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**CHEMICAL SCIENCES**

# Characterization, fractionation and mobility of trace elements in surface sediments of the Jequiezinho River, Bahia, Brazil

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**Abstract:** The Jequiezinho River is a temporary river. In the urban stretch it is impacted, with perennial flow coming from domestic sewage and rainwater. This study evaluated the geochemical distribution and potential mobility of some metals (Pb, Co, Ca, Cr, Mg, Cu, Fe, Mn, Ni and Zn) in sediments of the Jequiezinho River. Sediment samples were collected at ten different sites along the river. The silt/clay fraction was submitted to acid digestion and sequential extraction with analysis by FAAS. The results indicated that, in the more densely populated region, there was an increase in concentrations of Cr, Ni, Cu, Co, Pb, and Zn. The contents found were compared with the guideline values of TEL (Threshold Effect Levels) and PEL (Probable Effect Levels), not exceeding the maximum reference limits. The results indicated that Ca, Mg, Mn and Fe presented greater susceptibility to mobility and bioavailability suggesting the geochemical origin responsible for these high concentrations. The multivariate analysis showed that Cr, Ni, Cu, Co, Pb, and Zn presented a similar behavior, especially in locations with higher population density and the discharge of non-discriminated effluents, reflecting the anthropogenic contributions as responsible for the concentration increase.

**Key words:** Jequiezinho River, sediments, metals, sequential extraction.

## INTRODUCTION

Sediments are the layers of finely granulated mineral and organic particles that are in contact with the lower parts of natural water bodies, such as lakes, rivers and oceans (Baird & Cann 2011). Sediments can accumulate large amounts of chemical compounds such as metals, pesticides, polycyclic aromatic hydrocarbons (PAHs) and can consequently be transferred to the living organisms in contact with them. Due to this fact, sediments have been widely used to monitor and track possible sources of environmental contamination, functioning as efficient environmental indicators (Soares et al. 1999, Duodu et al. 2016, Unda-Calvo et al. 2019).

Some elements occur naturally in the soil at concentrations that vary according to their genesis, being classified as micro and macro elements (Resende et al. 1995), which are recognized as essential for life in concentrations adequate for the functioning of biological systems such as Fe, Mg, Ca, Mn and K. However, the increased availability of these elements in the environment, where the concentrations exceed the tolerable limit, lead to serious environmental problems (Silva 2006, Vareda et al. 2019).

Besides being considered water pollutants and food contaminants when in high concentrations, metals can also be transported by air, either as gases or as adsorbed species on suspended particulate matter (Baird & Cann 2011, Zhang et al. 2016). Although most pollutants adsorbed to the sediments are not readily available to aquatic organisms, the variation of some physical and chemical characteristics of water (pH, salinity, redox potential and the content of organic chelates) may lead to the release of metals into the aqueous phase, thus becoming an important pollution source (Soares et al. 1999).

In the sediment, depending on its chemical form, trace elements can exist in various forms. When these compartments do not undergo anthropic action, they are mainly linked to silicates and primary minerals and, therefore, to a low degree of mobility (Pereira et al. 2007). On the other hand, those chemical elements incorporated from anthropic activities are more mobile, associated to the organic matter present in the fine fraction of sediments or adsorbed in hydrated Fe/Mn oxides, or are bound to other phases of the sediment, such as carbonates, oxides, hydroxides and sulfides (Pereira et al. 2007, Kersten & Förstner 1989).

Sediment samples can be an important tool for assessing the pollution level of a water body (Förstner 2004, Turner & Taylor 2018). The determination of trace metals in sediments allows evaluating the level of contamination to which the water is subjected, as well as the present organisms. However, the total concentration does not provide enough data to evaluate contamination, since the present elements, depending on the chemical form, can affect bioavailability, toxicity, chemical interactions and mobility in the environment (Barreto et al. 2004, Morillo et al. 2008, Relic et al. 2010, Alan & Kara 2019). The study of exchangeable fractions (sequential extraction) can be used for a greater precision on the amount of metals present in the environment that could be mobilized by the chemical changes of the sediment (Adami et al. 1999, Hang et al. 2009, Rosado et al. 2016).

Sequential extraction consists of a variety of techniques widely used for the fractionation of metals in soils, sediments and other environmental matrices. It intends to assess the potential for mobility and availability of these metals in the environment (Gleyzes et al. 2002). The most widely used methods are those based on the multi-step extraction procedure, in which different reagents are consecutively used to extract metals from the fractions operationally defined (Pereira et al. 2007).

The Jequiezinho River is a temporary river that shows water runoff only in the rainy season and complete drought in the absence of rainfall. In the stretch that crosses the urban area of Jequié, it is quite impacted, with a perennial flow coming from the supply of domestic sewage. Studies conducted in the Contas River basin at points sampled near the Jequiezinho River indicate that there is a compromise of water quality in relation to the chemical parameters, very different from the other points along the basin (Dos Santos et al. 2009). This research aimed to evaluate the geochemical distribution and mobility of some metals (Cu, Pb, Co, Ni, Mg, Mn, Fe, Zn, Cr, Ca) and their pollution potential in sediments of the Jequiezinho River through a sequential extraction procedure.

## MATERIALS AND METHODS

### Study area

The Jequiezinho River is 58,300 m long and, together with the Pati River and Riacho Conceição, form the Jequiezinho River sub-basin (Figure 1). It is born in the municipality of Maracás (Bahia/Brazil) at an altitude of approximately 800m, passes through the rural region of Lafaiete Coutinho (Bahia/Brazil) and flows into the Contas River in the municipality of

Jequié (southwestern Bahia/Brazil) (Magalhães et al. 2016).

The urban area of Jequié is densely populated. In its limits, a landfill, roads and a fuel distribution pipeline can be found, generating a large amount of domestic sewage and other non-discriminated pollutants. The predominant climate in this area is typical of semiarid regions, dry most of the time, with periods of rainfall (December to March). The predominant vegetation is the Caatinga (a semiarid vegetation) which, together with the climate and the geomorphology of the region, makes it difficult to store water, giving the river a temporary character, with rainfall and extreme drought during the dry season (Magalhães et al. 2016).

The collection points were chosen strategically, according to the absence or presence of potential pollution sources, such as agricultural properties, landfills, fuel distributors, and domestic sewage. Points from rural zone, considered as non-impacted, were also collected, aiming to make comparisons. The collection sites were georeferenced using a GPS (Global Positioning System) (Table I).

## Sample collection

Samples were collected in two campaigns, the first in March/2018 (late rainy season) and the second in September/2018 (dry season). Ten samples were collected in each period at different points along the Jequiezinho River, comprising rural and urban areas.

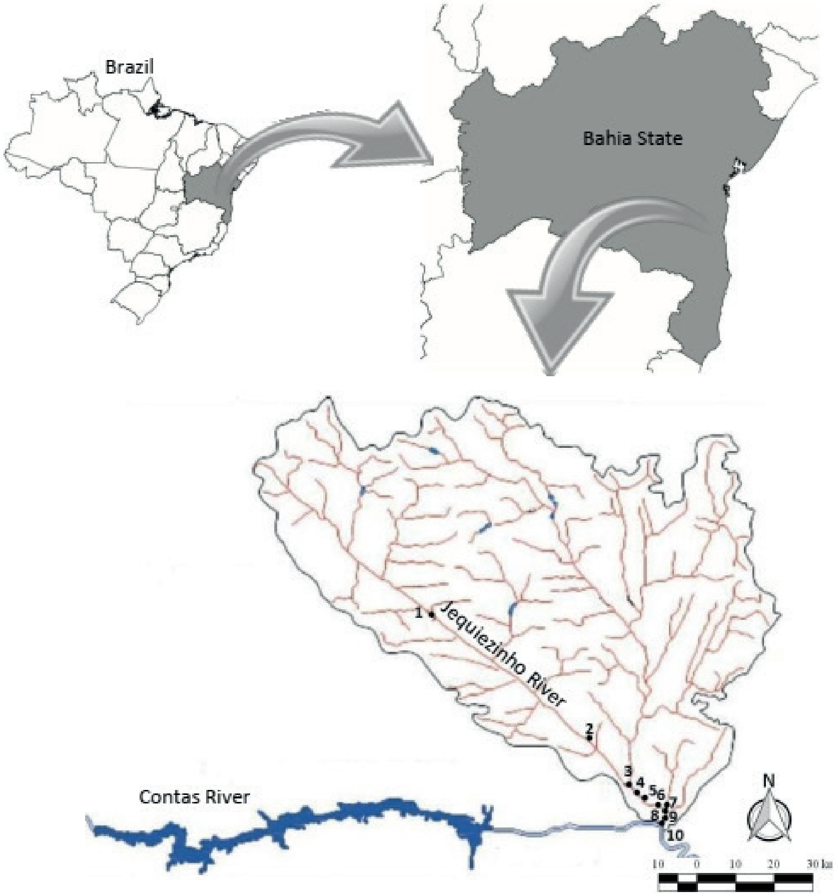

**Figure 1.** Sub-basin of the Jequiezinho River. Adapted from Magalhães et al. 2016.

Sampling was performed by removing approximately 2.0 kg of sediment from the superficial layer of the sediment (0-5 cm deep), discarding leaves and other surface materials at a distance of approximately 2.0 meters from the edge, using a polyethylene spatula; the material was then packed in sterile plastic bags, sealed and stored in a refrigerator at 5 °C until laboratory processing.

Seasonal variation is one of the main factors responsible for the dynamics of chemical species in aquatic environments, where irregular rainfall distribution may influence their mobility. Rainfall analysis for the region allowed characterizing two periods: rainy (Nov/2017 to Feb/2018) and dry season (April to October 2018) (Figure 2), and this criterion was used to schedule the collection of sediment samples.

During the whole study period, the water volume showed a strong climatic irregularity, with a deficit occurring in all the months of 2018. The collection made in March 2018 occurred in places with some volume of water, except in P2. On the other hand, in the second collection, the sampling points P1 to P4 had dried and the other points contained a small water flow, coming only from the discharge of sewage.

### Cleaning/material decontamination

All glassware, spatulas and polyethylene bottles were washed with neutral detergent and rinsed in running water until the product was completely removed. They were then immersed in 10% $HNO_3$ solution (v/v) for 24 hours and rinsed with deionized water for 3 (three) times, oven dried at 60 °C (glassware) or at room temperature

**Table I. Location/characterization of collection points of sediments.**

| Point | Description | Area type | Coordinates | Altitude (m) |
|---|---|---|---|---|
| P1 | Farm in Lafaiete Coutinho | Rural | S13.66675°<br>W040.29587° | 473 |
| P2 | Farm in Jequié | Rural | S13.81686°<br>W040.11827° | 215 |
| P3 | Next to a landifill | Rural | S13.82511°<br>W040.11406° | 210 |
| P4 | Residences, corrals, rainwater drainage | Urban | S13.82904°<br>W040.10888° | 208 |
| P5 | Bridge on the BR 116 highway | Urban | S13.83294°<br>W040.10407° | 206 |
| P6 | Bridge on a side road | Urban | S13.83688°<br>W040.09901° | 204 |
| P7 | Next to a fuel pipeline distributor | Urban | S13.84860°<br>W040.07506° | 182 |
| P8 | Residences, rainwater drainage | Urban | S13.86121°<br>W040.07612° | 180 |
| P9 | Residences, rainwater drainage | Urban | S13.86414°<br>W040.07737° | 180 |
| P10 | Confluence Jequiezinho River and Contas River | Urban | S13.866089°<br>W40.078423° | 178 |

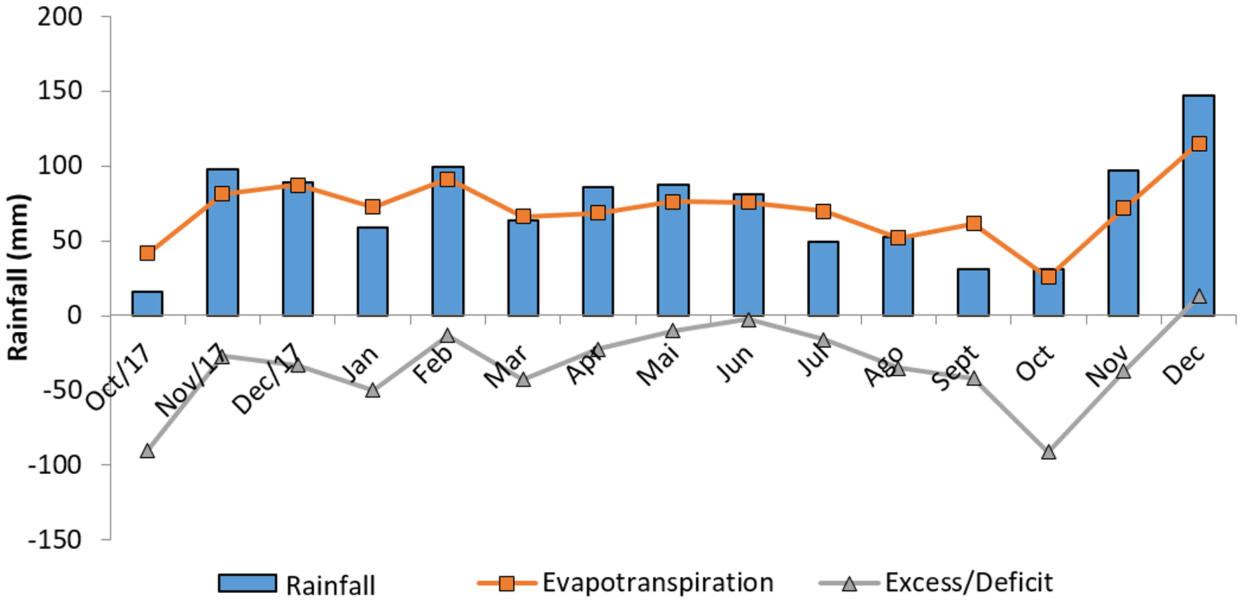

**Figure 2. Water balance from January to December 2018, in the municipality of Jequié. Source: CPTEC INPE: http://www.cptec.inpe.Br/proclima2/balanço_hidrico/balancohidrico. shtml. Accessed on 05/05/19.**

(other materials) and packed in boxes in order to preserve the decontaminated material.

### Sample treatment

The sediment samples were oven dried at 60°C for 24 hours. Subsequently, each sample was triturated with mortar and pistil, sieved in 250-µm mesh, transferred to decontaminated plastic bottles and sealed.

Pseudo-total digestion was based on the study of McGrath et al. (1985), using a mixture of 5.0 mL aqua regia (HCl p.a. + $HNO_3$ p.a. 3:1 v/v) for a mass of 0.5 g of sediment sample. Initially, the digestion occurred at room temperature for 16 hours and then heated in a digestion block at a temperature of (90 ± 5) °C with the tubes partially capped until the $NO_2$ release ceased. After this step, the samples were cooled, filtered and transferred to polyethylene bottles, set to 10 mL with deionized water, kept under refrigeration at 4 °C until metal determination. The accuracy of this decomposition method was evaluated by analysis of a certified reference material (NIST 1646a - Estuarine sediments).

The methodology used for fractionation by chemical extraction was based on Tessier et al. (1979), and consists of four fractionation stages. For each step, an aliquot with 1.0 g of dry sediment was added to a glass vessel along with the respective reagents, according to the protocol defined for each fraction (Table II). Finally, the suspension was filtered, set to 25 mL with deionized water, transferred to a polypropylene tube, and stored at 4 °C until metal determination.

All samples used in both pseudo-total and fractional extraction were analyzed in triplicate. The blank of the digestion procedure, containing all reagents except the sample, was prepared and treated under the same procedure described for the sediment samples.

### Instrumentation

For the pseudo-total digestion procedure of the sediment samples, glass tubes with reflux system (cold finger) heated in a microprocessed digital digestion block (TECNAL, TE-007MP) were used. In sequential extraction, 250-mL Erlenmeyer

**Table II. Procedures** following each step of sequential extraction.

| Fraction | Reagents | Final volume (mL) | Experimental conditions |
|---|---|---|---|
| Soluble | Deionized water | 25 | 1 h, room temperature, continuous stirring |
| Ion-changed | Ammonium acetate | 25 | 1 h, room temperature, continuous stirring |
| Carbonate bounded | Acetate buffer | 25 | 5 h, room temperature, continuous stirring |
| Organic matter bounded | $H_2O_2$ 30%/$HNO_3$ | 25 | 5 h, 85 °C ±2, periodic stirring |

were used in a horizontal shaker with a capacity of 16 flasks (Ethik Technology).

The analysis of Fe, Zn, Mn, Ca, Mg, Pb, Co, Cu, Ni and Cr was performed on a flame atomic absorption spectrometer (AAnalyst 200, Perkin-Elmer) fed with an air/acetylene mixture. Hollow cathode lamps of the respective metals were used as a radiation source. The wavelengths used were those recommended by the manufacture for Ca (422.7 nm), Cu (324.8 nm), Fe (248.3 nm), Mn (279.5 nm), Ni (232.0 nm), Zn (213, 9 nm), Pb (283.3 nm), Co (240.7 nm) Cr (357.9 nm) and Mg (285.2 nm) determination. The other operating conditions of the equipment were acetylene flow rate (2.0 L $min^{-1}$), air flow rate (13.5 L $min^{-1}$) and solution aspiration flow rate (5.0 mL $min^{-1}$).

### Statistical analysis

Principal component analysis (PCA) was used to evidence possible similarities among the samples and variables and to estimate the potential sources of contamination. Pearson's correlation analysis was used to determine the relationship between the metals studied. Hierarchical cluster analysis (HCA) was performed in a complementary manner to PCA to confirm the results and provide grouping of variables. The grouping method used was the Ward's Method, due to its capacity to produce a well-defined dendrogram.

## RESULTS AND DISCUSSION

### Total contents and metal fractionation

Sample digestion using aqua regia is strong enough to provide most of the elements to the solution, but it does not constitute a total digestion and therefore represents the "pseudo-total" concentration of these elements. This type of digestion provides, in addition to more labile metals, those of lower mobility that are associated with the crystalline oxides of iron and manganese, organic matter, sulfides and some more altered silicates (Ryan et al. 2002). Although not all the elements that comprise the sediment are available for analysis, the results obtained are sufficient to quantify the metals in the sediment, and this method is widely used in studies on chemical composition in environmental matrices.

### Quantification and evaluation of the behavior of metals in the Jequiezinho River

The elements Fe, Mg and Ca are present in the sediments at the highest concentrations (on average: 19479.24, 1590.35 and 1377.77 mg/kg, respectively), while the other elements had lower values, especially Co, which presented the lowest average (11.41 mg/Kg) in relation to the samples collected in the first campaign (Table III). In the samples collected in the second campaign, the elements presented a behavior similar to that of the previous campaign, between average concentrations in all the points sampled. The only exception was Mg, whose values were lower than those of Ca.

### Sediment quality guidelines

The reference values for the evaluation of the quality of the sediments come from data in the literature. The suggested limits are derived

**Table III. Descriptive statistics of metal concentrations by pseudo-total digestion in sediment samples from the Jequiezinho River.**

| | Average (mg/Kg) | Lowest value (mg/Kg) | Highest value (mg/Kg) | SD* |
|---|---|---|---|---|
| **End of the rainy season** | | | | |
| **Pb** | 25.21 | 17.69 (P3) | 38.99 (P8) | 6.60 |
| **Cu** | 16.68 | 5.491 (P4) | 40.92 (P8) | 12.2 |
| **Co** | 11.41 | 6.832 (P3) | 19.67 (P5) | 3.86 |
| **Cr** | 31.90 | 16.58 (P3) | 50.90 (P5) | 11.8 |
| **Ni** | 20.10 | 10.62 (P1) | 31.10 (P8) | 8.11 |
| **Mg** | 1590 | 84.43 (P1) | 3500.02(P8) | 1022 |
| **Mn** | 291.6 | 62.11 (P5) | 1033.14 (P3) | 279 |
| **Ca** | 1378 | 49.66 (P4) | 8631.70 (P8) | 2755 |
| **Zn** | 48.98 | 15.52 (P8) | 132.11 (P5) | 32.64 |
| **Fe** | $1.948 \times 10^4$ | $1.178 \times 10^4$ (P9) | 27862.82 (P5) | 4611 |
| **Dry season** | | | | |
| **Pb** | 22.20 | 12.77 (P10) | 36.73 (P4) | 7.30 |
| **Cu** | 15.88 | 4.092 (P5) | 45.10 (P4) | 12.3 |
| **Co** | 8.931 | 3.903 (P5) | 16.59 (P4) | 4.17 |
| **Cr** | 28.67 | 14.86 (P10) | 51.02 (P7) | 12.4 |
| **Ni** | 19.33 | 9.54 (P1) | 35.28 (P7) | 7.84 |
| **Mg** | 1607 | 326.2 (P1) | 2993 (P3) | 945 |
| **Mn** | 215.1 | 109.3 (P4) | 346.8 (P6) | 78.4 |
| **Ca** | 2466 | 99.39 (P1) | 7780 (P9) | 2940 |
| **Zn** | 55.66 | 23.96 (P5) | 99.38 (P4) | 22.7 |
| **Fe** | $1.544 \times 10^4$ | 8334 (P10) | $2.413 \times 10^4$ (P7) | 5336 |

***Standard deviation.**

from the contamination database and define the ranges between which relationships are established to various biological effects. In Brazil, the legal instrument that regulates sediment quality is CONAMA (Conselho Nacional do Meio Ambiente), Resolution 454/2012, which regulates the dredging and disposal of dredged sediments. The guiding values adopted in this document refer to official Canadian, North American and European publications.

In this study, the metal concentrations of the Jequiezinho River sediments were compared to the values of TEL (Threshold Effect Levels), that is, limit levels of effect on organisms and PEL (Probable Effect Levels) of probable adverse effects on organisms, established by the National Oceanic Atmospheric Administration (NOAA) (Table IV).

Results of the pseudo-total digestion are shown in Figure 3. It is noted that Cr contents were quite uniform at the points sampled for the two campaigns, with P4, P5, P7 and P8 showing values higher than the reference level (37.3 mg / kg) established by CONAMA. Nickel concentrations were also higher than the reference value (35.9 mg/Kg), except for P1 and P3. The points located in the urban area, especially P7, presented values close to the maximum predicted by the environmental legislation (35.9 mg/Kg).

Copper also had concentrations above level 1 at P4, P5 and P8 (37.7 mg/Kg), with a small seasonal variation. Lead did not exceed the limits in P1 to P3, P6 and P9, suggesting a low probability of adverse effects to the biological community. However, at P4, P5 and P8, the concentrations exceeded reference level 1 (35.0 mg/Kg). This increase found in the urban area of Jequié can be attributed to greater population density and the discharge of sewage directly into the river. Zn did not show high concentrations at most of the sample points, except for P5 which, at the first sampling (end of the rainy season), showed a significant concentration above reference level 1 (123 mg/Kg).

For Co, Fe, Ca, Mn and Mg, there are no boundary values in the Brazilian legislation for sediments. However, the presence of these metals in the environment can not always be attributed to anthropogenic action. These elements can also be made available through natural rock decomposition processes, which constitute the geology of the region, so the increase in the concentrations can be due to the transport of soil particles.

The results obtained for the samples in the two campaigns indicate that the elements Fe, Ca, Mg and Mn presented the highest concentrations for the pseudo-digestion of all sampling points, with Fe was the one with the highest concentrations. According to Ure et al. (1993), these elements tend to be present in large quantities in the soil, since they participate in the formation of the Earth's crust and can be seen as essentially lithogenic metals. However, although the others present relatively smaller values, they may be related to potential anthropogenic environments (Fernandes 1997).

A similar behavior for these elements was found by Correia (2014) in Contas sediments, where it was observed that Fe also presented

**Table IV. Reference values in dry matter (mg/Kg), classification levels according to CONAMA 454/2012 and sediment quality guide values expressed as TEL (level 1) and PEL (level 2).**

| Reference values | Cu | Co | Cr | Pb | Zn | Ni | Fe | Ca | Mn | Mg |
|---|---|---|---|---|---|---|---|---|---|---|
| Level 1 (mg/kg) | 35.7 | – | 37.3 | 35 | 123 | 18 | – | – | – | – |
| Level 2 (mg/kg) | 197 | – | 90 | 91.3 | 315 | 35.9 | – | – | – | – |

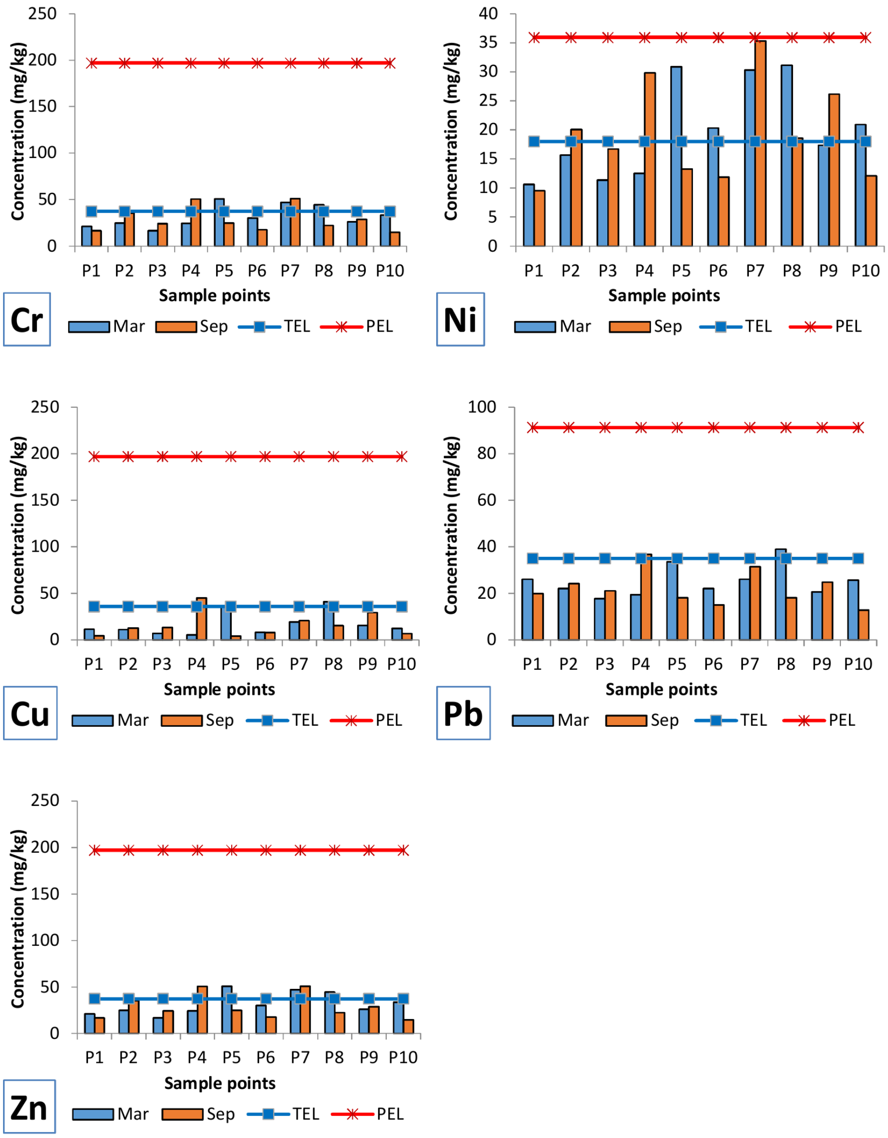

**Figure 3.** **Comparison of Cr, Ni, Cu, Pb and Zn concentrations in sediments of the Jequiezinho River with Canadian guideline values (TEL/PEL).**

high values. A study by Santos et al. (2007) concluded that the high concentrations of calcium found in the Pedras Dam, located in the Contas River, is due to the local geochemical composition. According to Fornari & Barbosa (1994), this region is located on a granulitic block called Jequié Complex, in which iron formations and quartzites predominate, justifying the presence of these metals in the environmental samples.

The correlation matrix formed by the metal concentrations in the sediment samples in the rainy season (Table V) indicates a significant correlation of Cr with Ni, Cu, Co and Pb, Ni with Cu, Cu with Pb and Mg with Ca. For the samples collected in the dry season (Table V), the high correlations between Cr and Ni, Co, Pb, Cu and Zn, and Co with Pb and Fe are highlighted.

Principal component analysis (PCA) in the samples collected for the two periods revealed two main components that, together, account for 79.23% of the total data variance (Figure 4).

PC1 contributed with 58.06% of the total variance of the metal levels between the

**Table V.** **Correlation matrix of the pseudo-total metal concentrations in sediments of the Jequiezinho River in (a) March 2018 and (b) September 2018 (in bold, significant correlation *p* <0.05).**

| | **Cr** | **Ni** | **Cu** | **Co** | **Pb** | **Mn** | **Mg** | **Fe** | **Ca** | **Zn** |
|---|---|---|---|---|---|---|---|---|---|---|
| **End of the rainy season** | | | | | | | | | | |
| **Cr** | 1.00 | | | | | | | | | |
| **Ni** | 0.98 | 1.00 | | | | | | | | |
| **Cu** | 0.81 | 0.83 | 1.00 | | | | | | | |
| **Co** | 0.80 | 0.72 | 0.74 | 1.00 | | | | | | |
| **Pb** | 0.78 | 0.78 | 0.94 | 0.78 | 1.00 | | | | | |
| **Mn** | -0.63 | -0.58 | -0.44 | -0.46 | -0.49 | 1.00 | | | | |
| **Mg** | 0.60 | 0.73 | 0.70 | 0.18 | 0.60 | -0.44 | 1.00 | | | |
| **Fe** | 0.42 | 0.24 | 0.29 | 0.78 | 0.45 | -0.25 | -0.37 | 1.00 | | |
| **Ca** | 0.32 | 0.44 | 0.68 | 0.08 | 0.63 | -0.25 | 0.85 | -0.34 | 1.00 | |
| **Zn** | 0.57 | 0.44 | 0.39 | 0.78 | 0.31 | -0.24 | -0.15 | 0.70 | -0.37 | 1.00 |
| **Dry season** | | | | | | | | | | |
| **Cr** | 1.00 | | | | | | | | | |
| **Ni** | 0.92 | 1.00 | | | | | | | | |
| **Cu** | 0.75 | 0.79 | 1.00 | | | | | | | |
| **Co** | 0.91 | 0.86 | 0.82 | 1.00 | | | | | | |
| **Pb** | 0.94 | 0.87 | 0.84 | 0.96 | 1.00 | | | | | |
| **Mn** | -0.28 | -0.37 | -0.60 | -0.31 | -0.34 | 1.00 | | | | |
| **Mg** | 0.21 | 0.51 | 0.29 | 0.27 | 0.18 | -0.36 | 1.00 | | | |
| **Fe** | 0.80 | 0.69 | 0.53 | 0.90 | 0.87 | -0.07 | 0.10 | 1.00 | | |
| **Ca** | -0.38 | -0.05 | 0.05 | -0.34 | -0.38 | -0.36 | 0.36 | -0.57 | 1.00 | |
| **Zn** | 0.72 | 0.84 | 0.96 | 0.80 | 0.79 | -0.55 | 0.46 | 0.51 | 0.17 | 1.00 |

sampling points, presenting the most significant values for Cr, Ni, Cu, Co, Pb, Fe and Zn. The metal distribution in PC1 associated the points located in the urban portion of the Jequiezinho River, considered as the most impacted portion of the studied environment, due to the contribution of sewage and other pollutants. This suggests that anthropogenic actions may somehow contribute to increased contamination by these metals. The formation of groups in relation to the collection periods (seasonality) was not observed, evidencing that the temporal conditions in the year 2018 did not significantly influence the quantification of these elements in the analyzed samples, probably due to the water deficit recorded over the study period, as previously shown.

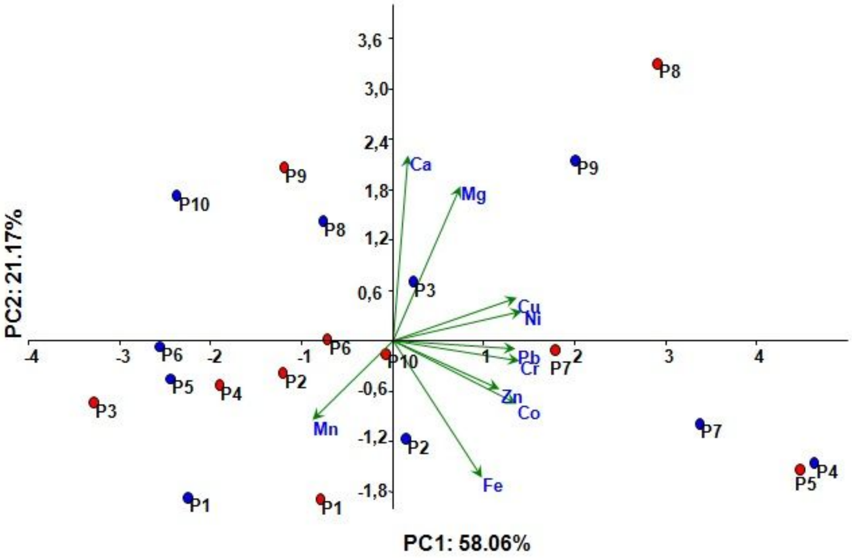

**Figure 4.** Bi-plot obtained by the overlapping of the scores and loadings graphs for the two sampling campaigns. Blue points: samples collected in the dry season. Red points: samples collected in the rainy season.

PC2 represented 21.17% of the total variance, with significant loads for Ca and Mg. These two elements, together with Fe, are considered abundant in the Earth's crust and are majorities in this study. Soil and sediment studies have used these elements as a reference geochemical element in the determination of the geochemical background to evaluate the geoaccumulation index. The analysis of PC2, therefore, accounts for the geochemical contribution to the concentrations of these elements.

The data were classified through hierarchical cluster analysis (HCA), and a double dendrogram was created from the metal concentration in relation to the sampling points. The horizontal dendrogram shows the clustering of the sampling sites (P1-P10), according to metal concentration. In the first sampling period, the points were separated into three major groups (Figure 5a). The first group was formed by the points P1-P4, P6, P9 and P10, which were responsible for the lowest concentrations of the studied metals, located in the area of lower population density, except for P9 and P10. The second group was formed by P5 and P7, as a function of the high concentrations of Ni and Cr and, finally, the third group containing only P8 related mainly to Ca and Mg contents.

The results of HCA are consistent with those of PCA, since they demonstrate a tendency of the samples to be grouped according to the collection site. The points located in the urban perimeter were those with the highest metal concentrations, in view of the population density and the release of effluents, which contribute as diffuse metal sources in the sediment.

The vertical dendrogram represents the results of the cluster analysis of the studied metals as a function of their concentration, according to the average Euclidean distances, demonstrating that they can be grouped into three distinct groups. The first group demonstrates that the Pb, Cu, Ca, Mg, Ni and Cr may exhibit similar behavior and geochemical origin, since their concentrations were increased in the most environmentally impacted locations. The second grouping was formed by Co, Fe and Zn, and Co and Zn correlated significantly with Fe, suggesting that they tend to concentrate on Fe oxides and hydroxides, corroborating the results of the correlation analysis. However, Mn showed no correlation with any other metal,

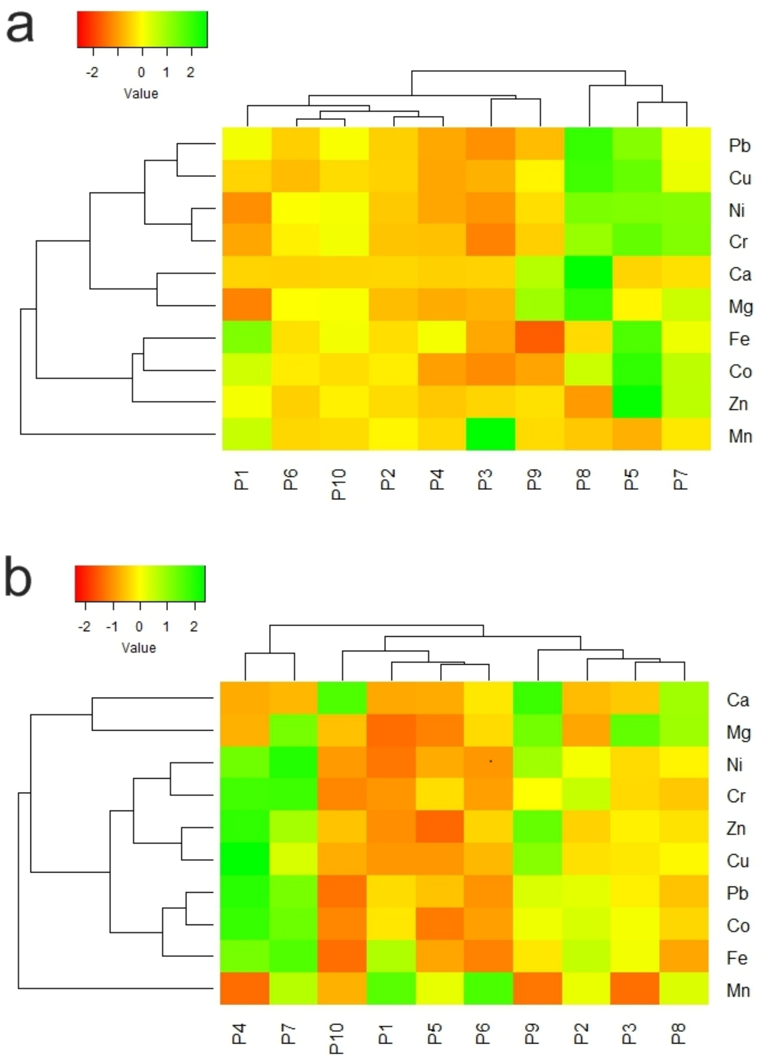

**Figure 5.** Results of the heat map for HCA from the concentration of the metals obtained by pseudo-total digestion in sediment samples of the Jequiezinho River (a) first campaign, (b) second campaign.

being isolated in the composition of the third grouping.

In the second collection period (Figure 5b), a behavior similar to the first was observed, where the sampling points of the urban area also presented the highest concentrations. The clusters formed by the metals indicate that they may have originated from similar sources, although the anthropogenic contribution on the concentrations presented is evident. The points P2, P3, P8 and P9 were responsible for the formation of the first group, P1, P5, P6 and P10 represented the second group due to the lower metal contents, except for Mn and Ca (P4 and P7), especially for Ni, Cr, Zn, Pb, Co and Fe.

Some studies indicate that Pb, Zn, As and Cd have the source of anthropogenic factors, such as emissions of exhaust from vehicles, disposal of household waste, application of phosphate fertilizers and pesticides, among others. (Shan et al. 2010, Ungureanu et al. 2016, Guan et al. 2018). The similarity between the collection periods (absence of effects related to seasonality) can be attributed to the water deficit observed in the region for the entire year of 2018, where the physical, chemical and biological processes responsible for the mobility of the chemical species did not change significantly, since the presence of water is critically important for the operation of this system.

## Sequential metal extraction

The study of chemical species fractionation allowed evaluating which element presented greater mobility potential among the analyzed fractions. According to Copaja et al. (2014), the distribution of trace elements through the different fractions of the sequential extraction procedure allows a better understanding of the bioavailability potential of these elements.

In general, the chemical elements extracted at each fractionation stage at the sampled sites showed similar behavior (Figures 6, 7), and the carbonate fraction was the most expressive; the soluble fraction had few contributions. The fraction of greater environmental interest (labile) presented poor results for most of the elements, except for Fe at the end of the rainy period and for Fe and Mg in the samples collected during the dry period.

In the first sample, Fe presented high percentages in fraction 1 (soluble fraction) for most of the sampling points, except in P8 and P9, where fraction 3 (metals bound to carbonates) had a higher value. In the second campaign, Fe presented a similar behavior, also extracted in the soluble and carbonate fractions.

Although Pb, Cu and Cr showed significant concentrations in the pseudo-total digestion, they did not appear in the fractions extracted sequentially, only Cr in F3 and F4 in the late rainy period and Cu in F3 in the second period, being considered of low geochemical mobility. Of all the elements evaluated, Mn is the most homogeneously distributed among all the fractions extracted. The concentration of Mn in the available fractions and mainly in the carbonate phase confirmed its high mobility potential, which does not necessarily mean that it is due to anthropogenic contributions, but it may also be due to the geochemical formation of the environment. The geochemical distribution of this element, concentrated in the carbonaceous phase, followed by the reducible one, was verified in other studies involving sediments where sequential extraction was applied (Teixeira et al. 1997, Kersten et al. 1995).

Zinc presented an association with the carbonate fraction for most of the collected samples, except for P7 (March/2018) and P1 (September/2018), with the highest concentrations recorded in the points located in the urban zone. This increase can be caused by the inflow of sewage into the river bed.

The concentration of Ni in the carbonate fraction did not show significant variations in any of the campaigns carried out. Considering that the values found in samples from rural areas, where anthropic sources are rare, are close to those determined in the urban area, it may be an indicative of the natural origin of this element.

Calcium and Mg are very abundant in aquatic environments. They participate in the formation of rocks and are released by weathering. Concentrations of Ca and Mg had a similar behavior in the samples collected in March 2018, especially in fractions 2 and 4. In the dry season, Mg was not significant in fraction 4, but presented significant values for fraction 1. Cobalt behavior in the two campaigns was very similar in relation to the extracted fractions, predominating in fraction 3. The occurrence of Co in mafic and granitic rocks mainly suggests that the contents found in the samples probably derive from the geochemical composition of the studied environment.

## Environmental implications and metal mobility

The metals associated with the potentially available fractions (F1 and F2) can be easily mobilized into the environment due to constant changes in physical and chemical parameters such as pH and temperature. Exchangeable, more labile fractions, are generally considered

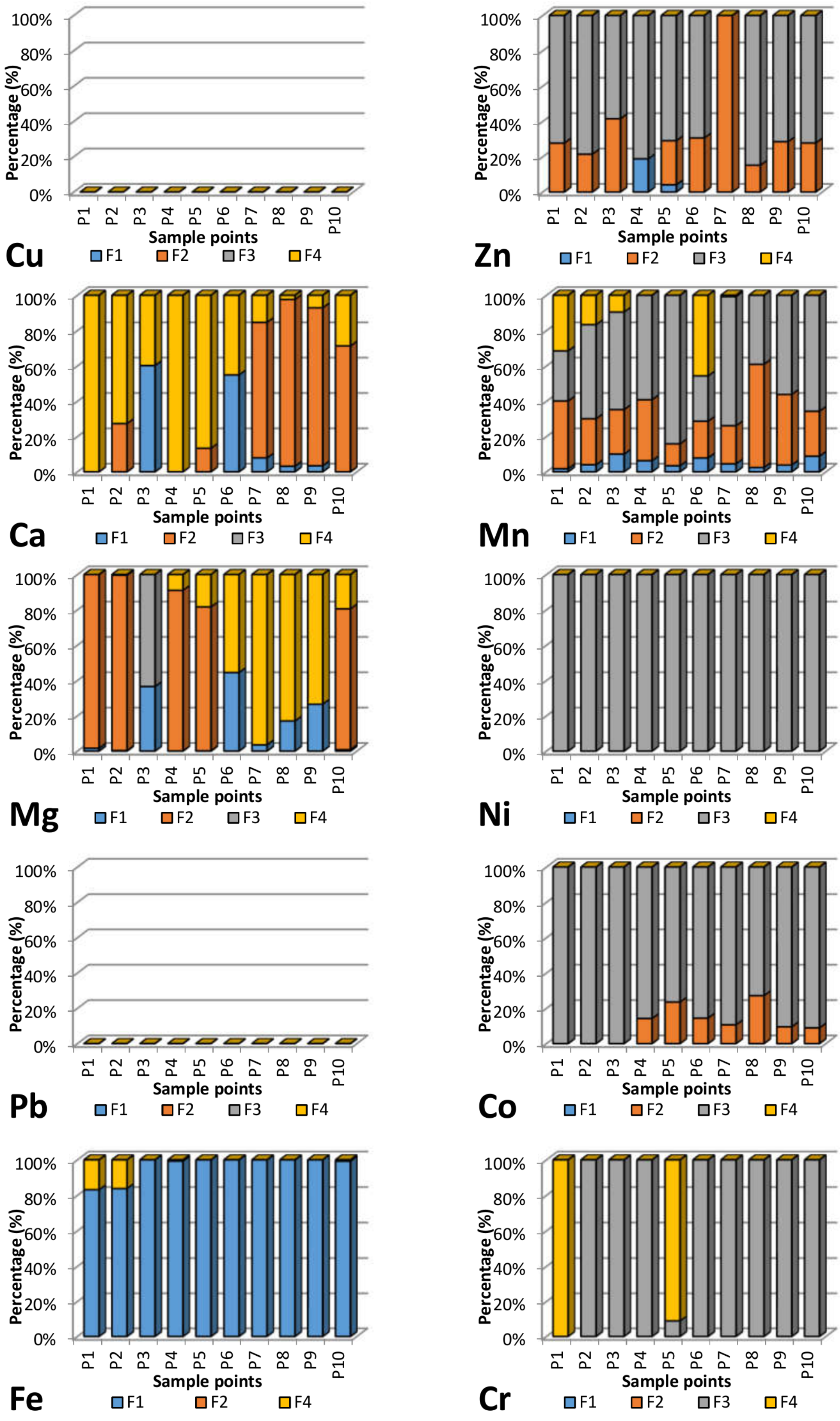

**Figure 6.** Geochemical distribution of Cu, Zn, Ca, Mn, Mg, Ni, Pb, Co, Fe and Cr in the sediment fractions of the Jequiezinho River, collected in March 2018. (F1 = soluble metal; F2 = easily exchangeable metals; F3 = metals bound to carbonates; F4 = metals bound to organic matter).

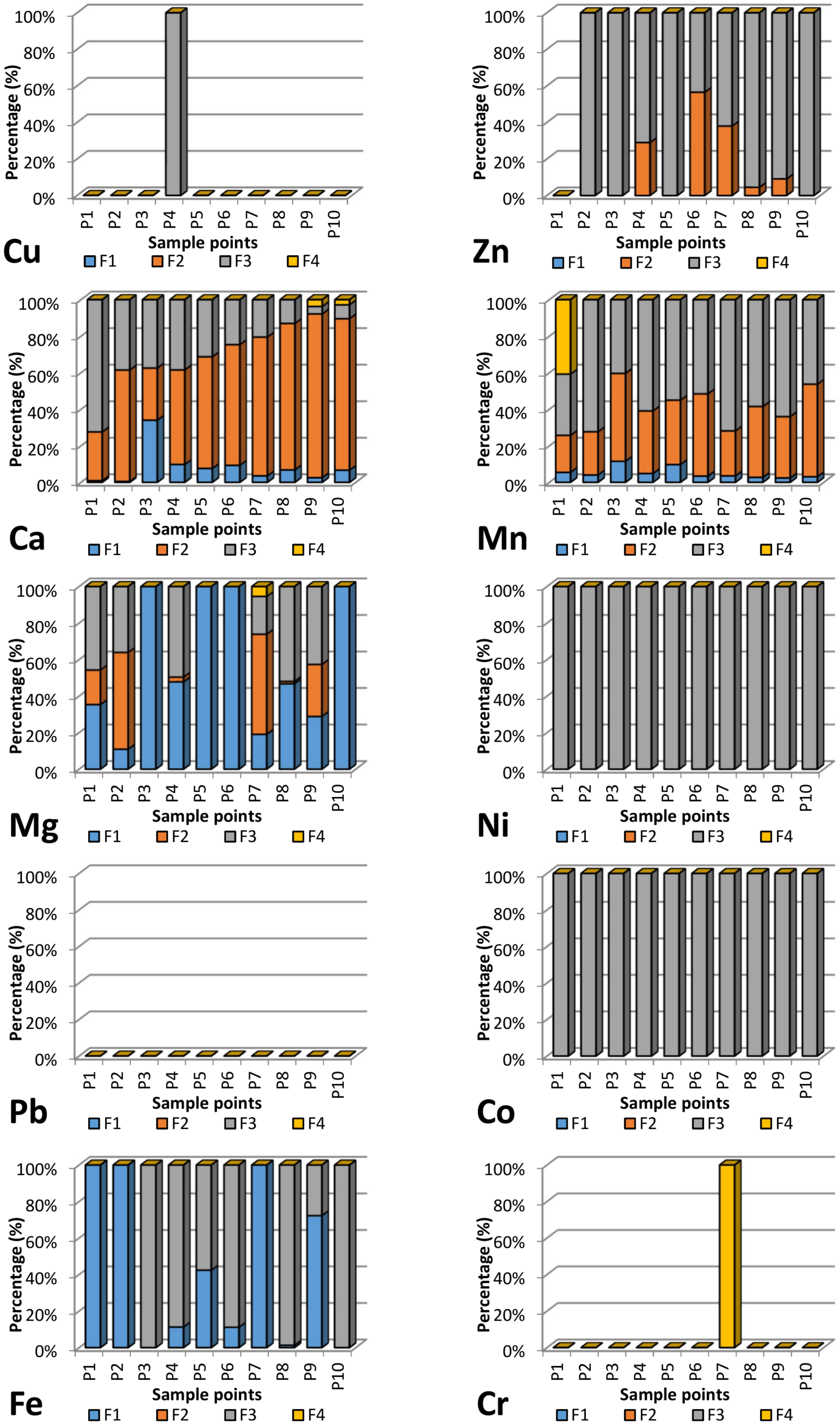

**Figure 7.** Geochemical distribution of Cu, Zn, Ca, Mn, Mg, Ni, Pb, Co, Fe and Cr in the sediment fractions of the Jequiezinho River, collected in September 2018. (F1 = soluble metal; F2 = easily exchangeable metals; F3 = metals bound to carbonates; F4 = metals bound to organic matter).

the most representative from the environmental point of view, since they are the bioavailable part of metals and, when sufficiently high, can cause toxicity to aquatic organisms (Sastre et al. 2001, Brady et al. 2016).

Fractions where the metals could be more easily available in the water column (extracted with water and ammonium acetate) were evaluated through the Mobility Factor (MF) proposed by Kabala & Singh (2001). This parameter is obtained from the sum of the concentrations obtained in the fractions F1 and F2 divided by the total sum of the sequentially extracted fractions, being expressed in percentage, according to the following equation:

$$MF = [F1 + F2 / \Sigma (F1 + F2 + F3 + F4)] \times 100$$

The mobility factor for each element analyzed indicates that the metals Mn and Mg presented the highest values, followed by Zn and Fe in the samples collected at the end of the rainy season. In the dry period, Mg presented the highest value, followed by Zn, Mn, Co and Fe. The mobility order varied seasonally, with Mn> Mg> Zn> Fe at the end of the rainy season and Mg> Zn>Mn> Co> Fe in the dry season (Table VI).

The percentages of metals associated with available fractions suggest that these elements are poorly adsorbed on the sediment surface. It can be easily dissociated from carbonates and made available to the environment, where they can be absorbed by the biological community. This behavior has been noted by other researchers such as Davutluoglu et al. (2011) and Usero et al. (1998) in studies conducted with river or marine sediments.

The occurrence of metals such as Mn, Mg, Fe, Zn and Co in the available fractions indicates the possible geochemical mobility of these elements in the sediments of the Jequiezinho River, which is not necessarily due to the anthropogenic contributions of the potential emission sources located in the catchment area of the Jequiezinho River. This phenomenon can also be determined by the environmental and geochemical constraints to which the environment is exposed.

The high values of FM can be interpreted as relatively high lability and biological availability of the metals in the sediment (Narwal et al. 1999). This suggests that Cu, Pb, Cu, Ni, and Cr were not detected in the most labile fractions, but, they were extracted in the pseudo-total digestion and are fixed in the crystalline structure of the stable and resistant weathering mineral silicates and, therefore, are unavailable in the environment (Bevilacqua et al. 2009, Brady et al. 2016).

## CONCLUSION

The results obtained with the pseudo-total digestion of the sediment samples from the Jequiezinho River allowed a quantitative evaluation of the concentration of metals in the environment. The sequential extraction made it possible to observe the phases in which the elements were available, allowing to predict their mobility, as well as their bioavailability to the organisms.

The applied Sediment Quality Values Guidelines (SQVG) indicate that some points present contamination by Cr, Ni, Cu and Pb. However, these metals were not observed in the less stable phases, demonstrating low mobility. The individual mobility factor suggests a greater mobility for Mg and Mn and lower for Zn, Co and Fe, directly influencing the availability of these elements.

The multivariate statistical analysis revealed that the elements Cr, Ni, Cu, Co, Pb, and Zn had a similar behavior in the urban portion of the Jequiezinho River, where sewage and other pollutants are discharged, thus reflecting

**Table VI.** Comparison of the average mobility (AM) of the extracted metals in the sediments of the Jequiezinho River in relation to the collection period.

| Collection point | Pb | Cu | Ni | Fe | Cr | Co | Mg | Zn | Mn |
|---|---|---|---|---|---|---|---|---|---|
| | % | % | % | % | % | % | % | % | % |
| **End of the rainy season** | | | | | | | | | |
| P1 | – | – | – | 1.30 | – | – | 15.97 | – | 14.70 |
| P2 | – | – | – | 0.39 | – | – | 8.48 | – | 9.91 |
| P3 | – | – | – | – | – | – | 70.72 | – | 100.62 |
| P4 | – | – | – | 0.02 | – | – | 10.39 | 11.48 | 32.29 |
| P5 | – | – | – | 0.02 | – | – | 22.40 | – | 5.32 |
| P6 | – | – | – | 0.05 | – | – | 18.33 | 14.29 | 15.64 |
| P7 | – | – | – | 0.02 | – | – | 7.04 | 1.29 | 7.13 |
| P8 | – | – | – | 0.01 | – | – | 5.25 | 1.07 | 16.08 |
| P9 | – | – | – | 0.05 | – | – | 4.28 | 4.61 | 35.14 |
| P10 | – | – | – | 0.00 | – | – | 15.72 | – | 42.22 |
| **Dry season** | | | | | | | | | |
| P1 | – | – | – | 1.22 | – | – | 96.28 | 3.06 | 7.99 |
| P2 | – | – | – | 0.24 | – | – | 54.43 | 2.88 | 4.44 |
| P3 | – | – | – | 0.12 | – | – | 91.30 | 6.02 | 0.77 |
| P4 | – | – | – | 7.00 | – | 15.11 | 79.74 | 3.00 | 3.95 |
| P5 | – | – | – | 0.94 | – | 10.28 | 34.03 | 5.82 | 7.26 |
| P6 | – | – | – | 0.11 | – | 10.59 | 44.84 | 2.93 | 13.41 |
| P7 | – | – | – | 0.35 | – | 7.98 | 22.47 | 17.85 | 4.73 |
| P8 | – | – | – | 0.04 | – | 18.32 | 18.15 | 47.46 | 38.56 |
| P9 | – | – | – | 0.30 | – | 9.05 | 20.53 | 5.92 | 8.88 |
| P10 | – | – | – | 2.78 | – | 6.80 | 33.10 | 2.89 | 2.64 |

the effects of the anthropogenic contribution. The distribution of the majority elements occurred throughout the study area, especially in isolated sites where there was no evidence of contamination sources, suggesting the geochemical formation of the environment as the most probable source.

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Darci Santos Silva, Rosane Moura Aguiar and Marcos Almeida Bezerra conceived the research that originated this manuscript. Darci Santos Silva and Uilliam Mozart Ferreira da Mata Cerqueira carried out the laboratorial experiments and applied the analytical methods. Darci Santos Silva, Rosane Moura Aguiar, Paulo Luis Souza Carneiro and Marcos Almeida Bezerra contributed in the statistical analysis. All authors discussed the results and contributed to write the final manuscript.