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Metal Contamination of Water and Sediments of the Vieira River, Montes Claros, Brazil

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Abstract

Vieira River is the main recipient of domestic and industrial wastewater in the city of Montes Claros, MG, Brazil. Until 2010, domestic sewage was dumped in it without any kind of treatment. Concentrations of arsenic (As), chrome (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) were determined in water and sediment samples in eight locations along the Vieira River during the dry season of 2015. Concentrations of Cu, Ni, and Zn detected in the water at some sites along the Vieira River were superior to the reference limits for toxicity. The concentration of Cu and Ni restricts the use of water for irrigation in some sites of the river. The level of sediment contamination was assessed by five approaches, including contamination factor (CF), pollution load index (PLI), geo-accumulation index (I_{geo}), cluster analysis (CA), and principal component analysis/factor analysis (PCA/FA). The results showed that Cr and the downstream sampling site nearest to the Wastewater Treatment Plant of the city of Montes Claros had the highest values of PLI, I_{geo}, and CF, which reinforces the influence of domestic and industrial wastewater discharge in pollution of the Vieira River. In addition, CA and PCA/FA reinforced the assumption that Cr comes from anthropogenic pollution sources.

The contamination of aquatic systems by metals presents considerable concern due to toxicity, abundance, persistence, and bioaccumulation of these chemical elements (Kuang et al. 2016; Xu et al. 2018; Yang et al. 2012). Metals are nonbiodegradable and persistent compounds, which, because of these characteristics, accumulate in vital organs of the human body, such as kidneys, bones, and liver, and are associated with serious health disorders, such as diarrhea, stomatitis, tremor, ataxia, paralysis, vomiting, convulsion, depression, and pneumonia (McCluggage 1991). The nature of the effects of these disorders can be toxic, neurotoxic, carcinogenic, mutagenic, or teratogenic (EU 2002).

The rapid growth of the world's population and the expansion of industrial and agricultural production contributed to large quantities of chemicals containing metals being discharged in rivers around the world in recent years (Islam et al. 2015; Srebotnjak et al. 2012). Metals accumulate in rivers mostly through atmospheric deposition, urban wastewater, and agricultural and industrial runoff (Cheng et al. 2013).

Metals discharged into a river system by natural or anthropogenic sources are found in the aqueous phase and in sediments (Mondal et al. 2018; Vu et al. 2017). Because of adsorption, hydrolysis, and precipitation, a large quantity of metal ions get deposited in the sediment, and only a small portion of them stay dissolved in water (Mondal et al. 2018). Studies on the pollution of water bodies by metals, considering only the aqueous phase, are not conclusive due to the seasonal variation of riverine flow and numerous changes associated with chemical elements due to dissolution, precipitation, sorption, and complexation. Therefore, the analysis of metals in riverbed sediments is essential to study metal pollution and assessment river system quality (Bhuyan and Bakar 2017; Islam et al. 2015; Mondal et al. 2018; Varol 2011) and is also an important step for measurement studies of contaminated ecosystems.

The Vieira River has significant importance for the water quality of the middle region of the São Francisco River basin, because it is the main recipient of domestic and industrial sewage from Montes Claros, MG, Brazil, the largest city in the region with approximately 400,000 inhabitants.

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The Vieira River basin is fully inserted in the municipality of Montes Claros and has a catchment area of approximately 580.1 km^2 and an extension of approximately 33.4 km (Leite and Rocha 2016). The Vieira River flows into the Verde Grande River, a tributary of the São Francisco River. The Verde Grande river basin is formed by 35 municipalities, Montes Claros being the largest, with approximately 45% of the basin inhabitants (ANA 2013). Therefore, The Vieira River is part of the São Francisco River basin, the fifth longest river in Brazil, with approximately 2863 km in extension.

The São Francisco River is the most important river in the arid and semi-arid region of Brazil, with a drainage basin of approximately 640,000 km^2. Approximately 70% of the water of the São Francisco River basin is used for irrigation, with greater demand in the middle and submiddle regions (CBHSF 2016). Despite the influence of water use in the Vieira River basin on quantity of water used, mostly, in irrigation downstream of Montes Claros, no scientific research regarding metal issues in the study area has been conducted so far. The present study can provide relevant information for the sustainability of the river basin ecosystems involved, especially regarding the risks to food security and the productive and ecological aspects of the areas that use water from the Vieira River.

Therefore, the objectives of this study are: (1) to assess the pollution status of the Vieira River by estimating the levels of metals in water and sediment, and (2) to identify sources of metal contamination in study area.

Methodology

Study Area

The Vieira River originates in the south of Montes Claros [near sampling site S1 (Fig. 1)] and crosses residential and industrial areas before joining the Verde Grande river. The Wastewater Treatment Plant (WTP) of Montes Claros is located between sites S2 and S3 (Fig. 1). Several industry plants are located west of sites S2, S3, and S4 (Fig. 1), including textile, biofuel, pharmaceutical, and mining industries. Approximately 1 km east from sites S2 and S3, another textile factory is located (Fig. 1). A small dam, located in site S6 (Fig. 1), diverts part of the Vieira River's waters to a superficial irrigation area that cultivates pasture to feed bovines to produce milk. Sites S7 and S8 (Fig. 1) are located at the mouth of the Vieira River and in the Verde Grande River, respectively.

The unpleasant odor and presence of solid residues and white foam in waters of the Vieira River are easily observed in the stretches crossing the city of Montes Claros and downstream from the WTP. Before 2010, this city did not have

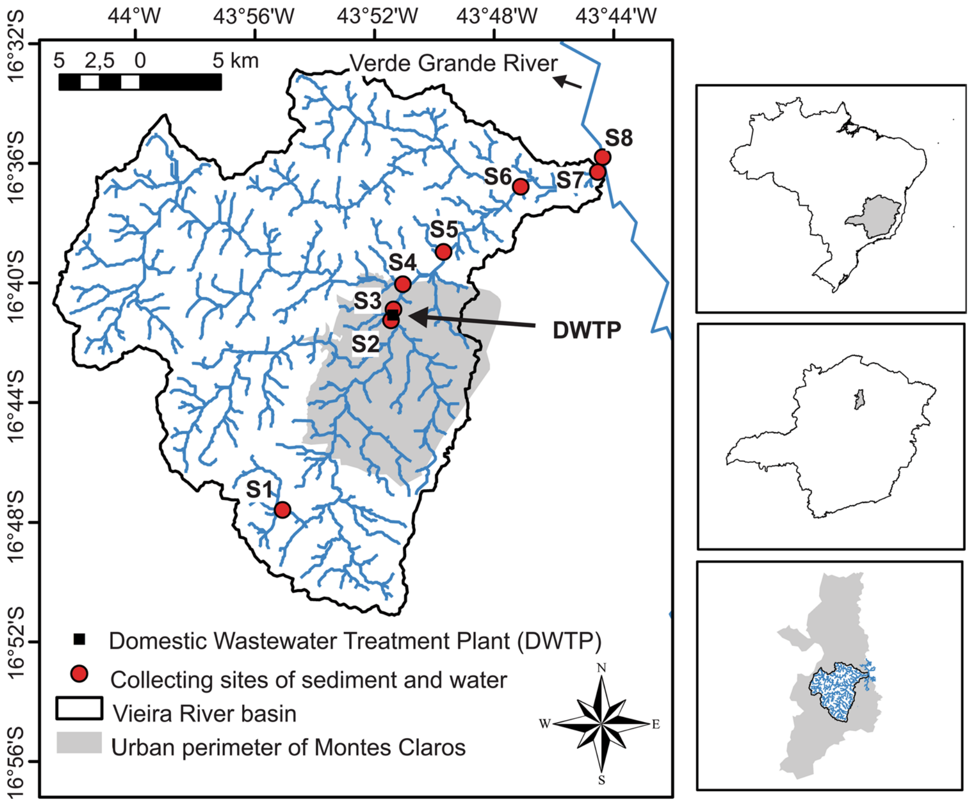

Fig. 1 Location map of sampling sites along the Vieira River

a WTP and domestic wastewater were discharged into the river without any kind of treatment.

Sample Collection

To assess the levels of metals contamination in the Vieira River, water and sediment samples were collected from eight sites (S1–S8) (Fig. 1) in July 2015. The unfiltered water and riverbed sediment samples were collected approximately 10 m from the Vieira River shore. The water samples were stored in polypropylene bottles that had been previously washed with HNO_3 (10%). To preserve the water samples, approximately 1.5 mL of HNO_3 (65%) was added to reduce their pH to values lower than 2. Sampling bottles were kept in coolers with ice during their transport to the laboratory, where they were stored in a refrigerator at temperatures between 0 and 4 °C until the quantification of metals (APHA 2012).

Three riverbed sediment samples were collected in each sampling site to form a composite sample. The samples were stored in plastic bags and transported to the laboratory, where they were dried in oven at 45 °C to gain constant weight. The dried samples were then ground using agate mortar and pistil and passed through 0.3-mm nylon sieve. Approximately 50 g of each sieved sample was stored in Falcon tubes for further analysis of metal content.

The pH and electric conductivity (EC) were measured *in loco* in each sampling site (S1 to S8) (Fig. 1) by using digital pH meter (HI98107 pHep, HANNA) and portable EC meter (HI98311 DiST$^{®}$5, HANNA), respectively.

Chemical Analysis

The metal concentration was analyzed using an atomic absorption spectrophotometer (AA FS240, Varian). The analytical curves were prepared from standard solutions obtained from Sigma Aldrich (Germany) and diluted in different concentration with ultrapure water (Mili-Q, Millipore). Elements Cr, Cu, Ni, Pb, and Zn were measured in the flame atomization mode, composed of ar-acetylene (acetylene 2.8 AA), and element As was determined by a hydrite generation system using argon (99.999% purity) and ar-acetylene (acetylene 2.8 AA) (Christophoridis et al. 2019; Santos et al. 2013). All analyses were performed in triplicate.

For metal analysis, 100 mL of the water sample was mixed with 10 mL of HNO_3 (65%, PA) and placed on a hot plate, where it evaporated to a volume of 10–20 mL (APHA 2012). The digested samples were then filtered through a quantitative filter paper (Unifil, C43, blue stripe) and transferred to Falcon tubes. The volume of each sample was adjusted to 25 mL using ultrapure water (Milli-Q, Millipore). The concentrations of As, Cr, Cu, Ni, Pb, and Zn were determined in an atomic absorption spectrophotometer.

To determine metal content in riverbed sediments of the Vieira River, 0.50 g of each sample was mixed with 9 mL of HNO_3 (65%, PA) and 3 mL of HCl (37%), and then subsequently microwave digested (Mars 6, CEM) (USEPA 1998). The digested samples were then filtered through a quantitative filter paper (Unifil, C42, blue stripe) and mixed with ultrapure water (Milli-Q, Millipore) until they reached a volume of 25 mL. The concentrations of As, Cr, Cu, Ni, Pb, and Zn were determined in an atomic absorption spectrophotometer.

Statistical Analysis

To understand the impact of metals present in the sediments, were calculated: contamination factor (CF), pollution load index (PLI), and geo-accumulation index (I_{geo}). The assessment of degree of contamination from metals using these coefficients has been successfully employed in several works (Islam et al. 2015; Kuang et al. 2016; Lu et al. 2017; Varol 2011).

CF is the ratio between the concentration of each metal in sediment samples and the background value (Eq. 1). The background value adopted were 0.23 mg kg^{-1} for As (Kabata-Pendias and Pendias 2001); 35.00, 25.00, 20.00, and 20.00 mg kg^{-1} for Cr, Cu, Ni, and Pb, respectively (Taylor and McLennan 1995) and 49.50 mg kg^{-1} for Zn (Turekian and Wedepohl 1961).

$$\mathrm{CF} = \frac{C_{\mathrm{metal}}}{C_{\mathrm{background}}} \tag{1}$$

The interpretation of the CF values was suggested by (Hakanson 1980), where $\mathrm{CF} < 1$ indicates low contamination; $1 < \mathrm{CF} < 3$ indicates moderate contamination; $3 < \mathrm{CF} < 6$ indicates considerable contamination; $\mathrm{CF} > 6$ indicates very high contamination.

The PLI gives an assessment of the overall toxicity status for each sample, and it also shows the contribution of each metal to the pollution. (Equation 2).

$$\mathrm{PLI} = \left(\mathrm{CF}_1 \times \mathrm{CF}_2 \times \mathrm{CF}_3 \times \cdots \times \mathrm{CF}_n\right)^{1/n} \tag{2}$$

where CF is the contamination factor, and n is the number of metal species. $\mathrm{PLI} < 1$ indicates that there is no metal pollution in the site, however, $\mathrm{PLI} > 1$ indicates that a pollution exists (Varol 2011).

The I_{geo} determines metal contamination in sediments, comparing current contents with background values (Eq. 3).

$$I_{\mathrm{geo}} = \log_2\left[\frac{C_n}{1.5B_n}\right] \tag{3}$$

where C_n is the measured concentration of metal n in the sediment and B_n is the background value of element n. The factor 1.5 is introduced in the equation to minimize possible variation in the background value, which can be attributed to lithospheric effects. The I_{geo} is classified in seven groups (Table 1).

Variance analysis (ANOVA) was performed, with 5% error probability, to verify differences between sampling sites, and in case of significance, the Tukey test ($p \leq 0.05$) was performed to identify homogeneities in the data sets. Correlations between the variables considered were tested using Pearson correlation coefficient with statistical significance defined at $p \leq 0.05$.

Multivariate analysis of the data set was performed through cluster analysis (CA) and principal component analysis/factor analysis (PCA/FA). The data were previously standardized to avoid misclassification due to differences in data size.

CA was performed in the data set through Ward's method (Ward 1963) with standardized Euclidean distances as similarity measure. FA was performed after PCA. PCA of the standardized variables was performed to extract the significant principal components (PCs) and reduce even more the contribution of variables with less significance.

Results and Discussion

Metal Contamination in Water Body

The concentration levels of As, Cu, Ni, and Zn in surface water of the Vieira River varied significantly ($p < 0.05$) among sampling sites. Zn was the metal with the highest average concentration, followed by Cu, Ni, and As. Cr and Pb were not detected in the Vieira River water in any of the sampling sites (Table 2). High concentrations of Zn and Cu are commonly found in wastewater (Kalavrouziotis et al. 2012; Kuang et al. 2016), and this fact has been corroborated in works with sewage sludge from Montes Claros' WTP (Horn et al. 2014).

The As was detected in higher concentrations in sites S7 and S8 water and in lower concentrations in sites S1

Table 1 Classification of pollution level in relation to the geo-accumulation index (I_{geo})

	Class 0	Class 1	Class 2	Class 3	Class 4	Class 5	Class 6
I_{geo}	$I_{\text{geo}} < 0$	$0 \leq I_{\text{geo}} < 1$	$1 \leq I_{\text{geo}} < 2$	$2 \leq I_{\text{geo}} < 3$	$3 \leq I_{\text{geo}} < 4$	$4 \leq I_{\text{geo}} < 5$	$I_{\text{geo}} \geq 5$
Pollution level	Practically unpolluted	Unpolluted to moderately polluted	Moderately polluted	Moderately to heavily polluted	Heavily polluted	Heavily polluted to extremely polluted	Extremely polluted

Table 2 Metal concentration (μg L^{-1}) in water samples of the Vieira River and maximum concentration (μg L^{-1}) permitted in water

Sites	As (μg L^{-1})		Cr (μg L^{-1})		Cu (μg L^{-1})		Ni (μg L^{-1})		Pb (μg L^{-1})		Zn (μg L^{-1})	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
S1	0.4d	0.09	0.0	0.00	82.6b	0.74	0.00f	0.00	0.0	0.00	189.1c	5.94
S2	0.6d	0.01	0.0	0.00	89.7b	1.14	0.00f	0.00	0.0	0.00	254.6c	49.44
S3	1.0c	0.09	0.0	0.00	150.3a	4.38	38.2c	1.64	0.0	0.00	392.4b	91.59
S4	1.2c	0.09	0.0	0.00	145.8a	18.14	21.8e	2.61	0.0	0.00	586.7a	1.85
S5	1.2c	0.03	0.0	0.00	18.6c	1.28	30.0d	1.86	0.0	0.00	158.4c	23.90
S6	1.7b	0.01	0.0	0.00	19.4c	2.61	52.3b	1.51	0.0	0.00	197.6c	23.25
S7	2.1a	0.22	0.0	0.00	15.5c	1.42	50.6b	1.01	0.0	0.00	148.9c	15.35
S8	2.3a	0.14	0.0	0.00	15.6c	2.28	77.9a	1.37	0.0	0.00	148.2c	7.79
Mean	1.3		0.0		67.2		33.8		0.0		259.5	
(CONAMA 2005)	33		50		13		25		33		5000	
(USEPA 2012)	100		100		200		200		5000		2000	
(WHO 2006)	100		100		200		200		5000		2000	
(USEPA 1999)	150		11		9		52		2.5		118	
(WHO 2011)	10		50		2000		70		10		–	

S1 and S2—upstream sites of the Wastewater Treatment Plant (WTP); S3 to S8—downstream sites of the WTP

SD standard deviation

Means followed by the same letter have no statistical difference (ANOVA; Tukey test, $p < 0.05$)

and S2. None of these values was higher than the recommended limits for use of water in irrigation (CONAMA 2005; USEPA 2012; WHO 2006) or fresh water (USEPA 1999; WHO 2011). Cu was detected in higher concentrations in sites S3 and S4 and in lower concentration in sites S5, S6, S7, and S8. In every site, Cu concentration exceeded the reference values for freshwater toxicity (USEPA 1999). Ni was detected in higher concentration in site S8 but not detected in sites S1 and S2. Ni concentration exceeded the recommended limits for use as fresh water in sites S6 and S8 (USEPA 1999; WHO 2011). Zn was detected in higher concentration in site S4, and in lower concentration in sites S1, S2, S5, S6, S7, and S8. In every site, Zn concentration exceeded the reference values for freshwater toxicity (USEPA 1999). Cu, Ni, and Zn concentrations did not exceed the limits recommended by international guidelines for use of water in irrigation. However, Cu and Ni were detected in concentrations higher than the established by the Brazilian legislation for use of water in irrigation in all sites and in S3, S5, S6, S7, and S8, respectively (CONAMA 2005) (Table 2).

The water samples collected in sites S3 and S4 had the highest concentrations of metals (Table 2), and these are the downstream sites nearest to Montes Claros's WTP (Fig. 1), which indicates anthropogenic pollution.

Between 1989 and 2009, Montes Claros practically doubled the occupied urban area in the Vieira River basin (Leite et al. 2011); also, before 2010, the domestic wastewater generated in the city was dumped into the Vieira River without any kind of treatment. This scenario supports the anthropogenic pollution thesis in sites S3 and S4 (Table 2).

The EC values of the Vieira River water had positive correlation with As ($r = 0.693$, $p < 0.05$) and Ni ($r = 0.706$, $p < 0.05$). Some metals also had positive correlation with each other: As with Ni ($r = 0.934$, $p < 0.01$) and Cu with Zn ($r = 0.867$, $p < 0.01$). The pH found in water along the Vieira River had no correlation with metal concentration (Table 3), a result similar to those of Kuang et al. (2016).

Metal Contamination in Riverbed Sediment

The average concentration of metals in riverbed sediments of the Vieira River followed a decreasing order of Cr > Zn > Cu > Pb > Ni > As. Concentration values of As, Cu, Ni, and Zn in riverbed sediments varied significantly ($p < 0.05$) between sampling sites. The sediments collected in site S3 showed the highest metal concentration along the Vieira River, which can be attributed to its proximity with Montes Claros' WTP. The sediment samples collected in sites S7 and S8 had lower concentration of metals, which is associated with the distance from Montes Claros' urban area, as it provides greater dilution of the pollutants generated by the city (Table 4).

The Brazilian legislation stablishes, in Resolution CONAMA 344/2004, two limit values (Level 1 and Level 2, shown in Table 5) for pollutant level found in sediments (CONAMA 2004). Compared with this legislation, the average levels of As, Cu, Ni, Pb, and Zn in sediments were below the limits stablished in Level 1, that is, these metals pose a low probability of adverse effects to biota. The average level of Cr in the sediments was above the limit stablished in Level 1, which indicates occasional adverse effects to biota (CONAMA 2004) (Table 5). The limit values indicated by Brazilian legislation have as reference the Canadian Council of Ministers of the Environment (CCME 2001).

Considering the toxicity reference values (TRV) proposed by (USEPA 1999), Cr and Cu were the only metals that had values above Level 1 limits (Table 5).

Compared with other rivers around the world, the average concentrations of As, Cr, Cu, Ni, Pb, and Zn in the Vieira River are lower. However, these metals, except As, have higher concentrations than the ones observed in the Pardo river, which suffers high anthropogenic impact, because it is located in a highly populated basin near areas of sugarcane cultures, with intense application of mineral fertilizers, pesticides and herbicides (Alves et al. 2014) (Table 5).

Cr values in riverbed sediments had positive correlation with Cu ($r = 0.787$, $p < 0.05$) and Zn ($r = 0.786$, $p < 0.05$) in water. Pb values found in riverbed sediments also had

Table 3 Pearson correlation matrix in water body

	As_W	Cu_W	Ni_W	Zn_W	EC	pH
As_W	1					
Cu_W	−0.614	1				
Ni_W	**0.934****	−0.521	1			
Zn_W	−0.317	**0.867****	−0.285	1		
EC	**0.693***	−0.376	**0.706***	−0.007	1	
pH	−0.150	0.395	−0.222	0.169	−0.357	1

Bold values represent correlation with significance

* and ** represent significance at the 0.05 and 0.01 probability level, respectively. Subscript W represents metal in water samples

Table 4 Metals concentration (mg kg^{-1}) in riverbed sediments of the Vieira River

Site	As (mg kg^{-1})		Cr (mg kg^{-1})		Cu (mg kg^{-1})		Ni (mg kg^{-1})		Pb (mg kg^{-1})		Zn (mg kg^{-1})	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
S1	0.2bc	0.13	27.6d	12.10	14.3b	1.33	14.1a	5.51	15.7ab	1.39	48.7a	2.86
S2	0.1cd	0.03	68.4bc	7.81	18.6b	18.58	9.8ab	3.71	13.7bc	6.66	52.0a	2.93
S3	0.5a	0.06	120.2a	20.27	43.5a	3.49	12.9a	2.72	23.1a	3.22	48.9a	0.08
S4	0.1cd	0.08	94.5ab	21.54	9.6b	1.52	10.5ab	8.23	10.4bc	4.08	45.8a	6.98
S5	0.2bcd	0.02	41.4cd	2.20	22.8ab	0.39	7.7ab	3.81	15.2ab	0.44	49.2a	1.77
S6	0.2bc	0.06	52.6cd	0.87	30.4ab	8.50	10.3ab	2.87	18.9ab	1.33	42.4ab	20.73
S7	0.0d	0.00	58.0cd	9.03	–	–	0.4b	0.48	5.2c	0.27	21.3b	3.05
S8	0.3b	0.06	28.6d	1.17	–	–	9.6ab	0.96	16.5ab	0.38	32.6ab	0.90
Mean	0.21		61.40		23.20		9.41		14.85		42.61	

S1 and S2—upstream sites of the Wastewater Treatment Plant (WTP); S3 to S8—downstream sites of the WTP

SD standard deviation

Means followed by the same letter have no statistical difference (ANOVA; Tukey test, $p < 0.05$)

Table 5 Metal levels in sediments (mg kg^{-1}) compared with different guidelines and studies around the world

River (location)	As (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})	References
Vieira River (Brazil)	0.21	61.40	23.20	9.41	14.85	42.61	This study
Pardo River (Brazil)	0.68	24.53	17.74	8.07	8.27	34.86	(Alves et al. 2014)
Hindon River (India)	–	101.78	59.33	–	41.20	58.29	(Suthar et al. 2009)
Korotoa River (Bangladesh)	25	109	76	95	58	–	(Islam et al. 2015)
Yanghe River (China)	–	44.25	25.4	–	20.9	74.3	(Kuang et al. 2016)
Tigris River (Turkey)	4.6	84.8	344.6	145.6	265.3	203.1	(Varol 2011)
Ergene River (Turkey)	25	160	65	64	99	177	(Hallı et al. 2014)
TRV	6	26	16	16	31	110	(USEPA 1999)
Level 1	5.9	37.3	35.7	18	35	123	(CONAMA 2004)
Level 2	17	90	197	35.9	91.3	315	(CONAMA 2004)

TRV toxicity reference value

positive correlation with As ($r = 0.921$, $p < 0.01$), Cu ($r = 0.785$, $p < 0.05$) and Ni ($r = 0.756$, $p < 0.05$) in riverbed sediments. Zn values found in riverbed sediments had correlation to As ($r = -0.862$, $p < 0.01$) in water and Ni ($r = 0.774$, $p < 0.05$) in sediments (Table 6). No obvious correlation was observed between metals in the river's sediments and water, which indicates that the metals found in water body is not from the natural source of contaminants release (e.g., riverbed sediments); that is, the anthropogenic discharge of pollutants may be the main source (Kuang et al. 2016).

The values of the contamination factors (CF) of the riverbed sediments followed a decreasing order of Cr > Cu = As > Zn > Pb > Ni. Cr was the only metal with average CF value that characterized moderate contamination. The other metals had average CF values lower than 1, which indicated low contamination (Hakanson 1980). Regarding Cr, the highest CF values were observed in sites S3 and S4, which indicates considerable contamination (Hakanson 1980). The CF values of Cu, As, and Pb were also higher in site S3, which is another indicative of an anthropogenic pollution source, given that this site is located just after Montes Claros' WTP. The CF values of Ni in all sampling sites showed low contamination (Hakanson 1980) (Table 7).

The pollution load index (PLI) in site S3, located near Montes Claros' urban zone and WTP, had higher values than the ones found in other sampling sites, and was the only one with value above 1, indicating the existence of pollution by metals. The PLI values of riverbed sediments of the Vieira River had the following descending order: S3 > S6 > S1 = S2 = S5 > S8 > S4 > S7 (Fig. 2).

Despite being located near the Vieira River's headwater, site S1 had pollution indexes higher than those of site S7 (Fig. 2; Table 7). This can be justified by the proximity of site S1 to pasture irrigation areas, which can result in pollution by chemical fertilizers.

CF and PLI values were higher in site S8 when compared to site S7 (Fig. 2; Table 7), which indicates contamination

Table 6 Pearson correlation matrix between average concentrations of metals in water body and riverbed sediments of the Vieira River

	As_W	Cu_W	Ni_W	Zn_W	As_S	Cr_S	Cu_S	Ni_S	Pb_S	Zn_S
As_W	1.000									
Cu_W	−0.614	1.000								
Ni_W	**0.933****	−0.521	1.000							
Zn_W	−0.317	**0.867****	−0.285	1.000						
As_S	−0.122	0.346	0.231	0.137	1.000					
Cr_S	−0.221	**0.787***	−0.136	**0.786***	0.320	1.000				
Cu_S	−0.476	0.403	−0.203	0.226	0.656	0.534	1.000			
Ni_S	−0.629	0.560	−0.371	0.347	0.674	0.143	0.519	1.000		
Pb_S	−0.271	0.241	0.083	0.033	**0.921****	0.197	**0.785***	**0.756***	1.000	
Zn_S	**−0.862****	0.557	−0.690	0.370	0.361	0.256	0.648	**0.774***	0.563	1.000

Bold values represent correlation with significance; * and ** represent significance at the 0.05 and 0.01 probability level, respectively. Subscript W represents metal in water samples. Subscript W and S represent metal content in water and sediment samples, respectively

Table 7 Contamination factors (CF) of metals in riverbed sediments of the Vieira River

Sites	CF values						Mean
	As	Cr	Cu	Ni	Pb	Zn	
S1	1.01	0.79	0.57	0.71	0.79	0.98	0.81
S2	0.48	1.95	0.74	0.49	0.68	1.05	0.90
S3	2.22	3.43	1.74	0.65	1.16	0.99	1.70
S4	0.51	2.70	0.39	0.52	0.52	0.92	0.93
S5	0.80	1.18	0.91	0.39	0.76	0.99	0.84
S6	1.05	1.50	1.22	0.52	0.95	0.86	1.01
S7	0.00	1.66	–	0.02	0.26	0.43	0.47
S8	1.36	0.82	–	0.48	0.82	0.66	0.83
Mean	0.93	1.75	0.93	0.47	0.74	0.86	

S1 and S2—upstream sites of the Wastewater Treatment Plant (WTP); S3 to S8—downstream sites of the WTP

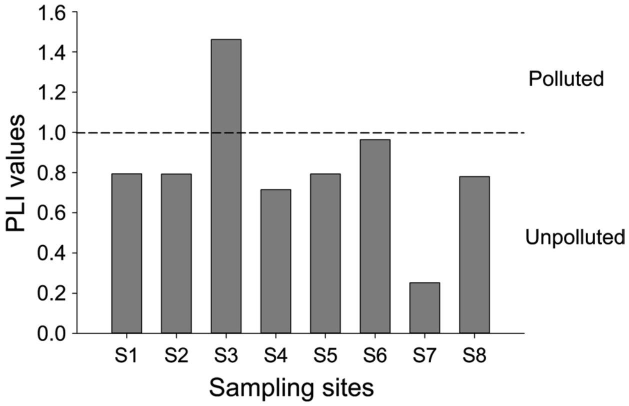

Fig. 2 Pollution load index (PLI) of metals in riverbed sediments of the Vieira River

of the Verde Grande river by some other pollution source outside the Vieira River basin. Site S8 is located in the Verde Grande river downstream to Vieira River mouth (Fig. 1).

The average values of geo-accumulation index (I_{geo}) of the riverbed sediments followed a decreasing order of Cr > As > Zn > Cu > Pb > Ni. Cr was the only metal with mostly positive I_{geo}, indicating pollution, reaching the maximum value of 1.20, which indicates moderate pollution (Table 1; Fig. 3). The I_{geo} values of As and Cu varied from −1.63 to 0.57 and from −1.96 to 0.21, respectively. Considering the positive I_{geo} of As and Cu, these values characterize riverbed sediments of the Vieira River as unpolluted to moderately polluted (Table 1; Fig. 3). All I_{geo} values of Ni, Pb and Zn were negative, indicating practically absence of pollution in sediments (Table 1; Fig. 3).

The sampling sites were grouped in three clusters (Fig. 4). Cluster 1 (S7) was located in the mouth of the Vieira River, most distant region from Montes Claros and with less accumulation of metals in riverbed sediments (Fig. 2; Table 7). Cluster 2 (S3), located in the nearest sampling site to the WTP of Montes Claros, had the highest levels of pollution (Fig. 2; Table 7). Cluster 3 (S1, S2, S4, S5, S6, and S8) had an intermediate level of pollution

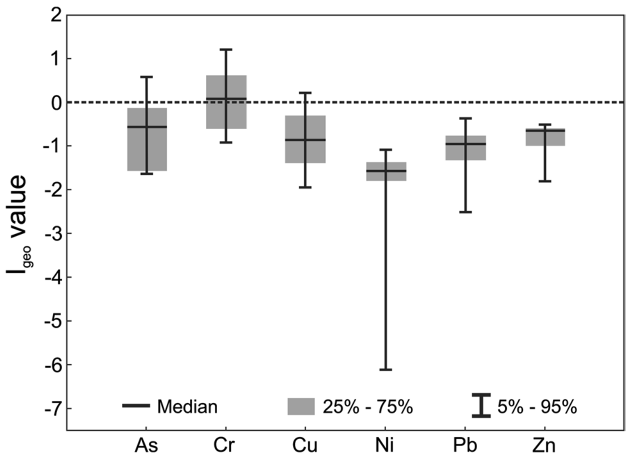

Fig. 3 Geo-accumulation indexes (I_{geo}) of metals in riverbed sediments of the Vieira River

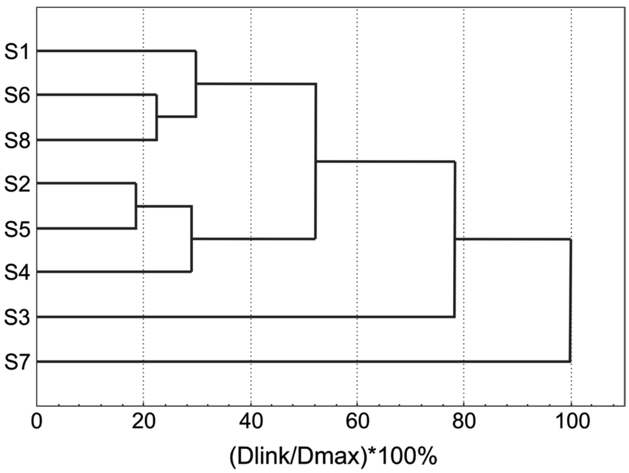

Fig. 4 Hierarchical dendrogram of sampling sites of riverbed sediments of the Vieira River

when compared to other clusters, but with indexes indicating absence of pollution (Fig. 2) or low contamination (Table 7) in these locations.

All metals analyzed were grouped in two clusters (Fig. 5). Cluster 1 is formed only by Cr—a metal found in greater proportion in riverbed sediments. Cluster 2 is formed by As, Pb, Ni, and Zn.

The approaches of PCA and FA were applied to further identify possible sources of contamination by metals. PCA of the entire data set (all metal concentrations in riverbed sediments) showed that the first two PCs explained about 81.34% of the total variance in the data set. The first PC, which represents 62.79% of the total variance, was correlated (loadings > 0.70) with As, Ni, Pb, and Zn. The second PC, which represents 18.66% of the total variance, was correlated with Cr (Table 8).

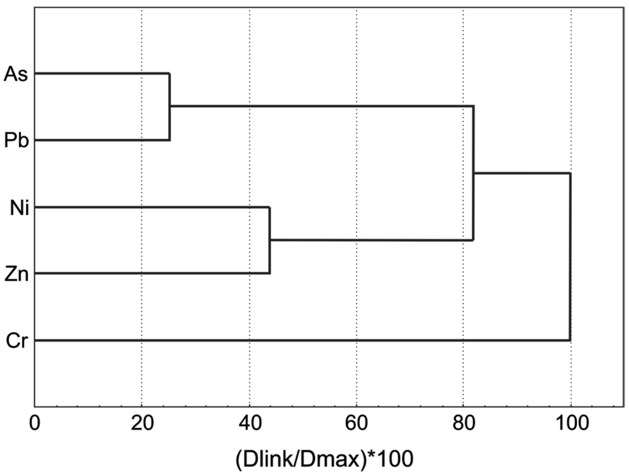

Fig. 5 Hierarchical dendrogram of metals found in riverbed sediments of the Vieira River

Table 8 Loadings of experimental variables in relation to the significant principal components to Vieira River data set

	VF1	VF2
As	**−0.868**	0.021
Cr	−0.360	**0.930**
Ni	**−0.903**	−0.222
Pb	**−0.928**	−0.126
Zn	**−0.762**	−0.048
Eigenvalue	3.139	0.933
Total variance (%)	62.79	18.66
Cumulative variance (%)	62.79	81.45

VF1 and VF2—first and second varifactor, respectively. Values in bold indicate significant loadings (> 0.70)

The relations among these metals based on two PCs are illustrated in two-dimensional space (2D) (Fig. 6). The metals assemble into two groups. As, Ni, Pb, and Zn are clustered in one major group, indicating similar standards and sources. Cr is apart from other metals, which implies a different source of pollution.

Cr is commonly used in textile manufacturing (Thuong et al. 2013), which can justify the high levels of this metal, in riverbed sediments of the Vieira River, in sampling sites S2, S3, and S4 (Fig. 1), which are located next to textile factories (Fig. 3; Tables 4, 5, 7).

As, Ni, Pb, and Zn occurrences can be attributed to their presence in natural sources, because these elements concentration in riverbed sediments was inferior to background values ($I_{geo} < 0$; Fig. 3). In addition, the significant correlations between these metals (Table 3) and their grouping in the same cluster (Fig. 5) reinforce the possibility that they originate from similar sources. In site S3, As concentrations

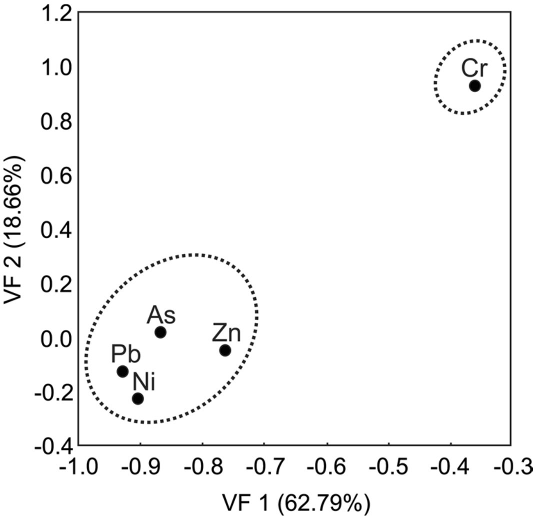

Fig. 6 Result of principal components analysis (PCA) considering the first two varifactor (VF)

in riverbed sediments was higher than the background values ($I_{geo} > 0$; Fig. 3), which can indicate an anthropogenic source of contamination. The As is used as a preservative for leather and wood, metal alloy additive, and in herbicides (Hallı et al. 2014; Thuong et al. 2013).

In general, the results of the principal component analysis (Fig. 6; Table 8) coincide with the cluster analysis (Fig. 5) of riverbed sediment.

Even though this study has identified levels of pollution by metals, especially by Cr and As, it is necessary to analyze the influence of forage grasses on the bioavailability of these pollutants. Most of the agricultural area of the Vieira River basin is intended for planting forage grasses (Leite et al. 2011). These species have high level of phytoliths (Webb and Longstaffe 2000), which, on the other hand, may mitigate the impacts of Vieira River water used for pasture irrigation.

Besides, this study suggested that chemical fractionation should be considered in future studies to provide a more accurate appraisal of the risk of metals in aquatic ecosystems. The speciation of metals affects their bioavailability and biological toxicity (Yang et al. 2014).

Conclusions

The higher concentrations of metals found in the sampling sites downstream of the city of Montes Claros, MG, near the industrial area and the discharge site of treated domestic sewage from this city, suggest that the Vieira River is polluted by metals due to anthropic actions, which can create an adverse effect on this ecosystem.

The Cu, Ni, and Zn concentrations in water in some parts of the Vieira River are above international reference limits for toxicity. The Cu and Ni concentrations restrict the use of water for irrigation in some parts of the river, following the criteria of Brazilian legislation.

The riverbed sediments of the Vieira River are polluted by Cr and the downstream sites nearest to the city of Montes Claros, MG showed greater metal contamination, which reinforces the influence of domestic and industrial wastewater discharge (from the Montes Claros sewage treatment plant and the industrial area located near this part of the river) on the water quality of the Vieira River.

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