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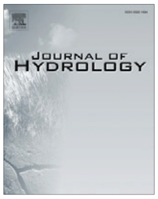

Isotopic and hydrochemical data as indicators of recharge areas, flow paths and water–rock interaction in the Caldas da Rainha–Quinta das Janelas thermomineral carbonate rock aquifer (Central Portugal)

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SUMMARY

An updated conceptual circulation model for the Caldas da Rainha and Quinta das Janelas thermomineral waters was developed. These thermomineral waters ($T \approx 33$ °C) are related to a huge syncline ascribed to the regional flow paths. Two diapiric structures were responsible for the uplift and subsequent folding of regional Jurassic carbonate rocks. Environmental isotopic (δ^2H and δ^{18}O) data indicates that the main recharge area of the thermomineral system is linked to the Jurassic limestones (Candeeiros Mountains, E border of the syncline). The thermomineral waters belong to the Cl–Na sulphurous-type, with a total mineralization of about 3000 mg/L. The thermomineral aquifer system seems to be "*isolated*" from anthropogenic contamination, which is typical for the local shallow groundwater systems, due to the existence of impermeable layers composed of a series of loamy and detritic rocks of the Upper Jurassic. The presence of ^{3}H in some thermomineral borehole waters, not accompanied by an increase in SO_4^{2-} and NO_3^-, could be ascribed to different underground flow paths and different mean residence time. The $\delta^{34}S_{(SO4)}$ and $\delta^{18}O_{(SO4)}$ values of dissolved sulphate of groundwaters of the Caldas da Rainha Spas indicate that the sulphate is the result of water–rock interaction with evaporitic rocks (e.g. gypsum and anhydrite) ascribed to the regional synclinal structure.

1. Introduction

In many parts of the world, carbonate rock formations hold water resources that are vital for the water supply (Andrews et al., 1982; Sharp and Clement, 1988; Kafri, 1996; Babidorics et al., 1998; Goldscheider et al., 2003). Also, carbonate aquifers probably constitute the most important thermomineral water resources, supplying spas all over the world (Goldscheider et al., 2010). Although the natural quality of such type of waters is often excellent, those (thermomineral or not) associated to karst aquifer systems are more vulnerable to contamination than other types of aquifers, thus requiring particular protection (Goldscheider and Drew, 2007).

The Caldas da Rainha region is located about 100 km north of Lisbon (Portugal), a few kilometres inland from the Atlantic Ocean coast, as shown in Fig. 1. The foundation of the city of Caldas da Rainha in the late 1400s was associated with the presence of thermomineral waters in the area. The Spa was found and initially supported by Queen Leonor (in fact, the name of the City can be translated into English as "*Queen's Hot Springs*"). The first Spa building was constructed directly over the place where, at that time, a group of hot sulphurous springs existed. These springs were highly appreciated by the local population who used them as treatment for various diseases. At the location of the most productive springs, with the largest sulphurous exhalations, two major natural swimming pools were built, the so-called "*Piscina da Rainha*" ("*Queen's swimming pool*") and the "*Piscina dos Homens*" ("*Men's swimming pool*"). There are however no records that the Queen has ever taken a bath in the swimming pool baptized with her title. These swimming pools are located in the basement of the Spa building, and are filled with the natural flow of the mineral spring waters. After a devastating fire that destroyed the ancient Thermal Hospital almost completely, the construction of a new building was ordered by king João V in 1747. At present the Caldas da Rainha thermomineral water concession operates several boreholes (AC1B, AC2, AC3 and JK1) supplying approximately a total of

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50 L/s of thermomineral water. The historic baths used thermomineral waters from springs discharging from the naturally flowing systems, while modern baths are entirely supplied by these boreholes.

Quinta das Janelas thermomineral water issues at a small dilapidated bath house on the estate with the same name near the village of Gaeiras in the Óbidos municipality, about 5 km south of the main Caldas da Rainha discharges. Its temperature of 30.9 °C and its sulphurous smell indicate that this thermomineral water has comparable characteristics as the Caldas da Rainha thermomineral waters.

The Caldas da Rainha thermomineral system has been described in a preliminary study (Marques et al., 2010). In this paper we present an updated and much enlarged study on the knowledge of both the Caldas da Rainha and Quinta das Janelas deep thermomineral systems, including new data providing important information on: (i) sources of groundwaters and location of recharge areas, (ii) underground flow patterns, (iii) "*age*" of the thermomineral waters, (iv) water–rock interaction processes occurring at depth and (v) the possible existence of mixing between different groundwater bodies. In fact, environmental problems associated with the use of low-temperature thermomineral waters are different, in many aspects, from those of utilizing high-temperature geothermal resources. In the case of thermomineral waters, the maintenance of water chemical quality is more important than in high-temperature geothermal exploitations, since spas are very dependent on both constant temperature and water quality (Albu et al., 1997). Thus, in this case the existence of possible mixing between deep thermomineral and local shallow groundwaters is of considerable concern. Caldas da Rainha Spas are located in a region with intensive agricultural land use. Therefore, pollution of the shallow groundwater with agro-chemicals during recharge and subsequent mixing may result in contamination of local thermomineral water resources (Albu et al., 1997).

The application of geochemical and isotopic methods in all stages of thermomineral exploration can provide information on water sources, mixing, and water–rock interactions that are difficult to obtain by any other techniques. Groundwater is a "*hidden resource*" for which pollution prevention, monitoring and restoration are more difficult than for surface waters due to its inaccessibility. This often results in a lack of understanding with regard to the extent of pollution risks and groundwater pressures (e.g. over-exploitation). Pollution from domestic, agricultural and industrial sources is, despite the progress in some areas, still a major concern, either directly or through discharges. While point sources have caused most of the pollution identified to date, there is evidence that diffuse sources are having an increasing impact on groundwater. For example, nitrate concentrations currently exceed the nitrate guideline values in approximately one third of groundwater bodies in Europe (Quevauviller, 2005, 2007).

2. Geological, geomorphologic and tectonic settings

Geologic and geomorphologic investigations are indispensable when studying carbonate aquifers. It is impossible to understand carbonate aquifer systems without taking into account the lithology of the different geological formations, the stratigraphy, fracturing, fault and fold structures, as well as the topography, the karst landforms and the landscape history (Goldscheider and Drew, 2007). According to Goldscheider et al. (2010), thermomineral water resources in carbonate rock aquifers are strongly related with deep regional flow systems, characterized by cross-formational hydraulic continuity. Groundwater circulation in such systems is generally gravity-driven, caused by topographic gradients (Tóth, 2009). Density gradients induced by temperature facilitate the upward flow of hot thermomineral waters toward springs, the most characteristic features of carbonate aquifer areas (Ford and Williams, 2007). In such hydrogeologic systems, fractures and faults are the major controls on groundwater flow Goldscheider et al. (2010).

According to Zbyszewski and Moitinho de Almeida (1960) the geological formations that occur in the Caldas da Rainha region are mainly of sedimentary origin, with prevalence of Jurassic limestones, sandstones and marls. There are also some magmatic rocks (dolerites) related to magma injections in the form of dykes and domes. The western part of the studied region is covered by Plio-Plistocene (E) sandy–silty sediments (Figs. 1 and 2).

In carbonate regions, groundwater circulation should be understood within the framework of epigenic and hypogenic flow systems (Klimchouk, 2007): (i) epigenic flow systems are directly influenced by the infiltration of meteoric waters and CO_2 from the atmosphere and soil, at high recharge altitudes, and are characterized by local shallow cold dilute groundwaters, (ii) hypogenetic systems are ascribed to regional, deep and hot thermomineral waters.

Structurally, the study region is dominated by a huge syncline that influences the regional flow path of the thermomineral waters. A schematic cross-section of the study region is shown in Fig. 2. The Caldas da Rainha and Quinta das Janelas thermomineral waters discharge from springs located close to a locally oriented N–S oblique fault (60°E), which puts the loamy and detritic rocks from the Upper Jurassic (D) and the marls (and evaporitic deposits) from the Hetangian–Retian (A) in contact. The Hetangian–Retian does not contain any aquifer and acts as an aquitard. At depth, the Jurassic series are mainly formed of limestones (B and C).

The origin of the syncline and anticline structures along the sedimentary basin is attributed to the rising of huge salt domes that are associated with the Hetangian marls, known as "*Dagorda marls*" ("Margas de Dagorda"). The ascension of the salt domes, in both the East and the West side of the basin resulted in anticline structures in the external zones and a large syncline structure in the inner part of the basin, and is responsible for the uplift and subsequent folding of the Jurassic formations (Zbyszewski, 1959). The two domes have been eroded and the Hetangian–Retian is now exposed at the surface. Overlying Pliocene (E) detritic deposits (mainly sands and argillaceous sandstones) form an unconfined aquifer.

3. Methodology

Between 2005 and 2006 (see Tables 1 and 2), several fieldwork campaigns were carried out in the study region in order to collect groundwater samples from boreholes and springs related to the thermomineral and local surface (stream) and shallow cold dilute groundwater systems, for chemical and isotopic (δ^2H, δ^{18}O, δ^{13}C, δ^{34}S, δ^{37}Cl, ^{3}H and ^{14}C) analyses.

Temperature (°C), electric conductivity (μS/cm) and pH were measured in the field. The chemical parameters of the water samples were determined at the Instituto Superior Técnico, Laboratório de Mineralogia e Petrologia (Portugal), using the following methods: total alkalinity was measured a few hours after collection by titration; atomic absorption spectrometry for Ca, Mg; emission spectrometry for Na, K, Li, Rb and Cs; colorimetric methods for Al, Fe_{total} and SiO_2; ion chromatography for SO_4, NO_3 and Cl; potentiometry for alkalinity which is here referred to as HCO_3. Sulphide was precipitated *in situ* as CdS. In the laboratory, CdS was titrated (by potentiometry) with sodium thiosulphate. Dry residuum (D.R.) was calculated following the US Geological Survey procedure, which calls for drying at 180 °C for 1 h (Hem, 1970).

Environmental isotopes (δ^2H, δ^{18}O and ^{3}H) were measured at the Instituto Tecnológico e Nuclear (ITN – Sacavém, Portugal). The δ^{18}O and δ^2H determinations were carried out using a SIRA 10 VG-ISOGAS mass spectrometer, following analytical methods described

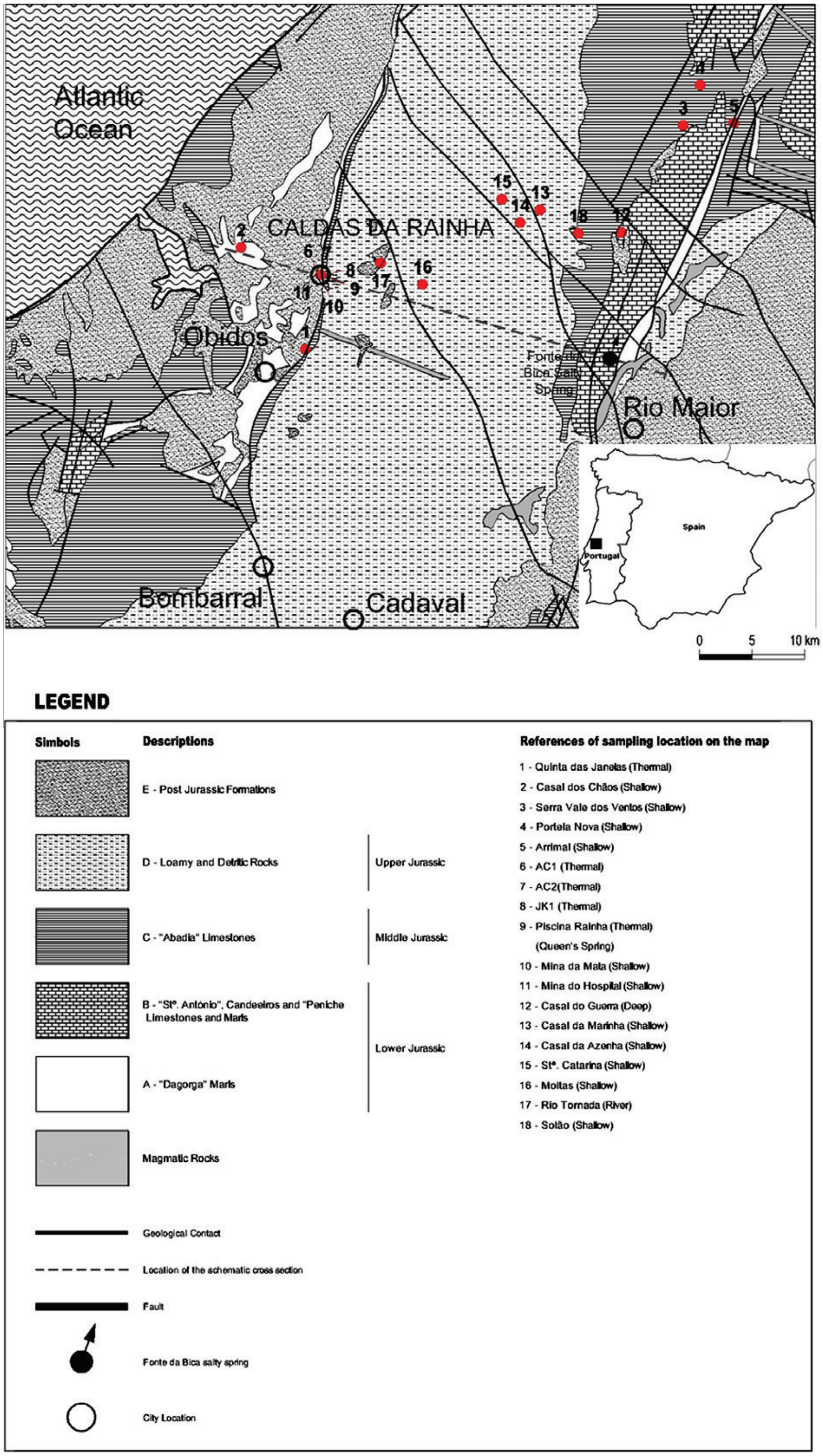

Fig. 1. Geographical location and simplified geology of the study region, showing water sampling locations and the approximate location of the schematic cross-section of Fig. 2. The sampling sites 6, 7, 8, 9, 10 and 11 are very close to each other on the open circle ascribed to Caldas da Rainha City location. Adapted from Zbyszewski and Moitinho de Almeida (1960) and from S.G.P. [Serviços Geológicos de Portugal] (1992).

by Epstein and Mayeda (1953) and by Friedman (1953) and Tanweer (1990), respectively. The results are reported in the usual δ notation in ‰ vs. V-SMOW. The accuracy of the measurements is 1‰ for δ^2H and 0.1‰ for $\delta^{18}O$. Tritium (^3H) contents in the water samples were determined using an electrolytic enrichment method followed by liquid scintillation counting measurements (PACKARD

TRI-CARB 2000 CA/LL) with a detection limit of 0.5 TU. The associated error to the measurements (≈0.6 TU) varies with the tritium concentration in the water samples. This analytical method is described in IAEA (1976). The $\delta^{34}S$ determinations were performed at the University of Calgary, Department of Geosciences, following analytical methods described by Giesemann et al. (1994) and Mayer and Krouse (2004). $\delta^{37}Cl$ was measured at Utrecht University using the method described by Eggenkamp et al. (1994). Cl^- in the samples was precipitated as AgCl, which was reacted with CH_3I to form CH_3Cl. $^{37}Cl/^{35}Cl$ ratios were subsequently determined on a VG-ISOGAS SIRA 24 mass spectrometer. The results are reported in δ notation in ‰ relative to SMOC (Standard Mean Ocean Chloride), which is, within error, a homogeneous reservoir and could thus be used as a reference standard (Godon et al., 2004), with a precision of 0.1‰.

The $\delta^{13}C$ and carbon-14 determinations were performed on the Total Inorganic Dissolved Carbon (TIDC), at the University of Georgia, Centre for Applied Isotope Studies, USA, by AMS. The radiocarbon content is given in pmC (percentage of modern Carbon) and the $\delta^{13}C$ values are reported in ‰ vs. V-PDB (Vienna–Peedee Belemnite) standard, with an accuracy of ±0.1‰.

The physico-chemical parameters and isotopic compositions of representative waters from Caldas da Rainha region are presented in Tables 1 and 2, respectively.

4. Results and discussion

4.1. Hydrogeochemical signatures

The traditional hydrogeochemical techniques can provide important information about the "*working*" of carbonate rock aquifer systems. In such regions, if a sufficient contrast of hydrogeochemical data exists, the hydrogeochemical approach can help to locate and quantify the geological formations ascribed to water mineralization. Thus, water geochemistry should be considered as a natural tracer that provides information about the structure and dynamics of carbonate rock aquifers. In addition, hydrogeochemical studies are often motivated by water quality problems and aimed at identifying the extent and origin of water contamination. On one hand, a good understanding of the functioning of a carbonate rock aquifer is necessary for a thorough diagnosis of water contamination. On the other hand, anthropogenic contaminants such as NO_3^- or Cl^- can sometimes also provide information about the characteristics of such type of aquifers (Goldscheider and Drew, 2007).

Caldas da Rainha (AC2, AC1B, JK1 and Pisc. Rainha) and Quinta das Janelas thermomineral waters (see Table 1) have discharge temperatures between 31 and 35 °C, and belong to the Cl–Na sulphurous *facies*. Dry residuum (D.R.) values are around 3000 mg/L for Caldas da Rainha and 2400 mg/L for Quinta das Janelas thermomineral waters (see Table 1). The presence of H_2S and HS^- in these thermomineral waters, responsible for the typical sulphurous odour, could be generated by microbial reduction of sulphates in contact with organic carbon (which accelerates karstification). According to Palmer (1995) calcite dissolution by H_2S can be described as follows:

$$H_2S + CaCO_3 = Ca^{2+} + HS^- + HCO_3^- \tag{1}$$

The generation of H_2S is generally accompanied by supersaturation with respect to calcite/dolomite (Goldscheider et al., 2010). However, in the present study, the computer code HIDSPEC (Carvalho and Almeida, 1989) was used to calculate the logarithm of the saturation index (log SI) for regionally widespread minerals such as calcite and dolomite. The results obtained indicate that the thermomineral borehole and spring waters are close to equilibrium with calcite (log SI = 0.01 and 0.06, respectively) but slightly undersaturated with respect to dolomite (log SI = −0.32 and −0.24, respectively). According to (Lauritzen and Bottrell, 1994), these results seem to indicate that microbial reduction of sulphates should be reduced.

The chemical signatures of the thermomineral waters reveal that Na^+, Ca^{2+}, HCO_3^-, SO_4^{2-} and Cl^- are the dominant species. The presence of HCO_3^-, Ca^{2+} (and even Mg^{2+}) seems to be related to water–limestone interaction, while Na^+, Cl^- and SO_4^{2-} concentrations are mainly associated with the presence and dissolution of halite and gypsum lenses found along the regional syncline. The presence of these saline and sulphate deposits has been confirmed by deep petroleum prospecting boreholes.

Quinta das Janelas thermomineral spring water ($T \approx 30$ °C), located about 5 km from the Caldas da Rainha Spa area, presents similar geochemical signatures, but significantly lower TDS values (≈2375 mg/L). This indicates that this water could be described as member of a similar thermomineral aquifer system (see Table 1).

The groundwaters percolating the C/B limestone formations (see Fig. 3) belong to the Ca–HCO_3^- type. The more mineralized waters are those sampled at a longer distance from the Candeeiros Mountains (see Fig. 2), the main recharge area (see Section 4.2.1). This fact is not surprising since, according to Goldscheider et al. (2010), thermal water resources in carbonate aquifers are part of deep regional groundwater flow systems, were high topographic gradients between elevated meteoric recharge areas and low-lying discharge zones result in high hydraulic gradients (see Fig. 2), which generally act as the most important driving force (Klimchouk, 2007).

The thermomineral confined carbonate aquifer (mainly related to the C limestone formations) is overlaid by an aquifer system composed by the Upper Jurassic (D) sandstones. The groundwaters associated with this upper aquifer system also belong to the Ca–HCO_3^- type, with relatively low D.R. values (ranging from 400 to 700 mg/L) and issue temperature between 12 and 19 °C. The above mentioned geochemical signatures can be observed in Table 1 and in the modified Schoeller–Berkaloff diagram of Fig. 3.

The vulnerability of freshwater resources in karst aquifers to contamination is common knowledge (Goldscheider and Drew, 2007; Goldscheider et al., 2010). However, thermomineral carbonate aquifer systems, due to their often deep and confined setting, are naturally well protected, renewable and quasi-infinite resources (Goldscheider et al., 2010). Contaminants may be released at lower concentrations over larger areas, representing diffuse sources. The most important diffuse sources are usually from the application of pesticides and fertilizers. While these compounds are frequently spread over larger areas, the application occurs as discrete events in time.

The contribution of the shallow cold dilute groundwaters ascribed to the D geological formation, to the possible anthropogenic impact on the Caldas da Rainha and Quinta das Janelas thermomineral waters is enhanced by the NO_3^-, Cl^- and SO_4^{2-} concentrations (see Table 1 and Fig. 3) determined in some of those waters samples. The NO_3^-, Cl^- and SO_4^{2-} concentrations could be related to

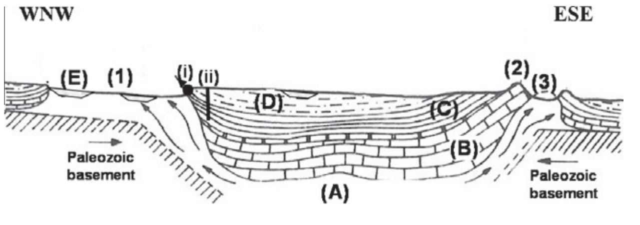

Fig. 2. Schematic geological and structural cross-section of the studied area. (1) Caldas da Rainha diapir; (2) Candeeiros Mountains; (3) Fonte da Bica diapir. The arrows indicate the movement directions. (i) thermomineral spring at Caldas da Rainha Spa; (ii) exploitation borehole of Caldas da Rainha thermomineral water. Adapted from Zbyszewski (1959). Legend as is Fig. 1.

Table 1
Representative physico-chemical composition of the waters from Caldas da Rainha region.

			in situ" determinations									Concentrations in mg/L										
Date Water source	Geological formation	Reference	T (°C)	pH	Cond (μS/cm)	Eh (mV)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al^{3+}	Fe_{total}	Li^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	HS^-	SiO_2	D.R.	Rb^+	Cs^+
24.11.05^{++}	E/A	Casal dos Chãos	16.4	5.20	368	289	30	6	24	5.6	0.10	n.d.	1.19	3	35	41	79	n.a.	10.2	233	0.020	0.410
24.11.05^{+}	B	Serra Vale dos Ventos	13.1	7.50	191.4	245	33	2	8	3.9	0.07	n.d.	1.16	114	9	8	7	n.a	1.4	122	0.010	0.350
24.11.05^{++}	C	Portela Nova	12.5	6.86	142.8	268	21	1	7	1.3	0.09	n.d.	1.12	37	7	8	35	n.a	4.1	98	0.010	0.350
24.11.05^{++}	C	Arrimal	14.5	7.15	503	249	80	4	14	7.1	0.08	n.d.	1.13	344	5	12	7	n.a	8.3	290	0.020	0.430
15.05.07$^{*,+}$	D	Q^a Janelas	30.9	6.98	2900	n.a.	291	55	339	5.4	n.a.	n.d.	n.d.	303	790	520	25	3.9	22.5	2200	n.a.	n.a.
30.12.05^{*,x}	C	Termas AC2	32.5	6.94	4360	n.a	258	54	608	9.7	n.a.	n.d.	n.a.	337	604	919	n.d.	3.2	16.7	2599	0.030	0.550
20.01.06^{*,x}	C	TermasAC1B	32.5	6.73	4670	n.a.	267	55	655	6.7	n.a.	n.d.	n.a.	320	637	1000	n.d.	4.0	18.7	2800	n.a.	n.a.
20.01.06^{*,x}	C	TermasJK1	33.5	6.83	4800	n.a.	273	57	675	7.3	n.a.	n.d.	n.a.	320	641	1000	n.d.	4.1	18.4	2800	n.a.	n.a.
20.01.06$^{*,+}$	C	Termas.PiscRainha	31.1	6.80	5260	n.a.	267	56	662	6.7	n.a.	n.d.	n.a.	317	639	1000	n.d.	3.4	18.5	2800	n.a.	n.a.
23.02.06^{+}	D	Mina da Mata	12.2	8.90	868	n.a.	129	32	72	2.6	n.a.	n.d.	n.a.	395	111	103	18	n.a.	13.8	676	n.a.	n.a.
24.04.06^{+}	D	Mina do Hospital	16.6	7.98	1075	n.a.	119	37	76	2.4	n.a.	n.d.	n.a.	399	129	105	12	n.a.	20.1	697	n.a.	n.a.
19.05.06^{x}	B	Casal do Guerra	18.3	7.68	605	n.a.	133	4	14	1.1	0.48	n.d.	0.01	295	14	26	22	n.a	21.7	325	n.d.	0.001
19.05.06^{x}	D	Casal da Marinha	14.9	7.44	1095	n.a.	75	38	70	31	0.14	n.d.	0.01	443	72	82	72	n.a	26.5	654	0.002	0.001
19.05.06^{x}	D	Casal da Azenha	16.5	7.36	1014	n.a.	69	38	59	2.8	0.09	n.d.	0.01	416	49	118	60	n.a	24.5	579	0.001	0.001
19.05.06^{++}	D	St^a Catarina	17.3	7.26	766	n.a.	88	30	16	1.3	0.08	n.d.	n.d.	411	45	37	22	n.a	21.1	440	n.d.	n.d.
19.05.06^{++}	D	Moitas	18.8	7.03	922	n.a.	115	24	24	2.7	0.03	n.d.	n.d.	445	60	50	36	n.a	24.1	503	0.001	0.001
19.05.06^{o}	D	Rio da Tornada	18.7	7.92	1104	n.a.	107	42	41	5.4	0.19	n.d.	n.d.	519	70	87	70	n.a	9.9	658	0.001	n.d.
26.10.06**	B	Casal do Guerra	n.a.	n.a.	n.a.	n.a	14	0.3	2.5	0.3	n.d.	n.d.	n.d.	5.1	1	2	n.d.	n.a	2.8	n.a	n.a	n.a
26.10.06**	B	Serra Vale dos Ventos	n.a.	n.a.	n.a.	n.a.	13	1.3	11.5	3	n.d.	n.d.	n.d.	2.1	3	12	4	n.a	0.7	n.a	n.a	n.a
03.11.06**	C	Solão-Benedita	n.a.	n.a.	n.a.	n.a.	5	0.3	3.8	1.4	n.d.	n.d.	n.d.	n.d.	1	1	1	n.a	0.1	n.a	n.a	n.a

Notes: n.a. – Not analysed; n.d. – not detected (below detection limit).

[*] Thermomineral.

[+] Spring.

[x] Borehole.

[**] Rain.

[o] Stream.

[++] Well.

Table 2
Representative isotopic ($\delta^{18}O$, $\delta^{2}H$ and ^{3}H) composition of the waters from Caldas da Rainha region.

Date	Geological formation	Reference	Isotope data			
			$\delta^{18}O$	$\delta^{2}H$	^{3}H	
24.11.05	D	Qª Janelas	−4.76	−28.4	0.1	±0.7
24.11.05	B	Serra Vale dos Ventos	−3.65	−19.9	2.4	±0.7
24.11.05	C	Portela Nova	−4.14	−26.8	1.1	±0.6
24.11.05	C	Arrimal	−3.23	−16.8	2.0	±0.6
30.11.05	C	Termas AC2	−4.39	−27.9	2.5	±0.6
20.01.06	C	TermasAC1B	−4.55	−20.2	2.8	±0.8
20.01.06	C	TermasJK1	−4.54	−29.0	1.1	±0.6
20.01.06	C	Termas.Pisc. da Rainha	−4.54	−18.9	−0.4	±0.8
23.02.06	D	Mina da Mata	−4.11	−24.4	1.7	±0.8
24.04.06	D	Mina do Hospital	−4.17	−21.0	n.a.	–
19.05.06	B	Casal do Guerra	−4.60	−22.5	2.5	±0.8
19.05.06	D	Casal da Marinha	−4.13	−22.1	0.8	±0.8
19.05.06	D	Casal da Azenha	−4.05	−26.2	1.1	±0.8
19.05.06	D	Stª Catarina	−3.68	−21.4	2.5	±0.8
19.05.06	D	Moitas	−3.97	−22.7	2.1	±0.8
19.05.06	D	Rio da Tornada	−4.00	−24.0	1.2	±0.7
26.10.06	B	Casal do Guerra	−5.99	−36.4	2.6	±0.6
26.10.06	B	Serra Vale dos Ventos	−6.29	−37.0	1.6	±0.6
03.11.06	C	Solão (Benedita)	−5.32	−30.1	2.2	±0.7

the fact that those samples (mostly from shallow boreholes and dug wells) are located, at low altitude sites, within areas with intensive agriculture. This fact might explain the higher SO_4^{2-} concentrations determined in Quinta das Janelas thermomineral waters. In fact, the Quinta das Janelas thermomineral spring issue in the D geological formation, and presently is abandoned and with no a protection area. This discussion will be pursued in the isotopic section.

4.2. Isotope approach

Carbonate aquifer systems can be characterized by natural tracers including isotopes. Isotopic data explain the origin and "*age*" of waters, and can show that possible mixing and carbonate reactivity are major variables. H and O isotopes can be used to demonstrate that most groundwaters from carbonate aquifers are normal meteoric waters (Marfia et al., 2004; Goldscheider and Drew, 2007; Azzaz et al., 2008). ^{2}H and ^{18}O contents of meteoric waters at a given geographic location vary over time. In part these variations reflect seasonal changes in temperature at single locations; they are greater in regions with large seasonal temperature changes than in areas where such differences are small (as in the study region). Normally, winter precipitation is more depleted in ^{2}H and ^{18}O than summer precipitation (Truesdell and Hulston, 1980). Most groundwaters from carbonate rock aquifers lie on or near the Global Meteoric Water Line (GMWL: $\delta^{2}H = 8\ \delta^{18}O + 10$) defined by Craig (1961) and are clearly derived from local precipitation that becomes substantially homogenized in groundwater reservoirs (Goldscheider and Drew, 2007).

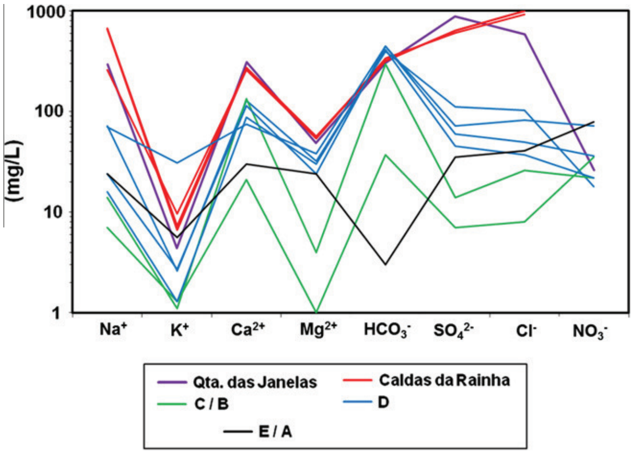

Fig. 3. Modified Schoeller–Berkaloff diagram of Caldas da Rainha and Quinta das Janelas thermomineral waters, and representative waters from the local aquifer systems ascribed to different geological formations.

Hydrogen also has a relatively short living radioactive isotope, tritium (^{3}H), with a half-life of 12.32 years (Lucas and Unterweger, 2000). ^{3}H can be used to estimate the "age" of water and due to the thermonuclear tests performed in the atmosphere during the 1960s can be applied as a tracer for groundwater recharged after 1953 (Gonfiantini et al., 1990; Gat et al., 2000). Most groundwaters from carbonate rock aquifers contain tritium that could be associated to the incorporation of modern water contaminated by thermonuclear fallout, or due to the "fast" flow-path velocities when compared with other fractured aquifers systems. Tritium is now, at a given location, about 100 times less abundant than in 1963. Nowadays, much of the "bomb-pulse" is not well defined in groundwater due to tritium decay and dispersion. Nowadays, unfortunately, the testing has originated a high doubt regarding the ^{3}H content at the time of recharge, making the ^{3}H content by itself useless as an absolute age-dating method. The application of tritium content in different groundwater case studies can be done using mathematical models (piston flow, well-mixed reservoir model, etc.) to simulate tracer distributions in aquifer systems (Deák et al., 1995). All different approaches require knowledge of the sources concentrations. Presently, the tritium peak is so narrow in most systems that the screen sizes on most boreholes includes water from periods several years above and bellow the tritium maximum (Zuber, 1986; Solomon et al., 1992; Richter et al., 1993; Reilly et al., 1994; Maloszewski and Zuber, 1996).

4.2.1. Oxygen-18, deuterium and tritium

The $\delta^{18}O$ and $\delta^{2}H$ values presented in Table 2 and displayed in Fig. 4 seem to indicate that the recharge of the Caldas da Rainha–Quinta das Janelas thermomineral aquifer systems is rather diffuse, being mainly related to the C (Middle Jurassic) geological formations (see Figs. 1 and 2). In fact, the Caldas da Rainha–Quinta das Janelas thermomineral waters are slightly depleted in heavy isotopes, compared to the isotopic composition of the shallow cold dilute groundwaters sampled in the D (Upper Jurassic) loamy and detritic formations. This isotopic difference supports the hypothesis of the existence of unrelated aquifer systems (see Fig. 4). On the other hand, when compared with Caldas da Rainha thermomineral waters, Quinta das Janelas thermomineral waters have a rather different chemical mineralization (e.g. in SO_4, Cl and NO_3). However, both thermomineral systems are close to each other from the isotopic (δ^2H and δ^{18}O) point of view, indicating similar recharge altitudes.

Two of the Caldas da Rainha thermomineral waters (from borehole AC1B and Piscina da Rainha) present deuterium enrichment (see Fig. 4). This trend could be related to isotopic fractionation between water and HS^-, as referred by Mook (2000) in similar studies.

The hydrogen and oxygen isotope ratios of shallow cold dilute groundwaters ascribed to the D formations should be considered as representative of local meteoric waters infiltrated at low altitude sites. Two groundwater samples (Portela Nova and Arrimal – see Table 2) related to the C Middle Jurassic geological formations presents a heavier isotopic composition (see Fig. 4). These waters were sampled in the Eastern border of the Candeeiros Mountains. This different isotopic content can be related with different underground flow path towards East, or most probably associated to the fact that Arrimal water sample represent a dugwell sample, under strong evaporation conditions, explaining the enriched isotopic composition.

Caldas da Rainha thermomineral borehole waters (e.g. AC1-B, AC2 and JK1) are characterized by the presence of ^{3}H (from 1.1 to 2.8 TU). To a first approach, these ^{3}H concentrations could be interpreted as the result of mixing with shallow groundwaters. In this case, the thermomineral spring waters with no ^{3}H and high mineralization should be considered as most representative of the deep thermomineral aquifer system. However, the presence of ^{3}H in the thermomineral borehole waters is not accompanied by an increase in SO_4^{2-} and NO_3^- which, in agricultural areas, are good indicators of anthropogenic contamination (see Fig. 5). These results indicate that the Caldas da Rainha thermomineral aquifer system is "*isolated*" from the anthropogenic contamination detected in the shallow cold groundwaters related to the D (Upper Jurassic) geological formations. Therefore, the presence of ^{3}H in those thermomineral borehole waters (showing similar geochemical signatures) seems to be related with a shallow and shorter underground flowpaths. In this case, the hypothesis of mixing with highly polluted shallow groundwaters seems to be unreliable. On the other hand, the possibility of mixing between these systems trough leaking borehole casing (small amounts of water) should be unable considering the tritium content in the atmosphere around 4 TU (Carreira et al., 2004) or even the peak of tritium during the thermonuclear tests performed during the 1960s. In this case, a small amount of mixing will not be detectable in the tritium content of the thermomineral water samples.

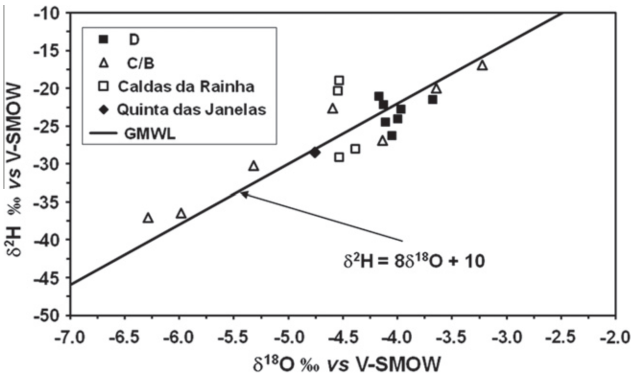

Fig. 4. δ^2H vs. δ^{18}O diagram for the Caldas da Rainha and Quinta das Janelas thermomineral waters and groundwaters ascribed to different geological formations. The Global Meteoric Water Line (GMWL) was plotted as reference.

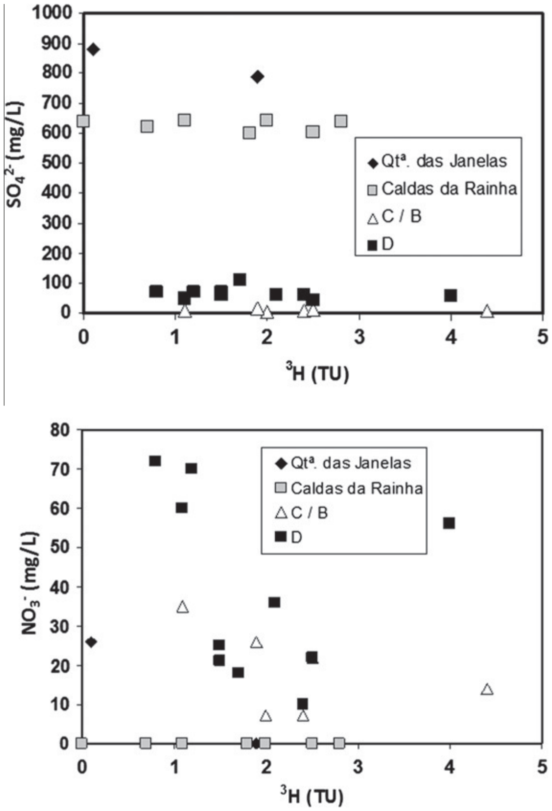

Fig. 5. Diagrams SO_4 vs. ^{3}H and NO_3 vs. ^{3}H for the Caldas da Rainha and Quinta das Janelas thermomineral waters and groundwaters ascribed to different geological formations.

4.2.2. Carbon isotopes in the thermomineral waters

The half-life of 5730 years for radiocarbon (^{14}C) makes it highly useful for dating carbon-bearing materials in the range of 100–50,000 years, which greatly facilitates studies of archeological materials (Goldscheider and Drew, 2007). Groundwater has also been dated, most commonly by determining the ^{14}C abundance in Dissolved Inorganic Carbon (DIC).

Carbon-14 dating technique can be routinely performed on DIC by use of accelerator mass spectrometry (AMS) or through a liquid scintillation counter (benzene synthesis). Most successful studies (e.g. Changkuon et al., 1989; Wang and Pang, 1995; Horvatincic et al., 1996) have been conducted using DIC ^{14}C measurements. Within the time length of the ^{14}C dating (the production rate of the global ^{14}C reservoir is more or less constant) the cosmogenic production is balance by radioactive decay. A simplest approach to carbon-14 dating of groundwater systems assumes that the ^{14}C "travel" with the water molecules along the flow path and the main mechanism that controls carbon-14 dating technique can be routinely performed on DIC by use of accelerator mass spectrometry (AMS) or through a liquid scintillation counter (benzene synthesis). Most successful studies (Changkuon et al., 1989; Wang and Pang, 1995; Horvatincic et al., 1996) have been conducted using DIC ^{14}C measurements. Within the time length of the ^{14}C dating method the production rate of the global ^{14}C reservoir, is more or less constant, the cosmogenic production is balance by radioactive decay. At simplest approach to carbon-14 dating of groundwater systems assumes that the ^{14}C "travel" with the water molecules along the flow path and the main mechanism that is varying the ^{14}C content of the groundwater is "pure" radioactive decay. Often, in several situations, like in Caldas da Rainha thermomineral system, this is not the case, the isotopic signature of the ^{14}C may be diluted, particularly by ^{14}C-free sources (Carreira et al., 2008). However the discussion when using the dating approaches the ^{14}C content of the groundwater is "pure" radioactive decay. Often, in several situations, like in Caldas da Rainha thermomineral system, this is not the case, since the isotopic signature of the ^{14}C may be diluted, particularly by ^{14}C-free sources (Carreira et al., 2008). However, the discussion related with the dating approach continues about the extent to which ^{14}C-free carbonate rocks dilute the ^{14}C content of recharge waters. As a result, absolute "*age*" determinations of groundwater using ^{14}C are limited to special cases where the absence of carbonate can be demonstrated or ^{14}C correction models can be validated.

There are various models to estimate the initial activity of the ^{14}C by applying the concentrations of the bicarbonate and CO_2 or the isotopic composition of carbon includes isotopic fractionation and mixing. A common and easy way is to estimate the initial ^{14}C activity, relating the $\delta^{13}C$ content of the DIC in the groundwater to the mixed carbon from carbonate rocks, with carbon from soil CO_2 and the fractionation factor between the different carbonate phases function of temperature (Salem et al., 1980).

The use of ^{14}C measurements in carbonate rock aquifers must be treated with great caution. The propensity of DIC to react with the carbonate matrix is very high and observed ^{14}C contents in carbonate rock aquifers are best viewed as a measure of the extent of isotopic exchange with the host rock. When coupled to $\delta^{13}C$ measurements, the extent of such isotopic change reaction becomes apparent and can be a valuable tool in water–rock reaction studies and in the calculation of groundwater ^{14}C apparent age. The ^{13}C enrichment is a consequence of the $\delta^{13}C$ value of limestone, usually ranging between 0‰ and 2‰ vs. VPDB, while the $\delta^{13}C$ of DIC that initially dissolves in groundwater depends on the conditions occurring during the dissolution of soil CO_2 (type of vegetation, pH, open or closed system, etc.), most frequently it ranges from −20‰ to −15‰. On the other hand, the ^{14}C depletion is a consequence of the ^{14}C content of limestone, normally equal to zero, compared to the initial value of DIC, which may be as high as 100 pmC (Gonfiantini and Zuppi, 2003).

As mentioned, according to the different methods, different ^{14}C "age" values of can be obtained for the groundwater systems, since are open systems to carbon. Considering the geological features of Caldas da Rainha and following the indications given by Gonfiantini and Zuppi (2003) in their research work within karst systems, located in different regions, an apparent carbon-14 age for Caldas da Rainha thermomineral system was calculated and the values obtained are varying between 4.4 (Caldas da Rainha AC3 borehole) up to 6.6 ka BP for Quinta das Janelas thermomineral spring waters (Table 3). According to those authors, groundwater in karst aquifers has often short residence time, and, as a consequence, the ^{14}C radioactive decay and the isotopic exchange effects may not be large enough to produce a significant correlation between ^{14}C activity and $\delta^{13}C$ of DIC. Furthermore, the income of ^{14}C to the groundwater associated to the thermonuclear testes in the atmosphere, can be followed by the high dispersion and mixing which are typical of karst aquifers, and may affect the relationship between carbon-14 activity and groundwater age.

In Table 3 carbon-14 groundwater ages are presented for the thermomineral waters of Caldas da Rainha region, obtained through the different mathematical models used, based on the initial ^{14}C content. The ages obtained range from 2.5 ka in Caldas da Rainha AC3 borehole up to 8.8 ka BP (Quinta das Janelas spring).

In order to use the proposed equation (Gonfiantini and Zuppi, 2003) one have to consider the second parameter referred by the authors, i.e., the isotopic fractionation $^{13}C/^{12}C$ enrichment factor in $CaCO_3$ precipitation should be constant, as temperature and pH do not show major variations. Caldas da Rainha and Quinta das Janelas are thermomineral systems, with a mean issue temperature around 32 °C.

In a first approximation, these results should be treated with caution since we deal with a carbonate aquifer system. In most cases, these types of aquifer systems have unique hydrogeological characteristics, such as the presence of conduits, which allow groundwater to flow rapidly over large distances. This is especially true for those carbonate formations that outcrop along all their extension. In these cases, carbonate rock aquifers evolve with time to karst aquifers as CO_2 in the infiltrating groundwater dissolves the carbonate rock, enlarging a proportion of the initial fractures into conduits and caves (see Moore et al., 2010). The orientation and extension of the flow system and conduit network may even change with time (Goldscheider and Drew, 2007).

However, this is not the case in the Middle/Lower Jurassic (C and B) carbonate rocks of the Caldas da Rainha–Quinta das Janelas thermomineral systems, which are "*sealed*" by the overlaying formations mainly composed of Upper Jurassic (D) loamy and detritic rocks. According to Zbyszewski and Moitinho de Almeida (1960), this complex is dominated by sandstones and clays.

Therefore, in this case study, thermomineral water circulation at depth along the C and B carbonate formations seems to be relatively slow due to the absence of large quantities of conduits and caves. Most thermomineral water flow must be related to the intersection of rock fractures and stratigraphic joints. The low ^{3}H contents detected in the thermomineral spring waters (Piscina da Rainha and Quinta das Janelas) seem to corroborate this hypothesis, validating the ^{14}C age determinations. On the other hand, Gonfiantini and Zuppi (2003) focus that the ^{14}C radioactive decay rate is about three times faster than the isotope exchange rate between limestone water and rock, suggesting only a small age correction.

As stated by Criss et al. (2007), groundwater in regional karst systems can be >1000 years old and the use of ^{14}C to estimate groundwater "*age*" has lead to diverse correction advances to estimate the extent of water–rock interaction with very old carbonates. Recently, Gonfiantini and Zuppi (2003) combined the radioactive decay equation with the stable isotope exchange model and concluded that the radioactive decay rate of ^{14}C is 3 times faster than the isotope exchange rate between karst water and rock. They suggested that in karst systems only a small age correction is necessary. Criss et al. (2007) stated that many studies that have used ^{14}C to characterize karst groundwater age point to similarly slow water–rock exchange rates in their simplified age-correction models. For example, Deák (1978) indicated ^{14}C "*age*" determinations of the hot (40–60 °C) spring water from the Buda karst (Hungary) from 5000 to 16,000 years old. In the case of Derbyshire thermal (27.5 °C) springs (UK), where the springs discharge from a karstified limestone aquifer of Dinantian age, Brassington (2007) reported that the thermal water is heated by circulation down to 1 km in depth, and groundwater "*age*" of 5000 years old, determined by isotopic methods. Therefore, in our case study, the ^{14}C "*age*" determinations can be seen as reliable results bearing in mind (i) the extension of the regional syncline and (ii) the geochemical signatures (Na, Cl, SO_4 and Ca concentrations) indicating a deep and long flow path through the subsurface rocks of the Hetangian–Retian (A) where the evaporitic deposits (gypsum, anhydrite and halite) are mainly found (Zbyszewski, 1959; Zbyszewski and Moitinho de Almeida, 1960).

The total dissolved carbon in thermomineral waters can be attributed to two main origins: organic and inorganic, and this will be revealed in the $\delta^{13}C$ values (Fig. 6). Considering an organic source, CO_2 can be produced from decay of organic matter with mean $\delta^{13}C$ values between −26‰ and −22‰. Among the inorganic sources, carbon in thermomineral systems may originate from: (i)

Table 3
Apparent "*ages*" of thermomineral waters. Ages estimated using different initial carbon-14 content and different methods.

Reference	pmC (%)	$\delta^{13}C$ ‰ vs. V-PDB	Radiocarbon apparent "*ages*" years BP ± 2σ			
			(100 pmC)[1]	(85 pmC)[2]	(55–65 pmC)[3]	(100 pmC)[4]
Caldas da Rainha AC2[x]	38.29 ± 0.18	−8.6	5184 ± 2303	6592	3685	3844 ± 2308
Caldas da Rainha AC3[x]	44.39 ± 0.20	−9.9	4386 ± 1949	5370	2462	3672 ± 2270
Piscina avxda Rainha[+]	37.58 ± 0.18	−7.8	5284 ± 2349	6747	3840	3280 ± 2340
Quinta das Janelas[+]	29.33 ± 0.14	−6.6	6623 ± 2944	8796	5889	4117 ± 2405

Notes: $\delta^{13}C_{aquifer} = 1 \pm 0.1‰$; $\delta^{13}C_{soil} = -23 \pm 2‰$, $\varepsilon_{13} = 8 \pm 0.5‰$.

[+] Spring.

[x] Borehole.

[1] Gonfiantini and Zuppi (2003).

[2] Vogel (1970).

[3] Geyh (1972) in Mook (2000); initial ^{14}C content for karst regions: mean age ± 690 years BP.

[4] Salem et al. (1980).

deep-seated (upper mantle) carbon showing $\delta^{13}C$ values ranging between −8‰ and −1‰, (ii) carbonate (marine origin) dissolution with $\delta^{13}C$ values close to 0‰, or (iii) from the dissolution metamorphism of carbonates producing CO_2 with slightly positive $\delta^{13}C$ values (Bergfeld et al., 2001; Truesdell and Hulston, 1980).

In the case of Caldas da Rainha–Quinta das Janelas thermomineral waters $\delta^{13}C$ values range from −9.9‰ to −6.6‰ vs. V-PDB, which are typical for carbonate dissolution enhanced by soil derived H_2CO_3 (mainly from the recharge areas). From data presented in Fig. 6 it can be concluded that waters of the Caldas da Rainha–Quinta das Janelas thermomineral aquifer systems show a simultaneous enrichment in $\delta^{13}C$ and depletion in ^{14}C, a result of isotopic exchange with the host aquifer rocks, originated from old marine carbonates.

4.2.3. Sulfur and oxygen isotopes ($\delta^{34}S_{(SO4)}$ and $\delta^{18}O_{(SO4)}$) in sulphate

Since chemical analysis of waters only can provide the concentration of sulphate, but not its source, an isotopic ($\delta^{34}S_{(SO4)}$ and $\delta^{18}O_{(SO4)}$) sampling campaign was carried out. A special emphasis was put on the thermomineral waters and on the shallow cold dilute groundwaters from the D geological formation, where diffuse sources of pollution in the catchment area are mainly from agriculture and livestock activities. Therefore, the objective of this campaign was to identify the origin of sulphate in Caldas da Rainha and Quinta das Janelas thermomineral waters.

Two groups with different $\delta^{34}S_{sulphate}$ and $\delta^{18}O_{sulphate}$ values were obtained (Fig. 7): Group 1 – encompasses deep groundwaters with high sulphate concentrations (between 600 and 800 mg/L), collected from springs and boreholes related to the thermomineral aquifer system, having $\delta^{34}S_{sulphate}$ and $\delta^{18}O_{sulphate}$ values between +14.9‰ and +19.1‰ and +11.1‰ and +16.2‰, respectively. Group 2 – is related to shallow cold dilute groundwater samples (with sulphate concentrations around 60 mg/L) from the D geological formations, collected from boreholes (≈100/150 m depth) and dug wells, displaying $\delta^{34}S_{sulphate}$ and $\delta^{18}O_{sulphate}$ values between +1.5‰ and 4.1‰ and +8.6‰ and +9.3‰, respectively (Table 4).

These results indicate two different sources of sulphate in the studied groundwaters. In the case of groundwaters ascribed to the Caldas da Rainha–Quinta das Janelas thermomineral aquifer systems, the sulphate is clearly the result of water–rock interaction with evaporitic sulphates (e.g. gypsum and anhydrite) found in the deeper component of the regional synclinal structure. In the second group, the sulphate concentrations are still considerable but clearly lower (below 60 mg/L) than in the first group, indicating

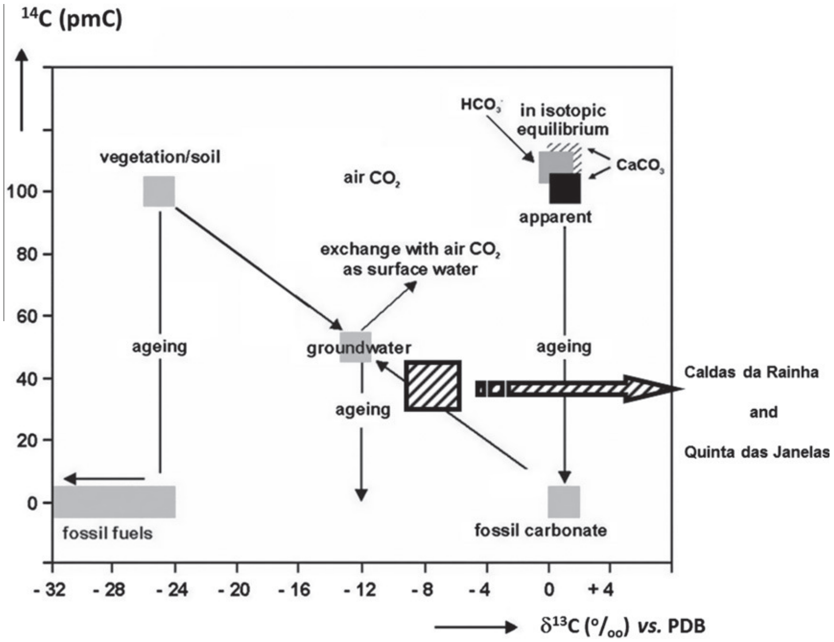

Fig. 6. Schematic diagram showing the relationships between $\delta^{13}C$ and ^{14}C in nature. Adapted from Mook (2000). The field of Caldas da Rainha and Quinta das Janelas thermomineral waters was plotted as reference.

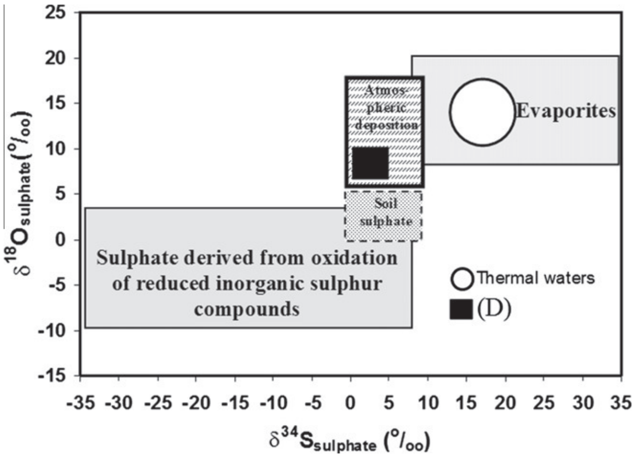

Fig. 7. Variation of $\delta^{34}S_{(SO4)}$ and $\delta^{18}O_{(SO4)}$ values observed in atmospheric, pedogenic and geogenic sulphates. Adapted from Mayer and Krouse (2004). The field of Caldas da Rainha and Quinta das Janelas thermomineral waters (Thermal waters) and of shallow cold dilute waters ascribed to the Upper Jurassic (D) geological formation were plotted as reference.

that the sulphate may be from atmospheric deposition that has cycled through the soil zone and infiltrated the groundwater. The influence of fertilizers used in agriculture activities should also not be ruled out.

4.3. Comparison between Caldas da Rainha and Quinta das Janelas mineral waters

Although the Caldas da Rainha and Quinta das Janelas thermomineral water systems clearly belong to one larger groundwater system and consist of related and comparable water types striking differences both in the chemical as well as the isotopic composition are found. In the chemistry most strikingly is a lower Na and Cl content found in Quinta das Janelas as compared to Caldas da Rainha. As far as the isotopic content is concerned some differences can also be found between the two thermomineral systems, The $\delta^{18}O$ and $\delta^{2}H$ mean values of Quinta das Janelas are slightly more depleted, while $\delta^{34}S_{(SO4)}$ and $\delta^{18}O_{(SO4)}$ are more enriched. Although, when these thermomineral water samples are represented in the $\delta^{2}H$ vs. $\delta^{18}O$ diagram, they plot close to each other (see Fig. 4). The depleted $\delta^{18}O$ and $\delta^{2}H$ values determined in the water samples of Quinta das Janelas might indicate a higher altitude for its recharge area. However from the isotopic point of view the two water samples from Caldas da Rainha group (Piscina da Rainha and Termas AC1B) are most probably indicating isotopic fractionation (evaporation/H_2S isotopic exchange, respectively). On the other hand, Quinta das Janelas thermomineral waters have the lower ^{14}C content. Finally Cl isotopes have a negative value (relative to SMOC) in Quinta das Janelas, and mostly positive values in Caldas da Rainha.

These geochemical and isotopic differences seems to indicate different origins of the two hydromineral systems or different underground flow paths by contacting with different geological layers leading to different isotopic signatures ($\delta^{34}S_{(SO4)}$; $\delta^{18}O_{(SO4)}$ and $\delta^{37}Cl$). As mention, the smallest ^{14}C content found in Quinta das Janelas indicate either a longer distance from the recharge area, or less permeable rocks so that the average flow rate is lower. Chemical data, with lower Na and Cl concentration in Quinta das Janelas suggest that the composition of the Margas da Dagorda formation, which is the main source of soluble salt in these thermomineral water systems regional flow path consists of relatively less halite compared to its gypsum content.

Positive $\delta^{37}Cl$ values in Caldas da Rainha thermomineral waters indicate that the NaCl it has dissolved out of the Margas da Dagorda formation is a first stage halite as halite precipitating from seawater is enriched in ^{37}Cl (Eggenkamp et al., 1995). However a more depleted $\delta^{37}Cl$ in Quinta das Janelas would indicate a late stage evaporite, which is in contradiction to the lower NaCl contents (relative to gypsum) in this thermomineral water. It is thus suggested that the Cl present in both systems is from different origins (earlier and later stage evaporites) and that the gypsum (Ca and SO_4) has been dissolved into the waters at different locations. The differences in both chemistry and isotopic compositions of the two described thermomineral systems thus indicate a different flow between recharge and discharge areas, notwithstanding the fact that the two systems have many similarities, which are the result form the fact that they originated form similar, but significantly different, water–rock interaction.

5. Conceptual model

A conceptual model is a stage in model development and usually will be used in setting up a monitoring network, deriving threshold values, determining the status of groundwater bodies, etc. Models used to consider, and to discuss about the ideas they are based on, are called conceptual models. A conceptual model is a qualitative, schematic representation of (or part of) reality. Usually a conceptual model consists of three elements, described at an abstract level (van Baest, 2004): i) the research element, the independent variable(s) subject to investigation, ii) the concepts, theoretical variables, all relevant variables with respect to the investigation and iii) the hypotheses, the relations between concepts.

Table 4
$\delta^{34}S_{(SO4)}$, $\delta^{18}O_{(SO4)}$ and $\delta^{37}Cl$ values observed in groundwaters from Caldas da Rainha region.

Reference		$\delta^{34}S_{(SO4)}$ (‰)	$\delta^{18}O_{(SO4)}$ (‰)	SO_4 (mg/L)	$\delta^{37}Cl$ (‰)
Quinta das Janelas (♦)$^{+}$	Group 1	19.1	16.2	802	−0.06
Piscina da Rainha (■)$^{+}$		17.1	13.3	600	0.26
AC2 (■)^{x}		17.8	11.1	604	0.28
AC3 (■)^{x}		14.9	14.8	600	0.28
JK1 (■)^{x}		–	–	–	0
Moitas$^{++,D}$	Group 2	4.1	9.3	56	–
Casal da Marinha^{x,D}		1.5	8.6	48	–
Casal da Azenha^{x,D}		–	–	–	0.06

Notes: (♦) and (■) Thermomineral waters.
$^{+}$ Spring.
^{x} Borehole.
$^{++}$ Dug well.
^{D} Upper Jurassic geological formation.

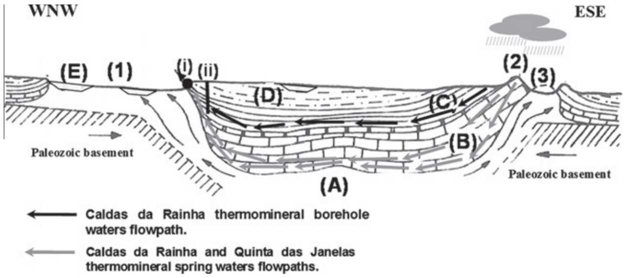

Fig. 8. "*Global*" conceptual hydrogeological model of Caldas da Rainha–Quinta das Janelas thermomineral water systems. Based on the geological cross-section presented by Zbyszewski (1959). No scale. Legend as is Fig. 1.

The conceptual circulation model "*build up*" for Caldas da Rainha thermomineral waters acknowledges the existence multi-layered aquifer systems, including independent aquifer systems. The hydrogeochemical characteristics and temperature of Caldas da Rainha thermomineral waters reflect a depth circulation.

The main recharge area of the Caldas da Rainha thermomineral system seems to be related to the geological formations C/B located at the E border of the Candeeiros Mountains (see Figs. 1 and 8). The discharge zone is located at the W border of the regional syncline, controlled by the locally oriented N–S oblique fault (60°E). In the Caldas da Rainha discharge flow area the thermomineral water flows through the limestone strata. In this area, the flow evolves from East to West, following the reverse inclination of limestone layers. When the groundwater flow reaches the "*Dagorda marls*" at the fault zone, the groundwater tends to percolate into the limestone located in the W block of the fault. From this limestone the water pass into the superficial sedimentary granular deposits located under the main building of Caldas da Rainha Spa, where the springs are located at the basement of the building.

The infiltrated meteoric waters percolate along the syncline (about 15 km length) promoting water–rock interaction. The presence of HCO_3^-, Ca^{2+} (and even Mg^{2+}) is probably related to the water–limestone interaction, while the Na^+, Cl^- and SO_4^{2-} concentrations should be mainly associated with the dissolution of halite, gypsum and anhydrite lenses found in the deeper parts of the regional syncline. The results of ^{14}C age determinations using four different methods (see Table 3) give radiocarbon ages varying from 2462 years BP (Caldas da Rainha AC3 up to 8796, with a mean value around 5000 years BP). Among the different methods that were used the one from Gonfiantini and Zuppi (2003) and the Salem et al. (1980) correction method seems, in Caldas da Rainha case study, those which are more "reliable". Applying the $\delta^{13}C$ content in the ages correction the data obtained are about 3500 years BP and 4000 years BP for Quinta das Janelas, corroborating the hypothesis of a longer and deeper underground circulation path.

The Caldas da Rainha thermomineral aquifer system seems to be "*isolated*" from anthropogenic contamination due to the existence of impermeable layers of the Upper Jurassic (D). $\delta^{34}S_{\ (SO4)}$ and $\delta^{18}O_{\ (SO4)}$ values of dissolved sulphate indicate that in the Caldas da Rainha thermomineral waters, the sulphate is clearly the result of water–rock interaction with evaporitic rocks at depth.

6. Concluding remarks and outlook

Usually, karst aquifers require specific investigation methods, since they are different from other hydrogeological environments such as fractured aquifers.

In the study region, carbonate rock formations hold important thermomineral water resources that are vital for the water supply of Caldas da Rainha Spas. The natural quality of this karst thermomineral water is excellent. The regional lithostratigraphy rock sequences have been used and interpreted as a hydrostratigraphy, enabling a hydrogeological subdivision of the rock sequences. A regional fault with important displacement seems to limit the thermomineral aquifer.

The hydraulic properties of Caldas da Rainha thermomineral–Quinta das Janelas carbonate rock aquifer can be explained assuming mainly the presence of a low permeability system with a high storage capacity, which is drained by a fissured (a network of fractures and bedding planes) porous aquifer (limestone rocks). The fissured-porous rocks contain flowing water in the fissures and stagnant water in the porous matrix. The water enters this system at the catchment surface and flows through several similar flowpaths (subsystems), being finally drained at springs. This simplified view of this carbonate rock thermomineral aquifer system is supported by the ^3H values and the ^{14}C "*age*" determinations.

Further studies, including exploration geophysics, aimed at improving knowledge about water storage and flow in such a peculiar groundwater system will play a very important role for delimiting contamination protection zones and for estimation of water resources. As support of previous hydrogeologic investigations, geophysical methods such as gravimetric, resistivity and electromagnetic, can provide important additional information on (i) detection of high porosity zones, (ii) delineation of aquifer dimensions and groundwater flow paths.

Although carbonate rock aquifers present a considerable degree of similarity, in terms of the manner in which they function, difficulties in the interpretation of smaller scale characteristics with the regional conceptual model requires a wide variety of data sources that will be extremely useful in conceptualizing carbonate rocks hydrogeology.

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