New Thermal Mineral Water from Aguas (Penamacor, Central Portugal): Hydrogeochemistry and Therapeutic Indications

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Abstract. Thermal mineral waters are a potential resource in the local and economic development of a region. The thermal area of Termas das Águas is in the inner region of central Portugal and its grant will enable the exploration and exploitation of this water resource for medical and therapeutic purposes through a thermal medical SPA. In Portugal, the classification and legalization of a thermal unit must provide a natural mineral water resource, recognized by Portuguese Energy and Geology General Directorate and integrated in a concession granted by the Portuguese Government. For this purpose, it will be necessary to have available mineral water, with physico-chemical and microbiological, temporal stability, ensuring water's high quality. The purpose of a certified mineral water includes a detailed geomorphological, geological and hydrogeological characterization of the survey area, as well as the water's compositional temporal stability. Only after the recognition conferred by the national agency as a natural mineral water, it is possible to start a medical-hydrological study, for this resource. This process follows an experimental period of 3 years, during which it is implemented the different and specific balneotherapy techniques associated with the therapeutic features of the mineral water. A final report, to be submitted to Portuguese General Directorate for Health, will gather the main results and conclusions, regarding the benefits of this natural resource on human health, and allow its inclusion as an official medical thermal SPA in the Portuguese Normative Decrees. The main subject of this research is the geological and hydrogeological characterization of Termas das Águas aquifer, as well as the mineral water quality study (AM4 – well). The main topics for the medical hydrological study, mainly related to rheumatic and respiratory diseases, are also presented to the medical SPA of Termas das Águas.

1. Introduction

Mineral waters that naturally ascend to the surface of the Earth, as spring or well waters, have always been a source of curiosity for mankind throughout history. Earlier, these waters were only used at locations where the surface was reached. Later, with the development of science and technology, most of these springs have been used for medical and commercial purposes. The geochemistry of mineral waters, and the thought of an existing relationship between different water types and the geological environment, is nowadays a keen subject for science and regional economics [1].

This work aims the Águas water's geochemistry characterization to be classified as a new mineral water – Termas das Águas (Penamacor, Central Portugal). The main results allow the recognition of its therapeutic benefit, by the Portuguese Ministry of Health. The principal therapeutic proprieties are associated with rheumatic and respiratory health treatments. The thermal area of Termas das Águas (Medical SPA) was exploited for a while, some years ago. However, it is unknown the precise date for the first thermal bath facilities. There is an inscription on the granite of the resort, alluding to the year of 1856 [2]. Initially, the Termas das Águas has operated in a traditional regime and it was not legalized. Nowadays, this thermal water is licensed by the Portuguese Ministry of Economy (DGEG - Energy and Geology General Directorate) and Ministry of Health (DGS - Directorate General of Health). The thermal water license [2] comprises several research studies in different steps:

- initial hydrogeological exploration with the identification and characterization of the thermal aquifer system and delineation of its main discharge zones [3-5];
- mechanical exploration, which allowed the delimitation of the well [6];
- specific and detailed hydrogeological studies, including water composition and water quality, and its temporal stability [2].

These studies allowed the achievement of the legal authorization to the natural mineral water exploitation [7-10] and further classification as a natural geological resource, granted with a national exploitation concession [11-12].

The thermal mineral water of Termas das Águas is abstracted from a vertical well (Fonte Santa well - AM4), 328 m deep, emplaced in a slightly altered coarse-grained granitic rock. The well is tubed from 0 to 120 m with an AISI stainless 306 steel, and thence in "open hole" until the 328 m. The water flows essentially from the drainage area, between 100-119 m deep, with a flow around 0.8 L/s. Mineral water resources must have therapeutic indications to be used in the thermal area as a Medical SPA according to Portuguese legislation [13]. The water from Termas das Águas was approved as a thermal water with therapeutic characteristics to rheumatic/musculoskeletal and respiratory diseases [14].

2. Geology and geomorphology

The thermal area of Termas das Águas is in the inner region of central Portugal, at the village of Águas, about 42 km NE of Castelo Branco and 5 km south of Penamacor (Figure 1).

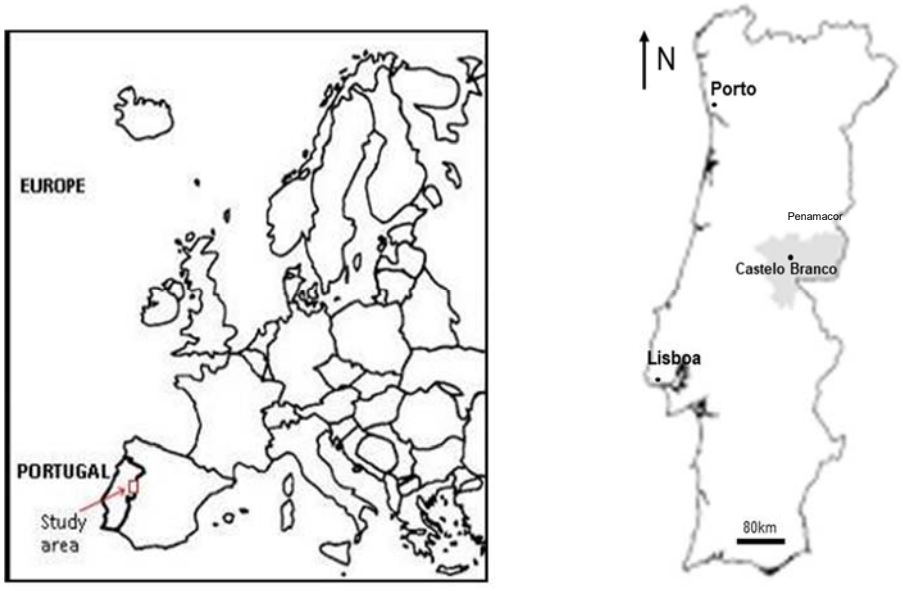

Figure 1. Location of the Termas das Águas area in the Europe and Portugal

The area belongs to the Central Iberian Zone of the Iberian Massif, near the Portuguese-Spanish border, and is in the Variscan granitic rocks from Penamacor-Monsanto pluton (area = 140 km^2), with 250-280 Ma, which intruded the Ante-Ordovician schist-metagraywacke complex (Figure 2a). NW-SE Ordovician quartzite rocks occur in the schist-metagraywacke complex and the Tertiary sediments in the south of the area [15].

The Termas das Águas area shows an elliptical shape (19km x 9km), with a NW-SE major axis. It is relatively flat with an elevation of 400 m high in the geomorphological unit called "Planura de Castelo Branco" [16]. The granitic rocks from Penamacor-Monsanto pluton are more permeable than the intruded schist-metagraywacke complex (Figure 2a). This complex is dominated by impermeable schists, where the aquifer's recharge is essentially due by the infiltration of precipitation and water in the granitic rocks. However, it should also be noted the infiltration observed from the outside to the drainage recharging reserves [9]. Near the Fonte Santa (AM4 well), the granites are covered by thin sandy-silty alluvium materials located in the stream of Ribeira das Termas; the main river through the survey area (Figure 2b).

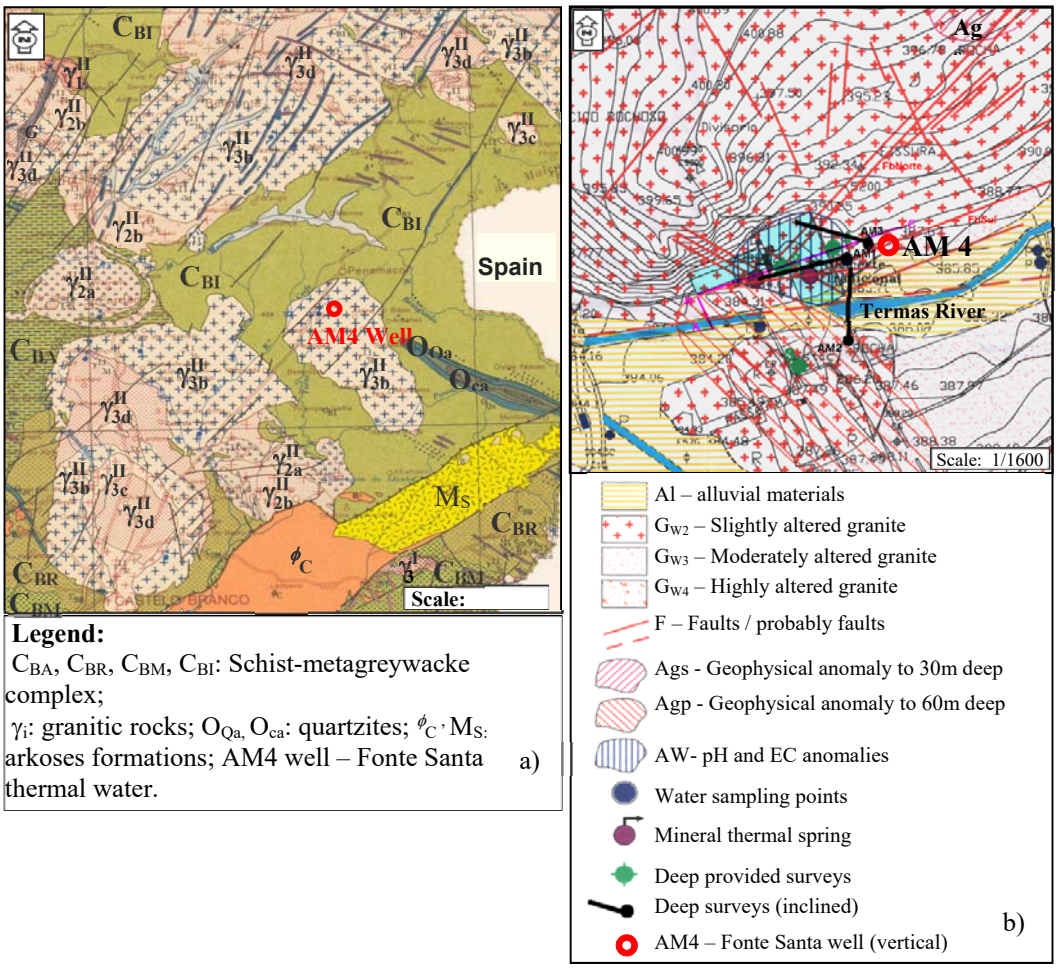

Figure 2. a) Geological setting; b) geology and tectonic from Termas das Águas area. AM4 - Fonte Santa water (adapted from [2])

There is a dominant N40ºE, vertical system of geological fractures, mostly very open, smooth and stretch over an extended region. These fractures represent recent faults that cross the granite and country

rocks. Nevertheless, there is a complex arrangement of fractures associated with semi-horizontal veins and promoting the occurrence of mineral water in restricted zones. The Penamacor-Monsanto granite pluton has modest slopes (< 10%), sometimes with very fractured and altered areas covered by a dense vegetation which enables the occurrence of anisotropic infiltration processes to the aquifer recharge.

3. Geohydrology

Penamacor-Monsanto pluton area records an annual average temperature between 13.5-15.5º C. The lowest values occur in the NW of the pluton, while the highest ones in the SE. The mean annual rainfall varies between 750-850 mm. The estimated water balance, to the Termas das Águas area, indicates the occurrence of a dry season followed by a wet period. The dry period occurs between May and October, with observed water deficits (DH), and achieving its maximum during July. Otherwise, the wet period, evidenced by water surplus (SH), occurs between November and April, with a water maximum in January. During the wet period, SH receives the contribution of runoff and groundwater flow with an overall value of 327.3 L/m^2. About 35% of this water contributes to the aquifer recharge with an estimated infiltration of 115 L/m^2 per year, allowing an annual recharge of $16x10^6$ m^3 [2].

Around the AM4 well, there are essentially granitic rocks, locally covered by a thick layer of alluvial sediments (Figure 2b). However, a complex system of fractures is associated to a sub-horizontal vein, promoting a restrict zone for water occurrence, below 20 m deep and essentially in the area between Fb_{north} and Fb_{south} faults (Figure 3). The mineralized aquifer comprises a slightly altered granitic rock (GW2; Figures 2b and 3), mainly fractured, which constitutes a confined to semi-confined fissured aquifer, with superficial runoff and infiltration groundwater recharge. The deepest aquifer's layer is around 3 m and effectively develops below the 20 m deep, with a vein structure system at the height of the aquifer [9]. The main hydraulic parameters of the mineralized aquifer were obtained experimentally as follows: k = 0.28 m/day - permeability and S = 26.6 $x10^{-4}$ - storage coefficient [2]. These parameters must be taken as a magnitude order value, since they represent an average obtained from several repetitions of the water flow test (AM3 well; Figure 3). The applied model is continuous and represents a porous medium, in a productive zone located between 20-120 m [9].

The water from Termas das Águas is sulphurous type and can be considered as an aquifer with low permeability, according to Lambe and Whitman [17]. The granitic rocks are represented by two groups: 1) slightly altered granite (GW2; Figure 3), corresponding to an unconfined aquifer in the first 20-60 m deep, generally with a lower to medium permeability increasing with fracturation; 2) moderate to highly altered granites (GW3-W4; Figure 3) represented by an aquifer, in the first 60 m deep, fissured and locally interstitial type in highest altered zones. The area concerns to an unconfined aquifer of variable permeability, ranging from low to medium, and increasing locally with fracturation. In the area, there is also an unconfined aquifer associated to the highest permeability of the alluvium formation of the Ribeira das Termas stream, which do not extend more than 3 m.

4. Water quality control

The Portuguese concession for water exploitation is based on a year of water composition control, including monthly physico-chemical and bacteriological analyzes, as well as, radiological control [11-12], to be recognized and certified by the Portuguese Ministry of Health, as a mineral medical SPA. The physico-chemical and bacteriological characteristics of Termas das Águas water - Fonte Santa well - AM4 – were determined during one year, between June 2008 and May 2009. Trace elements and radiological water contents were measured on October 2008 (Table 1 and 2). The water analyses were determined at the Laboratory of the IST (Instituto Superior Técnico, Portugal) and at the Public Health Laboratory from Castelo Branco (Portugal), according the national regulation NPEN ISO / IEC 170252005 [18].

All the water samples were colorless and translucent, without suspended material and with a hydrogen sulfide odor, as other thermal waters in Portugal. The physico-chemical parameters of the

thermal water of Termas das Águas indicate an alkaline, low mineralized water (222–324 mg/L) with substantial amounts of silica (15% of the total mineralization) (Table 1). This thermal water shows a significant geochemical stability, with a lower pH (pH range: 7.18- 8.23; Table 1) and fluoride content (F^-=2.3-3.9 mg/L) than the observed in the main Portuguese thermal waters. These features may introduce novel utilities concerning to hydrotherapy, particularly in the treatment of rheumatic and respiratory diseases.

The Piper diagram plotting outlines a classification for the mineral water as a bicarbonate-sodium type water (Figure 4). Water trace elements mostly occur below the detection limits, except for the elements B_2O_3> Mn> Cs> W> Al>Be>As_2O_3 (Table 1). Thermal water's organic compounds and radiological parameters of Termas das Águas are lower (Table 2) and below the Portuguese water's reference values, for human consumption [18]. Water's microbiological results were favorable and below the permitted values for human consumption (Table 2).

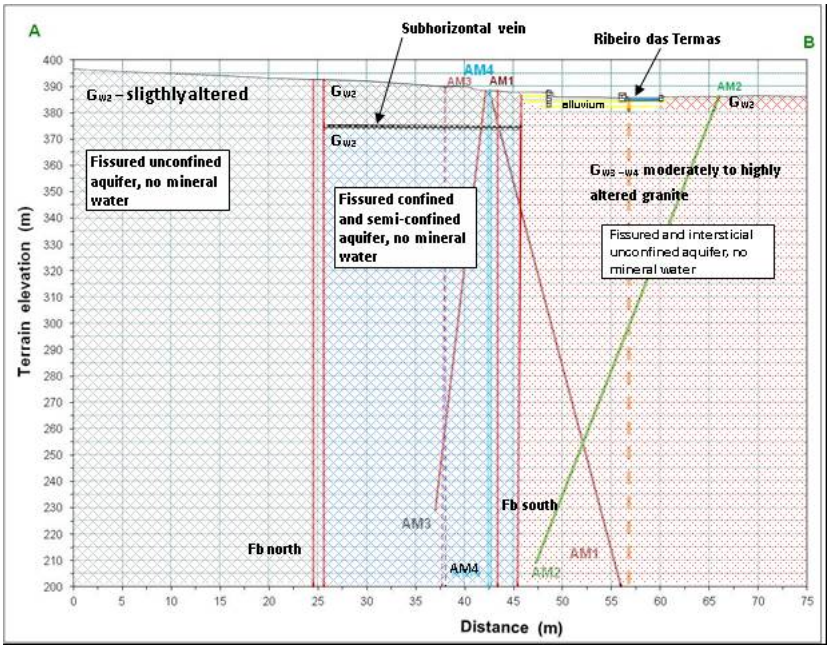

Figure 3. Local hydrogeological system from Termas das Águas area. AM1- 4 prospecting drills [2]

5. Experimental thermal bath

Considering that the Termas das Águas is a sulphurous water, which has some similarities with other Portuguese thermal medical waters, it was understood that were verified the conditions to investigate its efficacy for rheumatic and respiratory diseases.

In the old building of the thermal baths, of Termas das Águas, was installed an experimental *apparatus,* aiming the development of the needed medical-hydrological studies. The available thermal area was implemented with basic and/or complementary facilities, including: i) waiting room; ii) medical office; iii) women's and men's locker rooms; iv) balneotherapy area, with two hydromassage baths, one steam stretcher to the vertebral column and/or to the members, one jet shower and/or circular; and v) respiratory tract area, supported by a room with a nasal irrigation station and individual nebulization stations, two Sonic Aerosol stations, and one facial spray station (Figure 5).

Inside the AM4-well infrastructures are installed a pump to extract 0.7 L/s of 19º C water, and a water reservoir with 12 m^3 (Figure 5). The technical centre, including a boiler with heat exchangers and other associated systems, monitors the three implemented sulphur water's networks, at temperatures of 19º C, 42º C and 60º C) (Figure 5).

6. Medical-Hydrological studies

The medical-hydrological study was organized in the following specialities:

i) knee pain due to gonarthrosis;
ii) rhinosinusitis;
iii) lower back pain caused by lumbar spondylarthrosis.

The various studies were preceded by clinic protocols to be performed at the experimental SPA, submitted to the Technical Evaluation Committee of the Portuguese Ministry of Health (Table 1 and Table 2).

Table 1. Physico-chemical analysis from thermal water of Termas das Águas

	Oct/2008	Average	Minimum	Maximum	Standard Deviation		Oct/2008
pH [1]	7.7	7.56	7.18	8.23	0.32		
EC (µS/cm) [1]	286	266	213	310	29.5	Ag (µg/L) [2]	<2
Alkalinity ($CaCO_3$ mg/L) [1]	132	122.5	90.5	154	20.57	Al (µg/L) [2]	38
HS^- (mL I_2 0.01 N/L) [1]	11.8	8.8	4.4	13	3.1	As_2O_3 (µg/L) [2]	0.11
H_2S (mg /L) [1]	0.3	0.3	0.1	0.5	0.1	B_2O_3 (µg/L) [2]	540
CO_2 (mg/L) [2]	6.0	-	-	-	-	Ba (µg/L) [2]	<0.03
DO (mg/L) [2]	< 1	-	-	-	-	Be (µg/L) [2]	0.5
SiO_2 (mg/L) [1]	44	40	34	45	3,18	Br (µg/L) [2]	<100
Hardness (mg/L $CaCO_3$) [1]	3.1	3.5	2.4	4.8	0.77	Cd (µg/L) [2]	<1.0
Dry residue (mg/L) [1]	221	205	167	231	20.24	Co (µg/L) [2]	<2
TDS (mg/L) [1]	308	280	222	324	32.66	Cr (µg/L) [2]	<1.0
Na^+ (mg/L) [1]	71	65.3	50	77	8.02	Cs (µg/L) [2]	61
Ca^{2+} (mg/L) [1]	0.7	0.9	0.6	1.2	0.2	Cu (µg/L) [2]	<2
K^+ (mg/L) [1]	1.3	1.4	1.2	1.5	0.1	Hg (µg/L) [2]	<0.2
Mg^{2+} (mg/L) [1]	0.34	0.33	0.2	0.45	0.08	I (µg/L) [2]	< 5
NH_4^+ (mg/L) [1]	0.28	0.19	0.1	0.28	0.05	Mn (µg/L) [2]	75
Li^+ (mg/L) [1]	0.94	0.88	0.67	1.1	0.14	Mo (µg/L) [2]	<5
Fe^{2+} (mg/L) [1]	0.03	-	< 0.03	0.19	-	Ni (µg/L) [2]	<5
HCO_3^- (mg/L) [1]	160	147.2	109	183,0	24.12	Pb (µg/L) [2]	<3
CO_3^- (mg/L) [1]	< 2.0	-	< 2.0	< 2	-	Sb (µg/L) [2]	<1.0
Cl^- (mg/L) [1]	14	12	10	14	1.26	Se (µg/L) [2]	<0.4
SO_4^{2-} (mg/L) [1]	9	7.5	1.6	15	4.86	Sr (µg/L) [2]	0.01
F^- (mg/L) [1]	2.9	2.9	2.3	3.9	0.49	U (µg/L) [2]	<0.10
NO_3^- (mg/L) [1]	<0.3	-	<0.01	< 0.3	-	V (µg/L) [2]	<0.02
NO_2^- (mg/L) [1]	<0.01	-	<0.01	<1.0	-	W (µg/L) [2]	43
SH^- (mg/L) [1]	1.6	1.2	0.5	2.0	0.54	Zn (µg/L) [2]	<0.02

1. One monthly analyse from june 2008 to May 2009; 2. one analyse from October 2008. EC - Electrical Conductivity; DO - Dissolved Oxygen; TDS - Total Dissolved Solids.

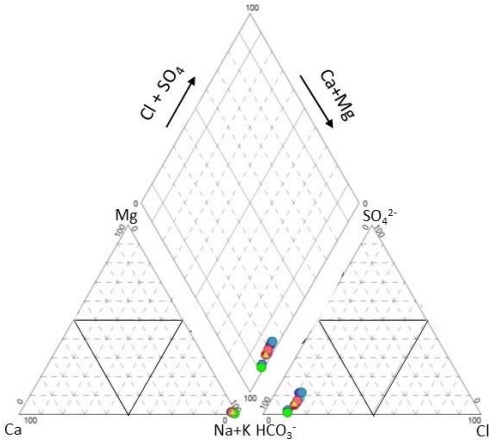

Figure 4. Piper classification of the thermal water from Termas das Águas

Table 2. Organic compounds, radiological and microbiological analyses of thermal water from Termas das Águas

Organic compounds and radiological parameters		
		AM4 - well
Organochlorines Pesticides (ng/L) [1]		< 20 ng/L
Organochlorines (ng/L) [1]		< 20 ng/L
Polynuclear Aromatic Hydrocarbons (PAH´S) [1]		< 0.005 µg/L
Radiological parameters [1]	α total	0.081 ± 0.013 Bq/L
	β total	0.134 ± 0.010 Bq/L
	Total dose	0.074 mSv/ano

Microbiological parameters		
	VP	**AM4 - well**
Total germs [2]	5 - 100	0 - 31
Total coliforms [2]	0	0
Fecal Coliforms [2]	0	0
Escherichia coli [2]	0	0
Faecal *streptococci* [2]	0	0
Clostridium [2]	0	0
Pseudomonas aeruginosa [2]	0	0

1. One monthly analyse from june 2008 to May 2009; 2. one analyse from October 2008. VP - permitted values [18]

The adopted methodologies followed the recommendations defined in the National Medical Academy, for thermal water's medical research [19]. In the different studies, specific methodologies were introduced, concerning to 14 consecutive days' treatment. For each test group, was applied a questionnaire, with the following schedule: i) the first day before the thermal treatment; ii) the last day of the thermal treatment; iii) three months after the thermal treatment; and iv) six months after the thermal treatment.

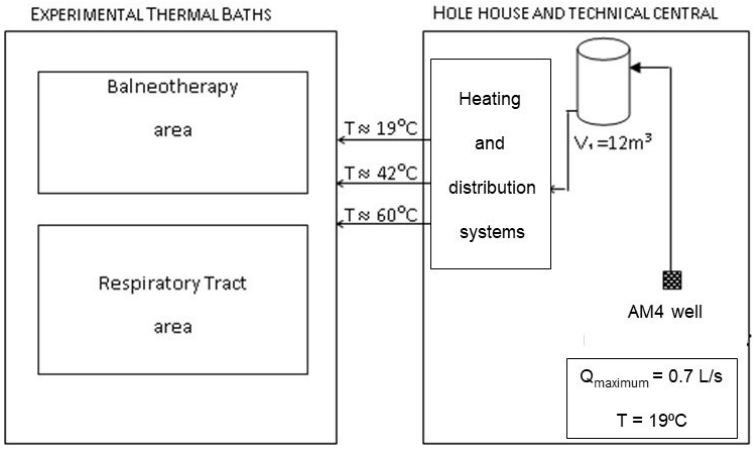

Figure 5. Schematic box representation of the water's system exploitation in the experimental medical-hydrological survey in Termas das Águas medical SPA.

The groups with knee pain due to gonarthrosis and rhinosinusitis studies for gonarthrosis and for rhinosinusitis were carried out between June and November 2012, while the group with lower back pain caused by lumbar spondylarthrosis between May and November 2014 [14]. The first group was represented by a small number of thermal bath users and was not completely conclusive. However, it

was extremely useful for future planning phases. Otherwise, the second group study indicates that a thermal treatment with sulphuric waters, namely the ones of Termas das Águas, is an effective therapeutic procedure and a possible alternative regarding to the traditional treatments.

In which concerns to the group of lower back pain caused by lumbar spondylarthrosis, the obtained results showed to be promising. The study was developed with 43 thermal users and the applied questionnaire contains the following steps:

- Socio-demographic and clinical variables,
- Pain assessment (Visual Analogue Scale-EVA),
- Medical Outcomes Study (SF36v2),
- Disability assessment (Oswestry Disability Index v2, ODIv2),
- Work absenteeism,
- Numbers of acute outbreaks/relapse,
- Needs to take medicines

During the fourteen days of thermal treatment, external administration techniques were involved [20-21] in addition to the specific physico-chemical properties of the natural mineral water, in the hydrotherapy facility. All the participants were submitted to the following treatments:

1. Hydromassage - is a therapeutic methodology which uses simultaneously the dynamic energy of the water, associated with its ideal temperature. The hydromassage is indicated to joint and muscular diseases. The treatment lasts 20 minutes with a water temperature around 38º C.
2. Jet Shower – is a hot water (T = 39º C) jet shower over the lumbar region, thrown at 5 m, for 4 minutes. This treatment is indicated for rheumatic diseases, providing anti-inflammatory, analgesic and relaxing effects. However, is contraindicated in acute attacks of low back pain.
3. Vichy shower-massage – this therapy contains five strategically positioned showers with hot water (T = 39º C) and associated massage for 15-20 minutes. It has a relaxing effect.
4. Steam into the vertebral column – is an individual steam bath (T = 42º C) with steam jets pointing directly to the musculoskeletal area, for 12 minutes. It promotes a good muscle-tendon relaxation followed by a muscular-articular analgesic effect.

The questionnaire was collected in all testing groups, during the fourteen days of the thermal treatment, after which all the SPA therapists formulated different assumptions and conclusions (Table 3).

The main conclusions show that:

- thermal bathers have reduced pain, disability and consumption of medicines;
- thermal bathers improved their “quality of life”, however did not influence the number of acute outbreaks/relapses showed by thermal bathers with Lumbar Spondylarthrosis;
- the beneficial effects occurred in a short to medium temporal scale (6 months);
- no consistent conclusions could be drawn regarding to a possible influence of the studied socio-demographic and clinical variables;
- there is a clear beneficial action on the studied pathologies;
- the treatment could be a complementary therapeutic option, effective in selected patients with Lumbar Spondylarthrosis.

7. Conclusions

The Termas das Águas medical SPA was not recognized as a certified “natural mineral water", over a long period. Nowadays, the physico-chemical water’s stability and adequate bacteriological conditions promote its classification as a natural mineral water by the Portuguese Ministry of Health and Economy.

The natural mineral water of Termas das Águas is an alkaline poorly mineralized water, slightly fluoride, and with substantial amounts of silica (about 14% of the total mineralization). The thermal water is a dominant bicarbonate-sodium type, with an average pH value of 7.56, electrical conductivity of 256 μS/cm and total mineralization of 280 mg/L. After the adaptation of the old thermal facilities,

into a small experimental bath, a medical-hydrological survey was carried out aiming the study of the thermal waters of Termas das Águas as an alternative therapeutic for rheumatic diseases (knee pain due to gonarthrosis and lower back pain caused by lumbar spondylarthrosis) and respiratory diseases (rhinosinusitis). The obtained results allowed the recognition of its therapeutic adequacy for both groups of diseases, by the Portuguese Directorate General of Health. According to this, the specific conditions were created for the construction of a new medical thermal SPA in the studied area. The new area of medical SPA from Águas (Penamacor) must be dimensioned according to the potential of the aquifer system.

Table 3. Formulated considerations and conclusions performed in the Medical SPA

	Considerations	Conclusions
1	There is a relationship between the pain intensity in patients with lower back pain caused by Lumbar Spondylarthrosis and the thermal treatment	Thermal treatment reduces the pain intensity in a short to medium temporal scale - the hypothesis is confirmed
2	There is a relation between "Life quality" in lower back pain caused by Lumbar Spondylarthrosis patients and the thermal treatment	The thermal baths benefited from an improvement in their quality of life (physical and mental), over six months – the hypothesis is confirmed
3	There is a relationship between the inability of patients with lower back pain caused by Lumbar Spondylarthrosis and the thermal treatment	The therapy was useful in reducing the patients disability, with a beneficial effect in a short to medium temporal scale - the hypothesis is confirmed
4	There is a relation between the number of days of work absenteeism and the number of acute outbreaks/relapses of patients with lower back pain caused by Lumbar Spondylarthrosis and the thermal treatment	The thermal treatment reduced work absenteeism days, but had no influence on the number of acute outbreaks/relapses - the hypothesis is partially confirmed
5	There is a relationship between the need to take medications for patients with lower back pain caused by Lumbar Spondylarthrosis and the thermal treatment	The reduction in medicine consumptions is associated with a reduction of pain and disability of the patients, within six months after treatment - the hypothesis is confirmed
6	Action mechanism	The observed effects increase in the months following the treatment (mostly 6 months after the thermal treatment). This situation could be associated with the gradual systemic release of substances accumulated in mineral waters, on the skin, and their effect over the time.
7	To evaluate possible relationships between socio-demographic and clinical factors, with the studied variables	Osteoarthrosis is more common in women
8	To investigate the relationship between active jobs and the results of thermal treatments	It was not possible to draw any conclusion relative to the thermalists professional activity and there was a significant heterogeneity

Considering the Portuguese medical SPA temporal evolution, the studied area, of Termas das Águas, show a natural aptitude to work as a "wellness thermals", orientated to tourism, ecotourism and leisure. This situation promotes the construction of hotel units, as well as catering areas, selling local products, handicrafts, animation, among many others. The study area is a small village with high local economic potential with a mineral thermal water to be used by its inhabitants and contribute to the national tourism economy.

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