

Mobility of metals in river sediments from a watershed in the Iron Quadrangle, Brazil

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RESUMO

A dinâmica do comportamento de metais em ambientes de água doce tem sido um dos principais focos de monitoramento ambiental nos últimos anos. O presente estudo investigou a distribuição de metais pesados nos sedimentos fluviais da bacia do rio Santa Bárbara (Minas Gerais, Brasil). A área de estudo sofreu com problemas relacionados à mineração e várias atividades de alto impacto, como agricultura, silvicultura e reflorestamento para produção de carvão vegetal. Os sedimentos superficiais foram coletados em quatro pontos nos rios Conceição, Caraça e Santa Bárbara. Esses sedimentos foram analisados quanto a frações trocáveis, redutíveis, oxidáveis e residuais, através do procedimento de extração sequencial proposto pelo European Community Bureau of Reference (BCR). Os resultados indicam que o Cd e Pb estão presentes principalmente na fração redutível, enquanto Fe, Ni, Cr e Zn foram predominantemente encontrados na fração residual, Mn e Cu são os elementos que proporcionalmente apresentam frações mais trocáveis e maior mobilidade. Fatores como pH e potencial redox influenciam diversos processos que alteram a mobilidade de metais, como adsorção e complexação. Os valores desses parâmetros mostraram que os pontos amostrados possuem características redutoras e ácidas. A identificação das etapas geoquímicas dos metais nos sedimentos permitiu a compreensão da contaminação no meio e a identificação de possíveis fontes. Isso possibilita a avaliação da qualidade dos sedimentos na microbacia estudada e serve de referência para o monitoramento do efeito antrópico ao meio ambiente.

Palavras-Chave: Rio Santa Bárbara, mineração de ferro, extração sequencial, elementos traço.

ABSTRACT

The dynamics of the behavior of metals in freshwater environments has been one of the main focuses of environmental monitoring in the last years. The present study investigated the distribution of heavy metals in the river sediments of the Santa Bárbara River Watershed (Minas Gerais, Brazil). The study area suffered from problems related to mining and several high impact activities, such as farming, forestry, and reforestation for charcoal production. Surface sediments were collected at four points in the Conceição, Caraça, and Santa Bárbara rivers. These sediments were analyzed for exchangeable, reducible, oxidizable, and residual fractions through the sequential extraction procedure that was proposed by the European Community Bureau of Reference (BCR). The results indicate that the Cd and Pb are mostly present in the reducible fraction, while Fe, Ni, Cr, and Zn were predominantly found in the residual fraction, Mn and Cu are the elements that proportionally present more exchangeable fractions and greater mobility. Factors such as pH and redox potential influence several processes which alter the mobility of metals, such as adsorption and complexation. The values of these parameters have shown that the sampled points have reducing and acidic characteristics. The identification of the geochemical stages of metals in sediments allowed for the comprehension of the contamination in the medium and the identification of possible sources. This enables the assessment of the quality of the sediments in the studied watershed and serves as a reference for the monitoring of the anthropic effect to the environment.

Keywords: Santa Bárbara River, iron mining, sequential extraction, trace elements.

1 INTRODUCTION

Understanding the dynamics of the behavior of metals in freshwater environments has been one of the main focuses of environmental monitoring studies in the last few years, which has been faced with the complexity of regulating, mitigating, and remediating contamination in water bodies (WARREN; HAACK, 2001). Metals can be distributed in water environments as soluble species in water, colloids, forms in suspension and in sedimentary phases. However, in contrast to organic pollutants, they cannot be removed through the natural decomposition process (PENG *et al.*, 2009). This characteristic puts them among the most serious pollutants within the natural environment because they cause adverse effects to the biota due to their toxicity, persistence and capacity of bio-assimilation and bioaccumulation by organisms.

To conduct a risk assessment of environmental samples affected by metal contamination, it is necessary to characterize the proportions of the elements in their several forms. The assessment should also be conducted under a wide range of possible conditions in natural systems. Once deposited in sediments, the metals can be adsorbed and form complexes, such as carbonates, iron and manganese oxides, organic carbon and sulfides (BURUAEM *et al.*, 2012). The formation of these complexes regulates distribution, mobility, bioavailability and, consequently, the metals' toxicity according to the environmental conditions (ZHANG *et al.*, 2015).

The mobility of these metals depends on a number of factors, such as the characteristics of the sediments and the physical-chemical form of the metal. These factors determine how much the elements are mobile, labile, or available to the species living in a certain medium (CAPPUYNS, 2012). The change of phase is controlled by processes such as decomposition/re-suspension, sorption/adsorption, and complexation/decomplexation (RUIZ, 2001). These processes are mainly controlled by pH, redox potential, and complexing agents dissolved in the organic matter (SALOMONS, 1998).

The determination of the mobility of these metals can be carried out through sequential extraction techniques (LI; CAI 2015). This is a very well-established method for the fractioning of metals content in soils and sediments. The process consists of the

application of reagents for a series of continuous extractions in soil or sediment samples, using pre-defined solutions, while taking factors such as the type of reagent, concentration, temperature, and time into account. The fractions provide information on the proportion of the metal which is associated with a determined geochemical phase (BEVILACQUA *et al.*, 2009). This enables the association of the chemical form of origin to the form of chemical or biological occurrence, in addition to its mobilization (CARVALHO *et al.*, 2012).

Given the diversity of the extraction procedures, the Community Bureau of Reference (BCR), based on the modifications of the method proposed by TESSIER *et al.*, (1979), has created a standardized extraction procedure in three stages, which are known as BCR (URE *et al.*, 1993). This procedure can be used to obtain metals in the exchangeable, reducible (metals associated to iron and manganese oxides), oxidizable (metals associated to organic matter and sulfides), and residual (metals associated to non-silica fractions of the sediments) fractions. The first reference material was the BCR CRM 601, certifying five elements (Cd, Cu, Cr, Ni, Pb, and Zn). However, modifications were required because there were several potential sources of irreproducibility in the stages of extraction, with the most important variables being pH and Hydroxylamine chloride. The new, revised protocol, BCR 701, contains the required alterations and involved the increase in concentration of the Hydroxylamine chloride and pH adjustment (RAURET *et al.*, 2001), improving the reproducibility as a function of the greater efficiency of dissolution of the reducible fraction of the analyzed matrix (NEMATÍ *et al.*, 2009). The process is intended to minimize errors in data treatment and sample analysis. In addition, it also identifies the most suitable analytical procedure and provides reference material for a comparison of the results.

In this context, the aim of this study was evaluate the influence of human activities and the natural features in the geochemical stages of metals in bottom sediments of Santa Bárbara River, important tributary of the Doce River, using the reference BCR-701. We correlated the results with the lithological and anthropic factors that influence this watershed.

2 MATERIALS AND METHODS

2.1 REGION OF STUDY

The Santa Bárbara River watershed has been intensively exploited by mineral extraction activities thanks to its location on the northeast portion of the Iron Quadrangle, a pre-Cambrian terrain with significant mining resources, especially gold and iron (COSTA *et al.*, 2010). In addition to mineral extraction, several high impact economic

activities have influenced the watershed, such as farming, forestry, and reforestation for charcoal production. The population of the watershed is estimated to be 200,000 people (Instituto Brasileiro de Geografia e Estatística or IBGE 2015). The soil is diversified and is formed by cambisols, latosols, outcrops and argisols.

2.2 SAMPLING STATIONS

The surface sediments were collected during March 2015, in the following four locations: a tributary of the Conceição River (Point 1), and three points along the main course of the Santa Bárbara river watershed (Points 2, 3, and 4), as shown in **Figure 1**.

The sampling points were selected to allow the assessment of the contributions of both point and diffuse pollution in the river. Point 1 (P1) receives all of the input of the Conceição River watershed, which has several mining activities for metal and non-metal minerals, including iron ore. Point 2 (P2) receives all of the contribution of the Conceição River and the Caraça stream, which

includes mining processes added to domestic discharges. Point 3 (P3) is influenced by contamination from the upstream points P1 and P2, in addition to domestic and industrial effluents, and it is the last point before the Peti dam, which was formed by the damming of the Santa Bárbara River. The Peti dam is used to generate electricity and it acts as a barrier that partially prevents the contamination flow throughout the course of the river (SILVA *et al.*, 2009). Point 4 (P4) is the last sampling point of the watershed and it receives all of input from the portion of the Santa Bárbara River downstream the Peti dam.

2.3 PHYSICAL AND CHEMICAL ANALYSIS OF SEDIMENTS

We also analyzed in situ the amounts of pH and redox potential (E_H) using portable digital multiparameter (Ultrameter II 6Psi, Myron L Company, USA).

The sediment samples were collected with the aid of a collecting scoop, and the material was conditioned in polyethylene bags. In the laboratory, the material was dried at room temperature and then their particles were disaggregated and homogenized using an agate mortar and pestle. The granulometric analysis was done

by sifting with 35 *mesh*, 70 *mesh*, 100 *mesh*, 230 *mesh* and < 230 *mesh* iron sieves,

obtaining granulometric fractions of 500 μm , 0210 μm , 149 μm , 63 μm , and < 63 μm , respectively. This meant that the dominant granulometric fractions at each point were below < 63 μm , which were used in the sequential extraction procedure. The finest fraction samples (silt and clay <63 μm) accumulate higher concentrations of contaminants than coarse particles (particles larger than 63 μm), which determine their wide use in the evaluation models of metal fractions in sediments (FÖRSTNER, 2004; HOROWITZ, 1985).

2.4 SEQUENTIAL EXTRACTION

The sequential extraction assay was carried out with 1 g of sediment. The standards were prepared with the same extraction solutions to minimize the matrix effects during the determinations by atomic absorption. The glassware and plastic containers were washed with Extran 5% detergent; they were then

rinsed and kept immersed in HNO_3 (30%) for 24 h, and they were then rinsed again with deionized water and dried in a kiln before initiating the procedure. All of the reagents had a high degree of analytical purity and the solutions were prepared using ultra-pure water, which was obtained from the purification

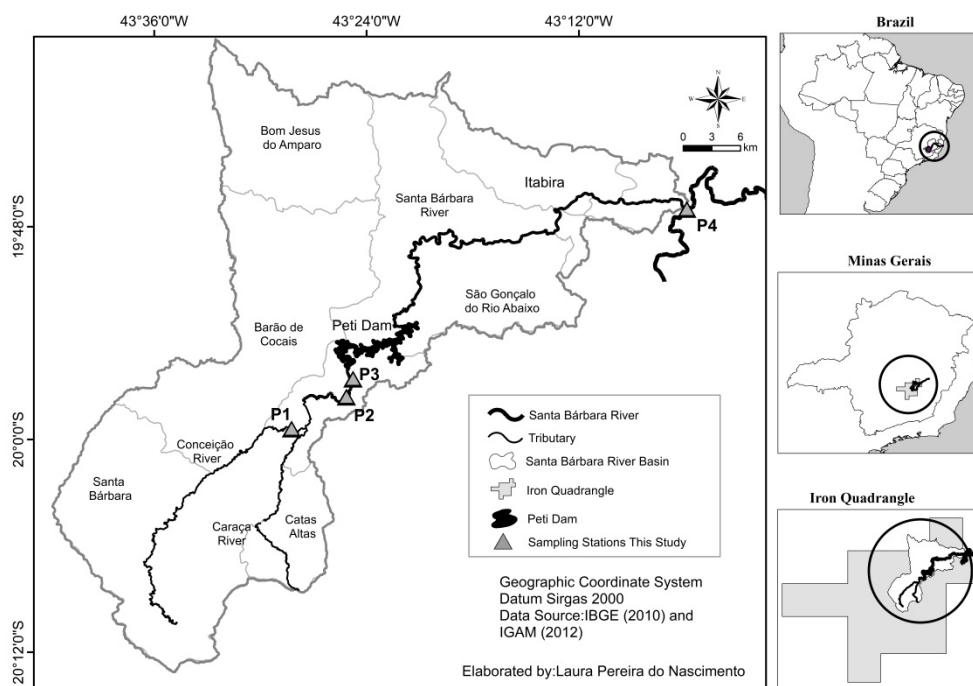


Figure 1
Locations of the sampling stations in the Santa Bárbara River in the Iron Quadrangle, Brazil.

system of the Millipore Model Milli-Q.

For sequential extraction through the BCR-701 method, the following reagents were used: 0.11 mol L⁻¹ acetic acid (CH₃COOH), 0.5 mol L⁻¹ hydroxylamine hydrochloride (NH₂OH.HCl), 8.8 mol L⁻¹ hydrogen peroxide (H₂O₂), and 1 mol L⁻¹ ammonium acetate (CH₃COONH₄). The reagents used analyses were of the Synth (Brazil) brand.

The sequential extraction process was carried out in four samples with granulometry <63 μm, based on the reference material BCR 701 of the Community Bureau of Reference. The samples were submitted in triplicate to the procedure proposed by Rauret et al (2001). The levels of Cd, Cr, Cu, Ni, Pb, Zn, Fe, and Mn were determined in the samples through the ICP- OES.

First Stage (F1): (Exchangeable Stage) 20 mL of 0.11 mol L⁻¹ acetic acid was added to the previously weighed sediment. The tubes were submitted to agitation for 16 h at room temperature using an end-over-end type shaker (Heidolph Model REAX 2). The tubes were then centrifuged at 3000 rpm for 30 minutes. The supernatant was transferred to a syringe coupled to a filter with a 0.45 μm membrane. The filtrate was maintained at 4 °C for determination of the metals and metalloids. The residue was washed. After the addition of 20 mL of deionized water, the residue was submitted to agitation for 15 minutes and centrifuged at 3000 rpm for 30 minutes. The

supernatant obtained from the washing was discarded.

Second Stage (F2): (Reducible Stage) 20 mL of 0.5 mol L⁻¹ hydroxylamine chloride acidified with HNO₃ (25 mL of HNO₃, 2 mol L⁻¹ for 1000 mL of the solution) was added to the residue from the first stage. The same procedures as those used in the first stage were used for the agitation, centrifugation, and filtration.

Third Stage (F3): (Oxidizable Stage) 5 mL of the 8.8 mol L⁻¹ hydrogen peroxide was added, drop by drop, to the residue from the second stage. The flask of the centrifuge was loosely capped and kept at room temperature for 1 h, with occasional manual agitation. Then, the flask was put in a beaker that was placed in a water bath at 85 ± 2°C for 1 h, with occasional agitation in the first 30 minutes. With the open flask, the volume was reduced to 1.5 mL. Again, another 5 mL of the 8.8 mol L⁻¹ hydrogen peroxide was added and the flask was submitted to the same temperature until the volume reached approximately 0.5 mL. After cooling, 20 mL of 1.0 mol L⁻¹ ammonium acetate was added. For the extract separation, the same procedures as those used in the first stage were used for the agitation, centrifugation, and filtration.

Residual Stage (F4): At this stage, the residue from the third stage was transferred to a beaker using the minimum possible amount of deionized water. A volume of 4.65 mL of regal

water (3.50 mL of HCl 37% p/p and 1.15 mL of HNO₃ 65% p/p) was added. For digestion and filtration, the same digestion procedure with regal water was used. The filtered material was collected in a 25 mL volumetric flask.

The metal concentrations in the supernatant extracts obtained in the sequential extraction

process were determined using an inductively coupled plasma/optical emission spectrometer (ICP-OES, Agilent Model 725, Agilent Technologies, Germany). Every procedure was carried out in the Environmental Geochemistry Laboratory (LGQA) at the Federal University of Ouro Preto (UFOP).

3 RESULTS AND DISCUSSION

3.1 PHYSICAL AND CHEMICAL ANALYSIS OF SEDIMENTS

The results of the present study show that all of the points are in acid and reducing medium. Lower pH and redox potential values were found in Points 1 and 2, respectively. The pH and redox values are shown in **Table 1**.

Table 1. pH and redox potential results for the sampling points

	pH	Redox potential (mV)
P1	6.32	143
P2	6.87	107
P3	6.60	134
P4	6.95	140

The pH and the redox potential are key parameters that directly influence the aquatic ecosystems due to their effects on the mobility of chemical species (PENG *et al.*, 2009). A decrease in pH increases the concentration of free ions, causing the desorption of the colloidal and particulate forms, and the dissociation of some organic and inorganic complexes (MARKICH *et al.*, 2002). The redox reactions control the oxidation state, and thus the mobility of the metals (VIOLANTE *et al.*, 2010). Some E_H values in different redox condition zones in sediments and soils can be interpreted as Salomons and Stigliani (1995):

- Oxidative zone (E_H = +300 mV): value associated with aerobic respiration;
- Nitrate and Mn⁴⁺ reduction zone (E_H between +100 to +300 mV): value associated with facultative anaerobic respiration;
- Fe³⁺ reduction zone (E_H between -100 to +100 mV): value associated with facultative anaerobic respiration;
- Sulfide reduction zone (E_H between -200 to -100 mV): value associated with anaerobic respiration; and

- Methane formation zone (E_H < -200 mV): value associated with anaerobic respiration.

The decrease in pH can promote the solubilization of carbonates and hydroxides, changing the desorption process of complex metallic cations by organic matter due to the competition of these cations with H⁺ ions; therefore, the lower the pH, the lower the metals retention capacity (QUINÁGLIA, 2006).

The redox potential of substances depends on two basic factors, which are the affinity of the molecules by electrons, and the concentration of reducers and oxidants in the medium, which is referred to as a redox pair DeLaune and Reddy (2005). The reducing agents are related to organic matter, and its several organic compounds and inorganic reducers, such as NH₄⁺, Fe²⁺, Mn²⁺. High redox potential values facilitate the sulfide and organic matter oxidation process, accelerating the release of complex/adsorbed metals (ZHANG *et al.*, 2014). On the other hand, in reducing environments, sulfides form insoluble complexes and decrease mobility (Quinágua, 2006).

The results of the granulometric classification according to Conselho Nacional do Meio Ambiente or CONAMA 454/12 (BRAZIL, 2012) are shown in **Table 2**, based on the granulometric composition of the predominant fraction in the sampling points. Point 1 presented greater proportions of medium sand, whereas Points 2 and 4 showed the predominance of silt. Greater concentrations of clay were found in Point 3.

The sampling points presented a variation with respect to their granulometric classification. Points 2, 3 and 4 were the most relevant considering this parameter because they all contain greater fractions of clay or silt.

Table 2. Dominant granulometric fraction of the sampling points

Samples	mm	Classification
P1	0.5 to 0.25	Medium sand
P2	0.062 to 0.00394	Silt
P3	0.00394 to 0.0002	Clay
P4	0.062 to 0.00394	Silt

The size of the particles which compose the sediments is essential for the comprehension of the occurrence of heavy metals in aquatic environments. It is one of the control parameters (MASLENNIKOVA *et al.*, 2012) because the accumulation of contaminants and their distribution is inversely proportional to the size of the fraction (FÖRSTNER, 2004). Finer grains contain most of the metals associated with sediments, indicating a strong positive relationship between the decreasing

3.2 SEQUENTIAL EXTRACTION

The obtained fractions (mg kg^{-1} and %) in each stage of the procedure are described in **Table 3**, and a graphic representation is shown in **Figure 2**. Stages 1, 2, 3, and 4 refer to the exchangeable, reducible (metals associated

3.2.1 EXCHANGEABLE FRACTION

The results indicate that cadmium, chrome, lead, and iron present minimum values, or even below the quantification limit of the device in this stage. The cadmium and lead fractions were below the quantification limit at all points (**Fig. 2**). At Point 1, chrome had a percentage of 0.46% and at Point 2 it was 0.12% of the total. Points 3 and 4 were below the quantification limit. The values for iron were below 1% at all of the sampling points, as observed by other authors, such as Pereira *et al.* (2007).

The copper exchangeable fraction extracted in the samples shows that Point 1 presented the greatest amount in the exchangeable stage, with 49.90%, followed by Point 2 with 22.50%, Point 4 with 10.99%, and Point 3 with 8.24%. The high amount of the extracted fraction at the exchangeable stage at Point 1 is likely to be due to the adsorption of the metal to the abundant fine particles in the medium. These particles are exposed by the stirring of the soil. They are directly influenced by mining activities, leached to water bodies and co-precipitated, especially when carbonates are present in the area. Fine particles such as clay minerals present a sorting or ionic exchange

size of the grain and the increase in metal concentration (HOROWITZ, 1985).

Finer sediments (clay and silt) are responsible for a significant portion of the transport of metals in water bodies, which are attached by adsorption to the surface of minerals, usually in particles $< 63 \mu\text{m}$ (CHAPMAN, 2002).

Clay minerals can obtain a negative net charge by ionic substitution where the ions Si^{+4} and Al^{+3} are replaced by similar size ions but with lower charge. The compensation of the negative charge occurs by association of cations (cation-exchange capacity) with the surface of the layers of these minerals, which is an important characteristic for sediments and colloids that present ion exchange capacity (MANAHAN, 2016).

with iron and manganese oxides), oxidizable (metals associated with organic matter and sulfides) and residual (metals associated with the non-silicate fraction of sediments) stages, respectively.

capacity caused by the electric charges in their crystallographic structure (RODRIGUES *et al.*, 2015a). The affinity of Cu^{2+} with these minerals favors the adsorption process under the surface of carbonaceous minerals (FERREIRA; SANTANA, 2012). The obtained results are attributes the highest values in this fraction to the dissolution of minerals such as the Chalcopyrite (CuFeS_2) (CHI, 2013), which is abundant in the studied area.

Manganese followed the same pattern as copper, being in the exchangeable stage predominantly at Point 1, with 42% of the total extracted, while Points 2, 3, and 4 presented between 26% and 29% of the extraction. These high concentrations indicate the affinity of Mn by carbonates (COPAJA *et al.*, 2014). Mn is associated with minerals and humus, and in this stage, it is sensitive to environmental changes, modifying its mobility under acidic conditions (YANG *et al.*, 2014). The manganese under the Mn^{2+} form, which is dominant in aquatic environments, is thermodynamically unstable in oxygenated environments, being oxidized to Mn^{3+} and Mn^{+4} (TRIBOVILLARD *et al.*, 2006). Of all

sampling points, Point 1 presented the highest redox potential value and the lowest pH, which justifies the higher indices found in the exchangeable stage. Tack *et al.* (1996) investigated the function of pH in sediments influenced by oxidation processes, and showed that the Mn solubility linearly increases as pH decreases, which suggest its association with carbonates. They found that the extracted fractions occur as a function of the dissolution of Ca and Mg carbonates because Mn^{2+} can replace Mg^{2+} in dolomites and Ca^{2+} in calcites, which are carried to the sediments (GAO *et al.*, 2010).

The highest zinc concentrations occurred at Point 1 with 17%, and Points 2, 3, and 4 presented nearly 10% of the total extracted. Point 1 presents higher zinc concentration, despite the predominant sandy texture, which decreases the adsorption of metals in the sediments. The pH may have contributed to these results. According to Rieuwerts *et al.* (1998), the adsorption of Zn is significant when observed in pH between 5.0 and 6.5.

3.2.2 REDUCIBLE FRACTION

The result of the Pb extraction showed that this element was only extracted in the reducible fraction at all of the sampling points (Fig. 2). Lead is a metal that is known to be preferably associated with iron and manganese oxides (HEM, 1985) and can be released to the medium if the sediment is submitted to reducing conditions. This explains the proportions found in the reducible fractions, suggesting the importance of these ions in the transport of this element (YUAN *et al.*, 2004). The higher levels can be from both anthropogenic and lithogenic sources. Point 4 receives contributions from domestic sewage, and possibly from sanitary landfill leachates, agricultural inputs and related to agriculture from the entire watershed downstream the Peti dam. These factors are responsible for the introduction of Pb in aquatic environments (OLIVEIRA; MARINS, 2011). Point 1 is extremely influenced by mineral processes that

Reddy *et al.* (1995) investigated the mobility of zinc in different media, and at pH levels of 6.6, 5.0, 4.0, 3.0, and 2.4 concluded that the availability of this element increases as pH decreases.

Nickel presented the highest percentage of the exchangeable stage, with 25.68%, at Point 1. Point 3 had nearly 9% of the total, and Point 2 had 7%. For Point 4, the concentrations were below the quantification limit. The considerable fraction in Point 1 indicates potential pollution by recent contamination (RAURET, 1998).

Sorption-desorption processes at this stage can be affected by changes in the ionic composition of the water and variations of the pH values (TESSIER *et al.*, 1979), which causes alterations in the liability of the elements (URE; DAVIDSON, 2008). Metals linked to this stage are considered potentially available for absorption by aquatic organisms (SINGH *et al.*, 2005) because they are more easily released into the environment.

evidence large amounts of Fe and Mn that dominate the local lithology.

Cadmium presented similar pattern. At Points 1, 2, and 4 it was only found in the reducible fraction, while for Point 3 the fractions were below the quantification limit. The affinity with Cd in this stage is mostly linked to manganese oxides, or it can be co-precipitated, mainly on mineral surfaces (HEM 1985). Its mobility is moderate to low in acid and reducing environments (SMITH; HUYCK, 1999), respectively, which is a characteristic of all of the sampling points.

The Cu at Point 1 registered 27%, at Point 2 it is the dominant fraction with 26%, at Point 3 it was nearly 21%, and at Point 4 it was 13%. Ni equals 35% at Point 1, 7% at Point 2, 13% at Point 3 and it was below the quantification limit at Point 4. High Ni and Cu concentrations at Point 1 are related to the association of the metal to iron and manganese

Table 3 - Results of sequential extraction.

Points	Fractions	Cd mg kg ⁻¹		Cr mg kg ⁻¹		Cu mg kg ⁻¹		Ni mg kg ⁻¹		Pb mg kg ⁻¹		Zn mg kg ⁻¹		Fe mg kg ⁻¹		Mn mg kg ⁻¹	
		M ± DP	M ± DP (%)	M ± DP	M ± DP (%)	M ± DP	M ± DP (%)	M ± DP	M ± DP (%)	M ± DP	M ± DP (%)	M ± DP	M ± DP (%)	M ± DP	M ± DP (%)	M ± DP	M ± DP (%)
Point 1	F1	<LQ	-	0,6±0,01	0,46±0,007	178,9±5,1	49,9±1,44	33,8±0,92	25,6±0,69	<LQ	-	24,3±2,5	17,1±1,80	224,2±8,4	0,13±0,004	1103,1±7,8	42,7±0,2
	F2	0,36±0,02	-	3±0,10	2,31±0,07	100,7±3,0	28,12±0,85	21,1±0,83	16,07±0,62	10,2±0,2	-	10,9±0,4	7,64±0,29	4147,7±54	2,3±0,03	834,1±3,5	32,3±0,1
	F3	<LQ	-	6,2±0,38	4,83±0,29	28,9±1,9	8±0,54	16,5±1,33	12,5±1	<LQ	-	9,1±0,85	6,4±0,59	445,9±10,2	0,2±0,005	39,17±0,72	1,5±0,02
	F4	<LQ	-	119,8±1,4	92,4±1,07	49,6±1,1	13,84±0,30	60,24±3,9	45,71±2,95	<LQ	-	98,2±4,9	68,9±3,43	173221±1660,7	97,2±0,93	605,3±1,64	23,4±0,0
Point 2	F1	<LQ	-	0,4±0,01	0,12±0,002	21,6±0,3	23,48±0,41	10,8±0,21	8,14±0,15	<LQ	-	11,2±1,9	10,32±1,80	18,34±1,95	0,01±0,001	393,33±0,6	26,07±0,6
	F2	0,3±0,006	-	2,2±0,09	0,61±0,02	24±1,0	26,14±1,18	9,93±0,49	7,43±0,36	6,5±0,54	-	7,6±0,60	6,98±0,55	3108,8±39,4	1,95±0,02	548,9±3,95	36,38±0,2
	F3	<LQ	-	12±0,8	3,33±0,23	7,6±0,50	8,33±0,5	10,02±0,2	7,5±0,17	<LQ	-	6,13±0,3	5,63±0,36	270,63±111,1	0,17±0,006	36,±1	2,44±0,04
	F4	<LQ	-	348,3±2,2	95,94±0,61	38,7±0,05	42,05±0,05	102,7±3,4	76,92±2,56	<LQ	-	83,9±3,3	77,06±3,03	155983±1240,5	97,87±0,8	529,72±1,4	35,11±0,0
Point 3	F1	<LQ	-	<LQ	<LQ	1,8±0,04	8,25±0,17	2,78±0,08	9,55±0,27	<LQ	-	9,82±0,8	10,92±0,95	5,07±0,65	0±0002	294,89±2,3	10,72±0,0
	F2	<LQ	-	0,7±0,02	1,05±0,03	4,8±0,19	21,44±0,83	3,77±0,19	12,95±0,65	6,19±0,1	-	8,3±0,64	9,23±0,71	1687±22,9	0,58±0,007	1636,7±1,5	59,52±0,0
	F3	<LQ	-	5,1±0,39	7,59±0,58	1,5±0,17	6,79±0,74	<LQ	-	<LQ	-	5,51±0,5	6,13±0,60	150,48±5,6	0,05±0,001	54,46±0,32	1,98±0,0
	F4	<LQ	-	61,1±1,2	91,37±1,90	14,4±1,15	63,52±5,07	22,56±2,2	77,5±7,55	<LQ	-	66,3±2,6	73,72±2,89	289266,1±2345	99,37±0,8	763,97±5,5	27,78±0,1
Point 4	F1	<LQ	-	3±0,17	10,1±0,55	<LQ	<LQ	<LQ	-	<LQ	-	9,95±2,9	9,93±2,98	47,05±4,6	0,02±1,94	306,25±4,3	29,01±0,4
	F2	0,3±0,02	-	1,9±0,11	3,24±0,18	4,1±0,06	13,5±0,19	<LQ	-	13,9±0,4	-	7±0,87	6,99±0,86	3206,1±36	1,36±0,02	284,9±3,1	26,99±0,2
	F3	<LQ	-	5,9±0,22	9,94±0,36	1,9±0,10	6,26±0,32	<LQ	-	<LQ	-	6,26±0,4	6,25±0,41	160,82±7,4	0,07±0,003	23,73±0,35	2,25±0,0
	F4	<LQ	-	51,7±0,91	86,821,52	21,4±0,42	70,14±1,37	13,68±0,48	-	<LQ	-	77±1,10	76,84±1,09	232637,9±2111,1	98,55±0,89	440,6±4,87	41,74±0,4

* M- Mean, DP- Standard deviation, LQ = Quantification Limit

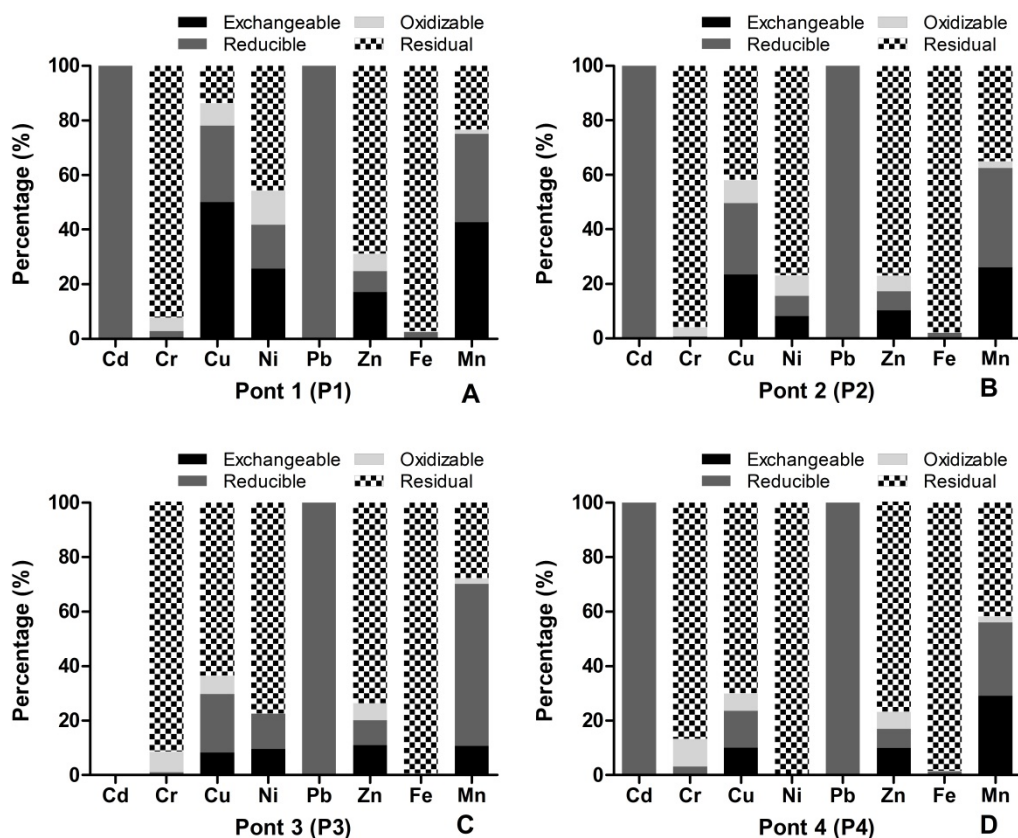
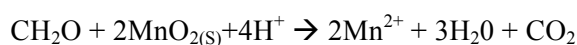


Figure 2
Results of the sequential extraction in Points 1 (A), 2 (B), 3 (C), and 4 (D).

oxides, which are released due to the instability of these elements under reducing conditions (YACOUB, 2012). Fe and Mn oxides are considered adsorbents and they are known to be easily leachable (TESSIER, 1979) and are abundant at this point due to the mining activities that influence the area.

The reducible fractions of Mn presented considerable concentrations at all points, and it



Mn and Fe oxides exhibit an especially high sorption capacity, and their production is mediated by the bacteria present in the sediments (MANAHAN, 2016). From this it

3.2.3 OXIDIZABLE FRACTION

The results indicate that the Cd and Pb concentrations were below the quantification limit at all of the sampling points (Fig. 2). For Cr, Zn, Fe, and Mn the indices signaled results below 8% in all of the samples. Cu ranged between 7–13% and Ni registered 12% at Point 1, 8% at Point 2 and was below the quantification limit at Points 3 and 4.

was predominant at Points 2 (36%) and 3 (59%). These two points are located in urban areas and they both have intensive contamination by domestic and industrial effluent discharge. High Mn concentrations have been attributed to the reductive dissolution of manganese oxides, as defined by the following reaction (PETRUNIC *et al.*, 2005).

can be inferred that the mobility is increased by the action of these microorganisms. Zn registered between 7–9%, whereas Fe and Cu were below 3% at all studied points.

The low metal concentrations at this stage are due to the location of the sampled points, which are within a region with high levels of humic substances (HS) (GONTIJO, 2012). High HS concentrations at the studied area due to the leaching of the pedological cover that is rich in humus, proving its capacity of complexation with metals such as Cu, Fe, Mn,

and Zn forming insoluble complexes. The insoluble complexes are formed as a result of the high molecular weight of the HS, which

3.2.4 RESIDUAL FRACTION

The concentrations that we found point to the predominance of the residual stage for Cr and Fe (> 90% at all points), Cu (P 4- 70%, P3- 63%, P2- 42%), Ni (P4 was the only quantified stage, P3 and P2 > 75% and P1 > 45%), Zn (> 70% at all points), and Mn (P4- > 40%). The other points presented reduced values, while Cd and Pb did not register indices at this stage.

The Cr results at the four points showed that the transport of this metal is associated with crystalline particles, reflecting a geochemical contribution that mostly comes from the local rocks and soils, which are unavailable in the medium (BEVILACQUA *et al.*, 2009). Although the residual fraction does not have a direct environmental importance for their lithogenic contributions, low values registered of this fraction can indicate the influence of aloctone pollutant sources that accumulate in the sediments (CORINGA *et al.*, 2016). A similar situation was described by Abreu (2005) in the Cachoeira Stream, also in the Quadrangle Iron. In this case, despite having found high amounts of chrome in the samples, larger amounts were extracted in the residual stage, with nearly 91% to 93% of the concentration, and small amounts were found in the other stages.

4. CONCLUSIONS

The identification of the geochemical stages of metals in sediments allowed for the comprehension of the contamination in the medium and the identification of possible sources. This enables the assessment of the quality of the sediments in the studied watershed and serves as a reference for the monitoring of the anthropic effect to the environment.

This study showed a variation in the predominance of fractions in the analyzed elements. The results obtained in the sequential extraction indicate that cadmium was mainly found in the reducible stage, as was lead. Iron, nickel and chrome obtained the higher values extracted in the residual fraction, indicating low mobility in the medium. Zinc presented a

slowly releases small amounts of metals depending on the decomposition processes in oxidant conditions (FILGUEIRAS *et al.*, 2002).

The high levels of Cu in the residual fraction (P2, P3, and P4) indicate its original mineralogy and reduced mobility in the water-sediment interface (SÁENZ *et al.*, 2003).

The dominance of the nickel proportion in the residual stage at all of the sampling points is in agreement with the literature (Yuan *et al.*, 2004), and this element can be considered immobile.

According to the results, where the values exceed 70% at all points, Zn presents low mobility in the environment and is not available for biological processes. Zn in the residual fraction is usually associated with minerals such as magnetite Fe_3O_4 (RODRIGUES *et al.*, 2015b), which is abundant in the studied area.

The results point out that Fe in this stage prevails, with over 97% of the total extracted in all samples. This indicates that it is mostly controlled by its mineralogy and the degree of weathering (SHARMIN *et al.*, 2010). The obtained concentrations indicate that the element is chemically stable and biologically inactive.

The predominant Mn residual fraction at Point 4 represents a low direct risk to the environment because this metal presents stronger associations with the crystalline structure of the minerals.

pattern similar to that observed for Fe, Ni, and Cr with a higher fraction linked to the residual stage, but with some recorded small fractions at every stage. Manganese was mostly found in the reducible and exchangeable stages. Copper was the element that presented greater variation of the fractions at all points, especially Point 1, with high concentrations in the exchangeable stage. Manganese and copper were the elements with greater mobility in the medium. Thus, small changes in the medium can offer these elements to the biota and cause bioaccumulation in the food chains. The granulometric analysis, redox potential and pH have proven to be important parameters for the comprehension of the distribution and mobility of these metals.

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