Assessment of recharge and flowpaths in a limestone thermomineral aquifer system using environmental isotope tracers (Central Portugal)

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We conducted chemical and isotopic analyses to develop and test a hydrogeological model of thermomineral water circulation in a limestone aquifer system at Caldas da Rainha (Central Portugal), contributing to future borehole-drilling and development strategies, with the aim of extracting waters with the best possible flow and/or temperature. The thermomineral waters ($T \approx 33\,°C$) discharge from springs and boreholes located close to a locally N–S-oriented oblique fault (60°E) that places loamy and detritic Upper Jurassic rocks and Hettangian-Rhaetian marls (and evaporitic deposits) in contact. [14]C determinations indicate a pmC content between 29.33 ± 0.14 and 44.39 ± 0.20 pmC. The presence of HCO_3^-, Ca^{2+} (and Mg^{2+}) are ascribed to water–limestone interactions, while Na^+, Cl^- and SO_4^{2-} concentrations are mainly associated with the dissolution of halite and gypsum lenses found along the regional syncline structure. The $\delta^{18}O$ values of Caldas da Rainha thermomineral water were slightly lower than those of shallow groundwater from the Upper Jurassic rocks, suggesting the existence of two distinct aquifer systems. The different isotopic composition of water also indicates that the main recharge of the thermomineral waters likely occurs in the Middle and Lower Jurassic limestone formations of the Candeeiros Mountains. The presence of [3]H (from 1.1 to 2.8 TU) in some thermomineral borehole waters (showing rather similar geochemical signatures) suggests mixing of small amounts of shallow groundwater with thermomineral waters, as a result of leaking borehole casing construction or a recharge when the ^{3}H content in the atmosphere was higher than that at present. Caldas da Rainha thermomineral waters having $\delta^{34}S_{sulphate}$ and $\delta^{18}O_{sulphate}$ values between $+14.9$ and $+19.1\,‰$ and $+11.1$ and $+16.2\,‰$, respectively, indicate that the sulphate is the result of water–rock interaction with evaporitic formations. The obtained chemical and isotopic data have informed the further development of a hydrogeological model that will be used by decision-makers, in order to contribute to the socio-economic development of the spa region.

Keywords: anthropogenic contamination; conceptual model; geochemistry; isotopes; isotope geochemistry; limestone aquifer; Portugal; thermomineral waters

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1. Introduction

In many parts of the world, carbonate rock formations hold thermomineral water resources that are vital for the water supply of numerous spas. Although the natural quality of those thermomineral waters is often excellent, limestone aquifer systems are more vulnerable to contamination than other types of aquifers, thus requiring special investigation and protection [1].

In the last few decades, the popularity of spas in mainland Portugal has increased considerably contributing to regional socio-economic development [2] through increased tourism. While increasing numbers of spa visitors often result in economic benefits for the region, it has also become necessary in some cases to find increased supplies of thermomineral waters when existing water sources accessed by natural springs or boreholes were insufficient to meet the demand of expanding spa facilities.

This paper examines the conceptual hydrogeological circulation model of the Caldas da Rainha thermomineral water. The key objective was to assess potential sites for future well drilling and development, with the aim of extracting waters with the best possible flow and suitable temperatures, and putting those waters to the widest possible use. To this end, a multidisciplinary approach was used through Geoscience disciplines such as Structural and Tectonic Geology, Hydrogeochemistry and Isotope Hydrology. The Caldas da Rainha thermomineral aquifer system (Figure 1) is hosted in deep fissured-porous Jurassic limestone formations [3]. Special emphasis was put on the characterisation of local/regional flow paths and the interaction between shallow cold ($\approx 17\,°C$) groundwaters with warm ($\approx 33\,°C$) thermomineral waters.

Figure 1. Geographic location of Caldas da Rainha thermomineral waters and simplified geology of the study region. Reproduced from G. Zbyszewski and F. Moitinho de Almeida, Carta Geolgica de Portugal, 1960.

2. Geological, geomorphological and hydrogeological setting

Geological and geomorphological investigations are indispensable when studying limestone hydrogeology. It is extremely difficult to understand a limestone aquifer system without taking into account the lithology of the different geological formations, the stratigraphy, fracturing, fault and fold structures, as well as the topography, the limestone landforms and the landscape history [1]. The geological formations that occur at Caldas da Rainha region are mainly of sedimentary origin, with prevalence of Jurassic limestones, sandstones and marls [3]. These Mesozoic strata are overlain by Plio-Pleistocene sandy–silty sediments.

The study region is characterised by a large syncline structure responsible for the regional flow paths of the thermomineral waters. Caldas da Rainha thermomineral waters discharge (at the W part of the syncline) from springs and boreholes located close to a locally N–S oriented oblique fault (60 °E), putting in contact the loamy and detritic rocks from the Upper Jurassic (J^{3-4}) and the marls (and evaporitic deposits) from the Hettangian-Rhaetian (J^1_{ab}) [3]. At depth, the middle and lower Jurassic series (J^3_b and J^2_{abc}, respectively) are mainly formed by limestones.

The regional diapiric structures were responsible for the uplift and consequent folding of the Jurassic formations. These two domes had been eroded and the Hettangian-Rhaetian (J^1_{ab}), the so-called 'Margas da Dagorda', becomes exposed at the surface. Overlying the marls are Pliocene (P) sediments that contain shallow unconfined aquifers in porous sands and argillaceous sandstones [3].

Fold structures often have a major impact on the groundwater drainage patterns, especially in shallow Karst aquifer systems with a high degree of stratigraphic flow control [1]. In contrast, hydrogeological studies have demonstrated that, in the case of the Caldas da Rainha thermomineral aquifer system, the influence of Karst flow control is extremely limited [4].

3. Sampling and methods

Several fieldwork campaigns were carried out between 2005 and 2008 in the study region in order to collect thermomineral water samples (from springs and boreholes – between 125 and 150 m depth) and cold dilute waters from shallow groundwater systems (from boreholes ≈150 m depth and dug wells ≈5 m depth).

Temperature (°C), electrical conductivity (μS/cm) and pH were measured in the field. Subsequently, water samples were filtered and preserved and returned to the laboratory for chemical and isotopic (δ^2H, δ^{18}O, δ^{13}C, δ^{34}S, δ^{37}Cl, ^{3}H and ^{14}C) analyses.

The chemical parameters of the surface water and shallow groundwater samples were determined at Instituto Superior Técnico, Laboratório de Mineralogia e Petrologia (Portugal), using the following methods: total alkalinity (here referred to as HCO_3) was measured a few hours after collection using standard titration techniques; atomic absorption spectrometry for Ca and Mg; emission spectrometry for Na and K; colorimetric methods for SiO_2 and ion chromatography for SO_4, NO_3 and Cl. Sulphide was precipitated *in situ* as CdS. In the laboratory, CdS was titrated (by potentiometry) with sodium thiosulphate. Total dissolved solids (TDS) were determined following the US Geological Survey procedure after drying at 180 °C for 1 h [5]. The chemical parameters of the thermomineral waters were determined at Laboratório de Análises of Instituto Superior Técnico, using the following methods: Ca, Mg, Na, K, Cl, SO_4 and NO_3 by ion chromatography; Fe by inductively coupled plasma; HCO_3, SiO_2, HS and TDS were determined using the same methods as described above. Table 1 contains representative data from five different sampling sites: (1) and (2) are thermomineral borehole and spring waters, respectively, and (3)–(5) are non-thermomineral waters ascribed to different geological formations. The data presented do not represent the mean values. The non-thermomineral waters are representative of the type of

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

	(1)	(2)	(3)	(4)	(5)
T (°C)	32.5	31.1	18.8	12.5	18.3
pH	6.73	6.80	7.03	6.86	7.68
Cond (μS/cm)	4670	5260	922	143	605
Ca (mg/L)	267	267	115	21	133
Mg (mg/L)	55	56	24	1	4
Na (mg/L)	655	662	24	7	14
K (mg/L)	6.7	6.7	2.7	1.3	1.1
HCO_3(mg/L)	320	317	445	37	295
SO_4(mg/L)	637	639	60	7	14
Cl (mg/L)	1000	1000	50	8	26
NO_3 (mg/L)	n.d.	n.d.	36	35	22
HS (mg/L)	4.0	3.4	–	–	–
SiO_2 (mg/L)	18.7	18.5	24.1	4.1	21.7
$\delta^{18}O$ (‰)	−4.39	−4.54	−3.97	−4.14	−4.60
δ^2H (‰)	−29.7	−18.9	−22.7	−26.8	−22.5
^3H (TU)	2.5 ± 0.6	0.0 ± 0.8	2.1 ± 0.8	1.1 ± 0.6	2.5 ± 0.8
$\delta^{34}S_{(SO4)}$ (‰)	17.8	17.1	4.1	–	–
$\delta^{18}O_{(SO4)}$ (‰)	11.1	13.3	9.3		
$\delta^{13}C$ (‰)	−8.6	−7.8	–	–	–
^{14}C (pmC)	38.29 ± 0.18	37.58 ± 0.18	–	–	–

Notes: Thermomineral waters and non-thermomineral waters ascribed to different geological formations. (1) Thermomineral borehole water; (2) thermomineral spring water; (3) shallow cold dilute dug well water – J^{3-4} (upper Jurassic) geological formation; (4) shallow cold dilute dug well water – J^3_b (middle Jurassic) geological formation; (5) shallow cold dilute borehole water – J^2_{abc} (lower Jurassic) geological formation; n.d., not detected (below detection limits).

waters that have been sampled in the different geological formations from shallow boreholes or dug wells.

The environmental isotopes (δ^2H, $\delta^{18}O$ and ^3H) were measured at Instituto Tecnológico e Nuclear (Sacavém, Portugal). $\delta^{18}O$ and δ^2H values were determined using a VG Isogas SIRA 10 mass spectrometer, following the analytical methods described in [6–8], respectively. The results are reported in δ notation in ‰ relative to V-SMOW. The precision of the measurements is 1 ‰ for ^2H and 0.1 ‰ for ^{18}O. The ^3H contents of the water samples were determined using an electrolytic-enrichment method followed by liquid scintillation counting measurements (PACKARD TRI-CARB 2000 CA/LL) [9]. The detection limit is 1 TU. The standard deviation associated with these measurements varies between ±0.6 and ±0.8 TU function of the tritium activity of the water sample.

The $\delta^{34}S$ determinations were performed at the University of Calgary, Department of Geoscience, following the analytical methods described in [10,11].

$\delta^{37}Cl$ was measured at Utrecht University by the method described in [12]. 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) [13] with a precision of 0.1 ‰.

The $\delta^{13}C$ and ^{14}C determinations were performed at the Centre for Applied Isotope Studies (CAIS), at the University of Georgia, USA. For radiocarbon analysis, the dissolved inorganic carbon (DIC) was extracted in vacuum by acidifying the water sample. The extracted carbon dioxide was cryogenically purified and catalytically converted to graphite. Graphite $^{14}C/^{13}C$ ratios were measured using the CAIS 0.5 MeV accelerator mass spectrometer. The sample ratios were compared with the ratio measured for the Oxalic Acid I (NBS SRM 4990) standard. The $^{13}C/^{12}C$ ratios were measured separately using a stable isotope ratio mass spectrometer and expressed as $\delta^{13}C$ with respect to PDB, with an uncertainty of less than 0.1 ‰.

4. Results and discussion

4.1. *Chemistry of the waters and ^3H contents*

Caldas da Rainha thermomineral waters with a temperature of circa $32\,°C$ were characterised by electrical conductivities exceeding $4500\,\mu S/cm$ and belong to the Cl–Na sulphurous-type, presenting a rather constant composition over time [14]. The presence of reduced species of sulphur is likely related to bacterial sulphate reduction [11]. The presence of HCO_3^-, Ca^{2+} (and Mg^{2+}) are related to water–limestone interactions, while Na^+, Cl^- and SO_4^{2-} concentrations are mainly associated with the dissolution of halite and gypsum lenses found along the regional syncline. In the case of the thermomineral waters, the computer code HIDSPEC [15] was used to calculate the logarithm of the saturation index (log SI) for regionally widespread minerals such as calcite, dolomite, halite and gypsum. 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). Both thermomineral borehole and spring waters are clearly undersaturated with respect to halite and gypsum ($-4.88 < \log SI < -0.44$). Similar results have been presented by [16,17]. The first case study [16] is related to the origin of some comparable Portuguese thermomineral waters ascribed to a similar geological environment. The second one [17] describes the hydrogeochemical properties of CO_2-rich thermomineral water in Turkey.

The groundwaters percolating the Middle and Lower Jurassic limestone formations (J_b^3/J_{abc}^2) belong to the Ca-HCO_3 type. The thermomineral limestone-confined aquifer is overlain by an aquifer system composed of the Upper Jurassic (J^{3-4}) sandstones. The groundwaters associated with this upper aquifer system belong also to the Ca-HCO_3 type (Table 1).

Most shallow groundwaters have elevated nitrate concentrations indicating anthropogenic impacts likely from agricultural practices. In contrast, no nitrate was detected in the thermomineral waters (Table 1). This may indicate that the Caldas da Rainha thermomineral aquifer system is 'geologically isolated' from anthropogenic contamination due to the presence of loamy and detritic rocks of the Upper Jurassic (J^{3-4}) geological formations. Environmental isotopes were used to further test this hypothesis.

Hydrogen has a relatively short living radioactive isotope, tritium (^3H), with a half-life of 12.32 years [18]. ^3H can be used to determine the 'age' of water and serves as a tracer for groundwater recharged after 1953. Tritium has also been used to detect mixing processes between groundwaters with different ages.

The presence of ^3H (from 1.1 to 2.8 TU) in some Caldas da Rainha thermomineral borehole waters is not accompanied by a significant change in the chemical composition (e.g. Cl and Na; Figure 2).

The presence of ^3H determined in some thermomineral borehole waters (1.1–2.8 TU), with quite similar geochemical signatures, suggests mixing of small amounts of shallow groundwaters with thermomineral waters, as a result of leaking borehole casing construction. This mixing hypothesis could be not noticeable in the chemistry of the thermomineral waters, since the potential mixed shallow groundwaters have very low mineralisation (TDS $\approx 100\,mg/L$, [4]), although perceptible in the ^3H content. On the other hand, another possible explanation needs to call to recharge of the thermomineral waters under different ^3H atmospheric content, when the atmospheric ^3H was much higher than today, derived from the vast amounts of thermonuclear tritium that have been injected into the upper troposphere and the stratosphere related to atmospheric detonations of thermonuclear devices [19]. Under this previous hypothesis, the different amounts of ^3H found in the thermomineral aquifer system could be ascribed to different underground flow paths (and different mean residence times) that will not be detectable in future campaigns. In this case, the
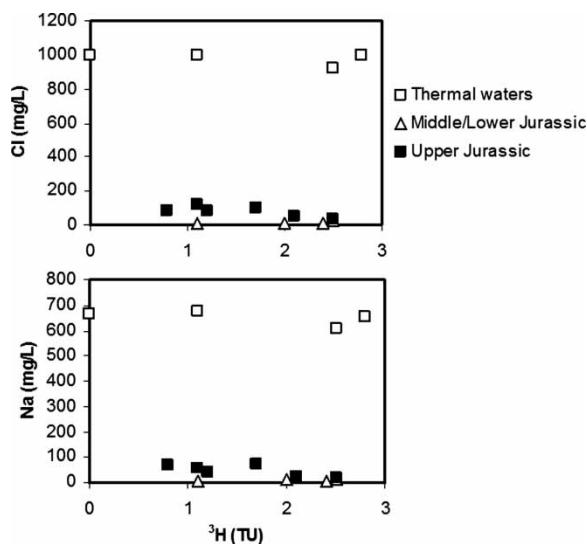
Figure 2. Diagrams Cl vs. ^{3}H and Na vs. ^{3}H for groundwaters ascribed to different geological formations.

thermomineral spring waters with no ^{3}H can be considered as most representative of the deepest thermomineral water flow system.

4.2. *Stable isotopes (δ^2H, $\delta^{18}O$ and $\delta^{13}C$)*

Among natural tracers that can be used to characterise the groundwater flow paths, stable isotopes can provide important information about limestone aquifer systems. Hydrogen (H) and oxygen (O) isotope abundance ratios can be used to evaluate whether limestone waters are derived from meteoric waters [20,21]. Most limestone waters lie on or near the Global Meteoric Water Line ($\delta^2H = 8\delta^{18}O + 10$) defined by Craig [22] suggesting a meteoric origin with the local precipitation becoming homogenised after infiltration into the groundwater reservoirs [1].

Figure 3 summarises the δ^2H and $\delta^{18}O$ values of the investigated thermomineral and groundwater samples. The Caldas da Rainha thermomineral aquifer has slightly more depleted $\delta^{18}O$ (and δ^2H) values than shallow groundwater sampled in the Upper Jurassic J^{3-4} loamy and detritic formations, indicating the presence of distinct aquifer systems. The lower isotopic composition is consistent with recharge of the thermomineral aquifer (mainly confined to the Middle and Lower Jurassic (J_b^3/J_{abc}^2) geological formations) at higher elevations at the Candeeiros Mountains at the western flank of the syncline (Figure 4). Two of the thermomineral water samples were characterised by elevated δ^2H values that may be attributed to water HS$^-$ isotopic exchange [23].

The total dissolved carbon in thermomineral waters may be attributed to two main origins: organic and/or inorganic carbon sources. CO_2 can be produced from the decay of organic matter with mean $\delta^{13}C$ values typically between -26‰ and -22‰. With respect to inorganic sources, carbon in thermomineral systems may originate from: (i) deep-seated (upper mantle) carbon with $\delta^{13}C$ values near -6‰, (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 [24–26]. Bacterial sulphate reduction should be considered as an additional source of 'dead' carbon in the system [11], and therefore the ^{14}C content (pmC) should be interpreted with caution (Section 4.3.). In the case of Caldas da Rainha thermomineral waters, $\delta^{13}C$ values of DIC range from -9.9 to -6.6‰ vs. V-PDB. These values are consistent with the water–rock
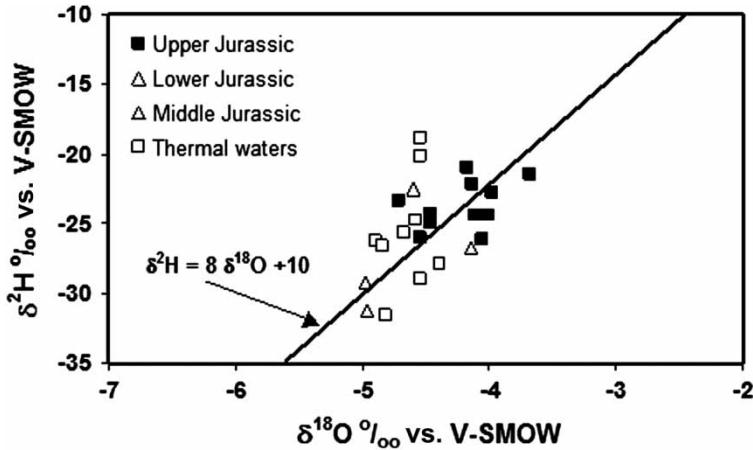
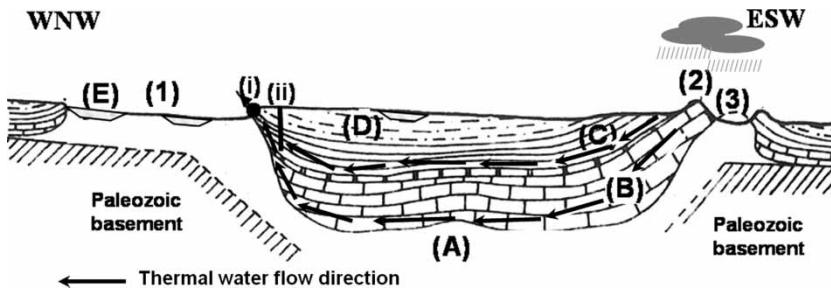Figure 3. δ^2H vs. δ^{18}O diagram for groundwaters ascribed to different geological formations.

Figure 4. Conceptual hydrogeological conceptual model of Caldas da Rainha thermomineral waters. (A) J^1_{ab}, (B) J^2_{abc}, (C) J^3_c/J^3_b, (D) J^{3-4} and (E) P. (1) Caldas da Rainha diapir, (2) Candeeiros Mountain and (3) Fonte da Bica diapir. The arrows indicate the movement directions. (i) Thermomineral spring at Caldas da Rainha Spa and (ii) exploitation borehole of thermomineral water. Adapted from [32].

interaction with carbonates, shifting the δ^{13}C values to less negative values as a result of mixing with H_2CO_3 produced from the decay of organic matter.

4.3. *Carbon-14 of the thermomineral waters*

Absolute 'age' determinations of groundwater using ^{14}C analyses are limited to special cases where the absence of carbonate can be demonstrated or ^{14}C correction models can be validated [27].

Groundwater dating by the use of ^{14}C measurements in limestone groundwaters must be treated with great caution since the reactivity of the carbonate matrix often significantly influences the ^{14}C contents of DIC in these types of aquifer. The obtained data are best viewed as a measure of the extent of isotopic exchange with the host rock. As stated by Criss *et al.* [28], groundwater in regional limestone systems can be >1000 years old. Recently, Gonfiantini and Zuppi [29] combined the radioactive decay equation with the stable isotope exchange model and concluded that the radioactive decay rate of ^{14}C is three times faster than the isotope exchange rate between limestone water and rock. The authors suggested that in limestone systems, only a small age correction is necessary.

The ^{14}C content obtained in the thermomineral groundwaters ranged between 29.33 ± 0.14 and 44.39 ± 0.20 pmC. The host formations for the thermomineral system are fissured-porous

Jurassic limestones. In such systems, significant delays of radiocarbon are expected with respect to water due to losses of ^{14}C due to matrix diffusion, leading to high ^{14}C ages. Furthermore, the sulphate reduction process occurring within the system adds dead carbon. Both factors play an important role in the decrease in the ^{14}C content. These processes will produce apparent ^{14}C ages higher than the true water ages.

These deep fissured-porous Jurassic limestone formations [3] are only exposed to the surface weathering processes in the recharge area. In fact, most limestone formations percolated by the thermomineral waters are covered by an extensive 'cap' of loamy and detritic rocks from the Upper Jurassic. The geochemical characteristics (Na, Cl, SO$_4$ and Ca concentrations) of the thermomineral water are also consistent with deep and long flow paths through the lower Jurassic formations where the evaporitic deposits are mainly found.

4.4. *Sources of SO$_4$ in the shallow and thermomineral waters*

Chemical analyses revealed significant differences between sulphate concentration of shallow groundwater and thermomineral water. Isotopic techniques (δ^{34}S$_{sulphate}$ and δ^{18}O$_{sulphate}$) were employed to identify the origin of sulphate not only in the thermomineral waters but also in the shallow groundwaters from the J$^{3\text{-}4}$ geological formation, where elevated nitrate contents had indicated water quality impacts from possible agricultural activities.

The isotopic composition of sulphate is summarised in Table 1. The obtained results indicated two distinct groundwater groups with different δ^{34}S$_{sulphate}$ and δ^{18}O$_{sulphate}$ values:

  (i) the Caldas da Rainha thermomineral waters having δ^{34}S$_{sulphate}$ and δ^{18}O$_{sulphate}$ values between +14.9 and +19.1 ‰ and +11.1 and +16.2 ‰, respectively, and
  (ii) the shallow groundwater samples collected from boreholes (∼150 m depth) and dug wells in the Upper Jurassic J$^{3\text{-}4}$ loamy and detritic formations displaying δ^{34}S$_{sulphate}$ and δ^{18}O$_{sulphate}$ values between +1.5 and +4.1 ‰ and +8.6 and +9.3 ‰, respectively.

In the case of Caldas da Rainha thermomineral waters (used in the local spa), the sulphate is clearly the result of the water–rock interaction with evaporitic formations at depth. In the shallow groundwaters sampled in the J$^{3\text{-}4}$ formations, where sulphate concentrations ranged between 40 and 60 mg/L, sulphate is most likely derived from atmospheric deposition that has cycled through the soil zone and infiltrated into the shallow aquifers. The influence of sulphate derived from fertilisers used during agriculture activities is another potential sulphate source [30].

4.5. *Chlorine (δ^{37}Cl) isotopic signatures of the thermomineral waters*

The chlorine isotope compositions of a thermomineral spring and two thermomineral water samples from boreholes in the Caldas da Rainha Spa were determined and δ^{37}Cl were consistent ranging from +0.2 to +0.3 ‰ vs. SMOC. Chloride in the thermomineral water from Caldas da Rainha is most likely originated from the Hettangian-Rhaetian (J$^1_{ab}$) 'Margas da Dagorda' formation that contains evaporites. NaCl that precipitates from saturated NaCl brines is enriched in ^{37}Cl [31] and has a more positive δ^{37}Cl value than the brine from which it precipitates. During progressive precipitation of NaCl from brine, the brine will become isotopically lighter due to the loss of ^{37}Cl, and assuming a constant isotope fractionation factor, the resulting precipitate will also be characterised by progressively lower δ^{37}Cl values. Assuming precipitation of evaporites from seawater with a δ^{37}Cl value of 0 ‰, the slightly positive δ^{37}Cl values in Caldas da Rainha thermomineral waters indicate that the Cl is derived from early formed NaCl evaporites.

5. Conceptual model and concluding remarks

Chemical and isotopic data presented in this paper are consistent with the following conceptual model. The main recharge area of the Caldas da Rainha thermomineral aquifer system seems to be the geological formations located on the eastern side of the Candeeiros Mountains (Figure 4). In fact, the δ^2H and δ^{18}O signatures of the thermomineral waters reflect the influence of altitude on meteoric recharge. The results obtained indicated that the Caldas da Rainha thermomineral aquifer has slightly lower δ^{18}O (and δ^2H) values than the shallow groundwater sampled in the upper Jurassic $J^{3\text{-}4}$ loamy and detritic formations, indicating the presence of distinct aquifer systems with different recharge altitudes. The lighter isotopic composition is consistent with the recharge of the thermomineral aquifer (mainly confined to the middle and lower Jurassic (J_b^3/J_{abc}^2) geological formations) at higher elevations at the Candeeiros Mountains at the western flank of the syncline (Figure 4).

The discharge zone is located at the western border of the regional syncline, close to a locally oriented N–S oblique fault. The infiltrated meteoric waters percolate along the syncline over a $\sim$15 km distance promoting a significant water–rock interaction. The conceptual circulation model 'build up' for Caldas da Rainha thermomineral waters acknowledges the existence of multilayered and independent aquifer systems. The hydrogeochemical characteristics and temperature of Caldas da Rainha thermomineral waters reflect deep flow paths with the thermomineral spring waters (with no ^{3}H) being the most representative of the deepest flow paths.

The Caldas da Rainha thermomineral aquifer system seems to be 'isolated' from anthropogenic contamination due to the existence of impermeable layers (D: $J^{3\text{-}4}$) in the upper Jurassic sedimentary bedrock sequence. The δ^{34}S$_{(SO4)}$ and δ^{18}O$_{(SO4)}$ values of the dissolved sulphate indicate that sulphate in the thermomineral waters is the result of the water–rock interaction with evaporitic formations at depth.

Groundwater is a 'hidden resource' which is much more important than surface water and 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 evidence regarding the extent of risks and pressures. Pollution from domestic, agricultural and industrial sources is, despite the progress in some areas, still a major concern.

Understanding the subsurface hydrological cycle is fundamental to the sustainable management of hydromineral resources at the regional or local level. We have demonstrated that a multidisciplinary approach including Structural and Tectonic Geology, Hydrogeochemistry and Isotopic Hydrology is vital to gain a better understanding of these highly complex hydrogeological systems.

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