Palaeowater in coastal aquifers of Spain

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Abstract: In the framework of the PALAEAUX project, three coastal aquifers have been studied in Spain, looking at the possible existence of Pleistocene or Early Holocene fresh groundwater, in addition to the formerly studied Llobregat Delta. They constitute representative situations of the most common coastal aquifers. The main characteristics of these four areas are:

- The Llobregat Delta system, studied since 1965, is placed to the southwest of Barcelona (NE Mediterranean coast of the Iberian Peninsula). It is a sedimentary fluvial formation of Pleistocene to recent age, which is representative of small size coastal alluvial formations with the deep confined aquifer open to the sea offshore. Marine sea water penetrated the deep Pleistocene layer during the Flandrian sea-level rise but afterwards relatively high freshwater heads upstream allowed its progressive flushing to the sea through the submarine outlet since 6000–8000 a ago. Freshwater turnover time is shorter than the Holocene duration and it has been renovated due to natural discharge of the aquifer to the sea. The renovation process has recently been accelerated due to intensive groundwater exploitation during the past century. Nowadays, only freshwater a few centuries old remains in low permeability areas of the confined Pleistocene aquifer.
- The Doñana sedimentary aquifer system corresponds to the ancient estuary of the Guadalquivir River (SW Spain). It contains old saline groundwater that has not been flushed away due to the low freshwater head. In this aquifer ^{39}Ar, ^{85}Kr, ^{3}H, ^{14}C and ^{13}C measurements have been used to ascertain the age structure of several mixed groundwater samples. After correction, the oldest fresh groundwater ^{14}C age is *c.* 12–15 ka but ^{39}Ar ages point to somewhat younger water. Neither the stable isotope contents nor the recharge temperature calculated from noble gases show a climatic signature for these waters.
- The Inca-Sa Pobla carbonate system is the northeast sector of the island of Mallorca. Brackish and salt groundwater in the coastal area has been found along the coastal strip of S'Albufera, displaying what seems a convective-like flow pattern inside the up to 200 m thick aquifer. The most consistent estimated average ^{14}C ages of the mixed water vary between 9 and 13 ka, i.e. Early Holocene–Late Pleistocene. Water ^{18}O and ^{2}H contents do not show a clear climatic signature.
- The Amurga volcanic Massif is on the southeast of the island of Gran Canaria. Brackish groundwater is found in the thick phonolite rock sequence. The unsaturated zone can be up to 200 m thick. Groundwater salinity is due to recharge under arid conditions and the influence of marine airborne salts. Groundwater ^{14}C age is possibly *c.* 11 ka, indicating a Late Pleistocene age water mixture. The small recharge due to aridity and the thick unsaturated zone explains this. Stable-water isotopes show no clear climatic signature.

The most important aquifers along the 5000 km of peninsular and island coastal areas in Spain are mainly unconsolidated sedimentary Plio-Quaternary formations and Triassic–Miocene carbonate massifs. The first ones consist of deltas, filled-up ancient estuaries and coastal lowlands that are mostly present in the SW Atlantic strip and along the Mediterranean shore. The carbonate massifs are common features along the Mediterranean coast of the Iberian Peninsula and the Balearic Islands, as well as in some areas of the north coast. Both the sedimentary and the carbonate formations constitute highly permeable, and often extensive and thick aquifers, usually intensively developed for agricultural, industrial, urban and touristic uses.

To a minor extent, the fractured granite and shale Palaeozoic formations along the northern and northeastern Spanish coast are also permeable enough as to be considered aquifers of local significance. In the Canary Islands, volcanic formations and the associated sediments, of Miocene–Recent age, may constitute coastal aquifers.

At the last glacial maximum (LGM) most of the Iberian Peninsula coastline, and also that of the Balearic and Canary Islands, was between 100 and 120 m below present sea level, with the coastline not far away from the present one. Sea-level rise started *c.* 15–12 ka ago and stabilized *c.* 6 ka ago. Taking into account the configuration of the existing coastal aquifers, fresh Pleistocene and Early Holocene groundwater can still be present in some areas, especially in the sedimentary formations where highly permeable alluvial layers are confined by estuarine and prodeltaic clayey wedges, although they do not necessarily cover the offshore end. In most cases, relatively high freshwater heads have pushed out the Pleistocene water, which has been replaced. Thus, only Holocene and recent freshwater is found. This is the case for the small Mediterranean deltas like the Llobregat River Delta. Currently, the natural situation has often been dramatically changed due to intensive groundwater development, and the existing freshwater may be totally or partially replaced by recent freshwater and marine water. In other cases, the freshwater head was not high enough to flush away the sea water encroached during the sea-level rise, and Late Pleistocene or Early Holocene salt and brackish groundwater is still present, often mixed in different proportions with recent water. This is the case for the biggest deltas (e.g. the Ebre and the Guadalquivir River Deltas), and also for some carbonate formations filling gravens open to the sea, like the Inca-Sa Pobla system on Mallorca island.

In very arid zones, like the southern flank of Gran Canaria island, the combination of the influence of aridic conditions during recharge and the supply of marine airborne salts has to be taken into account to explain the existence of brackish Pleistocene–Holocene groundwater above sea level under hydraulic conditions preventing marine intrusion. This is the case of the Amurga Massif.

In this paper the study cases of the Llobregat Delta, and the Doñana, the Inca-Sa Pobla and the Amurga aquifers are introduced. They have been selected to show typical situations to which many of the other coastal aquifer systems of Spain can be referred.

Llobregat River Delta aquifers, northeastern Iberian Peninsula

The Llobregat River Delta lies at the southwestern corner of the Barcelona Metropolitan area, on the northeastern Mediterranean coast of Spain (Fig. 1). It is a small sedimentary formation of *c.* 80 km², that extends into the river's lower valley up to some 20 km upstream. The alluvial aquifers in this area are an important component of the local water resources system, despite being so small. Under intensive exploitation, most of the recharge comes from river water, both by channel infiltration and recharge of irrigation excess water along the lower valley. The river drains *c.* 5000 km² and contributes a mean flow close to 20 m³ s⁻¹, which may vary between 4 and 2000 m³ s⁻¹.

The intensive development of the alluvial aquifers started late in the last century, first in the lower valley for supplying Barcelona and then in the delta where deep boreholes were flowing wells. There were industrial settlements making intensive use of groundwater at the delta boundaries and in the 1920s abstraction of large quantities of groundwater from the delta itself was begun. The massive use of groundwater to supply factories peaked in the 1970s. The use of groundwater for irrigation, although important, is a minor part of the total outflow since irrigation canals diverting river water upstream supply a large part of the area.

In 1955, a river-water treatment plant to produce drinking water was put into operation and the supply wells for Barcelona changed their use from continuous exploitation to emergency use, to respond to peak demands, river droughts, serious river pollution events and failures. Artificial recharge operates by increasing river infiltration through the bed (since 1954) and by injection, via special wells, of excess treated river water. Total groundwater abstraction peaked in the 1970s, at *c.* 4.5 m³ s⁻¹ of equivalent continuous flow, but currently it is *c.* 2.5 m³ s⁻¹, although variable from one year to another.

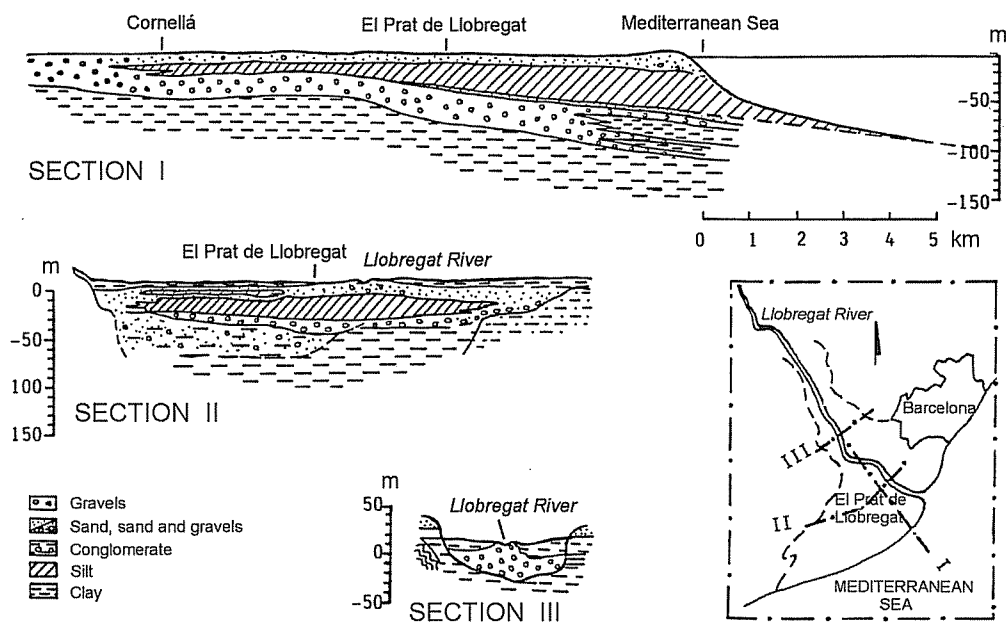The quality of river water is rather poor due to

Fig. 1. Geographical emplacement and geological structure of the Llobregat River Delta (after Custodio *et al.* 1992*b*).

the large and increasing population and industrialization of the basin, and especially due to the disposal of brines at the central part of the basin resulting from KCl mining and processing. At times of low flow, river water was brackish and in the late 1980s a pipeline was constructed to divert part of the brines directly to sea, partly alleviating the problem. The alluvial aquifers are affected by river-water salinity and are threatened by contamination from diverse sources that are the result of poor environmental control in previous decades. Recharge is also threatened by the reduction of rural areas due to the progressive urbanization of the area. If the aquifer system fails (e.g. drying of a large part, salinization, contamination) the investments needed to guarantee the water supply are so large that some citizen groups, including the active Groundwater Users' Association, demand action by the water authorities with help in environmental control and preservation of recharge.

The first comprehensive study was carried out by the Geological Survey of Spain and dates from the early twentieth century (Santa María & Marín 1910). However, detailed studies did not appear until the second half of the 1960s, led by the Eastern Pyrenees Water Authority and the Public Works Geological Service, followed by the Technical University of Catalonia and what is now the Foundation International Centre for Groundwater Hydrology. A series of studies, explorations, researches and projects have been carried out (see

Custodio 1981 and Custodio & Bruggeman 1987 for details). As a result, a large amount of groundwater data is available.

Geology and hydrogeology

The delta (see Fig. 1) is a Pleistocene and Holocene formation that consists of three layers: (1) a deep confined aquifer layer of Pleistocene alluvial sands and gravels; (2) an intermediate prodeltaic silty-clayey aquitard wedge with a high organic matter content; (3) a water-table aquifer of sandy deltaic plain and front Holocene sediments. The silty intermediate wedge and the sandy upper layer grew up under the sea-level rise of the Flandrian transgression that started *c.* 15 ka BP, i.e. after the last Pleistocene glaciation.

The confined deltaic aquifer is up to 10–15 m thick and lies directly over the Pliocene marls and clays that constitute the impervious bottom of the aquifer system. The Pleistocene layer outcrops landward in the lower river valley, where it merges with the highly permeable (up to 100–800 m d^{-1}) lower valley alluvial aquifer. Along the coastline the aquifer is *c.* 70 m deep and extends seaward, intersecting the sea bottom at *c.* 100 m depth, 3–4 km offshore from the central part of the delta coastline. The sediments are highly permeable and have a strong lateral heterogeneity related to sedimentary features like the existence of palaeo-channels.

The aquitard disappears and becomes sandy at the southern end of the lower alluvial valley and to the deltaic margins. The maximum thickness (40 m) of the prodeltaic wedge is in the centre of the delta coastline. In this area its vertical permeability is *c.* 2×10^{-5} m d^{-1}.

The upper Holocene layer is 10–20 m thick. In the left and right margins of the delta, and also northwards to the river valley, the water-table aquifer directly overlies the Pleistocene gravels, thus forming a single water-table aquifer. During the Flandrian transgression, sea-level rose, the
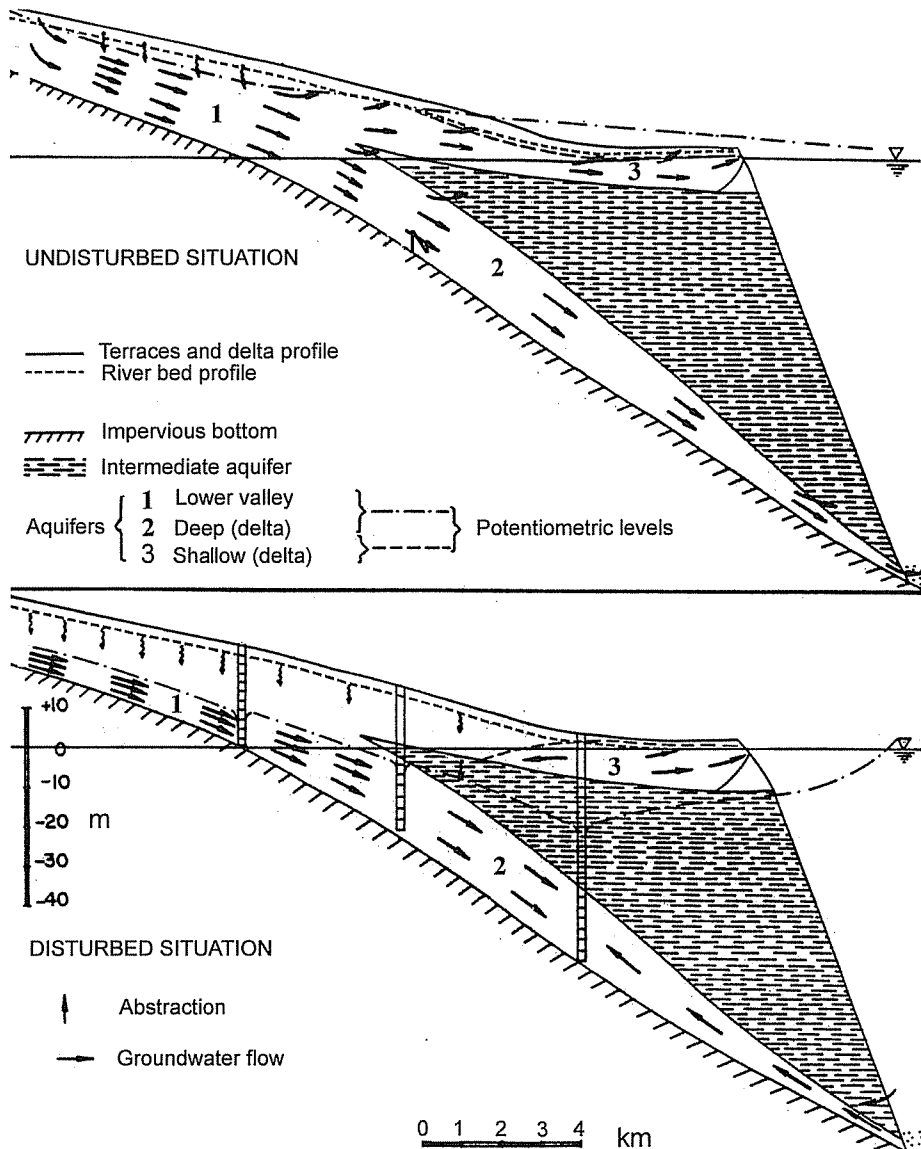
Fig. 2. Conceptual model of the aquifer system. Under natural conditions the water head between the two deltaic aquifers allowed groundwater to start upwards flow through the intermediate aquitard. The head at the inner boundary was high enough to allow discharge to the sea through the submarine outlet of the confined aquifer. Under the influence of present conditions, groundwater flows downwards through the aquitard and the discharge to the sea is changed for sea-water intrusion (after Iribar & Custodio 1993).

Pleistocene alluvial layer was filled with sea water and the Holocene prodeltaic clayey wedge trapped seawater while settling.
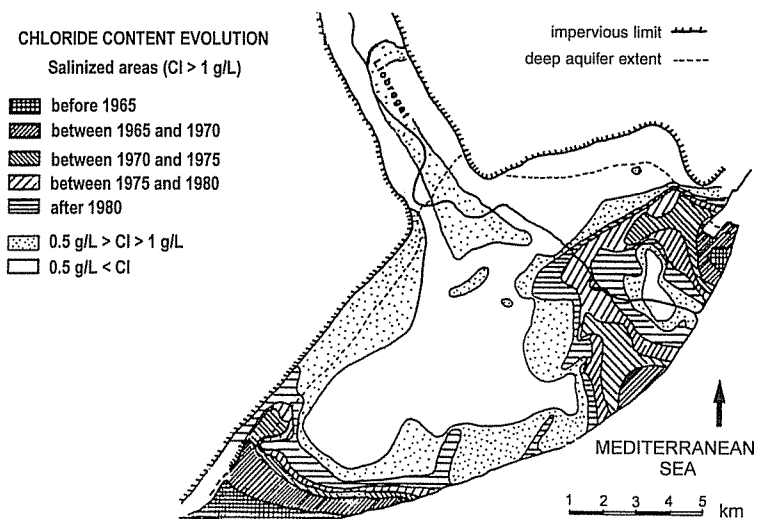
Before groundwater intensive development, the river drained the alluvial aquifer in the lower valley and the water head was high enough to maintain freshwater discharge to the sea through the confined deltaic aquifer outcrop in the well-confined central part of the delta (Fig. 2). In the delta itself, the water head difference between the two aquifers allowed upward flow of freshwater into the aquitard. This situation resulted in the flushing out of the original marine water of the deep aquifer over a period of a few thousands years, producing a variable dilution of connate marine pore water in the lower part of the aquitard. Currently, recharge to the lower valley aquifer and to the deltaic aquifers comes mainly through river-water infiltration, either through the actual riverbed or from irrigated fields. Recharge is artificially enhanced by controlled ploughing of the riverbed at the upstream part of the river valley and also by injection of surplus treated river water through wells. The discharge of the lower valley aquifer occurs through pumping and as underground transfer to the delta deep aquifer. The discharge of the deep confined delta aquifer takes place through pumping in the centre of the delta and in the margins. Before intensive development the discharge was through its submarine outcrop and to the margins of the delta, where the aquitard is missing or is rather permeable, thus allowing some vertical flow to the water-table aquifer.

The recent, intensive groundwater exploitation, mainly concentrated at the southern end of the river valley and in the centre of the delta, produced a widespread piezometric drawdown cone in the confined aquifer. Since the late 1960s the water table in the river valley has been permanently under the riverbed (except during exceptional floods), while the piezometric head of the deltaic confined aquifer is below sea level all along the coastline (Fig. 2). This allows the movement of groundwater landwards instead of seawards.

Hydrogeochemistry

By 1965 the sea-water encroachment in the deltaic confined aquifer was already showing up in some tracts of the coastline (Custodio 1967), while river water salinity, c. 700 mg l^{-1}, had already reached the pumping wells in the centre of the delta at the lowest point of the drawdown cone. Before 1925 the river had < 100 mg l^{-1} of Cl$^-$: salinity changes in the river water take 10 a to reach the pumping wells. Freshwater in the confined aquifer between this recently recharged river water and the intruding saline water is pre-1925 water that was recharged in the lower river valley, which was moving towards the offshore outflow area and is now moving landward, pushed by sea water that replaces it. In 1965, a wide strip of this pre-1925 water was seen

CHLORIDE CONTENT EVOLUTION

Salinized areas (Cl > 1 g/L)

before 1965
between 1965 and 1970
between 1970 and 1975
between 1975 and 1980
after 1980

0.5 g/L > Cl > 1 g/L
0.5 g/L < Cl

impervious limit
deep aquifer extent

MEDITERRANEAN SEA

1 2 3 4 5 km

Fig. 3. Progression of the marine-water intrusion into the deltaic-confined aquifer between 1965 and 1990. Saline water moves faster through areas of high permeability, like a palaeochannel placed to the right of the river mouth or along the side areas of the delta, where the intermediate silty wedge is thinner or missing and coarse sediments dominate (after Iribar & Custodio 1993).

but it has currently been depleted, except in some low permeability areas.

Groundwater chemistry in the deep confined deltaic aquifer is dominated by sea-water intrusion in the delta coastal area and by the reducing conditions created by organic-rich sediments at the upper boundary. Since the beginning of the process, two saline plumes have shown up in the northeastern part of the delta (Fig. 3), in response to the drawdown cone created by abstractions (Custodio et al. 1986; Iribar 1992; Iribar & Custodio 1993). The plume to the northeastern corner follows the coarse sediments at the boundary, and the other plume is close to the current position of the river, following a main palaeochannel of the Pleistocene river. Between the two plumes there is a shrinking area of low permeability containing some pre-1925 water that is being progressively depleted. The progression of these plumes is currently more or less arrested, since some brackish and saline water is being abstracted for cooling in some factories and for desalination, thus establishing an equilibrium between salinity inflow and salinity outflow. Small changes in abstraction quantities and patterns produce conspicuous shifts in salinity.

The southwestern saline groundwater is, in reality, unflushed connate marine water, although currently it is also moving landwards. In this area, local alluvial fan sediments coalesce with the Pleistocene deep gravel layer and the sandy Holocene deposits, forming a roughly single water-table aquifer with a rather low water head that prevents sea-water flushing from deep layers. Between the northeastern and the southwestern saline areas, pre-1925 groundwater is still found, since there the gravel layer is thin or absent, but a new saline plume is developing following the more permeable features.

Saline water and its variable mixing with fresh groundwater in the deep aquifer produced additional hydrochemical changes, mainly derived from cation exchange and redox reactions. The resulting and most significant changes are local hardening (where marine encroachment is recent) or softening (in areas where connate marine water is still being flushed out), and HCO_3^- content increase due to carbonate dissolution. No clear chromatographic pattern is found. The advection-dominated flow in the sea-water intruded areas prevents a clear salinity stratification in the relatively thin aquifer. In areas rich in organic matter there is SO_4^{2-} reduction.

Saline pore water in the aquitard was detected in the late 1960s, during the hydrogeological surveys. To ascertain the origin of this water, cores obtained during the 1970s and the pore-water salinity were studied by dilution (Peláez 1983). The aquitard was found to contain marine connate water, from its top down to a variable depth, where dilution starts to reach values characteristic of the deep aquifer freshwater at the bottom of the aquitard. Integrating this data with the conceptual historical flow model, the dilution was interpreted as the result of fresh-water upward flow from the deep aquifer to the upper one during a maximum of 6–8 ka BP, when natural flow conditions operated in the aquifer system. During this time only a small part of the saline water in the aquitard had been displaced.

Hydrogeochemical studies were made in order to explain the observed pore-water composition and to determine the hydrochemical processes that have modified the composition of the mixed water. Vertical Cl^- and Na^+ changes found in the central coastal area of the aquitard correspond to a longitudinal dispersivity (mainly due to molecular diffusion) of $1–2 \times 10^{-5}$ m^2 d^{-1}. The Na/Cl ratio indicated a progressive vertical cation exchange between Na^+ in the water and Ca^{2+} in the sediments as the flushing of sea water decreased upwards: these waters were ^3H free (Custodio et al. 1971).

Later, in the 1980s, new pore-water samples of the aquitard were obtained by squeezing (Manzano & Custodio 1987). Chloride, $\delta^{18}O$ and δ^2H measured values correspond to near-perfect conservative mixing curves. However, the vertical distribution of cations in the aquitard column showed a near perfect chromatographic distribution. It was deduced that the main controlling chemical reactions were cation exchange (Na^+ for Ca^{2+} and Mg^{2+}), calcite dissolution at the bottom of the aquitard and precipitation upwards, as well as SO_4^{2-} reduction (Manzano et al. 1990, 1993; Manzano 1993). The conceptual model was simulated with a reactive multicomponent transport model and very reasonable results were obtained (Fig. 4). The model for cation distribution at the base of the aquitard has recently been improved by adding redox changes (Xu et al. 1999).

Environmental isotopes

Environmental isotope studies carried out in the area since late in the 1960s were fundamental in confirming the origin of the water and the conceptual model of the flow system. Tritium-content distribution in the lower valley water-table aquifer, in samples taken from wells tapping the full aquifer thickness, follows what can be expected from an exponential mixing model (Zuber 1985; Custodio 1991). To compare samples from different dates and places along the aquifer, the variable aquifer storage and ^3H evolution with time has to be taken into account. Average turnover time for groundwater from wells in the lower valley varies between 2 and 4 a, in agreement with zero (under
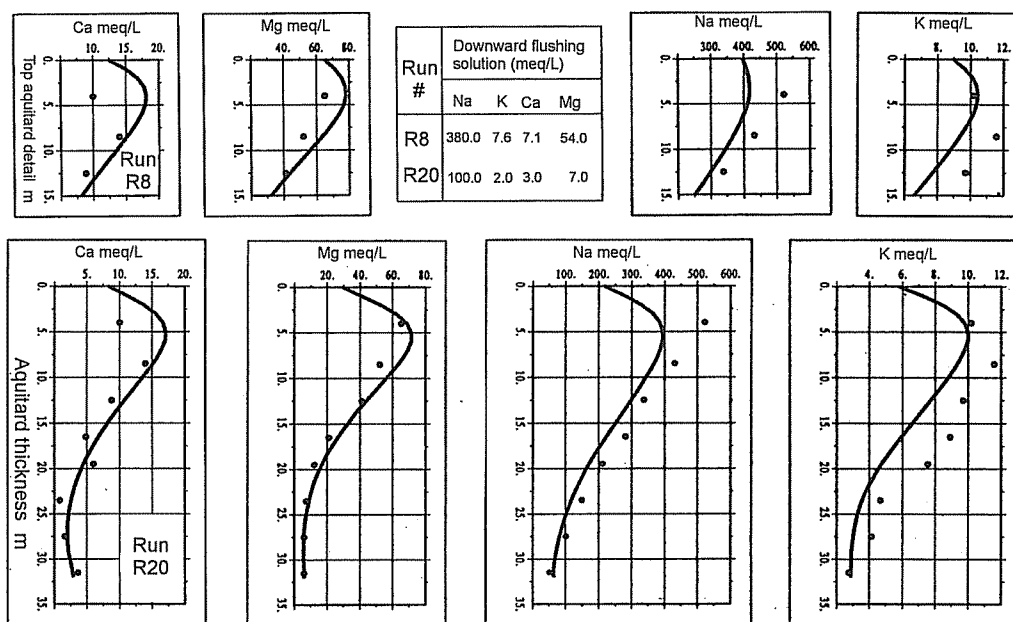
Fig. 4. Saline pore water in the aquitard (●) as a result of diluting connate marine water by upward flow of freshwater from the confined aquifer during the period of natural hydraulic conditions in the system (6–8 ka). The experimental curves show a perfect chromatographic sequence where cation exchange and carbonate dissolution play the main role. Continuous lines were simulated with a multicomponent reactive transport model using experimental values for the initial concentrations of pore water and freshwater in the underlying aquifer. Longitudinal dispersivity was calculated by inverse calibration of the Cl curve; the selectivity coefficients for the exchange reactions were calculated by combining experimental pore-water chemistry and the concentration of cations adsorbed in the sediments (after Manzano *et al.* 1993).

the riverbed) to 2 a (under the irrigated fields) of calculated transit time through the unsaturated zone and with the ratio of groundwater volume to average yearly abstraction. Groundwater spends *c.* 10 a getting from the recharge area to the wells in the confined aquifer in the centre of the delta. This agrees with transit times deduced from Cl⁻ (as mentioned above).

Tritium data in the deltaic-confined aquifer have been interpreted as being the result of well-mixed recharge groundwater in the lower valley that subsequently moves along the deep aquifer, according to a piston flow model. Tritium distribution in the aquifer between 1972 and 1976 showed high contents (> 10 TU) for young waters close to the recharge area, while towards the coast both freshwater and saline water were almost ^{3}H free. The boundary between both zones roughly agreed with the position of the main pumping wells, defining the minimum of the drawdown cone. This also agrees with the hypothesis that seawater intrusion started most recently in the 1950s or early 1960s, through the submarine outlet of the

deep aquifer that is 100 m deep and 3–4 km offshore. However, late in the 1970s the most saline coastal groundwater showed measurable ^{3}H contents (1–3 TU), indicating that the intruded marine water already had some thermonuclear influence (Fig. 5). Calculations based on data from 1982 to 1987 mean that the marine water had moved 4 km in *c.* 30 a; equivalent to a mean average permeability of *c.* 40 m d⁻¹ for this part of the deep aquifer (Custodio *et al.* 1992a).

Isotope contents in rainwater from Barcelona are $\delta^{18}O \cong -6.5 \pm 2.6\%$ and $\delta^2H \cong -41.6 \pm 25\%$ Standard Mean Ocean Water (SMOW) (Iribar 1992). Average river-water composition is $\delta^{18}O \cong -6.8 \pm 0.1\%$ and $\delta^2H \cong -51.5 \pm 3.97\%$ SMOW, which is lighter than local rainfall, as could be expected considering that the Llobregat River Basin encompasses heights of up to 2000 m in the Pyrenees. But the river has two dams and many ponding areas behind hydropower and irrigation diversion structures, where some isotopic evaporative fractionation occurs, which means a decrease in the ^{2}H excess. Recharge water in the
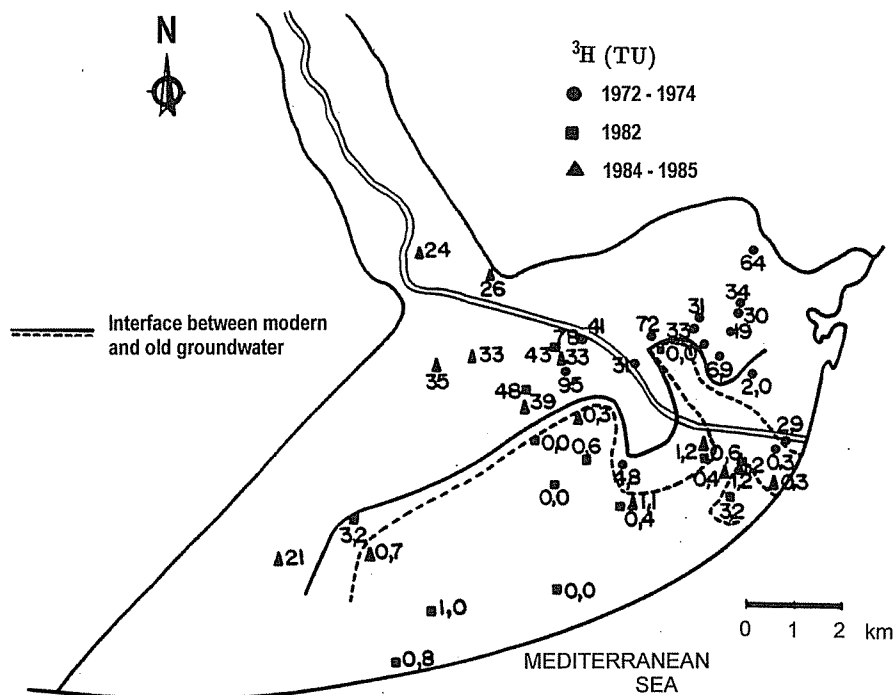
Fig. 5. Tritium content in water from wells in the deltaic-confined aquifer (Custodio *et al.* 1992*a*).

lower valley has an average composition of $\delta^{18}O \cong -6.5$ to $-7.0‰$ and $\delta^2H \cong -47$ to $-50‰$ SMOW, in agreement with the river water origin. Some local differences correlate perfectly with chemical changes. This indicates some lateral groundwater contribution as well as an enrichment by an additional fractionation process due to ponding in the irrigated fields, which decreases further the ^2H excess: this is especially clear towards the lower part of the valley.

Groundwater in the deltaic-confined aquifer show very small and non-discriminative differences: freshwater and young groundwater (with measurable ^3H contents) found between the recharge area and the centre of the delta has isotopic values similar to those in the lower valley. Older fresh groundwater (without ^3H) still present in the central coastal area between the two saline plumes seems to be a little bit lighter. The freshwater component of saline groundwater in the deep aquifer has a composition similar to the fresh old groundwater. The fresh groundwater in the western and eastern deltaic single aquifers is a little bit heavier, suggesting the influence of the isotopically heavier local recharge.

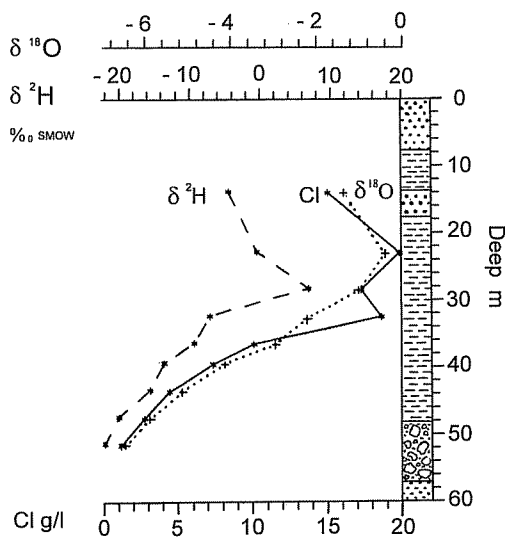Pore water in the aquitard has $\delta^{18}O$ and δ^2H values that correspond to a conservative mixing of

Fig. 6. Vertical distribution of $\delta^{18}O$, δ^2H (‰ SMOW) and Cl (g l^{-1}) in the aquitard pore water showing near-perfect conservative mixing between marine water (close to the aquitard top) and freshwater typical from the underlying confined aquifer (after Manzano *et al.* 1990).

freshwater from the deep aquifer and marine water during the period of natural (undisturbed) hydraulic conditions in the system (Fig. 6). Small deviations from the conservative mixing can be explained by fractionation during the water extraction from the cores (by squeezing). An exception is the uppermost sample, that corresponds to a mixing with groundwater of the upper water-table aquifer in a rather sandy layer.

Groundwater in the lower valley has total inorganic carbon dissolved $\delta^{13}C$ values of -12.9 to $-14.9\%o$ PDB, typical of groundwater in a carbonated medium with recharge following a reaction path open to soil CO_2. Carbon dioxide input takes place only during recharge, especially in the irrigation fields, where it comes from the soil and the degradation of water-contributed organic matter. This is in agreement with the observed increase of HCO_3^- contents in waters resulting from recharge of irrigation excess water. This suggests initial ^{14}C activities of 0.54–0.58 percentage of modern carbon (pmc) when there is no thermonuclear influence. Some samples, measured in 1972, showed ^{14}C activities of > 200 pmc, perhaps corresponding to the recharge through the riverbed without incorporation of C from the soil (Custodio *et al.* 1992*a*).

$\delta^{13}C$ data available in the deltaic-confined aquifer are somewhat heavier than in the valley. This could be due to an additional dissolution of calcite in the aquifer driven by different chemical processes such as NO_3^- and SO_4^{2-} reduction, and by mixing of salt water and freshwater.

Figure 7 shows the incorporation of water containing ^3H in samples lying to the right of the conservative mixing line between biogenic C ($\delta^{13}C \cong -25\%o$ PDB and $^{14}C \cong 100$ pmc) and C from the carbonate minerals (assuming $\delta^{13}C \cong 0\%o$ PDB and $^{14}C \cong 0$ pmc) in a system closed to soil CO_2 or in a system open to CO_2 with an equilibrium isotope fractionation constant between CO_2 and HCO_3^- of $\varepsilon = -8\%o$. Most of these waters have measurable ^3H contents: three samples are without ^3H but they are very close to the mixing line. Moreover, some of them are from saline zones and show the effect of cation exchange and of SO_4^{2-} reduction, so the lower ^{14}C activity could be due to CO_2 incorporation from carbonate minerals dissolution or to organic matter in the formations ($\delta^{13}C \cong -25\%o$ PDB but *c.* 8000 a old). Therefore, these samples may only be a few centuries old. Only one sample seems somewhat older (up to *c.* 3000 a BP), in agreement with being from an almost stagnant area in the central coastal zone of the aquifer.

Conclusions

Hydrochemical studies carried out since 1965 have provided a good knowledge of the groundwater flow system and its behaviour under human
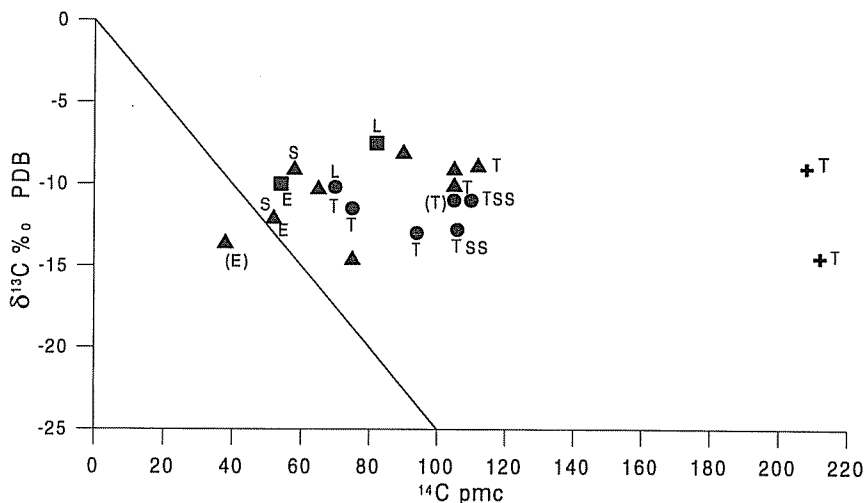
Fig. 7. ^{14}C (pmc) v. $\delta^{13}C$ (‰ PDB) in groundwater from the deltaic confined aquifer and from the lower valley water-table aquifer. T, ^3H is present; E, ^3H is absent; S, saline water; SS, very saline water; L, sample near the delta boundaries. Most of the samples show the presence of thermonuclear water and only one seems old (modified from Custodio *et al.* 1992*a*).

influence. Moreover, environmental isotope data have provided very useful tools to check out conclusions and calculations, as well as to solve some particular aspects.

River recharge can be identified through the high altitude isotopic signature of its headwaters, even if mixed with intruding sea water. Local contribution from nearby gullies and local rainfall can be separated from river recharge.

Groundwater in the confined deep aquifer is only a few centuries old due to the permanent discharge of this aquifer to the sea through its submarine outcrop since it was formed, and also to an increased renovation rate due to the intensive groundwater development since early in the 1960s. Isotopically depleted palaeowater is not present in the delta aquifers but some pre-1925 water is still there and is currently being depleted.

The study of vertical chemical and isotopic composition of pore water in undisturbed cores from the aquitard allowed values of vertical permeability to be obtained, they were then checked by numerical modelling. The chemical reactions responsible for the aquitard pore water vertical distribution were also validated by a flow and reactive numerical transport model. The results confirm a mixing of Holocene connate marine water and freshwater flowing upwards over a period of a few thousand of years as the origin for the pore water. The resulting chromatographic ionic distribution in some 40 m of aquitard thickness can be applied to understand the origin of the chemical variability observed in other coastal aquifers where the hydraulic evolution is not clear. It can also be used to forecast future changes.

The Doñana aquifer system, southwestern Iberian Peninsula

The Doñana natural region and aquifer is placed on the southwestern Atlantic coast of Spain, partly occupying the ancient estuary of the Guadalquivir River but also extending far to the north and west of it. A combination of geographical and biological special factors determine its high ecological value as habitat of a wild fauna and vegetation diversity. Water plays the main role in this richness, both as surficial water and groundwater. Most of the area is under the two highest protection figures for natural spaces that exist under Spanish law.

The Doñana National and Natural Parks together cover > 1000 km², but the natural region known as Doñana is *c.* 2500 km², shared between the provinces of Huelva, Sevilla and Cádiz. Most of the area is uninhabited except for people in charge of the study and management, the occasional developers of some natural resources and the

visitors. Some important towns surround the area, and the main economical activities are agriculture and tourism, both competing for groundwater, as does the preservation of the protected area.

Geology and hydrogeology

The aquifer system consists of unconsolidated Plio–Quaternary materials overlapping impervious Miocene marine marls. At the end of the Miocene, the precursor of the Guadalquivir River Valley was an elongated southwest–northeast marine basin from the Mediterranean Sea to the Atlantic Ocean, filling up with sediments coming from the Iberian Plate, to the north border, and from the African Plate, to the south. In the western sector of this trench, roughly between the present emplacement of the towns of Sevilla, Cádiz and Huelva, fluviomarine and alluvial sands settled during the Pliocene. During the Pleistocene and Holocene, the eastern part of this area subsided more than the western one, probably driven by tectonics, giving rise to the build-up of thick gravely Pleistocene layers and forming the wide Early Holocene Guadalquivir Estuary. The Flandrian (post-Würm) transgression almost replenished the estuary with clayey, silty and sandy interlayered sediments, but it was still a shallow, semi-closed bay with an extensive littoral sand barrier, in Roman times called Lake Ligur or Ligustinus. Nowadays, freshwater and brackish water marshes exist overimposed on the estuarine deposits (Vanney 1970; IGME 1982; Salvany & Custodio 1995).

The aquifer system has a surface area of 3400 km², a variable thickness from a few metres inland to more than 150 m along the coastline, and is roughly triangular in shape. The aquifer outcrops to the west and north, but to the southeast it deepens and become confined under *c.* 50 m thick Holocene estuarine clayey layers, with interlayered sands. The confined area is *c.* 1800 km² (Fig. 8).

The Pliocene fluviomarine sands overlapping the impervious Miocene marls have a moderate permeability. The Quaternary consists of permeable fluvial gravel layers and less permeable fluvial and eolian sands. Figure 8 shows a cross-section from the northern outcrop to the centre of the marshland through the area studied in the PALAEAUX project. There, the thicker gravel layers are Pleistocene and rest under the Holocene clays in the confined part of the aquifer. The thickness of the gravel layers decreases landwards, as they become wedge-shaped layers (Pleistocene and Holocene) among thick deltaic sandy layers of the unconfined area. The Holocene gravels also extend to the south, interlayered among the contemporaneous clays.
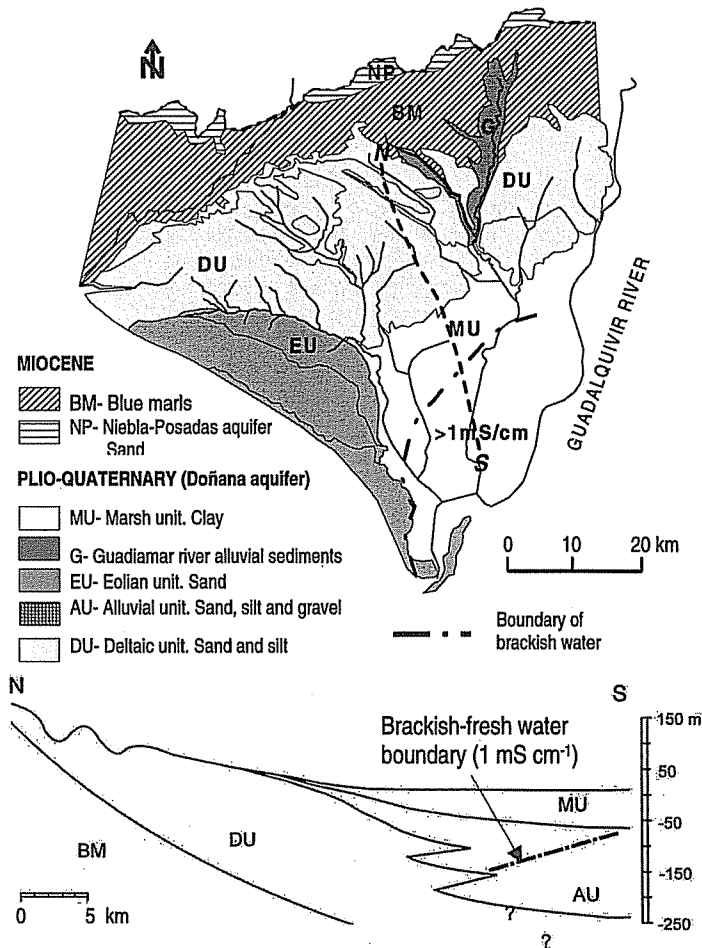
Fig. 8. Geology of the Doñana aquifer system and a cross-section along the studied area.

The aquifer system is recharged by rainfall in its cropping-out area, to the west and north of the marshes. Under undisturbed conditions, groundwater in the studied area flowed southwards towards the confined part of the aquifer. Groundwater discharge used to occur near the boundary between the unconfined and the confined areas, and as upward flows through the Holocene clayey sediments in the confined area. The southeastern sector of the confined aquifer is filled with saline groundwater that has not been flushed out due to the low hydraulic head existing since the Late Holocene sea-level stabilization (c. 6 ka BP; after Zazo et al. 1996). The natural flow pattern has been modified during the past three decades because of increasing pumping for irrigation in the area just to the north of the marshes, as well as around El Rocío (Trick 1998). Nowadays, most of the recharged

water is pumped out from the unconfined area (IGME 1982; Llamas 1991; Custodio & Palancar 1995), and some local flow reversals occur between the confined aquifer and the Holocene clay.

Head evolution in point boreholes screened at different depths show that, under current circumstances, vertical downwards water-head gradients exist both in the unconfined area and in some parts of the confined aquifer. Also, electrical conductivity (EC) and temperature (T) downhole logs in boreholes placed in both areas show the existence of vertical downwards groundwater flow. This is the result of a decreasing water head downwards due to groundwater abstraction.

Mean annual air temperature is c. 18°C: the vertical thermal gradient both in the unconfined and the confined areas is between 0.015 and 0.025°C m^{-1} [a preliminary study can be found in

Custodio *et al.* (1996]. EC varies between 0.3 mS cm^{-1} in the unconfined (recharge) area to > 40 mS cm^{-1} in the saline confined aquifer.

Hydrogeochemistry

Rainwater in the recharge area is of the NaCl type due to the airborne marine influence. Some calcite is the only reactive mineral present in the aquifer northern outcrop and groundwater here approaches the Na–Ca–Cl–HCO$_3$ type. In the western outcrop, almost pure silica sands prevent mineral additions from the aquifer material and concentration takes place only by evapotranspiration (Iglesias 1999). As groundwater flows to the south under the marshes it becomes increasingly brackish because of mixing with the saline water trapped in the southeastern sector. A broad mixing zone develops from the northwest to the southeast. Maximum salinity in the aquifer is generally a bit lower than that of sea water but some brines have recently been found near the Guadalquivir River mouth. Also, pore-water salinity in the Holocene clays increases upwards in the top 30 m, reaching values

twice that of sea water in the top 5 m. This is interpreted as being the result of repeated evaporation and dissolution processes of tidal seawater in the uppermost centimetres of the clays, and also in shallow-water bodies in the marshes (Baonza *et al.* 1984; Rodriguez-Arévalo 1988; Manzano *et al.* 1991; Custodio 1993*a*).

Looking to the chemistry of the major ions, Na/Ca and Na/Mg exchange seem to be the main chemical reactions that modify the mixing of fresh recent water and old saline water encroached to the southeast of the aquifer, as groundwater flows from the recharge to the confined area (north to south; Fig. 9). A chromatographic spatial distribution has not been found, although the few available sampling points southwards into the marshes (multiscreend boreholes and pumping wells) are not adequate to identify individual flow paths. A secondary modifying reaction seems to be sulphate reduction and gypsum precipitation processes: some of the samples both in the confined and in the unconfined areas are depleted in SO$_4^{2-}$ relative to the conservative mixing with sea water. However, in the recharge area some, but not all, of the samples display incorporation of SO$_4^{2-}$ and NO$_3^-$
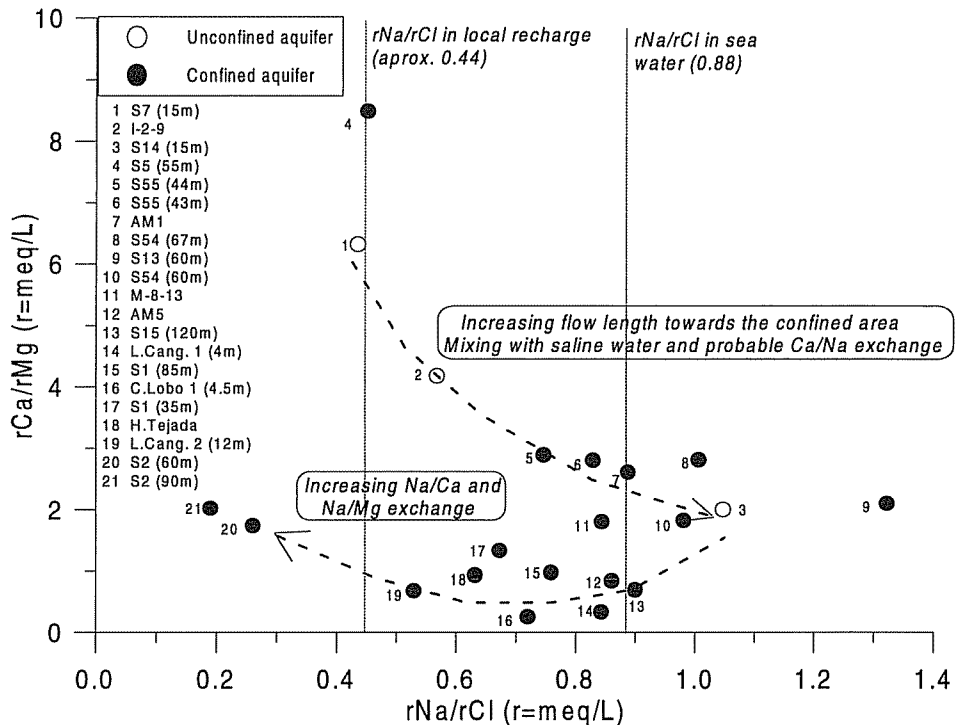

Fig. 9. Main hydrochemical reactions taking place in the mixing zone between freshwater from the unconfined aquifer and saline water in the confined aquifer.

from agricultural practices. No other major chemical reaction seems to be quantitatively significant.

Environmental isotopes

Residence times, based on ^3H calculations, have been estimated as being between a few years and > 40 a (Baonza et al. 1984; Poncela et al. 1992; Iglesias 1999). ^{14}C activity values measured in the 1980s were in the range of 100 to 7 pmc.

Groundwater becomes older southwards under the marshes, up to 14 ka after the Fontes & Garnier (1979) model. Baonza et al. (1984) found that some wells in the recharge area showed mean $\delta^{13}C$ values of total dissolved inorganic carbon (DIC) of c. −16‰, which was explained as being the result of isotopic equilibrium of carbonate species and CO_2 in an open system, with soil CO_2 coming from the decay of Calvin-type plants ($\delta^{13}C$ c. −25‰ PDB), and afterwards changing into a closed system for the dissolution of soil carbonates with average $\delta^{13}C = -4.7‰$ PDB (measured in sediments by the aforementioned authors). In the confined area, measured $\delta^{13}C$ values seemed to become heavier with increasing salinity. Also, some of the freshwaters under the clays showed very heavy $\delta^{13}C$ values of DIC (−4 to 2‰). This may be due to the input of heavy C from old organic matter (ubiquitous in the clay sediments) that is enriched in $\delta^{13}C$ due to CH_4 formation and separation. The actual presence of CH_4 has not been reported.

In the framework of the PALAEAUX project, some samples for detailed environmental isotope studies have been taken, mainly to determine the age structure of the deep waters and to detect possible admixtures of recent waters. The isotopes measured were: ^3H, ^2H, ^{18}O, ^{14}C, ^{13}C, ^{39}Ar and ^{85}Kr, which have been combined with major ion chemistry in the following discussion. Evidence of CH_4 has not been found in four groundwater samples taken for noble gases analyses. The wells reported by Baonza et al. (1984) as giving heavy C have not been resampled and they are further into the marshland.

Age structure of the waters. Results of isotope determinations are given in Table 1: Table 2 summarizes the composition of the gases collected for ^{39}Ar activity measurements. The amount of gas is increased by c. 30% compared to air-saturated water in samples from boreholes S54 and M-8-13; this is due to the considerable CO_2 content in the extracted gases. Table 3 contains the noble gas concentrations determined mainly to calculate recharge temperatures (RT).

An initial interpretation of the data states that recent-water components, in all wells, are smaller than c. 10%, even for boreholes M-8-13, I-2-9 and S54, which show the highest ^{39}Ar and ^{14}C values. Well I-2-9 is in the water-table aquifer area, while the other two are nearby but tap several layers of the confined aquifer. This limit of 10% for a recent admixture can be estimated from the ^3H content, if a maximum of 10 TU is assumed for present-day precipitation. An even lower limit of c. 1% is estimated for boreholes S54, S13 and S2 from the low ^{85}Kr activity (Table 1). These low values also demonstrate that the sampling intervals of 50–70 m below the surface are deep enough to prevent gas exchange between this water and the atmosphere, thus preventing the increase of ^{39}Ar activity from external sources.

A close look at ^3H, ^{85}Kr, O_2 and NO_3 data allows more detailed conclusions to be made:

(1) the water of borehole M-8-13 may contain c. 5% of recent water, as estimated from its ^{85}Kr activity of 3 dpm ml^{-1} and the amount of O_2 (1.75%) found in the extracted gases;

(2) data from borehole S13 are more complex: its ^{85}Kr content is really low, excluding c. > 1% of recent water. This, however, seems to be in contradiction to the measured ^3H, NO_3 and O_2 contents. A possible explanation assumes the admixture of a water component with an age of several decades. The $^3H/^{85}Kr$ ratio in the atmosphere was then much higher (Loosli et al. 2001). There is the suspicion that the formation surrounding the borehole screen still contains drilling water that was probably taken from one of the nearby agricultural wells;

(3) the NO_3 content of borehole S54 may also indicate some influence of fertilizers applied up to 30 a ago, when agriculture became intensive in the area.

From the above it can be concluded that most of the boreholes referred in Table 1 contain water that is older than c. 40 a; this is important because all wells, except S2, are close to the assumed recharge area.

The combination of ^{39}Ar and ^{14}C data allows a more precise estimation of the age of these deep waters:

(1) the low ^{39}Ar value in water from borehole S2 shows that the underground production of ^{39}Ar is c. < 10%. Therefore, the measured ^{39}Ar activities in boreholes M-8-13, S54 and S13 may be converted into ages: for borehole M-8-13 c. 170 a can be calculated, taking into account the aforementioned addition of 5% recent water (assuming the same age along the screen);

(2) assuming piston flow, a value of c. 400 a can be estimated for boreholes S54 and S13;

Table 1. *Isotope data and modelled ^{14}C ages in the Doñana aquifer*

Well	Sampling date	^{3}H (TU)	^{85}Kr (dpm ml^{-1})	^{39}Ar (dpm ml^{-1})	^{14}C (pmc)	$\delta^{13}C$ (‰)	^{14}C ages (a BP)			$\delta^{18}O$ (‰ SMOW)	$\delta^{2}H$ (‰ SMOW)
							Pearson*	Pearson†	Tamers		
I-2-9	04.06.97	0.39 ± 0.26			46.9	−14.3	1624	51	1328	−5.0	−30
M–8–13	04.06.97	0.17 ± 0.26	3 ± 0.3	70 ± 6	–	−12.0				−4.7	−26
S54	06.06.97	0.23 ± 0.25	0.34 ± 0.05	34 ± 4‡	51.7	−11.6	−942	−3515	73	−4.6	−26
AM5	06.06.97	0.3 ± 0.24			27.5	−13.5	5579	3763	5385	−4.6	−26
S13	05.06.97	1.15 ± 0.26	0.28 ± 0.04	28 ± 4	20.9	−13.0	7497	5509	7403	−5.0	−32
S2	06.06.97	0.48 ± 0.26	0.7 ± 0.11	< 10	7.34	−11.0	14 853	11 966	16 454	−4.3	−25
AM1	27.11.97	0.65 ± 0.69			33.6	−14.0	4224	2564	3955	−4.7	−29

* Ages based on Pearson model assuming $\delta^{13}C$ of $CaCO_3$ = 0‰.
† Ages based on Pearson model assuming $\delta^{13}C$ of $CaCO_3$ = 4.7‰ (after Baonza *et al.* 1984).
‡ Results of repeated measurements: 19 ± 4% and 46 ± 6% (preliminary).

Table 2. *Amount and composition of the extracted gases, and NO_3 content in water from the Doñana aquifer*

Sampling point	Extracted gas volume (ml l^{-1})	Sampling depth (m)	O_2 volume (%)	N_2 volume (%)	Ar volume (%)	CO_2 volume (%)	CH_4 volume (%)	N_2/Ar	NO_3 (mg l^{-1})
S54	18	68	−0.01	66.1	1.29	27.5	−0.01	51	3.0
S13	13	74	1.0	90	1.73	1.75	−0.01	52	1.9
S2	12	72	0.03	92.7	2.0	4.85	< 0.01	46.4	0.0
M-8-13	17	55	1.75	65.0	1.5	30.45	0.05	43.3	3.0

Table 3. *Noble gas contents and recharge temperatures (RT) in Doñana*

Sample	He × 10^8 (cm^3 STP g^{-1})	$^{3}He/^{4}He$ (× 10^7)	Ne × 10^7 (cm^3 STP g^{-1})	Ne excess (%)	Ar × 10^4 (cm^3 STP g^{-1})	Kr × 10^8 (cm^3 STP g^{-1})	Xe × 10^8 (cm^3 STP g^{-1})	RT (°C)
S13	8.13	10.31	2.38	29	3.73	7.95	1.06	19.7 ± 3.4
M-8-13	10.71	8.10	2.43	31	3.72	8.04	1.05	19.8 ± 1.8
S54	8.96	10.27	2.69	45	4.01	8.73	1.18	15.1 ± 1.2
S2	27.75	3.34	2.29	24	3.65	7.92	1.07	17.8 ± 1.7
Errors (%)	± 0.5%	± 0.5%	± 1%		± 1%	± 1%	± 1.8%	–

(3) the water of borehole S2 is older than the aforementioned three waters, based on its low ^{39}Ar activity and its ^{4}He content (Table 3). The ^{39}Ar activity shows a lower age limit of *c.* 900 a for borehole S2.

This age structure derived from ^{39}Ar activities may now be compared with the interpretation of ^{14}C and δ^{13}C measurements. Some of the samples measured for the PALAEAUX study have been analysed previously (in a 1984 study). The new ^{14}C and δ^{13}C determinations in or close to the recharge area generally confirm previous results, but heavy δ^{13}C values found by Baonza *et al.* (1984) have not been found during the PALAEAUX study, in which samples where collected somewhat closer to the infiltration area.

As in the 1984 study, the highest ^{14}C values (*c.* 50 pmc) show up in the northeast, decreasing along the recharge boundary to *c.* 20 pmc to the west. The lowest ^{14}C value found here, *c.* 7 pmc, is from the new drilling S2, which is screened in the deep layers (down to 200 m depth) of the multilayered aquifer in the confined area.

There is no relationship between δ^{13}C or ^{14}C and total DIC or the salinity content. Samples in the confined area with low ^{14}C contents have DIC $\cong$ 2 mmol l^{-1}, lower than in the unconfined area (DIC $\cong$ 6 mmol l^{-1}). So, neither calcite dissolution from the marine clays nor incorporation of C from the organic matter in the sediments seems

to be a quantitatively significant processes, although they probably contribute to some extent. The δ^{13}C–^{14}C relationship is in agreement with this: δ^{13}C values characteristic of the recharge area are also found in the confined aquifer as groundwater is being depleted in ^{14}C, mainly because of radioactive decay (Fig. 10). Vertical mixing of groundwater of different ages is probably the major modifying process, especially in the unconfined area where most of the sampling wells are multiscreened.

All of the measured values seem to fit a system closed to CO_2. In the confined area this is in agreement with the existence of thick clay layers on top and between the sand- and gravel-permeable layers. In the unconfined area it can be explained because of the aquifer configuration of alternated layers of different permeabilities (mainly sand, but also gravels and some silts).

Age information from ^{14}C data (in addition to the conclusions from ^{39}Ar) is given as model ages in Table 1:

(1) a strong argument in favour of Pearson's model ages (Ingerson & Pearson 1964) is provided by the results from borehole M-8-13: its ^{39}Ar age is *c.* 170 a (see above); a nearby and comparable well investigated in 1984 showed a ^{14}C activity of *c.* 55 pmc with a δ^{13}C value very similar to what has been measured now in well M–8–13;

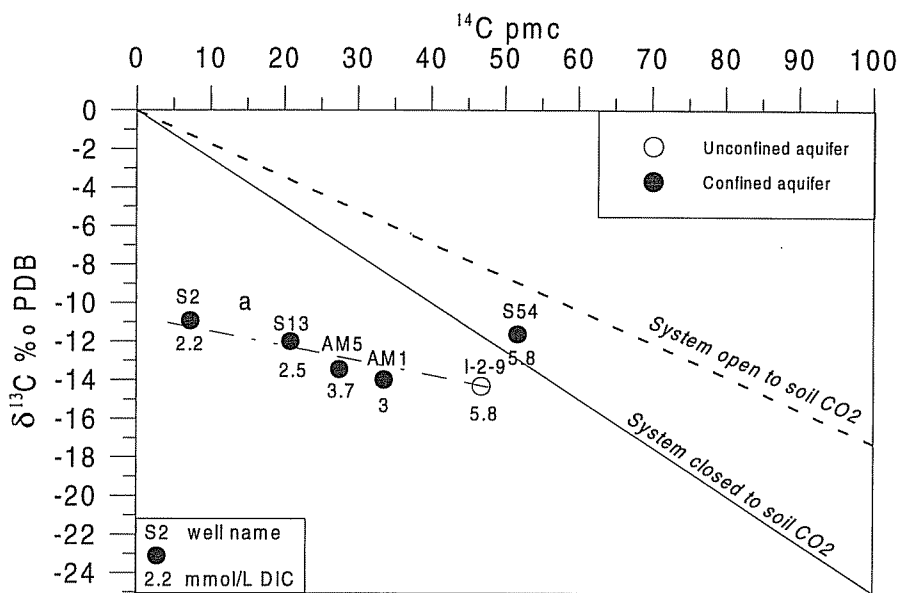**Fig. 10.** ^{14}C v. δ^{13}C in samples from Doñana analysed in the PALAEAUX project. The trend line indicates groundwater ageing in a downward flow. Marine water contribution to all the samples is < 1%.

(2) therefore, it can be concluded that the corrected ^{14}C ages of boreholes M-8-13, I-2-9 and S54, all placed close to the recharge area in the northeast, should be younger than a few hundred years, as given in Table 1;

(3) it also can be concluded that a model age of c. 12–15 ka seems appropriate for borehole S2, mainly because no change in $\delta^{13}C$ compared to young waters has been observed;

(4) an alternative to the average ^{14}C model age of borehole S13 is concluded from the ^{39}Ar–^{14}C comparison: it cannot be excluded that this water gets its ^3H, ^{85}Kr, ^{39}Ar and ^{14}C activity from an admixture which is several decades old. Thus, the main component could be water much older than c. 1 ka.

Stable isotopes. From previous work (Baonza et al. 1984; Manzano et al. 1991; Iglesias 1999), it is known that groundwater in the recharge area has the $\delta^{18}O$ and δ^2H signature of averaged local rain without significant fractionation by evaporation ($\delta^{18}O = -4.7$ to $-5.5‰$ SMOW, $\delta^2H = -28$ to $-33‰$ SMOW). New data obtained during the PALAEAUX project increased the information from the northern recharge area, showing that recharge water in this area is $\delta^{18}O \cong 0.5‰$ and $\delta^2H \cong 4‰$ heavier than in the western recharge area. This could be explained by enhanced fractionation previous to recharge in what was an area prone to ponding before the recent water-table drawdown.

Salinity increases along a north–south flow path from the water table to the confined aquifer, but does not fit a model of simple mixing with marine water in the confined area (Fig. 11). The saline end member seems to be heavier than local sea water, probably due to evaporation in former sea water fed lagoons. Mixed waters define a trend that could correspond to mixing with these saline pore waters in the Holocene clays; however, this hypothesis has yet to be checked.

No palaeoclimatic signature has been found in the freshwater component of the confined aquifer groundwater after correction of $\delta^{18}O$ and δ^2H values for the marine-water contribution. However, a pollen record described in the coastal area of Doñana which covers the last 18 ka, suggests no major climatic changes during this period, and that during the LGM the weather in the southwest of the Iberian Peninsula was humid and warm – not very different to the present climate (Zazo et al. 1996).

Noble gas recharge temperatures (RT). In principle, excess air can be determined from any of the noble gas concentrations; however, Ne is the most sensitive and therefore Ne excess values are given in Table 3. Excess air of c. 20–45% agrees with the N_2/Ar ratios given in Table 3. The excess air correction has been used to calculate the recharge temperatures (RT) from the other noble gas concentrations. Solubilities at 18°C and at an elevation of 50 m above sea level are the basis for this calculation; the results for boreholes S54 and
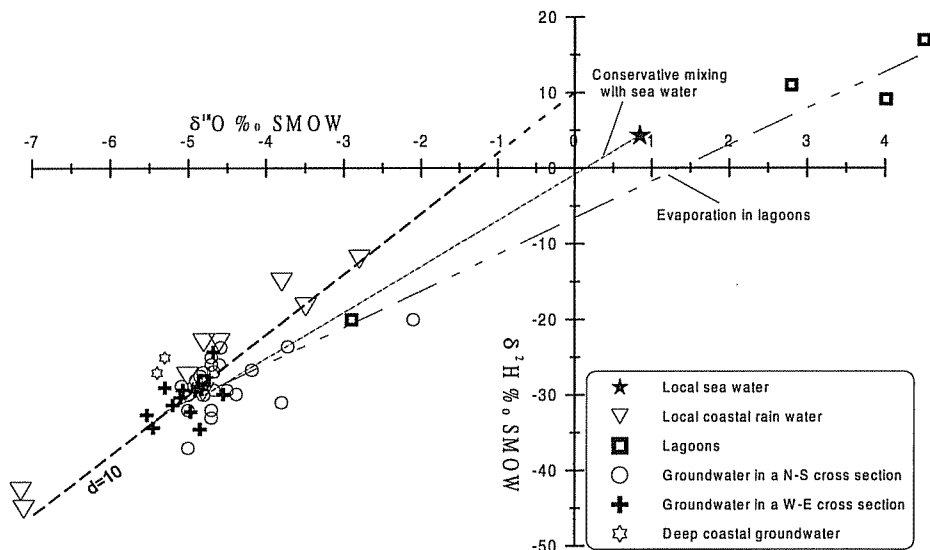
Fig. 11. Characteristic isotopic signature of different waters from the Doñana area. Increasing salinity along the north–south flow path could be explained by mixing with saline waters in the aquitard that had previously been evaporated in formerly sea-water-fed lagoons.

S2 show the smallest errors. All RT are within present-day mean annual air temperature.

Radiogenic ^{4}He is present in all samples (Table 3). Borehole S2 contains the highest radiogenic ^{4}He content and its ^{3}He/^{4}He ratio is closer to the end-member value for this ratio than the other three samples. If the ^{3}He/^{4}He ratio is plotted v. 1/^{4}He then an extrapolation of this end-member value is possible, showing that all measured ratios correspond to a mixing between air-saturated water (^{3}He/^{4}He = 1.35 × 10^{-6}) and an end-member with ^{3}He/^{4}He = 7 × 10^{-8}. This points to ^{3}He production by a Li-rich rock, or possibly to an admixture of He from deeper crustal layers; this also shows that tritiogenic ^{3}He content is very low and therefore ^{3}He/^{3}H dating is not possible.

Discussion

The situation observed in the Doñana aquifer suggests that approximately half of the confined Pleistocene aquifer has been freshened by fresh groundwater flowing to the southeast from the unconfined area, and probably discharging during some 6 ka inside the marshland as upward flow through the Holocene clays. The upward head gradient was still visible a few decades ago as flowing wells. Nowadays, the piezometric level of the confined aquifer is 1–2 m under the land surface, due to the drawdown produced by agricultural pumping in the water-table aquifer close to the northwestern and northeastern limit of the marshes.

Fresh groundwater heads prevailing since sea-level stabilization 6000 a BP have not been high enough to flush out all the saline water in the Pleistocene gravels and salt water probably remains in the southeasternmost extreme of the aquifer. Drilling to establish the conditions here is under way. In the saline waters studied, palaeoclimatic signatures are not present.

So, in the Doñana aquifer old saline water still exists extensively due to the aquifer structure and prevailing low water heads, and only a more or less wide strip contains freshwater. This situation means that no large reserves of old fresh groundwater are available. The case can be applied to forecast the probable groundwater quality changes in areas with moderate average recharge and low altitude, under a hypothetical future sea-level rise.

The Inca-Sa Pobla aquifer, Mallorca island

S'Albufera area is the northeastern extreme of the Inca-Sa Pobla aquifer system, in the northeast corner of the Mallorca island (Eastern Mediterranean Sea). S'Albufera means 'the lagoon', which still exists as the remnant of the Flandrian marine transgression during the first half of the Holocene period.

Geology and hydrogeology

The aquifer materials consist of a > 300 m thick sequence of marine carbonates (mostly limestones) and calcarenites ranging from the Upper Miocene (Tortonian) to the present (Gelabert 1998). They settled in a southwest–northeast subsiding trench some 35 km long and 7–15 km wide (Fig. 12). To the north and northwest the trench is limited by overthrusted Triassic, Jurassic and Cretaceous dolomites and limestones with marls and gypsum, forming the Serra de Tramuntana range that is up to 1400 m high. To the south and southeast the trench is limited by Tortonian and Pliocene calcarenites and by Plio-Quaternary molasses, forming smooth hills up to 100 m high. To the northeast the aquifer is limited by the Mediterranean Sea.

In some areas, two overimposed aquifers appear, an upper table one and a deep confined one, but in most of the area only a water-table aquifer exists. The system is recharged mainly by local precipitation and probably, to a minor extent, by lateral groundwater flow from the Serra de Tramuntana and from the southern hills. There are no significant permanent rivers and surface flows exist only after intense rainfall episodes. Groundwater flows northeastwards to the sea and discharges through pumping wells for agricultural and urban uses all along the aquifer, and as springs and diffuse upward outflow in the landward boundary of the S'Albufera wetland clay infilling.

To the west and northwest of the S'Albufera wetland, high vertical temperature gradients develop. The dominant hypothesis before the PALAEAUX project studies (1996–1999) was that saline groundwaters were stagnant, and their existence was due to mixing with deeper salt water moving upwards as a result of groundwater abstraction. This hypothesis has now been modified. Very low vertical temperature gradients were found in the rest of the area (Custodio *et al.* 1992*b*; Barón *et al.* 1994).

Detailed downhole EC and T logs in point and multiscreened boreholes in the Pleistocene–Holocene sediments and in the underlying Miocene–Pliocene have been recently carried out as part of the PALAEAUX project. Vertical and spatial distribution of EC, T and thermal gradients show a spatial pattern of what seems to be a dominantly convective flow network of saline water in the coastal sector of the aquifer. This pattern appears under and in the surroundings of S'Albufera wetland, down to > 200 m depth. Freshwater and saline water both flow downwards along the central axis of the basin where thermal
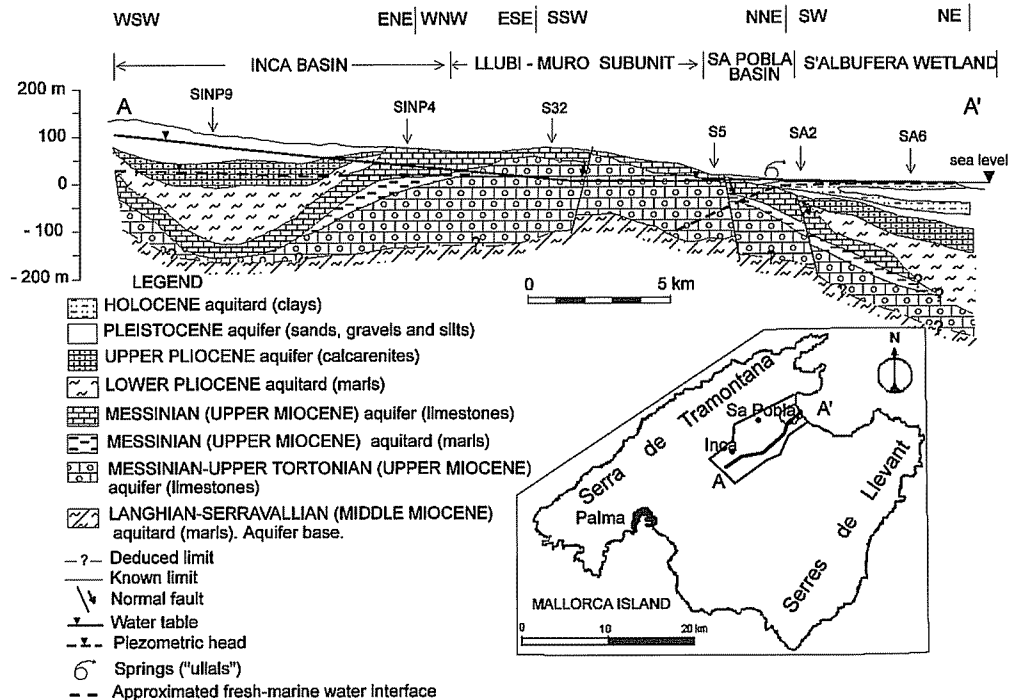
Fig. 12. Hydrogeological cross-section of the Inca-Sa Pobla aquifer system (Mallorca, Balearic Islands).

gradients are close to $0.00°C\ m^{-1}$. Close to the north-northwest and south-southeast boundaries of the basin, upward flow of saline groundwater exists. Here, thermal gradients are close to $0.03-0.035°C\ m^{-1}$ but values up to $0.05°C\ m^{-1}$ have been measured locally, as in borehole S20 (Fig. 13). Upward flows seem to concentrate through highly fractured (and probably karstified) areas, but this is yet to be confirmed. Due to the lack of adequate observation points, the relationship between these flows and the hydraulic gradients remain unknown. The small size of some geological bodies and the unclear existence of effective confining materials does not favour the existence of residual high potentiometric heads for the saline groundwater in deep formations inherited from higher sea stages in the past.

Hydrogeochemistry

Despite the multilayer configuration of the aquifer, all carbonate layers are hydraulically connected. The Upper Miocene deep limestone layer is the most transmissive unit (see Fig. 12) and although most of the pumping wells penetrate the full set of layers, they collect water mainly from this thick

Miocene layer. This enables comparisons between samples placed along a flow line along the deepest part of the aquifer.

Outside the coastal strip, groundwater in the Inca-Sa Pobla aquifer is of the Ca-carbonate type, the result of rock dissolution by recharged rainfall. Under and in the surroundings of S'Albufera wetland, groundwater is brackish and saline due to mixing with marine water. A thin freshwater layer exists around the northern and southern boundaries of the S'Albufera wetland, but to the west and northwest a wide stepwise transition zone develops that is characteristic of fissured and karstified rocks (Custodio & Bruggeman 1987). (Groundwater from the Serra de Tramuntana, to the north of the studied aquifer, is also of the calcium carbonate type.)

Groundwater salinity in the Inca-Sa Pobla system increases slightly downflow (to the northeast) in the first 25 km of the unit, but 10–12 km towards the coast mixing with saline water is already evident. In most of the aquifer system, groundwater flow in the uppermost tens of metres is mostly vertical downwards, allowing rain and irrigation excess water to penetrate. But through the deepest part of the unit, and from the southwest to northeast, horizontal
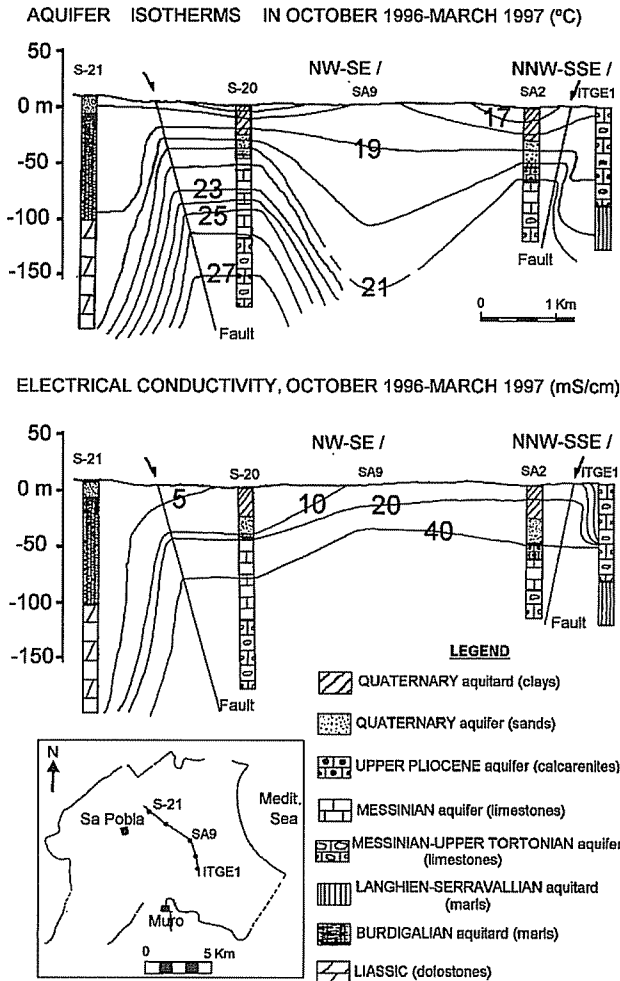
Fig. 13. Electrical conductivity (EC) and temperature (T) cross-section (October 1996–March 1997) of the coastal area of the Inca-Sa Pobla aquifer system (the S'Albufera area). Isolines follow EC logs in boreholes and they may be distorted to some extent by vertical water flows inside the boreholes. Consequently, isolines in the aquifer may be somewhat less varied.

flow seems to dominate up to the coastal area, where the aforementioned convective flows appear.

Although most of the freshwater is of the Ca-carbonate type, some spatial changes exist. Groundwater with the lowest salinity is found in the southwestern part of the system, where the recharge area begins. Only a few samples in the central part of the unit are of the sulphate calcium or sulphate magnesium type. Dolomite is rare in the aquifer, which is probably due to the influence of the Mg-rich Miocene marls that constitute the impervious bottom of the aquifer and which is risen in this central area (see Fig. 12). In a 10 km wide coastal fringe, groundwater is of the Na–Ca–Cl–

carbonate type, and closer to the sea is of the NaCl type.

As a result of convective flows, a detailed interpretation of the spatial water chemistry changes in the S'Albufera area has to be referred to the sampling depth and the hydraulic characteristics of each point. However, a look to the downflow evolution of some ionic ratios shows two different mixing trends between freshwater recharged along the unit and saline water encroached in the coast (Fig. 14):

(1) brackish and saline groundwater under and to the southeast of the S'Albufera wetland
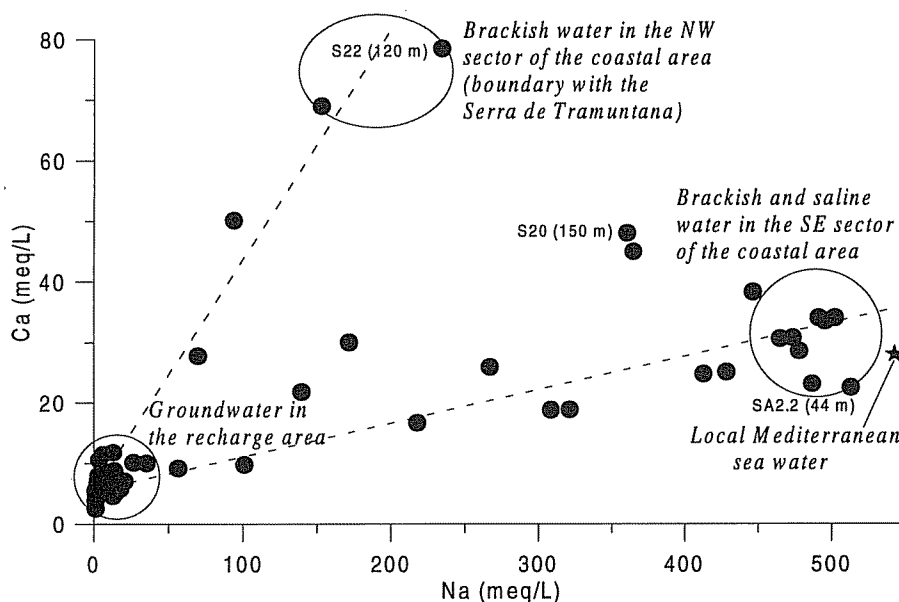
Fig. 14. Mixing trends between present-day recharge water and saline and brackish groundwater in the coastal area of the aquifer, as shown by Na–Ca relationships.

appears as the result of non-conservative mixing between current recharge water and Mediterranean sea water;

(2) brackish groundwater to the north and northwest of S'Albufera, along the boundary with the Serra de Tramuntana range, seems to correspond to a non-conservative mixing of present recharge water and a brackish groundwater with more than twice the Ca content and $rCa/rMg \cong 1$ $(r = meq \, l^{-1})$, four times that of the former area $(rCa/rMg \cong 0.25$, similar to that of sea water).

Several boreholes to the north 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.* 1992b). In a nearby area (S'Almadrava) a brackish spring water outflows several metres above sea level with what seems a simple mixing of freshwater and sea water. These flows could be maintained by deep lateral flows coming from water recharged in the nearby elevations of the Serra, which mix locally with saline water in the aquifer.

Along several boreholes, upward flows of saline water have been observed both along the northern and southern limits of the coastal sector of the aquifer, while in between they are vertical downwards. This scheme suggests a convective pattern that has yet to be studied in detail.

Environmental isotopes

Tritium contents in samples from 1997 decrease downflow from 6 to 8 TU (modern water) in the southwest, down to < 1 TU in the boundary of the S'Albufera wetland (Fig. 15). Even though data is scarce, a closer look gives useful information. Samples 1–4 tap the deep confined aquifer of the Inca Basin, but their high ^3H content (similar to current mean values in local rain water) indicates fast penetration of recharge water from the water table aquifer, which has a higher head.

Samples 5–12 are from wells and boreholes in the Llubí–Muro corridor, where a single aquifer exists. Samples 5, 6, 7 and 12 show that ^3H contents progressively decrease, which may be interpreted as a downflow increase of residence time. An EC and T downhole log performed in well 7 showed an anomalously high thermal gradient and the existence of deep upwards flow. The mixing pattern in the well determines, to some extent, the ^3H content, from very recent water (sample 9) to long residence-time water (sample 12).

Samples from boreholes and wells in the coastal area (samples 13–16 and white dots) have ^3H contents that are related to their depth but not to their salinity. In general, marine water is found c. 7–8 m below ground level at the coastline, at 10–15 m c. 3 km landwards, and 20–40 m in the periphery of the S'Albufera wetland. Samples 15 and 16, which are ^3H free, correspond to deep
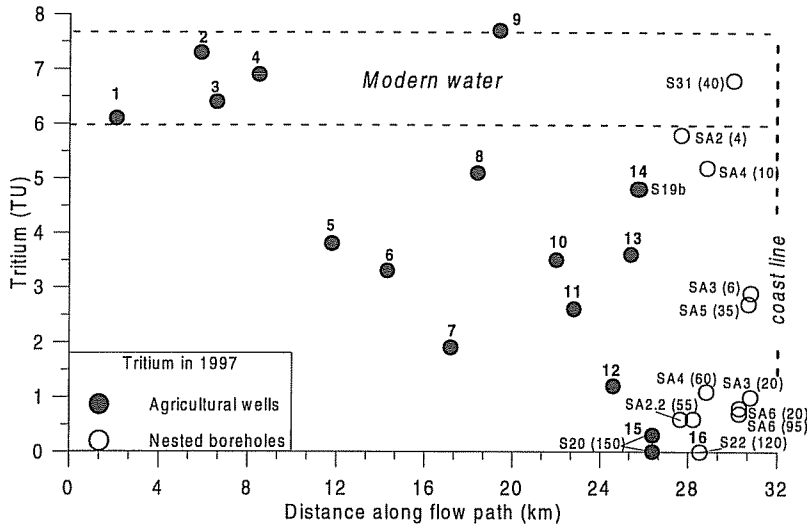
Fig. 15. Tritium content along a flow path through the deepest part of the Inca-Sa Pobla aquifer (samples 1–12) and at different depths in nested boreholes in the coastal area (figures in parentheses are sampling depths in metres).

saline waters under the Holocene S'Albufera sediments (see Fig. 12). The rest of the samples correspond to brackish and saline groundwater from different depths taken in nested boreholes (SA1–SA9 series in Fig. 15), showing the expected decrease in ^3H content with depth.

$\delta^{18}O$ and δ^2H in fresh groundwater fit the local meteoric line (excess $^2H = 13$–$15‰$), as do fresh components of mixtures. Looking at the relationship with salinity, two different freshwater components seem to be present (Fig. 16): (1) the signature is that of local rainwater ($\delta^{18}O \cong -5.5$ to $-6‰$; $\delta^2H \cong -32$ to $-36‰$); and (2) the signature is $c. 1‰$ lighter in $\delta^{18}O$ and $c. 8‰$ lighter in δ^2H than local rainwater. A recharge altitude high enough to explain this difference does not appear to be possible in the sector of the Serra de Tramuntana close to the wells. There is also the possibility of having freshwater recharge in past colder times, to the end of the last glacial period. The isotopic composition of the freshwater component given by:

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

where s, m and f are the isotopic compositions, and S, M and F the chloride contents of marine (salt) water, mixed water and freshwater, respectively. Assuming a Gaussian distribution of errors, the standard deviation, σ, can be calculated from:

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

where x is each one of the variables (s, m, S, M and

F). For the following values (in $g\,l^{-1}$): $S = 20$, $\sigma_S = 0.5$; $M = 10$, $\sigma_M = 0.3$; $F = 0.1$, $\sigma_F = 0.01$; $s = 0.0$, $\sigma_s = 0.3$; $m = -5.0$, $\sigma_m = 0.2$, giving $\sigma_f = 0.65$. If $M = 1$, $\sigma_M = 0.1$ and $m = -6.0$, $\sigma_m = 0.2$, with other values remaining the same, then $\sigma_f = 0.22$. This means that the difference of $c.$ $\delta^{18}O \cong 1.0‰$ could be significant.

Attempts to establish the age of this light freshwater component, and also that of the marine water, have been made through ^{14}C dating. The existence of saline groundwater under and in the surrounding area of the S'Albufera wetland, in the $> 200\,m$ thickness of the Holocene, Pliocene and Upper Miocene sediments (see Fig. 12), has been known since the 1980s (Custodio *et al.* 1992b). Due to the fact that groundwater use in the area takes place landwards of the wetland, studies to try to explain the origin of this saline water are very recent (Barón *et al.* 1994). ^{14}C activity of total dissolved inorganic carbon and ^3H contents in four groundwater samples from the coast decrease as the freshwater content increases (Fig. 17 and Table 4), which apparently points to an old freshwater component.

The $\delta^{13}C$ of samples SA2.2, S20 and S22 are lower than the simple mixing of freshwater sample S19b and sea water. The $\delta^{13}C$ of sea water is assumed to be close to $0‰$, since the fractionation factor between carbonate ($\delta^{13}C \cong 0‰$) and dissolved HCO_3^-, which is the dominant DIC species at sea water pH, is $c. 1‰$ (Fig. 17a). On the other hand, $\delta^{13}C$ values decrease as DIC increase in the three saline samples (Fig. 17b). This implies a
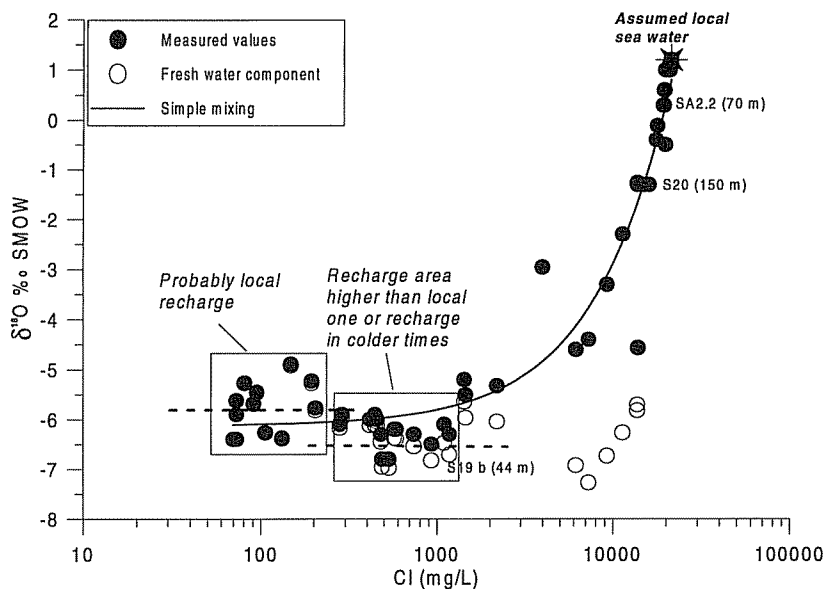
Fig. 16. $\delta^{18}O$ signature of groundwater and of the freshwater component after correction for the saline contribution. Looking at the recharge signature, two groups are apparent.

source for the light C different to that of mineral dissolution and C contribution from marine water, which would produce heavier isotope values. Sample SA2.2 is almost sea water (97%) but contains light C; however, its DIC coincides with that of sea water, suggesting that sea water in the ground exchanges ^{13}C with the organic matter in the formations, giving $\delta^{13}C$ values lighter than expected (Hornibrook *et al.* 2000). The process is not well understood at the moment but a decrease in pH due to reduction processes may shift the isotopic equilibrium with dominating HCO_3^- to another equilibrium, one in which H_2CO_3 is a significant fraction of DIC, having a fractionation factor of *c.* 8‰. Samples S20 and S22 seem to incorporate this light organic C in addition to exchange, since the DIC increases. The possibility of incorporating a third old water component with very light C seems less likely, since in a carbonate system $\delta^{13}C$ values of DIC lighter than −17‰ seem improbable.

A preliminary interpretation of ^{14}C ages following the model of mixing between soil-derived CO_2 ($\delta^{13}C \cong -25‰$ and $^{14}C = 100$ pmc), in a closed or open system with respect to recharge water, and a very old marine carbonate rock ($\delta^{13}C \cong 0‰$ and $^{14}C = 0$ pmc) gives Figure 18. Sample S19b appears to contain some thermonuclear ^{14}C and, in fact, contains ^{3}H. Sample SA2.2 (almost sea water) appears as modern to recent,

depending on the system, but this does not apply since infiltration of seawater was probably not through a CO_2-rich soil. Samples S20 and S22 seem old, with ages of *c.* 3000 and 12 000 a for closed system to soil CO_2, and of *c.* 8000 and 25 000 a for an open system. However, if CO_2 derived from organic matter in the sediments is taken into account, then this model fails. Corrections cannot be made since, at present, isotope and chemical characteristics of this organic matter is unknown. If this organic matter is old (^{14}C free) then the ages given above are clearly overestimates.

Discussion

In the Inca Basin-confined aquifer, most of the wells produce recently recharged water from the water-table aquifer. In most of the Sa Pobla Basin single aquifer, ^{3}H contents of pumped groundwater depend on the mixing pattern of each sampling point. Boreholes to the northwestern and southeastern boundaries of the aquifer show upwards flow of deep saline groundwater, with < 1 TU, while boreholes in the centre of the basin display downwards flow of modern, fresh groundwater and also of saline water. Nevertheless, ^{3}H contents of samples from the single aquifer from the Muro Corridor show some deep upwards flow of older groundwater.
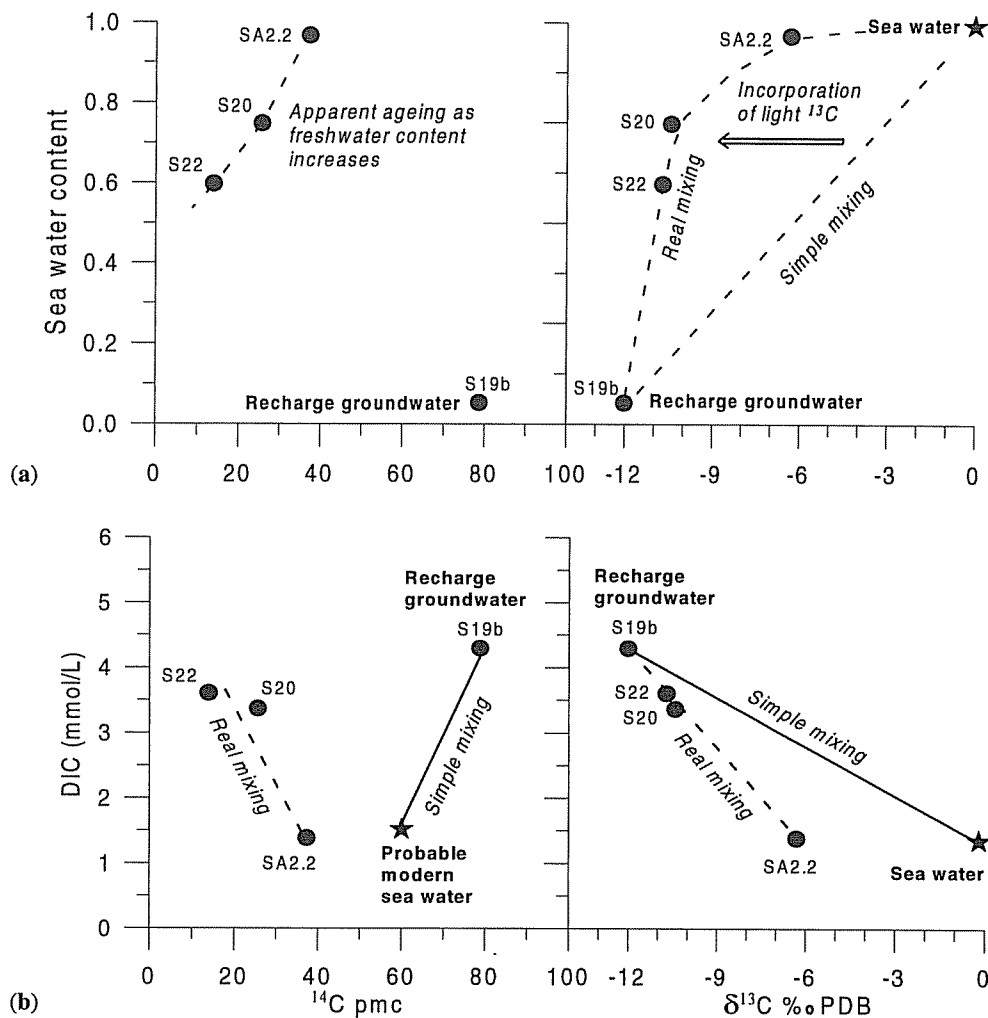
Fig. 17. (a) ^{14}C and $\delta^{13}C$ v. sea-water content in groundwater from the coastal area. Comparing with a conservative freshwater–salt water trend, samples SA2.2, S20 and S22 have $\delta^{13}C$ values lighter than expected. (b) ^{14}C and $\delta^{13}C$ v. total dissolved inorganic carbon (DIC) content in groundwater from the coastal area.

Table 4. *Calculated ages on the basis of ^{14}C and $\delta^{13}C$ data in the Inca–Sa Pobla aquifer*

Reference	Sampling date	^{14}C (pmc)	$\delta^{13}C$ (‰)	Sea water (%)	^{14}C ages (a BP)		^{3}H (TU)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
					Pearson*	Tamers†			
S19b (44 m)	11.11.97	78.8	−12.0	5	−4099	−2674	4.8 ± 0.5	−6.5	−38.5
SA2.2 (55 m)	10.11.97	37.4	−6.3	97	−3265	3336	0.6 ± 0.4	0.3	0.0
S20 (150 m)	07.11.97	25.7	−10.4	74	3990	7771	0.0 ±0.4	−7.1	−35.3
S22 (120 m)	07.11.97	14.0	−10.7	60	9240	13 307			

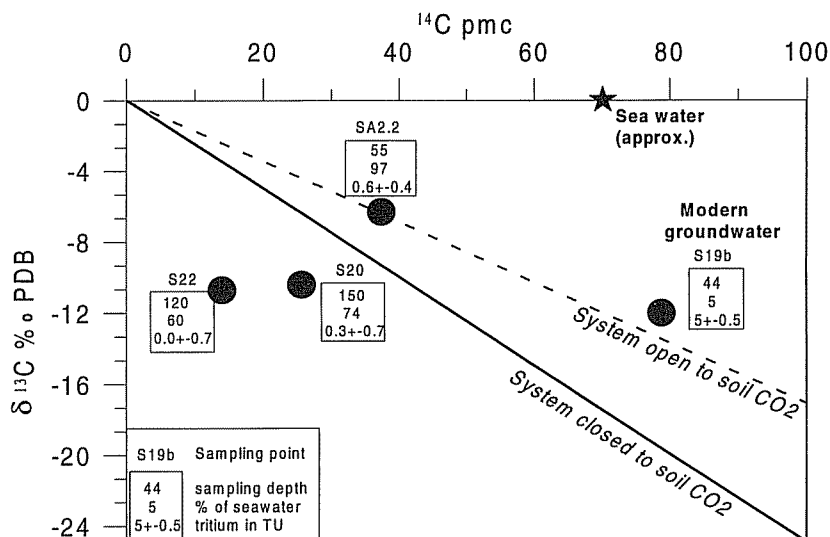* Ages based on Pearson model assuming $\delta^{13}C$ of $CaCO_3 = 0‰$.
† Ages based on Tamers model.

Fig. 18. ^{14}C v. $\delta^{13}C$ in groundwater from the coastal area of the Inca-Sa Pobla aquifer. $\delta^{13}C$ values are not corrected for a marine-water contribution. The theoretical evolution in a system closed to CO_2 is shown. Borehole SA2.2 is confined by 50 m of clay, thus a system closed to CO_2 can be assumed, indicating some thermonuclear ^{14}C contribution.

In most of the aquifer, fresh groundwater is of the Ca-carbonate type. In the coastal fringe (*c.* 7 km wide), groundwater is brackish and of the NaCl 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 constitute the lowermost transmissive layer.

The freshwater component of brackish groundwater in the coastal area seems to have a double origin: (1) in the southeastern sector it has the ^{18}O and ^2H signatures of local recharge ($\delta^{18}O \cong -6$ to $-6.5\%o$ and $\delta^2H \cong -35$ to $-40\%o$ SMOW); (2) in the northwestern sector it has the signature of a water recharged either at higher altitudes than the aquifer recharge area or local recharge under colder atmospheric temperatures than present-day ones, i.e. during the Pleistocene–Holocene change.

It is difficult to calculate the age of saline water, and of the freshwater and saline water components, due to what appears to be exchange and incorporation of C from organic matter in the sediments, which is of unknown age and characteristics. Although preliminary calculations may show ages of 3000–25 000 a, real ages may be much lower, although 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 upwards flow of freshwater along the freshwater–salt water interface in the surroundings of the S'Albufera wetland, taking with it some saline water. Nowadays, discharge also takes place through pumping, but these upward flows still sustain the springs and diffuse outflow occurring along the inner border of S'Albufera.

The lack of a hydraulic gradient for freshwater flow in the aquifer during the Holocene period prevented the freshening of the coastal sector. More than 200 m of Quaternary–Miocene sediments hold saline groundwater under the S'Albufera wetland and its discharge, mixed with the springs, is probably $< 0.5 \times 10^6$ m^3 a^{-1} in an area > 30 km^2; this means that most of this salt water is probably older than 5 ka. Hydraulic gradients favour the vertical mixing of heterochronous salt water and young freshwater, although the mechanism by which this takes place is not yet fully understood.

The Amurga Massif, Gran Canaria island

Geology and hydrogeology

Gran Canaria (1500 km^2) is one of the volcanic islands of the Archipelago of the Canaries (Fig. 19). To the southeast is the Amurga Massif, a wedge-shaped phonolite formation *c.* 5 Ma old, resting on rhyolitic ignimbrites and finally on Miocene basalts of the old edifice (*c.* 10 Ma) of the Gran Canaria island volcanic shield (ITGE 1992). The total surface area is *c.* 125 km^2; the highest point is
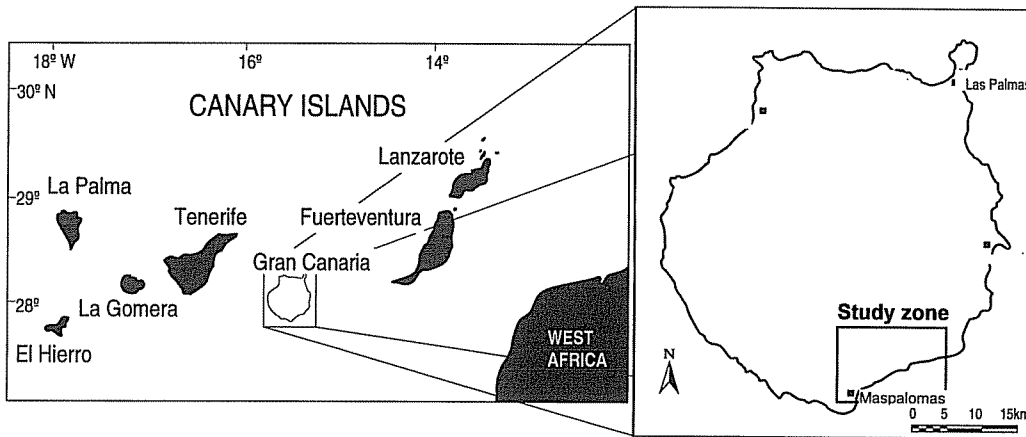
Fig. 19. Location of the Amurga Massif study area.

1191 m above sea level, at the apex of the wedge, and falls towards the coast with a mean slope of 0.086. The massif is dissected by deep gullies that produce a rough surface, with scarce interbasin flats and almost vertically walled canyons. The wedge is limited at the sides by two deeply incised main gullies (barrancos), Fataga to the west and Tirajana to the east. Only in the Tirajana Barranco does the old basement crop out. The coastal side presents cliffs and intermediate torrential alluvial fans.

The island of Gran Canaria is in the Saharan dry belt. Mean rainfall at sea level is < 200 mm a^{-1}, but increases up to 1000 mm a^{-1} on the highlands due to orographic effects of the dominating north-eastern trade winds and occasional southwestern Atlantic wet winds. Amurga is in the downwind dry part of the island with mean rainfall of c. 100 mm a^{-1} at the coast and < 250 mm a^{-1} at the small surface area at the top, but occasional intense and short downpours sometimes occur. High net sun radiation produces high potential evaporation, > 1500 mm a^{-1}. Only dispersed vegetation, of mostly euphorbiae, is present leaving a large part of the land surface open to direct sun radiation most of the time. A large part of the land is bare rock or rock debris, with some soil in between, part of which is wind-blown dust from the continent.

Most of the massif consists of phonolite lava flows running from close to the island centre to the coast, from metres to tens of metres thick, in a well-defined sequence containing well-developed interflow brecciae, and some interbedded ash-flow formations, which increase in frequency downwards.

Exploitation by means of deep boreholes (down to 250 m) started in the 1980s. Groundwater is brackish and thus unsuitable for human supply and agriculture. This prevented its use until the late 1980s, when an electrodialysis desalination plant started operation to convert this water (plus groundwater from the Tirajana Delta area and the Barranco of Fataga) from c. 4 g l^{-1} salinity into potable water for the large touristic complex of Maspalomas-El Inglés. Studies were carried out to establish the resources, origin of the water and the evolution of its salinity to ensure that the plant could operate as foreseen during its 25 a of economic life.

The regional water table is very deep, from tens to hundreds of metres below the interfluves, and is not intersected by the intramassif barrancos. There are no springs, except for a few, small perched ones, outflowing from some interflow brecciae or at the foot of large landslide masses along the two major barrancos, but groundwater fed vegetation strips can be seen. The Barranco de Fataga may collect up to 15 l s^{-1} of diffuse discharge and evapotranspirates a higher quantity. Along the coastal cliffs there were some water seeps at altitude above the beach and wet patches in the barranco mouths; they disappeared after land changes produced by current intensive urbanization and gardening.

Exploration and exploitation boreholes show a regional water table as illustrated in Figure 20. The whole area is not covered due to a lack of data; emplacement of drilling machinery on the rough land and penetration of the thick unsaturated zone is difficult. Pumping tests in the boreholes and exploitation data of the wells show transmissivity values in the range 50–800 m^2 day^{-1}, although there is a bias due to only considering the productive ones. Mean regional transmissivity may be an order of magnitude less.
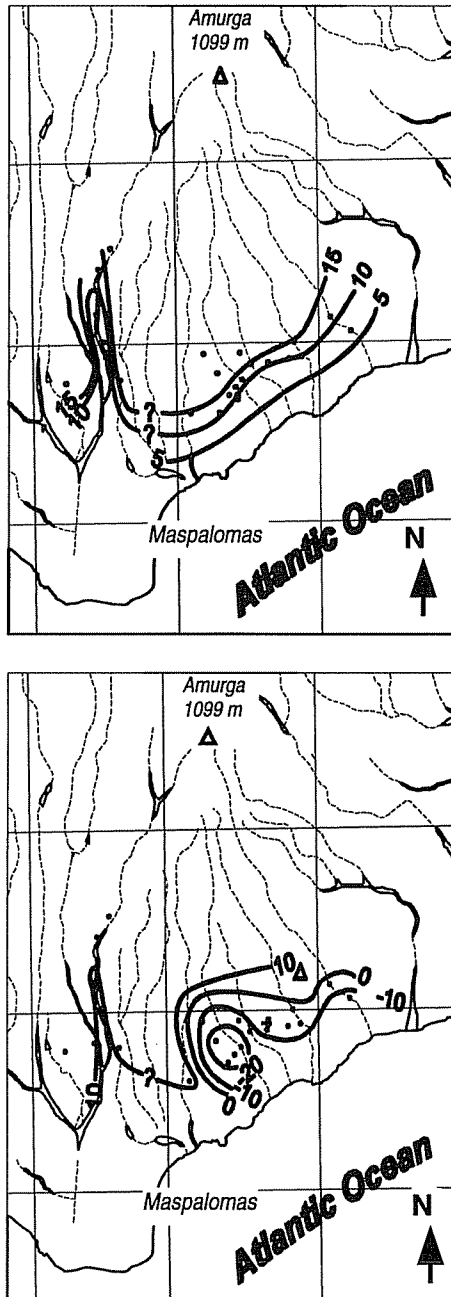
Fig. 20. Representation of the water table in the Amurga Massif, showing the situation both without (above) and with (below) the influences of exploitation.

The only source of recharge is rainfall infiltration. Most precipitation remains close to the land surface, where it evaporates. The discontinuous vegetal cover transpires a part and the remaining return to the atmosphere directly from bare land. Only a small fraction of precipitation escapes evaporation and produces recharge, which varies widely from year to year and is only significant in wet years. The long-term mean value is estimated as 2–4 mm a^{-1}.

Recharge moves downwards through the rock matrix. Even rainwater penetrating through fissures, directly or at the bottom of the barrancos, is probably suctioned through the fissure walls and incorporated into the matrix, and then moves downwards as diffuse flow. The unsaturated zone is very thick and there are frequent horizontal interlayers of brecciae, ash flows and ash falls. Then input to the saturated zone is smoothed and delayed with respect to recharge generation. Piston flow seems a reasonable model for recharge transfer description, although a crude one. In the saturated zone the combination of horizontal brecciae and scoriae with vertical fissures produces a three–dimensional (3D) water flow whose thickness is unknown but surely is up to some hundred metres thick.

Current groundwater abstraction from Amurga and the Barranco de Fataga Valley is *c.* 60 l s^{-1} (up to 80 l s^{-1}). This represents *c.* 10 mm a^{-1} for the whole Amurga Massif and up to 500 mm a^{-1} for the 2–3 km wide strip parallel to the coast, where most of the wells are placed; this is larger than the assumed recharge. Then, groundwater reserves are being depleted and there is a continuous water-table drawdown. Estimated drainable (effective) porosity is 0.03–0.07, which is in the range considered to be representative of other lava-dominated formations (Custodio 1978).

T and EC logs carried out in some of the, currently uncased, dismantled boreholes show homogeneous salinity along the penetrated saturated thickness but variable vertical thermal gradients (Fig. 21), from 0°C m^{-1} to a typical value of 0.03°C m^{-1}. No residual volcanic heat is seen, in agreement with the age of the rock and the lack of recent effusions. Some boreholes at the bottom of deep barrancos show anomalous high temperatures of the air in the borehole but normal thermal gradients; this is assumed to be the result of the topographic position in the canyon, well below the interfluve, and the intense sun action due to their north–south orientation. Some boreholes show no vertical temperature gradients over any part of their length, due to significant vertical flow of water inside the borehole, downwards or upwards, depending on the 3D flow pattern induced by groundwater abstraction.
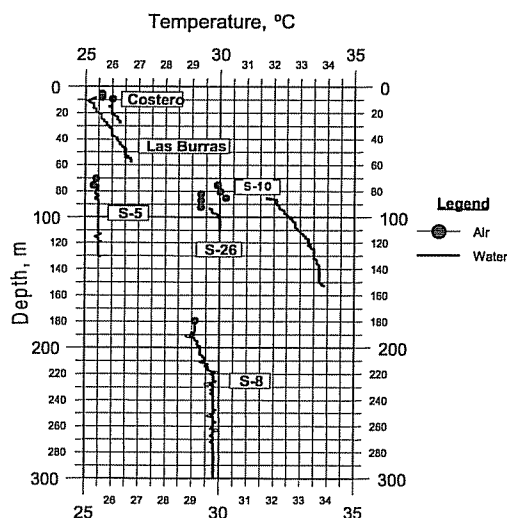
Fig. 21. Temperature logs measured in some boreholes in the Amurga Massif.

Hydrogeochemistry

Numerous water analyses from the pumping wells have been available since 1985. Most waters are of the NaCl type and cluster around some main poles. Most of the boreholes in the Amurga Massif yield quite similar brackish water (EC in the range of 4.5–6.3 mS cm^{-1}) that has not changed significantly over time, except for one case in which there is a clear evolution towards marine composition. This is the only well to show the possible effects of sea-water intrusion after the conspicuous sustained local water-table drawdown due to groundwater development.

Water from boreholes along the Barranco de Fataga are also brackish but with lower salinities than in the Amurga Massif (EC c. 1.7 mS cm^{-1}), and they are enriched in Na relative to Cl. This is interpreted as the effect of the more acidic nature of volcanic formations (rhyolites and thrachytes), different to that of the Amurga Massif but undergoing a similar process to become brackish.

Most groundwater is close to saturation with respect to calcite and amorphous silica, and slightly oversaturated with respect to dolomite. Equilibrium CO_2 pressure is 0.003–0.001 atm, i.e. an order of magnitude higher than in the atmosphere.

Salinity is assumed to be attributable to the effect of the arid environment (low precipitation that is evaporated almost completely) and relatively high airborne salinity due to the proximity to the coast and the relatively rough sea. A precipitation–recharge Cl balance in the areally variable input wedge-shaped land is in agreement with this

hypothesis (Custodio 1993b). The rCl/rBr ratio of 800–900 (r = meq l^{-1}) shows that Cl may be of marine origin (ratio of 655) with some fractionation, but not clearly from evaporites or residual evaporation brines, although further research is needed. This seems a common feature in the Canaries for brackish groundwater or groundwater related to recent volcanism, in spite of the lower ratio for fresh volcanic rocks. This may point to some partial evaporation of seawater near the coast (Custodio & Herrera 1990). The rSO$_4$/rCl ratio (c. 0.11) is typically marine. DIC is 0.5–2 (mean 1.2) meq l^{-1} for the small springs and seeps, and c. 3.3 meq l^{-1} for the wells.

Environmental isotopes

Water isotopes in Gran Canaria rainfall show a clear altitudinal effect and a similar pattern in the northern and southern halves. The meteoric line shows a slight ^{2}H excess ($d = \delta^2$H $-8\ \delta^{18}$O‰ SMOW), which is assumed to be due to the effect of the regional, relatively dry environment that enhances kinetic evaporation of sea water [see Gasparini (1989) and Gasparini $et\ al.$ (1990) for more details].

Groundwater clusters around a δ^2H v. δ^{18}O line of slope = 4, which indicates fractionation of rainfall before converting into recharge. This is in agreement with the aridity of the area and the lack of a continuous vegetation canopy. The intersection of this line with the local meteoric line corresponds to a weighted rainfall of δ^{18}O = -5.5‰ and δ^2H = -32‰ SMOW. However, considering the range of altitudes, a range of possible mean isotope compositions of rainfall can be expected for evaporation slopes of < 4, corresponding to intense fractionation of soil humidity when vapour transport in dry soil is important. In any case, this shows a recharge in agreement with the rainfall at mid-altitudes (high altitudes represent only a small surface area). No clear palaeoclimatic effect is observed, and if it does exist it is obscured by the wide range of the possible values.

All sampled groundwater from the boreholes have no measurable ^{3}H (< 1 TU and even < 0.2 TU), which means that there is no significant direct input of rainfall through fissures or through the boreholes from perched levels discharging into the unsealed inner space of the wells. One of the sample sets is close to the end of an extraordinary wet period and even direct recharge from the bottom of the barrancos seems diffused when moving downwards.

Radiocarbon analyses from two surveys separated by 10 years (Table 5) consistently show the percentage of modern C (pmc) contents to be generally low, and pumped water seems really old.

**Table 5.** *δ¹³C and ¹⁴C data on the Amurga and Fataga areas*

Well	Year	δ¹³C (‰ PDB)	¹⁴C (pmc)	DIC* (mmol l⁻¹)
Fataga 1	1986	−8.47	6.5 ± 0.9	5.6
Fataga 1	1997	−8.56	6.7 ± 0.2	5.0
Fataga 7	1986	−12.15	58.9 ± 0.9	2.0
Fataga 7	1997	−11.80	57.9 ± 0.4	2.0
Amurga 11	1986	−12.71	24.6 ± 1.0	2.2
Amurga 12	1986	−12.13	27.3 ± 0.7	2.3
Amurga 17	1997	−12.34	17.2 ± 0.4	3.0
Amurga 18	1997	−12.07	25.8 ± 0.5	2.4
Amurga 21	1986	−12.62	29.5 ± 0.7	3.7
Amurga 21	1997	−10.04	34.8 ± 0.3	4.9
Amurga 25	1997	−11.86	26.4 ± 0.3	2.2

* Total dissolved inorganic carbon.

DIC is high for almost bare soils in non-carbonate rocks; with the help of $\delta^{13}C$ data (see Fig. 22), three possible origins of DIC are proposed, or some combination of them:

(1) only soil CO_2 is incorporated, in an open system in which recharge is in equilibrium with the CO_2-rich unsaturated zone air. The work carried out by Gasparini (1989) shows that the $\delta^{13}C$ content of soil CO_2 is highly variable, without a clear relationship with site, depth, lithology or vegetal cover. Values close to −15‰ seem common (is it the effect of CAM-dominated vegetation?) but in the study area it
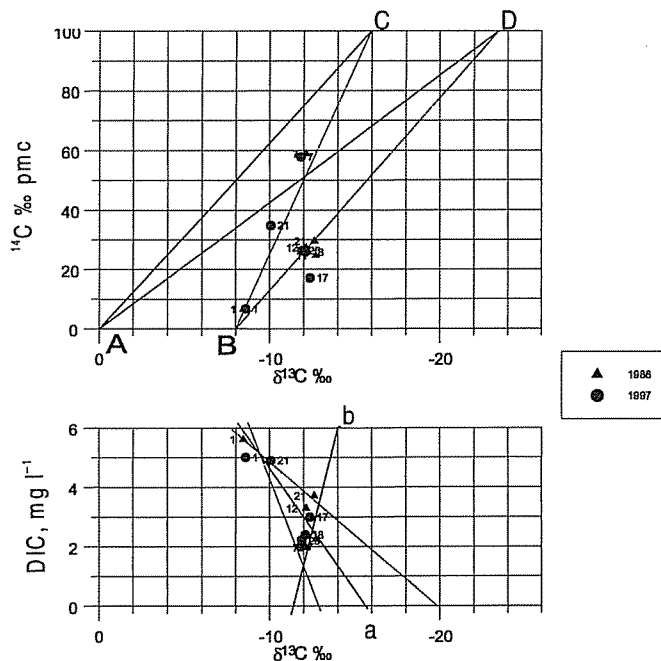
Fig. 22. ^{14}C and total dissolved inorganic carbon (DIC) content v. $\delta^{13}C$ and possible relationships. A, open system incorporation of volcanic CO_2; B, as A, but under closed system; C, open system incorporation of pedologic soil CO_2; D, as C, but under closed system; a, trend lines considering the Amurga and the Fataga wells; b, trend line considering only the Amurga wells.

ranges between −11‰ (bare soil) and −22‰. It is not known how $\delta^{13}C$ of CO_2 in soil air changes with depth and the effect of air CO_2 diffusion in barren areas. This may be important with measurements from a carbonate formation (Bosch & Custodio 1991);

(2) there is some volcanic CO_2 input that slowly diffuses from deep-seated magma chambers. This was not expected due to the long period of time since volcanic activity in this area, but it is not impossible since other areas of the island some kilometres away have subhistorical activity and there are wells producing CO_2-rich water. Then, some contribution by slow CO_2 diffusion from deep-seated layers cannot be ruled out; in fact, the boreholes at the bottom Fataga barranco seem clearly affected and a deep fault line along it. The composition of this CO_2 is not known but can be assumed to be close to $\delta^{13}C = −8‰$, although some fractionation is possible.

(3) soil and/or volcanic CO_2, moreover weathering silicate minerals, dissolve the carbonate infilling of the rock fissures and voids that can be seen in the cores of some deep boreholes. The $\delta^{13}C$ of these carbonates is not known but may be assumed to be in isotopic equilibrium with volcanic CO_2, or $\delta^{13}C \cong 0‰$ if formed at low temperatures, but may be as light as $\delta^{13}C \cong −8‰$ if formed at high temperatures, after taking into account the isotopic fractionation factors (Friedman & O'Neil 1977).

If, for the Amurga wells, it is considered that only soil-derived CO_2 is present, with some incorporation of carbonates in fissures and perhaps in airborne dust, the age correction yields values from recent to c. 11 ka. This last value seems to be the most consistent. If this age is accepted, this means that abstracted water from the Amurga Massif is mostly Late Pleistocene palaeowater. This is in agreement with the thick unsaturated zone and the small recharge values if piston flow or a dispersive mixing model, with a dispersion parameter less than the unsaturated thickness, is assumed.

Conclusions

- Salinity of groundwater is due to environmental aridity and relatively high airborne salinity. No direct seawater intrusion or trapped marine water existed under natural conditions.
- Abstracted water age is uncertain but a value of c. 11 000 a seems to be a reasonable compromise that is compatible with the small mean recharge, the thick unsaturated zone and the turnover time in the unsaturated zone.

- Groundwater was probably recharged under similar environmental conditions as those existing today. If a Late Pleistocene age is assumed for the groundwater, then this means that there is no significant isotopic shift due to climatic change at these latitudes (27°N).
- The thick unsaturated zone is responsible for the existence of what appears as palaeowater in the aquifer.

Concluding remarks

The situation observed in the Doñana aquifer suggests that approximately half of the confined Pleistocene aquifer has been freshened by fresh groundwater flowing during a period of some 6 ka. This situation applies to several other aquifers along the Spanish coast such as the Ebre Delta (Bayó *et al.* 1997). In these areas there are not large reserves of old freshwater but the known geological and water-head evolution during the Late Pleistocene–Holocene period can be used to forecast what may happen during a possible future elevation of sea level in areas with moderate average groundwater recharge and low topographic slopes. The characterization of the quality changes in the recharge water, due to mixing with trapped old salt water, is the main area to be addressed in these localities.

A different situation is that of the Llobregat Delta deep aquifer and other small deltas along the Mediterranean coast (Custodio & Bruggeman 1987), where salt water was flushed out to sea but sea water then later encroached under intensive groundwater development.

In the coastal area of the Inca-Sa Pobla aquifer, the whole aquifer thickness (Miocene–Holocene carbonated rocks and detritic sediments) contains brackish and saline water. This suggests that, during the Holocene, the only natural discharge mechanism of the aquifer was upward flow of freshwater along the freshwater–salt water interface in the surroundings of the S'Albufera wetland, together with upward flow of saline water along the northwestern and southeastern boundaries of the wetland. Some palaeoclimate signature in saline groundwater near the aquifer coastal area has not been discarded, although further isotopic and geochemical studies have to be carried out to confirm this.

The convective flows found in the S'Albufera area makes water chemistry interpretation dependent on the particular hydraulic configuration of each sampling point. Hydraulic gradients favour the vertical mixing of heterochronous salt water and young freshwater, although the mechanism is not yet fully understood. From the point of view of the study of palaeowaters, the main interest of this

aquifer lies, as in the case of Doñana, in the chemical changes affecting recharge water as well as in the quantification of the time needed for the mixing processes to take place.

In the Amurga Massif, groundwater salinity is due to environmental aridity and relatively high airborne salinity. No direct sea-water intrusion or trapped marine water existed under natural conditions. Abstracted water age is uncertain but a value of *c.* 11 ka may be a reasonable compromise. This is compatible with the small mean recharge, the thick unsaturated zone and the turnover time in the unsaturated zone. Groundwater was probably recharged under similar environmental conditions as those existing today. If a Late Pleistocene age is assumed for the groundwater, then this means that no significant isotopic shift appears due to climatic change at these latitudes (27°N).

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