CIÊNCIA e NATURA

UFSM

Ci. e Nat., Santa Maria, v. 42, Esp. Ed.: UNICEUMA, e5, 2020

DOI: 10.5902/2179460X41267

ISSN 2179-460X

Environment

Submitted 03/12/19 Accepted 08/12/19 Published 09/10/20

Evaluation of the quality of superficial sediment using principal components analysis of the physical–chemical attributes of the Mearim River – Brazil

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ABSTRACT

The Mearim River is one of the main rivers of Maranhão, which, over the years, has been affected from pollution caused by human activities such as deforestation, disposal of domestic effluents, and agricultural activities, among others. The objective of this research was to evaluate the environmental quality of the Mearim River through the study of the sediment in different periods. In order to investigate this question, four sampling points (P1- Balneário, P2-Cais, P3-Trizidela, and P4-Matadouro) were submitted to particle size analysis (clay, silt, and fine sand) and physico-chemical analyses (pH, organic matter, and inorganic and organic carbon). Two principal components were generated in principal component analysis, explaining 73% of the total variance among the parameters within the studied periods. The overall analysis of the data set by principal component analysis highlighted two clusters: one relating the attributes to three sampling points analyzed in the rainy season and another relating the attributes to four sampling points analyzed in the dry period. Multivariate analysis of the data showed that the organic matter, clay, and pH parameters were directly correlated with the dry period (correlation coefficients > 0.41), and inorganic matter (correlation coefficient = | 0,414 |) was more sensitive in the rainy season.

Keywords: Sediment; Mearim River; Principal component analysis

1 INTRODUCTION

Sediment can be considered the result of the interaction of all the processes that occur in an aquatic ecosystem (ESTEVES, 2011); it has great importance in the biogeochemical processes of these environments. Studies on sediments in aquatic environments initially focused on lake sediments (lentic environments) and later expanded into rivers (lotic environments) (ESTEVES, 2011). Rivers are the most important

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agent for sedimentary transport and distribution (CHISTOFOLETTI, 1980). This transport produces a continuous process of sedimentation that can cause several changes in the aquatic system and interfere with ecological processes (TUNDISI & TUNDISI, 2008)

Sediments can influence considerably the amount of dissolved substances in the waters of rivers and lakes, this characteristic is the result of the massive interaction of the water with the substrate forming the watershed, which gives the water a very complex chemical nature (TUNDISI & TUNDISI, 2008). Research has shown a strong relationship between the sediment and the water column; studies show that sediment should be considered as an environment of chemical interactions with the water column and the resident biota (SARAIVA, *et al*., 2009).

In river basins subject to human-influence, the sedimentary material present in the riverside differs from that in basins that still have natural characteristics. Deforestation of riparian forests, the construction of dams, and river drainage can directly influence the granulometric characteristics of fluvial sediment, while pollution affects the ionic constitution of the sediment. Sedimentary deposits contain the environmental history of the river basin to discover the environmental history. Deposits do not just present a current record of the geochemical characteristics of the environment, but they are also have an active role in the biogeochemical cycles of the elements (BELÓ; QUINÁIA; PLETSCH, 2010). Another problem lies in activities that promote pollution; these can affect considerably the concentrations of chemical compounds in the aquatic environment and, consequently, affect the quality of the sediments.

Sediments of continental aquatic ecosystems are formed by a great variety of organic and inorganic materials of autochthonous and allochthonous origin (CALLISTO, ESTEVES, 1996). The organic matter associated to the sediments causes modifications that influence the biogeochemical cycles of several elements, determining the way in which they are present (MARTINS *et al*., 2019). For example, the availability of elements is strongly influenced by the concentration of organic matter in aquatic environments (ESTEVES, 2011).

The Mearim River is one of the main rivers in the state of Maranhão, and over the years it has been affected by compaction caused by human activity in its watershed. Deforestation, the release of fresh domestic effluents and agricultural activity seem to be the main activities impacting the chemical makeup of the river's sediment (SEMATUR, 1991).

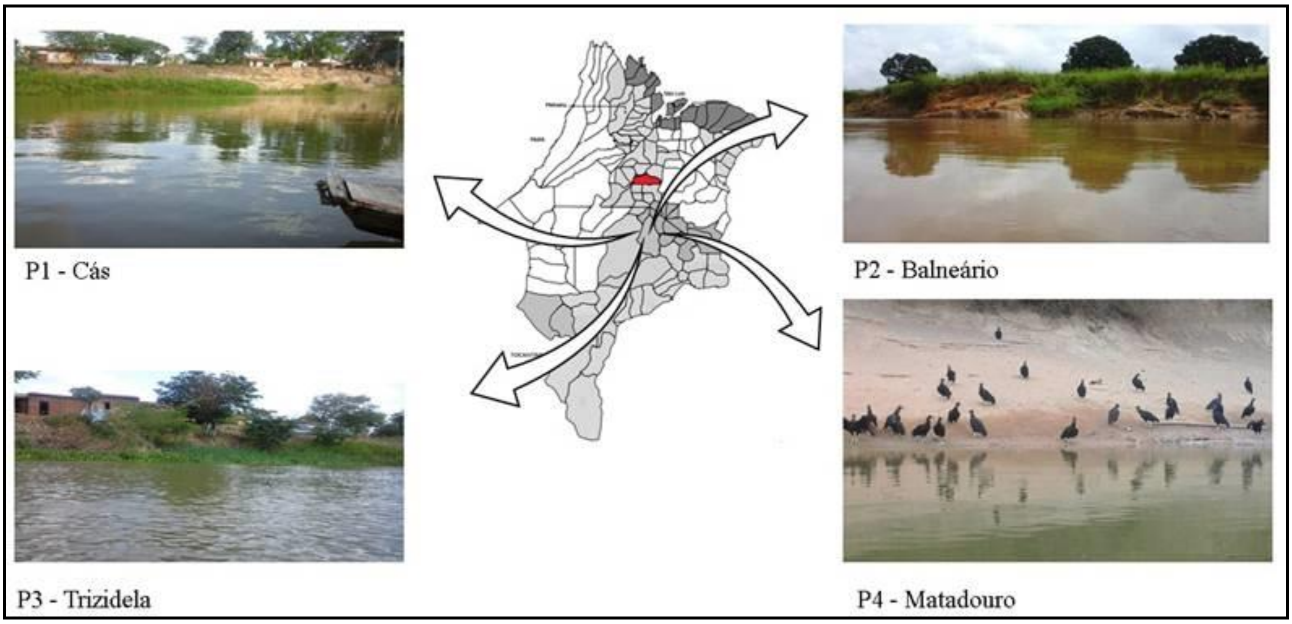
The objective of the present research is to evaluate the environmental quality of the Mearim River, in the municipality of Bacabal, through the sediment study.

2 METHODOLOGY

2.1 Study area

The Mearim River flows through the municipality of Bacabal (Figure 1) for approximately 1,150km^2, between the hydrographic basins of the Mearim and Tocantins rivers, near the city of Amarante (in Maranhão). The river's total length is approximately 686km, and it is navigable in the patch from its outfall at kilometer 41 of the Mearim River to the outfall of the Buriticupu River at kilometer 456 (MACEDO, 2005). The work was carried out in the vicinity of the municipality of Bacabal, predominantly in the part of the city that developed along the riverbank, since anthropic occupation is the main cause of bank erosion banks and silting of the river. However, the Mearim River has been suffering from various problems of silting, flooding, and deforestation. Conservation indexes in this region are low, due to marginal ciliary vegetation.

Figure 1 - Location of sampling points in the city of Bacabal in the State of Maranhão. Source: Authors, 2019



The main economic activity of the region is agriculture and livestock. The soil is characterized as yellow latosol and red yellow podzolic. The vegetation cover is classified as Dense Ombrophylous Forest (ATLAS DO MARANHÃO, 2006). The sediment samples were taken at four representative points along the banks of the Mearim River and named (P1) Balneário, (P2) Cais, (P3) Trizidela, and (P4) Matadouro. Samplings were carried out during the different seasonal periods: dry period (August 2013) and rainy season (November 2013).

2.2 Physical and chemical sediment variables

Sample collection was carried out in backwater areas, where there is a greater accumulation of fine material, with the aid of a 50cm long, 5cm diameter PVC pipe. The material removed was homogenized in a plastic bucket and placed in labeled plastic bags, kept in polystyrene boxes, and transported to the Environmental Sciences Laboratory of CEUMA University for physical and chemical characterization. Granulometric determination of the samples was carried out by means of mechanical processing in a set of sieves in combination with the piping technique (Stocks law), the materials' texture was classified based on the Wentworth (1992) granulometric scale and EMBRAPA (2017). The pH of the sediment was measured in 0.01 mol L^{-1} calcium chloride solution using a multiparameter sensor (HANNA, model HI9828).

Organic carbon analysis was performed by the method described by EMBRAPA (2017). The organic and inorganic content in the sediments was determined using the standard incineration procedure (SILVA and SILVA, 2014). The determination of the clay minerals present in the sediment samples was carried out at the Laboratory of Crystallography of the Institute of Chemistry of São Carlos (IQSC /USP) and in the Institute of Physics of São Carlos (IFSC /USP) using X-ray diffraction (DRX) (MUDROCK and MACKNIGHT, 1994 and SILVA, 2006). It should be emphasized that the results refer only to the qualitative analysis of the minerals, as their quantification was not worked.

2.3 Statistical analysis

Statistical analyses showed similarity among dry-season sampling points and among wet-season sampling points. The analyses were performed using Origin 8.0 and Minitab 17 software. Means and standard deviations were calculated for organic matter content, inorganic matter, organic carbon, pH, clay, silt, and thin sand. The data were evaluated by Analysis of Variance (ANOVA) using the Tukey test at $p < 0.05$ and compared among the sampling points (P1, P2, P3 and P4) and between the studied periods (rainy season and dry season).

For the set of analyses (organic matter, inorganic matter, organic carbon, pH, clay, silt, and thin sand), Principal Component Analysis (PCA) was performed for the mean values of three replicates in order to identify correlations between parameters and the rainy and dry periods (JOHNSON and WICKER, 1998; HONGYU, 2015; SILVA, *et al*., 2019).

3 RESULTS AND DISCUSSION

In view of the data from all analyses, it was possible to observe the variations between periods of dryness and rainfall in the region. Table 1 shows the physico-chemical parameters for the rainy and dry periods.

Table 1 - Organic matter, inorganic matter, organic carbon, and pH in sediment samples during the rainy and dry periods

		Rainy season		
Sampling points	**OM (%)**	**IM (%)**	**OC (%)**	**pH**
P1	7.26 ± 0.24a	92.42 ± 0.89a	6.45 ± 0.34a	6.48 ± 0.07a
P2	7.65 ± 0.39a	92.51 ± 0.55a	6.79 ± 0.25a	6.60 ± 0.01ab
P3	7.55 ± 0.06a	92.10 ± 0.95a	6.49 ± 0.31a	6.62 ± 0.07b
P4	9.51 ± 0.28b	91.26 ± 0.54a	6.82 ± 0.30a	7.22 ± 0.02c
		Dry season		
Sampling points	**OM (%)**	**IM (%)**	**OC (%)**	**pH**
P1	11.03 ± 0.27a	89.75 ± 1.39a	5.97 ± 0.71ab	7.51 ± 0.07a
P2	9.63 ± 0.44bc	90.32 ± 1.17a	5.13 ± 0.30a	6.75 ± 0.06b
P3	8.92 ± 0.12b	91.36 ± 0.57a	6.46 ± 0.33b	6.95 ± 0.05c
P4	9.75 ± 0.15c	90.54 ± 0.48a	6.54 ± 0.41b	7.77 ± 0.08d

Values are mean ± standard deviation (n = 3). OM (Organic Matter), IM (Inorganic Matter), OC (Organic Carbon). Different superscript letters indicate means that significantly differ at $p < 0.05$ (Tukey test).

From the organic and inorganic matter percentages, it was possible to observe a variation between the dry season and rainfall in the region. In August (dry season), values ranging from 8.92% to 11.03% were recorded for organic matter, and values ranging from 89.75% to 91.36% were recorded for inorganic matter. In the rainy season, the values ranged from 7.26% to 9.51% for organic matter and from 91.26% to 92.51% for inorganic matter. Organic matter higher than 10%, characterizing the sediment as organic (ESTEVES, 2011), was observed at only one sampling point.

Organic carbon is important for primary production, food chains, and biological succession. Organic carbon contents above 5% are considered high. In the study area, mean organic carbon percentages ranged from 5.13 and 6.54% in the dry season and from 6.45 to 6.82% in the rainy season. These data can be compared with those observed by Silva (2014) in a study in the Pindaré river in the municipality of Tufilândia-Maranhão. Silva (2014) measured dry season organic carbon values between 6.13 and 6.32%, and rainy season values between 5.15 and 5.99%. This information is significant when comparing environments, since these two rivers are influenced by their geological characteristics, with the Pindaré River the main tributary of the Mearim River (SILVA *et al*., 2017).

The sediment pH measured in the present study varied from 6.75 to 7.77 in the dry season and from 6.48 to 7.22 in the rainy season. The highest value observed for this parameter was in the dry season (7.77), and a close value was also observed in the rainy season (7.22), characterizing a near-alkaline pH in both two studied periods. The sampling points in the study are located in areas of potential contaminants of water and river sediment, including diesel oil spillage, oils from canoes and car washes, household waste, and other chemical substances.

Table 2 shows the results of the granulometric distribution and the qualitative determination of the clay minerals present in the sediment samples at the sample locations.

Table 2 - Granulometric distribution and clay minerals analysis in sediment samples in the rainy and dry seasons

		Rainy season		
Sampling points	**Clay (%)**	**Silt (%)**	**Thin sand (%)**	**Types of clay***
P1	5.10 ± 0.01a	4.89 ± 0.01a	89.93 ± 0.06a	
P2	3.45 ± 0.01b	5.33 ± 0.01b	84.94 ± 0.06b	K, Gb, Q, H
P3	4.61 ± 0.01c	6.33 ± 0.01c	89.06 ± 0.03c	
P4	5.57 ± 0.01d	7.34 ± 0.00d	87.10 ± 0.02d	
		Dry season		
Sampling points	**Clay (%)**	**Silt (%)**	**Thin sand (%)**	**Types of clay ***
P1	7.35 ± 0.04a	6.02 ± 0.02a	86.85 ± 0.12a	
P2	4.88 ± 0.01b	7.64 ± 0.04b	87.52 ± 0.08b	K, Gb, Q, H
P3	5.70 ± 0.10c	9.22 ± 0.01c	88.90 ± 0.13c	
P4	6.88 ± 0.01d	8.95 ± 0.58c	83.57 ± 0.32d	

Values are mean ± standard deviation (n = 3). *(K): kaolinite; (Gb): gibsite; Q: quartz; e (H): hematite. Different superscript letters indicate means that significantly differ at $p < 0.05$ (Tukey test).

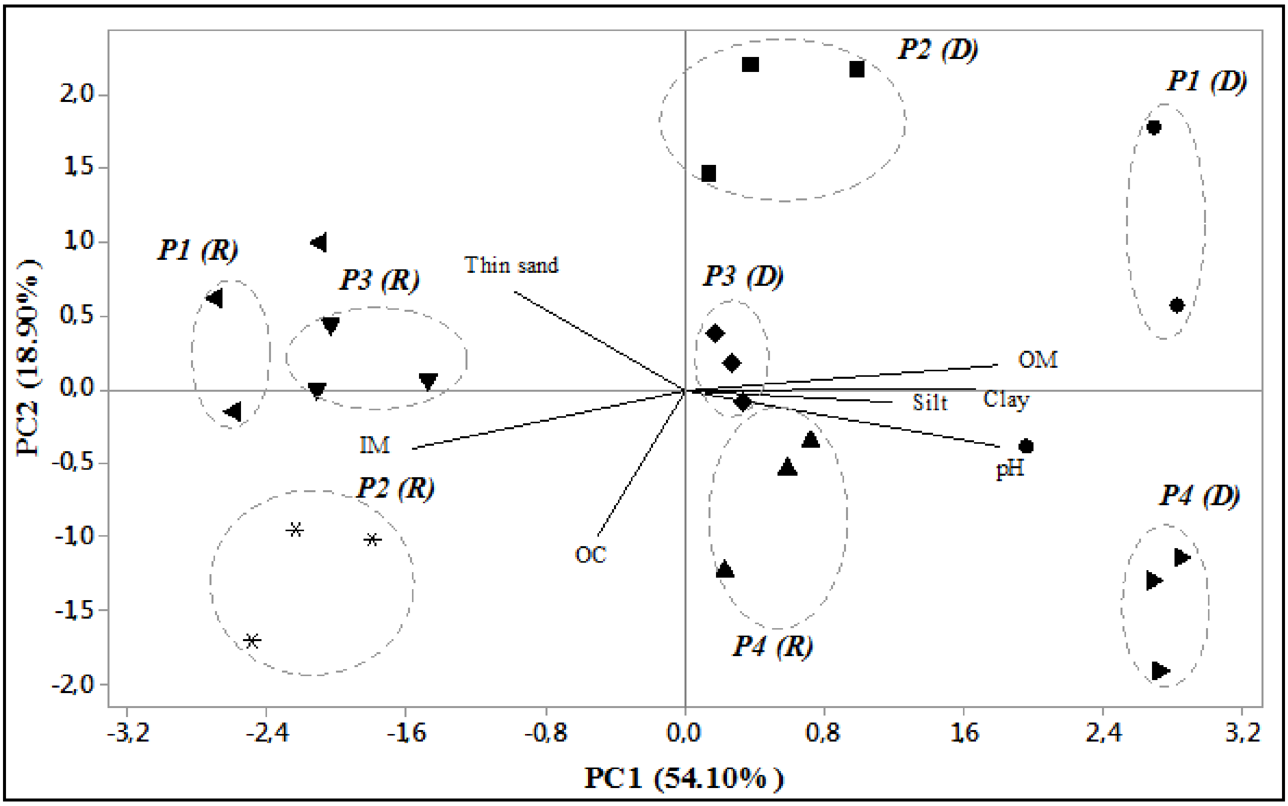
The results of the qualitative analysis of the minerals showed that all points were characterized as kaolinite, gibsite; quartz; and hematite and that there was a spatial and temporal granulometric variation in sediment composition. Greater levels of fine sediment sand were observed in the rainy season (89.93%), while the percentage found in the dry season was 88.90%. Clay and silt contents were higher during the dry period: 7.35% and 9.22%, respectively. The area under study is very sandy, and removal of riparian forests from the river banks provokes silting, further increasing the sand indices in the region.

Comparing the data obtained in this work with those of SILVA, *et al*., (2017), the authors of that study observed clay fractions from 0.01 to 1.55% and silt fractions from 7.00 to 33.35% in the municipality of Pindaré-Mirim. They found that sand content varied from 63.4 and 91.45% in the sediment.

The sediment's granulometric influences its capacity to absorb pollutants. Sediments of sandy composition favor the availability of pollutants to the water column, as opposed to sediments with fine granulation which adsorb pollutants more strongly. Silt and clay, due their large surface area in relation to their volume, have a greater capacity to retain pollutants (BURTON Jr., 2002).

PCA was used to investigate possible correlations between all variables studied and the samples regarding the effects of seasonality (TOSIC *et al*., 2019; XU *et al*., 2019). Initially, a statistical evaluation of the relationships between the seven variables in to the two periods studied was performed based on a matrix of correlated data, in which the variables were standardized. Figure 2 shows the PCA results for the physical–chemical and granulometric characteristics of the sediment in relation to the sampling points and their respective seasons.

Figure 2 – Principal Component Analysis (PCA) of physical–chemical and granulometric characteristics of the sediment. R: rainy season; D: dry season; (P1), (P2), (P3) e (P4): Sampling points. IM: Inorganic matter; OM: Organic matter; OC: Organic carbon. PC1: Principal component 1; PC2: Principal component 2



As shown in Figure 2, the first two dimensions of the PCA explain 73.00% of the variation among all the parameters studied. Looking at the spread of the data, two clusters can be observed: the cluster P1(R), P2(R), and P3(R) for the rainy season analysis and the cluster P1(D), P2(D), P3(D), and P4(D) for the dry season analysis. From the loadings and score plot (physical–chemical and granulometric characteristics), it can be inferred that the parameters pH, clay, and organic matter were high during the dry season, while silt content was low. In the rainy season, inorganic matter levels were high, but organic carbon content was low. The parameters organic matter, pH, clay, and silt, were positively correlated to the dry season, with higher levels during this season, while the parameters inorganic matter, thin sand, and organic carbon were correlated with the rainy season. Table 3 shows the correlation coefficients of the PCA (factors 1 and 2) for the physico-chemical and granulometric characteristics of the sediment.

Table 3 - Loadings of the variables for the first two principal components

Variables	PC1*	PC2*
OM	0.474	0.125
IM	-0.414	-0.303
OC	-0.132	-0.746
pH	0.475	-0.290
Clay	0.440	0.010
Silt	0.314	-0.066
Thin sand	-0.260	0.497
Total variance(%)	54.10	18.90
Cumulative variance (%)	54.10	73.00

*PC1: Principal component 1; PC2: Principal component 2. OM: Organic matter; IM: Inorganic matter; OC: Organic matter.

Interpretation of the correlation coefficients (Table 3) follows the same reasoning of a simple linear correlation analysis, so we can infer that the attributes with negative correlation coefficients (IM, OC, and thin sand) decrease with the change of season, that is, they have lower levels in the dry period, and the attributes with positive coefficients (OM, pH, clay, and silt) have lower levels in the rainy season. Wick *et al*. (1998), using principal components analysis, observed that the variables related to nutrient dynamics of soil organic matter contributed to explain 80% of the total data variance, confirming that variables such as soil biomass carbon and total organic carbon can be used as indicators in the evaluation of soil quality. The soil texture, pH, and organic matter, along with some metals, were evaluated as possible ecological indicators of soil quality by JUHOS *et al*. (2019) using statistical correlation analysis.

5 CONCLUSION

Physical and chemical characteristics are important in the dynamics of aquatic ecosystems. The values observed at the sampling points of the Mearim River are considered adequate to maintain aquatic life, according to CONAMA Resolution 357/2005. However, there are changes in water quality, due to the high levels of riverbank deforestation, silting, and erosion in the basin area. This study confirms the natural complexity of the studied ecosystems, as well as their high environmental fragility in relation to the anthropic actions, as exposed in our discussion.

Considering that the region is densely populated, these results demonstrate that besides natural entrance of material, there is an addtional entrance of material derived from anthropic use and occupation of the soil and domestic effluents and residues as a result of the practices of recreational activities. This condition, associated with the predominance of inorganic matter and the sediment acidity, favors the release of minerals to the water column, promoting the contamination of this environment.

Granulometric analysis showed a predominance of sand and silt in the sampled area, in both evaluated seasons. This can be associated with the proximity to deforested areas and lack of vegetation, which contribute to the erosion process.

ACKNOWLEDGMENTS

We would like to thank the Universidade CEUMA (UNICEUMA - São Luis - MA, Brazil).

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