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Geochemical and environmental characterization using multivariate tools in the Una River Basin - PE

Caracterização geoquímica e ambiental através de ferramentas multivariadas na Bacia Hidrográfica do Rio Una – PE

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Abstract: Knowing the dynamics of the chemical components in the soil system is essential in order to prevent the evolution of possible contaminants. The Una River Basin, located in the southern part of the state of Pernambuco, is negatively influenced by the use and occupation of the soil, which poses a risk to its ecological sustainability. There was a need to study the geochemical behavior of the watershed's soils as a geoenvironmental strategy to estimate their vulnerability and prospects for use and occupation. Twenty samples extracted from the Geochemical Atlas of Pernambuco were analyzed within the basin, which served as the basis for the research. The chemical elements: Al, Ca, K, Mg, P, S, As, Cr, Cu, Ni, Pb, Zn, Ba, Ce, Co, Cs, Ga, Hf, Mn, Mo, Nb, Sc, Se, Sn, Sr, Th, U, V, W, Y and Zr, were highlighted and then used to study descriptive statistics, multivariate statistics and the construction of heavy metal isopleth maps using the kriging technique. Possible anthropogenic contributions were demonstrated. The formation of specific groupings between the soil components was observed, which served as the basis for establishing the hafnium/aluminum ratio, which expresses the validity of the chemometric techniques used.

Keywords: Geochemical signature; Multivariate analysis; Una River.

Resumo: Conhecer a dinâmica dos componentes químicos no sistema do solo é imprescindível para evitar a evolução de possíveis contaminantes. A Bacia Hidrográfica do Rio Una, localizada na porção sul do estado de Pernambuco, sofre influências negativas quanto ao uso e ocupação do solo, isso oferece risco a sua sustentabilidade ecológica. Verificou-se a necessidade de estudar o comportamento geoquímico dos solos da bacia hidrográfica como estratégia geoambiental para estimar sua vulnerabilidade e perspectivas de uso e ocupação. Foram analisadas vinte amostras extraídas do Atlas Geoquímico de Pernambuco, no interior da bacia, as quais serviram como base para o desenvolvimento da pesquisa. Os elementos químicos: Al, Ca, K, Mg, P, S, As, Cr, Cu, Ni, Pb, Zn, Ba, Ce, Co, Cs, Ga, Hf, Mn, Mo, Nb, Sc, Se, Sn, Sr, Th, U, V, W, Y e Zr, foram colocados em evidencia, assim, seguiram para o estudo da estatística descritiva, multivariada e construção de mapas de isoteores dos metais pesados, pela técnica de krigagem. Ficaram demonstradas possíveis contribuições antrópicas. Observou-se a formação de agrupamentos específicos entre os componentes do solo que serviram de base para o estabelecimento da relação háfnio/alumínio a qual exprime validade para as técnicas quimiométricas utilizadas.

Palavras-chave: Assinatura geoquímica; Análise multivariada; Rio Una.

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1. Introduction

Given the existing challenges in guaranteeing the availability and quality of water, an essential resource for life, the proper use and conservation of soils is an essential alternative for maintaining environmental quality. The use of soil by humans and animals, when poorly managed, can negatively affect the quality of environmental resources (PIERONI, et al 2019).

The assessment and characterization of contaminated soils is challenging due to the intensity and variability of chemicals released into the environment (FERNANDÉZ, 2017). The mobility of these elements can be influenced by the specific surface area, texture and density of the soil, amount of organic matter, mineralogical composition, physical-chemical nature and content of trace elements present in the soil (OLIVEIRA; COSTA; CRUZ, 1998).

In this respect, there is a need to know the dynamics of contaminants in the soil system and consequently to develop monitoring with a view to mitigating environmental impacts. These dynamics are influenced by the presence of heavy metals, which are an indication of environmental quality (BARROS, 2010).

At the beginning of the 20th century, the methods used in this type of study were based on classical statistics, where parameters such as the mean and standard deviation were used to represent a phenomenon, assuming the central premise that variations between different locations were random (VIEIRA, 2000). However, Krige (1951) concluded that the information provided by variance alone is not enough to explain the phenomenon under study. For this, another parameter is needed, such as distance. This gave rise to the concept of Geostatistics, which takes geographical location and spatial dependence into account.

On this basis, geochemical analysis proposes the establishment of relationships between soils and possible contaminants (natural or anthropogenic), by determining the concentration of chemical elements, making it possible to monitor quantitatively and qualitatively, estimating the flow of elements during weathering, leaching processes and/or activities subject to environmental liabilities (CHADWICK et al., 1990).

Geostatistics, like chemometrics, aims to find and separate objects in a group of similar data, and also provides the possibility of multidimensional grouping through scientific procedures. In many situations, it is necessary to know certain characteristics, especially when measurements of different natures are obtained, so the Cluster Analysis method can be applied when there are similarities in the data set (VICINI, 2005).

The application of chemometric tools has become an essential activity in recent years. This is mainly due to the large quantity and nature of the data generated, based on the need to extract objective information (PEREIRA, 2022). Statistical processing of the results can act directly to solve problems in environmental applications (FERNANDÉZ, 2017).

This study aims to collaborate with the multivariate interpretation of geochemical results, in an attempt to elucidate with chemical details the vulnerability, perspectives of land use and occupation and also to improve the management of the areas of water scarcity of the Una River Basin - BHRU. Based on this, the characterization of the River Basin is of fundamental importance for the integrated management of natural resources, since the socio-economic aspects, observed together with the climatic, pedological, geological and land use and occupation properties, aim to improve the conditions for agricultural, urban and industrial activities (MARTINS, 2004).

2. Metodologia

2.1 Área de estudo

The chemical annotation carried out in this research took place in the geographical region of the Una River Basin - BHRU, which is located between 8º17'14” and 8º55'28‘’ south latitude, and 35º07'48‘’ and 36º42'10‘’ longitude west of Greenwich. In the territorial space of the Agreste and Zona da Mata mesoregions, state of Pernambuco, Brazil. The Una River rises at an altitude of 900m, and generally runs in a west-east direction. It runs for approximately 255km until it meets the Atlantic Ocean (Figure 1).

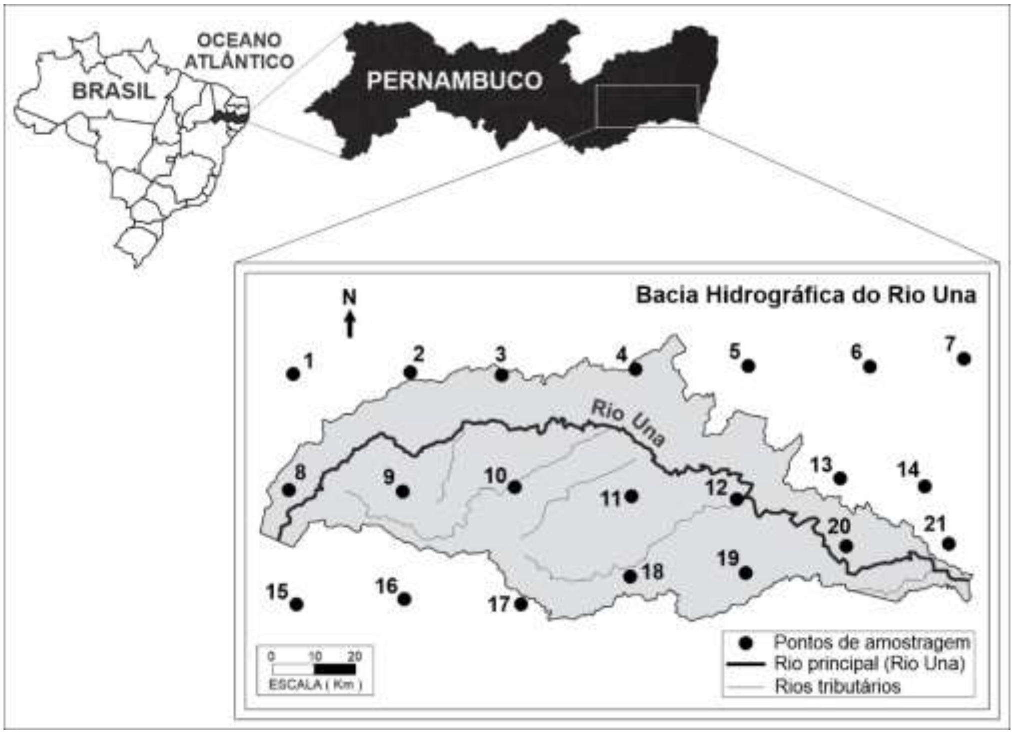

Figure 01 – Location map of the Una River Basin and the analysis points considered
Source: Authors (2024)

The BHRU is mostly made up of crystalline rocks, with migmatites and granites playing a roughly equal role. Occasional transcurrent destructive faults occur in these migmatites. The sedimentary area is represented by sandy-clay deposits of recent alluvium (SANTOS, 2013). The soils in the Una river basin are of the Planossolos, Vertissolos, Neossolo and Latossolos Distróficos types. It should be noted that in the semi-arid portion, the soils generally have the potential for economic use in pasture and agriculture. There are also shallow soils with low permeability, which have excess water in the rainy season and extreme dryness in the dry season.

Some studies on morphometric parameters based on radar images and surface geology data have shown that the Una River is located on three surfaces created by successive uplift and erosion events, which have controlled the compartmentalization of its watershed (FILHO, 2019).

The Una River basin clearly has two climatic patterns: it is hot and humid, with high annual rainfall totals of over 1,000 mm (ARAÚJO, 2022).

As for land use, the Agreste Mesoregion is dominated by rural properties where polyculture, dairy farming and sugar cane production are developed. In the Zona da Mata Sul, urban and industrial occupation of special steels, electronic products, irrigation equipment, boats, ships, hulls for oil platforms, chips, software, automobiles, batteries and petrochemical products stand out (FERNANDÉZ, 2017).

2.2 Data processing

Data from twenty-one samples from the geographical region of the BHRU contained in the Geochemical Atlas of Pernambuco (LIMA et al, 2017) were analyzed. The chemical elements (Al, Ca, K, Mg, P, S, As, Cr, Cu, Ni, Pb, Zn, Ba, Ce, Co, Cs, Ga, Hf, Mn, Mo, Nb, Sc, Se, Sn, Sr, Th, U, V, W, Y and Zr) were then highlighted.

Descriptive statistical analyses of the samples (mean, median, standard deviation and coefficient of variation) were carried out in order to evaluate the metal contents.

To assess the relationship between the elements studied, Hierarchical Cluster Analysis (HCA) was used to evaluate the relationships between the elemental concentrations of the set of samples in order to look for possibilities of grouping by similar characteristics.

To build the heavy metal isopleth maps, we used the pointwise ordinary Kriging technique with an interpolator based on semivariograms, which estimates the value of a variable at an unsampled position Z(xi) based on a spatial pre-analysis of the set of samples using experimental semivariograms (SOARES, 2016). In order to guarantee the accuracy of the estimates and verify the necessary hypotheses, samples were taken in and around the Una River Basin.

3. Results and discussion

The results are presented initially focusing on the chemical elements with a toxic effect, also known as heavy metals (As, Cr, Cu, Ni, Pb and Zn). They are compared with the reference values most commonly used in Brazil by the Companhia Ambiental do Estado de São Paulo - CETESB (2001), which establishes the quality criteria shown in Table 01, together with the average values obtained from the descriptive statistical analyses.

The metals Cr and Ni remained above the average percentage proposed by CETESB's VRQ. Point samples of elements above the quality reference values were identified at all the points studied; however, only Cr and Ni had indicator points overlapping the prevention values. This is due to the fact that, depending on the sample universe, their average value can be shifted to values lower than the reference, resulting in a mistaken statistical coincidence.

Table 01 – Reference values and average values for heavy metals (ppm).

Parameters	As	Cr	Cu	Ni	Pb	Zn
No. of observations	21	21	21	21	21	21
Average	1,10	46,50	7,47	15,21	12,98	23,15
Median	1,10	46,50	7,47	15,21	12,98	23,15
Minimum	0,50	8,00	1,10	2,50	4,40	3,00
Maximum	5,00	95,00	25,00	41,20	28,60	85,00
Standard Deviation	1,30	27,18	6,78	10,59	7,85	20,55
CV%	1,7	738,58	45,91	112,08	61,64	422,45
VQR CETESB	3,5	40	35	13	17	60
Prevention Value	15	75	60	30	72	86

Source: Adapted from CETESB (2001).

Trace elements are a group of elements with specific characteristics and naturally occurring in the environment, making up accessory minerals in rocks. Although these elements are associated with toxicity, they require differentiated treatment in terms of their function in biological systems, since several of them have proven essentiality for plants (Ni, Cu, Fe, Mn, Zn) and animals (Ni, Cu, Fe, Mn, Zn, Cr III) and others have no biological function (Pb, Cd and Cr IV). Trace elements are commonly associated with contamination episodes that affect living organisms and the ecosystem as a whole, in many cases these effects are associated with anthropogenic contamination (BIONDI et al., 2011).

The distribution of metals in the soil depends on their adsorption capacity during weathering; geomorphology; hydrology; and geochemical barriers, which prevent the further dispersion of metals (Miller, 1997). Metals can be transported free in solution, in the form of complexes or associated with clay minerals and organic compounds (Quantin et al., 2002; Sommer et al., 2000).

In order to highlight the real values obtained in this work for the geographical region in question, isopleth maps were made of the heavy metals described. Thus, the levels of As, Cr, Cu, Ni, Pb and Zn are shown in the form of kriging dispersion maps in the rectangle corresponding to the area of the Watershed under study (Figures 2 and 3).

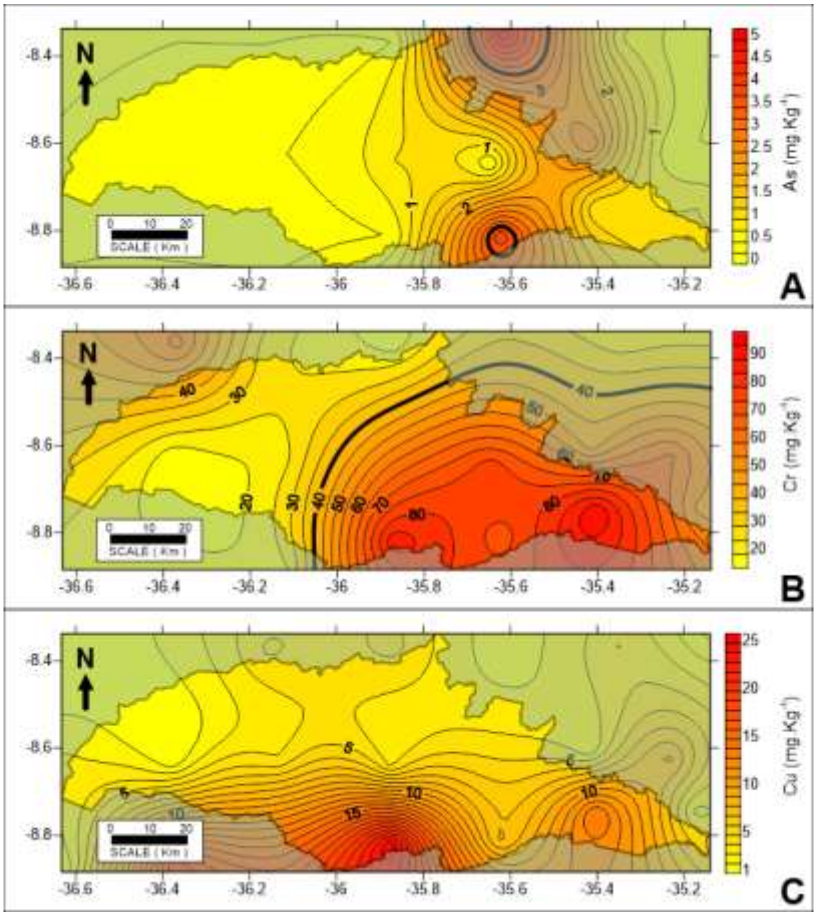

Figure 02 – Isoteor maps for Arsenic (A), Chromium (B) and Copper (C)
Source: Authors (2024)

Arsenic is a grayish semi-metallic chemical element, brittle and with a metallic luster in its elemental state, which is naturally present in the environment forming organic and inorganic complexes with different valence states, -3, +3, 0 and +5, highlighting the higher toxicity of inorganic compounds compared to organic compounds (ATSDR, 2007).

For Arsenic, figure 2A shows a small anomalous region, with levels above the reference of 3.5 mg/kg in the southernmost portion of the river basin, with a predominance of agricultural regions and an increase in population density. Natural sources of As include weathering of the source material through physical, chemical and biological processes and volcanic emissions (Alonso et al., 2014). From anthropogenic sources, As can be detected in activities involving the use of herbicides, phosphate fertilizers, mining, industrial waste and work related to wood preservation (Chirenje et al., 2003; Alonso et al., 2014; Roy et al., 2015).

Chromium is often found in the soil in combination with other elements, such as O, Fe, Pb, in the form of oxides. Cr can exist in nine different oxidation states, however, the Cr3+ and Cr6+ forms are the most common. Trivalent Cr, Cr(III), is the most stable form of Cr and exists naturally in the environment; hexavalent Cr, Cr(VI), comes essentially from anthropogenic pollution sources (CCME, 1999a).

The entire eastern region of the watershed studied has a strong interaction with Chromium, thus suggesting the great availability of clay material, justifying Ribeiro's (2013) assertion that Cr is strongly adsorbed by clay particles, organic matter and other electronegatively charged particles.

In the study on phytoremediation by Costa et al. (2021), they evaluated the capacity for chromium bioaccumulation in the sunflower plant species, and found good efficiency in the phytoextraction potential of this species when grown in contaminated soil. However, the oil extracted from the seeds grown in these conditions is not suitable for human consumption due to the high metal content. Thus, the importance presented in this context is that sunflower can be grown in the river's hydrographic region as an alternative for restoring the area, never as an economic alternative.

Like As, Cr (VI) derives from activities that are potentially harmful to the environment, such as the metallurgical industry (CCME, 1999), reaffirming the possible association between sources of pollution. Ribeiro (2013) states that solid Cr (VI) compounds are soluble in the soil and are extremely mobile, and can leach into groundwater.

Copper, when bivalent, has the ability to combine with various anions, and also migrates in the form of solutions of Cu and other metals such as Fe, Al and Mn, thus reducing mobility in the soil (GOLDSCHMIDT, 1958); (RIBEIRO, 2013), which explains the reduced Cu in sedimentary residues from some areas of the basin shown in figure 2C.

Cu is considered essential for basic plant nutrition, as it is one of the seven most important micronutrients, but large amounts of Cu produce a toxic effect capable of causing serious problems such as anemia and disorders in the central nervous and cardiovascular systems. However, the absence of Cu in animals and humans can cause neurological disorders, which is why it is also characterized as essential in human and animal nutrition, appearing as an important and necessary component in certain enzymes (SILLANPAA, 1972). The normal concentration of copper in the soil is 20mg/kg, with variations in the range of 6 to 80 mg/kg (McBride, 1994).

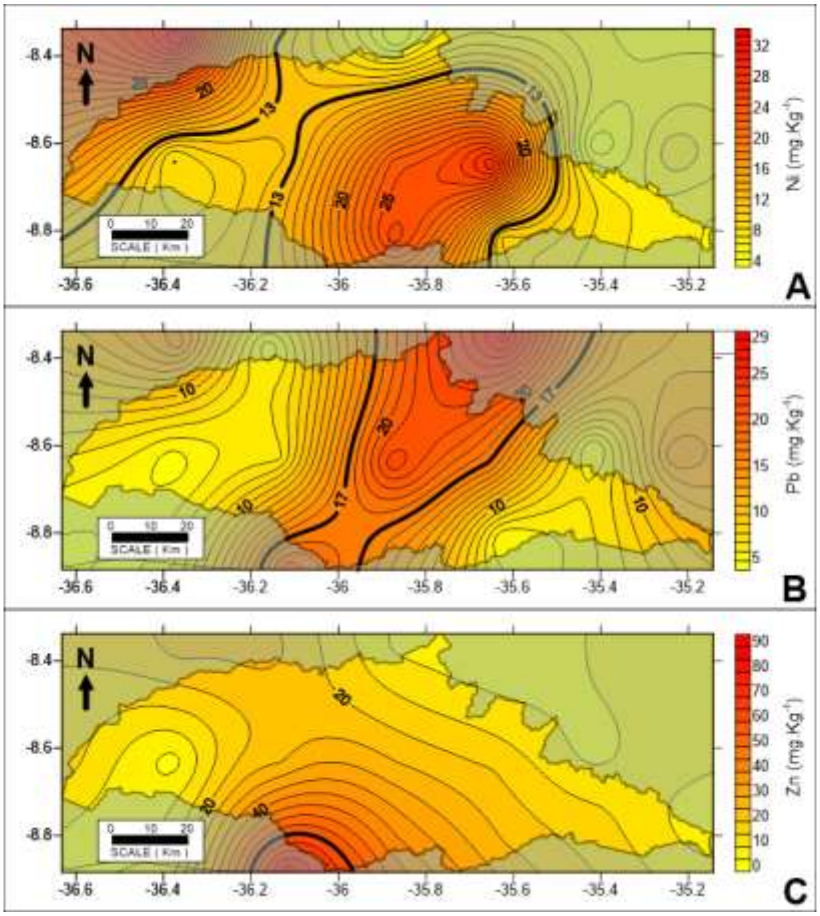

Figure 03 – Geographical distribution of Ni (A), Pb (B) and Zn (C).
Source: Authors (2024)

Nickel occurs naturally in the environment, but its presence in elemental form is rare (McGrath, S.P., 1995). Ni has a strong affinity with Fe and S, forming Fe sulphide compounds such as pentlandite [(Ni,Fe)9S8] in igneous rocks, millerite (NiS) and ulmanite (NiSbS) in mineralized areas. There are also minerals rich in Fe and Ni, which can be found naturally in soils due to rock weathering (McGrath, S.P., 1995).

Ni has an affinity for organic matter due to the presence of binding agents, humic substances or groups that form specific complexes or chelates with Ni2+ (KABATA-PENDIAS, 2011).

The main uses of Ni are the production of alloys, including Ni stainless steel, the manufacture of batteries, welding electrodes and the production of chemicals such as nickel sulphate, nickel chloride and some catalysts (DEPA, 2005).

These compounds can contribute negatively to soil contamination in the BHRU, being disposed of in an environmentally incorrect way through liquid effluents or through gaseous emissions by the industries that use them.

Figure 3A shows the effective presence of Ni in the western and central parts of the geographical region studied. It therefore assumes less geochemical interaction with clay and greater affinity with sandy minerals. McGrath (1995) proposes that Ni associated with soil geology is more effective in clays, which justifies the idea that the Ni present in the Una River Basin area is potentially from anthropogenic activities.

Lead is rarely found in its elemental form in the environment, with the 2+ ion being the predominant element in nature. It can easily form metallic alloys with other metals such as Cu and Zn.

There are concentrations of lead in areas with a high density of plantations (Agreste), from the north to the south in the central area of the isohyet map shown in figure 3B. The quality reference values (17mg/kg) established by CETESB (2001) are exceeded by the levels obtained in the analyses (up to 28.60mg/kg). These areas of contamination, probably caused by the application of chemical products in the sweet potato, cassava and banana plantations, may allow the incorporation of metals into the watercourses, which implies environmental damage for the entire aquatic and terrestrial ecosystem community along the watershed, (MONTOGMERY, 2008).

In addition to the proposed contamination hypothesis, there are various sources of Pb emissions into the atmosphere, such as forest fires, the burning of fossil fuels and animal production waste. In this sense, lead is deposited in the soil through precipitation when the atmospheric environment is contaminated (RIBEIRO, 2013).

Zinc is highly abundant in the earth's crust. However, it is not found in its elemental form in the environment, but is extracted from the mineral sphalerite [(ZnFe)S] (CCME, 1999b). Like Cu, Zn is an essential element in human nutrition because it is effectively related to enzymes (PEAKALL AND BURGER, 2003).

Figure 3C shows the distribution of Zn around the watershed, noting its uniform distribution throughout the geographical area, considering reference values lower than those established by current legislation, which infers the absence of Zn contamination. This idea is based on the statement proposed by (CCME, 1999a) in which Zn is one of the most mobile metals in the soil due to its high solubility in the presence of soil solutions with a neutral or acidic pH. In addition, when it is present in the environment, Zn remains in the soil, forming insoluble compounds, which is a significant environmental concern.

All the chemical elements analyzed were structured using the dendrogram below (figure 04). This diagram aims to graphically represent the relationship between objects or groups of objects in a cluster analysis. In this model, a hierarchy is respected based on the distance between them. The closer the objects are to each other, the smaller their correlation distance.

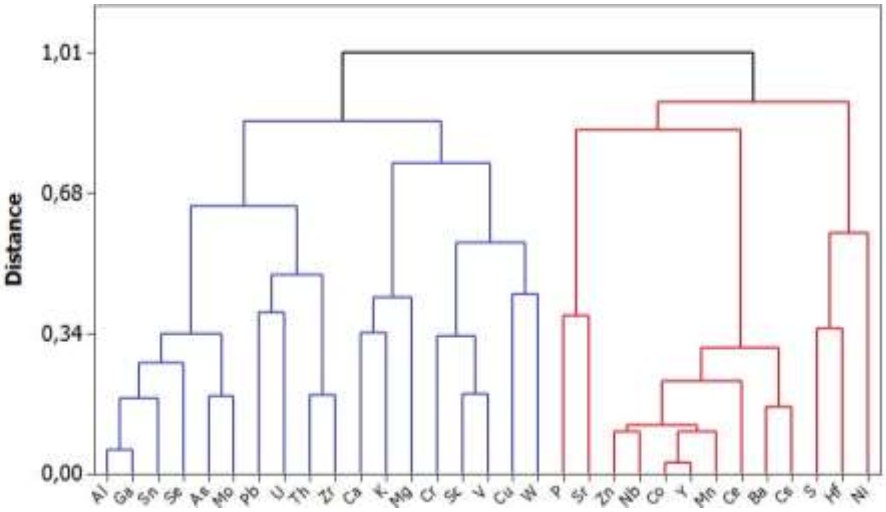

Figure 04 – Cluster graph between the chemicals analyzed
Source: Authors (2024)

The dendrogram compares the distribution of the chemical elements analyzed along the BHRU, forming two distinct groups, with group 1 on the left containing the elements most closely associated with the clay particles (Al, Ga, Sn, Se, As, Mo, Pb, U, Th, Zr, Ca, K, Mg, Cr, Sc, V, Cu, W). And group 2, to the right of the graph, contains the other elements, which, by analogy with the distribution, considering that the water regime is very decreasing towards the west, it can be suggested that this group is related to the sand fraction (P, Sr, Zn, Nb, Co, Y, Mn, Ce, Ba, Cs, S, Hf and Ni), corroborating the information proposed by (LIMA et al, 2017). In order to reduce the dimensionality of this system with the various chemical elements presented, the ratio between Hafnium and Aluminum was used, since these elements belong to each of the groups observed in the dendrogram. Thus, according to Zaaboub 2016, who found that the increase in the Hf/Al ratio may be related to areas with low hydrodynamic conditions, and that, in the study area, this geochemical signature shows that the closer to the coast, the lower the values of the Hf/Al ratio are verified, and on the other hand, the further west, the higher the values of the ratio evidenced, figure 5.

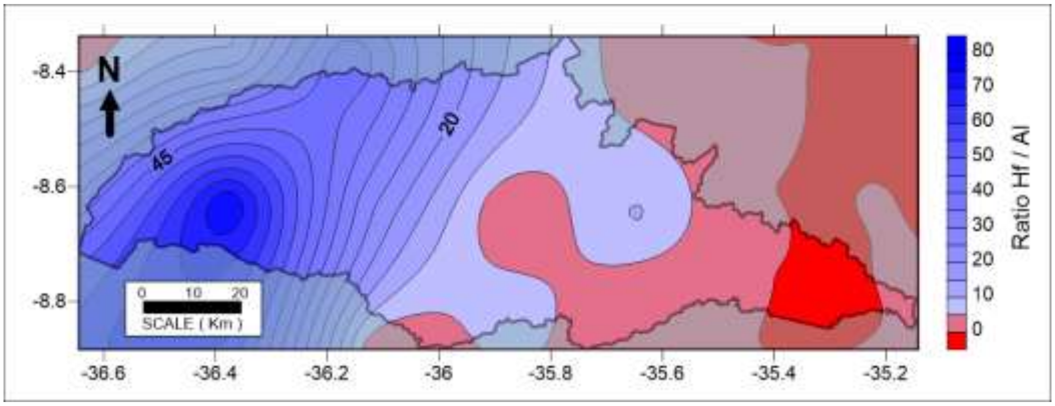

Figura 05 – Gráfico da relação geoquímica Ha/Al
Source: Authors (2024)

In general, the groupings observed by the multivariate statistical method can only be represented by these two chemical elements, although there is a gradient of dependence on this rule, which could mean which elements are subordinate to the result of the local water regime and which are of punctual (geogenic) origin or transported by another system. This corroborates the intention to test the origin and provenance of chemical elements, since the characteristics of soils, rocks and sediments in and around the BHRU can be indicative of its environmental quality. It is also important to note that Araújo 2022, in his results, showed an increase in precipitation over the course of the watershed from west to east, figure 6, and this behavior may be analogous to the distribution of Hf/Al geochemical signature values shown in this work.

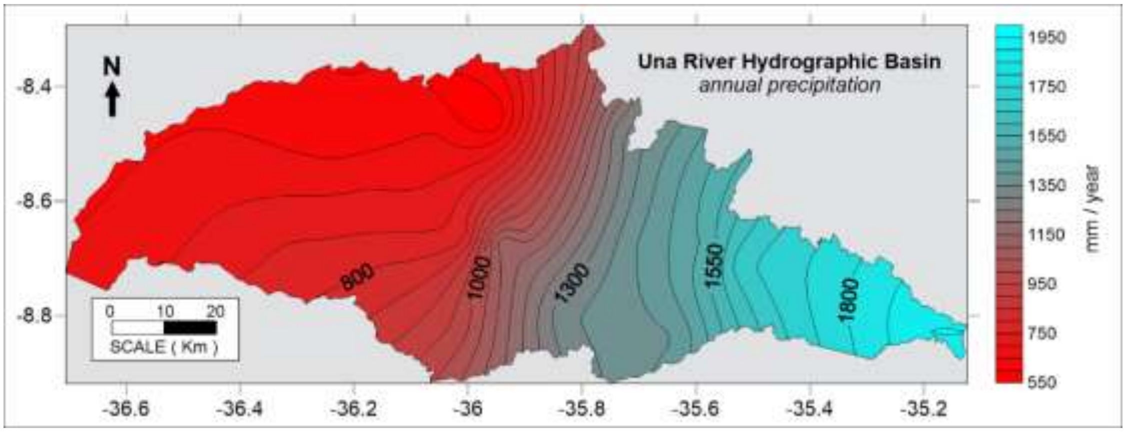

Figure 06 – Annual precipitation along the BHRU
Source: ARAÚJO, et al. 2022

This idea reinforces the hypothesis that the relationship established between the elements is valid and is associated with the climatology of the research region. The hafnium associated with the sand particle remains present in areas with lower rainfall, while the aluminum, found easily in the clay fraction, is more mobile on the surface and is accompanied by surface runoff throughout the watershed.

According to Chaves (2008), soil pollution is related to the accumulation and transportation of the elements contained in it, with the clay fraction being the main precursor of interactions in the solid and liquid phases of the soil. Therefore, considering the topographic gradient and the amount of rainfall, it is possible to infer a predominance of aluminum and hafnium or their respective associated elements. The higher the rainfall and consequently the surface runoff, the greater the concentration of aluminum in space.

4. Final considerations

Geostatistics made it possible to carry out a spatial analysis of the levels of Arsenic, Chromium, Copper, Nickel, Lead and Zinc in the Una River Basin - PE. The variables studied showed anomalous conditions when compared with current environmental legislation, which allowed us to suggest hypotheses about possible inappropriate forms of land use and occupation.

It was possible to observe that interpolation using the geostatistical kriging method can produce satisfactory results, capable of providing reliable inference of geochemical levels in unsampled areas. Chemometrics is therefore a viable alternative for obtaining an environmental diagnosis of areas with large surface areas and interconnected characteristics.

The Hf/Al ratio obtained is useful for determining, with greater probability, the presence of chemical elements associated with the grouping to which it is related. It was concluded that the higher the ratio, the lower the conditions for the Al-bonded group, as they are more closely correlated with Hf. Similarly, the lower the ratio, the higher the incidence of Al and the elements linked to the Hf group. This relationship can be explained by the region's climatic conditions.

The una river basin has geochemical characteristics favorable to environmental balance. In areas with possible anthropogenic contributions, phytoremediation proposals could be studied and added to later.

As this is a low-density study, the recommendations are limited to indicating areas where more detailed work should be carried out, increasing the number of samples and selecting strategic points capable of identifying anthropogenic contamination or natural occurrences.

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