Chapter

Chemical Quality of Rainwater and Surface Runoff Water in the Proximity of the Abstractions That Supply the São Pedro do Sul Medical Spa (Portugal)

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Abstract

São Pedro do Sul medical spa provides health services using hot natural groundwater superiorly classified as natural mineral water. The main source of supply of that medical spa, has been over time, the Traditional Spring, which in recent decades has been systematically controlled, and shows spectacular constancy in its chemical quality, if there are no outside contaminations. Within the context presented, the detailed physical-chemical quality of rainwater and surface runoff water was studied, in the proximity of the Traditional Spring, as there is a potential for them to infiltrate at depth and evolve into the natural mineral water aquifer system. Thus, in the present chapter, after presenting the physical-chemical quality of the natural mineral water from the Traditional Spring, as well as some elements of the literature on the physical-chemical quality of rainwater, the methodology of work is followed, and then the results obtained from the physical-chemical composition of rainwater and surface run-off water are presented and discussed, comparing them with the quality of the water from the Traditional Spring. Finally, the main conclusions are presented, and some recommendations are made on research into potential sources of pollution, which justify the poor quality of the rainwater studied.

Keywords: chemical composition, rainwater, surface runoff water, natural mineral water, São Pedro do Sul medical spa

1. Introduction

The medical spa of São Pedro do Sul (SPS), in Portugal, with a millenary tradition, was already used by the Romans about 2000 years ago. Currently, it is a great asset to the region, as it allows leveraging the local economy, due to its activity in thermalism and other associated and complementary activities, such as tourism. Thermalism is the activity practiced in the medical spa, namely the use of natural mineral water (NMW)

in some treatments, in the field of balneotherapy. SPS medical spa has two operating bathhouses (Thermal Centre and Queen D. Amélia Bathhouse) and has already reached around 25,000 users in classic thermalism per year; each user of classical thermal treatments attends a Bathhouse for about 2 weeks. In this process, the direct income with the treatments has already reached about 5 million euros/year [1].

The main source to supply the SPS medical spa, is the Traditional Spring (NT), which provides special groundwater with about 10 L/s of the sulphureous water type. There is also a well (AC1) that complements the supply of groundwater similar to the NT water. It is important to note that the water in the NT comes from a semi-confined aquifer system, of granite rocks, of the fissure type, very deep; its water, initially rain, infiltrates to great depths, in the order of several kilometers, and on its way acquires its specific chemical quality, function of the water/rock interaction, also acquiring temperatures above 100°C; in that process, and due to the geological singularities, the NMW resurfaces in the NT at about 68°C.

There is also, the superficial aquifer system, unconfined, in granitic rocks, more common in the region, with about 100 m depth, essentially of fissure type, and sometimes porous, when the granites are very weathered; in this superficial aquifer system, its waters are slightly acidic (pH <6.0) and generally have total mineralization (M_T) lower than 250 mg/L. Detailed studies on these situations can be seen in works by several authors [2, 3]. The chemical composition of the special groundwater, from NT, is very well characterized and is classified by the Portuguese state as a NMW for thermalism applications. The guarantee of its physical-chemical stability, besides other requirements, allows the use of that water as an equivalent of a medicine, with treatments for rheumatic and respiratory diseases being prescribed by a doctor.

The chemical composition of that water is analyzed over time and in a systematic way. Such quality control allows you to check, if anomalies are occurring, being sometimes its enigmatic causes.

Records in 2005, from physical-chemical analyses of the water of the NT, identified values of its trace component out of the common, namely of lead (Pb), zinc (Zn) and copper (Cu). This situation led to several interventions, namely the study of the chemical quality of the rainwater and surface runoff water in the area surrounding the NT. Thus, it is emphasized that it is the chemical quality of rainwater and surface runoff water in the medical spa area that this chapter focuses on, in order to try to understand whether changes in the water quality of the NT may result from them.

The SPS medical spa is located in an area called "Polo das Termas" of the São Pedro do Sul Hydromineral and Geothermal Field—CHGSPS (**Figure 1**).

The territory's characteristics are essentially a dispersed urban space, with some equipment for medical spa activities, and other associated and consequent ones, such as hotels, restaurants, and tourism. Green spaces predominate, although most of them present characteristics of brush and poorly regulated forest, interspersed with small family agricultural areas or scattered patches of houses.

The nearest town is São Pedro do Sul, about 3.5 km NE of the medical spa area. The town of São Pedro do Sul has only about 3600 inhabitants, being the municipality seat, with 14 parishes, in a global territory with 348.95km^2 of the area and 16,851 inhabitants (2011). The municipality of São Pedro do Sul, as well as the neighboring ones, each has 1 to 2 industrial parks with various factories, car workshops, and services, but without any apparent expression capable of causing record air pollution. There is also no known focus on air pollution in those municipalities.

About the chemical quality of the natural mineral water of the NT, it is presented in **Table 1** statistics of the results of physical-chemical analysis, between 1985 and

Figure 1.
Geographic framing of the study area (a) and image of SPS medical spa zone, with the location of its abstractions (Main spring—NT, and well AC1), and of its bathhouses (thermal center and queen D. Amélia bathhouse (b).

2014, including the results, of the most anomalous phase (2005–2006), and also of several years following the problem, which is now resolved.

The parameters that present a SD_R lower than 10% correspond to relatively very stable chemical elements. One obvious case in the opposite situation is Aluminium (Al), which presents an SD_R of 217%. This happens because although the water naturally includes some Al content, it sometimes appears with abnormal values, being understood as a consequence of local anthropic actions; in 2005–2006, and following years, there was no problem with Al. Other cases, clearly evident in bad situations, are those in which the values of certain chemical elements are suddenly very high, when the normal content of the chemical element being studied is below the detection limit, as is the case with Pb, Zn, and Cu.

That context led to the creation of an External Monitoring System (EMS) in the area surrounding the NT, which was presented in detail in: "Good practices of quality control in the area surrounding of natural mineral water abstraction of São Pedro do Sul medical spa (Portugal)" [1], and which will be presented in the methodology section of this chapter.

On hydrological elements of the study area, based on records between 1933 and 1960, in the São Pedro do Sul udometric station, the average annual precipitation was 1103 mm. The average annual air temperature in that region is around 13°C. From the monthly sequential hydrological balance for the same region, it is obtained annual surpluses of 675 mm [5]. In **Figure 2**, the evolution of precipitation throughout the year is presented, being noteworthy that the month with the lowest precipitation is July, with 11.8 mm, and the month with the highest precipitation is March with 175 mm.

Rainwater and surface runoff water quality studies in the context of the present work, as far as the authors know, are inexistent, because medical spas are normally located in special equipment areas associated with tourism and leisure, and in green parks, so there is no concern that rainwater in these areas may have harmful chemical elements; the fact is that if this happens, the water infiltrating around the natural mineral water abstractions areas may contaminate the resource and create public health problems. Studies on rainwater quality in contexts different from the present chapter are frequent in the literature; some considerations about this domain are presented in the follow-up, to facilitate the framing of the results of this study. Rainwater contains small amounts of dissolved and suspended substances. The

Parameter		N	min	ave	max	SD	SD_R (%)
pH		96	8.33	8.82	8.95	0.08	1
Conductivity – C (μS/cm)		96	351.00	405.08	485.00	26.14	6
Total Sulphuration (in I_2 0.01 N-mL/L)		96	16.00	21.30	34.00	3.70	19
Total Alkalinity—A_T (in HCl 0.1 N-mL/L)		94	22.00	23.68	25.00	0.70	3
Total Hardness-H_T (in p.p.10^5 of $CaCO_3$)		96	0.65	0.77	1.10	0.06	8
Total CO_2 (mmol/L)		80	1.81	2.06	2.50	0.09	4
Silica—SiO_2 (mg/L)		96	60.90	67.94	78.50	3.61	5
Dry Residue – R_D (at 180°C) – (mg/L)		95	291.30	304.77	326.00	6.27	2
Total Mineralization – M_T (mg /L)		96	333.00	359.68	385.00	8.68	2
Cations (mg/L)	Sodium (Na^+)	96	85.40	90.19	96.00	1.93	2
	Calcium (Ca^{2+})	96	1.60	2.99	4.40	0.30	10
	Potassium (K^+)	93	2.90	3.30	3.70	0.16	5
	Magnesium (Mg^{2+})	55	< 0.03	—	< 1.0	—	—
	Lithium (Li^+)	93	0.47	0.59	0.70	0.04	7
	Ammonium (NH_4^+)	96	0.16	0.33	0.47	0.04	13
	Iron (Fe^{2+})	21	< 0.075	—	0,100	—	—
Anions (mg/L)	Bicarbonate (HCO_3^-)	96	101.90	119.48	133.00	5.48	5
	Chloride (Cl^-)	96	25.10	27.89	37.00	1.53	5
	Sulphate (SO_4^{2-})	94	7.80	10.12	13.00	0.95	9
	Fluoride (F^-)	96	15.20	17.71	19.00	0.56	3
	Carbonate (CO_3^{2-})	96	3.00	4.69	9.50	1.10	23
	Nitrate (NO_3^-)	95	< 0.05	—	0.97	—	—
	Nitrite (NO_2^-)	96	< 0.002	—	< 0.02	—	—
	Bisulfide (HS^-)	96	1.70	3.26	5.60	0.64	20
	Silicate ($H_3SiO_4^-$)	87	7.00	11.89	15.10	1.69	14
	Phosphates ($H_2PO_4^-$)	3	< 0.04	—	< 0.04	—	—
Trace elements (mg/L)	Silver (Ag)	49	< 0.00004	—	< 0.0005	—	—
	Aluminium (Al)	51	0.0021	0.0437	0.6400	0.0950	217
	Arsenic (As)	53	0.0030	0.0045	0,0180	0.0022	49
	Boron (B)	51	0.3600	0.4263	0.4760	0.0245	6
	Barium (Ba)	53	< 0.0003	—	0.0063	—	—
	Beryllium (Be)	53	0.0003	0.0006	0.0014	0.0002	28
	Bismuth (Bi)	40	< 0.00002	—	0.0001	—	—
	Bromide (Br)	3	0.1300	0.1750	0.2600	0.0601	34
	Cadmium (Cd)	53	< 0.00002	—	0.0006	—	—

Parameter		N	min	ave	max	SD	SD_R (%)
	Cobalt (Co)	53	< 0.00001	—	0.0003	—	—
	Chromium (Cr)	53	< 0.0004	—	0.0124	—	—
	Cesium (Cs)	42	0.0460	0.0624	0.0721	0.0043	7
	Copper (Cu)	51	< 0.00005	—	0.0550	—	—
	Mercury (Hg)	47	< 0.00007	—	0.0003	—	—
	Iodide (I)	3	< 0.00006	—	0.0020	—	—
	Manganese (Mn)	52	0.0013	0.0020	0.0060	0.0009	45
	Molybdenum (Mo)	53	< 0.001	—	0.0060	—	—
	Niobium (Nb)	52	<0.00002	—	0.0001	—	—
	Nickel (Ni)	52	< 0.0002	—	0.0150	—	—
	Lead (Pb)	52	< 0.00006	—	0.0730	—	—
	Rubidium (Rb)	42	0.0530	0.0590	0.0670	0.0028	5
	Antimony (Sb)	53	< 0.00009	—	0.0070	—	—
	Selenium (Se)	49	< 0.00085	—	0.0013	—	—
	Tin (Sn)	53	< 0.00003	—	0.0010	—	—
	Strontium (Sr)	50	0.0570	0.0667	0.0730	0.0032	5
	Tantalum (Ta)	41	< 0.00001	—	0.00004	—	—
	Tellurium (Te)	48	< 0.00005	—	0.0003	—	—
	Thallium (Tl)	41	< 0.0001	—	0.0015	—	—
	Uranium (U)	47	< 0.00002	—	0.0001	—	—
	Vanadium (V)	53	< 0.0002	—	0.0009	—	—
	Yttrium (Y)	53	< 0.00001	—	0.00002	—	—
	Tungsten (W)	53	0.0370	0.0791	0.0990	0.0101	13
	Zinc (Zn)	53	< 0.0002	—	0.3140	—	—
	Zirconium (Zr)	41	< 0.00015	—	0.0002	—	—

N: number of samples; min: minimum, ave.: average, max: maximum, SD: standard deviation, and SD_R: relative standard deviation (SD/ave) × 100.

Table 1.
Statistics of the results of physical-chemical analyses of the natural mineral water collected in the traditional spring (NT), between 1985 and 2014 [4].

concentration of these substances as well as the pH can vary with time [7] and place [8]. Another very common situation in rainwater quality studies is related to the content of some chemical elements as a function of distance from the sea, namely Cl^- and Na^+. The most important compounds that can be found in rainwater are Cl^-, $S0_4^{2-}$, NO_3^-, NO_2^-, and HCO_3^- in anions, and Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+ in the cations [9]. Nowadays, the existence of immense industrial parks, of different types, spread all over the world, as well as the burning of fossil fuels for energy production, locomotion of vehicles and airplanes, or even the incineration of dangerous waste and others, leads to enrichment in the atmosphere of very potentially harmful chemical elements, which without these anthropogenic sources, they would never appear.

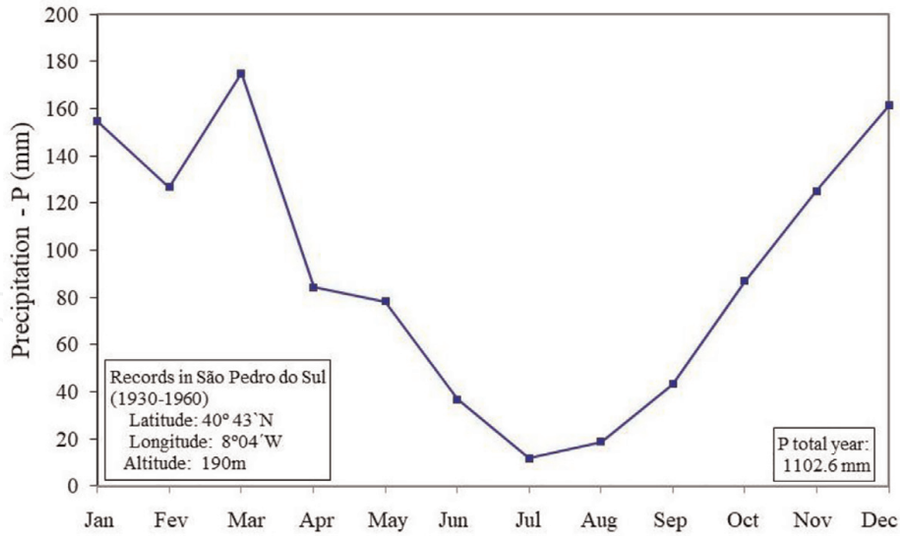

Figure 2.
Evolution of the average monthly precipitation in the region of SPS (from [6]).

There have been many studies on the quality of rainwater in different situations under the action of anthropic factors. The works of several authors dealing with the quality of rainwater in different situations are worth mentioning, showing very problematic cases [10–12], especially in situations where there is a need to collect rainwater to supply populations. In synthesis, the purity of rainwater in any region of the world should not be guaranteed whenever public health situations are involved.

2. Methodology

In this item it is important to mention that the natural mineral water abstractions (Traditional Springer—NT and Well AC1) are located in a garden zone, immediately upstream of the Queen D. Amelia Bathhouse (**Figure 3**). Surrounding that garden area, and upstream of it, there is a public street (Thermas garden street) that includes parking capacity for about 30 cars, besides the location of a hotel (Hotel do Parque), contiguously, with outdoor parking. The area surrounding the NT house, and in particular in the upstream sector (area NW and SW of the house) at the time when there were problems in the quality of the NT natural mineral water, had luxuriant vegetation and in particular banana trees. Following the detection of problems in the quality of NT natural mineral water, interventions were planned, organized into two groups:

2.1 Immediate interventions

I. to start using the NT as the main abstraction, because since 2002, with the beginning of the exploration of the young well AC1, the NT was only a complement; it should be noted that the natural mineral water aquifer system is of the semi-confined type, and the exploration of one abstraction interferes with the other; thus, from 2005 onwards, a great constraint was imposed on the exploitation of Well AC1, sometimes closing it totally, in order to raise the piezometric level of the natural mineral water aquifer system; in this way the infiltrations of rainwater and other waters in the garden area were minimized;

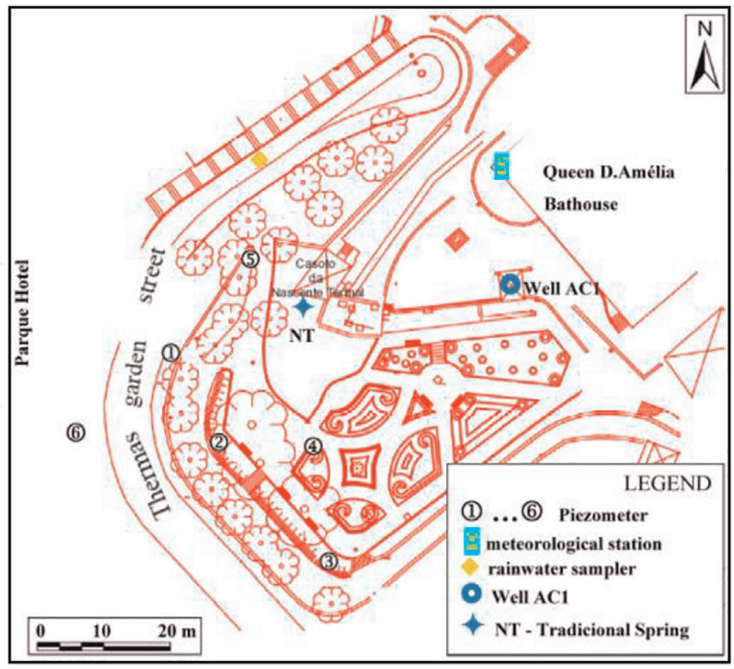

Figure 3.
Location of external monitoring equipment in the upstream zone of the natural mineral water abstractions of the SPS medical spa.

II. placing a gutter on the roof of the NT access house on the south and west sides, and harmonizing the situation with the surface runoff water so that it does not infiltrate locally; the external area of the roof of the NT house was also waterproofed;

III. check the drainage of surface groundwater in the surroundings of the NT house, in order to ensure that there are no leaks or infiltrations into the NT.

The interventions in (III) had unforeseen developments, very prolonged in time, and in particular because many meticulous excavations were carried out around the NT house, for having found underground water resurgences equal to that of the NT, which immediately interfered with its flow; part of the garden was eliminated, mainly the area with banana trees, substituting very organic earth, and others, namely by adequate clays that waterproofed the surrounding of the NT house.

2.2 Short-term intervention

Install an External Monitoring System (EMS), to control what happens over time to the environmental and groundwater quality resulting from possible infiltration from various sources such as agriculture or gardening, vehicle traffic, storm-water networks, or even the wastewater network.

Synthetically, the EMS consists of three main components: (i) piezometers for monitoring groundwater levels, conductivity, temperature, and for collecting water for physical-chemical quality control, namely heavy metals; (ii) a surface runoff water sampling system for physical-chemical analysis of the water resulting from the runoff of the street area; and (iii) a meteorological station with a precipitation collection system for physical-chemical analysis.

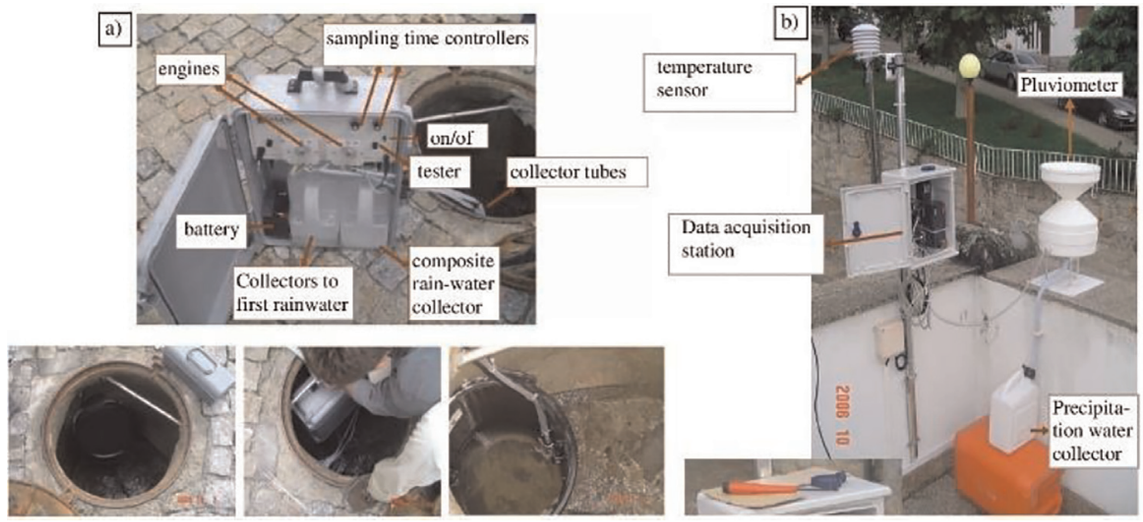

Figure 4.
Images of monitoring systems: (a) street surface runoff water sampling system; and (b) meteorological station with a precipitation collector.

The surface runoff water sampling system, installed in the Thermas garden street (**Figure 4**), consists of a PVC tank for storing surface runoff water, to which an automatic sampler is associated for taking water samples. The automatic sampler has two independent sampling circuits, allowing the differentiated collection in two polyethylene containers, each with a capacity of four liters. The two samplers made it possible to organize the samples with two designations: the simple sample, which is the one resulting from the first rainfall that goes into the PVC tank and from there is sucked continuously into the sampler; the composite sample results from intermittent sampling over time. Regarding the meteorological station, it was installed on the terrace edge of the Queen D. Amélia Bathhouse, in a place with the following coordinates: Latitude −40°44′20″N, Longitude −8°05′34″W, Altitude: 154 m. This point is about 55 km east of the coastline (Atlantic Ocean). That station consists of a modular data acquisition system which, among others, has a tilting type rainfall sensor with a sensitivity of 0.2 mm per tilting. The coating is made of UV-resistant plastic, so as not to alter the chemical parameters of the water and rain and is associated with a container to retain the water, thus enabling its subsequent analysis in the laboratory.

In order to evaluate the quality of rainwater and surface runoff water, it was established as a minimum sampling period of 1 year, with monthly collections, however, the period ended up being higher, because it did not always rain on the date scheduled for the collections, in addition to some occasional constraints of technical and logistical nature, so in order to have greater representativity of the results, the sampling period ended up being between October 2006 and October 2008. It should be mentioned that in this period systematic analyses of groundwater from the piezometers were also carried out, however, these are not the subject of studies in this chapter.

The physical-chemical analyzes were carried out almost globally by the Laboratory of INETI (current Laboratory of LNEG), except for the analyzes of the first two campaigns, which were carried out by the Laboratory of IST, still in 2006. Those laboratories are accredited in accordance with the rules of the European Union. In summary, the parameters to be researched were organized as follows: (i) global parameters (pH, conductivity-C, total alkalinity-A_T, total hardness-H_T, Silica-SiO_2, and total mineralization-M_T); (ii) major cations (Sodium-Na^+, Calcium-Ca^{2+},-Potassium-K^+, Magnesium-Mg^{2+}, Lithium-Li^+, Ammonium-NH_4^+, Iron-Fe^{2+}); (iii)

major anions (Bicarbonate-HCO_3^-, Chloride-Cl^-, Sulphate-SO_4^{2-}, Fluoride-F^-, Nitrate-NO_3^-, Nitrite-NO_2^-, Phosphates-$H_2PO_4^-$); and (iv) trace elements, such as details, for example, are presented in **Figure 5**. The analytical methods followed were:

Parameter		N	Min	Ave	Max	SD	SD_R (%)
pH		12	4.17	5.27	5.93	0.47	9
Conductivity - C (µS/cm)		12	8.00	32.03	75.00	22.46	70
Total Alkalinity - A_T (in HCl 0.1N - mL/L)		12	< 0,05	-	1.00	-	-
Total Hardness - H_T (in p.p.10^5 $CaCO_3$)		10	0.14	1.13	4.30	1.28	113
Silica - SiO_2 (mg/L)		12	< 0.3	-	1.10	-	-
Total Mineralization - M_T (mg /L)		9	2.20	9.91	24.40	6.39	64
C	Sodium (Na^+)	12	0.20	1.65	4.90	1.44	88
a	Calcium (Ca^{2+})	12	0.14	1.78	7.40	2.05	116
t	Potassium (K^+)	11	0.06	0.26	1.20	0.31	122
i	Magnesium (Mg^{2+})	12	0.04	0.31	0.90	0.28	89
o	Lithium (Li^+)	10	0.0001	0.0011	0.0033	0.0010	92
n	Ammonium (NH_4^+)	10	< 0.04	-	1.64	-	-
(mg/L)	Iron (Fe^{2+})	11	< 0.03	-	0.20	-	-
A	Bicarbonate (HCO_3^-)	11	<0.03	-	1.80	-	-
n	Chloride (Cl^-)	12	0.50	3.88	9.80	3.12	81
i	Sulphate (SO_4^{2-})	12	0.30	1.53	4.40	1.31	85
o	Fluoride (F^-)	12	< 0.07	-	0.53	-	-
n	Nitrate (NO_3^-)	12	< 0.12	-	2.30	-	-
(mg/L)	Nitrite (NO_2^-)	12	< 0.01	-	0.07	-	-
	Fhosphates ($H_2PO_4^-$)	12	<0,13	-	< 0,15	-	-
	Silver (Ag)	10	<0.00005	-	0.00057	-	-
	Aluminium (Al)	10	0.01000	0.09404	**0.32500**	0.09621	102
	Arsenic (As)	12	<0.0002	-	0.00540	-	-
T	Boron (B)	9	0.00130	0.00497	0.01140	0.00354	71
r	Barium (Ba)	10	0.01130	0.21026	**1.82100**	0.53719	255
a	Beryllium (Be)	10	<0.00004	-	0.00007	-	-
c	Bismuth (Bi)	10	<0.00001	-	<0.00006	-	-
e	Cadmium (Cd)	10	0.00007	0.00044	0.00191	0.00054	125
	Cobalt (Co)	10	0.00003	0.00079	0.00600	0.00175	222
e	Chromium (Cr)	10	<0.0002	-	0.00076	-	-
l	Cesium (Cs)	10	<0.00002	-	0.00059	-	-
e	Copper (Cu)	11	0.00060	0.00383	**0.01120**	0.00314	82
m	Mercury (Hg)	10	<0.00003	-	0.00010	-	-
e	Manganese (Mn)	10	0.00020	0.00609	0.01970	0.00598	98
n	Molybdenum (Mo)	10	<0.00002	-	0.00037	-	-
t	Niobium (Nb)	10	<0.00001	-	0.00001	-	-
s	Nickel (Ni)	10	0.00020	0.00138	0.00450	0.00142	103
	Lead (Pb)	10	0.00017	0.00063	0.00190	0.00050	80
(mg/L)	Rubidium (Rb)	10	0.00010	0.00079	0.00280	0.00091	114
	Antimony (Sb)	10	0.00014	0.00068	0.00170	0.00055	81
	Selenium (Se)	10	<0.0003	-	0.00060	-	-
	Tin (Sn)	10	0.00003	0.00700	0.01960	0.00709	101
	Strontium (Sr)	10	0.00090	0.00486	0.01450	0.00439	90
	Tantalum (Ta)	10	<0.00001	-	<0.00006	-	-
	Tellurium (Te)	10	<0.00002	-	<0.00021	-	-
	Thallium (Tl)	10	<0.00001	-	0.00001	-	-
	Uranium (U)	10	0.00005	0.00016	0.00050	0.00013	82
	Vanadium (V)	10	0.00020	0.00098	0.00400	0.00122	124
	Yttrium (Y)	10	0.00001	0.00012	0.00030	0.00010	87
	Tungsten (W)	10	<0.0002	-	0.00280	-	-
	Zinc (Zn)	11	0.01790	0.08959	**0.16900**	0.05164	58
	Zirconium (Zr)	10	<0.00004	-	0.00053	-	-

Figure 5.
Statistics of the results of physical-chemical analysis of rainwater collected from the meteorological station near the SPS medical spa.

pH-Potentiometry, C-conductimetry, A_T-acid/base volumetry; Na^+ and K^+ by Atomic Absorption Spectrometry, the Ca^{2+}, Mg^{2+}, and Li^+, by Inductive Plasma Emission Spectrometry, Fe^{2+} by Plasma Spectrometry; Cl^-, F^- and SO_4^{2-} by Ion Chromatography, SiO_2, NO_3^-, NO_2^-, NH_4^+, and $H_2PO_4^-$ by Molecular Absorption Spectrometry; metals and Boron by Inductively Coupled Plasma Mass Spectrometry; other elements, were evaluated by calculation, as is the case of: HCO_3^-, H_T and M_T.

3. Results and interpretation

3.1 Water quality in the climatological station—Rainwater

The results of all the physical-chemical analyses of the water collected in the container associated with the climatological station are presented in detail in **Table 2**, and their results in statistical terms together with consequent bar diagrams are presented in **Figure 5**.

From the results, the very low total mineralization is highlighted, as would be expected, but the fact that they have great oscillation in their quality is emphasized, with total mineralization ranging from 2.2 to 24.4 mg/L, and the majority ions having SD_R generally greater than 80%. These situations point to the fact that its chemical composition changes over time with some significance in relative terms. Regarding the majority ionic species, the predominance of the anion Cl^- and the cations Na^+ and Ca^{2+} is noteworthy, indicating its proximity to the Atlantic Ocean.

The pH is the only parameter that apparently shows relative stability (SD_R = 9%), corresponding to acidic waters. In the trace elements, we emphasize the fact verified for the elements: Ba, Co, Cd, and V, with $SD_R \geq 124\%$. These elements may have an intermittent origin, but even so, it should be noted that they are potentially very toxic to human health. The case of Ba presents a very singular and worrying situation; overall, it presents SD_R = 255% (**Figure 5**), reaching a value of 1.8 mg/L, which corresponds to the second most representative element, after Cl^- with 2.9 mg/L (analysis of March 2007, **Table 2**). Ba is reported to be a chemical element of the alkali-earth metal family, soft, silvery in appearance, with a high melting point and toxic [13]. Ba is mainly used in spark plugs, vacuum tubes, pyrotechnic rockets, and in fluorescent lamps, besides other uses such as in barium sulphate for white pigment in paintings and in glass, and also as barium carbonate in rat poison. The negative presence of Al, Zn, Cu, Pb, among others, should also be pointed out, with Al, for example, reaching values of 0.325 mg/L, which is higher than the parametric limit for drinking water [14].

3.2 Surface runoff water quality

The results of all the physical-chemical analyses of surface runoff water collected from the simple and composite samplers are presented in detail in **Tables 3** and **4** respectively, and their results in statistical terms together with consequent bar diagrams are presented in **Figures 6** and **7,** respectively.

From the outset it should be noted that in global terms there are no significant differences between the waters of the simple sampler and the composite sampler. The pH has in average terms almost the same value, with pH = 7.05 in the simple samples and pH = 7.09 in the composite samples. The total mineralization, also in average terms presents almost the same value, with M_T = 146.68 mg/L, in the plain samples

Date*		**2006 Dec**	**2007 Jan**	**2007 Feb**	**2007 Mar**	**2007 Apr**	**2007 May**	**2007 Jun**	**2007 Jul**	**2007 Oct**	**2007 Dec**	**2008 Mar**	**2008 Oct**
pH		5.40	5.55	5.81	5.28	5.93	5.41	5.62	5.21	5.23	4.87	4.74	4.17
C (μS/cm)		28.9	29.5	8.0	14.0	75.0	12.0	64.0	63.0	13.0	11.0	26.0	40.0
A_T (in HCl 0.1 N-mL/L)		<1	1.0	0.3	<0.1	—	<0.05	0.1	0.1	0.1	0.1	<0.2	<0.05
H_T (in p.p.10^5 $CaCO^3$)		1.8	4.3	0.2	0.2	2.2	0.4	1.5	0.14	—	0.2	0.3	—
Silica-SiO_2 (mg/L)		<0.3	0.4	0.2	0.3	1.1	<0.9	1.0	<0.9	<0.9	<0.9	0.4	0.9
M_T (mg /L)		13.0	14.0	7.0	6.9	—	6.7	24.4	2.2	—	3.5	11.5	—
Cations (mg/L)	Na^+	3.5	1.5	0.9	1.6	4.9	0.4	2.5	0.2	0.2	0.4	2.9	0.7
	Ca^{2+}	0.14	1.3	0.9	0.5	7.4	1.6	4.8	0.5	1.0	0.8	0.7	1.8
	K^+	0.1	0.2	0.2	0.1	1.2	0.2	0.4	<0.04	0.1	0.1	0.1	0.3
	Mg^{2+}	0.4	0.3	0.2	0.2	0.9	0.1	0.9	0.04	0.1	0.1	0.4	0.3
	NH_4^+	0.13	1.2	0.11	—	1.64	<0.04	—	—	<0.05	0.05	0.05	<0.05
	Fe^{2+}	<0.03	<0.03	<0.03	—	0.04	<0.10	0.20	<0.05	<0.05	<0.03	0.03	0.10
Anions (mg/L)	HCO_3^-	<1	1.2	1.8	<0.3	—	0.3	0.6	0.6	0.3	0.6	0.5	<0.03
	Cl^-	7.0	2.8	2.0	2.9	9.8	2.0	9.2	0.5	0.6	1.1	5.8	2.8
	SO_4^{2-}	1.2	3.1	0.5	0.8	4.4	1.2	3.6	0.3	0.7	0.5	1.1	1.0
	F^-	<0.1	<0.1	<0.07	<0.07	0.53	<0.07	0.2	<0.07	<0.07	<0.07	0.1	0.1
	NO_3^-	<0.3	2.3	0.2	0.5	1.8	0.9	1.1	<0.12	<0.12	<0.12	<0.12	<0.11
	NO_2^-	0.026	0.07	0.011	0.0	0.1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.1
	$H_2PO_4^-$	—	—	<0.13	<0.13	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15
Trace Elements (mg/L) $x10^{-3}$	Ag	—	—	<0.07	0.20	<0.3	<0.2	<0.05	<0.2	<0.2	<0.1	<0.5	0.57
	Al	—	—	11	10	101	39	211	36.8	115.5	51	40.1	325
	As	<1	<1	<0.2	1.1	0.5	5.4	0.6	<0.8	0.30	<0.2	0.40	<0.69

Date*		2006 Dec	2007 Jan	2007 Feb	2007 Mar	2007 Apr	2007 May	2007 Jun	2007 Jul	2007 Oct	2007 Dec	2008 Mar	2008 Oct
	B	—	—	1.80	—	8.0	3.1	11.4	1.3	3.0	2.0	4.4	9.7
	Ba	—	—	33.7	1821	23.8	11.3	54.3	15.5	21.9	27.8	22.2	71.1
	Be	—	—	0.01	0.02	0.04	0.01	0.05	<0.04	0.03	<0.06	<0.1	0.07
	Bi	—	—	<0.01	<0.01	<0.05	<0.02	<0.03	<0.01	0.01	0.01	<0.01	<0.06
	Cd	—	—	0.12	0.14	0.19	0.20	1.91	0.60	0.80	0.07	0.07	0.25
	Co	—	—	0.03	0.06	6.0	0.14	0.78	0.07	0.32	0.10	0.12	0.27
	Cr	—	—	<0.2	0.10	<1	0.10	0.70	<0.3	0.30	0.20	0.20	0.76
	Cs	—	—	0.04	0.10	0.09	0.05	0.11	<0.02	0.06	0.10	0.03	0.59
	Cu	—	4	0.60	1.50	7.60	2.10	11.20	1.10	2.20	5.20	1.20	5.40
	Hg	—	—	<0.05	0.08	0.10	0.05	0.07	<0.03	<0.05	<0.05	<0.1	<0.18
	Li	—	—	0.2	0.2	2.3	0.6	3.3	0.5	0.1	0.9	1.0	1.6
	Mn	—	—	1.00	1.20	19.70	5.20	0.20	1.40	9.80	5.40	4.10	12.90
	Mo	—	—	<0.02	<0.1	0.37	0.13	0.13	<0.3	0.03	0.02	0.01	0.07
	Nb	—	—	<0.02	<0.04	0.01	<0.01	0.01	<0.02	<0.02	<0.01	<0.02	<0.06
	Ni	—	—	0.20	0.30	3.30	0.80	4.50	0.50	1.00	0.40	<0.6	1.40
	Pb			0.17	0.27	0.41	0.27	1.10	0.39	0.88	0.48	0.41	1.90
	Rb	—	—	0.19	0.10	2.80	0.70	2.28	0.10	0.40	0.30	0.30	0.75
	Sb	—	—	0.16	0.14	1.61	0.40	1.70	0.24	0.58	0.34	0.55	1.10
	Se	—	—	<0.3	0.60	0.60	<0.5	<0.3	<0.8	<0.4	<0.3	<0.4	<0.4
	Sn	—	—	0.03	1.02	14.60	2.69	19.60	3.10	5.28	2.42	2.91	18.30
	Sr	—	—	1.40	2.00	14.50	2.90	11.80	0.90	4.90	0.90	3.20	5.10
	Ta	—	—	<0.02	<0.01	<0.01	<0.01	<0.05	<0.03	<0.01	<0.01	<0.02	<0.06

Date*		2006 Dec	2007 Jan	2007 Feb	2007 Mar	2007 Apr	2007 May	2007 Jun	2007 Jul	2007 Oct	2007 Dec	2008 Mar	2008 Oct
	Te	—	—	<0.03	<0.04	<0.04	<0.03	<0.08	<0.02	<0.03	<0.03	<0.1	<0.21
	Tl	—	—	0.01	<0.1	<0.02	<0.02	<0.05	<0.01	<0.02	0.01	<0.02	0.01
	U	—	—	0.10	0.05	0.20	0.08	0.50	0.05	0.22	0.10	0.07	0.21
	V	—	—	0.30	0.22	4.00	0.60	2.59	0.26	0.50	0.20	0.23	0.93
	Y	—	—	0.02	0.01	0.18	0.30	0.27	0.03	0.13	0.04	0.03	0.18
	W	—	—	<0.2	0.10	2.20	0.50	2.80	<0.4	<0.3	<0.2	0.30	0.21
	Zn		140.0	36.9	17.9	126.3	85.0	160.1	32.4	110.0	53.3	54.6	169.0
	Zr	—	—	<0.3	<0.04	0.37	<0.06	0.40	<0.10	0.30	<0.12	<0.20	0.53

**besides the dates on which rainwater was collected, other intermediate dates were also planned, but because in that period there was no rain, or in some cases technical and logistical problems occurred, the sampling was not effectively monthly sequential.*

Table 2.
Chemical composition of rainwater from the meteorological station near to the SPS medical spa, over time.

Date*		2006 Oct	2007 Jan	2007 Feb	2007 Mar	2007 Jun	2007 Jul	2007 Aug	2007 Sep	2007 Oct	2007 Dec	2008 Mar
pH		7.02	7.08	6.71	6.87	6.81	6.75	7.44	7.52	7.01	7.24	7.1
C (μS/cm)		94.9	215.0	137.0	61.0	101.0	120.0	226.0	296.0	251.0	193.0	184.0
A_T (in HCl 0.1 N-mL/L)		—	—	3.2	5.4	5.9	8.2	20.8	28.7	20.1	9.0	7.7
H_T (in p.p.10^5 $CaCO^3$)		40.0	88.0	5.4	2.8	3.2	4.6	10.9	14.0	11.1	8.7	8.7
Silica-SiO_2 (mg/L)		6.8	8.0	5.5	4.3	10.4	4.9	17.0	25.2	9.3	7.6	7.3
M_T (mg/L)		86.0	165.0	99.7	56.3	84.0	100.0	211.0	291.0	223.0	153.5	144.0
Cations (mg/L)	Na^+	3.0	3.7	1.4	1.9	7.1	3.0	5.8	5.4	3.0	1.7	1.0
	Ca^{2+}	13.9	32.0	20.2	9.3	10.5	16.4	40.3	49.9	41.0	32.5	32.8
	K^+	3.2	6.1	5.5	1.7	2.0	7.7	3.8	11.5	13.1	3.6	1.8
	Mg^{2+}	1.2	1.9	0.64	0.8	1.2	1.1	2.0	3.5	2.0	1.4	1.1
	NH_4^+	0.13	<0.05	0.05	—	—	—	<0.05	<0.05	<0.05	<0.05	0.001
	Fe^{2+}	0.03	<0.03	<0.03	<0.03	0.05	<0.05	<0.05	<0.03	0.10	< 0.03	< 0.03
Anions (mg/L)	HCO_3^-	47.4	68.5	19.5	32.9	36.0	50.0	127.0	175.0	123.0	54.9	47.0
	Cl^-	3.4	7.5	1.6	1.4	8.2	2.5	6.0	6.6	5.3	1.2	4.6
	SO_4^{2-}	5.8	35.0	35.2	2.3	5.0	11.0	5.5	6.9	16.4	32.5	27.7
	F^-	0.3	0.2	0.1	0.2	< 0.12	0.2	0.35	0.3	0.2	0.2	0.1
	NO_3^-	—	2.0	9.8	1.3	3.2	2.7	2.7	4.7	7.5	17.3	20.0
	NO_2^-	—	<0.01	<0.005	<0.005	<0.001	0.03	<0.01	<0.01	<0.01	0.001	0.001
	$H_2PO_4^-$	—	—	0.2	0.18	0.26	0.44	0.23	1.03	1.30	0.66	0.52
Trace Elements (mg/L) $x10^{-3}$	Ag	—	—	<0.07	0.10	<0.05	0.05	0.70	0.03	< 0.02	<0.1	<0.05
	Al	—	—	10.50	55.00	8.00	48.40	35.00	26.40	8.10	7.00	4.50
	As	7.1	13.0	8.50	6.40	5.00	9.00	12.00	38.60	12.30	8.00	8.70
	B	—	—	10.6	8.00	9.80	17.5	20.9	35.0	24.0	16.0	15.8

Date*		2006 Oct	2007 Jan	2007 Feb	2007 Mar	2007 Jun	2007 Jul	2007 Aug	2007 Sep	2007 Oct	2007 Dec	2008 Mar
	Ba	—	—	25.0	519.0	19.3	19.5	46.5	40.0	20.0	35.2	186.0
	Be	—	—	0.01	0.02	<0.02	<0.04	<0.03	0.05	<0.01	<0.06	<0.1
	Bi	—	—	<0.01	0.04	<0.03	<0.01	<0.01	0.02	<0.01	<0.01	<0.01
	Cd	<0.1	<0.1	0.08	11.90	0.13	0.12	0.13	0.66	0.03	0.02	0.13
	Co	—	—	0.07	0.02	0.03	0.03	0.08	0.19	<0.03	0.03	0.12
	Cr	—	—	0.50	2.10	0.90	3.20	1.00	0.80	0.60	0.70	1.40
	Cs	—	—	0.49	0.20	0.21	0.63	0.38	0.64	0.28	0.10	0.16
	Cu	5.0	2.0	4.00	2.60	1.70	3.80	1.60	9.30	3.50	2.50	1.90
	Hg	—	—	<0.05	0.06	<0.05	<0.03	<0.03	0.03	<0.05	<0.05	<0.1
	Li	—	—	13.8	1.5	2.5	4.6	3.3	7.4	4.5	7.7	19.4
	Mn	—	—	0.40	0.40	0.30	0.40	0.30	0.30	0.57	0.20	0.30
	Mo	—	—	0.77	1.20	1.09	3.10	4.00	4.25	3.70	1.35	1.72
	Nb	—	—	<0.02	<0.01	<0.01	<0.02	<0.04	0.02	<0.02	<0.01	<0.02
	Ni	—	—	1.00	0.40	<0.4	<0.1	<0.1	100	<1.0	<0.2	1.0
	Pb			0.09	0.21	0.10	1.11	0.11	0.07	0.25	0.30	0.07
	Rb	—	—	17.98	4.00	5.88	20.00	10.80	26.10	23.50	8.20	6.20
	Sb	—	—	1.02	0.61	0.73	0.78	0.69	0.56	1.48	1.37	1.52
	Se	—	—	<0.3	<0.6	<0.3	<0.8	<0.6	0.80	<0.4	<0.3	<0.4
	Sn	—	—	0.03	0.13	0.63	0.05	0.08	0.03	0.06	0.03	0.04
	Sr	—	—	50.60	20.20	32.20	38.00	79.10	144.0	76.60	82.60	69.10
	Ta	—	—	<0.02	<0.01	<0.05	<0.03	<0.05	0.01	<0.01	<0.01	<0.02
	Te	—	—	<0.03	<0.04	<0.08	<0.02	<0.05	0.03	<0.03	<0.03	<0.1
	Tl	—	—	0.02	0.01	—	0.02	0.02	0.01	0.03	0.02	0.02

Date*		2006 Oct	2007 Jan	2007 Feb	2007 Mar	2007 Jun	2007 Jul	2007 Aug	2007 Sep	2007 Oct	2007 Dec	2008 Mar
	U	—	—	0.80	1.97	0.45	1.48	11.30	8.22	2.14	1.31	0.76
	V	—	—	1.60	1.14	1.46	2.06	1.90	1.30	2.20	2.80	2.67
	Y	—	—	0.03	0.08	0.05	0.10	0.02	0.06	0.05	0.01	0.01
	W	—	—	0.20	0.40	0.40	0.70	1.30	1.70	0.61	0.60	0.70
	Zn	—	—	127.7	9.50	7.50	6.20	37.7	29.6	4.40	11.8	35.6
	Zr	—	—	<0.3	<0.04	<0.1	0.12	<0.2	0.17	<0.2	<0.12	<0.2

**besides the dates on which surface runoff water was collected, other intermediate dates were also planned, but because it had not rained in that period, or in some cases technical and logistical problems occurred, the sampling was not effectively monthly sequential.*

Table 3.
Chemical composition of surface runoff water, in simple sampler, in the rainwater sewerage system of Thermas garden street, next to the SPS medical spa, over time.

Date*		2006 Oct	2007 Jan	2007 Feb	2007 Mar	2007 Jun	2007 Jul	2007 Aug	2007 Sep	2007 Oct	2007 Dec	2008 Mar
pH		7.24	7.09	6.92	6.96	6.87	7.07	7.46	7.16	7.23	6.88	7.12
C (μS/cm)		115.0	221.0	136.0	76.0	106.0	134.0	190.0	239.0	290.0	205.0	182.0
A_T (in HCl 0.1 N-mL/L)		46.1	58.3	4.8	6.4	6.1	11.2	15.5	18.4	19.8	12.0	9.9
H_T (in p.p.10^5 $CaCO_3$)		48.0	92.0	5.5	3.5	3.3	5.9	8.2	10.1	12.9	9.3	8.7
SiO_2 (mg/L)		7.9	8.1	5.7	4.2	10.6	9.5	14.5	15.4	14.1	9.5	8.1
M_T (mg/L)		101.0	169.0	102.7	66.3	86.9	119.5	169.3	212.0	255.0	170.1	148.8
Cations (mg/L)	Na^+	3.2	3.5	1.5	1.9	7.6	3.2	5.4	4.7	4.5	2.2	1.2
	Ca^{2+}	16.8	34.0	20.8	12.1	11.1	21.2	30.0	36.0	45.8	34.0	32.6
	K^+	3.7	5.7	5.5	2.1	1.9	4.3	3.8	11.6	13.0	4.4	2.3
	Mg^{2+}	1.4	1.7	0.75	0.9	1.2	1.4	1.7	2.7	3.5	1.9	1.3
	NH_4^+	<0.05	0.05	<0.05	—	—	—	<0.05	<0.05	<0.05	<0.05	0.04
	Fe^{2+}	<0.03	<0.03	<0.03	<0.03	<0.05	<0.05	<0.05	<0.03	0.10	<0.03	<0.03
Anions (mg/L)	HCO_3^-	56.2	71.1	29.3	39.0	37.2	68.3	94.6	112.0	121.0	73.2	60.4
	Cl^-	3.1	7.5	1.6	1.5	8.7	2.7	5.4	5.9	6.7	1.8	3.4
	SO_4^{2-}	8.1	35.0	29.3	3.0	4.5	7.0	7.5	14.3	25.0	25.9	21.1
	F^-	0.4	0.2	0.1	0.2	<0.12	0.3	0.3	0.2	0.4	0.2	0.1
	NO_3^-	0.3	1.9	8.1	1.4	3.8	1.4	5.4	8.8	18.9	16.4	17.8
	NO_2^-	<0.01	0.023	0.01	<0.005	<0.01	<0.01	<0.01	—	<0.01	0.01	0.01
	$H_2PO_4^-$	—	—	<0.13	<0.13	0.27	0.22	0.7	1.15	1.64	0.63	0.43
Trace Elements (mg/L) x10^{-3}	Ag	—	—	<0.07	0.10	<0.05	0.03	0.05	0.05	<0.02	<0.1	<0.05
	Al	—	—	6.20	14.00	6.20	21.40	30.00	10.10	13.10	6.00	7.10
	As	40.0	11.0	8.30	7.40	6.10	18.90	13.40	30.00	18.20	10.50	8.70
	B	—	—	11.80	9.00	9.60	18.50	19.60	28.20	39.00	23.00	16.20

Date*		2006 Oct	2007 Jan	2007 Feb	2007 Mar	2007 Jun	2007 Jul	2007 Aug	2007 Sep	2007 Oct	2007 Dec	2008 Mar
	Ba	—	—	15.50	300.0	12.90	12.20	23.80	29.90	21.40	20.50	22.90
	Be	—	—	<0.01	0.01	<0.02	<0.04	<0.03	0.05	0.01	<0.06	<0.1
	Bi	—	—	<0.01	<0.01	<0.03	<0.01	<0.01	0.02	<0.01	<0.01	<0.01
	Cd	—	—	0.04	0.02	0.11	0.06	0.12	0.18	0.03	0.02	0.04
	Co	—	—	0.06	0.02	0.03	0.03	0.05	0.05	0.11	0.05	0.13
	Cr	—	—	0.70	1.50	0.50	2.20	1.30	0.05	2.30	1.30	1.70
	Cs	—	—	0.45	0.20	0.23	0.43	40.00	0.65	0.43	0.20	0.16
	Cu	5.00	2.00	1.30	1.60	1.40	2.20	3.00	4.30	4.80	2.50	1.80
	Hg	—	—	<0.05	0.05	< 0.05	<0.03	<0.03	<0.02	<0.05	<0.05	<0.1
	Li	—	—	13.2	1.7	2.8	2.6	2.7	5.6	4.9	7.1	15.2
	Mn	—	—	0.70	0.20	0.20	0.40	0.30	0.40	0.14	0.20	0.20
	Mo	—	—	0.87	1.40	0.97	5.20	3.27	4.39	5.58	1.69	1.48
	Nb	—	—	<0.02	<0.01	<0.01	<0.02	<0.04	0.02	<0.02	<0.01	<0.02
	Ni	—	—	0.80	<0.1	<0.4	<0.1	<0.1	<0.6	<1.0	<0.2	0.70
	Pb	—	—	0.08	0.08	0.10	0.27	0.09	0.06	0.19	0.08	0.06
	Rb	—	—	17.38	5.10	5.91	11.50	11.70	268.0	28.60	11.10	7.10
	Sb	—	—	0.54	0.06	0.55	0.92	1.28	0.81	1.37	1.20	1.27
	Se	—	—	<0.3	<0.6	<0.3	<0.8	<0.6	0.80	<0.4	<0.3	<0.4
	Sn	—	—	0.03	0.06	0.39	0.03	0.36	0.04	0.05	0.03	0.07
	Sr	—	—	51.90	25.50	33.10	45.60	66.30	97.70	65.30	88.20	73.40
	Ta	—	—	<0.02	<0.01	<0.05	<0.03	<0.05	<0.01	<0.01	<0.01	<0.02
	Te	—	—	<0.03	<0.04	<0.08	<0.02	<0.05	<0.03	<0.03	<0.03	<0.1
	Tl	—	—	0.02	0.01	0.05	0.01	0.03	0.02	0.03	0.02	0.02

Date*		2006 Oct	2007 Jan	2007 Feb	2007 Mar	2007 Jun	2007 Jul	2007 Aug	2007 Sep	2007 Oct	2007 Dec	2008 Mar
	U	—	—	1.00	3.37	0.52	5.49	6.40	4.71	5.87	1.82	1.09
	V	< 20.0	< 20.0	1.60	1.20	1.50	2.05	3.90	2.20	2.60	2.40	2.28
	Y	—	—	0.02	0.04	0.05	0.06	0.02	0.02	0.08	0.02	0.01
	W	—	—	0.20	0.30	0.40	0.80	0.09	1.50	0.82	0.60	0.50
	Zn	—	—	84.30	7.50	7.90	4.60	31.70	11.60	4.50	8.70	13.10
	Zr	—	—	<0.3	<0.04	<0.1	<0.1	<0.2	0.17	0.20	< 0.12	<0.2

**besides the dates on which surface runoff water was collected, other intermediate dates were also planned, but because it had not rained in that period, or in some cases technical and logistical problems occurred, the sampling was not effectively monthly sequential.*

Table 4.
Chemical composition of surface runoff water, in the composite sampler, in the rainwater sewerage system of Thermas garden street, next to the SPS medical spa, over time.

Parameter		N	Min	Ave	Max	SD	SD_R (%)
pH		11	6.71	7.05	7.52	0.25	4
Conductivity - C (µS/cm)		11	61.00	170.81	296.00	70.19	41
Total Alkalinity - A_T (in HCl 0.1N - mL/L)		9	3.20	12.11	28.70	8.31	69
Total Hardness - H_T (in p.p.10^5 $CaCO_3$)		11	2.80	17.95	88.00	24.23	135
Sílica - SiO_2 (mg/L)		11	4.30	9.66	25.20	5.92	61
Total Mineralization-M_T (mg /L)		11	56.30	146.68	291.00	68.32	47
C	Sodium (Na^+)	11	1.00	3.36	7.10	1.88	56
a	Calcium (Ca^{2+})	11	9.30	27.16	49.90	13.15	48
t	Potassium (K^+)	11	1.70	5.45	13.10	3.71	68
i	Magnesium (Mg^{2+})	11	0.64	1.53	3.50	0.77	50
o	Lithium (Li^+)	9	0.0015	0.0072	0.0194	0.0055	77
n	Ammonium (NH_4^+)	8	<0.05	-	0.13	-	-
(mg/L)	Iron (Fe^{2+})	11	<0.03	-	0.10	-	-
A	Bicarbonate (HCO_3^-)	11	19.50	71.02	175.00	46.54	66
n	Chloride (Cl^-)	11	1.20	4.39	8.20	2.41	55
i	Sulphate (SO_4^{2-})	11	2.30	16.66	35.20	12.67	76
o	Fluoride (F^-)	11	<0.12	-	0.35	-	-
n	Nitrate (NO_3^-)	10	1.30	7.12	20.00	6.30	89
(mg/L)	Nitrite (NO_2^-)	10	<0.001	-	0.03	-	-
	Fhosphates ($H_2PO_4^-$)	9	0.18	0.54	1.30	0.37	70
	Silver (Ag)	10	<0.00005	-	0.00070	-	-
	Aluminium (Al)	9	0.00450	0.02254	**0.05500**	0.01833	81
	Arsenic (As)	11	0.00500	0.01169	0.03860	0.00884	76
T	Boron (B)	9	0.00800	0.01751	0.03500	0.00790	45
r	Barium (Ba)	9	0.01930	0.10117	**0.51900**	0.15586	154
a	Beryllium (Be)	9	<0.00001	-	0.00005	-	-
c	Bismuth (Bi)	9	<0.00001	-	0.00004	-	-
e	Cadmium (Cd)	11	<0.0001	-	**0.01190**	-	-
	Cobalt (Co)	9	<0.00003	-	0.00019	-	-
e	Chromium (Cr)	9	0.00050	0.00124	0.00320	0.00083	67
l	Cesium (Cs)	9	0.00010	0.00034	0.00064	0.00019	56
e	Copper (Cu)	11	0.00160	0.00345	0.00930	0.00212	62
m	Mercury (Hg)	9	<0.00003	-	0.00006	-	-
e	Manganese (Mn)	9	0.00020	0.00035	0.00057	0.00010	28
n	Molybdenum (Mo)	9	0.00077	0.00235	0.00425	0.00131	56
t	Niobium (Nb)	9	<0.00001	-	0.00002	-	-
s	Nickel (Ni)	9	<0.0001	-	**0.10000**	-	-
(mg/L)	Lead (Pb)	9	0.00007	0.00026	0.00111	0.00031	122
	Rubidium (Rb)	9	0.00400	0.01363	0.02610	0.00787	58
	Antimony (Sb)	9	0.00056	0.00097	0.00152	0.00036	37
	Selenium (Se)	9	<0.0003	-	0.00080	-	-
	Tin (Sn)	9	0.00003	0.00012	0.00063	0.00018	152
	Strontium (Sr)	9	0.02020	0.06582	**0.14400**	0.03482	53
	Tantalum (Ta)	9	<0.00001	-	0.00001	-	-
	Tellurium (Te)	9	<0.00002	-	0.00003	-	-
	Thallium (Tl)	8	0.00001	0.00002	0.00003	0.00001	32
	Uranium (U)	9	0.00045	0.00316	**0.01130**	0.00364	115
	Vanadium (V)	9	0.00114	0.00190	0.00280	0.00055	29
	Yttrium (Y)	9	0.00001	0.00005	0.00010	0.00003	65
	Tungsten (W)	9	0.00020	0.00073	0.00170	0.00045	61
	Zinc (Zn)	9	0.00440	0.03000	**0.12770**	0.03669	122
	Zirconium (Zr)	9	<0.00004	-	0.00017	-	-

Figure 6.
Statistics of the results of physical-chemical analysis of water collected in the simple sampler, from surface runoff water at Thermas garden street, near the SPS medical spa, at different times of the year.

Parameter		N	Min	Ave	Max	SD	SD_R (%)
pH		11	6.87	7.09	7.46	0.17	2
Conductivity - C (µS/cm)		11	76.00	172.18	290.00	61.71	36
Total Alkalinity - A_T (in HCl 0.1N - mL/L)		11	4.80	18.95	58.30	16.55	87
Total Hardness - H_T (in p.p.10^5 of $CaCO_3$)		11	3.30	18.85	92.00	26.01	138
Sílica - SiO_2 (mg/L)		11	4.20	9.78	15.40	3.44	35
Total Mineralization – M_T (mg /L)		11	66.30	145.51	255.00	54.22	37
C	Sodium (Na^+)	11	1.20	3.54	7.60	1.82	52
a	Calcium (Ca^{2+})	11	11.10	26.76	45.80	10.54	39
t	Potassium (K^+)	11	1.90	5.30	13.00	3.52	66
i	Magnesium (Mg^{2+})	11	0.75	1.68	3.50	0.76	45
o	Lithium (Li^+)	9	0.0017	0.0062	0.0152	0.0046	74
n	Ammonium (NH_4^+)	8	<0.05	-	0.05	-	-
(mg/L)	Iron (Fe^{2+})	11	<0.03	-	0.10	-	-
A	Bicarbonate (HCO_3^-)	11	29.30	69.30	121.00	28.53	41
n	Chloride (Cl^-)	11	1.50	4.39	8.70	2.44	55
i	Sulphate (SO_4^{2-})	11	3.00	16.43	35.00	10.71	65
o	Fluoride (F^-)	11	< 0.12	-	0.40	-	-
n	Nitrate (NO_3^-)	11	0.30	7.65	18.90	6.69	87
(mg/L)	Nitrite (NO_2^-)	10	<0.005	-	0.023	-	-
	Fhosphates ($H_2PO_4^-$)	9	<0.13	-	1.64	-	-
	Silver (Ag)	9	<0.00002	-	0.00010	-	-
	Aluminium (Al)	9	0.00600	0.01268	0.03000	0.00778	61
	Arsenic (As)	11	0.00610	0.01568	0.04000	0.01014	65
T	Boron (B)	9	0.00900	0.01943	0.03900	0.00911	47
r	Barium (Ba)	9	0.01220	0.05101	**0.30000**	0.08819	173
a	Beryllium (Be)	9	<0.00001	-	0.00005	-	-
c	Bismuth (Bi)	9	<0.00001	-	0.00002	-	-
e	Cadmium (Cd)	9	0.00002	0.00007	0.00018	0.00005	76
	Cobalt (Co)	9	0.00002	0.00006	0.00013	0.00004	60
e	Chromium (Cr)	9	0.00005	0.00128	0.00230	0.00071	56
l	Cesium (Cs)	9	0.00016	0.00475	0.04000	0.01246	262
m	Copper (Cu)	11	0.00130	0.00272	0.00500	0.00131	48
e	Mercury (Hg)	9	<0.00002	-	0.00005	-	-
n	Manganese (Mn)	9	0.00014	0.00030	0.00070	0.00017	54
t	Molybdenum (Mo)	9	0.00087	0.00276	0.00558	0.00177	64
s	Niobium (Nb)	9	<0.00001	-	0.00002	-	-
	Nickel (Ni)	9	<0.0001	-	0.00080	-	-
(mg/L)	Lead (Pb)	9	0.00006	0.00011	0.00027	0.00007	60
	Rubidium (Rb)	9	0.00510	0.04071	**0.26800**	0.08064	198
	Antimony (Sb)	9	0.00006	0.00089	0.00137	0.00042	47
	Selenium (Se)	9	<0.0003	-	0.00080	-	-
	Tin (Sn)	9	0.00003	0.00012	0.00039	0.00014	117
	Strontium (Sr)	9	0.02550	0.06078	**0.09770**	0.02272	37
	Tantalum (Ta)	9	<0.00001	-	<0.00005	-	-
	Tellurium (Te)	9	<0.00002	-	<0.0001	-	-
	Thallium (Tl)	9	0.00001	0.00002	0.00005	0.00001	49
	Uranium (U)	9	0.00052	0.00336	0.00640	0.00219	65
	Vanadium (V)	9	0.00120	0.00219	0.00390	0.00074	34
	Yttrium (Y)	9	0.00001	0.00004	0.00008	0.00002	62
	Tungsten (W)	9	0.00009	0.00058	0.00150	0.00040	69
	Zinc (Zn)	9	0.00450	0.01932	**0.08430**	0.02425	126
	Zirconium (Zr)	9	<0.00004	-	0.00017	-	-

Figure 7.
Statistics of the results of physical-chemical analysis of water collected in the composite sampler, from surface runoff water at Thermas garden street, near the SPS medical spa, at different times of the year.

and M_T = 145.51 mg/L in the composite samples. The majority ionic composition in average terms, in both situations the three main cations and anions follow the same order, that is: $Ca^{2+} > > K^+ > Na^+$, and $HCO_3^- > SO_4^{2-} > NO_3^-$, respectively. In relation to trace elements, in both situations Ba and Sr. appear as predominant elements, and others with relatively significant values such as Rb, Zn, B, Al and As.

When comparing the two sets in terms of simple and composite samples, for the maximum values, it is worth noting that there are some slight differences, as for example in the M_T. The waters from the simple samples are slightly more mineralized (M_T = 291.0 mg/L) than the waters from the composite samples (M_T = 255 mg/L). Note that the simple samples are a consequence of the water from the first rainfall while the composite samples correspond to water not only from the first rainfall but from others collected over time. In principle, the first runoff tends to be more mineralized, as they are the ones that first come into contact with heavily polluted surfaces.

From the point of view of the stability of the various chemical elements in this type of water over time, significant changes can be noted from sample to sample; the majority of the elements, both major and trace, present SD_R greater than 50%, showing great changes over time. The most serious situations were observed for Ba, Sn and Zn in both types of samples (SD_R of 117 to 173%), as well as for Pb and U in the simple samples with SD_R of 122 and 115%, respectively, and finally, the cases of Cs and Rb, in the composite samples, with SD_R of 262 and 198%, respectively. In addition to the previous situation, there are cases in which it was not possible to perform total statistics because in most of the surveys some elements appear below the detection limit, and occasionally occur with relatively significant values, examples being Ni and Cd in the simple samples.

In comparative terms with rainwater quality, the following should be noted at the outset: (i) surface runoff water has a much higher pH than rainwater, as the latter have an essentially acidic character ($pH_{ave\text{-}rainwater}$ = 5.27), and surface runoff water have much higher values ($pH_{ave\text{-}surface\text{-}runoff} \cong 1.34 pH_{ave\text{-}rainwater}$ = 7.06), with a neutral character; (ii) surface runoff water has a much higher total mineralization than rainwater, which in average terms is: $M_{T\text{-}ave\text{-}surface\text{-}runoff} \cong 14.75 M_{T\text{-}ave\text{-}rainwater}$ = 146.2 mg/L; (iii) rainwater has almost zero values for Total Alkalinity (A_T), for silica (SiO_2), and even for Total Hardness (H_T), while surface runoff water reaches levels with some significance (maximum values: A_T = 58.3 0 mL/L, SiO_2 = 25.2 mg/L, H_T = 92.0 p.p.10^5 of $CaCO_3$; (iv) in rainwater, the elements of the major ionic component are: Cl^- in the anion, and Na^+ and Ca^{2+} in the cations; in surface runoff water the anions and cations, respectively, predominate in the following elements: $HCO_3^- > SO_4^{2-} > NO_3^-$; and $Ca^{2+} > > K^+ > Na^+$, emphasizing that Cl^- in particular ceases to have meaning and Na^+, never appears as the predominant cation; (v) Phosphate ion ($H_2PO_4^-$) in rainwater never appeared and in surface runoff water became part of the ensemble of anions observed; (vi) regarding the trace elements, it is emphasized the fact that the most representative element in rainwater was Ba, reaching a maximum value of 1.8 mg/L. In surface runoff water, it also continues to be the most representative element, although with slightly lower values, with maximum values of 0.52 mg/L and 0.30 mg/L, in simple and composite samples, respectively; (vii) regarding still other trace elements, as in rainwater, several chemical elements are still present, with particular attention to Zn, which in rainwater reaches 0.169 mg/L and in the simple sample of the surface runoff water reaches 0.130 mg/L; and (viii) about trace elements in surface runoff water, it is also worth noting the fact that these include with some significance Sr. (0.144 mg/L) and Ni (0.10 mg/L) in simple samples, and Rb (0.268 mg/L) in the composite samples, being noteworthy that these elements are not as important in rainwater.

3.3 Comparison between the quality of natural mineral water from the traditional spring and the quality of rainwater and surface runoff water

The chemical quality of NMW from the Traditional Spring (NT) of the SPS medical spa, was already studied by Lepierre in 1903 and 1928, at least in the global parameters and majority ions [5]. However, it was from 1985 onwards that a systematic control over time was carried out, as mentioned in the methodology section. The results obtained over 29 years (1985 to 2014) are presented in statistical terms in **Table 1**. These are in the basis of the present work because as already mentioned in item 1, this systematic control allowed us to verify, in 2005–2006, unusual results of Pb, Zn and Cu, leading to subsequent work, namely the study of the quality of rainwater and surface runoff water, to identify, and annul, or minimize the problem.

From a global point of view, it should be noted that the NMW of the NT (**Table 1**), in a universe of 96 samples over time: the M_T and pH have average values of 359.68 mg/L, and 8.82, respectively, with only SD_R of 2 and 1%, respectively. The rainwater, for those parameters, in average terms, was obtained: M_T = 9.91 mg/L and pH = 5.27, with SD_R of 64 and 9% respectively. The surface runoff water, also in average terms, for the simple samples: M_T = 146.68 mg/L and pH = 7.05, with SD_R of 47 and 4% respectively, and for the composite samples: M_T = 145.51 mg/L and pH = 7.09, with SD_R of 37 and 2% respectively.

It is emphasized the fact that, in global terms, the silica component (in the non-ionized form), in average terms, in NT, presents a SiO_2/M_T ratio = 19%, and with excellent stability (SD_R = 5%), while in rainwater that ratio is null, and in surface runoff water it is about 7%, with very large SD_R. Regarding the majority ions, the NT waters always present HCO_3^- and Na^+ as the most representative anion and cation, respectively, and very stable over time; in this water, the predominance of the ions, are according to the following order, from most to least representative: $HCO_3^- >> Cl^- > F^- > SO_4^{2-}$, for the anions, and $Na^+ >> K^+ > Ca^{2+}$ for the cations. In rainwater, the predominant anions, in average terms, are Cl^- and SO_4^{2-}, although occasionally Cl^- has a lower content than SO_4^{2-}; it should be noted that in these waters the HCO_3^- and F^- anions almost always have negligible contents. Still in rainwater, in terms of cations, the predominant ones are Na^+ and Ca^{2+}, almost with similar levels, and with some significance in relative terms the K^+ and Mg^{2+}.

In the case of surface runoff water in simple and composite samples, HCO_3^- is always the main anion, as it happens in NT waters; on average, $HCO_3^- >> SO_4^{2-} > NO_3^- > Cl^-$, although occasionally, except for HCO_3^-, the sequence is not always the same; still concerning anions, F^- is always present in NT waters, with an average value of 17.71 mg/L, and corresponding SD_R of 3%, and in surface runoff water appears almost without expression, having found the maximum value of F^- = 0.4 mg/L. Still in the case of surface runoff water in simple and composite samples, for the cations in average terms it was verified: $Ca^{2+} > K^+ > Na^+ > Mg^{2+}$, being of note that in the simple samples in fact Ca^{2+} was always the one with the highest content, being that the order of the other elements, in the individual analyses, was not always the same; in the composite samples, that order is always maintained in all the individual samples. Regarding the NT water, the first three cations are also predominant in this water, although in the inverse order ($Na^+ >> K^+ > Ca^{2+}$), being worth mentioning that the NT water does not present Mg^{2+}. Regarding trace elements, the NMW of the NT has a typical ensemble, which is acquired in the extensive path of the water particles, which at the beginning are rainwater, infiltrate the rock mass, and evolve over many kilometers, passing even, along some extensive veins, which are

sometimes rich in singular minerals, namely metals. According to the research already carried out (**Table 1**), the elements that are understood to form part of this ensemble, from the most abundant to the least abundant (using the average content as a reference), are presented in **Table 5**.

It is admitted that other elements, never surveyed so far, may occur, such as, for example, gold (Au). The case of Br was surveyed only three times and always appeared; to confirm order 3, many more surveys will have to be carried out, and to verify that the SD_R is less than 10%. The case of Al appears with a SD_R = 217%, which means that, besides being an element of the typical ensemble of NMW, contamination sometimes occurs because of anthropic actions. A less serious situation is found with the As and the Mn; there is a need to do more research on these elements to ascertain their order, without considering the elements with added anthropic component. The situation of Pb, Zn and Cu, surveyed many times in the studies over time (**Table 1**), are understood not to be part of the ensemble of natural trace elements of the NMW of the NT, as they were recorded many times below the limit of detection (l.d.) as can be seen in **Table 1** and especially in **Table 6**, where the cases of Pb and Cu, 43% of the times surveyed, the result was below the l.d., and Zn only 11% below the l.d., as it is often affected by anthropic actions. Other trace elements that have sometimes been recorded in the NMW of NT, and that in the 2005–2006 season were not of concern, but with the detailed analysis in the present chapter, one gets the notion that there is a great possibility of their occurrence being a consequence of anthropic actions; they are in particular: Ba, Ni, V, Cd, Co and U, since in some cases most of the times situations below the l.d. have been verified (**Table 6**).

For a joint analysis of the trace elements obtained in rainwater and surface runoff water, the chemical elements studied were organized according to the dosages obtained in the NMW of the NT, resulting in **Table 7**, with the elements organized into two large groups:

- *Group I*, which includes the chemical elements understood to be *part of the ensemble of the natural trace elements* of NMW. Crossing the results, of the three

Element	Order	N	min	ave	max	SD	SD_R (%)
Boron (B)	1	51	0.3600	0.4263	0.4760	0.0245	6
Bromide (Br)	2	3	0.1300	0.1750	0.2600	0.0601	34
Tungsten (W)	3	53	0.0370	0.0791	0.0990	0.0101	13
Strontium (Sr)	4	50	0.0570	0.0667	0.0730	0.0032	5
Cesium (Cs)	5	42	0.0460	0.0624	0.0721	0.0043	7
Rubidium (Rb)	6	42	0.0530	0.0590	0.0670	0.0028	5
Aluminium (Al)	7	51	0.0021	0.0437	0.6400	0.0950	217
Arsenic (As)	8	53	0.0030	0.0045	0,0180	0.0022	49
Manganese (Mn)	9	52	0.0013	0.0020	0.0060	0.0009	45
Beryllium (Be)	10	53	0.0003	0.0006	0.0014	0.0002	28

*[*] from **Table 1**; N: number of samples studied, min: minimum, ave.: average, SD: standard deviation, SD_R: relative standard deviation = (SD/ave)x100. Order: 1 is the most abundant, 10 is the least abundant.*

Table 5.
Main trace elements from chemical analyses carried out between 1985 and 2014 of NMW of the NT[*].

Ele.	N	n	l.d. (%)	l.d. (mg/L)	max (mg/L)	Observations
Pb	51	22	43	0.00006	0.0730	max was in 2005/3; from 2006/11 rn
Zn	53	6	11	0.0002	0.2270**	max occurred in 2005/3; from 2007/7 rn
Cu	51	22	43	0.00005	0.0550	max was observed in 2005/3; from 2008/6 rn
Al	51	0	0	—	0.640***	max was observed in 1989/10; it is admitted that from 1998/6 rn
Ba	53	6	11	0.0003	0.0063	max was observed in 2014/4
Ni	52	30	58	0.0002	0.0150	max occurred in 2005/3; from 2005/7 rn
V	53	27	51	0.0002	0.0009	max was observed in 2003/11; in 2005/8 rn
Cd	34	5	15	0.00002	0.0006	max was observed in 2012/1; in 2012/4 rn
Co	53	34	64	0.00001	0.0003	max occurred in 2005/3; in 2005/7 rn
U	47	27	57	0.00002	0.0001	max occurred in 2005/12; in 2006/2 rn

from **Table 1; l.d.: detection limit, l.d (%) = (n/N) × 100, N: number of samples studied, n: number of samples with results < l.d., max: maximum, rn: returned to normal.*
***note: in 2003, Zn = 0.3140 mg/L was punctually observed.*
****it is admitted that NMW, at its origin, has Al contents estimated at around 0.0021 mg/L.*

Table 6.
Detailed aspects of the occurrence of some trace elements in the NMW of the NT.*

types of waters, it is only extracted the clear notion, that the Al, in fact, could be a consequence of relations with the rainwater and surface runoff waters. Such an inference is the result of the high SD_R in the NT water, and the relative abundance of this element sometimes in rainwater and surface runoff water. It is admitted that As and Mn also have some interference with rainwater and surface water. The case of Br, with almost no information, should be investigated in the future in all water types.

- *Group II*, includes the chemical elements that is admitted *not do part of the ensemble of the natural trace elements* of NMW, or if they are part of the natural elements, their content is very low and close to the detection limit. This understanding results from the number of times they appear below the detection limit, and on the other hand by the significant quantities that at least some appear in rainwater and surface runoff water. It is important to mention that the occurrence of organic and other soils, which have been removed with the improvement works, around the NT will also contribute to the addition of some elements. Thus, in this group, it was subdivided into three subgroups: (i) *Sub-group II-a,* in which the chemical elements sometimes occur with *some significance*; it is understood that there will be a relationship with some elements in rainwater and surface runoff water, namely Zi, Cu, and particularly Ba, in addition to other elements in lesser influences such as Pb, Ni, and Sn; (ii) *Sub-group II-b*, includes the chemical elements, where they sometimes occur with *slight significance*; it is understood that there will be a relationship with some elements in rainwater and surface runoff water, namely in V, Cd, Co, Hg, and even U; (iii) *Sub-group II-c*, includes chemical elements where they sometimes occur with *very slight significance*; it includes the elements Ta, Y, and Ag; the occurrence of these elements admitted that may have nothing to do with rainwater and surface runoff water.

Group	Element	Traditional Springer—NT				Rainwater				Surface runoff water**			
		N	ave	max	SD_R(%)	N	ave	max	SD_R (%)	N	ave	max	SD_R (%)
I	B	51	0.4263	0.4760	6	9	0.0050	0.0114	71	9	0.0194	0.03900	47
	Br	3	0.1750	0.2600	34	—	—	—	—	—	—	—	—
	W	53	0.0791	0.0990	13	10	—	0.00280	—	9	0.0007	0.00170	61
	Sr	50	0.0667	0.0730	5	10	0.0049	0.01450	90	9	0.0658	0.14400	53
	Cs	42	0.0624	0.0721	7	10	—	0.00280	—	9	0.0048	0.04000	262
	Rb	42	0.0590	0.0670	5	10	0.0008	0.00280	114	9	0.0407	0.26800	198
	Al	51	0.0437	**0.640**	**217**	10	0.0940	**0.32500**	102	9	0.0225	0.05500	81
	As	53	0.0045	0,0180	49	10	—	0.00540	—	11	0.0157	**0.0400**	65
	Mn	52	0.0020	0.0060	45	10	0.0061	0.01970	98	9	0.0003	0.00070	54
	Be	53	0.0006	0.0014	28	10	—	0.00007	—	9	—	0.00005	—
II-a	Zn	53	—	0.3140	—	11	0.0896	**0.16900**	58	9	0.0300	0.12770	122
	Pb	52	—	0.0700	—	10	0.0006	0.00190	80	9	0.0003	0.00111	122
	Cu	51	—	0.0550	—	11	0.0038	**0.01120**	82	11	0.0035	0.00930	62
	Ni	52	—	0.0150	—	10	0.0014	0.00450	103	9	—	0.10000	—
	Cr	53	—	0.0124	—	10	—	0.00076	—	9	0.0012	0.00320	67
	Sb	53	—	0.0070	—	10	0.0007	0.00170	81	9	0.0010	0.00152	37
	Ba	53	—	0.0063	—	10	0.2103	**1.82100**	255	9	0.1012	**0.5190**	154
	Mo	53	—	0.0060	—	10	—	0.00037	—	9	0.0028	0.00558	64
	I	3	—	0.0020	—	—	—	—	—	—	—	—	—
	Tl	41	—	0.0015	—	10	—	0.00001	—	9	0.00002	0.00005	49
	Se	49	—	0.0013	—	10	—	0.00060	—	9	—	0.00080	—
	Sn	53	—	0.0010	—	10	0.0070	0.01960	101	9	0.00012	0.00063	152

Group	Element	Traditional Springer—NT				Rainwater				Surface runoff water**			
		N	ave	max	SD_R(%)	N	ave	max	SD_R (%)	N	ave	max	SD_R (%)
II-b	V	53	—	0.0009	—	10	0.0010	0.00400	124	9	0.00219	0.00390	34
	Cd	53	—	0.0006	—	10	0.0004	0.00191	125	9	—	0.01190	—
	Co	53	—	0.0003	—	10	0.0008	0.00600	222	9	—	0.00019	—
	Hg	47	—	0.0003	—	10	—	0.00010	—	9	—	0.00006	—
	Te	48	—	0.0003	—	10	—	<0.00021	—	9	—	0.00003	—
	Zr	41	—	0.0002	—	10	—	0.00053	—	9	—	0.00017	—
	Bi	40	—	0.0001	—	10	—	<0.00006	—	9	—	0.00004	—
	Nb	52	—	0.0001	—	10	—	0.00001	—	9	—	0.00002	—
	U	47	—	0.0001	—	10	0.0002	0.00050	—	9	0.0032	0.01130	115
II-c	Ta	41	—	0.00004	—	10	—	<0.00006	—	9	—	0.00001	—
	Y	53	—	0.00002	—	10	0.0001	0.00030	87	9	0.00005	0.00010	65
	Ag	49	—	<0.0005	—	10	—	0.00057	—	9	—	0.00070	—

*from **Table 1** and **Figures 5–7.***

**the present values were the ones that occur in greater dosage, among those obtained in the simple and composite samples; N: number of samples studied, ave.: average, max: maximum, SD_R: relative standard deviation.*

Table 7.
Comparison of trace element levels recorded in NMW from the NT of the SPS medical spa, with those recorded in local rainwater and surface runoff water.*

4. Conclusions

The natural mineral water (NMW) from the Traditional Spring (NT) of the São Pedro do Sul medical spa is fundamental to the public health of a considerable group of people who use that medical spa. As a result, the local economy, through direct revenues from thermal treatments and other indirect revenues from tourism, hotel, catering, and other activities, is very important to boost the economy of the entire region where the medical spa is located. The change in the chemical quality of NT water leads to the assumption that there is contamination and, as a result, the health authorities impose the closure of the use of that water. Therefore, the chemical composition of the water is analyzed systematically over time. Such quality control allows checking if anomalies are occurring, and sometimes their causes are enigmatic.

Infiltration of rainwater, or even of surface runoff water in the proximity of the NT has the potential to interfere with the water quality of the NT. There is also the possibility that other causes may be at the origin of these potential problems, such as the migration of chemical elements from the garden soils surrounding the NT house; these latter situations are not studied in this chapter. It is therefore on the chemical quality of rainwater and surface runoff water from the medical spa area, subjected to detailed physical-chemical analyses for about two years, that this chapter focuses, in order to try to understand if, from these may result in changes in the quality of the NMW of the NT.

Regarding rainwater (**Figure 5**), total mineralization (M_T) shows a variation from 2.2 to 24.4 mg/L and pH between 4.17 and 5.93. In relation to the majority ionic species, the predominance of the anion Cl^- (0.5 to 9.8 mg/L) and the cations Na^+ (0.2 to 4.9 mg/L) and Ca^{2+}(0.14 to 7.4 mg/L) is highlighted, denouncing its proximity to the Atlantic Ocean, which is only about 55 km to the west. In the trace elements, emphasis is given to the fact that elements Ba, Co, Cd, and V were found, with a relative standard deviation, SD_R, greater than 120%, pointing to intermittent origins; the case of Ba, presents a very singular and worrying situation, with SD_R = 255%, reaching a content of 1.82 mg/L, which corresponded to the second most representative element, after Cl^- with 2.9 mg/L (analysis March 2007, **Table 2**). It is also noted the almost systematic presence of other trace elements, such as Al, Zn, Cu, and Pb, and it should be emphasized that, for example, Al reaches values of 0.325 mg/L, which is higher than the parametric limit of water for human consumption.

About the surface runoff waters, which are the result of rain that falls in the garden area and street surrounding the NT site, at a maximum distance of about 250 m from the sampling site (**Figure 3**), it should be noted that there are no major differences in the chemical quality of the samples of the 1st rainfall (simple samples—**Figure 6**) with the samples collected in various moments during the rains (composite sample—**Figure 7**). From the point of view of the stability of the various chemical elements in this type of water over time, there are significant changes from sample to sample; most elements, whether majority or vestigial, have an SD_R greater than 50%, showing large changes over time. In comparative terms with rainwater quality, the following aspects are emphasized:

i. surface runoff waters have a higher M_T and pH than rainwater; in average terms, it is verified: (a) $M_{T\text{-ave-surface-runoff}} \cong 14.75 \times M_{T\cdot\text{ave-rainwater}} = 146.2$ mg/L; and (b) $pH_{\text{ave-surface-runoff}} \cong 1.34 \times pH_{\text{ave-rainwater}} = 7.06$;

ii. the surface runoff waters present contents with some significance of Total Alkalinity (A_T), silica (SiO_2), and even for Total Hardness (H_T), with

maximum values: A_T = 58.3 0 mL/L, SiO_2 = 25.2 mg/L, and H_T = 92.0 p.p.10^5 of $CaCO_3$, while in rainwater these parameters show almost zero values;

iii. on the elements of the majority ionic component while rainwater presents Cl^- in the anions, and Na^+ and Ca^{2+} in the cations, in surface runoff water predominate in the anions: $HCO_3^- > SO_4^{2-} > NO_3^-$, and in the cations: $Ca^{2+} > > K^+ > Na^+$, emphasizing that in particular Cl^- ceases to have significance and Na^+, never appears as the predominant cation; it is also mentioned that Phosphate ($H_2PO_4^-$) in rainwater never appeared and in surface runoff water became part of the set of anions observed;

iv. regarding the trace elements, it is emphasized that the most representative element, as in rainwater, continues to be Ba, despite having lower values, with a maximum value of 0. 52 mg/L; in relation to other trace elements, such as in rainwater, several chemical elements continue to be present, with particular attention to Zn, which in rainwater reaches 0.169 mg/L and in the simple surface runoff water sample it reaches reach 0.130 mg/L; on trace elements, in surface runoff water, it is also worth noting the fact that they include with some significance Sr (0.144 mg/L), Ni (0.10 mg/L), and Rb (0.268 mg/L), being of mention that these elements are not so important in rainwater.

On the NMW of the NT, that being a groundwater resulting from an extensive hydrogeological circuit, with its beginning as rainwater, which infiltrates at depth, and as it percolates along the essentially granite rock mass, in the various water/rock interactions, it acquires its own chemical composition. From a global point of view, based on the universe of 96 physical-chemical analyses carried out over time (**Table 1)**, it is noted that it has very good stability, particularly evident in the global physical-chemical parameters and the majority ionic component, which generally present SD_R of less than 10%. M_T and pH present mean values of 359.68 mg/L, and 8.82, respectively. It is emphasized that these are alkaline waters, while rainwater is acidic and surface runoff water is neutral. Still in the global parameters, it is emphasized the occurrence in the water of the NT, of: (i) Sulphuration, with average values of 21.3 mL/L, which is a parameter that corresponds to the total ionic water content of S_2^- specie, including simple and complex sulphury forms [15], and does not appear in the other waters; (ii) Non-ionized silica, with average value of 67.94 mg/L, which corresponds to a considerable representation in relation to the total mineralization (SiO_2/M_T = 19%); the silica, is almost null in rainwater, and in surface runoff water presents SiO_2/M_T = 7%. In relation to the majority ions, systematically, the most representative ions, from highest to lowest, are: $HCO_3^- > > Cl^- > F^- > SO_4^{2-}$, for the anions, and $Na^+ > > K^+ > Ca^{2+}$ for the cations; these situations are completely different from those seen in rainwater and surface runoff water. We point out the particularity of F^- that in the NT water occurs always, with an average value of 17.71 mg/L, which is relatively considerable, while in rainwater and surface runoff water, this element appears almost without expression, with the maximum value of F^- = 0.53 mg/L in rainwater. In relation to the trace elements in the NT water and comparison with what occurs in rainwater and surface run-off water, the elements are organized according to the following (**Table 7**):

- *Group I*: B > Br > W > Sr. > Cs > Rb > Al > As>Mn > Be, which correspond to the most systematically representative chemical elements and are understood to

be *part of the ensemble of natural trace elements* of NMW. These elements were always quantified whenever they were surveyed. Some present excellent SD_R, less than 10%, as is the case of B, Sr., Cs and Rb. We highlight the case of Al, which presents an SD_R = 217%, therefore sometimes with relatively high values, which is understood to be a punctual consequence of mixtures and/or infiltration of rainwater and surface runoff water; it is also admitted that As and Mn also have some interference with rainwater and surface runoff water.

- *Group II*, which includes the chemical elements that are admittedly *not part of the ensemble of natural trace elements* of NMW, or if they are part of the natural elements, their content is very low and close to the detection limit; this group is subdivided into three subgroups: (i) *Sub-group II-a:* Zn > Pb > Cu > Ni > Cr > Sb > Ba>Mo > I > Tl > Se > Sn, in which chemical elements sometimes occur with *some significance*; it is understood that there will be a relationship with some elements from rainwater and surface runoff, notably in the cases of Zi, Cu and particularly Ba, in addition to other elements in lesser influences such as Pb, Ni and Sn; (ii) *Sub-group II-b*: V, Cd, Co, Hg, Te, Zr, Bi, Nb, U, in which the chemical elements sometimes occur with *slight significance*; it is understood that there will be a relationship with some elements of rainwater and surface runoff water, namely in V, Cd, Co, Hg and even U; (iii) *Sub-group II-c*: Ta, Y, Ag, in which the chemical elements occur sometimes with *very slight significance*; their occurrence admittedly may have nothing to do with rainwater and surface runoff water.

The present work was triggered by the occurrence of abnormal levels of Zn, Cu and Pb in March 2005; however, when analyzing in detail the chemical situation during the 29 years of analyses of the water of the NT, occasionally there were problems with other elements, which have since been resolved, as shown in **Table 6**. The main action taken to solve these problems was the removal of organic and other soils from around the NT house, replacing them with impermeable clays, among others. Attention should continue to be paid to the monitoring of all the elements that constitute the External Monitoring System, namely the recording of the quality of groundwater from the piezometers, and, as far as possible, measures should be taken to eliminate all the traditional garden area, replacing it by situations that favor impermeable zones. Solutions should also be found to cancel traffic and parking in the area near the NMW abstractions.

Finally, we emphasize the occurrences of anomalous chemical elements from the domain of trace elements in rainwater, namely those that occur systematically, such as Ba, Al, Zn, Cu, Pb, Cd, Co, Mn, Ni, Rb, Sb, Sn, Sr., U, V and I. It will be important in the future to continue researching these chemical elements in rainwater, and to simultaneously study the direction of local and regional winds, in order to find out the origin of pollution from the air, as these chemical elements could be harmful to the NMW of the NT, and of course to public health in global terms, due to the possibility of these elements becoming associated with the surface waters of the region (rivers and reservoirs), common groundwater and even the quality of the air we breathe. It will also be very important to make an inventory of all the potential sources of pollution, both local and regional, including industrial parks, with a characterization of the various existing industries, car workshops, namely those that paint and wash vehicles automatically, and places of the waste incineration, among others.

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Conflict of interest

The data sets generated during and/or analyzed during the current study are available from the corresponding author on request after the publication of work.

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