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ORIGINAL ARTICLE

Environmental isotopes (δ^2H, $\delta^{13}C$, $\delta^{18}O$, ^3H, and ^{14}C) as a diagnostic tool in the appraisal of mineral water management and protection: two case studies—Portugal

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Abstract
Groundwater management and protection must be confronted under ethical and moral concerns, with regulations and water policies for proper and sustainable civilization development. Approximately half of the world population relies on groundwater as the main source of supply, representing a vital requirement for human life and progress. Often in many regions of the world, water authorities are facing scarcity and over-exploitation of the available fresh water reserves. In these circumstances, geoethical aims to represent a way to reach the entire community (water authorities, stakeholders, scientists, and the population in general), focusing on the importance and awareness of water sustainability. In this paper, two case studies from Portugal will be reviewed and discussed aiming to highlight the importance of isotope hydrology as a way to obtain a unique characterization of groundwater resources foreseeing a proper management and sustainability of the groundwater systems. The first case study, Melgaço-Messegães CO_2-rich mineral waters, is located in a granitic environment (NW Portugal). The study allowed to establish the preferential recharge altitude (delimitation of protection limits) based on the δ^2H and $\delta^{18}O$ content; the ^3H data indicates a mean residence time of 40 years; the carbon isotopes ($\delta^{13}C$ and ^{14}C values) highlight methanogenesis and/or mantle-derived carbon as the main carbon source. In the second case study, Moura−Ficalho aquifer (carbonate formations, SE of Portugal), the combined use of geochemical and isotopic (stable and radioactive) data allowed the identification of different (much smaller) flow velocities in the deepest layers of the Moura−Ficalho aquifer and the $\delta^{18}O$ data indicates recharge under different climate conditions.

Keywords Groundwater protection and management · Conceptual circulation model · Groundwater dating · Environmental isotopes · Protection zones

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Introduction

Groundwater represents 30% of the total fresh water availability in the globe, and hence, aquifers often stand for renewable water resources, with different replenishment rates. The global population increase, along with intensive agricultural practices and the rise of industrial use, have led to a growing demand for groundwater (GWP 2014; Boretti and Rosa 2019; Suhoschi 2022). In many regions of the globe, water managers are dealing with water scarcity and over-exploitation of accessible aquifers. Threats of anthropogenic pollution from the spills of contaminants and toxins into the groundwater can be identified all over the globe, ascribed to different sources like agriculture, industry, or urban activities (Re et al. 2014; Altenburger et al. 2015; Marques et al. 2021; Sacchi et al. 2021; Mansour et al. 2021).

As mentioned by Barbieri et al. (2021), not much has been written connecting climate change issues and water quality, a subject still little addressed by the scientific community. Water quantity and water quality are two fundamental issues in terms of water resources protection and management, particularly in regions where climate change is restraining the renewal of surface water systems. The previous authors also call attention to the impact of the population growth acceleration, and the changes in the land use and fertilizers load, all of these contributing to an increase of water withdrawal. Nowadays, in some well-known places of the globe (and in other regions in the near future), it will be expected a change in the water quality due to the climatic change variability, affected by the anthropogenic impact due to water withdrawal and pollution increase (Barbieri et al. 2021; Lasagna et al 2020).

According to Custodio (2021) groundwater management and protection must always be faced with an ethical and moral concern, with regulations like those that are applied to humans, and often ignored in nature and the environment. Water policies must consider water management and infrastructure preconditions for civilization development (UN Water 2022). Clean Water and Sanitation for all is one of the United Nations Sustainable Development Goals (SDG 6), a major target among the water proposals for global sustainable development. In the SDG 2022 Report, special attention is given to the misuse, poor management, over-extraction, and contamination of fresh water and groundwater resources, which have intensified water stress and deteriorated water-related ecosystems, with a direct impact on human health, economic activities, food, and energy supplies. Urgent action is needed to shift this current trend. To ensure a sustainable and equitable distribution of water resources to meet all needs is essential an ethical and moral behavior from stakeholders and the scientific community to achieve the average global implementation rate of improved water resources management (UN SDG 2022).

Groundwater ethics (hydrogeoethics) must deal with present and future scenarios, ascribed to the present climatic change predictions and the present dangerous anthropogenic inputs, from urban wastes, agriculture, and industry, directly or indirectly on the water resources (Peppoloni and Di Capua 2015). Barbieri et al. (2021) call attention to the fact that groundwater is more resilient to climate change if compared with surface water bodies. Even so, the changes in temperature and precipitation will affect groundwater quality, by an increase of anthropogenic pressures in the aquifer systems ascribed to a recharge decrease.

To be moral and geoethically acceptable, the "water community" should be objective, unprejudiced, and scientifically feasible. Hydrogeoethics play an important role in water policy-making, especially for groundwater management. An important issue to be addressed implies the community in general since approaches in science and technology are not unique solutions to environmental problems (Peppoloni and Di Capua 2015; Abrunhosa et al. 2021; Chaminé et al. 2021; Custodio 2021). To achieve a well-aware society with social, environmental, and economic agreements bound, the objectives must be linked to sound ethical and moral goals. In addition, the water scientific community, together with the available technology, must play an important role in water resources policy-making, contributing to the ways to move the objectives towards a higher level of water use, protection, and management (Farahmand et al. 2021).

Although, nuclear techniques have been introduced in hydrogeological studies more than fifty years ago, and the range of applicability has increased worldwide in different interdisciplinary fields, isotope techniques have not been widely used by numerous hydrogeologists and many countries as a routine approach. Most of the hydrological studies that were and are being carried out use traditional techniques like piezometric levels determinations (dynamic and static), maximum extraction flows rates, recharge rates, pumping tests, and hydrogeological parameters like the rock permeability and water conductivity coefficients, and transmissivity, to obtain an aquifer circulation model. These studies are also looking for additional information related to groundwater chemical composition, to check the viability for human consumption. These studies often go further and look for water–rock interaction processes, and analysis of hydrochemical indicators (e.g., ion content, mineral solubility, and saturation index). Parallel to these approaches some mathematical models can simulate the groundwater evolution within the aquifer system, an important issue for groundwater management allowing to predict the groundwater evolution and potential actions to be taken in case of anthropogenic pollution. Nevertheless, the characterization of the water isotopic composition (δ^2H, ^3H and $\delta^{18}O$) of even the isotopic composition of the dissolved components (e.g., $\delta^{13}C$, ^{14}C, $\delta^{15}N$, $\delta^{34}S$), have a key role in groundwater assessment, allowing to go further in the characterization of the groundwater resources.

Among the hydrogeological available technology to investigate and characterize groundwater systems, isotope hydrology can be used to report and characterize the origin and replenishment rates of groundwater. Understanding groundwater dynamics and chemical evolution along the flow path is almost impossible, without calling upon the variability and distribution of the environmental isotopes, namely through δ^2H, $\delta^{13}C$, $\delta^{18}O$, ^3H, and ^{14}C variation content, i.e., stable and radioisotopes naturally present in groundwater systems. Furthermore, groundwater pollution issues are complex. Among the isotope techniques, the use of tritium, carbon-13, and nitrogen content have proved to be an important fingerprint in the identification of main sources and quantification of contaminants (Galego Fernandes et al. 2009; Carreira et al. 2014b, 2019; Gooddy et al. 2016; Re et al. 2017; Zhou et al. 2018; Matiatos et al. 2021). A scientific assessment of the origin and replenishment rate of aquifer systems is critical in fulfilling their function as reliable long-term water supplies, either for human consumption, agriculture, or industrial uses. Stable and radioisotopes naturally present in groundwater can be used to learn more about the origin, mean residence time, and replenishment rates.

The use of isotopic approaches in hydrogeological studies related to water management and protection noted an exponential increase in the last decades. According to Aggarwal et al. (2005), the importance of isotope hydrology in hydrogeological research is being demonstrated by the increasing number of published papers in important scientific journals where isotopes are one of the tools applied in hydrogeological studies. These authors also mentioned that from less than 100 scientific papers on hydrological research from the period 1960–1965, the number increased exponentially for more than 7000 publications from 1995 to 2000. An example of this advancement, is Springer Sustainable Water Resources Management. Since its foundation in 2015 40 research papers were published in the framework of isotope hydrology in water characterization and management developments. The use of isotope hydrology is the result of the development of new measurement isotope techniques (laser absorption spectroscopy) and the increased number of water isotope laboratories (Wassenaar et al. 2012, 2018, 2021).

The environmental isotopes have demonstrated their importance as an indicative tool in the identification and characterization of different hydrological processes occurring during recharge and along the underground flow. Furthermore, this type of approach can give precise information concerning the main origin of groundwater degradation (Re et al. 2014; Altenburger et al. 2015; Marques et al. 2021; Sacchi et al. 2021; Mansour et al. 2021). The application of isotope techniques together with traditional hydrogeological tools can able to provide valuable insights to understand the aquifer systems dynamics, namely in the: (i) identification of mixing processes between different water bodies; (ii) identification of the water salinization origin; (iii) estimation of the preferential recharge altitudes, and (iv) estimation of mean groundwater flow velocities and mean residence time (Ravikumar and Somashekar 2011; Saccon et al. 2013; Hamed et al. 2014; Duckett et al. 2020; Blarasin et al. 2021; Kammoun et al. 2021; Almeida et al. 2022; Bahir et al. 2022; Marques and Carreira 2022).

In groundwater management and protection, the estimation of preferential recharge altitudes often represents a key tool for the proper sustainability of these resources. Stable isotopic signatures of the water (^{18}O and ^2H values), within a regional isotopic context, represent important environmental tracers in the evaluation of water vapor masses moving through the continents, providing the identification of the main source of the recharge. Besides, $\delta^{18}O$ and δ^2H content patterns in precipitation, known in the scientific literature as the "altitude effect", allow to establish protection limits based on the regional isotopic composition. This type of approach is based on the lowering of temperature with increasing elevation in mountain regions. Usually, the increase in altitude leads to condensation and consequently precipitation of the water masses. This evolution implies an isotopic fractionation with depletion of heavy isotopes in precipitation with altitude. This altitude effect has been used in numerous hydrological studies to identify the preferential recharge areas and to investigate the interconnection between water bodies (Araguás-Araguás et al. 2000; Gonfiantini et al. 2001; Darling et al. 2005; Carreira et al. 2009, 2011, 2014a, 2014b; Liotta et al. 2013; Giustini et al. 2016). Besides, in this approach, the regional isotopic composition has been also applied in the identification of palaeowaters; meteoric waters infiltrated under different climatic conditions, for example during a colder period (Carreira 1998; Darling et al. 2003; Galego Fernandes and Carreira 2008; Carreira and Marques 2018; Carreira et al. 2019).

The use of environmental radioactive isotopes in groundwater research allows the estimation of the water age (groundwater dating using, for example, ^3H and ^{14}C content), an indication of the recent recharge−replenishment rates, infiltration rates in the unsaturated zone, flow velocities determination, and delineation of wellhead and aquifer protection zones. Furthermore, the variety of potential information that can be obtained using isotope techniques is unique, and this type of methodology does not require the knowledge of hydraulic proprieties or, in some isotopes, even the knowledge of the aquifer matrix. Among the isotopic approach of dating modern groundwater (within 50–60 years), tritium is often used in the characterization of shallow groundwater systems as an indicator of aquifer vulnerability to anthropogenic actions. Besides, the tritium content is used in the characterization of groundwater dynamics and identification of mixing between different water (e.g., Ravikumar and Somashekar 2011; Hamed et al. 2014). Furthermore, the seasonal ^{3}H variations in the atmosphere, the so-called spring leak (Rozanski et al. 1991; Mook 2000), can be used as a fingerprint of an active recharge of the aquifer, in relatively shallow groundwater systems.

The tritium content in the atmosphere/precipitation is the result of two distinct processes: (i) a natural origin—in the upper layers of the atmosphere from the reaction of (thermal) neutrons, produced by the interaction of cosmic rays with nitrogen atoms; (ii) an artificial (anthropogenic) origin—as result of thermonuclear bombs, nuclear reactors, and reprocessing units, for example. Regardless of its origin, natural or artificial, ^{3}H in the atmosphere is rapidly oxidized to atmospheric water vapor ($^{1}H^{3}HO$) and enters the Hydrological Cycle through precipitation and isotopic exchange between air and ocean water bodies (Mook 2000).

The main advantage of groundwater dating with tritium is ascribed to its behavior, i.e., the ^{3}H content in the groundwater is not affected by microbial degradation, retardation, absorption, and chemical processes with the aquifer matrix, and does not change in contaminated reducing environments. Conversely, the disadvantages are significant, namely, the natural limits and the actual concentration of ^{3}H in the atmosphere that make it difficult to apply this isotope in a quantitative way (groundwater dating). However, the content measured in the water systems allows a different type of approach, i.e., in a qualitative way.

Carbon-14 present in the Carbon Cycle has its origin connected with two distinct processes, similar to tritium: a natural origin, resulting from the interaction of cosmic radiation with nitrogen atoms in the upper layers of the atmosphere, and, an artificial origin, related to anthropogenic activities, like nuclear power plants, nuclear reactors, and thermonuclear power tests. The ^{14}C atoms in the atmosphere, after oxidation, will be part of the carbon dioxide ($^{14}CO_2$) molecules that will be mixed with non-radioactive atmospheric CO_2, and subsequently, participate in the Carbon Cycle, i.e., in the bio, litho, and hydrosphere reservoirs.

Carbon enters the hydrological cycle mainly by chemical processes associated with the dissolution of atmospheric and soil CO_2 (plant respiration) and/or through the dissolution of carbonate minerals (aquifer matrix). When carbon in the aqueous system is primarily of biogenic origin (soil CO_2), the activity of ^{14}C of a water body characterizes exclusively the activity of this species of organic origin. However, in most groundwater systems the carbon dissolved in water is of organic and mineral origin, i.e., the ^{14}C activity will reflect the percentage of mixing between the different C sources. The different carbon origins pose limitations in groundwater dating with carbon-14. Nonetheless, understanding the mean residence time of the groundwater allows the acquisition of information regarding a high or low vulnerability to anthropogenic actions, important for the proper management and protection of water resources.

Beyond the light "state of the art" of some stable and radioactive isotopes behavior in the hydrological cycle, in this paper two case studies will be reviewed and discussed, in which the isotope hydrology combined with other Geosciences tools, proved to be essential in the characterization of different types of groundwater resources, showing how the use of nuclear techniques (environmental isotopes interpretation) are fundamental in decision making for the proper management of water resources. A comparative study of two hydromineral aquifers located in the Portuguese mainland will be presented: Melgaço CO_2-rich mineral waters, located in a granitic environment (NW Portugal), and Moura−Ficalho aquifer, located in carbonate formations (SE of Portugal). Knowledge of mean preferential recharge altitude, groundwater flow paths, identification of mixing processes, and groundwater dating are important tools for (i) the development of hydrogeological conceptual circulation models and (ii) proper management and protection of the aquifer systems. The combination of isotopic and geochemical data interpretation in a hydrogeological context will be reviewed and discussed, bearing in mind that the main objective is the demonstration of the importance of applying nuclear techniques in groundwater characterization as additional tools to traditional hydrological approaches. In addition, a secondary objective was achieved in the Moura−Ficalho aquifer where it was possible the identification of paleoclimate fingerprints encoded in groundwater composition (stable isotopic signatures), representing potential past climatic archives. Through the use of this type of hydrogeological methodology, the authors would like to call attention to the fact that "hydrogeoethics" is not simply professional geoethics, but also important for the awareness of hydrogeoscientists to the cultural and social role that all should play to provide protection and respect for geoecosystems.

The main goal of this work is to present and validate how isotope hydrology can help geoscientists, water authorities, and stakeholders to have a more proactive and geoethical attitude. The combination of isotopic and geochemical data interpretation in a hydrogeological context will be reviewed and discussed, bearing in mind that the main objective is the development of conceptual hydrogeological circulation models, key issues for good management of the groundwater resources, in which isotope hydrology can fill up inaccuracies, gaps, and misconceptions occurring during hydrogeological research.

Since in the present work, the review of two hydrogeological case studies, in the Portuguese mainland, will use similar methodological approaches, in both cases, the structure will be the same, and as follows:

- Geological and hydrogeological setting;
- Hydrogeochemical approach;
- Isotopic assessment;
- Concluding remarks.

Sampling and analytical approach

Melgaço region (N Portugal—granitic environment)

Groundwater samples were collected along 3 fieldwork campaigns (02/2002; 02/2006 and 07/2006) from boreholes (CO_2-rich mineral water systems) and springs (at different altitude sites) representative of the shallow cold dilute groundwater systems (Carreira et al. 2014a). The chemical analyses were performed at Centro de Petrologia e Geoquímica do Instituto Superior Técnico (CEPGIST), using the following analytical methods: atomic absorption spectrometry for Ca and Mg determinations; emission spectrometry for Na and K analysis; colorimetric methods for dissolved SiO_2, Fe_{total}, F and Al quantifications; ion chromatography for SO_4, NO_3, and Cl concentrations; potentiometry for alkalinity measurements (here referred to as HCO_3), carried out at CEPGIST laboratory. The quality control was based on the ionic balance calculation for each water sample. The isotopic composition was determined at Centro de Ciências e Engenharias Nucleares do Instituto Superior Técnico (C^2TN/IST) laboratories, previous Instituto Tecnológico e Nuclear—ITN). The δ^2H and $\delta^{18}O$ measurements (vs. V-SMOW) were performed by mass spectrometry (SIRA 10–VG ISOGAS) following the analytical methods proposed by Friedman (1953) and Epstein and Mayeda (1953), and the results were reported in δ notation. The accuracy is ± 1‰ for δ^2H and ± 0.1‰ for $\delta^{18}O$. The ^3H content of the water samples (reported in Tritium Units, TU) was determined using electrolytic enrichment followed by liquid scintillation counting (PACKARD TRI-CARB 2000 CA/LL), standard deviation ranges between ± 0.6 and ± 1.1 TU, depending on Tritium content in the water sample (IAEA 1976).

The $\delta^{13}C$ and ^{14}C determinations were performed at the Geochron Laboratories/USA by accelerator mass spectrometry (AMS), in the Total Dissolved Inorganic Carbon. The $\delta^{13}C$ values are reported in ‰ *vs.* V-PDB, with an accuracy of ± 0.1‰. The ^{14}C content is given in pmC (percentage of modern Carbon).

Moura–Ficalho region (S Portugal—limestone environment)

Between July and September 2014, two fieldwork campaigns were carried out in Moura–Ficalho region to collect groundwater samples and to achieve an isotopic characterization of Moura–Ficalho hydromineral system (Carreira et al. 2019). Water samples were collected for δ^2H, $\delta^{13}C$, $\delta^{18}O$, ^3H, and ^{14}C determinations in 5 boreholes and 1 representative spring of the deeper hydromineral system, and 2 springs from the shallow cold dilute groundwater systems. Temperature, pH, and electrical conductivity were measured in situ.

Chemical determinations (Na, K, Ca, Mg, Li, HCO_3, SO_4, Cl, NO_3, F, and SiO_2) were performed at Laboratório Nacional de Engenharia e Geologia—Portugal (LNEG) laboratory, namely by atomic absorption spectrometry (for Ca and Mg), emission spectrometry (for Na and K), colorimetric methods (for dissolved SiO_2, Fe_{total}, F and Al), ion chromatography (for SO_4, NO_3 and Cl) and potentiometry for alkalinity measurements (here referred to as HCO_3). The quality control was based on the ionic balance calculation for each water sample. The isotopic determinations were performed at C^2TN/IST. The δ^2H and $\delta^{18}O$ contents in the water samples were determined by laser spectroscopic analysis (LGR-24d from Los Gatos Research), and the results were reported in δ notation (‰ vs V-SMOW). The $\delta^{13}C$ and carbon-14 content were measured in the total dissolved inorganic carbon (TDIC) extracted in the field as $BaCO_3$ in a pH environment higher than 9.0 (IAEA 1981). In the laboratory, along a vacuum line, chemical reactions converted the $BaCO_3$ into benzene. The counting rates of the ^{14}C were obtained using a liquid scintillation counter (PACKARD TRI-CARB 4530). The errors associated with this technique increase with the decrease of the ^{14}C content in the sample. It is important to mention that the errors associated with this methodology began with the sampling method (converting all the inorganic carbon dissolved in the water to barium carbonate, open atmosphere to CO_2), and after, in the laboratory, the errors can be ascribed to the change of $BaCO_3$ to CO_2 and after to benzene. The ^{14}C content in the TDIC is expressed as a percentage of modern carbon (pmC). During the benzene synthesis, a CO_2 gas sample is collected for $\delta^{13}C$ determination, and measured by mass spectrometry using a SerCon Geo 20–20 mass spectrometer. The isotopic composition of $\delta^{13}C$ is reported to V-PDB in ‰, with an associated error of 0.1‰. Tritium content in the water samples was determined using an electrolytic enrichment method followed by liquid scintillation counting measurements (PACKARD TRI-CARB 2000 CA/LL). The associated error is ≈ 0.6 TU, varying with the tritium concentration in the water samples. The analytical method is described in IAEA (1976).

Case study 1—Melgaço-Messegães hydromineral system

Geological and hydrogeological setting

Melgaço-Messegães CO_2-rich mineral groundwater system is located in the NW Portugal, in a geological environment mainly composed of granitic and granodioritic rocks (Fig. 1). Regionally three types of granitic formations are recognized in the region, considering their internal deformations and structural relationships (Ribeiro and Moreira 1986; Moreira and Simões 1988). These authors proposed the following groups: (i) syntectonic granites with flakes of muscovite, biotite, and metamorphic minerals and strongly correlated with migmatitic rocks; (ii) late tectonic granites associated with granodiorites, exhibiting the abundant presence of biotite and muscovite. The internal deformation points to an origin linked to the last Hercynian deformation phase; and (iii) post-tectonic granites: usually characterized by the presence of mega-crystals of K-feldspar and biotite (Ferreira et al. 1987). Fluvial deposits, sandstones, and conglomerates of Quaternary age are the most recent geological formations in the region usually found along the Minho River banks. The main fracture systems are represented by strike-slip faults, predominantly ENE-WSW, WNW-ESE, NNE-SSW, and NNW-SSE (Fig. 1).

According to Soares de Carvalho (1992), these linear structures are of late Hercynian age, and still active during the Meso-Cenozoic. The regional geomorphology is well-marked by the contrast between the high plateaus at the top of individual remnant blocks and the carved valleys controlled by these fractures. The geomorphologic structures range from 100 m a.s.l along the Minho River banks to altitudes in the order of 800 to 900 m a.s.l in the SE area of the region. The CO_2-rich mineral waters issue along NNW-SSE fractures.

Water geochemistry and isotope fingerprints

Hydrogeochemical approach

A huge difference is observed in the mineralization between Melgaço-Messegães CO_2-rich mineral waters and the regional shallow cold dilute groundwater systems; the mineral waters are characterized by a dry residuum (DR) between 365 and 1515 mg/L, while the shallow cold dilute

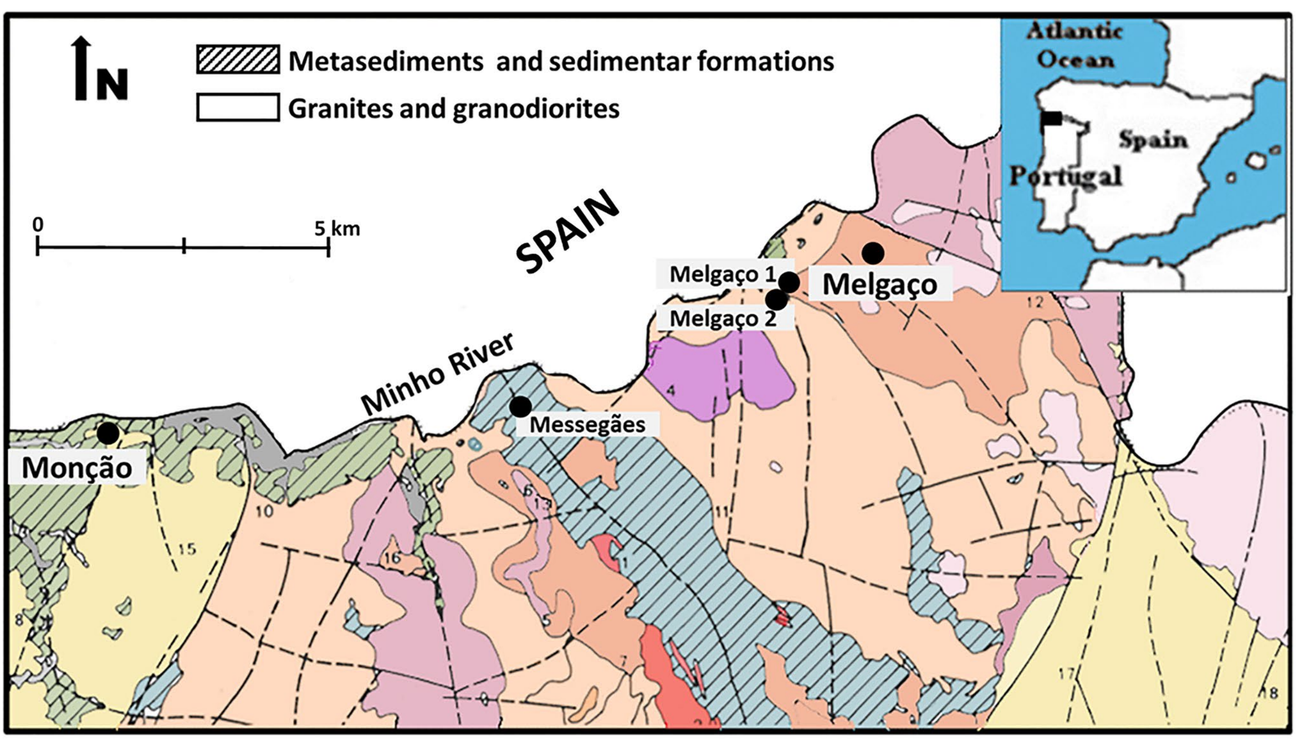

Fig. 1 Simplified geological map of the study region. Filled circle marks the location of the mineral water boreholes. The filled areas represent the metasedimentary rocks and sedimentary formations; the solid filled areas stand for granites and granodiorites. Adapted from Ribeiro and Moreira (1980)

groundwaters show a DR between 24 up to 120 mg/L, as Table S1. In the shallow groundwater systems, a correlation between the groundwater temperature with the time of the year (15.0 ºC in February to 18.3 ºC in July) was identified pointing to relatively shallow groundwater flow paths. The temperature fluctuation is not clear in the CO_2-rich mineral groundwater system, indicating a deeper circulation; the values range from 16.2 °C at Messegães to 19.5 °C at Melgaço2. The geochemical facies of the mineral and shallow groundwater systems are also different; the CO_2-rich mineral waters are Ca-HCO_3 and Na-Ca-HCO_3-type waters, while the local shallow cold dilute groundwater are Na-HCO_3-type waters (Fig. 2).

The high CO_2 gas content found in the CO_2-rich mineral waters is responsible for the water–rock interaction increase promoting the feldspars hydrolysis. In fact, as stated by Criaud and Fouillac (1986) and by Greber (1994), in CO_2-rich hydromineral systems, CO_2 gas can play an important role in influencing the physical and chemical signatures of the fluids, enhancing water–rock interaction knowing that the solubility of CO_2 in water increases with decreasing temperature. The chemical facies (Ca-HCO_3 type) of the CO_2-rich waters suggests interaction with Ca-rich plagioclases (hydrolysis) along the underground flow paths occurring in granodioritic terrains (Ribeiro and Moreira 1986; Farias et al. 1987). Different geochemical signatures can be observed within the shallow cold dilute groundwater systems, ascribed to the different samples location, frequently downhill in areas of intensive agricultural activities, being the Human impact enhanced by the increase in NO_3^-, Cl^- and SO_4^{2-} content (Fig. 2).

Oxygen-18 and deuterium assessment

The Local Meteoric Water Line (Fig. 3a) was defined using the isotopic composition of the local shallow cold dilute groundwater samples (Local MWL, $\delta^2H = 7.85\ \delta^{18}O + 9.42$, data in Carreira et al. 2014a; as Table S2). The equation obtained is similar to the Global MWL defined by Craig in 1961 (Mook 2000). In this study, the "altitude effect" was used successfully in the estimation of the preferential recharge areas of the CO_2-rich mineral waters. Likewise, through the isotopic composition of the water samples, the possible interconnection between the two groundwater systems was investigated. The data from the scientific literature point to a mean isotopic gradient (isotopic depletion) varying between − 0.15 to − 0.5‰ in $\delta^{18}O$, and in δ^2H, from − 1.5 to − 4 ‰ per l00 m of elevation. According to Mook (2000), the average rate of isotopic depletion in ^{18}O content is around − 0.26‰/100 m. At the Melgaço area the isotopic gradient obtained for $\delta^{18}O$ was − 0.15‰ per 100 m of altitude (Fig. 3b). This result is in conformity with the literature data, using the discharge altitude of the spring waters (shallow cold dilute groundwater systems) instead of the infiltration altitude, since these spring waters are representative of local/shallow circulation systems. The

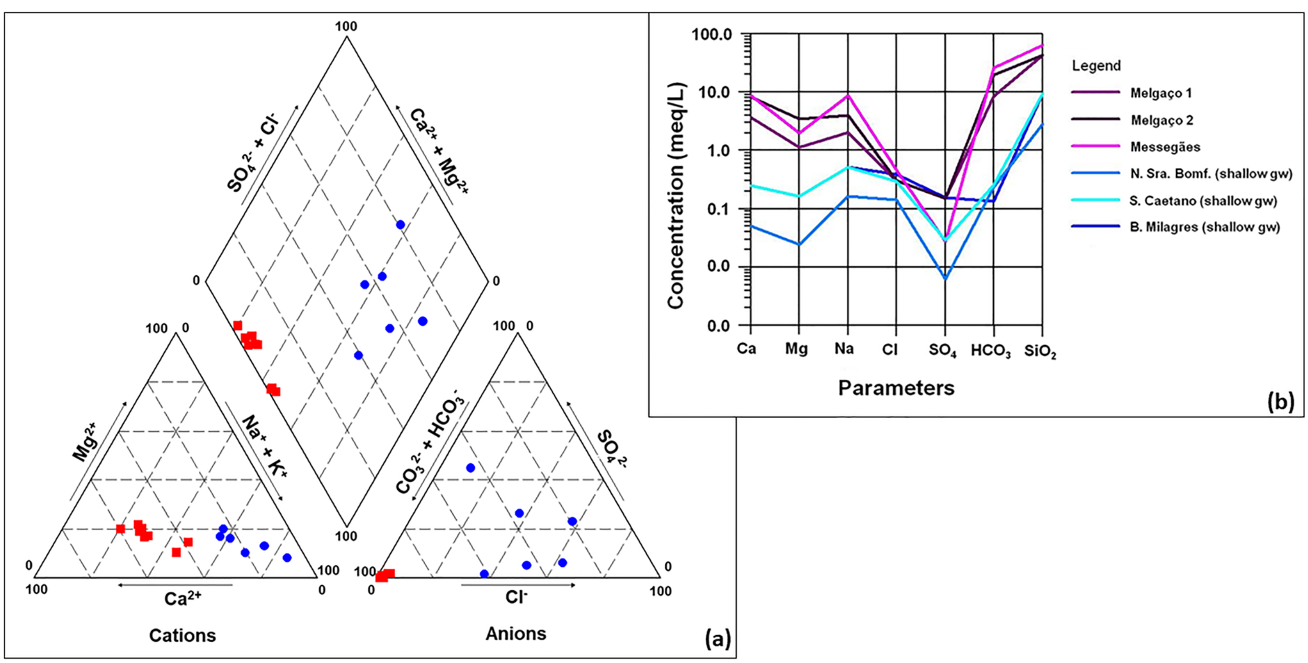

Fig. 2 **a** Piper diagram of Melgaço and Messegães CO_2-rich mineral waters. The symbol (blue circle) stands for shallow cold dilute groundwater systems and (red square) for CO_2-rich mineral waters. **b** Schoeller plot, where the mean chemical composition of the shallow cold dilute and CO_2-rich mineral waters (Melgaço 1; Melgaço 2 and Messegães) is represented

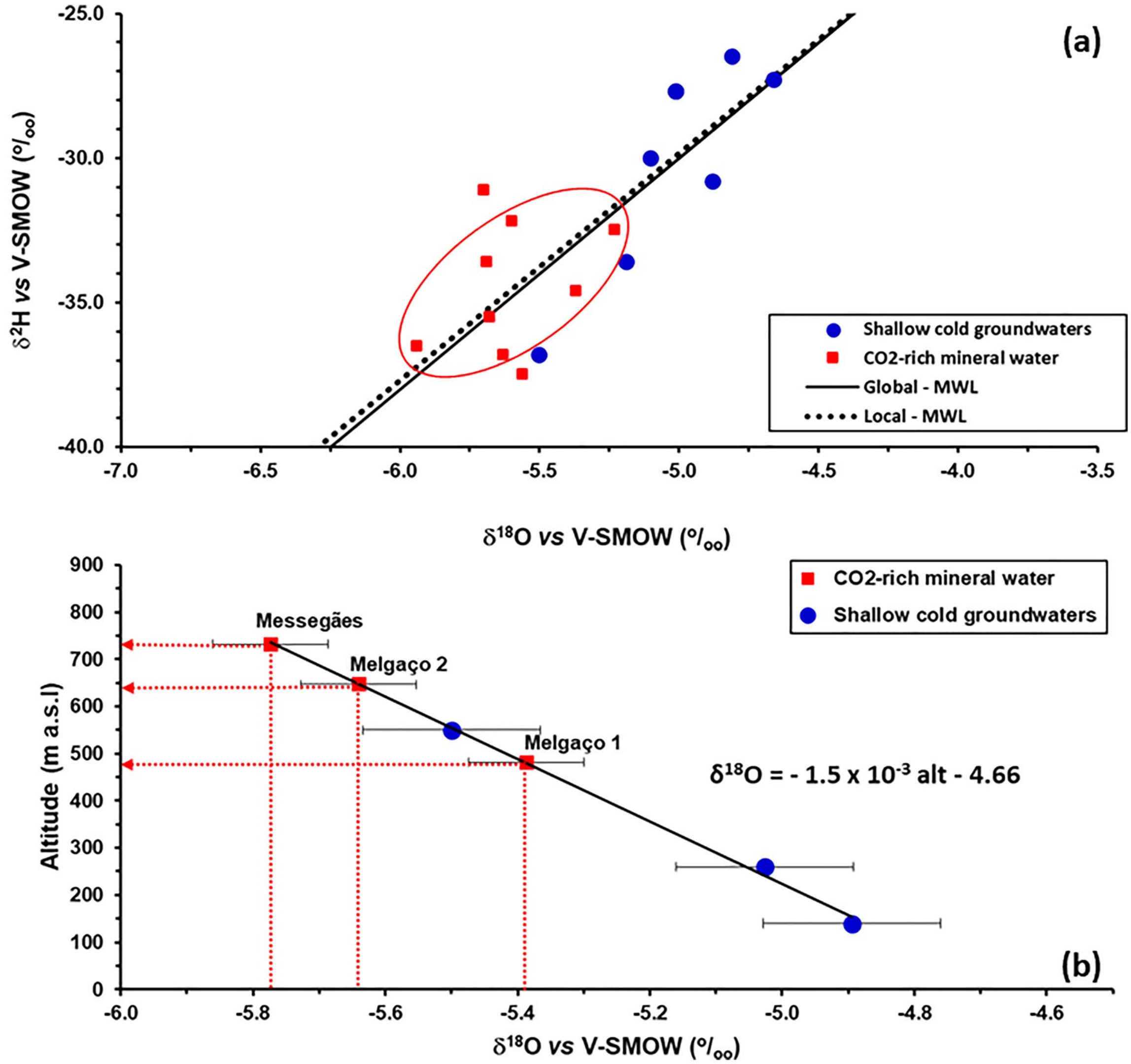

Fig. 3 **a** δ^2H *vs.* δ^{18}O from Melgaço area. **b** Estimation of the recharge altitude of the CO_2-rich mineral water systems using $\delta.^{18}$O values (adapted from Carreira et al 2014a)

preferential recharge altitudes of the CO_2-rich mineral water were calculated applying the altitude gradient equation. The obtained values range between 480 m a.s.l (Melgaço 1) and 730 m a.s.l. (Messegães). These elevations are pointing to a recharge area located south of Minho River towards Peneda Mountain (Carreira et al. 2014a).

Tritium and carbon-14

In the studied shallow cold dilute groundwater systems, the ^{3}H content ranged between 5.2 ± 0.6 TU (October 1999) and 2.1 ± 0.6 TU (February 2003). The CO_2-rich mineral waters show the lowest ^{3}H concentrations from 0 TU up to 2.2 TU (Carreira et al. 2014a). The lowest ^{3}H values are found in the water samples that have the highest mineralization, pointing to a longer circulation path and higher water–rock interaction (Fig. 4). The Messegães CO_2-rich mineral borehole water, with the higher recharge altitude (730 m a.s.l.), has the lowest tritium content indicating a higher residence time favoring water–rock interaction (Carreira et al. 2014a). The ^{3}H half-life is 12.32 years (Lucas and Unterweger 2000) which makes tritium an ideal tracer in the identification of active recharge of the aquifers systems. In addition, being part of the water molecule, the geochemical reactions with soil gases and possible biogeochemical reactions will not affect its abundance, reason why ^{3}H is the ideal tracer for recent recharge events (Cartwright et al. 2017). Considering the tritium input found in the Porto meteorological station (4.5 TU – mean arithmetic weight value, in Carreira et al. 2006), at least 40 years of mean residence time should be considered for the hydromineral systems (Carreira et al. 2014a).

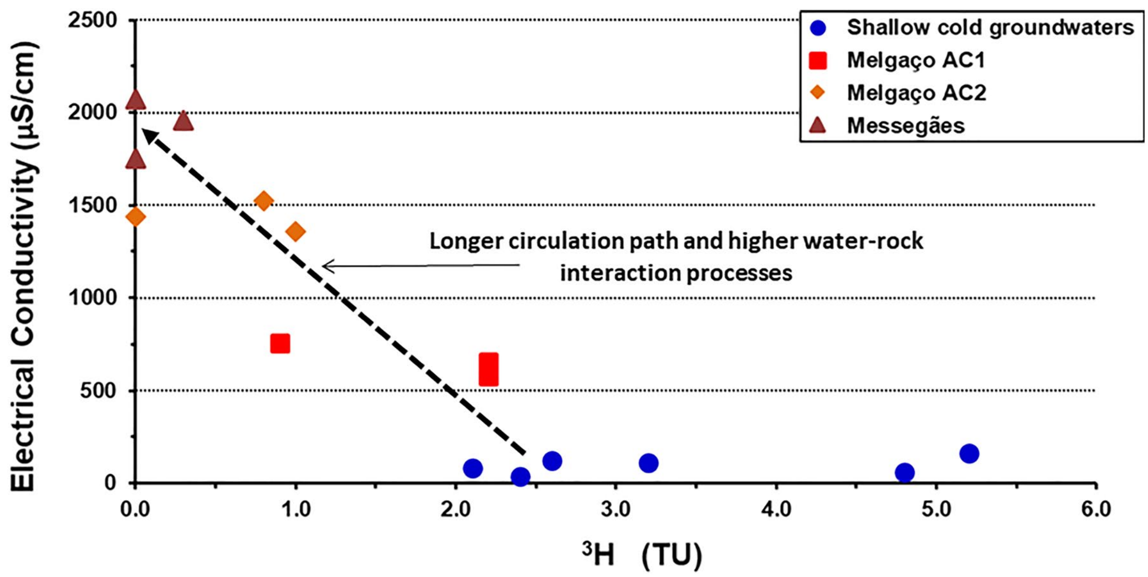

Fig. 4 Electrical conductivity vs. tritium (^{3}H) content

According to Carreira et al. (2014a), based on low ^{14}C content and positive δ^{13}C composition: $^{14}C = 2.33 \pm 0.07$ pmC and $\delta^{13}C = 4.7‰$ (Melgaço 1), and $^{14}C = 1.01 \pm 0.04$ pmC and $\delta^{13}C = 4.7‰$ (Melgaço 2), these CO_2-rich mineral waters seem to represent very old groundwater systems. Considering the geological and structural setup of the region, those authors suggested a deep-seated—upper mantle CO_2 source for the CO_2-rich mineral waters together with methanogenic processes (redox reactions involving methane) leading to the δ ^{13}C positive values.

Melgaço-Messegães: concluding remarks

The oxygen-18 content of Melgaço-Messegães of CO_2-rich mineral waters favor a conceptual circulation model where the preferential recharge area (between 480 and 730 m a.s.l) is located south of Melgaço, at Peneda Mountain. Groundwater flow paths are connected to the regional fault systems, issuing these waters when appropriate conditions are created. The preferential recharge altitudes agree with a longer circulation path (low tritium content) for Messegães CO_2-rich mineral water and a shorter circulation path associated with Melgaço 1 mineral water. The δ^{13}C determinations carried out on TDIC of the CO_2-rich mineral waters are pointing to the hypothesis of: i) methanogenesis (^{13}C enrichment) and ii) mantle-derived CO_2 inducing a decrease in the radiocarbon content in the TDIC to negligible values.

Case study 2—Moura–Ficalho hydromineral system

Geological and hydrogeological setting

Located on the left bank of the Guadiana River, Baixo Alentejo region (S of Portugal) Moura–Ficalho aquifer is ruled by the existence of a karst-fissured aquifer, settled between Vila Verde de Ficalho and Moura. The Moura–Ficalho aquifer system is located in a Portuguese semi-arid region, where water managers are dealing with annual low recharge rates, water scarcity, and sometimes over-exploitation of accessible water resources. Moreover, anthropogenic pollution ascribed to urban activities and agriculture is a major issue of concern. This groundwater resource is the main and most extensive aquifer of the region. A comprehensive study of this aquifer was initiated by Costa before 1991 (Costa 1991; Ribeiro et al. 2002), and later reinitiated in 2014 by Carreira et al. (2019). With a total area of 187 km^2 of which 85 km^2 correspond to outcrops of carbonate rocks. Considering the regional annual weak precipitation values, for continuous development of the region from an urban, industrial and agricultural point of view, is essential a good knowledge of Moura–Ficalho aquifer system, regarding proper hydrogeoetical exploitation of these groundwater resources.

The Moura–Ficalho aquifer is mainly composed of Lower Cambrian carbonate layers mostly represented by dolomites, calcitic marbles, and dolomitic limestones (Oliveira 1991). Three main reliefs with SE-NW direction dominate the region; these elongated hills represent anticlinal folds of carbonate rocks. The base of the aquifer is made of impermeable black schists (Costa 1998). The average thickness of the Moura–Ficalho aquifer is large; the top of the aquifer was intersected at 84 m depth (Moura village) while the base lies below 690 m (Costa 1998). According to hydraulic studies, a double hydraulic conductivity was identified in the aquifer, connecting two distinct flow networks; one more superficial characterized by high-velocity flow through big karstic conducts, and a second, deeper, characterized by low velocity flow through small fractures or openings. According to Costa (2008), the storage capacity of the Moura–Ficalho aquifer is dependent on the small fractures network, although both network fractures (the more superficial and the deeper ones) are present in the aquifer flow (Fig. 5).

Water geochemistry and isotope fingerprints

Hydrogeochemical approach

In the Moura–Ficalho aquifer system, groundwater circulation occurs mainly in a carbonate environment, responsible for the Ca/Mg–HCO_3 facies. The groundwater pH is around 7.4 and the electrical conductivity varies between 724 µS/cm and 1063 µS/cm. The relatively high conductivity values found in this carbonate system are attributed to the water–rock interaction namely with the Cenozoic detrital deposits covering the recharge zone of the mineral aquifer, responsible for the Cl and Na concentration in the water systems (Costa 2008). In this region, an increase in the agricultural areas over the last decade was reported, being responsible for the increase of nitrate content in the aquifer (Fig. 6a; as Table S3), although concentrations do not exceed 40 mg/L (Costa 2008). In Fig. 6b, Casal de Sto. André, with the higher bicarbonate content (496 mg/L) and the lowest Cl concentration (45 mg/L), is isolated from all the remaining water samples.

All water samples are saturated with respect to calcite and to dolomite; the $SI_{calcite}$ varies between 0.3 and 0.7 in Casal de St. André and Três Bicas springs, respectively, and the $SI_{dolomite}$ between 0.4 at Messangil spring, up to 1.1 at Três Bicas spring (Fig. 6c, d). According to Costa (2008) and Carreira et al. (2019), the variation in the saturation indexes of the water is due to the lithological heterogeneities found in the region. In the Piper diagram representation (Fig. 7), only Casal de Sto. André groundwater is plotted apart, "isolated" from all the remaining samples. Casal Sto. André groundwater sample has the highest Mg^{2+} and HCO_3^- content and the lowest Cl^- and SO_4^{2-} concentration, indicating large water–rock interaction processes with dolomite rocks. In the region, diffuse sources of pollution associated with local industry, are well known. This local industry, located near Moura village, uses brine processes for food conservation and seems to be the cause/origin for the increase in Cl and Na contents, measured in the groundwater, not expected in a karstified carbonate aquifer far from the coastal region and without saline domes.

In karst systems, the water flows rapidly through the conduits with occasional opportunities to be filtered (Goldscheider et al. 2010). Pollutants can travel over larger areas as anthropogenic inputs like fertilizers and pesticides, or from agricultural soils enriched with nitrogen, phosphorous, and heavy metals, for example, representing diffuse pollution sources (Van der Perk 2007; Azzaz et al. 2008; Lepiller et al. 2007; Foster et al. 2013; Marques et al. 2013). This can therefore explain the high Na and Cl content and the electrical conductivity values (> 1000 µS/cm) observed in the Moura–Ficalho carbonate aquifer. In any type of aquifer system, groundwater pollution is complex and particularly in semi-arid regions, like the case of Moura–Ficalho aquifer system, where the identification of pollutants source, and dispersion impact, are important issues regarding water resources protection. Also, the question concerning the replenishment rate of aquifer systems is critical in fulfilling their function as reliable long-term water supplies, either for human consumption, agriculture or industry uses.

Oxygen-18 and deuterium assessment

When the isotopic composition of the groundwater samples is represented in an orthogonal diagram δ^2H-$\delta^{18}O$ (Fig. 8), Casal de Sto. André samples stand out by their isotopic depletion, around 0.3‰ in $\delta^{18}O$ and 3‰ in δ^2H, in comparison with the other groundwater samples (Carreira et al. 2019). This isotopic shift (depletion) is impossible to explain based on the regional fractionation with altitude, knowing that no important topographic differences can be found in the region. One of the initial assumptions in isotope hydrology is that groundwater composition should mimic the topography and climate of the region (Mook 2000). The regional groundwater isotopic composition ($\delta^{18}O$ and δ^2H values) is defined by the isotopic signatures of the recharge and regional precipitation composition (Craig 1961; Dansgaard 1964; Rozanski et al. 1992; Aráguas-Aráguas et al. 2000; Gourcy et al. 2005). Therefore, the above-mentioned isotopic depletion in both ^{18}O and ^2H is most probably ascribed not to an isotopic altitude fractionation effect (different preferential recharge altitudes), which is not feasible in the region, but to precipitation infiltration under different climatic conditions, the colder climate during the LGM (Carreira et al. 2019).

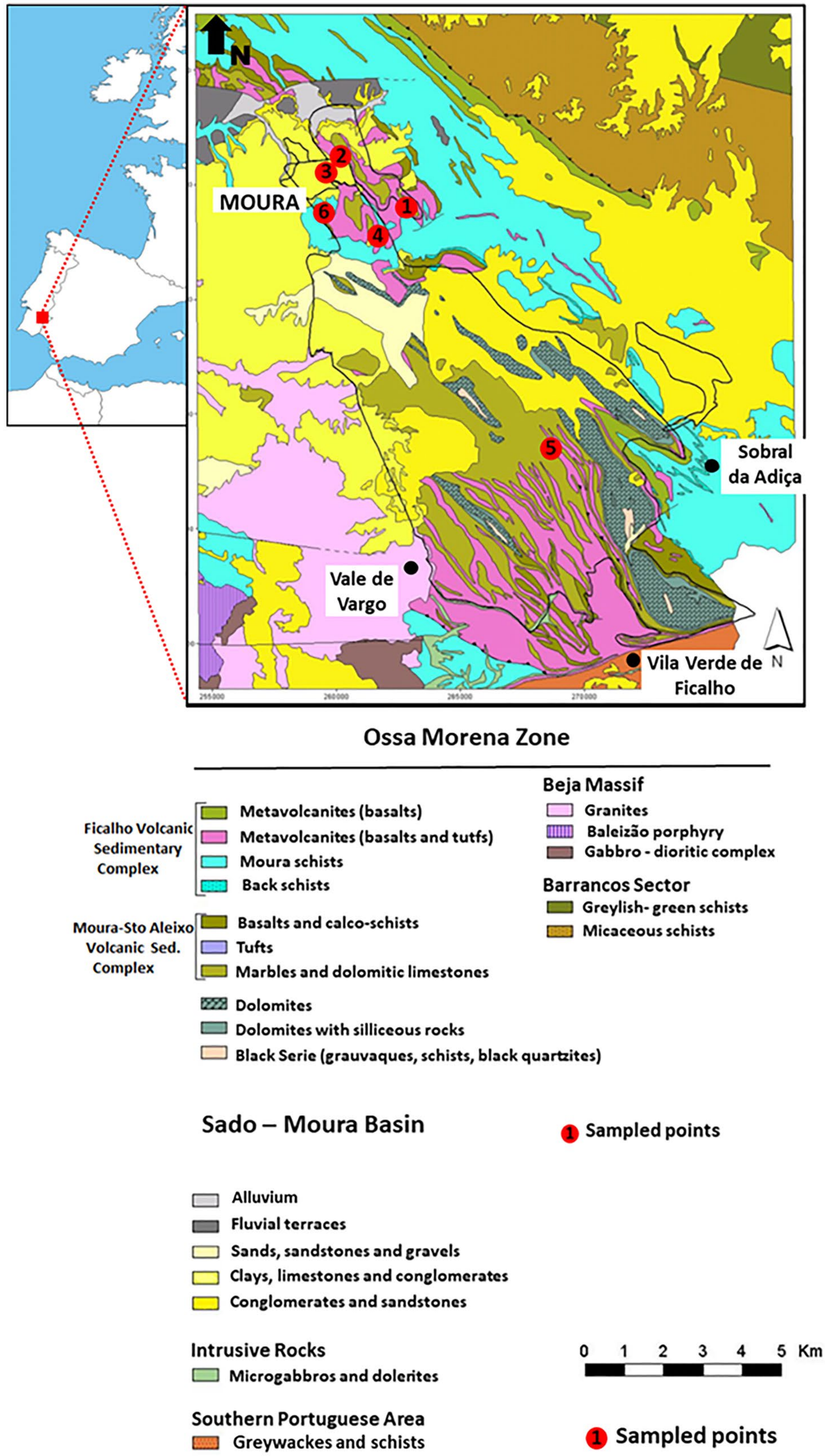

Fig. 5 Geological map and location of the sampling points, Moura–Ficalho aquifer, adapted from Carreira et al. (2019)

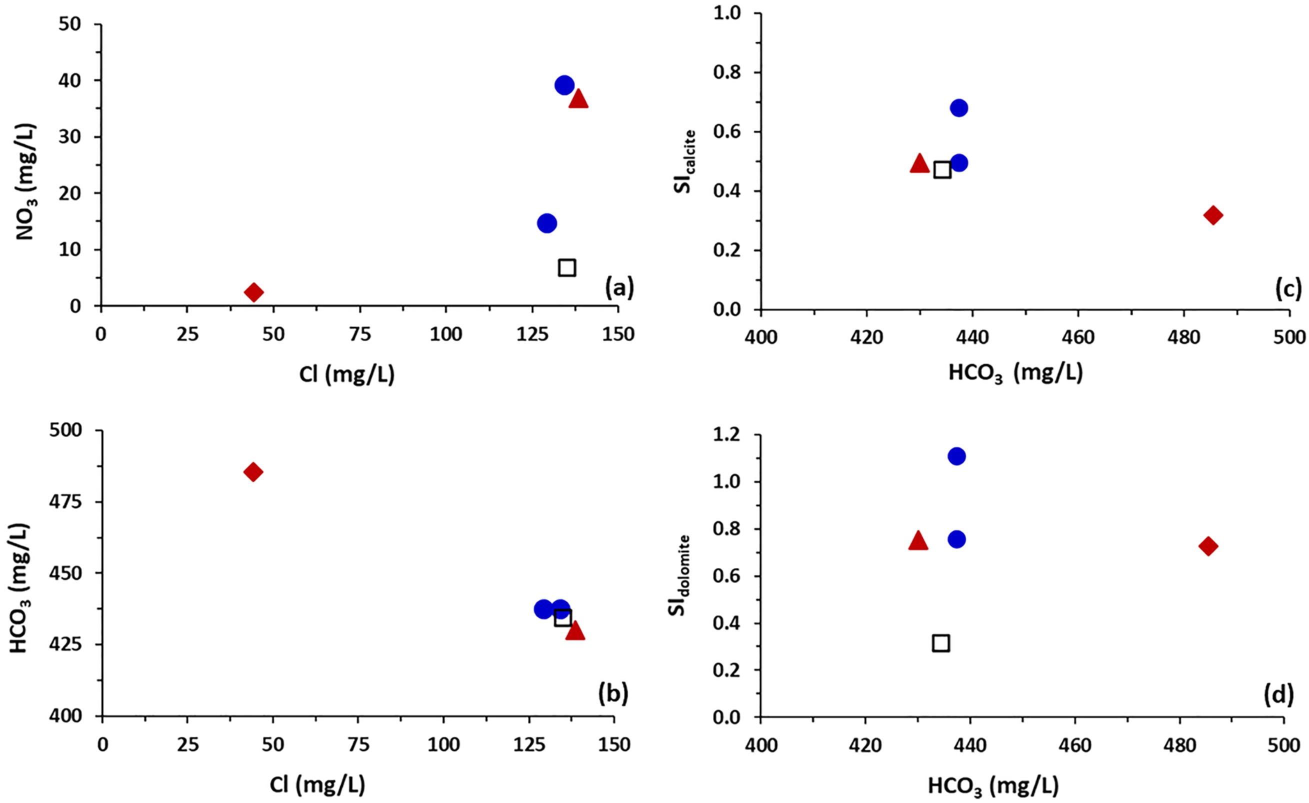

Fig. 6 Water–rock interaction for Moura–Ficalho mineral water samples: **a** NO_3 vs. Cl; **b** HCO_3 vs. Cl; **c** Calcite saturation index vs. HCO_3; **d** Dolomite saturation index vs. HCO_3. The (red triangle) symbol stand for the mean composition of Fonte da Telha groundwater sample, the (blue circle) stands for Três Bicas spring and borehole mean composition, the (!) for Messangil spring and (red diamond) Casal de Sto. André mean composition

Carbon-14

The ^{14}C content in the TDIC of Moura–Ficalho groundwater system varies between 11.0 ± 0.12 pmC at Casal de Sto André to 79.28 ± 0.34 pmC at Fonte da Telha borehole (Table S4). Carreira et al. (2019) applied a graphical ^{14}C approach to assess the predominant geochemical mechanisms occurring in the groundwater system, which can modify the initial radiocarbon content (Han et al. 2012; Han and Plummer 2016), i.e., dissolution of soil CO_2, mixing with organic matter, carbonates dissolution or precipitation, etc.

The isotopic composition of Moura–Ficalho mineral waters points to an additional source of organic carbon present in all water samples (Fig. 9a), expressed by an isotopic depletion in the ^{13}C in comparison with the current soil CO_2 composition. The depletion observed may also indicate silicates weathering, by additional carbonic acid (increase of DIC and decrease of $\delta^{13}C$ and ^{14}C). The last hypothesis was considered feasible by Carreira et al. (2019), due to the presence of metavolcanic intercalations and discontinuous levels of siliceous rocks (Oliveira 1991; Costa 2008). In addition, when the ^{14}C content is plotted *vs.* $\delta^{13}C$ or *vs.* 1/DIC (Fig. 9a and c) Casal Sto. André water sample stands apart suggesting the presence of further geochemical processes. Additionally to the organic matter mixing, and open conditions to CO_2, other hypotheses were formulated to account for different geochemical evolution through the dissolution of inorganic carbon from mixing with older groundwater or by reaction with fossil organic matter (Fig. 9a).

To estimate de apparent ^{14}C groundwater ages Carreira et al. (2019) considered the Gonfiantini model (Gonfiantini and Zuppi 2003). This groundwater age model uses a straightforward geochemical evolution and was selected considering that $\delta^{13}C_{TDIC}$ values are relatively homogeneous, between − 15.5 to − 13.6 ‰. The mean apparent carbon-14 ages obtained range from 1.9 up to 17.4 ka BP in the deeper part of Moura–Ficalho aquifer (Fig. 9d). Again, Casal de Sto. André deviation is well noticed both in the apparent ^{14}C ages and stable isotopic composition ($\delta^{18}O$ depletion).

Casal de Sto. André apparent ^{14}C age place the recharge of this sample during the Last Glacial Maximum (LGM), i.e., under a colder climate environment if compared with the regional modern mean temperatures (Edmunds 2005). In Moura–Ficalho region, the $\delta^{18}O$ difference within the groundwater samples is − 0.35‰. According to Goy et al. (1996) and Zazo et al. (1996), Great Britain and all Central

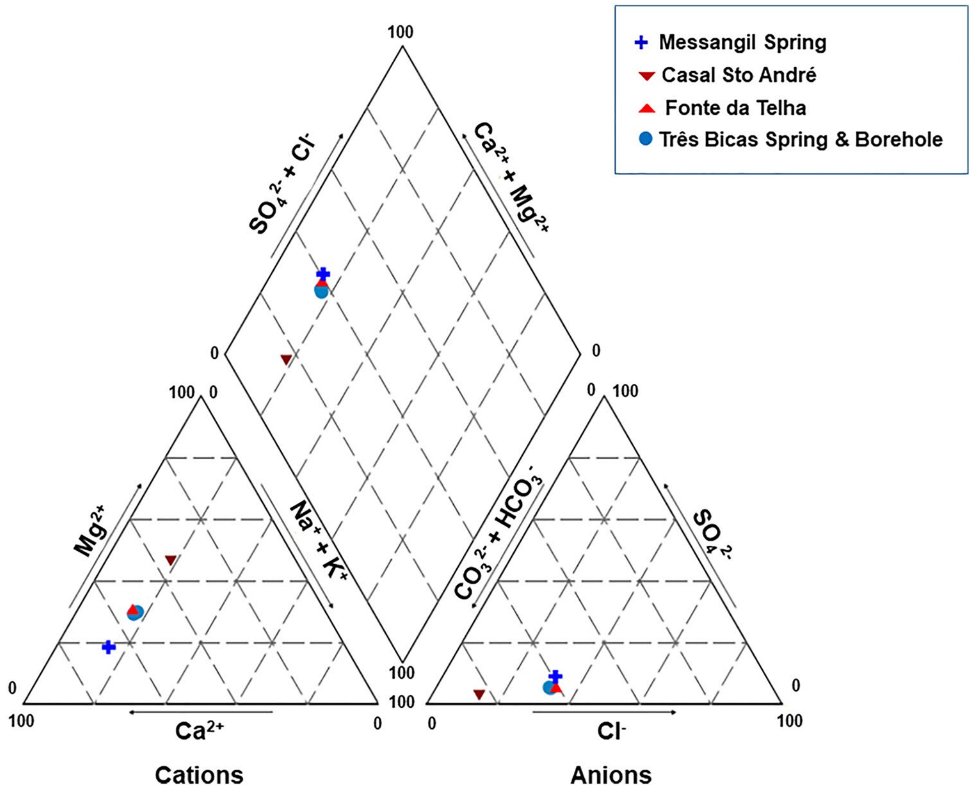

Fig. 7 Representation of the Moura–Ficalho groundwater mineral water samples in a Piper Diagram. Adapted from Carreira et al. 2019

Europe were covered by an ice mass during LGM, while the Iberian Peninsula experienced a colder climate of about 5–6 °C, a hypothesis supported by noble gases measurements (Carreira et al. 1996; Carreira 1998; Bush et al. 2001; Edmunds 2005).

The information obtained through the radiocarbon is important as an example of how groundwater systems can act as archives of ancient climatic variation, but also to give information to the water authorities and stakeholders about the (i) replenishment rates of groundwater, and (ii) mean residence time, allowing the estimation of the mean groundwater velocities within an aquifer system. The assessment of the origin and replenishment rate of aquifer systems is critical in fulfilling their function as reliable long-term water supplies, either for human consumption, agriculture or industry uses.

Moura–Ficalho—concluding remarks

The combined use of geochemical and isotopic tracers (stable and radioactive environmental isotopes) proved to be highly effective to determine the flow velocity in the deepest layers of Moura–Ficalho aquifer, allowing to differentiate, within the carbonate aquifer, groundwater circulation ascribed to karstified and fissured zones, standing as an important tool in the development of the conceptual circulation model, namely:

– The isotopic and chemical deviations observed between Casal de Sto André spring and the other water samples, in Moura–Ficalho aquifer, can be explained assuming that this aquifer has different flow regimes: a groundwater flow within karstified zones and another groundwater flow within fissured carbonate media. These different groundwater fluxes should be responsible for the differences obtained in the radiocarbon apparent ages. Três Bicas (borehole and spring waters) and Fonte da Telha spring waters represent the faster and shallower flow related to the karstified system, while Casal de Sto. André spring waters stands for the slow-flowing groundwater in the fissured carbonate media inducing much older groundwater apparent ages (Fig. 10).

Final remarks

In many parts of the world, groundwater levels are rapidly declining as groundwater withdrawal far exceeds the natural recharge, with strong possibilities of decreasing the water quality. Understanding the nature of recharge and the groundwater flow is essential to characterize the possible changes that can be induced under different withdrawal

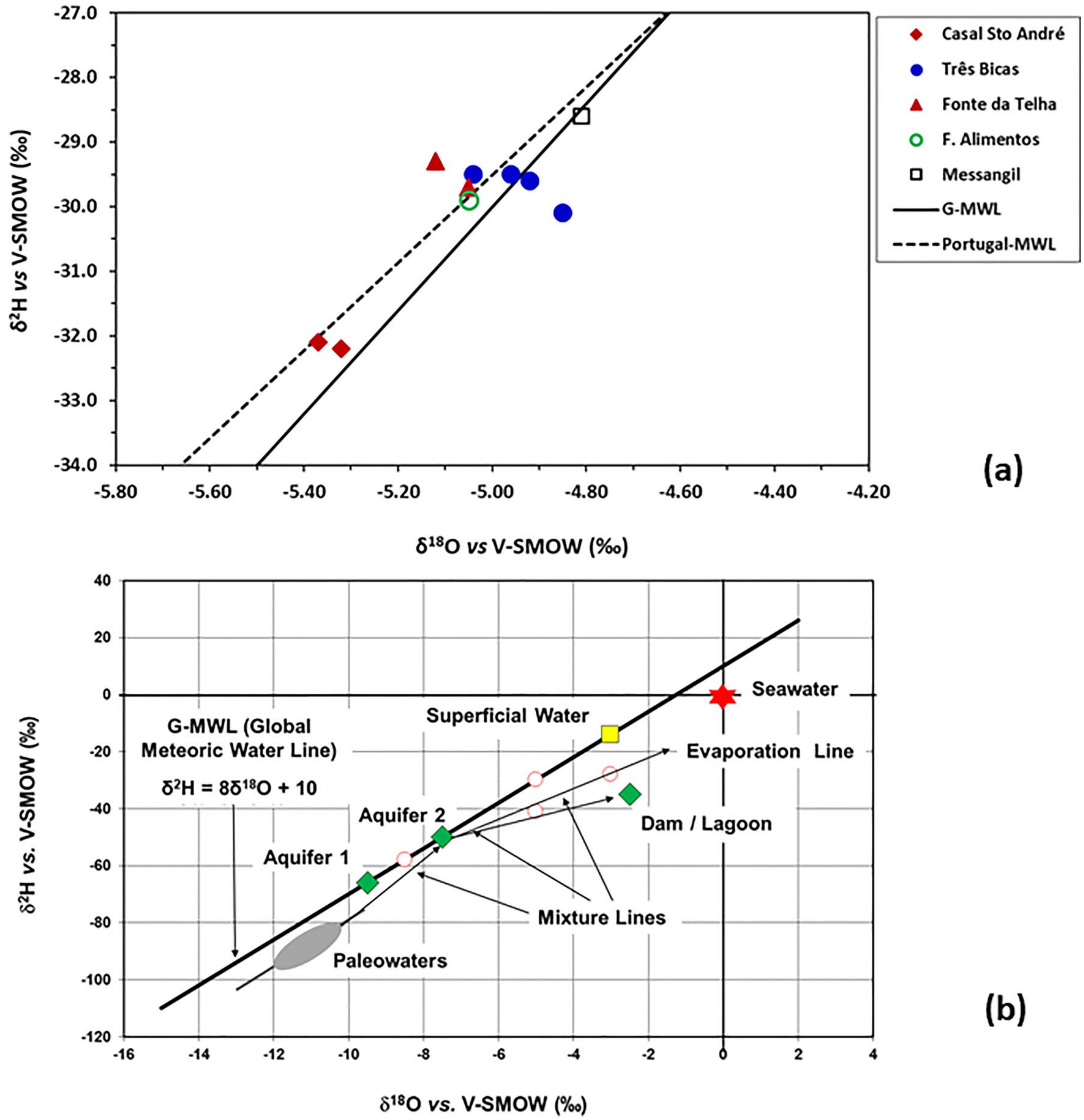

Fig. 8 **a** δ^2H vs. δ^{18}O. G-MWL stands for the Global Meteoric Water Line ($\delta^2H = 8\delta^{18}O + 10$) and Portugal-MWL stands for the Portuguese Meteoric Water Line ($\delta^2H = 6.8\delta^{18}O + 4.5$, Carreira et al. 2009), adapted from Carreira et al 2019. **b** δ^2H vs. δ^{18}O isotopic composition of water samples ascribed to different processes, adapted from Carreira et al. (2014b) and references therein

regimes which will affect not only the water resources but consequently the development and economic stability of a given region. The responsibility of the water authorities and stakeholders to water resources calls for a strong engagement of the community with a hydrogeoethical concern. Although groundwater is more resilient to climate change when compared with surface water bodies, the increase in anthropogenic pressures put them in a fragile equilibrium. Geoscientists and, in particular, people related to water management and protection, must reflect on the hydrogeoethical implications of their work to achieve a responsible interaction with the environment, orienting other professionals and society towards responsible interactions with the Earth system.

Chaminé et al. (2021) enhanced the need for a balanced groundwater fingerprint in sustainable water resources, to aim a proper management, in which society must play an essential role. The individual and collective actions sharing societal responsibility should be based on eco-responsibility and water ethics (UN–Water 2022). Under the threat of a climatic change scenario, expected to increase seasonality variability, present-day problems with water-stressed all over the world are expected to rise to different levels. Under this scenario, it becomes imperative that all

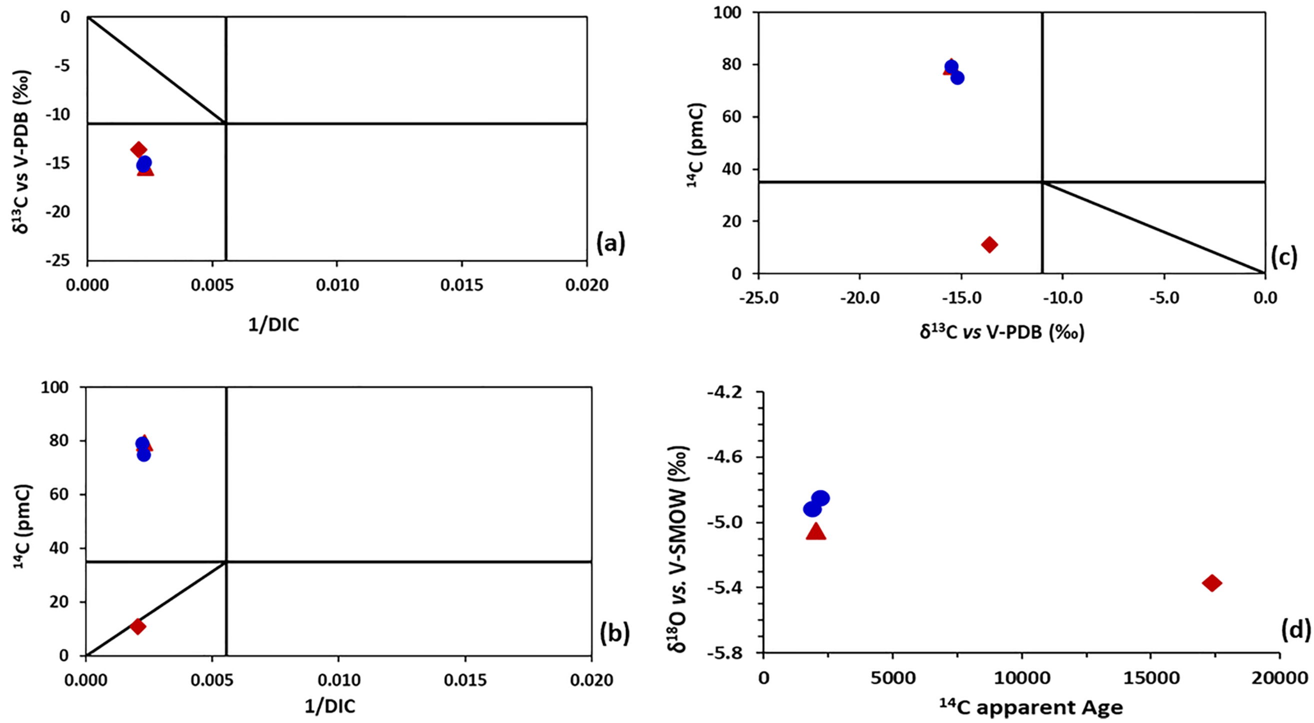

Fig. 9 Graphical method to evaluate predominant geochemical processes occurring in groundwater systems for radiocarbon dating **a** ^{14}C vs. δ^{13}C; **b** δ^{13}C vs. 1/DIC and **c** ^{14}C vs. δ^{13}C. **d** δ^{18}O vs ^{14}C groundwater apparent age. The (red triangle) symbol stand for Fonte da Telha groundwater sample, the (blue circle) stands for Três Bicas spring and borehole and (red diamond) Casal de St. André, adapted from Carreira et al (2019)

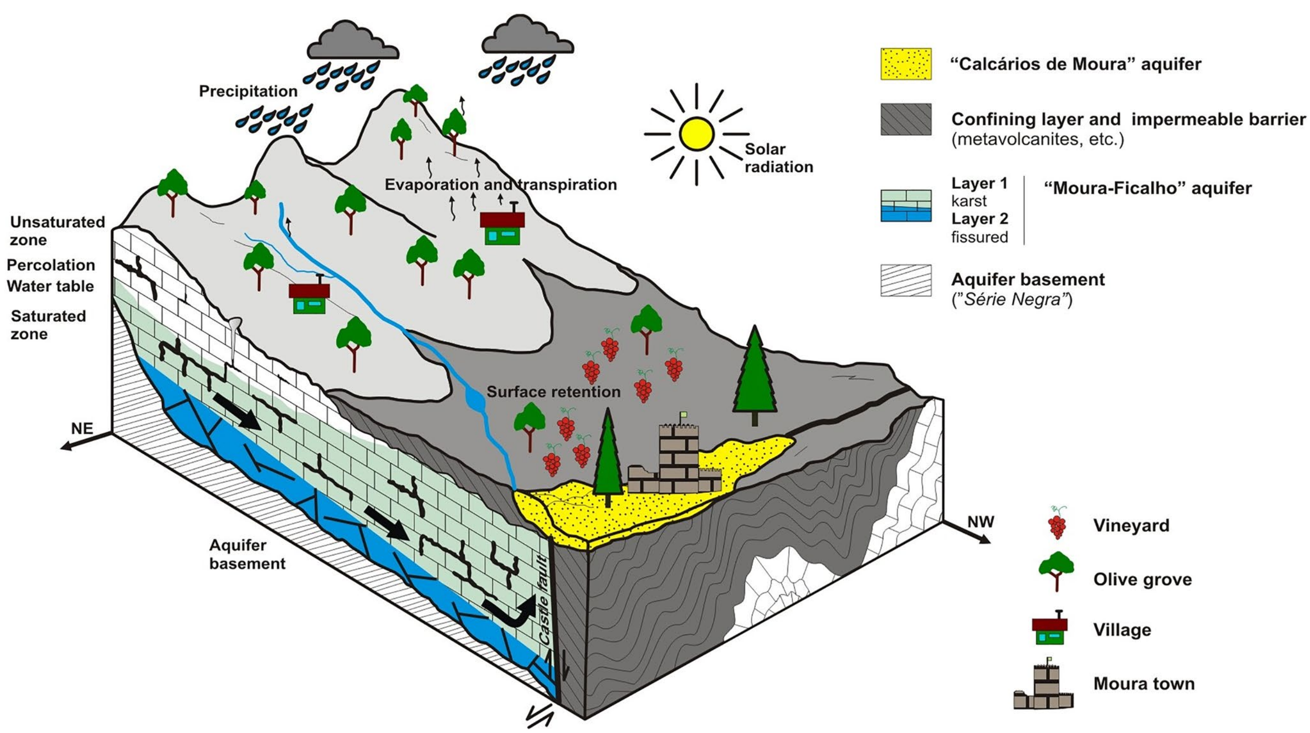

Fig. 10 Moura–Ficalho aquifer conceptual circulation model (Carreira et al. 2019)

society must be responsible for water resources protection and proper management.

The comparison of hydrogeological case studies can be used to display some of the key features that should aim to define and characterize the systems and the problems and how to solve them. These features are geology, tectonic structure, recharge, discharge, geochemistry (dominant anions and cations, TDS, pH), and isotopic characterization (stable and radioactive isotopes). Based on this approach, several studies have been carried out by the team, for example in aquifers located in coastal regions, presenting issues related to the increase of salinization (due to anthropogenic activities), as well as other pollution issues which were characterized using similar approaches, namely at Sines coastal aquifer, Portugal (Fernandes et al. 2008), Lower Sado basin, Portugal (Carreira et al. 2014b), Essaouira basin, Morocco (Ouhamdouch et al. 2019; Bahir et al. 2021), or even at Santiago Island, Republic of Cape Verde (Carreira et al. 2022). Not forgetting other case studies ascribed to different geological environments like the Serra da Estrela Mountain region, Portugal (Carreira et al. 2011) or the CO_2-rich thermal and mineral waters issuing in the north of Portugal (Marques et al. 2012; Carreira et al. 2021).

With this concern, the present work was focused on a comparative study of groundwater systems in different lithological and climatological environments, where geochemistry and environmental stable and radioactive isotopes played an important role for better understanding the aquifer systems dynamics and geochemical evolution. With this work, the authors intended, in a summarized way, to present some of the potentialities of the use of radioactive and stable environmental isotopes in the characterization of aquifer systems dynamics and how the information obtained can help hydrogeologists, stakeholders and national water authorities to develop a hydrogeoethical perspective concerning the sustainable management of groundwater resources. The use of traditional techniques together with the isotope hydrology approach is highly effective when all the different tools are put together, providing extremely helpful information to characterize water resources.

The use of nuclear techniques has proved numerous times to give unique information and better knowledge on water resources dynamics and vulnerability, namely in (i) the identification of preferential recharge altitudes; (ii) groundwater dating and replenishment (mean residence time); (iii) the identification of pollution sources (e.g., salinization, nitrates origin), information that can be very valuable for the Water Authorities and stakeholders concerning the proper management and sustainability of water resources.

In the context of water protection and management, the isotope hydrology methodologies can give unique information about the response of groundwater systems to climatic change, knowing their vulnerability to anthropogenic actions under low recharge scenarios.

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Availability of data and materials Not applicable.

Code availability Not applicable.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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