# REFERENCE VALUES FOR HEAVY METALS IN SOILS OF A BASIN IN THE COASTAL ZONE OF NORTHEAST BRAZIL

## *VALORES DE REFERÊNCIA PARA METAIS PESADOS EM SOLOS DE UMA BACIA NA ZONA COSTEIRA DO NORDESTE DO BRASIL*

## *VALORES DE REFERENCIA PARA METALES PESADOS EN SUELOS DE UNA CUENCA EN LA ZONA COSTERA DEL NORESTE DE BRASIL*

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### ABSTRACT

The presence of heavy metals in the soil poses a threat to both ecosystems and human health. In order to assess the effects of human activities on soil contamination, the environmental monitoring authorities need reference parameters for these contaminants. These parameters, known as Quality Reference Values (QRVs), indicate the natural concentrations of heavy metals in soils unaffected by human interventions and should be established as essential guidelines. Although there are already studies on QRVs in Brazil, the lithological variability justifies the need for more detailed approaches. The objective of this study was to establish QRVs for Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in the soils of the Jaboatão River basin, state of Pernambuco, Brazil. The results revealed that the metals Cr, Cu, and Ni contained some undetected data. The QRV values (mg kg-1) were: 0.43 for Cd, 6.76 for Co, 5.41 for Mn, 21.23 for Pb, and 152.17 for Zn. The values for Co, Pb, and Zn exceeded the QRVs for Pernambuco, established by the State Environmental Agency (CPRH), but did not surpass the Prevention Values set by national legislation.

### KEYWORDS

Geochemistry, soil pollution; trace elements.

### *RESUMO*

*A presença de metais pesados no solo representa uma ameaça tanto para os ecossistemas quanto para a saúde humana. A fim de avaliar os efeitos das atividades humanas na contaminação do solo, os órgãos responsáveis pelo monitoramento ambiental necessitam de parâmetros de referência para esses contaminantes. Estes parâmetros, conhecidos como Valores de Referência de Qualidade (VRQs), são indicativos das concentrações naturais de metais pesados em solos não afetados por intervenções humanas e devem ser estabelecidos como guias essenciais. Embora já existam estudos de VRQ no Brasil, a variabilidade litológica justifica a necessidade de abordagens mais detalhadas. O objetivo do presente trabalho foi estabelecer os VRQ para Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb e Zn nos solos da bacia do rio Jaboatão, estado de Pernambuco, Brasil. Os resultados permitiram verificar que os metais Cr, Cu e Ni contiveram parte dos dados não detectados. Os valores de VRQ (mg kg-1) foram: 0,43 para Cd, 6,76 para Co, 5,41 para Mn, 21,23 para Pb e 152,17 para Zn. Os valores de Co, Pb e Zn*

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*foram superiores aos VRQs de Pernambuco, estabelecidos pela Agência Estadual de Meio Ambiente (CPRH), porém não ultrapassaram os Valores de Prevenção estabelecidos pela legislação nacional.*

## *PALAVRAS-CHAVE*

*Impactos ambientais; políticas públicas; geração de resíduos sólidos; Cariri.*

## *RESUMEN*

*La presencia de metales pesados en el suelo plantea amenazas para los ecosistemas y la salud humana. Para evaluar el impacto de las actividades humanas en la contaminación del suelo, los organismos encargados del monitoreo ambiental requieren parámetros de referencia, conocidos como Valores de Referencia de Calidad (VRQ). Estos indican las concentraciones naturales de metales pesados en suelos no afectados por intervenciones humanas y deben establecerse como guías esenciales. A pesar de existir estudios de VRQ en Brasil, la variabilidad litológica justifica enfoques más detallados. Este trabajo buscó establecer los VRQ para Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb y Zn en los suelos de la cuenca del río Jaboatão, en Pernambuco, Brasil. Los resultados revelaron que los metales Cr, Cu y Ni contenían datos no detectados. Los VRQ (mg kg-1) fueron: 0,43 para Cd, 6,76 para Co, 5,41 para Mn, 21,23 para Pb y 152,17 para Zn. Aunque los valores de Co, Pb y Zn superaron los VRQ de Pernambuco establecidos por la Agencia Estatal de Medio Ambiente (CPRH), no sobrepasaron los Valores de Prevención de la legislación nacional.*

## 1. INTRODUCTION

Among soil contaminants, trace elements stand out as they become hazardous to humans and biota when pollution levels are reached. These chemical elements are found in soils either naturally or anthropogenically. Their natural levels depend on the original material, pedogenetic processes, and soil development. Anthropogenic activities lead to an increase in the content of these elements, requiring knowledge of their natural concentrations for the prevention and monitoring of soil and water pollution. In environmental studies, natural concentrations of chemical elements are commonly referred to as "quality reference values" or "geochemical reference values" (Hernández-Crespo; Martín, 2015).

Various methods have been developed to determine Quality Reference Values. Generally, they are divided into direct, indirect, and integrated methods. Direct methods use samples from preserved areas to establish averages and medians of chemical element concentrations. On the other hand, indirect methods use a large number of samples, statistical tools, and spatial analysis to distinguish values related to anthropogenic contamination from Quality Reference Values. In this regard, the integrated method is most suitable, as samples are collected in preserved areas, and the results are subjected to statistical calculations (Galuszka; Migaszewski, 2011; Dung et al., 2013; Hernández-Crespo; Martín, 2015).

Several statistical techniques have been proposed. Generally, these techniques identify outliers in a studied dataset, which may result from contaminations (Matschullat et al., 2000; Reimann et al., 2005; Rothwell; Cooke, 2015). The most recommended techniques include "mean + 2 x Standard Deviation" (Redon et al., 2013), upper limit of Tukey's boxplot, inflection point of a cumulative frequency graph (Reimann et al., 2005; Mikkonen et al., 2017), "median + 2 x Absolute Median Deviation" (Reimann et al., 2005; Rothwell; Cooke, 2015; Mikkonen et al., 2017), 75th and 90th percentiles of the sample universe (Paye et al., 2010; Santos; Alleoni, 2013; Ander et al., 2013; Oliveira et al., 2014; Fernandes et al., 2018; Serafim et al., 2019).

In 2009, the National Environment Council (CONAMA) issued Resolution No. 420, requiring each state to establish its soil quality guideline values. The values indicated by the resolution are: Quality Reference Value (QRV), Prevention Value (PV), and Investigation Value (IV). Biondi et al. (2011), following CONAMA criteria, estimated the natural levels of some chemical elements for representative soils in Pernambuco. In 2014, the State Environmental Agency of Pernambuco (CPRH) issued Instruction No. 7, establishing QRV for Pernambuco.

Determining representative values facilitates monitoring and ensures stricter legislation. However, these values may present possible geochemical anomalies that interfere with the defined levels. Therefore, it is necessary to detail local realities, as various soil formation factors generate significant spatial variability (Cembranel et al., 2017).

The Jaboatão River watershed belongs to a region in the state of Pernambuco with high population density. Additionally, it faces industrial waste discharge into watercourses, lack of sanitation infrastructure, improper solid waste disposal, irregular settlements, deforestation, and the use of pesticides and chemical fertilizers driven by sugarcane cultivation. Given its increasing urbanization, it is urgent to determine local reference levels that can serve as a basis for assessing environmental impacts caused by economic and demographic growth.

In this context, the objective is to establish Quality Reference Values for the elements aluminum (Al), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) for the Jaboatão River watershed, based on the guidelines contained in CONAMA Resolution 420/2009.

## 2. MATERIAL AND METHODS

### 2.1 Study area

The Jaboatão River watershed is located between the coordinates 8º01' and 8º17' South and 34º54' and 35º18' West of Greenwich. It encompasses parts of six municipalities: Vitória de Santo Antão (Zona da Mata Sul), Moreno, São Lourenço da Mata, Jaboatão dos Guararapes, Recife, and Cabo de Santo Agostinho (Metropolitan Region) (Figure 1). It has a drainage area of 422 km², with the main watercourse extending over 75 km from its source in Vitória de Santo Antão to the Atlantic Ocean (CPRH, 2020; APAC, 2024).

The land use and occupation in the watershed are divided among urban areas, sugarcane cultivation, polyculture, Atlantic Forest areas, mangroves, and industrial occupation, encompassing various types of industries (chemical, food products, metallurgical, textile, beverages, paper, cardboard, plastic, electrical materials, sugarcane and alcohol production, clothing, footwear, mechanical, transportation equipment, pharmaceuticals, and veterinary products) (CPRH, 2020).

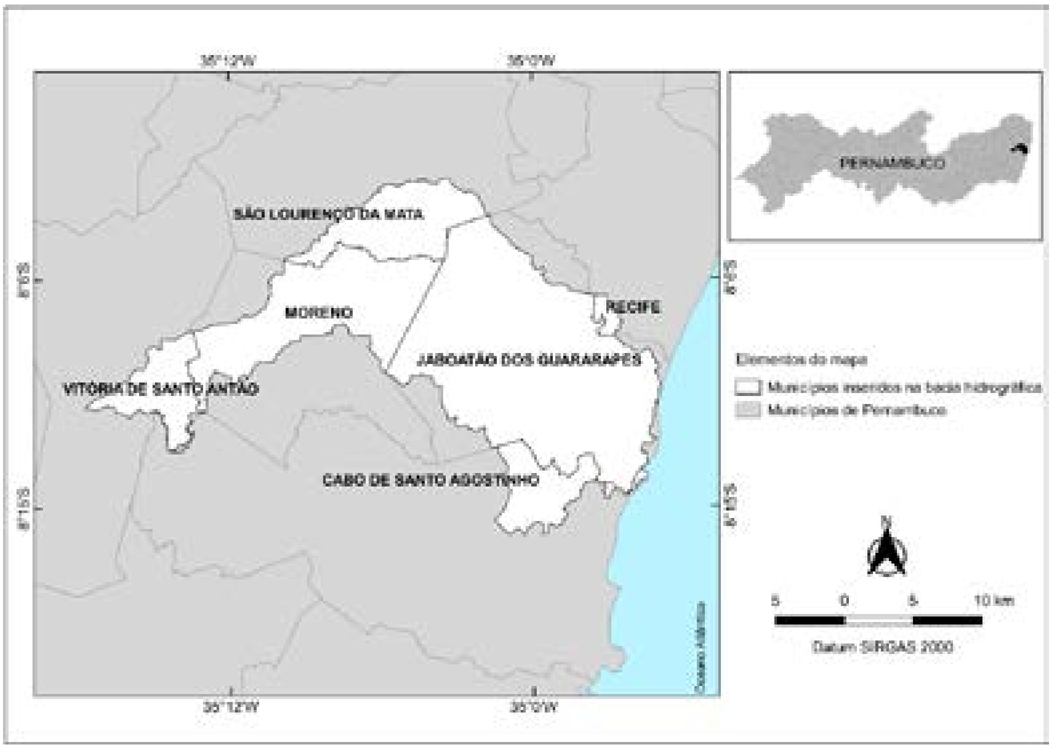

**Figure 2:** Location of the Jaboatão river watershed. Source: Authors, 2024.

### 2.2 Soil Sampling

For the study, sampling points were pre-defined and distributed throughout the Jaboatão River watershed, with the assistance of QGis® 3.10.6 and Google Earth Pro©, following criteria to be located in forested areas and away from civilization. Through visual analysis of the forest conservation status, prioritizing preserved or minimally anthropogenically influenced areas, 16 points were selected. Samples were collected at these points using a stainless steel Dutch auger. At each sampling point, single samples were collected, resulting in 32 samples—16 at the 0–0.20 m layer (surface) and 16 at the 0.20–0.40 m layer (subsurface), both in relation to the soil surface.

The geographic coordinates and altitude of the sampling points were georeferenced with the assistance of QGis® 3.10.6. The map of low and medium soil intensity recognition for the state of Pernambuco (Araújo Filho et al., 2000) served as a base to determine soil classes in the study area, and the geological diversity map of the state of Pernambuco (CPRM, 2014) was used as a reference for identifying the geological context of the region. The identification of sampling points according to municipalities, soil classes, geological context, and geographic coordinates is presented in Table 1.

### 2.3 Soil Analysis

The soil samples were air-dried, mechanically crumbled using a wooden roller, and sieved through a 2.0 mm mesh stainless steel sieve (ABNT 10) to obtain Air-Dried Fine Earth (ADFE).

The physical and chemical characterization analyses performed included: particle size distribution using the pipette method (EMBRAPA, 2017), hydrogenionic potential (pH) in soil-water suspension (1:2.5) (EMBRAPA, 2017), Total Organic Carbon (TOC) by wet oxidation with external heating, modified Walkley-Black method by Yeomans and Bremner (2008), and potential Cation Exchange Capacity (CEC) by the ammonium acetate and sodium acetate method (Freire et al., 2016).

### 2.4 Determination of Natural Contents

For the quantification of elements, the ADFE samples were ground in an agate mortar and sieved through a 0.053 mm mesh sieve (ABNT 230) to obtain a fine powder.

The extraction of trace and major elements was carried out following the method 3050B from the United States Environmental Protection Agency (USEPA, 1996a). This method is a pseudo-total digestion technique for most samples, as it involves a very strong acid digestion that will dissolve nearly all elements that can become "environmentally available." The method does not extract elements bound in silicate structures, as they are generally not mobile in the environment.

The quantification of elements was performed using flame atomic absorption spectrometry. The accuracy of the analysis was assessed using certified reference material for metals, Trace Metals - Sandy Clay 1, CRM049 – 50 g Sigma-Aldrich.

| Point | Municipality | Soil Class[1] | Geological Context[2] | Coordinates (S/W) | Altitude (m) |
|---|---|---|---|---|---|
| 1 | Vitória de Santo Antão | Yellow Ultisol | Subalkaline Granitic (Igneous) | 8°11'56"/35°13'53" | 281 |
| 2 | Moreno | Red-Yellow Ultisol | Gneiss and Migmatite (Metamorphic) | 8°08'11"/35°12'35" | 263 |
| 3 | Moreno | Red-Yellow Ultisol | Gneiss and Migmatite (Metamorphic) | 8°07'56"/35°11'16" | 189 |
| 4 | Moreno | Yellow Ultisol | Subalkaline Granitic (Igneous) | 8°09'07"/35°10'41" | 227 |
| 5 | Moreno | Red-Yellow Ultisol | Gneiss and Migmatite (Metamorphic) | 8°07'30"/35°10'20" | 220 |
| 6 | Moreno | Yellow Ultisol | Subalkaline Granitic (Igneous) | 8°08'10"/35°08'30" | 163 |
| 7 | São Lourenço da Mata | Red-Yellow Ultisol | Gneiss and Migmatite (Metamorphic) | 8°05'14"/35°08'32" | 150 |
| 8 | Moreno | Red-Yellow Ultisol | Gneiss and Migmatite (Metamorphic) | 8°06'44"/35°06'59" | 147 |
| 9 | Moreno | Yellow Oxisol | Gneiss and Migmatite (Metamorphic) | 8°08'32"/35°05'25" | 112 |
| 10 | Moreno | Red-Yellow Ultisol | Gneiss and Migmatite (Metamorphic) | 8°06'25"/35°04'38" | 148 |
| 11 | São Lourenço da Mata | Red-Yellow Ultisol | Gneiss and Migmatite (Metamorphic) | 8°02'22"/35°03'26" | 101 |
| 12 | Jaboatão dos Guararapes | Yellow Oxisol | Intensely Deformed Granitoid (Igneous/ Metamorphic) | 8°10'59"/35°02'49" | 96 |
| 13 | Jaboatão dos Guararapes | Red-Yellow Ultisol | Gneiss and Migmatite (Metamorphic) | 8°05'20"/35°01'17" | 88 |
| 14 | Jaboatão dos Guararapes | Red-Yellow Ultisol | Gneiss and Migmatite (Metamorphic) | 8°06'51"/34°59'41" | 37 |
| 15 | Jaboatão dos Guararapes | Red-Yellow Ultisol | Intensely Deformed Granitoid (Igneous/ Metamorphic) | 8°09'32"/34°59'36" | 16 |
| 16 | Jaboatão dos Guararapes | Gleyic Gleisol | Clayey, Clayey-sand, and Sandy Sediments (Sedimentary) | 8°13'15"/34°59'19" | 13 |

**Table 1:** Identification of the 16 points sampled in the Jaboatão river basin.

(1) Araújo Filho et al., 2000; (2) CPRM, 2014

### 2.5 Quality Reference Values

To obtain the Quality Reference Values (QRV), the boxplot graphical representation was initially used to identify and remove anomalous values from the sample universe (CONAMA, 2009). Subsequently, the results of trace and major element concentrations were utilized to calculate the QRV for the Jaboatão River watershed according to statistical methods proposed by Redon et al. (2013), equation 1, Reimann et al. (2005) and Mikkonen et al. (2017), equation 2, Reimann et al. (2005), Rothwell and Cooke (2015), and Mikkonen et al. (2017), equation 3 for the upper inner limit of Tukey's boxplot and the 75th and 90th percentiles recommended by CONAMA (2009).

$$\text{QRV}=\text{mean}+2\text{SD} \tag{1}$$

$$\text{QRV}=\text{median}+2\text{MAD} \tag{2}$$

$$\text{QRV}=\text{Q3}+1{,}5\text{Q3}-\text{Q1} \tag{3}$$

where SD is the standard deviation, MAD is the median absolute deviation, and Q1 e Q3 are the first and third quartiles, respectively.

The obtained data were organized and subjected to descriptive analysis, normality hypothesis testing, analysis of variance (ANOVA), with means compared by Tukey's test at $p < 0,05$, as well as Pearson correlation analysis ($p < 0,1$), using the SISVAR software (Ferreira, 2011), and Microsoft Excel XLSTAT (version 2019.3.2) (Addinsoft, 2019). For multivariate analysis, factor analysis with factors extracted by principal components was used. The axes were rotated using the Varimax method. Factors with eigenvalues greater than 1.0 were chosen, and factor loadings greater than 0.6 were considered significant (Kaiser, 1960; Davis, 1986).

## 3. RESULTS AND DISCUSSION

### 3.1 Soil properties

The descriptive statistics of the chemical and physical properties for the two soil layers studied are presented in Table 2. Tukey's test at $p < 0.05$ showed statistical significance between the two layers for total organic carbon (TOC). On the other hand, the other analyzed parameters did not show statistical significance between the different layers.

The hydrogen potential (pH) of the samples ranged from 3.96 to 5.85 with an average value of 4.59 (Table 2); thus, the soils in the region are considered acidic. Soil pH has a significant effect on the dynamics of chemical elements in soils, as acidic conditions favor the solubilization and mobilization of cationic metals in the soil (Arias et al., 2005; Zeng et al., 2011; Almeida Júnior et al., 2016).

COT levels were higher in the surface and lower in the subsurface, ranging from 11.29 to 27.30 g kg-1 with an average of 17.75 on the surface, and 7.32 to 22.73 g kg-1 with an average of 13.85 in the subsurface (Table 2). A higher amount of organic carbon on the soil surface can contribute to the retention of chemical elements, as organic matter in soil samples actively participates in the immobilization of these elements in the soil (Tume et al., 2014). This behavior can be attributed to the generation of adsorption sites with a prevalence of negative charges that act, through ionic bonding, as a chelating agent in the soil solution (Garcia-Mina, 2006).

Cation exchange capacity (CEC) values varied from 2.58 to 13.57 cmolc kg-1, with an average of 5.50 cmolc kg-1 (Table 2). The potential for high CTC variation may be related to contributions from organic matter in tropical soils, in addition to minerals with high specific surface area (Eze et al., 2010).

The sand fraction ranged from 65.99 to 712.13 g kg-1, with an average of 533.46 g kg-1; the silt fraction ranged from 74.00 to 453.93 g kg-1, with an average of 128.97 g kg-1; and the clay, the most reactive soil fraction, varied from 146.00 to 419.90 g kg-1, with an average of 279.99 g kg-1 (Table 2). The texture classes of the analyzed soil samples were: loamy sand (59%), loamy clay (13%), loamy sand (9%), sandy loam (9%), clayey (6%), and clayey-silty (3%).

| Variables | Layer[1] | Mean | Median | Minimum | Maximum | Standard Deviation |
|---|---|---|---|---|---|---|
| pH H2O | 1 | 4.56 | 4.41 | 4.07 | 5.85 | 0.49 |
| | 2 | 4.63 | 4.62 | 3.96 | 5.04 | 0.28 |
| | All | 4.59 | 4.58 | 3.96 | 5.85 | 0.39 |
| CEC (cmol$_c$ kg-$^1$) | 1 | 6.30 | 5.94 | 3.44 | 13.59 | 2.47 |
| | 2 | 4.69 | 4.31 | 2.58 | 12.16 | 2.10 |
| | All | 5.50 | 4.82 | 2.58 | 13.59 | 2.40 |
| COT (g kg-$^1$) | 1 | 19.75 | 20.77 | 11.29 | 27.30 | 4.48 |
| | 2 | 13.85 | 13.48 | 7.32 | 22.73 | 3.75 |
| | All | 16.80 | 16.41 | 7.32 | 27.30 | 5.05 |
| Sand (g kg-$^1$) | 1 | 521.64 | 558.24 | 65.99 | 712.13 | 151.01 |
| | 2 | 484.34 | 490.88 | 314.20 | 625.51 | 85.96 |
| | All | 502.99 | 533.46 | 65.99 | 712.13 | 122.35 |
| Silt (g kg-$^1$) | 1 | 154.99 | 125.98 | 77.99 | 453.93 | 98.95 |
| | 2 | 149.36 | 137.98 | 74.00 | 289.96 | 61.34 |
| | All | 152.17 | 128.97 | 74.00 | 453.93 | 81.03 |
| Clay (g kg-$^1$) | 1 | 259.10 | 253.98 | 146.00 | 405.94 | 62.07 |
| | 2 | 308.72 | 312.97 | 155.98 | 419.90 | 66.71 |
| | All | 283.91 | 279.99 | 146.00 | 419.90 | 68.21 |

**Table 2:** Chemical and physical properties of soil samples in the Jaboatão river basin.

(1) 1- surface (average of 16 samples); 2 – subsurface (average of 16 samples); All – mean of 32 samples (surface e subsurface).

### 3.2 Recovery of trace elements

The certified reference material used to verify that the extraction and quantification of elements occurred effectively has certified values based on the digestion method 3050B, 3051, or equivalent pseudo-total digestion methods.

The recovery rates of elements in the certified material ranged from 89 to 99% (Table 3), falling within the recommended range (USEPA, 1996b). Therefore, these results ensure the quality of the United States Environmental Protection Agency (USEPA) method 3050B for soil sample digestion, indicating the reliability of the results obtained in the analysis of trace and major elements.

| Element | Certified Value[1] | Determined Value | Recovery |
|---|---|---|---|
| mg kg-1 | | | % |
| Al | 10,300.00 (1,610.00) | 9,194.67 (646.84) | 89 |
| Cd | 87.90 (1.71) | 87.13 (0.81) | 99 |
| Co | 217.00 (4.77) | 215.67 (0.82) | 99 |
| Cr | 134.00 (2.26) | 132.90 (0.51) | 99 |
| Cu | 133.00 (2.52) | 132.13 (0.29) | 99 |
| Fe | 6,610.00 (253.00) | 6,531.67 (10.27) | 98 |
| Mn | 1,120.00 (36.80) | 1,094.33 (4.64) | 97 |
| Ni | 287.00 (5.71) | 284.33 (1.25) | 98 |
| Pb | 340.00 (7.24) | 335.33 (2.49) | 98 |
| Zn | 443.00 (7.92) | 438.00 (2.16) | 99 |

**Table 3:** Certified values [mean (standard deviation)], determined values [mean (standard deviation)] and percentage recovery of trace elements in certified material after submitting to USEPA method 3050B.

(1) Certified material values (Trace Metals - Sandy Clay 1, CRM049 – 50 g Sigma-Aldrich)

### 3.3 Natural levels of trace elements

Some elements showed high variations (Table 4) in their concentrations, such as Mn and Ni, which exhibited variations above 100%, due to different geological contexts for Mn and the low number of samples with detectable Ni levels. However, Al, Fe, Cd, Co, Pb, and Zn had variations lower than 65%.

Tukey's test did not show statistical significance between the concentrations of chemical elements for the two soil layers studied. Therefore, the averages of surface and subsurface samples were analyzed.

The average concentrations of elements followed the following decreasing order, in mg kg-1: Al > Fe > Zn > Mn > Pb > Cr > Co > Ni > Cu > Cd. Overall, the values were lower than those reported by Paye et al. (2010) in soils from Espírito Santo, except for Pb and Zn. The low values reflect the geological context of the Jaboatão River watershed, which is mainly composed of metamorphic rocks, predominantly gneisses, migmatites, quartzites, and granites (CPRM, 2014).

The average Al content was 16.27 g kg-1 (Table 4); the studied areas showed abundance in Al levels, as Al is dominant in the structure of secondary minerals, forming the majority of the clay fraction in weathered and acidic soils, similar to the soils in the region (Marques et al., 2004; Benedetti et al., 2011).

Fe presented a lower average concentration (3.89 g kg-1) (Table 4) than in studies conducted by Almeida Júnior et al. (2016) for soils in the state of Paraíba (14.31 g kg-1), Silva et al. (2015) for soils in the Ipojuca River watershed in Pernambuco (16.05 g kg-1), and Biondi et al. (2011) for soils in the Zona da Mata region of Pernambuco, with an average value of 21.42 g kg-1. However, they observed a wide variation in Fe levels, ranging from 0.70 g kg-1 to 94.50 g kg-1. In some locations with Yellow Argisol and Red Argisol, with sedimentary sandy and clay-sandy origin materials, as well as gneisses and migmatites, the levels are similar to those in the present study, and these authors attributed the large differences to the diversity of source materials.

Mn concentrations (Table 4) ranged from 4 to 407.10 mg kg-1 with an average value of 64.06 mg kg-1, where 88% of the samples had values below 200 mg kg-1, corroborating the results of Biondi et al. (2011) for soils in the state of Pernambuco. These authors attributed the low values to the weathering of the region's soils. However, the values were low when compared to studies in other states of Brazil, such as Espírito Santo with 131.69 mg kg-1 (Paye et al., 2010), Rio Grande do Norte with 3,300.00 mg kg-1 (Preston et al., 2014), and Pará with 100.40 mg kg-1 (Fernandes et al., 2018).

| Element | Layer[1] | n[2] | Mean | Median | Min[3] | Max | Standard Deviation | Coeficient of Variation (%) |
|---|---|---|---|---|---|---|---|---|
| Al (g kg$^{-1}$) | 1 | 16 | 15.75 | 16.22 | 11.38 | 17.53 | 1.73 | 11 |
| | 2 | 16 | 16.79 | 17.13 | 11.52 | 19.29 | 1.96 | 12 |
| | All | 32 | 16.27 | 16.58 | 11.38 | 19.29 | 1.90 | 12 |
| Fe (g kg$^{-1}$) | 1 | 16 | 3.84 | 3.91 | 2.98 | 4.10 | 0.29 | 7 |
| | 2 | 16 | 3.95 | 4.01 | 3.31 | 4.25 | 0.24 | 6 |
| | All | 32 | 3.89 | 3.98 | 2.98 | 4.25 | 0.27 | 7 |
| Cd (mg kg$^{-1}$) | 1 | 16 | 0.31 | 0.26 | 0.02 | 0.71 | 0.19 | 61 |
| | 2 | 15 | 0.41 | 0.35 | < LD | 1.09 | 0.24 | 57 |
| | All | 31 | 0.36 | 0.35 | < LD | 1.09 | 0.22 | 60 |
| Co (mg kg$^{-1}$) | 1 | 16 | 5.56 | 5.30 | 1.01 | 9.69 | 2.29 | 41 |
| | 2 | 16 | 5.89 | 6.21 | 1.61 | 11.10 | 2.28 | 39 |
| | All | 32 | 5.72 | 5.75 | 1.01 | 11.10 | 2.26 | 39 |
| Cr (mg kg$^{-1}$) | 1 | 9 | 12.80 | 7.46 | < DL | 37.16 | 12.14 | 95 |
| | 2 | 9 | 21.41 | 17.46 | < DL | 45.81 | 14.98 | 70 |
| | All | 18 | 17.10 | 11.64 | < DL | 45.81 | 13.95 | 82 |
| Cu (mg kg$^{-1}$) | 1 | 2 | 2.83 | 2.83 | < DL | 3.57 | 1.05 | 37 |
| | 2 | 2 | 3.78 | 3.78 | < DL | 5.63 | 2.62 | 69 |
| | All | 4 | 3.30 | 2.83 | < DL | 5.63 | 1.72 | 52 |
| Mn (mg kg$^{-1}$) | 1 | 16 | 64.88 | 32.11 | 4.92 | 407.10 | 106.34 | 164 |
| | 2 | 16 | 63.25 | 30.19 | 4.00 | 353.57 | 103.07 | 163 |
| | All | 32 | 64.06 | 30.53 | 4.00 | 407.10 | 103.02 | 161 |
| Ni (mg kg$^{-1}$) | 1 | 6 | 2.93 | 0.98 | < LD | 12.54 | 4.44 | 152 |
| | 2 | 7 | 3.89 | 1.24 | < LD | 14.20 | 5.42 | 139 |
| | All | 15 | 3.37 | 1.08 | < LD | 14.20 | 4.73 | 140 |

**Table 4:** Descriptive statistics of trace element contents of soils sampled in the Jaboatão river basin.

(1) 1 – surface; 2 – subsurface; All – average of all samples. (2) n – number of samples with content detected by the method. (3) < DL – less than the detection limit.

| Element | Layer[1] | n[2] | Mean | Median | Min[3] | Max | Standard Deviation | Coeficient of Variation (%) |
|---|---|---|---|---|---|---|---|---|
| Pb (mg kg-$^1$) | 1 | 16 | 19.11 | 19.69 | 8.61 | 27.07 | 5.56 | 29 |
| | 2 | 16 | 18.34 | 19.38 | 6.77 | 22.77 | 4.43 | 24 |
| | All | 32 | 18.73 | 19.69 | 6.77 | 27.07 | 4.96 | 26 |
| Zn (mg kg-$^1$) | 1 | 16 | 111.14 | 109.02 | 11.54 | 217.03 | 68.38 | 62 |
| | 2 | 16 | 120.46 | 129.50 | 12.15 | 238.83 | 77.57 | 64 |
| | All | 32 | 115.80 | 111.36 | 11.54 | 238.83 | 72.09 | 62 |

**Table 4:** Descriptive statistics of trace element contents of soils sampled in the Jaboatão river basin.

(1) 1 – surface; 2 – subsurface; All – average of all samples. (2) n – number of samples with content detected by the method. (3) < DL – less than the detection limit.

The Cd concentrations ranged from 0.02 mg kg-1 to 1.09 mg kg-1 (Table 4), with only one sample not detecting Cd. The average Cd content (0.36 mg kg-1) (Table 4) in soils of the Jaboatão River basin is very close to that determined by Fernandes et al. (2018) for soils in Pará (0.32 mg kg-1), but higher than those found by Santos and Alleoni (2013) for soils in Mato Grosso and Rondônia, where Cd levels were below the detection limit in all samples, as well as for São Paulo (CETESB, 2014), and Espírito Santo (Paye et al., 2010).

In six samples, Cd exceeded the Quality Reference Value (0.5 mg kg-1) defined by CPRH (2014) for Pernambuco. However, none exceeded the Prevention Value (1.3 mg kg-1) determined by CONAMA (2009). Values above the Quality Reference Values (QRV) may be associated with natural geochemical enrichment or factors such as topography and weathering intensity (Burak et al., 2010; Santos; Alleoni, 2013), as the levels found are within the literature-reported range for soils derived from igneous rocks of 0.1-0.3 mg kg-1, metamorphic rocks between 0.1-1.0 mg kg-1, and sedimentary rocks of 0.3-1.0 mg kg-1 (Alloway, 1990).

Co concentrations ranged from 1.01 to 11.10 mg kg-1 with an average of 5.72 mg kg-1 (Table 4). The average content was similar to that found by Almeida Júnior et al. (2016) for soils in Paraíba (5.97 mg kg-1) and lower than the content found by Paye et al. (2010) for soils in Espírito Santo (8.64 mg kg-1). Like Biondi et al. (2011), high Co values were observed for Gleisol. This author indicates that in the Zona da Mata region of Pernambuco, there is a tendency for Co to be maintained in soils located in floodplain environments, where leached elements from soils located at higher elevations are transferred and retained during the formation time. This phenomenon results in higher levels than in other soils in the region.

Approximately 78% of Co values are above the Quality Reference Value (QRV) determined by CPRH (2014), which corresponds to 4.00 mg kg-1. However, none exceeded the Prevention Value (PV) determined by CONAMA (2009), which corresponds to 25.00 mg kg-1. As the samples were collected in areas with minimal anthropogenic interference, quantifying higher values than the QRV determined by CPRH (2014) reinforces the need for determining the QRV for the Jaboatão River basin.

Cr concentrations (Table 4) varied from below the detection limit to 45.81 mg kg-1, with an average content of 17.10 mg kg-1. Cu presented concentrations ranging from below the detection limit to 5.63 mg kg-1, with an average value of 3.30 mg kg-1, and for Ni, values ranged from below the detection limit to 14.20 mg kg-1, with an average content of 3.37 mg kg-1. All three elements had average values lower than those found by Almeida Júnior et al. (2016) for soils in the state of Paraíba and also lower than those found by Silva et al. (2015) for soils in the Ipojuca River watershed in Pernambuco. The low values reflect the geological context of the Jaboatão River basin, where the majority is composed of metamorphic rocks and clay-sandy sediments, which are naturally poor in Cr, Cu, and Ni (CPRM, 2014; Araújo et al., 2018).

Pb values (Table 4) ranged from 6.77 to 27.07 mg kg-1, with an average of 18.73 mg kg-1. This value was higher than those of soils in Espírito Santo (8.79 mg kg-1) (Paye et al., 2010), Mato Grosso and Rondônia (8.10 mg kg-1) (Santos; Alleoni, 2013), São Paulo (10.10 mg kg-1) (Nogueira et al., 2018), and Pará (3.69 mg kg-1) (Fernandes et al., 2018). However, it corroborates the values reported by Biondi et al. (2011) for soils in the Zona da Mata region of Pernambuco (16.85 mg kg-1) and Silva et al. (2015) for soils in the Ipojuca River basin in Pernambuco (19.48 mg kg-1).

Zn concentrations (Table 4) ranged from 11.54 to 238.83 mg kg-1, with an average of 115.80 mg kg-1. Most of the values found were much higher than those found in the study by Silva et al. (2015) for soils in the Ipojuca River basin, located in Pernambuco (45.41 mg kg-1). In the present study, the average value for soils derived from igneous rocks was 152.53 mg kg-1, and for soils derived from alluvial sediments, it was 12.95 mg kg-1. Oliveira e Costa (2004) also observed low Zn values for soils originating from gneiss and sediments and high values for soils derived from basalt.

Of the analyzed soil samples, about 84% had Pb values above the Quality Reference Value (QRV) (13.00 mg kg-1) determined by CPRH (2014), and about 81% of the analyzed soil samples exceeded the QRV (35.00 mg kg-1) determined by CPRH (2014) for Zn. However, all values were below the Prevention Value defined by CONAMA (2009) for Pb (72 mg kg-1) and Zn (300 mg kg-1), indicating that the evaluated soils do not pose risks to human health.

The highest Pb values were found in Oxisols, Ultisols, and Gleissol derived from Gneiss and Migmatites, Granitoids, and Alluvial Sediments. Kabata-Pendias and Pendias (2001) stated that soils derived from acidic rocks, granite, gneiss, and sandy and clayey sediments are materials that have high Pb levels. The most significant Zn values were found in Ultisols and Oxisols with a subalkaline granite and granitoid origin, indicating the possibility of this source material being rich in Zn (Kabata-Pendias; Pendias, 2001).

In addition to the source material, urban centers and local highway traffic may have influenced the concentrations of Pb and Zn. Studies conducted in São Paulo (Figueiredo et al., 2009), the Sydney watershed in Australia (Birch et al., 2011), and the Rio das Mortes watershed in Minas Gerais (Zuliani et al., 2017) have confirmed a close relationship between the distribution of Pb and Zn with urban centers characterized by high population density and vehicular emissions.

### 3.4 Quality reference values (QRV)

The concentrations of trace elements were used to determine the Quality Reference Value (QRV), with anomalous values previously removed through Boxplot, as recommended by CONAMA Resolution No. 420/2009. The elements Cr, Cu, and Ni did not exhibit a homogeneous distribution along the Jaboatão river basin, and in the majority of samples, they were not detected. Therefore, they were classified as less than the practicable limit of quantification (< LQP) (Table 5) and excluded from further procedures (CONAMA, 2009).

The "median + 2 x MAD," a method less sensitive to outliers, generated QRV very close to those determined by the 90th Percentile for most elements (Table 5). The 75th Percentile is the most conservative method; however, this technique tends to underestimate reference values, categorizing normal values as contamination, leading to the restriction or remediation of areas that are not actually contaminated in practice.

Among the analyzed methodologies, the upper limit of Tukey's boxplot and the "mean + 2 x SD" may have overestimated the QRV. On the other hand, the "median + 2 x MAD" showed values closer to the 90th Percentile (Table 5). Therefore, the 75th Percentile was adopted as the most suitable method for determining the QRV of the elements Al, Cd, Co, Fe, Mn, Pb, and Zn found in the soils of the Jaboatão river watershed.

Table 6 compares the QRV obtained for the Jaboatão river basin with other QRV established in Pernambuco. The values of Co, Pb, and Zn were higher than the QRV determined for the state of Pernambuco. However, none exceeded the prevention value determined by CONAMA (2009), Co (25.00 mg kg-1), Pb (72.00 mg kg-1), and Zn (300.00 mg kg-1), indicating that the evaluated soils do not pose potential risks to human health or the ecosystem of the region.

The values obtained in this study for Pb and Zn (Table 5) were higher than the QRV reported in other regions of Brazil: Espírito Santo (8.92 and 49.32 mg kg-1) (Paye et al., 2010), São Paulo (17.00 and 60.00 mg kg-1) (CETESB, 2015), Mato Grosso and Roraima (8.10 and 6.80 mg kg-1) (Santos; Alleoni, 2013), Rio Grande do Norte (16.18 and 42.44 mg kg-1) (Preston et al., 2014), Paraíba (14.62 and 33.65 mg kg-1) (Almeida Júnior et al., 2016), and Pará (6.40 and 21.00 mg kg-1) (Fernandes et al., 2018).

There are some similarities and clear differences between the concentrations in different regions of the state of Pernambuco. These differences emphasize the need to determine Quality Reference Value by regions, taking into account the geomorphological, pedological, and geological diversity of each region (Cembranel et al., 2017).

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| Element | P75 | P90 | Median + 2 x MAD | Mean + 2 SD | Upper limit from Boxplot |
|---|---|---|---|---|---|
| Al (g kg-$^1$) | 17.33 | 18.27 | 18.44 | 18.62 | 18.83 |
| Fe (g kg-$^1$) | 4.04 | 4.09 | 4.11 | 4.17 | 4.22 |
| Cd (mg kg-$^1$) | 0.43 | 0.52 | 0.53 | 0.61 | 0.70 |
| Co (mg kg-$^1$) | 6.76 | 7.95 | 8.54 | 9.23 | 10.49 |
| Cr (mg kg-$^1$) | <LQP | <LQP | <LQP | <LQP | <LQP |
| Cu (mg kg-$^1$) | <LQP | <LQP | <LQP | <LQP | <LQP |
| Mn (mg kg-$^1$) | 35.41 | 40.90 | 46.68 | 51.82 | 60.22 |
| Ni (mg kg-$^1$) | <LQP | <LQP | <LQP | <LQP | <LQP |
| Pb (mg kg-$^1$) | 21.23 | 22.08 | 23.07 | 23.94 | 26.51 |
| Zn (mg kg-$^1$) | 152.17 | 170.52 | 175.71 | 197.16 | 222.27 |

**Table 5:** Quality reference values for the soils of the Jaboatão river watershed, calculated through various statistical methods after the removal of anomalous values.
P75 - 75th Percentile; P90 - 90th Percentile; MAD - Median Absolute Deviation; SD - Standard Deviation; <LQP - less than the Limit of Quantification Practicable.

The "median + 2 x MAD," a method less sensitive to outliers, generated QRV very close to those determined by the 90th Percentile for most elements (Table 5). The 75th Percentile is the most conservative method; however, this technique tends to underestimate reference values, categorizing normal values as contamination, leading to the restriction or remediation of areas that are not actually contaminated in practice.

Among the analyzed methodologies, the upper limit of Tukey's boxplot and the "mean + 2 x SD" may have overestimated the QRV. On the other hand, the "median + 2 x MAD" showed values closer to the 90th Percentile (Table 5). Therefore, the 75th Percentile was adopted as the most suitable method for determining the QRV of the elements Al, Cd, Co, Fe, Mn, Pb, and Zn found in the soils of the Jaboatão river watershed.

Table 6 compares the QRV obtained for the Jaboatão river basin with other QRV established in Pernambuco. The

The values obtained in this study for Pb and Zn (Table 5) were higher than the QRV reported in other regions of Brazil: Espírito Santo (8.92 and 49.32 mg kg-1) (Paye et al., 2010), São Paulo (17.00 and 60.00 mg kg-1) (CETESB, 2015), Mato Grosso and Roraima (8.10 and 6.80 mg kg-1) (Santos; Alleoni, 2013), Rio Grande do Norte (16.18 and 42.44 mg kg-1) (Preston et al., 2014), Paraíba (14.62 and 33.65 mg kg-1) (Almeida Júnior et al., 2016), and Pará (6.40 and 21.00 mg kg-1) (Fernandes et al., 2018).

There are some similarities and clear differences between the concentrations in different regions of the state of Pernambuco. These differences emphasize the need to determine Quality Reference Value by regions, taking into account the geomorphological, pedological, and geological diversity of each region (Cembranel et al., 2017).

| Element | Jaboatão river basin[1] | Pernambuco[2] | Ipojuca river basin[3] | Fernando de Noronha Island[4] |
|---|---|---|---|---|
| Al (g kg-$^1$) | 17.33 | - | - | - |
| Fe (g kg-$^1$) | 4.04 | - | 13.02 | - |
| Cd (mg kg-$^1$) | 0.43 | 0.50 | 0.08 | - |
| Co (mg kg-$^1$) | 6.76 | 4.00 | - | 19.61 |
| Cr (mg kg-$^1$) | <LQP | 35.00 | 15.00 | 266.13 |
| Cu (mg kg-$^1$) | <LQP | 5.00 | 3.53 | 41.49 |
| Mn (mg kg-$^1$) | 35.41 | - | 91.80 | - |
| Ni (mg kg-$^1$) | <LQP | 9.00 | 3.30 | 58.75 |
| Pb (mg kg-$^1$) | 21.23 | 13.00 | 13.12 | - |
| Zn (mg kg-$^1$) | 152.17 | 35.00 | 30.12 | 117.58 |

**Table 6:** Quality Reference Values for Al, Fe, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn for soils in the Jaboatão river basin, Pernambuco, Ipojuca river basin and Fernando de Noronha Island.
(1) This study; (2) CPRH (2014); (3) Silva et al. (2015); (4) Fabrício Neta et al. (2018).

### 3.5 Factor analysis

The set of 32 samples was used to perform Pearson correlation analysis. Significant and positive correlations (data not shown) were found among most of the variables analyzed. These correlations allowed the use of variables in the data matrix for the factor analysis.

Through principal component factor analysis, three factors were identified (Table 7). These factors account for 70.68% of the total variation in the data. The chosen factors had eigenvalues > 1 (Kaiser, 1960; Davis, 1986).

The first factor explains over 24% of the total variation and is composed of the elements Mn and Ni, which exhibited higher factor loadings. This suggests that they originate from the same source, as high correlations between trace elements are likely related to a common source material (Chandrasekaran et al., 2015).

The second factor explains nearly 25% of the total variance and includes Al, Fe, and Zn. Al and Fe are the two main constituents of the lithosphere, indicating a common source material.

According to Costa et al. (2002), tropical soils' mineralogy is mainly composed of kaolinite, iron oxides (hematite, goethite, and maghemite), aluminum oxides (gibbsite), and minor proportions of 2:1 type minerals (vermiculite). Adsorption of metallic ions can occur on iron and aluminum oxides and on the peripheries of silicate clays through the formation of covalent or electrostatic bonds with the functional groups on the oxide surface.

| Element | Factor Axis[1] | | |
|---|---|---|---|
| | Factor 1 | Factor 2 | Factor 3 |
| Al | -0.120 | **0.784** | 0.211 |
| Cd | -0.356 | -0.129 | **0.752** |
| Co | 0.258 | 0.086 | **0.825** |
| Cr | 0.183 | 0.537 | -0.148 |
| Cu | 0.498 | 0.350 | -0.235 |
| Fe | 0.225 | **0.887** | 0.260 |
| Mn | **0.904** | 0.008 | 0.045 |
| Ni | **0.938** | 0.156 | -0.098 |
| Pb | -0.425 | 0.323 | 0.628 |
| Zn | 0.089 | **0.717** | -0.571 |
| Eigenvalues | 3,143 | 2,317 | 1,609 |
| Total Variance (%) | 24,254 | 24,779 | 21,655 |
| Cumulative Variance (%) | 24,254 | 49,033 | 70,688 |

**Table 7:** Quality Reference Values for Al, Fe, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn for soils in the Jaboatão river basin, Pernambuco, Ipojuca river basin and Fernando de Noronha Island.
Eixos fatoriais rotacionados pelo método Varimax

Even at low concentrations, Al and Fe oxides influence the adsorption of elements such as Zn (Alleoni et al., 2005). Both Fe and Zn may coexist in the soil source material and be released due to rock weathering (Sheng et al., 2012), explaining why these elements are in the same group.

Cd, Co, and Pb are represented by the third factor, explaining 22% of the total variation. This group includes some of the trace elements that pose significant environmental concerns, such as Pb and Cd, suggesting possible anthropogenic influence. Meanwhile, Co is more frequently associated with ores of Cu, Fe, Ni, and Pb, from which it is obtained as a byproduct (Preston et al., 2014).

## 4. CONCLUSIONS

The concentrations of Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were determined for 16 locations at two depths in the Jaboatão river watershed in Pernambuco. The abundance of elements in the Jaboatão river watershed followed the following descending order: Al, Fe, Zn, Mn, Pb, Cr, Co, Ni, Cu, and Cd. Chromium, copper, and nickel were not representative throughout the entire watershed. The calculation method deemed most appropriate for determining the Quality Reference Value (QRV) in the region was the 75th Percentile, with the following values (mg kg-1): Cd (0.43), Co (6.76), Mn (35.41), Pb (21.23), and Zn (152.17).

The QRV for the Jaboatão river watershed is lower than in other regions of Brazil, except for Co, Pb, and Zn. However, they did not exceed the Prevention Values established by CONAMA Resolution 420/2009, ensuring that the soils do not pose risks to human health and the ecosystems of the region. The principal component analysis, which grouped the metals Mn and Ni (Factor 1), Al, Fe, and Zn (Factor 2), and Cd, Co, and Pb (Factor 3), suggests the natural origin of these elements in the studied soils.

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