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Metal dynamics in a tropical watershed: The São Francisco river and its compartments

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ABSTRACT

Water ecosystems are one of the most threaten environments due to anthropogenic pressures, among them the contamination of metals that are toxic to every life form. The main objective of this paper was to investigate the role of each compartment of a river system in metal dynamics using metal sediment concentration. To accomplish the objective sediments from several sites in a tropical river drainage basin were sampled comprising different types of compartments: : the river channel, the dry and wet inundation area and marginal lagoons, as well a pristine site with no anthropogenic impact. A Principal Component Analysis and the calculation of the Enrichment Factor and Index of Geoacummulation were conducted. The results showed that was no great difference of Index of Geoaccumulation among the different compartments. However, the Enrichment Factor was higher in wet inundation areas followed by dry soils from inundation areas and dry lagoons. Principal Component Analysis selected the metals Fe, Cu and Mg in axis 1, while axis 2 selected Mg and Ba. Although there was not a clear separation in the results of the multivariate analysis among sites across a transect, the analysis separated the compartments in relation to the concentration of metals. The results showed that each compartment had its own dynamics in relation to accumulation of metals present in the river basin. The study shows the importance of studying different types of habitats of a drainage basin to stablish best management practices.

Keywords: metals, river, compartments, sediment, São Francisco river

RESUMO

Ecossistemas aquáticos são um dos mais ameaçados hoje em dia devido a pressões antrópicas, sendo entre elas uma das mais importantes a contaminação por metais que são tóxicos a todas formas de vida. O principal objetivo desse trabalho foi o de investigar o papel de cada compartimento de um sistema fluvial na dinâmica de metais usando a concentração destes no sedimento. Para isso sedimentos de diferentes pontos em uma bacia de drenagem tropical foram amostrados abrangendo diferentes tipos de compartimentos: o canal do rio, áreas de inundações húmidas e secas, lagoas marginais, e um ponto sem pressão antrópica. Uma Análise de Componente Principal (PCA) e o cálculo do Fator de Enriquecimento (FE) e o Índice de Geoacumulação (Igeo) foram realizados. Os resultados demonstraram que não houve grandes diferenças de Igeo entre os pontos amostrados. Entretanto, o EF foi maior nas áreas de inundações húmidas seguida pelas secas e lagoas secas. O PCA selecionou os metais Fe, Cu, e Mg no eixo 1, enquanto que o eixo 2 selecionou Mg e Ba. Apesar de não ter ocorrido uma grande separação dos pontos dos amostrados através de um transecto, a análise separou os compartimentos em relação à concentração de metais. Os resultados demonstraram que cada compartimento tem sua própria dinâmica em relação ao acúmulo de metais presentes na bacia de drenagem. O estudo mostrou a importância de se estudar diferentes tipos de habitats de uma bacia de drenagem para o estabelecimento de práticas de manejo.

Palavras-chave: metais, rio, compartimentos, sedimentos, rio São Francisco

1. INTRODUCTION

World population growth and the intensification of different forms of land use and occupation have increased environmental pressure on natural habitats. River systems, in this context, are impacted by changes in water quality, as well as a significant reduction in the amount of water available for a wide range of human uses and ecosystem functioning.

In relation to water quality, there has been great concern regarding the contamination of rivers by metals (Islam *et al.* 2015). The main sources of metals for the environment are related to wastewater from industrial and mining activities, atmospheric input, soil erosion and surface runoff from agriculture practices (Carman *et al.* 2007, Pizarro *et al.* 2010, Díaz-Alba *et al.* 2011, Jiao *et al.* 2015). The presence of metals in water is of great concern due to their toxicity, persistence and cumulative nature (Díaz-Alba *et al.* 2011, Nemati *et al.* 2011). In most cases, in natural environments, without anthropogenic influence, the concentration of metals is low and derived mainly from soil particles and rock weathering (Reza & Singh 2010). The metals that occur in minerals usually have low mobility, as they are linked to their crystalline structure. On the other side, those of anthropogenic origin have weak fixation to the substrate, allowing them to have high mobility (Heltai *et al.* 2005, Passos *et al.* 2010, Ghrefat *et al.* 2012, Saleem *et al.* 2015).

In countries in economic and social development such as Brazil, the discharge of industrial and domestic effluents in rivers is a recurrent practice that generates strong impacts on river systems and diminishes the possibilities of using water resources. Another important source of pollution is the diffuse pollution generated by runoff in urban areas and in regions of agricultural activities. Diffuse pollution refers to those materials that are carried by surface runoff from rainwater, some of these materials are metals, oils, phosphates and nitrates, residues of burning, organic compounds and other residues of the most varied sources. The treatment for diffuse pollution is very complex and difficult to apprehend, since it is necessary to define the sources of pollution and their composition, as well as the quantity of materials carried by the rainwater. Diffuse material continuously accumulates on surfaces and is easily carried in the first rainfalls. Potential for pollutant accumulation and rainwater collection are variables that depend essentially on soil type, prevailing anthropogenic uses and site topography. (Dotto & Paiva, 2006).

The presence of metals in watercourses is an important health issue due to the possibility of humans and animals contamination (Weber *et al.* 2013). Metals can be toxic, have long persistence in water and show bioaccumulation and bio-magnification in the food chain. Metals can accumulate in fish tissue, thus posing a threat to humans that use this type of protein in their diet. (Yousafzai *et al.* 2010, Harguinteguy *et al.* 2014)

Once in the aquatic environment, metals can be in dissolved or particulate forms (Tuna *et al*. 2007). Over time, metals in the particulate fraction can settle and become integral part of sediments. Metals that are present in sediments can be released to the water column due to changes of pH, redox potential and resuspension (Sundelin & Eriksson 2001, Roberts 2012, Hill *et al.* 2013). Consequently, metals are constantly being deposited in the sediments and released to the water column as dissolved and particulate fractions.

The fluvial system can be divided in different compartments, each one showing varied dynamics and resulting in different features and environments. The river channel, the inundation area (that can be wet or dry during some periods of the year) and marginal lagoons (wet or dry) stand out as important environments for the maintenance of the hydrosedimentological dynamics of the river.

In most cases, there is no previous treatment on these altered waters, nor the ability of monitoring by the environmental agencies, which generates recurrent contexts of water pollution. Due to the geographical situation, rivers are often the only source of drinking water for the local population. Increasing wastewater inflow from different human activities is

decreasing the water quality of these natural water bodies, and its potential use. In recent years, due to the contexts of scarcity, but mainly also to the poor water management capacity, some Brazilian states have experienced problems related to the amount of water available for human supply. With the reduction of water quantity, its quality has become one major problem for the management of water resources and the compatibilization of multiple uses, as proposed by the national water resources policy.

The São Francisco river drains an extensive area of the Brazilian territory, being its firsts springs located in the state of minas Gerais (southeast region of Brazil) and the river mouth in the border of the states of Sergipe and Alagoas (northeastern region). It is one of the most important rivers for the country and its basin is responsible for supplying water for a population of approximately 14.2 million (7.5% of the Brazilian population) in a territory with different economic activities. This river is of great importance because it drains vast arid lands in Brazil, being the only source of water for the local population.

The water resources of the main channel and its tributaries are used for different purposes, with emphasis on human consumption, energy production, irrigation and intense agricultural activities, disposal of wastewater from domestic and industrial activities. Therefore, the quality of its waters is of great concern, since the decrease in quality can have strong social and economic impacts. Several studies have already shown that metal contamination of its waters and sediments is an important issue in the drainage basin of São Francisco river (Horn & Baggio 2011; Horn *et al.* 2012; Horn *et al.* 2014; Palmares *et al.* 2016). However, these studies were conducted mainly in the river channel, not addressing the different compartments of the river system.

The main objective of this study was to verify if the different compartments of the São Francisco river have different metal dynamics. The specific objectives were:

1) Determine the concentration of metals in the different compartments;
2) Verify if there is difference in metal concentration in the different compartments and which metals accumulate in each compartment;
3) Determine the Enrichment Factor and Index of Geoaccumulation for each compartment;
4) Determine which of the compartments are the main retention site of metals.

2. MATERIAL AND METHODS

2.1 STUDY AREA

The São Francisco River watershed covers an area of eight federal units in Brazil: Minas Gerais, Bahia, Goiás, Pernambuco, Alagoas, Sergipe and the Distrito Federal (Brasília). Its drainage basin represents 8% of Brazilian territory with a drainage area of 634.000 km². The São Francisco River has an extension of over 2.700 km, with its springs located in Minas Gerais State (Canastra National Park) and the River mouth situated in the State of Alagoas. The River drains five states and 521 municipalities. It covers an area with middle to high hydric deficit and in many regions is the primary source of water for the local population. This extensive drainage basin is divided into four distinct zones (Patrus *et al.,* 2001): A) the Upper São Francisco (from its spring till the city of Pirapora/Minas Gerais), B) The Middle São Francisco (Pirapora till the Sobradinho Lake in Bahia State), C) Sub medium São Francisco (Remanso till Paulo Afonso, both in Bahia State) and D) Low São Francisco (Paulo Afonso till the Atlantic Ocean in Alagoas State).

The study area belongs to the upper to middle São Francisco River basin, covering an area from its springs until Pirapora city, all located in Minas Gerais State (Fig. 1). The climate of the region is classified (Köppen) as Aw, a typical raining tropical climate, with hot and humid summer months, and "dry" winter. The raining season with mean precipitation of 12 mm occurs from November until March.

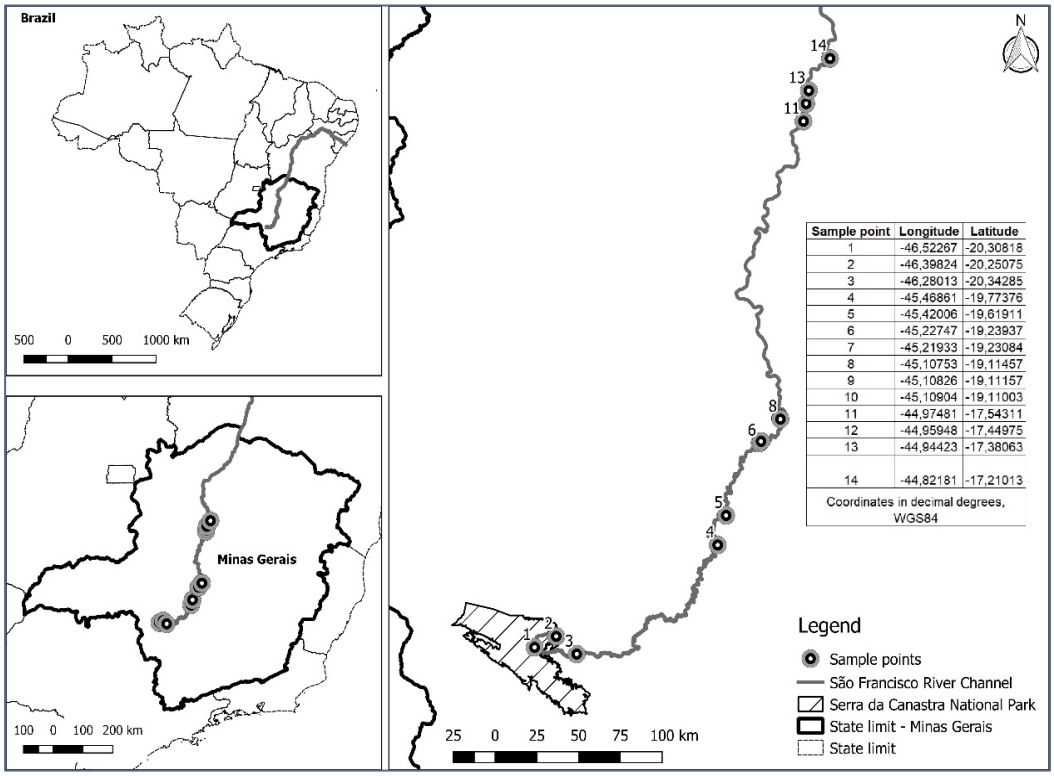

Figure 1
Map of São Francisco river and sampled sites.

Different compartments of the river were sampled: Sediment from a pristine area right after de Canastra National Park; sediments in the margin of the river; sediments in wet inundation areas; sediments from marginal lagoons; soils from dry inundation area or dry marginal lagoons (Table 1). The main anthropic pressures are related to industrial and agricultural activities and house holding. Among the industrial activities, there are zinc processing, metallurgy (iron and silicon) and textile industries. The agricultural activities are diverse and range from small ranches until the production of corn, soy, cotton, coffee, eucalyptus, *Pinus* sp. and livestock and fish farms. There is also the disposal of domestic effluents without previous treatment in its waters.

The sediments were sampled in February 2017 and April 2017. Fourteen sites were sampled since right after its springs till marginal lagoons in Pirapora City. Depending on the site different samples were taken, in different areas or depths (Table 1). The samples were retrieved with a nonmetallic shovel, placed in plastic bags, kept on ice till its transport to the laboratory. In the laboratory, the samples were kept under 4°C till the beginning of the analyses.

2.2 ANALYTICAL METHODS

Sediments were oven dried at 30 °C for 24 horas. Samples were grounded and passed through a mesh of 0.063 mm, which is the fraction where metals can be found (Salomons and Forstner, 1984). The particle size separation was carried out in accordance with the NBR 7181 (ABTN 1984). The fine sediment (0.063 mm) was subjected to acid digestion in microwave MARS-CEM in accordance to the method SW-846-3051 – US EPA (US EPA 1998). About 0.50 g of fine fraction of the sediment was digested with 10 ml of concentrated nitric acid (HNO3) for 10 minutes (ramp time) and temperature stabilization at 180 ° C and pressure (350 psi) for 4'30"(hold time). Samples were then filtered in cellulose filter (0.45 µm)

and analyzed in an ICP-OES (Spectroflame from Spectro Analytical Instruments). The concentration of Mg, Al, Ca, Cr, Fe, Co, Cu, Cd, Ti, Mn, Ni, Zn, Ba and Pb were determined. The results are reported in $mg.kg^{-1}$ on a dry weight basis.

Table 1 - Description of sampled sites Where A: Sediments from marginal lagoons, B: Soils from inundation area or dry lagoons, C: Sediment from wet inundation areas, D: Sediment from pristine area of the river and E: Sediment from impacted areas of the river.

ID	Type of Sampled Site	Site	Place of sampling	Sampling depth	Type of Sample	Coordinates
1	D	Pristine River	Margin of the river	0-5 cm	Sediment	--46,5227/-20,3082
2	E	Impacted River	Margin of the river	0-5 cm	Sediment	-46,3982/-20,2508
2-1	E	Impacted River	Margin of the river	5-10 cm	Sediment	
3	C	Inundation Area	Wet	0-5cm	Sediment	-46,2801/-20,3429
4	E	Impacted River	Margin of the river	0-5cm	Sediment	-45,4686/-19,7738
4-1	E	Impacted River	Margin of the river	5-10 cm	Sediment	
5	A	Gentil	1 m inside the lagoon	0-5cm	Sediment	-45,4201/-19,6191
5-1	A	Gentil	1 m inside the lagoon	5-10 cm	Sediment	
6	B	Inundation Area	Dry	0-5	Soil	-45,2275/-19,2394
6-1	B	Inundation Area	Dry	0- 10 cm	Soil	-45,2193/-19,2308
7	C	Inundation Area	Wet	0-5 cm	Sediment	-45,2193/-19,2308
8	B	Riacho Farm	Dried Lagoon 1	0-5cm	Soil	-45,1075/-17,5431
8-1	B	Riacho Farm	Dried Lagoon 1	5-10 cm	Soil	
9	B	Riacho Farm	Dried Lagoon 2	0-5cm	Soil	-45,1083/-19,1116
9-1	B	Riacho Farm	Dried Lagoon 2	5-10 cm	Soil	
10	B	Riacho Farm	Dried Lagoon 3	0-5cm	Soil	-45,1090/-19,1100
10-1	B	Riacho Farm	Dried Lagoon 3	5-10 cm	Soil	
11-1	A	Guim Lagoon	Inundation area	0-5cm	Sediment	
11-2	A	Guim Lagoon	1 m inside the lagoon	0-5cm	Sediment	-44,9748/-17,5431
11-3	A	Guim Lagoon	5 m inside the laggon	0-5cm	Sediment	
11-4	A	Guim Lagoon	Middle of the lagoon	0-5cm	Sediment	
12-1	A	Atoleiro Lagoon	Inundation area	0-5cm	Sediment	
12-2	A	Atoleiro Lagoon	1 m inside the lagoon	0-5cm	Sediment	-44,9595/-17,4497
12-3	A	Atoleiro Lagoon	5 m inside the laggon	0-5cm	Sediment	
12-4	A	Atoleiro Lagoon	Middle of the lagoon	0-5cm	Sediment	
13-1	A	Pontal Lagoon	Inundation area	0-5cm	Sediment	
13-2	A	Pontal Lagoon	1 m inside the lagoon	0-5cm	Sediment	-44,9442/-17,3806
13-3	A	Pontal Lagoon	5 m inside the laggon	0-5cm	Sediment	
13-4	A	Pontal Lagoon	Middle of the lagoon	0-5cm	Sediment	
14-1	A	Formoso Lagoon	Inundation area	0-5cm	Sediment	
14-2	A	Formoso Lagoon	1 m inside the lagoon	0-5cm	Sediment	-44,8218/-17,2101
14-3	A	Formoso Lagoon	5 m inside the laggon	0-5cm	Sediment	
14-4	A	Formoso Lagoon	Middle of the lagoon	0-5cm	Sediment	

*Geographic coordinates were measured in Datum WGS1984.

2.3. DATA ANALYSIS

The results were used in a Principal Component Analysis (PCA). The PCA consists of a multivariate analysis that is used to predict and describe structural patterns, using a large data set. This analysis describes the structure of a database quantifying the degree of association between the variables and objects (samples), thus defining biological communities and areas or periods of the same ecological characteristics (Pla 1986, Valentin 1995). The PCA technique is of assortment in which the variables are positioned on two or more axes so that their positions provide information on their similarities and differences. This technique is used to simplify, condense and represent synthetically vast data sets (Jollife 1986, Pla 1986, Valentin 1995). Statistical analyzes were performed using Statistica software version 7.1 for Windows (Stat Soft Inc. 2006).

The Enrichment Factor (EF) was calculated by the following formula (Loska & Wiechula 2003):

$$EF(\%) = \frac{C - Cmin}{(Cmax - Cmin)} * 100$$

Where C is the mean metal concentration, C max and C min are the maximum and minimum concentration respectively. As this calculation deals with mean, maximum and minimum values the EF was calculated grouping the data for each different compartment. As the intention was to verify the enrichment related to the pristine site the values observed for this site were used as the minimum concentration.

The Index of Geoaccumulation (Igeo) was calculate by the following formula (Loska & Wiechula 2003):

$$Igeo = \frac{Log2(Cn)}{1.5 * Bn}$$

Where *Cn* is the concentration of the metals in the sample, *Bn* is the background concentration. The metal concentration measured in the pristine site were used as a background concentration.

3. RESULTS AND DISCUSSION

The pristine site had the lowest concentration for almost all measured metals. Only for Ca, Cu and Ti the concentrations were not the lowest in the pristine site. The minimum and maximum concentration (in $mg.kg^{-1}$) in all sample sites were as followed: Mg: 85-2176, Al: 1605-53823, Ca: 243-1571, Cr: < 0.001-37, Fe: 742-5342, Co: < 0,0068-10.2, Cu: 10.8-40, Cd: not detected in any sample, Ti: 15.6-168, Mn: 10.2-778, Ni: 8.8-18.4, Ba: 19.6-273 and Pb: < 0,0349-68 (Table 2). Several analyses (i.e. plots, PCA) were done trying to stablish a relationship between the distance from the pristine site and the other sites and the increased concentration of metals (Data not shown). No clear relationship was stablished, as the concentration of metals were variable among the distance from the pristine site. This indicates that there is not an increase in metal concentration with distance from the main spring of São Francisco river. In a first thought this relation was supposed to be clear. As much as the river flows from pristine sites till areas of high human activity its is fair to suppose that metals concentration will increase with the distance as more effluent from human activities reach the river. As more contaminated effluents enters the river it is expected that they will settle and accumulate in the sediments. That was not the case. There was not a clear pattern of increasing metal concentration with distance from the pristine site (data not shown), although the PCA showed a separation among sites which will be presented latter. This indicates that other issues are more important in determining metal concentration in the sediments of the different compartments. Ciazela *et al*. (2018) states that metal concentration in the bottom sediments of freshwater ecosystems are controlled by a variety of human and environmental factors. Among them we can cite: 1) grain size fractionation, 2) chemical fractionation, 3) vicinity of urban areas, and 4) geogenic input (Ciazela *et al.* 2018).

The Enrichment Factor (EF) was very high for all types of compartment (Table 3). Toxic elements like Pb, Cu and Cr had values that reached 88,6%, 99,6% and 83,8% respectively (Table 3). The Compartment C which is the sediments from wet inundation areas had the highest values for most of metals, followed by Compartment B which are dry soils from inundation area and dry lagoons. On the other side, sediments from marginal lagoons had the lowest values for EF. Although marginal lagoons of the São Francisco hydrographic basin have been shown to accumulate metals in its sediments (Trindade 2016), it seems that the inundation areas are the sites where accumulation is more prominent. This result shows the importance of inundation areas to absorb impacts caused by pollution of rivers. The main mechanism that leads the inundation area (dry or wet) to have highest EF than the other compartments

Table 2 - Metal concentrations in sampled sites. Data in dry weight basis.

Sites	Mg	Al	Ca	Cr	Fe	Co	Cu	Cd	Ti	Mn	Ni	Zn	Ba	Pb
							mg.kg^{-1}							
1	85	1605	633	< 0,011	742	< 0.0068	11.5	< 0.0029	23.9	10	< 0.0133	8.8	19.7	< 0.0349
2	595	11118	896	7,9	33098	7.13	26.4	< 0.0029	76.4	619	2.26	30.0	66.1	19.2
2-1	1069	20650	984	16,5	42460	8.58	32.0	< 0.0029	168.1	778	7.03	51.1	109.1	27.7
3	592	11413	512	11,0	31519	10.16	25.8	< 0.0029	100.0	757	3.93	30.1	62.1	22.4
4	480	53824	1461	10,7	35118	< 0.0068	24.3	< 0.0029	21.0	37	< 0.0133	26.3	79.4	43.3
4-1	1183	49902	1279	24,5	29510	1.05	31.5	< 0.0029	68.8	48	8.35	47.1	150.2	68.3
5	635	31135	1346	35,7	30173	0.84	29.5	< 0.0029	63.8	76	8.13	41.8	55.5	36.9
5-1	376	21358	848	25,8	32849	< 0.0068	27.7	< 0.0029	35.8	78	3.76	26.5	37.7	27.9
6	557	14940	1571	19,1	30900	3.50	32.6	< 0.0029	61.5	336	< 0.0133	62.5	51.2	20.5
6-1	563	18683	951	15,2	31058	1.98	39.8	< 0.0029	67.8	280	4.28	52.0	56.4	23.0
7	410	11324	693	16,3	35667	3.77	26.0	< 0.0029	37.7	463	2.58	20.2	48.8	17.3
8	420	14217	310	9,9	27368	< 0,0068	22.5	< 0.0029	63.1	129	< 0.0133	11.9	48.7	16.7
8-1	439	15860	244	12,3	28970	2.64	25.8	< 0.0029	82.4	118	2.98	11.7	51.5	18.6
9	571	20642	378	24,2	34028	1.92	28.1	< 0.0029	75.0	95	1.51	25.5	79.7	25.6
9-1	479	15868	360	19,8	29349	1.39	27.1	< 0.0029	62.5	88	1.43	25.6	58.9	22.2
10	571	15750	534	16,9	28660	< 0.0068	30.3	< 0.0029	65.7	104	1.56	32.1	69.1	16.0
10-1	498	13490	342	18,4	27833	2.31	31.5	< 0.0029	55.4	98	3.79	22.6	55.7	23.7
11-1	422	12500	244	21,0	14941	< 0.0068	10.8	< 0.0029	35.0	72	< 0.0133	29.6	133.6	28.9
11-2	658	10000	273	18,0	19206	< 0.0068	19.0	< 0.0029	24.6	104	< 0.0133	54.2	154.8	24.7
11-3	764	11360	350	22,5	11590	< 0.0068	23.1	< 0.0029	31.3	80	< 0.0133	40.3	178.8	26.4
11-4	629	8745	395	15,2	11225	< 0.0068	21.8	< 0.0029	15.7	96	< 0.0133	39.6	219.2	22.9
12-1	2015	14402	425	21,5	17412	< 0.0068	16.1	< 0.0029	64.7	170	< 0.0133	40.2	273.8	32.1
12-2	678	10098	387	15,9	19559	< 0.0068	12.5	< 0.0029	19.0	266	< 0.0133	40.0	155.2	19.3
12-3	1002	9971	352	15,7	24846	9.34	17.9	< 0.0029	34.1	328	< 0.0133	60.3	193.6	26.4
12-4	1248	16740	428	23,1	23269	5.78	19.5	< 0.0029	52.7	302	6.00	59.6	226.9	29.3
13-1	1350	10548	571	16,9	17740	< 0.0068	15.5	< 0.0029	48.6	113	< 0.0133	75.0	111.2	23.8
13-2	2176	9353	382	17,2	19794	< 0.0068	13.5	< 0.0029	50.1	96	< 0.0133	46.5	97.8	22.1
13-3	1337	10608	483	16,6	18863	< 0.0068	14.3	< 0.0029	43.3	142	< 0.0133	64.7	110.3	21.3
13-4	1379	10667	580	19,4	17931	< 0.0068	16.9	< 0.0029	57.5	130	< 0.0133	70.0	119.0	24.2
14-1	1659	11317	664	32,2	30356	< 0.0068	19.0	< 0.0029	53.6	437	< 0.0133	64.9	149.4	30.6
14-2	1749	19951	533	34,2	39431	1.93	23.7	< 0.0029	83.3	265	< 0.0133	85.4	161.8	34.3
14-3	1954	20067	734	37,1	53942	10.24	40.1	< 0.0029	75.5	314	18.49	119.9	159.7	29.4
14-4	1401	12048	523	24,7	38317	1.82	17.5	< 0.0029	55.3	306	< 0.0133	69.0	112.9	28.6

Detection minimum limit in mg.kg^{-1}: Mg: 0,0219, Al: 0,0652, Ca: 0,118, Cr: 0,011, Fe:, Co: 0,0068, Cu: , 0,0099, Cd: 0,0029, Ti: 0,009, Mn:<0,015, Ni: 0,0133, Zn: 0,0018, Ba: 0,0207, Pb<0,0349

is not clear. It could not be found in the scientific literature any possible explanation for this fact. However, one explanation might be as inundation areas are more prone to have the influence of both the river and surface run off, some of metals that come with these allochthonous water might deposit in these areas before they reach the river. In addition, when these areas are wet the water usually is stagnant; there is no movement, which allows the metals particles to settle. Somehow when these areas get dry the metals can bind to soil particles and become retained in these sites.

Even though compartments B and C had the highest values, all other compartments show high EF. Its important to point out that background values for the calculation of EF were based on metal concentration founded in the pristine site. This indicates that the São Francisco river basin is receiving a considered load of metals that are being retained in its sediments and soils. As pointed out in this important hydrographic basin there is both industrial and agricultural activities which generate effluents with possible metal contamination. Among them we can cite zinc processing industry, metallurgy (iron and silicon) and textile industries. Both fertilizers and agrochemicals are known to contain metals, and in this area there is a large production of corn, soy, cotton, coffee, eucalyptus, *Pinus* sp. Other studies have already shown that sediment metal contamination is an important issue in São Francisco hydrographic basin (Horn & Bagio 2011; Horn *et al.* 2012, Trindade 2016). Our results show that sites with anthropogenic pressures are showing a very high metal enrichment when compared with sites with no impacts in this hydrographic basin.

The Index of Geoaccumulation was also high in the sampled sites for most metals. Values varied from 6,9 till 20,6. But there was no significant difference among sites (Table 4). However, the results show that there is high contamination of all sediments by all metals analyzed when comparing with data of other aquatic systems throughout the world (Tamin *et al.* 2016, Dai *et al.* 2017).

Table 3 - Enrichment Factor (%) in the different types of sampled sites. Where A: Sediments from marginal lagoons, B: Soils from inundation area or dry lagoons, C: Sediment from wet inundation areas, D: Sediment from pristine area of the river and E: Sediment from impacted areas of the river.

	Enrichment Factor (%)												
Type of sample sites	Mg	Al	Ca	Cr	Fe	Co	Cu	Ti	Mn	Ni	Zn	Ba	Pb
A	52.86	41.76	-14.59	61.73	44.70	16.24	29.35	38.62	41.56	17.89	43.44	50.22	73.67
B	90.60	78.04	-0,.9	74.38	88.24	56.07	68.11	73.96	45.94	51.94	45.31	67.77	83.39
C	82.00	99.54	-50.99	83.88	94.06	68.57	99.64	59.02	80.34	82.78	76.68	84.33	88.66
E	67.99	61.79	63.07	60.84	82.23	48.82	83.15	41.36	46.90	52.82	70.51	62.46	57.98

Table 4 - Index of Geoaccumulation in the different types of sampled sites. Where A: Sediments from marginal lagoons, B: Soils from inundation area or dry lagoons, C: Sediment from wet inundation areas, D: Sediment from pristine area of the river and E: Sediment from impacted areas of the river.

	Igeo												
Type of sample sites	Mg	Al	Ca	Cr	Fe	Co	Cu	Ti	Mn	Ni	Zn	Ba	Pb
A	15.82	19.47	14.66	10.29	20.29	8.01	10.08	11,18	13.27	8.73	11.57	13.03	10.57
B	14.82	19.80	14.73	9.86	20.69	6.96	10.70	11.88	12.92	7.05	10.53	11.69	10.19
C	14.77	19.30	15.05	9.57	20.86	8.46	10.52	11.77	15.04	7.50	10.45	11.61	10.13
E	15.43	20.60	15.97	9.60	20.91	7.83	10.65	11.86	13.24	8.18	11.04	12.42	10.97

The Principal Component Analysis (PCA) showed interesting results (Fig. 2, Table 5). The PCA explained 72,2% of the data variability. The PC1 with 45,1% of the variability selected Fe, Cu and Mg, while PC2 with 27,1% selected Mg and Ba (Table 5). When PCA selects the elements it means that the occurrence and concentration of these are the most influential in the percentage data variability. The metals Ba, Mg, Zn, Cr and Pb seem to occur in the same pattern in the selected sites. While Ni, Fe, Cu, Ti, Co, Ca, Mn and Al were placed in another cluster in the PCA. The different Components of the PCA might be showing different dynamics of metal. While PC1 might be representative of the bulk concentration of metals occurring in the sediments, PC2 can be representing the contribution from anthropogenic activities (pollution).

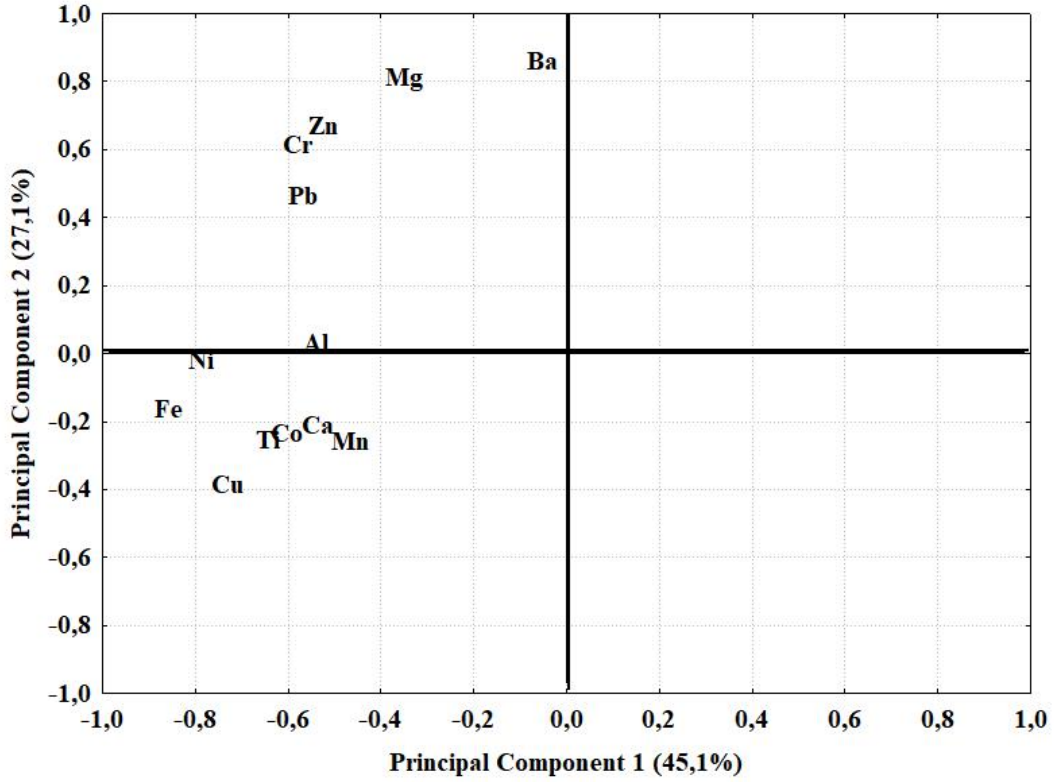

Figure 2
Results of the Principal Component Analysis (PCA) placing the elements with each respective loadings.

Table 5 - Results of the loadings of the elements and the percentage of the explained variability of the data from the PCA. Values in bold are the selected loadings that are the most important in explaining the variability of the component.

Elements	PC 1	PC 2
Mg	-0,349052	**0,766644**
Al	-0,539857	-0,016400
Ca	-0,533589	-0,257922
Cr	-0,577863	0,569693
Fe	**-0,855918**	-0,208539
Co	-0,602699	-0,282094
Cu	**-0,729492**	-0,433832
Ti	-0,642035	-0,301015
Mn	-0,465353	-0,306932
Ni	**-0,786939**	-0,068387
Zn	-0,524285	0,623913
Ba	-0,050607	**0,813874**
Pb	-0,565754	0,417629
% Expained. Variability	45.1%	27.1%

The plot of the sampled sites did not show a clear result (Fig. 3). Although it separated the sites located far apart from the spring (11 till 14), the other sites did not show a clear separation in relation to the transect across the river length. However, the pristine site (1) was placed far apart from all the other sites. This result is an indication that the pristine site has a statistical difference in metal concentration in relation to the other sites with anthropogenic pressures. The results of the PCA reinforces the results showed by EF and Igeo that there is a clear enrichment of metals in different compartments of the São Francisco river basin, and it is strongly related to the impact of the effluents of human activities.

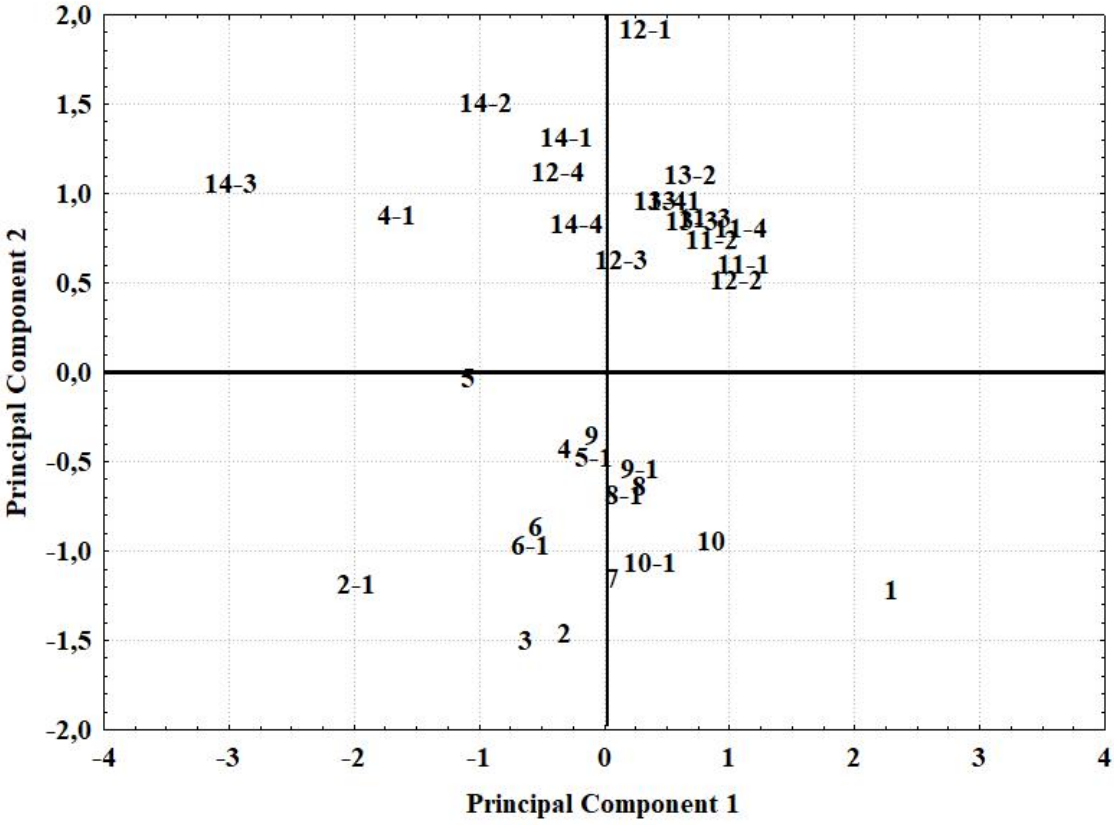

Figure 3
Score plot of the sampling sites position in relation to the results of the PCA. The numbers are across a transect from a pristine site close to the spring till the marginal lagoons further apart in Pirapora city.

When the different compartments sampled were plotted in relation to the PCA an interesting result was found (Fig. 4). The sediment of the lagoons were placed together and in the position of the cluster selected by PCA 2. And the other compartments were placed in relation to PCA 1. Other point was that the pristine site (D) was placed again far apart from the other sites showing that it can be used as a background site. And the other compartments although did not show a clear separation among them were placed close to each other. The results show that each compartment had its own dynamics in relation to the accumulation of metals present in the river basin. It also shows that the distance from the springs is not the major factor influencing the metal concentration, instead the type of habitat is more important in determining the accumulation of metals, as it was shown by EF and PCA.

Its clear that the marginal laggons were placed with the metals in PCA 2 which we discussed that could be indicating metals resulting from anthropogenic activities. This results shows that these types of habitats are important compartments retaining metals (Trindade 2016).

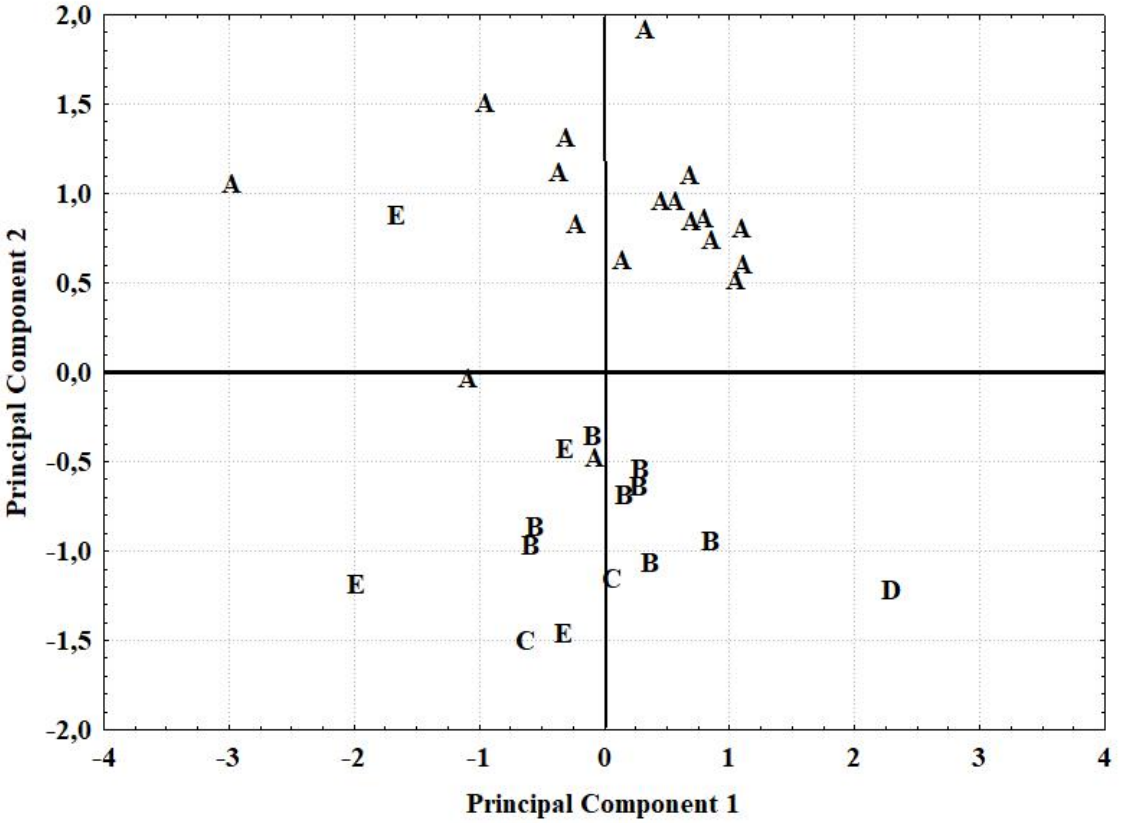

Figure 4
Score plot of the different compartments in relation to the results of the PCA. Where A: Sediments from marginal lagoons, B: Soils from inundation area or dry lagoons, C: Sediment from wet inundation areas, D: Sediment from pristine area of the river and E: Sediment from impacted areas of the river.

It is not clear which mechanism that can explain why the different compartments have different metal dynamics. We should expect that the distance from the pristine areas will correlate with metal concentration, which was not the case for all data analyses conducted. Our data showed that there is a difference in the type of metals that accumulates in each type of habitat. Moreover, habitats like inundation area show higher metal accumulation than the other types of habitats sampled. And each type of habitat has its own dynamics as they were all separated in the PCA. To our knowledge this is the first study to address sediment metal contamination in different types of habitats of river systems. We could not find in the scientific literature any other study that addressed metal contamination in sediments of different habitats in a river hydrographic basin. More studies must be conducted to find if there is a pattern on metal accumulation in different compartments of a river system.

4. CONCLUSIONS

The results of this study have shown that metal dynamics are different in each type of habitat present in river system. The article presents the hypothesis that the differences in the accumulation of metals may be associated mainly with the fluvial dynamics of each sedimentary environment, especially considering the influence of the waters and the consequent mobilization of the sediment deposited by the increase of the competence and capacity of the river system in the wet periods. These dynamics must be taken into account to stablish environmental management practices for both protection and recovery of rivers polluted by metals.

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