Determinação de clusters de enriquecimento/empobrecimento em solos tropicais – um caso de estudo na República Dominicana

Determination of spatial enrichment/impoverishment Clusters in Tropical soils – a Dominican Republic case study

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Resumo: Em cenários geoquímicos complexos multivariados torna-se fundamental a redução da dimensionalidade. No estudo apresentado a construção de mapas funcionou como uma ferramenta de visualização de padrões espaciais de teores químicos (Al, Ca, Fe, K, Mg, Mn, Na, Si, Ti, P, Ba, Co, Cr, Sr, V, Cu, Ni, Pb, Zn e de LOI), permitindo a identificação de áreas enriquecidas. Foram recolhidas 18 amostras de solo, em duas bacias de drenagem Dominicanas, caracterizadas por litologias de natureza ígnea ácida, intermédia, e em menor extensão, básica. Afloram também rochas de natureza detrítica, pelo que foi possível identificar assinaturas geoquímicas distintas em ambas as bacias. A Análise em Componentes Principais (ACP) foi utilizada para redução da dimensionalidade e para avaliação do grau de associação dos atributos. As variáveis selecionadas foram depois modeladas usando metodologias da geoestatística. Os três primeiros Componentes Principais foram estimados em toda a área por Krigagem Ordinária (KO). Seguiu-se a extracção de clusters de maior significância, aplicando "Local G-clustering". Foi assim possível delimitar zonas de enriquecimento/empobrecimento.

Palavras-chave: Caracterização Geoquímica; Krigagem Ordinária; Local G-clustering; República Dominicana

Abstract: When considering complex scenarios involving several covariates, such as in environmental characterization, a clearer reality, through the dimensional reduction of data, can be achieved. Indeed, maps work as a visualization tool of contaminant spatial patterns, allowing the identification of enriched areas. Eighteen soil samples were gathered in two Dominican drainage basins, characterized by acidic, intermediate, and to a lesser extent basic lithologies. Detrital rock outcrops are also identified, which allowed the identification of distinct geochemical signatures, in both watersheds. A set, of 19 elements (Al, Ca, Fe, K, Mg, Mn, Na, Si, Ti, P, Ba, Co, Cr, Sr, V, Cu, Ni, Pb, Zn and LOI) was measured in the soil. Principal Components Analysis (PCA) was used for dimensionality reduction and for the evaluation of the attributes' association grade. The selected covariates underwent geostatistical modelling. Ordinary kriging and Local G clustering allowed the definition of High/Low enrichment clusters and the spatial delimitation of enrichment/impoverishment compartments.

Keywords: Geochemical Characterization; Ordinary Krigging; Local G-clustering, Dominican Republic

1. Introduction

The Dominican Republic is characterized by tropical wet climate intensified by periods of extreme hydrometeorological events that occur almost every year. Since this island has evolved from an island-arc, most of the geological suites are igneous, varying from acid to basic composition, however there is a quite diversity, which includes volcano-sedimentary (VS) rocks, tonalites, sandstones, conglomerates and intermediate volcanic rocks. The lithology conjugated with the climate conditions and the rough topography contribute to high erosion rates and consequently to soil impoverishment (Araújo et al., 2018; Araújo et al., 2019; Fonseca et al., 2019). This study aims at determining and evaluating geochemical enrichment and impoverishment, caused by those factors in two dams drainage basins (Tavera and Sabana Yegua), in order to get a geochemical characterization and the definition of clusters of High/Low enrichment of major and trace elements. Principal Component Analysis (PCA) together with a spatial approach through variography, Ordinary Kriging (OK) and G-clustering was used.

2. Study area

Tavera and Sabana Yegua's drainage basins (Fig. 1) are separated by the Central Mountain Range (CMR), which crosses Hispaniola Island from East to West. Tavera's dam is located at the North side of CMR and Sabana Yegua's at South. The main lithological difference between both drainage basins, is the fact that Sabana Yegua has almost 1/3 of its area occupied by detrital and carbonated rocks, while Tavera nearly hasn't.

Tavera has higher weathering rates since it has steeper slopes and greater rainfall, when compared to Sabana Yegua, which is in a more arid area.

3. Material and Methods

Before the analytical procedure, soil samples were milled through a standard agate ring mill, reaching the granulometry of 200 mesh. Geochemical analysis of major (Si, Al, Fe, Mg, Ca, Na, K, P, Mn, Ti) and minor elements (Cu, V, Zn, Co, Ba, Sr, Cr, Pb, Ni) in soils were performed by ICP-OES (Perkin-Elmer OPTIMA 8300). For the analysis of major and trace elements in resistate minerals (Sr, Cr, V) samples were homogenized with an alkali fusion flux (Spectroflux) and introduced in a graphite crucible followed by melting at 1000ºC. The resulting pearl was dissolved in a nitric solution. The remaining metals were analysed after total digestion of samples in a tri-acidic solution (HCl-HNO_3-HF) in a high-pressure microwave unit. This procedure aims to avoid metals volatilization (Xu et al., 2012). Quality control for chemical analyses was carried out by using analytical replicates and Certified Reference Materials (CRMs) with an accuracy of R<5%.

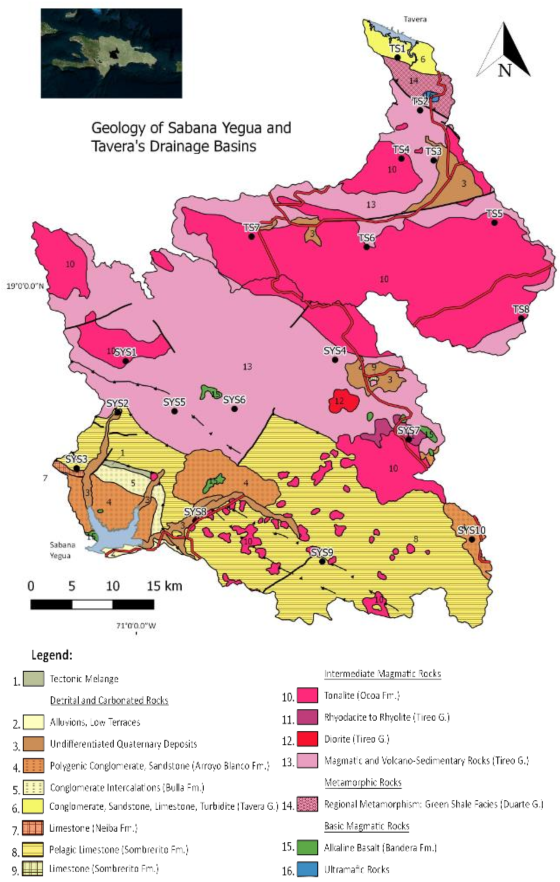

Fig.1 – Sabana Yegua and Tavera's lithology.

For the characterization of geochemical spatial distribution, a three-step methodology was adopted as follows:

(1) Principal Components Analysis (PCA) for reducing dimensionality and evaluate variable association (Tabs.1 and 2). The aim of PCA is to reduce the dimensionality of data while simultaneously preserves the within variability structure (variance-covariance) (e.g. Zuo et al., 2016). The XlStat 2013.1.01 software was used for computational purposes. Selected attributes were subjected to a structural analysis, and experimental variograms were computed (Matheron, 1963; Journel & Huijbregts, 1978; Gringarten & Deutsch, 2001) **(2)** spatial prediction through Ordinary Kriging (OK), aiming to predict the values for the variables at any arbitrary spatial location within the study region, was computed (Goovaerts, 1997). For the computation, the Space- Stat Software V. 4.0.18, was used. **(3)** Finally, LocalG clustering was performed. This technique allows measurement of the association degree of that results from the concentration of weighted points (or region represented by a weighted point) and all other weighted points included within a radius of distance from the original and defining clusters of high (high-ring) and low (low-ring) significance (Getis & Ord, 1992).

Tab.1 – Correlations between covariates and PCA's new Factors (F1; F2; F3)-Sabana Yegua

	F1	F2	F3
Al %	0,083	0,626	-0,638
Ca %	0,189	0,383	0,522
Fe %	0,868	0,349	-0,108
K %	-0,800	0,546	-0,017
Mg %	0,101	0,558	0,680
Mn %	0,898	0,350	-0,146
Na %	-0,303	0,255	0,577
Si %	-0,658	0,163	0,402
Ti %	0,358	0,006	-0,368
P_2O_5 %	-0,156	0,767	-0,090
LOI %	0,095	-0,386	-0,624
Ba ppm	-0,697	0,548	-0,340
Co ppm	0,904	0,049	0,123
Cr ppm	0,714	0,032	0,270
Sr ppm	-0,325	0,782	0,089
V ppm	0,911	0,000	-0,057
Cu ppm	0,754	0,135	0,089
Ni ppm	0,928	0,012	0,281
Pb ppm	0,110	0,583	-0,641
Zn ppm	0,723	0,512	-0,006

4. Results and Discussion

The characterization of clusters of Low and High content was achieved using the kriged maps and Local G clustering.

The spatial distribution for the analysed elements, revealed to be as not conclusive in Tavera basin, probably due to the small number of sampling points, the low geological diversity and the existence of only one drainage sub-basin (Yaque del Norte River). Unlike it, in Sabana Yegua, the richer geological diversity distributed by 3 sub-basins, showed a spatial distribution, which allowed to rank distinct spatial "hotspots" (Fig. 2), as follows:

(1) Al, P_2O_5, Sr, Pb Cluster: this cluster, located in the East sector, includes soils originated from magmatic, VS rocks, rhyodacites and tonalites with abundant intercalations of basaltic rocks. The weathering products of these rocks, rich in macronutrients (Ca, Mg) and metallic micronutrients (Fe, Mn, Cu and Zn) enhance the vegetal development and the microorganism's activity, giving rich-organic soils. The high topography of this sector boosts the development of deep soils, which can be mobilized to lower areas, explaining the extension of this cluster to South. Basalts and VS rocks, often composed by basic tuffs, could be the main source of metals, such as Pb. This sector is also enriched in immobile elements, such as Al. This element might outcome from the abundant feldspars of the VS lithologies. Due to its geochemical immobility it is hardly leached to lower areas.

Tab. 2 – Correlations between covariates and PCA's new Factors (F1; F2; F3) - Tavera

	F1	F2	F3
Al %	0,581	-0,282	0,703
Ca %	0,407	0,697	0,104
Fe %	0,973	-0,060	-0,076
K %	-0,244	-0,731	0,478
Mg %	0,235	0,808	0,385
Mn %	0,276	0,416	-0,647
Na %	-0,493	0,278	0,768
Si %	-0,737	0,020	-0,417
Ti %	0,900	-0,314	-0,184
P_2O_5 %	0,033	-0,429	-0,416
LOI %	0,932	0,076	0,128
Ba ppm	-0,732	-0,432	0,005
Co ppm	0,326	0,531	0,011
Cr ppm	0,257	-0,756	0,110
Sr ppm	-0,751	0,506	0,207
V ppm	0,880	-0,254	0,183
Cu ppm	0,594	0,685	0,260
Ni ppm	0,732	-0,471	0,246
Pb ppm	0,814	-0,412	-0,321
Zn ppm	0,560	0,746	-0,262

(2) C, H, N, S, LOI Cluster corresponds to soils from carbonate rocks. The high levels of Ca and Mg in the weathering products enable the enrichment in these organic elements. The lack of Ca and Mg in the soils of this cluster might be due to the high erosion rates and great mobility of these elements, which are easily leached to lower areas in loosely-bounded forms.

(3) Metals cluster: located in the upland of the Northern sector, this cluster is a good example of the metals immobility, owing to the near neutral pH (pH 6-7) of soils. These elements have as main sources the VS rocks with basic-intermediate composition. **(4)** Sr, Ba, Si Cluster: correspond to a wide area of carbonated rocks, in lowlands at the Southern part of the basin. Although having distinct chemical mobility, Sr and Ba are commonly associated and represent important constituents of carbonate minerals, due to its high affinity with Ca. Apparently, Si enrichment in a sector of carbonate rocks is dubious; however, the slight higher content of this element could be a result of physical weathering of abundant intercalations of tonalitic rocks and the occurrence of quartz-rich detrital deposits. (**5)** Na Cluster: the high mobility of Na with high contents in plagioclases, common mineral in most of the basin lithologies, is denoted by its enrichment in small dispersed clusters in flattened areas of low relief.

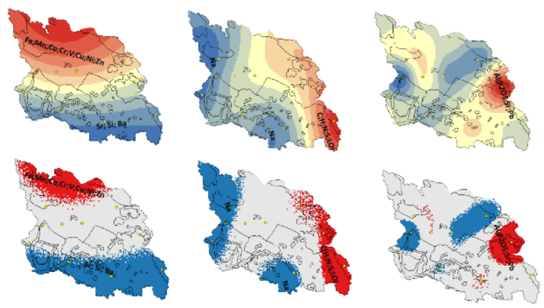

Fig. 2 – a) Spatial distribution (OK) for Sabana Yegua of PCA factors: F1, F2 and F3; b) G Clusters for Sabana Yegua

5. Conclusions

This work aims the definition of geochemical data spatial patterns, in soils from two small Dominican drainage basins, through KO coupled with G-clustering. In which concerns to Tavera data revealed to be inconclusive. However, for Sabana Yegua it was possible to determine and identify clusters of natural enrichment, allowing to raise hypothesis about geochemical mobility and elements' fate.

Future complementary work is keen for a better understanding of geochemical mobility, as well as, for a better understanding of the involved sedimentary processes, including the analysis of more elements, namely Rare Earth Elements.

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References

Araújo, J. F., Nogueira, P. M., Fonseca, R. M., Pinho, C. G., Araújo, A. A., 2018. Caracterização geoquímica de sedimentos de fundo de barragens Dominicanas. Geonovas, 31, 73-84.

Araújo, J. F., Fonseca, R., Pinho, C., Roseiro, J., Nogueira, P. 2019. Effects of geological and climatic conditions on the enrichment of nutrients in sediments accumulated in Tavera and Sabana Yegua tropical dam lakes (Dominican Republic) - General Assembly 2019 (Áustria), Vol. 21, EGU2019-9352.

Fonseca, R., Pinho, A. C., Araújo, J. 2019. Impact of extreme climatic events on the spatial and temporal distribution of major and trace elements in bed sediments of reservoirs in the Dominican Republic - General Assembly 2019 (Áustria), Vol. 21, EGU2019-5957.

Getis, A., Ord, J.K., 1992. The analysis of spatial association by use of distance statistics. Geogr. Anal. 24, 189–206

Goovaerts, P., 1997. Geostatistics for Natural Resources Evaluation. University Press, New York, Oxford, 483 p.

Gringarten, E., Deutsch, C.V., 2001. Teacher's aide variogram interpretation and modeling. Math. Geol.33, 507-534.,

Journel, A.G., Huijbregts, C.J., 1978. Mining Geostatistics. Academic Press, San Diego, 600 p.

Matheron, G., 1963. Principles of geostatistics. Econ. Geol. 58, 1246–1266, DOI:10.2113/gsecongeo.58.8.1246.

Xu, G., Hannah, J. L., Bingen, B., Georgiev, S., Stein H. J., 2012, Digestion methods for trace element measurements in shales: paleoredox proxis examined. Chemical Geology, 324-325, 132-147.

Zuo, R., Carranza, E.J.M., Wang, J., 2016. Spatial analysis and visualization of exploration geochemical data. Earth Sci. Rev. 158, 9–18.

https://www. xlstat.com/en/ (12/01/2019)

https://www.biomedware.com/software/ sp cestat/ (12/01/2019)