

Pleistocene saline groundwater in the Doñana aquifer system (SW Spain)

Marisol Manzano, Emilio Custodio, and Heinz H. Loosli

Abstract The Doñana Plio Quaternary and fluvio marine aquifer system contain old saline groundwater not fully flushed due to the prevailing low freshwater head. The situation observed suggests that a strip of the confined Pleistocene aquifer has been freshened by fresh groundwater flowing to the SE from the unconfined area, and probably discharging during some 6000 years 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 to 2 m under land surface due to the drawdown produced by agricultural pumping in the water table aquifer close to the boundary of the marshes. ^{39}Ar , ^{85}Kr , ^3H , ^{14}C and ^{13}C measurements informs that the oldest fresh component of mixed groundwaters is around 12–15 ka, but ^{39}Ar age points to somewhat younger water. Neither the water stable isotope contents nor the recharge temperature calculated from noble gases show a clear climatic signature for these waters. The Doñana 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. This situation applies to several other aquifers along the European coast where large reserves of old fresh water are present.

Index Terms Coastal aquifer, saline water, palaeowater, freshening, Doñana

I. INTRODUCTION

COASTAL aquifers are complex units in which past sedimentary evolution linked to sea level changes in the Pleistocene–Holocene may still condition groundwater salinity distribution. This is partly the result of a series of unsteady states affecting mostly large hydrogeological units in which groundwater turnover time is measured from hundreds to thousands of years. This is the case of Doñana, as it is also the

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case of a set of European coastal aquifers studied in projects PALAEAUX and BaSeLiNe [2].

The Doñana natural region and the aquifer are placed in the SW Atlantic coast of Spain, partly occupying the ancient estuary of the Guadalquivir river but also extending far to the N and W throughout some 3000 km² (Fig. 1). It is a singular, fluctuating space, where the confluence of geographical and biological factors determine its biodiversity and high ecological value as habitat of wild fauna. Doñana is internationally known as a Ramsar Convention protected area for wildlife and waterfowl. Around 1100 km² are protected under the legal figures of National Park (where human activities are severely restricted) and Natural Park (where some controlled farming and light tourism activities are allowed, like pine collection, charcoal production and walking). Surface water and groundwater play a key role in this natural space.

Most of the protected area is inhabited except for people in charge of the protection and research, the occasional developers of some natural resources and the visitors. Outside the protected zones large areas are used for intensively irrigated agriculture, currently the main economical activity. It developed late in the 1970' when a groundwater-based irrigated farming development plan started after studies carried out by the FAO and the Spanish Government. Tourism is the second most relevant economical activity. It is mainly beach-based, though in the last years environmental tourism is fastly growing. It is concentrated both in time, spring and summer, and space in Matalascañas and Mazagón coastal resorts, with a joint capacity for ca. 300,000 people. The closest important towns (Huelva, Sevilla and Cádiz) are between 70 and 130 km far and only villages exist within the area.

II. GEOLOGY AND HYDROGEOLOGY

At the end of the Miocene, the precursor of the Guadalquivir river valley was an elongated SW–NE marine basin extending from the Mediterranean to the Atlantic and filling up with sediments coming from the Iberian Plate, to the N border, and from the African Plate, to the S. In the W sector of this trench, roughly between the present emplacement of the towns of Sevilla, Cádiz and Huelva, fluvio–marine and alluvial sands settled during the Pliocene. During the Pleistocene and Holocene the eastern part of this area subsided more than the western one, forming the wide early Holocene Guadalquivir

estuary and giving place to the building up of thick gravelly almost replenished the estuary with clayey, silty and sandy interlayered sediments, although it was still a shallow, semi-closed bay at Roman times, with an extensive littoral sand barrier. Nowadays, fresh and brackish marshes exist overimposed to the estuarine deposits [7][17][19].

The aquifer system consists of unconsolidated Plio-Quaternary materials overlapping impervious Miocene marine marls. It has a surface area of 2700 km², a variable thickness from a few meters inland to some 150 m at the coastline, and a roughly triangular shape. The aquifer outcrops to the W and N, but to the SE it deepens and become confined under a 50 to 70 m thick estuarine and marshy clay layer nowadays separated from the sea by a recent littoral sand spit. The confined area is about 1800 km².

Fig. 1 includes a cross-section from the northern outcrop to the centre of the marshland through the studied area. The Pliocene fluvio-marine sands overlapping the impervious Miocene marls have a poor permeability. On top of them, Pleistocene sand and gravel layers give rise to the more transmissive part of the aquifer. They become confined southward under the Pleistocene and Holocene clays and grow thin to disappear [17]. To the west of the marshes the Quaternary consists of a thin cover of permeable fluvial gravel layers and less permeable fluvial and eolian sands interlayered among the contemporaneous clays.

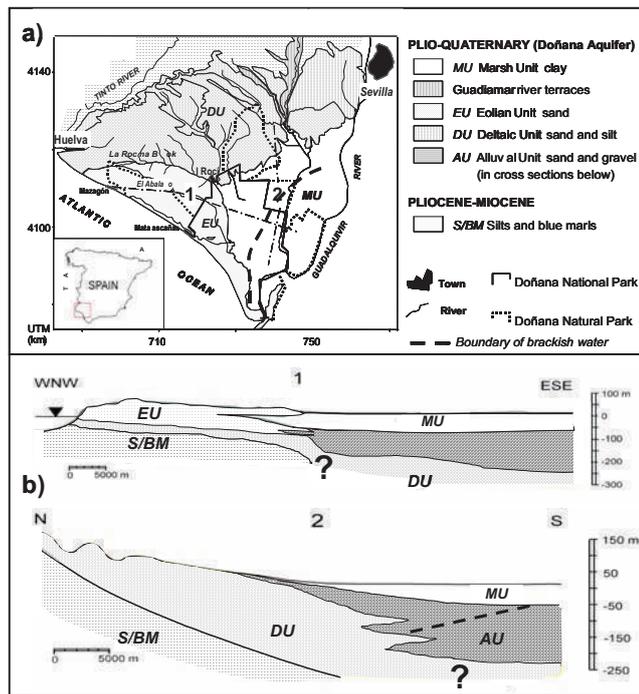


Fig. 1. Location, geology and geometry of the Doñana aquifer system. The aquifer limits coincide with these of the Plio Quaternary sediments.

Aquifer recharge takes place by rain infiltration in the sandy areas to the N and W of the marshes, and to some extent by excess irrigation water in the agricultural areas, which use local groundwater. At a regional scale groundwater flow is mostly to the S and SE, that is to the area confined under the marshes, to a main brook called La Rocina, and to the ocean.

Pleistocene layers. The Flandrian (post-Würm) transgression Under natural conditions discharge takes place as seepage to the ocean, to the streams and the many small lagoons and shallow water Tables sites placed on top of the eolian sands, as phreatic evapotranspiration, as upward flows near the boundary (ecotone) between the sands and the clays, and perhaps through the Quaternary clays in the confined area, although this is probably a minor term of the water budget.

The natural flow pattern, prevailing during millennia, has been modified during the past three decades because of increasing pumping for irrigation, mainly just to the N and NW of the marshes. Nowadays, a large fraction of the recharged water is pumped out from the unconfined area [4][11][18], and some local flow reversals occur between the confined aquifer and the overlying Quaternary clay, thus contributing to the progressive salinization of formerly fresh groundwater irrigation wells [3]. Head changes in boreholes screened at different depths and electrical conductivity and temperature downhole logs show the existence of vertical downward groundwater flow, as a result of the vertical hydraulic gradient reversal due to deep groundwater abstraction.

The SE sector of the confined aquifer contains almost stagnant, old connate marine water which has not been flushed out due to the low hydraulic head prevailing since the late Holocene sea level stabilisation some 6 ka BP [20].

EC of groundwater varies between 0.3–0.5 mS cm⁻¹ in the unconfined (recharge) area to more than 40 mS cm⁻¹ in the saline confined aquifer.

The conceptual model established to explain current salinity distribution is:

- during the Pleistocene, with a low sea level (about 120 m below current elevation), the distal part of the alluvial unit was below seawater and containing saline groundwater, the more proximal areas with freshwater,
- when the sea level rised fine sediments under marine and brackish environments begin to be deposited in the broad lower Guadalquivir stuary, introducing saline water in some areas, but also confining the aquifer with its salinity pattern. This pattern has been progressively modified by buoyancy density readjustements and diffusion, and also by the penetration of freshwater at the boundaries when this has been hydraulically possible,
- when the sea level finally stabilized freshening at the boundaries continued if heads allowed it and some relatively recent freshwater could replace brackish (mixed) and saline water along a strip.

The existence of the Pleistocene fresh and saline water can be known by their chemistry and especially their environmental radioisotope content, as will be commented below. The freshwater part is a non-renewable water resource.

III. MATERIALS AND METHODS

The saline groundwater of the Doñana confined aquifer has been studied in order to ascertain its extent, age, and the origin of its chemistry.

Both historical and newly obtained chemical and isotopic data have been studied. Previous information on major components and environmental isotopes is abundant and was interpreted in former studies [1][6][12][16]. More recently some tens of water samples have been collected within the framework of different recent projects between 1999 and 2001 [2], especially following two N-S and NW-SE sections along the main regional groundwater paths under natural conditions, from the water Table to the confined aquifer in the centre of the marshes (see Fig. 1). Most of the new samples are from short-screened boreholes, several are from multi-screened boreholes or wells, and a few ones are lagoon waters. Major and some minor components have been analysed as well as the isotopes of water (^3H , $\delta^{18}\text{O}$ and $\delta^2\text{H}$), of inorganic dissolved C ($\delta^{13}\text{C}$ and ^{14}C) and dissolved noble gases (^{39}Ar and ^{85}Kr). Major component analyses were performed at the Geological Survey of Spain (IGME, Madrid, Spain) by ICP-AES and standard techniques, including 24 fresh and brackish waters samples analysed for Br and Cl by slow flow ion chromatography to characterise the origin of water salinity, which in this case is marine. Tritium was analysed at the CEDEX lab in Madrid (Spain); $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analyses were performed at the CSIC lab in Granada (Spain) and at the CEDEX, and $\delta^{13}\text{C}$ and ^{14}C were analysed at the CEDEX and also at University of Bern (Switzerland), where the other nobles gas analyses were carried out.

The code PHREEQC-Version 2 [15] has been used to check the hydrogeochemical conceptual model proposed for groundwater hydrochemistry evolution along flow paths. The full set of available data has been considered.

IV. GROUNDWATER HYDROCHEMISTRY

A. Solute sources in groundwater

The only source of recharge is rainfall infiltration. Locally, return irrigation flows from local groundwater sources exist, though they do not constitute a net recharge contribution. The groundwater chemistry primary sources are rainfall composition and aquifer mineralogy, although some polluting activities within and outside the recharge area play a relevant role in the chemistry of recent recharge water, and also the marsh annual flooding with allochthonous water. But this last source is available only on the clay-lined area and its effect is restricted.

Local rainwater is of the Na-Cl type and slightly acidic. Ionic ratios shows that wet and dry deposition of marine salts are the main solute source, although only about 30% of S in rainwater can be accounted for a marine origin. In areas without agricultural influence the remaining 70% may be attributed to recycling from local dust and to S derived from sulphide particles from the W of the aquifer recharge area, following the dominant wind direction. The source of these

particles can be open pit mining activities in the numerous sulphide one mines of the Portuguese-Spanish Pyrite Belt, which crops out to the N and NW of Doñana, and/or the emissions from Huelva industrial pole, placed some 30 km to the NW.

Aquifer mineralogy is dominated by amorphous silica, with some minor spatial differences due to the K and Na feldspars (microcline and albite) accompanying minerals. Illite, chlorite and kaolinite are minor components. Carbonate, mostly CaCO_3 , is present either as detrital grains or as shell remains except in the upper eolian and fluvio-marine sand layers of the western water-Table sector, where they have been already leached by acidic rainfall infiltration. A down flow increase of Ca and HCO_3 may indicate a sluggishly flowing part of the aquifer under natural conditions, although the current situation could be changed by the effect of pumping.

B. Groundwater chemistry evolution along flow paths

At a regional scale groundwater salinity ranges three orders of magnitude. Most of the waters seems to be either the result of mixing of two end members or an evolution of them:

- i) A fresh water member, with electrical conductivity (EC) $< 1 \text{ mS cm}^{-1}$ (often in the $0.3\text{--}0.5 \mu\text{S cm}^{-1}$ range) and mostly of the Na-Cl type, which may locally evolve towards a Na/Ca-Cl/ HCO_3 type water when carbonate sources are present or had been found,
- ii) A saline water member, originally sea water, sometimes subjected to evaporation in natural ponds, with EC up to 80 mS cm^{-1} and mostly of the Na/Ca-Cl/ HCO_3 type, which means with some chemical interaction with the ground. Re-circulation of evaporated seawater when the marshes were open to the sea is also a possible origin [9].

The fresh water member is the most characteristic groundwater found in the watertable areas down to 40–50 m depth. The saline member is characteristic of the aquifer confined under the marshes. Saline water may also form locally in the eolian sands around phreatic lagoons as a result of intense evaporation. Many saline groundwater samples are really the result of vertical mixing between fresh groundwater flowing upward through or close to the marshy clays- and saline pore water, both underneath and trapped in the low permeability sediments above. In fact, pore water salinity in the Quaternary clays increases upward in the top 30 metres, reaching values twice that of seawater in the top 5 m. This is interpreted as the result of repeated evaporation and dissolution processes of water of the uppermost centimetres of the clays, and also in shallow water bodies in the marshes [1][3][9][12]. The observed groundwater chemical changes along main regional flow paths and with depth and the proposed processes are as follow:

- Along a W to E flow path (Fig. 2): shallow and middle depth groundwater is acidic, of the Na-Cl type and low mineralization ($\text{EC} < 0.5 \text{ mS}\cdot\text{cm}^{-1}$). This water has been interpreted as the result of slightly evaporated rain water dissolving soil CO_2 and remnants of Na/K feldspars. At greater depths ($> 50 \text{ m}$, depending on the site) groundwater

mineralization increases and water become of the Ca-HCO₃ type as a result of calcite dissolution. Flowing to the east, as groundwater approaches the marine and estuarine sediments it becomes brackish and saline, mostly because of mixing with saline groundwater. A saline groundwater body (> 40 mS·cm⁻¹) exists in the coastal area, which is locally more concentrated than seawater.

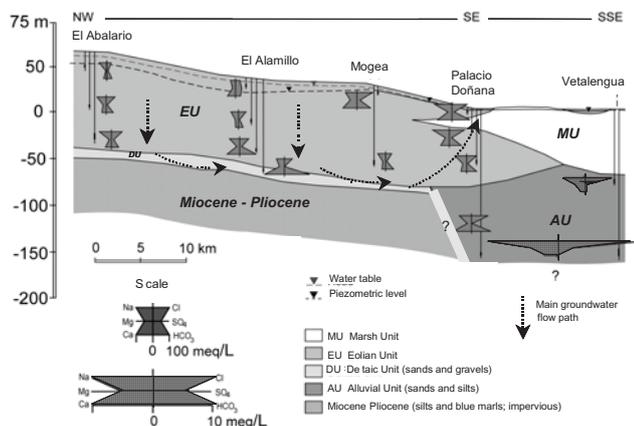


Fig. 2. Groundwater chemical evolution along main flow paths W E. The section goes from El Abalarío, in the water Table western area, to the marshes (see Fig. 1).

- Along a N to S flow path (Fig. 3): in the northern water-Table area the aquifer is thinner (< 50 m) and consists of silts and siliceous and carbonate containing silty sands. Phreatic and deeper groundwaters are of the Ca-HCO₃ or Na-Ca-HCO₃-Cl type, but as they reach the confined area evolve rapidly to a Na-Cl type and become brackish and finally salty. In the upper part of the unconfined areas, down to 25–35 m deep [14], groundwater chemistry shows the impact of human activities like agriculture, which appears as high NO₃

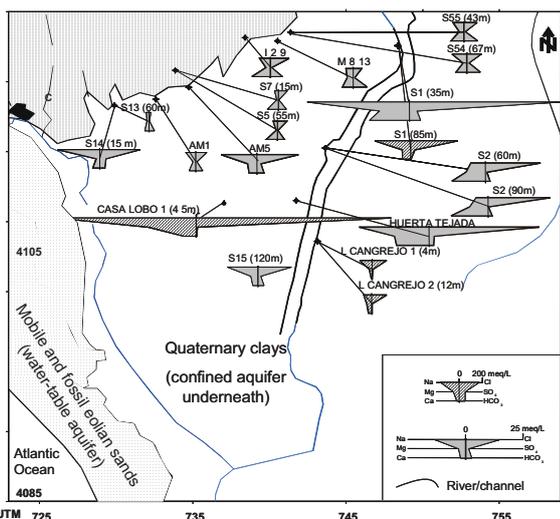


Fig. 3. Groundwater chemical evolution along main flow paths N-S.

A wide mixing strip develops from NW to SE under the marshes, with salinities ranging from 1 up to 80 mS·cm⁻¹. Its geometry is not well known due to scarce wells and the difficulties to drill adequate observation boreholes in the marsh area and to obtain representative samples in a multilayer aquifer. However, specific modifications with respect to conservative mixing can be identified at a local observation scale, and the following proposed interpretation has been checked through modelling with PHREEQC, taking into account the following processes:

- equilibrium with calcite, which eventually lead to dissolution or precipitation,
- sulphate reduction,
- cation exchange of Na and Ca (or Mg) in moving fresh-saline water fronts. A chromatographic spatial distribution is difficult to be observed because the few available sampling points southward in the marshes are not adequate to get samples that identify individual flow paths; they correspond to multi-screened boreholes and pumping wells that yield mixtures,
- incorporation of inorganic C from sedimentary organic matter.

Thus, groundwater chemistry evolution in the confined aquifer reflects the usual pattern found when fresh and saline water mixes. However, as described below, the saline member here is not recent marine water but evolved marine palaeowater.

V. INFORMATION PROVIDED BY ENVIRONMENTAL ISOTOPES

A. Recharge conditions

Groundwater in the recharge area has the δ¹⁸O and δ²H signature of averaged local rain without significant fractionation by evaporation: δ¹⁸O = -4.7 to -5.5 ‰ SMOW, δ²H = -28 to -33 ‰ SMOW [1][6][12][13]. A detailed look to phreatic waters from the western and northern recharge areas shows that two groups can be made since groundwater is ~0.5 ‰ (for ¹⁸O) and ~4 ‰ (for ²H) heavier in the North-East than in the West (Fig. 4), where eolian sandy soils predominate and water recycling is less important. The salinization follows a mixing trend mixing between fresh and marine water (Fig. 4).

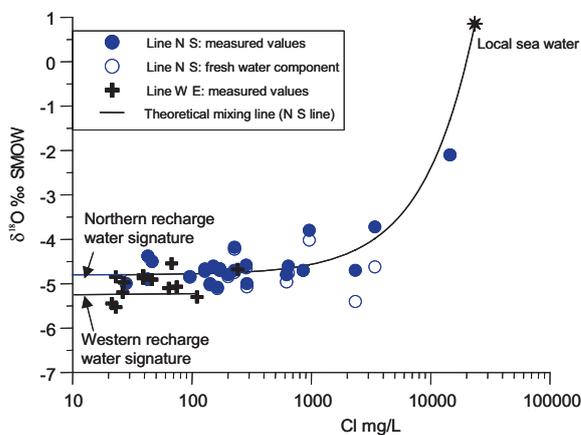


Fig. 4. Recharge water signature in the water Table area. In the northern area recharge water seems to be slightly heavier than in the western one which is attributed to evaporative fractionation due to water recycling in the groundwater-irrigated area.

B. Carbon isotope geochemistry

Soil gas samples indicate $\delta^{13}\text{C}$ values of CO_2 about -23 to -25‰ in the eolian sandy recharge areas. This corresponds to soil CO_2 derived from Calvin type plants ($\delta^{13}\text{C} \sim -25\text{‰}$ PDB). There groundwater may be only slightly heavier if still acidic and free of soil carbonates, but most often values are around -16‰ PDB. This can be explained as the result of isotopic equilibrium of dissolved carbonate species and soil CO_2 in an open system, whose result depends on pH. Afterwards conditions may change into a closed system, in which there is a progressive dissolution of soil carbonates with average $\delta^{13}\text{C} = 0.0$ to -6.4‰ PDB, as measured by Baonza *et al.* [1] in local sediments. These authors [1] found that the $\delta^{13}\text{C}$ values measured in the confined area tended to be heavier the greater the salinity. They also found that some of the fresh waters under the marsh clays had very heavy DIC ($\delta^{13}\text{C} = -4$ to $+2\text{‰}$), which they explained as due to the input of heavy C from evolved, old organic matter ubiquitous in the clay sediments. This enrichment may be due to CH_4 formation, although the actual presence of CH_4 has never been reported. Probably it escaped or migrated. There are no isotopic analyses available of this organic matter.

Measured ^{14}C activity values vary between almost 100 pmc and about 7 pmc, what means up to 15 ka after the Fontes and Garnier model [5]. The ^{14}C ages indicate that groundwaters in the waterTable areas are less than a few centuries old, but it becomes much older southward and eastward under the marshes.

C. Age of the old groundwater

The old measurements of $\delta^{13}\text{C}$ and ^{14}C from samples of 1981 [1] are given in Table 1, with other relevant data. Sample situation is indicated in Fig. 5 (LACKS). Groundwater becomes apparently older towards the marshland, without significant changes in water stable isotopes except the mixing with saline water. In order to check the previous conceptual mixing model, to detect possible admixtures of recent and old components, and to determine the age structure of the deep mixed waters, new sampling to measure major ion chemistry, dissolved gasses, and ^3H , ^2H , ^{18}O , ^{14}C , ^{13}C , ^{39}Ar and ^{85}Kr have been carried out. Evidence of CH_4 has not been found in the four groundwater samples taken for noble gases analyses.

Results of these new isotope determinations are given in Table 2. Table 3 gives the results of ^{85}Kr and ^{39}Ar analyses. Table 4 summarizes the composition of the gases collected. In samples from boreholes S54 and M-8-13 the amount of extracted gas is increased by about 30% compared to air-saturated water due to the considerable CO_2 content. This large amount of CO_2 responds to an equilibration CO_2 pressure three orders of magnitude greater than in air and is assumed to come from ground organic matter. A detailed study is still lacking. This means that in these cases most DIC is not of recharge soil CO_2 origin but sedimentogenic, and the

calculated age (most models are not applicable) is not that of groundwater but that of organic matter in the sediments. Table 5 contains the noble gas concentrations determined mainly to calculate recharge temperatures (RT) of assumed palaeowaters.

To explain the low tritium content in groundwater, assuming a maximum of 10 TU for 1999–2001 precipitation, the recent water component in all wells should be less than about 10%, even for boreholes M-8-13, I-2-9 and S54, which show the highest ^{39}Ar and ^{14}C activity values. Well I-2-9 is in the water Table aquifer area, while the other two are nearby but penetrate several layers of the confined aquifer. An even lower limit of about 1% is estimated for boreholes S54, S13 and S2 from the low ^{85}Kr activity (Table 3). These low ^{85}Kr values also demonstrate that the sampling intervals of 50–70 m below surface are deep enough to prevent significant gas exchange between this water and the atmosphere, thus discarding the possible increase of ^{39}Ar activity from anthropogenic sources.

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

- The water of borehole M-8-13 may contain about 5% of recent water, as estimated from its ^{85}Kr activity of 3 dpm mL^{-1} Kr and the amount of 1.75% O_2 found in the extracted gases (old water should be oxygen free);

- Data from borehole S13 are more complex: its ^{85}Kr content is really low, which excludes more than about 1% of recent water. This however seems to be at odds with the measured ^3H , NO_3 and O_2 contents. A possible explanation assumes the admixture of a water component several decades old, when the $^3\text{H}/^{85}\text{Kr}$ ratio in the atmosphere was much higher [10]. The $^3\text{H}/^{85}\text{Kr}$ ratio in TU/(dpm mL^{-1} Kr) value for 1970 was around 10 and about 0.5 for 1999 for activities in the atmosphere in the indicated year. Consequently there is the suspicion that the formation surrounding the borehole screen still contains remnants of drilling water, which was probably supplied from one of the nearby agricultural wells;

- The NO_3 content of borehole S54 may also indicate some influence of fertilizers but they may correspond to those applied up to 30 a ago, when agriculture and farming became intensive in the area.

- From what has been said it can be concluded that most of the boreholes referred in Table 2, which are close to the assumed recharge area, except S2, contain water that is not recent, and therefore it should be older than about 40 years.

The combination of ^{39}Ar and ^{14}C data allows a more precise estimation of these “old”, deep waters age taking into account that the low ^{39}Ar value in water from borehole S2 shows that the underground production of ^{39}Ar is below about 10 dpm mL^{-1} . Therefore the measured ^{39}Ar activities in boreholes M-8-13, S54 and S13 may be converted into ages. For borehole M-8-13 about 170 years can be calculated, taking into account the above mentioned addition of 5% recent water. Assuming piston flow a value of about 400 years can be estimated for boreholes S54 and S13.

TABLE 1. CHEMICAL AND ISOTOPIC DATA FROM BAONZA ET AL. [1] CORRESPONDING TO SAMPLING IN JANUARY AND JUNE 1981. ONLY POINTS IN OR NEAR THE MARSHLAND ARE INCLUDED. SOME POINTS HAVE TWO ³H MEASUREMENTS.

Identification	$\delta^2\text{H}$ ‰ SMOW	$\delta^{18}\text{O}$ ‰ SMOW	^3H TU	$\delta^{13}\text{C}$ ‰ PDB	^{14}C pmC	Pearson's age, years	HCO ₃ mg/L	Cl mg/L	NO ₃ mg/L
1 Veta la Arena	27.1	5.0	3.4±2.3/4.0±0.8	14.6	10.1±1.8	15350	171	99	6.4
3 Mari López Chico	26.4	4.6	1.3±2.8/1.2±0.8	13.2	19.3±4.5	9400	122	2407	0.3
4 Mari López	28.9	4.8	1.5±2.7	10.5	7.4±1.3	15950	140	287	
5 El Cornejo	31.5	5.0	2.0±1.7	18.6	25.0±1.5	9450	177	103	0.5
7 Lucio Aguasrubias	27.1	4.4	3.7±1.6/0.1±1.2	14.3	23.1±1.4	8400	177	1487	2.4
8 La Señuela bis	9.8		0.8±1.0	4.4	38.5±2.6	1950	73	7248	
9 El Puntual	25.8	5.3	0.0±2.7	17.3	41.6±2.2	4750	98	46	
11 Martinazo		5.1	1.1±1.5	13.0	27.6±1.7	6350	91	35	
12 La Algaida		5.4	2.4±1.3	20.1	78.8±1.7	450	64	39	1.9
13 HatoVilla/SotoChico		5.5	3.8±1.3/0.7±1.9	14.7	45.4±3.0	2950	104	37	0.5
15 El Lobo	24.0	4.7	1.6±1.3	9.6	14.1±3.1	10100	152	92	0.7
16 Venta Perico Planeta	33.7	5.5	2.4±1.3/0.2±1.2	11.1	8.1±1.2	15500	107	48	0.3
17 Casa Raposo		5.5	4.3±1.1	12.3	21.2±5.2	8200			
18 Casa La Galvija		5.6	3.0±1.3	9.0	33.5±1.3	2600	116	122	0.3
19 M 1 4		5.3	1.3±1.6	4.0	15.7±2.8	5100	165	49	0.5
20 M 2 6	28.3	5.1	1.6±2.8	12.4	19.0±2.7	9150	98	37	0.7
21 M 8 16		4.9	6.4±2.4	11.5	54.6±1.3	50			
24 M 5 7			2.3±1.3	3.1	15.6±2.4	4250	159	90	
26 M 6 5	27.1	5.2	1.7±1.2		12.6±2.2		134	198	
27 M 7 1	30.5	5.6	0.6±1.2	+2.4	18.7±2.1		183	708	
29 M 7 7			1.0±1.2	0.1	10.8±2.2		116	368	

Pearson's ages after $\delta^{13}\text{C}$ (soil CO₂) = 21.5‰ and $\delta^{13}\text{C}$ (calcite) = 0‰

TABLE 2. CHEMICAL AND ISOTOPIC DATA FROM YEARS 1997-2001 SAMPLINGS.

Identification (depth)	Sampling date	$\delta^2\text{H}$ ‰ SMOW	$\delta^{18}\text{O}$ ‰ SMOW	^3H UT	$\delta^{13}\text{C}$ ‰ PDB	^{14}C pmC	Pearson's age, years	HCO ₃ meq/L	Cl meq/L	NO ₃ meq/L
1 SGOP8 S3 (42-46m)	nov 00	27	4.5	0.00±0.14	20.2	75.1	1852	0.7	0.84	0.03
2 Mogea S16 (64-72m)	nov 00	29	5.3	0.11±0.15	21.1	76.9	2017	0.65	0.5	0.00
3 Vetalengua S56 (80m)	nov 00	26	3.1	0.06±0.15	13.0	46.9	2101	3.00	166.00	0.17
4 M 7 1	jul 01	27	4.6	0.15±0.13	12.5	13.2	12259	2.74	12.05	0.03
5 M 1 1	jul 01	27	4.9	0.18±0.13	12.3	12.2	12777	2.02	7.18	0.00
6 M 2 6	jul 01	29	4.9	0.01±0.13	13.0	11.5	13723	1.1	1.55	0.00
7 Alamillo-S24 (106-110 m)	nov 00	30	5.2	2.2±0.19	15.5	53.1	2528	2.1	0.64	0.00
8 SGOP1 S4 (134-145m)	nov 00	29	5.2	0.15±0.15	19.5	73.2	1772	0.7	0.84	0.03
9 P Doñana-S49 (150-158 m)	nov 00	28	5.1	0.99±0.15	14.2	14.7	12423	1.6	1.40	0.00
10 P Doñana-S50 (52-60m)	jul 01	30	5.1	0.25±0.13	19.5	60.7	3320	0.3	0.90	0.02
11 L MariLópez-S2	jul 01	26	4.5	0.44±0.14	11.9	31.2	4740	1.92	10.87	0.00
12 S FAO	jul 01	28	4.6	0.06±0.13	11.3	7.4	16210	0.92	2.03	0.00
13 I 2 9	jun 97	30	5.0	0.39±0.26	14.3	46.9	2889	5.24	8.12	0.27
14 M 8 13	jun 97	26	4.7	0.17±0.26	12.0	79.1	2880	6.1	3.61	0.05
15 P Resina-S54	jun 97	26	4.6	0.23±0.25	11.6	51.7	353	5.51	4.26	0.05
16 AM5	jun 97	26	4.6	0.3±0.24	13.5	27.5	6827	3.05	18.00	0.15
17 AM1	nov 97	29	4.7	0.65±0.69	14.0	33.6	5471	3.00	4.80	0.03
18 Raposo-S13	jun 97	32	5.0	1.15±0.26	13.0	20.9	8784	2.38	0.79	0.03
19 C Bombas-S2	jun 97	25	4.3	0.48±0.26	11.0	7.34	16055	4.00	132.00	0.01

Pearson's ages after $\delta^{13}\text{C}$ (soil CO₂) = 21.5‰ and $\delta^{13}\text{C}$ (calcite) = 0‰

TABLE 3. ISOTOPIC NOBLE GAS ANALYSES IN WATER FROM FOUR BOREHOLES, CARRIED OUT IN JUNE 1997.
(¹) pcm = per cent modern

Sample identification	⁸⁵ Kr dpm/mL Kr	³⁹ Ar pcm (¹)
M.8.13	3±0,3	70±6
S 54	0.34±0.05	34±4 9±4 (²) 46±6 (²)
S 13	0.28±0.04	28±4
S 2	0.70±0.11	<10

(²) repeated measurement in the same sample

TABLE 4. AMOUNT AND COMPOSITION OF THE EXTRACTED GASES, AND NO₃ CONTENT IN GROUND WATER FROM THE DOÑANA AQUIFER.

Sampling point	sampling depth m	extracted gas vol. mL L ⁻¹	O ₂ vol. %	N ₂ vol. %	Ar vol. %	CO ₂ vol. %	CH ₄ vol. %	N ₂ /Ar	NO ₃ mg L ⁻¹
S54	68	18	0.01	66.1	1.29	27.5	0.01	51	3.0
S13	74	13	1.0	90	1.73	1.75	0.01	52	1.9
S2	72	12	0.03	92.7	2.0	4.85	<0.01	46.4	0.0
M 8 13	55	17	1.75	65.0	1.5	30.45	0.05	43.3	3.0

TABLE 5. NOBLE GAS CONTENTS AND RECHARGE TEMPERATURES (RT) IN DOÑANA

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

After its low ³⁹Ar activity and its high ⁴He content the water of borehole S2 appears as much older than the other three waters in Table 4. The ³⁹Ar activity shows a lower age limit of about 900 years for borehole S2, and probably much older (the half-life of ³⁹A is 269 years).

This age structure derived from ³⁹Ar activities may be compared with the interpretation of ¹⁴C and δ¹³C measurements. The new ¹⁴C and δ¹³C determinations in or close to the recharge area generally (Table 2) confirm the 1984 [1] results, of Table 1, but the heavy δ¹³C values of the first survey have not been found since samples were collected somewhat closer to the recharge area. The highest ¹⁴C values (around 50 pmc) show up in the NE, decreasing along the recharge boundary to about 20 pmc to the W. The lowest ¹⁴C value here found, about 7 pmc, is from a new borehole (S2) screened in the deep layers (down to 200 m depth) of the multilayered confined aquifer.

Samples from the confined area, with low ¹⁴C contents, have DIC ≈ 2 mmol L⁻¹, which is lower than some samples from the unconfined area (DIC ≈ 6 mmol L⁻¹), but close to what is found in other areas. So neither calcite dissolution from the

marine clays, nor incorporation of C from the organic matter in the sediments seems to be quantitatively significant geochemical processes, although they probably contribute to some extent, except if there is a region of extensive carbonate deposition. The δ¹³C - ¹⁴C relationship is shown in Fig. 6. δ¹³C values characteristic of the recharge area are also found in the confined aquifer as groundwater is being depleted in ¹⁴C, mainly because of radioactive decay due to increasing age. Vertical mixing of groundwater with different ages is probably a major process, especially in the unconfined area, where most of the sampling wells are multiscreened ones.

Most of the measured values seem to fit a system closed to CO₂. 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 fine sand, but also gravels and some silts) and vertical head gradients.

Age information from ¹⁴C data is given in tables 1 and 2. A strong argument in favor of using Pearson's 14C age interpretation model [8] is from the results from borehole M-8-13, since its ³⁹Ar age is about 170 a (see above) and a

nearby and comparable well investigated in 1984 showed a ^{14}C activity of about 55 pmc with a $\delta^{13}\text{C}$ value very similar to what have been measured now in well M-8-13. 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 NE, should be younger than a few hundred years, as given in Table 2.

An age around 12–15 ka seems appropriate for water from borehole S2, mainly because no change in $\delta^{13}\text{C}$ compared to young waters has been observed.

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. Then, the main component could be water which is much older.

D. Noble gas recharge temperatures (RT)

Ne excess values over air saturation at ambient temperature of 18°C and at an elevation of 50 m above sea level are given in Table 4. Excess air of about 20–45% agrees with the N_2/Ar ratios. The excess air correction has been used to calculate the recharge temperatures from the other noble gas concentrations. The results for boreholes S54 and S2 show the smallest errors. All RT are within present day mean annual air temperature.

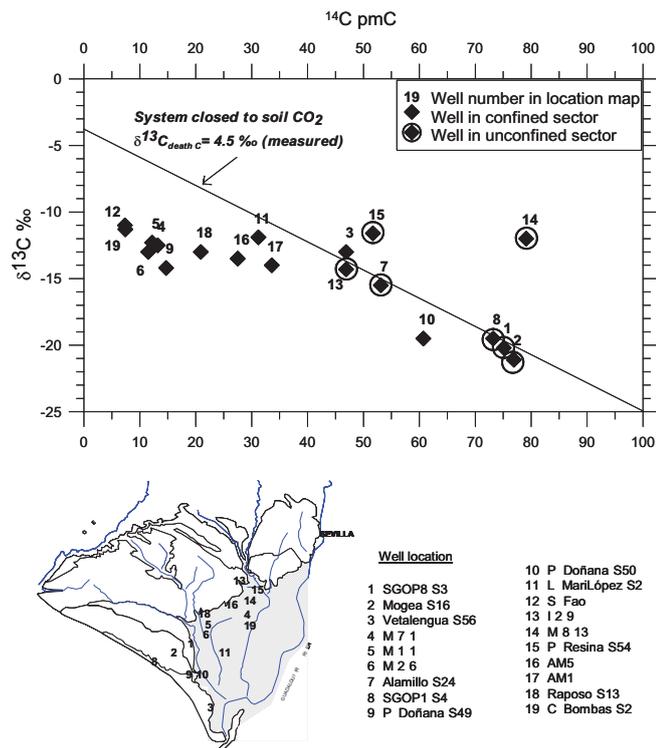


Fig. 5. $\delta^{13}\text{C}$ and ^{14}C content evolution in groundwater from the water-table aquifer to the confined sector under the marshes. Values, dates and other information are in Table 2. Tritium contents are clearly different to zero only in wells 7,9 and 18.

VI. DISCUSSION AND CONCLUSIONS

The situation observed in the Doñana aquifer suggests that a strip of the confined Pleistocene aquifer still contains old water, only partly replaced by young fresh groundwater flowing to the SE from the unconfined area, and probably discharging during several thousand years inside the marshland as upward flow through the Holocene clays. The upward head gradient was still visible a few decades ago as flowing wells, but nowadays the piezometric level of the confined aquifer is 1 to 2 m under land surface due to the drawdown produced by agricultural pumping in the water Table aquifer close to the NW and NE limit of the marshes. But due to the aquifer structure and low fresh groundwater heads prevailing since sea level stabilisation 6 ka BP, groundwater flow have not been enough to flush out all the fresh and saline water in the confined Pleistocene sands and gravels. Salt water older than 15 ka remains in the southeast most extreme of the aquifer. In the old groundwater samples that have been studied recharge palaeo-temperature is not essentially different from present conditions.

A detailed multi-isotopic study combined with hydrochemistry shows that most of the water samples are actually admixtures of groundwater components with different ages. In many cases vertical mixing in the aquifer is the most reasonable cause, but in some newly drilled boreholes with a short, well-confined screen, the most probable origin of the young component is drilling water still remaining in the terrain. This is due to moderate to low permeability values.

The Doñana 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. This situation applies to several other aquifers along the European coast where large reserves of old fresh water are present. The study of their 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 the sea level in areas with moderate average groundwater recharge and low topographic slopes. The characterisation of the quality changes in the recharge water due to mixing with trapped old salt water is the main question to be addressed in these areas.

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