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Hydrogeochemical Studies of a Groundwater with a View to its Classification as Mineral Water for a New Medical Spa in Portugal

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Abstract. Natural mineral waters are a high quality underground water resource and are becoming increasingly scarce. According to Portuguese legislation this resource is organized into two main types: bottled water and thermal waters. There are some cases where the same water due to its singularities is used in both situations. It is important to stress that groundwater to be considered a natural mineral has to comply with very demanding technical requirements and only after a considerable number of studies and procedures can it be proposed superior to the state to recognize this resource as mineral water. The present work corresponds to a recently licensed natural mineral water, with application in thermal activity, in classic thermalism and wellness thermalism, and that after its licensing it was designated "Termas de São Miguel", in the municipality of Fornos of Algodres, in the district of Guarda, in Portugal. It should also be pointed out that there was no pre-existence of thermal baths, neither from Roman times, nor from any other period. It was all done from scratch. Thus, in this paper, the main aspects that lead to the licensing of the new natural mineral water are summarized, giving greater emphasis to the hydrogeochemical studies that were absolutely central in the whole process. Thus, in a first phase the geomorphological, geological, hydrogeo-environmental and hydrogeological aspects are presented and, in the whole, led to the elaboration of the geohydraulic model of the resource. In a second phase, the elements on the stability of the quality in terms of hydrogeochemicals, the respective classifications in chemical terms, are presented in detail, and their characteristics are compared with mineral waters of other Portuguese Medial Spas. Finally, some final considerations are made on the potential applications of the water under study, and the main conclusions are presented.

1. Introduction

The first works with the intention of performing a Medical Spa in Fornos de Algodres (Figure 1) were carried out in 2010 [1], which resulted in a proposal to locate several drilling holes and hydrogeological research. Several studies were carried out, with reference to the final work titled "Hydrogeological study for direct attribution of concession as Mineral Water in Thermal Activity" [2], being the fundamental document for the Portuguese government to license the new natural mineral water, whose extract of the Exploration Agreement, was published in the Portuguese Decree of October, 2015 [3]. However, some of the main results were presented at the National Water Congress in Evora (Portugal) in 2018. It should be noted that the fundamental abstraction that serves as a basis for the exploration of the new mineral water is a vertical hole (Hole F2) of 230 meters of depth.

According to the Portuguese legislation [5], groundwater to be licensed must be a process associated with an application addressed to the Minister, with a set of documents, including an original hydrogeological study, with results of 12 physical-chemical and bacteriological analyzes, including the essential indicators proving the quality of groundwater, from samples collected from a abstraction at regular intervals of one month. At least one detailed physicochemical analysis, including the search for radioactive elements, should be included. The present paper is dedicated in essence to show the main indicators of quality and the water stability of the Hole F2 (principal groundwater abstraction).

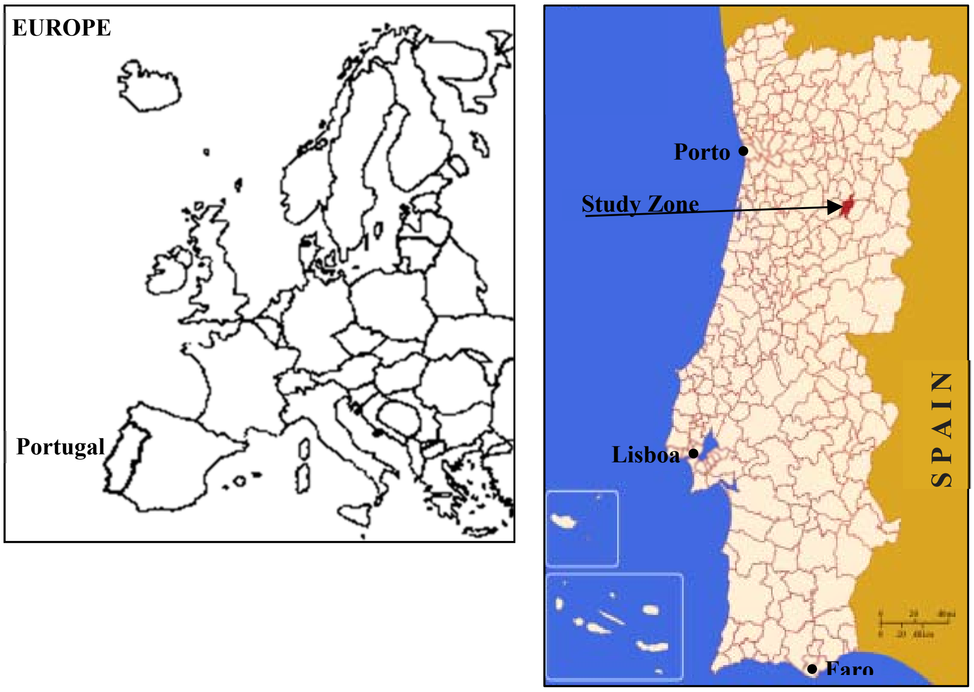

Figure 1. Location / geographical setting of the São Miguel Thermal Baths, in the municipality of Fornos de Algodres, in the Center-North region of Portugal.

2. Methodology

The F2 Hole resource was submitted to monthly physical-chemical control at the LNEG Laboratory (National Laboratory of Energy and Geology) between February 2013 and February 2014. The water for the radioactive study was collected on 12/12/2013, and analyzed in the Laboratory of ITN (Technological and Nuclear Institute). The bacteriological control of the resource was carried out in parallel with physical-chemical control and in the same period, with monthly harvests, and analyzed in the MICROCHEM Laboratory, certified by the European standards for this purpose. The techniques or methods used in the quantification of the various parameters and/or chemical elements are generally in convergence with EN ISO/IEC 17025, imposed by Portuguese law [6].

3. Geomorphology and Geology

The Hole F2 is located at an elevation of 641m approximately, in a small, very flat sub-basin, called Ribeiro das Ínfias, which is part of the Mondego River Basin. That area is a relatively mild, plateau area. The Ribeiro das Ínfias sub-basin presents an elliptical shape in plan (Figure 2), with an axis greater than 2.2 km approximately in the NE-SW direction, and with the minor axis of only about 0.43 km, discharging its surface flows directly to the Mondego River.

The geological units that occur in the area closest to the Hole F2, from the oldest to the most recent, are as follows [7]: i) Schist and Greywacke Complex (XSa), Cambrian age; (ii) Granitoids of Hercynic age: ii-a) Granite of fine to medium grain, essentially with biotite and amphibole ($\gamma'f$), ii-b) Granite of medium grain two-mica with megacrystals ($\gamma\ \pi' m_v$), ii-c) Porphiroid granite of medium grain with biotite

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(γπm); ii-d) Porphiroid granite of coarse grain with biotite, with aplite-pegmatite masses and veins(γπg); ii-e) Granite of fine to medium grain, essentially with muscovite (γap); e iii) alluvial sediments (a), Holocene.

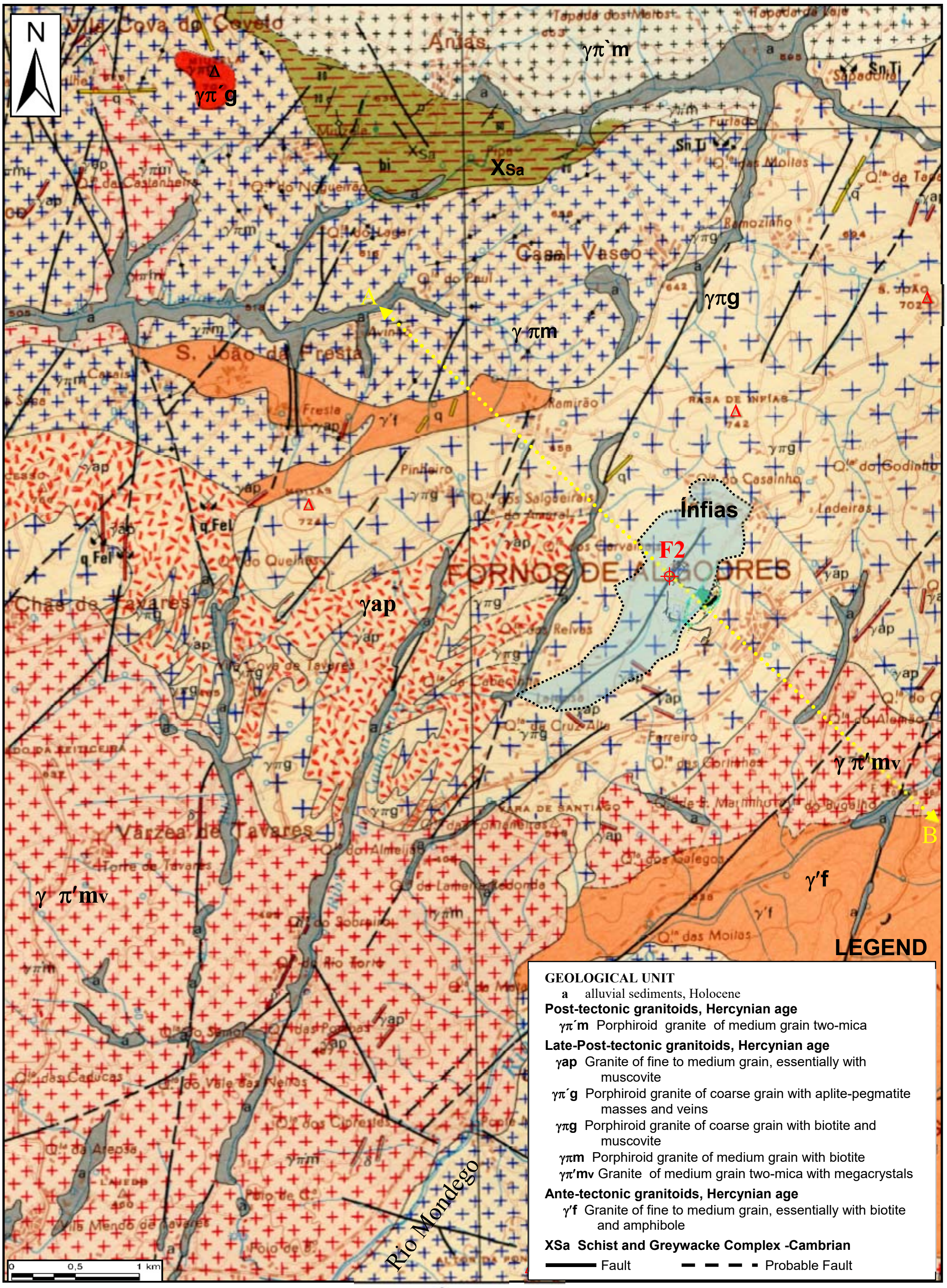

Figure 2. Geological framework of Ribeiro das Ínfias basin area, in the Geological Map of Portugal to scale 1/50000 (from Gonçalves et al., 1990 [7])

It should be noted that it is the unit γπg, constituted of porphiroid granite of coarse grain with biotite, that occurs exclusively in the Ribeiro das Ínfias basin, which is the Hole F2 basin (Figure 2). It is also worth mentioning the particularity of the occurrence of a fault practically in the central zone of the Ribeiro das Ínfias basin, being this structure that allows to relate the groundwater captured in F2 Hole with the aquifer system of depth. A geological section of the zone is shown in Figure 3, which shows the proximity of the fault with Hole F2, so that the groundwater abstracted is necessarily related to it.

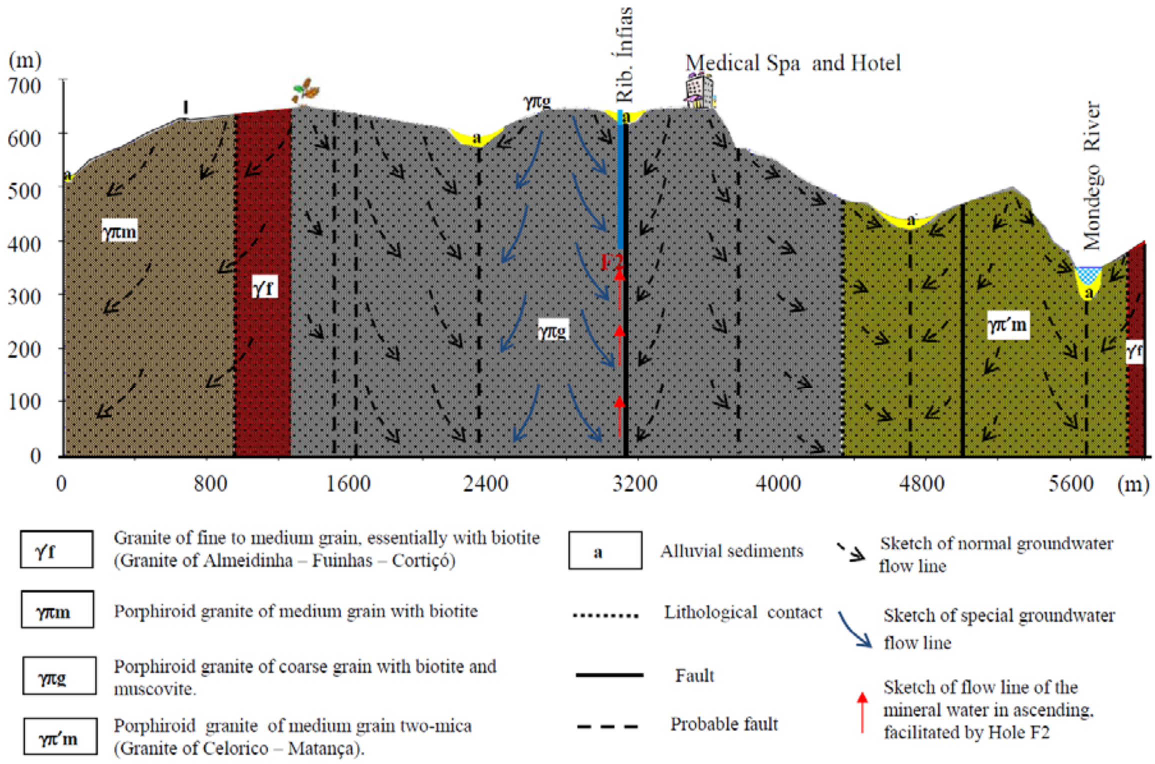

Figure 3. Hydrogeological model of the new natural mineral water captured in the Hole F2 [2]

4. Hydrogeological Aspects

Before developing the hydrogeological aspects proper, some climatological elements were studied in order to calculate the monthly sequential hydrological balance, and to have a notion about the potential deep recharges. The main results of the hydrological balance, following the methodology of Thornthwaite and Mather (1957, in [8]) are presented in Table 1.From these results the following conclusions are drawn: i) it is verified the occurrence of a dry period and a humid period; the first is translated by the water deficit (DH), which runs from June to September, while the wet period is translated by the water surplus (SH) that runs from October to May; ii) DH reaches the maximum value in August; (iii) SH reaches the maximum value in January. The total value of SH (409.2 mm) is that it contributes to the recharge of groundwater in the area under study.

In order to identify the hydrogeological situation, it was carried out with detail the survey of the main groundwater points in the basin under study and of some zones surrounding, namely for heights higher than the altitude of the Ribeiro das Ínfias basin. Twenty-six water points were recorded, consisting essentially of wells and punctually by mines, springs, fangs (small dams located on springs, in places of topographic breaks) and holes. It is emphasized that the fundamental objective was to know the type of resource of each water point, in order to clarify the hydrogeological model with the maximum of possible consistency.

Table 1. (*) Monthly sequential hydrological balance (mm) for the Fornos de Algodres region.

Parameter	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
P	123.9	100.7	90.5	73.9	67.7	36	12.8	14.4	39.8	84.8	102.5	124.1	871.1
ETP	14.21	18.82	30.88	45.17	64.05	96.11	113.90	107.19	80.97	49.68	26.29	15.06	662.3
ETR	14.21	18.82	30.88	45.17	64.05	81.18	47.68	26.46	42.46	49.68	26.29	15.06	461.9
DH	-	-	-	-	-	14.93	66.22	80.73	38.51	-	-	-	200.4
SH	109.7	81.88	59.62	28.73	3.65	-	-	-	-	0.00	16.55	109.04	409.2

P- Precipitation; ETP - potential evapotranspiration; ETR - real evapotranspiration, DH - water deficits; SH - water surplus
(*) it is assumed that the vegetation usable capacity (nu = 100mm), is complete at the beginning of the dry period (June).

The *in situ* parameters measured were, whenever possible, the following: depth / length of the capture, depth of water level, flow, pH, Eh (redox potential), conductivity, temperature and total dissolved solids (TDS). Of all the records, the results of the Hole F2, are highlighted, because this is the mineral water abstraction of the São Miguel Medical Spa, in order to serve as reference to the results of the other water points, being the following: pH = 5.70, conductivity = 83.67 µS/cm, temperature = 13.3°C, Eh = 16.3mV, and TDS = 77.0mg/L. In relation to the other water points, there is a great variety of situations, which, assuming that there is no chemical pollution, it is evident that there are several hydrogeological cells, supplied by extensive fractures, in some cases connecting several sub-basins, and the mineralogical composition of the materials crossed greatly condition the existing type of water. It is noteworthy that results were obtained in the following ranges: pH = 5.09 to 6.49; conductivity = 41 to 316 µS/cm; temperature = 10.9 to 14.4°C, Eh = -7.2 to 50.73mV, and TDS = 36.4 to 290.5 mg/L.

The Hole F2 , is the result of a vertical survey, performed to rotopercussion, in the year 2012, 230m deep. The obtained lithology's were as follows: 0 - 7 m: alluvial deposits; 7 - 22 m: granite heavily altered (W4); 22-24m: little altered granite (W3); 24 - 49m: slightly altered granite (W2), 49 - 230m granite without alteration to slightly altered (W1 / W2).

To evaluate the potential of the main water point resource, Hole F2, a flow test was performed, the results of which were presented in detail in Ferreira Gomes et al. (2018) [7]. From these results it is emphasized the establishment of the admissible flow rate (Q_{ad}), as 69 m^3/day, which in steady state only leads to lowering of the water level about 5 m in the hole itself.

In terms of hydrogeological units, for the zone of Hole F2, three hydrogeological units are considered for the site, according to the following, from top to bottom:

- Alluvial deposits; are reservoirs with permeability of the interstitial type, medium, and constitute a free-type aquifer, about 7 m thick in the groundwater abstraction area;
- Surface granitic formation; consisting of essentially porphiroid granite with biotite, with about 18 m of thickness in the zone of the groundwater abstraction; presents a permeability essentially of the interstitial type because the granite is very altered; in the groundwater abstraction area is an aquitard, that is, it constitutes a geological formation with normal groundwater and very low permeability, because it ends up confining the mineral aquifer;
- Deep granite formation; consisting of porphiroid granite of coarse grain with biotite, the depth below 22 m in the groundwater abstraction zone; has a fissural-like permeability because the granite is usually no alterated or slightly altered; in the groundwater abstraction area constitutes a confined to semi-confined aquifer with low overall permeability but punctually along some fractures of medium and sometimes higher permeability.

The hydraulic characterization of the water aquifer captured by Hole F2 was advanced by Ferreira Gomes (2014) [2] based on the results of the flow test, taking into account hydrogeological mass geometry and the characteristics of the groundwater abstraction, assuming a confined aquifer, continuous in the horizontal and equivalent to a porous medium, applying the Jacob Method (*in* [9]) in transitional regime, considering the productive zone between 30 and 48.5m, using the average of the results corresponding to the various flow rates, obtained the following parameters: hydraulic conductivity, k=5.22x10^{-6} m/s; transmissivity, T=9.70x10^{-5} m^2/s; and storage coefficient, S=3.36x10^{-3}.

5. Quality of Resource

The results of the physical-chemical analyzes are presented in detail in Table 2. They are organized in 4 groups: global parameters, anions, cations, and vestigial species. It is worth mentioning that DPR (relative standard deviation) values for the first three groups are almost always less than 10%, evidencing a very good quality stability throughout the year. In Figure 4, examples of the results of the main parameters are shown in graphic terms, where it is confirmed that there is no trend of evolution of the various parameters. This convergence of results is also visible in Figure 5, with observation of the results in the classic diagrams of Stiff and Piper, where the results end up overlapping because they are very close to the mean of the results.

In the case of the fourth group of results, vestigial species, it was not possible to obtain results with low DPR values, because its very small amount, coupled with slight natural fluctuations and associated with errors inherent to the test methodology, sometimes leads in terms large swings around the mean. Of these secondary elements, it is to emphasize their occurrence, of greater importance, according to the following: Li> Sr> As> Rb> U> Be> Mo. This knowledge has utility for the establishment of the hydrogeological model, in the defense of the quality of the resource in relation to contaminating intruder elements and in the use of the groundwater under study.

Also, in terms of the quality of the resource under study, and taking into account the levels of all chemical elements, including trace species, they are below the maximum permissible limits to ensure their potability in human consumption [10]. a situation to be highlighted in order to be able to predict the ingestion of this resource.

Analyzing the results in terms of the classification of the resource, it is possible to refer to some of the main classifications of the literature, which are natural groundwater: i) Hypothermal water, in relation to the temperature (T) considering T = 13.3ºC, which is the value at the head of Hole F2 (classification according to Herculano de Carvalho et al., 1961, *in* [11]; ii) Hyposaline water, in relation to the total mineralization (Mt), considering the average value of Mt = 77.9 mg / L obtained during the legalization period (classification according to the Institute of Hydrology of Lisbon, *in* [11]; iii) Soft water, in relation to hardness (D), considering the average value of D = 14.8 mg / L $CaCO_3$, obtained in the period of legalization (classification according to Custódio and Llamas, 2001 [9]); iv) Acid water, in relation to the pH values (pH <7,00), considering the average value of 5.89, obtained during the legalization period; v) Silicate water, considering the high percentage of silica (Si) in the non-ionized form, in relative terms with the total mineralization (Mt), which was Si/Mt = 32%, and vi) Bicarbonate-Sodium water, in relation to its as shown by the projection on the Piper diagram (Figure 5), using the mean values obtained during the legalization period.

Still from the point of view of the quality of the resource of the Hole F2, it is worth noting that the monthly control in the period of legalization, made by the MICROCHEM Laboratory, was verified as microbiologically adequate water to the classification of the resource as natural mineral water.

In order to compare the studied water with other mineral waters already consecrated in Portugal and presented in the classic catalog "Medical spas and Bottled Water in Portugal" [12], the chemical compositions of the waters belonging to the same chemical group of the studied water, are presented in Table 3. We emphasize the greater proximity of the quality of the water under study with the natural mineral water of Monfortinho, which is also classified as that of the present study by Bicarbonate-Sodium, due to the fact that its main ions are bicarbonate (HCO_3^-) and Sodium (Na^+).

Table 2. Results of physical-chemical analysis in the water of the Hole F2, during a hydrological year, in order to obtain the classification as mineral water to be used in a new medical Spa (from [2]).

Parameter		2013.2 14	2013.3 13	2013.4 10	2013.5 22	2013.6 18	2013.7 10	2013.8 28	2013.9 25	2013.11 12	2013.12. 4	2014.1 23	2014.2 19	Min	med	max	DPR (%)
pH		5.96	5.99	6.15	6.12	5.71	5.51	5.92	5.67	5.86	5.88	6.04	5.82	5.51	5.89	6.15	3
Cond. ($\mu S.cm^{-1}$)		69	70	70	70	70	72	72	70	71	70	72	72	69.00	70.67	72.0	1
Hardness - mg/L $CaCO_3$		14	14	15	13	15	16	15	15	15	15	15	15	13.00	14.75	16.0	5
Silica (mg/L)		24.7	25.3	26.1	25.6	25.7	26	23.9	24.2	24.7	24.5	23.7	25.3	23.70	24.98	26.1	3
Rs to180º(mg/L)		66.0	67.0	67.0	67.0	67.0	69.0	65.0	64.0	67.0	65.0	66.0	69.0	64.00	66.58	69.0	2
Mt (mg/L)		77.2	78.4	78.2	78.8	78.6	80.9	77.0	75.2	77.7	76.1	77.1	80.0	75.20	77.93	80.9	2
Cations (mg/L)	Na^+	9.30	9.30	8.80	9.30	9.10	9.60	9.30	9.00	9.10	9.20	9.40	9.60	8.80	9.25	9.60	2
	K^+	1.00	1.10	1.10	1.10	1.10	1.00	0.94	1.00	1.10	1.10	1.10	1.20	0.94	1.07	1.20	6
	Mg^{2+}	1.10	1.00	1.00	1.10	1.00	1.10	1.10	1.00	1.10	1.00	1.10	1.10	1.00	1.06	1.10	5
	Ca^{2+}	4.10	4.10	4.00	3.90	3.80	4.30	4.00	4.10	3.80	4.00	4.10	3.80	3.80	4.00	4.30	4
	NH_4^+	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.10	<0.10	< 0.1	< 0.1	< 0.1	-
Anions (mg/L)	F^-	0.21	0.22	0.22	0.16	0.22	0.24	0.24	0.19	0.22	0.19	0.21	0.27	0.16	0.22	0.27	12
	Cl^-	7.00	7.00	7.10	6.90	6.90	7.20	6.90	7.00	7.60	7.20	7.50	7.40	6.90	7.14	7.60	3
	HCO_3^-	23.10	23.40	23.40	23.70	23.60	24.20	23.50	22.20	22.30	22.00	22.80	22.80	22.00	23.08	24.20	3
	SO_4^{2-}	0.71	0.64	0.62	0.56	0.64	0.63	0.75	0.69	0.62	0.70	0.61	0.98	0.56	0.68	0.98	15
	$H_2PO_4^-$	0.34	0.35	0.32	0.34	0.32	0.38	0.35	0.27	0.33	0.33	0.37	0.35	0.27	0.34	0.38	8
	NO_3^-	5.60	6.00	5.70	6.10	6.10	6.20	6.00	5.70	6.90	5.80	6.40	7.10	5.60	6.13	7.10	7
	NO_2^-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-
Trace elements (mg/L)x 10^{-3}	Li	18.40	-	-	16.80	16.90	19.40	29.60	19.90	18.40	17.70	27.30	28.20	16.80	21.26	29.60	22
	Be	0.72	-	0.57	0.50	0.52	0.47	0.63	0.51	0.88	0.44	0.75	0.70	0.44	0.61	0.88	22
	B	3.90	<19.4	-	4.30	3.40	6.60	<13.4	3.60	<4.6	3.70	6.90	5.00	-	-	-	-
	Al	4.10	<16.7	14.50	13.60	4.20	9.20	7.40	3.30	4.00	3.70	20.30	5.30	-	-	-	-
	V	0.36	<2.2	<1.1	0.44	0.37	<0.49	<1	<0.59	0.34	0.33	-	0.50	-	-	-	-
	Cr	<0.16	<1.2	<2	<0.42	0.46	0.43	<5.1	<0.66	<0.89	<0.82	<0.96	<0.96	-	-	-	-
	Fe	<34.7	<79	<41.3	<8.6	<26.5	11.10	-.	<50.9	<57.4	<75.7	<46.6	<46.6	-	-	-	-
	Mn	3.10	2.40	2.80	2.60	2.30	2.80	1.90	0.90	1.20	0.42	1.60	1.20	0.42	1.94	3.10	43
	Co	0.03	<0.34	<0.71	<0.09	0.03	0.04	<0.12	<0.04	<0.05	<0.01	<0.05	<0.05	-	-	-	-
	Ni	<1.4	<21.9	<9.9	<0.98	<0.95	<0.74	<3	<0.19	<1.2	<0.59	<0.68	<0.68	<0.19	-	-	-
	Cu	<0.24	<1.3	<1.9	<0.4	0.06	<0.17	<0.49	<0.41	<0.46	<0.06	<0.29	<0.29	<0.06	-	-	-
	Zn	0.45	<2.5	<2.4	<1.6	<3.1	<0.77	0.73	<1.8	1.30	0.92	1.10	0.97	<0.77	-	-	-
	As	6.40	5.80	6.20	5.80	6.80	7.20	9.30	5.80	6.60	5.80	8.30	8.60	5.80	6.88	9.30	17
	Se	<1.5	<3	<3	<1.1	<0.4	<0.52	<1.8	<16.9	<0.9	<0.6	<0.87	<0.87	<0.4	-	-	-
	Rb	5.60	4.80	5.80	5.00	5.90	5.30	6.40	5.50	5.80	5.60	7.60	8.00	4.80	5.94	8.00	16
	Sr	15.90	14.30	17.10	13.70	15.20	17.90	19.40	16.50	19.10	16.40	24.80	26.00	13.70	18.03	26.00	20
	Y	<0.02	<0.06	0.01	0.01	0.01	0.03	0.01	<0.01	0.01	<0.01	<0.05	<0.05	<0.01	-	-	-
	Zr	<0.23	<0.16	<0.16	0.32	<0.08	<0.17	<0.41	<0.06	<0.08	<0.1	<0.17	<0.17	<0.06	-	-	-
	Nb	<0.02	<0.01	<0.01	<0.01	<0.01	<0.03	<0.04	<0.01	<0.01	<0.01	<0.02	<0.02	<0.01	-	-	-
	Mo	0.24	0.22	0.27	0.25	0.26	0.26	0.34	-	0.21	-	0.32	0.29	0.21	0.27	0.34	15
	Ag	<0.16	<1.2	<0.24	0.04	<0.1	<0.04	<0.27	<0.12	<0.03	<0.02	<0.03	<0.03	<0.03	-	-	-
	Cd	<0.03	0.95	<0.08	<0.02	<0.01	<0.07	<0.13	<0.14	<0.01	0.13	0.02	0.03	<0.01	-	-	-
	Sn	<0.02	<0.03	<0.03	<0.01	<0.1	<0.03	<0.02	0.01	<0.27	<0.04	<0.07	<0.07	<0.01	-	-	-
	Sb	<0.04	<0.04	<0.04	<0.05	<0.06	<0.06	<0.24	<0.16	<0.03	<0.04	0.14	<0.03	<0.03	-	-	-
	Cs	0.53	<1.1	<1.1	0.74	0.60	0.53	<6.1	0.57	0.72	2.20	1.80	0.83	<1.1	-	-	-
	Ba	0.78	0.95	1.00	1.40	0.80	0.78	0.60	0.94	0.93	<1.0	4.10	1.10	<1.0	-	-	-
	Te	<0.06	<0.05	<0.05	<0.05	<0.04	<0.02	<0.09	0.02	<0.02	<0.03	<0.03	<0.03	--	-	-	-
	W	<0.07	<1	<0.38	<0.08	<0.05	<0.12	<4.3	0.08	<0.9	<0.12	0.07	0.06	<0.05	-	-	-
	Hg	<0.07	<0.1	<0.1	<0.06	<0.04	<0.05	<0.51	<0.02	<0.07	<0.06	0.08	<0.02	<0.02	-	-	-
	Pb	<0.17	<0.05	<0.87	0.03	<0.04	<0.16	<0.1	0.04	<0.03	0.12	<0.04	<0.04	<0.03	-	-	-
	Bi	<0.03	<0.08	<0.09	<0.01	<0.01	<0.02	<0.24	<0.02	<0.02	<0.01	<0.01	<0.01	<0.01	-	-	-
	U	1.70	1.60	1.70	1.60	1.80	2.10	2.50	1.80	2.00	1.60	2.40	2.60	1.60	1.95	2.60	18

Rs - dry residue, Mt - total mineralization, min – minimum, med –medium, max – maximum, DPR = (standard deviation / medium)x100.

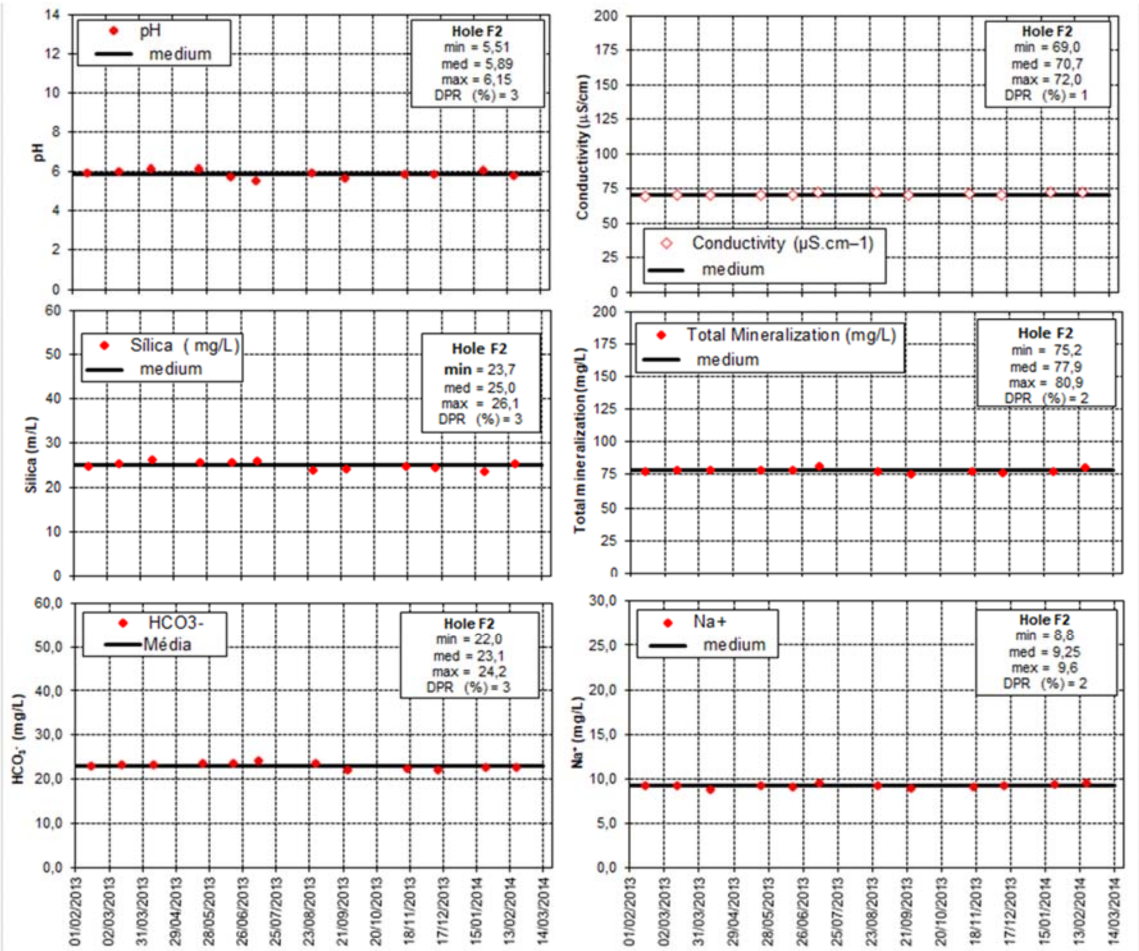

Figure 4. Results of main physico-chemical parameters when measuring the stability of the quality of the resource of the Hole F2 for its licensing as natural mineral water.

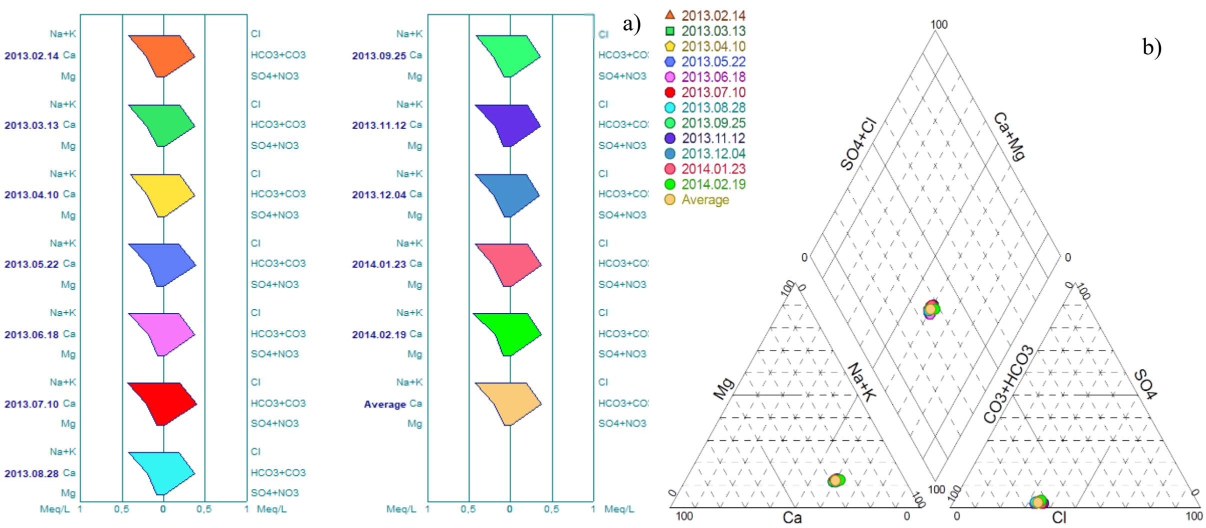

Figure 5. Results in graphical terms (a-Stiff diagrams, b) Piper diagram) of the main physical-chemical parameters when assessing the stability of the quality of the resource of the Hole F2 for its licensing as natural mineral water.

Table 3. Comparison of the main chemical composition of the studied water with the chemical composition of the Portuguese mineral waters that belong to the same chemical group: Hyposaline and Silicate waters.

Parameter		Hole F2- Present study	Luso [12]	Monfortinho [12]	Ladeira de Envendos [12]
pH		5.89	5.40	5.70	4.70
Conductivity (µS/cm)		70.7	50.5	36.0	38.0
Hardness - mg/L $CaCO_3$		14.8	7.4	8.8	4.2
Silica (mg/L)		25.0	10.9	18	10.1
Dry residue to 180º - Rs (mg/L)		66.6	37.0	40.0	25.8
Total mineralization -Mt (mg/L)		77.9	40.2	48.7	26.2
Cations (mg/L)	Na^+	**9.3**	**6.4**	**4.6**	**3.9**
	K^+	1.1	0.7	1.0	0.4
	Mg^{2+}	1.06	1.30	1.30	0.60
	Ca^{2+}	4.0	0.9	1.4	0.6
	NH_4^+	< 0.1	<0.1	<0.1	<0.1
Anions (mg/L)	F^-	0.22	< l.d.	0.03	<ld
	Cl^-	7.1	**9.2**	4.6	**6.5**
	HCO_3^-	**23.1**	7.9	**15.2**	1.2
	SO_4^{2-}	0.68	1.80	0.60	2.60
	$H_2PO_4^-$	0.338	0.058	0.090	0.027
	NO_3^-	6.13	1.14	1.86	0.34
	NO_2^-	< 0.01	< 0.01	< 0.01	< 0.01
(Silica/Mt)*100		32	27	37	39

l.d. – detection limit

6.Application Applications

About water applications of the Hole F2, the fact that the quality of the studied groundwater to be very close to the quality of other already classified waters and with very well defined applications, allows to have a notion of potential applications. In this sense, the official uses and respective therapeutic indications of the Portuguese waters that are in the same chemical group of the water studied in Table 4 are presented.

Table 4. Use and therapeutic indications of Portuguese natural mineral waters classified in the same group as the water in study (Hyposaline and Silicate).

	Hole F2 -Fornos de Algodres	Luso [12]	Monfortinho [12]	Ladeira de Envendos [12]
Use	-	Balneotherapy, Ingestion, Bottling	Balneotherapy, Ingestion	Balneotherapy, Ingestion, Bottling
Therapeutic indication	-	Circulatory system, Respiratory system, Nephro-urinary, Rheumatic and Musculoskeletal Diseases	Digestive system, Skin diseases	Digestive system, Skin diseases, Rheumatic and Musculoskeletal Diseases

In the following, in a space as a experimental medical spa, equipped with techniques suitable for a set of thermal applications (bathtubs, Vichy shower, jet shower, steam springs to the column, sauna, Turkish bath, dynamic swimming pool, aerosols, nasal irrigators in spraying and nebulization, among others) an investigation was carried out in the field of Medical Hydrology [13], culminating in the legalization of the thermal mineral water of the Spa of S. Miguel, in diseases of the rheumatic and muscular- skeletal and respiratory system [14].

7. Conclusion

It is emphasized that a set of hydrogeological and related studies carried out in a very detailed way in an area with potential, after providing a quality groundwater abstraction, may lead to the society making available a new resource, the natural mineral water, and from this result the various advantages, in the economic field, public health, tourism and social, with the birth of a new Medical Spa.

It is also emphasized that Portugal is currently in a phase where there are medical-hydrological studies, with the responsibility of a medical researcher, but in perfect harmony with a professional in the area of geosciences. This "attitude" is going to give scientific credibility to the thermalism, with the emergence of new medical spa and resorts with the use of mineral water, where there are always two responsible: one in the area of geosciences whose main mission is to explore the natural mineral water, with the strict maintenance of their quality, the other is a doctor whose primary mission is to ensure that users have an adequate use of the resource.

Thus, Portugal offers a new Medical Spa, the Spa of São Miguel, which uses thermal mineral water of the type Hyposaline and Silicate, captured in a Vertical Hole, from an aquifer system of granite rocks, confined type and with permeability of the fissural type.

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