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Classification of natural mineral and spring bottled waters of Portugal using Principal Component Analysis

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ABSTRACT

Considering its area, Portugal is one of the world's richest countries in mineral and spring waters. There are 33 different types of bottled water, 18 of which are classified as natural mineral water and the remaining as spring water. The majority of these waters are of low mineralisation in comparison to most European bottled waters.

Principal component analysis was used to identify the main geotectonic interrelationships among physico-chemical parameters, enhancing similarities and dissimilarities, and contributing to a new typology of bottled waters, based on their hydrochemical characteristics and geological occurrence.

1. Introduction

Portugal, according to its size, population and geological diversity, is one of the richest countries in the World with respect to the number and variety of natural springs, some of which with proven medicinal properties that were known since ancient times (Lepierre, 1930).

About 400 springs are known in Portugal:

- springs classified as natural mineral water by a legislative Act before the Decree-Law of 1990 (Decree 15401 of 1928) and
- springs with exceptional physico-chemical properties, which have been verified by specialists or their therapeutic qualities have been known over a long time.

Natural mineral water, recognised as exceptional water, is not subject to maximum admissible values. Nevertheless, some reference values do exist and are defined by the EU Directive 2009/54/EC. In the case of natural spring water (as well as water for human consumption) the levels of physico-chemical parameters are established by the Decree-Law 243/2001.

Natural mineral water has qualities that distinguish it from other natural water, such as the level of physico-chemical parameters. Although nature does not "produce" two natural waters with exactly the same chemical composition, it is, however, possible to group them into classes or types, based on some similarities of their physico-chemical properties.

Overall, natural mineral and spring waters in Portugal are in general low mineralisation waters, a fact that is unlike the majority of bottled waters sold in other European countries, thus, revealing the taste of the Portuguese for this type of waters.

From the marketing point of view, mineral and spring waters are outstanding economic valuable natural resources, representing a non negligible income for the regions where they occurred through bottling industries, with significant impact on tourism.

Bottled natural mineral waters contributed with 203 million € (2008) to the Portuguese economy, and spring waters with 58.4 million € according to the statistics of DGEG — Direcção-Geral de Energia e Geologia (General Directorate of Energy and Geology).

Water is essential to life support systems, and with the impact of climate change and anthropogenic activities to water resources, quantity and quality are becoming more rare and valuable for water resources. Hence, the importance to conserve and protect this natural resource.

In the natural mineral water industry the tolerance, with respect to the deviation of physico-chemical and microbiological qualities, is actually very small. For this reason, there is a growing need to develop robust methodologies for water quality assessment to support decision makers in elaborating water management plans at national and municipal levels.

Several statistical studies have already been carried out to analyze in more detail some important hydrothermal water resources of Portugal. Special emphasis was given to the use of the Mann–Kendall test to evaluate trends in water quality parameters in Pedras Salgadas and Vidago waters (Ribeiro and Lourenço, 1999; Lourenço and Ribeiro, 2007), and the application of multivariate statistics analyses

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to assess the hydrochemical patterns of the same waters (Lourenço, 2000; Ribeiro and Lourenço, 2000).

2. Legislative frame of the bottled water sector

The certification of each natural water type in Portugal is well established with different Decree-Laws as shown in Fig. 1. According to the Decree-Law 90/90 natural mineral water is integrated in the public domain, while spring water, is considered to be privately owned (Decree Law 84/90).

With these laws, new concepts and roles were introduced in terms of defining geological water resources, and how to explore and manage them.

When natural mineral water is classified under Portuguese legislation as a hydromineral resource (Decree-Law 86/90), its exploration and management is under the control of the DGEG, after a favourable review (in terms of resource qualification) by the Direcção-Geral de Saúde (General Directorate of Health).

Natural spring water is, with respect to technical requirements (Decree-Law 84/90), subjected to very similar testing processes, before exploitation and commercialisation.

From a purely geological perspective, natural mineral waters have specific physico-chemical characteristics that distinguish them from "normal" spring waters, with the most distinctive characteristic being their total mineralisation or other physico-chemical parameters (such as pH, CO_2, silica, etc.), exceeding the levels of "normal" waters, or higher temperatures than the average ambient temperature.

According to the Schoeller classification (Custódio and Llamas, 1996), thermal water has a temperature of 4 °C above the average ambient temperature.

A natural mineral water, as defined by Portuguese legislation, is bacteriologically safe, of deep circulation, with physico-chemical properties that are stable within the annual variation range, and from which therapeutic qualities may result, or it may simply have favourable effects on human health. Spring water is also defined as natural, generally of deep circulation, free of bacteria, although it can have a larger annual variation range in its physico-chemical parameters, corresponding to a shorter ground residence time, when compared with mineral water.

In the Portuguese legislation, the most distinctive characteristic that distinguishes natural mineral from spring water is the overall stability of the physico-chemical parameters of the former, even if there is a change in the level of a specific parameter. This stability is the result of a slow and deep circulation process where the water/rock interaction can take tens to thousands of years, and/or there is a contribution from deep fluid fluxes that affects its final chemical composition.

3. Location and structural geology

On mainland Portugal there are 33 qualified ground water bottled types of which 18 are classified as natural mineral and 15 as spring waters. In some of these waters free CO_2 is added. The result is that, the same water can be sold under the commercial name of non-carbonated or carbonated.

Their distribution across the country is uneven, with a greater concentration in the northern and central parts, mainly justified by Portugal's division in areas with distinct geological and structural characteristics.

Taking into account the occurrence of bottled mineral and spring waters, Portugal can be divided in two great geotechtonic areas (Fig. 2).

In the first area, located in northern Portugal, the occurrence and circulation of waters are controlled by deep faults, involving fluids coming from the depth, generated in metamorphic and/or magmatic environments. In the second area, located in central and southern Portugal, the mineral and spring waters are mostly influenced by rock dissolution processes.

In the first area, situated in the northern and central region of the Hesperic Massif, namely in the Galiza-Trás-os-Montes zone (Fig. 2), the waters are normally issuing from granitic outcrops of Hercynian age. The area is well known for its natural CO_2 rich waters.

Their geographical location is well correlated with regional fault systems, such as the "Penacova-Régua-Verin Fault" (with a NNE–SSW direction), the "Vilariça Fault" (with a NNE–SSW direction) and the "Rio Minho Fault" (with a ENE–WSW direction). They occur within the granite and schist, usually at the intersection of major regional faults, since they normally provide the best conditions for the rising of fluids from deep crustal zones (Lourenço, 2000).

These waters are generally classified as hypo-thermal, with high mineralisation contents (>1 g/L) and fluoride concentrations higher than 1 mg/L and high levels of CO_2 about 1000 mg/L. They are mainly sodium bicarbonate type waters, except Melgaço water, a calcium bicarbonate hydrochemical facies type.

The physico-chemical characteristics of these waters cannot be explained only by water–rock reactions, since the geochemical phenomena responsible for these features are most likely generated in deep crustal zones responsible for the high amounts of CO_2, and the relatively high concentrations of certain elements, such as fluoride, boron and bromine.

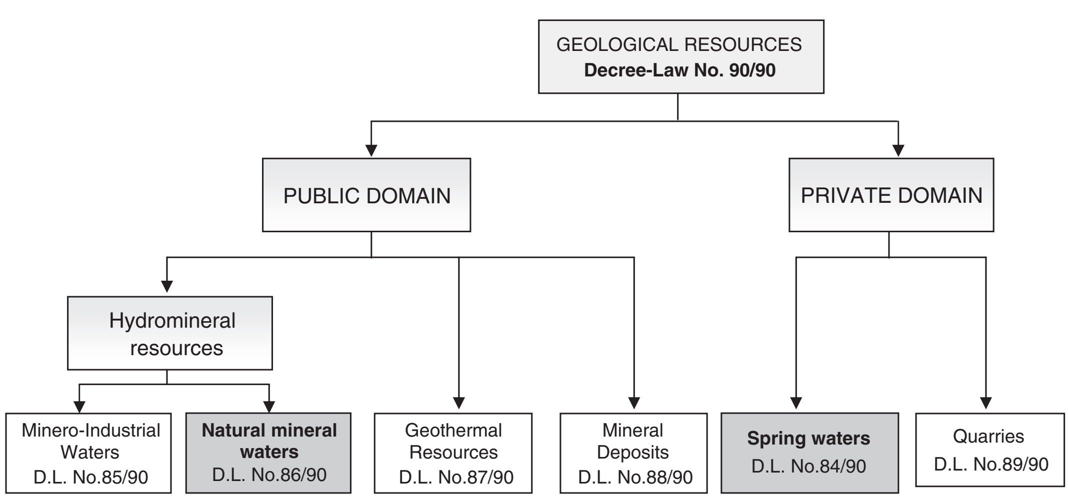

Fig. 1. Organisation chart of the Decree-Law No. 90/90.

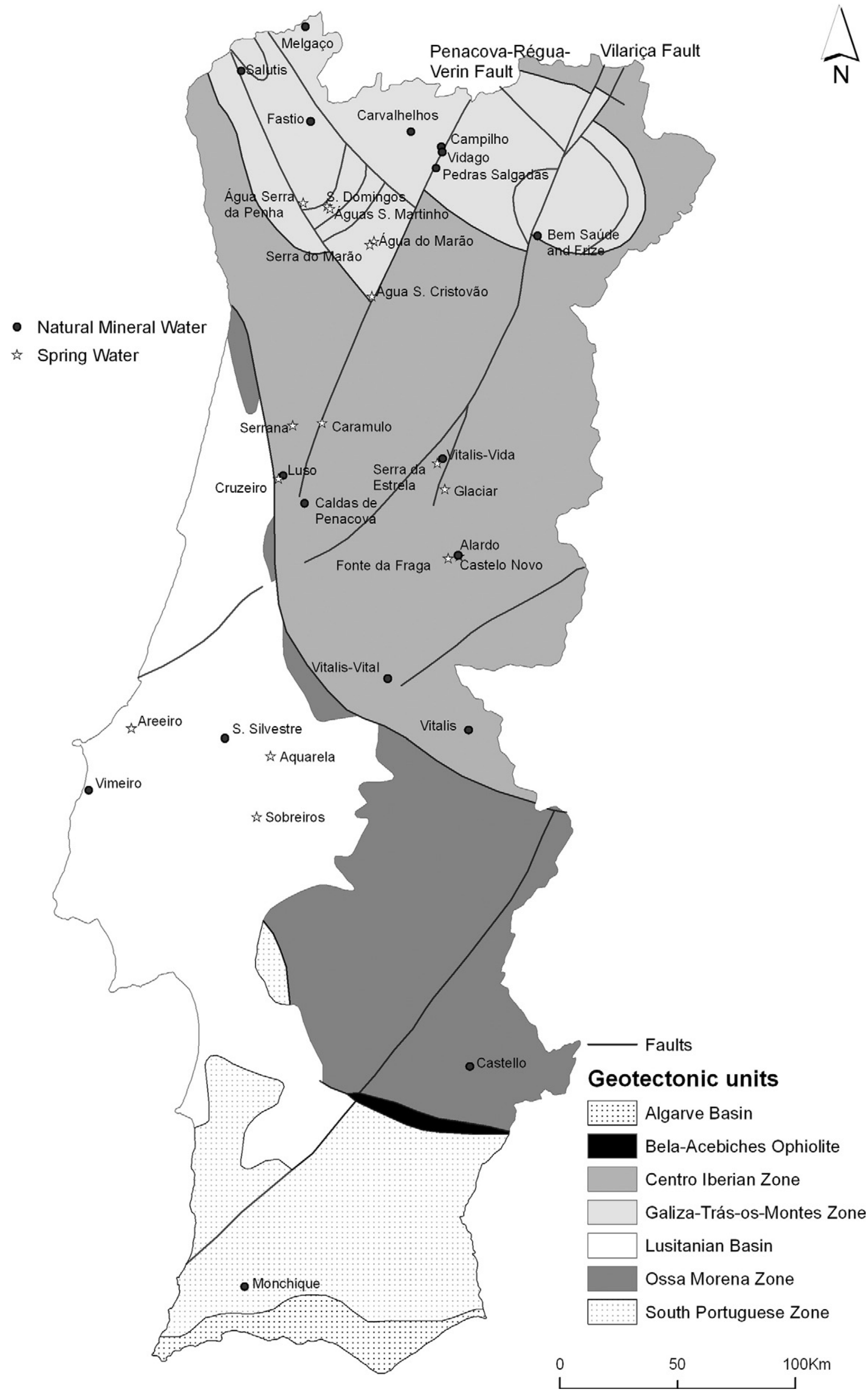

Fig. 2. Location of natural mineral and spring waters in Portugal and geotectonic regions.

Table 1
Characteristics of natural bottled mineral and spring waters of Portugal.

Name	Abbrev.	Natural mineral water		
		Non-carbonated	Carbonated	Natural CO_2
Alardo	ALAR	•		
Bem-Saúde	BSAU			•
Campilho	CAMP		•	
Castello	CAST		•	
Carvalhelhos	CAR**l**	•	•	
	CAR**g**			
Vitalis-Vida[a]	VIDA	•		
Fastio	FAST	•		
Frize	FRIZ			•
Luso	LUSO	•	•	
Melgaço	MELG			•
Pedras Salgadas	PSAL			•
Penacova	PENA	•		
Salus-Vidago	SALUS			•
Vitalis-Vital	VITA	•		
Monchique	MON**l**	•	•	
	MON**g**			
Salutis[a]	SALU	•		
Vimeiro	VIM**l**	•	•	
	VIM**g**			
Vitalis	ALIS	•		
São Silvestre	SSIL	•		

Name	Abbrev	Spring water	
		Non-carbonated	Carbonated
Água do Marão[a]	MARA	•	
Areeiro[a]	AREE		•
Caramulo	CARA	•	
Castelo Novo[b]	NOVO	•	
Cruzeiro	CRU**l**	•	•
	CRU**g**		
Fonte da Fraga	FFRA	•	
Glaciar[a]	GLAC	•	
Penha	PENH	•	
S. Martinho[a]	SMAR	•	
S. Domingos	DOMIN	•	
S. Cristóvão[a]	SCRI	•	
Serra da Estrela	SEST	•	
Serra do Marão[a]	MARAO		•
Serrana[a]	SERR	•	
Aquarela do Mundo[b]	AQUA	•	
Nestle[b]	NEST	•	

l – Non-carbonated.
g – Carbonated.
[a] Analysis performed on the bottled water (2001).
[b] Complete analysis performed in the well (2008).

Within the second area, the mineralisation of waters is mostly controlled by the equilibrium rock–water interactions, and, consequently, depends on the nature of the minerals present, among other factors. The highest mineralised water in this area (Vimeiro water with total mineralisation >1000 mg/L), is related to evaporitic minerals, like halite and gypsum, and to carbonate rocks that occur at the contact of diapiric structures. The Castello water is also related to carbonate rocks, and is of intermediate mineralisation. Several other water types in this

Table 2
Hydrochemical types of bottled waters in Portugal.

Hydrochemical type	Main characteristics	Number of bottled waters	% bottled waters
Low mineralisation water	Total mineralisation <100 mg/L; Silica content >25% of the total mineralisation	23	59
Weakly mineralisation water	Total mineralisation between 100 and 1000 mg/L. Presence of an ionic dominant pair: HCO_3^-–Na^+ HCO_3^-–Na^+–Ca^{2+} HCO_3^-–Ca^{2+}–Mg^{2+}	8	20.5
Medium mineralisation water	Total mineralisation between 1000 and 1500 mg/L. Presence of an ionic dominant pair: Cl^-–HCO_3^-–Na^+–Ca^{2+}	2	5.1
High mineralisation water	Total mineralisation >1500 mg/L. Presence of an ionic dominant pair: HCO_3^-–Na^+ HCO_3^-–Ca^{2+} Fluoride content >1 mg/L; High amount of CO_2	6	15.4

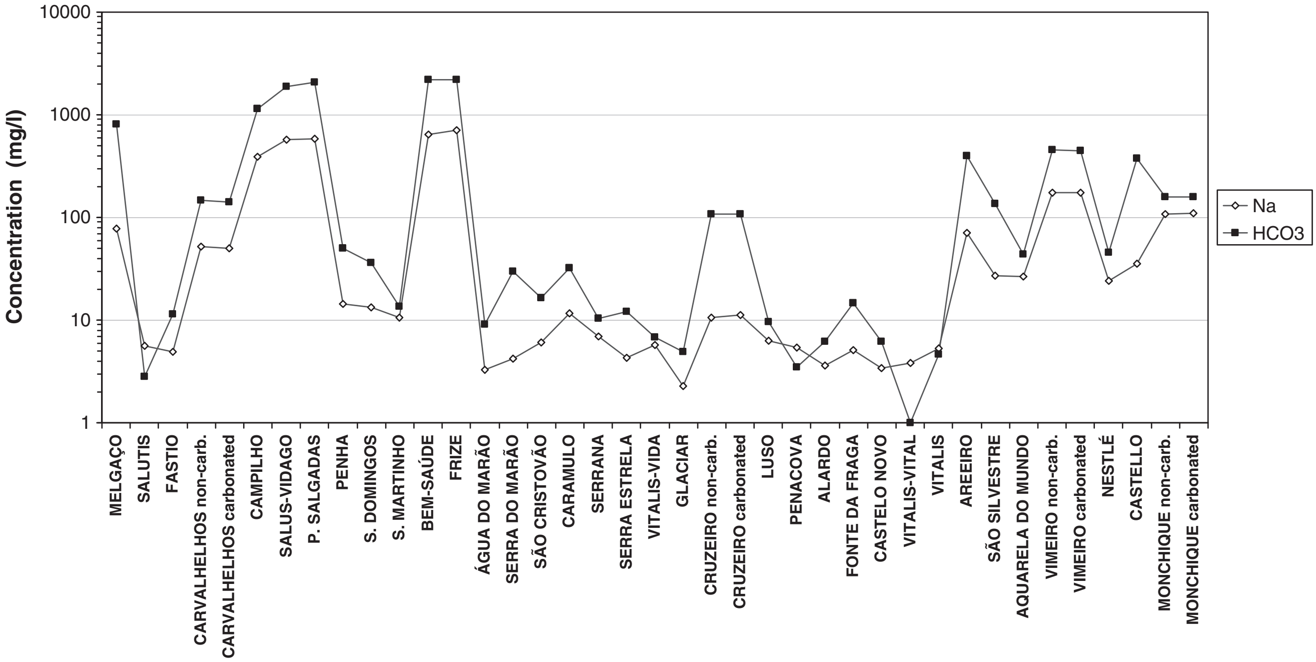

Fig. 3. Profile of concentrations of Na^{+} and HCO_3^{-} in mineral and spring waters bottled in Portugal (logarithmic scale).

area are less mineralised, and are associated with sandstone layers of upper Jurassic or Miocene age (S. Silvestre, Aquarela, Sobreiros).

Further, in the second area, but in the Centro-Iberian Zone, there are low mineralisation water types, which are derived from the circulation of meteoric water moving through fissures in mostly granitic rocks (Serrana, Caramulo, Serra da Estrela, Glaciar, Fonte da Fraga, Alardo, Castelo Novo) and quartzitic formations (Luso, Caldas de Penacova, Vitalis). Their most significant characteristic is the low amount of dissolves salts. Generally, sodium is the dominant cation, associated with bicarbonate or chloride, and the silica values are greater than 25% of total mineralisation.

4. Hydrochemical data

The quality of natural mineral and spring waters is controlled by a monitoring programme implemented by the ex-Instituto Geológico e Mineiro (Geological and Mining Institute, presently, DGEG) since 1986 (comprising 3 to 4 simple physico-chemical analyses per year

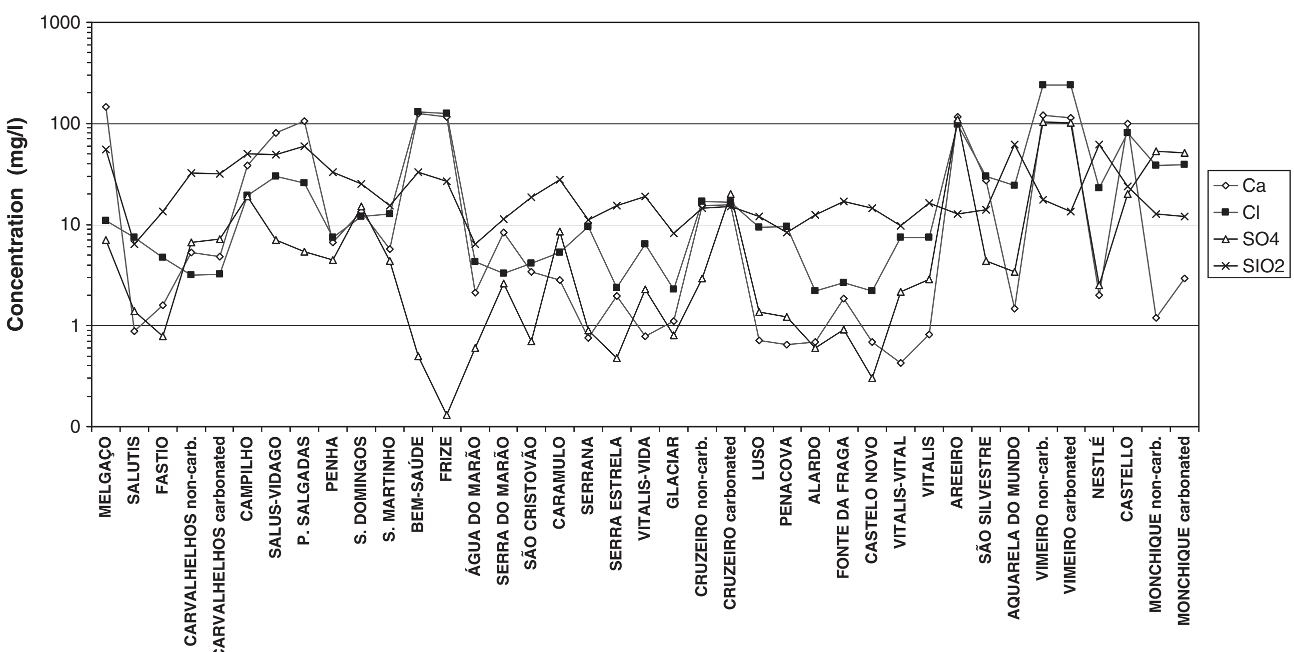

Fig. 4. Profile of concentrations of Ca^{2+}, Cl^{-}, SO_4^{2-} and SIO_2 in mineral and spring waters bottled in Portugal (logarithmic scale).

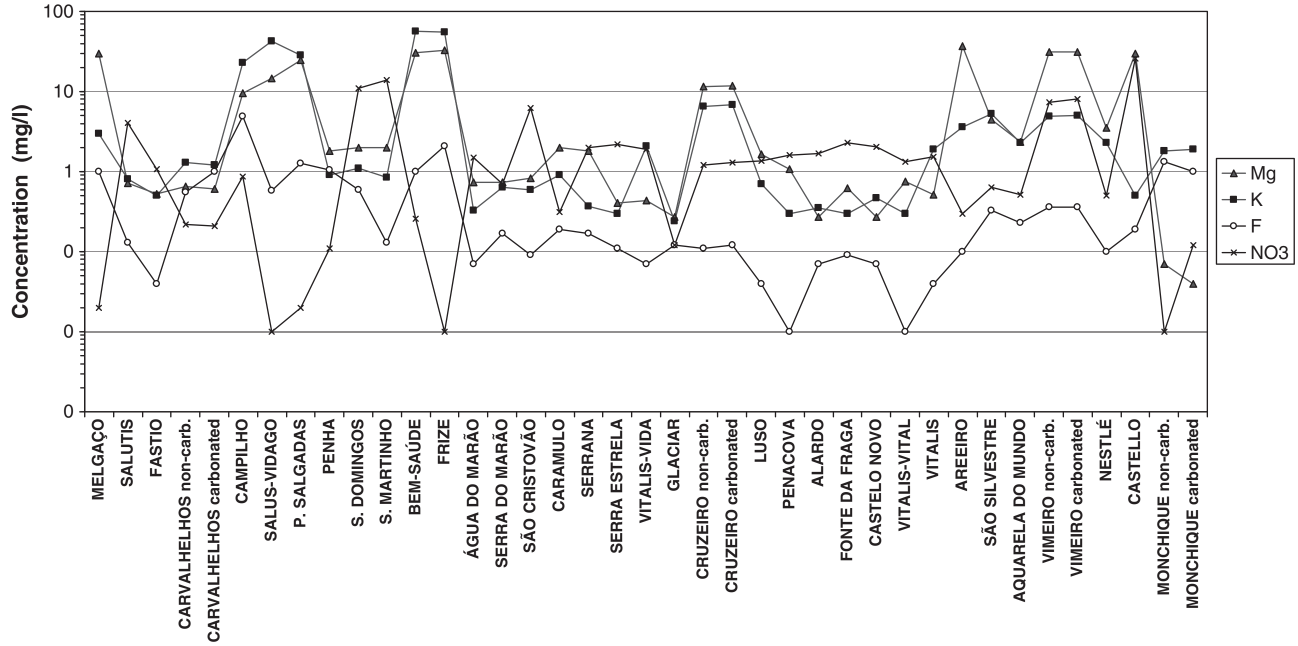

Fig. 5. Profile of concentrations of Mg^{2+}, K^{+}, F^{-} and NO_3^{-} in mineral and spring waters bottled in Portugal (logarithmic scale).

and one complete analysis every 4 or 5 years). The bacteriological control, however, is done weekly or two times per month, depending on usage.

The chemical analysis of water refers to an evaluation of the physico-chemical parameters that constitute the major and minor properties of the system.

Table 3
PCA matrix (39 bottled waters × 10 parameters). For explanation of abbreviations refer to Table 1.

Abbrev.	Ca	Mg	Na	K	HCO_3^-	Cl^-	SO_4^{2-}	F^-	NO_3^-	SiO_2
ALAR	0.68	0.27	3.60	0.35	6.20	2.20	0.60	0.07	1.70	12.50
BSAU	126.00	30.20	647.00	56.30	2181.00	129.00	0.50	1.00	0.26	33.20
CAMP	38.10	9.49	387.00	22.80	1147.00	19.30	19.00	4.90	0.86	49.70
CAST	99.90	29.50	35.60	0.50	378.00	80.40	20.00	0.19	25.90	24.00
CARl	5.32	0.66	52.00	1.30	148.00	3.14	6.59	0.55	0.22	32.50
CARg	4.76	0.61	50.20	1.20	141.00	3.20	7.17	0.99	0.21	31.50
VIDA	0.79	0.44	5.70	2.10	6.80	6.40	2.30	0.07	1.90	18.80
FAST	1.60	0.53	4.90	0.50	11.50	4.70	0.79	0.04	1.07	13.50
FRIZ	115.00	33.10	704.00	55.00	2182.00	125.00	0.13	2.11	0.01	26.70
LUSO	0.71	1.64	6.30	0.70	9.60	9.38	1.36	0.04	1.36	11.90
MELG	145.00	30.00	77.90	3.00	810.00	10.90	7.01	1.00	0.02	54.60
PSAL	105.00	24.60	579.00	28.60	2059.00	25.60	5.33	1.27	0.02	59.50
PENA	0.65	1.08	5.40	0.30	3.50	9.55	1.21	0.01	1.61	8.40
SALUS	80.00	14.50	572.00	42.50	1897.99	29.80	6.97	0.58	0.01	48.70
VITA	0.43	0.75	3.80	0.30	1.00	7.39	2.14	0.01	1.32	9.70
MONl	1.20	0.07	109.00	1.80	160.00	38.20	53.3	1.34	0.01	12.60
MONg	2.9	0.04	110.00	1.90	160.00	39.10	51.1	1.00	0.12	12.10
SALU	0.88	0.72	5.60	0.80	2.80	7.50	1.40	0.13	4.10	6.40
VIMl	120.00	31.20	174.00	4.90	455.00	237.00	104.00	0.36	7.36	17.40
VIMg	114.00	30.90	176.00	5.00	449.00	238.00	101.00	0.36	8.08	13.40
ALIS	0.81	0.52	5.30	1.90	4.60	7.38	2.88	0.04	1.54	16.20
MARA	2.10	0.730	3.30	0.33	9.10	4.30	0.60	0.07	1.50	6.40
AREE	115.00	37.00	71.00	3.60	398.00	98.00	110.00	0.10	0.30	12.80
CARA	2.82	2.01	11.60	0.90	32.00	5.29	8.50	0.19	0.31	27.70
CRUl	15.30	11.60	10.50	6.60	109.00	16.80	2.91	0.11	1.21	14.50
CRUg	15.80	11.70	11.20	6.90	109.00	16.70	20.00	0.12	1.30	15.00
FFRA	1.86	0.62	5.10	0.30	14.70	2.65	0.91	0.09	2.30	16.90
GLAC	1.10	0.27	2.30	0.24	4.90	2.30	0.80	0.12	0.12	8.20
PENH	6.70	1.79	14.50	0.90	50.50	7.45	4.41	1.04	0.11	32.90
SMAR	5.70	2.00	10.50	0.85	13.50	12.60	4.40	0.13	13.90	15.30
SSIL	27.30	4.45	27.30	5.30	136.00	29.70	4.33	0.33	0.64	13.90
SCRI	3.40	0.82	6.10	0.60	16.40	4.10	0.70	0.09	6.20	18.70
SEST	1.95	0.41	4.30	0.30	12.20	2.37	0.48	0.11	2.18	15.50
MARAO	8.40	0.73	4.20	0.63	30.10	3.30	2.60	0.17	0.70	11.40
SERR	0.76	1.80	7.00	0.37	10.40	9.50	0.90	0.17	2.00	11.20
AQUA	1.47	2.35	26.50	2.30	43.90	24.20	3.40	0.23	0.51	62.10
NEST	2.00	3.50	24.00	2.30	45.50	23.00	2.50	0.10	0.50	62.00
DOMIN	13.4	2.00	13.30	1.10	36.30	12.00	15.00	0.60	11.00	25.00
NOVO	0.68	0.27	3.4	0.47	6.2	2.2	0.3	0.07	2.02	14.5

Table 4
Eigenvalues, % of explained variance, and cumulative variance %.

Factors	Eigenvalue	% of explained variance	Cumulative variance %
1	4.996	49.96	49.96
2	2.320	23.20	73.16
3	0.877	8.77	81.93
4	0.767	7.67	89.59
5	0.619	6.19	95.78
6	0.252	2.52	98.30

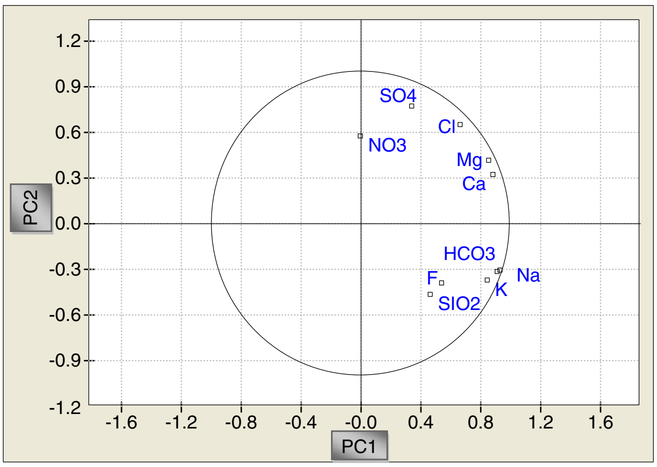

Fig. 6. Projection of variables in the 1st factorial plane.

The extensive level of acquired laboratory information, with respect to both quantity and quality, requires an efficient data statistical analysis to be able to highlight any specific characteristics and to group the sampled waters into different water types.

The chemical composition that a water displays in the bottled product should be considered as the result of a set of changes occurring in the original fluid, which depend on various factors, such as water pathways, the pH changes due to the system's degasification, etc. (Canto Machado, 2000).

The bottled waters discussed above are shown in Table 1 and concern mineral and spring water bottled on mainland Portugal in 2009. On each water sample, an analysis was performed on the bottled water in 2009 by the Laboratory of Geochemistry for Resource Management, through the programme "MinWas", or, in the absence of such data, the last analysis performed on the bottled product after 2001, or the last complete analysis performed on the well.

A total of 39 analyses of bottled water were considered in this study.

Table 5
Principal Component loadings of the 10 variables.

Variable	Mean	Stand. dev.	Principal Component (PC)					
	(mg/L)		1	2	3	4	5	6
Ca^{2+}	30.5	46.7	**0.889**	0.319	0.104	−0.008	0.184	0.226
Mg^{2+}	8.3	12.0	**0.856**	*0.407*	0.082	−0.020	0.168	0.226
Na^{+}	101.8	191.4	**0.911**	−0.315	−0.034	−0.168	−0.119	−0.119
K^{+}	6.8	14.1	**0.848**	−0.377	−0.004	−0.318	−0.105	−0.101
HCO_3^-	340.8	633.6	**0.929**	−0.306	0.056	−0.165	−0.019	0.016
Cl^-	33.6	56.8	*0.666*	***0.645***	−0.157	−0.032	−0.038	−0.258
SO_4^{2-}	14.8	28.6	0.346	**0.765**	−0.406	0.286	−0.004	−0.079
F^-	0.5	0.9	*0.544*	−0.396	−0.135	***0.513***	−0.495	0.124
NO_3^-	2.7	4.9	0.002	*0.573*	**0.751**	0.052	−0.311	−0.071
SiO_2	23.0	15.9	*0.476*	−0.466	0.287	***0.510***	***0.429***	−0.174

Table 6
Principal Component loadings of the 39 bottled waters. For explanation of abbreviations refer to Table 1.

Abbrev.	PC1	PC2	PC3	PC4	PC5	PC6	PC7
ALAR	−0.512	−0.067	−0.039	−0.144	−0.022	0.032	0.009
BSAU	1.864	−0.380	0.029	−0.625	0.002	−0.110	0.118
CAMP	1.017	−0.890	−0.159	0.975	−0.796	0.133	0.067
CAST	0.372	1.037	1.273	0.093	−0.261	0.127	−0.029
CARl	−0.286	−0.263	−0.044	0.170	0.114	−0.065	−0.009
CARg	−0.255	−0.295	−0.077	0.258	0.000	−0.020	0.024
VIDA	−0.457	−0.090	−0.002	−0.080	0.036	−0.035	0.009
FAST	−0.497	−0.078	−0.066	−0.144	0.014	0.025	0.021
FRIZ	1.956	−0.472	−0.082	−0.469	−0.332	0.036	0.177
LUSO	−0.484	−0.041	−0.066	−0.162	−0.008	0.028	0.033
MELG	0.701	−0.104	0.238	0.412	0.620	0.572	0.124
PSAL	1.418	−0.669	0.210	0.039	0.295	0.043	−0.226
PENA	−0.513	−0.012	−0.073	−0.204	−0.047	0.042	0.028
SALU	1.231	−0.684	0.121	−0.319	0.203	−0.220	−0.302
VITA	−0.515	−0.029	−0.084	−0.186	−0.027	0.036	0.018
MONl	−0.133	0.087	−0.482	0.250	−0.319	−0.079	−0.166
MONg	−0.162	0.117	−0.451	0.162	−0.246	−0.102	−0.176
SALU	−0.512	0.041	0.039	−0.195	−0.164	0.044	0.000
VIMl	0.979	1.406	−0.281	0.165	0.051	−0.229	0.121
VIMg	0.941	1.422	−0.259	0.110	−0.023	−0.229	0.132
ALIS	−0.469	−0.073	−0.038	−0.114	0.025	−0.018	0.011
MARA	−0.525	−0.025	−0.086	−0.216	−0.078	0.080	0.020
AREE	0.669	1.072	−0.548	0.124	0.336	0.331	−0.274
CARA	−0.379	−0.147	−0.060	0.070	0.159	−0.050	−0.007
CRUl	−0.239	0.006	−0.040	−0.179	0.065	0.130	0.080
CRUg	−0.202	0.098	−0.114	−0.112	0.065	0.099	−0.035
FFRA	−0.481	−0.075	0.018	−0.087	0.009	0.003	0.003
GLAC	−0.526	−0.081	−0.151	−0.187	−0.038	0.082	0.030
PENH	−0.271	−0.282	−0.064	0.296	0.026	0.003	0.096
SMAR	−0.429	0.269	0.592	−0.048	−0.308	−0.100	−0.110
SSIL	−0.232	−0.022	−0.111	−0.132	−0.004	0.072	0.111
SCRI	−0.461	0.013	0.234	−0.055	−0.070	−0.043	−0.034
SEST	−0.489	−0.076	0.004	−0.100	−0.008	0.015	0.008
MARA	−0.469	−0.071	−0.106	−0.137	−0.018	0.079	0.020
SERR	−0.476	−0.033	−0.041	−0.139	−0.061	0.043	0.040
AQUA	−0.184	−0.353	0.163	0.438	0.505	−0.344	0.088
NEST	−0.188	−0.338	0.178	0.405	0.543	−0.333	0.084
DOMI	−0.299	0.157	0.430	0.188	−0.228	−0.092	−0.112
NOVO	−0.503	−0.074	−0.008	−0.122	−0.008	0.015	0.007

In some of these mineral and spring waters (Carvalhelhos, Luso, Monchique, Vimeiro and Cruzeiro) CO_2 is added and so, the same water can be sold under two types of commercial name: non-carbonated and carbonated (see Table 1).

The carbonated and non-carbonated waters represent 20% and 67%, respectively, of the total number of bottled mineral and spring waters sold in Portugal. The remaining 13% are natural CO_2 waters.

Table 2 shows the hydrochemical types of sampled bottled water, of which 59% are low mineralisation waters, and 15.4% high mineralisation ones, corresponding to natural CO_2 waters (with exception of Campilho), mainly sodium bicarbonate type, with high concentrations of certain elements, such as fluoride. The remaining 26.6% are classified as weakly or medium mineralisation waters.

Graphs of relative anion and cation concentrations were drawn for all waters listed in Table 2.

Fig. 3 displays profiles of HCO_3^- and Na^+ concentrations of all the 39 waters sampled. About 12.8% have concentrations higher than 1000 mg/L HCO_3^- (Campilho, Salus-Vidago, Pedras Salgadas, Bem-Saúde, Frize,) and 23.1% higher than 100 mg/L Na^+ (Campilho, Salus-Vidago, Pedras Salgadas, Bem-Saúde, Frize, Vimeiro non-carbonated, Vimeiro carbonated, Monchique non-carbonated and Monchique carbonated) with maximum values occurring in natural CO_2 water Frize (2182 mg/L HCO_3^- and 704 mg/L Na^+), Bem-Saúde (2181 mg/L HCO_3^- and 647 mg/L Na^+), Pedras Salgadas (2059 mg/L HCO_3^- and 579 mg/L Na^+), and Salus-Vidago (1897.99 mg/L HCO_3^- and 572 mg/L Na^+).

Fig. 4 displays profiles of Ca^{2+}, Cl^-, SO_4^{2-} and SiO_2 concentrations values. The graph shows that 15.4% of waters have concentrations

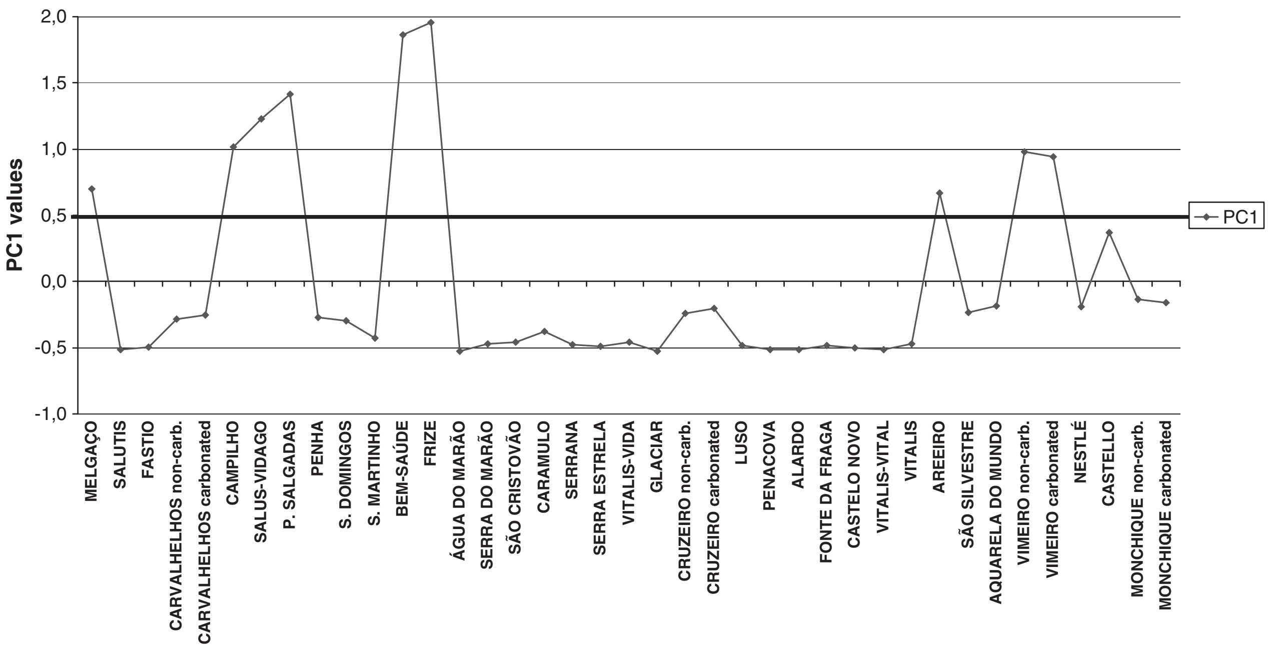

Fig. 7. Profile of 1st Principal Component for the 39 bottled waters.

higher than 100 mg/L Ca^{2+} (Melgaço, Pedras Salgadas, Bem-Saúde, Frize, Areeiro and Castello), 12.8% higher than 100 mg/L Cl^- (Bem-Saúde, Frize, Areeiro, Vimeiro non-carbonated and Vimeiro carbonated), 7.7% higher than 100 mg/L SO_4^{2-} (Areeiro, Vimeiro non-carbonated and Vimeiro carbonated), and 12.8% higher than 50 mg/L SiO_2 (Melgaço, Campilho, Pedras Salgadas, Aquarela do Mundo, Vimeiro and Nestlé). The highest silica contents are observed in Nestlé and Aquarela spring waters, with values exceeding 35% of their total mineralisation.

Concentrations of

- Ca^{2+} >100 mg/L can be observed in Melgaço, Penha, Bem-Saúde, Frize, Pedras Salgadas, Areeiro, Vimeiro non-carbonated and Vimeiro carbonated waters,
- Cl^- >100 mg/L in Bem-Saúde, Frize and Vimeiro water, and
- SO_4^{2-} >100 mg/L in Areeiro, Vimeiro non-carbonated and Vimeiro carbonated waters.

Some of these waters correspond to CO_2 rich waters controlled by deep faults, involving flow of fluids from depth, and others (Areeiro, Vimeiro non-carbonated and Vimeiro carbonated) are related to evaporitic minerals, like halite and gypsum, and to carbonate rocks that occur at the contact of diapiric structures.

Fig. 5 displays Mg^{2+}, K^+, F^- and NO_3^- concentrations values. The graph shows that 7.7% of waters have concentrations higher than 10 mg/L Mg^{2+} (Melgaço, Salus-Vidago and Pedras Salgadas), 12.8% of waters have concentrations higher than 10 mg/L K^+ (Campilho, Salus-Vidago, Pedras Salgadas, Bem-Saúde and Frize), 7.7% of waters have

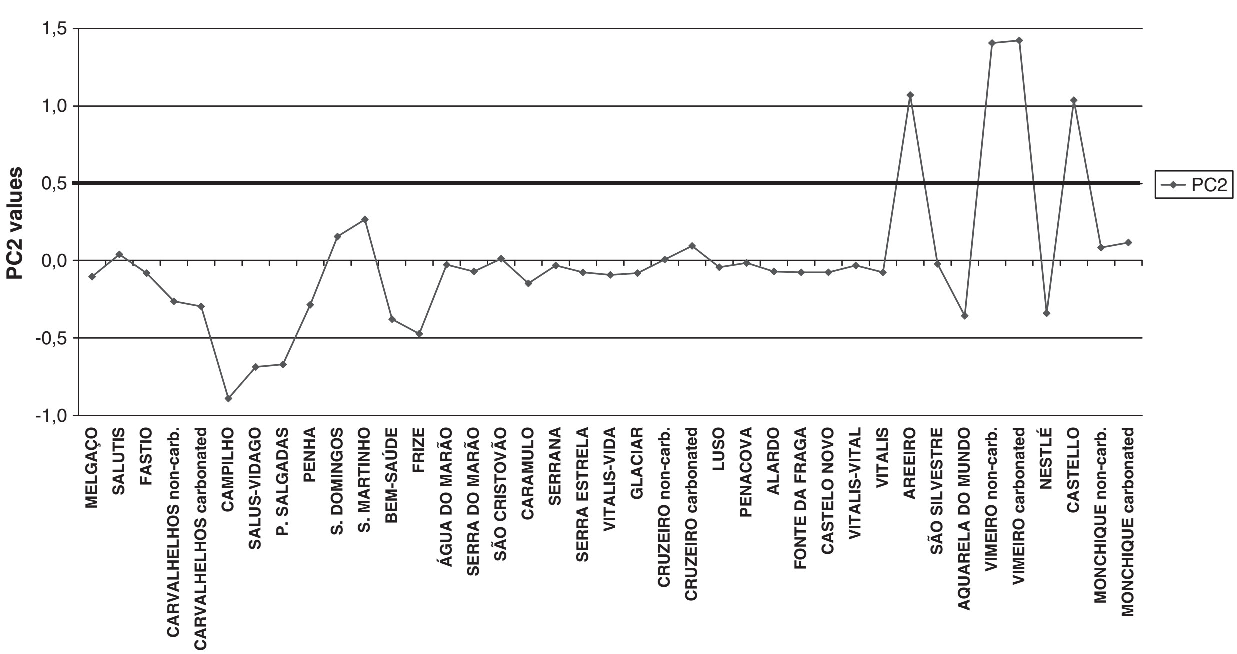

Fig. 8. Profile of 2nd Principal Component for the 39 bottled waters.

concentrations higher than 10 mg/L NO_3^- (S. Domingos, S. Martinho and Castello), and 23.1% of waters have concentrations higher than 1 mg/L F^- (Melgaço, Carvalhelhos carbonated, Campilho, Pedras Salgadas, Penha, Bem-Saúde, Frize, Monchique non-carbonated and Monchique carbonated).

The maximum of Mg^{2+} and K^+ concentrations are mainly observed in CO_2 rich waters, and the highest F^- concentration is detected in the high mineralisation waters Campilho and Frize.

The highest concentrations of NO_3^- (>10 mg/L) are detected in Castello, S. Domingos and S. Martinho.

5. Principal Component Analysis

While univariate statistical analysis of a large amount of data could be cumbersome and cause misunderstanding and error in the interpretation, multivariate statistical techniques are more robust and, thus, become more useful for environmental data treatment and for identification of anomalous patterns. An example of these techniques is Principal Component Analysis (PCA). PCA reduces a large number of variables (e.g. measured physical parameters, anions and cations) to a smaller number, the principal components (PC), allowing to determine which factors (group of parameters) account for the numerical variation of the clusters (Güller et al., 2002) Also, the definition of PCs helps to extract related variables, giving more information than single parameters and to infer the processes that control water chemistry.

In most of the cases, PCA is applied to the linear correlation matrix. To obtain this matrix, data are first standardised by mean centering each column (i.e. the column mean is subtracted from each of the values in the column) within the original data matrix, and then dividing each of the values within each column by the column standard deviation. With PCA, the large data matrix is reduced to two smaller ones that consist of PC scores and loadings. PC loadings are the eigenvectors of the correlation, or covariance matrix depending on PC scores, and, therefore, contain information on all of the variables combined into a single number, with the loadings indicating the relative contribution that each variable makes to that score. PCs are calculated in such a way so that they take into account the correlations present in the original data, but are uncorrelated (orthogonal) to one another. The first PC explains most of the variance within the original data, and each subsequent component explains progressively less. Typically, the data can be reduced to two or three dimensions that account for the majority of the variance within the original dataset. However, in some cases more dimensions may have to be included (Singh et al., 2004).

The loadings are then evaluated to determine the variables that are responsible for these correlations. Variables with the greatest positive and negative loadings make the largest contribution. The loadings can, therefore, be examined to provide further insight into the processes that are responsible for the similarities in the variables (e.g. element concentrations) in surface water (Ribeiro et al., 1999; Thyne et al., 2004).

In this study, PCA was applied to a matrix of concentrations of 10 parameters (columns) observed in 39 bottled waters (lines), which are tabulated in Table 3.

Table 4 shows the eigenvalues, the percentage of explained variance and its cumulated values. The first three factors explain 81.93% of the total variance of the original matrix.

Analysing the projections of the variables on the 1st factorial plane by plotting PC1 against PC2 (Fig. 6) and respective PC loadings (Table 5), it is concluded that the 1st axis explains almost 50% of the total variance, which is a typical mineralisation axis with all the parameters occurring in its positive side. In particular, HCO_3^-, Na^+, Ca^{2+}, Mg^{2+} and K^+, parameters with the highest loadings (>0.8) that contribute significantly for its interpretation.

The 2nd axis, that explains about 23% of the total variance, discriminates sulphate-chloride type waters, with PC loadings higher than 0.6 from another type composed by SiO_2 and F^- (PC loadings lower than −.39).

Finally, the 3rd principal component axis is clearly a pollution index, mainly derived by agricultural activities, as can be confirmed by the high PC loading on NO_3^- (>0.75; see Table 5).

The interpretation given for the associations depicted by the first three principal component axes enables the classification of bottled waters into different hydrochemical types.

Table 6 shows the PC loadings of all 39 bottled waters. A profile of the first three new variables are represented in Figs. 7, 8 and 9, in a similar way to Figs. 3, 4 and 5, which show the raw data. These new

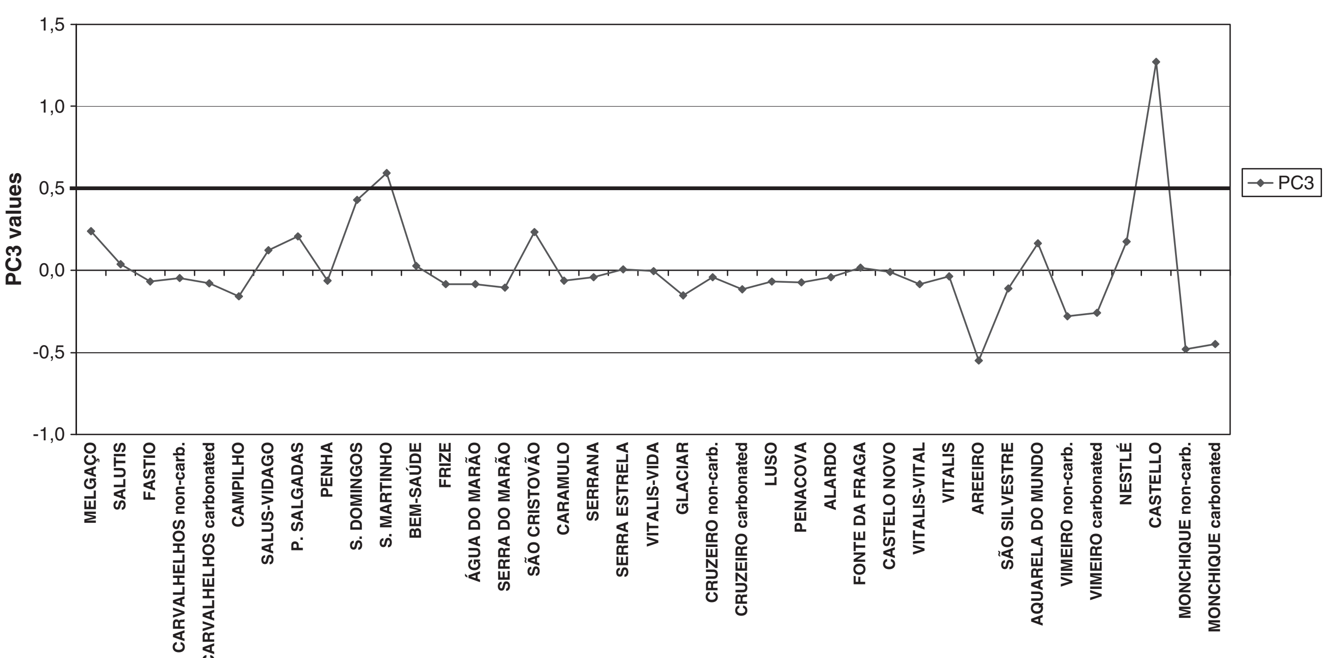

Fig. 9. Profile of 3rd Principal Component for the 39 bottled waters.

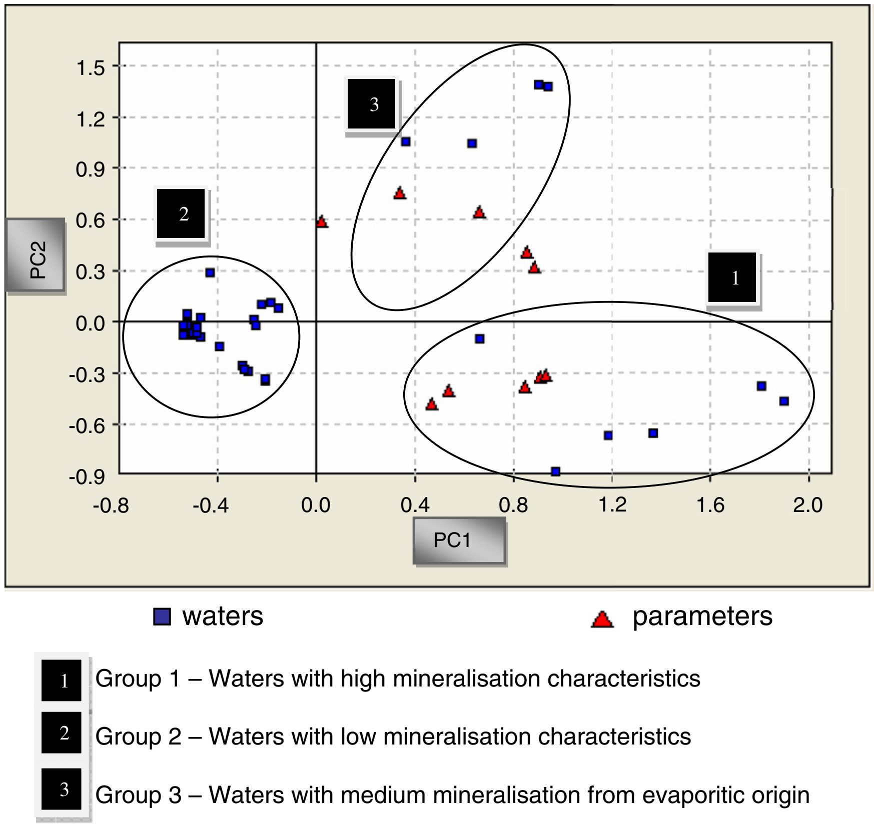

Fig. 10. Projection of the three hydrochemical groups in the 1st factorial plane.

profiles are now a synthesis of the hydrochemical profiles of the 10 original parameters.

Fig. 7 shows the profile of PC1. Considering the reference limit of 0.5 for the PC1 value the mineral and spring waters can be divided in two distinct groups, the high and low mineralisation waters. The former type includes Bem-Saúde, Frize, Pedras Salgadas, Salus-Vidago, Campilho, Areeiro, and Vimeiro bottled waters.

Fig. 8 shows the profile of PC2, where low and high SO_4^{2-}/Cl^{2-} waters are displayed. Considering the reference limit of 0.5 for the PC2 value the mineral and spring waters can be again divided in two distinct groups, the low and high SO_4^{2-}/Cl^{2-} content bottled waters. The former type include Castello, Areeiro and Vimeiro, being the last ones related to evaporitic minerals, like halite and gypsum, and to carbonate rocks that occur at the contact of diapiric structures.

Fig. 9 shows the profile of PC3, which shows waters that are more vulnerable to pollutions sources. This is the case of Castello water, located in Alentejo. The intensive agriculture, the high pollution risk due to carbonate aquifer lithology, and the overexploitation of groundwater resources in the vicinity of the Castello's mineral water concession (Pisões-Moura) contributed to the high nitrate concentrations (28 mg/L) monitored in the hydromineral aquifer.

Finally, the interpretation of the first two principal component axes enables the classification of the bottled waters studied into three hydrochemical groups (Fig. 10):

Group 1 – High mineralisation waters,
Group 2 – Low mineralisation waters, and
Group 3 – Medium mineralisation waters from evaporitic origin.

6. Conclusions

The application of descriptive methods of Multivariate Data Analysis, such as PCA, has shown that this technique is an effective tool in the identification of the main structural interrelationships among the physico-chemical parameters of bottled waters, enhancing their similarities and dissimilarities, and contributing, therefore, to a new typology of the mineral and spring waters bottled in Portugal, based on their hydrochemical characteristics and geological occurrence.

PCA, applied to a matrix of 39 bottled waters and 10 parameters, generated three new synthetic variables, the Principal Components (PCs), with the following clear physical meanings: mineralisation, sulphate-chloride and nitrate pollution, enabling, therefore, the classification of the mineral and spring waters of Portugal into three hydrochemical groups.

In order to control the quality of bottled mineral and spring water in Portugal the monitoring programme should be strengthened and extended to cover a large number of public and private bottled water industries.

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