Multivariate analysis of the water quality variation in the Serra da Estrela (Portugal) Natural Park as a consequence of road deicing with salt

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ABSTRACT

The concentration of some anions (Cl, F, NO_3, and SO_4), cations (Na, K, Ca, and Mg), pH and conductivity was determined in seven sampling points in the Serra da Estrela Mountains (Portugal) to verify if the application of road deicing with salt provokes impact in the water quality. Multivariate chemometric data analysis techniques of clustering and factor analysis were used. Preliminary analysis shows an overall conductivity increase in late spring and a decrease in late summer. A strong association between sodium chloride and the conductivity was observed by cluster analysis. Factor analysis supports the previous results and shows that the variation of the concentration of sodium chloride is the main source of the variance of the data along the year. In conclusion, the spreading of salt during the winter creates a local and seasonal impact on the water quality.

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1. Introduction

The Serra da Estrela is the highest mountain range in the Portuguese mainland, and is an important condensation barrier to the moist air masses from the Atlantic that enter the Iberian Peninsula from the west, playing an important role in the impact on the local water cycle (Fig. 1). This granite mountain range in central Portugal features glacier valleys and many depressions with natural lakes and ponds in its central part above 1400 m elevation [1]. The mountain range is part of the Iberian Central Cordillera and is limited by two steep fault scarps with a relative relief of over 1000 m. The upper area shows two plateaus, divided by the NNE–SSW tectonic lineament of the Zêzere and Alforfa valleys. The western plateau is highest at 1400–1993 m, while on the eastern plateau altitudes stay below 1750 m.

The climate is Mediterranean with warm, dry summers and a wet season from October to May with a mean annual precipitation of 2500 mm at the top of the mountain, while the plateaus show more than 2000 mm [2]. In winter, mainly in December, January and February, the precipitation is frequently in snow form. Registrations over 20 years show an average of 38 and 60 days of snow per year in the soil of two areas: Lagoa Comprida and Penhas da Saúde [3]. During the winter, the snow and low temperatures promote ice formation in

soil and roads, creating many traffic problems which the motorway operator (Estradas de Portugal, S.A.) solves with the spreading of deicing agents. The primary deicing agent is rock salt, consisting mainly of sodium chloride (NaCl), which is an effective deicing substance for temperatures down to −9 °C [4]. Its cost is moderate, the storage, handling and dispersing on the roads is relatively easy [5]. Road salt applications can keep roads free of ice for safe winter travel. However, this practice is questioned because the water from the melting snow dissolves the salt and transports it into streams or lakes through advective transportation or infiltrates the soil into the groundwater. This environmental transportation may lead to an increase of the salt content of the natural soil and water affecting the chemistry and biota of the natural compartments [6]. The population reduction of some amphibian species, embryo malformation, metal ion mobilization and toxicity of plants are only some examples of road deicing salt effect in the biota [7–10].

The analysis of the effect of road deicing salt on water quality has been carried out using a univariate approach. However, multivariate statistical techniques have been shown to be powerful tools for data exploration and analysis when environmental data sets are being researched. This paper focuses on the application of a multivariate strategy based on hierarchical clustering analysis, linear discriminate analysis, principal component analysis and factor analysis to help in the determination of the relation between the water quality and the road deicing with salt in seven different sampling points in the Serra da Estrela Natural Park (Portugal) collected between 26 October 2006 and

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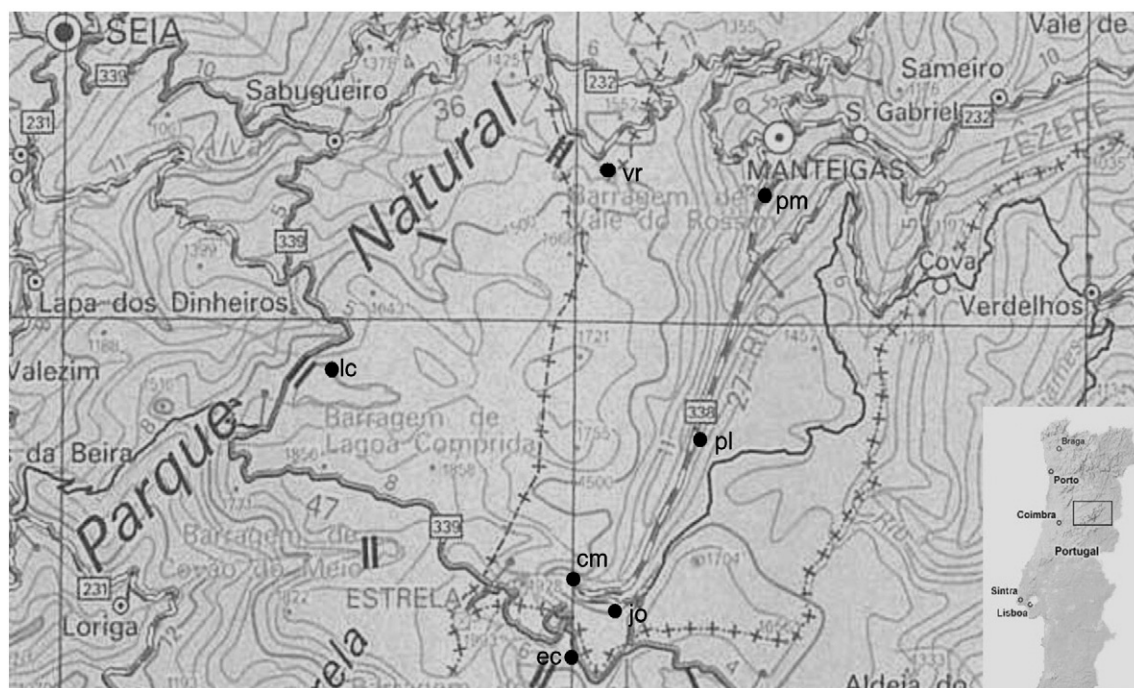
Fig. 1. Water sampling sites at Serra da Estrela Natural Park: **pm**— 40º 23′ 01,22″ N, 7º 32′ 44,71″ W; **pl** — 40º 19′ 52,92″ N, 7º 34′ 15,20″ W; **cm** — 40º 19′ 41,40″ N, 7º 35′ 14,46″ W; **jo** — 40º 19′ 28,45″ N, 7º 34′ 39,80″ W; **ec** — 40º 19′ 13,13″ N, 7º 35′ 20,26″ W; **lc** — 40º 21′ 50,30″ N, 7º 38′ 41,02″ W; **vr** — 40º 24′ 02,49″ N, 7º 35′ 15,05″ W.

7 January 2008. This mountain is a pristine area, with no significant anthropogenic pollution aside from car traffic. The observed trends in the natural water quality parameters were correlated with the road salt applications and the main factor provoking those variations identified.

2. Experimental section

2.1. Sampling sites

Water samples were collected in the following seven locations in the Serra da Estrela area (Fig. 1): **pm** — Ponte Manteigas; **pl** — Fonte Paulo Luis Martins; **cm** — Covão d'Ametade; **jo** — Fonte da Jonja; **ec** — Espinhaço de Cão; **vr** — Vale de Rossim; **lc** — Lagoa Comprida. Four of the samples are surface waters (**pm**, **cm**, **vr** and **lc**) and the other three (**pl**, **jo** and **ec**) are shallow groundwater. The sampling sites **vr** and **lc** are quite distant from the Zêzere Glacier Valley and its waters should not be affected by the addition of salt on the roads. The same is true for site **pl**, whose water source, although located within the Zêzere Valley area, is not affected because its remote origin is not conducive to salt

contamination. These three points can constitute a pristine natural setting for the area under research.

Twenty-two water samples were collected from 26 October 2006 to 7 January 2008, all of which were subjected to chemical analysis for the determination of the following parameters (data set one): conductivity; pH; sodium ion (Na); fluoride ion (F); chloride ion (Cl); nitrate ion (NO_3); and, sulfate ion (SO_4). Fourteen water samples collected from 16 May 2007 to 7 January 2008 were subjected to further chemical analysis for the quantification of the following cations (data set two): calcium (Ca); magnesium (Mg); and potassium (K).

2.2. Deicing agent

Tests conducted on deicing salt samples (5 samples) showed a purity of 96% NaCl and an average composition of 0.58 and 0.38 kg of sodium and chloride ions, respectively, per kg of salt. These results corroborate the fact that NaCl is 40% sodium and 60% chloride by weight. Accordingly, taking into account the amount of salt used in the winter of 2006–07, an addition of 457 and 299 tons of Cl and Na ions, respectively, were used on the roads of the Serra da Estrela.

Table 1
Univariate statistical analysis of conductivity (cond.), pH, anions (F, Cl, NO3, and SO4) and cations (Na, Ca, Mg, and K) between 26 October 2006 and 7 January 2008[a].

| Parameter	Sampling point						
	vr	lc	pl	pm	jo	cv	ec
Cond	17(4)	22(5)	34(7)	32(12)	29(35)	71(32)	185(73)
pH	6.9(0.5)	6.3(0.8)	5.7(0.3)	6.9(0.5)	5.8(1.0)	5.8(0.4)	6.1(0.4)
Na	1.3(0.2)	2.5(0.2)	2.8(0.1)	2.9(0.6)	2.0(0.2)	9.1(4.8)	16.3(7.0)
F	0.1(0.03)	0.1(0.04)	0.2(0.1)	0.2(0.04)	0.2(0.1)	0.2(0.04)	0.4(0.1)
Cl	1.6(0.7)	3.8(0.3)	3.9(0.3)	2.9(0.7)	1.0(0.2)	16.0(8.9)	50.0(20.0)
NO_3	0.3(0.4)	0.3(0.2)	1.4(0.5)	0.6(0.4)	1.8(1.7)	0.4(0.5)	2.1(0.7)
SO_4	0.6(0.1)	0.6(0.1)	0.9(0.1)	0.9(0.2)	0.4(0.2)	0.9(0.3)	0.6(0.1)
Ca	0.3(0.1)	0.3(0.1)	0.8(0.2)	0.8(0.2)	0.2(0.1)	1.0(0.6)	9.9(2.4)
Mg	0.1(0.04)	0.1(0.03)	0.4(0.2)	0.1(0.03)	0.04(0.04)	0.1(0.1)	1.4(0.2)
K	0.2(0.1)	0.2(0.1)	0.3(0.04)	0.2(0.1)	0.3(0.1)	0.7(1.6)	0.6(0.1)

[a] Concentrations in mg L^{-1}.
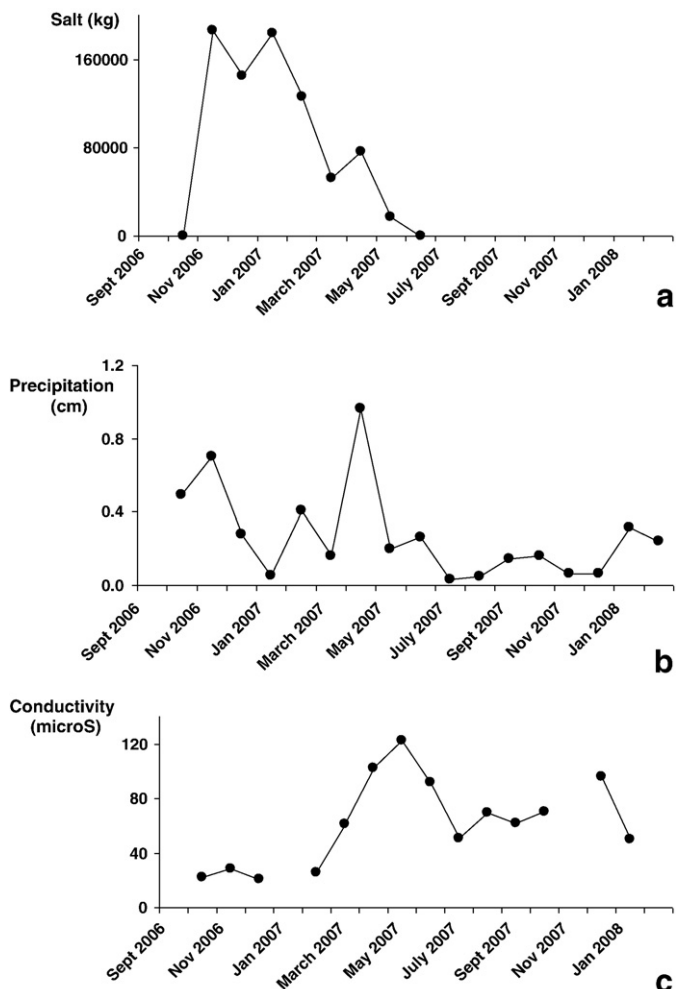
Fig. 2. Average monthly data (September 2006 to January 2008) of salt amount added, precipitation, and conductivity variation in Covão d'Ametade water.

2.3. Analytical procedures

Water samples were analyzed using a Dionex-IX120 ion chromatography (Dionex Corp., Sunnyvale, USA) to determine the anion concentration of F, Cl, NO_3, and SO_4, according to the ISO 10304-1:2007 Standard. The cations K, Na, Ca, and Mg were determined by atomic absorption spectroscopy, using a GBC 906AA spectrometer as described in the ISO 9964:1993 and ISO 7980:1986 Standards. pH measurements were made with a pH meter (Tritilab TIM 900, Radiometer), while conductivity measurements were performed with an Orion conductimeter (model 150). All analytical parameters were determined in the laboratory.

Table 2
Classes detected by cluster analysis and composition.

Class	
1	jo10, jo11, jo12, jo13, jo15, jo16, jo17, jo18, jo19, jo20, cv1, cv2, ec1, ec5
2	jo2, jo3, jo5, jo6, jo7, jo8, jo9, jo14, jo21
3	pm1, pm2, pm3, pm5, pm6, pm7, pm9, pm10, pm11, pm12, pm13, pm14, pm15, pm16, pm17, pm18, pm19, pm20, pm21, cv3, cv4
4	cv5, cv6, cv7, cv13, cv14, cv15, cv16, cv17, cv18, cv19, cv21
5	cv8, cv9, cv10, cv11, cv12, cv20
6	ec2, ec3, ec4, ec6, ec7, ec8, ec9, ec10, ec11, ec12, ec14, ec15, ec16, ec17, ec18, ec19, ec20

Table 3
Average values (standard deviations under parenthesis) of the variable of the detected classes (data set one)[a].

Class	Cond	pH	Na	F	Cl	NO₃	SO₄	Np
1	**22(8)**	5.6(0.3)	**2.1(0.6)**	0.17(0.03)	**1.6(1.8)**	0.7(0.4)	0.3(0.1)	14
2	**21(5)**	5.5(0.2)	**1.9(0.1)**	0.25(0.04)	**1.0(1.2)**	2.3(0.7)	0.5(0.2)	9
3	**30(9)**	6.9(0.4)	**3.0(0.7)**	0.22(0.03)	**3.1(1.3)**	0.6(0.4)	0.8(0.2)	21
4	**66(14)**	5.7(0.4)	**7.8(1.4)**	0.16(0.02)	**14(2)**	0.6(0.6)	0.9(0.2)	11
5	**111(14)**	5.6(0.1)	**16(3)**	0.18(0.05)	**28(4)**	0.2(0.2)	1.3(0.2)	6
6	**211(48)**	6.1(0.3)	**19(5)**	0.40(0.1)	**57(12)**	2.3(0.2)	0.6(0.1)	17

The most important variables are indicated in bold.
[a] Cond — conductivity; Na, F, Cl, NO₃, and SO₄ — concentrations (mg L^{-1}) of the ions sodium, fluoride, chloride, nitrate and sulfate, respectively; Np — number of points.

2.4. Multivariate chemometric analysis

A multivariate chemometric classification of the waters was carried out, first, using a non-supervised approach (non-linear mapping and hierarchical clustering) followed by a brief supervised analysis (linear discriminate analysis). Non-linear mapping (ALSCAL) and hierarchical cluster analysis was used as an unsupervised exploratory technique to detect natural similarities among the parameters analyzed in the water [11]. Squared Euclidean distance was consistently used as the similarity index for clustering, using the average linkage and centroid method. Raw data was standardized based on Z-scores by variable. The discriminant capacity power of the variables was assessed through linear discriminant analysis (LDA) [12,13]. All the statistical multivariate analysis was performed using SPSS 17.0 software for Windows (SPSS Inc., Chicago, IL, USA).

3. Results and discussion

3.1. Preliminary analysis

The univariate statistical analysis of the collected data is shown in Table 1. The preliminary analysis of this table shows an overall lower mineralization in all samples, which reflects low water–rock interaction associated with short surface/underground circulation paths. The water from sites **ec** and **cv** show the highest concentration of Na and Cl ions and conductivity value. These sites are in a topographic elevation near the area of highest addition of salt to the roads and they form a small retention basin that results in the accumulation of water run-off. The other two sites likely to suffer from contamination by sodium chloride (**jo** and **pm**) have a substantially lower value because of dilution effect — in the case of site **pm** (sampling in the Zêzere river, at a distance of approximately 20 km) and the small contribution area, in the case of site **jo**. The remaining water sampling points at **pl**, **lc** and **vr** should not be influenced by the addition of salt to the roads, and the corresponding chemical water composition is taken as characteristic for the region. These last three sampling sites further do not show a marked variation in composition during the year. The analysis of the univariate trend concentrations for the sampling sites studied provide the following information: (i) significant increase in the conductivity and sodium and

Table 4
Average values (standard deviations in parenthesis) of the variable of the detected classes (data set two)[a].

Class	Ca	Mg	K	Np
1	0.2(0.1)	0.1(0.02)	0.3(0.1)	10
2	0.3(0.1)	0.1(0.06)	0.3(0.1)	4
3	0.8(0.2)	0.1(0.03)	0.2(0.1)	14
4	0.6(0.3)	0.1(0.07)	0.2(0.1)	9
5	1.43(0.6)	0.1(0.12)	1.6(2.8)	5
6	11.3(2.1)	1.5(0.13)	0.7(0.1)	12

[a] Ca, Mg, and K — concentrations (mg L^{-1}) of the ions calcium, magnesium, and potassium, respectively; Np — number of points.

Table 5
Discrimination capacity among the detected clusters of the variables.

Variable	Wilks' Lambda	F
Cond	**0.091**	**143.780**
pH	0.257	41.632
Na	**0.110**	**116.830**
F	0.155	78.771
Cl	**0.060**	**223.890**
NO$_3$	0.215	52.557
SO$_4$	0.236	46.538

The most discriminating variables are indicated in bold.

chloride ions concentration between May and July in water sites **cv** and **ec**; (ii) significant increase in conductivity between May and July in the water sampling points **jo** and **pm**; and (iii) small changes for all the water parameters analyzed in the sampling points **pl**, **lc** and **vr**.

Fig. 2 shows the average monthly data (between September 2006 and January 2008) of the amount of salt added to the roads (Fig. 2a), precipitation in the Serra da Estrela (Fig. 2b), and water conductivity at the site of Covão d'Ametade (**cv**) (Fig. 2c). Analysis of this figure shows that the largest amount of salt is added during the months of December, January and February with the highest recorded rainfall occurring in April, as a consequence of leaching of soluble salts (mainly the deicing salt), originating an increase of the water conductivity one month later, in May. This delay suggests that the change in the water quality observed in the late spring season could be due to the addition of salt in the roads. However, the ionic composition variation must be analyzed in order to detect which ions are provoking the conductivity variation or if this variation results from a global ionic strength variation. After July, the conductivity of the water tends to decrease to a basal level. Further information about the variation observed can only be obtained after a multivariate analysis of the water quality parameters.
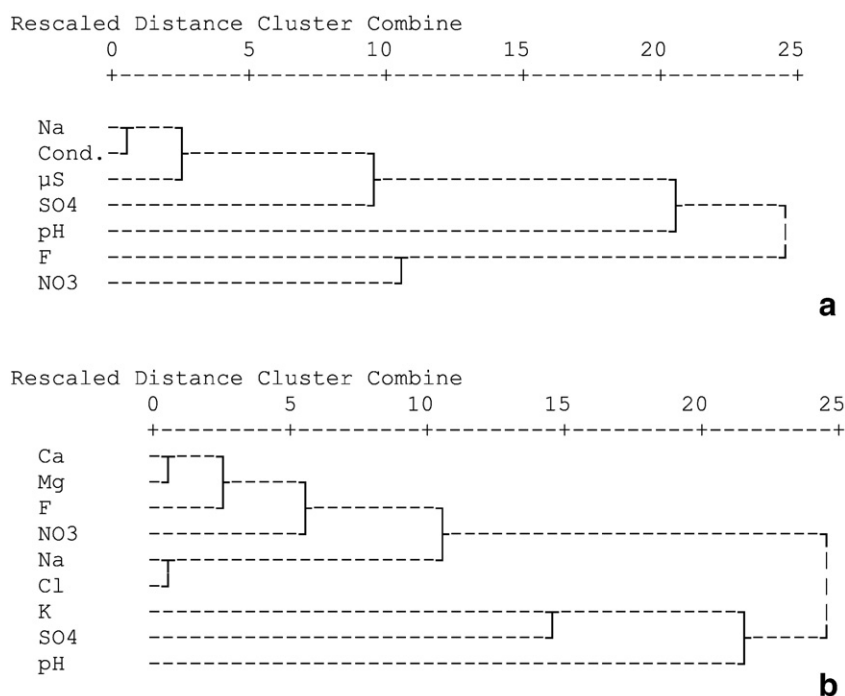
3.2. Cluster analysis

Clustering techniques comprise a series of unsupervised chemometric procedures that involve a measurement of either the distance or similarity between samples. Samples are grouped into clusters according to their similarity — the assumption is that the spatial proximity of the samples in the space of the variables reflects the similarity of their properties [14–16].

The dendogram obtained by cluster analysis of data set one shows the existence of six classes whose composition is presented in Table 2. The analysis of the sample composition of the six classes shows that samples were clustered according to their site of origin. However, some of the samples corresponding to one sampling site were subdivided into two classes; specifically, **classes 1** and **2** correspond to **jo** samples; and **classes 4** and **5** correspond to **cv** samples. This result shows that the natural clustering criterion in this data set is the sample origins, which suggest that the sampling sites **jo**, **pm**, **cv** and **ec** have quite different water compositions and/or chemistries. Moreover, the cluster analysis results show that the water samples from the sampling sites **jo** and **cv** have marked variations during the sampling period because they were divided into two clusters.

In order to obtain quantitative information about the water quality of the detected classes of samples, Tables 3 and 4 (data set one and data set two, respectively) show the corresponding average values and the standard deviations. The analysis of this table clearly shows the existence of an increasing trend in the conductivity variable — the increasing trend corresponds to the increasing class number. **Classes 1** and **2**, constituted by water samples from sampling site **jo**, show the lowest and most similar conductivity values (about 22 μS), differing only in ionic composition. **Class 3** corresponds to water samples from sampling site **pm** and shows a relatively low conductivity of 30(9) μS. **Classes 4** and **5**, constituted by water samples from sampling site **cv**, show quite different and relatively high conductivity values, 66(14) and 111(14) μS respectively. **Classes 6** corresponds to water samples from sampling site **ec** and shows the highest conductivity of 211(48) μS.

In order to assess which variables, besides conductivity, show the highest discrimination capacity for the detected classes, a linear discrimination analysis was carried out and Wilks' Lambda and F-tests were calculated (Table 5). The analysis of this table shows that the three most discriminating water parameters are chloride and sodium

Fig. 3. Dendrograms obtained by cluster analysis of seven and nine significant parameters in data set one (a) and data set two (b) based on the squared Euclidean distance measure and Ward's method.

Table 6
Extracted component matrix and varimax rotated component matrix by principal component analysis method of the variables Cond, pH, Na, F, Cl, NO$_3$, and SO$_4$ ions.

Variable	Component			Rotated component		
	1	2	3	1	2	3
Cond	**0.966**	0.111	−0.107	**0.977**	−0.025	−0.040
pH	−0.063	**0.542**	**0.823**	−0.048	0.141	**0.976**
Na	**0.925**	0.243	−0.240	**0.968**	0.157	−0.103
F	0.864	−0.126	0.372	.800	**−0.421**	0.287
Cl	**0.975**	0.103	−0.098	**0.984**	−0.037	−0.034
NO$_3$	0.654	**−0.511**	0.248	0.545	**−0.674**	0.007
SO$_4$	0.052	**0.883**	−0.217	0.205	**0.867**	0.189

The most significant loadings are indicated in bold.

ions as well as conductivity — the smaller the value of Wilks' Lambda and the higher the *F*-tests, the higher the discriminating capacity of the variable [17,18]. This result shows that the classes are discriminated mainly based on the water conductivity and sodium chloride concentration. Also, this result suggests that the conductivity of the water samples is mainly conditioned by the sodium chloride concentration and that the other ion concentrations show a relatively small effect on the conductivity trend observed.

To obtain further information about the similarity of the variables, cluster analysis was performed and the corresponding dendograms are shown in Fig. 3. Fig. 3a shows the dendogram of data set one and shows that the conductivity and sodium and chloride ions are similar or constitute a well-defined factor of variation of that data set. This result confirms the previous results that water conductivity is markedly associated with the sodium chloride concentration. To analyze the similarity among more variables, but using a smaller number of water samples, the variables of data set two were subjected to cluster analysis and the dendogram obtained is shown in Fig. 3b. The analysis of this figure confirms the association of sodium and chloride ions and reveals another association among the calcium, magnesium and fluoride ions. The first association corresponds to a salinity factor and the second to a solubility factor (calcium fluoride shows low solubility and magnesium has a geological source similar to calcium).

3.3. Factor analysis

Principal component analysis (PCA) was applied to data set one and the extracted eigenvalues, which explained up to 99% of the variance, were: 3.9 (56%); 1.4 (20%); 1.0 (14%); 0.5 (6%); 0.2 (2%). As a result, the first three components that account for 90% of the total variance were further studied as follows.

Table 6 presents the loadings of the three main components. The components are characterized by relatively high loadings for the following variables: (first component) conductivity, sodium and potassium ions; (second component) pH, sulfate and nitrate ions; (third component) pH. To confirm the component composition, a Varimax rotation was applied to these components, resulting in the three factor model shown in Table 6. The rotated loadings enhanced the composition of the first factor (conductivity, sodium and potassium ions), similarly the second factor was simplified by enhancing the loadings of sulfate and nitrate ions and reducing the loading of the pH (a two variable factor); finally, the third factor was clarified, by enhancing the loading of pH, which became a one component factor. The chemical interpretation of the three factors is thus simplified: factor one — salinity induced by the addition of road deicing agent; factor two — geological variation of the two anions sulfate and nitrate; factor three — natural environmental water pH variations.

The PCA score plot, shown in Fig. 4 (with the first two principal components accounting for 76.5% of the total variance), confirms that the conductivity is highly associated with the sodium chloride in the data set under investigation. Indeed, these three variables are quite close in the projection plot.

These results strongly support that the main source of variance in the data is due to an annual variation of sodium chloride in the water samples studied (which is reflected in the conductivity) — greater than 50% of the data variance. Because the only external source of sodium chloride in the area under study is the anthropogenic spreading of deicing salt during winter, this operation is responsible for that source of variation. From an environmental perspective, the data analyzed supports a local and potentially seasonal impact observed in the water quality.

4. Conclusions

The application of a multivariate approach to the road deicing environmental problem was successful. Chemometric techniques, like hierarchical clustering analysis, linear discriminate analysis, and principal component analysis, allow for the identification of the main factor of variability of the water quality, specifically the addition of road deicing salt.
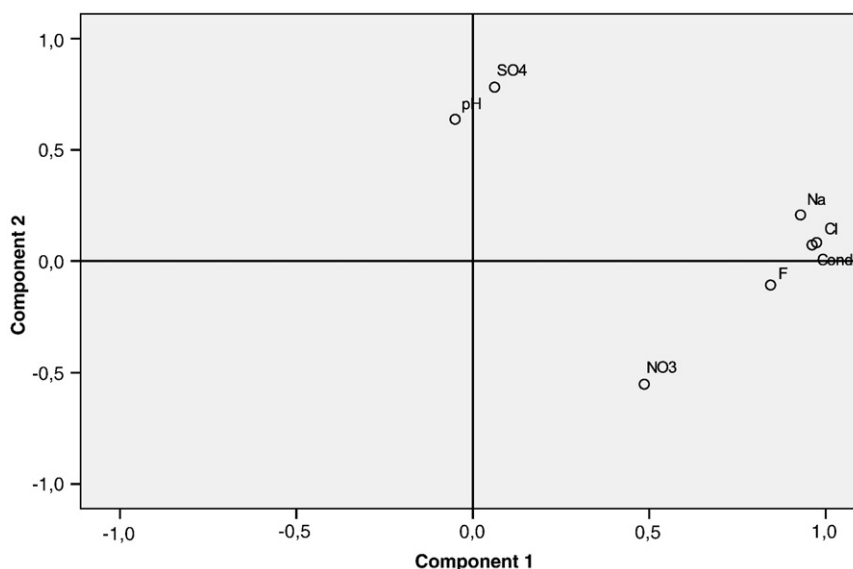

Fig. 4. PCA score plot of data set one for the four sampling points (**cv**, **ec**, **pm**, and **jo**).

Clustering techniques show, as expected, that the water conductivity is mainly conditioned by the sodium chloride concentration. The principal component analysis results obtained in this study show that deicing salt is the main source of variation in the water quality in the Serra da Estrela Natural Park during the year. This common operation during the winter provokes an increase of the sodium and chloride ion concentration of the surface water of the most vulnerable water sites. However, the increase of sodium chloride concentration is seasonal, from late spring and early autumn.

Similar sodium chloride concentration trends were observed by Novotny et al. [5]. However, no information was obtained about the impact on groundwater or about the environmental and ecological impact of seasonable salinization. Nevertheless, the chloride concentrations in the Serra da Estrela water never exceed the chronic and acute level defined for aquatic life by Minnesota Pollution Control Agency, which is 230 and 860 mg L^{-1}, respectively [5]. Indeed, all the chloride ion concentrations obtained in this study are much lower than that. Water quality degradation could be due to mobilization of trace elements, like heavy metals, *via* ion exchange, as a result of the use of NaCl as a deicing agent [19,20]. The influence of this phenomenon on groundwater quality is another important aspect because the magnitude of contamination is higher than in the surface [21,22]. These situations need to be researched in future studies, especially in the most sensitive areas of the Natural Park.

Acknowledgments

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