4.5 | -5.6 | -33.0 | - | - | |
| 28 | Ionian Sea | 13. 7.1971 | - | 8.03 | 593.2 | 2.42 | 0.35 | 1.4 | +1.3 | + 9.0 | - 3.30 ± 0.5 | 111.9 ± 1.0 | |
| 29 | Adriatic Sea | 14.10.1973 | - | - | 583.4 | 2.25 | 0.33 | 1.5 | +0.83 | + 7.5 | - 2.60 ± 0.5 | 81.0 ± 0.8 | |

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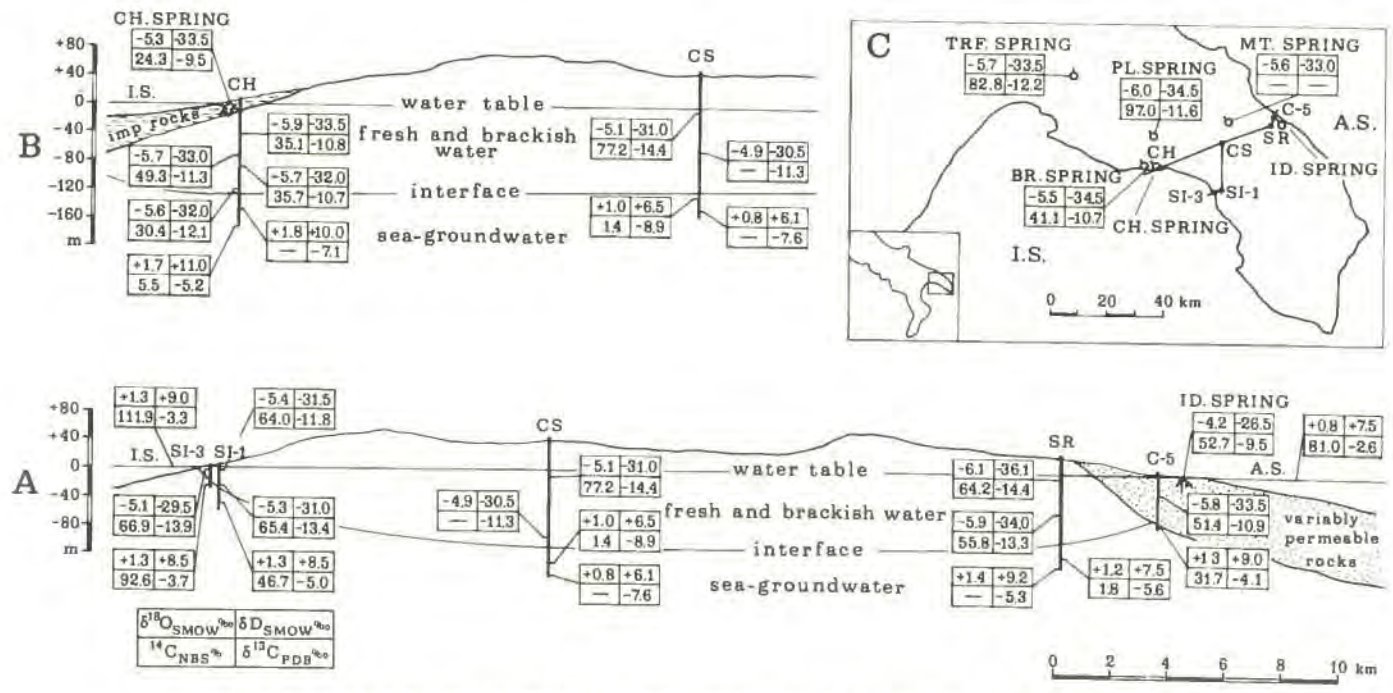


FIG. 4. Location of wells and springs and schematic sections showing isotope data (I.S.: Ionian Sea; A.S.: Adriatic Sea).

on water from the Chidro (CH.) and Idume (ID.) Springs are shown in parts A and B of Fig. 4. The samples of well waters were taken in the absence of vertical currents, except for the sample of fresh water from the C-5 Well.

The locations of the wells and springs, the directions followed by the sections in parts A and B, the isotope data of the Boraco (BR.) Spring, and the locations and isotope data of three minor springs (MT., PL. and TRF.) issuing from small perched aquifers, are all shown on the map (part C) in Fig. 4.

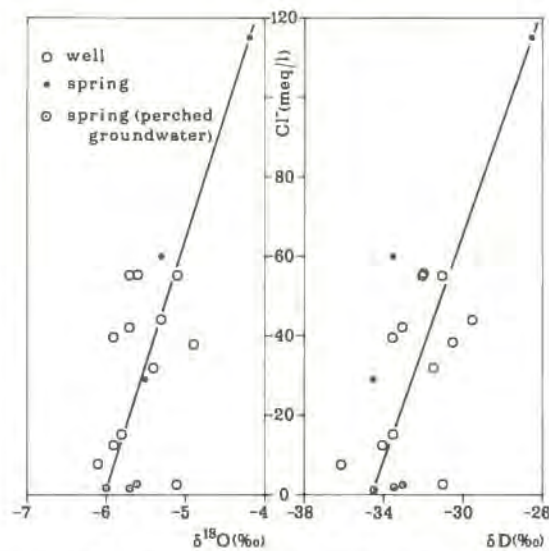


FIG. 5. Relation between $\delta^{18}\text{O}$ and Cl^- content and between δD and Cl^- content for fresh and brackish groundwaters.

3.1. ^{18}O and deuterium

The average $\delta^{18}\text{O}$ and δD contents of the perched groundwaters are -5.8‰ and -33.7‰ respectively. These values are slightly below the mean ($\delta^{18}\text{O} = -5.4\text{‰}$, $\delta\text{D} = -32.1\text{‰}$) of the fresh and brackish waters floating above the sea-groundwaters.

It is said that the waters above the interface are often brackish because of contamination from the underlying sea-groundwaters.

As far as the isotope data are concerned¹, it is apparent from Fig. 5 that the relationship between the chloride ion contents on the one hand and the $\delta^{18}\text{O}$ and δD values on the other is not clearcut, though it can be readily recognized. In Fig. 6, where the δD and $\delta^{18}\text{O}$ values are compared, the fresher waters ($\text{Cl}^- < 15$ meq/litre) are practically indistinguishable from those which are not so fresh ($\text{Cl}^- = 15-115$ meq/litre).

¹ See also Ref.[8] and E. Tongiorgi in discussion to Ref.[9].

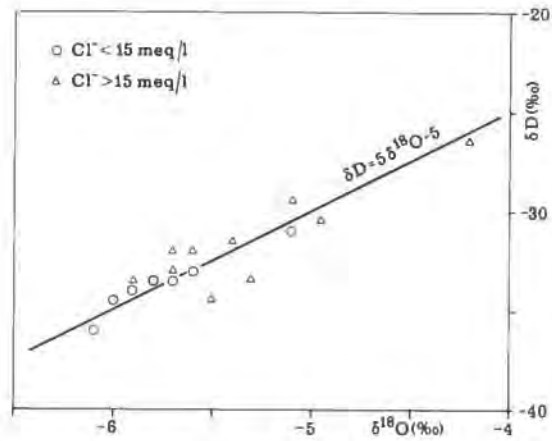


FIG. 6. Relation between $\delta^{18}\text{O}$ and δD for fresh and brackish groundwaters.

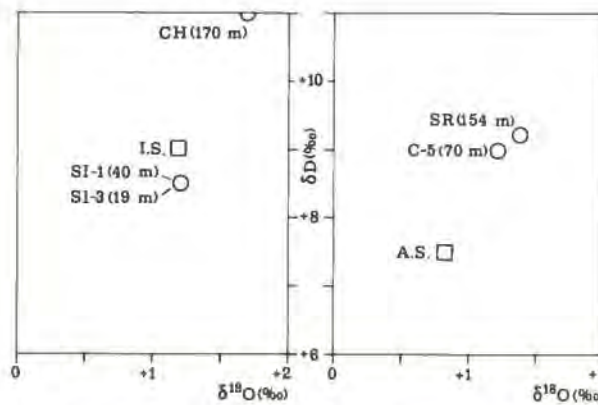


FIG. 7. Relation between $\delta^{18}\text{O}$ and δD for seawater (I.S.: Ionian Sea; A.S.: Adriatic Sea) and for sea-groundwaters of the Ionian (CH, SI-1 and SI-3) and Adriatic (C-5 and SR) coastal areas.

What, in fact, happens in the $\delta\text{D}-\delta^{18}\text{O}$ diagram (Fig. 6) is that the factors which together determine the isotope content of the waters that percolate into the subsurface (mainly seasonal influence of the isotope contents and of the rainfall; diffused or concentrated infiltration conditions, in relation to the evaporation of the surface run-off waters) are such as partially to mask the effects of contamination caused by the underlying sea-groundwaters. Furthermore, the factors that together determine the chemical composition of the waters that penetrate below ground (mainly the influence of the distance from the shoreline [10] and dissolution, during rainy periods, of the salts, left on the ground surface through evaporation of the rainwaters during dry periods) are responsible for the dispersion of the pairs of values that may be observed in the $\text{Cl}^- - \delta^{18}\text{O}$ and $\text{Cl}^- - \delta\text{D}$ diagrams (Fig. 5).

The average isotope contents of the sea-groundwaters are a little higher than those of the sea itself, the former averaging $\delta^{18}\text{O} = +1.31\text{‰}$, $\delta\text{D} = +8.48\text{‰}$, and the latter $\delta^{18}\text{O} = +1.07\text{‰}$ and $\delta\text{D} = +8.25\text{‰}$.

In particular, in the case of the San Isidoro area, the sea-groundwaters and the Ionian Sea have stable isotope contents that are very similar (Fig. 7). The isotope data, in good agreement with the results of hydrogeological investigations [3, 11], thus point to the existence of a direct connection between the sea on the one hand and the groundwaters on the other.

With regard to the coastal areas where communication between the sea and sea-groundwaters is hindered by irregularly permeable or impervious formations, the heavy isotope contents of the sea-groundwaters on the Ionian and Adriatic sides of the peninsula are well above those of the waters of the Ionian and Adriatic seas respectively (Fig. 7). Hence ingress of the seawater occurred when climatic conditions were different from what they are at present.

3.2. ^{13}C

It is well known that the behaviour of the carbon isotopes (^{13}C and ^{14}C) is closely bound up with the chemistry of CO_2 and of the carbonates. The latter is a rather complex subject and even today many aspects are not completely clear [12]. The application of carbon isotopes to the study of groundwaters therefore still involves many unknowns.

As far as the groundwaters of the Salentine Peninsula are concerned, the relationships between pH and bicarbonate, free carbon dioxide and total carbonate values (Table I) do not satisfy the theoretical equations.

In fact, the concentrations of bicarbonates and free CO_2 are closely connected with the chemical composition and the salt contents. So, as appears from about a hundred chemical analyses from several wells and springs (Fig. 8), the variation of the bicarbonate concentration as a function of the salt contents is clear; consequently, the bicarbonate concentration changes with the value of pollution from the sea-groundwater also.

Figure 8 also shows that the confined brackish groundwaters have a greater bicarbonate content.

On the contrary, the chemical analyses of 23 samples from Well SR show a linear variation of the bicarbonate concentration as a function of the salt contents.

In good agreement with this, the bicarbonate concentrations of the fresh and brackish groundwaters studied are, on average, about twice those of the subjacent sea-groundwaters² (Fig. 9).

Average bicarbonate concentrations of the sea-groundwaters are similar to those of the seawaters, but the total carbonate values — and hence free carbon dioxide — are markedly higher (Fig. 9). In actual fact, the sea-groundwaters are in equilibrium with a much higher CO_2 partial pressure (that of the soil air) than that of the atmosphere, with which the seawater is in equilibrium. These differences in concentration indicate that the ingress of seawater into the land mass leads to the migration of CO_2 from the fresh and brackish groundwaters towards the subjacent intruded seawater, because of the greater partial pressure of CO_2 in the underground environment (Fig. 9).

² The differences in concentration measured at nearby points in the same body of groundwater can often be explained by CO_2 enrichment as a result of greater mobility of the water [13, 14].

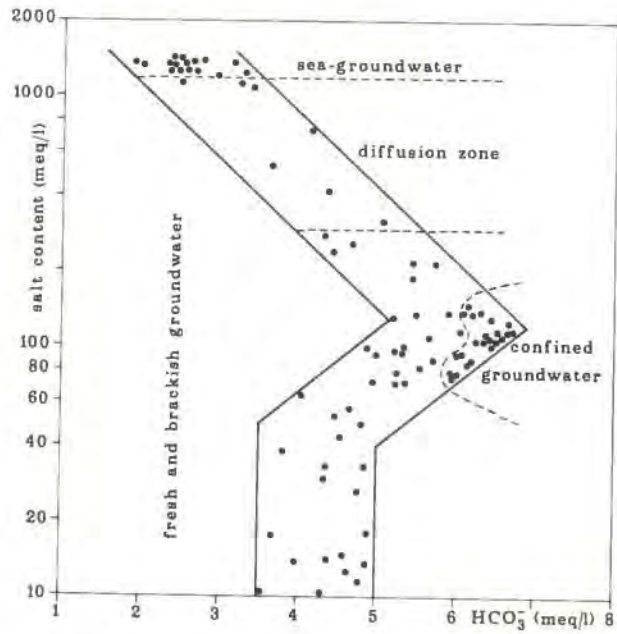


FIG. 8. Variation of bicarbonate concentrations as a function of salt contents.

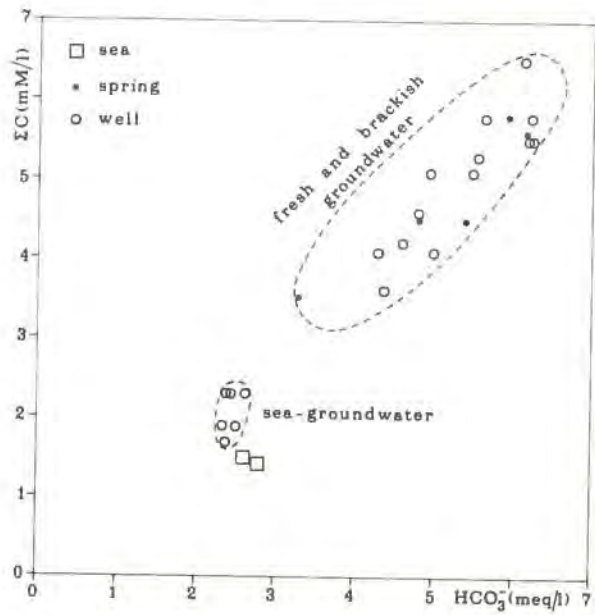
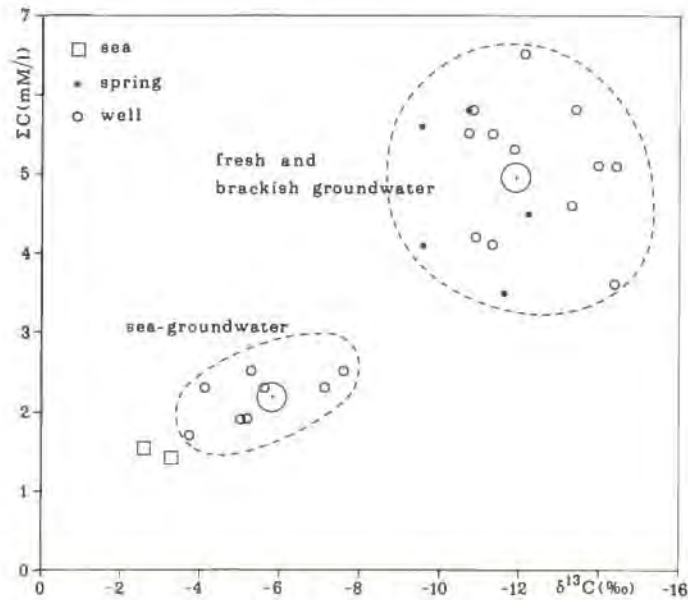


FIG. 9. Relation between ΣC and HCO_3^- ($HCO_3^- + CO_3^{2-}$ for the seawater).

FIG. 10. Relation between ΣC and $\delta^{13}C$.

This phenomenon might lead to CO_2 being attracted from the soil air and migration of CO_2 from the sea-groundwaters towards the sea. However, evidence is not available to support this hypothesis.

The isotope data confirm the phenomenon of gaseous CO_2 migration from the fresh and brackish water towards the underlying intrusive seawaters. The $\delta^{13}C$ content of the sea-groundwater ($\delta^{13}C = -5.8\text{‰}$, on average) is explained by the migration of CO_2 from the fresh and brackish groundwaters ($\delta^{13}C = 11.9\text{‰}$, on average) towards the subjacent intrusive sea-groundwaters, which originally had a $\delta^{13}C$ content averaging -2.9‰ (Fig. 10). It must also be pointed out that the sea-groundwaters show distinct layering of $\delta^{13}C$ at depth: as depth increases, the $\delta^{13}C$ content of sea-groundwaters also increases (Wells CH, CS and SR; Fig. 4 and Table I).

Hydrodynamic dispersion and, to a lesser extent, molecular diffusion, attributable to fluctuations of the interface — as a result of seasonal recharge [15] and fluctuations in sea level because of tidal movement and changes in atmospheric pressure [16] — as well as to differences in water density because of temperature and to differences in permeability because of the existence of preferential groundwater flow paths, all lead to the pollution of the fresh groundwaters by salt through the subjacent sea-groundwaters. This phenomenon is also clearly illustrated by the relation that exists between the Cl and $\delta^{13}C$ contents (Fig. 11).

In addition, the $\delta^{13}C$ values demonstrate the very considerable exchange that occurs at present between seawater and the sea-groundwaters in the San Isidoro area, where there is direct contact between the groundwaters

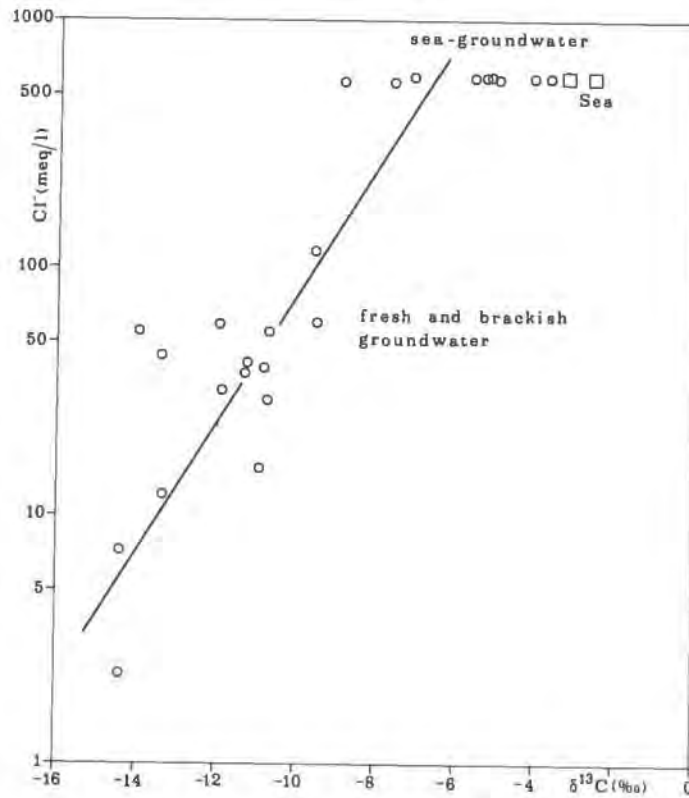


FIG. 11. Relation between Cl⁻ and δ¹³C.

and the sea. As already noted, there are numerous marine estavelles along the coast which act as swallow holes for seawater during high tides and when the atmospheric pressure is low [3]. In the SI-3 Well drilled some 250 m from the shoreline, the sea-groundwater has a δ¹³C content of -3.7‰, which is very close to that of the Ionian Sea (Fig. 4).

3.3. ¹⁴C

From present knowledge of the solution of mineral CaCO₃ it is not always possible to arrive at a really accurate estimate of the age of the groundwaters.

In our case, however, the determination of ¹⁴C contents holds out interesting possibilities for resolving hydrogeological problems connected with the intrusion of seawater into the peninsula.

The decrease of the ¹⁴C contents of the fresh and brackish groundwaters with depth in the CH Well, and the relatively low figures obtained in the

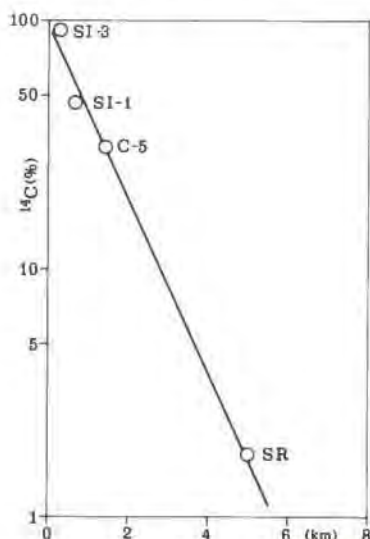


FIG.12. ¹⁴C contents of sea-groundwater as a function of the distance from the shoreline.

waters of the nearby Chidro spring (¹⁴C = 24.3%) indicate that this drains deep brackish waters near the interface. This is in good agreement with the temperature data and the ²²²Rn and CO₂ contents of the waters [13, 17].

The ¹⁴C content of the sea-groundwater in the SI-3 Well (92.6%) ties in with the δ¹⁸O, δD and δ¹³C contents of this water, indicating considerable renewal of the sea-groundwater in the Ionian Sea (¹⁴C = 111.9%). It must also be pointed out that the pollution of the fresh water by salt through the underlying sea-groundwater leads to the apparent rejuvenation of the fresh water³; the CO₂ migration from the fresh and brackish water towards the subjacent sea-groundwater leads instead to the apparent increase in age of the latter waters.

The relatively high ¹⁴C values of the sea-groundwater in the SI-1 Well lying 0.6 km inland (¹⁴C = 46.7%) and in the C-5 Well lying 1.4 km inland (¹⁴C = 31.7%) again point to the existence of relatively recent communication with the sea,⁴

The low ¹⁴C contents of the sea-groundwaters in the central part of the Salentine Peninsula (CS Well: ¹⁴C = (1.4 ± 1.4)%; SR Well: ¹⁴C = (1.8 ± 0.6)% and the Chidro Spring area (CH Well: ¹⁴C = (5.5 ± 0.2)%), where communication

³ On the contrary, where the sea-groundwater ¹⁴C contents are lower than those of the overlying water, the salt pollution leads to the apparent increase in age of the fresh water. Likewise, the salt pollution affects the ¹⁸O, D and ¹³C contents.

⁴ In this connection it should be observed that whereas the Ionian Sea has a ¹⁴C content of 111.9% (sample taken off Porto Cesareo, 3 km from the shore, at a depth of 8 m), that of the Adriatic is 81% (sample taken 3 km off the coast of Lecce at a depth of 13 m). A second sample taken from the Adriatic 3 km off the coast north of Bari at a depth of 8 m gave a ¹⁴C content of 82%. At present we are unable to give any plausible explanation for the abnormally low ¹⁴C values in the Adriatic.

between the sea and the groundwaters is hindered by a thick bed of impervious clay, indicate that here the intrusion of seawaters and CO₂ migration (see above) are ascribable either to a very slow, continuous process or that they occurred relatively rapidly in the past, as a result of marked changes in sea level. The first of these hypotheses would appear to be borne out by the exponential decrease in the ¹⁴C contents with the increase in the distance inland (Fig. 12).

4. CONCLUSIONS

Environmental isotope investigations enable certain aspects of the ingress of seawater into the carbonate aquifer of the Salentine Peninsula be clarified.

In those parts of the coast where there is unimpeded communication between the sea and the groundwaters (e.g. in the San Isidoro area), it is apparent that inflow of seawaters is recent. The data obtained with ¹⁸O, deuterium, ¹³C and ¹⁴C bear this out.

In the central part of the peninsula and the Chidro Spring area the ¹⁴C content of the sea-groundwaters is 5.5% or lower. Even in the very unlikely case that only 50% of the total carbon present in the water samples is of biogenetic origin, this means that the age of the sea-groundwaters is 17 730 years or more.⁵ The waters therefore pre-date the beginning of the Flandrian transgression. The sea-groundwater on the Adriatic side instead shows a Flandrian age (C-5 Well; older than 3500 years).

In the coastal area of the Chidro Spring and in the central parts of the peninsula, the sea-groundwaters have a higher heavy isotope content than present-day seawater. These sea-groundwaters therefore derive from old waters from an ingressive sea when climatic conditions were different from those now prevailing.

Possible pollution of the sea-groundwaters as a result of harmful substances dumped in the sea, and hence pollution of the superjacent fresh and brackish waters through the sea-groundwaters, is only likely to become significant along those stretches of coast where the seawaters are in direct communication with the groundwaters.

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⁵ As stated, the bicarbonate contents of the sea-groundwaters are similar to those of the sea, but the free carbon dioxide values, and hence total carbonates, are much higher — almost double. Hence the carbon dioxide introduced into sea-groundwater by migration has not dissolved any more mineral carbonate.

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DISCUSSION

R. R. LETOLLE: The $\delta^{13}C$ values usually obtained in the Western Mediterranean are closer to zero than those reported by you. Are your values representative of the mean?

G. S. TAZIOLI: I do not think that the $\delta^{13}C$ values reported by us for the Ionian and Adriatic Seas or our ^{14}C values for the Adriatic Sea are representative of the mean. In my opinion, they are influenced by local, albeit fairly widespread, effects.

In this connection I would mention that two samples collected by us in the Adriatic at points almost 150 km apart yielded similar $\delta^{13}C$ and ^{14}C values: -1.77‰ and -2.60‰ for $\delta^{13}C$, and 82% and 81% for ^{14}C . We have begun to investigate this interesting problem, looking into, among other things, the possibility of seasonal variations.

Lastly, I would add that we have obtained a $\delta^{13}\text{C}$ value of -0.5‰ with samples collected in the Ionian Sea at a depth and a distance from the coast less than in the case of the samples mentioned in the paper.

B. T. VERHAGEN: With regard to a slide which you showed in your oral presentation but which does not appear as a figure in your paper, I was puzzled by the ^{14}C concentrations in the sea-groundwater. The ^{14}C content of the seawater was given as 112%, compared with a value of 92% at some distance into the aquifer and 47% still further down. This suggests a fairly rapid flow from the sea into the aquifer beneath the fresh-water lens. Do you know what mechanism is involved?

G. S. TAZIOLI: We think the movement of seawater towards the aquifer in the San Isidoro area is, as you say, rapid — although it is limited to the coastal zone. The ^{14}C value of 92% measured in the sea-groundwaters at a distance of 250 m from the shore is the result of dilution of the ^{14}C in the intrusive seawater caused by the migration of aquifer CO_2 towards the subjacent sea-groundwaters.

J. DOWGIALLO: Is it possible to delimit fresh waters from brackish waters in the axial zone of the Salentine Peninsula?

G. S. TAZIOLI: On the Salentine Peninsula there is generally an increase in salt concentration as one moves from the axial zone towards the coast, the fresh waters occurring well away from the coast. It is accordingly possible to delimit the zones of fresh water (*sensu stricto*) on a hydro-chemical map. Incidentally, the shape of these zones is very irregular; even the thickness of the fresh-water lens might vary by several metres from place to place.

J. DOWGIALLO: Can one use the Ghyben-Herzberg formula to determine the depth of the fresh (brackish) water/saltwater interface?

G. S. TAZIOLI: As we have values for the density of the fresh and brackish waters, the Ghyben-Herzberg formula enables us to determine the depth of the interface with sufficient precision for practical purposes. In the case of areas near the coast, differences between the calculated depth and the real depth are due not so much to the fact that the formula applies only to static regimes as to simultaneous variations in the level of the phreatic surface and the interface, the latter variations being caused by fluctuations in the sea level, mainly as a function of the atmospheric pressure (see Ref. [16]).

M. LEVIN LIPSIN: Have detailed isophreatic maps been made of zones of interest on the Salentine Peninsula?

G. S. TAZIOLI: Yes, isophreatic maps much more detailed than the one shown in Fig. 1 have been made of the Chidro Spring and Idume Spring zones (see Refs [2] and [1] respectively).

M. LEVIN LIPSIN: Have you tried to determine the concentrations of soluble salts or the amount of water imbibed by the "impermeable" material?

G. S. TAZIOLI: No, we have not.

M. LEVIN LIPSIN: Could the soluble salts infiltrate the clays in the Chidro Spring zone?

G. S. TAZIOLI: Not to any significant extent according to the data available to us at present.

M. LEVIN LIPSIN: Could you please describe briefly how the land is used in the region where you carried out your study?

G. S. TAZIOLI: Most of the region is cultivated (olives, almonds and grapes). Very little land is left fallow, and there is not much scrubland.

M. LEVIN LIPSIN: Could you give some information about the wells in the region?

G. S. TAZIOLI: There are several hundred dug wells and drilled wells in the region, and the specific discharge of the drilled wells is roughly 1 litre/s·m.

M. LEVIN LIPSIN: How did you carry out sampling?

G. S. TAZIOLI: That depended on the depth at which sampling was carried out and on the sample volumes required; we used either pumps with inlets immersed to the desired depth or samplers with remote-controlled valves.