

#### Article

# High Aluminum content in the aquifer of Camaçari industrial pole, state of Bahia, Brazil: Correlation with natural and anthropogenic environmental factors using multivariable analysis

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Abstract: This work used multivariable analysis to correlate groundwater high aluminum content in the area of the Liquid Effluent Treatment Center-CETREL of the Camaçari Industrial Pole, with natural environmental factors: geology, hydrogeology, precipitation, soil and vegetation; and anthropic: equipments of treatment and disposal of industrial waste from CETREL. This company made available data from 99 monitoring wells, period 2006–2016, with aluminum content above (0.2mg/L) the limit established by the Ministry of Health Ordinance Nº 888, 5 April 2021. Previous studies have indicated that there is no correlation of aluminum in groundwater of the Camaçari Industrial Pole with other metallic contaminants; also, that aluminum in the studied region is disseminated in the geological matrix, clayey soils, and poor and leached Cerrado soils. The Kruskal-Wallis test indicated significant correlation of high aluminum content with the treatment/disposal areas, geology, soil and vegetation; and no correlation with precipitation and hydrogeology. The four environmental factors indicating the highest average aluminum content ( $\pm C_{95\%}$ ), in descending order, are: Clayey Soils, Organic Sludge Farm I, Marizal Formation, and Herbaceous-Subshrub Vegetation. The multivariable analysis indicated that, the most influential factors on the high aluminum content in groundwater of the CETREL region, are all ultimately associated with the leaching of aluminum present in the solid matrix. As CETREL processes are not correlated with aluminum residues, the results were an important information for the company environmental managers.

Keywords: multivariate analysis; high aluminum content; groundwater; CETREL-BA

# **1. Introduction**

The Liquid Effluent Treatment Center—CETREL is responsible for the treatment of the resulting effluent from the industrial processes of the Camaçari Industrial Pole (PIC), State of Bahia, Brazil; as well as by the disposal of industrial residues in equipments built for this purpose.

The Water Resources Management Plan (PGRH) was implemented by CETREL in 1992, with guidelines for the monitoring, protection and conservation of water in the PIC's area. The PGRH has 24 sampling stations for surface water and bottom sediments, in the Jacuipe, Capivara Pequeno, Capivara Grande, Imbassaí, Ganhador, Joanes and Camaçari rivers; and in some containment basins.

In 2017, the groundwater monitoring network had: 1354 Monitoring Wells (PM); 233 Multilevel Monitoring Wells (PMM); 196 Production Wells (PP); and 94 Extraction Wells (PE); with some of these wells already out of operation. The monitoring of PIC's groundwater identified the presence of high aluminum content in the region groundwater, fact not well understood by the CETREL hydrogeologists, us aluminum is not processed by the industrial pole (PIC). Thus, these studies had the objective to investigate the influence of environmental factors, natural or anthropic, on the high aluminum content of the region groundwater.

Among the natural factors that most influence the quality of groundwater are the precipitation, geology, hydrogeology, soils and vegetation. Aluminum is one of the most abundant metallic elements in the earth's crust [1]. Aluminum content in groundwater depends on the rocks that contain the element, in addition to fluorides, sulfates, organic matter and clay [2]. They also depend on temperature and pH, being soluble in acidic or alkaline pH values [3]. According to Ordinance N° 888, 5 April 2021 of the Ministry of Health (Brazil 2021), the maximum value of aluminum in drinking water is 0.2 mg/L.

Aluminum in the soil can undergo dissolution to neutralize the entry of acids and acid rain [4], with consequent migration of this element to groundwater. The work by Silva et al. [5], found aluminum content in groundwater from tubular wells and Amazon wells, above the potability limits of Ordinance 888/2021 (0.2 mg/L), and CONAMA Resolution 357/2005 (0.1 mg/L). The high aluminum content was attributed to the soil rich in kaolinite, whose weathering makes aluminum available; associated with the pH of the groundwater that was at levels below the recommended.

The seasonal distribution of the precipitation and temperature are important in the processes of disaggregation and decomposition of rocks and soils. The works by Guerra and Negrão [6] and Negrão [7] present the quality of groundwater in the State of Bahia associated with precipitation and the predominant rock type in the hydrogeological domains. Scopel et al. [8] agree that the chemical characteristics of groundwater are closely related to the types of rock drained.

Soils result from physical, chemical and biological weathering, leaching the primary rock, being constituted by mineral and organic compounds that account for the diversity of soils [9,10]. In countries with a tropical climate, soils are highly leached, and nutrients migrate to groundwater contributing to its chemical composition [11].

Vegetation development depends on the mineralogical and textural constitution of the soil, and on water availability. However, vegetation also influences the weathering of rocks and soil formation, by decomposing organic matter, increasing the concentration of  $CO_2$  in the soil, acidifying water, and favoring the dissolution of minerals present [12]. Carvalho [13] found that the Cerrado vegetation generally coincides with acidic soils of low fertility, deficient in bases, and high aluminum saturation in the deeper layers of the soil profile.

Vegetation also contributes to the constitution of aquifers by intercepting rainwater, providing better infiltration conditions and reducing surface runoff [14]. In fractured aquifers in semiarid regions, especially in dry seasons, the greener vegetation may coincide with the aquifer lineament zone [15]. Vegetation also contributes to reducing evaporation, and the partial filtration of impurities [16]. In crystalline fractured aquifers, however, Costa [17] found that vegetation had low influence on groundwater quality.

# 2. Materials and methods

## 2.1. CETREL: Location and climate

CETREL's area, with approximately 4530 hectares, is located between coordinates E: 585400 and 583300; and N: 8599200 and 8596400, in the municipality of Camaçari, State of Bahia (**Figure 1**). CETREL is located in the Jacuipe River basin, on the watershed of the Capivara Pequeno River and the Capivara Grande River subbasins, in a terrain overlapping the São Sebastião aquifer, the main aquifer of the Reconcavo Sedimentary Basin



**Figure 1.** Location of CETREL's industrial plant. Source: ROCHA [18].

According to the Köppen-Geiger classification, the Camaçari region has an Af climate, humid tropical with little rain in summer and rainy in autumn and winter (**Figure 2**). Data from CETREL's rainfall and climatological stations indicate average annual rainfall of 1354 mm, and average local temperature of 25 °C.



Figure 2. Climate map of Brazil and Camaçari municipality, according to the Köppen-Geiger climate classification. Source: Adapted from Alvares [19].

#### **2.2. CETREL: Effluent treatment processes**

CETREL started its activities in 1978, being responsible for the supply, distribution and reuse of water; treatment and final disposal of effluents and industrial residues; in addition to the environmental management of the PIC and its area of influence. Treatment processes include: transport, treatment and final oceanic disposal of industrial effluents; Class II solid waste landfills; and liquid and solid waste incinerators. The final disposal of industrial solid waste began only in 1984. The territories related to the management of solid waste at CETREL are indicated in **Figure 3**.



Figure 3. CETREL industrial plant and limit of treatment process areas. Source: ROCHA [18].

#### 2.2.1. CETREL: Treatment processes

Since the beginning of its activities, in 1978, the ETE uses the activated sludge process for the treatment of industrial effluents. Its facilities are distributed in:

- Equalization Basin (BEQ): In precast plates fitted with joints, on a concrete base, without bottom waterproofing;
- Aeration Tanks (TA): The 04 aeration tanks (TA-1 to TA-4) have a reinforced concrete bottom, in the form of a board with wooden joints, without bottom waterproofing. The slopes are formed by compacted clay, covered by an inverted filter composed of stones, graded gravel, gravel, bidim and sand.
- Secondary Decanters (DS): The decanters (DS-1 to DS-6) are made of concrete with a foundation directly on the ground, without waterproofing at the bottom. The decanters (DS-7 to DS-12) are in pre-molded plates fitted with joints on a concrete base, without bottom waterproofing;
- Thickeners (ESP): The thickeners (ESP-1 to ESP-5) are in concrete with a foundation directly on the ground, without base waterproofing;
- Aerobic Digesters (DG): The digesters (DG-1 and DG-2) have a reinforced concrete base in the form of a board with wooden joints, without waterproofing the base. The slopes are in compacted clay covered with an inverted filter composed of stones, graded gravel, gravel, bidim and sand. The digester (DG-3) consists of a reinforced concrete box with foundations directly on the ground, without bottom waterproofing;

- Lagoa dos Patos I and II: All the sludge generated in the ETE treatment processes (after the ESP and DG stages) was released in the Lagoa dos Patos I and II in the region, until 1982. After 1982, the Landfarming process began in the Farms (Fazenda de Lodo I and Fazenda Bali) and the Lagoa dos Patos started to receive only rainwater contribution.
- Organic Sludge Farms (FL): The Organic Sludge Farm I was built with ten cells (Cells 0 to 9) and the Organic Sludge Farm Bali contains seven additional cells (Cells 11 to 17). For the construction of FLs, after the earthworks of the area (cuts and embankments), a layer of compacted clay 0.4 m thick and hydraulic conductivity of a design of 10<sup>-7</sup> cm/s, constitutes the bottom base. During the removal of the processed sludge, 0.2 m of clay thickness is also removed (sacrifice layer), in order to guarantee the total removal of the sludge. A new layer of clay is then replaced.

#### 2.2.2. CETREL: Solid waste disposal areas

From 1984 to 1993, the CETREL disposed the PIC's industrial solid waste in buried trenches, called Organic Trenches. These were horizontal excavations, below ground level, functioning as isolated cells. They had a layer of compacted clay (0.4 m thick) and a design hydraulic conductivity of  $10^{-7}$  cm/s. A PVC blanket was placed over the clay layer. Twenty-five (25) ditches were built, occupying an area of 39 h, with approximately 49,051.7 m<sup>3</sup> of disposed solid waste.

In 1994, the disposal of industrial solid waste started to use an Industrial Landfill, built with a vertical design. The base is formed by a layer of compacted clay, with a thickness between 0.7 and 0.8 m, and hydraulic conductivity of a project of  $10^{-7}$  cm/s, covered by a blanket of High-Density Polyethylene (HDPE) of 2.0 mm thick, plus a layer of soil-cement to protect the blanket. For the final coverage, layers of compacted clay, HDPE blanket and biosolids manufactured by CETREL are used.

#### 2.2.3. CETREL: Area for oily waste biodegradation

The oily residues are disposed at the Organic Sludge Farms I, and Bali, where they are treated by the Landfarming process, using the soil macrobiotic itself [20].

According to Miyazawa et al. [21], the application of biosolids generated by industrial sludge farms can improve the physicochemical characteristics of the soil, such as acidity correction [22], however, it can produce a deleterious action, when they undergo chemical and biological reactions capable of altering the mobility of metals incorporated into the soil matrix.

# 2.3. CETREL: Analytical data and geographical location of tubular wells

The data stored in the database [23], were extract using the EQuIS Professional 6.5 software, a management system used by CETREL. The following data were used: well identification, sampling date, geographic coordinates, lithological description and static level, analytical results of aluminum contents, in addition to inorganic and physicochemical parameters.

Only aluminum results with values above 0.2 mg/L (BRASIL [24]), were used. Of the 170 active CETREL monitoring wells, were discarded: 39 wells with aluminum < 0.2 mg/L and 32 wells (without lithological description); leaving 99 wells selected for this study.

To investigate the pH distribution in groundwater of the CETREL region, descriptive statistics were performed using monitoring data from 100 tubular wells, obtained in the period 1992–2016, with a total of 2423 samples.

#### 2.4. Maps for the environmental factors

Using ArcGis 10.4.1. software, maps were prepared for the following data: water quality; precipitation, geology, hydrogeology, pedology, vegetation, areas of Industrial Landfill, E.E. Atlantica Basin; E.E. Capivara Basin; ETE; Organic Sludge Farm I; Organic Sludge Farm Bali, and Organic Trenches; in addition to the climate data for the State of Bahia [19].

#### 2.5. Average aluminum content in the confidence interval (±95%).

The average aluminum contents in the confidence interval ( $\pm 95\%$ ) were calculated, according to Connecticut [25]. Using the USEPA ProUCL 5.1 Software, the arithmetic mean ( $\pm 95\%$ ) was calculated, and the statistical distribution (normal, log-normal, gamma and non-parametric distribution) most suitable for the analysis was applied.

## 2.6. Assigning grades to environmental factors

A quali-quantitative method for assigning grades was developed to represent the influence of the variable upon the aluminum content. For a total of (334) samples, the grades were based on the average aluminum content ( $\pm 95\%$ ), for the groundwater samples with aluminum (>0.2 mg/L). As the number of variables for each environmental factor was in the range 2–7, was established a criterion of grades from 1 to 7, directly proportional to the average aluminum content ( $\pm 95\%$ ).

#### 2.7. Statistical data analysis

After defining the grades for the variables, statistical tests, parametric and nonparametric, evaluated the influence of environmental factors on high aluminum content.

The parametric test Pearson's linear correlation, is applied to quantitative data in which the conditions of Gaussianity, homoscedasticity and model independence are reasonably met. If the number of data is (>33), the Gaussian normal distribution becomes an adequate probabilistic model to fit the data statistically. In the unilateral test, the minimum absolute value for the Pearson correlation coefficient to be significant is (r = 0.165), for a number of samples ( $n \ge 100$ ) and 95% confidence level [26].

The non-parametric test Kruskal-Wallis [27] analyzes whether the results for aluminum content in groundwater belong to the same population, or, if they are similar. If the null hypothesis ( $H_0$ ) is rejected, then the aluminum content values are distinct, and the variable influences the result.

The non-parametric test Kruskal-Wallis post-hoc after Nemenyi is applied when  $(H_0)$  is rejected from the Kruskal-Wallis test, in order to identify which variables, among those that are part of the environmental attribute, presented similar correlations with the aluminum content, and those with distinct correlations.

# 3. Results and discussion

# 3.1. Environmental factors maps

# 3.1.1. Geology

**Figure 4** shows the geological map of the CETREL region indicating the presence of alluvial deposits from the Quaternary and the Marizal and São Sebastião formations.



**Figure 4.** Geological map of the municipality of Camaçari and the CETREL region. Source: Adapted from CPRM [28].

The Marizal Formation consists of sandstones and basal conglomerates, in addition to siltstones, shales and limestones [29]. Throughout the PIC region, this formation reaches depths of 30 to 50 m and is superimposed on the São Sebastião Formation [30].

The São Sebastião Formation consists of coarse, poorly classified and friable sandstones that may be intercalated with clays, which may present laminar layers of iron oxide (BAHIA [31]). The sandstones of the São Sebastião Formation are the most important aquifers in the State of Bahia, capable of supplying the demand for drinking water in the Reconcavo Baiano region [32], reaching depths up to 3000 m [30].

Quaternary Alluvial Deposits are sediments deposited in riverbeds; floodplains and associated lakes [33]. They can have very varied textural characteristics, in addition to a complex distribution of clay, silt and gravel.

#### 3.1.2. Hydrogeology



**Figure 5** shows the hydrogeology map of the CETREL region, which is associated with the domains of Detrital Covers and Sedimentary Basins.

Figure 5. Map of hydrogeological domains of the municipality of Camacari and the CETREL region. Source: Adapted from CPRM [34].

Detrital Covers are composed of sedimentary rocks (from the Tertiary and Quaternary periods) and are divided into deep and shallow covers [34]. The Shallow Covers are characterized by quaternary detrital deposits, constituted by sand from dunes and alluviums and by tertiary deposits from the Barreiras Formation. When they are thick, can store large volumes of water recharged directly by rainwater or indirectly by streams [7].

In the municipality of Camaçari, the Marizal and São Sebastião formations occur, which, in combination, generate an important large-scale aquifer system with excellent conditions for storage, recharge and production of groundwater [7].

## 3.1.3. Pedology

**Figure 6** shows the pedology map of the CETREL region and the municipality of Camaçari, with six soil types. The soil Hydromorphic Spodosols is predominant in the CETREL region.



Figure 6. Pedological map of the municipality of Camaçari and the CETREL region. Source: Adapted from CPRM [35].

The Hydromorphic Spodosols predominate in the CETREL region, due to the high soil moisture from the proximity of several water bodies. Spodosols are a sandy soil, constituted by quartzites, sandstones or quartz sediments, not exceeding 5% of clay contents, poor in nutrients and with high permeability [36]. In this soil, the processes of degradation of organic matter, mineralization and loss of nutrients are accelerated by the low adsorption capacity of the elements to the soil matrix, which increases the levels of chemical elements in the groundwater composition [37].

The CETREL area is inserted in the Geomorphological Unit Tabuleiro do Reconcavo, a board mostly dissected, consisting of sands and clays from the Marizal Formation [38]. Much of this area has geomorphological variations due to floristic degradation and extensive mineral extraction activity. In areas close to CETREL, the content of metallic contaminants (aluminum, arsenic, cadmium, calcium, lead, cobalt, copper, chromium, iron, magnesium, manganese, mercury, potassium, selenium, sodium, vanadium and zinc), from sediments belonging to the formations, Marizal and São Sebastião, and alluvial sediments, are well below the reference values of several legislation. Also, Pearson's Linear Correlation Matrix, showed that aluminum did not correlate with any other metal, indicating to be an element of different origin [38].

Due to the homogeneity of pedology data in the CETREL area (Figure 6), was taken as representative of the soil in the 99 wells location, the column of sediments above the static level, as recommended by Marques [39]. For very deep lithological profiles, the soil was described to a maximum depth of five (5.0) meters. For profiles with a variety of lithological compositions, the layer thickest and closest to the base

was the soil representative. For profiles with embankment layers up to five meters of depth, the designation was "landfill", being disregarded for correlation analysis of high aluminum contents.

Some pedology classifications were discarded, due to small number of cases such as: clay-silt-sandy (PM-024/273); silt (PM-024/275); silt-sand-clay (PMM-024/203); silt-clay (PM-024-282); and silt-sandy (PM-024/274). **Table A1** (Appendix) shows the soils considered in the lithological profiles.

#### 3.1.4. Vegetation

**Figure 7** shows the vegetation map of the municipality of Camaçari and the CETREL region. According to CPRM [40], the Cerrado vegetation predominates in the region.



Figure 7. Vegetation map of the municipality of Camaçari and the CETREL region. Source: Adapted from CPRM [40].

The municipality of Camaçari is located in the Atlantic Forest Biome. According to the Forest Inventory and Floristic Diagnosis [41] it is predominant the Dense Ombrophylous Forest vegetation, in addition to Campo Cerrado, Restinga and anthropogenic areas.

In most of the PIC's region predominates the tableland area, with a floristic association of Cerrado, with small shrubby vegetation and frequent herbaceous plants SICM [42]. The Cerrado vegetation mixes with species of greater size and density, increasing the region's floristic diversity. The occurrence of species from Atlantic Forest Biome, classify the area as a transition zone towards the seasonal-Ombrophylous Forest.

Due to the homogeneity of the Vegetation map in the CETREL area (**Figure 7**), the vegetation surrounding the wells, limited to a radius of 50 meters due to the high anthropization of the area, was taken as representative. This vegetation was classified into the following classes: Degraded area (original characteristics altered beyond the natural recovery limit). Exotic vegetation (non-native species). In the PIC's area, a Forest Ring was established in 1972, with exotic trees, mainly pine and eucalyptus. Herbaceous vegetation (plants with a soft or malleable stem, usually creeping, and/or plants whose stem does not undergo secondary growth throughout its development). Sub-shrubby vegetation (plants with woody stems that branch along the ground and are smaller than trees). Arboreal vegetation (woody-trunked trees) with branches well above ground level.

## 3.1.5. Precipitation

**Figure 8** shows the isohyet map of the municipality of Camaçari and the CETREL region, to represent the climate, as an environmental attribute. Precipitation data for the period 2007–2017 were used in the isohyet map using the ArcGIS 10.4.1 Inverse Distance Weighted (IDW) tool. Due to the small variation in precipitation values, the precipitation ranges are: 1379–1384 mm, 1384–1389 mm, and 1389–1394 mm.



Figure 8. Map of Isohyets of the municipality of Camaçari and the region of CETREL. Source: ROCHA [18].

# 3.2. Distribution of the pH in the groundwater of the CETREL region

**Table 1** presents the pH statistical data from 100 wells in the CETREL region (2423 groundwater samples), monitoring period 1992–2016. Also presents from the literature, information on pH ranges and its importance for the solubility of aluminum in groundwater.

Table 1. Descriptive Statistics for the pH Parameter in 100 tubular wells in the CETREL region, period 1992–2016.

pH ranges	Number of samples	Average pH	References	pH interval	Solubility or aluminum content (mg/L)
Monitoring Results		Bibliographic Information			
1.00-4.00	145	3.78	CETESD (201()	1.00-5.49	0.50–1.0
4.01-5.00	925	4.57	CETESB (2016)	1.00-5.49	0.50–1.0
5.01-5.49	471	5.23	Santos (2003)	2.85-5.77	2.91–3.96
5.50-6.00	343	5.72	CETESB (2016)	5.5-6.0	Low solubility
<6.0			Rosalino (2011)	<6.0	Soluble
Sum	1884 (77.8%)				
6.01-6.50	222	6.25			
6.51-7.50	173	6.83	CETESB (2016)	6.5–7.5	Low solubility; 0.001-0.05
7.51 - 8.00	18	7.7			
	413 (17.0%)				
8.01-10.00	38	9.12	CETESB (2016)	>8.00	Soluble; medium to strong alkalinity
10.01-12.0	88	11.05	Rosalino (2011)	>9.00	Soluble; alkali
Sum	126 (5.2%)	Weighted Average			
Total	2423	5.46			

Source: ROCHA [18].

Based on **Table 1**, the pH distribution in the groundwater of the CETREL region is: pH < 6.0 (77.8%) and pH > 8.0 (5.2%), totaling 83% of the samples in the favorable range for aluminum solubility. Also, the weighted average pH of (5.46) characterizes an acidic groundwater, favorable to the solubility of aluminum.

# **3.3.** Association between high aluminum content and environmental variables

**Table A2** (Appendix) presents a few examples for aluminum content in the groundwater of the CETREL region, for areas of the treatment processes. This resulted from the interpolation process using the softwares: EQUIS Professional 6.5 (to load information from the monitoring wells) and ArcGIS 10.4.1 (to load information from the thematic maps). The procedure was similar for all environmental variables.

#### 3.3.1. Statistical data analysis results

**Tables 2–4** present the results of the statistical tests between the average aluminum contents in the  $\pm 95\%$  confidence interval, and the various environmental factors. The **Table 2** presents the results for Pearson's Correlation, even though this is a parametric method, applied for a pair of continuous variables. This work had only one of the variables as continuous, the high aluminum content in groundwater.

	Aluminum	Areas	Precipitation	Geology	Hydrogeology	Pedology	Vegetation
Aluminum	1.000						
Areas	0.280	1.000					
Precipitation	0.178	0.555	1.000				
Geology	0.213	0.401	0.154	1.000			
Hydrogeology	0.080	0.448	0.113	0.781	1.000		
Pedology	0.176	0.135	0.087	-0.164	-0.213	1.000	
Vegetation	0.179	0.020	-0.030	0.168	0.133	-0.100	1.000

Table 2. Pearson's correlation matrix for aluminum content and environmental factors.

Source: ROCHA [18]. Note: Significance for (*p*-Value > 0.165)

Table 3. Kruskal-Wallis test results for aluminum content and environmental factor	ors.
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Parameter	<i>p</i> -Value							
	Areas	Precipitation	Geology	Hydrogeology	Pedology	Vegetation		
Aluminum	0.000937	0.05354	0.02851	0.05141	0.04222	0.01742		
Source: ROCHA [18] Note: Significance for $(p-Value < 0.05)$								

Source: ROCHA [18]. Note: Significance for (p-Value < 0.05).

Table 4. Results of the Kruskal-Wallis post-hoc after Nemenyi test for aluminum content in the treatment process areas.

	ЕТЕ	Bali organic sludge farm	Organic trenches	Industrial landfill	E.E. Atlantica basin
Bali Organic Sludge Farm	1.000	-	-	-	-
Organic Trenches	1.000	1.000	-	-	-
Industrial Landfill	1.000	1.000	1.000	-	-
E.E. Atlantica Basin	0.250	0.907	0.344	0.520	-
Organic Sludge Farm I	0.018	0.420	0.029	0.064	0.715

Source: ROCHA [18].

Using Pearson's Correlation, all environmental factors are significantly correlated with the high aluminum content in groundwater (first column), except for hydrogeology, with (p-Value = 0.08).

Tables 3 and 4 present the results for Kruskal-Wallis Test, a non-parametric method, applied for non-parametric variables, even though one of the variables were continuous, the high aluminum content in groundwater.

Using the Kruskal-Wallis test, the environmental factors (disposal areas, geology, pedology and vegetation) indicate an association with the aluminum content (p-value < 0.05), while the factors (precipitation and hydrogeology), with (p-Value > 0.05), indicate no association (thus, the Null hypotheses  $[H_0]$  is accepted). In fact, there is no significant variability in both factors in the CETREL area: the precipitation ( $\Delta = 15$ mm), and hydrogeology (predominate the sedimentary basins).

Applying the Kruskal-Wallis post-hoc after Nemenyi Test, to the variables "areas of treatment processes", because they presented high significance by the Kruskal-Wallis test (p-Value = 0.000937), the data indicate complete correlation between the variables (ETE, Bali Organic Sludge Farm, Organic Trenches and Industrial Landfill), or, they have a similar influence on the aluminum content. And, there is an intermediate correlation between the variables (E.E. Atlantica Basin and Organic Sludge Farm I), and (E.E. Atlantica Basin and Industrial Landfill).

# 3.3.2. Average aluminum content ( $\pm C_{95\%}$ ) versus grades for the environmental factors

**Table 5** shows the average aluminum contents ( $\pm C_{95\%}$ ) associated to the environmental factors; the assigned grades, and the choice of statistical distributions used by USEPA's ProUCL 5.1 Software, as the following: 1 = Non-parametric (95% Chebyshev); 2 = Gamma (95% Adjusted Gamma); 3 = Non-parametric (95% Hall's Bootstrap); 4 = Log-normal (95% H-UCL); 5 = Normal (95% t-Student).

**Table 5.** Environmental factors, average aluminum content ( $\pm C_{95\%}$ ), grades, and the statistical distributions.

Treatment process area	Aluminum C95% (mg/L)	Grade	Statistical distributions
Organic Sludge Farm I	22.92	7	1
E.E. Atlantica Basin	13.67	6	1
Industrial Landfill	11.42	5	1
E.E. Capivara Basin	6.137	4	2
Organic Trenches	4.672	3	1
Bali Organic Sludge Farm	3.343	2	3
ETE	3.273	1	1
Precipitation Ranges (mm)			
1.389–1.394	9.494	3	4
1.379–1.384	8.787	2	1
1.384–1.389	3.480	1	1
Geology			
Marizal Formation	22.15	3	1
São Sebastião Formation	11.86	2	1
Alluvial Deposits	5.019	1	1
Hydrogeology			
Sedimentary Basins	9.300	2	1
Detrital Coverage	5.645	1	1
Pedology			1
Clay	28.98	5	2
Clayey sand	6.328	4	1
Sandy-clay	5.771	3	1
Sand	5.509	2	1
Silt Sand	1.182	1	4
Vegetation			
Herbaceous subshrub	17.97	5	5
Arboreal	8.988	4	1
Exotic	8.725	3	1
Sub-shrub-tree	4.801	2	1
Degraded Area	4.316	1	1

Source: ROCHA [18].

For the significant environmental factors according to the Kruskal-Wallis test, the four (4) highest average aluminum contents ( $\pm C_{95\%}$ ) in groundwater of the CETREL region are summarized in **Table 6**, respectively: clayey soil, disposal area; geology; and vegetation.

**Table 6.** Environmental factors and average aluminum content ( $\pm C_{95\%}$ ).

Source: ROCHA [18].

Clayey soil ( $C_{95\%} = 28.98 \text{ mg/L}$ ), predominantly composed of aluminum silicates [43], exerts the greatest influence on the high aluminum content in groundwater. According to Oliveira [38], aluminum in the PIC's region was not correlated with another metallic contaminant. Therefore, aluminum certainly originates from the clayey soil, which is predominant in the CETREL region.

The Organic Sludge Farm I ( $C_{95\%} = 22.92 \text{ mg/L}$ ), where the land-farming process takes place, carries bio-solids that can undergo chemical and biological reactions, capable of changing the mobility of metals that are incorporated into the underlying soil structure [21].

The Marizal Formation ( $C_{95\%} = 22.15 \text{ mg/L}$ ) on which the CETREL area is located, produces predominantly sandy clayey soil, thus justifying the presence of a high aluminum content in groundwater.

The Herbaceous-Subshrub vegetation ( $C_{95\%} = 17.97 \text{ mg/L}$ ), is typical of Cerrado. According to Carvalho [13], it usually coincides with acid soils with base deficiency and high aluminum saturation in the deeper layers of the soil profile. Most of the PIC's area occurs in a tableland area, with a Cerrado type floristic association [42]. The combination of vegetation and soil justifies the influence of the high aluminum content in groundwater.

# 4. Conclusions

Multivariable statistical methods were able to correlate the high aluminum content in groundwater of the CETREL region with natural and anthropic environmental factors present in the area.

The attribution of quality grades, using the average aluminum content in the confidence interval ( $\pm 95\%$ ), to represent the influence of the variables of each environmental factor, upon the groundwater aluminum content, proved to be adequate.

The Kruskal-Wallis test revealed significant correlations between high aluminum content with the factors: treatment process areas, geology, pedology and vegetation. And no significance for the factors: precipitation and hydrogeology.

The most influential environmental factor on high aluminum content is clayey soil, followed by the Organic Sludge Farm I, then, the Marizal Formation and the typical Herbaceous-Subshrub vegetation of Cerrado region, for last. It is concluded that the high aluminum content in groundwater in the CETREL region, ultimately, results from the leaching of aluminum from the soil matrix to the groundwater, predominantly favorable to the solubility of this metal.

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# References

- Terrell D. Assessment of groundwater quality in a kaolin mining area: impacts and prospects for remediation, municipality of Mogi das Cruzes, SP (Portuguese). Available online: http://www.teses.usp.br/teses/disponiveis/44/44138/tde-25042008-160351/.../DT.pdf (accessed on 20 June 2024).
- 2. CETESB. Quality of Fresh Waters in the State of São Paulo, Appendix E Environmental and Health Significance of Quality Variables (Portuguese). Available online: https://cetesb.sp.gov.br/aguas-interiores (accessed on 20 June 2024).
- 3. Rosalino MRR. Potential effects of the presence of aluminum in drinking water (Portuguese) [Master's thesis]. Universidade Nova de Lisboa; 2011.
- 4. Hama P. Study of the Influence of Acid Rain on Aluminum Concentration in Soils Near a Coal Power Plant (Portuguese) [Master's thesis]. The University of the South Pacific; 2001.
- Silva KWS. Aluminum concentrations and pH in water available for consumption in the community of Segredinho, Pará, Brazil (Portuguese). Available online: http://www.abq.org.br/cbq/2019/trabalhos/5/1637-24521 (accessed on 20 June 2024).
- 6. Guerra AM, Negrão FI. Hydrogeological Domains of the State of Bahia (Portuguese). In: Anais do IX Congresso Brasileiro de Águas Subterrâneas. ABAS; 1996.
- 7. Negrão FI. Hydrogeology of the State of Bahia: quality, potential, availability, vulnerability and degree of pollution (Portuguese) [PhD thesis]. Universitário de Xeoloxía, Universidade da Coruña; 2007.
- 8. Scopel RM, Teixeira EC, Binotto RB. Hydrochemical characterization of groundwater in the area of influence of future hydroelectric plant installations (Portuguese). Bacia hidrográfica do Rio Taquariantas/RS. Brasil. Revista Química. São Paulo: Nova. 2005; 28(3): 383–392.
- 9. Luchese EB, Favero LOB, Lenzi E. Fundamentals of Soil Chemistry (Portuguese), 2nd ed. Rio de Janeiro; 2002. p. 155.
- 10. Cajazeiras CC. A. Quality and Use of Groundwater and the Relationship with Waterborne Diseases, Crajubar Region/CE (Portuguese). Programa de Pesquisa e Pós-Graduação em Geologia [Master's thesis]. Universidade Federal do Ceará; 2007.
- Moreira-Nordemann LM. Geochemistry and the Environment. Space Research Institute-INPE (Portuguese). Laboratório de Geoquímica Ambiental. São José dos Campos; 1987. pp. 89–107.
- Branco PMO. Weathering and erosion (Portuguese). Available online: http://www.cprm.gov.br/publique/Redes-Institucionais/Rede-de-Bibliotecas---Rede-Ametista/Canal-Escola/O-Intemperismo-e-a-Erosao-1313.html (accessed on 2 June 2024).
- 13. Carvalho AR. Soil attributes associated with variations in vegetation in a cerrado fragment, Assis, SP (Portuguese) [Master's thesis]. Universidade de São Paulo; 2008.
- 14. Rizzi NE. The forest's role in maintaining water quality for human use (Portuguese). Revista Floresta. 1985; 15(12): 54-65.
- Andrade JBM. Factors influencing the salinization potential and processes of fractured aquifers in the upper Vaza-Barris river basin, Uauá region, Bahia, Brazil (Portuguese) [Marster's thesis]. Instituto de Geociências, UFBA, Salvador; 2010. p. 137.
- Follmann FM, Foleto EM. Importance of Vegetated Areas in the Natural Conservation Area of the Santa Maria Basal Sandstone Aquifer, Santa Maria, RS (Portuguese). Boletim Goiano de Geografia. 2013; 33(1). doi: 10.5216/bgg.v33i1.23630
- 17. Costa WD. Hydrogeology of fissured media (Portuguese). In: Hidrogeologia: conceitos e aplicações. 3rd ed. Rio de Janeiro: CPRM, LABHID, UFPE; 2008. pp. 121-151.

- 18. Rocha RPR. Study of the correlation of aluminum and iron levels in groundwater with environmental factors in the CETREL region (Portuguese). UFBA; 2017.
- 19. Alvares CA, Stape JL, Sentelhas PC, et al. Köppen's climate classification map for Brazil. Meteorologische Zeitschrift. 2013; 22(6): 711–728. doi: 10.1127/0941-2948/2013/0507
- 20. Tomasoni E, Araújo JS, Jerônimo CEM. Bioremediation process of hydrocarbon-contaminated soils by the Landfarming technique using sanitary sewage (Portuguese). Available online: https://tratamentodeagua.com.br/artigo/biorremediacao-solos-contaminados-landfarming/ (accessed on 20 June 2024).
- Miyazawa M, Gimenez SMN, Fernandez F, et al. Effect of sewage sludge on heavy metal levels in soil and plants (Portuguese). In: Andreoli CV, Lara AI, Fernandes F (editors). Reciclagem de Biossólidos: Transformando problemas em soluções. Curitiba, Companhia de Saneamento do Paraná; 1999. pp.204–225.
- 22. Silva NRS. Techniques for Recovering Degraded Areas, with a Focus on the Use of Organic Fertilizers (Portuguese) [Bachelor's thesis]. UFBA; 1999.
- 23. CETREL. Water Resources Quality Monitoring Program. Water Resources Management Plan for the Camaçari Industrial Estate (Portuguese). Camaçari. Bahia; 2016.
- BRASIL. Consolidation Ordinance GM/MS No. 888, of 04/05/2021, amends Annex XX Control and surveillance of the quality of water for human consumption and its standard of potability, of Ordinance GM/MS, No. 5, of 09/28/2017 (Portuguese). Ministério da Saúde. Diário Oficial da União, Brasília, DF; 2021.
- 25. Connecticut. Guidance for Calculating the 95% Upper Confidence Level for Demonstrating Compliance with the Remediation Standard Regulations. Connecticut. USA; 2014.
- 26. Barbetta PA. Statistics Applied to the Social Sciences (Portuguese), 5th ed. Editora da UFSC; 2005. p. 340.
- 27. Pohlert T. The Pairwise Multiple Comparison of Mean Ranks Package (PMCMR). Available online: https://cran.rproject.org/web/packages/PMCMR/vignettes/PMCMR.pdf (accessed on 20 June 2024).
- 28. CPRM. Geodiversity map of Bahia (Portuguese). Serviço Geológico do Brasil; 2010.
- 29. Fonseca PP. Geological Mapping and Geoenvironmental Zoning of the Camaçari Industrial Estate Region using Digital Orthophotos (Portuguese). ABAS. 2004: 77.
- 30. Santos PRP. Study of the vulnerability to pollution of the Marizal aquifer in the region of influence of the Camaçari Industrial Complex (PIC)—BA (Portuguese) [Master's thesis]. Universidade Federal da Bahia; 2010.
- 31. Bahia. Secretaria da Indústria, Comércio e Mineração do Estado da Bahia—SICM. Plano Diretor: Polo Industrial de Camaçari, Camaçari, Bahia; 2013. p. 134.
- 32. Mariano AH. Hydrogeological and Petrophysical Analysis of the São Sebastião Aquifer in the Miranga Field, Recôncavo-BA Basin (Portuguese). ABAS; 2002. p. 104.
- 33. Suguio K. Quaternary geology and environmental change (Portuguese). Oficina de Textos; 2012.
- 34. CPRM. Map of Bahia's Hydrogeological Domains (Portuguese). Serviço Geológico do Brasil; 2010
- 35. CPRM. Soil map of Bahia (Portuguses). Serviço Geológico do Brasil; 2010.
- Araújo MSB, Schaefer CE, Sampaio EVSB. The formation process of spodosols and the associated transport of phosphorus (Portuguese). Revista de Geografia. Recife. Pernambuco. 2006; 23(3).
- 37. Neu V. Influence of vegetation cover on nutrient cycling via soil solution in the Manaus-AM region. Dissertation (Portuguese) [Master's thesis]. University of São Paulo; 2005.
- 38. Oliveira AC. Study of the concentration of metals in soils of the Marizal, São Sebastião and Alluvial Cover formations, in a pilot area around the Camaçari Industrial Estate, Ba. Geology Degree Monograph (Portuguese). UFBA; 2014. p. 79.
- Marques JHS. Study of the Vulnerability of Aquifers in the Municipality of Salvador, Bahia-Brazil, with a View to Preventing Pollution and Assessing Non-Potable Water Potential (Portuguese) [Master's thesis]. MEPLIM, UFBA; 2012.
- 40. CPRM. Vegetation Map of Bahia (Portuguese). Serviço Geológico do Brasil; 2010.
- 41. Bahia. Forest Inventory and Floristic Diagnosis for the Duplication of BA-530 (Via Atlântica) (Portuguese). Secretaria de Infraestrutura. Departamento de Infraestrutura de Transportes da Bahia—DERBA; 2014. p. 97.
- 42. SICM. Secretariat of Industry, Commerce and Mining of the State of Bahia (Portuguese). Plano Diretor Polo Industrial de Camaçari. 2013; 134.
- EMBRAPA. Brazilian Agricultural Research Corporation (Portuguese). Sistema Brasileiro de Classificação de Solos; 2013. p. 353.

# Appendix

Poços	N.A.	Composição	Poços	N.A.	Composição		
Profundidade até 1.0 m							
PM-024/012	1.13	A	PM-024/016	1.7	Argila-arenosa		
PM-024/013	1.31	Areia-argiiosa					
Profundidade até 2.0 m							
PM-024/014	2.21	A	PM-024/024	2.82	Areia-argilosa		
PM-024/015	2.1	Argna-arenosa	PM-024/314	2.39	Argila-arenosa		
PM-024/017	2.1	Argila	PM-024/315	2.5	Argila		
Profundidade até 3.0 m							
PM-024/018	3.47	Argila-arenosa	PM-024/019	3.78	Argila		
Profundidade até 5	5.0 m						
PM-024/100	8.36	Areia-argilosa	PM-024/318	11.55	Areia-argilosa		
PM-024/101	8.62	Areia	PM-024/320	4.07	Areia		
PM-024/104	10.35	Argila	PM-024/222	9.93	Areia-siltosa		
PM-024/224	7.27	Aterro	PM-024/223	7.72	Areia-argilosa		
PM-024/225	6.88	Aterro	PM-024/516	14.4	Argila-arenosa		

Table A1. Exemplo de Composição Pedológica de Poços Tubulares da área da CETREL.

Table A2. Exemplo de Resultados Analíticos para o Alumínio por Área de Processo de Tratamento.

Identificação da Amostra: Poço-Data Amostragem	Teor de Alumínio (mg/L)	Identificação da Amostra: Poço-Data Amostragem	Teor de Alumínio (mg/L)
Bacia da E.E. Atlântica			
PM-024/014-AS20120417	45.6	PM-024/013-AS20120417	11.8
PM-024/024-AS2015T1020	22.0	PM-024/019-AS2016T2279	11.31
PM-024/012-AS20120417	18.9	PM-024/019-AS20120417	10.4
PM-024/017-AS20120417	15.6	PM-024/013-AS2015T2253	8.1
PM-024/013-AS2016T2273	12.97	PM-024/014-AS2013T1010	0.22
Aterros Industriais			
PM-024/104-AS2016T2286	18	PM-024/101-AS2016T1033	0.31
PM-024/104-AS2015T2267	11	PM-024/101-AS2015T1027	0.24
Valos Orgânicos			
PM-024/207-AS2014T1083	2.9	PM-024/206-AS20110923	0.58
PM-024/206-AS20120831	1.0	PM-024/206-AS2015T1082	0.44
PM-024/221-AS2014T2307	0.62	PM-024/206-AS2016T2345	0.252