A Análise em Componentes Principais como instrumento de identificação de sedimentos contaminados na área mineira de Aljustrel

Principal Components Analysis as a tool for identifying contaminated stream sediment samples in the Aljustrel mining area

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Abstract

In the Aljustel mining area, a case study illustrating the application a novel PCA (Principal Components Analysis) based methodology aiming at generating homogeneous sub-sets of stream sediment samples is presented. On the grounds of significant associations of elements, the typology produced by the proposed methodology is interpreted in geochemical/environmental terms.

The proposed methodology relies on the following steps:

(i) The matrix of n samples *vs.* concentrations in p elements obtained by field work and analytical procedures is submitted to a PCA, which leads to a small (p'<<p) number of axes summarizing groups of elements with a strong internal linear correlation.

(ii) Once interpreted each axis by the geochemical/environmental signature of the group of elements which are associated with it by the highest correlation criterion, the samples to be assigned to such an axis are selected directly in the same factorial space displaying the groups of elements, by imposing a cut-off to their projection.

(iii) The sub-sets of samples linked to contamination, whose separation from the geological background is optimized by ensuring that the above mentioned cut-off leads to a maximum internal homogeneity, are plotted in the geographical space in order to outline polluted zones in the case study area.

The case study main results consists of producing five significant sub-sets of samples, two of them characterized by conveying a different type of contamination (mechanical *vs.* chemical dispersion), and the remaining expressing the local geological context, interpreted in terms of different formations.

Keywords: contamination, Aljustrel, PCA, geochemical/environmental signatures

Resumo ou Resumen

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Palavras chave ou Palabras clave: palavra, palabra, palavra, palabra, palavra

Introduction and methodology

In mining areas where there is a significant amount of waste piles and important tailing ponds resulting from ancient exploitations, an important issue is how to differentiate associations of elements induced by contamination from those that are characteristic of the geological background. In order to approach the problem under a statistical perspective, groups of elements were identified by their high correlation with the axes produced by the PCA of the matrix containing the concentrations of an array of elements assayed in a set of stream samples covering the area to be characterized in geochemical-environmental terms.

The groups of elements emerging from the above outlined procedure must be related with sub-sets of samples where they are prevalent. This can be accomplished by selecting, in the common factorial space onto both samples and element concentrations are projected (Vairinho et. al, 1990, ANDAD), the samples that are associated with the axis that convey the relevant information on groups of elements, previously interpreted on the grounds of their geochemical/contamination signature. When the selection of samples linked with each axis is not straightforward, i.e., when there is a noteworthy overlapping of sample projection onto the factorial plane, a discriminant analysis based procedure is applied, in order to obtain a minimum within group variance, maximizing by this token the homogeneity of the final sub-sets of samples.

When the optimal separation between sub-sets of samples is reached, those can be plotted in the geographical space, giving rise to maps where polluted areas can be spotted.

This methodology was applied to the Aljustrel mining area, aiming at identifying contaminated stream sediment samples.

Aljustrel Area Geological Context

The deposits of the Aljustrel mining area form two northwest trending belts that are hosted within the upper part of the Volcanic Siliceous Complex (VS não bate com mapa), near the contact of the overlying Flysch Group.

North of Mesejana fault (marcar mapa) fault, the rocks that host the deposits are down dropped and exposed only in erosional windows through Tertiary sediments of the Sado Basin Formation. (*vd.* Fig. 1 não pode aparecer VSV e VSS, só um é que interessa).

The geology of the Aljustrel area has been described by Schermerhorn and Stanton (1969), Andrade and Schermerhorn (1971), Barriga (1983), Barriga and Fyfe (1988 and 1998), Barriga *et. al* (1997), Relvas (1990), Dawson *et al.* (2000, 2001 and 2003), Carvalho and Barriga (2000) and others. (cortar muito).

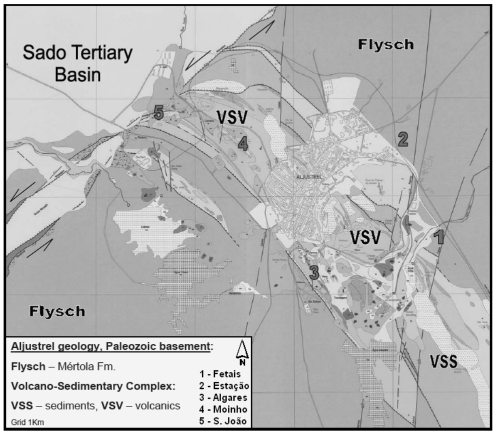

Fig. 1 – Local geology of Aljustrel mining area.

Sampling and Analytical Procedures

In order to characterise the contamination sources and the pattern of dispersion associated with contamination in the case study area, a geochemical/environmental sampling campaign was carried out. In a first stage, reported in this paper, 67 stream sediments samples were collected, according with the spatial distribution depicted in Fig. 2.

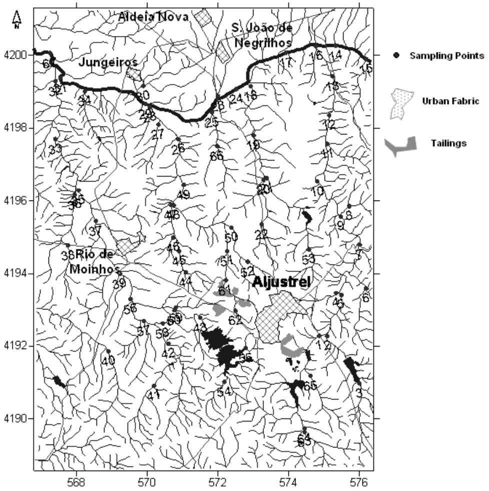

Fig. 2 – Spatial distribution of stream sediments samples.

Stream sediment samples were oven dried before dry sieving at a temperature of 40°C, until a constant weight was attained. Samples were disaggregated and passed through a 177 µm aperture plastic sieve. The fine-grained (< 177 µm) fraction of the stream sediment samples was submitted to multielemental analysis in an accredited Canadian laboratory (ACME Anal. ISO 9002 Accredited Lab-Canada). A 0.25 g split was digested in a 4-acid solution (HNO3, $HClO_4$, HCl, HF) at high temperature. The solutions were analyzed by Inductively Coupled Plasma-Emission Spectrometry (ICP-ES) for 41 chemical elements (Ag, Al, As, Au, Ba, Be, Bi, Ca, Ce, Cd, Co, Cr, Cu, Fe, Hf, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, S, Sb, Sc, Sn, Sr, Ta, Th, Ti, U, V W, Y, Zn and Zr cortar os que não aparecem). The accuracy and analytical precision were determined using analyses of reference materials and duplicate samples in each analytical set.

Statistical Treatment and Discussion of Results

The concentrations provided by chemical analysis were arranged under the form of a matrix cross-tabulating n lines (samples or individuals) per p columns (elements or variables). This matrix was submitted to a PCA, in order to detect, in the first sep of the proposed methodology, the main groups of elements that emerge from data. The results of PCA that permit the interpretation of all variables are given in Fig. 3, 4 and 5, referring to 4 axes that explain 73% of the original information.

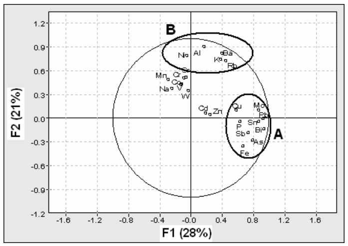

Fig. 3 – Projection of variables in the axis 1 and 2 of PCA.

Selecting the elements whose correlation is maximum with axes 1 and 2, the interpretation of Fig. 3 leads to groups A and B

Group A, highly correlated with axis 1, reflects the association between Cu, Mo, Pb, Sn, P, Sb, Bi, As and Fe, similar to the polymetallic sulphide deposits that occur in the area, therefore revealing a type of contamination driven mainly by mechanical transport.

Group B (N, Al, Ba, K and Rb) is strongly correlated with axis 2 and reveals an association consistent with the local formation denoted in Fig.1 as Flysh, where the phyllites, quartzites and greywackes are dominant.

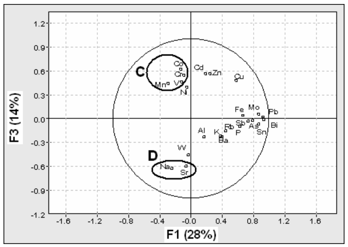

Fig. 4 – Projection of variables in the axis 1 and 3 of PCA.

From the analysis of Fig. 4, two groups (C and D) emerge, both with strong correlation with factor 3 and revealing associations consistent with the local geology.

Group C shows the association between Co, Cr, V and Mn, which is characteristc of the (pôr isto certo com a Fig. 1)Volcano-Sedimentary Complex, mainly composed by siliceous schists, acidic tufts, lavas and basic tufts. The presence of Mn in this group can be explained by influence of Moinho and Feitais areas, rich in this element.

Group D, composed by Na and Sr, discloses the influence of the conglomerates and argillaceous sandstone of the Sado Tertiary Basin.

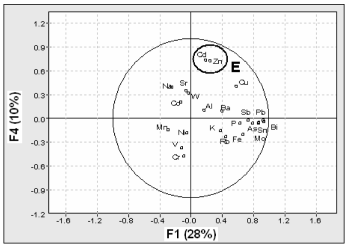

Fig. 5 – Projection of variables in the axis 1 and 4 of PCA.

Group E, highly correlated with factor 4 as displayed in Fig. 5 shows the association between Cd and Zn, revealing mainly the contamination driven by chemical dispersion from the tailings pond source.

In order to identify sub-sets of samples linked to axis 1 (type A contamination) and 4 (type E contamination), samples were projected in Fig. 6 and 7 onto the same axes displayed in Fig. 3 and 4, respectively.

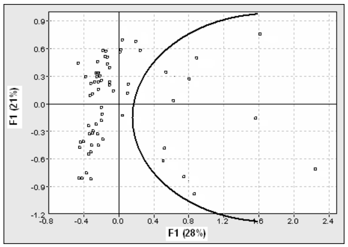

Fig. 6 – Projection of samples in the axis 1 and 4 of PCA.

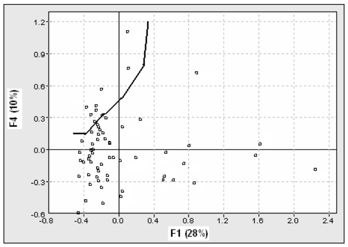

Fig. 7 – Projection of samples in the axis 1 and 4 of PCA.

The sub-set of samples associated with A-type contamination was selected by imposing a cut-off to their projections onto axis1 in Fig 6, and the same procedure was applied to Fig. 7, *mutatis mutandi,* to obtain the E-type samples. Such cut-offs (O.5 for axis 1 and 0.3 for axis 4) were derived from a discriminant criterion: the boundary should be placed in the position where the groups of samples exhibit a maximum dissimilarity. This corresponds to a maximum internal homogeneity, measured by a parameter denoted discriminant power, which is defined by the fraction of the total variance that is conveyed by the between-group variance.

Once selected the A and E type samples, they were mapped in Fig. 8 and 9, labelled by a symbol that indicates that they exceed the prescribed cut-offs.

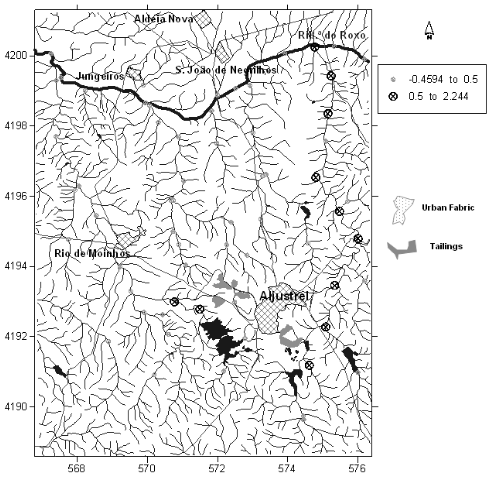

Fig. 8 – Spatial distribution of the contaminant factor summarizing the association Cu, Mo, Sn, Sb, P, Bi, As, Fe and Pb (Group A).

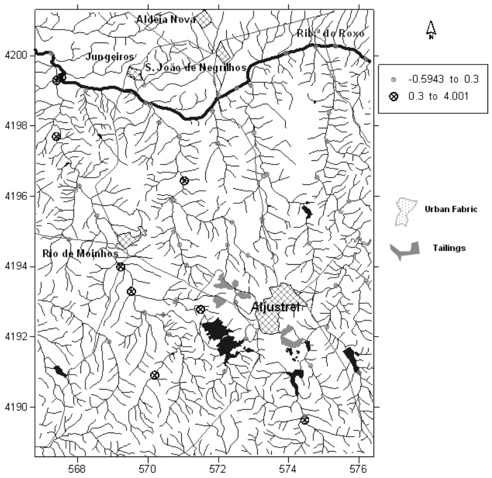

Fig. 9 – Spatial distribution of the contaminant factor summarizing the association Cd and Zn (Group E).

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Conclusions

A novel application of PCA, aiming to derive directly from the factorial space a typology of individuals (interpreted in terms of variables) gave outstanding results when applied to the Aljustrel mining area. In fact, the proposed methodology allowed to obtain sub-sets of samples with a sound geochemical /environmental significance. In particular those samples associated with different kinds of contamination were identified and characterized, providing maps of polluted areas.

Acknowledgments

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