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## Good Practices of Quality Control in the Area Surrounding of Natural Mineral Water Abstraction of São Pedro Do Sul Medical Spa (Portugal)

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# Good Practices of Quality Control in the Area Surrounding of Natural Mineral Water Abstraction of São Pedro Do Sul Medical Spa (Portugal)

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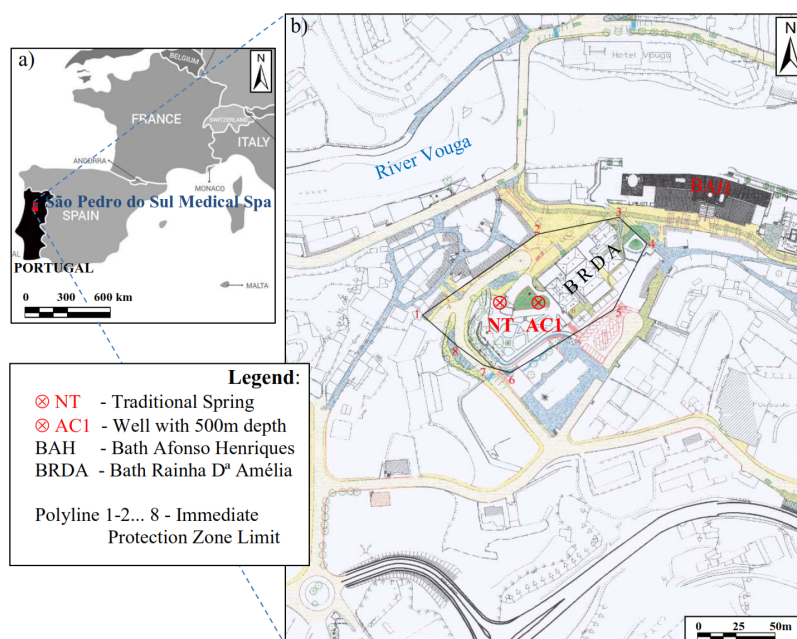
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**Abstract.** São Pedro do Sul medical spa is a space with a millenary tradition in providing health services from the natural hot groundwater. The main source of supply of this thermal unit, was along the time, the Traditional Spring, which in the last decades has been controlled, and shows to have constancy in the flow rate, with about 10 L/s, with a temperature of 68.6°C in the origin. From 1999 onwards, with the construction of new abstraction, Well AC1, with 500m deep, with a maximum flow rate of 12.2 L/s, at 67°C, the exploitation potential of this resource increased. Due to the fabulous characteristics of the resource's potential (hot natural mineral water), there has been over time a great development in the spa medical activity, having already frequented these spa 25450 users per year, reflecting a maximum annual turnover of 5.4 million euros, coming from thermalism alone. Currently, there are two Bathhouses in operation and the resource is used, not only for therapeutic and wellness thermalism but also for geothermal uses and yet in the cosmetic area. This situation becomes the perfect scenario for attracting investment, increasing the circulation of people and goods, but also in the interest of building new bathhouses, hotels and restaurants and subsequently new roads, gardens, public drinking water and sanitation networks. All this pressure causes a lot of potential damage to the environment, including the underground water environment, and could eventually lead to the closure of the medical spa, if the natural mineral water from the abstractions become contaminated. In Portugal, there are several legally imposed defensive mechanisms of the mineral aquifer system, namely the implementation of the Protection Perimeter, but also the analytical control of the natural mineral water, at the abstraction head, both in chemical and microbiological terms, in addition to the orientation to have an automatic, on-line, record system associated to the abstractions, monitoring parameters such as: water level, flow rate, temperature, pH and conductivity of the water captured. However, the São Pedro do Sul medical spa go further, implementing an external monitoring system, consisting of: i) double piezometers (to sample groundwater at different depths), ii) street rainwater samplers, and iii) records precipitation and respective quality. Thus, in this paper, after a brief presentation of the importance of the resource and the physical aspects of the place (geology, hydrogeology and quality of the resource), the fundamental elements of the implemented external monitoring system and its main results are presented, showing that precipitation itself is already contaminated, that street rainwater sample presents chemical elements that are highly harmful to public health, and that groundwater sometimes presents very worrying results. Finally, some actions are mentioned that have been implemented to minimize the potential for contamination of natural mineral water from abstractions and the mineral aquifer system.



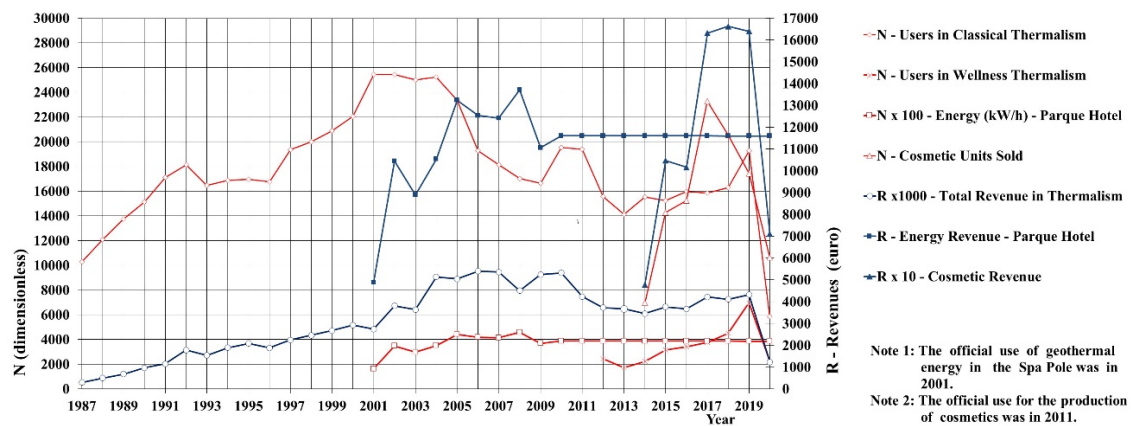
## 1. Introduction

São Pedro do Sul Medical Spa (SPS medical spa), in Portugal (Fig.1), is at the top at the national ranking, with regard to direct revenues from its resource, which comes essentially from the frequency of users in the therapeutic spa, which are in the spa for about 15 consecutive days, leveraging the local economy, in the area of hotels, restaurants and tourism. The increase, whether in tourist/clients flows or in animation activities available for their entertainment has a huge impact on the environment and consequently, jeopardizing the resource quality (hot natural mineral water). The potential resource contamination increases, additionally, with new buildings constructions, car parks, aqua-play spaces, among others, in the vicinity of natural mineral water abstractions, if their construction does not follow strict rules, so that they do not conflict with the natural mineral water geohydraulic circuits. Thus, "External Monitoring" implementation brings a greater knowledge from several environmental components, and being unprecedented in Portugal, on the Thermalism sector, it is considered essential to explain its components and characteristics, in addition to the main results obtained, so that these good practices can be disseminated, discussed, improved and extended to other medical spas around the world.



**Figure 1.** Geographical framework of SPS medical spa (a), and its natural mineral water abstractions (Traditional Spring and Well AC1), its Thermal Bath buildings currently in operation, and Immediate Protection Zone (b).

SPS medical spa users' evolution over time, respective revenues, as well as other more recent applications, such as the energy supplied to the "Hotel do Parque", and the production of cosmetic products, have already been addressed in other papers [1,2,3], however it is considered important to show its updates in Figure 2. The values obtained in 2020 stand out, on the negative side, since they were attached with the COVID-19 phenomenon, which led to the closure of the Medical Spa, throughout almost every year. Positively, however, in the sense of highlighting the resource's potential, it stands out, the 2006 revenues, obtained only from the therapeutic thermalism, which totaled 5.6 million euros; the cost of energy sold to the "Hotel do Parque", which in 2008 reached a maximum of 13700 euros, and also, the value obtained through the most recent resource application (cosmetics production) which reached, in 2018, the impressive amount of 166200 euros. It is noteworthy the fact that the use of geothermal energy, which currently supplies energy for heating the interior space, and heating of sanitary water, of 2 hotels and the 2 Spa Bathhouses [4,5,6], is being expanded to heat another 12 buildings, using the Traditional Spring and Well AC1.



**Figure 2.** Evolution of the main applications of hot natural mineral water, and respective revenues of the São Pedro do Sul Medical Spa.

## 2. Geological and hydrogeological aspects of the São Pedro do Sul Medical Spa area

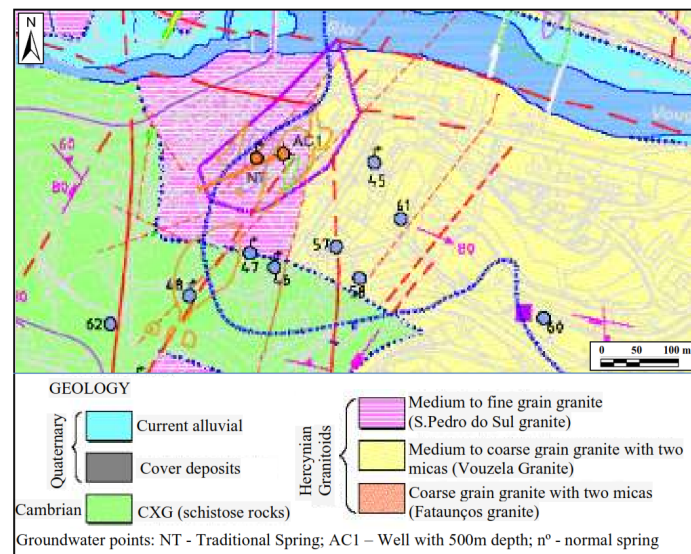
The geological aspects of São Pedro do Sul Thermal Spa region have already been documented in several works [2,7,8,9], however, for this paper it is important to present a notion of the local geology from the nearest surroundings to the Medical Spa, where “External Monitoring” was implemented. The local geological map (Fig.3) distinguishes the granitic terrains where the motorization systems were installed, and in particular those where the piezometers were installed, which belong to the geological unit “São Pedro do Sul Granite”, constituting medium-grain granites to thin, generically very altered. This is the same geological unit, where the natural mineral abstractions arise (NT and Well AC1). It is also important to point out that, in this area, there are several geological faults, constituting, as a whole, a zone of high shear, occurring only locally in the NT site, unaltered granite, and in the generality surrounding area, the granite is completely decomposed.

Regarding hydrogeological aspects, it is mentioned that natural mineral water comes from a confined, very deep, fissural-type aquifer system, and ends up naturally re-emerging on the surface, due to the combination of several fractures, some very extensive on the surface and deep; local artesianism is favored due to the fact that the recharge is at relatively high levels, favored by the fact that the water in depth acquires a temperature above 100°C [10,11]. In hydraulic terms, the mineral aquifer system, by behaving as a confined aquifer, in which the piezometric surface is much higher than the water table, and above the topographic surface (Fig.4), naturally leads to a reduction on the contamination problems, since eventual contaminated surface infiltration, when reaching the saturated zone, tend not to advance in depth. A problematic situation can occur when top priority is given to mineral water production from AC1 well, because the piezometric surface drops a lot, and, in continuous, and in the long term, it facilitates the descent of contaminants in depth. This situation would be aggravated if pumping were carried out in the well itself. It is precisely for this reason that AC1 well is used only in artesianism, and with a flow rate of less than about 7 L/s, to minimize the potential for local contamination. It should be noted that, when AC1 well debits a flow rate greater than 7 L/s, there is a notorious interference with NT flow [2], and therefore the resource exploitation is oriented giving priority to the NT flow, with an approximate flow rate of 10L/s, and the remaining from well AC1, in order to allow a total flow rate lower than 17 L/s.

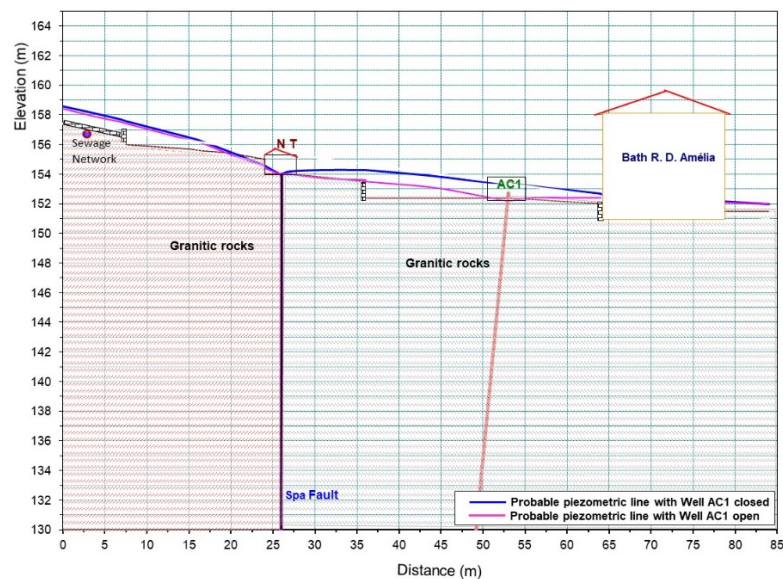
## 3. Resource Quality (Natural Mineral Water)

SPS medical spa natural resource, in chemical terms, has been subject of intense and rigorous research, due to its importance in Portuguese thermalism context, namely the water from the Traditional Spring. Some of these results, from punctual analysis (from 1903, 1928, 1985, 1989, 1994 and 1998) were presented by Ferreira Gomes et al in 2001 [8].





**Figure 3.** Geological map of the area of the natural mineral water discharge of SPS Medical Spa.



**Figure 4.** Sketch of the piezometric surface of the confined, fissural and very deep aquifer system at SPS medical spa.

Other study, based on more recent chemical analyses, were carried out by Almeida et al [12], with analysis between 2005 and 2013, in a total of 40 samples for NT water, for 9 consecutive years. The results allowed to confirm the spectacular chemical stability of this resource, whose water is classified as sulphureous, sodium-bicarbonate, fluoridated and alkaline. However, in a specific internal work, when reflecting about the results obtained from the external monitoring, object of this paper, a more thorough study [13] was developed with all available results since 1985, as they are generally considered to be carried out with methodologies similar to those currently standardized, until 2014. These analyses were carried out by the laboratories of the IST (Lisbon) and the LNEG (São Mamede de Infesta). The results were evaluated individually, parameter by parameter, in order to analyze any trends over time, perform basic statistics, and detect any anomalous points; Tables 1 and 2 present the statistical elements of all results, and Figure 5 presents some graphs as an example.

**Table 1.** Statistics of the results of physical-chemical analyses, in terms of main parameters, of the water collected in the Traditional Spring, between 1985 and 2014 [13].

Parameter	Number of samples - N	Minimum	Average	Maximum	Standard Deviation - DP	DP <sub>Relative</sub> DPR- %	
<b>pH</b>	96	8.33	8.82	8.95	0.08	1	
<b>Conductivity - <math>\mu\text{S}/\text{cm}</math></b>	96	351.00	405.08	485.00	26.14	6	
<b>Total Sulphuration (in <math>\text{I}_2</math> 0.01N) - mL/L</b>	96	16.00	21.30	34.00	3.70	19	
<b>Total Alkalinity (in HCl 0.1N)-mL/L</b>	94	22.00	23.68	25.00	0.70	3	
<b>Total Hardness (in p.p.10<sup>5</sup> de <math>\text{CaCO}_3</math> - °f)</b>	96	0.65	0.77	1.10	0.06	8	
<b>Total CO<sub>2</sub> - mmol / L)</b>	80	1.81	2.06	2.50	0.09	4	
<b>Silica (<math>\text{SiO}_2</math>) - mg/L</b>	96	60.90	67.94	78.50	3.61	5	
<b>Dry Residue (at 180°C) - mg/L</b>	95	291.30	304.77	326.00	6.27	2	
<b>Total Mineralization - mg /L</b>	96	333.00	359.68	385.00	8.68	2	
<b>Cations (mg/L)</b>	<b>Sodium (<math>\text{Na}^+</math>)</b>	96	85.40	90.19	96.00	1.93	2
	<b>Calcium (<math>\text{Ca}^{2+}</math>)</b>	96	1.60	2.99	4.40	0.30	10
	<b>Potassium (<math>\text{K}^+</math>)</b>	93	2.90	3.30	3.70	0.16	5
	<b>Magnesium (<math>\text{Mg}^{2+}</math>)</b>	55	< 0.03	-	< 1.0	-	-
	<b>Lithium (<math>\text{Li}^+</math>)</b>	93	0.47	0.59	0.70	0.04	7
	<b>Ammonium (<math>\text{NH}_4^+</math>)</b>	96	0.16	0.33	0.47	0.04	13
	<b>Iron (<math>\text{Fe}^{2+}</math>)</b>	21	< 0.075	-	0,100	-	-
<b>Anions (mg/L)</b>	<b>Bicarbonate (<math>\text{HCO}_3^-</math>)</b>	96	101.90	119.48	133.00	5.48	5
	<b>Chloride (<math>\text{Cl}^-</math>)</b>	96	25.10	27.89	37.00	1.53	5
	<b>Sulphate (<math>\text{SO}_4^{2-}</math>)</b>	94	7.80	10.12	13.00	0.95	9
	<b>Fluoride (<math>\text{F}^-</math>)</b>	96	15.20	17.71	19.00	0.56	3
	<b>Carbonate (<math>\text{CO}_3^{2-}</math>)</b>	96	3.00	4.69	9.50	1.10	23
	<b>Nitrate (<math>\text{NO}_3^-</math>)</b>	95	< 0.05	-	0.97	-	-
	<b>Nitrite (<math>\text{NO}_2^-</math>)</b>	96	< 0.002	-	< 0.02	-	-
	<b>Bisulfide (<math>\text{HS}^-</math>)</b>	96	1.70	3.26	5.60	0.64	20
	<b>Silicate (<math>\text{H}_3\text{SiO}_4^-</math>)</b>	87	7.00	11.89	15.10	1.69	14
	<b>Phosphates (<math>\text{H}_2\text{PO}_4^-</math>)</b>	3	< 0.04	-	< 0.04	-	-

The results analysis, obtained over these 30 consecutive years, it was found that there was no any trend, being common, in the global physical parameters and majority ions, a more frequent situation of standard deviation around the mean (DPR) of less than 10%, except rare exceptions. In trace species, the DPR values are sometimes high. That can be explained due to the fact that they occur in very small quantities, and any fluctuation, even caused by adjustments in laboratory practices, can lead to this situation. Occasionally, the DPR assumes very high values, as in Aluminum (Table 2); such a situation is orienting for any problem in that parameter. Another peculiarity, concerning trace species, is the detection and quantification of some chemical elements which, as a general rule, are below detection limits. It is the case of Cu, Ni, Pb and Zn species. It is emphasized that only with a perfect notion of the history of chemistry, over time, the external monitoring system will become more effective in favor of defending the quality of the mineral aquifer system.

#### 4. External Monitoring System

Considering the location of the Traditional Spring, its relationship with the morphological and hydrogeological aspects, it was decided to carry out the monitoring organized into three main components (Fig. 6): i) Installation of double piezometers, for monitoring water levels, conductivity, temperature, and for water collecting for physical-chemical quality control, namely heavy metals; the piezometers were installed according to the elements shown in Figure 7. Each piezometer has two tubes, one more superficial (3m deep) and other deeper (6m deep) in order to investigate the situation at different depths (Fig.7a,b); ii) Installation of a street rainwater sampler (Fig.7c), for physical-chemical analysis of water resulting from runoff from the street area with the car park adjacent to Hotel do Parque; and, iii) Installation of a meteorological station with a precipitation collector system for physical-chemical analysis (Fig.7d).

The installation work of the various components took place from July to October 2006. During the execution of the boreholes for the piezometers installation, soil samples were collected, every meter, to be later studied, in terms of the main heavy metals. Due to the results, it was decided to remove some soils, especially near the NT guardhouse. The records of the water levels and respective conductivity and temperature in piezometers, in an initial experimental phase, were carried out in a systematic way, monthly from October 2006 to May 2014. Detailed physical-chemical analysis of groundwater samples from the piezometers, from rainwater, stormwater, occurred almost monthly from October 2006 to October 2008. Sometimes, in some months, samples were not obtained from the meteorological station and the rainwater sampler, as in some periods there was no precipitation.

**Table 2.** Table 2. Statistics of the results of physical-chemical analyses, in terms of trace elements, of the water collected in the Traditional Spring (NT), between 1985 and 2014 [13].

<b>Trace species (mg/L)</b>	<b>Silver (Ag)</b>	49	< 0.00004	-	< 0.0005	-	-
	<b>Aluminium (Al)</b>	51	0.0021	0.0437	0.6400	0.0950	217
	<b>Arsenic (As)</b>	53	0.0030	0.0045	0.0180	0.0022	49
	<b>Boron (B)</b>	51	0.3600	0.4263	0.4760	0.0245	6
	<b>Barium (Ba)</b>	53	< 0.0003	-	0.0063	-	-
	<b>Beryllium (Be)</b>	53	0.0003	0.0006	0.0014	0.0002	28
	<b>Bismuth (Bi)</b>	40	< 0.00002	-	0.0001	-	-
	<b>Bromide (Br)</b>	3	0.1300	0.1750	0.2600	0.0601	34
	<b>Cadmium (Cd)</b>	53	< 0.00001	-	0.0006	-	-
	<b>Cobalt (Co)</b>	53	< 0.00001	-	0.0003	-	-
	<b>Chromium (Cr)</b>	53	< 0.0004	-	0.0124	-	-
	<b>Cesium (Cs)</b>	42	0.0460	0.0624	0.0721	0.0043	7
	<b>Copper (Cu)</b>	51	< 0.00005	-	0.0550	-	-
	<b>Mercury (Hg)</b>	47	< 0.00007	-	0.0003	-	-
	<b>Iodide (I)</b>	3	< 0.00006	-	0.0020	-	-
	<b>Manganese (Mn)</b>	52	0.0013	0.0020	0.0060	0.0009	45
	<b>Molybdenum (Mo)</b>	53	< 0.001	-	0.0060	-	-
	<b>Niobium (Nb)</b>	52	< 0.00002	-	0.0001	-	-
	<b>Nickel (Ni)</b>	52	< 0.0002	-	0.0150	-	-
	<b>Lead (Pb)</b>	52	< 0.00006	-	0.0730	-	-
	<b>Rubidium (Rb)</b>	42	0.0530	0.0590	0.0670	0.0028	5
	<b>Antimony (Sb)</b>	53	< 0.00009	-	0.0070	-	-
	<b>Selenium (Se)</b>	49	< 0.00085	-	0.0013	-	-
	<b>Tin (Sn)</b>	53	< 0.00003	-	0.0010	-	-
	<b>Strontium (Sr)</b>	50	0.0570	0.0667	0.0730	0.0032	5
	<b>Tantalum (Ta)</b>	41	< 0.00001	-	0.00004	-	-
	<b>Tellurium (Te)</b>	48	< 0.00005	-	0.0003	-	-
	<b>Titanium (Ti)</b>	1	-	0.0110	-	-	-
	<b>Thallium (Tl)</b>	41	< 0.0001	-	0.0015	-	-
	<b>Uranium (U)</b>	47	< 0.00002	-	0.0001	-	-
	<b>Vanadium (V)</b>	53	< 0.0002	-	0.0009	-	-
	<b>Yttrium (Y)</b>	53	< 0.00001	-	0.00002	-	-
	<b>Tungsten (W)</b>	53	0.0370	0.0791	0.0990	0.0101	13
	<b>Zinc (Zn)</b>	53	< 0.0002	-	0.3140	-	-
	<b>Zirconium (Zr)</b>	41	< 0.00015	-	0.0002	-	-

## 5. Results

The results of the evolution levels of the piezometers and their water physical-chemical parameters (conductivity and temperature) are extremely important to understand what is happening in the involvement of mineral water abstractions, in order to make decisions about, not only, in the water flow rate in exploration, but also on anthropic actions at the place. As an example, the results from piezometer 3 are shown in Figure 8. In order to carry out a rigorous analysis, the results will have to be analysed simultaneously with what happens in terms of exploration in the mineral water abstractions, namely in Well AC1. Therefore, Well AC1 started its exploration, with its open use at 100% ( $Q \approx 12L/s$ ) in 2002, and remained so, until June 2005. Since July 2005 it has generally been around 40 to 50%, with rare

exceptions, namely in the flow test phase. Thus, for example, careful analysis in Figure 8 on what occurred in August 2012, there was a high level in the 3m piezometer, noting that it was in counter-cycle, because in a common situation, the level should be very low because it was the peak of summer, and the opposite was verified. Investigating the reason, it turned out that the garden had been over-watered. To reconfirm this situation, in that period, was the simultaneous occurrence of relatively high conductivity, which is the result of irrigation water that crosses contaminated soil levels becomes more mineralized and more conductive, evolving to the piezometer.

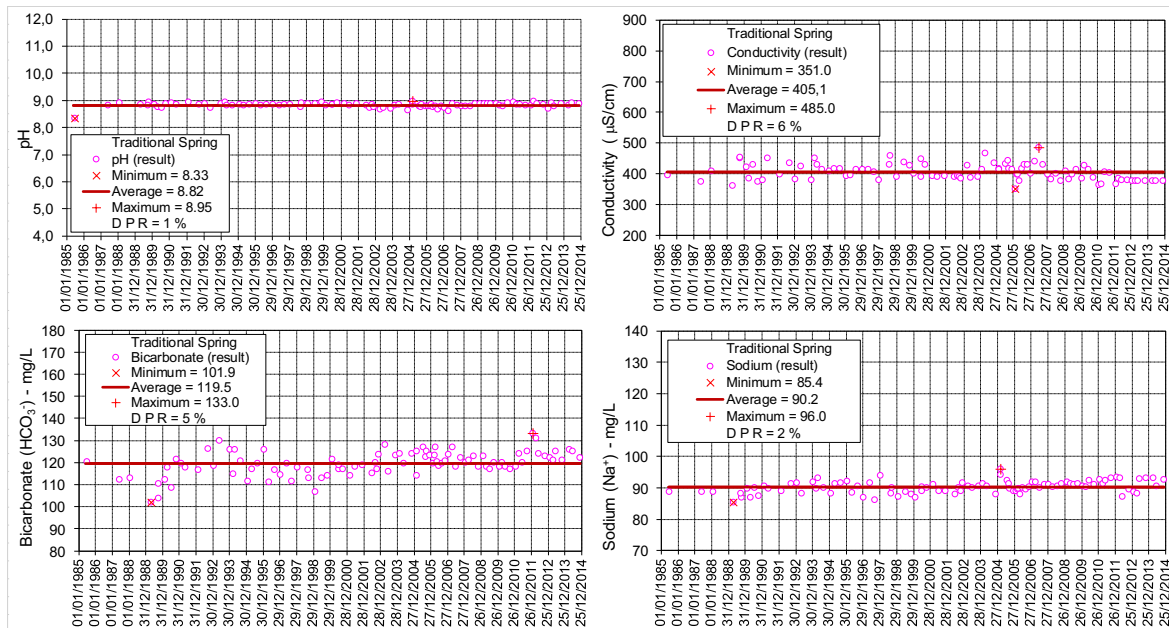


Figure 5. Examples physical-chemical analysis results from the Traditional Spring (NT) water, between 1985 and 2014.

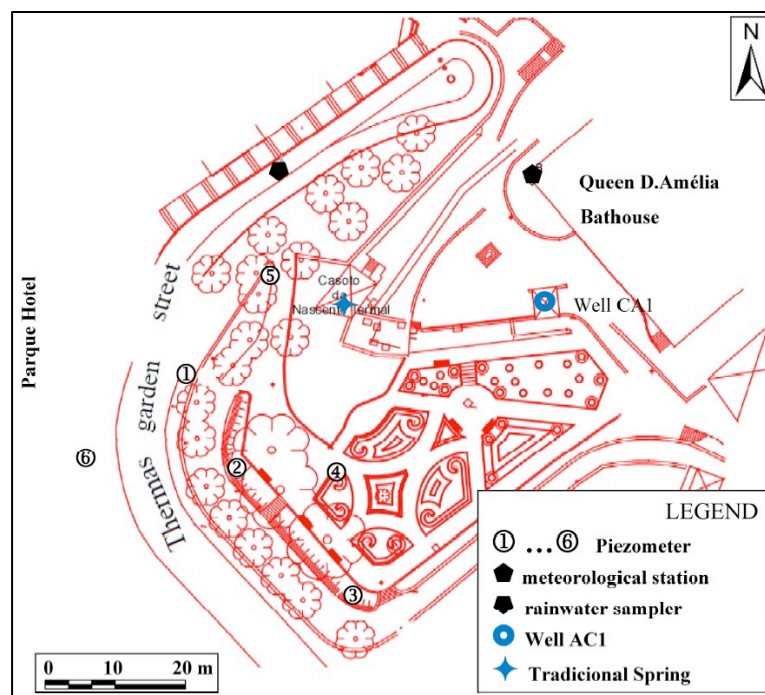
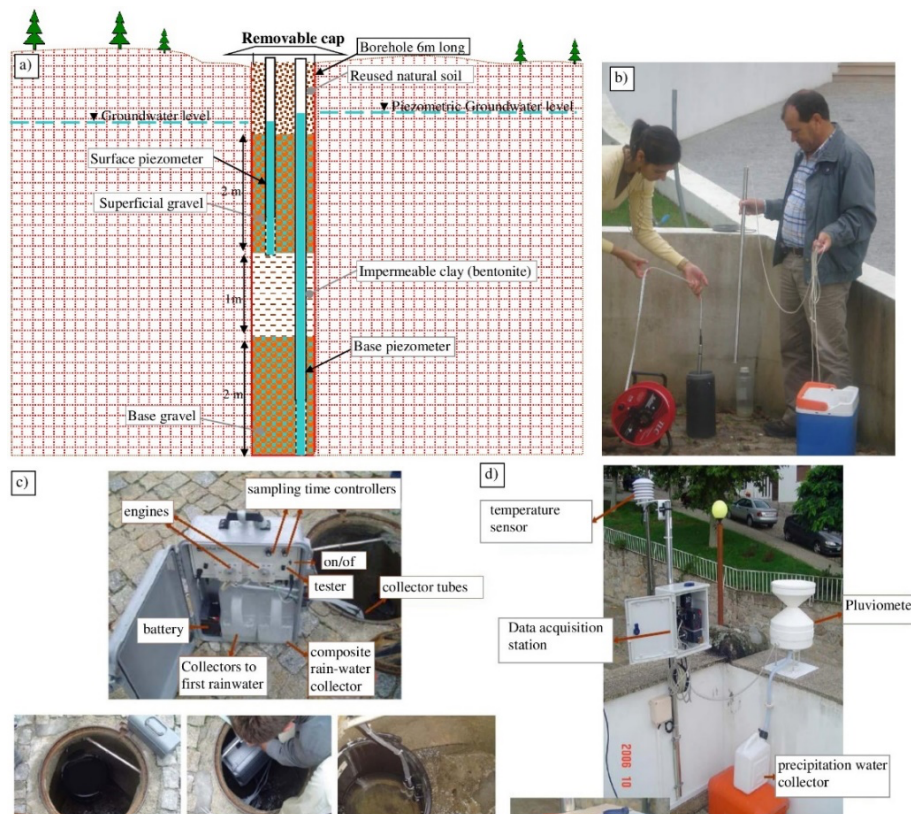


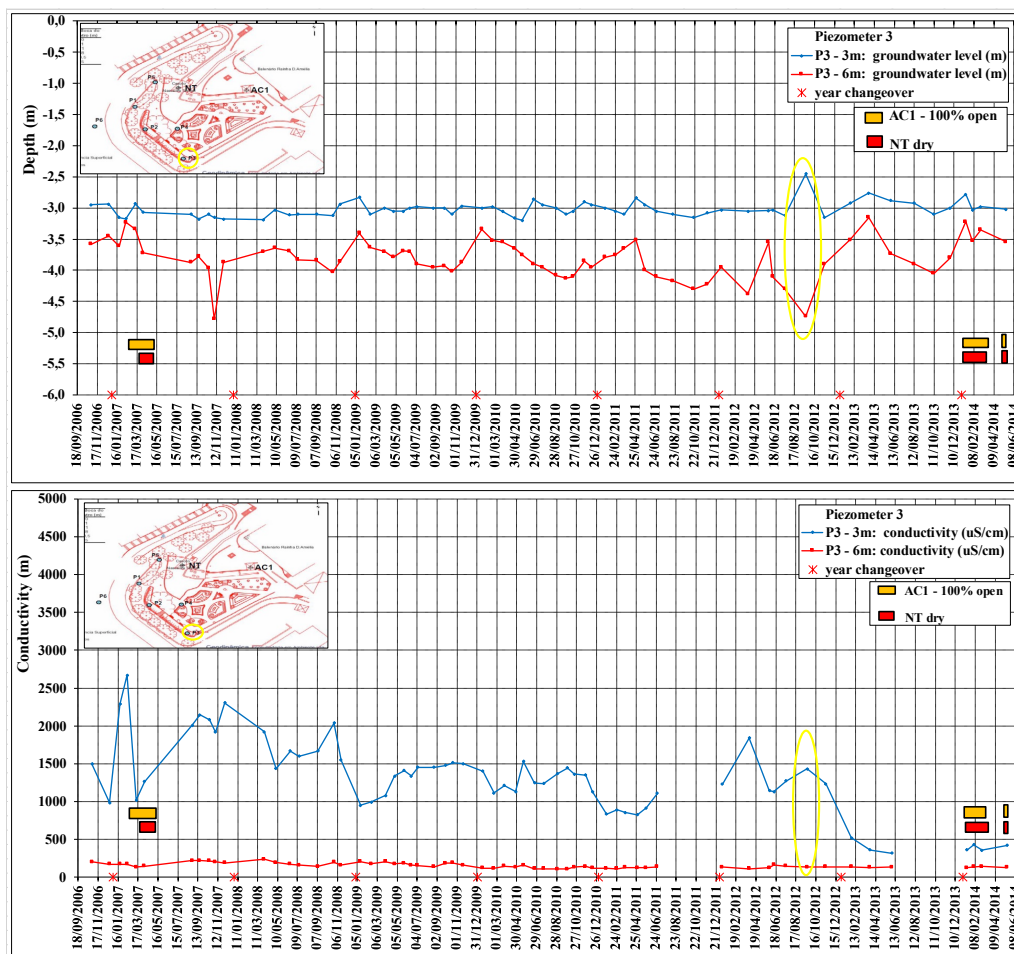
Figure 6. Location of external monitoring equipment around the SPS medical spa.





**Figure 7.** Figure 7. Elements of the external monitoring system in SPS medical spa area: a) double piezometers scheme; b) operating moment on the piezometer 6; c) image of the street rainwater sampler, d) image of the meteorological station with a precipitation collector system.

About the results of water chemism in the piezometers, much could be said because the results are enormous, however the following aspects can be highlighted: i) the water in the same piezometers over time shows large oscillations in quality, this situation is more evident in the 3 m piezometers, with relative standard deviations (DPR) in major ions often exceeding 40%; in the 6 m piezometers, DPR is often over 25%; ii) the waters from the various piezometers present themselves very different, being, in relation to the main ions, from sulphated-sodic, sodium bicarbonate, and calcium-bicarbonate waters; it is also noteworthy the fact that iron, sometimes appears with very significant values, reaching values of 46mg/L, when normally, NT natural mineral water does not present this element; it should be noted that, regarding NT natural mineral water, some piezometers have less mineralized water while others have greater mineralization's; finally, regarding the trace species, several situations are verified in piezometers waters, highlighting the fact that some trace species arise with values much higher than those present in the NT water, in particular for Pb, Al, As, Zn, Cu, Mo and U. Concerning the samples from the street rainwater sampler, they are the result of rainwater that falls nearby, and especially on the street, which has a parking area, and which ends up flowing to the rainwater sewer system. From the results, the low total mineralization (about 146 mg/L) stand out, even so, much higher than the underground water mineralization from some piezometers, evidencing the possible risk infiltration of these rainwater in the area, in addition to the fact that they have significant levels of trace species such as Ba, Al, Zn, Ni, Cd, V, and even U. Finally, regarding the results of the analysis of the water from the climatological station collector, the very low total mineralization is highlighted, as expected, but the negative emphasis is on the fact that they have great oscillation in quality, with total mineralization varying between 2.2 to 24.4 mg/L, and the main ions have DPR generally greater than 80%, and present trace elements such as Al, Ba, Zn, Cu, Pb, Sn, Sr, and many others, noting that Al sometimes presents values that exceed the parametric limit for drinking water.



**Figure 8.** Results of the levels recordings in piezometer 3, in the 3m and 6m deep tube, and also the conductivity over time, between 2006 and 2014, from the external monitoring system in the SPS medical spa area.

## 6. Conclusions and Recommendations

Regarding the results of the external monitoring of the São Pedro do Sul Medical Spa, the following situations should be highlighted: i) there is a great apprehension around the water quality from the meteorological station, since, in addition to the instable quality of the rainfall water, they are polluted, and are, habitually rich in some harmful elements to public health, specifically Al, Zn, Cu and Pb; ii) the street runoff water quality was found to be even more contaminated than rainwater, evidencing the anthropogenic pressure, namely the circulation and vehicle parking, pointing to the necessity to not allow this sort of infiltrations in the natural mineral water abstraction area; iii) regarding the groundwater quality from the more superficial piezometers (3m deep) the situation is very heterogeneous, revealing local anthropic actions from various domains, which leads to the presence of trace species at much higher values than those that occur in natural mineral waters, namely in the cases of Pb, Al, As, Zn, Cu, Mo and U. Situation less worrying, occurs in 6m piezometers waters, even though, sporadically there are also situations of some apprehension, which increases, especially in areas where the Well AC1 exploration is related to the levels of some piezometers, namely in P4 and P5.

As a closing note and recommendation: i) the infiltrations of rainwater in the mineral water abstractions area should be minimized, or even annulled, if possible, as well as the runoff water; all excess watering in the green areas must also be void; any action in the area close to the abstractions must be prudently thoughtful, since the possible free movement of people and goods, car circulation and

parking, to urban occupation, which leads to the implementation of drinking water and sanitation networks that, in cases of malfunction, can be fluid percolation foci, in a downward direction to the mineral aquifer system; ii) the previous situation is enhanced due to the fact that the land is highly contaminated and when occurs water percolation in those lands, this will drag some contaminants in a downward direction, direct to the aquifer; although some contaminated surface land has already been removed, and some tree species have even been abolished, such as banana trees near the Traditional Spring, the same type of action should be continued for areas where the results of soils analysis, resulting from drilling to install of the piezometers, showed contamination.

Finally, it is emphasized that until all potential problems are solved, in the context of the exploitation of the mineral aquifer system by the mineral water abstractions (NT and Well AC1), the exploitation of Well AC1 should be contained with about 40 to 50% of its maximum capacity, in order to maintain the piezometric level relatively high and above the topographic surface.

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