

IAEA, dec 2007 STI/PUB/1310

ISBN 978-92-0-110207-2

**Advances in Isotope Hydrology
and its Role in Sustainable Water
Resources Management
(IHS-2007)**

**Proceedings of a Symposium
Vienna, 21-25 May 2007**

Vol. 1



IAEA

International Atomic Energy Agency

**GROUNDWATER AND ITS FUNCTIONING AT THE
DOÑANA RAMSAR SITE WETLANDS (SW SPAIN):
ROLE OF ENVIRONMENTAL ISOTOPES TO DEFINE
THE FLOW SYSTEM**

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Abstract

Out of the largely fluctuating surface water marshes, many of the environmental characteristics of the Doñana ecosystems depend on groundwater outflow and shallow watertable. Groundwater flow in the dominantly sandy Plio-Quaternary aquifer is complex and is currently undergoing important changes due to groundwater development. The use of environmental isotopes ^{18}O , ^2H , ^3H , ^{13}C , ^{14}C , ^{34}S , ^{39}Ar and ^{85}Kr has been very successful for defining recharge areas, flow patterns, transit times and the conceptual flow model. The importance of vertical groundwater flow in unconfined areas, as well as the behaviour of pre-Holocene confined water has been assessed. Thus, mixing patterns and chemical evolution can be explained. Lagoons are mostly aquifer discharge areas in which water evaporates. Some of the solutes remain trapped in bottom sediments and some are flushed out in wet events. This pattern is being changed due to the intensive aquifer development in some areas and negative ecological impacts are appearing.

1. INTRODUCTION

The Doñana aquifer system is situated in the SW coast of Spain, between the Guadalquivir River and the Portuguese border, and covers some 2700 km²

(Fig. 1). The climate is Mediterranean with an Atlantic influence. Mean rainfall is 500–600 mm, with a very high inter-annual variability. The mean yearly temperature is around 18°C.

A large part of the area (1100 km²) is strongly protected by the Spanish law. Also, Doñana is a Ramsar Convention area since 1990. Most of the Doñana core area is inhabited, but outside the protected zones large areas have been used for intensive agriculture developed late in the 1970s. Beach-based tourism is also an important economic activity.

Several hydrodynamic studies and groundwater flow modelling at regional and local scales have been performed to understand the aquifer functioning [1] and its relationship with the many wetlands of the watertable areas [2]. Hydrochemical and environmental isotopes studies have been performed to establish a conceptual model for groundwater chemistry origin and evolution, to obtain insights into groundwater recharge, transit and residence times, and to define the role of groundwater in wetlands [3–6].

2. BACKGROUND TO AQUIFER GEOLOGY AND HYDROGEOLOGY

The aquifer system consists of detrital, unconsolidated Plio-Quaternary sediments overlapping impervious Miocene marine marls (Fig. 1). The Pliocene materials are marls and silts. The Quaternary sediment consists of deltaic and alluvial silts, sands and gravels to the north, and littoral, alluvial and eolian sands to the west. The mineralogy consists of amorphous silica with minor contents of K-, Na-feldspars, illite, chlorite and kaolinite. Carbonates are present only locally.

To the southeast, the coarse sediments are covered by a thick (50–80 m) sequence of estuarine and marshy clays separated from the ocean by a recent sand spit. The sandy area to the north and west roughly behaves as an unconfined aquifer, while under the marsh area (1800 km²), a large confined aquifer has developed.

Recharge occurs mainly by rain infiltration in the sandy areas. At a regional scale groundwater flows to the confined area and to the ocean. Discharge takes place as seepage to the ocean, to the streams and the many wetlands situated on top of the sands, as evapotranspiration and as upward flows around the marshes. The SE sector of the confined area contains old marine water not flushed out due to the low hydraulic head prevailing since the late Holocene sea level stabilisation some 6 ka BP [5, 7]. Intensive groundwater abstraction since early in the 1980s for irrigation and to supply touristic areas has induced piezometric and watertable drawdown [1, 8].

GROUNDWATER AND ITS FUNCTIONING AT THE DOÑANA RAMSAR

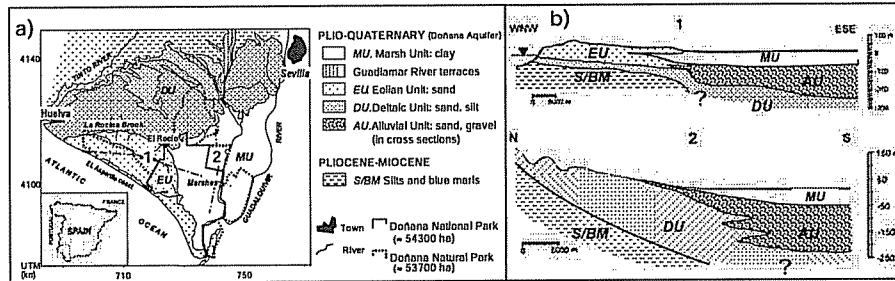


FIG. 1. Location, geology and geometry of the Doñana aquifer system. The freshwater wetlands are situated on top of the Eolian Unit (EU).

Pumping concentrates around the marshes, so it has partially depleted natural discharge to streams, phreatophytes and seepage, and has induced changes in vegetation and in wetlands hydrology [2, 8].

3. ISOTOPES AS TOOLS TO UNDERSTAND THE FLOW SYSTEM

Until 1990 the monitoring network consisted of multiscreened agricultural wells. Thus, groundwater samples and piezometric measurements integrated flow lines with different transit times and heads. As in many areas groundwater flow is mostly vertical, the information obtained did not allow insights into vertical gradients, chemical variations with depth or travel times. Early in the 1990s a dedicated monitoring network of nested boreholes was designed and built.

The study of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in rain water, surface water, phreatic and deeper groundwater samples from the whole aquifer confirmed the conceptual model for recharge origin and mechanisms:

- (1) Local rain water values fit the Mean World Meteoric Water Line (Fig. 2a).
- (2) Shallow groundwater in the watertable areas has the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signature of averaged local rain without significant fractionation: $\delta^{18}\text{O} = -4.7$ to -5.5‰ SMOW, $\delta^2\text{H} = -28$ to -33‰ SMOW. However, detailed examination of phreatic waters from the western and northern recharge areas shows that groundwater is $\sim 0.5\text{‰}$ (for $\delta^{18}\text{O}$) and $\sim 4\text{‰}$ (for $\delta^2\text{H}$) heavier in the north than in the west (Fig. 2b). This difference appears to result from higher groundwater recycling of evaporated water (due to irrigation) in the north zone, where the aquifer is much thinner than to the west [5].

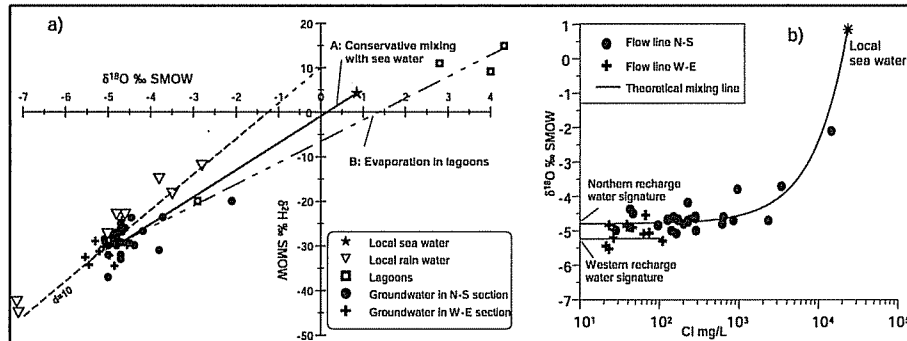


FIG. 2. a) Isotopic signature of ground and surface water showing evaporation and mixing processes. b) Observed isotopic fractionation in recharge water of the northern unconfined area.

Changes in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values along regional and local groundwater flow lines show the occurrence of three modifying processes:

- (1) A slight evaporative concentration of recharge water in the northern recharge area with respect to the western one (already mentioned).
- (2) Mixing of fresh and saline groundwater. This mixing occurs through two different mechanisms: by deep mixing of fresh and marine groundwater under the marshes, along regional flow lines; by incorporation of sea spray to very shallow groundwater and surface water around the lagoons located near the coastal sand spit. Trend A in Fig. 2a is defined by both types of samples.
- (3) Evaporative concentration of water from surface bodies in lagoons situated on certain phreatic flow lines. Trend B in Fig. 2a indicates evaporation of water prior infiltration; samples on this line are from both lagoon waters and nearby shallow groundwater [2, 5, 6].

Tritium studies helped define the groundwater flow model in different areas and to estimate transit and residence times. Studies carried out before 1990 [3, 4] had many uncertainties due to the impossibility of sampling individual flow lines. In the 1990s, the new nested boreholes allowed clarification of the groundwater flow network by measuring vertical head evolution, and establishment of flow paths through the study of flow paths that facilitate the study of chemical evolution and travel times. A significant advance was examination of different flow models to interpret ^3H data combining the different types of sampling points available, their location either in a recharge or discharge area, and the sampling methods used [9]. The work was supported by modelling (MULTIS [10]), and provided great knowledge about transit and residence times across the aquifer:

GROUNDWATER AND ITS FUNCTIONING AT THE DOÑANA RAMSAR

- **Recharge areas:** shallow groundwater (<15 m) is recent and spent between one and a few years to reach the watertable. Groundwater between 20 and 25 m depth have transit times of 15–34 years; for depths >25 m transit times are >34 years, and groundwater at >40 m depth was recharged before 1954.
- **Discharge areas:** springs in the El Asperillo coastal cliff and along La Rocina brook have short turn-over times of 6–7 years. Deeper (>30 m) groundwater close to La Rocina was recharged before 1954. Discharging groundwater along the western boundary between the marshes and the sands has transit times around 30 years at 20–25 m depth, and for depths >25 m it was recharged before 1954. The springs of El Asperillo had higher ^3H contents than expected, but the study to build-up the local input function showed that rain water contaminated with artificial ^3H and generated in 1986 in Gibraltar (to the E of Doñana) reached the area. This contaminated rain was detected in shallow coastal flows and also at shallow depths in some agricultural wells.
- **Confined area:** both the old wells and the new nested boreholes contain groundwater recharged before 1954. In spite of being pumped for cleaning several times, some new boreholes still have some remains of drilling water, as shows the presence of measurable ^3H and NO_3^- .

The ^{13}C and ^{14}C data were used to build the hydrochemical model and estimate groundwater ages. Soil gas samples indicate $\delta^{13}\text{C}$ values of CO_2 about -23 to -25‰ in the eolian sandy recharge areas, which corresponds to soil CO_2 derived from Calvin type plants ($\delta^{13}\text{C} \sim -25\text{‰}$ PDB). Groundwater may be only slightly heavier if they remain acidic and free of soil carbonates, but most often values are around -16‰ PDB. This difference 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. Downflow in the saturated zone 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 [3] in local sediments. These authors found that the $\delta^{13}\text{C}$ values measured in the confined area tended to be heavier the greater the salinity, and that some of the fresh waters under the marsh clays had very heavy DIC ($\delta^{13}\text{C} = -4$ to $+2 \text{‰}$). The marsh clay data can be explained explained by input of heavy C from evolved, old organic matter ubiquitous in the clay sediments, though isotopic analyses of this organic matter are not available.

The ^{14}C activity values measured in the 1980s [3] were in the range between almost 100 pMC and about 7 pMC, which means up to 15 ka according to the Fontes and Garnier model [11]. The ^{14}C ages indicated that groundwaters in the watertable areas are less than a few centuries old. Groundwater becomes much

TABLE 1. CHEMICAL AND ISOTOPIC DATA FROM THE 1997-2001 SAMPLING.

Identification (depth)	Samp. date	HCO ₃ ⁻ meq/L	NO ₃ ⁻ meq/L	³ H UT	δ ¹³ C ‰ PDB	¹⁴ C pMC	Pearson's age, years ¹	³⁹ Ar pcm	⁸⁵ Kr dpm/mL Kr	CO ₂ Vol. %	RT (°C)
SGOP8-S3 (44 m)	Nov. 00	0.7	0.03	0.00±0.14	-20.2	75.1	1852				
Mogea-S16 (68 m)	Nov. 00	0.65	0.00	0.11±0.15	-21.1	76.9	2017				
Vetalengua S56 (80 m)	Nov. 00	3.00	0.17	0.06±0.15	-13.0	46.9	2101				
M-7-1	Jul. 01	2.74	0.03	0.15±0.13	-12.5	13.2	12259				
M-1-1	Jul. 01	2.02	0.00	0.18±0.13	-12.3	12.2	12777				
M-2-6	Jul. 01	1.1	0.00	0.01±0.13	-13.0	11.5	13723				
Alamillo-S24 (108 m)	Nov. 00	2.1	0.00	2.2±0.19	-15.5	53.1	2528				
SGOP1-S4 (140 m)	Nov. 00	0.7	0.03	0.15±0.15	-19.5	73.2	1772				
P.Doñana-S49 (155 m)	Nov. 00	1.6	0.00	0.99±0.15	-14.2	14.7	12423				
P.Doñana-S50 (56 m)	Jul. 01	0.3	0.02	0.25±0.13	-19.5	60.7	3320				
L. MariLópez-S2	Jul. 01	1.92	0.00	0.44±0.14	-11.9	31.2	4740				
S.FAO	Jul. 01	0.92	0.00	0.06±0.13	-11.3	7.4	16210				
I-2-9	Jun. 97	5.24	0.27	0.39±0.26	-14.3	46.9	2889				

GROUNDWATER AND ITS FUNCTIONING AT THE DOÑANA RAMSAR

M-8-13 (55 m)	Jun. 97	6.1	0.05	0.17±0.26	-12.0	79.1	-2880	70±6	3±0.3	30.45	19.8±1.8
P. Resina-S54 (68 m)	Jun. 97	5.51	0.05	0.23±0.25	-11.6	51.7	353	34±4/30±10	0.34±0.05	27.5	15.1±1.2
AM5	Jun. 97	3.05	0.15	0.3±0.24	-13.5	27.5	6827				
AM1	Nov. 97	3.00	0.03	0.65±0.69	-14.0	33.6	5471				
Raposo-S13 (74 m)	Jun. 97	2.38	0.03	1.15±0.26	-13.0	20.9	8784	28±4	0.28±0.04	1.75	19.7±3.4
C. Bombas-S2 (72 m)	Jun. 97	4.00	0.01	0.48±0.26	-11.0	7.34	16055	<10	0.70±0.11	4.85	17.8±1.7

¹ Pearson's ages after $\delta^{13}\text{C}$ (soil CO_2) = -21.5% and $\delta^{13}\text{C}$ (calcite) = 0‰

older southward and eastward under the marshes without significant changes in water stable isotopes, except the mixing with saline water. In order to check this conceptual mixing model, to detect possible admixtures of recent and old components, and to determine the age structure of the deep mixed waters, a new sampling to measure dissolved gasses, and ^3H , ^2H , ^{18}O , ^{14}C , ^{13}C , ^{39}Ar and ^{85}Kr were carried out in 1997–2001 (Table 1). The new ^{14}C data are coherent with the previous ones, but the heavy ^{13}C values measured by [3] were not found. Also, there is no clear relationship between ^{14}C and ^{13}C and the DIC contents (Fig. 3). Thus, the dominant model for groundwater age in the confined aquifer is that the observed decrease of ^{14}C activities downward flow is mostly due to groundwater aging. However, for some samples this interpretation is not true (see below).

The presence of measurable ^3H , ^{39}Ar and ^{85}Kr in some of the oldest groundwater samples (Table 1) indicate that they are admixtures of old and recent components. For the old wells mixing can be explained by the joint sampling of recent and old flow lines, but for single screened boreholes it can only be explained by remnants of drilling water in the low permeability sediments. To explain the ^3H contents in old 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 the youngest samples showing the highest ^{39}Ar and ^{14}C activity values. An even lower limit of about 1% is estimated for boreholes S54, S13 and S2 from the low ^{85}Kr activity. The low ^{85}Kr values demonstrate that the sampling intervals of 50–70 m below surface are deep enough to prevent significant gas exchange between water and the atmosphere, thus discarding the possible increase of ^{39}Ar activity from anthropogenic sources [5].

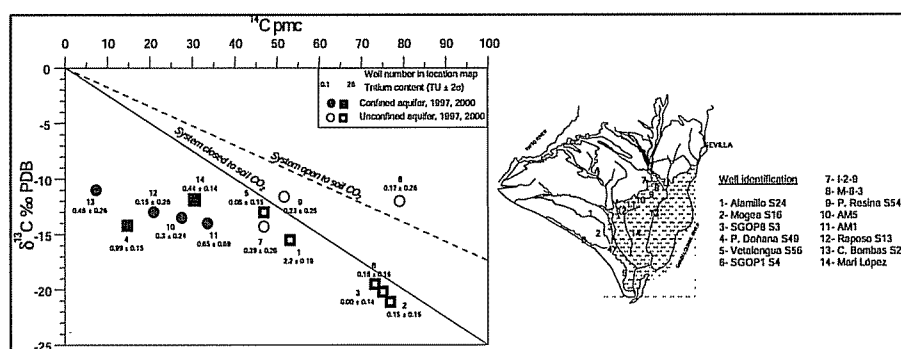


FIG. 3. $\delta^{13}\text{C}$ and ^{14}C in groundwater of the unconfined and confined areas. Values and other information are in Table 1. Tritium contents are clearly different from zero in wells 7, 9 and 18.

GROUNDWATER AND ITS FUNCTIONING AT THE DOÑANA RAMSAR

In some samples the amount of extracted gas is higher than 30% compared to air-saturated water. This excess corresponds to an equilibration pressure three orders of magnitude greater than in air and is assumed to come from organic matter in the sediments. This observation implies that in these cases most DIC is not from soil CO₂ but is sedimentogenic, and thus the calculated age is not that of groundwater, but of organic matter in the sediments. A detailed study is still lacking.

Noble gas concentrations were determined in four samples to calculate recharge temperatures of assumed palaeowaters. Evidence of CH₄ was not found. No palaeoclimatic signature was found in the freshwater component of the confined aquifer groundwater after correction of δ¹⁸O and δ²H values for marine water contribution (RT in Table 1) [5]. This result agrees with the information from a pollen record described in the coastal area of Doñana which covers the last 18 ka and suggests no major climatic changes during this period, and that during the last glacial maximum weather in the southwest of the Iberian Peninsula was humid and warm, and not very different to the present one [7].

4. THE GROUNDWATER ROLE IN WETLANDS AS INDICATED BY ISOTOPES

The numerous wetlands of Doñana have diverse geo-morphological origin and hydrology, but most of them are directly dependent on groundwater. The two most common wetland types are small erosive or eolian depressions located at the foot of stabilised dune fronts and small watercourses. Both types are mostly seasonal and their location is related to local or medium-scale groundwater flow paths. Water chemistry in those wetlands reflects mostly groundwater composition, which is highly stable in time. In general, it is of the sodium-chloride type or intermediate between sodium-chloride and calcium-bicarbonate. However, some of the lagoons show temporary changes in mineralization and ionic type which depend on modifications in the balance between water inputs and outputs and on bio-geo-chemical reactions. These reactions may produce significative temporal changes in water salinity, pH and ion composition.

Studies under way to improve the knowledge of wetlands processes include δ¹⁸O_{H₂O} and δ²H and δ³⁴S and δ¹⁸O_{SO₄}. The preliminary results indicate that around certain lagoons regional or local groundwater flow systems develop along the year, driven by seasonal changes in the hydraulic gradient direction between the ponds and the nearby watertable [2]. This implies that major chemical changes occurring in the wetland water bodies are transferred

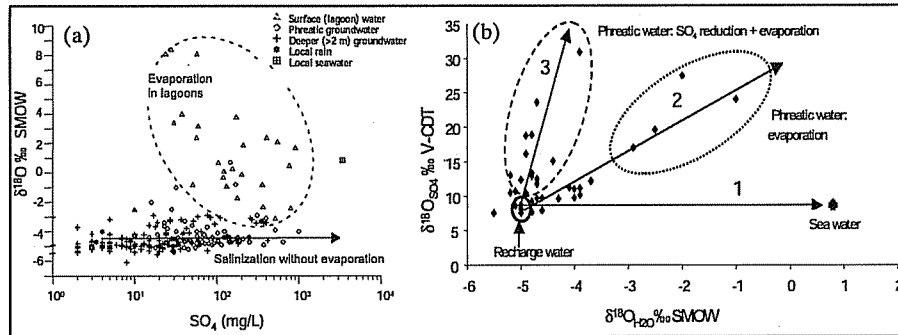


FIG. 4. a) The groundwater salinization trend without isotopic enrichment results from solid sulphur and sulphate salt dissolution. b) Groundwater samples along trend 2 show mostly evaporation; samples along trend 3 show mostly SO_4 reduction.

to the nearby shallow groundwater. In some lagoons strong evaporation in the dry season causes sodium chloride, calcium sulphate and possibly calcium carbonate precipitation and accumulation in the basin floodable zone, often accompanied by sulphate reduction and sulphur accumulation in the bottom sediments. In the next wet season, a large fraction of these salts is re-dissolved and transferred to the surrounding phreatic water along with sulphur, oxidized to sulphate (Fig. 4). This input modifies the salinity of shallow groundwater and, eventually, its ionic composition. The process is seasonal around some lagoons, but in other cases sulphate concentration in groundwater is increasing in the last years, thus pointing to enhanced oxidation of S accumulated in lake sediments.

5. CONCLUSIONS

The previous isotopic studies carried out in Doñana, combined with the improvement of the observation network and integration of chemical and hydrodynamic studies, have contributed greatly to the knowledge of the groundwater flow network, transit and residence times and the role of groundwater in the wetlands. With respect to the last subject, studies under way combining $\delta^{18}O_{H_2O}$, δ^2H , $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$, show that although groundwater composition dominates wetlands chemistry at the regional scale, some reactions taking place within the lagoons influence the composition of the nearby shallow groundwater. Changes in water salinity, ion composition and isotopic concentration originated in the lakes can be traced downflow in the aquifer. In wetlands well connected to the groundwater flow these changes are just seasonal,

GROUNDWATER AND ITS FUNCTIONING AT THE DOÑANA RAMSAR

but in some areas where accumulated watertable lowering due to pumping has turned former permanent or seasonal wetlands into sporadic ones, evidence of irreversible groundwater composition changes are already noticeable. Thus, intensive groundwater abstraction is having a serious impact not only on groundwater discharge to wetlands by seepage and evapotranspiration, but also on wetlands functioning and groundwater chemistry.

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