ABSTRACT

This paper is dedicated to update knowledge on the Caldas de Manteigas thermal waters, issuing at the Manteigas–Nave de Santo António–Torre sector, Serra da Estrela High Mountain area (Central Portugal, Iberian Massif). The geological, morphostructural, hydrogeochemical, isotopic and climatic information were used to outline a conceptual circulation model comprising the main components of the thermal system, with a special emphasis on the recharge areas and the deep thermal water component. The recharge of the local thermal waters was studied based on the spatial and temporal variability of the isotope ($\delta^{18}$O, $\delta^2$H and $^3$H) contents in the water. According to the isotopic gradient in the study area (-0.12 ‰/100 m of altitude) and considering the mean isotopic composition of the thermal waters ($\delta^{18}$O$_{mean}$ = -7.8 ‰ vs. V-SMOW), the recharge of the thermal system should take place in the main tectonic valleys situated near and above 1600 m a.s.l., namely: i) the NNE-SSW section of the Zêzere valley, corresponding to the main BVMFZ lineament; ii) the Nave de Santo António col, also lying over this lineament; iii) the Covão da Ametade and Candeeira valleys, corresponding to conjugate faults of the main structure. These recharge areas consist of a sedimentary layer of alluvium and quaternary glacial deposits overlying tectonised granite and receiving water influx both from vertical infiltration of precipitation (rain and snow) and lateral flow from the local shallow aquifers. (máx. 250 words)

Keywords – Thermal waters, geochemistry, isotopes, geophysics, conceptual circulation model.
1 INTRODUCTION

This study is strongly related to one of the central water research issues of this millennium: “High Mountain Areas Hydrology” (see UNESCO IHP-VI Programme: http://www.unesco.org; AURELI, 2002). Special emphasis is dedicated to thermal waters and non-thermal groundwaters issuing at the Manteigas–Nave de Santo António–Torre sector, situated in Serra da Estrela High Mountain area (Central Portugal). Mountain areas are the source of most of the larger river systems all over the world, and usually represent some of the blackest “black boxes” in the hydrological cycle. The seasonality and spatial variability of local groundwaters and the complex role of soils, geomorphology, geology, climate, land use and human activities on the hydrology of mountain areas are rather difficult to model, even when relevant data are available. Nevertheless, mountain river basins provide the best opportunity to increase knowledge on the relationship between those complex variables as well as their impacts on the water quality at different elevation zones, under different cultural settings (CHALISE, 1994).

The study area (Fig. 1) corresponds to the Zêzere river drainage basin upstream of Manteigas village, to which corresponds an area of 28,04 km². This area presents specific geomorphologic, climatic and geotectonic characteristics which contribute to control the recharge and flow paths of Caldas de Manteigas thermal waters (issue temperature of about 42°C). Since Serra da Estrela Natural Park as well as Zêzere river basin extends up to the highest elevation zones in Portuguese mainland, they provide unique places for integrated studies, which will help in developing a scientific basis to understand and deal with the present-day hydrogeology and groundwater resources problems at mountain areas.

Figure 1 Morphotectonic features from Central Portugal, Serra da Estrela mountain region. Major faults: PCTSZ: Porto-Coimbra-Tomar strike-slip shear zone; VCRFZ: Vigo-Vila Nova de Cerveira-Régua fault zone; VRPFZ: Verin-Régua-Penacova fault zone; BVMFZ: Bragança-Vilariça-Manteigas fault zone; SLF: Seia-Lousã fault zone. Taken from ESPINHA MARQUES et al. (2006).
In order to assess the interrelation between local surface waters (recharge waters) and groundwaters, an integrated multidisciplinary (geomorphology, structural geology, geochemistry, isotope hydrology, applied mineralogy, geophysics and GIS mapping) approach is being launched, under the scope of the HIMOCATCH R&D Project "Role of High Mountain Areas in Catchment Water Resources, Central Portugal".

2 STUDY AREA

2.1 Geomorphology and climate

The Serra da Estrela (Fig. 1) is the highest mountain in the Portuguese mainland (with an altitude reaching 1993m a.s.l.) and is part of the Cordilheira Central, an ENE-WSW mountain range that crosses the Iberian Peninsula. This region shows distinctive climatic and geomorphologic characteristics that play an important role on the local water cycle. The river Zêzere drainage basin upstream of Manteigas, corresponds to an area of ca. 28 km² with an altitude ranging from 875m a.s.l., at the streamflow gauge measurement weir of Manteigas, to 1993m a.s.l., at the Torre summit (Fig. 2).
The relief of the study region is consists mainly of two major plateaus, separated by the NNE-SSW valley of the Zêzere river (VIEIRA, 2004: see Fig. 3): the western Torre–Penhas Douradas plateau (1450-1993m a.s.l.) and the eastern Alto da Pedrice–Curral do Vento plateau (1450-1760m a.s.l.). Late Pleistocene glacial landforms and deposits are a distinctive feature of the upper Zêzere catchment, since the majority of the plateau area was glaciated during the Last Glacial Maximum (e.g. DAVEAU et al., 1997, VIEIRA, 2004).

According to DAVEAU et al. (1997), the Serra da Estrela climate has Mediterranean features, with mean annual precipitation reaching 2500 mm in the most elevated areas. Precipitation seems to be mainly controlled by the slope orientation and the altitude (VIEIRA and MORA, 1998). Mean annual air temperatures are below 7ºC in most of the plateau area and, in the Torre vicinity, they may be as low as 4ºC.

2.2 Geology and tectonics

The Serra da Estrela Mountain (the highest mountain in Portuguese mainland) is located in the so-called Central-Iberian Zone of the Iberian Massif (RIBEIRO et al., 1990).

The geological and tectonic conditions outline some of the major hydrogeologic features and processes, such as infiltration, aquifer recharge, type of flow medium (porous vs. fractured), type of groundwater flow paths, or hydrogeochemistry.

Fractured mediums occur in poorly weathered rocks. Such mediums may be present very close to the surface (especially on granitic outcrop dominated areas, with thin or absent sedimentary cover) or bellow the referred porous geologic materials. The main regional hydrogeological units (Fig. 4) correspond to i) sedimentary cover, including alluvium and quaternary glacial deposits; ii) metasedimentary rocks, which include schists and graywackes; and iii) granitic rocks. On the other hand, an important issue connected to the infiltration and aquifer recharge in the Serra da Estrela region consists on the identification of areas of prevailing fractured or porous circulation mediums (ESPINHA MARQUES et al., 2005). In particular, the porous mediums are dominant in the alluvium and quaternary glacial deposits as well as in the most weathered granites and metasedimentary rocks. Porous mediums usually occur at shallower depths (typically less than 50m).

The main regional tectonic structure is the NNE-SSW Bragança-Vilarica-Manteigas fault zone, which controls thermal occurrences. This megastructure is part of a late-Variscan fault system that was reactivated by the alpine compressive tectonics and originated the uplift of the mountain as a horst in a pop-up structure (RIBEIRO et al., 1990).
It is well known the advantages of remote sensing imagery for recognizing lineaments: regional linear or slightly curvilinear features, outstanding their digital format, high spectral resolution, homogeneity in data collection, and the synoptic view that they allow (AVERY and BERLIN, 1985). Such lineaments, being caused by linear alignment of regional morphological features, such as streams and rivers, escarpments, and mountain ranges, and by tonal features, are usually considered the presumable surface expression of fractures or fault zones (DRURY, 1993; SIEGAL and GILLESPIE, 1980).

In this paper we report the results from the analysis of the satellite image obtained by the SPOT and LANDSAT satellites and aerial photo maps. For the total data integration it was also employed the free Google Earth program.

From the satellite image analysis we identified more than two hundred well expressed lineaments with lengths superior to 1 km, totalling circa 700 km. Notwithstanding, in some cases, they correspond to fractures, while most of them are the expression of tectonic features - faults. A preliminary statistic from the remote sensing interpretation show seven power families (Fig. 5), from the more significant of 205 measures observed: N30 to 35E - 66 measures; N40 to 45E - 43 measures; N50 to 55E - 32 measures; N120 to 125E - 23 measures; N90 to 95E - 19 measures; N135 to 145 - 15 measures; N10 to 15E - 7 measures.
3 SAMPLING AND RESEARCH METHODS

Water samples for geochemical and isotopic analysis were collected from river waters, shallow cold dilute groundwaters (spring waters – “normal” waters) and from the Caldas de Manteigas thermal waters (Fig. 6).

Temperature (°C), pH, Eh (mV) and electrical conductivity (μS/cm) of the waters were determined “in situ”. Total alkalinity was measured a few hours after collection. The following methods were applied for chemical analyses performed at the Laboratório de Mineralogia e Petrologia of Instituto Superior Técnico (LAMPIST): atomic absorption spectrometry for Ca and Mg; emission spectrometry for Na, K, Li, Rb and Cs; colorimetric methods for SiO₂, Fe_total, F and Al; ion chromatography for SO₄, NO₃ and Cl; potentiometry for alkalinity, here referred to as HCO₃. The δ²H and δ¹⁸O measurements (vs. V-SMOW, Vienna - Standard Mean Ocean Water) were performed by mass spectrometry (SIRA 10–VG ISOGAS) at the Instituto Tecnológico e Nuclear (ITN - Portugal) following the analytical methods of EPSTEIN and MAYEDA (1953) and FRIEDMAN (1953), with an accuracy of ± 1 ‰ for δ²H and ± 0.1 ‰ for δ¹⁸O. The ³H water content (reported in Tritium Units, TU) was also determined at ITN, using electrolytic enrichment followed by liquid scintillation counting method (standard deviation around ± 0.6 TU, depending on tritium content of the water). ¹⁴C determinations in waters were performed at the Geochron Labs/USA by accelerator mass spectrometry (AMS). A preliminary geophysical study (3 VES with an AB/2 spacing varying between 1 m and 200 m) was carried out at the Nave Sto. António in order to investigate the basin fill as well its basement. The Nave de Sto António col is located at an elevation of 1540 m a.s.l., and is one of the main potential recharge areas.

Figure 6 Water sampling sites at Serra da Estrela Natural Park. (a) Caldas de Manteigas Spas, thermal waters - borehole; (b) Zêzere river, near the Spas; (c) Espinhaço de Cão spring and (d) Nave de Stº António spring.
4 RESULTS AND DISCUSSION

4.1 Hydrochemistry

In this section, the geochemical signatures of the sampled waters will be used to derive information on groundwater's origin and geochemical history.

The infiltrated waters begin to interact with sediments or rocks as soon as they enter the unsaturated zone. After this process, they continue to react, with a more or less degree of extent in the saturated zone. Recently infiltrated groundwaters will contain CO₂ and oxygen, and the acid-base reactions are dominant (e.g. weathering of silicates – feldspars). The result of these reactions is the elevation of groundwater pH, the production of HCO₃⁻ and the release of base cations and silica to the solution.

Concerning local “normal” groundwaters (surface waters and shallow cold dilute groundwaters) the geochemical signatures can be defined as:

i) HCO₃⁻-Na-type waters displaying low total dissolved solids. These spring waters could be considered as good signatures of local recharge. The relatively higher mineralization detected in two of these spring waters could be ascribed to a long shallow underground flow path, allowing higher water-rock interaction and,

ii) Na-Cl-type waters, also characterized by relatively low mineralization. The clear Na-Cl geochemical signatures found within some of the waters of this group (Fig. 7) could be ascribed to the local use of NaCl to promote snowmelt in the roads during the winter season, clearly detected in the field through the higher electric conductivity values.

At greater depths (up to several hundred metres) the infiltrated groundwaters tend to evolve, increasing salinity and pH, with a gradual preponderance of Na over Ca with depth. Sulphate also becomes obvious, probably derived from the oxidation of sulphide minerals. Most reaction rates increase with increasing temperature, and thus thermal waters, by nature, usually present the highest mineralization.

At the study area, the thermal waters (with output temperatures around 45ºC) are characterised by the following main features:

i) relatively high pH values (≈ 9),
ii) TDS values usually in the range of 160 to 170 mg/L,
iii) HCO₃⁻ is the dominant anion,
iv) Na is the dominant cation,
v) the presence of reduced species of sulphur (HS⁻ ≈ 1.7 mg/L),
vi) high silica values (usually around 50 mg/L) representing a considerable percentage of total mineralization and
vii) high fluoride concentrations (up to 7 mg/L).

As indicated by the chemical composition of the Caldas de Manteigas thermal waters, the reservoir rock should be mainly granite, being the thermal waters mineralization strongly dominated by the hydrolysis of Na-plagioclases through the reaction:

\[ 2NaAlSi₃O₈ + 9H₂O + 2H⁺ + 2HCO₃⁻ = Si₂O₅Al₂(OH)₄ + 2Na⁺ + 2HCO₃⁻ + 4 H₄SiO₄ \]

The strong HCO₃⁻-Na signatures of Caldas de Manteigas thermal waters can be clearly seen in the Stiff diagram of (Fig. 7).
Figure 7: Stiff diagrams for the sampled waters, during the Winter (A) and Summer (S) field work campaigns. Taken from ESPINHA MARQUES et al. (2005).
4.2 Isotope hydrology

Isotope hydrology has been used for more than 25 years in the study of water flow resulting from snowmelt (KENDALL and MCDONNELL, 1998). The assessment of snowmelt contribution to stream and groundwater flow is complex due to isotopic fractionation during snow formation, accumulation, ablation and phase change during melt. For this reason, comprehensive sampling of meltwater, instead of snow, is generally recommended for hydrological studies. Therefore, fieldwork campaigns at Serra da Estrela were performed in April, after the beginning of snowmelt period.

The seasonal variation of the stable isotopic composition of precipitation is reflected in the comparatively low $\delta$-values in the snowfall, which will be reflected in the $\delta^{18}$O and $\delta^{2}H$ contents of meltwater. Although isotope changes take place in the precipitated water during both snowpack storage and melting, meltwater is usually considerably depleted in stable isotopes as compared to the annual mean precipitation or groundwater. This shift could provide a very useful tracer signal for hydrogeological studies in mountainous areas (KENDALL and MCDONNELL, 1998).

The isotopic composition of the water samples (stream, shallow groundwaters and thermal waters) varies between -8.0 to -7.2 $\%_o$ in $\delta^{18}$O and between -52 to -42 $\%_o$ in $\delta^{2}H$ (Fig. 8). In the diagram of Figure 8, where the long term weighted mean value of precipitation collected at Penhas Douradas meteorological station (located at an altitude of 1380 m a.s.l.) is shown ($\delta^{2}H = -43.3 \%_o; \delta^{18}$O = -7.20 $\%_o$ in CARREIRA et al., 2005), one can observe a progressive depletion in heavy isotopes ascribed to the lowering of temperature with increasing elevation in mountains regions (the Global Meteoric Water Line GMWL is shown as reference).

We can also observe that $\delta^{2}H$ vs $\delta^{18}$O values of some sampled waters show a rather significant deviation from the GMWL which could be attributed to precipitation at high altitudes and/or snowmelt contribution, resulting in a high deuterium excess $d$ ($d = \delta^{2}H - 8 \delta^{18}$O), as described in KENDALL and MCDONNELL (1998). This deviation is more effective in the waters sampled during September 2003 and April 2004 campaigns.

![Figure 8](image)

Figure 8 $\delta^{2}H$ vs $\delta^{18}$O diagram for the studied waters.

The thermal waters do not show any evidences of mineral/water exchange reactions in a high temperature environment. In fact, no shift towards a heavier $\delta^{18}$O composition, due to exchange with oxygen isotopically heavier silicates, is observed. These results are consistent with the issue temperature of the thermal waters. Reservoir temperatures (between 98ºC and 103ºC) given by the quartz geothermometer, indicate a maximum depth of about 3.8 km reached by the Caldas de Manteigas thermal water system, considering a geothermal gradient of about 25ºC/km (MARQUES et al. 2006).
The methodology used to study the recharge of thermal waters was based on the spatial variability of the isotope contents in the water. The spatial variability was based on the relationship between $\delta^{18}O$ and altitude of recharge. This methodology was conducted by sampling shallow cold dilute groundwaters (spring waters – “normal” waters) and river waters at different altitude sites, as is based on the assumption of the conservative behaviour of the stable isotopes (the contents of $\delta^{18}O$ and $\delta^2H$ in the discharge zones represents the contents in the recharge zone, IAEA 1981).

The obtained $\delta^{18}O$ isotopic gradient for the study area was -0.12 ‰/100 m of altitude of altitude (Fig. 9). According to this gradient, and considering the mean isotopic composition of the thermal waters in the region ($\delta^{18}O_{\text{mean}} = -7.8$ ‰ vs. V-SMOW), the upper valley of Zêzere river, with altitudes ranging between 1600 and 1800 m a.s.l., should be faced as a potential catchment area of this thermal water system. The main recharge seems to occur laterally. The Bragança-Vilarica-Manteigas fault zone should play an important role in conducting the laterally infiltrated meteoric waters towards the discharge zone at the Caldas de Manteigas Spa.

Tritium ($^3H$), the radioactive isotope of hydrogen, occurs naturally in the rainfall at levels less than 20 TU. Between 1952 and 1963, atmospheric tests of hydrogen bombs produced large quantities of $^3H$, inducing rainfall tritium levels over 1000 TU (ROZANSKI et al., 1991). Since then, tritium in rainfall as declined, although in many places modern rainfall still contains tritium levels above natural background (MOOK, 2000). Now a days, the usefulness of tritium as a dating tool is declining since tritium in rainfall is approaching natural background levels. Nevertheless, groundwaters displaying > 1 TU can be interpreted as to have been modern groundwaters (recharged during the last four decades).

In the case of Caldas de Manteigas thermal waters (boreholes AC2 and AC3) tritium contents below the detection limit were observed (MARQUES et al., 2006). These $^3H$ signatures indicate long residence times ascribed to a groundwater circulation reaching considerable depth, confirming the results of chemical geothermometers. On the other hand, higher $^3H$ concentrations (between 2 and 6 TU) were detected on the local shallow cold dilute groundwaters (“normal” groundwaters), indicating that they are recent and have relatively short underground flow paths (MARQUES et al., 2006).

Carbon-14 data have been used to calculate the “apparent age” of Caldas de Manteigas thermal waters. One water sample (borehole AC2) was collected for $^{14}C$-age determinations (AMS determinations; Geochron Laboratories, USA). The $^{14}C$ age obtained was 10540 ± 80 years BP (pmC =
26.93 ± 0.27 and δ^{13}C = -17.6 \text{%o}. The study of carbon isotopes is more complex than that of O or H, due to the existence of a number of different sources of carbon. In most groundwaters, only part of the bicarbonate carbon is recent and derived from biogenic CO₂. The rest could be derived from aquifer carbonate (which is not the case), being far older than the half-life of 5730 years, having dead carbon (negligible 14C content). Nevertheless, the interpretation of 14C data (having some limitations) provides a limit on maximum age. δ^{13}C values of -17.6 \text{%o} ascribed to Caldas de Manteigas thermal waters (borehole AC2) suggest an organic origin for the carbon.

The depth of about 3.8 km reached by the Caldas de Manteigas thermal water system (given by the chemical geothermometers), suggest that 14C-dating of the thermal waters seems to provide rather reliable results.

4.3 Geophysics

A preliminary geophysical study was carried out at the Nave Sto. António in order to investigate the basin fill as well its basement. The Nave de Sto António col (Fig. 10) is located at an elevation of 1540 m a.s.l., and is one of the main potential recharge areas.

![Figure 10 Location of the dipole-dipole profile at the Nave de Sto. António area (in the upper valley of Zézere river). Adapted from Carta Militar Nº 223, Instituto Geográfico do Exército, 1/25000](image)

A 600 m dipole-dipole profile had been carried out in the south part of basin (Fig.10), using a dipole distance of 10 m. The pseudo-section (Fig.11) shows a high resistive uppermost layer with resistivity greater than 4000 ohm-m, followed by a less resistive deep zone with apparent resistivity values of 1500-2000 ohm-m. The highest resistivity values appear in the south-eastern part of the profile and correspond to the granite rock that outcrops to SE of the profile.

From these preliminary results some conclusion can be drawn: i) the fill of the basin is dominated by sand with different granulometry, and other particulate rock materials (e.g. blocks, etc.), ii) the deeper part of the basin (resistivity values lesser than 2000 ohm-m) seems to have a non uniform topography and may has different degrees of weathering.
5 CONCEPTUAL MODEL

A conceptual model of a hydrothermal system is a simplified representation of the reality. The conceptualisation process implies the comprehension of the aquifer nature, its broad characteristics and the physical and chemical processes involved. Some of the most important features to consider include lithology, the geologic and geometric characteristics of the system’s limits, the spatial variability of hydraulic parameters, hydrogeochemistry, surface water-groundwater interactions, recharge, discharge, among others.

The hydrogeologic system existing in the river Zêzere basin upstream Manteigas comprises three main types of aquifers: i) shallow unconfined aquifers, hydraulically connected to the vadose zone; ii) shallow semi-confined aquifers; iii) a deep thermal aquifer. Waters from aquifer types i) and ii) have TDS $\approx 40$ mg/L, pH $\approx 6$ and temperature $\approx 10^\circ$C whereas the Caldas de Manteigas thermal waters have TDS $\approx 160$ mg/L, pH $\approx 9.5$ and temperature $\approx 42^\circ$C.

The recharge of shallow aquifers seems to take place mostly in the plateaus; an additional part of the recharge may occur in the slopes of the Zêzere valley and its tributaries; the discharge areas are located in the Zêzere and Candeeira valley-bottoms and in the Nave de Santo António col (see Fig. 2). The recharge of the deep thermal aquifer seems to take place on more permeable zones of the granitic massif, associated to tectonic structures. Such zones correspond to the main tectonic valleys in the basin, which simultaneously act as discharge areas of the shallow aquifer subsystem (Fig. 12).

Figure 11 Apparent resistivity pseudo-section of the dipole-dipole profile.

Figure 12 Scheme of the thermal aquifer recharge: a conceptual hydrogeological model. Taken from ESPINHA MARQUES et al. (2006).
Part of the groundwater flowing from the shallow aquifers reach the surface and outflows in springs or along the river bottoms, while another part circulates downward through the tectonic structures, eventually reaching the thermal reservoir (Fig. 12).

As pointed out by the morphostructural and isotopic data, the recharge areas should be the following (see Fig. 2): i) the NNE-SSW section of the Zêzere valley, corresponding to the main BVMFZ lineament; ii) the Nave de Santo António col, also lying over this lineament; iii) the Covão de Ametade and Candeeira valleys, corresponding to conjugate faults of the main structure. The thermal waters from Caldas de Manteigas spa discharge in an area located ca. 800 m a.s.l. The water ascending from the deep reservoir spurts out in an area with distinct structural features affecting the granitic massif: the intersection of the main NNE-SSW structure by WNW-ESE conjugate structures and the presence of a geologic limit separating different granitic facies.

The results of studies performed under the scope of HIMOCATCH Project will be used to help the development of reliable management practices to preserve thermal water quality, based on the identification of i) recharge areas, ii) underground flow paths, iii) sources of pollution and iv) the processes affecting natural hydrogeologic conditions. Thermal waters should be considered one of the most important georesources at the Serra da Estrela Natural Park. In fact, Caldas de Manteigas Spa is one of the most important focus for local and regional development.

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