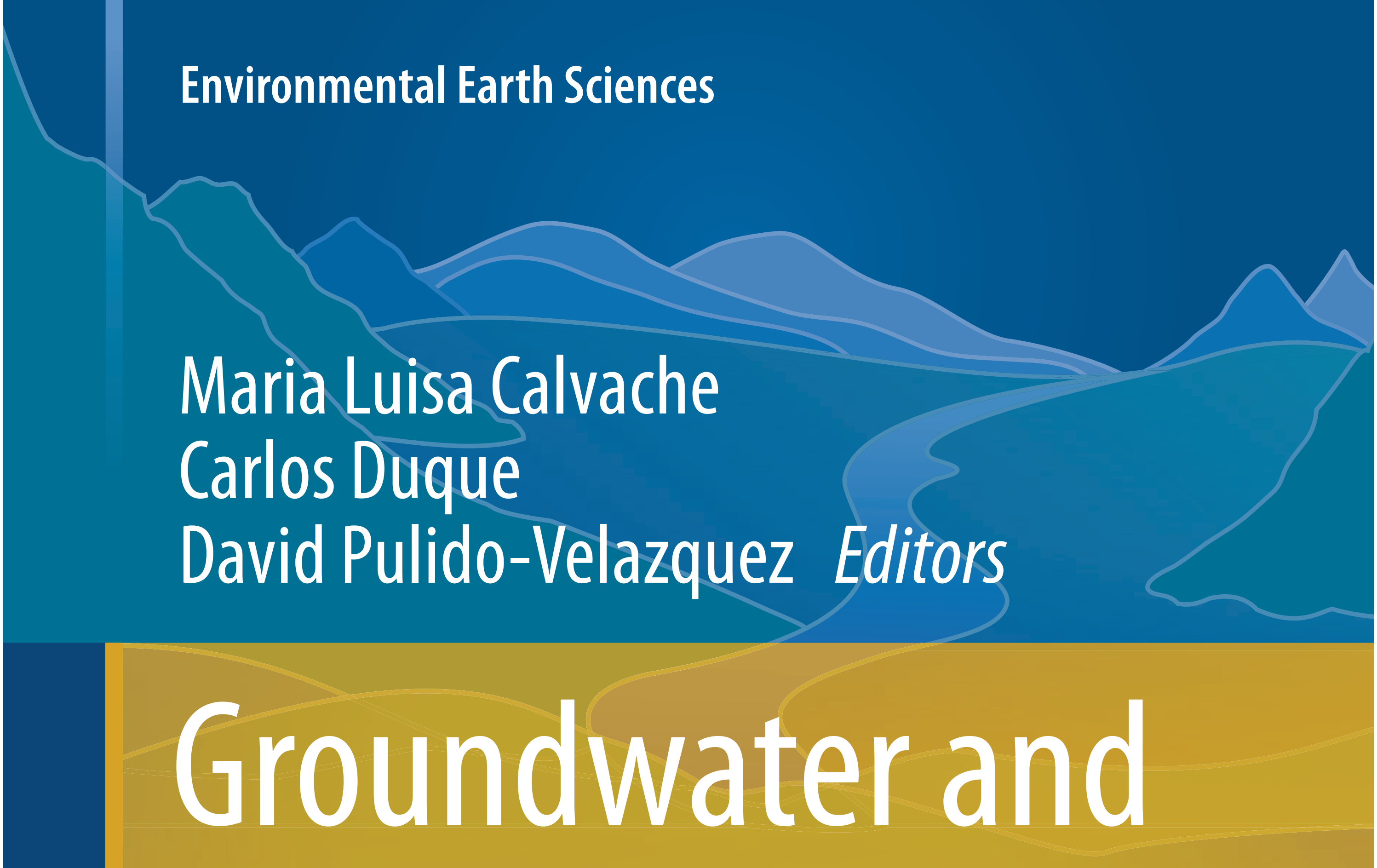

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Maria Luisa Calvache
Carlos Duque
David Pulido-Velazquez *Editors*

Groundwater and Global Change in the Western Mediterranean Area

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Editors

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Editors
Maria Luisa Calvache
Department of Geodynamics
University of Granada
Granada
Spain

David Pulido-Velazquez
Spanish Geological Survey (IGME)
Granada
Spain

Carlos Duque
Department of Geoscience
Aarhus University
Aarhus
Denmark

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calvache@ugr.es

Groundwater Salinity and Environmental Change Over the Last 20,000 Years: Isotopic Evidences in the Lower Sado Aquifer Recharge, Portugal

P. M. Carreira and J. M. Marques

1 Introduction

Steady increase in the salinity of most of the major aquifers being used for water supply in coastal regions, in particular in areas under arid and semi-arid conditions, provide evidences of water quality deterioration (Jalali 2007; Bouchaou et al. 2008). This increase of mineralization in groundwater resources is often due to inflow of saline dense water during heavy withdrawals of fresh water from coastal aquifers and/or mobilization of saline formation waters by over-exploitation of inland aquifer systems. Not only seawater mixing is responsible for water resources degradation. Because of the different income sources for groundwater quality deterioration, it is necessary to identify and characterize the specific processes involved. Among the different approaches, isotope techniques are particularly effective for identifying the source of salinity and renewability of groundwater (Carreira et al. 2014; Re and Sacchi 2017).

The Lower Tagus-Lower Sado basin is located in Setúbal-Lisbon region and represents an important water resource for a vast region. The highly populated urban and industrialized areas of Setúbal and Lisbon are supplied by this system, which has been extensively exploited over the last decades. In order to find out the source of salinization in these groundwater systems chemical (Cl^-, HCO_3^-, SO_4^{2-},

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P. M. Carreira (✉)
Centro de Ciências e Tecnologias Nucleares (C2TN), Instituto Superior Técnico,
Universidade de Lisboa, Estrada Nacional 10, km 139, 7, 2695-066 Bobadela, LRS, Portugal
e-mail: carreira@ctn.tecnico.ulisboa.pt

J. M. Marques
Centro de Recursos Naturais e Ambiente (CERENA), Instituto Superior Técnico,
Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

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Ca^{2+}, Mg^{2+}, Na^+ and K^+) and isotopic (δ^2H, $\delta^{13}C$, $\delta^{18}O$, ^3H and ^{14}C) analyses were performed on groundwater samples collected in 43 boreholes. In the region under investigation there is a growing concern that these groundwater systems maybe threatened by further exploitation (not controlled) due to mixing with the shallow aquifers (highly polluted), seawater intrusion processes in the coastal areas, or either by brine dissolution detected at depth by geophysical studies (Astier 1979).

Isotope methodology applied (stable and radioactive environmental isotopes) were particularly effective for identifying the source of salinity and renewability of groundwater. Since most of the recharge is derived from direct infiltration of precipitation, the groundwater will reflect the isotopic composition of that precipitation. However, if most of the recharge is derived from surface water (rivers or lakes) instead of precipitation, the groundwater will reflect the mean isotopic composition of the contributing river or lake and possible mixture between different aquifer units. The difference in isotopic composition allows for differentiation of precipitation sources, and hence of recharge mechanisms and in some case the presence of paleowaters (Fig. 1).

The isotope techniques were used to distinguish the importance of the following processes which may lead to the salinization of groundwater: (i) leaching of salts by percolating water; (ii) seawater intrusion (present or past) of salt water bodies such as seawater, brackish surface water or brines; and (iii) concentration of dissolved salts through evaporation. Environmental isotope studies were applied in order to assess the origin of salinization, being complement by geochemical investigations, which, in some cases, were not able to undoubtedly solve the questions. The case study that will be presented is situated south of Lisbon in a very industrialized region, the Lower Tagus-Sado sedimentary basin (central Portugal), where groundwater salinization occurs, and reaching values of several grams of Total Dissolved Solids (TDS)/L. The source of this high mineralization could be: (a) actual seawater intrusion; (b) dissolution of a brine structure at depth or mixing with ancient seawater trapped during the basin formation.

Stable isotopes provide an effective label for seawater and freshwater to enable tracing of seawater intrusion, as well as identifying other processes that may be responsible for groundwater salinization. Evolution of stable isotope concentration of water during different processes related to water salinization is presented in Fig. 1. In studies dealing with seawater intrusion and identification of groundwater salinization process, it is often common to consider both isotopic and hydrochemical evolution. Such an approach will enable a clear distinction to be made of the salinization process (or processes), for cases where freshwater salinity may be caused by direct seawater intrusion, leaching of salt formations, mineral dissolution, or salt accumulation due to evaporation, as often encountered in irrigated areas (Edmunds and Droubi 1998). During the processes of salt formations or mineral dissolution leaching, the stable isotope content of the water is not affected while the salinity of water increases (Fig. 1). This is a unique feature which will enable identification of such processes based on isotopic and geochemical data.

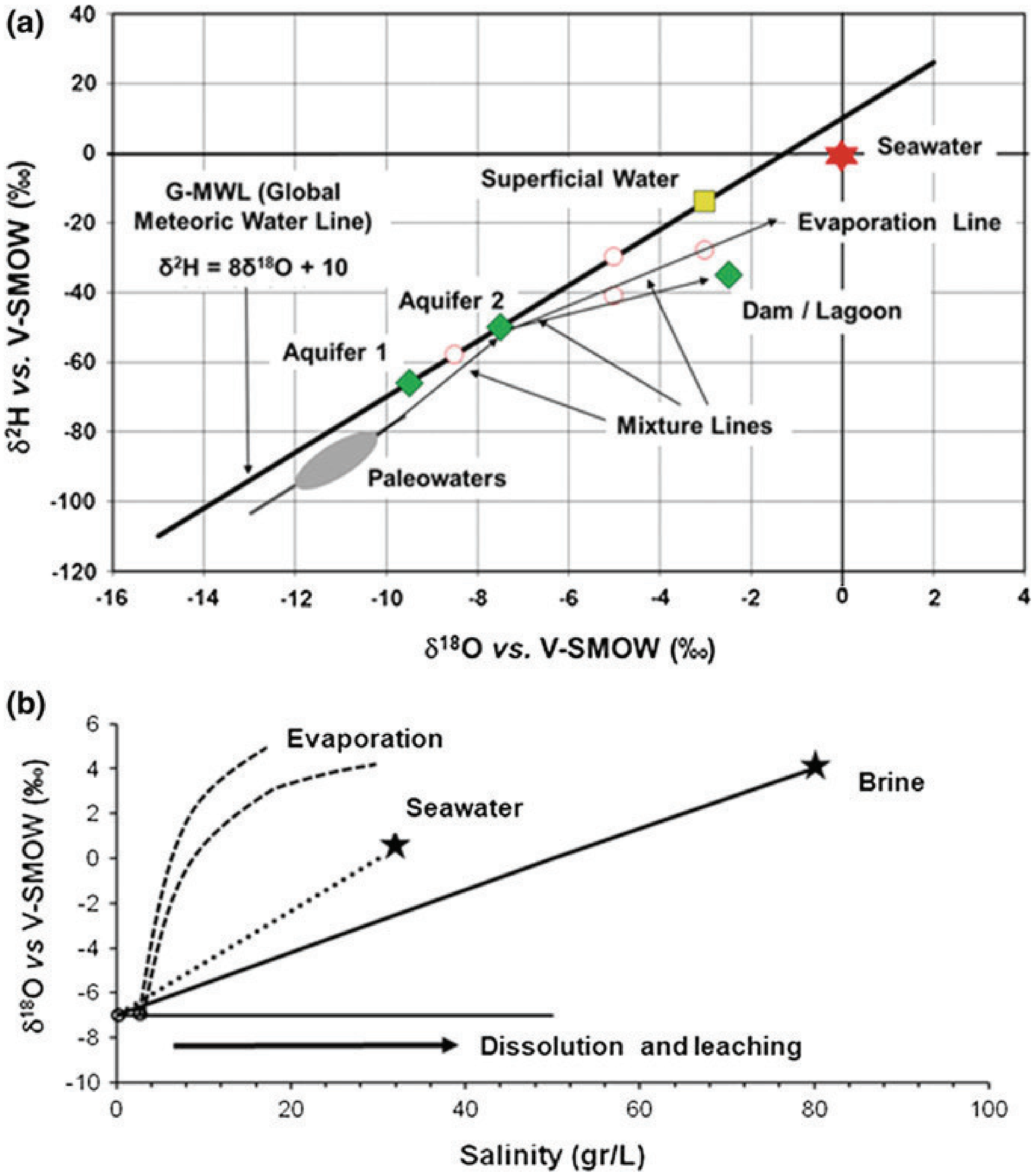

Fig. 1 **a** δ^2H versus δ^{18}O: change in isotopic composition of the groundwater associated with different processes. The symbols Aquifer 1, Aquifer 2, Dam/Lagoon and superficial water stand for hypothetic mean isotopic composition of different water systems. **b** δ^{18}O versus salinity: change in isotopic composition of water, ascribed to different salinization processes

2 Analytical Procedures

At Lower Tagus-lower Sado basin a total of 45 water samples were collected. Stable isotopes (δ^2H, δ^{13}C and δ^{18}O) were measured using a SIRA 10 mass spectrometer, the results are in delta notation (δ), the ^{18}O and ^{2}H are reported to V-SMOW, while ^{13}C reported to V-PDB. Carbon-14 determinations were carried out in the precipitate barium carbonate of the total dissolved inorganic carbon

(TDIC) in situ, and after measured by liquid scintillation counter. The ^{14}C activity is given in pmC (percentage of modern carbon). The tritium measurements were obtained using electrolytic enrichment followed by liquid scintillation counting and the results are in TU (Tritium Units).

3 Results and Discussion

3.1 Hydrogeological Setup

From the geological point of view the Lower Tagus-Lower Sado basin is characterized by a synclinal structure composed by Tertiary sediments, mainly formed by marine deposits (Fig. 2). Three main groundwater systems can be identified in the region: (i) a shallow Quaternary aquifer constituted by alluvial deposits presenting high transmissivity values, underlie by the (ii) Pliocene and Miocene formations. The Miocene deposits are composed by sandstones and limestones of marine origin related with different marine transgression and regression events. These deposits show an average thickness around 200–300 m, although in the central part of the basin these values increase up to 800 m. Finally, (iii) fluvial terraces made of sands and clays represent the Pliocene layers (Fig. 3).

Geophysical studies performed in the region, reveal two important fault systems. The first located in the Lower Tagus valley with a N30ºE direction, and the other the so-called Setúbal-Pinhal Novo fault runs N-S and are responsible for a graben structure which allows the rising of a brine formation or ancient seawater trapped in the sediments (Fig. 3).

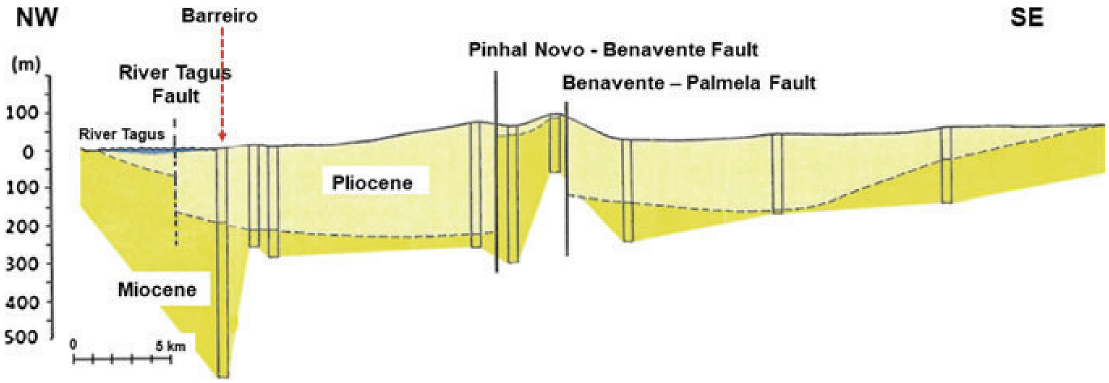

Fig. 2 Schematic cross section of the Lower Tagus-Lower Sado basin (adapted from Simões 1998)

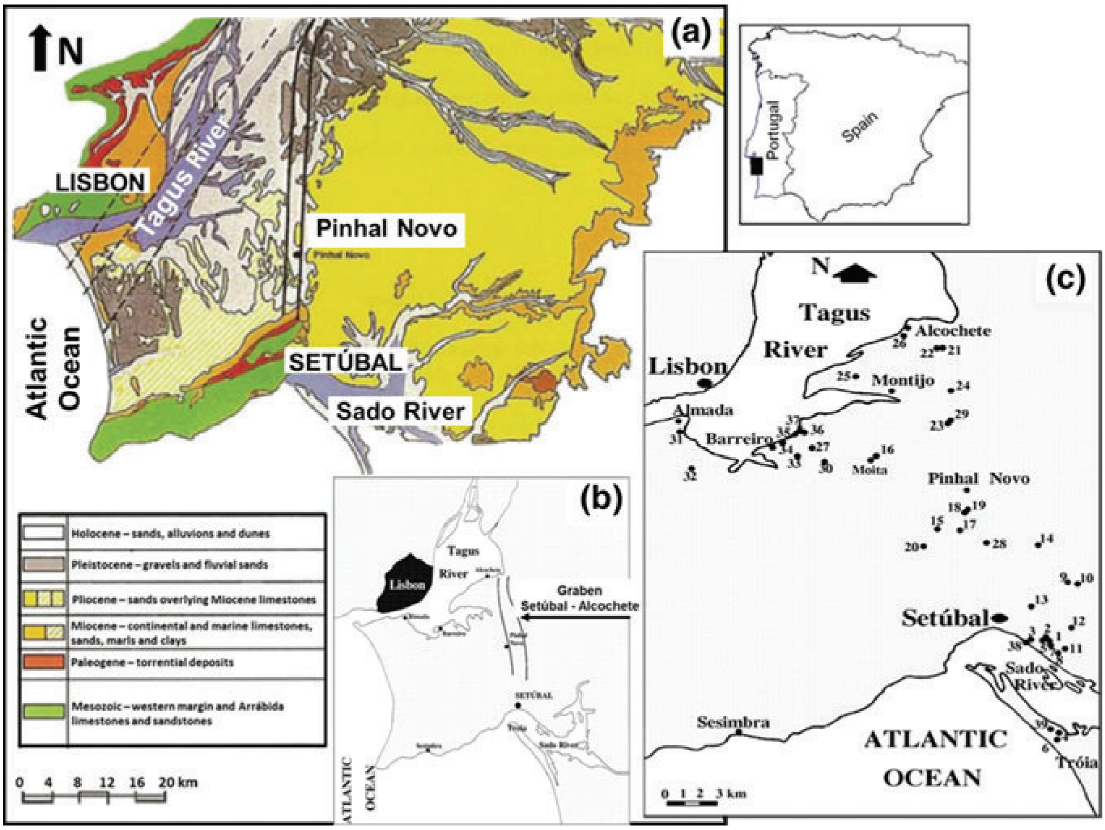

Fig. 3 Sketch of the Lower Tagus-Lower Sado basin. **a** Setubal-Alcochete graben; **b** schematic map of the region; **c** location of the sampling sites (adapted from Simões 1998)

3.2 *Hydrogeochemistry*

The hydrochemical evolution, of groundwaters ascribed to the different aquifer systems, is characterized by a progressive increase in the TDS varying from 80 mg/L up to 2565 mg/L in the Pliocene aquifer while in the Miocene the mineralization ranges between 200 mg/L and 7800 mg/L.

In the central part of the basin, groundwaters are used for human and agriculture supply, and an increase of the water salinization was identified. Two different evolution trends were recognized in the ratio Ca^{2+}/Na^{+}, both apart from the seawater—fresh water mixing line, reflecting flow paths with different Ca^{2+} content (carbonate minerals). Besides the trend observed can be due also to different ionic exchange proportions as the ion exchange mechanism is able to influence the ion concentration of the groundwater, and since the adsorption by the aquifer matrix of Na^{+} with release of Ca^{2+}, is a process which is triggered by intruded seawater (Fig. 4).

The magnitude of ion exchange processes in groundwater chemical composition can be assessed by the equation presented by Pennisi et al. (2006). Those authors combine the Ca^{2+} and Na^{+} with the conservative ion Cl^{-} content of the groundwater samples. Through this approach, the difference between the analytical data and the

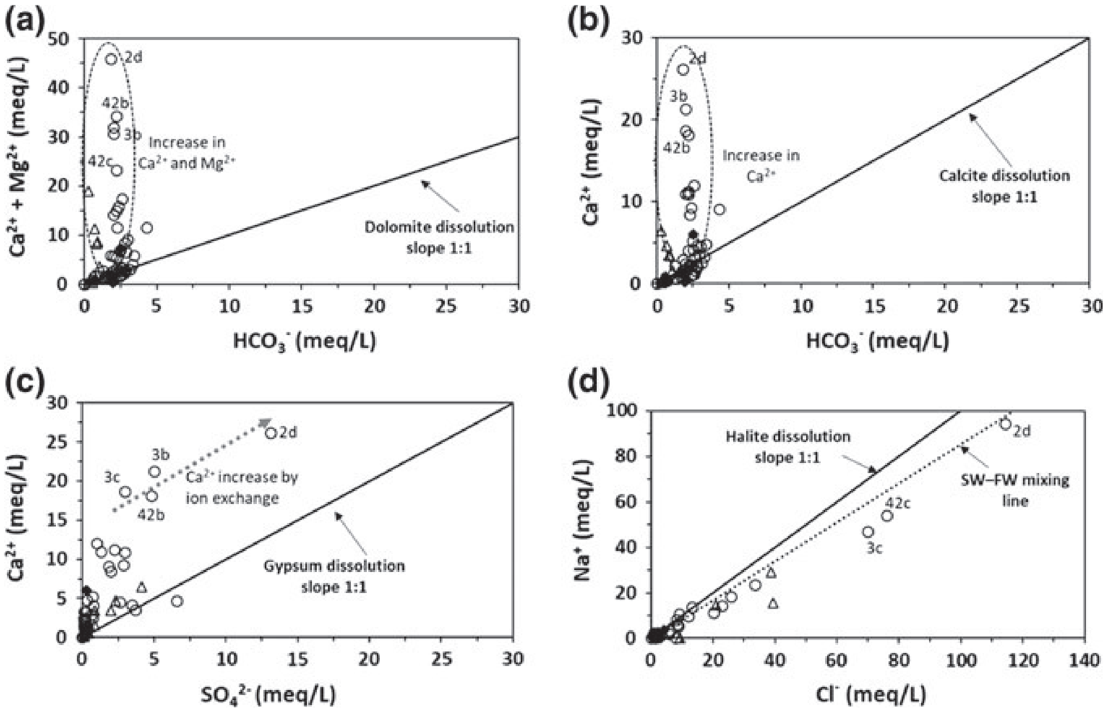

Fig. 4 Water-rock interaction between different solutes for Lower Tagus-Lower Sado groundwater samples: **a** Ca^{2+} + Mg^{2+} versus HCO_3^-; **b** Ca^{2+} versus HCO_3^-; **c** Ca^{2+} versus SO_4^{2-} and **d** Na^+ versus Cl^-. The (Δ) symbols stand for the Pliocene groundwater samples, the (♦) stands for the Mio-Pliocene groundwater samples and (○) for the Miocene groundwater samples from Lower Tagus-Lower Sado basin

expected ion content in the groundwater is calculated if a seawater intrusion mechanism is assumed to be present in the groundwater system (Eq. 1).

$$\begin{aligned}\Delta n\mathrm{X} &= n\mathrm{X(m)} - n\mathrm{X(c)} \\ &= n\mathrm{X} - [n\mathrm{X}(0) + (n\mathrm{Cl(m)} - n\mathrm{Cl}(0))(n\mathrm{X(sea)}/n\mathrm{Cl(sea)})]\end{aligned} \tag{1}$$

The $n_{(\mathrm{m})}$ stands for the measured concentration and $n_{(\mathrm{c})}$ for the expected content by mixing with seawater for ion X, based on the conservative ion Cl^-, where $n_{\mathrm{X}(0)}$ and $n_{\mathrm{Cl}(0)}$ stand for the concentrations of ions X and Cl^- in groundwater not affected by salinization. In the Sado basin, these values represent the mean content of the groundwater samples with an electrical conductivity above 300 µS/cm. The research area is part of a sedimentary basin where cation exchange process can easily occur with the uptake of sodium dissolved in the groundwater and release of calcium, by the aquifer matrix. Most of groundwater samples present Na^+ deficit ($\Delta n_{\mathrm{Na}} < 0$) and an excess of Ca^{2+} ($\Delta n_{\mathrm{Ca}} > 0$), supporting the hypothesis that the missing in sodium and increase of calcium is ascribed to cation exchange mechanisms.

3.3 Isotopic Signatures

For most of the groundwater samples representing the Miocene aquifer no tritium was found, only in three water samples an average content around 1.2 ± 0.5 TU was determined. For all the remaining samples (26) the tritium content was zero TU. Moreover, in the shallow aquifer (Pliocene aquifer) the tritium content varies between 1 and 3 TU.

Radiocarbon was determined in 13 boreholes on the Total Dissolved Inorganic Carbon (TDIC). The ^{14}C content varies from 71.9 ± 0.7 pmC to 88 ± 0.8 pmC in the TDIC of the Pliocene groundwater samples, and from 2.9 ± 0.3 pmC up to 45.6 ± 0.9 pmC in the Miocene groundwater samples.

A common and easy way is to estimate the initial ^{14}C activity, relating the $\delta^{13}C$ content of the TDIC in the groundwater to the mixed carbon from carbonate rocks, with carbon from soil CO_2 and the fractionation factor between the different carbonate phases function of temperature (Salem et al. 1980; Gonfiantini and Zuppi 2003). This simple model was chosen since, in all analysed water samples the Saturation Index (SI) for calcite is lower than −1.69, and in parallel, the $\delta^{13}C$ measured in the TDIC of the groundwater samples is around −10‰.

The estimated apparent carbon-14 ages varies between modern (borehole 5 and 27) in the Pliocene aquifer system, up to 27.9 ± 3.4 ka Before Present (BP) in the Miocene aquifer system (borehole 3). Looking to the apparent groundwater ages, estimated for the deepest aquifer, all the values (with the exception of borehole 31) present ages higher than 15.9 ± 3.2 ka BP, with an average age around 20 ka BP, indicating the presence of paleowaters.

A dispersion groundwater samples with the increase of salinization and apparent groundwater age can be observed pointing out to brine dissolution mechanism in the southern part of the basin (boreholes AC1, JK1 and 38), as the mechanism responsible for the deterioration of the water quality. However, in the northern part of the basin modern seawater intrusion seems to play the major role in the groundwater mineralization in the shallow aquifer (Fig. 5), since the increase of salinization is not followed by a groundwater ageing increase.

In order to corroborate the origin of the groundwater mineralization in the Lower Sado-Lower Tagus basin, the isotopic composition ($\delta^{18}O$) was plotted as a function of the Cl^- content (Fig. 6a). Borehole 2 is plotted on the seawater—fresh water mixing line, followed by the JK1 from the depth aquifer and from Pliocene samples 5 and 27, only the sample AC1 is displaced from this trend. Looking to this distribution pattern the oxygen-18 and deuterium content and chemistry are not sufficient to clarify the groundwater mineralization origin.

Nevertheless, combining all the available information (isotopes and chemistry), is possible to establish a different approach to explain the salts origin: mixing with modern seawater should lead to a ^{14}C activity increase. However, in Sado-Tagus basin this relationship (salinization and age) is not observed. The increase of salts in the groundwater system should be ascribed to ancient seawater trapped in the sediments and coeval of the sedimentary basin formation, allowing distinguishing

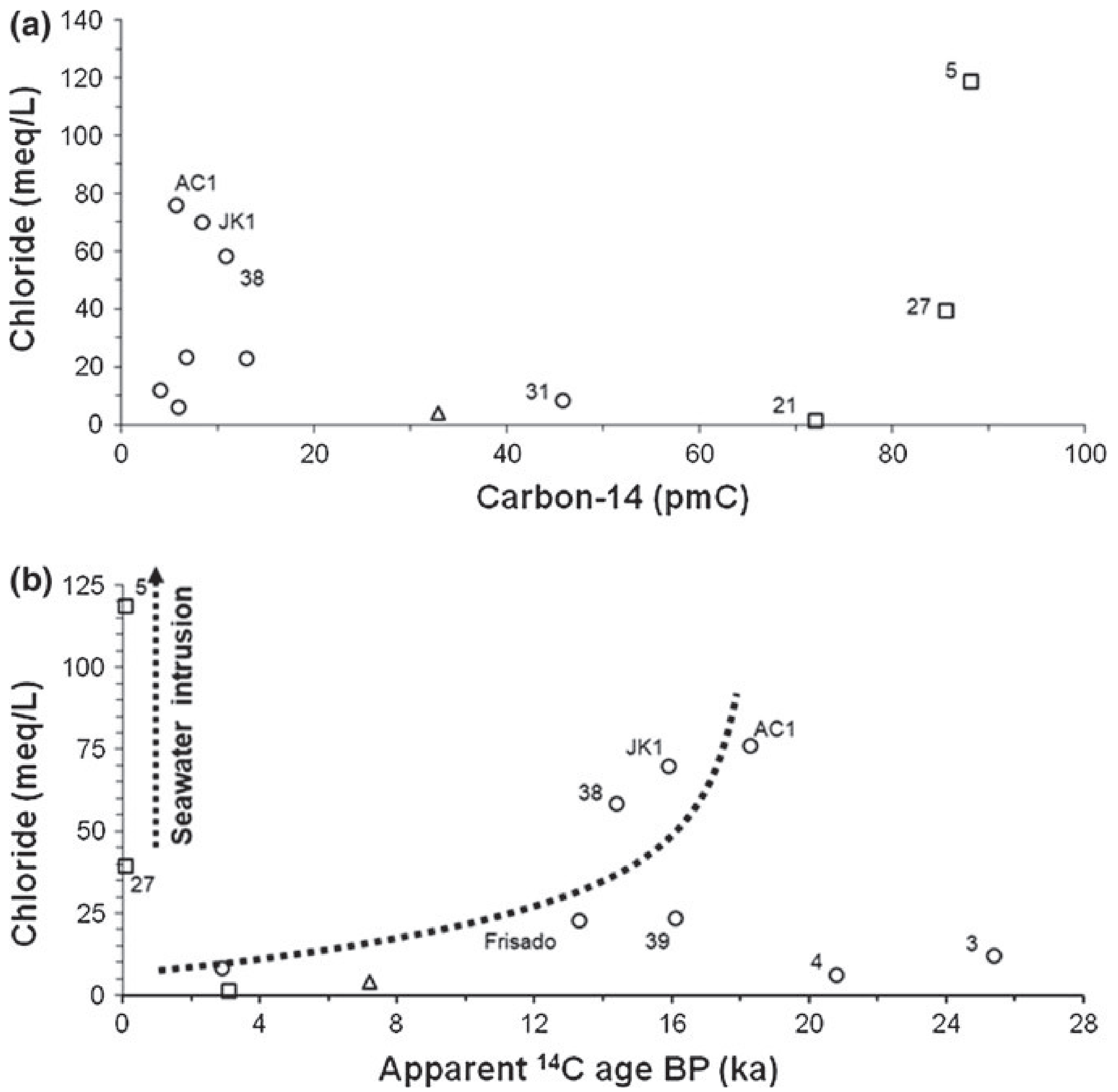

Fig. 5 Results from Lower Tagus-Lower Sado basin: **a** Cl^- versus carbon-14 content; **b** Cl^- versus apparent carbon-14 groundwater age. The (□) symbols stand for the Pliocene groundwater samples, the (Δ) stands for the Mio-Pliocene groundwater samples and (○) for the Miocene groundwater samples from Lower Tagus-Lower Sado basin

paleo-marine and modern seawater intrusion by combining radiocarbon and hydrogeochemical data.

A small enrichment in the heavy isotopes is observed within the groundwater samples, of about 2‰ in deuterium and 0.2‰ in oxygen-18 in Miocene groundwater samples, indicating that the recharge have occurred under different climatic conditions (Fig. 6b).

Similar isotopic enrichment has been also observed in another coastal aquifer in Portugal (Aveiro Cretaceous Aquifer (Carreira et al. 1996) and Morocco (Edmunds 2005). The authors indicate a possible explanation to the heavy isotope enrichment related to the isotopic enrichment of the global ocean during glacial time, due to the preferential storage of isotopically depleted water in the polar ice caps. Aveiro being a coastal aquifer, like the Lower Tagus-Lower Sado, is recharged mainly by

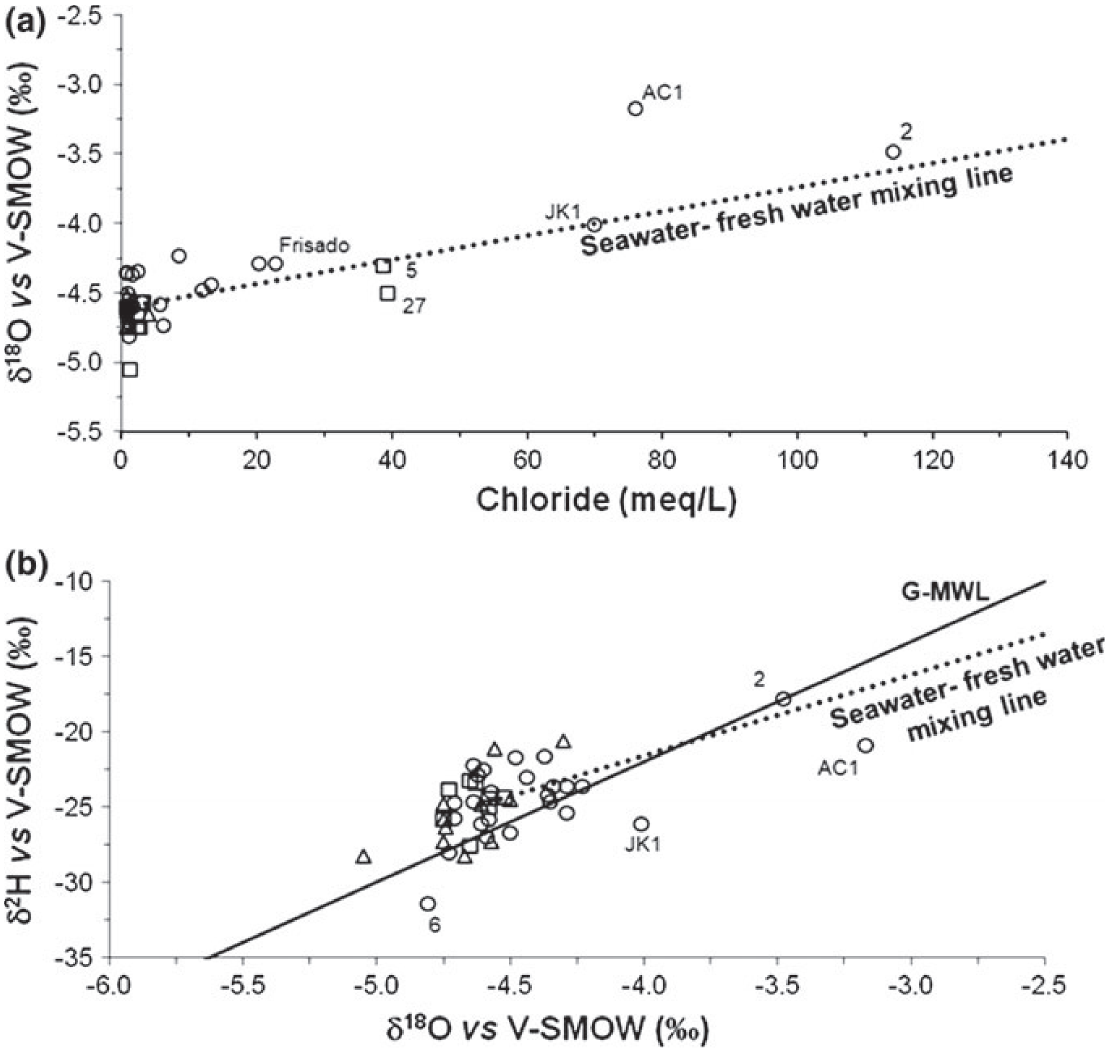

Fig. 6 Results from Lower Tagus-Lower Sado basin: **a** Cl versus $\delta^{18}O$ content; **b** $\delta^{18}O$ versus $\delta^{2}H$, seawater—freshwater mixing line is plotted, G-MWL stands for the Global Meteoric Water Line. Symbols as in Fig. 5

precipitation originating from the first step condensate, this newly formed groundwater may reflect, in the first instance the fluctuations of the isotopic composition of the ocean in the source regions.

4 Final Remarks

Groundwater resources mineralization can be ascribed to different sources such as: agriculture activities; seawater intrusion (active or ancient); dissolution of brines at depth; dissolution of evaporitic minerals dispersed in the geological matrix of the aquifer or even concentrated in saline domes, for example. Under a climate change perspective, groundwater resources of good quality must be considered as strategic resources. A different climatic scenario, under higher mean annual temperatures, associated with a decrease in the precipitation amount, will lead to additional environmental arid conditions in the Mediterranean region.

Salinization of aquifers in coastal areas can be the result of different connected processes related to both seawater intrusion and water-rock interaction mechanisms. Stable isotopes provide an effective label for sea water and freshwater to enable tracing of sea water intrusion, as well as identifying processes that may be responsible for water salinization through the evolution of stable isotope concentration of water during different processes related to water salinization.

In the Lower Tagus-Lower Sado basin the groundwater samples when plotted in a Cl^- versus Ca^{2+} logarithmic diagram, are displaying a Ca^{2+} enrichment, distributed along a pattern more or less analogous to the seawater—fresh water mixing line, most probably ascribed with brine dissolution. On the other hand, the apparent groundwater ages estimated for the Miocene aquifer present an average around 20 ka BP indicating the presence of paleowaters. In the northern part of the basin modern seawater intrusion seems to play the major role in the groundwater mineralization in the shallow aquifer, since the increase of salinization is not followed by a groundwater ageing increase. The use of single tracers (chemical or isotopes data) to identify and characterize salts origin in groundwater systems used alone is much less effective than, used in combination with each other. The combined use of geochemical and isotopic tracers (stable and radioactive environmental isotopes) has proved to be highly effective.

Climate changes, on which seawater rise must be included, add an additional demanding topic in water resources, with spatial-temporal uncertainty as well as vulnerability assessment. The assessment of the evolutional trend on water resources near the coastline under different climate scenarios and spatial-temporal uncertainties is essential for decision making, such as preservation and good management. Demand for good water quality will by consequence, rapidly increase, leading to salinization processes.

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