

The sulphurous mineral waters of Entre-os-Rios (NW Portugal): a hydrogeochemical assessment

M.J. Afonso

Laboratory of Cartography and Applied Geology, Department of Geotechnical Engineering (DEG), School of Engineering (ISEP), Polytechnic of Porto; Centre GeoBioTec/UA, Aveiro, Portugal.

M.R. Ferreira

Laboratory of Cartography and Applied Geology, School of Engineering (ISEP), Polytechnic of Porto, Porto, Portugal.

J. Teixeira and H.I. Chaminé

Laboratory of Cartography and Applied Geology, DEG, School of Engineering (ISEP), Polytechnic of Porto; Centre GeoBioTec/UA, Aveiro, Portugal.

Keywords: Sulphurous mineral waters, Hydrogeochemistry, Entre-os-Rios thermal baths, NW Portugal.

Abstract

The hydromineral waters of Entre-os-Rios are one of the most important sulphurous waters in Portugal and their hydrochemical status revealed a good consistency through the last hundred years.

1 Introduction

The NW region of the Iberian Peninsula in general and particularly mainland Portugal are rich in hydromineral resources mostly encompassed by the alkaline sulphurous waters. In Portugal these waters are mainly localised in the so-called Ancient Massif, being related with the regional geotectonic framework. The infiltration of meteoric waters may reach great depths giving these waters special physico-chemical characteristics. These hydromineral waters frequently emerge with higher temperatures than the remaining normal groundwaters.

The main goal of this study was to evaluate the hydrogeochemical evolution of the sulphurous mineral waters of Entre-os-Rios, in order to a better understanding of the hydrogeological conceptual model of this hydromineral system.

2 Entre-os-Rios hydromineral waters: regional background

Entre-os-Rios thermal baths (formerly *Torre* thermal baths) are sited in a place called *Lugar da Torre*, in the village of Eja, municipality of Penafiel, Porto district (NW Portugal), (Figure 1). Entre-os-Rios site

is recognised in the region for the thermal spa tradition, which dates back at least to the middle of sixteenth century (e.g., Ortigão [1], Baptista [2], Amorim [3], Ferreira da Silva [4], Acciaiuoli [5]).

In Entre-os-Rios area three aquifer systems coexist, a shallow unconfined granitic aquifer and an unconfined to semi-confined granitic aquifer, both with normal groundwater, and a confined granitic aquifer, deep seated, with mineral water flow. The hydromineral resources of Entre-os-Rios are controlled by lithology (geological contact between a porphyritic coarse-grained granite and granodiorites, and also by the presence of two-mica microgranite) and tectonic constraints (fracture systems N-S to NNE-SSW and ENE-WSW, and also the regional fracture systems NW-SE and NE-SW), (Figure 1), (Medeiros et al. [6], [7], Pereira et al. [8], LABCARGA [9], Teixeira [10]).

2.1 Materials and methods

Hydrochemical data was collected, both from the old thermal springs (*Torre*, *Curveira*, *Arcos esquerda* and *Arcos direita*) and from the *Barbeitos* well. Hydrochemical analyses were assembled from the 1938-2012 period, including organoleptic characteristics (smell, colour, and turbidity), several physico-chemical properties (e.g., temperature, pH, electrical conductivity, and sulphuration), major anions and cations (e.g., bicarbonate, fluoride, sodium, and lithium) and minor elements (e.g., lead, tungsten, and boron). Also, some historical data from the end of nineteenth century to the early twentieth century were integrated.

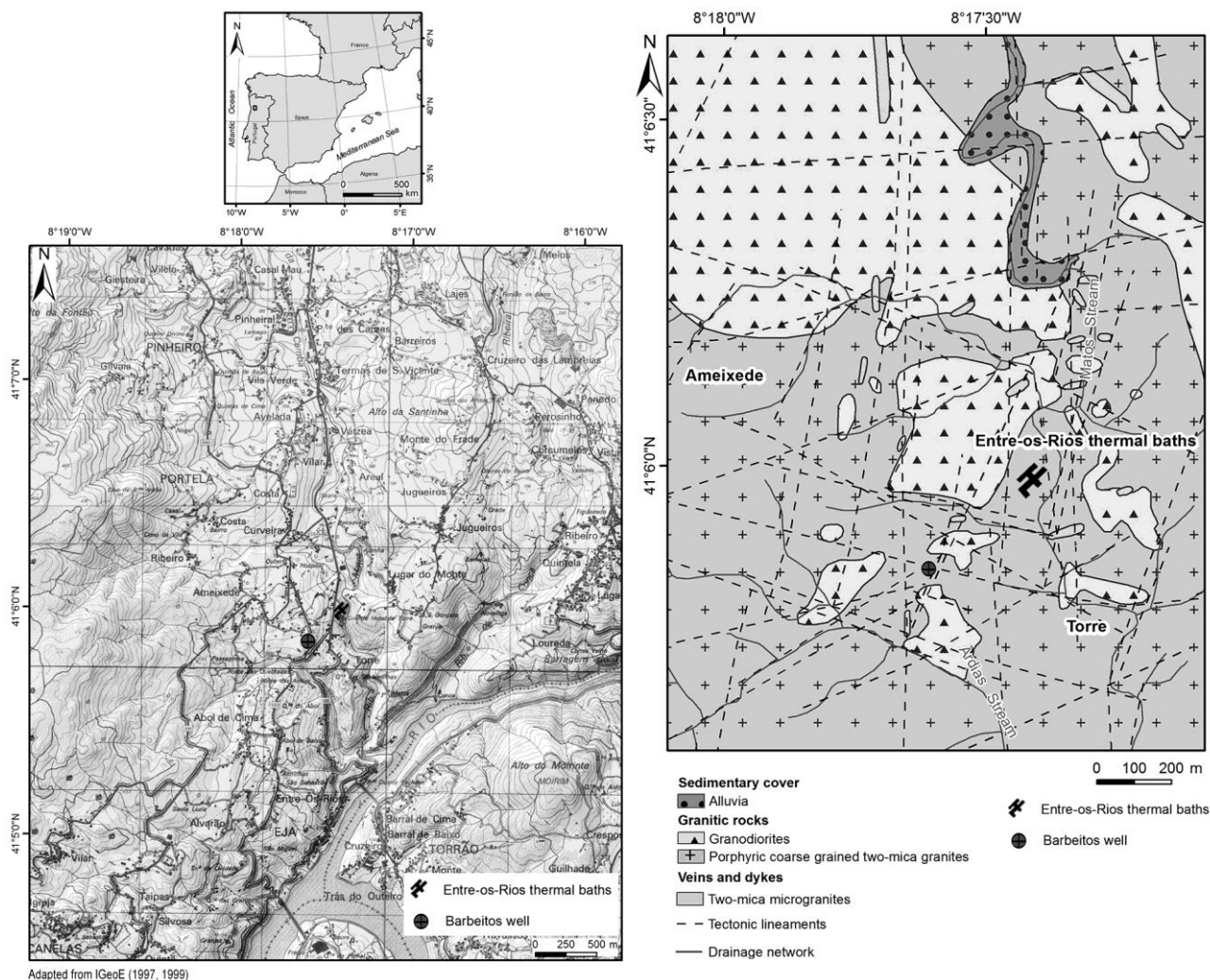


Figure 1. Entre-os-Rios thermal baths: regional geographic setting (left) and geotectonic background (right), (adapted and updated from Medeiros et al. [6], [7], Pereira et al. [8], LABCARGA [9], Teixeira [10]).

2.2 Results and discussion

The mineral waters of Entre-os-Rios are colourless, with no turbidity and have a characteristic foul odor of rotten eggs, given by hydrogen sulphide. These waters are cold, with median temperatures ranging from 17°C to 21°C, electrical conductivities ranging 550-650 $\mu\text{S}\cdot\text{cm}^{-1}$, sulphydric, carbonated and highly fluorinated (ca. 20 $\text{mg}\cdot\text{L}^{-1}$). The hydrogeochemical facies is mostly Sodium-Bicarbonate; this facies is quite different from the normal groundwater that are Sodium-Chloride-Sulfate.

In order to illustrate the hydrogeochemical evolution of these mineral waters, pH and total sulphuration were selected.

These waters are clearly alkaline (Figure 2), with similar pH in the old thermal springs (median values of 8.68, 8.59, 8.41 e 8.84) and *Barbeitos* well (median value of 8.81).

Regarding total sulphuration, the values for the old thermal springs are limited to the 1979-1990 period. Median values range from 18 to 24.9 $\text{mg}\cdot\text{L}^{-1}$ (Figure 3). These waters are recognized, since the 19th century (e.g., Ferreira da Silva [4], Machado [11]), for having one of the highest values in Portuguese sulphurous mineral waters.

All these results are in good agreement with Machado [12], [11], [13], Calado [14], Teixeira [10] and Ferreira [15].

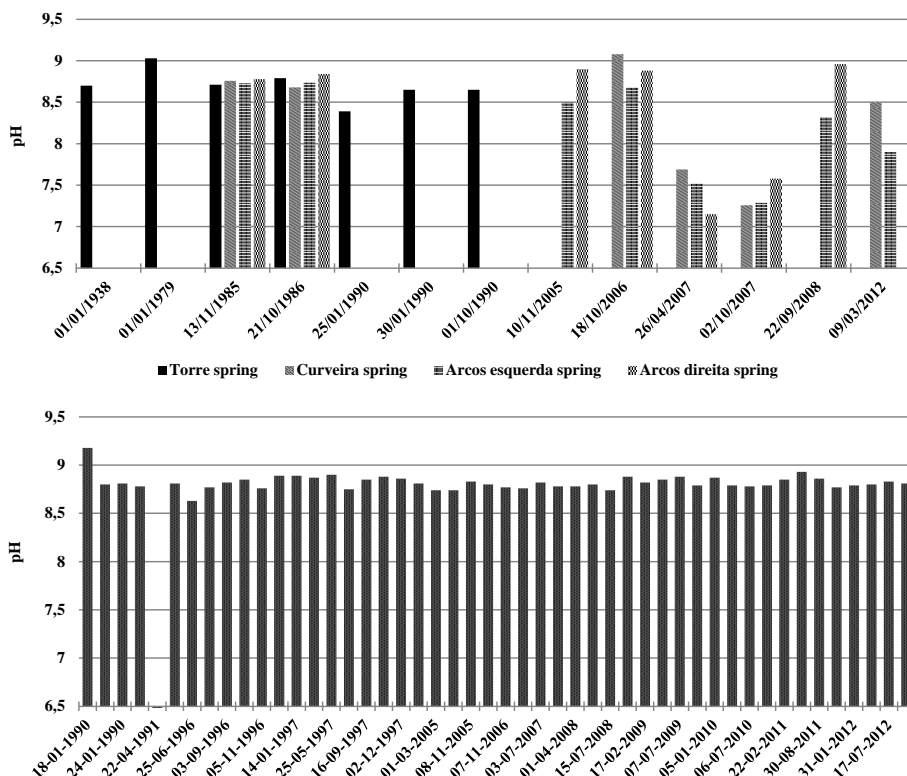


Figure 2. pH values from the old thermal springs (top) and from the *Barbeitos* well (bottom) for the period 1938 to 2012.

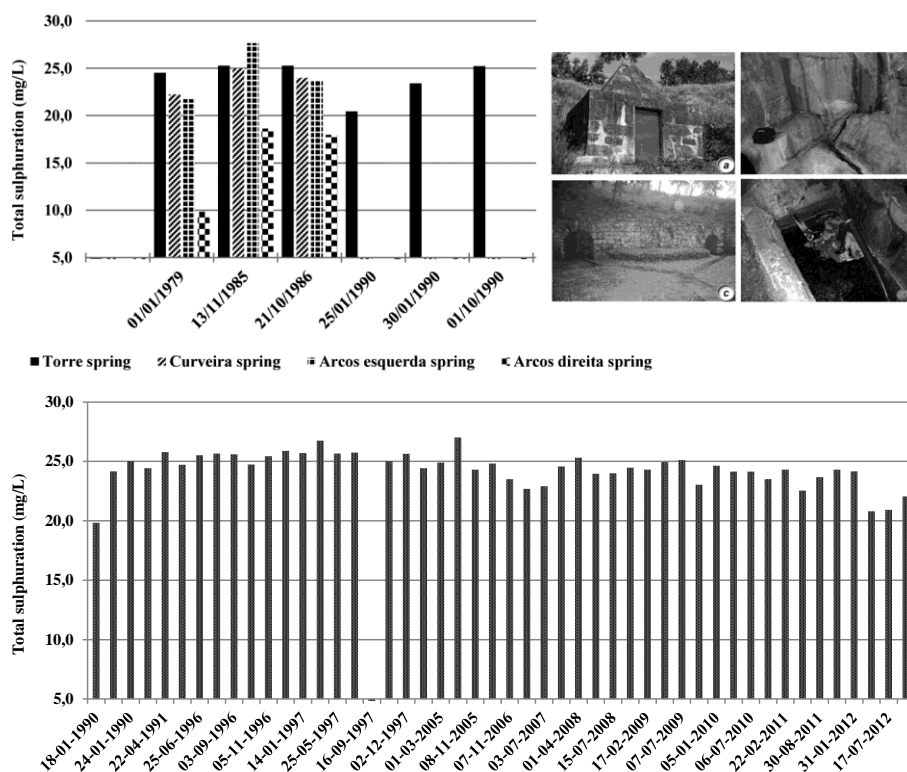


Figure 3. Total sulphuration values from the old thermal springs (top left) and from the *Barbeitos* well (bottom) for the period 1979 to 2012. Several aspects of the old thermal springs (top right): a) *Torre* spring's old building; b) *Torre* spring; c) entrances for *Arcos esquerda* and *Arcos direita* springs; d) Tank where *Curveira* spring is collected.

3 Concluding remarks

The hydromineral waters of Entre-os-Rios are controlled both by lithology and tectonic constraints.

Chemical analyses revealed that these waters have a good constancy throughout the last hundred years. They have a characteristic odor of hydrogen sulfide, a low temperature (17-21°C), a relatively low mineralisation, are clearly alkaline (8.41<pH<8.81), sulphidric, carbonated, highly fluorinated, with high concentrations of total sulphuration, and their hydrogeochemical facies is dominantly Sodium-Bicarbonate. These characteristics are definitely different from the normal groundwater of the region.

This preliminary study helped to improve our knowledge of these hydromineral systems and to refine the regional hydrogeological conceptual model.

Acknowledgments

Special thanks are due to INATEL Foundation, namely A. Vilela and M.C. Soares, for allowing the access to the archive of Entre-os-Rios thermal baths. Thanks are also due to J.M. Carvalho, M.R. Carvalho and J. M. Marques for all discussions. The present work is dedicated to the late Chemist Maria José do Canto Machado (SFM/IGM/LNEG), outstanding Hydrochemist, who assessed the almost thermomineral waters and groundwaters in Portugal.

References

- [1] Ramalho Ortigão. Banhos de Caldas e águas minerais. Livraria Universal, Magalhães & Moniz Editores, Porto, 1875.
- [2] Albino M. S. Baptista. As águas d'Entre-os-Rios e a sua Estância (Torre). Typographia a vapor da Empreza Guedes, Porto, 1912.
- [3] Henrique S. Amorim. Therapeutica Thermal (águas de Entre-os-Rios). Dissertação Inaugural apresentada á Escola Medico-Cirurgica do Porto, Typographia de A.F. Vasconcellos, Succ, Porto, 1900.
- [4] António J. Ferreira da Silva. As águas minerais de Entre-os-Rios (Estância da Torre): memória e estudo químico e bacteriológico, Typographia a vapor da Empreza Guedes, Porto, 1909.
- [5] Luiz M. C. Acciaiuoli. Le Portugal hydrominéral. Direction Générale des Mines et des Services Géologiques. 2 volumes, Lisbonne, 1952/1953.
- [6] Artur C. Medeiros, Ludgero Pilar, Amílcar P. Fernandes. Carta Geológica de Portugal, na escala 1/50000. Notícia Explicativa, Folha 13-B (Castelo de Paiva). Serviços Geológicos de Portugal, Lisboa, 1964.
- [7] Artur C. Medeiros, Eurico Pereira, Armando Moreira. Carta Geológica de Portugal, na escala 1/50000. Notícia Explicativa, Folha 9-D (Penafiel). Serviços Geológicos de Portugal, Lisboa, 1980.
- [8] Eurico Pereira, António Ribeiro, Gaspar S. Carvalho, Fernando Noronha, Narciso Ferreira, José H. Monteiro. Carta Geológica de Portugal, escala 1/200000. Folha 1. Serviços Geológicos de Portugal, Lisboa, 1989.
- [9] LABCARGA – Laboratório de Cartografia e Geologia Aplicada. Estudo geomorfológico e geológico-estrutural da concessão hidromineral HM-23 de Entre-os-Rios (Quinta da Torre) e área envolvente: implicações no desenvolvimento de recursos hídricos subterrâneos. LABCARGA|ISEP, Porto, (unpublished report), 2009.
- [10] José A. Teixeira. Hidrogeomorfologia e sustentabilidade de recursos hídricos subterrâneos. Universidade de Aveiro (PhD Thesis), 2011.
- [11] Maria José Canto Machado. O quimismo das águas sulfúreas portuguesas. Estudos, notas e trabalhos do Serviço de Fomento Mineiro, 30:37-49, 1988.
- [12] Maria José Canto Machado. Estudo químico completo das águas das várias nascentes das Termas de Entre-os-Rios. Direcção-Geral de Geologia e Minas, Laboratório, Secção de Hidroquímica, Relatório n.º11, São Mamede Infesta, 1987.
- [13] Maria José Canto Machado. Estudo físico-químico completo da água do furo de Barbeitos das Termas de Entre-os-Rios. Direcção-Geral de Geologia e Minas, Laboratório, Secção de Hidroquímica, Relatório n.º11, S. Mamede de Infesta, 1991.
- [14] Carlos M. A. Calado. A ocorrência de água sulfúrea alcalina no Maciço Hespérico: quadro hidrogeológico e quimiogénese. Universidade de Lisboa (PhD Thesis), 2001.
- [15] Maria do Rosário N. Ferreira. Evolução hidrogeoquímica das águas sulfúreas de Entre-os-Rios: avaliação preliminar. Instituto Superior de Engenharia do Porto (MSc Thesis), 2013.