Characterization of the functioning of the Motril–Salobreña coastal aquifer (SE Spain) through the use of environmental tracers

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Abstract

Environmental tracers were used to characterize the origin and determine the age of the groundwater in the Motril–Salobreña aquifer (south-eastern Spain). The stable isotope concentrations ($\delta^{18}O/\delta^2H$), compared to the results obtained in previous studies, indicate that most of the recharge during the sampling period was from irrigation return flow and the carbonate Escalate aquifer. The combined dating of ^3H, ^3He, ^4He, ^{85}Kr, and ^{39}Ar allowed establishing the presence of modern water throughout the aquifer, although with different mixing percentages. Thus, there is a large zone characterized by a fluvial domain with 100% young waters (< 5 years) due to the circulation of water through an area of high permeability sediments. In the discharge zone of the aquifer, older water is located (age > 170 years), and the percentage of young water is reduced (22.5%). This is explained by the greater distance that groundwater travels (aquifer thicknesses is over 250 m) and the lower permeability of the aquifer in the deeper sectors.

Introduction

Groundwater dating has become a very useful technique for studying sources of aquifer recharge (Woolfenden and Ginn 2009), the calibration of numerical models (Sanford 2011), the description of groundwater flow distribution (Broers 2004), the hydrodynamic description of groundwater at a regional scale (Sültenfuβ et al. 2011), and to infer apparent groundwater age (Cook and Böhlke 2000). The applications of this approach also include the assessment of pollutant transport and the vulnerability of aquifers (Manning et al. 2005; Åkesson et al. 2015), the quantification of groundwater flow (Reilly et al. 1994), and groundwater mixing processes (Benettin et al. 2013; Underwood et al. 2018).

The concept of "groundwater age" has been described in several studies (Davis and Bentley 1982; Sanford 2011; IAEA 2013) as the average age of the water molecules in a sample or the average residence time of those molecules in the subsoil (Bethke and Johnson 2008). McCallum et al. (2015) provide a detailed description of the terms that are commonly used for groundwater age. They define the age distribution in an aquifer system as the representation of the collected samples in which the environmental tracers are measured; the mean age referring to the average of the distribution. This age distribution represents the transport processes experienced by a conservative tracer. Knowing the characteristics of this distribution improves the understanding of solute transport processes within the aquifer (Engdahl et al. 2012).

As indicated by the International Atomic Energy Agency (IAEA 2013), the study of groundwater age in a

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specific place requires knowledge of all the processes by which groundwater flows to a given sampling location. The net result of the action of all of the processes, which occur from the moment the water enters the aquifer system until it reaches the location where the sample is taken, determines the age distribution. The preferred groundwater flow lines are complex and difficult to predict because water mixtures are typically produced at different scales within the aquifer (Phillips and Castro 2003).

Although there might be large differences between apparent tracer age and the mean age or advective age, the use of these age measures in groundwater models can still yield favorable results (McCallum et al. 2015). As Goode (1996) illustrates, although groundwater age is not directly measurable, it is adequate for a conceptual model that, when two bodies of water are mixed, the average age of the mixture is the mean age weighted by the mass of both components.

There are three main inter-related factors that directly affect groundwater age distribution within an aquifer system: (1) the hydrodynamic mechanisms, (2) the hydrogeological configuration, and (3) the entry and exit conditions that are imposed in the system. In relation to the first factor, the most important transport processes that affect the movement of groundwater are advection and diffusion (Phillips and Castro 2003). The other factors refer to the fact that the age distribution of groundwater is also conditioned both by the heterogeneity and geometry of the aquifer in question, as well as by spatial variations in the recharge and discharge of the system (McCallum et al. 2015). In fact, large-scale heterogeneities and the mixture of multiple components can lead to a large dispersion in the age values obtained (Weissmann et al. 2002; Corcho-Alvarado et al. 2007; Underwood et al. 2018).

The application of dating methods in coastal aquifers can provide valuable knowledge about the residence times of groundwater in the system, a matter of great importance for the management of coastal water resources. Age distribution modeling turns out to be an integrated method of great utility for the characterization of the behavior of coastal aquifers, especially when these aquifer systems are quite heterogeneous, as is the case of the Motril–Salobreña coastal aquifer (Calvache et al. 2016).

Groundwater dating can be performed by measuring the concentration of one or more environmental tracers. In fact, several authors have shown that the age distribution of groundwater in a borehole cannot be determined from the analysis of a single tracer and, therefore, requires a multi-tracer method (Corcho-Alvarado et al. 2007; Sültenfuβ et al. 2011; Visser et al. 2013).

The environmental tracers used in this study were $\delta^{18}O/\delta^2H$, ^3H, ^3He, ^4He, ^{85}Kr, and ^{39}Ar. In addition to covering the expected range of ages for the groundwater in the aquifer, this combination of tracers is intended to reduce ambiguity in the translation of tracer concentration to mean ages of groundwater (Suckow 2014).

Transient tracers such as ^3H, ^3He, and ^{85}Kr are sensitive to young groundwater components, with residence times of less than about 50 years (Corcho-Alvarado et al. 2007; Underwood et al. 2018). Thus, the combination of ^3H, ^3He, and ^{85}Kr is used for dating and quantifying the fraction of young waters (< 50 years approx.), using the ΔNe factor as an indicator of possible degassing of water or the contribution from excess air (Sültenfuβ et al. 2011). In contrast, ^{39}Ar is used to cover an older range of ages (50–1000 years), and the stable isotopes $\delta^{18}O/\delta^2H$ are used to identify the most recent water inputs to the system (0.1–3 years), according to Suckow (2014). $^4He_{rad}$ is used here as a qualitative indicator of age (Solomon 2000).

The present study aims to characterize the Motril–Salobreña aquifer, the main detrital coastal aquifer of Granada province, using a hydrochemical and isotopic approach, and to determine the groundwater age distribution through the combination of several environmental tracers. With this, it will be possible to elucidate the dynamics of groundwater flow within the aquifer and the factors that control it, and relate these data to the degree of vulnerability of the aquifer.

Hydrogeological context of the study site

The detrital Motril–Salobreña aquifer, with an area of 42 km², is located along the Mediterranean coast in southeastern Spain (Fig. 1). It is an aquifer that is mainly composed of deposits from the Guadalfeo River, as well as other, smaller fluvial streams. It is a heterogeneous formation composed of sediments with highly variable grain sizes but with a high fraction of coarse grains, concentrated mainly in the northernmost sector. The thickness of the aquifer ranges from 30 to 50 m in the northernmost sector, within the fluvial domain, to more than 250 m in the southern sector, near the coastal margin, in the deltaic domain (Duque et al. 2008).

Recharge from the Guadalfeo River constitutes one of the main water entrances to the aquifer. Another important input is irrigation return flows from the intense agricultural activity that characterizes the area, where there is cultivation of subtropical and orchard products that are irrigated most of the year. To a lesser extent, direct infiltration also occurs from precipitation (of little importance due to scarce rainfall, 350 mm/year, and to high evapotranspiration (18 °C of average annual temperature) and sub-surface through the carbonate Escalate aquifer that is connected to the Motril–Salobreña aquifer in the northern sector.

The aquifer is mainly bounded by metapelitic materials (schists and phyllites) constituting the impervious substrate of the aquifer. The southern limit is the Mediterranean Sea.
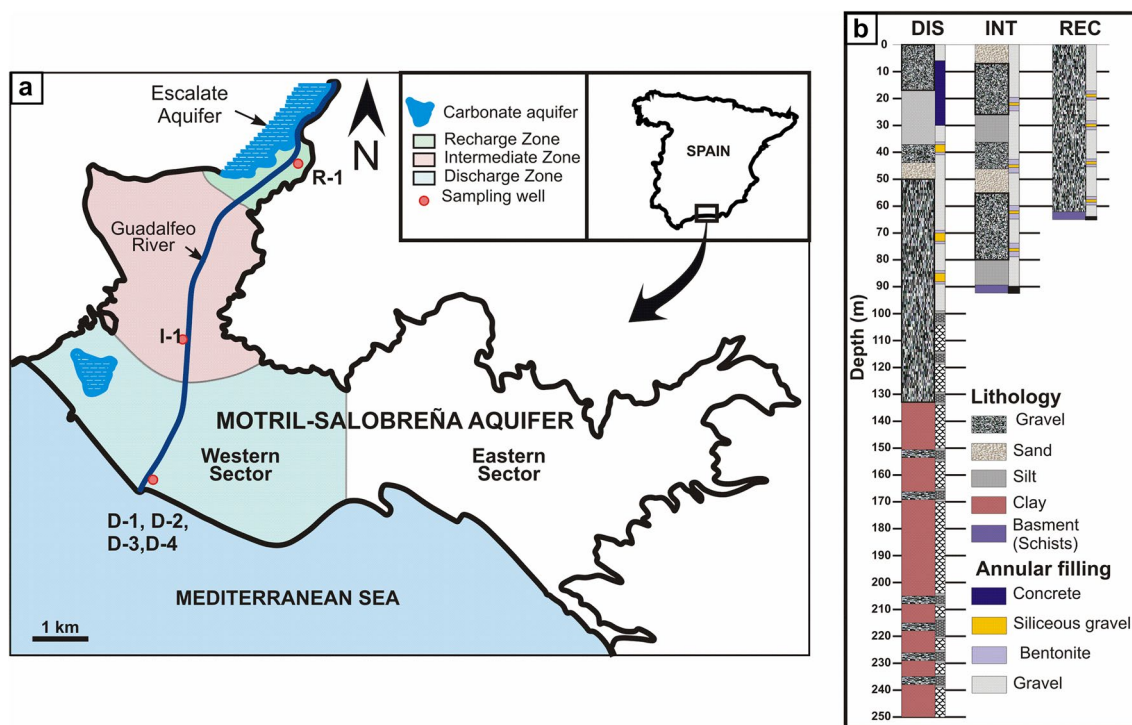
Fig. 1 a Location of the Motril-Salobreña aquifer and sampling wells. b Lithology and annular filling of the sampling wells

In the Motril–Salobreña aquifer, an initial differentiation can be made between the western and eastern sectors (Fig. 1). The western sector is heavily influenced by the Guadalfeo River and is where the most important recharge and discharge processes take place and where the most important connections with the external hydrogeological systems that limit it take place (Ibáñez 2005; Calvache et al. 2006). The eastern sector is fed by sporadic fluvial courses and its importance in terms of both reserves and water resources is much lower. Likewise, within the western sector, several zones have been differentiated according to their hydrogeological characteristics (Fig. 1): a recharge zone (REC), an intermediate zone (INT), and a discharge zone (DIS).

The REC zone is the aquifer sector where the main recharge takes place. This zone includes the contact between the detrital aquifer with the karstic Escalate aquifer and where the main replenishment of the aquifer by the river occurs. The aquifer in this zone has a variable thickness with maxima between 50 and 60 m, and is composed of a succession of gravels, sands, and silts, with a predominance of gravels and coarse sands. The INT zone is considered to be a transition zone between the REC and DIS zones, with aquifer thickness between approximately 60 and 100 m. It is composed of gravels, sands, and silts with a higher fraction of silts and fine sands than the REC zone. In this zone, the river still contributes considerable recharge, although the entry of irrigation return flow from the agricultural activity

is greater. The DIS zone has the highest variation in aquifer thickness, from approximately 100 m to more than 250 m near the coastal edge. The upper 140 m is composed of a sequence of gravels, sands, silts, and mixed layers (sands and silts with gravels). At greater depths (up to 250 m), thick clay layers predominate with some intercalations of gravels and sands (Fig. 1b). The recharge in this area is mainly due to irrigation return flows. The recharge of the river in the DIS zone is minimal because the water table approaches the riverbed, and the river changes from losing to gaining. Another characteristic feature of this area is the artesian character of the deepest wells, which can yield flows up to 24 L/s due to the upward flow components that are produced by the effect of the salt wedge in the fresh water discharge zone (Calvache et al. 2011).

Methodology

Characteristics of the sampling wells

Twelve samples of groundwater were collected for dating at different depths in six wells that were distributed in the three different zones of the aquifer. The samples were named according to the zone and the depth to which they correspond (Fig. 2).
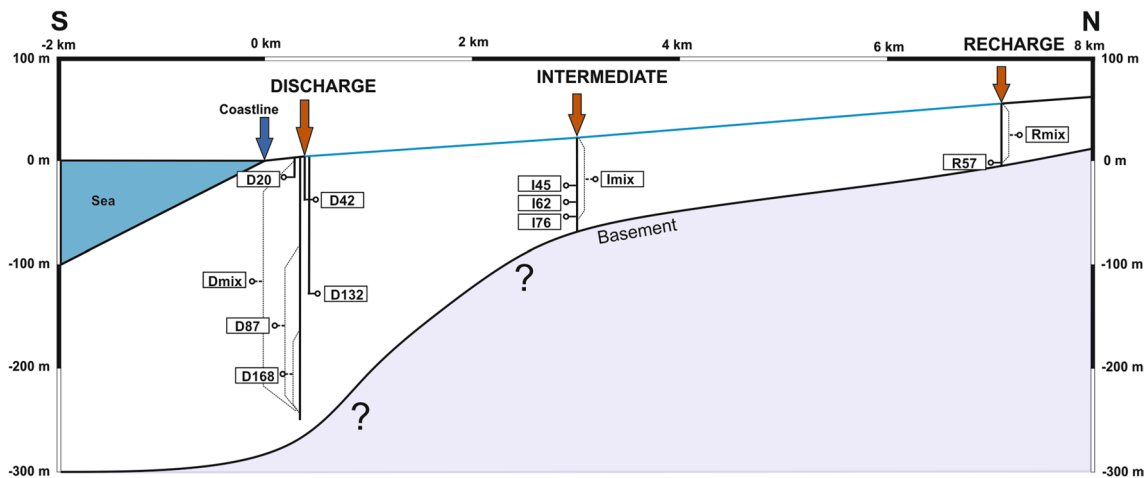
Fig. 2 Schematic profile of the sampled sector that follows approximately the Guadalfeo River. The relationship between the horizontal and vertical scaleis 1:10 (modified from Sánchez-Úbeda 2017)

In the recharge zone, there is only one borehole (R-1) that reaches the basement of the aquifer at 62 m depth. The borehole has four screened sections at different depths (Fig. 1b). The annular space that remains between the tubing and the sediments is filled with clean gravel in the screened sections and bentonite in the blind sections to isolate the groundwater flow in the different bore screens. In this survey, two water samples were taken, one at a depth of 57 m (R57) and another corresponding to a mixture of all of the screened sections (Rmix).

In the intermediate zone, there is a borehole of 90-m depth (I-1) that also reaches the impermeable substratum with four screened sections. In this case, water samples were collected at 76-m depth (I76), at 62-m depth (I62), at 45-m depth (I45), and with water mixture from all different screened sections (Imix).

Three piezometers, D-1, D-2, and D-3, and one borehole, D-4, located a few meters away from each other, were sampled in the discharge zone. From one of the piezometers (D-1), which had a total depth of 20 m and a bore screen of 2 m at the lower end, sample D20 was collected. D-2 has a total depth of 42 m and with a bore screen of 3 m at the lower end, from which sample D42 was collected. Piezometer D-3 has a total depth of 132 m with a bore screen of 3 m at the lower end (sample D132). Finally, borehole D-4 has a total depth of 250 m and has 12 different screened sections, each of which is 3-m long, except for one that is 6-m long (Fig. 1b). Here, three groundwater samples were collected at 168-m depth (D168), at 87-m depth (D87), and a mixture of all screened sections (Dmix). Figure 2 details the depth or depth range from which each of the analyzed samples originated.

Sampling and environmental tracers

The sampling survey was done from May 5th to May 7th of 2015. Groundwater was pumped from specific depths by isolating certain sections of the borehole by means of two packers (one above and one below the bore screen) in some cases and isolating with one packer from a certain depth and pumping interval in the screened sections above. The pumping was performed with a Grundfos® BTI/MP1 pump or with a 48 L Rolatec® RL machine from the Scientific Instrumentation Center of the University of Granada (to which the packers were connected). In all cases, the sample was collected after an estimated purge time, depending on the dimensions of the well and the volume of water to be displaced. Only in the DIS zone pumping was unnecessary since the samples were collected from the artesian wells, by inserting a thin PVC pipe up to the required sampling depth.

Part of the hydrochemical analysis was carried out in situ with the HI 9828 multiparameter equipment (Hanna Instruments) which measured temperature, conductivity, pH, and Eh. The remaining measurements were made in SCADA laboratories (Granada, A-019-AU), where they obtained concentrations of major elements (HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, Ca^{2+}, Mg^{2+}, Na^+, and K^+).

The environmental tracers were analyzed in the Climate and Environmental Physics Institute of the University of Bern (Switzerland) (^{85}Kr and ^{39}Ar) and in the Noble Gas Laboratory of the Institute of Environmental Physics (University of Bremen, Germany) (^3H, ^3He, ^4He and Ne).

Method of dating with ^{3}H–^{3}He

^{3}H–^{3}He age (τ) refers to the time when water enters the saturated zone, while ^{85}Kr includes possible delay in the unsaturated soil zone (Gerber et al. 2018):

$$\tau = \frac{1}{\lambda} \cdot \ln\left(1 + \frac{^3\text{He}_\text{tri}}{^3\text{He}}\right), \tag{1}$$

where ^{3}He$_\text{tri}$ is the ^{3}He produced by the decay of ^{3}H, $\lambda = \ln(2)/t_{1/2}$ is the decay constant, and $t_{1/2}$ is the half-life of ^{3}H, which is 12.32 years according to Lucas and Unterweger (2000). The ^{3}He$_\text{tri}$ must be differentiated from the other sources of ^{3}He as the concentration from the ^{3}He in equilibrium with the atmosphere (^{3}He$_\text{equi}$), which originates from the additional dissolved air due to the partial dissolution of air bubbles (excess air, Aeschbach-Hertig et al. 1999) and ^{3}He produced in rocks and released to groundwater. As ^{3}He is part of atmospheric air, Ne can be used as parameter for excess air and degassing of water (Sültenfuβ et al. 2011). The ^{3}He$_\text{tri}$ is then the result of the expression:

$$^3\text{He}_\text{tri} = {}^3\text{He}_\text{sample} - {}^3\text{He}_\text{equi} - {}^3\text{He}_\text{excess} - {}^3\text{He}_\text{rad}, \tag{2}$$

where ^{3}He$_\text{sample}$ is the total concentration measured in the sample, ^{3}He$_\text{equi}$ is the concentration in conditions of equilibrium with the atmosphere which is a function of temperature, salinity and atmospheric pressure during infiltration, ^{3}He$_\text{excess}$ is the additional amount due to the partial dissolution of air (bubbles) near the water table (subsaturated zone), and ^{3}He$_\text{rad}$ (radiogenic) is the concentration that is produced in rocks and is released into the water. Sültenfuβ et al. (2011) contains a detailed description of these terms, as well as the laboratory sampling and analysis procedure.

Method of dating with ^{85}Kr

The dating method based on ^{85}Kr (half-life of 10.76 years) is used in hydrogeology to identify fractions of infiltrated young groundwater over the past 50 years (Lehmann et al. 2003). The activity concentration of ^{85}Kr is expressed in terms of the ratio ^{85}Kr/Kr in a sample, measured in disintegrations per minute of ^{85}Kr per ml of Kr, dpm/cm^{3}Kr. For this reason, the evaluation of water age through ^{85}Kr is not affected by solubility processes, recharge temperature, or excess air. The application of ^{85}Kr is especially useful in combination with ^{3}H, which has a similar half-life (12.32 years). The atmospheric activity of ^{85}Kr is increased steadily over the last 50 years due to its release by the nuclear fuel reprocessing plants (Zimmermann et al. 1989; Lehmann et al. 1991; Bauer et al. 2001; Winger et al. 2005). The ^{85}Kr atmospheric 2015 was 82 dpm/cm^{3}Kr.

Method of dating with ^{39}Ar

The ^{39}Ar method (half-life of 269 years) covers the time gap for dating between the indicators of residence times of young waters [such as the methods based on ^{3}H–^{3}He, ^{85}Kr, or chlorofluorocarbons (CFCs)] and radiocarbon methods for the oldest waters (Sültenfuβ et al. 2011). In this specific case, the radiocarbon-based method was not used because the uncertainties of the method and ^{39}Ar was considered to be sufficient to reach the older ages that exist within the aquifer, given the recent formation of the Guadalfeo River delta.

The atmospheric concentration of ^{39}Ar is caused by the interaction of cosmic rays with the atmosphere. The equilibrium activity concentration of 1.67×10^{-2} Bq/m^3 (Loosli 1983), corresponds to an atmospheric ratio of ^{39}Ar/Ar of approximately 10^{-15} (Loosli 1983; Loosli et al. 1989). This atmospheric value for ^{39}Ar is globally constant and represents the initial value for freshly recharge young water (100% modern, Corcho-Alvarado et al. 2007; Yechieli et al. 2019; Avrahamov et al. 2018; McCallum et al. 2017).

Method of dating with radiogenic helium 4 (^{4}He$_\text{rad}$)

Radiogenic helium 4 (^{4}He$_\text{rad}$) is produced by the decay of α particles from the decay series of uranium (U) and thorium (Th) nuclei in the aquifer matrix. ^{4}He$_\text{rad}$ is useful as a qualitative age indicator (Solomon 2000) and is calculated with the following expression:

$$^4\text{He}_\text{rad} = {}^4\text{He}_\text{sample} - {}^4\text{He}_\text{equi} - {}^4\text{He}_\text{excess} \tag{3}$$

If the accumulation rate of ^{4}He$_\text{rad}$ in water is constant over time and space in the aquifer, the concentration of ^{4}He$_\text{rad}$ increases linearly with time and represents relative age differences. The age estimation range of ^{4}He is 50 to > 100,000 years. However, Solomon et al. (1996) indicate that it is possible to detect ^{4}He$_\text{rad}$ in young waters in an age range between 10 and 1000 years when the groundwater percolates aquifers formed by sediments from recent erosion. In such cases, ^{4}He$_\text{rad}$ is pre-accumulated in the source rock and diffusively released in elevated quantities into the water after erosion (Sültenfuβ et al. 2011).

Results

Hydrochemical and isotopic analyses of groundwater

The hydrochemical analysis of the samples indicates that these are waters with similar characteristics, except those

Table 1 Results of the hydrochemical analysis of groundwater

Sample	Well	Sampling depth (m)	Temp. (°C)	pH	Eh (mV)	EC 25 °C (µS/cm)	HCO_3^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	TDS (mg/L)
R57	R-1	58	16.07	7.73	73	682	265	24	81	3	69	29	22	1.6	596
Rmix	R-1	19–44	17.54	7.59	89	682	335	50	84	3	69	31	43	1.5	617
I45	I-1	45	18.04	7.42	156	672	329	46	76	4	72	30	23	1.6	582
I62	I-1	62.3	17.81	7.43	143	671	329	44	80	4	73	31	21	1.6	584
I76	I-1	76	17.91	7.66	−23	669	357	44	81	4	72	30	21	1.7	611
Imix	I-1	22–76	17.98	7.38	167	679	320	44	74	4	73	29	21	1.6	568
D20	D-1	20	18.60	7.62	−200	665	381	59	0	0	52	29	41	1.3	564
D42	D-2	42	18.48	7.77	−145	824	354	64	111	0	75	36	35	1.7	676
D87	D-4	87–250	17.85	7.24	17	1103	342	146	121	8	81	35	82	2.5	818
D132	D-3	132	17.86	8.38	87	3605	329	816	328	3	17	20	655	3.2	2172
D168	D-4	168–250	18.01	7.24	−53	8728	259	2077	523	6	141	132	1312	9.2	4461
Dmix	D-4	0–250	17.77	7.39	24	1023	360	126	116	7	78	35	69	2.1	794

corresponding to the discharge zone (Table 1). They have relatively high concentrations of Cl^-, Na^+, and SO_4^{2-} ions, as well as high electrical conductivity (EC) and total dissolved solids (TDS), as a consequence of being located in the vicinity of the freshwater–saltwater interface. The content of HCO_3 decreases in sample D168, probably due to the influence of seawater that leads to supersaturation and precipitation of calcium carbonate.

The redox potential decreases with depth and even becomes negative (reducing conditions), which is consistent since the influx of atmospheric oxygen becomes more difficult and the waters are likely older, more stagnant, and impoverished. In the discharge zone, there are alterations of this pattern in the 20-m and 40-m boreholes where very negative values are found. This observation may be related to the presence of a thick layer of black silt that is rich in organic matter, which could indicate oxygen-reducing or impoverished conditions due to the abundance of organic matter.

EC and TDS increase with depth and towards the discharge zone because the residence time increases and there may be mixture of fresh water and salt water. The content in the main anions shown in a Piper diagram (Fig. 3) clearly indicates the progressive mixing with salt water that the samples have in the discharge zone as the depth increases. Exceptions to this trend are found in samples D20, which shows sulfate reduction, and D132, which is likely affected by exchange processes (relative increase in Na with respect to Ca and Mg).

Using the conservative condition of chloride ion, and considering that the chloride concentration of fresh water is approximately 60 mg/L and that of sea water is 21.813 mg/L (average of the hydrological year 2007–2008), the percentages of seawater present in the samples collected at different depths in borehole D-4 and in piezometer D-3 are estimated (Table 2). Sample D168 contains the highest percentage of salt water, reaching almost 10%. It is noteworthy that at 87-m depth, the salt water mixture is only 0.4% even though it is located 300 m from the coastal edge, which indicates that there is no saltwater intrusion. Likewise, the fact that the mixture sample Dmix has the lowest percentage of salt water of all samples taken in D4 is striking. It is assumed that the highest proportion of water contribution to this artesian well must come from a high permeability level that occurs at a depth of less than 87 m and supplies low-salinity water.

The isotopic data from this study were compared to results from a larger study of the entire Motril–Salobreña aquifer (Fig. 4, Duque et al. 2011). First, there is agreement between both studies because all of the data from this study are included within the zone marked by the isotopic signal of groundwater analyzed in Duque et al. (2011) (Fig. 4). However, there is a feature that distinguishes both studies; in this study, the isotopes $\delta^{18}O/\delta^2H$ showed a good fitting to
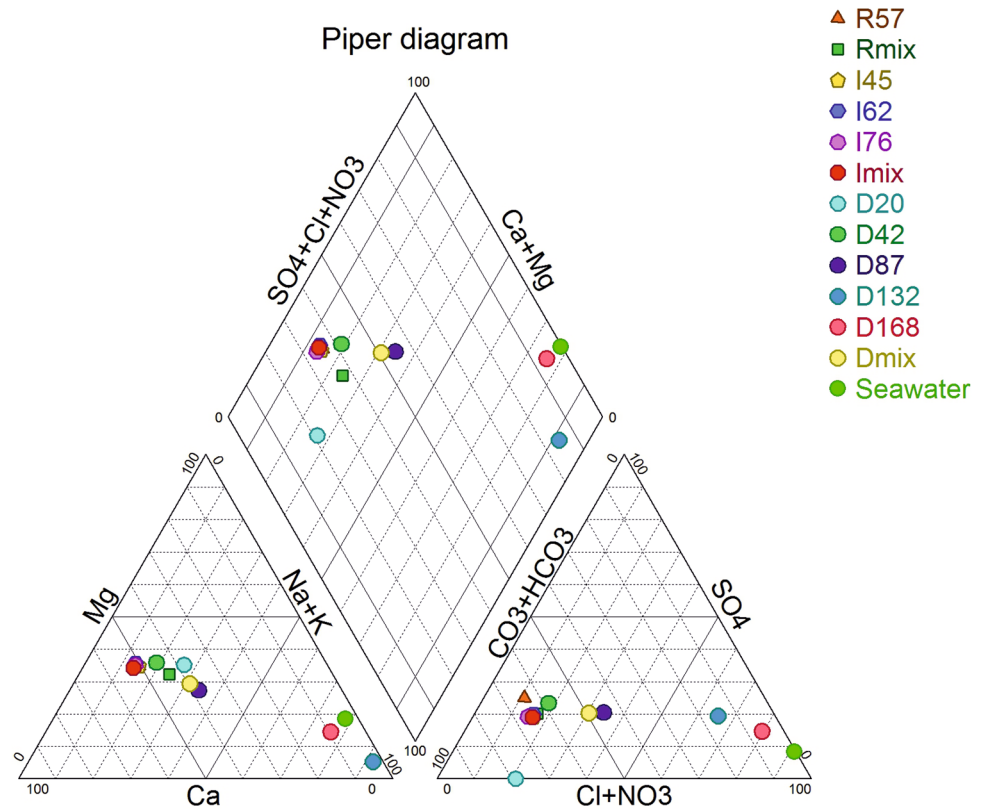
Fig. 3 Pipper graph for all the groundwater samples

Table 2 Cl⁻ concentration and percentage of seawater in the D-4 samples in the discharge area

| Sample	Cl⁻ (mg/L)	% sea water
D87	146	0.4
D132	816	3.5
D168	2077	9.3
Dmix	126	0.3

the global meteoric line (GML, whose equation is $\delta^2H = 8\ \delta^{18}O + 10$, Craig 1961). However, the data of Duque et al. (2011) fitted slightly better to the western Mediterranean meteoric line (WMML, whose adjustment equation is $\delta^2H = 8\ \delta^{18}O + 13.7$, Celle-Jeanton et al. 2001). This difference may be because in this study, the samples were collected in the vicinity of the Guadalfeo River, whereas in Duque et al. (2011), the entire aquifer was sampled. Therefore, the influence of the river in these samples will be dominant compared with data Duque et al. (2011). The water of the Guadalfeo River has its origin from Sierra Nevada, brought by precipitation fronts from the Atlantic Ocean that has a distinct isotopic mark. However, in the rest of the aquifer, the surface recharge may be more affected by precipitation fronts coming from the Mediterranean since the high altitude of the Sierra Nevada (3482 m) prevents the arrival of the Atlantic fronts.

The samples collected from the REC and INT zones have less negative isotopic values, showing a closer relationship to the isotopic signal that is characteristic of the water coming from the carbonate Escalate aquifer; whereas, the samples taken in the DIS zone and a deep sample of the INT zone have more negative isotopic values that are closer to the isotopic signal found in groundwater used for irrigation. There are two samples that deviate from this trend, D20 and D168. Sample D20 has a more negative isotopic signal, indicating a clearer influence of the river compared to others. Sample D168 presents the highest values of the isotopic ratio, approaching the high values of $\delta^{18}O$ and δ^2H measured in the Mediterranean Sea in this zone (averages of 0.52 and 3.62, respectively).

Groundwater dating

The age data estimated with the different environmental tracers show a high degree of agreement, especially for young waters (Table 3) as evidenced by the high degree of correspondence in the apparent ages obtained through the $^3H/^3He$ ratio and ^{85}Kr (Fig. 5). However, although the linear relationship is very good, it shifts slightly with respect to the 1:1 line, mainly at younger ages, which indicates that the ages obtained from ^{85}Kr are slightly older. The results obtained in older waters with different tracers are apparently not as coherent as in the previous

Fig. 4 Relationship between the stable isotopes δ18O and δ2H and error bars for all the analyzed samples. The dashed line corresponds to the Western Mediterranean Meteoric Line (OMML), and the dotted line to the Global Meteoric Line (GML). The circles represent the zones of influence of the different origins of the ground-water, determined in a previous isotopic study in the area (Duque et al. 2011)
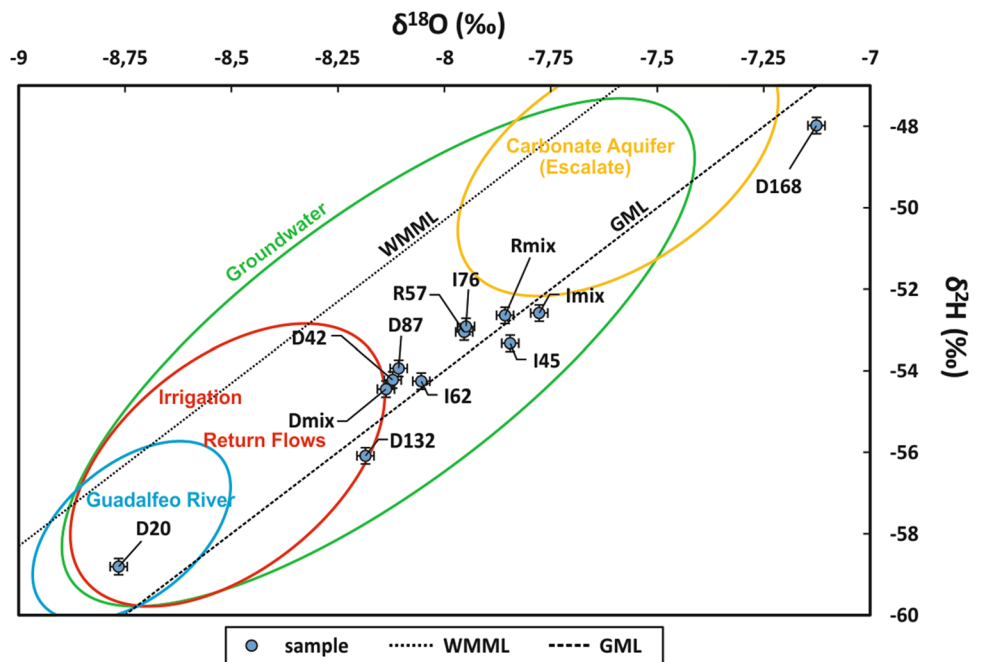
case. Thus, the ages that we obtain from ^{85}Kr are younger than the results contributed from ^{39}Ar.

The results obtained with the different environmental tracers indicate a predominance of young groundwater in the sector of the Motril–Salobreña aquifer that is close to the Guadalfeo River. Young groundwater was found in the recharge, intermediate, and discharge zones, as indicated by the ^{3}H values close to approximately 2TU (value of the ^{3}H concentration in recent precipitation) in almost all samples (Fig. 6a). In addition, the values of ^{85}Kr between 70 and 80 dpm/cm^{3}Kr (concentration of Kr measured in the atmosphere in 2015) that are observed in most of the samples are close to the recent atmospheric level (Fig. 6b).

However, older waters also appear in the DIS zone where the largest detrital aquifer thicknesses occur. In this area, near the coastal edge, a gradient in the values of age in relation to the depth is observed, obtaining higher percentages of older waters at greater depths. The apparent ages obtained in this case vary from a few years (assumed minimum ages of 2.5 years) as found in sample D42 to the apparent maximum age of 170 years for sample D132, with intermediate values of 25 years in sample D87. It is presumed that the age found for sample D168 was even higher; however, it was not possible to obtain these data because the sample was lost during the process of gas transfer in the laboratory, preventing the determination of ^{39}Ar in the sample.

Discussion

Although the groundwater that was dated from the recharge and intermediate zones of the aquifer is very young, less than 5 years old and seemingly related to the direct recharge by the Guadalfeo River, the isotopic signals of stable isotopes found in these waters indicate that it is closest to the Escalate carbonate aquifer and to the irrigation water. Therefore, the young water circulating in the aquifer in the REC and INT zones in the vicinity of the Guadalfeo River comes mainly from irrigation (which in turn comes from the Guadalfeo River) and from the Escalate aquifer. Thus, it can be argued that the Escalate aquifer groundwater is also very recent, an issue that can be justified by the minimal extension of the aquifer. These young groundwater components extend over a large part of the aquifer owing to the high values of the hydraulic conductivities and the low saturated thickness of a significant portion of the Motril–Salobreña aquifer.

The discharge zone contains older water, greater than 170 years, because in this part of the aquifer, the thickness of the aquifer is much greater (greater than 250 m) and the sediments are less permeable, leading to higher residence time in groundwater that circulate in the near coastal area. The presence of the salt wedge forces the

Table 3 Groundwater dating results for the tracers used

Sample	85Kr (dpm/cm³Kr)	Error (dpm/cm³Kr)	39Ar (%mod.)	Error (%)	Age85Kr (year)	Age39Ar (year)	Error (year)	3H (TU)	Error (TU)	3He_tri (TU)	Error (TU)	Age 3H/3He (year)	4He_rad (cm³STP/kg)	ΔNe (%)
R57								2.30	0.1	0	0.5	0	2×10^{-6}	26
Rmix	80	2.9			2.5			2.25	0.1	0	0.5	0	2×10^{-6}	26
I45	75.1	3.7			2.5			2.30	0.1	0	0.5	0	2×10^{-6}	28
I62	79.6	6.8			2.5			2.26	0.1					
I76	74.7	2.9	100	7	2.5	0	27.2	2.35	0.1					
Imix								2.42	0.1	0	0.5	0	5×10^{-6}	31
D20								0.45	0.04	0	0.5	0	1×10^{-6}	20
D42								2.50	0.1	0.5	0.5	3.5	1×10^{-5}	44
D87								2.20	0.1	6.5	0.5	24.5	3×10^{-5}	140
D132	5.1	0.3	65	10	41	167	59.7	1.57	0.08	14.5	0.5	41.5	3×10^{-5}	42
D168			94	6		24	24.8	1.40	0.07					
Dmix	47.2	2.3			12			2.14	0.1	1.8	0.5	10.5	2×10^{-5}	56

The concentrations of each tracer are shown, as well as the corresponding age. The gaps without data indicate that this tracer has not been analyzed for that sample or that the analysis could not be performed
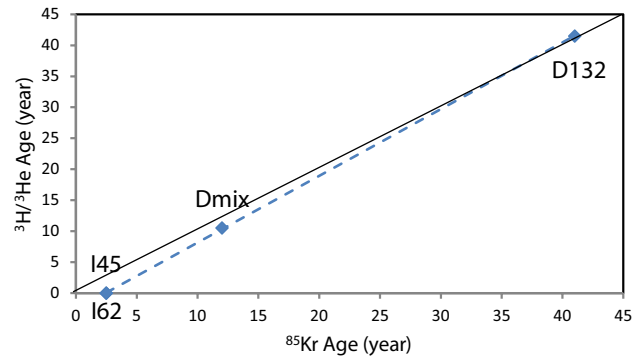

Fig. 5 Linear correlation between the ratio of ages ^{3}H/^{3}He and ages of Kr. The dashed line denotes the linea fit between the samples
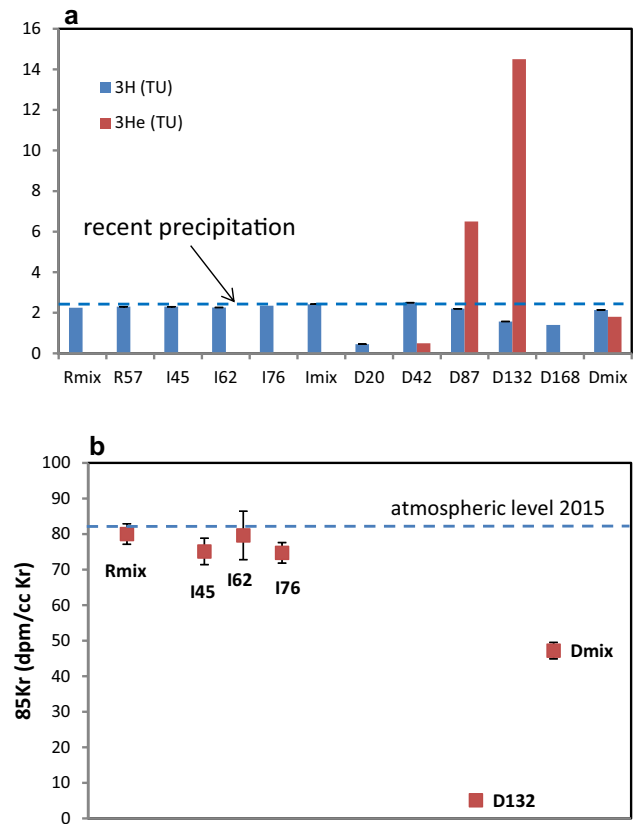

Fig. 6 a Concentration of ^{3}H and ^{3}He in the samples analyzed. The dashed line indicates the concentration of 3H in recent precipitation. **b** Concentration of ^{85}Kr in the samples analyzed. The dashed line indicates the atmospheric level of ^{85}Kr in 2015. The data represented are shown in Table 3

deep flow to rise in the area of the coastal edge, producing a mixture of groundwater at the surface. As a result, there are large differences in the ages observed in the same borehole according to the depth sampled. For example, in borehole D-4, the age obtained by ^{85}Kr is 2.5 years at a depth of 76 m (I76), but the same tracer provides an age

of 12 years for the sample mixture (Dmix) that indicates the presence of older groundwater that rise, increasing the age found above 76 m.

Sample D20 shows completely anomalous results for all the methods applied. On the one hand, it has a low redox potential indicating the existence of reducing conditions that justify the absence of SO_4^{2-} and NO_3^- in the sample. The isotopic signal is different than the other samples and becomes closer to those of the Guadalfeo River. In addition, the sample shows very low values in ^3H concentrations, which would indicate that the sample may contain a high percentage of old waters. All these features seem to indicate the presence of a low level of permeability (level of dark-colored silts enriched in organic matter), which at some point was an area flooded with river water and was isolated from the remainder of the aquifer by a sealed, impermeable material that maintained the initial characteristics without mixing with other younger waters.

In some cases, the age determination with the different methods may be contradictory for the same sample; depending on the tracer used, different ages were obtained. For example, for sample D132, the concentrations of ^{85}Kr and ^3H–^3He coincide and provide values close to 41 years; however, the concentration of ^{39}Ar suggests an age of 167 years. These different ages correspond to average apparent ages of a mixture of waters of very different ages. Thus, the 41 years of D132 may correspond to the youngest fraction of this sample. To verify this, the results of this study were compared with those recorded in the rainfall in Madrid (Fig. 7). The $^3H + ^3He$ concentration of the oldest sample, D132, fits with the concentrations of ^3H record in precipitation from Madrid at the calculated recharge period, which indicates agreement of the tracer concentration with the age obtained. However, the concentration of the tracer in sample D132 (16.2TU) is much lower than

the average value observed in precipitation from that time (71.9TU for years 73 and 74 of Madrid). The ratio between both ages indicates that 22.5% of the sample is 41-year-old water.

The use of several environmental tracers allowed to verify the adequacy of the results and establish the apparent age of groundwater. In this case, the results were checked comparing the three samples (I76, Dmix, and D132), in which the three tracers ^3H, ^{85}Kr, and ^{39}Ar were measured. Although the ages provided are different, this is because different proportions of water are dated at different ages. This is supported by the coherence of the results obtained by the three tracers of the percentage of young water obtained with each of the tracers used. Starting from the hypothesis that the Dmix sample would be a mixing of the youngest water, I76 (2.5 years with ^{85}Kr and ^3H and 0 years with ^{39}Ar), and the oldest, D132 (41 years with ^{85}Kr and ^3H and 167 years with ^{39}Ar), the percentage of young water would be given by the following relationship:

Table 4 Estimation of the percentage of young water in the Dmix sample from the comparison between samples D132 and I76

Sample	^{85}Kr (dpm/cm^{3}Kr)	^3H (TU)	^{39}Ar (% modern)
I76	74.7	2.35	100
D132	5.1	1.57	65
Dmix	47.2	2.14	94
Percentage of young water in Dmix			
^{85}Kr	60.49		
^3H	73.08		
^{39}Ar	82.86		
Average	72.14		

Fig. 7 Comparison of the ^3H and ^3He contents between the samples analyzed and the historical rainfall series in Madrid since 1970
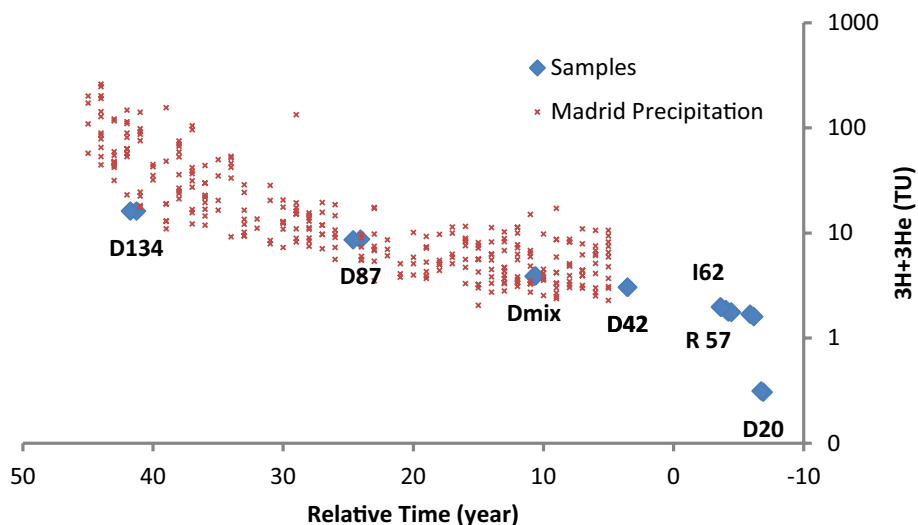
$$\%modernwater = \frac{concentrationDmix - concentrationD132}{concentrationI76 - concentrationD132}.$$

The percentage of young water in the Dmix sample obtained from the three tracers is very similar, with an average value of 72% (Table 4).

Conclusions

From the concentration of environmental tracers (^{3}H, ^{3}He, ^{85}Kr, and ^{39}Ar), estimated groundwater ages in the Motril–Salobreña aquifer range from 5 to more than 170 years. Its distribution indicates the presence of variable percentages of young waters in almost all sector studied, as well as a pronounced gradient towards older waters at depth, especially in the discharge zone of the aquifer.

Transport times of less than 50 years (even less than 5–10 years) would be justified by the fast flow in the shallower half of the aquifer due to high permeable sediments. The deeper half of the aquifer would be characterized by lower permeability, slower flow and longer residence time of groundwater.

The presence of so young waters in a large sector of the aquifer indicates a high velocity of groundwater transit and a consequent low regenerative capacity in the face of the pollution. Therefore, it can be deduced from this that the Motril–Salobreña aquifer is very vulnerable to contamination in a thick superficial fringe (aprox. 50 m), either due to pollution that occurs on the surface of the aquifer, such as agriculture, or that which occurs laterally from the sea, such as saltwater intrusion.

The percentage of young waters varies in the aquifer, from 22.5% in the oldest sample (D132) to 72% in the mixing water from this same well (Dmix) to 100% upstream of borehole I76.

Establishing the age of groundwater with a set of environmental tracers allowed associating the apparent age with the percentage of mixing of younger waters. The use of a single tracer can lead to unrealistic age results.

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