IJSRM
INTERNATIONAL JOURNAL OF SCIENCE AND RESEARCH METHODOLOGY
An Official Publication of Human Journals
HUMAN

Human Journals
Research Article
December 2022 Vol.:23, Issue:2

Environmental Investigation of the Source of Pollution in Superficial Sediments Using Chemometric Tools in the Ipojuca River, Brazil

IJSRM
INTERNATIONAL JOURNAL OF SCIENCE AND RESEARCH METHODOLOGY
An Official Publication of Human Journals
HUMAN

Joelmir Chaves Diniz*[1], Alex Souza Moraes[1], Enjôlras de Albuquerque Medeiros Lima[1], Otávio Pereira dos Santos Junior[2]

[1] Department of Chemistry, Federal Rural University of Pernambuco (UFRPE). Dom Manuel de Medeiros Street, s/n - Dois Irmãos, Recife, Pernambuco, Brazil, Zip code: 52171-900;

[2] Department of Chemistry, Federal Institute of Education, Science and Technology of Pernambuco (IFPE)., Brazil

Submitted: 22 November 2022
Accepted: 28 November 2022
Published: 30 December 2022

HUMAN JOURNALS
www.ijsrm.humanjournals.com

Keywords: Environmental Pollution, Toxic Metals, Enrichment Factor and Chemometrics Tools

ABSTRACT

Urban pollution when combined with untreated industrial waste can dangerously exacerbate the toxicity levels in the sediments of water bodies. The Ipojuca River, which crosses the city of Caruaru in Northeast Brazil, is known to be contaminated because it receives a large load of contaminants from domestic sewage and effluents, mainly from the textile sector. The study was carried out through the analysis of 14 samples of bottom sediments collected in the Ipojuca River in its tributaries, approximately 500 meters away from each point, adding up to an extension of approximately 10 km. The samples were analyzed by ICP-OES for 37 chemical elements, and pointed out enrichment of some heavy metals in some stretches with notorious presence of domestic sewage and industrial effluents with the highest values found above the USEPA standards (Cu > 180 mg. Kg^{-1}, Ni > 50 $mg.Kg^{-1}$, Pb > 90 $mg.Kg^{-1}$, Zn > 600 $mg.Kg^{-1}$). The Principal Component Analysis showed that there is a relationship between the areas with the highest presence of textile laundries and the stretches with the highest metal enrichment in the Ipojuca River, including As, Cr, Cu, Ni, Pb and Zn. In general, the geochemical signature carried out in this study, present in the sediments of the Ipojuca River, indicates the unnatural enrichment of many chemical elements and toxic effect due to the input of material from industrial activities. Such results can contribute to the strengthening of decision-making by public managers regarding decontamination actions to protect human health.

1. INTRODUCTION

Water is one of the most important natural resources for humanity, and it is of paramount importance for the existence and permanence of life on the planet. Not only because it is essential for human and animal hydration, but also because of its participation in the development of various human activities such as agriculture and industry, in addition to the maintenance and balance of terrestrial ecosystems. (MORAES, 2011; CASTRO, 2012)

According to Saraiva (2019), economic progress and population growth drive industrial, commercial and agricultural activities' increase., And when this escalation occurs in an unsustainable way, there is a contribution to the contamination of surface and underground water resources mainly by the release of tailings containing metals (GABRIEL 2017), organic materials, fertilizers and pesticides (ADDO-BEDIAKO *et al*. 2021), oils (SOARES *et al*. 2021), toxic percolates from dumps, among others.

The characteristics and richness of water are deeply linked to fresh water and, therefore, there is a distortion in the ways human beings act towards water. For example, approximately two thirds of the Earth is covered by water, of these, about 97% is salty and, thus, initially unfit for consumption. So just under 3% of the water is fresh. Since more than 2.5% is frozen in Antarctica, Arctic and glaciers making it unavailable for immediate use/consumption, there is less than 0.5% available for contiguous use. (National Water Agency – ANA 2019). In addition, a large part is in underground aquifers and a small portion in surface waters. On that account, it is understood that it would be natural to take greater care with the fresh water available on the surface, firstly, because it was easier to obtain for use, whether for consumption or for agricultural and/or industrial activities, and secondly, due to the small percentage available on land. However, and unfortunately, this is not what happens. According to Moraes (2011), the quality of most of these bodies of water is unfit for human consumption, requiring a higher degree of treatment. This inadequacy is linked to the degradation of water sources caused by the growth and diversification of human activities (LIU *et al*. 2020). In addition to scarcity (CASTRO 2012), world society is facing a decline in water quality.

Accordingly, it is possible to notice and even associate the damage to surface water resources in places with growth and development of anthropic activities. For example, according to

Minaríkova (2020) the Danube River Basin (present in 14 countries in the European continent) is harmed by various sources of pollution, such as agricultural, industrial and urban effluents and navigation (hydrophobic organic); Gabriel (2017) verified concentrations of toxic metals in the lower course of the Rio Doce, (state of Espírito Santo, Brazil), being of anthropic origin, especially due to the disaster involving the rupture of the *Fundão* dam, in Mariana (state of Minas Gerais, Brazil). In the study by Moraes (2011), a moderate anthropic contribution of copper and zinc metals in the upper Tietê basin (state of São Paulo, Brazil) was found at all analyzed points and, in some, other types of contaminants also (for example, surfactants).

It is evident that surface freshwater resources are subject to anthropic disturbances. Therefore, we target our attention to the river basin of the Ipojuca River, in the state of Pernambuco, in the Brazilian Northeast. A state that historically suffers from water scarcity and has the Ipojuca River over 320 km long, with signs of contamination evident in the urban vicinity (SILVA et al., 2019; OLIVEIRA et al., 2021; SILVA et al., 2017). In this way, it is imperative to know the real situation regarding river's quality, so that there is concise and objective information to help the population, the public power and the private sector to reduce the direct and indirect damage to water resources.

Given the above, the evaluation of sediment samples associated with geochemical quality indices has proved to be an excellent tool to verify the level of contamination. (ISLAM et al., 2020) According to Moraes (2009) and Addo-Bediako et al. (2021), knowledge of the quality of sediments present in aquatic bodies is extremely significant for the diagnosis of the health of ecosystems. Therefore, the present study aimed to (i) carry out an assessment of the concentration of metals and non-metals in surface sediment samples of the Ipojuca River in the stretch that cuts through the city of Caruaru-PE, where there is direct contact with urbanization and well-defined industrial activities; assess (ii) the degree of contamination and damage to the river ecosystem; and obtain (iii) to obtain the grouping of enriched metals and metalloids in surface sediments, by means of chemometric techniques.

2. MATERIAL AND METHODS

2.1 STUDY AREA

The Ipojuca River has an extension of approximately 320 km and its basin covers an area of 3,435.34 km^2, corresponding to 3.49% of the area of the State of Pernambuco. With an orientation mostly in the west-east direction, with its source in the city of Arcoverde, with the water bed running through the *sertão*, *agreste*, forest area and metropolitan region to its mouth in the Atlantic Ocean (its estuary has been significantly altered in recent years). As a result of the installation of the Suape Port Complex The fluvial regime of the Ipojuca River, in general, is intermittent, becoming perennial from its middle course, near the city of Caruaru.

During the course, a total of 25 municipalities are inserted, among which 14 are directly in the basin and 11 are only partially. Mainly, the municipalities of Bezerros, Caruaru, Escada, Chã Grande, Gravatá, Ipojuca, Primavera, São Caetano and Tacaimbó stand out. Its main tributaries, on the right bank, are Liberal creek, Taquara creek and Mel creek and, on the left bank, Coutinho creek, Mocós creek, Muxoxo creek and Pata Choca creek. The Liberal stream, its most important tributary, has its sources in the municipality of Alagoinha, which drains along its 47 km length, areas of the municipalities of Alagoinha, Pesqueira and Sanharó, and empties into the Ipojuca River. (APAC 2021)

Among the cities that cross the Ipojuca River Basin, Caruaru, located in the Agreste Central Development Region, is the most representative, in terms of population and industrial activities, with emphasis on the textile industry (CONDEPE 2011).Due to that, the present research covers the stretch of the Ipojuca River Basin, located in the urban center of the municipality of Caruaru-PE, restricting the areas of the Ipojuca River close to the textile industries. Among the sampling points are the Salgado stream and the Mocós stream. (Figure 1)

.

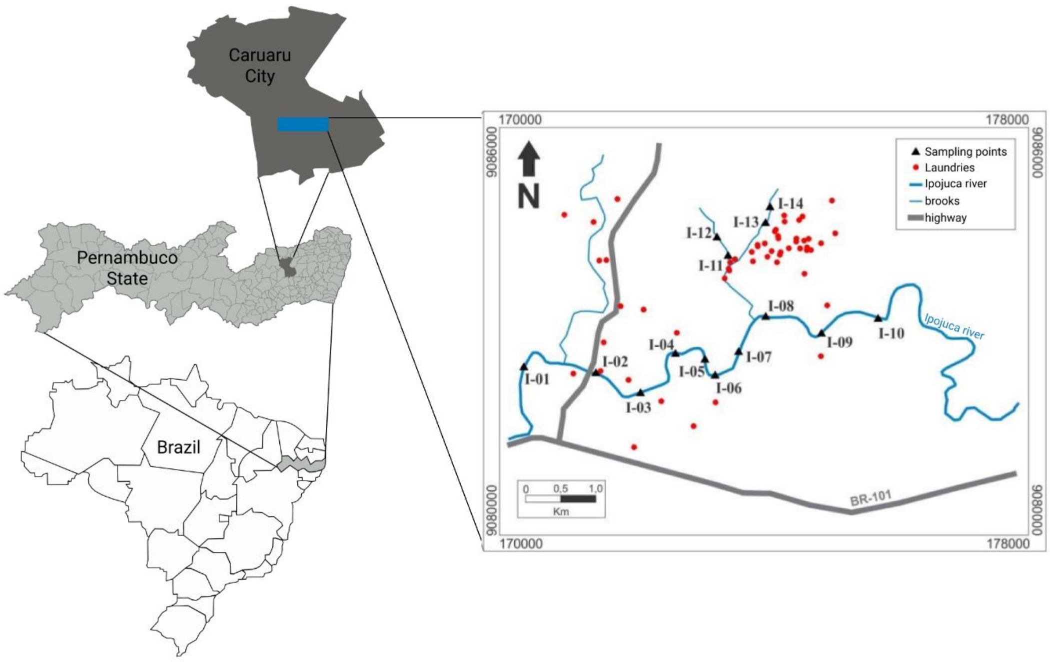

Figure 1: location of sampling points along the Ipojuca River in the city of Caruaru

As in the study area there is a prominent presence of the textile industrial sector, purposely, to determine the sampling points, a survey was carried out of the laundries registered in the Union of the Spinning and Weaving Industry in General of the Municipality of Caruaru - Sinditêxtil, with proximity to the stretch of the Ipojuca river in the urban center of Caruaru-PE. (Figure 2)

2.2 SAMPLING AND MEASUREMENTS

14 sampling points were determined (figure 1), all collection points were georeferenced by the universal transverse mercator system (UTM), as shown in table 1.

Table 1: Georeferencing of sampling points

Points	Description	UTM coordinate (Zone 25)	
		S	S
I01	Extensive presence of laundries, before the tributary of the creek dos mocós.	9082369.90	170153.30
I02	Extensive presence of laundries, post tributary of the creek dos mocós	9082297.32	171172.60
I03	Extensive presence of laundries, before the open market in Caruaru	9082017.00	171863.35
I04	Extensive presence of laundries, open market in Caruaru	9082593.60	172375.86
I05	Extensive presence of laundries	9082497.25	172870.28
I06	Extensive presence of laundries	9082296.85	172957.90
I07	Without the presence of laundries, pre-tributary of the salty stream	9082627.60	173390.94
I08	Extensive presence of laundries, tributary of the salt stream	9083155.50	173699.26
I09	Extensive presence of laundries	9082866.50	174515.00
I10	Extensive presence of laundries, upstream, with a distance of 115 km from the mouth of the Atlantic Ocean.	9083115.60	175346.60
I11	Intensive presence of laundries, salty stream	9084199.52	173179.20
I12	Intensive presence of laundries, salty stream	9084484.20	172876.71
I13	Intensive presence of laundries, salty stream	9084793.87	173835.34
I14	Intensive presence of laundries, salty stream	9084984.14	173734.25

Note: the average distance between the points is 500 meters

At each sampling point, three sediment samples were collected (with the aid of a VanVeen dredger) in the first half of 2018, totaling 14 sediment samples. Subsequently, they were packed in sterilized polyethylene bags and closed with a double-locked security seal (double sock seal) with an identification code, for traceability of the collection point. Immediately, they were sent to the Construction Materials Laboratory, in the Rural Technology Department of DTR/UFRPE, for processing. The samples had a preliminary treatment of drying in an oven at 60°C for 24 hours and, afterwards, with the aid of a porcelain mortar, the dried samples were disaggregated and homogenized. Then, approximately 10g of each sample was separated and sent for analysis.

Before the analysis, the sample was prepared, which consisted of submitting a 1.0g aliquot of each sample to decomposition and solubilization with aqua regia (a mixture of hydrochloric acid and nitric acid in the proportion 3:1) on a hot plate at 100°C for 12 hours. Subsequently, the samples were left to rest at room temperature. Finally, the samples were filtered, added to a 50 ml volumetric flask and the volume measured with a 5% HNO_3 solution. After preparation, the samples were analyzed by the atomic emission spectrometry technique with the inductively coupled plasma source method (ICP-OES), the respective elements in each sample: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Sc, Se, Sn, Sr, Th, Ti, Tl, U, V, W, Y, Zn and Zr (37 elements). It is important and necessary to state that analytical grade reagents and solutions were used in this study.

2.3 TOXICOLOGY AND QUALITY

To evaluate and characterize the contamination in sediments, the approach of Long et al (1995; 1998) was used, which determined the values of ERL - Effect Range Low (minimum concentration of a metal that can generate adverse effects) and ERM - Effect Range Medium (average concentration likely to have harmful effects). (Table 2) Since values below the ERL have no adverse effects, while concentrations above the ERM will likely have adverse effects. This approach was used by USEPA (1998) and the National Council for the Environment (CONAMA) of Brazil, through Resolution 454/2012, which establishes two threshold levels that can cause some adverse effect on the biota, for eight metals.

Table 2: Reference values proposed by Long et al., (1995), used by USEPA (1998) and Conama 454/12 (2012) for metals.

Metals		As	Cr	Cu	Pb	Ni	Zn
USEPA (1995) ERL and ERM	ERL*	8.2	81	34	47	21	150
	ERM*	70	370	270	220	52	410
CONAMA 454/12 (2012) dredged material, fresh water, level 1 and 2.	Level 1*	5.9	37.3	35.7	35	18	123
	Level 2*	17	90	197	91.3	35.9	315

Adapted by: authors. *Values in $mg.kg^{-1}$

Based on Table 2, the concentrations of metals in sediments expressed in relation to ERL and ERM values are: Good – if the concentrations of all nine metals are below the ERL Limit; intermediate – if the concentration of some metal is between ERL and ERM; and Weak – if the concentration of any metal is above ERM. And according to CONAMA 454/12 (2012), they are classified into two levels: Level 1 – threshold below which there is less probability of adverse effects to the biota; and Level 2 – threshold above which there is a greater probability of adverse biota effects.

2.4 ENRICHMENT FACTOR (EF)

The Enrichment Factor (EF) is a geochemical index used as a method to identify contamination and/or environmental pollution by anthropogenic action (ZHUANG et al., 2021; ISLAM et al., 2018). It is a widely used indicator for studies of sediments and soil quality, as it indicates the concentration of the contaminating metal that is present in relation to reference values (geochemical background) (MORAES 2013; ZHUANG et al., 2021).

To assess the enrichment factor, the formula described by Thomas & Meybeck (1996) was used, equation 1, which states that sediment samples from the bottom of rivers, streams and estuaries provide values of reasonable concentrations for comparison. Therefore, the chemical analysis of the particulate matter can be compared with the world average content (background).

$$EF = \frac{[element/Al]sample}{[element/Al]background} \qquad \text{equation 1}$$

The EF result can be classified into 6 categories: 1 > EF, no enrichment; 1 < EF < 3, low enrichment; 3 < EF < 5, moderate enrichment; 5 < EF < 10 moderately severe enrichment; 10 < EF < 25, severe enrichment; 25 < EF < 50, very severe enrichment; and 50 < EF, extremely severe enrichment. (Birch and Olmos, 2008).

2.5 STATISTICS AND CHEMOMETRICS

Descriptive statistical parameters were analyzed, such as minimum and maximum values, standard deviation, mean and coefficient of variation. Also, chemometrics was used through principal component analysis (PCA) in order to look for regularities or patterns, to assist in the investigation of possible sources of contamination.

3. RESULTS AND DISCUSSION

3.1 GENERAL

The methodology used, and previously described, is an extremely widespread technique to work with profiles similar to the current one (MORAES 2009; MORAES 2011; KEN et al. 2017; GABRIEL 2017; SLAM et al. 2018; RÉGIS et al. 2018; CONRAD et al. 2018; CONRAD et al. al. 2019; SILVA et al. 2019; SLAM et al. 2020; MAO et al. 2020; ADDO-BEDIAKO 2021), with the necessary adaptations. However, an extra and randomly chosen analysis was performed to verify the repeatability of the results and the reliability of the procedures and equipment used. Thus, 21 elements were quantified and the results were separated into two groups, per unit of measurement $mg.kg^{-1}$ and % (percentage) and the relative standard error calculated for the groups, 1.36% and 2.38%, respectively. This indicates good reproducibility, as according to the National Health Surveillance Agency (ANVISA 2003, 2017), it should be less than 5%.

3.2 CONCENTRATION OF ELEMENTS IN SEDIMENTS

A total of 37 elements were analyzed, being Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Sc, Se, Sn, Sr, Th, Ti, Tl, U, V, W, Y, Zn and Zr, in 14 sample points (figure 1). Of these, 10 elements showed concentration levels below the limit of quantification (in $mg.kg^{-1}$) at all points, Ag (<1), B (<10), Bi (<10), Cd (<1), Sb (<5), Se (<10), Sn (<10), TI (<10), U (<10) and W (<10). With the exception of Cadmium and Silver, there are not many studies in the recent literature with these elements in environmental monitoring via sediment sampling (GABRIEL 2017; SLAM et al. 2018; SILVA et al. 2019; SLAM et al. 2020; ZHUANG et al. 2021). However, even without palpable results, the authors believe in the importance of keeping track of monitoring the levels, especially for monitoring and database. For Cd, it was verified in Moares (2011) and Slam (2020), the presence in concentrations below the quantification limit of the identification and quantification technique used in this study. However, it is a basis for future studies, especially if there are possible anthropogenic contributions such as mining, production, consumption and industries (e.g., batteries, pigments, alloys, electronic components), fossil fuels, cement and phosphate fertilizers. (Moraes 2011)

Table 3 shows the mean concentrations in the sediment at 14 sampling points per element, plus statistical values such as minimum and maximum, Standard Deviation (SD), Coefficient of Variation (CV) and background values, with the global concentration of Shales (TUREKIAN AND WEDEPOHL 1961) and the content of the upper continental crust, UCC, (RUDNICK AND GAO 2014). It was found that the mean concentrations of the elements Zn and Pb were higher than the corresponding ones in Shales and UCC. Result also obtained by Zhuang et al. (2021). And the average concentration of P was higher exclusively when compared to Shales and, on the other hand, the concentrations of Cu and La were higher with their peers in UCC, respectively. On this tangent, he conjectured that the maximum points of concentrations per element for Cu, Mo, P, Pb, Th and Zn obtained higher concentrations than the background in Shales and UCC. And As and La had their highest concentrations only when compared to UCC, also found by Zhuang et al. (2021) referring to As.

Table 3: Mean concentration values (mg.kg-1 or %), the elements in sediment samples in the Ipojuca River. aTurekian and Wedepohl (1961); bRudnick and Gao (2014); *: SD: standard

Elements		Average	Minimum	Maximum	SD[*]	CV[*]	Shales[a]	UCC[b]
Al	%	0,89	0,42	2,06	0,45	50%	8	15,4
Ca		0,43	0,16	1,23	0,29	66%	2,21	3,59
Fe		1,62	0,97	3,01	0,64	40%	4,72	5,04
K		0,2	0,11	0,36	0,07	34%	2,66	2,8
Mg		0,18	0,09	0,47	0,1	54%	1,5	2,48
Mn		0,02	0,01	0,04	0,01	40%	0,09	0,1
Na		0,05	0,02	0,11	0,03	48%	0,96	3,27
P		0,09	0,03	0,47	0,11	122%	0,07	0,15
Ti		0,07	0,03	0,17	0,03	48%	0,46	0,64
As	$mg.kg^{-1}$	3,29	2,5	8	2	61%	13	4,8
Ba		159,64	73	467	98,4	62%	580	628
Be		0,68	0,5	2	0,42	62%	3	2,1
Co		3,36	1,5	8	2,07	62%	19	17,3
Cr		19,36	1	63	17,36	90%	90	92
Cu		36,21	4	199	48,38	134%	45	28
La		34,93	12	84	20,21	58%	92	31
Li		10,21	5	21	5,56	54%	66	24
Mo		0,82	0,5	4	0,93	114%	2,6	1,1
Ni		9,57	1	58	14,09	147%	68	47
Pb		23,57	9	83	17,9	76%	20	17
Sc		1,71	1,5	3	0,54	32%	13	14
Sr		32,14	17	94	19,75	61%	300	320
Th		8	5	18	4,49	56%	12	10,5
V		16,21	9	43	8,86	55%	130	97
Y		8,07	3	19	4,01	50%	26	21
Zn		111,14	39	603	142,9	129%	95	67
Zr		1,9	0,5	5	1,64	86%	160	193

deviation; CV: coefficient of variation. The coefficient of variation (CV) obtained per element in relation to the 14 sample points showed high data dispersity, indicating that the concentration values are heterogeneous, namely, there was a path from 32% (Sc) to 147% (Ni). Of the 27 elements analyzed, 8 (Sc, K, Fe, Mn, Ti, Na, Y, Al) obtained CV ≤ 50%, 14 (Mg, Li, V, Th, La, As, Sr, Ba, Co, Be, Ca, Pb, Zr and Cr) presented CV between 50 and 100%; and 5 (Mo, P, Zn, Cu and Ni) with CV > 100%. (Figure 2) This dispersion can be explained by different variables such as seasonality, mineralogical composition of the region and anthropic contribution. (ISLAM et al. 2018; SILVA et al. 2019; SABINO, LAGE E NORONHA 2017; GABRIEL 2017) According to Jain et al. (2007), sometimes, variations in metal concentrations can also be influenced by changes in geological characteristics, lithological inputs, hydrological effects, cultural influences and type of vegetation cover. Given that, for Zhuang et al. (2021) the uneven distribution in the sediment is significantly affected by human activities. The anthropic contribution by several aspects, for the context of the study, can be accentuated because the sampling points of the Ipojuca River are located in an urban center, with a strong presence of companies in the textile sector (laundries) and the street market.

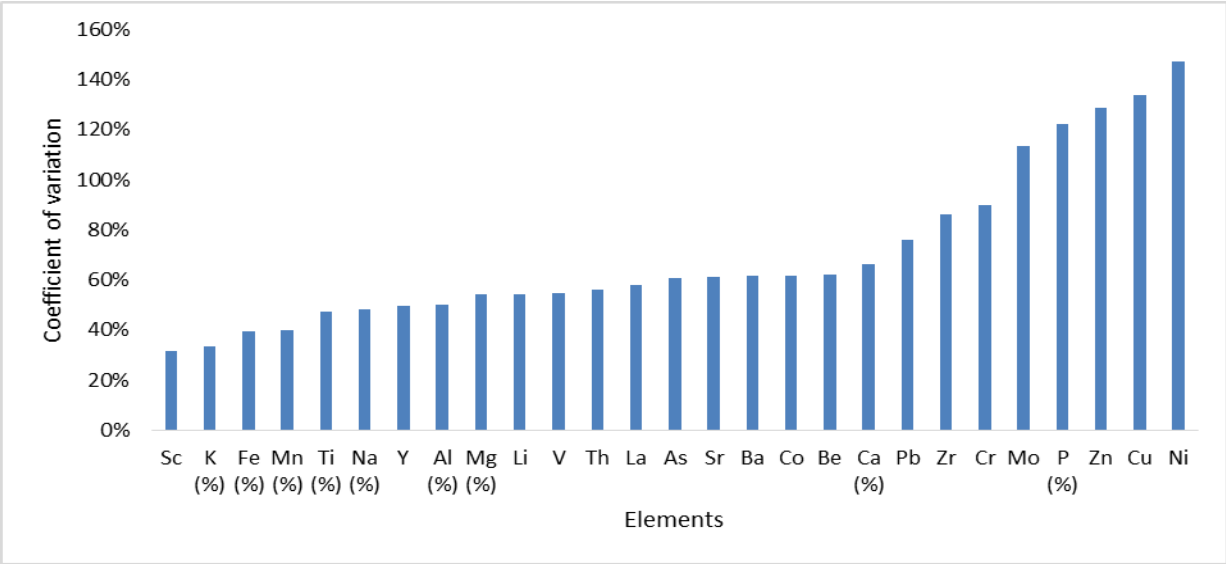

Figure 2: Coefficient of variation of 27 elements analyzed in the Ipojuca River.

Note: the elements that do not show the unit of measurement displayed are in $mg.kg^{-1}$.

At point I01 (figure 1), it was found that Th (18 $mg.kg^{-1}$) had a higher concentration than the background in Shales and UCC, and As (8 $mg.kg^{-1}$) and La (54 $mg.kg^{-1}$), were more concentrated in direct comparison to the UCC. Currently, there are no studies on the presence of Th in sediment samples, although Freitas (2008), in his study on thorium and rare earth recovery, cites some non-nuclear applications for thorium, such as: alloy component for magnesium, tungsten coating on electronic valve filament, oxide used in laboratory crucibles for high temperature, conversion of ammonia to nitric acid, oil cracking, scientific instruments due to high refractive index and low dispersion. As, unlike Th, is a much-studied element in sediment samples (SLAM et al. 2020; ZHUANG et al. 2021; SILVA et al. 2019; OLIVEIRA et al., 2021; SILVA et al., 2017), this is often because it is an integral element of the reference table for toxicology adopted by USEPA (1998), initially cited by Long et al. (1995) and adopted as a reference base in Brazil, through CONAMA 454 (2012). For Zhuang et al. (2021), As concentration is affected by traffic and industrial sources. It is worth noting that Ken et al., (2017), confirmed the main origin of as, from industrial sources. It is also possible to note that agricultural activities can be a source of As contamination of surface water bodies via surface runoff/erosion, leaching and harvests (SHI et al., 2019) La, as well as Th has no history of studies in sediment samples (MORAES 2009; MORAES 2011; KEN et al. 2017; GABRIEL 2017; SLAM et al. 2018; RÉGIS et al. 2018; CONRAD et al. 2019; SILVA et al. 2019; SLAM et al. 2020; MAO et al. 2020; ADDO-BEDIAKO 2021). However, according to Figueiredo et al., (2020) it's considered a contaminant belonging to Rare Earth Elements, having its fundamental use in several areas, such as electronic technology, medical products, industries and agriculture, in the latter, with special emphasis on bactericides or fertilizers. Kulaksiz and Bau (2011) draw attention that the increasing application of La in technologies and industries provides a greater allocation of this in aquatic ecosystems, through domestic sewage and industrial emissions. Figueiredo et al. (2020), in their study with Glass Eels (Anguilla anguilla) with exposure to a concentration of 1.5 $\mu g.L^{-1}$, proved that La has toxicological and bioaccumulation effects. In addition, these are accentuated with increasing temperature. Moreover, they reinforce the importance of more studies for a better understanding of the effects of lanthanum on the ecosystem, as well as monitoring in the face of technological and industrial changes of the current times. A little earlier, Oral et al., (2010), in their study on cytogenetic toxicity and development in sea urchin embryos in the presence of cerium and lanthanum, the results suggested damage analogous to the first stages of life of organisms.

At point I02, La, Th and Pb showed higher concentrations than their background pair in UCC, 38, 12 and 24 ($mg.kg^{-1}$), respectively. The values of La and Th were lower than at point I01. Pb, like As, has an input influenced by traffic and industrial sources (ZHUANG et al. 2021), also by production and processing operations of the metal and by the iron and steel industries (MORAES

2011) and by atmospheric deposition (MAO et al., 2020) Its presence in the ecosystem is worrisome, as it does not bring desirable beneficial or nutritional effects to human health, and is still a toxic metal with the ability to bioaccumulate. In humans, it can cause several clinical manifestations, according to the exposure time, ranging from allergy, diarrhea or vomiting to organ damage, brain dysfunction, cancer, which can lead to death (MORAES 2011) and hearing problems, in growth, impaired brain development, reduced synthesis of vitamin D (GABRIEL 2017). Islam et al (2018) in their research on the Halda River, obtained an average Pb concentration of 18.2 mg.kg^{-1}, that is, 31.9% lower than that found in the current study.

At point I03, the elements Pb, Th and Zn obtained a higher concentration than their peers at Shales and UCC, 28, 13 and 111 (mg.kg^{-1}), respectively; P (0.08%) had a higher concentration in relation to the Shales background; and Cu (31 mg.kg^{-1}) and La (43 mg.kg^{-1}) with concentration higher than the reference in UCC. Zn is a prominent element in research and/or, as well as, with evidence of signs of anthropogenic disturbance. Namely in the Chongming Islands River, China (MAO et al., 2020); on the Halda River, in South Asia, in Bangladesh (ISLAM et al. 2020); upstream of the Danjiang River, China (ZHUANG et al. 2021); in the Rio Ouro tropical watershed, Brazil (SCHWANTES et al. 2021); in San Quintín Bay, a lagoon on the North Pacific coast of Mexico (MARTINEZ et al. 2021); in port areas of Mucuripe Bay, a semi-arid ecosystem, Brazil (MOREIRA et al. 2021); and on the River Seine Paris, France (LE GALL et al. 2018) The increase in zinc concentration in surface waters can be caused by agricultural activities (MAO et al., 2020), by traffic and industrial sources (ZHUANG et al. , 2021). It can also be used as an indicator of burning fuel oil and untreated industrial waste (ISLAM et al., 2020). P, as a contaminant, is a direct indicator of human action, mainly due to the discharge of domestic and industrial sewage, without prior and/or adequate treatment. In agreement, Chen et al. (2016) stated that, on one hand, chemical fertilizers, recycled manure, atmospheric deposition and seeds are the main sources of P input to forests and agricultural land, on the other hand, in an urbanized location the main sources of P are from human and animal waste. However, the transport of phosphorus from forest landscapes and agricultural lands to the river network mainly occurs through runoff and leaching (non-point sources). In contrast, a considerable proportion of P from urbanized areas enters the river network through direct sewage discharge (point sources). Similarly, phosphorus is an essential macronutrient for the biota, however, it is also a common pollutant, as it is a common component, in excess, of discharge in many regions of the world, to the receiving surface waters (CARACO 1993), reaffirmed by Mallin and Cahoon (2020), who reinforce that P, once in the receiving waters, becomes a pollutant, either dissolved or associated with suspended solids. Cu in the conception of Zhuang et al. (2021), has its origin mainly from agricultural and natural sources. In the study by Ke et al. (2017), in the Liaohe River in a protected area in China, the origin of Cu was from natural sources. Following this reasoning, Mao et al. (2020) in their study on river sediments in the Chongming Islands, where industrial activities were limited, found that most of the anthropogenic Cu input came from agricultural activities.

At point I04, the elements Cu (199 $mg.kg^{-1}$), Mo (4 $mg.kg^{-1}$), Pb (83 $mg.kg^{-1}$), Zn (603 $mg.kg^{-1}$) and P (0. 47%) achieved higher concentrations than their peers in Shales and UCC. And La (84 $mg.kg^{-1}$) and Ni (58 $mg.kg^{-1}$) presented higher concentrations than their reference in UCC. Of the 27 elements analyzed, with the exception of the elements As, Cr, Li, Na, Th and Ti, the remainder (Al, Ba, Be, Ca, Co, Cu, Fe, K, La, Mg, Mn, Mo, Ni, P, Pb, Sc, Sr, V, Y and Zn), presented all the maximum values, in concentration, at this sampling point. It is worth noting that this point has a strong and direct contact with urbanization, due to its proximity to the street market. We reinforce that the urban context is decisive, for example: for Ke et al. (2017) in the study of the Liaohe River (protected area in China), Ni input was categorized as by natural sources; Zhuang et al., (2021) Ni was supplied by agricultural and natural sources; Martinez et al. (2021) also associated Ni enrichment as a possible reflection of changes in agricultural activities, probably due to the inclusion and popularization of agrochemicals use. Baltas et al. (2019), corroborate the contribution of Ni from agricultural sources.

At point I05, the concentrations of Pb and Zn presented higher concentrations than their reference in Shales and UCC, 24 and 99 ($mg.kg^{-1}$), respectively. At point I06, Cu (42 $mg.kg^{-1}$) and Zn (83 $mg.kg^{-1}$), with a higher concentration than their peers in UCC. At point I07, La (64 $mg.kg^{-1}$) and Pb (20 $mg.kg^{-1}$), with higher concentration than UCC and Th (14 $mg.kg^{-1}$), with higher concentration than Shales and UCC. At point I08, As, Cu and Pb, with concentrations above the reference in UCC, 8, 44 and 18 ($mg.kg^{-1}$), respectively. Point I09 did not show higher values. At point I10, the values of Cu (39 $mg.kg^{-1}$), Pb (20 $mg.kg^{-1}$) and Zn (79 $mg.kg^{-1}$) were above the UCC and P (0.09%) above from Shales. At points I11 and I12, only Zn presented a higher concentration than UCC, 74 and 70 ($mg.kg^{-1}$), at the same time. At point I13, the values of

La (32 mg.kg^{-1}) and Zn (87 mg.kg^{-1}) were higher than the UCC; Pb (24 mg.kg^{-1}) was higher in Shales and UCC; and P (0.08%) was higher than Shales. Finally, at point I14, P (0.01%) had a higher concentration than Shales and Zn (77 mg.kg^{-1}) had a concentration above UCC.

In comparative terms, 9 elements (Th, As, La, Pb, Cu, Zn, P, Ni and Mo) presented, in at least one point, a superior value in at least one of the backgrounds. Furthermore, in table 4, a comparison was made with studies carried out in other countries, with elements that showed more evidence in the research (As, Cr, Cu, Ni, Pb and Zn). The elements showed concentrations equal to or higher than those found around the world, in at least one study.

Table 4: comparison with studies carried out in rivers contaminated by trace metals around the world.

Reference	Sites			Parameters			
		As	Cr	Cu	Ni	Pb	Zn
		mg.kg^{-1}					
Ke *et al.* (2017)	Liaohe River protected, China	9,88	35,06	17,82	17,73	10,57	50,24
Le Gall et al. (2018)*	Seine River floods, France	2-14	16-75	14-90	8-34	15-214	69-402
Mao et al. (2019)	Yangtze River, Chongming Islands, China	11,02	43,5	30,7	33,4	35,8	116,5
Conrad et al. (2019)	Hearnes Lake, Austrália	8,8	6,3	9,5	na	11,6	24,3
Islam et al. (2020)	Halda river, Bangladesh	6,51	90,7	17,8	37	18,2	54,5
Zhung et al. (2021)	Danjiang River, China	10,1	81,6	46,7	37,5	38,9	139
Martinez et al. (2021)*	San Quintín Bay, North Pacific, Mexico	5,9-48	18,8 - 96,3	15,6-31,9	11,6-53,6	3,8-21,9	23,7-108,3
Addo-Bediako et al. (2021)	Spekboom River, South Africa	3,06	1091,6	19,9	446,06	5,46	54,9
Current Study	Rio Ipojuca, Brazil	3,29	19,36	36,21	9,57	23,57	111,14

na: not rated. * Authors chose to present the results in range format.

It is noted in table 4 that the elements Cu, Pb and Zn are highlighted in concentration in the current study; As, Cr and Zn in the study Ke et al (2017) in a protected area in China; As, Cr, Cu, Ni, Pb and Zn in the research by Le Gall et al (2018), after floods in the Siena River; As, Cr, Cu, Ni, Pb and Zn in the assessment by Mao et al (2019) in the Yangtze River, with input from atmospheric deposits and agriculture; As was featured in Conrad et al's (2019) investigation of Lake Hearnes; As, Cr, Cu, Ni and Pb were highlighted in the diagnosis by Islam et al (2020) in the Halda River; As, Cr, Cu, Ni, Pb and Zn showed greater influence in the Zhung et al (2021) research on the Danjiang River, with agriculture, transport and industry activities being the main sources of contamination; As, Cr, Cu, Ni, Pb and Zn stood out in the study by Martinez et al (2021) in San Quintín Bay, with contamination associated with change in technology used in agriculture (irrigation and fertilization systems); and Cu and Ni were highlighted in the Addo-Bediako et al (2021) survey on the Spekboom River, and the source of contamination mainly from Cu and Ni, is associated with mining, agriculture and wastewater treatment plant. Therefore, it is evident that the level of concentration of elements in sediments of a river is associated with social, economic, industrial structure and with natural events to which the surface waters of those rivers are be subjected. That is, in each study context there is a signature of elements and their intensities.

3.3 TOXICOLOGY AND QUALITY

For characterization of sediment toxicity and quality assessment, the references were established by the Environmental Protection Agency of the United States of America – USEPA (1998), defined by Long et al. (1995) and by the National Environmental Council of Brazil, Conama 454 (2012), respectively. (Table 2). They are expressed in chemical species linked to anthropic pollution, using the ERL (Effects Range Low) and ERM (Effects Range Mean) resource; and Level 1 and Level 2 threshold classification.

Of the elements studied, As, Cr, Cu, Pb, Ni and Zn were evaluated in terms of toxicity and quality, by way of comparison and the results are shown in figure 3. For USEPA (1998), this method provides a uniform perspective to evaluate contaminants in sediments at levels within and between estuaries.

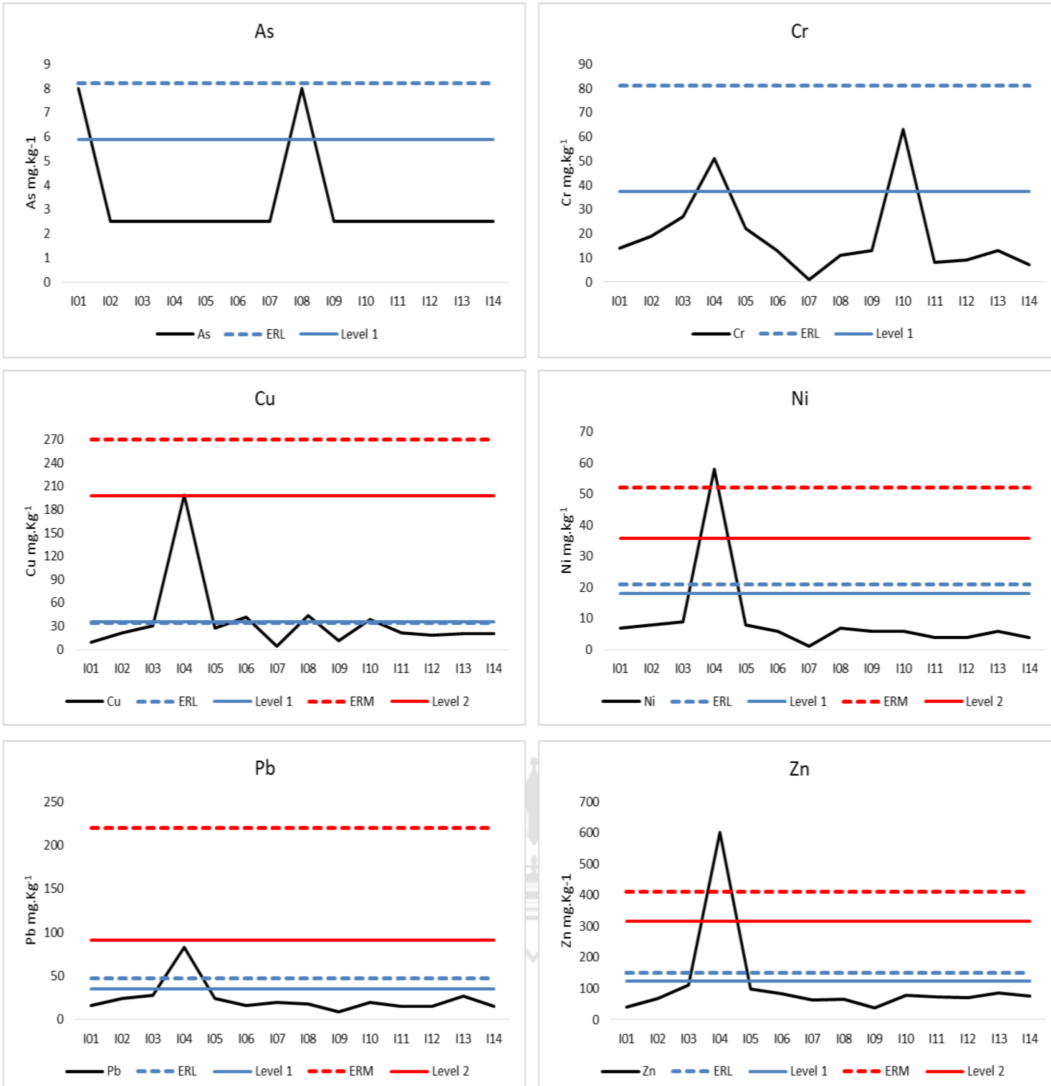

Figure 3: comparison of toxic metals from the Ipojuca River with toxicity and quality according to USEPA (1998) and Conama 454 (2012), respectively. **Source**: Long et al (1995), USEPA (1995) ERL and ERM, Conama 454/12 (2012) freshwater, level 1 and level 2.

For toxicity, As and Cr, in all 14 analyzed points in the Ipojuca River, presented values of concentrations lower than the ERL, thus, the undesirable biological effects rarely happen, being classified as “Good”. The concentrations of Cu were between the values of ERL and ERM for 4 sampling points, I04, I06, I08 and I10, as well as the concentration of Pb in I04, indicating that adverse biological effects occasionally occur, classified as "Intermediate". And, the concentrations of Ni and Zn were higher than the ERM at point I04, they are probably very toxic and classified as “Weak”.

For quality, Conama 454 (2012), which states the chemical characterization of the material to be dredged, was used and its chemical classification was carried out in order to assess the degree of contamination of river sediments. Classified as Level 1 (threshold below which a low probability of adverse effects on the biota is predicted) and Level 2 (threshold above which a probable adverse effect on the biota is predicted). As, Cr and Pb presented higher concentrations than Level 1 and lower than Level 2, at points I01 and I08; I04 and I10; and I04, respectively. Indicating, an intermediate probability of adverse effects to the biota. Cu had concentrations between levels 1 and 2, for points I06, I08 and I10; and higher than level 2 at point I04, presenting an intermediate and likely probability, with an adverse effect on the biota. Ni and Zn demonstrated concentrations above level 2 at the I04 point, with a probable adverse effect on the biota.

The comparisons of toxicity and quality of the sediment samples, indicated the toxicity for Cu, Pb, Ni and Zn in which some adverse effects on the biota are expected, in the points that are between ERL and ERM and/or above the ERM, according to USEPA (1998). And the quality according to Conama 454 (2012), recommends a probable adverse effect on the biota for values above threshold 2, and all at point I04 (Cu, Ni and Zn). It is important to note that the Zn and Ni elements had their values above level 2 and ERM and also at point I04.

3.4 ENRICHMENT FACTOR (EF)

To obtain the enrichment factor (EF), the global Shales concentration proposed by Turekian and Wedepohl (1961) and the content of the Upper Continental Crust (UCC) proposed by Rudnick and Gao (2014) were used as a reference (geochemical background). For both, the normalizing element was Aluminum (Al).

When comparing with the background Shales (TUREKIAN AND WEDEPOHL 1961), of all the elements studied (26), the Zr, Na and K, presented the EF <1 (11.5%) (without enrichment) in all analyzed points. That is, in at least one point there was enrichment, even if low, referring to 23 (88.5%) chemical elements. All 14 analyzed points exhibited values of EF>1, followed by the number of enriched elements per sampling point, 16(I01), 19(I02), 16(I03), 20(I04), 20(I05), 22(I06), 12(I07), 23(I08), 23(I09), 23(I10), 22(I11), 22(I12), 22(I13) and 21(I14). And the elements Be, Fe, La, Mn, Mo, P, Pb, Th, Y and Zn are enriched at all sample points. And with emphasis on heterogeneity and high EF values for As with low (1.1) to severe (11.4) enrichment; the Ba from low (1.8) to moderate (3.6); the Cu from low (1.3) to severe (18.2); the Fe from low (1.7) to moderate (4.6); the La from low (2.8) to moderately severe (5.1); the Mn from low (1.1) to moderate (3.7); the Mo from low (1.1) to moderately severe (6.0); P from moderate (3.1) to severe (26.1); Pb from moderately severe (5.1) to severe (16.7); the Th from low (1.6) to severe (10.0); the Y from low (1.7) to moderate (4.2); and Zn from low (2.7) to severe (24.6) (figure 4). Cr showed 11 sample points enrichment, 10 with low enrichment and 1 with moderately severe enrichment (8.4). In addition, the point with the least enrichment for all elements was I07, with 12 enriched elements, from low (1.1) to moderately severe (8.5).

The area of the present study showed an exaggerated enrichment of elements, being metals and non-metals, in all analyzed points and with different classifications, corroborating with heterogeneity verified by the coefficient of variation (figure 3). For Régis et al. (2018), in a study to assess the quality of sediments in the Capibaribe River Estuary (Brazil), stated that synergy between contaminants may also have increased toxicity. This fact can be accentuated in this work, due to the number of enriched elements and also because there is a concentration of metals between ERL and ERM and above ERM (USEPA 1998), with adverse biological effects and probably very toxic, respectively. And quality, according to Conama (2012), indicates a probable adverse effect on the biota (Figure 3). The enrichment of the elements is worrying, and even more so in sediments, as these are fundamental to the aquatic ecosystem, and in the view Islam et al (2020) sustain biodiversity, provide a habitat for many benthic organisms and play an important role in maintaining quality of the aquatic environment.

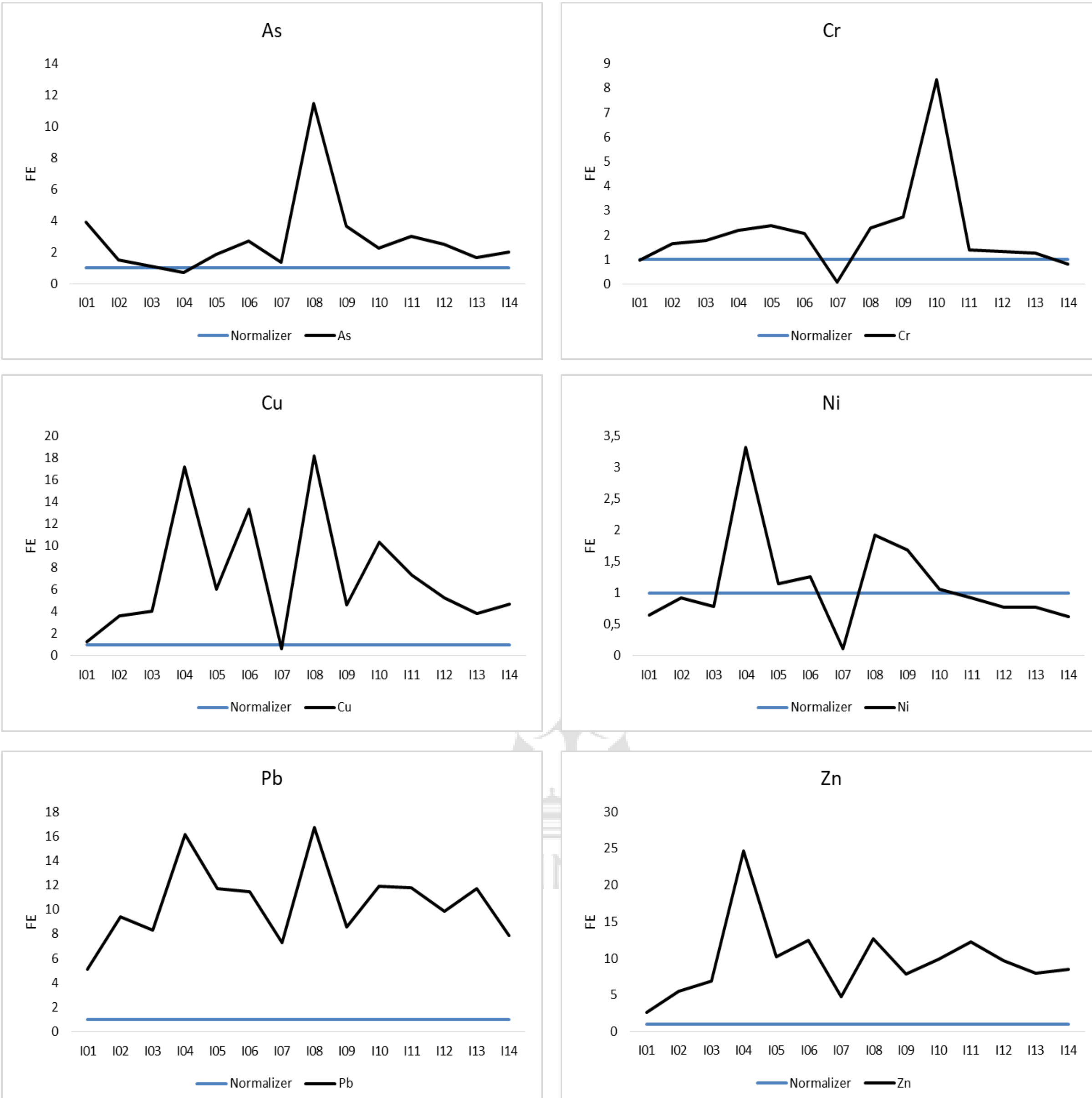

Figure 4: Enrichment factors for toxic metals in the Ipojuca River. With the normalizing element aluminum and the background, according to Turekian and Wedepohl (1961) in Shales

Note: Values under or over the blue line indicate no enrichment; values above indicate enrichment.

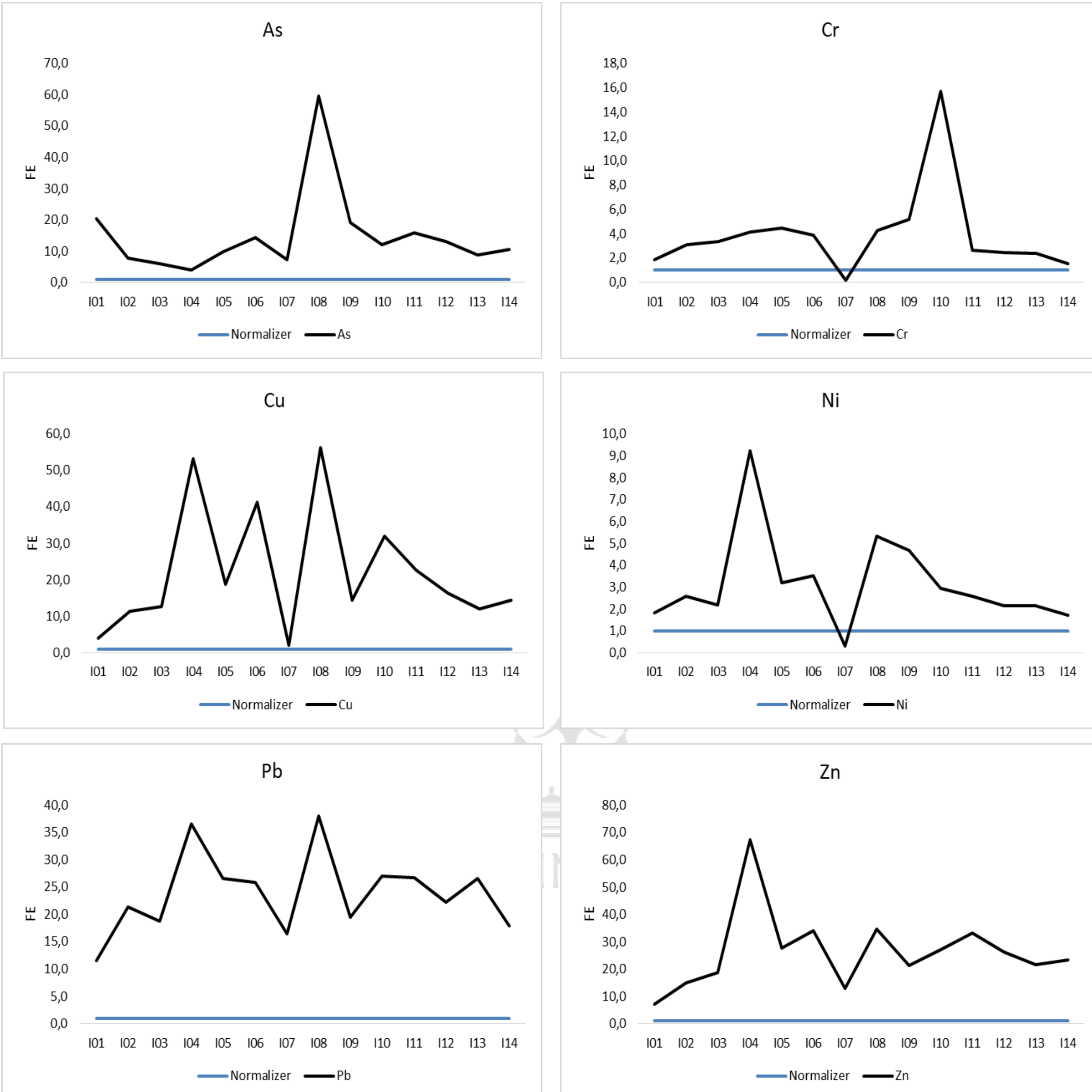

Figure 5: Enrichment factors for toxic metals in the Ipojuca River. With the normalizing element aluminum and the background according to Rudnick and Gao (2014) for the content of the upper continental crust (UCC).

Note: Values under or over the blue line indicate no enrichment, so values above indicate enrichment.

When comparing with the UCC background (RUDNICK AND GAO 2014), of all the elements studied (26), the Zr and Na, presented the EF <1 (7.7%) (without enrichment) in all analyzed points. That is, for this background reference, 24 elements showed some type of enrichment. All

14 analyzed points had enriched elements, EF>1, and higher when compared to Shales, that is: 20 elements (I01 sample point), 24(I02), 22(I03), 22(I04), 24(I05), 24(I06), 20(I07), 24(I08), 24(I09), 24(I10), 24(I11), 24(I12), 24(I13) and 24(I14).

The elements As, Ba, Be, Co, Cu, Fe, La, Li, Mn, Mo, P, Pb, Sc, Th, V, Y and Zn (17) showed enrichment, FE >1, at all sampling points. From low enrichment (example Co, EF=1.2) to extremely severe (Zn, EF=67.3), (figure 6). The FE calculated with the UCC background compared to the Shales, it is possible to verify a greater expressiveness in the enrichment of the elements and, also, a greater number of enriched elements per sampling point. The heterogeneity of EF by element in the sample course was also observed. Among them, As with moderate enrichment (3.9) to extremely severe (59.7); the Ba from low (1.6) to moderately severe (6.4); the Be from moderate (3.3) to moderately severe (8.7); the Cr from low (1.9) to severe (15.7); Cu from moderate (2.0) to extremely severe (56.3); the La with severe (15.8) to very severe (28.9) enrichment; o Li from moderate (2.9) to severe (11.3); the Mn from low (1.9) to moderately severe (6.0); the Mo from moderately severe (5.2) to severe (27.5); low (1.8) to moderately severe (9.2) Ni; P from low (2.8) to severe (23.4); Pb from severe (11.5) to very severe (37.5); the Th from moderate (3.6) to severe (21.9); and Zn from moderately severe (7.3) to extremely severe (67.3).

The sampling points with the lowest number of enriched elements were I01 and I07, with 20 enriched elements. Points I03 and I04 presented 22 enriched elements. And the rest, they were left with 24 enriched elements. It is important to report that at all sampling points, at least 4 elements had EF >10.

3.5 CHEMOMETRIC ANALYSIS

3.5.1 Multivariate analysis of concentration

Principal Component Analysis (PCA) of the concentration values of the 27 metals and non-metals, at the 14 sampling points, were used for exploratory analysis. Of the 27 main components generated, the first two, PC1 (63%) and PC2 (13%), explained 79% of the variance, as shown in figure 6.

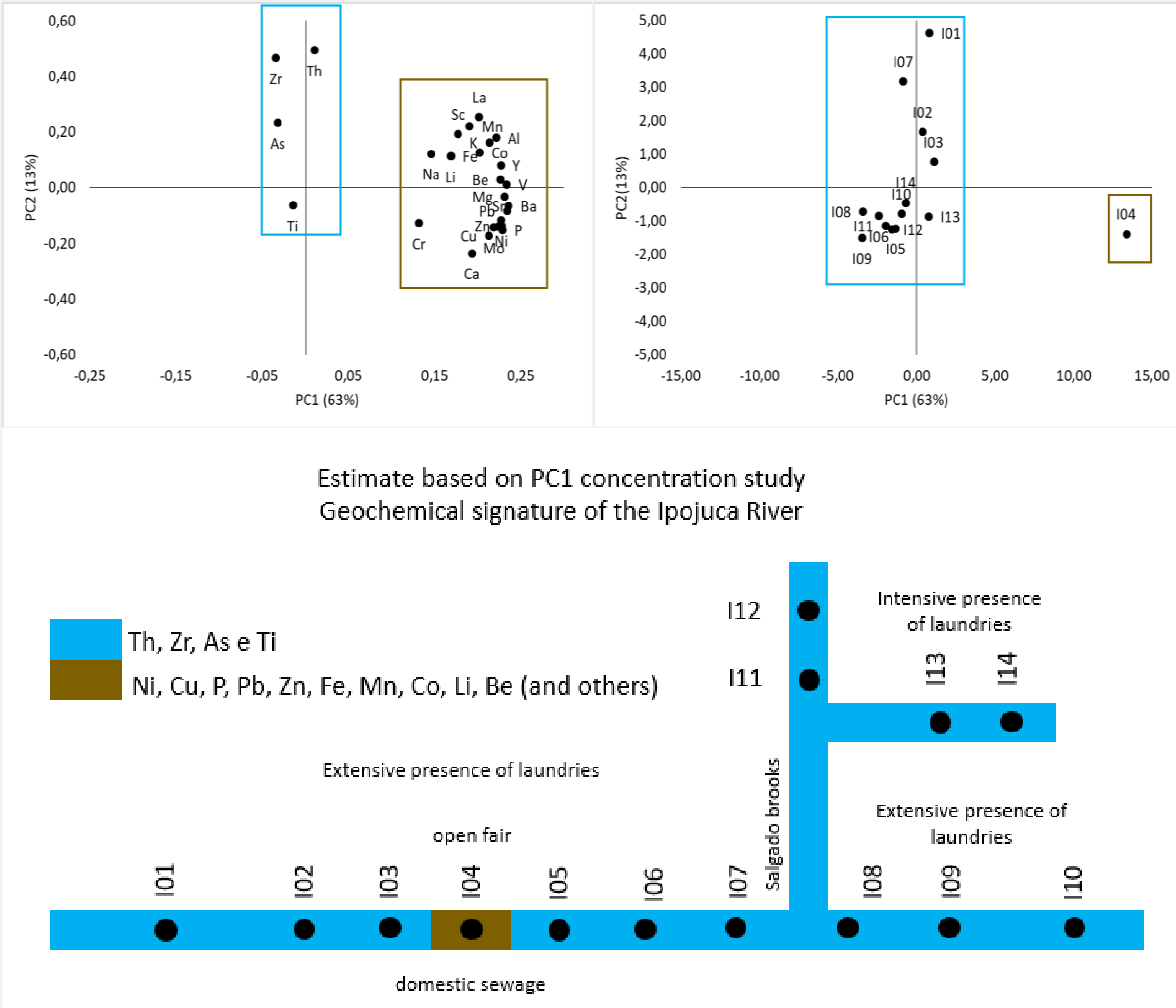

Figure 6: Top, principal component analysis, PC1vsPC2, scores (left) and loadings (right), with PC1 interpretation of concentration (of the 27 elements studied). Bottom, estimate of the geochemical signature of the Ipojuca River, based on analysis of the first principal component of the raw data.

It is possible to notice the formation of two groups according to the first principal component (PC1), highlighted in light blue and gold colors, with the associated elements Zr, Th, As, Ti; and Al, Ba, Be, Ca, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sc, Sr, V, Y and Zn, respectively. The second group was entirely associated with the sampling point I04, evidenced by the participatory portion of contamination from domestic sewage. It also suggests that the sediments have a more clayey characteristic (fine sediments), consequently more absorptive at that point.

The PC2 brought the information that the points I01 and I07 move away from the others, which may indicate a lower influence of contaminant inputs in these locations. Contrary to point I04.

3.5.2 Multivariate analysis of the enrichment factor

The principal component analysis (PCA) of the calculated values for the enrichment factor (EF) of 26 elements analyzed in the 14 sample points obtained was based on the Turekian and Wedepohl (1961) background (it was found that there would be no significant change in the results, if the EF obtained through the reference of Rudnick and Gao (2014) was used). Thus, of the 26 PCs generated, 3 were collected and the cumulative contribution was 66%, that is, it can explain approximately ¾ of the data, with only three components. See figure 7.

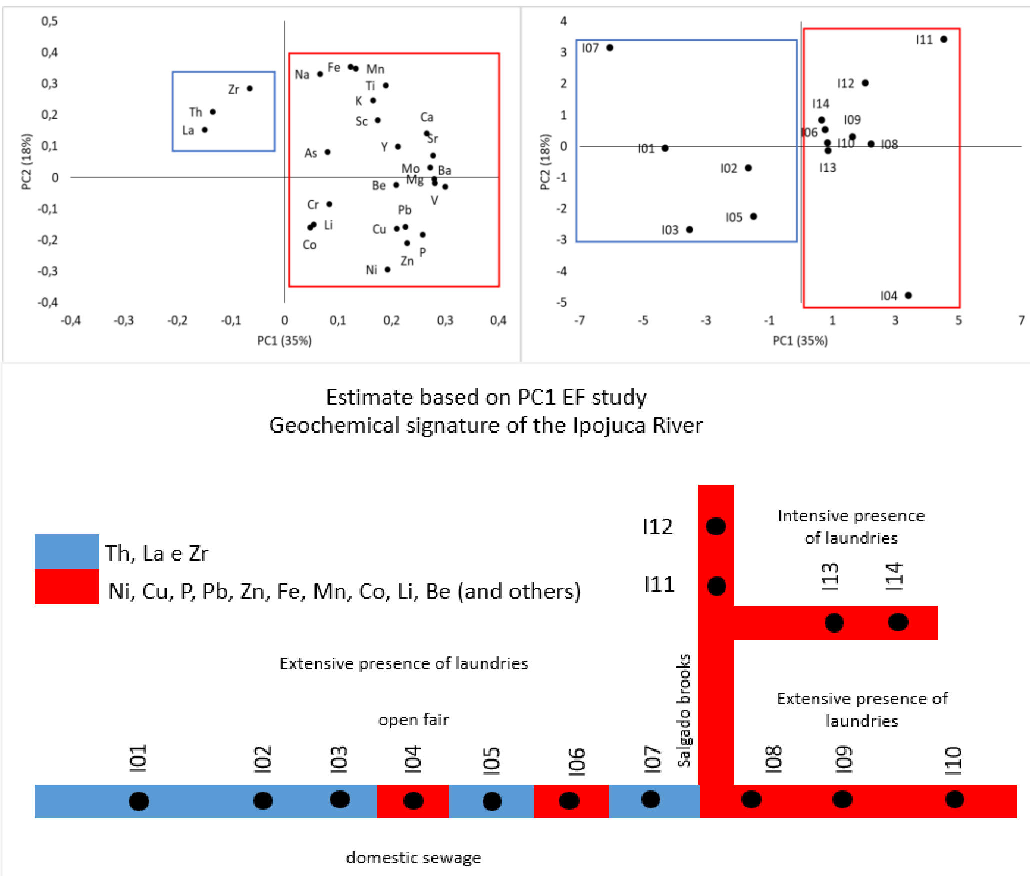

Figure 7: Top, principal components analysis, PC1vsPC2, scores (left) and loadings (right), with PC1 interpretation. Of the enrichment factors (EF) of 26 elements analyzed in the 14 sampling points of the Ipojuca River. Lower, the estimate of the geochemical signature of the Ipojuca

River, based on the analysis of the first principal component of the enrichment factors of the 26 elements.

The study of PC1 orthogonal to PC2 (figure 7) showed the formation of two distinct groups. The group evidenced by the dark blue color, formed by the sampling points (I01, I02, I03, I05 and I07) and with the elements (Th, La and Zr), on the negative axis of PC1; and the red group for sample points (I04, I06, I08, I09, I10, I11, I12, I13 and I14) and in elements (As, Ba, Be, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sc, Sr, Ti, V, Y and Zn) on the positive axis PC1. These two groups are well defined in terms of the enriched elements and also the sampling points. Which is to say that there is a correlation between some elements and the sampling point. Following the reasoning, the positive axis group of PC1 comprises 88% of the elements studied and, therefore, carries a totally different characteristic from the negative axis group with specific collection points (figure 1) and, still, with more representation because they are in the positive axis of PC1. It is important to emphasize that the elements of this group are mainly associated with sample points I09, I10, I11, I12, I13 and I14, accentuated in points I11, I13 and I14, which are in a geographical arrangement with a strong presence of companies in the sector textile (laundries). Still, it is possible to notice two zones of differentiation, points I04 and I11, in which the first point has an aggravation that is disposal without treatment of domestic sewage. For Islam et al (2020), in general, elements that belong to a group or the same main component and present significantly positive correlations, in the multivariate statistical analysis, probably indicate similar sources or origins (that is, the same effluent, industry or by-product of an organic compost). And based on the groups formed, two geochemical behaviors were noted in the study area, as shown in Figure 7.

When analyzing PC2, three groups are formed (positive, intermediate and negative bands), highlighted in different colors as shown in Figure 8, and it demonstrates the distribution of sample points correlated with the elements in the studied stretch. The level of heterogeneity can be seen, due to the magnitude and direction of the coefficients, printed prominently in points I04, I07 and I11. Although the collection sites I07 and I11 participate in the positive axis of PC2, the distance between them and the opposition indicates that the concentration of the chemical composition is different.

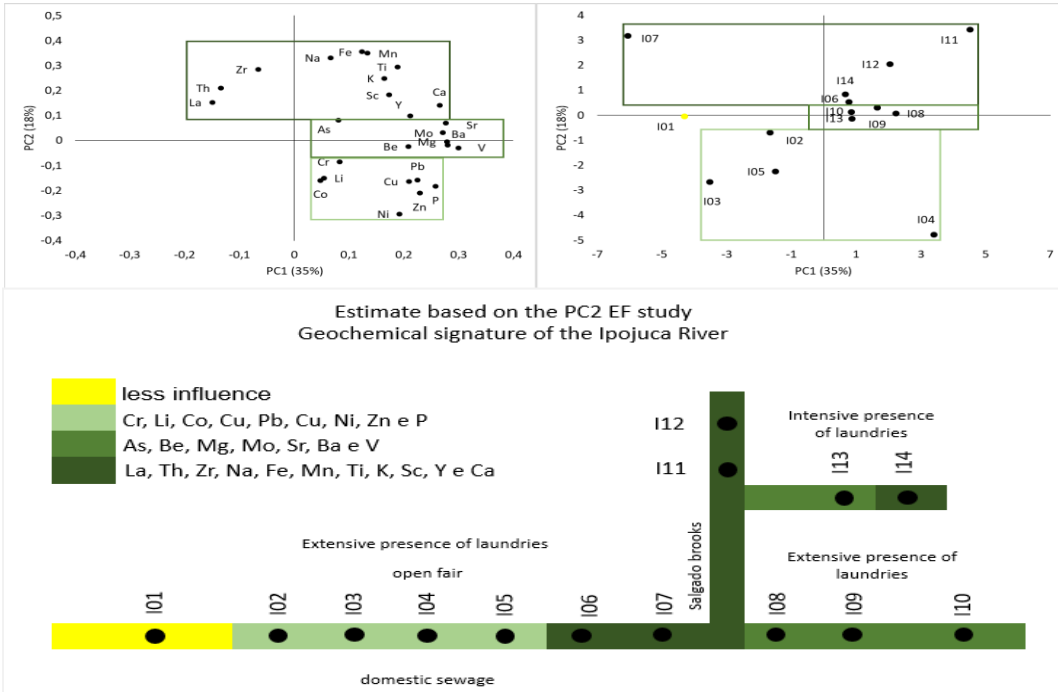

Figure 8: Top, principal components analysis, PC1vsPC2, scores (left) and loadings (right), with PC2 interpretation. Of the enrichment factors (EF) of 26 elements analyzed in the 14 sampling points of the Ipojuca River. Lower, estimate of the geochemical signature of the Ipojuca River, based on the analysis of the second principal component of the enrichment factors of the 26 elements.

Point I04 indicates a different characteristic from I07 and I11, but it is more similar to point I11. And both share textile industries in their vicinity. It is worth mentioning and repeating that this sampling point is associated with the elements Ni, Zn, P, Cu and Pb. With the exception of P, the toxicity and quality of the sediments indicated an intermediate and/or likely probability of some adverse effect on the biota. (USEPA 1998; CONAMA 454 2012). Furthermore, it suggests how harmful human action can be to surface waters, as it is a place with direct discharge of domestic sewage (without preliminary treatment) and close to the commercial pole/free market in Caruaru.

In addition to that, it is possible to notice a brief association at point I07 (point without direct influence of textile companies) with La, Th and Zr, making it possible that these elements originate mainly from natural sedimentary processes in the studied region. And the point I01 was the one that presented the least anthropic interference. And based on the groups formed, three geochemical behaviors were noted in the study area.

The configuration of the principal component analysis with PC1 orthogonal to PC3 (figure 9), with interpretation of PC3, strengthened the confirmation of the association of point I07 with the elements Th, La and Zr. This sampling point is located in the central range of the analyzed extension. However, it does not present companies in the textile sector in its proximity. It was also noted that the sites I02, I03 and I05 carry a feature closer to the points I09, I11, I12, I13 and I14 with lower intensity, and without the direct influence of domestic sewage disposal.

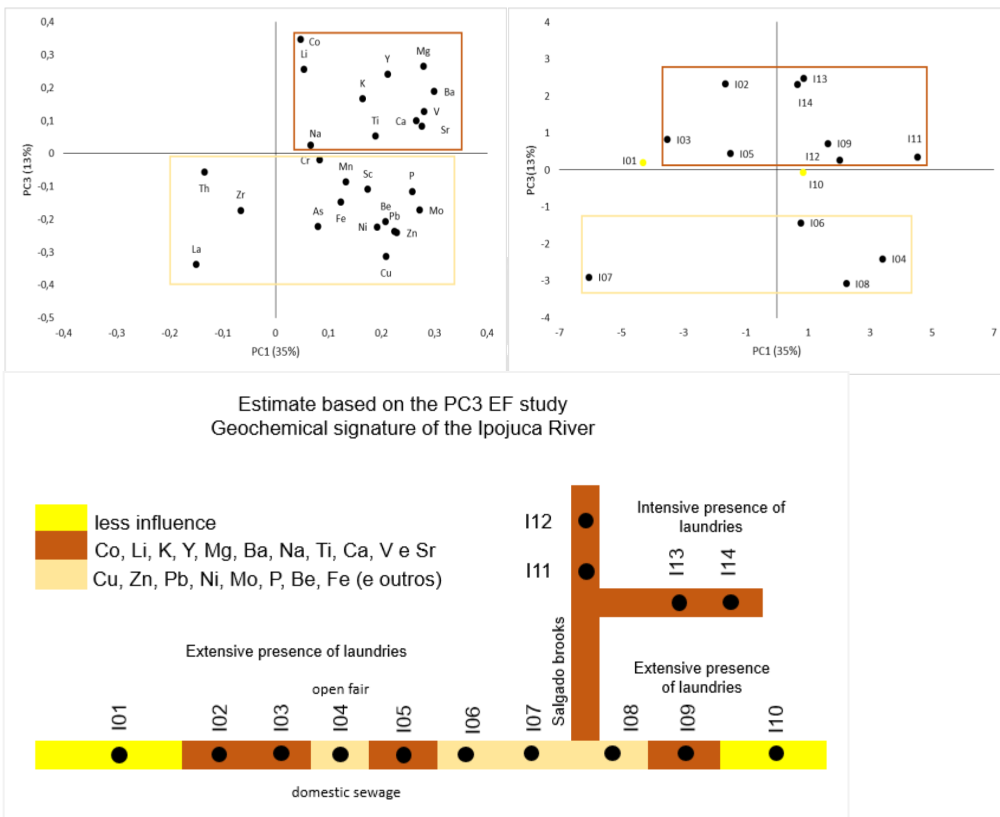

Figure 9: Top, principal components analysis, PC1vsPC3, scores (left) and loadings (right), with PC3 interpretation. Of the enrichment factors (EF) of 26 elements analyzed in the 14 sampling points of the Ipojuca River. Lower, estimate of the geochemical signature of the Rio Ipojuca, based on the analysis of the third principal component of the enrichment factors of the 26 elements.

As can be seen, the intensity of contaminating elements present in the study region increases in the same proportion of intensification of laundries and also, with greater contact with urban areas. In accordance with this, points I01 (upstream) and I10 (downstream), which are the extremes of the analyzed fraction of the river and further away from direct human action and without close contact with laundries, have lower levels of contamination. For Saraiva et al (2009), the development of industrial, commercial and/or agricultural activities in a non-sustainable way contributes to the contamination of surface and underground water resources as a result of the release of tailings. It is important to stress that the comparative values of toxicology and quality indicated that Cu, Pb, Ni and Zn can cause some adverse effects on the biota. (USEPA 1998; CONAMA 454, 2012).

It was found with the ACPs the existence of different chemical elements with different concentrations when traveling along the analyzed section of the Ipojuca River and with a strong influence of the number of laundries in the vicinity of the river. The proportion of elements with altered concentration (based on world references proposed by Turekian and Wedepohl (1961) and Rudnick and Gao (2014)), enriched from moderate to severe and that may cause some adverse effect on the biota (USEPA 1998), in the Ipojuca River in the stretch of the city of Caruaru, is closely related to the textile/laundry industry. Added to this, for Neamtu et al (2002), the textile industry has a characteristic of its own, which is to use a high amount of water in its processes, generating a high volume of effluents. These generally contain high loads of dissolved salts, surfactants, suspended solids and organic matter, mainly in the form of complex dye molecules. In the same sense, Ghaly et al (2014) state that textile effluents are rich in dyes and various chemicals, some are non-biodegradable and carcinogenic, representing a major threat to health and the environment if not properly treated.

4. CONCLUSIONS

The Ipojuca River is of great importance for the state of Pernambuco, firstly because of its length and secondly because part of its course is close to the cities. However, it was possible to check and verify that the proximity to the cities harms the river and its surface waters, as evaluated in the studied stretch in the municipality of Caruaru and with the comparison to international studies. Contamination is an undeniable fact, in view of the altered concentration values when compared to the world average, elements with moderate to extremely severe enrichment factor, with probable toxicity to the biota and the combination of toxic elements in the medium, Cu, Pb, Zn, P and Ni.

Chemometrics, specifically with principal component analysis, allowed relating and grouping the elements with the most representative enrichment factors and associating them with two sources of contamination, textile effluents and domestic sewage. And the level of degradation observed in the geochemical signature is accentuated with the increase in the density of laundries in the vicinity of Rio. In addition, the contamination caused by untreated textile effluent brings an additional alert, due to its complexity in its composition and the formation of by-products, such as nitrogen compounds, sulfonates and metals. And, it suggests that the trace metals Cu, Pb and Zn are associated with the source of contamination from textile effluents. And, P and Ni levels were raised by the disposal of domestic sewage, which is an enhancer of contaminants in sediments.

Finally, further studies are needed to better understand the environmental disturbance. It is essential that environmental authorities and executive and legislative public bodies exercise strict supervision and prioritize the studied stretch of the Ipojuca River, starting at points I04 and I11. It is important that academic institutions continue their studies and research, so that side by side with the competent bodies they can interrupt and/or reverse the situation of environmental disturbance of the Ipojuca River.

FINANCING:

This research has not received any specific grants from funding agencies in the public, commercial, or not-for-profit sectors.

REFERENCES

1. ADDO-BEDIAKO, A., NUKERI, S. & KEKANA, M. (2021) Heavy metal and metalloid contamination in the sediments of the Spekboom River, South Africa. **Applied Water Science**, 11, 133 (2021). https://doi.org/10.1007/s13201-021-01464-8

2. ANA, **National Water Agency. Brazil has about 12% of the world's fresh water reserves on the planet.** Brasilia, 03/15/2019. Available at: <https://www.ana.gov.br/noticias-antigas/brasil-tem-cerca-de-12-das-reservas-mundiais-de-a.2019-03-15.1088913117> Last accessed28 /02/2021.

3. ANVISA (2003). **National Health Surveillance Agency**. Resolution RE No. 899, of May 29, 2003.

4. ANVISA (2017). **National Health Surveillance Agency**. Resolution RDC No. 166, of July 24, 2017.
5. APAC, Pernambuco Water and Climate Agency. **Hydrographic basins – Ipojuca River**. 2021 Available at: < http://200.238.107.184/bacias-hidrograficas/40-bacias-hidrograficas/196-bacia-do-rio-ipojuca > Last accessed 02/28/2021.
6. BALTAS, H., SIRIN, M., GÖKBAYRAK, E., OZCELIK, A. E., (2019) A case study on pollution and a human health risk assessment of heavy metals in agricultural soils around Sinop province, Turkey, **Chemosphere**. V. 241, February 2020, 125015. https://doi.org/10.1016/j.chemosphere.2019.125015
7. BIRCH, GAVIN & OLMOS, MARCO. (2008). Sediment-bound heavy metals as indicators of human influence and biological risk in coastal water bodies. **ICES Journal of Marine Science**, Volume 65, Issue 8, November 2008, Pages 1407–1413. https://doi.org/10.1093/icesjms/fsn139
8. CARACO, N. F.. Disturbance of the phosphorus cycle: A case of indirect effects of human activity. 1993. **Trends in Ecology & Evolution.** V. 8, Issue 2, February 1993, Pages 51-54. https://doi.org/10.1016/0169-5347(93)90158-L
9. CASTRO, C. N.. **Water management: international and Brazilian experiences. Texts for discussion**, n. 1477. Brasília: IPEA, 2012
10. CHEN, C. W., KAO, C. M., CHEN, C. F., DONG, C. D., (2007) Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. **Chemosphere**, Volume 66, Issue 8, January 2007, Pages 1431-1440. https://doi.org/10.1016/j.chemosphere.2006.09.030
11. CHEN, D.; MINPENG, HU,; WANG, J.; GUO, Y.; DAHLGREN, RA Factors controlling phosphorus export from agricultural/forest and residential systems to rivers in eastern China, 1980–2011. **Journal of Hydrology**, Volume 533, February 2016, Pages 53-61. http://dx.doi.org/10.1016/j.jhydrol.2015.11.043
12. CONDEPE, PERNAMBUCO STATE PLANNING AND RESEARCH AGENCY. (2011) **Pernambuco Hydrographic Basins: regional study of structuring actions in the water planning unit of the Ipojuca River**. Condepe/Fidem: Recife. P. 39-43, 2011.
13. CONRAD, S. R., SANTOS, I. R., WHITE, S., & SANDERS, C. J.. (2019). Nutrient and Trace Metal Fluxes into Estuarine Sediments Linked to Historical and Expanding Agricultural Activity (Hearnes Lake, Australia). **Estuaries and Coasts,** 42(4), 944-957. https://doi.org/10.1007/s12237-019-00541-1
14. NATIONAL ENVIRONMENT COUNCIL (CONAMA). (2012). **Resolution No. 454 : Establishes general guidelines and reference procedures for the management of material to be dredged in waters under national jurisdiction.** Official Federal Gazette, Conama, 2012.
15. FIGUEIREDO, C., RAIMUNDO, J., LOPES, A. R., LOPES, C., ROSA, N., BRITO, P., DINIZ, M., CAETANO, M., GRILO, T. F. (2020). Warming enhances lanthanum accumulation and toxicity promoting cellular damage in glass cells (Anguilla anguilla). **Environmental Research.** V. 191, December 2020.110051. https://doi.org/10.1016/j.envres.2020.110051
16. FREITAS, A. A. DE,. (2008) **Recovery of thorium and rare earths via peroxide from the residue originated in the thorium purification unit** . 2008, p. 84. Dissertation (Master of Science in the Area of Nuclear Technology – Materials) - Institute of Energy and Nuclear Research, University of São Paulo, São Paulo, 2008.
17. GABRIEL, F. Â.. **Study of geochemical and environmental monitoring of water and sediment quality in the lower course of the Rio Doce, Espírito Santo, Brazil.** 2017, p. 216. Dissertation (Master's in Environmental Engineering) - Federal Rural University of Pernambuco, Recife, 2017.
18. GHALY, A. E., ANANTHASHANKAR, R., ALHATTAB, M., RAMAKRISHNA, V. V. (2014) Production, characterization and treatment of textile effluents: a critical review. J **Chem Eng Process Technol**, v. 5, no. 1, p. 1-19, 2014. ISSN: 2157-7048. https://doi.org/10.4172/2157-7048.1000182
19. ISLAM, M. A; DAS, B.; QURAISHIC, S. B.; KHANA, R.; NAHERA, K; AND ET. AL. (2020) Heavy metal contamination and ecological risk assessment in water and sediments of the Halda river, Bangladesh: A natural fish breeding ground. **Marine Pollution Bulletin**. 160, 111649. 2020. https://doi.org/10.1016/j.marpolbul.2020.111649
20. ISLAM, M. A., HOSSAIN, M. B., MATIN, A., ISLAM SARKER, M. S.. (2018) Assessment of heavy metal pollution, distribution and source apportionment in the sediment from Feni River estuary, Bangladesh, **Chemosphere** (2018). https://doi.org/10.1016/j.chemosphere.2018.03.077

21. JAIN, C. K., MALIK, D. S. & YADAV, R. (2007) Metal Fractionation Study on Bed Sediments of Lake Nainital, Uttaranchal, India. **Environ Monit Assess.** 130, 129–139. https://doi.org/10.1007/s10661-006-9383-6

22. KE, X., GUI, S., HUANG, H., ZHANG, H., WANG, C., GUO, W., (2017) Ecological risk assessment and source identification for heavy metals in surface sediment from the Liaohe River protected area, China, **Chemosphere**. V. 175, May 2017, 473-481. https://doi.org/10.1016/j.chemosphere.2017.02.029

23. LE GALL, M., AYRAULT, S., EVRARD, O., LACEBY, J. P., GATEUILLE, D., LEFÈVRE, I., MOUCHEL, J. M. AND MEYBECK, M. (2018) Investigating the metal contamination of contamination sediment transported by the 2016 Seine River flood (Paris, France). **Environmental Pollution**. V 240, September 2018, 125-139. https://doi.org/10.1016/j.envpol.2018.04.082

24. LIU, Q., SHENG, Y., JIANG, M., ZHAO, G., LI, C., (2020). Attempt of basin-scale sediment quality standard establishment for heavy metals in coastal rivers. **Chemosphere** 245, 125596. https://doi.org/10.1016/j.chemosphere.2019.125596

25. LIU, Q., SHENG, Y., JIANG, M., ZHAO, G., LI, C., 2020. Attempt of basin-scale sediment quality standard establishment for heavy metals in coastal rivers. **Chemosphere**, V. 245, 125596. ISSN 0045-6535. https://doi.org/10.1016/j.chemosphere.2019.125596

26. LONG, E. R., MACDONALD, D. D., SMITH, S. L., CALDER, F. D.. Incidence of adverse biological effects within ranges of Chemical concentrations in marine and estuarine sediments. **Environmental management**, vol. 19, no. 1, p. 81-97, 1995. https://doi.org/10.1007/BF02472006

27. LONG, E. R.; FIELD, L. J.; MACDONALD, D. D. Predicting toxicity in marine sediments with numerical sediment quality guidelines. **Environmental Toxicology and Chemistry**, v. 17, no. 4, p. 714-727, 1998. https://doi.org/10.1002/etc.5620170428

28. MALLIN, M. A.; CAHOON, L. B.. The Hidden Impacts of Phosphorus Pollution to Streams and **Rivers. BioScience** (2020), V.70, Issue 4, April 2020, Pages 315–329. https://doi.org/10.1093/biosci/biaa001

29. MAO, L., LIU, L., YAN, N., LI, F., TAO, H., YE, H., WEN, H., Factors controlling the accumulation and ecological risk of trace metal (loid)s in river sediments in agricultural field. **Chemosphere** (2020). https://doi.org/10.1016/j.chemosphere.2019.125359

30. MARTINEZ, T. C.; FERNÁNDEZ, A. C. R.; CABEZA, J. A. S; BERNAL, L. H. P.; GIL, J. M. S.; (2021) Influence of agricultural system transition on trace element contamination in salt marsh and seagrass sediments from the coastal Ramsar site. **Ecotoxicology and Environmental Safety**. V. 214, May 2021, 112045. https://doi.org/10.1016/j.ecoleng.2021.106194

31. MINARIKOVA, M. B., SMEDES, F., RUSINA, T. P., VRANA, B..(2020) Application of equilibrium passive sampling to profile pore water and accessible concentrations of hydrophobic organic contaminants in Danube sediments. **Environmental Pollution**. 267 (2020) 115470, 2020. https://doi.org/10.1016/j.envpol.2020.115470

32. MORAES, A. S. **Geostatistics applied to environmental geochemistry in the study of the quality of sediments in the Tatuoca River, industrial port complex in Suape**. 2009, p. 73. Dissertation (Master in Geosciences) - Federal University of Pernambuco, Recife, 2009.

33. MORAES, G. M. de. **Distribution of heavy metals in bottom sediments in the upper Tietê basin: enrichment factors and pollution classes.** 2011, p. 158. Dissertation (Master of Science) - University of São Paulo, Piracicaba, 2011.

34. MOREIRA, L. B., CASTRO, I. B., FILLMANN, G., PERES, T. F., BELMINO, I. K. C, SASAKI, S. T., TANIGUCHI, S., BICEGO, M. C., MARINS, R. V., LACERDA, L. D. de, LOTUFO, L. V. C., ABESSA, S. D. M. (2021) Dredging impacts on the toxicity and development of sediment quality values in a semi-arid region (Ceará state, NE Brazil). **Environmental Research**. V. 193, February 2021, 110525. https://doi.org/10.1016/j.chemosphere.2017.11.023

35. NASCIMENTO, L. P., REIS, D. A., ROESER, H. M. P., SANTIAGO, A. DA F. (2018) Geochemical evaluation of metals in river systems affected by human activities in the Iron Quadrangle. **Sanitary and Environmental Engineering.** 2018, v. 23, no. 04. ISSN 1809-4457. https://doi.org/10.1590/S1413-41522018165852

36. NEAMTU, M., SIMINICEANU, I., YEDILER, A., KETTRUP, A. (2002). Kinetics of decolorization and mineralization of reactive azo dyes in aqueous solution by the UV/H2 O2 oxidation. **Dyes and Pigments**, v. 53, p. 93-99, 2002. ISSN 0143-7208. https://doi.org/10.1016/S0143-7208(02)00012-8

37. OLIVEIRA, A. F, B. DE, GOMES, B. R. S., FRANÇA, R. S., MORAES, A. S.., BATAGLION, G. A., SANTOS, J. M. (2021) Assessment of Urban Contamination by Sewage in Sediments from Ipojuca River in Caruaru City, Pernambuco, Brazil. **J. Braz. Chem. Soc** ., Vol. 00, No. 00, 1-10, 2021. https://dx.doi.org/10.21577/0103-5053.20210133.

38. ORAL, R., BUSTAMANTE, P., WARNAU, M., D'AMBRA, A., GUIDA, M., PAGANO, G. (2010). Cytogenetic and developmental toxicity of cerium and lanthanum to sea urchin embryos. **Chemosphere**. V. 81, September 2010, pages 194-198. https://doi.org/10.1016/j.chemosphere.2010.06.057

39. RÉGIS, C. G., SOUZA-SANTOS, L. P., YOGUI, G. T., MORAES, A. S., & SCHETTINI, C. A. F. (2018). Use of Tisbe biminiensis nauplii in ecotoxicological tests and geochemical analyzes to assess the sediment quality of a tropical urban estuary in northeastern Brazil. **Marine Pollution Bulletin**, 137, 45–55. https://doi.org/10.1016/j.marpolbul.2018.10.011

40. RUDNICK, R. L. , GAO, S., 2014. Composition of the continental crust . In: Treatise on **Geochemistry**. V. 3, 2003, Pages 1-64. https://doi.org/10.1016/B0-08-043751-6/03016-4

41. SABINO, C. V. S.; LAGE, L. V.; NORONHA, C. V. DE.. (2017) Seasonal and temporal variation of water quality at a point in the Gameleiras Stream using robust chemometric techniques. **Sanitary and Environmental Engineering**. Rio de Janeiro, v. 22, no. 5, p. 969-983, Oct. 2017. http://dx.doi.org/10.1590/s1413-41522017158455.

42. SARAIVA, V. K., BORN, M. R. L. DO, PALMIERI, H. E. L., JACOMINO, V. M. F.. (2009) Sediment quality assessment - case study: Sub-basin of Ribeirão Espírito Santo, tributary of the São Francisco River. **Química Nova**, Vol. 32, No. 8, p. 1995-2002, 2009. https://doi.org/10.1590/S0100-40422009000800003

43. SCHWANTESA, D.; JUNIOR, A. C. G.; MANFRINC, J.; CAMPAGNOLO, M. A.; ZIMMERMANN, J.; JUNIOR, E. C.; AND BERTOLDO, D. C.; Distribution of heavy metals in sediments and their bioaccumulation on benthic macroinvertebrates in a tropical Brazilian watershed. **Ecological Engineering (2021)**. V. 163, 1 May 2021, 106194. https://doi.org/10.1016/j.ecoleng.2021.106194

44. SHI, T. R., MA, J., WU, F. Y., JU, T. N., GONG, Y. W., AND ET. AL..(2019) Mass balance-based inventory of heavy metals inputs to and outputs from agricultural soils in Zhejiang Province, China. **Science of The Total Environment** 649, 1269-1280. https://doi.org/10.1016/j.scitotenv.2018.08.414

45. SILVA, Y. J. A. B. DA S., CANTALICE, J. R.B., NASCIMENTO, C.W. A. DO, SINGH, V. P., AND ET. AL. (2017) Bedload as an indicator of heavy metal contamination in a Brazilian anthropized watershed, **Catena**, V. 153, 2017, Pages 106-113, ISSN 0341-8162. https://doi.org/10.1016/j.catena.2017.02.004

46. SILVA, Y. J. A. B. DA, CANTALICE, J. R. B., SINGH, V.P., NASCIMENTO, C. W. A. DO, WILCOX, B. P., (2019) Heavy metal concentrations and ecological risk assessment of the suspended sediments of a multi-contaminated Brazilian watershed. **Acta Scientiarum. Agronomy**, 41, e42620. Epub March 28, 2019. https://dx.doi.org/10.4025/actasciagron.v41i1.42620

47. SOARES, E. C., BISPO, M. D., VASCONCELOS, V. C., SOLETTI, J. I., AND ET. AL. (2021) Oil impact on the environment and aquatic organisms on the coasts of the states of Alagoas and Sergipe, Brazil - A preliminary evaluation, **Marine Pollution Bulletin**, Volume 171, 2021, 112723, ISSN 0025-326X. https://doi.org/10.1016/j.marpolbul.2021.112723

48. THOMAS, R.; MEYDECK, L. (1996) **The use of particulate material**. IN: CHAPMAN, D. Water Assessments – A guide to use of biota, Sediments an Water in Environmental Monitoring. 2nd ed. UNESCO/WHO/UNEP, 1996. chap. 4, 134-181.

49. USEPA, (1998). **EPA's Contaminated Sediment Management Strategy**. Washington, USEPA, EPA-823-R-98-001.

50. WEDEPOHL, K. H.. The composition of the continental crust. **Geochimica et cosmochimica** Acta, v. 59, no. 7, p. 1217-1232, 1995. https://doi.org/10.1016/0016-7037(95)00038-2