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# Isotopic, geochemical and geophysical studies to improve Caldas de Monção thermomineral waters conceptual circulation model (NW Portugal)

## Contribuição de estudos isotópicos, geoquímicos e geofísicos para o melhor conhecimento do modelo conceptual de circulação do sistema termomineral de Caldas de Monção (NW de Portugal)

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### Resumo

Tendo por objectivo aperfeiçoar o modelo conceptual de circulação das águas termominerais de Caldas de Monção, foram realizados estudos hidrogeológicos (isotópicos, fisico-químicos e geofísicos) na região envolvente das Caldas de Monção (NW de Portugal). Foram realizadas análises químicas (espécies maiores e menores) e isotópicas ( $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ,  $^3\text{H}$  e  $^{14}\text{C}$ ) em amostras de águas subterrâneas colhidas em furos de captação (sistema termomineral) e em nascentes representativas dos sistemas aquíferos mais superficiais e de fraca mineralização. Foram igualmente colhidas amostras de água do rio Minho para análises químicas e isotópicas. Em simultâneo, procedeu-se à realização de trabalhos de geofísica que incluíram a aquisição de perfis de resistividade eléctrica correlacionáveis com a circulação das águas termominerais da região. As águas subterrâneas de Monção classificam-se como bicarbonatadas-sódicas, revelando forte dependência do ambiente geológico local (fundamentalmente formações graníticas). Os resultados das análises isotópicas realizadas parecem indicar que: i) a contribuição das águas do rio Minho para o sistema termomineral deverá ser nula a inexistente; ii) a área de recarga do sistema termomineral deverá

situar-se a sul de Caldas de Monção, em torno dos 400 m de altitude (com base nos valores de  $\delta^{18}\text{O}$ ); iii) as idades aparentes das águas subterrâneas obtidas através do método de  $^{14}\text{C}$  em amostras de água do sistema termomineral foram respectivamente  $14.11 \pm 1.69$  ka BP e  $18.56 \pm 2.32$  ka BP nos furos AC2 e AC1, respectivamente, apontando para um sistema de circulação longo e profundo. Os dados isotópicos obtidos ( $^{14}\text{C}$ ) estão de acordo com a temperatura de emergência e área de recarga do sistema termomineral.

Palavras-Chave: Águas termominerais, isótopos ambientais ( $^{18}\text{O}$ ,  $^3\text{H}$  e  $^{14}\text{C}$ ), geocronologia, altitudes de recarga, Caldas de Monção (NW de Portugal)

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## 1. INTRODUCTION

Most of the Portuguese groundwater resources are found in sedimentary basins, ranging from Mesozoic to Quaternary age. However, in the studied region (NW part of Portugal), the geological environment is basically composed by Variscan granites and granodiorites. Monção region is situated at the northwest part of Portugal and located in Galicia-Trás-os-Montes Zone (FARÍAS *et al.*, 1987; RIBEIRO *et al.*, 1990) (Fig. 1). In this region, until the end of the 19<sup>th</sup> century, the natural conditions of the shallow (cold dilute) and deep (thermomineral) groundwater resources had not been seriously degraded by Human intervention. Groundwater resources have been utilized locally and slowly, and the exploitation was generally compensated by natural regeneration. Nevertheless, in the last decades, local groundwater resources have become progressively more endangered, both in quality and quantity, by accelerated modification of their natural conditions due to industrial and/or agricultural activities.

In order to update the knowledge on Caldas de Monção low-temperature geothermal system, with a special emphasis dedicated to the identification of the altitude of recharge areas, underground flow paths and possible existence of mixing between shallow and deep groundwaters, joined isotopic, geochemical and geophysical studies have been carried out in the surroundings of Caldas de Monção spas.

## 2. STUDY AREA: GEOLOGICAL BACKGROUND

M.L. RIBEIRO & MOREIRA (1986) and MOREIRA & SIMÕES (1988), among

others, have described in detailed the geology of Caldas de Monção area. In figure 1 a schematic geological map of the studied region is presented. Locally, three types of granitic rocks can be distinguished (based on their structural relationships and internal deformations). According to FERREIRA *et al.* (1987) this group of Variscan (or Hercynian) granitic rocks can be divided into:

i) sin-tectonic granites (D<sub>3</sub> deformation phase): with minute flakes of muscovite and biotite, usually presenting metamorphic minerals, and strongly correlated with migmatitic rocks;

ii) tardi-tectonic granites (frequently associated with the granodiorites): with a large presence of biotite (muscovite is a secondary mineral). The degree of deformation observed points out to an origin associated with last events of the Variscan D<sub>3</sub> deformation phase;

iii) post-tectonic granites: usually characterized by the presence of megacrystals of potassium feldspar and biotite. The lack of metamorphic minerals in these granites points to an age younger than the last Variscan deformation phase.

Fluvial deposits — sandstones and conglomerates (sometimes with clay layers) — of Quaternary age constitute the most recent formations in the region, well displayed in the surroundings of Caldas de Monção spas and along the Minho River margins.

The main fracture network systems are represented by tectonic lineaments (strike-slip faults), with directions ENE-WSW, WNW-ESE, NNE-SSW and NNW-SSE, of late Variscan age, and still active during the Meso-Cenozoic (SOARES de CARVALHO, 1992). The geological studies



carried out in Monção region have pointed out to that the fracture system ENE-WSW (left strike-slip fault) is related to morphology of the Minho River valley that is expressed by this structure.

The regional geomorphology of the area seems to favour a conceptual circulation model being the recharge area of the aquifer at south of Caldas de Monção uphill. The thermomineral borehole waters and springs are along the ENE-WSW structures, indicating that ascending path is controlled by this fracture system, issuing these waters when found appropriated conditions. On other hand, it seems that main groundwater circulation path is along the NNW-SSE direction.

### 3. SAMPLING AND METHODS

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

The environmental isotopes ( $^{13}\text{C}$ ,  $^{18}\text{O}$ ,  $^3\text{H}$  and  $^{14}\text{C}$ ) were measured at Instituto Tecnológico e Nuclear / Departamento de Química by the Grupo de Química Analítica e Ambiente (Sacavém / Portugal). The water samples (50 ml) collected for deuterium and oxygen-18 determinations

were kept in polyethylene bottles of high density. In laboratory, the determinations of  $^{18}\text{O}$  and  $^2\text{H}$  were carried out using a mass spectrometer SIRA 10 VG-ISOGAS. EPSTEIN & MAYEDA (1953) and FRIEDMAN (1953) have described the analytical methods used in the determinations of oxygen-18 and deuterium, respectively.

Usually the stable isotope content measured in solids, liquids or in gas samples ( $^{18}\text{O}$  and  $^2\text{H}$  results) are reported in  $\delta$  notation, which represents the relative deviations of the sample with respect to a standard value, defined by the following equation:

$$\delta \left( \text{‰} \right) = \left[ \left( R_{\text{sample}} / R_{\text{standard}} \right) - 1 \right] \times 1000$$

R stands for the ratio  $^2\text{H}/^1\text{H}$ ,  $^{13}\text{C}/^{12}\text{C}$  or  $^{18}\text{O}/^{16}\text{O}$  in the sample and  $R_{\text{standard}}$  represent the same ratio determined in the standard.

The average ocean composition ('Standard Mean Ocean Water' - SMOW) is accepted as the reference standard for  $^2\text{H}$  and  $^{18}\text{O}$  in water determinations. However, this standard has been replaced by the V-SMOW ('Vienna - Standard Mean Ocean Water'), and represents by definition the zero, i.e.,  $\delta^{18}\text{O}_{\text{V-SMOW}}$  and  $\delta^2\text{H}_{\text{V-SMOW}}$  are 0 ‰ (GAT *et al.*, 2001). The accuracy of the measurements are 1 ‰ in deuterium determinations and 0.1 ‰ for oxygen-18.

Environmental concentrations of tritium in natural waters are usually given as an isotope ratio in terms of TU ('Tritium Unit'). One TU has an isotopic ratio of  $^3\text{H}/^1\text{H} = 10^{-18}$ . One litre of water with a concentration of 1TU produces 7.2 dpm (desintegrations per minute; 0,12 Bq/l) (PAYNE, 1983). The

half-life of the tritium is 12.32 a, and emits low-energy beta radiation ( $E_{\max} = 18.6$  keV) (LUCAS & UNTERWEGER, 2000). The tritium measurements were carried out in all water samples using first an electrolytic enrichment method, and then all samples were measured by liquid scintillation counting method (PACKARD TRI-CARB 2000 CA/LL). The detection limit of this equipment (liquid scintillation counting) 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 described in I.A.E.A. (1976).

The  $^{14}\text{C}$  measurements were carried out on the thermomineral waters and determined on the Total Dissolved Inorganic Carbon (TDIC) extracted in the field as  $\text{BaCO}_3$  in a pH environment higher than 9.0 (I.A.E.A., 1981). The barium carbonate obtained *in situ* is, in laboratory, transformed into benzene and the counting rates of the  $^{14}\text{C}$  are measured 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, increasing with the lowest content in  $^{14}\text{C}$ . Carbon-14 is a radioactive isotope that has a half-life of 5730 a, emitting beta radiation ( $E_{\max} = 156$  keV). Environmental carbon-14 concentrations are expressed as a percentage of modern carbon (pmc). The modern carbon-14 value is referred to 1950 and is equal to 95% of the radiocarbon concentration of the NBS oxalic standard (PAYNE, 1983). During the benzene synthesis a  $\text{CO}_2$  gas sample is collected for  $\delta^{13}\text{C}$  determinations. The isotopic composition is reported to V-PDB (international standard); the associated error to this measurement is  $0.1 \text{ ‰}$ .

Temperature, electrical conductivity and pH were determined *in situ*. The water samples collected for chemical analysis were stored in two polyethylene bottles (1 L), one acidified with HCL for analysis of the major cations (Ca, Mg, Na and K), and the other was reserved unacidified for the major anions determinations ( $\text{Cl}$ ,  $\text{SO}_4$ ,  $\text{NO}_3$  and  $\text{HCO}_3$ ). The chemical parameters were determined at the Laboratório de Mineralogia e Petrologia – LAMPIST (Instituto Superior Técnico, Lisbon / Portugal), using the following methods: atomic absorption spectrometry for Ca and Mg; emission spectrometry for Na, K and Li; colorimetric methods for F and  $\text{SiO}_2$ ; ion chromatography for  $\text{SO}_4$ ,  $\text{NO}_3$  and Cl; potentiometric titration for alkalinity.

Geophysical studies have been performed near Caldas de Monção. Resistivity survey was carried out with the main goal to detected low resistivity zones that can be connected to the circulation of the thermomineral system. These investigations were developed by the Instituto de Ciências da Terra e do Espaço – ICTE, Lisbon / Portugal.

## 4. RESULTS OBTAINED AND DISCUSSION

### 4.1 Water's geochemistry

The mean temperature values of the thermomineral waters at the wellhead are around  $48 \text{ °C}$ , while the shallow cold hydrological systems present issue temperatures around  $14 \text{ °C}$ . The dry residue in the thermomineral waters range between 420 up to 470 mg/l, while in the shallow cold dilute groundwater samples the dry residue varies between 24 up to 120 mg/l

Table 1 – Representative physico-chemical composition of the thermomineral and shallow cold dilute groundwaters from Caldas de Monção area.

Ref.	Type	Date	Temp.	pH	E.Cond.	Na	K	Ca	Mg	Li	Al	HCO <sub>3</sub>	SO <sub>4</sub>	Cl	NO <sub>3</sub>	F	SiO <sub>2</sub>
AC1	(tw)	10/99	48.1	7.31	633	132	5.6	11.2	0.74	0.46	0	267	8.71	37.17	0.02	11.56	95.70
		02/02	52.0	7.05	670	130	5.9	13.0	0.75	0.44	0	319	8.43	29.23	0.56	10.92	79.82
		02/03	47.7	6.72	619	135	5.4	12.1	0.75	1.18	0.08	310	8.20	41.64	0	26.10	88.98
AC2	(tw)	10/99	45.0	6.98	693	156	5.7	17.75	1.15	0.56	0	322	6.27	36.83	0.02	9.35	89.50
		02/02	46.5	7.06	741	152	6.5	20.15	1.30	0.56	0	404	5.75	28.21	0.56	8.14	72.31
		02/03	42.2	6.55	793	138	5.8	20.05	1.25	1.48	0.1	390	5.92	43.76	0	10.91	80.08
S.Saúde	(tsp)	10/99	42.0	7.78	643	138	5.8	12.75	0.80	0.46	0	271	7.91	38.65	0.55	11.28	94.80
B.Mila. (NS1)	(sp)	10/99	16.0	6.13	162	17.8	1.8	6.70	3.50	0	0	12.2	9.69	1.68	23.79	0	24.4
		02/02	14.4	6.55	114	11.6	1.3	4.00	1.65	0	0	15.1	8.48	9.00	9.22	0.47	20.95
		02/03	12.8	5.78	123	12.0	1.4	5.00	2.00	0.02	0.05	8.1	7.40	13.8	12.79	0	20.05
S.Caet. (NS2)	(sp)	10/99	13.3	5.30	62	10.5	2.1	0.84	0.56	0	0	8.2	1.15	9.17	4.17	0	22.8
		02/03	11.7	5.12	80	9.2	0.98	1.38	0.85	0.02	0.05	15.8	1.40	10.35	3.40	0	20.05
Sr+Bon. (NS3)	(sp)	02/03	13.1	4.48	39	3.8	0.22	1.00	0.30	0.02	0.06	14.2	0.30	5.07	1.34	0	6.14
R.Minho	(river)	10/99	17.5	7.38	114	5.3	1.25	6.70	2.75	0	0	24.3	11.27	6.53	3.07	0	5.30
		02/03	10.4	6.55	112	6.3	1.02	7.04	1.90	0.02	0.12	20.2	9.60	6.26	4.38	0	8.50

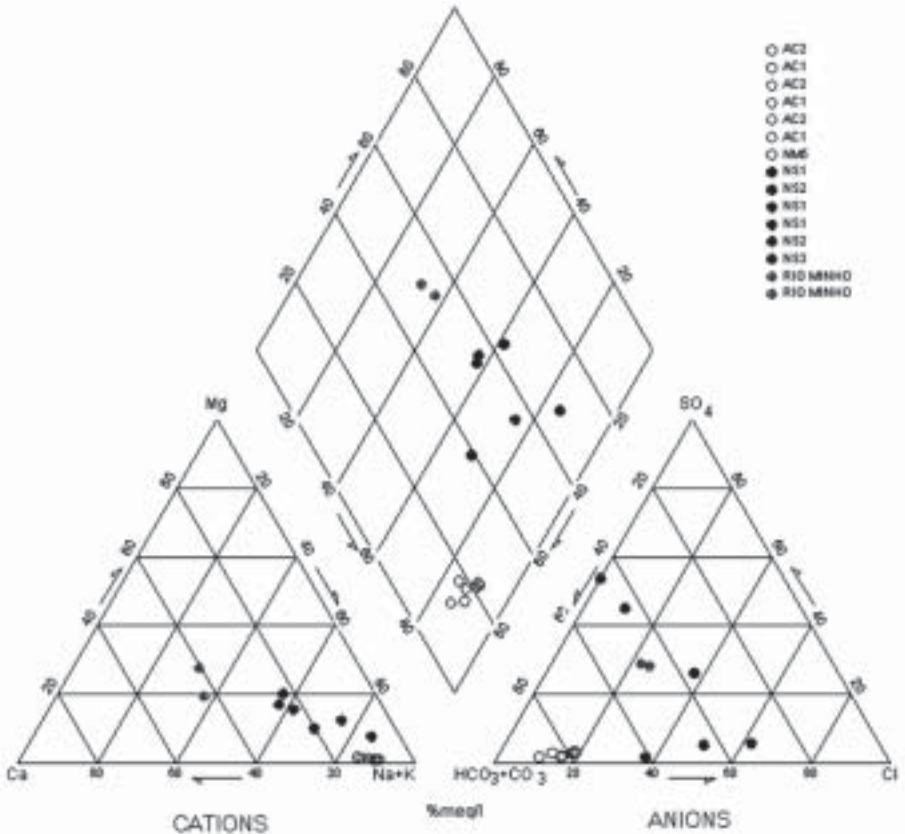
Notes: The concentrations are expressed in mg/L. Temp. stands for output temperature of the waters (°C). E.Cond. represents electrical conductivity in µS/cm, values obtained *in situ*. (tw) – thermomineral borehole waters; (sp) – thermomineral spring waters; (tsp) shallow cold dilute waters; (°) data from NASCIMENTO (2000).

(Table 1). An enormous gap in the mineralization content is observed between these two groups of waters systems (Fig. 2), although both hydrological systems present the same  $\text{HCO}_3\text{-Na}$  water *facies*.

The dispersion observed in the Piper Diagram (Fig. 2) should be related to the fact that in shallow cold dilute groundwater system the water samples were collected at different springs located down hill, frequently in areas of intensive agricultural activities, being the Human impact enhanced by the increase in  $\text{NO}_3^-$ , Cl and

$\text{SO}_4^{2-}$  concentrations. By contrary, the thermomineral water samples originate a define cluster of data points.

In Caldas de Monção geothermal area, the possibility of mixing between the geothermal fluids with the local cold dilute groundwater systems (or even mixing with Minho river waters) should be faced as an important environmental issue which should be addressed either in the exploitation and future development of these geothermal resources or in the delimitation of wellhead protection areas. An important aspect in the



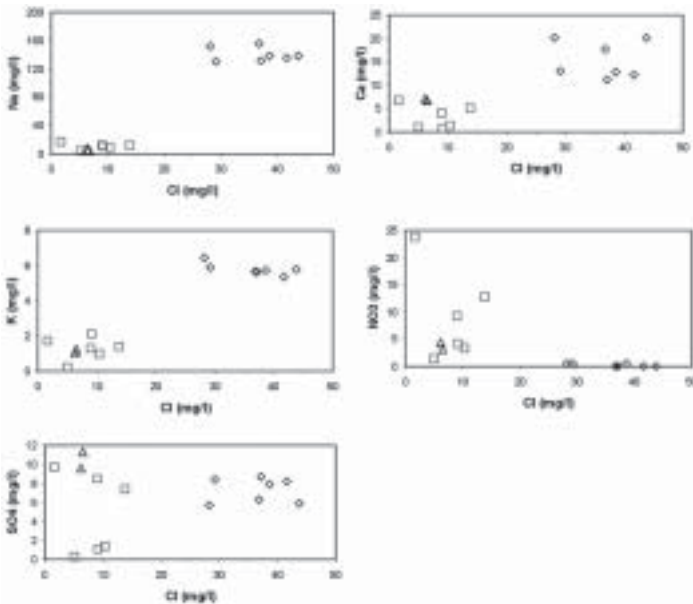
**Fig. 2.** Piper Diagram showing the hydrogeochemical signatures of the thermomineral (AC1, AC2 and NM5) and of the shallow cold diluted water (NS1, NS2 and NS3) systems. The watersamples from Minho River are also plotted.



low-temperature geothermal systems is the maintenance of the chemical quality of the water, for the reason that spas are very much dependent on both constant temperature and water quality. Therefore, the effects of mixing between the geothermal system and the shallow cold dilute waters (or even with Minho River waters) should to be investigated.

According to the Piper diagram, no mixture between these systems seems to occur. However, since chloride is a conservative element often used to identify mixing processes in geothermal fluids (GARCIA, 1986; MARINI & SUSANGKYONO, 1999; MARQUES *et al.*, 2003), chemical data (sodium, calcium, potassium, nitrate and sulphate) were plotted against chloride content (Fig. 3). Two

clusters of samples can be observed in all diagrams: one representing the geothermal borehole water samples and the other one representing the shallow cold dilute water samples and Minho river water samples. No mixture seems to occur between these two groups. It is important to refer that in the diagram  $\text{SO}_4^{2-}$  versus Cl the dispersion of the water samples from the shallow cold dilute system is well marked. The higher  $\text{NO}_3^{2-}$  and  $\text{SO}_4^{2-}$  concentrations should be associated to the geographic location of “Bica dos Milagres” spring. This spring is located at low altitude down hill within an area of intensive land use for agriculture purposes; nevertheless, it is important to emphasise that these two parameters ( $\text{NO}_3^{2-}$  and  $\text{SO}_4^{2-}$ ) are below the recommended maximum values in drinking waters for Human use.



**Fig. 3.** (a)  $\text{Na}^+$  versus Cl; (b)  $\text{Ca}^{2+}$  versus Cl; (c)  $\text{K}^+$  versus Cl; (d)  $\text{NO}_3^{2-}$  versus Cl and (e)  $\text{SO}_4^{2-}$  versus Cl diagrams for the water samples collected in 1999 (after NASCIMENTO, 2000), in 2002 and during 2003 field campaigns. The different symbols stand for: ( ) thermomineral borehole waters; ( ) shallow cold dilute waters; ( $\Delta$ ) Minho river waters.

**Table 2**– Caldas de Monção region, factor loadings (varimax normalized, using *Statistic 6*).

	Factor 1	Factor 2	Factor 3
T	0.9752	0.1161	0.0623
EC	0.9929	0.0484	-0.0459
Na	0.9885	0.1128	0.0233
K	0.9848	0.0747	0.0790
Ca	0.9348	-0.1115	-0.1018
Mg	-0.1705	-0.9632	0.0280
Li	0.7974	0.0628	-0.5756
Al	-0.4313	0.1363	-0.9784
HCO <sub>3</sub>	0.9719	0.1307	-0.0925
SO <sub>4</sub>	0.5294	-0.7132	0.1956
Cl	0.9335	0.2404	-0.1397
NO <sub>3</sub>	-0.5337	-0.8300	0.0942
SiO <sub>2</sub>	0.9707	0.0947	0.0643
<b>Variance (%)</b>	<b>68.68</b>	<b>17.48</b>	<b>9.36</b>

Principal Components Analysis (PCA) was applied in the study area using all data available from the thermomineral and shallow cold diluted water systems; all physical and chemical parameters obtained concerning these systems were used in this statistical method of analysis. In spite of this approach, the goal was to discriminate the relationship between the systems, the samples and the parameters, in particularly those in small concentrations that sometimes are neglected and could be derived from the Human impact activities, and which could be present in the thermomineral water resources of the region (MELLOUL, 1995).

PCA analyses were performed using STATISTIC 6 (STATSOFT INC., 2001). Three factors with eigenvalues over 1 were obtained (Table 2). Factor 1 contributes with 67 % of the total variance of the group and is the main responsible for the water characterization. This factor represents the groundwater evolution reflecting a high water rock interaction processes. Factor 2 and Factor 3 are characterizing agriculture

contamination (Human impact in the water resources) and water-rock interaction mechanisms. The parameters Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> dominant in the Factor 2 variance are those found in fertilizers used in vineyards and potato plantations, very common in the northern part of Portugal (see internet website: Adubos de Portugal, <http://www.adp-adubosdeportugal.com>). On the other hand, the last factor obtained, Factor 3, is dominated by aluminium most probably associated with water-granite interaction (hydrolysis of feldspars).

Using the factor loadings and plotting Factor 2 as a function of Factor 1 (Fig. 4), the separation between the thermomineral waters and the shallow cold diluted water systems (NS1, NS2 and NS3) is clear. In addition, in the diagram it is possible to distinguish the agriculture contamination, found among the spring samples (shallow cold dilute systems) recognized along the Factor 2 axis. Within the shallow cold dilute systems the evidence of anthropogenic influence / contamination due to intensive

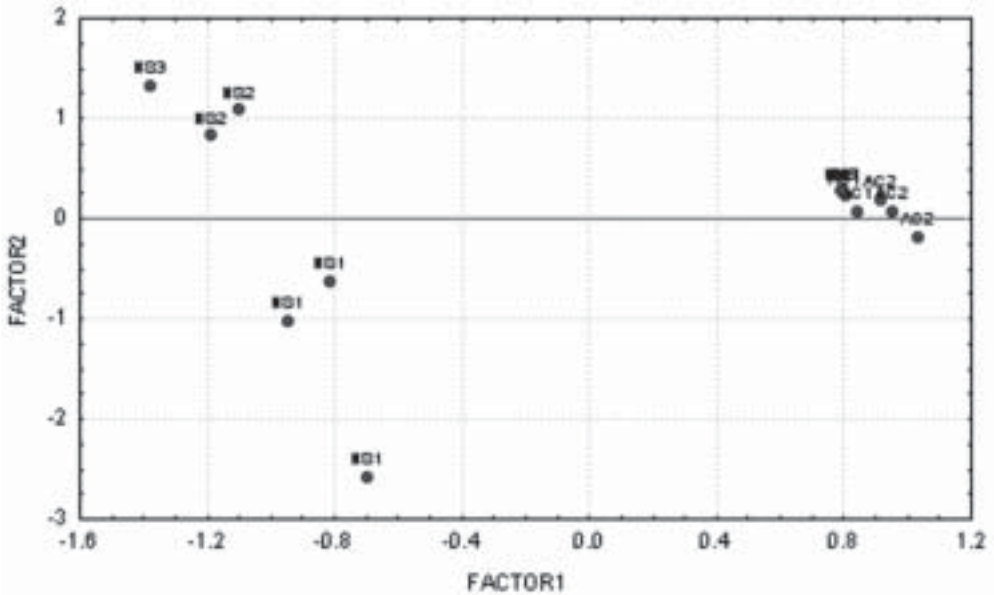


Fig. 4. Factor2 versus Factor1 (Principal Components Analysis). Anthropogenic influence (agriculture contamination) in the shallow groundwater system associated with spring NS1.

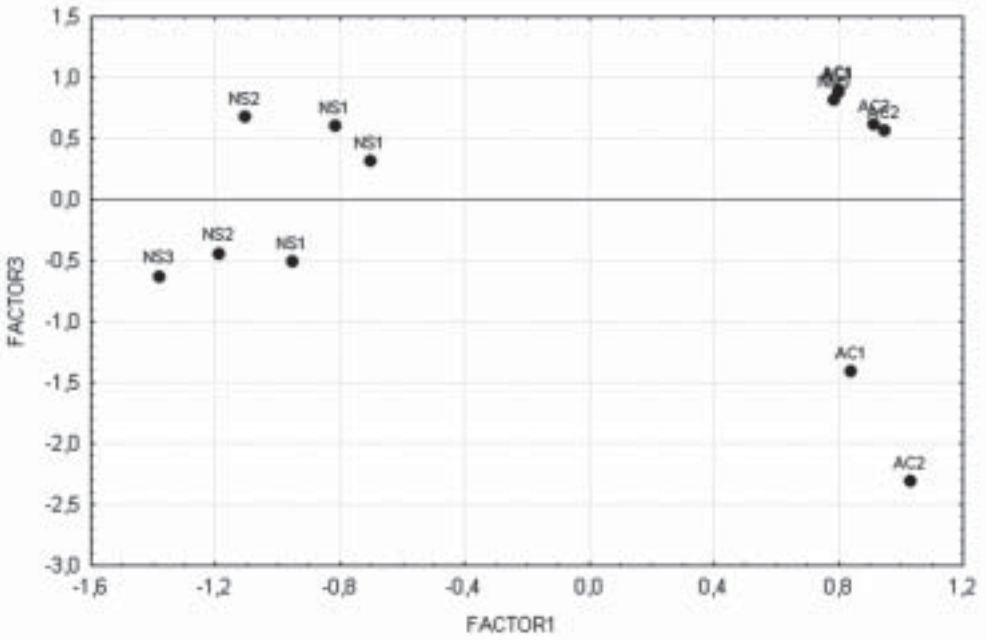
land use by agriculture seems to be well-established, considering that F2 is dominated by parameters usually used in fertilizers compositions added in agriculture practices.

Factor 3 represents 9.4% of the total variance of the system and the aluminium content in the groundwater samples represents the main parameter in the water systems characterization. This parameter is most probably associated with feldspar hydrolysis. Plotting F3 versus F1 (Fig. 5), a different position of the water samples is observed, i.e. samples from the thermomineral water system collected during February 2003 (AC1 and AC2) plot relatively far from the usually cluster. This shift is related with higher aluminium content in the groundwater that was also found in the other samples from the shallow cold diluted

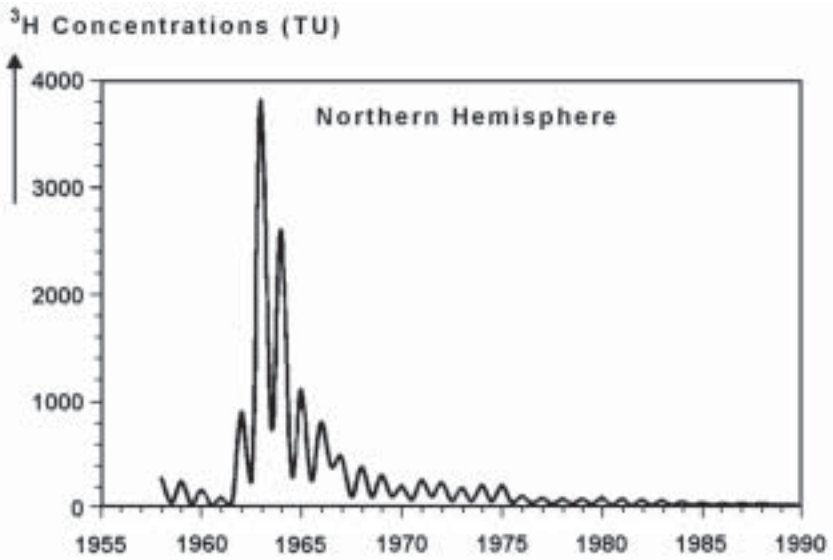
systems and Minho River from February 2003 (see Table 1).

In Table 3 it is plotted the correlation matrix obtained using all parameters from the thermomineral system and from the cold dilute groundwater systems. A strong correlation is observed between the aluminium content and the lithium and bicarbonate, revealing the high influence of the water - granite interaction processes. Also, the anthropogenic activities are enhanced by the strong correlation coefficient between the nitrates and the magnesium in the water systems.

The non-existence of a cluster associated with the spring NS1 belonging to the shallow cold dilute groundwater system could be due to the fact that one of the NS1 water samples was collected at the end of the dry season, when local groundwater systems



**Fig. 5. Principal Components Analysis: Factor 3 versus Factor 1. Influence of water rock interaction mechanisms within the thermomineral system.**



**Fig. 6. Smoothed curve representing the average  $^3\text{H}$  content of precipitation over the continental surface of the northern hemisphere (MOOK, 2000).**

**Table 3** - Correlation matrix obtained using all available information (thermomineral water and shallow cold dilute systems).

	Temp	E.C.	Na	K	Ca	Mg	Li	Al	HCO <sub>3</sub>	SO <sub>4</sub>	Cl	NO <sub>3</sub>	SiO <sub>2</sub>
Temp	1												
E.C.	0.97	1											
Na	0.98	0.99	1										
K	0.97	0.98	0.98	1									
Ca	0.87	0.95	0.92	0.91	1								
Mg	-0.29	-0.20	-0.27	-0.23	-0.00	1							
Li	0.74	0.81	0.77	0.75	0.78	-0.22	1						
Al	-0.07	0.01	-0.05	-0.12	0.02	-0.17	0.52	1					
HCO <sub>3</sub>	0.96	0.99	0.98	0.97	0.95	-0.27	0.83	0.06	1				
SO <sub>4</sub>	0.47	0.46	0.43	0.46	0.45	0.52	0.27	-0.27	0.36	1			
Cl	0.92	0.93	0.94	0.91	0.82	-0.41	0.86	0.13	0.92	0.33	1		
NO <sub>3</sub>	-0.61	-0.57	-0.62	-0.57	-0.42	0.90	-0.53	-0.19	-0.64	0.30	-0.71	1	
SiO <sub>2</sub>	0.96	0.95	0.97	0.96	0.84	-0.27	0.74	-0.08	0.92	0.50	0.96	-0.59	1

present higher contents in SO<sub>4</sub> and in NO<sub>3</sub> related to agricultural practices (NASCIMENTO, 2000).

#### 4.2. Isotopic features of Caldas de Monção groundwatersystems

The radioactive isotope of tritium (<sup>3</sup>H) and the stable isotopes deuterium (<sup>2</sup>H) and oxygen-18 (<sup>18</sup>O) are rare components of the water molecule H<sub>2</sub>O, when compared with the <sup>1</sup>H and <sup>16</sup>O abundance in natural water (<sup>1</sup>H = 99.985 % and <sup>16</sup>O = 99.759 %). They offer a broad range of possibilities for studying processes within the water cycle and trace groundwater evolution and characterization of its flow paths. Tritium being an environmental radioactive isotope originated in the high levels of atmosphere has also an anthropogenic origin associated to the release to the atmosphere during the test phase for hydrogen bombs. The very low natural levels were overwhelmed by the concentrations several orders of magnitude

higher (Fig. 6). Since then, Tritium levels have been progressively decreasing due to washout processes and the admixture of moisture from the oceans. Tritium in precipitation has been monitored of 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 through different compartments of the Hydrological Cycle. For example, groundwater, which does not contain tritium, must have infiltrated as rain before 1952, since the natural concentrations have already decayed below the detection limit.

Another example for the use of tritium in groundwater systems is given by CLARK & FRITZ (1997). These authors present a qualitative approach to the applicability of <sup>3</sup>H determinations in hydrogeological systems located in continental regions. For instance, concentrations lower than 0.8 TU (near the detection limit of the liquid scintillation counters but still measurable)

are catalogued as submodern being the recharge prior to 1952; for values between 0.8 to about 4 TU the groundwater could represent a mixture between submodern and recent recharge. Modern groundwater between 5 to 15 TU, the recharge of the system should have occurred in the range of 5 to 10 years. When the concentration in tritium is above 15 they consider the presence of anthropogenic origin related with the hydrogen bomb test.

The above range of values presented by CLARK & FRITZ (1997) is very useful in a qualitative approach of the systems; it is relevant to focus that this range of values is more specific for north hemisphere continental region. Considering the isotope precipitation record of the Portuguese Network Isotopes in Precipitation set up by ITN, we found tritium concentrations in precipitation over Portugal from 4.5 up to 5.3 TU respectively in coastal areas (Porto meteorological station, NW Portugal) and in continental regions (Portalegre meteorological station, South Portugal). These values represent the mean arithmetic of the weighted means of tritium in modern precipitation from 1988-1997 (CARREIRA *et al.*, 2003). These data enable the establishment of timescales; for example, groundwater, which does not contain tritium, must have infiltrated as rain before 1952 because of the natural concentrations have already decayed below the detection limits.

As far as the stable isotope are concerned the labels in a different way were used in hydrogeological research. The water molecule containing deuterium ( $^2\text{H}$ ) or oxygen-18 ( $^{18}\text{O}$ ) is heavier than a normal  $^1\text{H}^1\text{H}^{16}\text{O}$  molecule; the water vapour forming precipitation will be depleted in

heavy isotopes relative to the ocean water. On the other hand, condensation-forming raindrops from a cloud reverses this process, since the heavier molecules condensate first, *i.e.* the rain is isotopically enriched, and moisture is subsequently depleted as the rain out continues. The isotopic fractionation during phase transitions (vapour-liquid-solid) is temperature dependent, so a water sample is thus labelled depending on the environmental conditions it has experienced. According to this the signatures of isotopes in precipitation are not static; they respond to both synoptic climatology and global climate change. The observed isotope distribution in space and time can be related to a number of environmental parameters, which characterize not only the source region but also a given sampling site.

Seasonality, amount of precipitation, altitude dependence, continentality, the role of local temperature, together with the source specific fractionation between oxygen-18 and deuterium, all these effects can contribute to the isotopic content of a precipitation sample and consequently in the isotopic composition of the groundwater systems. In mid and high latitudes the isotopes in monthly precipitation are high correlated with temperature.

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  $\delta$  values. This feature is called "*altitude effect*" (DANSGAARD, 1964; ROZANSKI *et al.*, 1982, 1992, 1993). Also, there is an apparent tendency to observe more negative  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values in precipitation with increasing distance from the coast; this feature is known as a "*continental effect*", from this process clouds moving inland become progressively depleted in

heavy isotopes, giving to the hydrogeology researchers a tool (isotopic signatures) which reflects the topography of the continents. The lowering of temperature with increasing elevation in mountains regions usually leads to enhanced condensation and, therefore, to a progressive depletion in heavy isotopes of precipitation 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  $-0.50$  ‰  $100\text{ m}^{-1}$  for oxygen-18 and about  $-1$  to  $-4$  ‰  $100\text{ m}^{-1}$  for deuterium (ARAGUÁS-ARAGUÁS *et al.*, 2000; GONFIANTINI *et al.*, 2001).

Tritium concentrations were measured in all water samples, as a qualitative indicator of age. The values obtained range between 0 and 5.2 TU, in the shallow cold dilute groundwater systems (Table 4). The tritium concentrations measured in these waters indicate a local recharge and a rather short residence time. For comparison, the tritium record measured at Porto meteorological station (Serra do Pilar, approximately 100km South from Caldas de Monção) presents a mean arithmetic value of 4.5 TU (monthly record from 1988 to 2000 (ITN data base; IAEA, 1994; CARREIRA *et al.* 2003).

In the appraisal of Table 5, presenting data obtained from different fieldwork campaigns carried out in the region during October 1999 (reported in NASCIMENTO, 2000) and February 2002, 2003, we can observe a rather similar isotopic composition ( $\delta^{18}\text{O}$  and tritium) in the thermomineral waters collected from boreholes AC1 and AC2. This hydrothermal system does not show significant variations in time (1999-2003). From this set of results only in the

borehole AC1 (1999) a shift in tritium content is observed (from 4.1 TU measured in 1999 towards zero TU). Depletion in oxygen-18 was also found. In a first approximation, this deviation in the tritium content and depletion in oxygen-18 could represent mixing with another water bodies, more depleted and younger than the geothermal mineral system. Nevertheless, some remarks can be made considering the range of data obtained. The absence of  $^3\text{H}$  in the geothermal mineral borehole waters indicates a relatively long residence time, at least higher than 40 years, if one considers the tritium input to be in the same order of magnitude as found in Porto meteorological station (4.5 TU – mean arithmetic weight value).

In order to see some correlation / feature between the isotopic composition ( $\delta^{18}\text{O}$  and  $^3\text{H}$ ) within the thermomineral groundwater system and the cold dilute systems including Minho river water, all the available data were plotted (Fig. 7). A shift can be observed in the group of water samples collected during the 1999 campaign. The deviations in diagram of figure 7A and 7B are simply related to the tritium content found in the water samples collected in 1999, although we can not detect any shift in the tritium content within the precipitation record of Porto meteorological station during 1999 (*Portuguese Network Isotopes in Precipitation*).

At Caldas de Monção area the isotopic gradient for  $\delta^{18}\text{O}$  (“*altitude effect*”) is  $-0.18$  ‰ per  $100\text{ m}$  of altitude; this value is according with the data presented by several authors, e.g. GAT (1980); YURTSEVER & GAT (1981); ARAGUÁS-ARAGUÁS *et al.* (2000) and GONFIANTINI *et al.* (2001). The isotopic gradient presented range between  $-0.15$  to  $-0.50$  ‰  $\delta^{18}\text{O}$   $100\text{ m}^{-1}$ ,

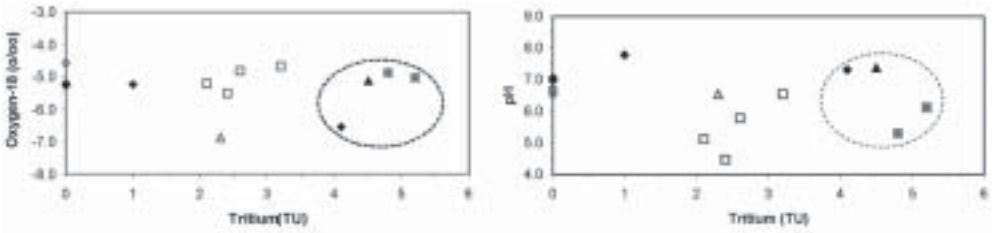


Fig. 7. (A)  $\delta^{18}\text{O}$  versus  $^3\text{H}$ ; (B) pH versus  $^3\text{H}$ . ( $\rightarrow$ ) thermomineral waters – 1999; ( $\bullet$ ) thermomineral waters – 2002 and 2003; ( $\square$ ) cold dilute groundwater systems – 1999; ( $\square$ ) cold dilute groundwater systems – 2002 and 2003; ( $\triangle$ ) – Minho river 1999; ( $\text{\textcircled{D}}$ ) – Minho river 2003.

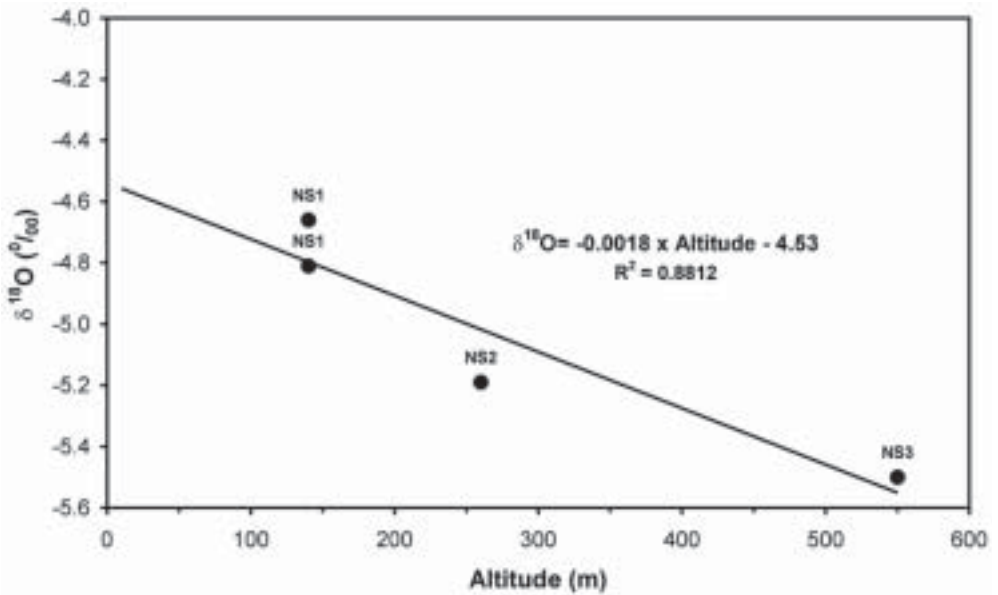


Fig. 8. Relation of  $\delta^{18}\text{O}$  values as a function of the altitude of sampling sites.



**Table 4** - Shallow cold dilute groundwater samples from Caldas de Monção area - isotopic composition, discharge altitude and issue temperature.

Samples	Sampling date	Altitude (m)	Temp. (°C)	Elec.Cond. (μS/cm)	δ <sup>18</sup> O (‰)	<sup>3</sup> H (TU)
NS1	10/1999*	140	16.0	162	-5.01	5.2 ± 1.0
	02/2002		14.4	114	-4.66	3.2 ± 0.6
	02/2003		12.8	123	-4.81	2.6 ± 0.6
NS2	10/1999*	260	13.3	62	-4.88	4.8 ± 1.1
	02/2003		11.7	80	-5.19	2.1 ± 0.6
NS3	02/2003	550	13.1	39	-5.50	2.4 ± 0.5
River Minho	10/1999*		17.5	114	-5.10	4.5 ± 0.9
	02/2003		10.4	112	-6.87	2.3 ± 0.6

Note: \* Data from NASCIMENTO (2000).

**Table 5** – Caldas de Monção – isotopic composition and issue temperature of thermomineral waters from boreholes AC1 and AC2.

		AC1	AC2
October 1999*	T (°C)	48.1	45.0
	δ <sup>18</sup> O	-6.54	-5.20
	<sup>3</sup> H	4.1 ± 1.0	0 ± 1.0
February 2002	T (°C)	52.0	46.5
	δ <sup>18</sup> O	-5.19	-5.25
	<sup>3</sup> H	0 ± 0.6	0 ± 0.6
February 2003	T (°C)	47.8	42.2
	δ <sup>18</sup> O	-5.22	-4.77
	<sup>3</sup> H	0 ± 0.6	0 ± 0.6
	δ <sup>13</sup> C (o/oo)	-7.06	-6.25
	<sup>14</sup> C (pmc)	4.82 ± 1.00	7.43 ± 0.34

Note: \* Data from NASCIMENTO (2000).

with an average rate of depletion of about -0.26 ‰ calculations based on the isotopic composition of precipitation water samples. In Monção region the isotopic gradient was established using the discharge altitude of the springs (cold dilute groundwater systems) and not the infiltration altitude. Nevertheless, the values obtained are reasonable and in agreement with the literature data. Using the isotopic signatures

of the thermomineral waters samples from the boreholes AC1 and AC2, the recharge altitude of Caldas de Monção geothermal system was estimated to range between 300 m and 600 m with a mean altitude value around 400 m a.s.l. (Fig. 8) (at the South of Caldas de Monção). The recharge altitude values obtained at Caldas de Monção geothermal system are in agreement with those proposed by LIMA & OLIVEIRA da

SILVA (2001), on the basis of the precipitation record.

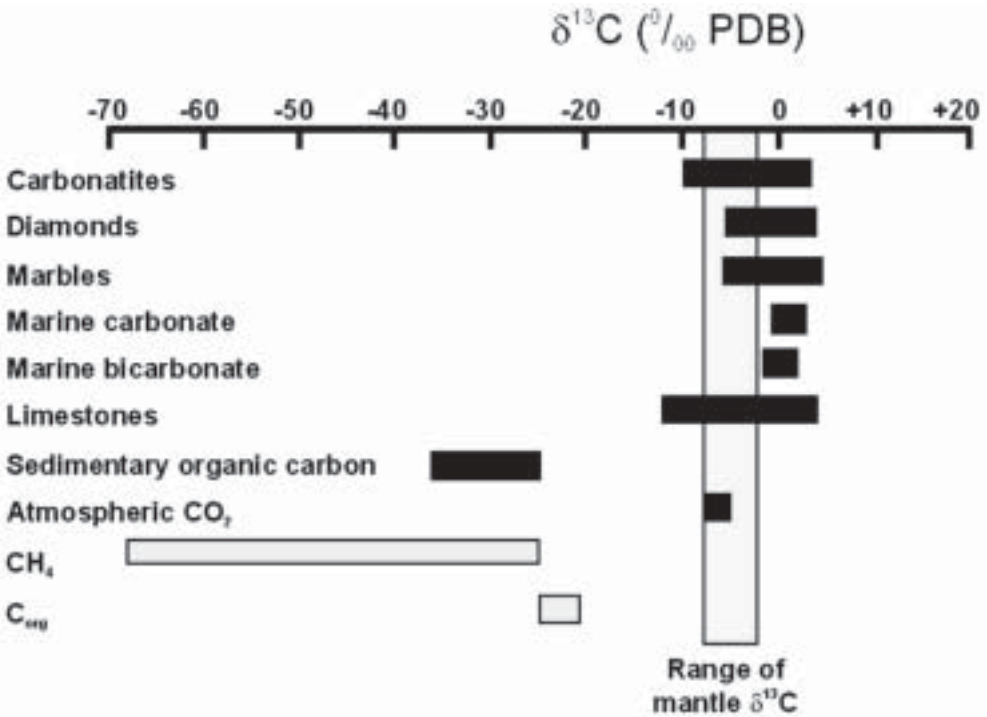
One of the main objectives of this study was the identification of possible mixture between Minho river waters with the geothermal system. The isotopic composition can be considered as a fingerprint of each system, reflecting the characteristics of the regions (altitude, temperatures, etc.). Minho river isotopic composition ( $\delta^{18}\text{O}$ ) indicates that most of the flow contributions proceeds from high elevations (see Table 4). According to LOUREIRO & MACHADO (1986), the source of 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, in Cantabrian Mountain Range) about 1500 m a.s.l.. The geographic/topographic characteristics of Minho river water source are responsible for the deviations measured in the isotopic composition revealing a depletion of about  $1.5 \text{ ‰}$  in oxygen-18. This isotopic fingerprint in Minho river waters allows us to consider that the contribution of this superficial water system to the recharge of the Caldas de Monção thermomineral system should be non-existence or extremely small. Besides, due to its source location and contribution of Sil river, the water samples from Minho river, although being a superficial water system were not considered in the altitude gradient calculations.

Carbon-14 determinations were carried out at the boreholes AC1 and AC2 from the thermomineral system (Table 5). The low  $^{14}\text{C}$  content determined in the Total Dissolved Inorganic Carbon (TDIC) of AC1 ( $4.82 \pm 1.00 \text{ pmc}$ ) and in AC2 ( $7.43 \pm 0.34 \text{ pmc}$ ) and the absence of tritium in these two

borehole waters support the hypothesis of a long residence time of the thermomineral groundwaters. Groundwater dating with  $^{14}\text{C}$  is complex due to the geochemical reactions that can occur within the aquifer. The radiometric age of the groundwater is that of the dissolved carbon, which may not be that of the water.

The carbon-14 age calculations were based upon the assumption that the initial activity of the dating material is 100 % modern  $\text{CO}_2$  activity (100 pmc); the  $\delta^{13}\text{C}$  of the aquifer matrix is  $1 \pm 1 \text{ ‰}$ ; the  $\delta^{13}\text{C}$  for the  $\text{CO}_2$  in the soil zone is  $-25 \pm 2 \text{ ‰}$ ; the fractionation factor  $\epsilon_{\text{HCO}_3}$  is  $8 \pm 0.5 \text{ ‰}$ , and the error associated to the measurements of the TDIC is  $0.5 \text{ ‰}$ . A close system model was used (SALEM *et al.*, 1980) to calculate the apparent carbon-14 age of the thermomineral waters. The mathematical model chosen includes mixture of soil  $\text{CO}_2$  and carbonates dissolution in the soil with isotopic differences. The apparent groundwater age obtained using this model were  $14.11 \pm 1.69 \text{ ka BP}$  for AC2 and  $18.56 \pm 2.32 \text{ ka BP}$  in AC1. Although the carbon-14 apparent groundwater ages are in agreement with what we expected, i.e., the younger water (AC2) has the lower issue temperature and also is more enriched in oxygen-18 (recharge area at lower altitudes), one has to center the attention to the carbon-13 values. The total dissolved carbon in mineral waters can be attributed to two main origins: organic and inorganic, that will be revealed in the  $\delta^{13}\text{C}$  values (Fig. 9). Considering an organic source,  $\text{CO}_2$  can be produced from decay of organic matter with mean  $\delta^{13}\text{C}$  values around  $-26 \text{ ‰}$  to  $-22 \text{ ‰}$ . Among the inorganic sources, carbon in hydromineral systems may originate from:

- i) deep-seated (upper mantle) carbon



**Fig. 9 - The range of  $\delta^{13}\text{C}$  values for different carbon-bearing substances as they compare to the  $\delta^{13}\text{C}$  values of the mantle carbon (vertical bar). Adapted from BERGFELD *et al.* (2001).**

showing  $\delta^{13}\text{C}$  values ranging between  $-8\text{‰}$  and  $-1\text{‰}$ , *ii*) dissolution of limestones (marine origin) with  $\delta^{13}\text{C}$  values close to  $0\text{‰}$ , or *iii*) metamorphism of carbonates producing  $\text{CO}_2$  with slightly positive  $\delta^{13}\text{C}$  values (TRUESELL & HULSTON, 1980; BERGFELD *et al.*, 2001).

The  $\delta^{13}\text{C}$  determinations carried out on Total Dissolved Inorganic Carbon (TDIC) of the Caldas de Monção thermomineral system give values in the range of  $-7.06\text{‰}$  in AC1 borehole and  $-6.25\text{‰}$  in AC2 borehole, indicating an origin for the  $\text{CO}_2$  in this waters that can be related with mixture between atmospheric  $\text{CO}_2$ , decay of organic matter and a deep-seated (upper mantle).

### 4.3. Geophysical studies

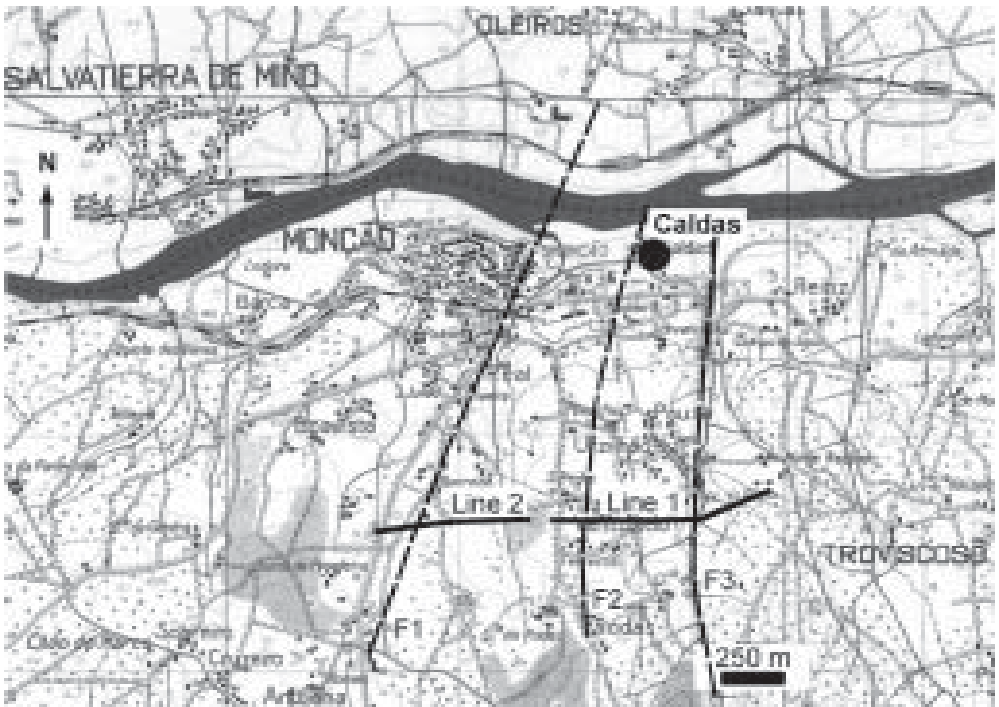
Geophysical surveys have been performed near Caldas de Monção with the objective to detect low resistivity zones that are predictably connected to the thermomineral circulation groundwater system. According to the geological studies the strike slip regional faults NNE-SSW and NW-SE to E-W are dominants, and basically control all the important hydrogeological systems in Northern part of Portugal (Fig. 10). Therefore, resistivity survey, comprising dipole-dipole lines, has been designed to cross the main fault system, tentatively associated to the Monção hydrogeological system.

Figure 11 shows the field apparent resistivity pseudo-section corresponding to one of the dipole-dipole surveys (line #2), carried out southwards of Caldas de Monção (dipole length of 10 m). The total length of this profile is 480 m. The field data was inverted using the RES2DINV code (LOKE & BARKER, 1996). The obtained resistivity model is presented in figure 11 and its main characteristics are:

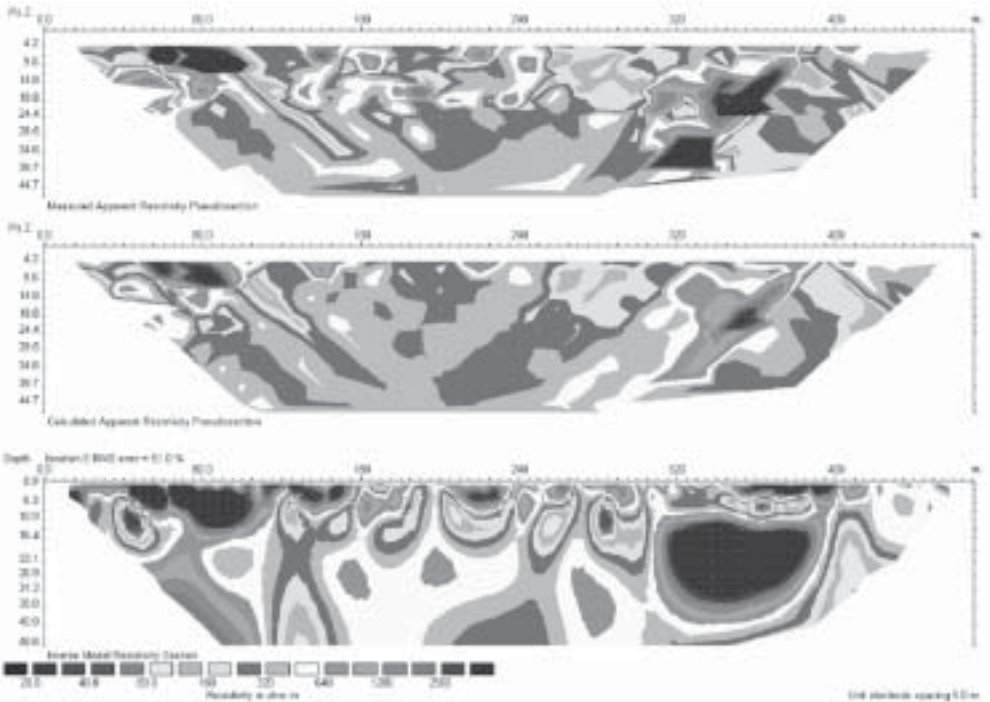
- an overburden with a thickness ranging from 6 to 20 m and resistivity ranging from 200 to 3000 ohm-m;
- a more homogeneous resistivity distribution (600 ohm-m in average) at depths greater than 20 m;
- the presence of three relatively low-resistivity (100 to 300 ohm-m)

anomalous zones crossing all the section at 100 m, 260-300 m and 400 m coordinates.

The high resistivity zones, in the overburden, are related to non-altered granite, which shows a few of fracture zones that appear as conductors on the profile. The low-resistivity zone in the western part of the profile (coordinate 100 m) is well correlated with a mapped fault (Fig. 10) that runs NNE-WWS in the Monção village direction (fault F1). Taking into account the resistivity contrast (from 600 to 60-100 ohm-m), this fractured zone is filled with high-conductivity material, probably clay and mineralised water. Therefore, the low-resistivity zones, at coordinates 260-300 m and 400 m, have been also interpreted as



**Fig. 10.** Location of two dipole-dipole lines carried out on the topographic map of Caldas de Monção region (1:25.000).



**Fig. 11. Field apparent resistivity pseudo-section, model response and resistivity model corresponding to the dipole-dipole line #2, carried out southwards of Caldas de Monção (dipole length of 10 m).**

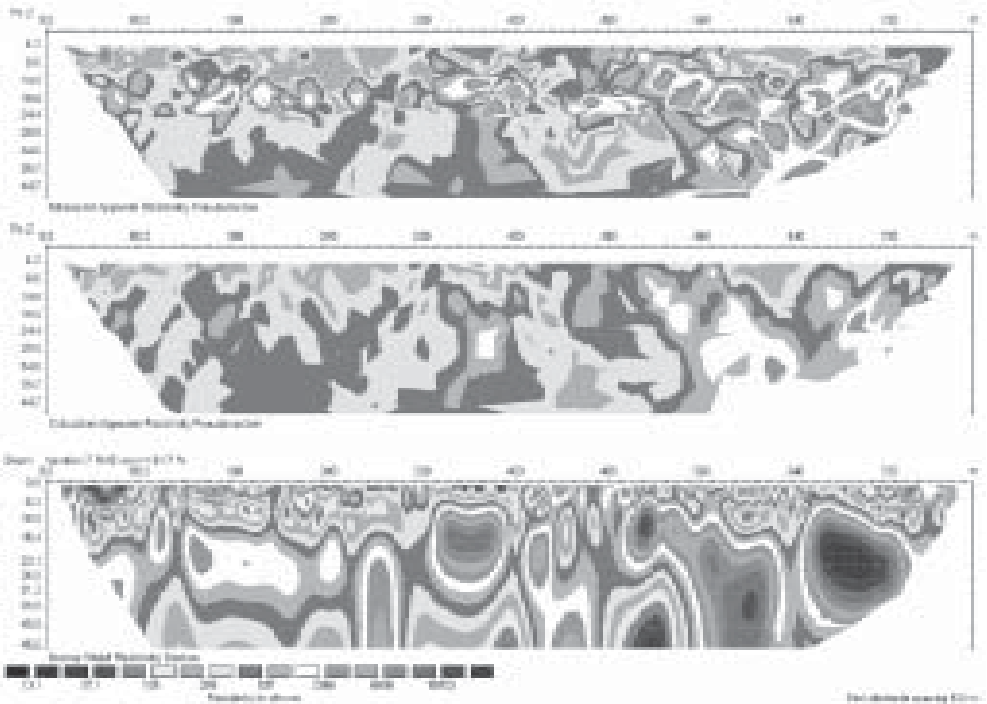
due to the presence of fracture zones filled with clay and mineralised water.

The same criteria were applied to the resistivity model obtained from line #1 (Figure 12) which reveals low resistivity zones well correlated with faults marked F2 and F3 in (Fig.10). These fault systems cross the area in direction of the Caldas de Monção spas. The obtained models suggest those fault system should go deep into the granite massive as predicted by geological studies.

## 5. CONCLUDING REMARKS

Isotopic composition ( $\delta^{18}\text{O}$ ) of the waters and the regional geomorphology of the area seem to favour a conceptual circulation model

of the Caldas de Monção thermomineral waters characterized by a recharge area at south of Caldas de Monção (uphill, around 400m a.s.l). The underground flow paths, which should be rather deep and long (apparent  $^{14}\text{C}$  ages between  $14.11 \pm 1.69$  ka BP and  $18.56 \pm 2.32$  ka BP), are associated with the fault systems (F1, F2 and F3 and their NW-SE associated systems), issuing these waters when appropriate conditions are found. In fact, the geophysical results confirm the presence of NNE-SSW fault systems southwards of the spas. The models suggest that those tectonic systems may be deep and filled with mineralised water. The higher issue temperature and apparent age presented by thermomineral waters from



**Fig. 12.** Field apparent resistivity pseudo-section, model response and resistivity model corresponding to the dipole-dipole line #1, carried out southwards of Caldas de Monção.

borehole AC1 could be ascribed to a deeper and longer circulation path from recharge to discharge. The  $\delta^{13}\text{C}$  determinations carried out on Total Dissolved Inorganic Carbon (TDIC) of the Caldas de Monção thermomineral system, give values in the range of  $-7$  to  $-6$  ‰, indicating an origin for the  $\text{CO}_2$  in these waters that can be related with mixture between atmospheric  $\text{CO}_2$ , decay of organic matter and a deep-seated (upper mantle  $\text{CO}_2$ ).

Caldas de Monção thermomineral waters are used for local spa facilities, source for local and regional social and economic development. So, the increase of knowledge

on the local hydrogeology is extremely important for the sustainable use of this important georesource.

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