

## **SALINE GROUNDWATER IN THE INCA-SA POBLA AQUIFER, SE OF MALLORCA ISLAND (BALEARIC ISLANDS, SPAIN)**

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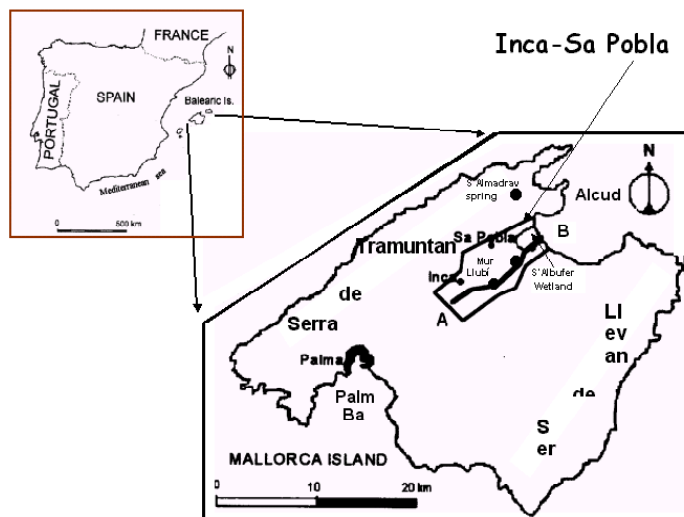
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### **ABSTRACT**

The Inca-Sa Pobla carbonate aquifer (NE of Mallorca Island, Spain) lies between the centre of the island and the coast, along some 40 km of rolling plains. In some areas two superposed aquifers are found, while in other areas there is a single water-table aquifer. Groundwater flows from the inland part (SW) to the coast (NE), dissolving calcium/magnesium carbonates, and at about 10 km from the coast groundwater becomes brackish and saline due to mixing with salt water. Chemical and environmental isotope evolution along a main flow path points to mostly unconfined flow. Tritium contents decrease along flow, reaching minimum values (<1TU) in the deepest coastal groundwaters. The fresh component of brackish water in the coastal area has two different stable isotope signatures: that of present local recharge, and a lighter one that seems to be either water from the mountain highlands or a remnant of palaeowater recharged in colder times, probably during the Pleistocene-Holocene change. <sup>14</sup>C ages of the brackish waters seem to be between recent and some 10 to 13 ka old, showing an apparent ageing as freshwater content increases, but the possible incorporation of organic matter carbon from the sediments makes groundwater age uncertain.

### **INTRODUCTION**

Mallorca is the largest of the Balearic Islands, in the Western Mediterranean Sea. Although the island's main economic activity is tourism, agriculture is still locally important in the rural areas of its central and NE part, along the Inca-Sa Pobla rolling plain (Figure 1). Urban water supply demand is continuously growing. Human and agricultural uses compete for groundwater in the Inca-Sa Pobla area, where there is one of the main pumping fields (Llubí) to supply the capital, Palma de Mallorca, as well as other supply wells for the local towns. Local good-quality water resources in the island are becoming scarce, especially in dry years. As a consequence, especial measures have been undertaken to satisfy water demand by introducing treated water reuse in some agricultural areas, desalination of brackish groundwater and seawater, and even resorting to the occasional conveyance of Ebre River water from Tarragona (E of the Iberian Peninsula) by vessel. But in spite of the water stress, quantitative knowledge of the island's groundwater resources still present some question marks.



*Figure 1 Situation of the Inca-Sa Pobla aquifer.*

During the last years several detailed hydrogeological studies have been carried out by the Technical University of Catalonia, the Balearic Islands Water Authority, and the Geological Survey of Spain (IGME), to update and improve previous studies. The most recent studies deal with the main springs of the Serra de Tramuntana (Sa Costera, Ses Ufanes), and the Inca-Sa Pobla Miocene-to-Quaternary basin, which include the characterization of the geochemical reactions that control groundwater composition, and the study of the origin and age of the brackish and salt water existing in the coastal area of Sa Pobla, NE coast of Mallorca (Figure 1). This paper introduces some results of the study carried out by the Technical University de Catalonia in collaboration with the Balearic Water Authority in the area between 1997 and 1999 in the framework of the EU project PALAEAUX (ENV4-CT95-0156). This project aimed at the characterization of the Pleistocene-Holocene climate change signature remaining in several coastal aquifers of Europe.

## **MATERIALS AND METHODS**

Some 25 monitoring points were sampled along a line roughly following a hypothetical groundwater flow path going from SW to NE along the deepest part of the aquifer (Figure 2). Shallow wells were avoided as much as possible. The sampling points mostly consisted of drilled wells (most of them fully screened or multiscreened) along the first 25 km of aquifer, and point boreholes (with a short screen) drilled in the coastal sector of the aquifer to monitor the position of the salt-water interface. Samples from the wells correspond to a mixture of the water inflowing through the screens. Samples from the boreholes were collected by means of a submersible bottle, after bailing. Sampling depth was selected from downhole electrical conductivity and temperature logs. In some cases these logs showed the existence of vertical upward and downward flows along the borehole. The selection of points and depths tried to follow as much as possible a hypothetical flow path.

Previous information on environmental isotopes in the aquifer was limited to the surroundings of S'Albufera wetland, in the coastal area. For the present study the following parameters were analysed: major ions, tritium, oxygen-18 and deuterium; pH, temperature, electrical conductivity and alkalinity were measured in situ. Data on  $^3\text{H}$ ,  $^{18}\text{O}$  and  $^2\text{H}$  content in groundwaters of the coastal area, around the S'Albufera wetland, from field surveys carried out in 1991-1993 have been included. Four samples for  $^{13}\text{C}$  and  $^{14}\text{C}$  were taken from boreholes of the coastal area for a first appraisal of the C behaviour.

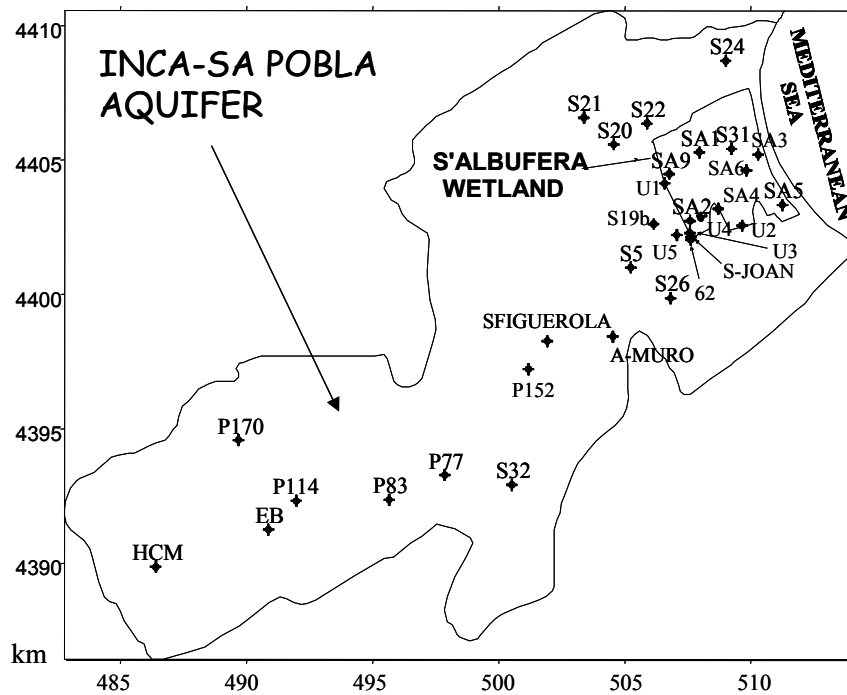


Figure 2 Wells and boreholes used in the study.

## HYDROGEOLOGY

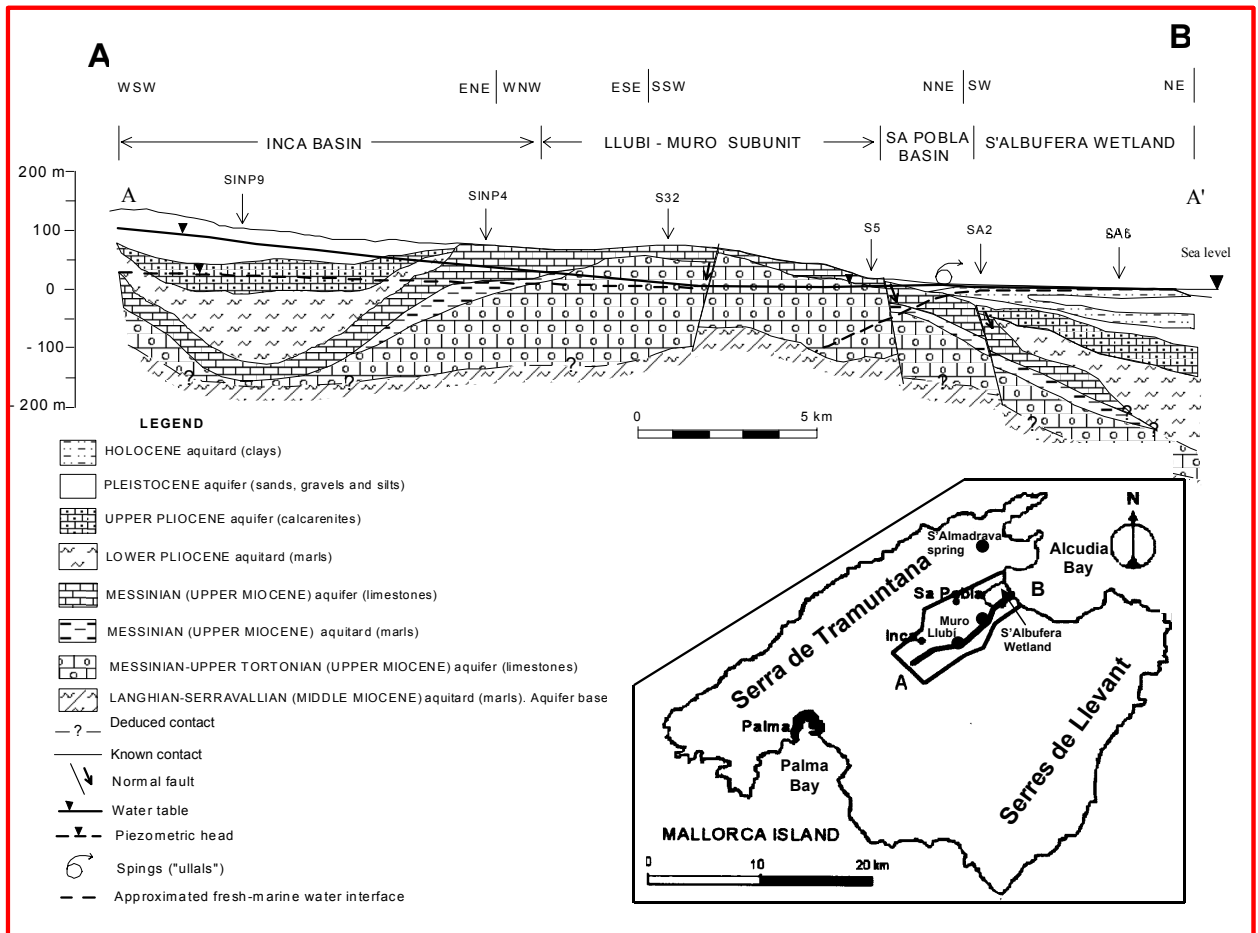
Geologically, Mallorca Island is part of the folded, faulted and thrust belt fringing the northern boundary of the African Plate. The Alpine orogeny originated in Mallorca two ranges of thrust Mesozoic and early Cenozoic carbonate materials (dolostones and limestones) separated by a pressure relief graven in between. The island is then formed by: 1) an SW-NE oriented, abrupt mountain range 90 km long and 1440 m high (Serra de Tramuntana), with high cliffs along the NW coast; 2) a SW-NE southern ridge (Serra de Llevant) less than 500 m high; and 3) a central graven, filled up with upper Tertiary sediments, up to 540 m high but mostly below 100 m above sea level, which forms a corridor between Palma Bay (SW) and Alcudia Bay (NE).

Average rainfall in Mallorca varies from less than 500 mm/a near the SE coast to as much as 1400 mm/a in central Serra de Tramuntana. Most of the rains fall in early autumn and in the late winter period. No permanent rivers exist, except for some springs whose water infiltrates soon downstream. Only after storms there is some ephemeral flow. A large part of groundwater recharge takes place along the Serra de Tramuntana. A part of it finds its way into the sea along the cliffs of the northern coast as springs and diffuse outflow; the rest collects along the inner boundary with the central corridor, where some highly transmissive formations occur.

The Inca-Sa Pobla Plain and aquifer is in the NE half of the central corridor. It is a north-eastward subsiding basin filled by a sequence of dominantly Upper Miocene (Messinian) to Quaternary carbonate sediments, with a total thickness of 150-250 m (Figure 3). Langhian-Serravallian (Middle Miocene) marls form the basement. To the N the aquifer is bounded by the Jurassic and Cretaceous permeable limestones of the Serra de Tramuntana, which seem to allow some lateral, not easy to quantify, flow to the Inca-Sa Pobla system. The S boundary consists of Tertiary marls and calcarenites forming low elevations. To the W the aquifer boundary is a hydrogeological divide in the centre of the island, where groundwater diverts either to the SW (to the Palma plain and aquifer) or to the NE (to the Inca-Sa Pobla aquifer). The eastern boundary is the Mediterranean Sea.

The aquifer is a gently sloping and faulted sequence of dominantly permeable materials with some discontinuous, low permeability interlayers. Abrupt lateral changes are frequent due to the transgressive and regressive conditions in which the sediments settled, as well as some faulting. From SW to NE three geologic and morphologic structures are observed (Figure 3): two subsiding basins at

the extremes of the unit (the Inca and the Sa Pobla basins), where the maximum aquifer thicknesses are found, and the Llubi-Muro threshold, which is an area where the aquifer base is elevated.



**Figure 3** Geological cross-section of the Inca-Sa Pobla aquifer system. A-B: sampled section.

From bottom to top the aquifer consists of the following units:

- 1- 50 to 150 m thick karstified, very permeable Tortonian to Messinian (Upper Miocene) reef limestones and calcarenites. It extends all along the area and constitutes the main aquifer. It shows fast lateral sedimentary changes.
- 2- A few to 50 m thick local patches of Messinian marl between units 1 and 3, confining the reef limestones below.
- 3- 40 to 80 m thick Messinian limestones, somewhat less permeable than the underlying ones, which are present in the whole area.
- 4- A few to 120 m thick lower Pliocene marly aquitard, which is only present in the two extreme basins.
- 5- A few to some 70 m thick Upper Pliocene calcarenite and shelly unit, which is present in the two basins but not in the central part of the aquifer (Llubi-Muro area). It is permeable and locally karstified.
- 6- A few to 30 m thick Pleistocene sandy, gravelly and silty unit, mainly in the two extreme basins, although it can be locally absent, especially in the centre.
- 7- A few to 40 m thick Holocene clays settled in the Sa Pobla basin during the Flandrian transgression and now underlying the S'Albufera wetland. They contain connate marine pore water.
- 8- Holocene to present-day permeable sands, gravels and silts, on top of the whole system. Its maximum thickness (15-20 m) is in the Inca and the Sa Pobla basins.

Thus, in the Inca basin there is a Tortonian-Messinian (reef limestones and calcarenites) deep confined aquifer, and an upper Pliocene (calcarenites) water table aquifer. The aquitard (lower Pliocene marls) extends downflow along some 15 km. To the NE of that point, across the Llubí-Muro area and most of the Sa Pobla basin, a single aquifer exists. The aquitard is also present near the coast in the Sa Pobla basin, in the subsiding area nowadays occupied by S'Albufera wetland. The wetland is a remnant of the Holocene Flandrian transgression (18 to 6 ka BP), and extends over some 30 km<sup>2</sup>.

Rain infiltration is the main source of recharge, but some lateral transfer from the Serra de Tramuntana carbonates (to the NW) could take place as well, especially to the upper aquifer of the Inca basin. Irrigation excess water also recharges the Sa Pobla basin, where agriculture is intensive, but it comes from locally abstracted groundwater.

Groundwater discharge is through pumping wells for agricultural and urban use, all along the area, and as springs and diffuse upward outflow in the inner border of the S'Albufera wetland clayey filling. In the past these springs were the main groundwater discharge.

Despite the multilayer configuration of the aquifer all the carbonate layers are hydraulically linked. The Upper Miocene deep limestone layer is the most transmissive unit and pumping wells get the water mainly from this thick layer.

In most of the aquifer groundwater flow in the uppermost tens of metres has mostly a vertical downward component. But through the deepest part of the unit, and from SW to NE, horizontal flow seems to dominate up to the coastal area, where convective flows of saline water seem to be present (Barón et al., 1997; Manzano et al., 2001).

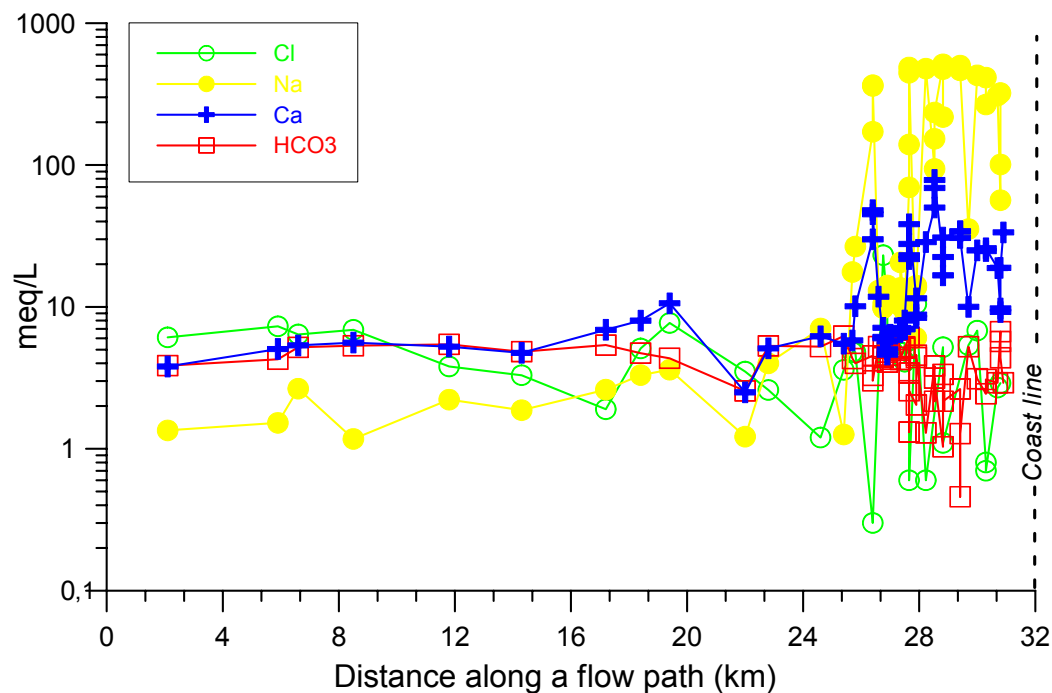


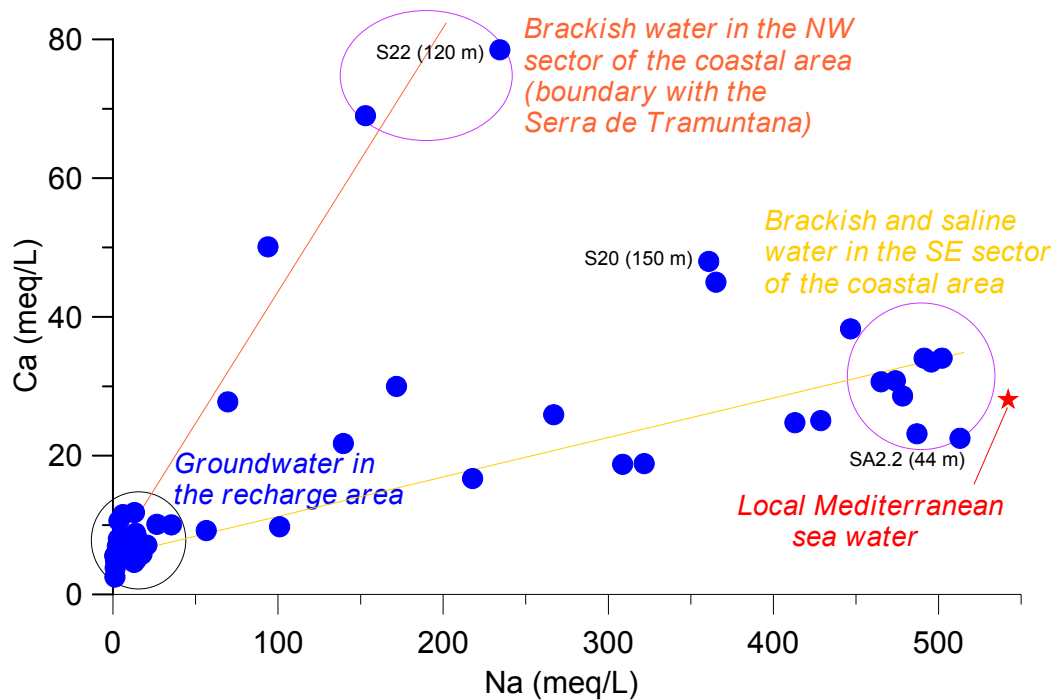
Figure 4 Groundwater salinity evolution, roughly following a flow line from SW to the coast (NE).

## HYDROCHEMISTRY

Groundwater along the sampled section is of the calcium bicarbonate type, and is saturated with respect to calcite. But in the 7 km-wide fringe closest to the coast it becomes saline, and of the sodium chloride type due to seawater influence (Figure 4). Groundwater from the Serra de Tramuntana is also of the calcium bicarbonate type. A thin freshwater layer exists around the N and S boundary of the wetland, but to the W and NW a wide transition zone develops.

A look at the evolution of some ion ratios (Ca/Na and Ca/Mg) shows two different mixing trends between freshwater recharged all over the unit and saline water encroached in the coastal fringe (Figure 5); some samples appear in between:

- 1) brackish and saline groundwater under and to the SE of S'Albufera wetland seems to be mostly the result of conservative mixing between fresh water and Mediterranean seawater,
- 2) brackish groundwater to the N and NW of S'Albufera seems to be a mixing of fresh water and a different brackish groundwater with more than twice the Ca content and a Ca/Mg ratio four times that of the saline water existing to the SE.



**Figure 5** Mixing trends between fresh groundwater and saline and brackish groundwater in the coastal area.

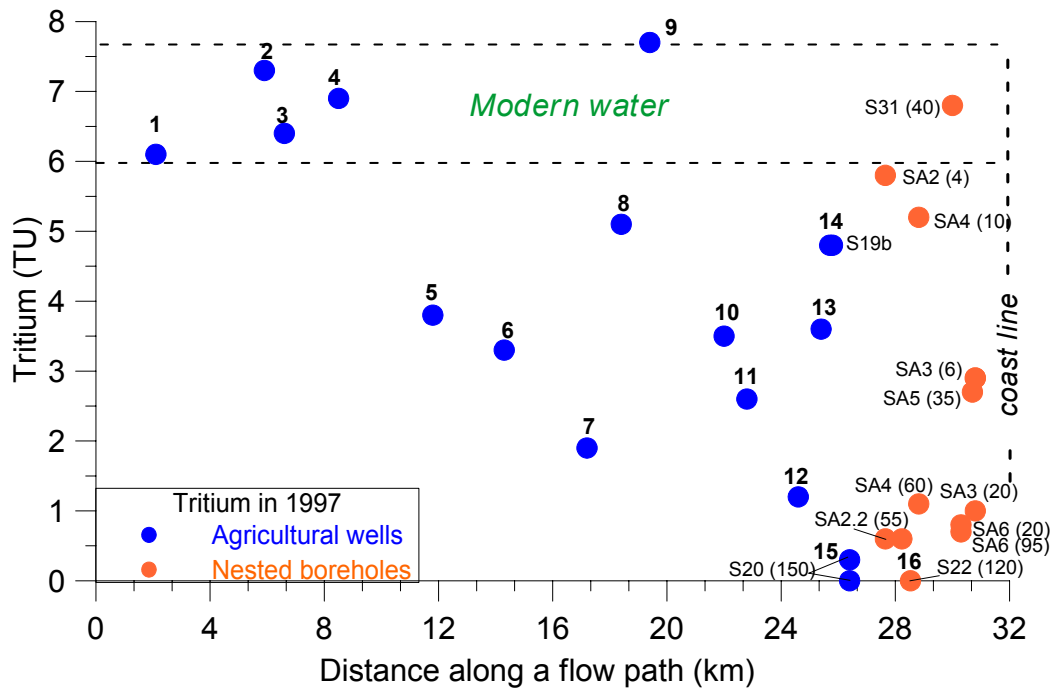
Several boreholes to the N of the wetland, close to the boundary with the Serra de Tramuntana range present upward flow of brackish groundwater as well as anomalously high vertical thermal gradients (Custodio et. al., 1992; Manzano et al., 2001). In a close-by area (S'Almadrava) a brackish spring outflows several metres above sea level of what seems a simple mixing of fresh and seawater. These flows may be explained by deep lateral flows coming from the nearby elevations of the Serra de Tramuntana, which mix locally with saline water in the aquifer.

Along several boreholes upward flows of saline water have been observed both along the N and S limit of the coastal sector of the aquifer, while in between there are downward vertical flows. This scheme suggests a convective pattern, which has yet to be studied in detail.

## ENVIRONMENTAL ISOTOPES

Tritium content in samples from 1997 decreases downflow from 6-8 TU (recent water) in the SW down to < 1 TU in the boundary of S'Albufera wetland (Figure 6).

Samples 1 to 4 tap the deep confined aquifer of the Inca basin, but their high tritium content (similar to current mean values in local rain water) indicates rapid penetration of recharge water from the higher head, water-table aquifer.



**Figure 6** Tritium contents along a flow path through the deepest part of the aquifer (samples 1 to 12), and at different depths in nested boreholes in the coastal area (figures between brackets give the sampling depth in m).

Samples 5 to 12 are from wells and boreholes in the Llubí-Muro threshold, where a single aquifer exists. Samples 5, 6, 7, and 12 show that tritium contents progressively decrease. This may be interpreted as a downflow increase of residence time. An electrical conductivity and temperature downhole log performed in well 7 showed an anomalously high thermal gradient and the existence of deep upward flow. The mixing pattern in each well determines to some extent the tritium content, from very recent water (well 9) to long residence time water (well 12).

Samples from boreholes and wells in the coastal area (samples 13 to 16 and white dots) have  $^3\text{H}$  contents, which are related with their depths but not with their salinity. In general marine water is found some 7-8 m below ground level at the coastline, 10-15 m some 3 km landward, and between 20 and 40 m in the periphery of S'Albufera wetland. Samples 15 and 16 are tritium free, and they correspond to deep saline waters under the Holocene S'Albufera sediments (see Figure 3). The rest of the samples correspond to brackish and saline groundwater from different depths taken in nested boreholes (SA1 to SA9 series in Figure 5). They show the expected decrease of tritium content with depth.

$\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in fresh groundwater fit the local meteoric line (Figure 7), as well as do the fresh water components of mixtures. Looking at their relationship with salinity, two different freshwater components seem to be present (Figure 8): 1) one with the signature of local rain water ( $\delta^{18}\text{O} = -5.5$  to  $-6$  ‰;  $\delta^2\text{H} = -32$  to  $-36$  ‰), 2) a second one which may be about 1 ‰ lighter in  $\delta^{18}\text{O}$ , and about 8 ‰ lighter in  $\delta^2\text{H}$  than local rain water. A recharge altitude that is high enough to explain this difference seems not possible in the sector of the Serra de Tramuntana close to the wells, but only at longer distances. So there is also the possibility of fresh water recharged in colder times in the past being present, probably from the end of the last glacial period (some 18-15 ka BP).

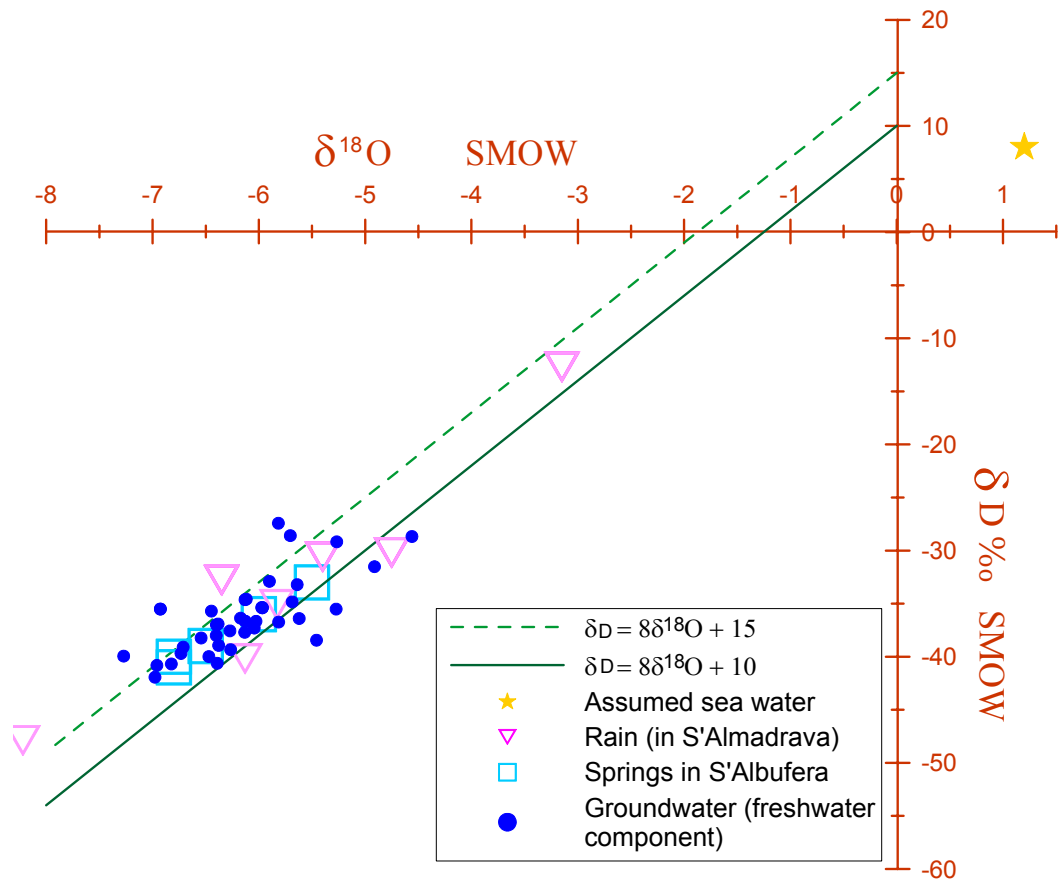


Figure 7  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in different waters of the area. Full dots are freshwater values corrected for marine water contribution according to the chloride content. Rainwater is from a nearby basin.

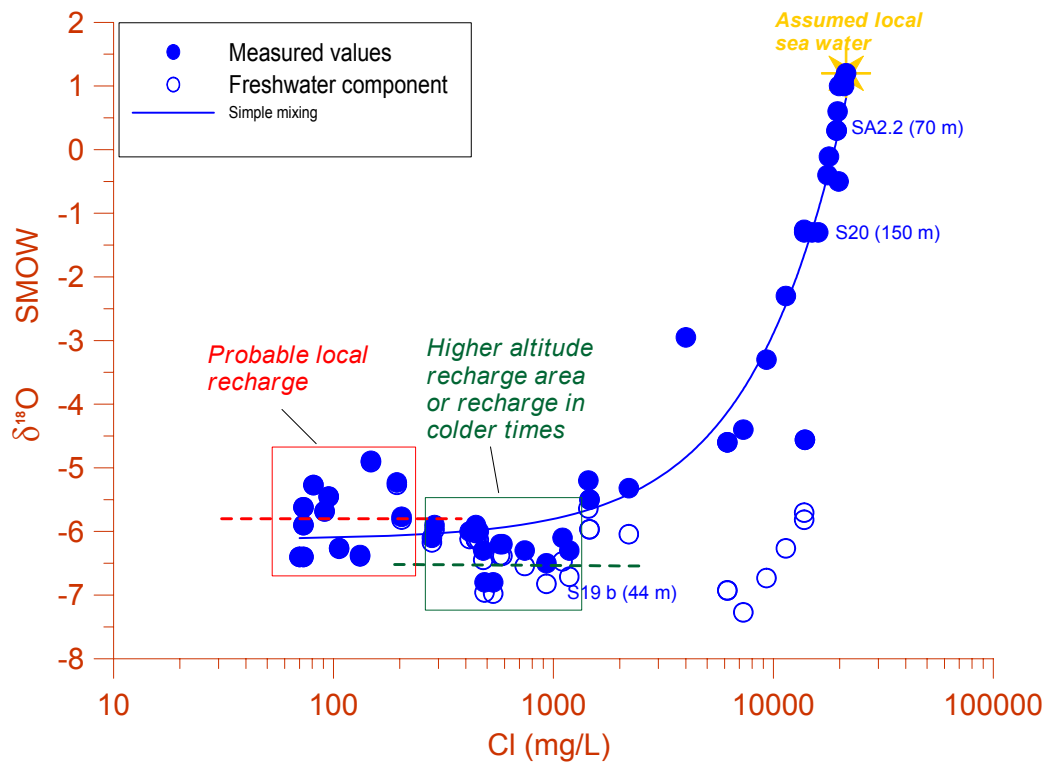


Figure 8  $\delta^{18}\text{O}$  signature of groundwater and of the fresh water component after correcting for saline contribution.



The isotopic composition of the freshwater component is given by:

$$f = \frac{m(S-F) - s(M-F)}{S-M}$$

being s, m, f, S, M, F the isotopic composition and chloride content of marine (salt), mixed and freshwater, respectively.

Assuming a gaussian distribution of errors, the standard deviation  $\sigma_f$  of the isotopic composition of the freshwater component, f, is:

$$\sigma_f^2 = \sum_x \left( \frac{\partial f}{\partial x} \right)^2 \sigma_x^2$$

in which x represent each one of the variables (s, m, S, M, F). The result is:

$$\sigma_f^2 = \frac{1}{(S-M)^4} \left[ (S-F)^2 (S-M)^2 \sigma_m^2 + (M-F)^2 (S-M)^2 \sigma_s^2 + (s-m)^2 (M-F)^2 \sigma_S^2 + (s-m)^2 (S-F)^2 \sigma_M^2 + (s-m)^2 (S-M)^2 \sigma_F^2 \right]$$

For the following values (in gL<sup>-1</sup> and ‰ respectively):

S	$\sigma_s$	M	$\sigma_M$	F	$\sigma_F$	s	$\sigma_s$	m	$\sigma_m$	$\sigma_f$
20	0.5	10	0.3	0.1	0.01	0.0	0.3	-5.0	0.2	0.64
20	0.5	1	0.1	0.1	0.01	0.0	0.3	-6.0	0.2	0.21

This means that the difference of about 1.0 in  $\delta^{18}O$  could be significant.

### ORIGIN OF THE FRESH COMPONENT IN COASTAL GROUNDWATER

The existence of saline groundwater under and in the surroundings of the S'Albufera wetland, in the up to more than 200 m thickness of the Holocene, Pliocene and Upper Miocene sediments (see Figure 3), is known since the 1980's (Custodio et al., 1992). Due to the fact that groundwater use in the area takes place landward of the wetland, studies to try to explain the origin of this saline water are recent (Barón et. al., 1997).

<sup>14</sup>C activity of dissolved inorganic carbon (DIC) and tritium content in four groundwater samples from the coast decrease as freshwater content increases (Figure 9), which apparently points to an old fresh water component.

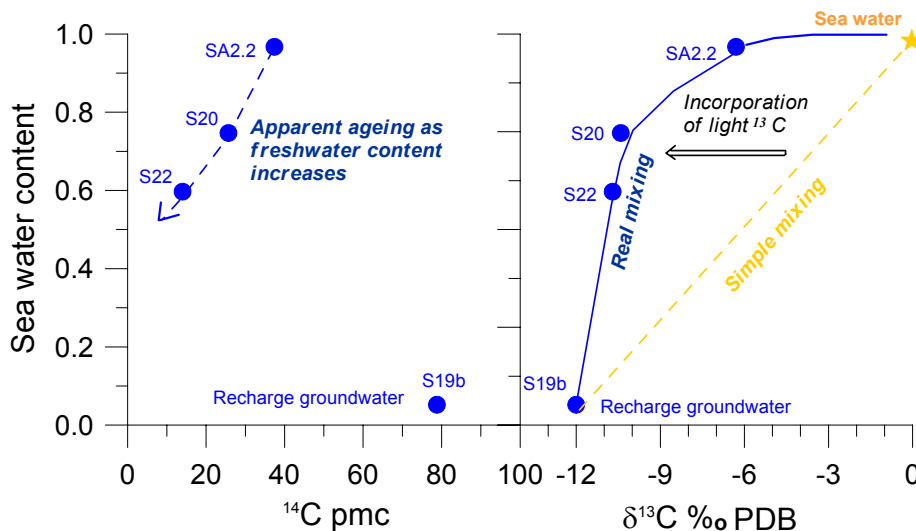


Figure 9 <sup>14</sup>C activity and  $\delta^{13}C$  in three saline samples and one freshwater sample from the coastal area (see situation in Figure 2).

The  $\delta^{13}\text{C}$  of samples SA2.2, S20 and S22 is lower than the simple mixing of freshwater sample S19b and seawater. The  $\delta^{13}\text{C}$  of seawater is assumed close to 0 ‰ since the fractionation factor between carbonate ( $\delta^{13}\text{C} \approx 0$  ‰) and dissolved  $\text{HCO}_3^-$ , which is the dominant DIC species at seawater pH, is about 1 ‰.

On the other hand,  $\delta^{13}\text{C}$  values decrease as total DIC increases in the three saline samples (Figure 10). This implies a source for the light C different to mineral dissolution and C contribution from marine water, which would produce heavier isotope values. Sample SA2.2 is almost seawater (97 %), but contains light C and its DIC coincides with that of seawater. This suggests that seawater in the ground receives  $^{13}\text{C}$  from the organic matter in the formations, which can be expected light (Hornibrook et. al., 2000) and the excess DIC is precipitated as  $\text{CaCO}_3$ . The process is not well understood at the moment. A decrease of pH due to reduction processes may shift the isotopic equilibrium with dominating  $\text{HCO}_3^-$  to another equilibrium in which  $\text{H}_2\text{CO}_3$  is a significant fraction of the total DIC, which has a fractionation factor around 7 to 8 ‰. Samples S20 and S22 seem to incorporate this light organic carbon in addition to exchange, since the DIC increases. The possibility of incorporating a third old water component with very light carbon seem less probable since in a carbonate system  $\delta^{13}\text{C}$  values of DIC lighter than -17 ‰ seem improbable.

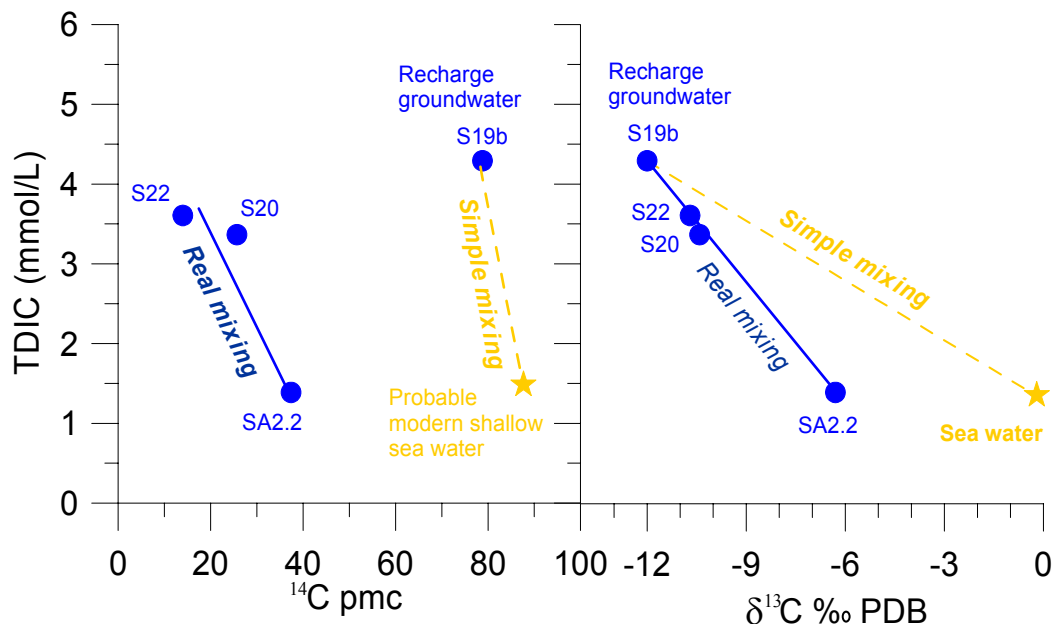


Figure 10  $^{14}\text{C}$  activity and  $\delta^{13}\text{C}$  versus the total dissolved inorganic carbon content in the samples of Figure 9.

## AGE OF THE BRACKISH WATERS IN THE COASTAL AREA

A preliminary interpretation of  $^{14}\text{C}$  ages following the model of mixing between soil-derived  $\text{CO}_2$  ( $\delta^{13}\text{C} \approx -25$  ‰ and  $^{14}\text{A} = 100$  %), in a closed or open system with respect to  $\text{CO}_2$ , and a very old marine carbonate rock ( $\delta^{13}\text{C} \approx 0$  ‰ and  $^{14}\text{A} = 0$  %) would produce Figure 11. Sample S19b contains some thermonuclear carbon, and in fact it contains tritium. Sample SA2.2 (almost seawater) appears as modern to recent, depending on the interpretation, but this does not apply since infiltration of seawater was probably not through a  $\text{CO}_2$  rich soil. Samples S20 and S22 seem old, with ages of about 3000 and 12000 years for closed system to soil  $\text{CO}_2$ , and of about 8000 and 25000 years for an open system.

But this model fails if it is considered that  $\text{CO}_2$  derived from organic matter in the sediments is incorporated. Corrections cannot be made since at present carbon isotope and chemical characteristics of this organic matter are unknown. If this organic matter is old ( $^{14}\text{C}$  free) the ages above indicated are clearly overestimated.

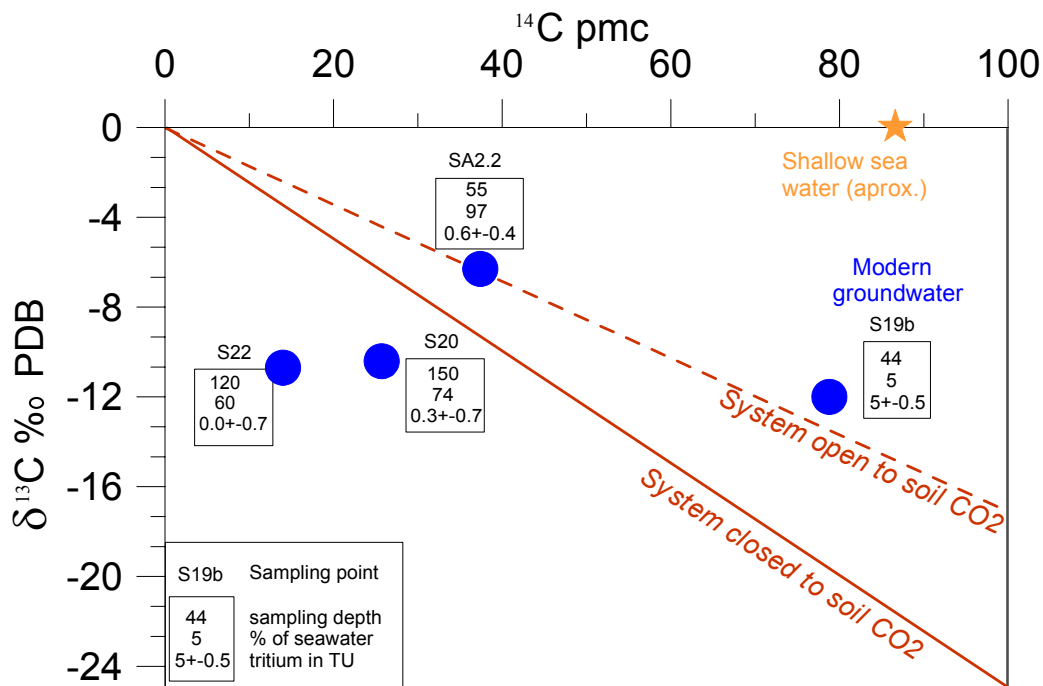


Figure 11  $^{14}\text{C}$  activity versus  $\delta^{13}\text{C}$  in the samples of Figure 9.

## CONCLUSIONS

In the Inca basin confined aquifer most of the wells produce recently recharged water from the water table aquifer. In most of the Sa Pobra basin single aquifer tritium contents of pumped groundwater depends on the mixing pattern of each sampling point. Boreholes to the NW and SE boundaries of the aquifer show upward flow of deep saline groundwater, which is almost tritium free (<1 TU), while boreholes in the centre of the basin display downward flow of modern, fresh groundwater and also of saline water. Nevertheless, the tritium content of samples of the single aquifer from the Llubí-Muro threshold shows some deep upward flow of older groundwater.

In most of the aquifer fresh groundwater is of the calcium-carbonate type. In the coastal fringe (some 7 km wide) groundwater is brackish and of the sodium-chloride type due to the mixing with marine water in the Holocene clays and in the underlying Pliocene calcarenites and marls, as well as in the Miocene limestones that constitutes the lowermost transmissive layer.

The fresh water component of brackish groundwater in the coastal area seems to have a double origin:

- to the SE sector it has the  $^{18}\text{O}$  and  $^2\text{H}$  signature of local recharge ( $\delta^{18}\text{O} \cong -6$  to  $-6.5$  ‰;  $\delta^2\text{H} \cong -35$  to  $-40$  ‰ SMOW);
- to the NW sector it has the signature of a water recharged either at higher altitude than the aquifer recharge area, or locally but under colder atmospheric temperatures than the present ones, namely during the Pleistocene-Holocene change.

It is difficult to calculate the age of saline water and its fresh and saline water components due to what seems exchange and incorporation of carbon from organic matter in the sediments, which has unknown age and characteristics. Although preliminary calculations may show ages between 3000 and 25000 years, real ages may be much less. But mixing of an old component with a young one cannot be precluded.

In the past, the only natural discharge mechanism of the aquifer system was upward flow of fresh water along the fresh-salt water interface in the surroundings of S'Albufera wetland, taking with it some saline water. Nowadays, discharge takes also place through pumping, but still these upward flows sustain the springs and diffuse outflow occurring along the inner boundary of S'Albufera.

The lack of hydraulic gradient for fresh water flow in the aquifer during the Holocene period prevented the freshening of the coastal sector. More than 200 m of Quaternary to Miocene sediments hold saline groundwater under S'Albufera wetland, and its discharge, which is produced as a saline component to the springs, is probably less than  $0.5 \cdot 10^6 \text{ m}^3 \text{ a}^{-1}$  in an area larger than  $30 \text{ km}^2$ . This means that most of this salt water is probably older than 5 ka.

## ACKNOWLEDGEMENTS

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