Role of high mountain areas in catchment hydromineral resources – Northern/Central Portugal: environmental issues

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Abstract

This study summarizes the results of geological, geomorphological, tectonic, geochemical, geophysical, hydrogeological and isotopic techniques in hydromineral resources assessment (issue temperature between 27ºC and 45ºC). Two case studies are presented: i) *Serra da Estrela* mountain region, the highest mountain in Portuguese mainland and ii) *Serra do Marão* mountain region. A special emphasis is dedicated to the recharge and discharge processes and the role of snowmelt as a source of hydromineral resources. Since local Spas are particularly dependent on water quality, the existence of mixing between hydromineral waters and local shallow groundwaters is also considered.

Keywords: geochemistry, isotopes, geophysics, tectonics, high mountain areas hydrogeology, hydromineral resources, environmental issues, Portugal.

1 Introduction

Mountain areas represent some of the blackest "*black boxes*" in the hydrological cycle (Chalise [1]). The complex role of soils, geomorphology, geology, climate and land use on the hydrology of mountain areas, are rather difficult to model. Nevertheless, mountain river basins provide the finest opportunity to increase knowledge on the relationship between those variables as well as their impacts on the water quality at different altitude zones [1]. This study attempts to present, under an environmental multidisciplinary approach, the assessment of two hydromineral systems in different mountain regions, located in Central/Northern Portugal, fig. 1, highlighting the environmental problems. Both areas present particular climatic, geomorphologic and geotectonic characteristics that contribute to control the recharge/discharge processes as well as the flow paths.

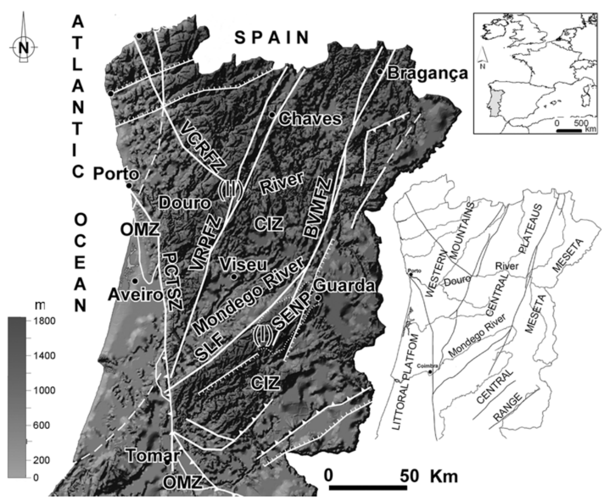

Figure 1: Morphotectonic features at Serra da Estrela National Park (SENP) (I) and Caldas do Moledo (II) mountain regions. Explanation: PCTSZ: Porto-Coimbra-Tomar strike-slip shear zone; VCRFZ: Vigo-Vila Nova de Cerveira-Régua fault zone; VRPFZ: Verin-Régua-Penacova fault zone; BVMFZ: Bragança-Vilariça-Manteigas fault zone; SLF: Seia-Lousã fault zone; CIZ – Central-Iberian Zone, OMZ – Ossa-Morena Zone.

At *Serra da Estrela National Park* (SENP) a special emphasis will be dedicated to: i) the recharge and discharge processes, ii) the role of snowmelt as a source of groundwater resources and iii) the local environmental issues which could affect the surface water-shallow groundwater-groundwater interactions.

At Caldas do Moledo region, coupled geomorphological, geotectonical, geochemical and isotopic data made it possible to improve knowledge on i) the hydrogeological conceptual model of the discharge area, based on the relations between shallow groundwaters and deep mineral waters, and ii) the local anthropogenic impacts on the groundwaters.

2 Climate, geomorphology and geology

2.1 Serra da Estrela region (Central Portugal)

The relief of the study region consists mainly of two major plateaus (*ca.* 1450-1993 m a.s.l.), separated by the NNE-SSW valley of Zêzere River (Vieira [2]). Late Pleistocene glacial landforms and deposits are a distinctive feature of the upper Zêzere catchment, fig. 2, since the bulk plateau area was glaciated [2]. The ice sheet that covered most northern and central Europe 18,000 years BP did not reach the study region, where only mountain glaciers were present.

Climate has Mediterranean features: mean annual precipitation reaches 2500 mm in the highest areas, and is mainly controlled by slope orientation and altitude. Mean annual air temperature is below 7ºC in most of the plateau areas and, in the highest sites (*e.g.* Torre surroundings) it may be as low as 4ºC (Vieira and Mora [3]).

Serra da Estrela Mountain is located in the so-called Central-Iberian Zone of the Iberian Massif (Ribeiro *et al* [4]), mainly composed by Variscan granitic rocks and Precambrian-Cambrian metasedimentary rocks, as well as alluvia and Quaternary glacial deposits.

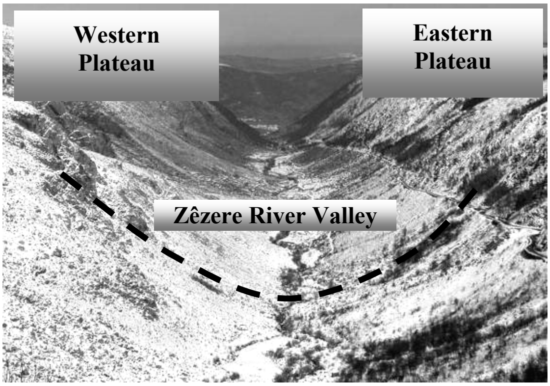

Figure 2: The U-shaped Zêzere River Valley (Eastern and Western Plateaus).

2.2 Caldas do moledo region (Northern Portugal)

The main geomorphologic feature of the Caldas do Moledo region is the Douro River valley, fig.3a, bordered by the Marão Mountain ridge (*ca.* 1415m a.s.l.) to the north and by the Meadas Mountain ridge to the south. The average annual temperature is about 15 ºC. The climate in the Douro region is influenced by the Marão Mountain which acts as a barrier that protects the region from the humid west winds from the Atlantic Ocean. Annual rainfall ranges from 1200 mm to 380 mm. It is heavier in December and January and, during the wettest months, it may be as low as 7 mm (D.G.R.A.H. [5]).

Caldas do Moledo region is also located in the Central-Iberian Zone of the Iberian Massif [4]. The most abundant lithotypes are metasedimentary rocks of lower Cambrian age (Schist-Greywacke Complex, Douro Group), also including significant aplite and pegmatite veins (Teixeira *et al* [6]), suggesting the existence of an important underlying granitic rock mass Espinha (Marques *et al* [7]).

The most important tectonic structures in the region are the NNE-SSW Verin-Régua-Penacova fault zone (VRPFZ), where the hydromineral resources issue, see fig. 1, and the WNW-ESE to NW-SE Vigo-Vila Nova de Cerveira-Régua fault zone, VCRFZ [7].

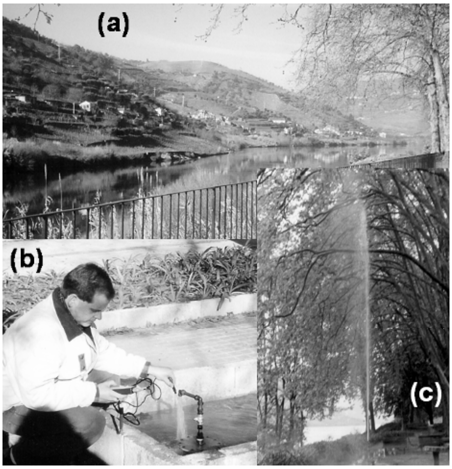

Figure 3: Caldas do Moledo: (a) Douro River valley; (b) mineral water sampling at the Spa – (c) artesian borehole AC1 (45ºC).

3 Research methods

Three water-types were sampled: river waters, shallow cold groundwaters (spring waters – so called "normal" waters) and mineral waters (*e.g.* at Caldas de Manteigas and Caldas do Moledo Spas). Temperature (ºC), pH and electrolytical conductivity (EC: in μS/cm) were determined *in situ*, fig. 4. Water samples were specifically treated – ultrafiltration. Total alkalinity was measured a few hours after collection. The chemical analyses of the waters were performed at the Laboratório de Mineralogia e Petrologia of Instituto Superior Técnico (LAMPIST) by the following methods: atomic absorption spectrometry for Ca^{2+} and Mg^{2+}; emission spectrometry for Na^+, K^+ and Li^+; colorimetric methods for SiO_2 and F^-; ion chromatography for SO_4^{2-}, NO_3^- and Cl^-; potentiometry for alkalinity, here referred to as HCO_3^-. For HS^- determinations, CdS was titrated by potentiometry with sodium thiosulphate. The δ^2H and $\delta^{18}O$ measurements (*vs.* V-SMOW) were performed by mass spectrometry (SIRA 10–VG ISOGAS) at the Instituto Tecnológico e Nuclear (ITN) following the analytical methods of Epstein and Mayeda [8] and Friedman [9] (accuracy of ± 1.0 $^o/_{oo}$ for δ^2H and ± 0.1 $^o/_{oo}$ for $\delta^{18}O$ measurements). The ^3H concentrations in the waters (in TU) were determined at ITN, using electrolytical enrichment followed by liquid scintillation counting method (PACKARD Tri-Carb 2000 CA/LL (standard deviation around ± 0.6 TU).

Figure 4: Sampling sites at Serra da Estrela Natural Park: (a) Caldas de Manteigas Spa, mineral waters – artesian borehole AC2 (42ºC); (b) Jonja spring; (c) Zêzere River; (d) Vale Formoso spring.

4 Results and discussion

4.1 Serra da Estrela region

Most "normal" groundwaters belong to the Na-Cl and HCO_3-Na *facies*, with low TDS, considered as good signatures of local recharge and hydrolysis of Na-plagioclases, respectively. The high Na-Cl concentrations found in some of the waters of this group (*e.g.* Espinhaço de Cão and N. Sto. António, see fig. 5) could be ascribed to the local use of NaCl to promote snowmelt in the roads during the winter season. Mineral waters from Caldas de Manteigas Spa are characterised by the following main features: high pH values (≈ 9), EC values around 300 μS/cm, the presence of reduced species of sulphur (HS^- ≈ 1.7 mg/L), silica values (around 50 mg/L) representing a significant % of TDS values and high F^- concentrations (up to 7 mg/L), indicating that the reservoir rock should be mainly the granite. The strong HCO_3-Na signatures of Caldas de Manteigas mineral waters can be clearly seen in the Stiff diagram of fig. 5.

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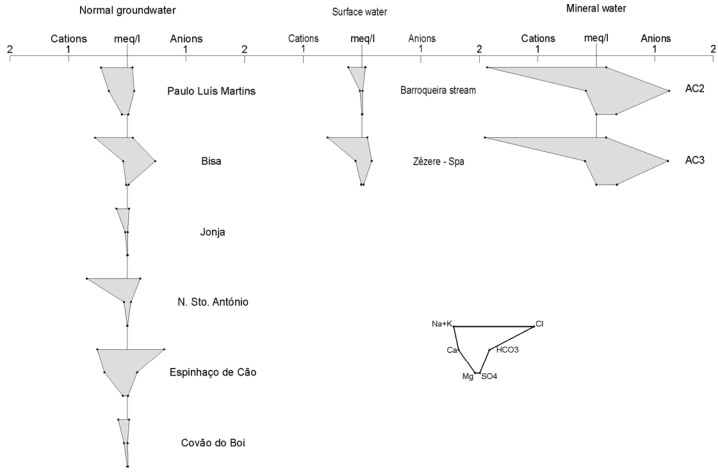

Figure 5: Representative Stiff diagrams of the studied waters. Adapted from Espinha Marques [10].

Since the isotopic content of snow pack is mainly controlled by variations in the isotopic content of individual precipitation events (Kendall and McDonnell [11]), sampling of melt water, instead of snow, is generally suggested for hydrological studies. Therefore, fieldwork campaigns at Serra da Estrela were performed in April (after the beginning of the snowmelt period) and September (the end of the summer season).

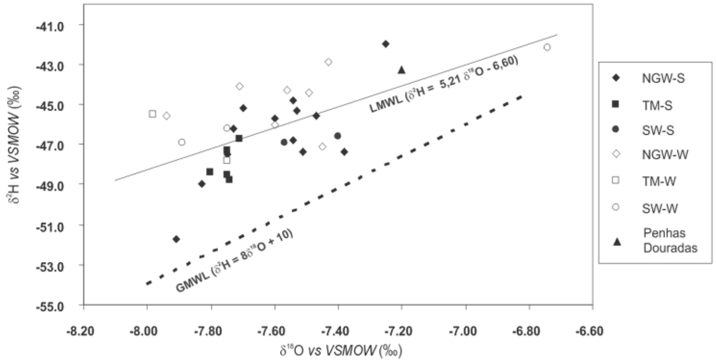

Figure 6: δ^2H *vs.* δ^{18}O diagram. LMWL - Local Meteoric Water Line; NGW - normal groundwaters; TM - mineral waters; SW - surface water; S summer; W winter; ▲ - P. Douradas precipitation. Adapted from [10].

A progressive depletion in heavy isotopes, fig. 6, ascribed to the recharge altitude of the sampling sites was observed (the Global Meteoric Water Line - GMWL - is shown as reference).

Two important isotopic signatures, fig. 6, should be highlighted: i) no influence of a lighter isotope component was detected in the groundwater samples from winter (April) campaigns, and ii) a deviation in the isotopic composition of the mineral water sample collected from borehole AC2 (winter 2004). The first signature can be explained by a high residence time leading to a mixing process between different groundwater bodies, with the tendency to the homogenisation of the isotopic composition. This process should occur mainly in the porous medium (dominated by alluvia and Quaternary glacial deposits) and the most weathered granitic rocks. In the second situation, the most reliable explanation should be attributed to an analytical error.

The recharge altitude of the hydromineral system was estimated by sampling spring waters at different altitudes. The $\delta^{18}O$ isotopic gradient was $-0.14^{o}/_{oo}/100$ m of altitude [10]. Therefore, the upper valley of Zêzere River, should be a potential catchment area of Caldas de Manteigas hydromineral system [10].

Since Nave de Santo António col (near Torre area), located at an elevation of 1540 m a.s.l., is one of the main potential recharge areas, three VES with an AB/2 spacing varying between 1 m and 200 m have been carried out in the southern part of basin. The VES soundings were inverted assuming a layered earth model and the results are presented in fig. 7. Preliminary results show that it is difficult to have a clear picture of the basin. Nevertheless, one can consider that the fill (20-40 m) is dominated by sand strata with different granulometry, and other particulate rock materials (*e.g.* blocks, etc.). The deeper part of the basin (resistivity values smaller than 2000 ohm-m) has a non-uniform topography and may consist of granite with different degrees of weathering [10].

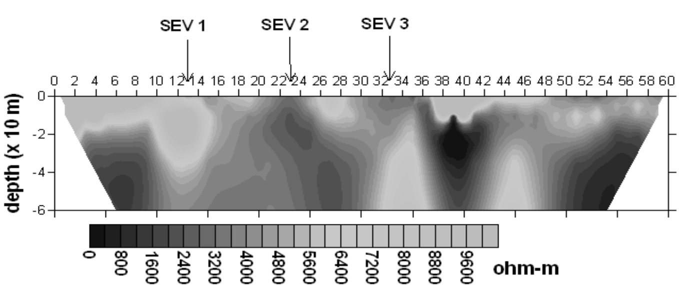

Figure 7: Apparent resistivity pseudo-section of the dipole-dipole profile. Adapted from [10].

4.2 Caldas do Moledo region

At Caldas do Moledo region, spring and borehole mineral waters emerge with temperatures between 27ºC and 45ºC. Their geochemical signatures are quite similar to those of Caldas de Manteigas Spa waters: pH values between 8.0 and 9.0, TDS values in the range of 200 to 350 mg/L, HCO_3 is the dominant anion, Na is the dominant cation, the presence of reduced species of sulphur ($HS^- \approx 2.5$ mg/L, high silica values ($\approx$ 50 mg/L), and F^- concentrations up to 10 mg/L.

These geochemical signatures indicate that in Caldas de Manteigas hydromineral system the reservoir rock should also be the granite.

All water samples lie on or close to the GMWL indicating that they have a meteoric origin, fig. 8. The Local Meteoric Water Line (LMWL) $\delta^2H = (9.28\pm0.84)\ \delta^{18}O + (20.21\pm4.20)$ was established using all the available data from local mineral and shallow groundwater systems Marques *et al* [12]. From the observation of the diagram of fig.8 one can consider that i) no oxygen-isotope shift due to water-rock interaction at high temperatures was found, and ii) the contribution of Douro River waters to the recharge of the hydromineral system should be inexistent.

The altitude dependence of the isotopic composition of Caldas do Moledo hydromineral system was determined by $\delta^{18}O$ values of springs in the Spa area and its bordering mountains. As stated by Marques *et al* [13] the isotopic gradient for $\delta^{18}O$ was -0.12°/₀₀/100 m of altitude, reflecting the influence of geographical parameters depending on the local climate and topography.

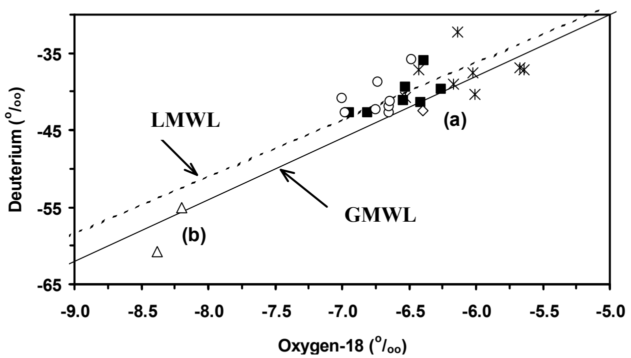

Figure 8: δ^2H vs $\delta^{18}O$ plot for water samples from Caldas do Moledo area. Taken from [12]. (○) mineral borehole waters; (■) mineral spring waters; (∗) shallow cold spring waters; (△) Douro River waters; (◊) Porto precipitation.

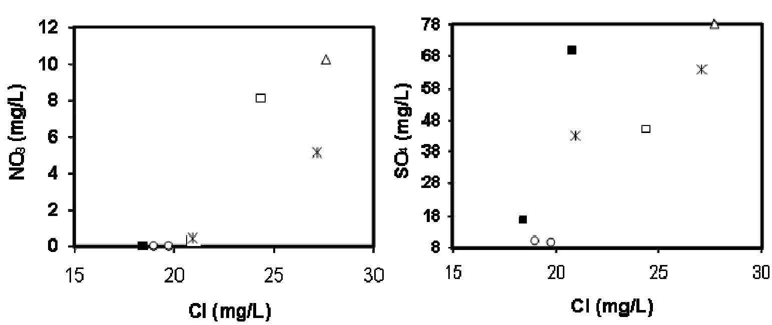

Figure 9: NO_3^- *vs.* Cl and SO_4^{2-} *vs.* Cl diagrams for water samples from Caldas do Moledo area: symbols as in fig. 8; (□) a mineral spring with distinct geochemical and isotopic signatures [14].

Espinha Marques *et al* [14] have showed a trend towards high SO_4^{2-} and NO_3^- concentrations as one passes from the hydromineral system to the shallow cold groundwaters, fig. 9. This trend supports the hypothesis of mixing between hydromineral fluids with local shallow groundwaters characterised by relatively high K^+, Ca^{2+}, NO_3^-, SO_4^{2-} and Cl^- concentrations (usual components of the most common fertilisers used in the vineyards, at the northern part of the country). Nevertheless, mineral waters from boreholes AC1 and AC2 do not show any evidence of anthropogenic contamination.

5 Conceptual models, environmental issues and outlook

Regarding Caldas de Manteigas hydromineral system, the Bragança-Vilariça-Manteigas fault zone, see fig.1, plays an important role in conducting the infiltrated meteoric waters towards the discharge zone, ascribed to the intersection of the main NNE-SSW structure with the conjugate WNW-ESE configuration, near Caldas de Manteigas Spa. The main environmental problem detected is ascribed to local use of NaCl to promote snowmelt in the roads during the winter season. In the case of Caldas do Moledo hydromineral system, the recharge area is located on the WNW-ESE Vigo-Vila Nova de Cerveira-Régua fault zone, which conducts the infiltrated meteoric waters towards the Verin-Régua-Penacova fault zone, see fig. 1, responsible for creating the mineral waters ascent. Geochemical and isotopic results point out to the existence of anthropogenic contamination of some mineral spring waters related to the intense use of fertilizers in the Portwine vineyards. This paper describes rather similar mineral waters, with analogous conceptual models but different environmental issues. The data obtained was used to define areas at higher contamination risk for further detailed multidisciplinary studies.

Acknowledgements

This study was granted by the Portuguese Foundation for Science and Technology (FCT) and FEDER EU funds, contract POCTI/CTA/44235/02.

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