

Fluid/mineral equilibrium calculations, isotopes and geophysics as a multidisciplinary approach to the characterization of Monção hydrothermal system (NW-Portugal)

Paula M. Carreira¹, José M. Marques², M. Rosário Carvalho¹, Fernando A. Monteiro Santos³, Hugo Matias³, Rafael Luzio³ & Dina Nunes¹

¹*Instituto Tecnológico e Nuclear. Estrada Nacional n° 10, Sacavém, Portugal*

²*Instituto Superior Técnico. Av. Rovisco Pais, Lisboa, Portugal*

³*Centro de Geofísica da Universidade de Lisboa, Edifício C, Lisboa, Portugal*

ABSTRACT: Geochemical, environmental isotopes and geophysical data from thermal and cold waters demonstrate the role of combined hydrogeological tools to improve knowledge of the conceptual circulation model of Monção hydrothermal system. Geophysical data show low resistivity zones ascribed to the thermal waters circulation in a granitic environment. The isotope signatures indicate that the aquifer recharge area is located to the south of the Monção Spas, up hill between 300 and 600 m a.s.l. The waters issue at 48°C, and are of Na-HCO₃ type. The mineral/solute equilibrium and the geothermometric results show that Monção thermal waters are non-equilibrated due to the high CO₂ content. The estimated deep temperatures derived from Na-K geothermometers give the most reliable deep temperatures, in the range of 110 to 126°C. Considering a mean geothermal gradient of 30°C/km at Monção region, the thermal aquifer is between 3.2 and 3.7 km deep.

1 INTRODUCTION AND GEOLOGICAL SETTING

One of the main objectives of groundwater modelling is to determine the most likely working models to explain hydrogeological observations. With this goal, some integrated studies (hydrogeochemical, isotopic and geophysical) were carried out at Monção region, North of Portugal. An important aspect in the low-temperature geothermal system is the maintenance of the chemical quality of the water, considering that Spas are very dependent on both constant temperature and water quality. Therefore, the effects of mixing between the hydrothermal system and the shallow cooler waters (or even with Minho River water) were investigated. Furthermore, in the research region the intense land use for agriculture (vineyards) is a major pollution risk. With this objective an integrated interpretation of the results was applied to update understanding of the Caldas de Monção low-temperature geothermal system. Special emphasis was placed on the characterization of: (i) aquifer temperatures of the Monção thermal waters from the chemical composition of the discharge fluids;

(ii) low resistivity zones to identify thermal waters flow paths; (iii) mixing processes between shallow and deep groundwater systems and, (iv) altitude of the recharge areas of the hydrothermal system. The better understanding of the aquifer structure will help in the definition of strategic sites for drilling, bearing in mind that Monção Spas are expanding their activities in response to increased demand. The boreholes located near the Minho River enable the better understanding of the structure and geometric characteristics of the hydrothermal system.

Three types of granitic rocks were identified based on their geometric relationships and internal deformation (Fig. 1). According to Ribeiro and Moreira (1986) and Moreira and Simões (1988) the rocks can be divided into: (i) *sin-tectonic granites*: with minute flakes of muscovite and biotite, presenting metamorphic minerals, and strongly correlated with migmatitic rocks; (ii) *late-tectonic granites* (frequently associated with the granodiorites): with abundant biotite (muscovite is a secondary mineral). The degree of deformation suggests an origin associated with the last Hercynian deformation phase (F3); (iii) *post-tectonic granites*: usually characterized by the presence of mega crystals of potassium feldspar and biotite. The lack of metamorphic minerals in these granites point to an age younger than the last Hercynian deformation phase. Fluvial sandstones and conglomerates of Quaternary age (sometimes with clay layers) constitute the most recent formations in the region, particularly near the Caldas de Monção Spas and along the Minho River margins.

The main fracture systems in the region are represented by structural lineaments (strike-slip faults), trending ENE-WSW, WNW-ESE, NNE-SSW and NNW-SSE, of late Hercynian age, and still active during the Meso-Cenozoic. The geological studies carried out in Monção region have indicated that the fracture system ENE-WSW (left strike-slip fault) is responsible for the morphology of the Minho River valley. The thermal borehole waters and

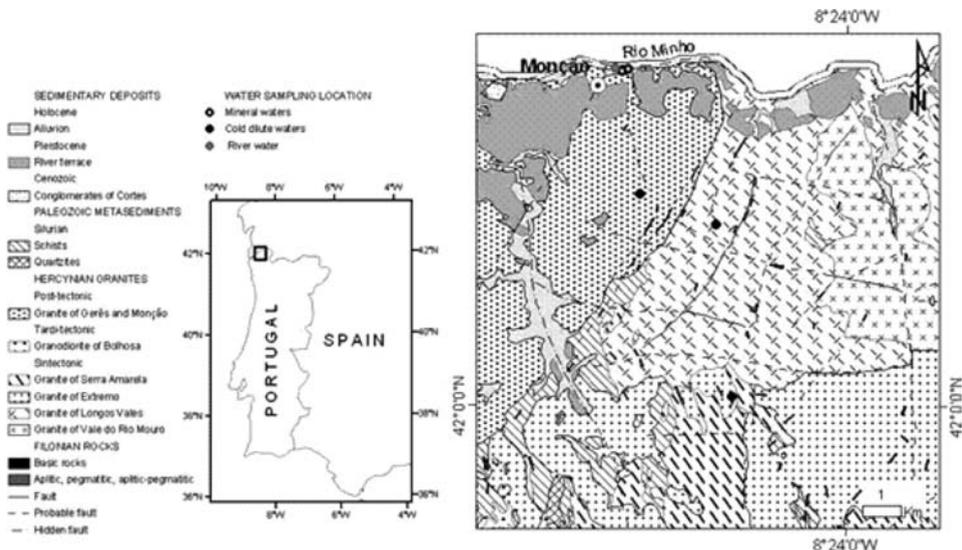


Figure 1. Geological sketch map of region (after Pedrosa, 1999). The location of water sampling sites is presented (for both thermal and shallow cold dilute water systems).

springs are located along the ENE-WSW structures, the groundwater flowpath being controlled by this fracture system.

2 SAMPLING AND METHODS

Two fieldwork campaigns were carried out at Monção region, the first during February 2002 and the second one in February 2003. Groundwater samples were collected from boreholes (thermal system) and springs (located at different altitude sites) representing the shallow cold dilute systems (local circulation). Isotopic determinations ($\delta^2\text{H}$, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, ^3H and ^{14}C) and chemical analysis (major and minor species) were carried out. During these campaigns two water samples were collected from Minho River for isotopic and chemical analysis.

The environmental isotopes (^2H , ^{13}C , ^{18}O , ^3H and ^{14}C) were measured at Instituto Tecnológico e Nuclear (Portugal). The ^{18}O and ^2H determinations were carried out using a mass spectrometer SIRA 10 VG-ISOGAS. Epstein and Mayeda (1953) and Friedman (1953) have described the analytical methods used in the determinations of oxygen-18 and deuterium respectively. The results are reported in δ notation in ‰ reported to V-SMOW with the accuracy of the measurements are 1‰ for ^2H and 0.1‰ for ^{18}O .

The ^3H was determined for all water samples using an electrolytic enrichment method and measured by liquid scintillation counting (PACKARD TRI-CARB 2000 CA/LL). The detection limit of this equipment is 0.5 TU. The associated error to the measurements varies with the tritium concentration in the samples, although usually is around 0.6 TU. The analytical method is describe in I.A.E.A. (1976).

The ^{14}C measurements were carried out on the Total Dissolved Inorganic Carbon (TDIC) extracted in the field as BaCO_3 in a pH environment higher than 9.0 (I.A.E.A. 1981). The barium carbonate obtained *in situ* is transformed into benzene in the laboratory and the counting rates of the ^{14}C are obtained using a liquid scintillation counter (PACKARD TRI-CARB 4530). The errors associated to this method vary with the amount of carbon available in each sample, and are greatest for the lowest ^{14}C content expressed as a percentage of modern carbon (pmC).

During the benzene synthesis a CO_2 gas sample is collected for $\delta^{13}\text{C}$ determinations (by mass spectrometer). The isotopic composition is reported to V-PDB in ‰. The associated error to this measurement is 0.1‰.

Temperature ($^{\circ}\text{C}$), electrical conductivity (E.Cond., $\mu\text{S}/\text{cm}$) and pH were measured *in situ*. The water samples collected for chemical analysis were stored in two polyethylene bottles (1 L), one acidified with HCl for analyses of Ca, Mg, Na, K, Li, Al and SiO_2 , the other was reserved unacidified for the F, Cl, SO_4 and NO_3 determinations. The chemical parameters were determined at Laboratório de Mineralogia e Petrologia of Instituto Superior Técnico (Portugal), using the following methods: atomic absorption spectrometry for Ca and Mg; emission spectrometry for Na, K and Li; colorimetric methods for Al, F and SiO_2 (the samples were specifically treated – ultrafiltration before Al measurements); ion chromatography for SO_4 , NO_3 and Cl; potentiometry for alkalinity, here referred to as HCO_3 .

Geophysical studies have been performed near Caldas de Monção Spas. Resistivity surveys were carried out with the main goal to detect low resistivity zones that may be connected to the thermal circulation system. These investigations were developed by the Instituto de Ciências da Terra e do Espaço (Portugal).

3 GEOPHYSICAL APPROACH

Resistivity surveys have been performed near Caldas de Monção Spas to detect low resistivity zones that represent the thermal water circulation system. The survey comprised two dipole-dipole lines that have been designed to cross the main fault system, tentatively associated to the Monção hydrogeological system (Fig. 2A). Fig. 2B shows the field apparent resistivity pseudo-section corresponding to the dipole-dipole line #2, carried out southwards of Caldas de Monção (dipole length of 10 m). The total length of this profile is 720 m. The field data was inverted using the RES2DINV code (Loke and Barker 1996). The resistivity model is presented in Fig. 2.

The main characteristics of this model are (i) overburden with a thickness ranging from 6 to 20 m and resistivity ranging from 200 to 3000 ohm-m; (ii) a more homogeneous resistivity distribution (600 ohm-m in average) at depths greater than 20 m; and (iii) the presence of three relatively low-resistivity (100 to 300 ohm-m) anomalous zones crossing all the section at 100 m, 260–300 m and 400 m coordinates.

Previous geological studies that have been performed in the region highlight the strike slip regional faults that trend NNE-SSW and NW-SE to E-W, and which basically control all the important hydrogeological systems in northern Portugal (Pedrosa, 1999). The high resistivity zones, in the overburden, are related to non-altered granite, which possess a few fracture zones that act as conductors within the profile. The low-resistivity zone in the western part of the profile (coordinate 100 m) is well correlated with a mapped fault (Fig. 2A) that runs NNE-SSW in the Monção village direction. Taking into account the resistivity contrast (from 600 to 60–100 ohm-m) this fractured zone has to be infilled with high conductivity material, probably clay and mineralized water. Therefore, the low-conductivity zones, at coordinates 260–300 m and 400 m, have been interpreted as fracture zones filled with clay and mineralized water. The same criteria was applied to the resistivity model obtained from line #1, which reveals low resistivity zones that correlate with faults marked F2 and F3 in (Fig. 2A). These fault systems cross the area towards the Caldas de Monção Spas. The models suggest that those fault systems should go deep into the granitic massif as predicted by geological studies.

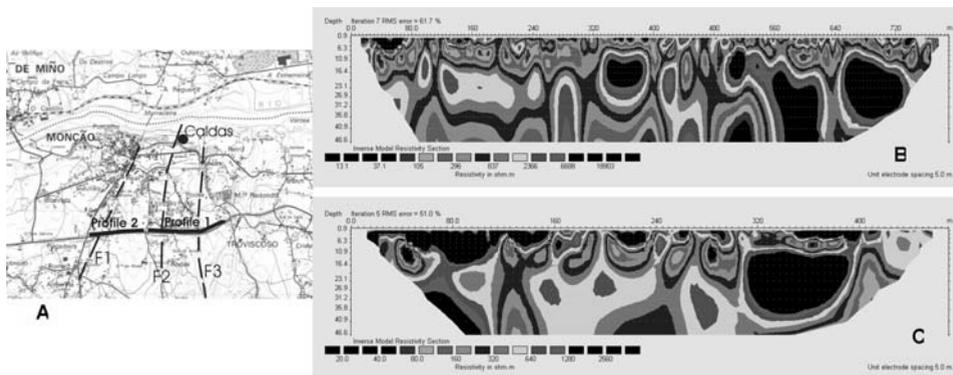


Figure 2. (A) Location of the two dipole-dipole lines plotted on the topographic map of Caldas de Monção area (1: 25000); (B) Field apparent resistivity pseudo-section corresponding to the dipole-dipole line #1, carried out southwards of Caldas de Monção; (C) Field apparent resistivity pseudo-section corresponding to the dipole-dipole line #2, carried out southwards of Caldas de Monção.

4 ISOTOPIC APPROACH OF CALDAS DE MONÇÃO GROUNDWATER SYSTEMS

4.1 Stable isotopes features

In general, the distribution of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ mimics the topography of the continents; mountains chains are marked by more negative δ values. This feature is called “*altitude effect*” (Dansgaard, 1964; Rozanski et al., 1982; 1992; 1993). The lowering of temperature with increasing elevation in mountain regions usually leads to enhanced condensation and, therefore, to a progressive depletion in heavy isotopes in rain with altitude. This “*altitude effect*” has been used in numerous hydrological studies to identify the recharge areas and to investigate the origin and interconnection of water bodies. The vertical isotope gradient varies between -0.15 and -0.50‰ 100 m^{-1} for oxygen-18 and about -1 to -4‰ 100 m^{-1} for deuterium (Araguás-Araguás et al., 2000; Gonfiantini et al., 2001).

Using the isotopic composition of the shallow cold groundwater samples the equation of the Local Meteoric Water line (Fig. 3A) is $\delta^2\text{H} = 10.17 \delta^{18}\text{O} + 20.19$ (the isotopic composition of the water samples are presented in Tables 1 and 2). In the same diagram is the isotopic composition of Minho River and the Global Meteoric Water Line (GMWL). The isotopic gap found between the two river samples should be attributed to the different sampling periods (end of summer season – October 1999 and middle of wet season – February 2003). In the Caldas de Monção area the isotopic gradient obtained for $\delta^{18}\text{O}$ (“*altitude effect*”) was -0.18‰ per 100 m of altitude (Fig. 3B). This isotopic gradient was estimated using the discharge altitude of the springs (cold dilute groundwater systems) and not the infiltration altitude, in view of the fact that these are local circulation systems, with small circulation paths.

Based on the isotopic gradient of the region and the isotopic signatures of the thermal waters, the recharge altitude of Caldas de Monção hydrothermal system was estimated. The values obtained range between 300 m and 600 m with a mean altitude around 400 m a.s.l. (at the South of Caldas de Monção). The recharge altitude values obtained at Caldas de Monção low-temperature geothermal system are in agreement to those proposed by Lima (2001), on the basis of the precipitation record.

One of the main objectives of this study was the identification of possible mixture between Minho river water with the hydrothermal system. The isotopic composition can be considered as a fingerprint of each system. Minho river depleted isotopic composition (February,

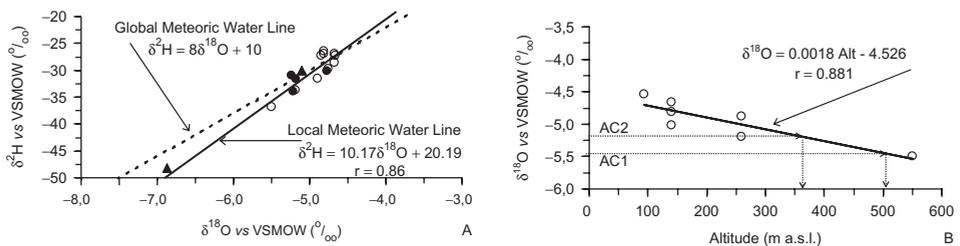


Figure 3. (A) $\delta^2\text{H}$ vs $\delta^{18}\text{O}$ for groundwater samples from Caldas de Monção area; (B) Relation of $\delta^{18}\text{O}$ values as a function of the altitude of sampling sites. The arrows indicate the estimation of the mean altitude of the hydrothermal system (boreholes AC1 and AC2). The different symbols stand for: (●) thermal borehole waters; (○) shallow cold dilute waters; (▲) Minho river water.

Table 1. Data from shallow cold dilute groundwater samples from Caldas de Monção area – discharge altitude, issue temperature, electrical conductivity and isotopic composition.

Samples	Sampling date	Altitude (m)	Temp. (°C)	Elec.Cond. ($\mu\text{S}/\text{cm}$)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	^3H (TU)
NS1	Oct-99*	140	16.0	162	-5.01	-27.7	5.2 ± 1.0
	Feb-02		14.4	114	-4.66	-27.3	3.2 ± 0.6
	Feb-03		12.8	123	-4.81	-26.5	2.6 ± 0.6
NS2	Oct-99*	260	13.3	62	-4.88	-31.5	4.8 ± 1.1
	Feb-03		11.7	80	-5.19	-33.6	2.1 ± 0.6
NS3	Feb-03	550	13.1	39	-5.50	-36.8	2.4 ± 0.5
River Minho	Oct-99*		17.5	114	-5.10	-30.0	4.5 ± 0.9
	Feb-03		10.4	112	-6.87	-48.2	2.3 ± 0.6

Note: * Data from Nascimento (2000).

2003) indicates that most of the flow contributions derive from high elevations. According to Loureiro and Machado (1986), the source of the Minho River is located about 750 m a.s.l. on Meira Mountain (NW-Spain) receiving an important recharge contribution of the Sil River also in NW Spain (Jistreda Mountain – Cantábric Mountain Range) about 1500 m a.s.l.. The Minho River geographical and topographical features are well marked in the isotopic composition variation, a depletion of about 1.5‰ in oxygen-18 (see Table 1). In a first approach this isotopic fingerprint in Minho river water suggests that the contribution of this superficial water body to Monção hydrothermal system should be extremely small or even non-existent.

4.2 *Dating Caldas de Monção thermomineral groundwater system*

Within the environmental radioisotopes, tritium cannot be detected in waters with more than approximately 50–60 years due to its short half-life (τ) (^3H : $\tau = 12.32$ years: *in* Lucas and Unterwager, 2000). Among the radioactive isotopes with a half-life higher than 10^3 years, carbon-14 ($\tau = 5730$ years: *in* Mook, 2000) represents the most important tool in groundwater dating.

Tritium concentrations were measured in all water samples (Table 1 and Table 2), as a qualitative indicator of age since it is important to mention that the tritium being an environmental radioactive isotope originated in the high levels of the atmosphere has also an anthropogenic origin associated with the release to the atmosphere from the test phase for hydrogen bombs. Tritium in precipitation has been monitored by IAEA/WMO since the bomb tests in late 1952 (Gonfiantini et al., 1990; Rozanski et al., 1991), these data enable the establishment of timescales for transport of water, e.g., groundwater, which does not contain tritium, must have infiltrated as rain before 1952, since the natural concentrations have already decayed below the detection limit.

The tritium concentrations measured in Monção shallow cold dilute groundwater systems indicate a local recharge and a rather short residence time (Table 1). When these groundwater content is compared with the precipitation tritium record measured at Porto meteorological station (Serra do Pilar, approximately 100 km south from Caldas de Monção), similar values are observed. The precipitation data present a mean arithmetic value of 4.5 TU (monthly record from 1988 to 2000, ITN data base *in*: Carreira et al., 2003). Furthermore, it is important to notice that the isotopic records of the *Portuguese Network Isotopes in*

Table 2. Data from Monção hydrothermal system – issue temperature, electrical conductivity, pH and isotopic composition (boreholes AC1 and AC2).

	Date	Temp. (°C)	E.Cond. (μS/cm)	pH	δ ¹⁸ O (‰)	δ ² H (‰)	³ H (TU)	δ ¹³ C (‰)	¹⁴ C (pmC)
AC1	Oct-99*	48.1	633	7.31	-6.54	-45.2	4.1 ± 0.6		
	Feb-02	52.0	670	7.05	-5.19	-31.6	0 ± 0.6		
	Feb-03	47.8	619	6.72	-4.77	-33.9	0 ± 0.6	-7.06	7.43 ± 0.34
AC2	Oct-99*	45.0	693	6.98	-5.20	-35.2	0 ± 1.0		
	Feb-02	46.5	741	7.06	-5.25	-30.9	0 ± 0.6		
	Feb-03	42.2	793	6.55	-5.22	-30.0	0 ± 0.6	-6.25	4.82 ± 1.00

Note: *Data from Nascimento (2000).

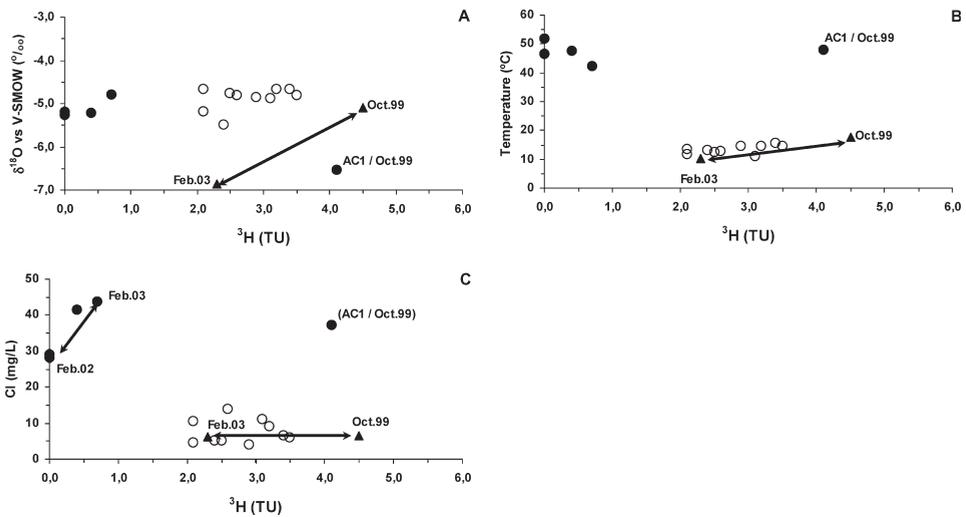


Figure 4. (A) δ¹⁸O(‰) vs ³H (TU); (B) Temperature (°C) vs ³H (TU); (C) Cl⁻ (mg/L) vs ³H (TU) for the water samples collected in 1999 in 2002 and during 2003 fieldwork campaigns. Symbols as in Fig. 3.

Precipitation reported (monthly arithmetic average of the weighted means of tritium in modern precipitation over Portugal from 1988–2000) have found tritium concentrations varying between 4.5 TU and 5.3 TU in coastal and in continental regions, respectively (Carreira et al., 2003).

The ³H content found in the shallow cold dilute groundwater systems range between 2.1 TU and 5.2 TU, reflecting local recharge and short residence times. However, the absence of ³H in the thermal borehole waters indicates a relatively long residence time, at least greater than 40 years (Table 2), if the tritium input is of the same order of magnitude as found in Porto meteorological station (4.5 TU – mean arithmetic weight value).

Fig. 4 shows a rather similar isotopic composition (δ¹⁸O and tritium) in the thermal waters collected from boreholes AC1 and AC2. In a first approach, the isotopic deviation in tritium content and depletion in oxygen-18 (AC1/ Oct. 99) could represent mixing with other water bodies (e.g. Minho River waters), more depleted and younger than the waters from the thermal system.

However, this mixing hypothesis is not enhanced in Fig. 4, either in the isotopic composition of all hydrothermal samples. Based on the ^3H content measured in the shallow aquifer, Minho River or precipitation data, no mixing is apparently occurring in the hydrothermal system or the contribution to other water bodies should be extremely small. The observed isotopic gap in $\delta^{18}\text{O}$ values between the two river samples could be explained by seasonal variation (October and February represent the end of the dry and rainy season, respectively).

The $\delta^{13}\text{C}$ determinations were performed at Monção hydrothermal system (TDIC), giving values of -7.06‰ in AC1 and -6.25‰ in AC2 boreholes, suggesting an origin for the CO_2 that can be related with mixture between atmospheric CO_2 , decay of organic matter, dissolution of limestone, deep-seated (upper mantle) CO_2 or metamorphism of carbonates producing CO_2 with slightly positive $\delta^{13}\text{C}$ values (Truesdell and Hulston, 1980; Bergfeld et al., 2001). However, limestone dissolution is unlikely, because no carbonate matrix is found in the system. Based on the geology and tectonic structure of the region the more reasonable source of carbon would be deep CO_2 (upper mantle origin).

Carbon-14 determinations were also carried out on the thermal waters, boreholes AC1 and AC2. It is important to mention that this radioisotope is present in the atmosphere, soil, aquifer matrix, etc. In fact, radiocarbon dating of groundwater in the simplest form assumes that: the ^{14}C moves with the water molecules along the flow path with a hydraulic gradient and the only mechanism enable to change the carbon-14 content within the groundwater systems is radioactive decay [$A = A_0 e^{-\lambda t}$; where A stands for the measured activity of ^{14}C in the sample; A_0 initial ^{14}C activity; λ the decay constant for ^{14}C and t stands for time]. The time can be re-arranged to provide an estimation of the groundwater "age" [$t = -\lambda^{-1} \ln (A/A_0)$]. In order to apply these equations, it is important to estimate the initial concentration of ^{14}C (A_0) at the time when the recharge occurs. Problems can arise when the measurements are performed in the Total Dissolved Inorganic Carbon (TDIC) as a consequence of the different incomes of carbon to the water system since the dissolved inorganic carbon in the surface is not conservative and potentially interacts with soil and aquifer carbonate matrix and organic matter, leading to a dilution of the initial ^{14}C content, and this results in an overestimation of the groundwater age.

At Caldas de Monção Spas the low ^{14}C content, determined in the Total Dissolved Inorganic Carbon (TDIC) in AC1 ($4.82 \pm 1.00 \text{ pmC}$) and in AC2 ($7.43 \pm 0.34 \text{ pmC}$) borehole waters, together with the absence of tritium support the hypothesis of a long residence time for the thermal waters. A close system model was used to calculate the apparent carbon-14 age of the thermal waters.

The carbon-14 age calculations was based upon the assumption that the initial activity of the dating material is 100% modern CO_2 activity (100 pmC); for the $\delta^{13}\text{C}$ of the reservoir was adopted the value of $-3 \pm 1\text{‰}$ (assuming the main origin is deep CO_2 (Bergfeld et al., 2001); the $\delta^{13}\text{C}$ for the CO_2 in the soil zone is $-25 \pm 2\text{‰}$; the fractionation factor ϵ_{HCO_3} is $8 \pm 0.5\text{‰}$, and the error associated to the measurements of the TDIC is 0.5‰. The chosen mathematical model, therefore, includes mixture of soil CO_2 with deep CO_2 since in the region no other source is known to explain the high bicarbonate content. The apparent groundwater age obtained is $11.39 \pm 2.68 \text{ ka BP}$ for AC1 and $13.13 \pm 3.59 \text{ ka BP}$ for AC2 borehole waters.

The radiometric age obtained in the hydrothermal system does not reflect the "true" groundwater age, since the most dissolved carbon has its origin in the upper mantle (^{14}C free), and the age reflects its source: dissolved carbon from deep CO_2 (upper mantle). Using simple mass balance calculations for a two-component system, an estimation can be made

of the maximum amount of upper mantle CO₂ at Monção hydrothermal system. $\delta^{13}\text{C}$ values of upper mantle CO₂ was assumed to be -3‰ (Bergfeld et al., 2001) and for the shallow aquifer $\delta^{13}\text{C}_{\text{CO}_2} -22.9\text{‰}$ (Marques et al., 2000). For a two-component system carbon isotope values indicate that the fraction of upper mantle CO₂ in Monção could be as high as 79–83%.

5 WATER CHEMISTRY APPROACH

Groundwater samples were collected from the two boreholes (AC1 and AC2) ascribed to the Caldas de Monção Spas, from the shallow cold dilute groundwater systems and from Minho River. The mean temperature of Caldas de Monção thermal waters (at the wellhead) is around 48°C, while the shallow cold dilute groundwater systems issue at temperatures around 14°C. A gap in the degree of mineralization is observed between these two water systems. The thermal waters are characterized by dry residuum between 420 to 470 mg/l, while the shallow cold groundwater systems have dry residuum values varying between 24 up to 120 mg/l. Both hydrogeological systems present the same HCO₃-Na *facies*. The Human impact in the shallow cold groundwater systems is enhanced by the increase in NO₃⁻, Cl⁻ and SO₄²⁻ concentrations. By contrast, the thermal water samples fall in a tight cluster of data points. Chloride is a conservative element often used to identify mixing processes in thermal fluids (Marini and Susangkyono, 1999; Marques et al., 2003). Therefore, geochemical data (Ca, Na, K, NO₃, SO₄ and HCO₃) were plotted against chloride content (Fig. 5).

Two clusters of water samples can be observed, one representing the hydrothermal system and another representing the shallow cold dilute groundwaters and Minho river water. In the diagram SO₄²⁻ versus Cl⁻ the dispersion of the water samples from the shallow cold dilute system is well marked. The highest NO₃²⁻ and SO₄²⁻ concentrations should be associated to the geographic location of “Bica dos Milagres” spring. This spring is located at low altitude within an area of intensely cultivated land. However it is important to emphasize that these two parameters (NO₃²⁻ and SO₄²⁻) are below the recommended maximum values in drinking waters for human use. It seems that no mixing process seems to occur between the thermal waters and the local shallow/surface waters (including Minho river water).

6 GEOTHERMOMETRIC APPROACH

The aquifer temperatures of Caldas de Monção thermal waters have been estimated with aqueous geothermometers (Table 3). These geothermometers are all based on the assumption that specific temperature dependent mineral/solute equilibrium is attained in the reservoir. The deep temperatures range from a minimum of 76°C (Na/Li geothermometer from Fouillac and Michard, 1981) to a maximum of 135°C using the quartz geothermometer (Fournier, 1977). This range of values may be due to lack of equilibration between the respective solutes and hydrothermal minerals as result of deep CO₂ gas input.

Reed and Spycher (1984) have proposed that the state of equilibrium between water and the many hydrothermal minerals as a function of temperature can provide the best estimate of reservoir temperature. Waters that are far from equilibrium with hydrothermal minerals will not show convergence of mineral equilibrium at any specific temperature. Reed and Spycher (1984) consider their procedure a valuable tool to distinguish between equilibrated

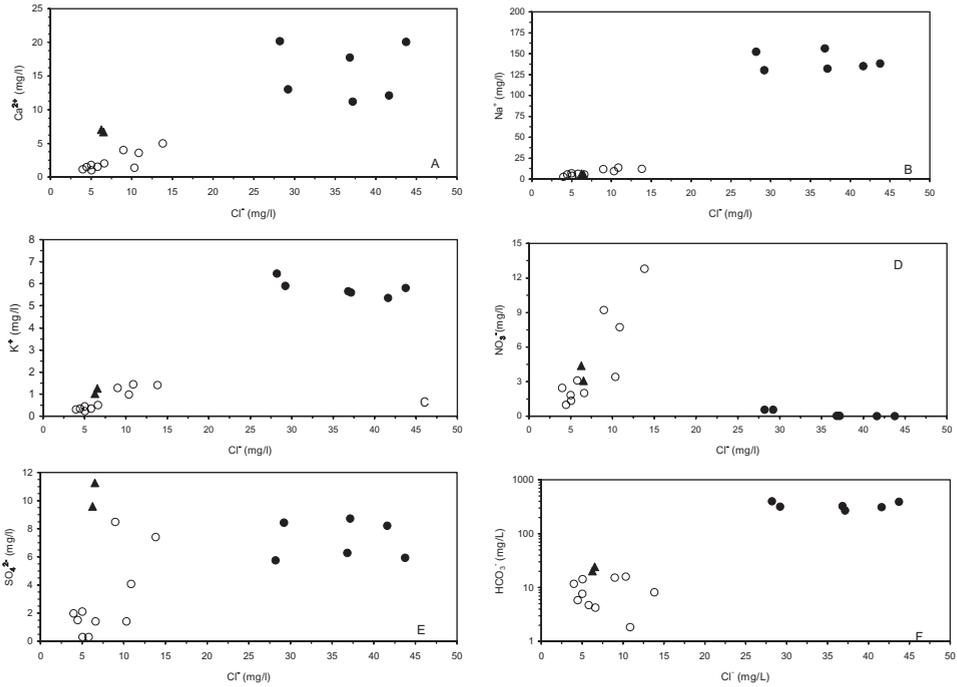


Figure 5. (A) Ca^{2+} vs Cl^- ; (B) Na^+ vs Cl^- ; (C) K^+ vs Cl^- ; (D) NO_3^{2-} vs Cl^- ; (E) SO_4^{2-} vs Cl^- and (F) HCO_3^- vs Cl^- diagrams for the water samples collected in 1999 (Nascimento 2000), 2002 and 2003 fieldwork campaigns. Symbols as in Fig. 3.

Table 3. Summary of results from aqueous geothermometric calculations applied to Monção thermal waters. Geothermometers used are from: (1) Fournier (1977); (2) Fournier and Truesdell (1973); (3) Arnórsson et al. (1983); (4) Kharaka and Mariner (1989); (5) Fouillac and Michard (1981).

Aqueous Geothermometers

Well/Spring	Date	Calcedony (1)	Calcedony (1)	Quartz- H = 0 (1)	Quartz- S = 0 (1)	Na/K (2)	Na/K (3)	Mg/Li (4)	Na/Li (5)
Monção-AC1 ⁺	Oct-99	108	106	131	135	102	121	110	80
Monção-AC1 ⁺	Feb-02	97	97	122	125	107	126	109	81
Monção-AC1 ⁺	Feb-03	103	102	127	131	97	116	139	151
Monção-AC2 ⁺	Oct-99	104	103	128	131	90	110	109	78
Monção-AC2 ⁺	Feb-02	91	91	118	120	102	121	108	77
Monção-AC2 ⁺	Feb-03	97	97	123	125	101	121	138	135
Sr ⁺ Saúde ⁺⁺	Oct-99	107	106	130	134	100	120	109	76

Note: (+) stands for borehole waters; (++) stands for spring waters.

geothermal waters and waters that have departed from equilibrium due to boiling or mixing with shallow colder waters.

The reservoir temperature was predicted on the basis of the temperature dependent equilibrium between many mineral phases and the water. The WATCH program version 2.0

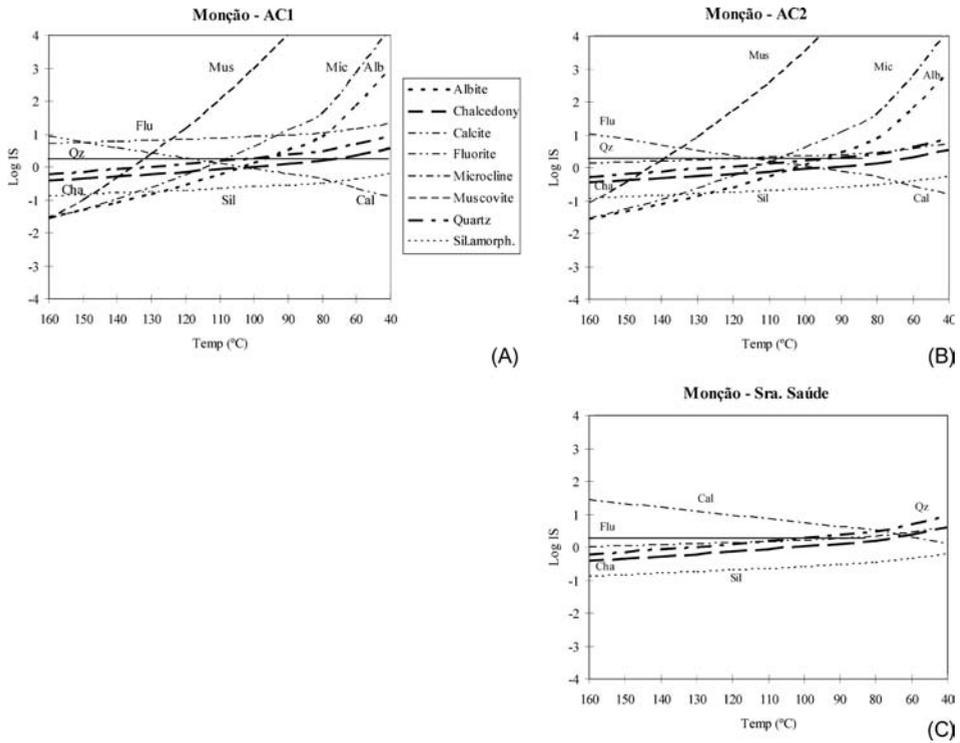


Figure 6. The saturation state of Monção thermal waters for selected minerals *versus* temperature: (A) water from AC1 well; (B) water from AC2 well; (C) water from N^o Sra. Saúde spring. The legend represented in (A) is equivalent for (B) and (C).

(Arnórsson and Bjarnason, 1994) was used to calculate the deep-water composition of Monção thermal aquifer and the state of equilibrium between the water and the minerals as a function of temperature (Fig. 6). The range of possible intersection temperatures is enormous, if one considers all the minerals for which thermodynamic data are available in the programme. The minerals likely to be present in the aquifer matrix have been considered. For most of the minerals, the deep equilibrium temperatures range from 105 to 130°C (Fig. 6). Nevertheless, the estimated temperature for the deep water of the Sra^a Saúde thermal spring is lower (Fig. 6(C)) because of the lack of aqueous aluminium data and, probably, because of silica re-equilibration during upflow.

The mineral/solute equilibrium and the geothermometric results obtained through the WATCH programme show that Monção thermal waters are non-equilibrated waters due to the high value of dissolved CO₂. As the geothermometric temperatures based on the silica minerals equilibrium are strongly dependent on the fluid pH, the estimated deep temperatures from the application of the conventional Na-K geothermometers give the most reliable deep temperatures, in the range of 110 to 126°C (Arnórsson et al., 1983).

The deep water composition of the Monção hydrothermal system was calculated using the WATCH programme and considering: (i) 120°C as deep temperature; (ii) conductive cooling in the upflow; (iii) that the total CO₂ analysed is already present in reservoir water (not updated during upflow). The Monção hydrothermal water supplying the AC1 and AC2

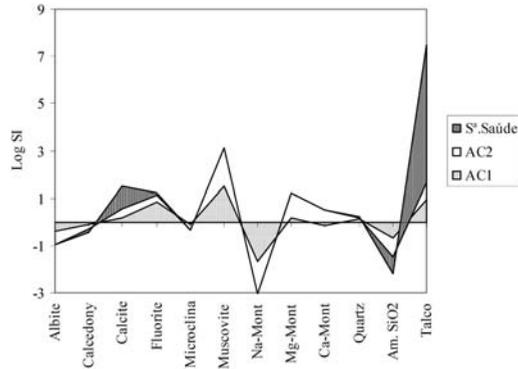


Figure 7. Water saturation state for some minerals, at the reservoir temperature of 120°C.

wells has pH around 6.70–6.85, with PCO_2 of 0.209–0.402 bar-abs and enthalpy close to 500 kJ/kg. The deep pH obtained for the spring water is higher (pH of 7.63) probably due to the lost of $\text{CO}_2(\text{g})$ during upflow.

In the aquifer, at 120°C, the water is slightly oversaturated in calcite, fluorite, Mg-montmorillonite, Ca-montmorillonite, muscovite, quartz, and talc (Fig. 7), which mean an excess of Ca, K, and Mg for the used reference equilibrium temperatures. The waters are undersaturated with respect to albite, chalcedony, Na-montmorillonite and amorphous silica. This can be explained by ionic exchange reactions or mixing of waters with different geochemical signatures. Assuming the aquifer temperature of 120°C and a mean geothermal gradient of 30°C/km at Monção region (Duque et al., 1998), the Caldas de Monção thermal aquifer is situated between 3.2 and 3.7 km at depth.

7 CONCLUSIONS

The regional geomorphology of the region favours a conceptual circulation model for Caldas de Monção hydrothermal system where the recharge area is located at South of Caldas de Monção, between 300 and 600 m a.s.l. (based on $\delta^{18}\text{O}$ values). The groundwater flow paths are associated with the NNE-SSW fault systems and their NW-SE associated systems. The geophysical models suggest that the tectonic systems may be deep and filled with mineralized water. The low ^{14}C (TDIC) content (between 4.82 ± 1.00 pmC and 7.43 ± 0.34 pmC) of Caldas de Monção thermal waters together with the absence of ^3H support the hypothesis of a long circulation path through the subsurface rocks. This hypothesis is corroborated by the minimum depth reached by the Caldas de Monção thermal water system (3.2–3.7 km) estimated by the geothermometric approach, considering that the thermal aquifer temperature is at 120°C. The $\delta^{13}\text{C}$ determinations give values in the range of -7 to -6% , indicating a “complex” origin for the CO_2 in these waters (mixture between atmospheric CO_2 , decay of organic matter and mainly by upper mantle CO_2). Geophysical, isotopic and geochemical studies performed at Caldas de Monção region have increase knowledge on the interaction between local shallow cold groundwater systems and the low-temperature geothermal waters. The better understanding of the Monção hydrothermal aquifer will help in the definition of drilling strategies, and prevent physico-chemical fluid alterations during further aquifer exploitation.

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