The use of multivariate statistical analysis to evaluate spatial and temporal water contamination in Germunde coal mine (Portugal)

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ABSTRACT

Mine water pollution is a widespread problem in the whole world. In Portugal, since the early nineties, several actions aiming to study and to characterize the seriousness and the extend of pollution due to abandoned mines were performed. Germunde Colliery is an underground coal mine closed in 1994. Since then, some water-quality monitoring (1998, 2003, and 2004) has been made with the goal of studing the evolution of surface and groundwater. The abandoned network comprises both mines that have flooded naturally as well as free-draining mines that have not flooded. Mine waste deposit drainage is also analyzed. Different water types evolution are expected to exist.

In order to achieve spatial / temporal patterns of hydrochemistry data set, multivariate statistical techniques were applied. Principal Component Analysis (PCA) and Correspondence Analysis allow the identification of structural relationships (similarities and/or oppositions) between various hydrochemical descriptors as well as geological features and mining infrastructures.

The results will emphasize the major pollution risk areas providing valuable information to implement groundwater monitoring network.

Finally cluster analysis (CA) techniques were applied in order to classify groups of variables with similar characteristics.

INTRODUCTION

Drainage from coal mines is one of the most important environmental legacies of industrial economics. Several problems are associated with coal mine drainage such as: sedimentation of chemical precipitates, soil erosion, loss of aquatic habitat, corrosion of metal structures due to contact with acid water (Williams *et al*, 2002) and acid water generated by the oxidation of pyrite reacts with parent rock, resulting in the leaching of many elements (Sullivan & Yelton, 1988).

The presence of mining contamination in waters in the study area is generalized, although, it's more emphasized in adits and spoil. The contaminated waters have $Mg\text{-}SO_4^{2-}$ facies with low pH and the presence of metals is very high especially iron, manganese, aluminium, zinc, nickel, beryllium and yttrium.

Multivariate data analysis is used here to classify and characterize structural relationships between variables and samples and to study the contribution of each one to the structure of hydrochemical data. Furthermore these techniques are powerful tools to distinguish the different processes of pollution.

MATERIAL AND METHODS

Study Area

The Germunde coal mine is part of the Douro Carboniferous Basin (BCD - Bacia Carbonífera do Douro). It is located in the NW of Portugal and it's composed by a narrow NW-SE strip of continental Carboniferous terrains.

The study area is located on the left margin of the Douro River and bounded by the Germunde Mine infrastructures in the NW and the Arda River in the SE (figure 1).

The SW and NE borders of the coal mine are formed by the Upper Precambrian and/or Cambrian Schist Complex ("Complexo Xisto - Grauváquico") and the Ordovician Formations, respectively.

The Carboniferous rocks of this area consist of a basal breccia overlayed by a complex system of coal flakes, intercalated by conglomerates, sandstones and schists. The whole system trends to 140ºE and dips between 60º and 90º towards NE (Pinto de Jesus, 2001).

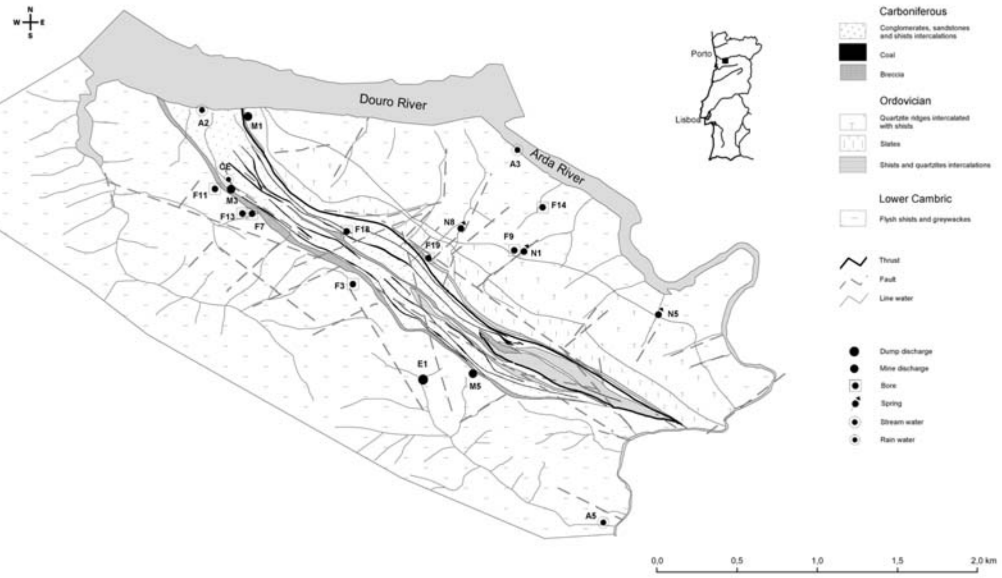

Figure 1: Location of the sampling points overlying a section of "Planta Geológica do Sector Germunde-Arda, E.C.D." (Gaspar *et al*, 1993)

Important conjugated NW-SE and NE-SW faults can be observed across the whole basin. The former direction coincides with the axial surface of the Valongo anticline. Minor faults can also be found, their directions varying from NNE-SSW to NNW-SSE, and from ENE-WSW to WNW-ESE.

Vertical discontinuities can also be observed at the surface caused by subsidence (Chaminé and Silva, 1997). Although exploitation of coal in Germunde started in the beginning of the twentieth century, only in 1966, with the modification of exploration method (without refilled), subsidence began to be the main responsible for the fracturing in the neighbourhood of the stopes and to its propagation to the surface, causing many problems of surface degradation (Gaspar *et al*, 1994).

Monitored parameters and analytical methods

The monitoring network was implemented to observe mine waters (shaft, adits and spoil) and their impact by acid mine drainage or "unpolluted" waters like bores, springs and streams (figure 1). This sampling strategy was designed in order to cover a wide range of determinant sites, which reasonably represent the water quality in the study area. According to the water-quality monitoring program, six field campaigns (winter / summer) were performed during 1998, 2003 and 2004 in order to have a proper study of the spatial and temporal patterns of both surface and groundwater (Table 1). During summer, some samples were not collected because these sites had dried up.

During field campaigns - pH, temperature (T), electrical conductivity (EC), reduction-oxidation potential (Eh) and total dissolved salts (TDS) - were measured *in situ*. Physical parameters, major and minor ions and trace element were analysed in the laboratory following standard protocols.

Sampling Station	Type	May 98	October 98	April 03	October 03	June 04	October 04
A1	Stream	A	B	D	E	F	G
A2	Stream	A	B	D	E	F	G
A3	Stream	A	B	D	E	F	G
A5	Stream	A	B	D			
F3	Bore	A	B	D	F	F	G
F7	Bore	A	B	D	E	F	G
F9	Bore	A	B	D	E	F	G
F11	Bore			D	E	F	G
F13	Bore			D	E	F	G
F14	Bore			D	E	F	G
F18	Bore			D			
F19	Bore			D		F	
N1	Spring	A	B				
N8	Spring			D	E	F	G
M1	Adit	A	B	D	E	F	G
M3	Adit	A	B	D		F	G
E1	Dump	A	B	D	E	F	G

Table 1 – Identification of sample points and correspondent campaign.

Data treatment and multivariate statistical methods

Exploratory data analysis was carried on 6 field water-campaigns. The boxplots of the elements pH, SO_4^{2-}, Mg^{2+}, Al, Fe, Mn, Zn and Ni are shown in figure 2.

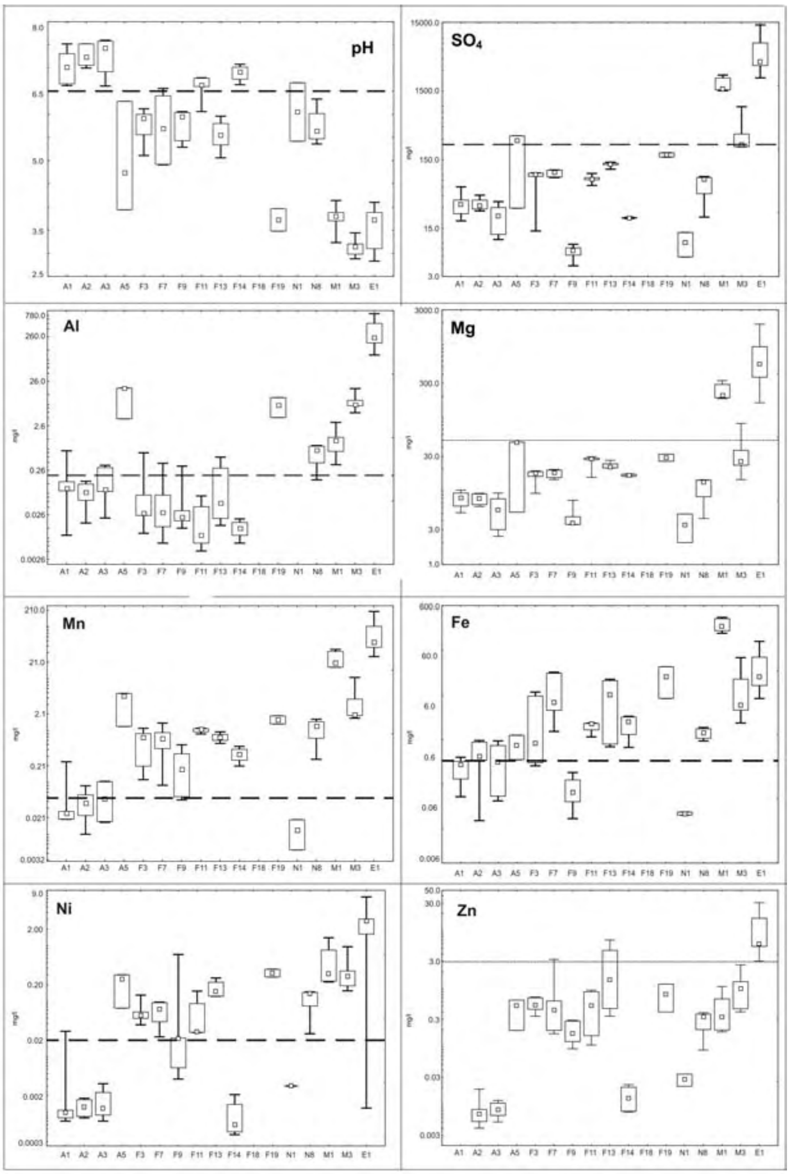

Figure 2: Boxplots illustrating distribution of pH, SO_4^{2-}, Al, Mg, Mn, Fe, Ni and Zn (y axes in logarithmic scale). Broken line represents the parametric value from Directive 98/83/CE. Dash line (in Mg and Zn) represent the maximum admissive value from Portuguese law (D.L. 236/98).

In all boxplots it's possible to distinguee 3 kind of groups: superficial waters (streams), groundwaters (springs and bores) and mine / spoil. Exceptions inside these major groups (like A5, F19, N8 in Al boxplot) reveals acid drainage. In general, the group of values on each type of station is very close to each median values.

SO_4^{2-} boxplot shows clearly the high concentrations of this anion in mine discharges. It is clear the positive symmetry between SO_4^{2-}boxplot and Mg boxplot. Comparing pH, Ni and Zn boxplots we can observed that when we have lower pH the presence of Ni and Zn in water raise. This is due to the increase of mobility of these ions with low pH.

Cluster analysis (CA) was used to highlight groups of samples with similar characteristics.

Hierarchical methods are the most widely applied clustering techniques in Earth Sciences (Davis, 1986). Various aggregate and distance criteria were used. The best dendogram was obtained with the Euclidean distance using raw data.

Principal Component Analysis (PCA) allows us to reduce a set of observed variables into a smaller set of artificial variables called principal components (PC). This technique attempts to reveal the correlation structure of the variables allowing interpretation of geological processes affecting the hydrochemical data.

PCA was applied in two scenarios (two different correlation matrixes) that combined distinct sets of samples. On the first scenario all the samples were included. The second scenario was applied after the result obtained by CA and two clusters of samples, which represent the most contaminated waters, were taken off. The variables selected were the same.

RESULTS AND DISCUSSION

Figure 3 represents the dendogram obtained by CA. A total of 78 water analyses were grouped into six statistically significant clusters at (D_{link}/D_{max}) x 100 < 45. Each cluster contains a set of samples with similar hydrochemistry facies.

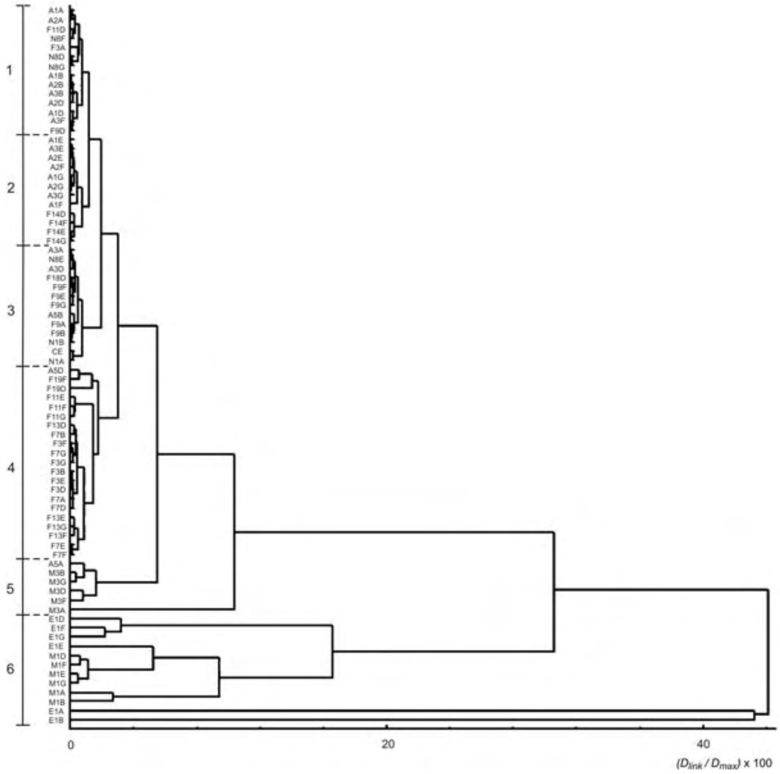

Figure 3: Dendogram obtained by the hierarchical cluster analysis using raw data

Clusters 1, 2 and 3 represent hydrochemical variations of unpolluted waters or relatively low pollution waters by ARD. Cluster 4, 5 and 6 represent a set of contaminated waters, with concentrations increasing from 4 to 6. Cluster 4 represents bores and stream (A5D) affected by mine flood or drainage, with waters of Mg-SO_4^{2-} facies although the concentration of these elements is lower than in cluster 5 and 6.

Cluster 5 represents adit M3 which is a free-draining level that has not flooded with seasonal variations and stream A5 which is characterized by a higher degree of pollution once it is a receiver of spoil discharge. Cluster 6 is build with water analysis of spoil (E1) and by adit M1 which represent the discharge of flooded level. Note that samples collected in the same site (for example F3 or F11) for different campaigns can appear in a different cluster. This reveals that the mixture of waters can occur (by fractures) during the variation of the seasonal level.

PCA was therefore applied first in the entire data set (1st scenario) and then, in the 2nd scenario where the principal contaminated waters from adits and spoil were left out (clusters 5 and 6 of CA). This strategy was used because these samples appear to overshadow other potentially interesting hydrogeochemical processes.

Tables 2 and 3 shows the *pxp* correlations matrixes, revealing the existence of bivariate linear correlations between variables. According to Davis (1986) values larger than 0.5 or smaller than -0.5 indicate significant correlation. As we can see they show some significant differences.

Correlations between the major ions SO_4^{2-}, Ca^{2+}, Mg^{2+}, Si and metals Zn, Mn, Be, Y, Li and Al are very high on the 1st scenario, which are highly correlated with EC and hardness. This is a testimony of mineral weathering process as a source of mine water contamination. A good example is ratio Al / Si: in non/weakly contaminated waters their correlation is inexistent but when mine water contaminations exists a strong correlation between them exists due to weathering of aluminium-silicates. In table 3 these correlations are weaker or disappear. Ca^{2+}, HCO_3^- and alkalinity present a very strong correlation.

Figure 4 shows the projection of variables on the 1st factorial plan, build with the 1st (F1) and 2nd (F2) axes for all data set (1st scenario).

F1 accounts for 51.78% of the variation of the initial matrix data. This axis shows an opposition between EC, hardness, SO_4^{2-}, Ca^{2+}, Mg^{2+}, SiO_2, Li, Mn, Zn, Co, Ni, Be, Y, Sr, Al, Si (negative side) and pH (positive side). In ARD this negative correlation is typically observed between pH and concentrations of many metals and metalloids, base cations and sulphate (Banks, 2004). This correlation is due to genetic co-variation (generation of protons, sulphate and metals in sulphide weathering reactions) and pH-dependent solubility of many ARD related metals. The relative position of Fe in this 1st factorial plan is explained by the fact that the relationship between pH and Fe is not straight-forward due to the multiplicity of “sink” reactions which operate when water is very aggressive (Wood *et al*, 1999). F2 explains 12.71% of total variance. Variables alkalinity (Alc) and HCO_3 are located in the positive side in opposition to Cl, Na, K and Fe, projected in negative part of the axis, which can be attributed to water mineralization.

Figure 5 shows the projection of samples on the 1st factorial plan. We can distinguish here 3 groups: spoil discharges (1), mine discharges (2) and a third group formed by bores, springs, streams and rain water (3). As we can see, the contaminated sites are in the negative side of F1, according to interpretation of the 1st factorial plan (see figure 4). Figure 5 reveals a decrease of contamination in spoil discharge and mine adits groups since 1998. For the other hand bores group don’t have the same hydrochemical variations which are associated with similar variations of flow, recharge and piezometer level in the terrain.

Table 2: ***pxp*** **correlation matrix based on all data set (1st scenario)**

Variable	pH	EC	Alc.	Hard.	Cl^-	SO_4^{2-}	NO_3^-	F^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	SiO_2	HCO_3^-	Li	Fe	Mn	Zn	Cu	Co	Ni	Ba	Be	Y	Sr	Al	Si
pH	**1.00**																										
EC	**-0.60**	**1.00**																									
Alc.	**0.70**	-0.32	**1.00**																								
Hard.	**-0.52**	**0.96**	-0.28	**1.00**																							
Cl^-	-0.37	-0.01	-0.21	-0.11	**1.00**																						
SO_4^{2-}	**-0.52**	**0.99**	-0.29	**0.97**	-0.08	**1.00**																					
NO_3^-	-0.14	0.41	-0.21	0.40	-0.09	0.42	**1.00**																				
F^-	-0.34	0.36	-0.22	0.23	0.32	0.31	0.19	**1.00**																			
Na^+	-0.45	0.19	-0.28	0.09	**0.65**	0.09	0.19	0.08	**1.00**																		
K^+	-0.27	0.20	-0.22	0.15	0.12	0.11	0.20	-0.03	**0.55**	**1.00**																	
Ca^{2+}	**-0.51**	**0.89**	-0.24	**0.83**	0.05	**0.83**	0.33	0.36	0.30	**0.52**	**1.00**																
Mg^{2+}	-0.48	**0.96**	-0.26	**0.98**	-0.12	**0.98**	0.43	0.21	0.08	0.10	**0.81**	**1.00**															
SiO_2	-0.42	**0.55**	-0.08	**0.55**	0.31	**0.57**	0.05	0.07	0.33	-0.25	0.32	**0.59**	**1.00**														
HCO_3^-	**0.70**	-0.32	**1.00**	-0.28	-0.21	-0.29	-0.21	-0.22	-0.28	-0.22	-0.23	-0.26	-0.09	**1.00**													

Li	**-0.50**	**0.95**	-0.28	**0.93**	-0.04	**0.97**	0.43	0.41	0.05	0.00	**0.76**	**0.95**	**0.59**	-0.28	**1.00**												
Fe	-0.47	**0.46**	-0.30	0.41	0.13	0.36	0.16	0.06	**0.53**	**0.85**	**0.75**	0.35	0.01	-0.30	0.23	**1.00**											
Mn	**-0.50**	**0.98**	-0.28	**0.97**	-0.11	**1.00**	0.42	0.26	0.07	0.10	**0.82**	**0.99**	**0.57**	-0.28	**0.97**	0.35	**1.00**										
Zn	-0.41	**0.89**	-0.23	**0.90**	-0.09	**0.94**	0.38	0.16	0.02	-0.10	**0.64**	**0.94**	**0.66**	-0.23	**0.93**	0.13	**0.94**	**1.00**									
Cu	-0.36	0.34	-0.23	0.39	-0.06	0.33	0.02	0.13	-0.11	-0.15	0.19	0.28	0.21	-0.23	0.29	-0.02	0.32	0.38	**1.00**								
Co	-0.47	**0.96**	-0.26	**0.96**	-0.16	**0.99**	0.42	0.21	0.02	0.02	**0.75**	**0.98**	**0.60**	-0.26	**0.96**	0.27	**0.99**	**0.96**	0.34	**1.00**							
Ni	-0.45	**0.59**	-0.28	0.49	0.03	**0.56**	0.13	0.43	0.03	0.01	**0.50**	0.48	0.32	-0.28	**0.53**	0.16	**0.52**	0.48	**0.71**	**0.51**	**1.00**						
Ba	0.19	-0.24	0.19	-0.20	-0.03	-0.22	-0.09	-0.04	-0.14	0.00	-0.18	-0.21	-0.25	0.20	-0.21	-0.13	-0.22	-0.18	0.05	-0.22	-0.18	**1.00**					
Be	-0.45	**0.92**	-0.25	**0.91**	-0.15	**0.96**	0.37	0.24	-0.03	-0.08	**0.69**	**0.94**	**0.60**	-0.25	**0.94**	0.15	**0.95**	**0.95**	0.47	**0.97**	**0.67**	-0.22	**1.00**				
Y	-0.42	**0.92**	-0.24	**0.92**	-0.14	**0.96**	0.41	0.33	-0.05	-0.11	**0.68**	**0.95**	**0.60**	-0.24	**0.97**	0.12	**0.96**	**0.96**	0.38	**0.98**	**0.57**	-0.20	**0.97**	**1.00**			
Sr	-0.08	**0.64**	0.14	**0.61**	-0.05	**0.62**	0.30	0.21	0.18	0.37	**0.74**	**0.61**	0.20	0.15	**0.56**	0.45	**0.61**	**0.51**	0.03	**0.57**	0.27	0.07	**0.51**	**0.53**	**1.00**		
Al	-0.41	**0.92**	-0.22	**0.92**	-0.15	**0.96**	0.39	0.26	-0.07	-0.11	**0.67**	**0.95**	**0.59**	-0.22	**0.96**	0.11	**0.97**	**0.97**	0.39	**0.98**	**0.56**	-0.20	**0.98**	**0.99**	**0.52**	**1.00**	
Si	**-0.52**	**0.75**	-0.24	**0.73**	0.17	**0.76**	0.26	0.04	0.37	-0.08	**0.52**	**0.77**	**0.88**	-0.24	**0.74**	0.21	**0.77**	**0.80**	0.26	**0.78**	0.38	-0.35	**0.76**	**0.74**	0.34	**0.75**	**1.00**

Table 3: *pxp* correlation matrix without clusters 5 and 6 (2nd scenario)

Variable	pH	EC	Alc.	Hard.	Cl^-	SO_4^{2-}	NO_3^-	F^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	SiO_2	HCO_3^-	Li	Fe	Mn	Zn	Cu	Co	Ni	Ba	Be	Y	Sr	Al	Si
pH	**1.00**																										
EC	-0.29	**1.00**																									
Alc.	**0.60**	0.31	**1.00**																								
Hard.	-0.36	0.40	-0.05	**1.00**																							
Cl^-	-0.46	**0.55**	-0.13	0.02	**1.00**																						
SO_4^{2-}	**-0.58**	**0.79**	-0.21	0.36	0.44	**1.00**																					
NO_3^-	0.04	-0.32	-0.20	-0.15	0.00	-0.39	**1.00**																				
F^-	-0.12	**0.58**	0.29	0.19	0.13	**0.53**	-0.32	**1.00**																			
Na^+	-0.28	0.39	-0.12	-0.11	0.88	0.21	0.15	-0.14	**1.00**																		
K^+	0.09	-0.20	-0.09	-0.17	0.02	-0.26	0.47	-0.18	0.17	**1.00**																	
Ca^{2+}	**0.61**	0.47	**0.87**	-0.01	-0.08	0.00	-0.15	0.37	-0.03	0.01	**1.00**																
Mg^{2+}	-0.45	**0.91**	0.14	0.32	**0.50**	**0.89**	-0.39	**0.57**	0.27	-0.36	0.22	**1.00**															

SiO_2	-0.35	**0.54**	0.08	0.02	**0.76**	0.42	-0.36	0.14	**0.66**	-0.41	-0.01	**0.58**	**1.00**														
HCO_3^-	**0.60**	0.30	**1.00**	-0.05	-0.13	-0.21	-0.20	0.29	-0.12	-0.08	**0.87**	0.14	0.08	**1.00**													
Li	-0.48	**0.55**	-0.04	0.21	0.46	**0.71**	-0.42	**0.53**	0.13	-0.27	-0.04	**0.69**	**0.51**	-0.04	**1.00**												
Fe	**-0.55**	0.36	-0.25	**0.59**	0.30	0.41	-0.25	-0.04	0.25	-0.24	-0.24	0.32	0.34	-0.25	0.28	**1.00**											
Mn	**-0.59**	**0.51**	-0.22	0.21	0.19	**0.81**	-0.29	**0.50**	-0.06	-0.34	-0.21	**0.77**	0.28	-0.23	**0.65**	0.24	**1.00**										
Zn	-0.25	0.31	-0.18	0.13	**0.53**	0.39	-0.15	0.14	0.42	-0.07	-0.10	0.35	0.42	-0.18	0.42	0.14	0.17	**1.00**									
Cu	**-0.53**	0.26	-0.26	**0.90**	0.07	0.33	-0.10	0.11	-0.06	-0.12	-0.24	0.23	0.03	-0.26	0.24	**0.62**	0.22	0.28	**1.00**								
Co	**-0.74**	0.43	-0.40	**0.61**	0.09	**0.73**	-0.19	0.41	-0.14	-0.18	-0.33	**0.58**	0.10	-0.40	**0.60**	**0.50**	**0.77**	0.18	**0.65**	**1.00**							
Ni	**-0.56**	0.25	-0.36	0.35	0.26	0.47	-0.15	0.18	0.08	-0.02	-0.35	0.40	0.21	-0.36	0.42	0.33	0.49	0.35	0.44	**0.59**	**1.00**						
Ba	0.02	0.01	0.12	0.03	-0.02	-0.06	0.02	0.20	-0.09	0.17	0.17	-0.09	-0.16	0.13	0.01	0.06	-0.12	0.08	0.26	-0.02	-0.02	**1.00**					
Be	**-0.65**	0.38	-0.39	0.36	0.12	**0.69**	-0.25	0.22	0.04	-0.24	-0.34	**0.53**	0.20	-0.39	0.41	**0.61**	**0.76**	0.14	0.42	**0.79**	0.46	-0.05	**1.00**				
Y	-0.43	0.34	-0.25	0.22	-0.03	**0.68**	-0.11	0.32	-0.22	-0.18	-0.19	**0.56**	0.00	-0.25	0.39	0.19	**0.83**	0.03	0.21	**0.67**	0.36	-0.08	**0.72**	**1.00**			
Sr	**0.53**	0.33	**0.52**	-0.06	-0.03	0.01	0.00	0.25	0.06	0.24	**0.78**	0.06	-0.12	**0.53**	-0.09	-0.17	-0.26	0.00	-0.22	-0.31	-0.27	0.32	-0.30	-0.21	**1.00**		
Al	-0.46	0.36	-0.24	**0.52**	-0.11	**0.65**	-0.06	0.35	-0.31	-0.19	-0.18	**0.54**	-0.09	-0.24	0.36	0.27	**0.77**	0.05	0.49	**0.76**	0.41	-0.05	**0.68**	**0.92**	-0.23	**1.00**	
Si	-0.39	0.45	-0.08	-0.01	**0.72**	0.37	-0.22	-0.03	**0.73**	-0.37	-0.13	0.48	**0.90**	-0.09	0.29	0.38	0.26	0.33	0.00	0.08	0.15	-0.27	0.31	0.01	-0.17	-0.10	**1.00**

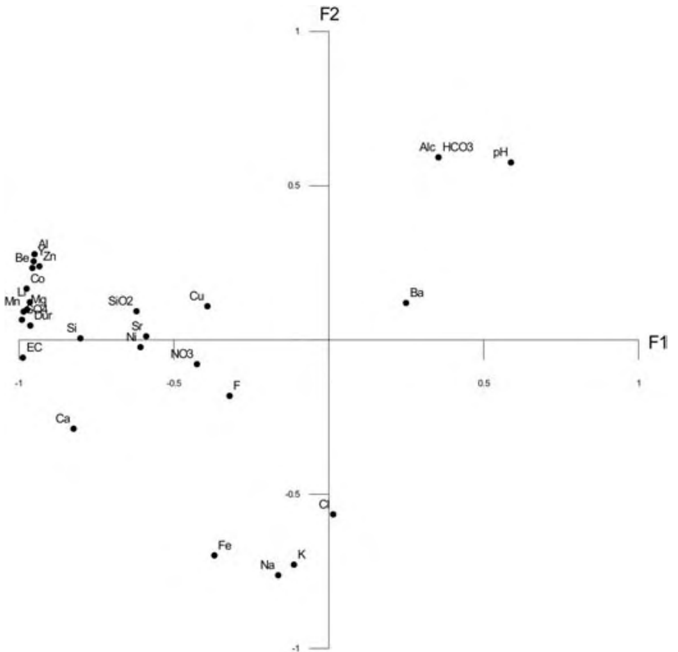

Figure 4: Projection of variables on the 1st factorial plan, 1st scenario

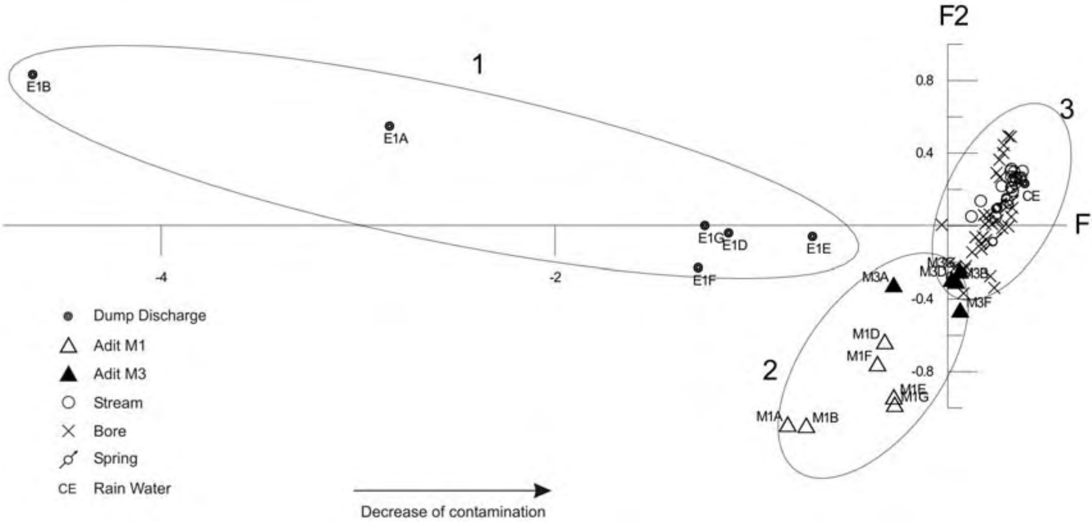

Figure 5: Distribution of different water samples on the 1st factorial plan, 1st scenario

In Figure 6 the 2nd scenario is project. The first factorial plan explains 34% of the variance and it is positively correlated with pH and negatively correlated with SO_4^{2-}, Mg, Mn, Co, Be. Correlations among Co, Be, Al and Y are high. The second factor explains 17% of the variance and it's positively correlated with alkalinity (Alc), Ca^{2+}, HCO_3^- and EC.

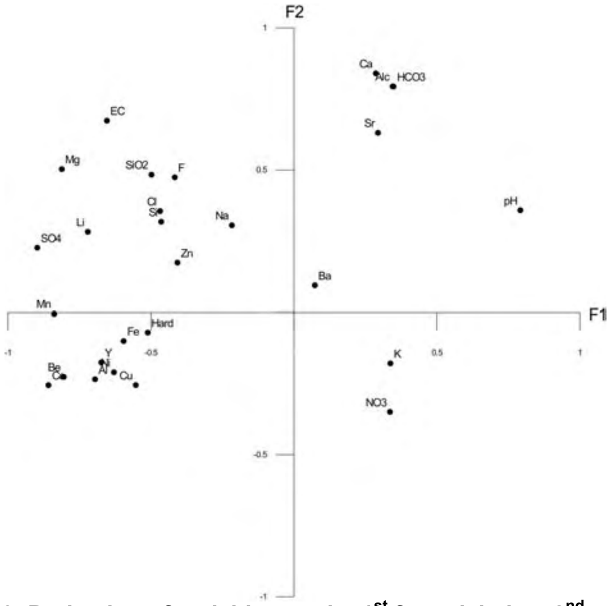

Figure 6: Projection of variables on the 1st factorial plan, 2nd scenario

Figure 7 is the projection of samples included in the matrix of the 2nd scenario. Here, the samples included on the third group of Figure 5 are projected among all factorial plan. It permits the hydrochemical fingerprint visualization of each water sample.

First factorial plane separates the region where acid-base (neutralization) reactions occur (positive loadings) of environments were oxidation reactions dominates (negative loadings). The presence of samples from the same site in different quadrants reveals mixture of waters by fractures.

Second factorial plan separates the regional facies waters – HCO_3^- with positive loadings and Cl^- facies with negative loadings.

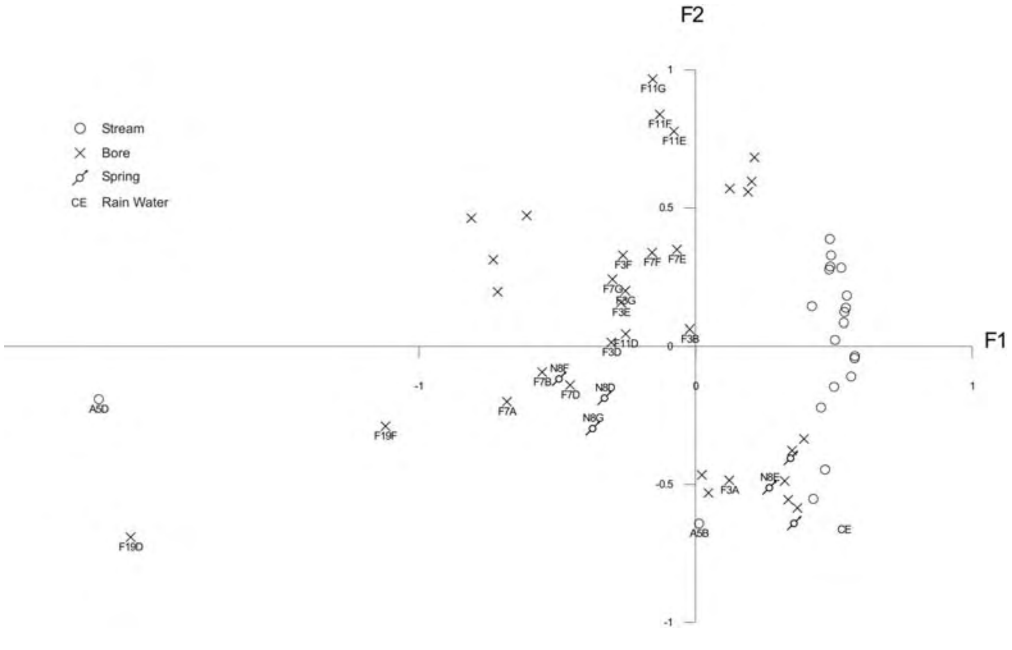

Figure 7: Distribution of different water samples on the 1st factorial plan, 2nd scenario

FINAL CONSIDERATIONS

Multivariate statistical techniques are a good approach to the identification of hydrochemical variations in a dataset. They allow us to distinguish unpolluted waters from contaminated waters by ARD. They also allow us to distinguish the chemical elements associated with ARD. The use of distinguish scenarios permit different approaches and different visualizations of temporal and spatial variations in waters hidrochemistry. Both scenarios denounce the same hidrogeochemical processes. Therefore, if we hadn't have realized these distinct approaches some reactions occurring in bores and springs would have stayed overshadowed by the degrees of contamination samples of adits and spoil.

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