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Relationship Between Metal Water Concentration and Anthropogenic Pressures in a Tropical Watershed, Brazil

Isabela Claret Torres[1]
Elizêne Veloso Ribeiro[2]
Walace Magalhães Trindade[3]
Antônio Pereira Magalhães Júnior[4]
Adolf Heinrich Horn[5]*

[1,2,3] Post-Graduation Program in Geography
Geoscience Institute
Federal University of Minas Gerais.

[4] Geography Department
Geoscience Institute
Federal University of Minas Gerais.

[5] Environmental Geochemistry Laboratory,
Geology Department
Geoscience Institute
Federal University of Minas Gerais

Av. Antônio Carlos, 6627
Belo Horizonte – MG/Brazil
CEP 31270-901

[1] iclarett@hotmail.com
[2] elizenev@yahoo.com.br
[3] wallacegeografo@yahoo.com.br
[4]magalhaesufmg@yahoo.com.br
[5]hahorn@gmail.com

* corresponding author

Resumo
Nos países em desenvolvimento, os rios são usados para eliminar as águas residuais de muitas atividades humanas que podem resultar em uma entrada de metais para os corpos d'água. A bacia hidrográfica do São Francisco é de extrema importância para o Brasil, pois drena grandes áreas, a maioria delas com alto déficit hídrico. Além de ser um importante recurso hídrico para a população local, várias atividades antropogênicas são desenvolvidas em sua bacia hidrográfica e comprometem a qualidade de sua água. O objetivo principal foi abordar a relação entre a concentração de metais e as pressões antropogênicas no rio São Francisco. A análise de componentes principais foi utilizada para determinar a relação entre as atividades humanas ea concentração de água no metal e verificar se havia uma tendência sazonal. Vários metais em forma particulada e dissolvida foram medidos em água a partir de 59 pontos, coletados durante uma estação "úmida" e "seca", e analisados utilizando ICP-OES. Os resultados mostraram que houve uma clara correlação da concentração de partículas de metal com a estação "úmida", enquanto as formas dissolvidas foram mais altas na estação "seca". As partículas em suspensão também mostraram concentrações claramente mais altas durante a estação "úmida", indicando importante entrada de escoamento superficial relacionada às atividades agrícolas. Maior concentração de partículas de metal foi encontrada em áreas com práticas agrícolas onde os metais dissolvidos foram as principais formas em locais industriais. Os resultados indicam que os metais associados às partículas do solo entram no rio com escoamento superficial. Por outro lado, o tratamento de efluentes industriais está sendo bem sucedido na retenção de metais em partículas, mas descarte metal em forma dissolvida no rio.
Palavras-Chave: Concentração de metais; Fracção particulada, fracção dissolvida, pressões antropogénicas; contaminação da água; Bacia hidrográfica do São Francisco.

Abstract
In developing countries, Rivers are used to dispose wastewater from many human activities that may result in an input of metals to the water bodies. The São Francisco watershed is of extreme importance to Brazil as it drains large areas most of them with high hydric deficit. Besides being an important water resource to the local population several anthropogenic activities are developed in its watershed and compromise its water quality. The main objective was to address the relationship between metal concentration and anthropogenic pressures in São Francisco River. A Principal Component Analysis was used to determine a relationship between human activities and water metal concentration and to verify if there was a seasonal trend. Several metals in particulate and dissolved forms were measured in water from 59 points, collected during a "wet" and "dry" seasons, and analyzed using ICP-OES. The results showed that there was a clear correlation of particulate metal concentration with "wet" season, while the dissolved forms were highest in the "dry" season. The suspended particulate matter also showed

clearly higher concentration during the “wet” season indicating important surface runoff input related to agricultural activities. Higher particulate metal concentration was found in areas with agricultural practices where the dissolved metals were the main forms in industrial sites. The results indicate that metals associated with soil particles enter the river with surface runoff. On the other side the treatment of industrial effluents are being successful in retaining metals in particulate but dispose metal in dissolved form in the river.
Keywords Metal concentration; particulate fraction, dissolved fraction, anthropogenic pressures; water contamination; São Francisco watershed.

1. INTRODUCTION

With the growth of the world population there has been an increase of pressure on natural habitats. Among the natural systems that are experiencing impacts resulting from anthropogenic activities the Rivers are the ones that are suffering with issues relating to water quantity and quality. In relation to water quality there has been great concern related to the contamination of Rivers by metals (Islam *et al.* 2015). The main sources of metals to the environment are related to wastewater from industrial and mining activities, atmospheric input, soil erosion and wastewater from agriculture practices (Carman *et al.* 2007, Pizarro *et al.* 2010, Díaz-de Alba *et al.* 2011, Jiao *et al.* 2015). The presence of metals in natural waters is of great concern due to their toxicity, persistence and cumulative nature (Díaz-de 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). Metals occurring in minerals have, usually, low mobility as they are linked to their crystalline structure, on the other side the ones from anthropogenic origin presents 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).

Once in the aquatic environment, metals can be in dissolved or particulate fractions (Tuna *et al.* 2007). With 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 presence of metals in Rivers is an important health issue due to the possibility of humans and animals contamination (Weber *et al.* 2013). Metals can accumulate in fish tissue, thus posing a threat to humans that use this type of protein in their diet. Metals can be toxic, has long persistence in water and show bioaccumulation and bio-magnification in the food chain (Yousafzai *et al.* 2010, Harguinteguy *et al.* 2014).

In developing countries like Brazil, the discharge of industrial and domestic effluents in Rivers is a common practice. Other important source of pollution in these countries is the surface runoff from agricultural activities. In most cases, there is no previous treatment of this wastewater resulting in pollution of water resources. Due to geographic situation, Rivers are often the only source of potable water for the local population and the increasing input of wastewater from different human activities are decreasing the water quality of these natural water bodies. In recent years the southeast states of Brazil are suffering with issues related to water quantity. With the decrease of water quantity its quality became the major issue for water managers.

The São Francisco River drains an extensive area from southeastern to the northeastern part of Brazil. It is one of the most important Rivers in this country and the main water resource for a population of 14.2 million (7.5% of the Brazilian population). This River is of great importance as it drains vast arid lands in Brazil, being the only source of water for the local population. The main stream and its tributaries are being used for human consumption, for energy production, irrigation, wastewater disposal from domestic and industrial activities. In the drainage basin there is intense farming activities. Hence, is of great concern the quality of its water. Besides its national importance, relevant studies concerning concentration of metals in its water connecting to theirs possible sources has not been conducted. This study use data from fieldwork to address concentration of metals (dissolved, particulate and total) in São Francisco River (upper to middle parts of the River) and some of its tributaries. With multivariate analyses, we tried to stablish a connection between metal concentration with seasonality and anthropogenic activities.

Multivariate analyses are being largely used in environmental studies, which deals with large data set. Among multivariate analyses, the Principal Component Analysis (PCA) is widely applied in studies concerning anthropogenic impacts to the environment. The PCA use large data sets to predict and describe patterns among samples, conditions, and seasonality. This analysis quantifies the degree of association between the variables and objects (samples), thus defining biological communities and areas or seasons of the same ecological characteristics (Pla 1986, Valentin 1995). In this type of analysis, the variables are positioned on two or more axes, which defines similarities and differences among them (Jollife 1986, Pla 1986, Valentin 1995).

The main objective of this study was to address the relationship between the metal water concentration and anthropogenic pressures in São Francisco watershed, Brazil. The specific objectives were:

1) Measure the concentration of particulate and dissolved metal water concentration in São Francisco River and its tributaries;

2) Verify if there is a seasonal pattern on the distribution of particulate and dissolved metals.

3) Stablish the impact of anthropogenic activities on particulate and dissolved metal concentration on the waters of a section of São Francisco River and its tributaries.

2. MATERIALS AND METHODS

2.1. Study Area

The São Francisco River watershed covers an area of seven states in Brazil: Minas Gerais, Bahia, Goiás, Pernambuco, Alagoas, Sergipe states and 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 and the River mouth situated in the State of Alagoas. The River drains five states and 521 cities. 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 city 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 the Hydroelectric Power Station and its lake upstream of Três Marias until its confluence with das Velhas River, in 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 months (Ribeiro *et al.* 2012). Through November until March, there is the rainy season with means of 12 mm.

The main anthropic pressures are related to industrial, urban and agricultural activities. 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., livestock and fish farms (Ribeiro *et al.* 2012). There is also the discharge of wastewater from domestic activities in the main River.

2.2 Sampling

Water quality and metal concentration were monitored at fifty nine sampling points in the months of March (“wet” season) and July (“dry” season) of 2008 (Fig.1 and Table 1). Among these sampling points, there are 12 tributaries of São Francisco River. At these points, water was sampled before and after their confluence with main River. Table 1 shows the description of the sampling points with the observed main anthropic influences. Water samples were placed in polyethylene bottles that were previously washed with nitric acid 10% and placed in a cooler with ice, transported to the laboratory and kept at 4 °C until the analyses. In the field, water quality parameters were measured. The water pH, temperature, electrical conductivity and total dissolved solids were measured with a pH/EC/TDS/Temp Waterproof Family/HI198129 (HANNA Instruments). The dissolved oxygen was stablished with an Oxygen Meter (DO-5510, HANNA Instruments) and turbidity with a turbidity probe HI 93703 (HANNA Instruments).

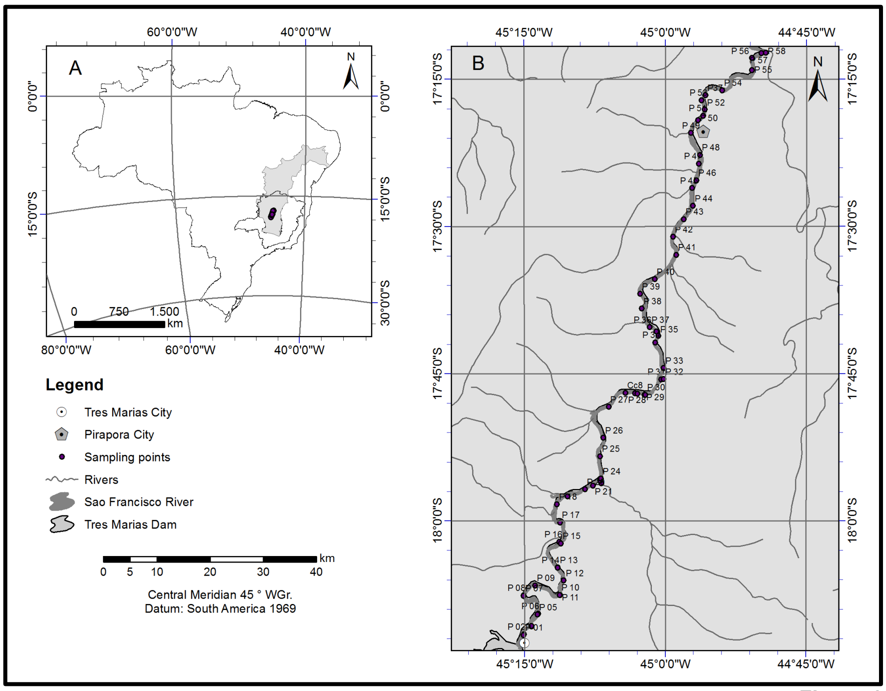

Figure 1
Map of the São Francisco watershed location in Minas Gerais State/Brazil and the sampling points in São Francisco River and its tributaries

2.3. Analytical Methods

In the laboratory, total suspended solids were measured by filtering a known volume of water in 0.45 µm filter (micropore) that were previously dried in the oven (24h at 90°C) and weighted. After filtering, the filters were placed again in the oven for the same season and temperature and weighted again. By the difference of weight between the filters before and after the filtration the total suspended solids were stablished. The data is reported in $mg.L^{-1}$.

Metal concentrations in the dissolved and particulate fractions were measured in the laboratory. Total metal concentration was determined by the sum of these two fractions and is reported in $mg.L^{-1}$. For the analyses of dissolved metals, a known amount of water was vacuum filtered in filters of cellulose nitrate of 0.45 µm porosity and 47 mm of diameter. Thirty milliliter of the filtered water was acidified with nitric acid until the pH reached the value of two. This procedure was done in duplicate. The samples were placed in a refrigerator and kept at 4°C until the analyses in an ICP-OES (Spectroflame from Spectro Analytical Instruments). The filter residue was used to determine metals in the particulate fraction. The filters were subjected to acid digestion in microwave MARS-CEM in accordance to the method SW-846-3051 – US EPA (US EPA 1998). Briefly, the filter was cut with a plastic tweezer that was previously decontaminated and digested with 5 ml of concentrated nitric acid (HNO_3) for 10 minutes (ramp time) and temperature stabilization at 180 °C and pressure (350 psi) for 4'30" (hold time). The total opening time in the microwave was 40 min. After this season, the tubes were opened in a hood for 10 min, and transferred to volumetric of 10 mL. The samples were filtered and kept under refrigeration until the analyses in the ICP-OES. The concentration of magnesium (Mg), aluminum (Al) , calcium (Ca), chromium (Cr), iron (Fe), cobalt (Co), copper (Cu), cadmium (Cd), titanium (Ti), manganese (Mn), nickel (Ni), zinc (Zn), barium (Ba) and lead (Pb) were determined and are reported in $mg.L^{-1}$.

Statistical analyses and figures were performed using *Statistica* software version 7.1 for Windows (Stat Soft Inc. 2006).

Table 1 Description of sampling points with main anthropogenic pressures

Point	UTM 23K	Localization	Main Anthropic Pressure
01	473386,714 7987336,043	São Francisco River	Urban (U)
02	473445,913 7988477,070	Barreiro Grande Stream	Industry/Urban (I/U)
03	474848,803 7989999,519	São Francisco River	Industry/Urban (I/U)
04	474888,503 7989960,816	Consciência Stream	Industry/Urban (I/U)
05	475965,216 7992172,356	São Francisco River	Ranches (R)
06	476100,304 7992339,606	Aldedo Dourado Stream	Ranches (R)
07	473372,199 7995699,950	São Francisco River	Ranches (R)
08	473333,556 7995791,047	Lucinda Stream	Ranches (R)
09	475537,838 7997631,060	São Francisco River	Ranches (R)
10	480141,799 7995850,688	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
11	480227,558 7995826,358	Espírito Santo River	Eucalyptus/*Pinus* plantation (E/P)
12	480930,189 7998563,852	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
13	479810,129 8001006,845	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
14	479787,933 8001045,650	São José Stream	Eucalyptus/*Pinus* plantation (E/P)
15	480336,777 8005527,101	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
16	480074,663 8005848,783	Abaeté River	Eucalyptus/*Pinus* plantation (E/P)
17	480198,946 8009511,343	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
18	479652,601 8012910,210	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
19	481676,855 8014408,070	São Francisco River	Coffee/Eucalyptus/*Pinus* plantation (C/E/P)
20	484939,994 8015726,896	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
21	486405,054 8016427,325	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
22	487715,673 8017401,789	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
23	487946,394 8016827,995	Rio de Janeiro River	Eucalyptus/*Pinus* plantation (E/P)
24	487864,550 8017723,175	São Francisco River	Livestock (L)
25	487741,785 8021950,168	São Francisco River	Agriculture (A)
26	488312,765 8025414,386	São Francisco River	Agriculture (A)
27	489357,836 8031229,147	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
28	494279,834 8033804,101	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)

Table 1 continuing

Point	UTM 23K	Localization	Main Anthropic Pressure
29	496067,625 8033490,178	Tapera Creek	Livestock/Eucalyptus/*Pinus* plantation (L/E/P)
30	496217,862 8033483,503	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
31	499200,749 8036394,193	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
32	499682,877 8036444,487	Pedras River	Eucalyptus/*Pinus* plantation (E/P)
33	499644,353 8038521,840	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
34	498139,142 8043311,842	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
35	498681,579 8044577,980	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
36	497061,026 8046187,983	Cedro Stream	Eucalyptus/*Pinus* plantation (E/P)
37	497055,477 8046205,212	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
38	495596,811 8049700,155	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
39	495267,937 8052467,211	São Francisco River	Eucalyptus/*Pinus* plantation (E/P)
40	498029,847 8055215,801	São Francisco River	Agriculture/Soy (A/S)
41	502055,253 8059781,208	São Francisco River	Coffee plantation (C)
42	501449,142 8063191,471	São Francisco River	Coffee plantation (C)
43	503466,925 8066483,748	São Francisco River	Agriculture (A)
44	505155,409 8069009,961	São Francisco River	Sugar Cane plantation (SC)
45	505071,806 8072348,162	Formoso River	Soy/Corn/Coffee plantation (S/C/C)
46	505823,754 8073790,123	São Francisco River	Livestock (L)
47	506315,426 8076945,423	São Francisco River	Livestock (L)
48	506538,375 8078584,231	São Francisco River	Urban (U)
49	504826,242 8082699,238	São Francisco River	Urban (U)
50	504804,518 8082839,466	Pedras Stream	Urban (U)
51	506176,894 8085153,601	São Francisco River	Urban (U)
52	506861,909 8085715,962	São Francisco River	Industry/Urban (I/U)
53	507309,031 8086562,500	São Francisco River	Industry/Urban (I/U)
54	507448,410 8087085,455	São Francisco River	Industry/Urban (I/U)
55	506839,436 8088854,217	São Francisco River	Ranches (R)
56	510705,325 8090704,511	São Francisco River	Horticulture (H)
57	516327,508 8094502,886	São Francisco River	Horticulture (H)
58	516257,580 8096792,899	São Francisco River	Horticulture (H)
59	518074,461 8097696,912	São Francisco River	Sugar Cane plantation (SC)

3. Results and Discussion

The Table 2 shows the mean and standard deviation of water quality parameters from all sampling locations during the "dry" and "wet" seasons.

In relation to water quality parameters the data showed that the majority of the points had pH around neutrality. The water samples were in general well oxygenated. Although these parameters did not show a marked season effect, the concentration of electrical conductivity, total dissolved solids, total suspended solids and turbidity showed a different result. While electrical conductivity and dissolved solids had higher values in the "dry" season, turbidity and suspended solids had higher values during the "wet" season. These results show that there is a higher input of solids to São Francisco River and its tributaries during the "wet" season. This indicates that its surrounding land is not well preserved and that a considerable amount of particulates enters the water bodies by surface runoff (Table 2). This is probably caused by exposed soil surface resulted from agricultural practices that prepares the soil for plantation. On the other side the electrical conductivity and total dissolved solids results show that there is a concentration effect during the "dry" season and lower levels of water in these water bodies.

Except for the concentration of Ca and Mg, the dissolved metal concentration was low in most of the sampling sites (Table 3). The values varied, in the "wet" season, from 0.06 to 42 $mg.L^{-1}$ for Mg, 0.54 to 33.8 $mg.L^{-1}$ for Ca, 0.003 to 29.2 $mg.L^{-1}$ for Zn, 0.001 to 2.61 $mg.L^{-1}$ for Mn, 0.003 to 0.51 $mg.L^{-1}$ for Fe, 0.003 to 0.27 $mg.L^{-1}$ for Al, 0.0013 to 0.122 $mg.L^{-1}$ for Cd, 0.014 to 0.058 $mg.L^{-1}$ for Pb, 0.007 to 0.03 $mg.L^{-1}$ for Ba, 0.005 to 0.013 $mg.L^{-1}$ for Ni,0.001 to 0.006 $mg.L^{-1}$ for Cr, 0.0015 to 0.0018 $mg.L^{-1}$ for Cu. The metals Co (0.0029 $mg.L^{-1}$) and Ti (0.0003 $mg.L^{-1}$) showed no variation among sites.

In the "dry" season values varied from 0.15 to 14.0 $mg.L^{-1}$ for Mg, 0.66 to 10.0 $mg.L^{-1}$ for Ca, 0.001 to 0.37 $mg.L^{-1}$ for Zn, 0.0016 to 0.23 $mg.L^{-1}$ for Fe, 0.015 to 0.124 $mg.L^{-1}$ for Pb, 0.0037 to 0.08 $mg.L^{-1}$ for Al, 0.0029 to 0.040 $mg.L^{-1}$ for Co, 0.0015 to 0.0143 $mg.L^{-1}$ for Cr, 0.0016 to 0.013 $mg.L^{-1}$ for Mn, 0.0074 to 0.0088 $mg.L^{-1}$ for Ba, 0.0013 to 0.0039 $mg.L^{-1}$ for Cd and 0.0011 to 0.002 $mg.L^{-1}$ for Cu. The metals Ti (0.003 $mg.L^{-1}$) and Ni (0.0053 $mg.L^{-1}$) did not show major differences on concentration among sites during the "dry" season. In general, there was no clear trend in dissolved metal concentration when comparing the "wet" and "dry" seasons. An opposite result was found for the particulate fraction. A clear trend of higher values during the "wet" season for the particulate metal concentration can be noticed by the dataset. The solid fraction showed higher values when comparing with dissolved metals, being the main form of metals found in São Francisco River and its tributaries waters during whole the year.

The predominance of particulate fraction of metals in Rivers is also reported in other studies. Sulkin and Zhang (2014) reported that particulate metals are predominant in Amur River in Russia. Heavy metals released to aquatic system are generally bound to particulate matter (Suthar *et al.* 2009).

The concentration of metals in particulate matter is influenced by the parent material mineral composition, the grain size distribution, hydrological regimes and human activities (Bravo *et al.* 2009; Carvalho *et al.* 1999, Chen *et al.* 2000, Lair *et al.* 2009). Fine-grained particles (e.g. clay minerals, oxides, chelates) are the main carrier of metals in the aquatic ecosystems due to their large specific surface area (Clifton *et al.* 1997, Che *et al.* 2003, Bi *et al.* 2014). The adherence or absorption of metals by fine particles depend largely on physico-chemical conditions of the environment (Calmano *et al.* 1993, Singh *et al.* 1999).

The amount of particulate fraction varied during the "wet" season from 8 to 608 $mg.L^{-1}$ for Al, 16 to 321 $mg.L^{-1}$ for Fe, 0.9 to 110 $mg.L^{-1}$ for Mg, 3 to 67 $mg.L^{-1}$ for Ca, 0.2 to 12 $mg.L^{-1}$ for Mn, 0.1 to 10 $mg.L^{-1}$ for Ti, 0.004 to 7.6 $mg.L^{-1}$ for Cr, 0.14 to 7.2 $mg.L^{-1}$ for Zn, 0.1 to 7.2 $mg.L^{-1}$ for Ba, 0.01 to 3.1 $mg.L^{-1}$ for Ni, 0.11 to 1.67 $mg.L^{-1}$ for Cu, 0.013 to 1.14 $mg.L^{-1}$ for Pb, 0.002 to 0.35 $mg.L^{-1}$ for Co and 0.0013 to 0.057 $mg.L^{-1}$ for Cd.

In the "dry" season the values showed a smaller variation of 1.2 to 150 $mg.L^{-1}$ for Fe, 1.1 to 104 $mg.L^{-1}$ for Al, 1.5 to 20 $mg.L^{-1}$ for Ca, 0.2 to 6.7 $mg.L^{-1}$ for Mg, 0.0 to 1.4 $mg.L^{-1}$ for Mn, 0.0003 to 1.1 $mg.L^{-1}$ for Ti, 0.00 to 0.77 $mg.L^{-1}$ for Zn, 0.103 to 0.546 $mg.L^{-1}$ for Cu, 0.00 to 0.48 $mg.L^{-1}$ for Ba, 0.015 to 0.24 $mg.L^{-1}$ for Pb, 0.00 to 0.13 $mg.L^{-1}$ for Cr,

Table 2 Mean and Standard Deviation of the water quality parameters measured in th e water of São Francisco River and some of its tributaries

Parameter	"wet" Season	"dry" Season
Temperature (°C)	26.5 ± 0.9	22.9 ± 1.1
Dissolved Oxygen (mg.L^{-1})	5.3 ± 1.06	6.9 ± 0.7
pH	7.1 ± 0.3	7.7 ± 0.2
Electrical Conductivity (µS.cm^{-1})	43.4 ± 40.1	110.4 ± 388.6
Dissolved Solids (mg.L^{-1})	24.04 ± 27.07	57.6 ± 199.6
Suspended Solids (mg.L^{-1})	137.4 ± 113.2	6.01 ± 26.4
Turbidity (NTU)	170.4 ± 132.2	7.2 ± 1.7

Table 3 Mean and Standard Deviation of the dissolved, particulate and total metal concentration (mg.L^{-1}) measured in the water of São Francisco River and some of its tributaries

Parameter	Dissolved (mg.L^{-1})		Particulate (mg.L^{-1})		Total (mg.L^{-1})	
	"wet" Season	"dry" Season	"wet" Season	"dry" Season	"wet" Season	"dry" Season
Mg	2.17 ± 5.62	2.24 ± 1.69	13.11 ± 14.97	0.68 ± 0.86	15.0 ± 15.4	2.8 ± 1.7
Al	0.075 ± 0.068	0.007 ± 0.013	104.9 ± 82.9	6.15 ± 13.8	103.2 ± 83.4	4.3 ± 3.4
Ca	4.76 ± 4.07	5.96 ± 1.17	11.05 ± 8.87	4.69 ± 3.39	15.5 ± 9.8	10.4 ± 2.9
Cr	0.002 ± 0.001	0.003 ± 0.003	0.34 ± 1.00	0.008 ± 0.018	0.34 ± 1.0	0.009 ± 0.006
Fe	0.086 ± 0.086	0.018 ± 0.038	141.1 ± 75.8	7.67 ± 20.11	138.7 ± 77.4	5.0 ± 4.7
Co	0.003 ± 0.001	0.004 ± 0.005	0.05 ± 0.05	0.004 ± 0.009	0.05 ± 0.05	0.007 ± 0.005
Cu	0.001 ± 0.001	0.0011 ± 0.0001	0.52 ± 0.27	0.160 ± 0.070	0.53 ± 0.28	0.15 ± 0.05
Cd	0.004 ± 0.016	0.0014 ± 0.0005	0.002 ± 0.007	0.001 ± 0.0005	0.006 ± 0.023	0.0027 ± 0.0005
Ti	0.0003 ± 0.0001	0.0003 ± 0.0001	2.01 ± 1.58	0.07 ± 0.16	1.97 ± 1.58	0.048 ± 0.065
Mn	0.050 ± 0.350	0.0019 ± 0.0016	2.39 ± 1.68	0.178 ± 0.190	2.35 ± 1.72	0.16 ± 0.10
Ni	0.005 ± 0.001	0.005 ± 0.001	0.14 ± 0.42	0.011 ± 0.002	0.14 ± 0.42	0.016 ± 0.000
Zn	0.55 ± 3.89	0.021 ± 0.050	0.78 ± 0.91	0.21 ± 0.13	1.31 ± 4.73	0.24 ± 0.13
Ba	0.016 ± 0.010	0.007 ± 0.001	1.01 ± 0.99	0.019 ± 0.064	1.01 ± 1.00	0.018 ± 0.010
Pb	0.03 ± 0.01	0.039 ± 0.033	0.18 ± 0.16	0.019 ± 0.030	0.21 ± 0.16	0.054 ± 0.033

0.0029 to 0.068 $mg.L^{-1}$ for Co and 0.011 to 0.025 $mg.L^{-1}$ for Ni. The Cd did not show variability on concentration (0.0013 $mg.L^{-1}$) when comparing the sites during the “dry” season.

As expected the total fixed metal concentration followed the same pattern than the particulate fraction. Both these forms of metals followed the same pattern found for total suspended solids. There was a tendency of higher concentration of metals during the “wet” season indicating an input of these metals in particulate form from the surrounding land by surface runoff. Li and Zhang (2010) reported the same trend of higher values of metals in Han River in China, and attributed this pattern to the increase in surface runoff. It can be noted that there was high variability on the standard deviation values indicating that metal concentration was highly variable among sites.

In terms of total concentration during the “wet” season the highest to lowest values of total metals concentration showed the following sequence: Fe > Al > Ca > Mg > Mn > Ti > Zn > Ba > Cu > Cr > Pb > Co > Cd. In the “dry” season, the order of concentration was Ca > Fe > Al > Mg > Zn > Mn > Cu > Pb > Ti > Ba > Co > Cd (Table 3).

As previously noted the data were used in a Principal Component Analysis (PCA) to verify if there is season variation on the data set, and if there is a pattern of distribution of metals among sites and if they relate to anthropogenic pressures. The results of particulate and dissolved metal fractions were used in the PCA.

Before performing the PCA, the outliers were identified and excluded from the analyses data set. Two outliers were detected: sampling points P04 (Consciência Stream) and P16 (Abaeté River), both from the “wet” season. These points had high values for some of the parameters influencing the analyses. The point P04 receives effluents from zinc processing industry and shows high electrical conductivity values (320 $\mu S.cm^{-1}$) and total Zn concentration (36.32 $mg.L^{-1}$) in the “wet” season. The point P16 is under the influence of *Pinus* sp. and eucalyptus plantation and have high values of suspended solids (760 $mg.L^{-1}$), Al (608 $mg.L^{-1}$) and Fe (106 $mg.L^{-1}$), indicating that the shores are not well preserved and high quantity of solids input to this River during the raining season. This point has also diamond mining activities, which could be also interfering with solids input to the River. In relation to industries is important to highlight the presence of textile industries, which could be interfering with metal values observed in this point.

The PCA results are shown in Figures 2 to 5. The PCA analysis explained 54.6 % of the total variability with Principal Component 1 (PC1) explaining 45.9 % and Principal Component 2 (PC2), 9 % (Fig. 2). The PC1 selected most of the metals in the particulate fraction (Mg, Al, Ca, Cr, Pb, Mn, Co, Ti, Ba, Fe, Zn and Ni) and PC2 selected Zn in dissolved fraction. This result indicates that these metals in particulate fraction showed the same variability in the data, as they clustered together in the same position in the PCA. Other pattern was detected for the dissolved fraction. It seems to have three distinct groups for the dissolved fraction: 1) with Zn, Mg, Ca, Mn and Cr, 2) with Ni, Co, Pb, Cd and Cu and 3) with Ba, Al and Fe. It is important to highlight that the group 3 (Ba, Al and Fe in the dissolved fraction) showed similar variability than the particulate fraction.

The plot of the sampling locations following the results of PCA showed that the points P19, P26, P38, P28, P25 P54 had highest values for the metals selected by PC1 and points P03 and P04 for the parameter selected by PC 2 (Fig. 3). Except the point P04 that is located in Consciência Stream, all other points are located in São Francisco River. It is important to highlight that point P04 is under the influence of zinc processing industry and was placed in the position of dissolved zinc in the PC2. There is a not clear trend in the distribution of particulate and dissolved metal concentration in relation to the sampling points.

On the other side the plot of seasonality in relation to the loadings of PCA showed a clear trend in metal distribution(Fig. 4). The results reinforce the data that there is a strong season effect on water metal concentration at São Francisco River and its tributaries. The “wet” season is placed in the location of the highest particulate metal concentration selected by PC1 while the dissolved fraction is positioned with the “dry” season. The results indicate that during “wet” season the main source of metal is in particulate form, while during the “dry” season the metals are found in the dissolved fraction. This is a strong indication that surface runoff is the main mechanism of metal input to these water bodies during raining season.

However, sediment resuspension during raining season cannot be discarded. In the Pardo River (Minas Gerais State, Brazil), Alves *et al.* (2014) also reported higher levels of metals during the rainy season. Kang *et al.* (2010) found the same result in the study of metal concentration in several water bodies in Yeongsan Watershed in South Korea.

It can be clearly seen a correlation between different element concentration at "dry" and "wet" seasons. In "dry" season the elements are subdivided (dissolved groups), probably due to different sources. There is a clear trend from lower to higher values for PC1 from the "wet" to the "dry" season.

The highest concentration of dissolved metal concentration during the "dry" season must be related to the low water level and the concentration effect. With the "dry" season and with low water level the impact of the disposal of effluents in dissolved forms is more pronounced than in the "wet" season. Consequently, the dissolved metal concentration appears to increase during the "dry" season. The opposite occurs with the particulate fraction. With the raining season, there is an increase of surface runoff and the land is washed to the Rivers carrying particles to the water bodies. Consequently, there is an increase in particulate and the metal associated with this fraction.

When the anthropic influences are plotted based on the results of PCA there is an indication that surface runoff is the primary mechanism of particulate metal input to these water bodies (Fig. 5). While agricultural practices like Eucalyptus, *Pinus*, coffee, soy, corn, sugar cane plantation are mainly plotted in the position of particulate metals selected by PC1, most of the sites under the influence of urban and industrial activities are plotted in the position of dissolved fraction. However, is important to point out that agriculture practices were also related to the metal in dissolved forms. This indicates that the main source of particulate metals in the waters is related to the agriculture practices. Furthermore, the main process of input of metals from agriculture practices are from surface runoff.

Islam *et al.* (2015) in the study of metal concentration in the waters of Korotoa River in Bangladesh reported high Cu levels and attributed to surface runoff from farmed land. In Brazil, Alves *et al.* (2014) linked the high levels of Zn in River Pardo waters to the fertilizers and fungicides in agriculture. In the study of metal concentration in soils under agricultural practices and a control in the Napan River drainage basin (China), Yang *et al.* (2013) reported higher levels of Cu, Zn, Pb and Cd in the land used for agriculture. The same result of higher values of metals in agricultural lands of River Han in China was reported by Li and Zhang (2010). It is well known that the application of fertilizer and pesticides can increase the concentration of metals in agricultural soils (Li and Zhang 2010; Yang *et al.* 2013). Alloway and Ayres (1994) reports that agricultural practices are one of the greatest non point sources of metals. The main source of metals used in agriculture are fertilizers (Cd, Cr, Mo, Pb, U, V, Zn); pesticides (Cu, As, Hg, Pb, Mn, Zn); wood preservatives (As, Cu, Cr) and effluents from birds and livestock production (Cu, Zn) (Alloway & Ayres 1994).

On the other hand, Kang *et al.* (2010) reported higher levels of metals in the water bodies of Yeongsan Watershed in South Korea located in urban localities than in agriculture fields. However, Kang *et al.* (2010) concluded that the main source of Al and Fe are from agriculture practices and Zn, Cu and Ni are from industrial activities. In our study, most of the particulate metals showed the same variability, in other words, most of them had higher values in the same sampling location. Moreover, according to PCA results the main land use with higher particulate metal concentration were related to agricultural practices. In another study in the Guadalquivir River, Spain, Mendiguchía *et al.* (2007) reported that PCA identified three distinct zones (urban, agriculture and industrial) in relation to nutrient and dissolved metal concentration. In our study, there seems to have also a separation between major land use types and metal concentration, showing that the particulate fraction is mainly related to agricultural activities in the "wet" season and the dissolved forms with industrial and urban effluents in the "dry" season. A similar result was found by Han *et al.* (2013), which studied eight Rivers in Japan under industrial and urban pressures, reported that the metals analyzed were mainly in dissolved form. The pattern of higher dissolved metal related to industrial activities must be due to the effluents treatment. It seems that the effluent treatment is being efficient in removing the particulate metal, but is failing in the removal of the dissolved fraction. On the other side, the higher concentration of particulate fraction in Rivers under agricultural practices is expected. In agricultural land most of the soil is exposed and is subject to be carried with surface runoff during the raining season. Consequently, natural occurring metals and the ones from anthropogenic origins (derived from fertilizer and pesticides) are bound to fine particles of soils and carried with surface runoff to water bodies from surrounding land.

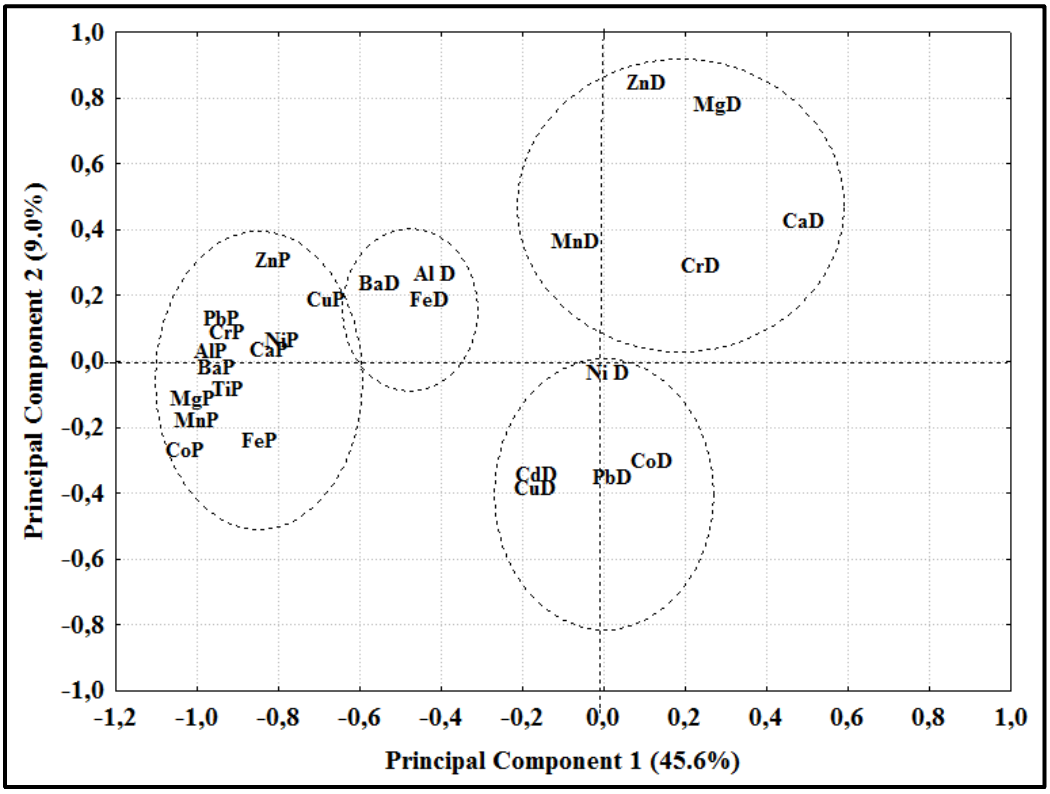

Figure 2
Results of Principal Component Analysis from the Principal Component Analysis (PCA) with the loadings of particulate (P) and dissolved (D) metal concentration São Francisco River and its tributaries waters

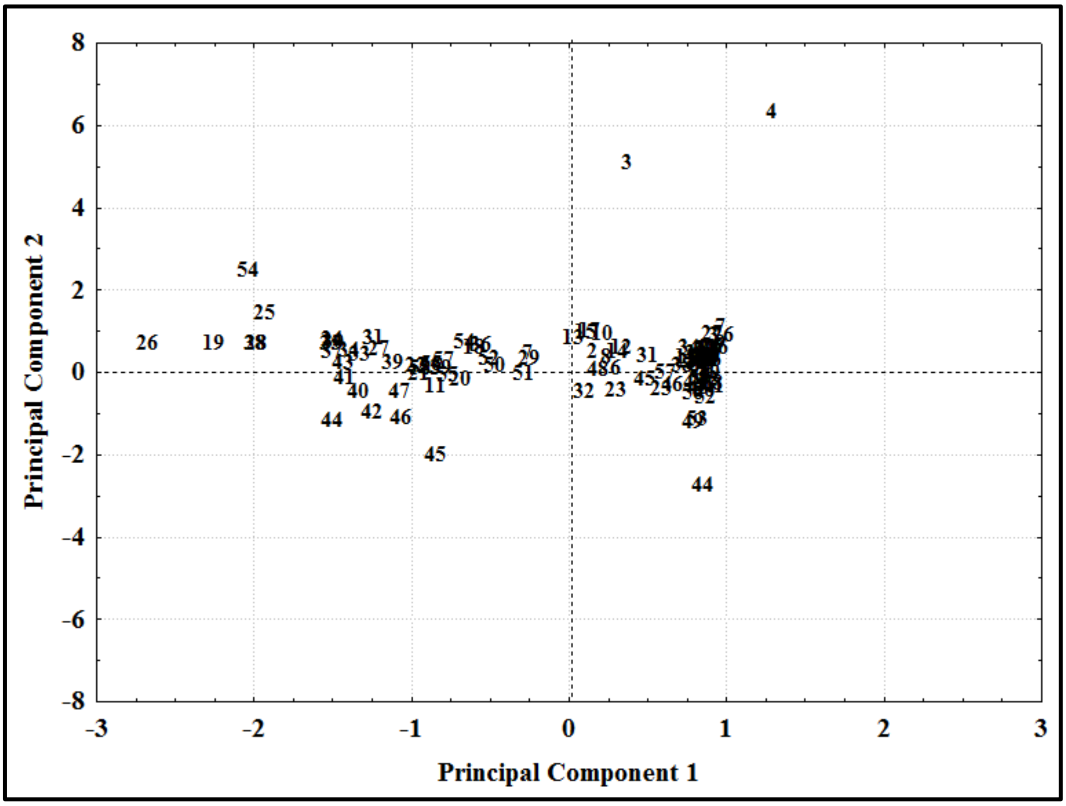

Fig. 3
Plot of the scores of the sampling points based on the results of PCA

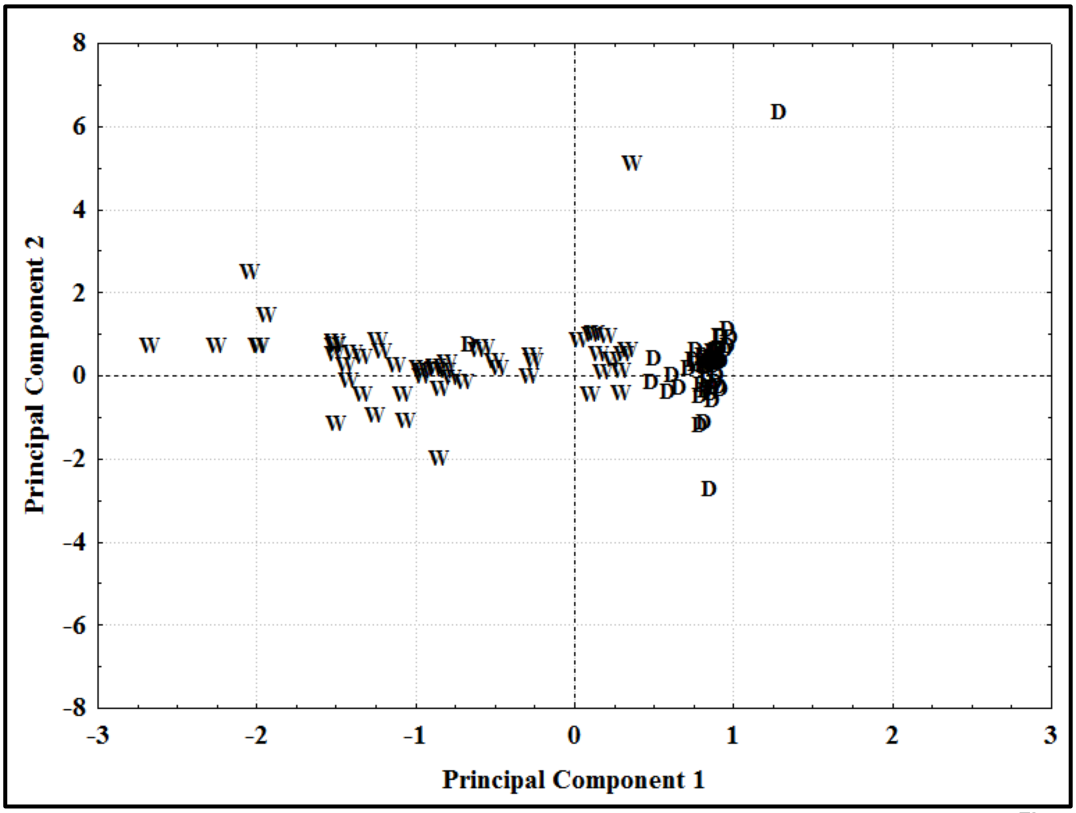

Fig. 4
Plot of the scores of the “dry” (D) and “wet” (W) seasons based on the results of PCA

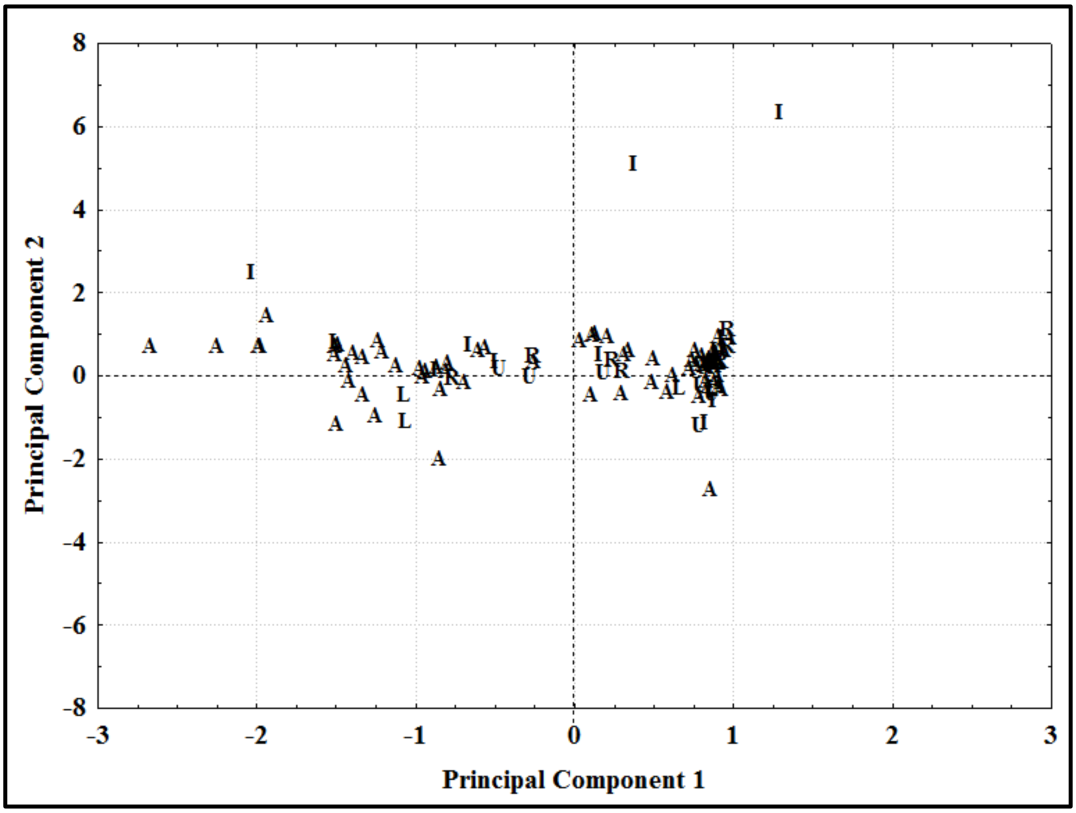

Fig. 5
Plot of the scores of the anthropic influences based on the results of PCA.
Where: A – Agriculture, R – Ranch, L – Livestock, I – Industrial, U – Urban

4. CONCLUSIONS

The results showed that there was a clear trend of higher particulate metal concentration during the "wet" season, while the dissolved forms were highest in the "dry" season. The suspended particulate matter also showed a clear trend of higher concentration during the raining season indicating that the shores are not well preserved. There was no clear trend of the distribution of particulate and dissolved metal concentration among sites. However, it seems that metals in particulate form were mainly related to agricultural practices while the dissolved forms were related to industrial activities. The results indicate that metals associated with soil particles from fertilizers and pesticides enters the Rivers with surface runoff, especially in the raining season. On the other side the treatment of industrial effluents are being successful in retaining metals in particulate form but fail in treating the dissolved metals that are disposed in the River. The results showed that is a close link between water metal concentration and anthropogenic pressures in São Francisco watershed.

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