Hydrogeological study of A High Mountain Área (Serra da Estrela, Central Portugal): a multidisciplinary approach

Estudo hidrogeológico de uma área montanhosa (Serra da Estrela, Portugal central): uma abordagem multidisciplinar

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Abstract

The results of a preliminary hydrogeological study of the river Zêzere catchment upstream of Manteigas (Serra da Estrela Natural Park, Central Portugal) are presented. In this mountain region, different types of groundwater and surface water (used in several economic activities) occur. The methodology adopted in this study emphasizes the way how Geology, Geomorphology, Geophysics, Geochemistry, Soil Science and Hydrogeology contribute to the description of the hydrological phenomena taking place in the catchment, such as infiltration and aquifer recharge and groundwater flow and geochemistry — allowing to develop better hydrogeologic conceptual models. The hydrological modelling in course includes the use of the VISU-AL BALAN code, which is being coupled to a GIS. The hydrogeochemical techniques are highlighted as well as its preliminary results concerning major and minor elements. The thermomineral water study includes the identification of the reservoir's geologic material, the characterization of water-rock interaction and geothermometry.

Key words: Mountain areas, geotectonics, geomorphology, hydrogeology, management of hydric resources, hydrogeochemical techniques, Portugal Centre.

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INTRODUCTION

This paper is strongly connected to one of the most crucial water-related research issues of this millennium: "High Mountain Areas Hydrology" (AURELI, 2002). Special emphasis will be dedicated on thermal (*e.g.*, Caldas de Manteigas thermal waters; CARVALHO, 1996) and non-thermal groundwaters issuing in Serra da Estrela High Mountain area (Central Portugal). Surface water systems will also be considered. The selected study area is located in the vicinity of a regional morphostructure — Bragança–Vilariça–Manteigas fault zone [BVMFZ] — on the sector that intersects the central massif of Serra da Estrela.

The study area corresponds to the river Zêzere drainage basin upstream of Manteigas village and presents specific geomorphologic, climatic and geotectonic characteristics which certainly contribute to control local thermal groundwaters recharge and circulation. Besides the presence of important thermal water resources (allowing the installation of the Caldas de Manteigas Spa), the research area is characterised by the existence of other strategic groundwater resources (*e.g.,* high quality drinking water for bottling and domestic use at Manteigas village) which seem to be also strongly dependent on geomorphology (recharge areas) and geotectonics (active faults responsible for groundwater circulation). Surface water resources have been taken into consideration because of the basin's contribution to the storage at the Castelo do Bode large dam, the main source for Lisbon's water supply.

A broad characterization of the hydrogeologic regime existing in the region is presented, in terms of its geotectonic, climatic and geomorphologic features. Relevant aspects of the geophysical behaviour of the BVMFZ, based on seismicity and magnetotelluric studies, are reviewed. The hydrologic importance of soils and land cover is also examined.

Preliminary hydrogeochemical results on the local surface waters and shallow and deep groundwaters will be presented and discussed. One of the earliest tasks consisted of the hydrogeologic inventorying of surface and groundwater ocurrences. These waters were monitored for one hydrologic year. During this period, two fieldwork campaigns were carried out. The hydrochemical results (major and minor elements) were used to derive information on groundwater's geochemical history, with a special emphasis on surface water/groundwater interactions. Maximum subsurface temperatures experienced by Caldas de Manteigas thermal waters will be recorded by two types of chemical geothermometers. Such information will be extremely helpful in geothermal resource evaluation, since it also reflects the depth of groundwater circulation, based on an understanding of regional tectonics and geothermal gradients.

In order to address what is happening on the interrelation between local surface waters (recharge waters) and groundwaters, an integrated multidisciplinary approach is being launched, under the scope of the HIMOCATCH R&D Project *"Role of High Mountain Areas in Catchment Water Resources, Northern/Central Portugal: Serra da Estrela and Serra do Marão case studies".*

GEOMORPHOLOGICAL AND CLIMATOLOGICAL BACKGROUND

The Serra da Estrela (Fig. 1) is part of the *Cordilheira Central*, an ENE-WSW mountain range that crosses the Iberian Peninsula, and is the highest mountain in the Portuguese mainland. Associated to a maximum altitude of 1993m a.m.s.l., this mountain shows particular climatic and geomorphological characteristics that play an important role and impact on the local water cycle, and, particularly, on the hydrogeological sub-cycle.

The Zêzere river catchment upstream of the village of Manteigas and its surroundings corresponds to an area of *ca.* 28 km^2 with an altitude ranging from 875m a.m.s.l., at the streamflow gauge measurement weir of Manteigas, to 1993m a.m.s.l., at the Torre summit. The relief of this sector of Serra da Estrela is dominated by two major plateaus, separated by the NNE-SSW valley of the Zêzere river (VIEIRA, 2004; VIEIRA *et al.* 2005): the Torre-Penhas Douradas plateau (1450-1993m a.m.s.l.), located in the western side, and the Alto da Pedrice–Curral do Vento plateau (1450-1760m a.m.s.l.). These plateaus are composite, show flat surfaces at distinct altitudes and present a few wide valleys. Late Pleistocene glacial landforms and deposits are a distinctive feature of the Zêzere catchment, since the majority of the plateau area was glaciated during the Last Glacial Maximum (*e.g.*, DAVEAU *et al.* 1997, VIEIRA, 2004).

The Serra da Estrela climate (DAVEAU *et al.*, 1997; VIEIRA & MORA, 1998; VIEIRA, 2004) is Mediterranean with dry and warm summers; the wet season extends from October to May, with a mean annual precipitation of *ca.* 2500mm in the Torre summit, while the plateaus show more than 2000mm. The main precipitation control factors seem to be the slope orientation and the altitude. In fact, the western side of the mountain presents a larger number of days with rainfall, but a slightly lower total amount than the eastern part, which in turn shows a smaller number of days with rain. A general raise in the precipitation with the altitude is noticeable. However, on a local scale, the distribution of the precipitation is hard to interpret due to its relation to the behaviour of the air mass fluxes and to complex air divergence and convergence mechanisms controlled by the mountain morphology.

Monthly temperature averages (VIEIRA & MORA, 1998) from Penhas Douradas, Lagoa Comprida and Penhas da Saúde meteorological stations reveal that Serra da Estrela is characterized by a simple thermal regime. The warmest month is July and the coldest is January. Mean annual air temperatures are below 7ºC in most of the plateaus area and, in the Torre vicinity, they may be as low as 4ºC.

The available data concerning snow precipitation are scarce and of poor quality. Nevertheless, the hydrologic importance of snow provides good reasons for intensifying the research concerning the snowfall and snow cover patterns. So far, the spatial and temporal irregularity of snow related phenomena has been referred in earlier studies (*e.g.,* ANDRADE *et al.*, 1992; MORA & VIEIRA, 2004). Since the snowfall above 1700m a.m.s.l. may represent a significant fraction of the annual precipitation, the aquifer recharge from snowmelt will be estimated through the use of isotopic methods and geomathematical modelling.

GEOTECTONICAL, GEOPHYSICAL AND HYDROGEOLOGICAL SETTING

The Serra da Estrela mountain is located in the Central-Iberian Zone of the Iberian Massif (RIBEIRO *et al.*, 1990). The geological conditions represent an essential part of the hydrologic setting since they impose some of the main features of the hydrogeologic systems (Fig. 2), such as the infiltra-

tion and aquifer recharge processes, the type of flow medium (porous *vs.* fractured), the type of groundwater flowpaths, or the hydrogeochemistry.

The main lithotypes occurring in the region are (fig. 3): i) Variscan granitic rocks; ii) Precambrian-Cambrian metasedimentary rocks; iii) alluvium and Quaternary glacial deposits. The most important regional tectonic structure is the NNE-SSW Bragança-Vilariça-Manteigas fault zone, which controls the thermomineral occurrences.

The Bragança-Vilariça-Manteigas left-lateral strike-slip fault zone (BVMFZ) is one of the major structures of the late-Variscan fault system network in NW Iberia (Fig. 1). Its reactivation during Cenozoic times by the alpine compressive tectonics, together with the reactivation of major ENE-WSW trending reverse faults (such as the Seia-Lousã fault), originated the uplift of the Serra da Estrela Mountain as a horst in a pop-up structure (RIBEIRO *et al.*, 1990). A left-lateral movement with upthrusting of the eastern block towards WNW can be put in evidence, representing the predominant tectonic style of the reactivated BVMFZ in Plio-Quaternary times; fault slip-rates ranging from 0.2 to 0.5 mm/year (see CABRAL, 1989, 1995) for the Upper Pliocene to Quaternary tectonic activity.

Instrumental seismicity associated to the BVMFZ demonstrates its present day activity (*e.g.,* RIBEIRO, 1984; MOREIRA, 1985; VELUDO, 2004). It is presented here the location (Fig. 4) of the epicentres of several seismic events that occurred in the BVMFZ or in associated structures, between 1964 and 2004. The epicentres distribution indicates that whole segments of the BVMFZ are active. The magnitude of the seismic events ranging from 1 to 6, demonstrate the variable seismic activity in the area.

The BVMFZ has been the subject of geophysical studies in the last decades, which allowed a better characterisation of different tectonic structures connected to the BVMFZ. During 1996 and 1998, thirty magnetotelluric (MT) soundings were carried out in the northern tip of the Vilariça basin (MONTEIRO SANTOS *et al.,* 2000, 2002). The interpretation of these data produced an image of the internal electrical resistivity distribution of the basin (fig. 5). The main characteristics of the MT models and the interpretation of its features are as follows (MONTEIRO SANTOS *et al.*, 2000): i) the upper-
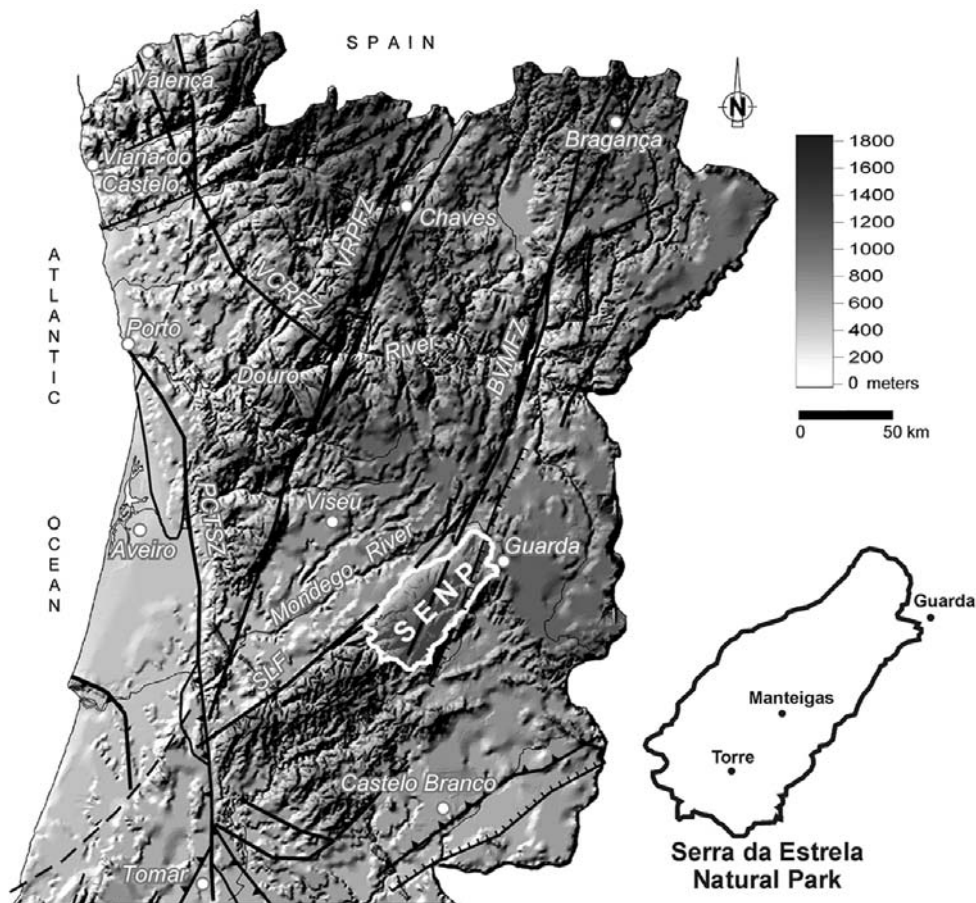
Fig 1. Morphotectonic features from Central Portugal, Serra da Estrela mountain region. Major faults: PCTSZ – Porto-Coimbra-Tomar strike-slip shear zone; VCRFZ – Vigo-Vila Nova de Cerveira-Régua fault zone; VRPFZ – Verin-Régua-Penacova fault zone; BVMFZ – Bragança-Vilariça-Manteigas fault zone; SLFZ – Seia-Lousã fault zone.

most lithologies of the Parautochthonous show an average resistivity of 100-200 ohm m; ii) the transition zone between Lower Allochthonous-Parautochthonous and the Parautochthonous is represented by a 350m thickness layer with a resistivity of 200-500 ohm m; iii) the Autochthonous metasediments (dominated by quartzites, pelites and graywackes), display distinct resistivity values, ranging from 500 to 4000 ohm m, defining different layers; iv) the sedimentary filling of the tectonic basin is a good conductor, presenting average resistivities of 20-100 ohm m. The low resistivity of this zone is mainly due to the water content of the sedimen-

tary units. The models suggest that this conductor is deeper within the northeastern part of the basin, whose floor tilts towards the north and southwards; v) at depths of 2km, in the western part of the studied area, the resistivity increases up to values greater than 4000 ohm m. We interpret the deepermost part of this layer as the Iberian gneiss basement; vi) the resistivity gradients revealed in the upper crust were associated with the main fault that controls the formation and evolution of the tectonic basin in Quaternary times.

The studies in course (*e.g.,* ESPINHA MAR-QUES, *in prep*.; ALMEIDA, *in prep*.; AFONSO et

al., 2005) are taking into consideration the hydrogeologic importance of the fracture network, with particular emphasis on understanding the fault system geometry, the processes of opening and sealing of fractures, the stress fields and the seismic pumping occurrence. For this purpose, scale studies from outcrop to satellite imagery will be accomplished. In particular, remote sensing and tectonic analysis will be used to characterise the main tectonic lineaments. Data obtained from computational analysis of digital terrain models and from geological/geomorphological structures are complemented by field data acquired using traditional mapping methods. Results will be integrated in a Geographic Information System (GIS).

In order to understand groundwater's recharge and circulation related phenomena (particularly thermomineral waters), infiltration and recharge areas are being identified and delimited by means of hydrogeochemical, isotopic (MARQUES *et al.*, 2005) and hydrogeomorphologic criteria. In addition, groundwater circulation paths must be characterised and groundwater contribution to streamflow estimated. Thus, lithology, water chemistry, morphostructure, climate, soil type and land cover should altogether be considered.

An important issue connected to the infiltration and aquifer recharge processes consists in the identification of areas of prevailing fractured or porous circulation mediums. 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). On the other hand, fractured mediums occur in poorly weathered granitic or metasedimentary areas. Such mediums may be present very close to the surface (especially on granitic outcrop dominated areas, with thin or absent sedimentary cover) or below the referred porous geologic materials.

INFILTRATION, SOILS AND LAND COVER

Soils are especially relevant in hydrologic studies, as they contribute to control both the volume and the water chemistry in hydrologic systems. The amount of water that moves from the topographic surface into the soil or the rock masses — in other words, that infiltrates — as consequence of a precipitation event, directly influences the aquifer recharge as well as the short-term stream response. The major factors usually pointed out as affecting infiltration — and runoff — are the amount and characteristics of precipitation (or irrigation), the soil physical and chemical features (*e.g.,* saturated hydraulic conductivity at the surface, clay mineralogy, presence of water-repellent substances), previous soil water saturation, surface slope and roughness, land cover and amount of evapotranspiration (*e.g.,* DINGMAN, 1994).

The soil features in this sector of Serra da Estrela result from the way how the formation factors act. The soil system is described (JENNY, 1994), by the following factors: parent material, climate, topography, organisms and time. Human action is often referred as an additional item to be considered (*e.g.,* GAUCHER 1981). The soil study included several fieldwork campaigns carried out through 2004. During these campaigns, soil samples were collected (Fig. 6) in order to obtain a physical, chemical, geochemical and mineralogical characterisation.

The main soil physical properties considered in the study are texture, structure, bulk density, particle density, porosity, colour, water retention and hydraulic conductivity. Other properties considered are pH, organic matter content, cation exchange capacity and exchangeable cations. Soil mineralogy focuses on clay mineralogy; soil geochemical analysis considered 36 chemical elements. The soil hydraulic conductivity was studied using the Guelph permeameter field method. During 2004, around 50 tests were conducted in most of the soil sampling sites.

The soil clay mineralogy and geochemistry is closely related to a detrital origin (absolute predominance of quartz, mica/illite and feldspars; more significant values of Al, Fe and K). Nevertheless, some distinctive features are evident, such as: samples related to granites show higher amounts of phyllosilicates (but show a decrease in illite whereas kaolinite increases); samples showing more significant values of Al, Fe and K are those related to granites and to glacial deposits located on slope and/or base of slope sites, whereas Ca shows higher values in samples related to glacial deposits located on slope, base of slope and plateau sites (ROCHA *et al.*, 2005).

Fig 2. Some aspects of the study area and the research work: a) Zêzere valley; b) Nave de Santo António, Cântaro Magro and Cântaro Gordo area; c) hydrochemical field analysis; d) snow cover at Nave de Santo António; e) soil profile in a granitic area; f) glacial deposit at Manteigas.
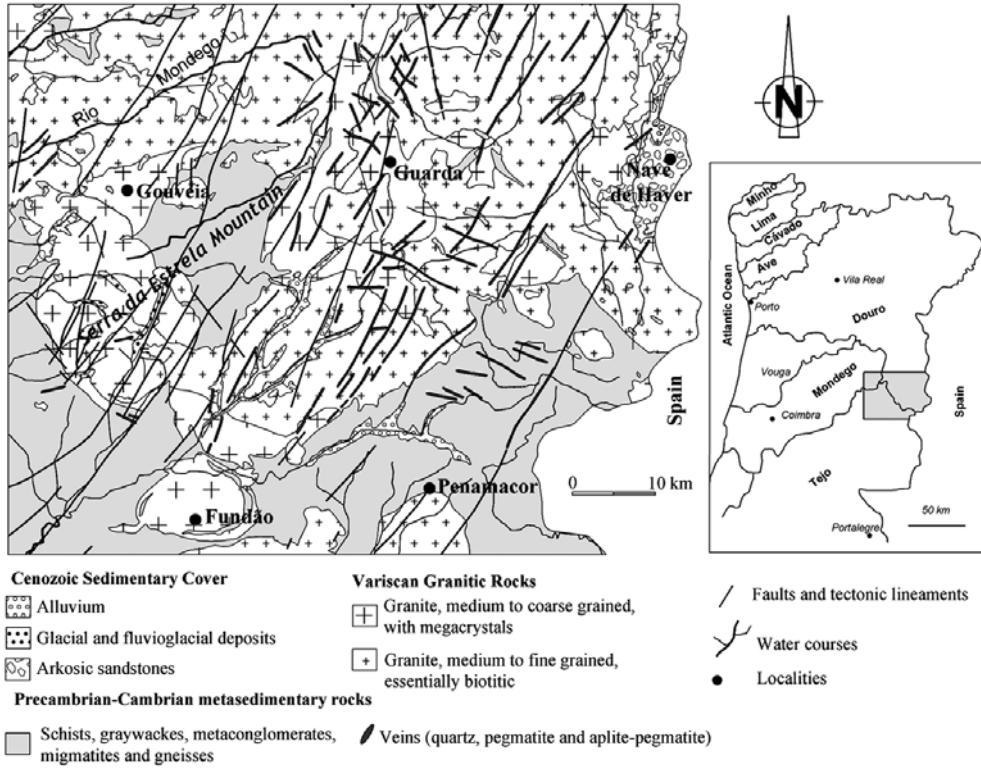
Fig 3. Geological map of the Serra da Estrela region, Central Portugal (simplified after OLIVEIRA et al., 1992)

Land cover has an important impact on a number of hydrological processes. The amount of infiltration varies considerably depending on whether vegetation is or is not present and on vegetation type. In the study region, several categories of land cover such as grassland, heathland, or forests are more favourable for infiltration than granitic or metasedimentary outcrop areas or exposed soils, mostly because of a runoff slowing effect.

It is included (Table 1) a preliminary description of some hydrologically relevant soil system characteristics at each sampling site. Soil classification according to the FAO-UNESCO criteria is being produced but is not yet available.

HYDROLOGICAL MODELLING

Hydrological models are being used to evaluate water resources in the basin. These models, which solve the water balance equations in the upper soil, the unsaturated zone and the aquifer, will provide estimates of aquifer recharge in the catchment. For this purpose, the computer code VISUAL BALAN V2.0, developed at the University of A Coruña (ETSI), will be used (SAMPER *et al.* 1999, 2000, 2005).

VISUAL BALAN V2.0 is a lumped hydrologic code which solves the water balance equation in the soil, the unsaturated zone and the aquifer. The code requires only a few parameters and incorporates user-friendly interfaces for data input and post-processing of results. It evaluates hydrologic components in a sequential manner. In addition to the water balance equation in the upper soil, the code also solves the water balance equations in the unsaturated zone and in the underlying aquifer. This allows the computation of daily groundwater levels as well as basin water discharge rates. Computed heads and streamflows can be compared to measured values for the purpose of model testing and
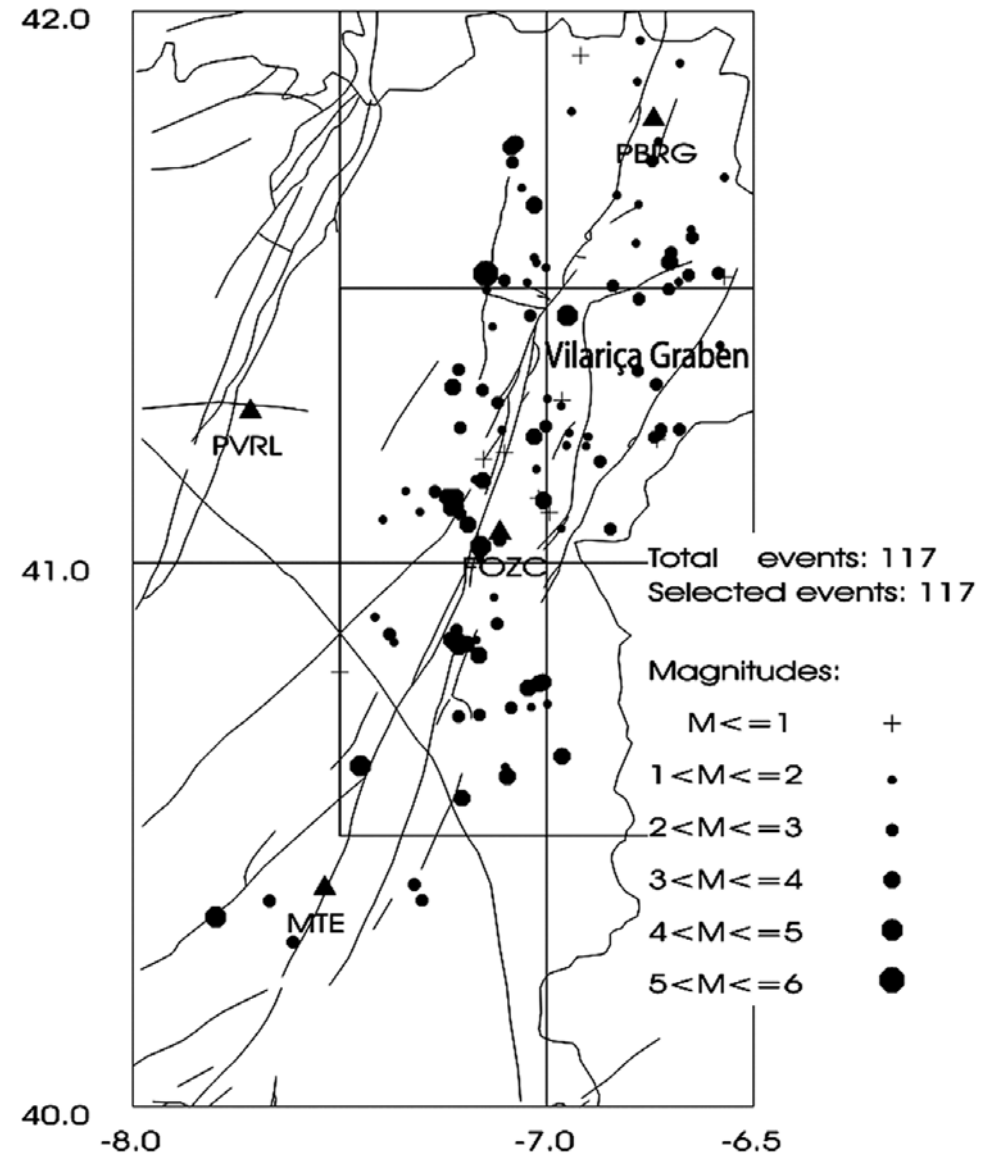
Fig 4. Seismicity connected to the Manteigas-Vilariça-Bração fault system and surrounding structures, recorded between 1964 and 2004 (VELUDO, 2004). Triangles – seismic stations (FOZC – Vila Nova de Foz Côa; MTE – Manteigas; PBRG – Bragança; PVRL; Vila Real); circles – earthquake epicentres.
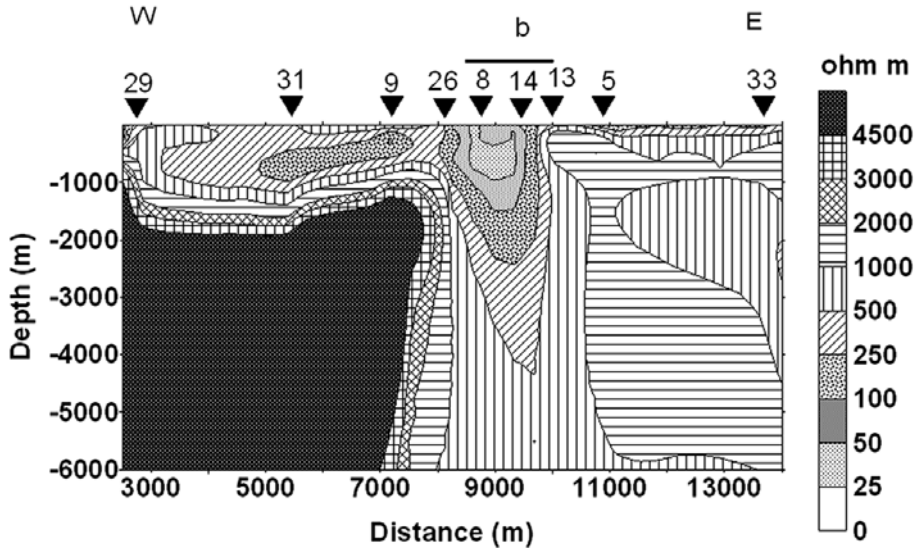
Fig 5. 2-D resistivity model obtained from joint TE-TM mode data (apparent resistivities and phases) collected across the Vilariça graben. The line marked with a b shows the approximate location of the basin (MONTEIRO SANTOS et al., 2000).

Type	Reference	chalcedony (1)	quartz (2)	Na/K (3)	K^2/Mg (4)
Spring (a)	Fonte Santa	57	88	59	52
Borehole (a)	AC2	68	98	71	n.d.
Borehole (a)	AC3	72	102	67	n.d.
Borehole (b)	AC2	73	103	78	n.d.
Borehole (b)	AC3	73	103	58	n.d.

(a) 1st fieldwork campaign; (b) 2nd fieldwork campaign. n.d. stands for not estimated (no Mg in water)
(1) Fournier & Truesdell (1974) *in* Fournier (1977)
(2) Truesdell (1975) - cooling by conduction
(3) White & Ellis (1970) *in* Truesdell (1975)
(4) Giggenbach (1988)

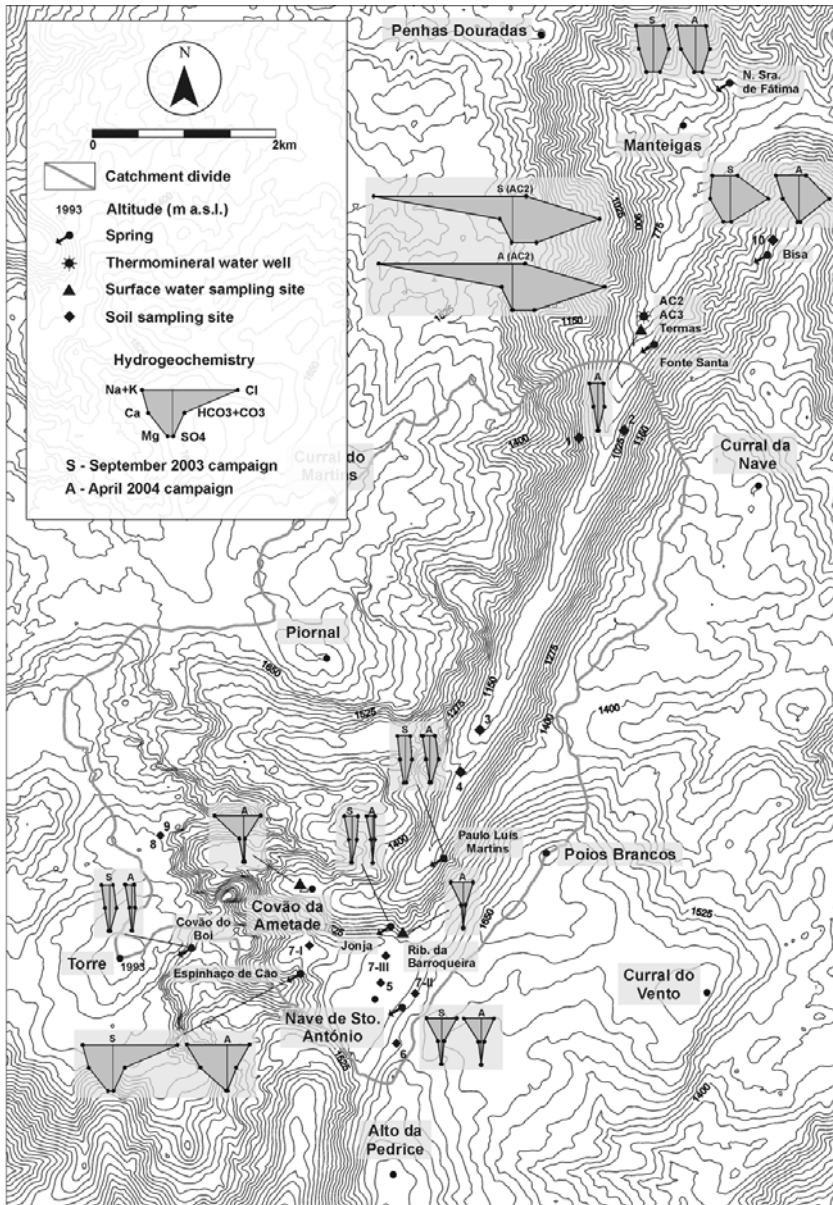Table 1 — Main soil system characteristics of the studied area.

Fig 6. Water and soil sampling points; major ion hydrogeochemical results.

calibration. VISUAL BALAN V2.0 accounts for irrigation sources and return flows. It also considers snow precipitation, melting and runoff. Two advanced options have been incorporated recently: i) Automatic parameter estimation using groundwater level and streamflow data and ii) Sensitivity analyses of hydrologic components to model parameters.

Since VISUAL BALAN V2.0 is a lumped hydrologic model, it is more suited for homogeneous and small basins. Therefore, as the studied basin is complex and exhibits a large spatial variability affecting most of its features, the basin is subdivided into several hydrologically homogeneous sub-basins where independent water balances can be performed. Results of each sub-basin are subsequently lumped to obtain the results for the whole basin.

The hydrological model is based on temperature and precipitation data from Penhas Douradas meteorological station (1383m a.m.s.l.). The possibility of using auxiliary data from other stations such as that at Manteigas (815m a.m.s.l.) is open to consideration. A preliminary definition of sub-basins, closely related to the definition of hydrogeomorphological units, is illustrated (Fig. 7). Several criteria are being considered in order to accurately represent the complexity of the hydrological system: geology, geomorphology, hydrogeology, climate, soil type and land cover. During this delimitation process, special attention has been paid to the available geological and geomorphological maps (*e.g.*, FERREIRA & VIEIRA 1999; VIEIRA, 2004). Due to the strong temperature and precipitation vertical gradients, climate data has to be analyzed carefully. Preliminary model testing and calibration has been performed by comparing computed streamflows to measured values from Manteigas streamflow gauge station.

GEOGRAPHICAL INFORMATION SYSTEM APPLICATION

Geographical Information System technology is particularly appropriate for handling hydrogeological data (SINGHAL & GUPTA, 1999). The development of a GIS applied to this sector of Serra da Estrela Natural Park will certainly help to develop and improve conceptual models comprising the main components of hydrogeologic systems, namely: i) recharge areas, ii) groundwater circulation zones and iii) discharge areas. Such an approach is particularly suitable for handling a great variety of data that must be spatially integrated in a coherent manner (Fig. 8) which, as referred earlier, is the case of the study area.

The methodological framework followed in this research offers important benefits for regional water resources management, especially in what concerns to groundwater exploration, to the definition of well-head protection areas and to the assessment of aquifer pollution vulnerability.

VISUAL BALAN V2.0 has recently been coupled to a GIS (SAMPER *et al.*, 2005). This procedure was carried out by extending the capabilities of the original code. For that purpose, a pre-processor has been developed as an input interface to VISUAL BALAN V2.0. Beginning from a digital elevation model and using the geomorphologic data in the GIS the pre-processor interprets model input data: sub-basin delineation, drainage network, morphologic parameters (average slope, characteristics, soil type and land cover/land use). Additional improvements are expected to be able to perform modelling of complex basins considering the spatial variation of model parameters (distributed parameter model) and surface runoff propagation. GIS will provide average parameter values for each sub-basin delineated by the pre-processor in the first step. Available meteorological data from different stations will be processed in the GIS to create maps that describe the spatial variability of weather variables. This information will be then processed to obtain series of average values for each sub-basin, in the same way as morphologic parameters. Connectivity between sub-basins will be established and so flow accumulation will be calculated for each sub-basin. A further step is planned in the future to be able to apply the balance equations to smaller areas, taking full advantage of the capabilities of the GIS.
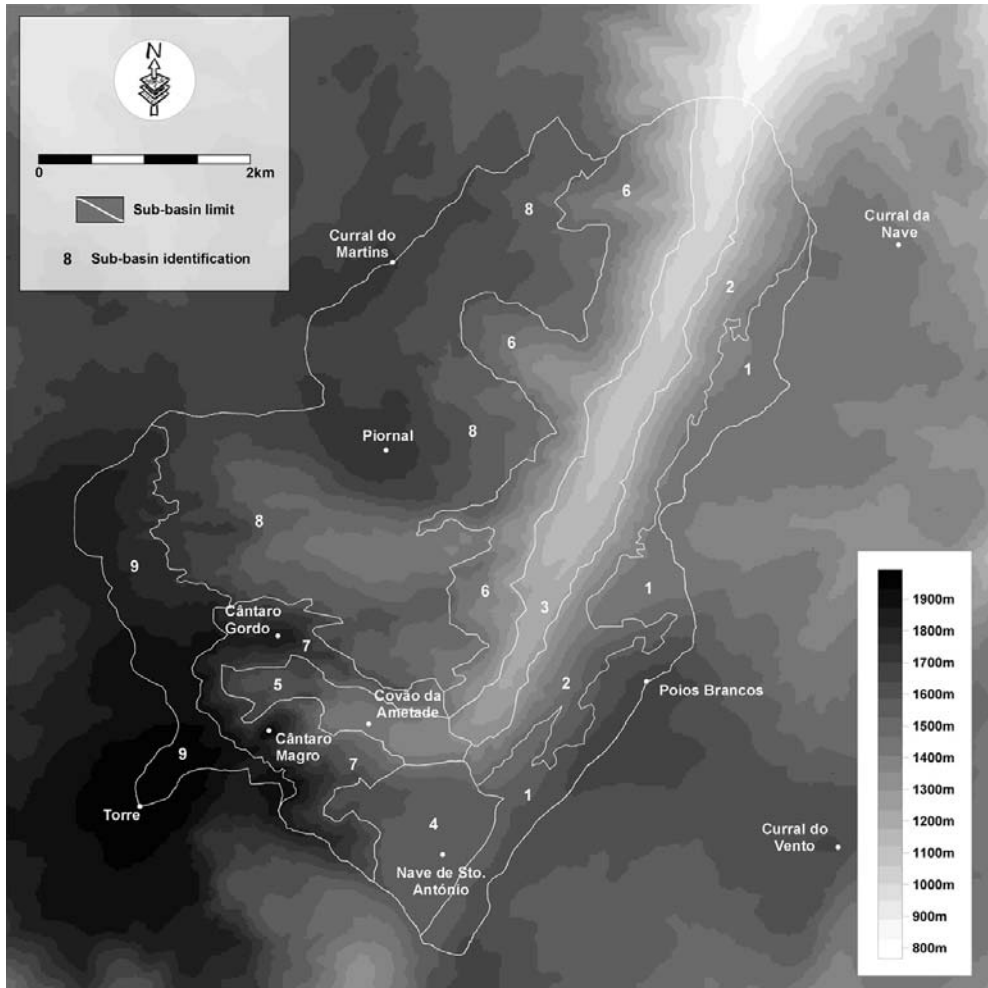
Fig 7. Sub-basin limits: 1 – Eastern plateau; 2 – Zêzere valley eastern slopes; 3 – Lower Zêzere valley floor; 4 – Nave de Santo António col; 5 – Upper Zêzere valley floor; 6 –Zêzere valley western slopes; 7 – Cântaros slopes; 8 – Lower western plateau; 9 – Upper western plateau.

HYDROGEOCHEMICAL APPROACH

Surface manifestations of thermomineral waters circulation are a subject of great scientific and economic interest. Thermomineral waters and shallow cold groundwaters spurting out in the same area should be observed and studied in detail, as they provide a significant amount of information at relatively low costs. This information may be used in the appraisal of the thermomineral water resources of a potential area for development.

In the present chapter, some of the geochemical techniques employed in thermomineral water investigations in the Caldas de Manteigas area, in order to update local and/or regional conceptual circulation models, are outlined. Preliminary results on the major and minor element composition of local surface waters and of shallow and deep groundwaters will be presented and discussed.

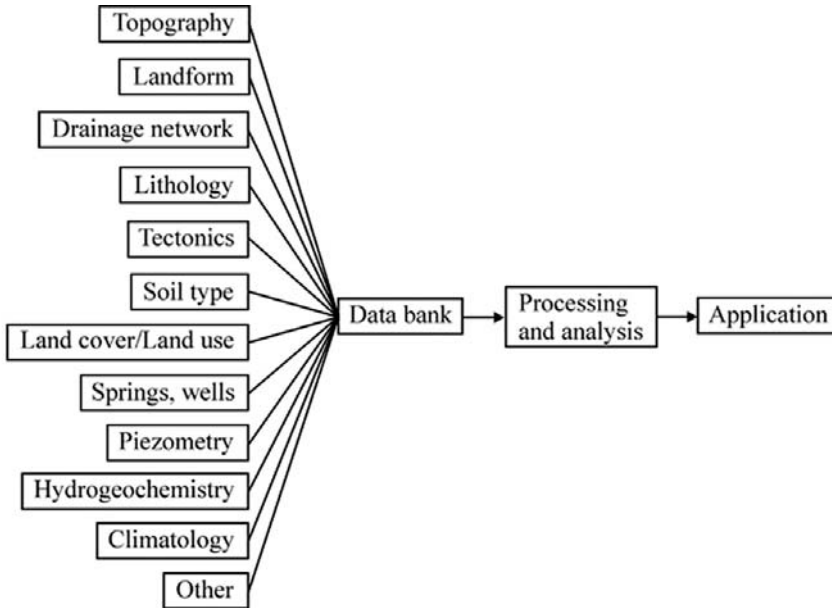The hydrogeochemical study in course illus-

Fig 8. Data integration in a GIS (modified after SINGHAL & GUPTA, 1999).

trates the considerable number of ground and surface water types coexisting in a relatively restricted area, thus reflecting the hydrologic complexity of the basin.

In order to embrace the various hydrologic subsystems occurring in the region, three main water categories were considered: i) shallow cold groundwaters; ii) deep thermomineral groundwaters and iii) surface waters from the river Zêzere and its tributaries.

A hydrogeologic inventory and the definition of a network of surface and ground water monitoring points (springs, boreholes and streams) was carried out (Fig. 6). Subsequent fieldwork campaigns were conducted in September 2003 and April 2004 in order to collect water samples for chemical and isotopic (oxygen-18, deuterium and tritium) analysis. The resulting hydrogeochemical information (major and minor element composition) is being applied to estimate geochemical evolution of groundwater, including its origin and interaction between water and the aquifer rock minerals.

Temperature (ºC), pH and electrical conductivity (iS/cm) of the waters were determined in the field. 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, Lisbon): atomic absorption spectrometry for Ca and Mg; emission spectrometry for Na, K, Li, Rb and Cs; colorimetric methods for SiO_2, Fe_{total}, F and Al; ion chromatography for SO_4, NO_3 and Cl; potentiometry for alkalinity, here referred to as HCO_3. Representative data of the waters sampled during the 1st (September 2003) and 2nd (April 2004) fieldwork campaigns are presented (tables 2 and 3).

At Caldas de Manteigas area, the thermomineral waters (with output temperatures around 45ºC) are characterised by the following main features:

i) relatively high pH values ($\approx$ 9).

ii) TDS values usually in the range of 160 to 170 mg/L.

iii) HCO_3 is the dominant anion.

iv) Na is the dominant cation.

v) the presence of reduced species of sulphur ($HS^-\approx 1.7$ mg/L).

vi) high silica values (usually around 50 mg/L)

representing a considerable percentage of total mineralization.

vii) high fluoride concentrations (up to 7 mg/L).

As indicated by the chemical composition of the Caldas de Manteigas thermomineral waters, the reservoir rock should be mainly granite, being the thermomineral waters mineralization strongly dominated by the hydrolysis of plagioclases. The strong HCO_3-Na signatures of Caldas de Manteigas thermomineral waters can be clearly seen in the Stiff diagram (Fig. 6).

Concerning the non-thermal waters sampled in the studied region (surface waters and shallow groundwaters), two groups can be defined through the geochemical signatures derived from the Stiff and Piper diagrams (Figs 6 and 9), namely:

- Group I) This first group encloses the so-called "normal" surface (Zêzere river – sampling point close to the Caldas de Manteigas spas) and shallow groundwaters (Covão do Boi, Jonja, Paulo Luís Martins, Bisa and N. Srª. de Fátima spring waters). All of these waters belong mainly to the HCO_3-Na *facies* (a relatively higher Ca concentration was found only in Bisa spring during the field work campaign of September 2003), displaying different total dissolved solids (TDS) values. The lower mineralization found in Zêzere river and Covão do Boi, Jonja and Paulo Luís Martins spring waters reflects low water-rock interaction associated with short surface/underground circulation paths. These spring waters could be considered as good signatures of local recharge. The relatively higher mineralization detected in Bisa and N. Srª. de Fátima spring waters could be ascribed to long shallow underground flow path, allowing higher water-rock interaction. It should be stated that Bisa spring is located in a forestated area where soils are enriched in organic matter. This important source of additional CO_2 could be responsible for a higher water-rock interaction, expressed in the following equation:

$$2NaAlSi_3O_8 + 9H_2O + 2H^+ + 2HCO_3^- =$$
$$Si_2O_5Al_2(OH)_4 + 2Na^+ + 2HCO_3^- + 4$$
$$H_4SiO_4$$
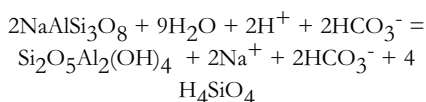
The role of CO_2 is strongly related with the pH of the solution since $2H^+ + 2HCO_3^-$ is, in fact, $2H_2CO_3$, or $2CO_2 + H_2O$.

- Group II) This second group of waters encloses surface (Zêzere river – sampling points close to Covão da Ametade and Jonja stream) and shallow groundwaters (Nave de Stº António and Espinhaço de Cão spring waters). This group of waters is also characterized by relatively low mineralization, but presents clear Na-Cl geochemical signatures. The Na-Cl *facies* found within some of the waters of this group could be ascribed to the local use of NaCl to promote snowmelt in the roads during the Winter season. These geochemical signatures can be clearly seen in the Piper diagram (see Fig. 9). In the case of Espinhaço de Cão spring the rather different Stiff diagrams indicates that water chemistry could be strongly controlled by other sources of anthropogenic contamination rather than the local use of NaCl for snow melting, since there are important differences in the Na/Cl ratios from the 1st to the 2nd field work campaign. The different geochemical signatures found in Espinhaço de Cão spring can be clearly detected in the field through the higher electric conductivity values (see Tables 2 and 3).

Chemical geothermometry is one of the most important geohydrologic tools in the exploration of thermomineral water resources. The main objective of geothermometric interpretation is to use the chemistry of hot springs in order to estimate chemical and physical properties of the reservoir fluid. This methodology depends upon the temperature dependence of the concentrations of certain species, the chemical equilibrium between minerals and water and various chemical reactions. During the last two decades many chemical geothermometers have been proposed, both qualitative and quantitative. Those used in this paper include the chalcedony and quartz geothermometers (FOURNIER & TRUESDELL, 1974 *in*: FOURNIER, 1977; TRUESDELL, 1975 – cooling by conduction), the feldspar (Na/K) geothermometer (WHITE & ELLIS, 1970 *in*: TRUESDELL, 1975) and the K^2/Mg geothermometer (GIGGENBACH, 1988). The results obtained are presented (see Table 4).

Bearing in mind that the reservoir fluid may

Reference	T °C	pH	Cond	Na	K	Ca	Mg	Li	Al	Fe$_{total}$	HCO$_3$	SO$_4$	NO$_3$	Cl	F	Rb	Cs	SiO$_2$	D.R.
Paulo L. Martins *	8.4	6.0	39	2.4	0.24	1.5	0.28	n.d.	n.d.	0.05	6.0	0.8	0.40	2.5	n.d.	n.d.	n.d.	11.5	19.2
Fonte Santa **	20.1	9.7	223	40.0	0.76	4.9	0.22	0.13	n.d.	0.05	74.4	12.3	n.d.	5.5	5.80	0.02	n.d.	36.6	135.4
C. Manteigas AC2 **	42.6	9.7	272	45.0	1.06	3.4	n.d.	0.15	n.d.	0.06	76.9	17.1	n.d.	7.4	6.40	0.02	n.d.	46.1	166.0
C. Manteigas AC3 **	42.2	9.7	265	44.0	0.96	3.3	n.d.	0.15	n.d.	0.05	78.0	15.8	0.1	7.2	6.04	0.02	n.d.	50.4	165.2
Bisa *	11.5	6.3	45	5.2	1.02	5.7	1.20	n.d.	n.d.	0.08	33.2	0.9	0.2	3.9	n.d.	n.d.	n.d.	22.6	53.4
N. Sr³. de Fátima *	14.8	6.3	58	5.2	0.64	4.1	1.15	n.d.	n.d.	0.05	13.9	4.9	4.2	5.3	n.d.	n.d.	n.d.	15.3	54.0
Jonja *	10.7	5.7	15	2.4	0.08	0.9	0.08	n.d.	n.d.	0.03	4.4	0.3	0.3	3.2	0.17	0.01	n.d.	11.6	16.0
Nave Sto. António *	9.5	5.5	26	4.9	0.14	1.1	0.08	n.d.	n.d.	0.04	2.3	0.3	1.0	7.8	0.18	0.01	n.d.	8.4	26.0
Espinhaço Cão *	12.4	7.1	102	9.8	0.32	7.0	0.84	0.01	0.03	0.04	10.7	0.6	1.5	33.3	0.06	0.01	n.d.	21.2	82.2
Covão do Boi *	12.3	6.9	10	2.5	0.12	1.2	0.10	n.d.	n.d.	0.07	6.4	0.8	0.6	2.0	0.14	0.01	n.d.	12.8	36.6

Concentrations in mg/L; Conductivity (Cond.) in μS/cm; n.d. = not detected (below detection limit). D.R. stands for dry residuum. (*) cold spring waters; (**) thermomineral waters.

Table 2 – Representative physico-chemical data of the waters from the studied region. 1st fieldwork campaign (September 2003).

Reference	T °C	pH	Cond	Na	K	Ca	Mg	Li	Al	Fe$_{total}$	HCO$_3$	SO$_4$	NO$_3$	Cl	F	Rb	Cs	SiO$_2$	D.R.
Paulo L. Martins *	7.0	5.9	18	2.3	0.24	1.1	0.06	n.d.	0.05	0.04	7.5	1.1	0.3	2.7	0.4	n.d.	n.d.	8.9	20.4
Jonja *	7.5	5.5	9	1.9	0.12	0.5	0.02	n.d.	0.05	0.04	1.8	n.d.	n.d.	1.1	n.d.	n.d.	n.d.	10.2	18.6
Covão do Boi *	8.7	5.7	9	2.0	0.22	0.8	0.02	n.d.	0.03	0.04	3.0	0.4	0.1	1.2	n.d.	n.d.	n.d.	10.3	18.4
Espinhaço de Cão *	7.8	6.2	150	13.0	0.62	7.8	0.20	n.d.	0.04	0.06	8.0	0.3	1.7	11.5	0.2	n.d.	n.d.	18.8	93.4
Nave Sto. António *	7.5	5.5	35	5.6	0.26	0.8	0.02	n.d.	0.03	0.04	2.7	0.1	0.5	6.5	n.d.	n.d.	n.d.	8.4	25.4
Bisa *	9.6	5.9	64	7.0	0.94	4.6	0.20	n.d.	0.02	0.18	26.4	0.9	0.2	3.6	n.d.	n.d.	n.d.	22.3	50.4
N. Sr de Fátima *	11.3	5.8	72	5.9	0.62	4.2	0.22	n.d.	0.02	0.07	12.6	4.6	5.1	5.3	n.d.	n.d.	n.d.	16.0	47.2
C. Manteigas AC2 **	43.2	9.0	286	43.0	1.14	3.1	n.d.	0.14	0.01	0.05	79.6	14.8	n.d.	6.2	6.7	0.01	0.01	51.2	163.0
C. Manteigas AC3 **	45.0	9.0	316	52.0	0.98	3.1	n.d.	0.14	0.01	0.05	79.7	14.3	0.2	6.4	6.8	0.01	0.01	51.4	159.6
Jonja stream #	10.0	6.1	20	4.1	0.12	0.6	0.02	n.d.	0.05	0.07	2.2	0.2	0.9	5.1	n.d.	n.d.	n.d.	5.6	20.2
Zêzere River (Covão da Ametade) #	5.1	5.2	88	9.7	0.12	1.3	0.04	n.d.	0.07	0.09	1.4	0.8	0.1	8.7	n.d.	n.d.	n.d.	3.2	40.4
Zêzere River (Spas) #	8.4	6.4	19	2.6	0.12	1.2	0.04	n.d.	0.07	0.12	5.8	0.6	0.2	3.0	n.d.	n.d.	n.d.	6.0	19.0

Concentrations in mg/L; Conductivity (Cond.) in μS/cm; n.d. = not detected (below detection limit). D.R. stands for dry residuum. (*) cold spring waters; (**) thermomineral waters; (#) stream and river waters.

Table 3 – Representative physico-chemical data of the waters from the studied region. 2nd fieldwork campaign (April 2004).
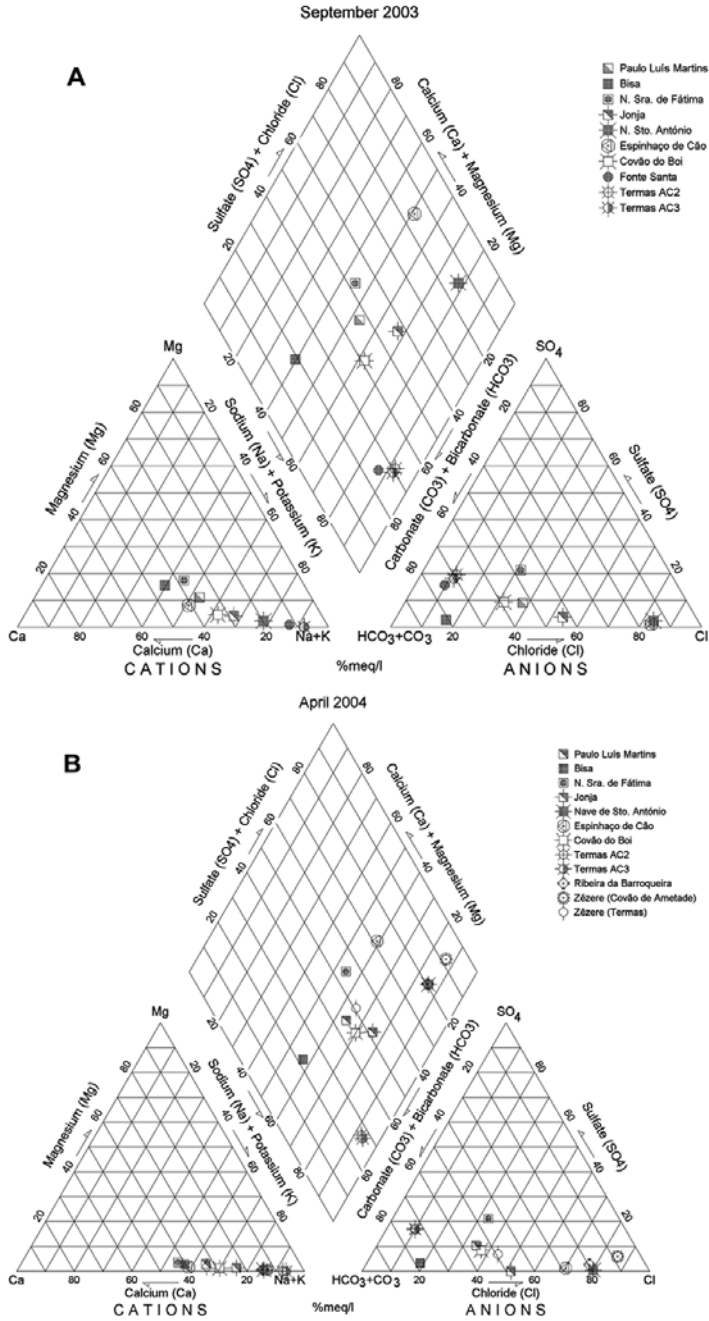
Fig 9. Major ion hydrogeochemistry: a) September 2003 campaign; b) April 2004 campaign.

become mixed with cold groundwater at shallow levels and could change its chemistry by leaching and reaction with wall rocks on the way to the surface, the results obtained from the application of several chemical geothermometers should be interpreted with great caution. In the near future, the results of chemical geothermometry will be correlated with the results from the geophysical and geotectonical surveys that will be performed in the region, under the scope of the HIMOCATCH R&D Project. Such information will be extremely helpful in thermomineral water resources evaluation, since it also reflects the depth of groundwater circulation, based on an understanding of regional tectonics and geothermal gradients.

Using reservoir temperatures given by the quartz geothermometer (applied to Caldas de Manteigas AC2 and AC3 borehole waters), and considering a mean geothermal gradient of 30ºC/km, we can estimate a maximum depth of about 3.2km reached by the Caldas de Manteigas thermomineral water system. This value was obtained considering that:

$$depth = (T_r - T_a) / gg = (100 - 5) / 30 = 3.2 \ km$$

where T_r is the reservoir temperature (ºC), T_a the mean annual temperature (ºC) and gg the geothermal gradient.

Geochemical data of Fonte Santa thermal spring waters seems to corroborate a mixing process with local shallow groundwaters. This trend requires the shallow groundwaters diluting Fonte Santa thermal spring waters to be derived from local infiltration. The mixing process should be responsible for the higher Ca and Mg dissolution. Effectively, the Ca and Mg concentrations are lower in AC2 and AC3 thermal borehole waters, whereas these metals are higher in Fonte Santa thermal spring waters. Furthermore, Ca and Mg are very often added to cooled waters by a reaction with the rock, as stated by several authors, particularly with regard to waters of the French Massif Central (*e.g.*, MICHARD *et al.*, 1978, 1981; CRIAUD & FOUILLAC, 1986). Further fieldwork campaigns will clarify the above mentioned hypothesis, based on systematic isotopic (^{18}O and ^{2}H) signatures of the waters.

In future studies involving the interpretation of chemical geothermometry special emphasis will be put on the evaluation of the overall chemical characteristics of the waters, as they correlate to equilibrium with alteration minerals.

CONCLUDING REMARKS

Crystalline rocks, particularly granites and metasedimentary units, dominate the Serra da Estrela Mountain region. The hydrogeological characterisation of this kind of hard-rocks is complex, due to the high heterogeneity and anisotropy of the fracture network that stores and conducts the water. It is usual to consider that the flowpaths are mainly governed by the fissured medium hydraulic conductivity, faulting and weathering, resulting on non-continuous productive zones. Nevertheless, it is clear that in the Variscan Iberian Massif, lithology and structure play a major role on the productivity of regional hydrogeological units and related water wells.

Some differences detected in local shallow cold groundwater's characteristics could be the result of water circulation paths varying in length and residence time and/or anthropogenic contamination, such as the local use of NaCl for snow melting. The combined chemical and isotopic data suggests that the Caldas de Manteigas thermomineral waters could be derived from regional groundwater sources. The quartz geothermometer indicates reservoir temperatures of approximately 100ºC.

Combining information ascribed to the geochemical and isotopic signatures of groundwaters, hydrogeologists can strongly support their conclusions on the origin of waters and recharge areas, groundwater quality and contaminant processes, water-rock interactions occurring at depth and resource renewability.

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between local surface waters (recharge waters) and groundwaters, an integrated multidisciplinary approach is being launched under the scope of the HIMOCATCH Project *"Role of High Mountain Areas in Catchment Water Resources, Northern/Central Portugal"*, granted by the Portuguese Foundation for Science and Technology (FCT), contract Nr. POCTI/CTA/44235/2002. PEF and JC acknowl-

Type	Reference	chalcedony (1)	quartz (2)	Na/K (3)	K^2/Mg (4)
Spring (a)	Fonte Santa	57	88	59	52
Borehole (a)	AC2	68	98	71	n.d.
Borehole (a)	AC3	72	102	67	n.d.
Borehole (b)	AC2	73	103	78	n.d.
Borehole (b)	AC3	73	103	58	n.d.

(a) 1st fieldwork campaign; (b) 2nd fieldwork campaign. n.d. stands for not estimated (no Mg in water)
(1) Fournier & Truesdell (1974) *in* Fournier (1977)
(2) Truesdell (1975) - cooling by conduction
(3) White & Ellis (1970) *in* Truesdell (1975)
(4) Giggenbach (1988)

Table 4 - Reservoir temperatures (ºC) of Caldas de Manteigas thermomineral waters, estimated from chemical geothermometry.

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