REVISTA DE CIÊNCIAS AMBIENTAIS - RCA (ISSN 1981-8858)
http://www.revistas.unilasalle.edu.br/index.php/Rbca
Canoas, vol. 8, n. 2, 2014

FRACTIONATION OF CHEMICAL ELEMENTS FROM THE ALLUVIAL TERRACES AND CUTBANKS OF THE GUALAXO DO NORTE BASIN, EASTERN-SOUTHEASTERN OF THE QUADRILÁTERO FERRÍFERO, MG, BRAZIL

Aline Sueli de Lima Rodrigues[1]
Guilherme Malafaia[2]
Adivane Terezinha Costa[3]
Hermínio Arias Nalini-Jr.[3]

ABSTRACT

The present study aimed to determine, via sequential extraction (method adapted from the Community Bureau of Reference), the different ways in which the elements Fe, As, Pb, Mn, Ba, Zn and Ni are associated with sediments of the alluvial terraces and cutbank from river Gualaxo do Norte Basin (east-southeast of the QuadriláteroFerrífero, Minas Gerais, Brazil). In order to complement data obtained by sequential extraction, were included sedimentological description and interpretation of facies, as well as mineralogical and grain-size analysis of samples collected in each profile. The results show high concentrations of the elements Pb, As, Fe, Mn and Ba in soil samples. However, only a small percentage of these features are readily bioavailable by being associated with the exchangeable fraction. Special attention should be given to the elements Ba and Ni, which can be mobilized in case of reduction of pH, when the release of acid drainage from tailings from mining activities. Regarding the toxic elements As and Pb, these show up predominantly associated with the residual fraction (suggesting a geogenic source), although the analysis of stratigraphic profiles reveal that large concentrations of these elements appear to be associated with anthropogenic activities such as gold mining in the region studied. In these cases, stimulates the development or adaptation of extracting a specific protocol, considering the characteristics of samples (rich in iron, poor in organic matter, with or without the presence of sulfides).

Keywords: heavy metal; fluvial sediments; mining

RESUMO

Fracionamento de elementos químicos dos terraços aluviais e da bacia do Gualaxo do Norte, leste-sudeste do Quadrilátero Ferrífero, MG, Brasil. O presente estudo objetivou determinar, via extração seqüencial (método adaptado a partir do Bureau de Referência de Romunidade), as diferentes maneiras em que os elementos Fe, As, Pb, Mn, Ba, Zn e Ni são associados com sedimentos dos terraços aluviais e da bacia do Rio Gualaxo Norte (leste-sudeste da Quadrilátero Ferrífero, Minas Gerais, Brasil). A fim de complementar os dados obtidos por extração

---

[1] Professora do Depto. de Gestão Ambiental, Instituto Federal Goiano - Campus Urutaí, Urutaí, GO, Brasil. Email para correspondência: alineifgoiano@gmail.com

[2] Professor do Depto. de Ciências Biológicas, Instituto Federal Goiano - Campus Urutaí, Urutaí, GO, Brasil.

[3] Professor(a) do Depto. de Geologia,Universidade Federal de Ouro Preto – UFOP, Ouro Preto, MG, Brasil.

seqüencial, foram incluídas descrição sedimentológica e interpretação de fácies, bem como, análise mineralógica e granulometria de amostras coletadas em cada perfil. Os resultados mostram altas concentrações dos elementos Pb, As, Fe, Mn e Ba em amostras de solo. No entanto, apenas uma pequena percentagem desses recursos são prontamente biodisponíveis por estar associado com a fração trocável. Atenção especial deve ser dada aos elementos Ba e Ni, que podem ser mobilizados em caso de redução do pH, quando a liberação de drenagem ácida de rejeitos das atividades de mineração. Sobre os elementos tóxicos As e Pb, estes aparecem predominantemente associados com a fração residual (sugerindo uma origem geogenic), embora a análise dos perfis estratigráficos revelam que grandes concentrações desses elementos aparecem para ser associadas com atividades antropogênicas, tais como a mineração de ouro na região estudada. Nesses casos, estimula o desenvolvimento ou adaptação de extrair um protocolo específico, considerando as características de amostras (ricos em ferro, pobre em matéria orgânica, com ou sem a presença de sulfetos).

Palavras-chave: metais pesados; sedimentos fluviais; mineração

INTRODUCTION

Environmental geochemistry, understood as the study ofthe inter-relationships betweennatural and artificial compounds/chemical elements and theenvironment, aims atassessing, predicting and controlling possible foci of soil, sediment, superficial water, underground water and atmospheric pollution (Eby, 2004). In this context, an interesting research field has been thegeochemical analysis of fluvial sediments, once the contaminationof these sediments has been consideredan important environmental issue.

Förstner et al. (2004) stress out that the chemical analysis offluvial sedimentsisan important tool for assessing water quality, becausethese sedimentsplay important rules in theaquatic environment, such as: i) “memory effect”in depositionenvironments, because sediment layers are temporally and sequentially accumulated; ii) support to life, because, besides representing an essential part of the aquaticecosystem,which is composed ofa variety of habitats andenvironments, they supply nutrients for the aquatic organisms; iii) secondary source of contaminants, involving mobilizationof contaminated particles followed byliberation of contaminantsvianatural or artificial re-suspension of sediments, and iv) final contaminant reservoir, once they have the capacity to immobilize potentially dangerous elements, *e.g.* toxic metals.

As discussed by Rezende et al. (2011) and shared by other authors (Hakanson, 1992; Altug e Balkis 2009), sediments are matrixes composed of detrital, inorganic or organic particles, which are relatively heterogeneous in terms ofphysical, chemical and biological characteristics. Frequently sediments are composed of fine-grained particles, which are in contact with the bottom of natural water bodies, such as lakes, rivers and oceans. Because of their capacity to accumulate pollutants, the determination of toxic elements in sedimentshelps assess the pollutant geochemical cycle (Rezende et al., 2011). Besides, sediments constitute a temporarystore and can act as metal sinks or sources by means of adsorption/desorption and precipitation/dissolution reactions (Lindell et al., 2010).

Sediments can liberatetoxic elements to the environmentdepending on variations of certain factors, such as pH, dissolved oxygen, salinity, redox potential, ionic strength, complexing agents and bacterial decomposition. Several studieshave indicated that thesevariations can break some links between metals and sediments, making these metals available to the water column (Alves et al., 2001; Kwon e Lee, 2001; Lima et al., 2001; Jordão et al., 2002; Zabetoglou et al., 2002; Pardo et al., 2004; Corbi et al., 2006). In this sense, as stressed out by Quináia et al. (2009), the total concentration of a certain metal in sedimentsis not information enough on contamination. To know how metals are linked to sediments can help obtain information on how much the waters around these sediments are prone tocontamination that can happen with changes in the environment (Zimmerman e Weindorf, 2010, Castillo et al., 2011; Nemati et al., 2011; Passos et al., 2011; Seddique et al., 2011; Sharif et al., 2011).

In this context, the objective of the presentstudy is to determine, via sequential extraction, the different forms in which the elements Fe, As, Pb, Mn, Ba, Zn and Ni can be associated with cutbank sediments and alluvial terraces of the Gualaxo do Norte River basin(Minas Gerais, Brazil). This basin is located in the eastern-southeastern portion of the Quadrilátero Ferrífero, well-knownfor encompassing some of the largest mineral deposits of the world (Deschamps et al., 2002; Roeser e Roeser, 2010).

MATERIAL AND METHODS

Sediment samples were collected from four sections located in alluvial terraces (T01, T02 and T03) and a cutbank (B01) of the Gualaxo do Norte River basin. These sectionswerechosenbecause the study area has been historically exploited for gold and for iron and manganese ores in the last decades.

The Gualaxo do Norte River headwaters are located northeast of Ouro Preto and northwest of Mariana (Figure 1). The four sections were described andthe facies were characterized according to Miall (1978, 1985, 1996), taking into consideration the sedimentary structures, grain size, textures, mineralogical composition, and any possible anthropogenic contribution. Faciesinterpretation was useful to the understanding of the dynamics of the elements along the geological time.

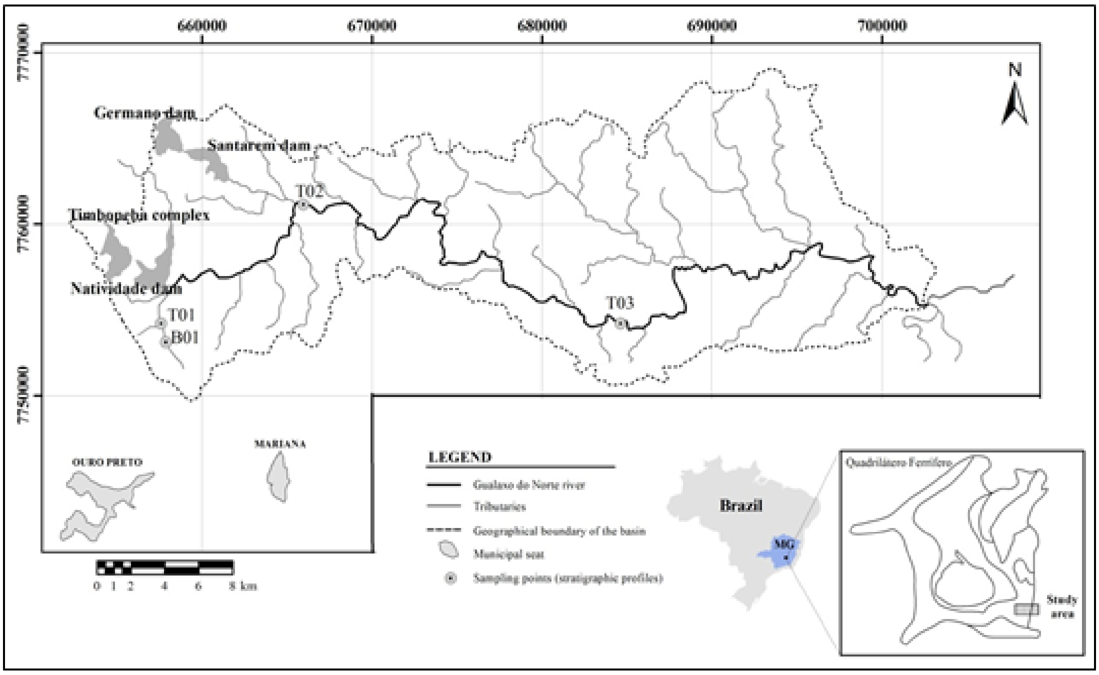
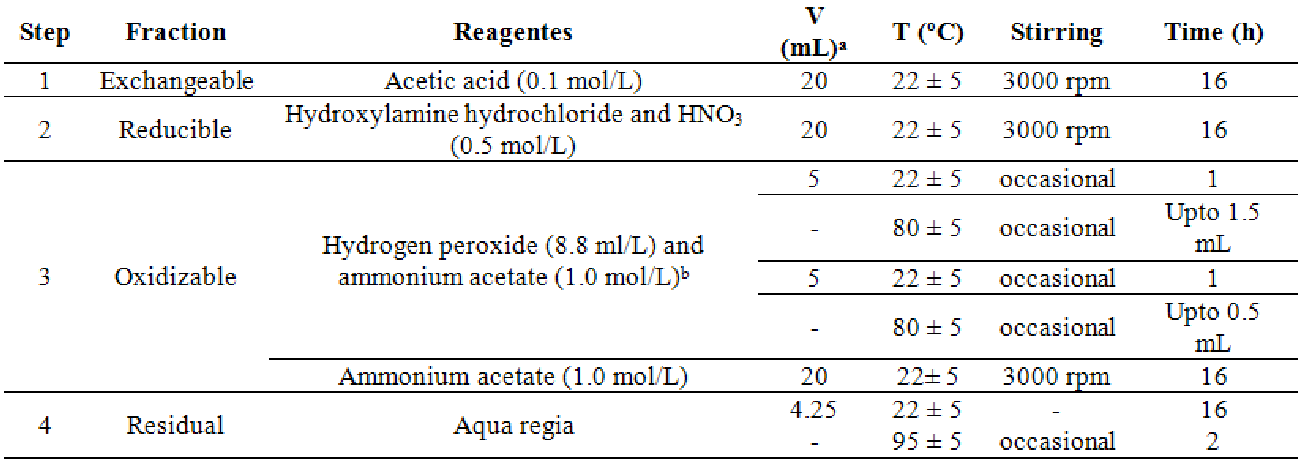


Figure 1. Location of the Gualaxo do Norte River Basin in Minas Gerais (Brazil) and of the sampling points.

Samples from all facies identified during the description of the sections were collected (n=25). Aliquots from these samples, of grain size smaller than 63 µm, were partly digested with aqua regia, adopting a method modified after López-Sánchez et al. (2002). To the 1 to 1.0005 galiquots, 7 mL HCl (12 mol/L) and 2.3 mL HNO_3 (15.8 mol/L) were added.The solutions were kept in 100 mL beakers covered with watch glasses, firstly at room temperature for 16 hoursand then at 70-80 ºC for two hours. The solutions were filtered using 0.045 µm cellulose membranes andtransferred to 50 mL flasks. The analyses performed with a SPECTRO CIROS CCD optical emission spectrometer at theEnvironmental Geochemistry Laboratory (DEGEO, UFOP).

After partial digestion, aliquots of 0.5 g ± 0.0003 g from the 25 samples (grain size <63 µm) underwent sequential extraction, procedure basedon López-Sánchez et al. (2002). The method adopted is an adaptation of the procedure proposed by the Community Bureau of Reference (BCR). In general lines, the procedure consisted in successive extractions that helped determine and certify the metals in four stages: exchangeable, reducible, oxidizable and residual. The results of the sequential extractionwere validatedby means of duplicate analysis of LKSD-2 reference material (CANMET, 2011). Table 1 lists the reagents and experimental conditions under which the sequential extraction took place.

Table 1. Reagents and experimental conditions under which the sequential extraction took place.



Step	Fraction	Reagentes	V (mL)[a]	T (°C)	Stirring	Time (h)
1	Exchangeable	Acetic acid (0.1 mol/L)	20	22 ± 5	3000 rpm	16
2	Reducible	Hydroxylamine hydrochloride and HNO_3 (0.5 mol/L)	20	22 ± 5	3000 rpm	16
3	Oxidizable	Hydrogen peroxide (8.8 ml/L) and ammonium acetate (1.0 mol/L)[b]	5	22 ± 5	occasional	1
			-	80 ± 5	occasional	Upto 1.5 mL
			5	22 ± 5	occasional	1
			-	80 ± 5	occasional	Upto 0.5 mL
		Ammonium acetate (1.0 mol/L)	20	22± 5	3000 rpm	16
4	Residual	Aqua regia	4.25	22 ± 5	-	16
			-	95 ± 5	occasional	2

[a] Value adjusted to 0.5 g of each sample. [b] pH adjusted using concentrated nitric acid.

RESULTS AND DISCUSSION

The stratigraphic description of cutbank andalluvial terracesections helped identify five sedimentary facies, namely A, As, Ar, Ct and G. Contrarily to facies As and G, no sedimentary structures were identified in facies A, As and Ct. Chart 1 presents the description and interpretation of the five facies.

Chart 1. Description and interpretation of the facies identified in the cutbank and alluvial terrace sections.

Facies	Description/interpretation
Ct	Characterized by the presence of gravels and stratigraphically disordered boulders. The predominant minerals are quartz, magnetite, hematite, feldspar, gibbsite, kyanite and tourmaline. This facies is interpreted as a channel with direct or indirect interference of mining activities as panning or dragging.
A	Characterized by very fine-to medium-grained sands. The predominant minerals are quartz (which occurs in granitic pegmatites and hydrothermal veins), muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$), hematite ($Fe_2O_3$), and clay minerals. This facies is interpreted as part of the succession of point bar deposits, probably generated under a lower flow regime. According to Christofoletti (1981), point bar deposits areformed by the erosion of concave margins, which are deposited by lateral accretion in the convex margins of the following meanders.
As	Characterized by medium-to coarse-grained sand, with evidence of pebbles and gravels. This facies is interpreted as an active channel environment deposit. The predominant minerals are quartz and clay minerals.
Ar	Characterized by fine-to very fine-grained sand with ripple cross lamination. The predominant minerals are quartz, muscovite, magnetite and clay minerals. This facies can be interpreted as bar-top and levee/low velocity deposit.
G	Characterized by clay. This facies is interpreted as a flood plain or flood lagoon. Suspended sediments are deposited after flooding. Quartz, muscovite and clay minerals predominate in this facies. Lamination is sometimes identified.

The sections are represented in figure 2.

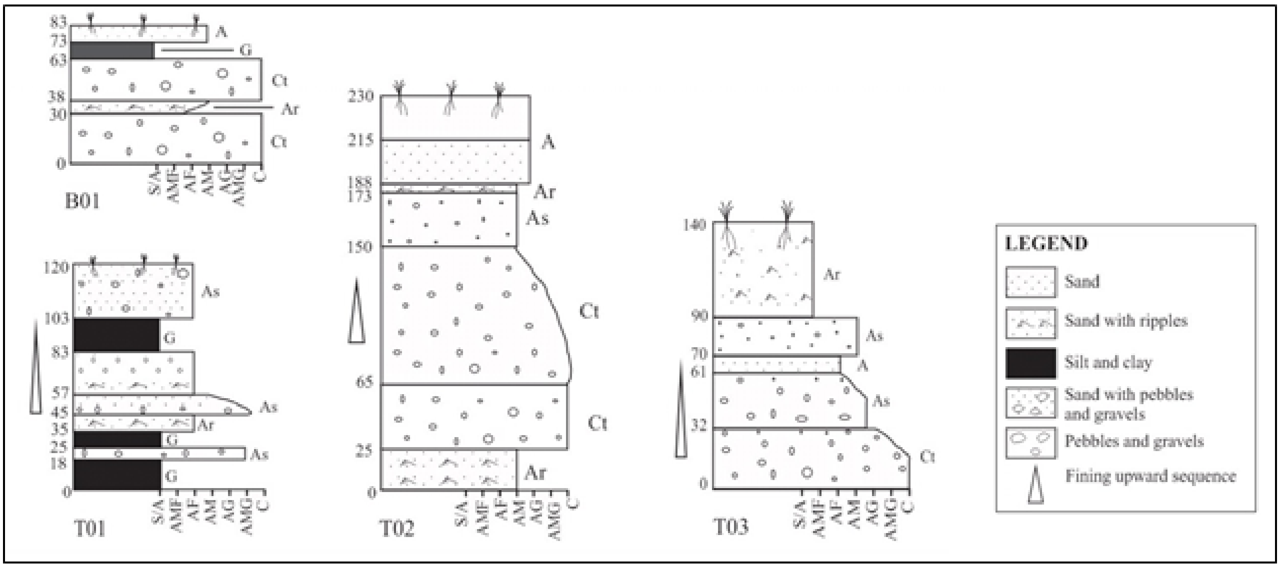


Figure 2. Description of cutbank (B01) and alluvial terrace (T01, T02 and T03) sections along the Gualaxo do Norte River basin, Minas Gerais, Brazil.

Table 2 presents the results of the recovery rates (RR) obtained for the certified elements.For the majority of elements, RR was satisfactory (>80%). As a control of the analytical method, two samples were randomly chosen for a triplicate sequential extraction. The results show good reproducibility of the data obtained separately in all extraction steps. The coefficients of variation (CV) for the majority of the samples were less than 10% (Table 3).

Table 2. Results (in mg.kg^{-1}) of the sequential extraction for reference material LKSD-2.

Element (mg/kg)	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**V**	**Zn**
VO$_1$	16.62	29.15	31.67	4.12	1497.3	22.45	50.23	175.26
VO$_2$	16.47	30.47	33.03	4.18	1516.8	22.38	54.72	186.54
M	16.55	29.81	32.35	4.15	1507.0	22.42	52.48	180.90
VC	17	29	36	3.50	1840	23	48	200
RR (%)	**97.3**	**102.8**	**89.9**	**118.6**	**81.9**	**97.5**	**109.3**	**90.5**

Legend: VO: sum of the concentrations obtained in each step of the sequential extraction (the subscript numbers indicate duplicate analyses). M: mean values (M=½ (VO$_1$+VO$_2$)). VC: certified value. RR: recovery rate – RR = [(M/VC)*100].

The following tables (3-7) present the concentrations obtained in each step of the sequential extraction, the results obtained from the aqua regia digestion (ARD), and RR for each sample. For the majority of these samples, RR was satisfactory (80%<RR< 120%).

Table 3. Results (in mg.kg^{-1}) of the sequential extraction for triplicate analyses.

Samples	**E**	**E1-Exchangeable**			**E2-Reducible**			**E3-Oxidizable**			**E4-Residual**		
		M	SD	CV	M	DP	CV	M	SD	CV	M	SD	CV
T01 (0-18)	Fe	0.8	0.2	*26.6*	16006.3	591.0	*3.7*	37.2	1.6	*4.4*	288170.0	11815.7	*4.1*
	As	-	-	-	-	-	-	-	-	-	460.0	6.3	*1.4*
	Pb	-	-	-	10.7	0.1	*1.2*	-	-	-	34.2	0.5	*1.3*
	Mn	220.9	5.6	*2.6*	16282.0	421.1	*2.6*	412.2	13.0	*3.1*	2631.0	64.6	*2.5*
	Ba	18.7	0.3	*1.5*	1912.7	44.8	*2.3*	9.3	0.0	*0.5*	116.7	4.3	*3.6*
	Zn	1.1	0.2	*21.4*	7.0	0.4	*5.5*	3.8	0.5	*13.8*	73.5	2.1	*2.8*
	Ni	-	-	-	14.0	0.3	*2.2*	7.1	0.3	*4.6*	21.8	0.5	*2.2*
T03 (65-150)	Fe	1.8	0.03	*1.7*	7440.7	449.0	*6.0*	102.0	22.1	*21.6*	202651.7	6539.3	*3.2*
	As	-	-	-	-	-	-	-	-	-	71.8	2.2	*3.1*
	Pb	-	-	-	16.8	0.2	*1.4*	-	-	-	12.9	1.7	*13.6*
	Mn	258.2	0.2	*0.1*	8484.7	369.3	*4.4*	115.4	9.3	*8.0*	1386.3	22.5	*1.6*
	Ba	13.4	0.1	*0.8*	525.3	22.0	*4.2*	3.7	0.4	*11.1*	27.8	2.2	*7.9*
	Zn	1.5	0.2	*13.9*	4.4	0.6	*13.6*	0.7	0.1	*8.9*	39.3	1.5	*3.7*
	Ni	-	-	-	7440.7	0.2	*4.5*	102.0	-	-	14.2	0.9	*6.2*

Legend: E: chemical element (mg.kg^{-1}). (-): values below quantification limit (LQ) of the technique used. M: arithmetical mean of the triplicate data; SD: standard deviation; CV: coefficient of variation [(DP/M)*100].

Table 4. Results (in mg.kg^{-1}) from the sequential extraction procedure applied to samples of section B01.

Sedimentary facies		**Fe**	**As**	**Pb**	**Mn**	**Ba**	**Zn**	**Ni**
B01(0-30)	E1	0.2	<2.4	<2.8	658.0	36.7	3.5	<1.9
B01(30-38)		0.2	<2.4	<2.8	692.0	38.0	3.1	<1.9
B01(38-63)		0.4	<2.4	<2.8	438.7	27.9	2.6	<1.9
B01(63-73)		0.6	<2.4	<2.8	643.0	43.6	1.9	<1.9
B01(73-83)		1.3	<2.4	<2.8	293.6	26.5	1.1	<1.9
B01(0-30)	E2	9,272.0	<2.4	8.7	13,373.0	1,171.0	7.6	6.9
B01(30-38)		28,306.0	<2.4	15.7	30,085.0	1,765.0	10.4	12.0
B01(38-63)		9,442.0	<2.4	10.1	12,825.0	1,049.0	6.1	6.2
B01(63-73)		10,443.0	<2.4	12.1	16,504.0	1,620.0	6.3	8.0
B01(73-83)		8,722.0	<2.4	6.5	11,289.0	993.0	6.0	6.5
B01(0-30)	E3	95.3	<2.4	3.7	206.7	4.7	2.1	<1.9
B01(30-38)		142.6	<2.4	<2.8	196.4	6.5	1.8	2.0
B01(38-63)		87.7	<2.4	<2.8	190.5	5.2	2.3	2.1
B01(63-73)		315.6	<2.4	<2.8	230.3	13.0	2.0	2.5
B01(73-83)		91.9	<2.4	<2.8	155.3	5.2	2.0	2.1
B01(0-30)	E4	526,691.0	84.7	50.2	2,250.0	32.1	60.4	8.0
B01(30-38)		497,523.0	162.2	48.0	2,540.0	49.6	68.9	13.3
B01(38-63)		479,896.0	76.1	47.8	2,042.0	31.9	50.2	7.0
B01(63-73)		411,249.0	220.0	40.7	2,547.0	78.4	59.2	14.5
B01(73-83)		272,019.0	92.5	29.9	1,303.0	26.9	41.0	8.3
B01(0-30)	Sum	536,058.5	92.0	65.3	16,487.7	1,244.4	73.6	18.7
B01(30-38)		525,971.8	169.5	69.2	33,513.4	1,859.1	84.2	29.2
B01(38-63)		489,426.1	83.4	63.5	15,496.2	1,114.1	61.2	17.2
B01(63-73)		422,008.2	227.3	58.4	19,924.3	1,755.1	69.4	27.0
B01(73-83)		280,834.2	99.8	41.9	13,040.9	1,051.6	50.1	18.7
B01(0-30)	ARD	421,769.0	161.0	90.1	16,966.0	1,221.0	60.8	18.9
B01(30-38)		426,938.0	213.0	97.2	26,850.0	1,934.0	71.3	27.0
B01(38-63)		417,204.0	151.0	86.6	14,440.0	1,121.0	56.0	17.6
B01(63-73)		342,611.0	273.0	85.4	18,864.0	1,902.0	67.4	28.6
B01(73-83)		250,543.0	141.0	65.0	12,180.0	1,059.0	44.3	18.5
B01(0-30)	RR (%)	127.0	57.0	73.0	97.0	102.0	121.0	99.0
B01(30-38)		123.0	80.0	71.0	125.0	96.0	118.0	108.0
B01(38-63)		117.0	55.0	73.0	107.0	99.0	109.0	98.0
B01(63-73)		123.0	83.0	68.0	106.0	92.0	103.0	94.0
B01(73-83)		112.0	71.0	65.0	107.0	99.0	113.0	101.0

Legend: E1: exchangeable fraction; E2: reducible fraction; E3: oxidizable fraction; E4: residual fraction; ARD: aqua regia digestion; RR (%): recovery rate, where: RR = [(E1+E2+E3+E4)/ARD]*100. Numbers preceded by symbol < indicate that concentration was below LQ.

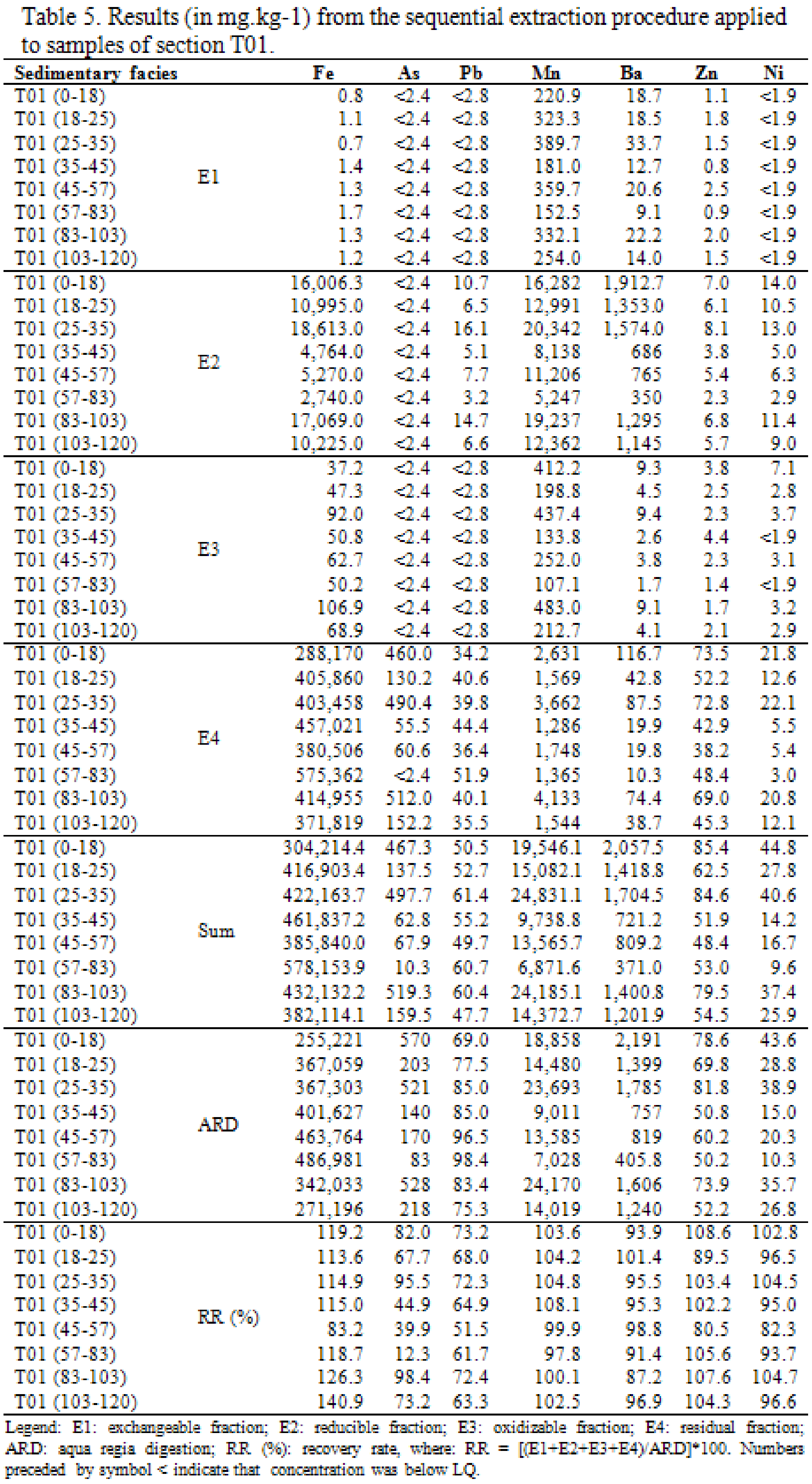


Table 5. Results (in mg.kg-1) from the sequential extraction procedure applied to samples of section T01.

Sedimentary facies		Fe	As	Pb	Mn	Ba	Zn	Ni
T01 (0-18)	E1	0.8	<2.4	<2.8	220.9	18.7	1.1	<1.9
T01 (18-25)		1.1	<2.4	<2.8	323.3	18.5	1.8	<1.9
T01 (25-35)		0.7	<2.4	<2.8	389.7	33.7	1.5	<1.9
T01 (35-45)		1.4	<2.4	<2.8	181.0	12.7	0.8	<1.9
T01 (45-57)		1.3	<2.4	<2.8	359.7	20.6	2.5	<1.9
T01 (57-83)		1.7	<2.4	<2.8	152.5	9.1	0.9	<1.9
T01 (83-103)		1.3	<2.4	<2.8	332.1	22.2	2.0	<1.9
T01 (103-120)		1.2	<2.4	<2.8	254.0	14.0	1.5	<1.9
T01 (0-18)	E2	16,006.3	<2.4	10.7	16,282	1,912.7	7.0	14.0
T01 (18-25)		10,995.0	<2.4	6.5	12,991	1,353.0	6.1	10.5
T01 (25-35)		18,613.0	<2.4	16.1	20,342	1,574.0	8.1	13.0
T01 (35-45)		4,764.0	<2.4	5.1	8,138	686	3.8	5.0
T01 (45-57)		5,270.0	<2.4	7.7	11,206	765	5.4	6.3
T01 (57-83)		2,740.0	<2.4	3.2	5,247	350	2.3	2.9
T01 (83-103)		17,069.0	<2.4	14.7	19,237	1,295	6.8	11.4
T01 (103-120)		10,225.0	<2.4	6.6	12,362	1,145	5.7	9.0
T01 (0-18)	E3	37.2	<2.4	<2.8	412.2	9.3	3.8	7.1
T01 (18-25)		47.3	<2.4	<2.8	198.8	4.5	2.5	2.8
T01 (25-35)		92.0	<2.4	<2.8	437.4	9.4	2.3	3.7
T01 (35-45)		50.8	<2.4	<2.8	133.8	2.6	4.4	<1.9
T01 (45-57)		62.7	<2.4	<2.8	252.0	3.8	2.3	3.1
T01 (57-83)		50.2	<2.4	<2.8	107.1	1.7	1.4	<1.9
T01 (83-103)		106.9	<2.4	<2.8	483.0	9.1	1.7	3.2
T01 (103-120)		68.9	<2.4	<2.8	212.7	4.1	2.1	2.9
T01 (0-18)	E4	288,170	460.0	34.2	2,631	116.7	73.5	21.8
T01 (18-25)		405,860	130.2	40.6	1,569	42.8	52.2	12.6
T01 (25-35)		403,458	490.4	39.8	3,662	87.5	72.8	22.1
T01 (35-45)		457,021	55.5	44.4	1,286	19.9	42.9	5.5
T01 (45-57)		380,506	60.6	36.4	1,748	19.8	38.2	5.4
T01 (57-83)		575,362	<2.4	51.9	1,365	10.3	48.4	3.0
T01 (83-103)		414,955	512.0	40.1	4,133	74.4	69.0	20.8
T01 (103-120)		371,819	152.2	35.5	1,544	38.7	45.3	12.1
T01 (0-18)	Sum	304,214.4	467.3	50.5	19,546.1	2,057.5	85.4	44.8
T01 (18-25)		416,903.4	137.5	52.7	15,082.1	1,418.8	62.5	27.8
T01 (25-35)		422,163.7	497.7	61.4	24,831.1	1,704.5	84.6	40.6
T01 (35-45)		461,837.2	62.8	55.2	9,738.8	721.2	51.9	14.2
T01 (45-57)		385,840.0	67.9	49.7	13,565.7	809.2	48.4	16.7
T01 (57-83)		578,153.9	10.3	60.7	6,871.6	371.0	53.0	9.6
T01 (83-103)		432,132.2	519.3	60.4	24,185.1	1,400.8	79.5	37.4
T01 (103-120)		382,114.1	159.5	47.7	14,372.7	1,201.9	54.5	25.9
T01 (0-18)	ARD	255,221	570	69.0	18,858	2,191	78.6	43.6
T01 (18-25)		367,059	203	77.5	14,480	1,399	69.8	28.8
T01 (25-35)		367,303	521	85.0	23,693	1,785	81.8	38.9
T01 (35-45)		401,627	140	85.0	9,011	757	50.8	15.0
T01 (45-57)		463,764	170	96.5	13,585	819	60.2	20.3
T01 (57-83)		486,981	83	98.4	7,028	405.8	50.2	10.3
T01 (83-103)		342,033	528	83.4	24,170	1,606	73.9	35.7
T01 (103-120)		271,196	218	75.3	14,019	1,240	52.2	26.8
T01 (0-18)	RR (%)	119.2	82.0	73.2	103.6	93.9	108.6	102.8
T01 (18-25)		113.6	67.7	68.0	104.2	101.4	89.5	96.5
T01 (25-35)		114.9	95.5	72.3	104.8	95.5	103.4	104.5
T01 (35-45)		115.0	44.9	64.9	108.1	95.3	102.2	95.0
T01 (45-57)		83.2	39.9	51.5	99.9	98.8	80.5	82.3
T01 (57-83)		118.7	12.3	61.7	97.8	91.4	105.6	93.7
T01 (83-103)		126.3	98.4	72.4	100.1	87.2	107.6	104.7
T01 (103-120)		140.9	73.2	63.3	102.5	96.9	104.3	96.6

Legend: E1: exchangeable fraction; E2: reducible fraction; E3: oxidizable fraction; E4: residual fraction; ARD: aqua regia digestion; RR (%): recovery rate, where: RR = [(E1+E2+E3+E4)/ARD]*100. Numbers preceded by symbol < indicate that concentration was below LQ.

Table 6. Results (in mg.kg^{-1}) from the sequential extraction procedure applied to samples of section T02.

Sedimentary facies		**Fe**	**As**	**Pb**	**Mn**	**Ba**	**Zn**	**Ni**
T02(0-25)	E1	2.3	<2.4	<2.8	293.1	5.3	1.8	<1.9
T02(25-65)		0.4	<2.4	<2.8	587.0	10.0	2.2	3.0
T02(65-150)		1.8	<2.4	<2.8	258.2	13.4	1.5	<1.9
T02(150-173)		8.7	<2.4	<2.8	199.7	9.9	6.0	<1.9
T02(173-188)		2.9	<2.4	<2.8	281.5	15.3	2.1	<1.9
T02(188-215)		16.7	<2.4	<2.8	282.4	15.0	2.8	2.0
T02(215-230)		14.4	<2.4	<2.8	529.0	23.8	4.1	<1.9
T02(0-25)	E2	2,068.0	<2.4	7.10	3,539.0	146.0	2.6	4.6
T02(25-65)		7,927.0	<2.4	21.50	13,538.0	444.2	5.6	10.4
T02(65-150)		7,440.7	<2.4	16.80	8,484.7	525.3	4.4	5.5
T02(150-173)		2,861.0	<2.4	9.80	1,752.0	86.3	5.0	3.0
T02(173-188)		2,168.0	<2.4	8.70	2,537.0	181.5	4.3	5.7
T02(188-215)		2,164.0	<2.4	5.20	3,770.0	243.3	4.9	6.2
T02(215-230)		4,527.0	<2.4	13.20	3,866.0	188.6	5.3	4.7
T02(0-25)	E3	64.3	<2.4	<2.8	13.6	0.7	1.3	<1.9
T02(25-65)		275.9	<2.4	<2.8	105.2	3.9	0.9	<1.9
T02(65-150)		102.0	<2.4	<2.8	115.4	3.7	0.7	<1.9
T02(150-173)		121.7	<2.4	<2.8	20.2	3.9	0.7	<1.9
T02(173-188)		104.1	<2.4	<2.8	30.0	2.7	1.0	<1.9
T02(188-215)		85.0	<2.4	<2.8	24.7	2.2	1.1	<1.9
T02(215-230)		248.5	<2.4	<2.8	116.1	3.0	1.1	<1.9
T02(0-25)	E4	434,507.0	30.90	41.70	848.0	6.1	44.3	10.5
T02(25-65)		286,514.0	104.10	31.10	1,876.0	33.7	54.7	14.9
T02(65-150)		202,651.7	71.80	12.90	1,386.3	27.8	39.3	14.2
T02(150-173)		175,956.0	11.40	18.00	410.2	12.2	32.1	17.4
T02(173-188)		173,942.0	11.70	15.80	529.0	11.0	35.9	23.4
T02(188-215)		350,283.0	<2.4	31.90	654.0	10.3	44.0	28.1
T02(215-230)		215,050.0	<2.4	20.60	1,171.0	14.0	40.9	20.2
T02(0-25)	Sum	436,641.6	38.20	54.40	4,693.7	158.1	50.0	18.9
T02(25-65)		294,717.3	111.40	58.10	16,106.2	491.8	63.4	30.2
T02(65-150)		210,196.1	79.10	35.30	10,244.6	570.3	45.9	23.4
T02(150-173)		178,947.4	18.70	33.40	2,382.1	112.4	43.8	24.2
T02(173-188)		176,217.0	19.00	30.10	3,377.5	210.5	43.2	32.9
T02(188-215)		352,548.7	10.30	42.70	4,731.1	270.8	52.8	38.2
T02(215-230)		219,839.9	10.30	39.30	5,682.1	229.4	51.4	28.7
T02(0-25)	ARD	441,344.0	98.20	93.90	4,848.0	171.0	49.2	17.8
T02(25-65)		240,116.0	139.00	73.90	15,143.0	526.0	56.7	28.1
T02(65-150)		193,030.0	101.00	47.00	10,406.0	657.0	54.9	24.2
T02(150-173)		154,086.0	39.70	45.20	2,625.0	127.0	41.5	22.9
T02(173-188)		175,170.0	35.70	48.70	3,503.0	234.0	44.9	36.6
T02(188-215)		379,719.0	27.10	81.10	4,712.0	277.0	56.4	46.4
T02(215-230)		205,553.0	27.20	55.00	5,727.0	238.0	48.1	29.8
T02(0-25)	RR (%)	98.9	38.90	57.90	96.8	92.5	101.6	106.3
T02(25-65)		122.7	80.10	78.70	106.4	93.5	111.8	107.3
T02(65-150)		108.9	78.30	75.10	98.4	86.8	83.7	96.8
T02(150-173)		116.1	47.10	73.80	90.7	88.5	105.6	105.7
T02(173-188)		100.6	53.20	61.90	96.4	90.0	96.2	89.9
T02(188-215)		92.8	37.90	52.60	100.4	97.8	93.5	82.4
T02(215-230)		107.0	37.80	71.50	99.2	96.4	106.8	96.4

Legend: E1: exchangeable fraction; E2: reducible fraction; E3: oxidizable fraction; E4: residual fraction; ARD: aqua regia digestion; RR (%): recovery rate, where: RR = [(E1+E2+E3+E4)/ARD]*100. Numbers preceded by symbol < indicate that concentration was below LQ.

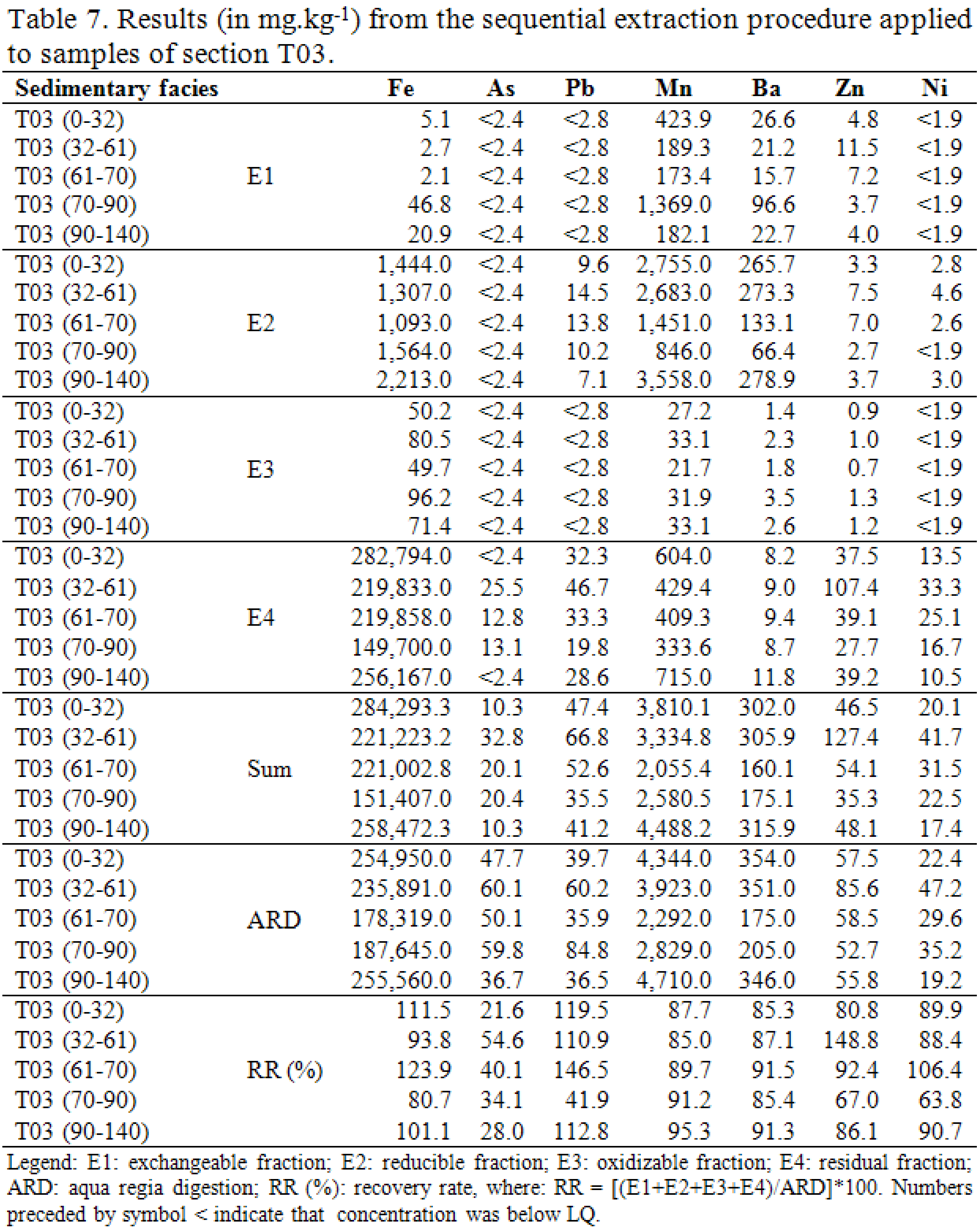


Table 7. Results (in $mg.kg^{-1}$) from the sequential extraction procedure applied to samples of section T03.

Sedimentary facies		Fe	As	Pb	Mn	Ba	Zn	Ni
T03 (0-32)	E1	5.1	<2.4	<2.8	423.9	26.6	4.8	<1.9
T03 (32-61)		2.7	<2.4	<2.8	189.3	21.2	11.5	<1.9
T03 (61-70)		2.1	<2.4	<2.8	173.4	15.7	7.2	<1.9
T03 (70-90)		46.8	<2.4	<2.8	1,369.0	96.6	3.7	<1.9
T03 (90-140)		20.9	<2.4	<2.8	182.1	22.7	4.0	<1.9
T03 (0-32)	E2	1,444.0	<2.4	9.6	2,755.0	265.7	3.3	2.8
T03 (32-61)		1,307.0	<2.4	14.5	2,683.0	273.3	7.5	4.6
T03 (61-70)		1,093.0	<2.4	13.8	1,451.0	133.1	7.0	2.6
T03 (70-90)		1,564.0	<2.4	10.2	846.0	66.4	2.7	<1.9
T03 (90-140)		2,213.0	<2.4	7.1	3,558.0	278.9	3.7	3.0
T03 (0-32)	E3	50.2	<2.4	<2.8	27.2	1.4	0.9	<1.9
T03 (32-61)		80.5	<2.4	<2.8	33.1	2.3	1.0	<1.9
T03 (61-70)		49.7	<2.4	<2.8	21.7	1.8	0.7	<1.9
T03 (70-90)		96.2	<2.4	<2.8	31.9	3.5	1.3	<1.9
T03 (90-140)		71.4	<2.4	<2.8	33.1	2.6	1.2	<1.9
T03 (0-32)	E4	282,794.0	<2.4	32.3	604.0	8.2	37.5	13.5
T03 (32-61)		219,833.0	25.5	46.7	429.4	9.0	107.4	33.3
T03 (61-70)		219,858.0	12.8	33.3	409.3	9.4	39.1	25.1
T03 (70-90)		149,700.0	13.1	19.8	333.6	8.7	27.7	16.7
T03 (90-140)		256,167.0	<2.4	28.6	715.0	11.8	39.2	10.5
T03 (0-32)	Sum	284,293.3	10.3	47.4	3,810.1	302.0	46.5	20.1
T03 (32-61)		221,223.2	32.8	66.8	3,334.8	305.9	127.4	41.7
T03 (61-70)		221,002.8	20.1	52.6	2,055.4	160.1	54.1	31.5
T03 (70-90)		151,407.0	20.4	35.5	2,580.5	175.1	35.3	22.5
T03 (90-140)		258,472.3	10.3	41.2	4,488.2	315.9	48.1	17.4
T03 (0-32)	ARD	254,950.0	47.7	39.7	4,344.0	354.0	57.5	22.4
T03 (32-61)		235,891.0	60.1	60.2	3,923.0	351.0	85.6	47.2
T03 (61-70)		178,319.0	50.1	35.9	2,292.0	175.0	58.5	29.6
T03 (70-90)		187,645.0	59.8	84.8	2,829.0	205.0	52.7	35.2
T03 (90-140)		255,560.0	36.7	36.5	4,710.0	346.0	55.8	19.2
T03 (0-32)	RR (%)	111.5	21.6	119.5	87.7	85.3	80.8	89.9
T03 (32-61)		93.8	54.6	110.9	85.0	87.1	148.8	88.4
T03 (61-70)		123.9	40.1	146.5	89.7	91.5	92.4	106.4
T03 (70-90)		80.7	34.1	41.9	91.2	85.4	67.0	63.8
T03 (90-140)		101.1	28.0	112.8	95.3	91.3	86.1	90.7

Legend: E1: exchangeable fraction; E2: reducible fraction; E3: oxidizable fraction; E4: residual fraction; ARD: aqua regia digestion; RR (%): recovery rate, where: RR = [(E1+E2+E3+E4)/ARD]*100. Numbers preceded by symbol < indicate that concentration was below LQ.

Only a small percentage of the elements is associated with the exchangeable fraction, *e.g.* Zn insections B01 and T01, and Ba, Zn and Mn in sections T02 and T03. SectionT03 presents the highest percentages associated with this fraction (*ca*. 55% for Ba and 53% for Mn). These results show that these elements are bioavailable in natural conditions and are susceptible to remobilization.

Regarding there ducible fraction, for all sections (B01, T01, T02 and T03) Mn, Ba and Ni were the elements that yielded the highest percentages extracted in thisfraction, attesting the association of these elements with amorphous Mn and Feoxides-hydroxides. It seems that the retention of these metals by Mn and Feoxides-hydroxides in the sediments analyzedoccurs both by deposition of sediments originally enriched in these metals and by remobilization of these metals in eachsection. As stressed out by Gerrard (1992), remobilization can result from variations ofredox conditions as a function of water level fluctuations. The author explains that whenthe water level rises, Fe and Mnin oxides-hydroxidesare reduced, Fe (III) to Fe (II) and Mn (III, IV) to Mn (II), causing the release of metals to superficial and/or underground waters. When the water level falls, the mobilized species are oxidized and reprecipitate as amorphous Fe and Mn oxides-hydroxides, which can adsorb or co-precipitate contaminating metals (Hudson-Edwards et al. 1998).

Barium is a hazardous element for biota and human health. High Ba concentrations were found insection B01 (especiallyat 0-30 cm – 1.171 mg.kg^{-1},and at 38-63 cm – 1.765 mg.kg^{-1}). Infacies Ct, these concentrations are predominantly associated with the reducible fraction. In these intervals, more than 90% of the extracted percentage is in this fraction. Accidental decreases in pH can occur in these sediments, caused, for example, by discharge of acid drainage coming from mining tailings. Barium could be freed from there ducible fraction, and be mobilized by a more bioavailable form.

The sections that presented the highest Ni concentrations were not necessarily those with high percentages in there ducible fraction. Sediments from sections T01, T02 and T03 presented the highest Ni concentrations. For section T01 (0-18 cm, facies G, 43.6 mg.kg^{-1} Ni), less than 40% Ni were extracted from the reducible fraction.For sections T02 (188-215 cm, facies A, 46.4 mg.kg^{-1} Ni) and T03 (32-61 cm, facies As, 47,4 mg.kg^{-1} Ni), the percentages of Ni extracted were less than 20% in the reducible fraction.

The highest Mn concentrations were found in sections B01 (30-38 cm, facies Ar, 26.850 mg.kg^{-1} Mn; 63-73 cm, facies G, 18.864 mg.kg^{-1} Mn) and T01(83-103 cm, facies G, 24.170 mg.kg^{-1} Mn; 25-35 cm, facies G, 23.693 mg.kg^{-1} Mn; 0-18 cm, facies G, 18.858 mg.kg^{-1} Mn). More than 75% of the extracted Mn is in the reducible fraction. It is worth mentioning that the availability of Mn is possibly affected by the mining activities in the study area.

Only a small percentage of elements were found associated with the oxidizable fraction. The highest percentages of Ni (7.4 to 12.4%) were associated with this fraction in section B01, and both of Ni (9.1 to 20.9%) and Zn (2.2 to 8.4%) were associated with this fraction in section T01. The highest percentages of Zn (1.5 to 2.6%) were associated with the oxidizable fraction insections T02 and T03.

It is interesting to note that the residual fraction seems to be an important repository of several elements. In section B01 the contribution of this fraction to the individual Fe and As fractions was significant (94.6 to 98.3% and 100% respectively), which can indicate that in the sections analyzed there is a tendency of elements to assume non-bioavailable forms. Besides, a high percentage of Zn, Pb and Ni were associated with the residual fraction in facies of section B01. Similar behavior was observed insections T01, T02 and T03.

Especially in relation to the last results, it is worth to stress out that Pb and As are highly toxic to humans and that Zn in excess is considered toxic. According to Garlipp et al. (2008), Zn concentrations in sediments can vary a lot. Coarser-grained sandy sediments can contain lower Zn concentrations, as observed in the 0-30 cm and 38-63 cm intervals in section B01, 25-150 cm insection T02, and 0-32 cm in section T03, in all cases in facies Ct. Clayey sediments, as in 0-18 cm, 25-35 cm and 83-103 cm intervals in section T01 (allfaciesG), can contain high Zn concentrations, as described by Larsen and Gaudette (1995). In terms of fractionation, residual Zn is generally associated with clay latticesand a variety of minerals, including ilmenite ($FeTiO_3$) and magnetite (Fe_3O_4 or $FeO.Fe_2O_3$), which were identified in some samples. Non-residual Zn is mainly found associated with theFe and Mn oxide-hydroxide fractions of many oxidized sediments. In contrast, in reduced sediments most of the element is associated with sulfides and organic matter (Garlipp et al. 2008).

Regarding Pb, we believe that most of it, in sections B01, T01, T02 and T03, is concentrated in the mineral matrix of the particles, being one part associated with aluminosilicates (residual fraction) and another part with Fe and Mn oxides-hydroxides, especially Fe (reducible fraction). The mineralogical analyses, both by optical stereoscopy and x-ray diffractometry, revealed the predominance of silicate mineralssuch as quartz, muscovite, kaolinite and talc in the samples analyzed, and minor Fe oxides, such as hematite, goethite and magnetite, and lack of sulfide minerals (either arsenopyriteor pyrite). Considering that the elements present in the residual fraction are those mainly linked to silicates, the mineral composition of the samples corroborates with the hypothesis of Pb being associated with these minerals. The mineral analysis shows the predominance of clay minerals, followed by Feoxides. It seems that Pb, identified in the reducible fraction, is, in fact, associated with Fe oxides-hydroxides that cover clay particles, as indicated by the strong correlation between Al concentrations (not shown) and Pb (aluminosilicate clayparticles). On the other hand, the lack of sulfideminerals explains the absence of Pb associated with the oxidizablefraction.

A similar reasoning can be applied to As. Our results corroborate with other studies developed in the Quadrilátero Ferrífero, which also stressed out that most of As seems to be associated with the residual fraction (Guimarães, 2005; Pereira et al., 2007; Varejão et al., 2011). Guimarães (2005) carried out a chemical characterization of the water and bottom sediments of the Cachoeira River Dam, located in the southeastern portion of the Quadrilátero Ferrífero and observed, by means of sediment fractionation, that not only As, but also Cd, Cr, Cu, Ni and Zn are predominantly associated with the residual fraction of the sediments. Pereira et al. (2007), studying the distribution of some metals in superficial sediments of the upper Velhas River basin (SW part of the Quadrilátero Ferrífero) and the mobility of these elements, found that As and Cr have similar behavior, being preferentially found associated with the residual fractionand are, consequently, less mobile in all sites analyzed. More recently, Varejão et al. (2011), also studying the southeastern part of the Quadrilátero Ferrífero, between Ouro Preto and Mariana, detected high As concentrations, which are related to the historical gold mining activities in the region.

High As percentages are associated with the residual fraction in all sections analyzed, the mobilization to the aquatic environment not being probable in natural conditions. In this case, similarly to Pb, the lack of sulfide minerals in the samples analyzed (B01, T01, T02 and T03), attested by the mineralogical analysis explain arsenic has not been identified associated with the lattice, for example, the arsenopyrite or pyrite enriched element.

CONCLUSIONS

Based on the exposed above, it can be concluded that:

- The fluvial sediments analyzed in this study present high concentrations of elements of importance under the environmental and public health points of view, such as Pb, As, Fe, Ba and Mn. However, only a few are promptly bioavailable, as these elements are associated with the exchangeable fraction. Special attention should be given to Ba and Ni, because they can be mobile under decreasing pH conditions, such as acid drainage generated by mining tailings.

- High Fe, As and Pb concentrations were detected in sedimentary facies interpreted as channels with direct or indirect interference of mining activities, such as panning or dragging (suggesting anthropogenic contributions of elements to the environment). However, these concentrations are predominantly associated with the residual fraction, corroborating to the hypothesis that these elements should be non-bioavailable (geological origin). In these cases, considering the difficulty to clearly define the origin of these elements (anthropogenic, geogenic or geogenic with anthropic contribution), it seems plausible to adapt or create a specific protocol for some of these elements, such as As and Pb. Certainly the characteristics of the samples to be analyzed by a certain sequential extraction protocol should be taken into consideration, in particular samples similar to many of this study, which are very rich in Fe, poor in organic matter, having or lacking sulfides.

ACKNOWLEDGMENTS

The authors wish to thank the Brazilian Council for Scientific and Technological Development (*Conselho Nacional de Desenvolvimento Científico e Tecnológico* – CNPq, Projects 577211-2008-0 and 476881-20072, the Program for Centers of Excellence (*Programa de Apoio a Núcleos de Excelência* – PRONEX), linked to the Minas Gerais Research Foundation (*Fundação de Amparo à Pesquisa do Estado de Minas Gerais* – FAPEMIG, CRA-APQ-00415-09), and to the Coordination for the Improvement of High Education Personnel (*Coordenação de Aperfeiçoamento de Pessoal de Nível Superior*– CAPES) for the scholarship granted to the first author.

REFERENCES

ALTUG, G.; BALKIS, N. 2009. Levels of some toxic elements and frequency of bacterial heavy metal resistance in sediment and sea water.**Environmental Monitoring and Assessment**, **149**(1-4):61-69.

ALVES, F. L. et al. 2001. River sediment analysis by slurry sampling FAAS: determination of copper, zinc and lead. **Journal of the Brazilian Chemical Society**, **12**(6):799-803.

CASTILLO, M. L. A. et al. 2011.Fractionation of heavy metals in sediment by using microwave assisted sequential extraction procedure and determination by inductively coupled plasma mass spectrometry. **Microchemical Journal**, **98**(2):234-239.

CANMET. Mining and Mineral Sciences Laboratories. LKSD-1 to LKSD-4. Disponível em: <http://www.nrcan.gc.ca/sites/www.nrcan.gc.ca.minerals-metals/files/pdf/mms-smm/tect-tech/ccrmp/cer-cer/lksd-1-eng.pdf>. Acesso em: 8 dez. 2011.

CHRISTOFOLETTI, A. 1981. **Geomorfologia fluvial**. São Paulo: Edgard Blücher Ltda., 313p.

CORBI, J. J. et al. 2006. Diagnóstico ambiental de metais e organoclorados em córregos adjacentes a áreas de cultivo de cana-de-açúcar (Estado de São Paulo, Brasil). **Química Nova**, **29**(1):61-65.

DESCHAMPS, E. et al. 2002. Soil and Sediment Geochemistry of the Iron Quadrangle, Brazil: the case of arsenic. **Journal Soils e Sediments**, **2**(4):216-222.

EBY, G. N. 2004. **Principles of environmental geochemistry**. Belmont: Thomson Brooks/Cole, 514p.

FÖRSTNER, U. et al. 2004. Historical contaminated sediments and soils at the river basin scale. Examples from the Elbe River catchment area. **Journal Soils and Sediments**, **4**(4):247-260.

GARLIPP, A. B.; SILVA, C. A. R.; AMARO, V. E. 2008. Concentração de elementos maiores e traços no material particulado em suspensão no estuário de Curimataú, Nordeste do Brasil. **Geochimica Brasiliensis**, **22**(1):189-200.

GERRARD, J. 1992. **Soil geomorphology, an integration of pedology and geomorphology**. London: Chapman and Hall, 269p.

GUIMARÃES, A. T. A. 2005. **Avaliação geoquímica ambiental da barragem do ribeirão da Cachoeira, sudeste do Quadrilátero Ferrífero, Ouro Preto, MG**. Dissertação (Mestrado em Ciências Naturais) – Universidade Federal de Ouro Preto, 133p.

HAKANSON, L. 1992. Sediment variability. In: G. A. Burton-Jr (Ed.). **Sediment Toxicity Assessment**. Boca Raton: Lewis Publishers, p. 19-36.

HUDSON-EDWARDS, K. A. et al.1998. Chemical remobilization of contaminant metals within foodplain sediments in an incising river system: implications for dating and chemostratigraphy. **Earth surfaceprocesses and landforms**, **23**(8):671-684.

JORDÃO, C. P.; PEREIRA, M. G.; PEREIRA, J. L. 2002. Metal contamination of river waters and sediments from effluents of kaolin processing in Brazil. **Water, Air and Soil Pollution**, **140**(1-4):119-138.

KWON Y. T., LEE C. W. 2001.Ecological risk assessment of sediment in wastewater discharging area by means of metal speciation. **Microchemical Journal**, **70**(3):255-264.

LARSEN, P. F.; GAUDETTE, H. E. 1995.Spatial and temporal aspects of sedimentary trace metal concentrations in mid-coast Maine. **Marine Pollution Bulletin**, **30**(7):437-444.

LIMA, M. C. et al. 2001. Especiação de cobre e chumbo em sedimento do rio Tubarão (SC) pelo método Tessier. **Química Nova**, **24**(6):734-742.

LINDELL, L.; ÅSTRÖM, M. E.; SARENBO, S. 2010. Effects of forest slash and burn on the distribution of trace elements in floodplain sediments and mountain soils of the Subandean Amazon, Peru. **Applied Geochemistry**, **25**(8):1097-1106.

LÓPEZ-SÁNCHEZ, J. F. et al. 2002. Extraction procedures for soil analysis. In: P. Quevauviller et al. (Orgs.). **Methodologies for soil and sediment fractionation studies**. Cornwall: MPG Books, p. 111-132.

MIALL, A. D. 1978. Facies types and vertical profiles models in braided river deposits: a summary. In: A. D. Miall (Ed.). **Fluvial sedimentology**. Canadian Society of Petroleum Geologists, Memoir 5, p. 597-604.

_____. 1985. Architectural-element analysis: a new method of facies analysis applied to fluvial deposits. **Earth-Science Reviews**, **22**(4):261-308.

_____. 1996. **The geology of fluvial deposits**: sedimentary facies, basin analusis and petroleum geology. Michigan: Springer, 582p.

NEMATI, K. et al. 2011.Comparison of unmodified and modified BCR sequential extraction schemes for the fractionation of heavy metals in shrimp aquaculture sludge from Selangor, Malaysia. **Environmental Monitoring and Assessment**, **176**(1-4):313-320.

PARDO, R. et al. 2004. Application of two- and three-way principal component analysis to the interpretation of chemical fractionation results obtained by the use of the B.C.R. procedure. **Analytica Chimica Acta**, **523**(1):125-132.

PASSOS, E. A. et al. 2011. Metal fractionation in sediments of the Sergipe River, northeast, Brazil**. Journal of the Brazilian Chemical Society**, **22**(5):828-835.

PEREIRA, J. C. et al. 2007. Distribuição, fracionamento e mobilidade de elementos traço em sedimentos superficiais. **Química Nova**, **30**(5):1249-1255.

QUINÁIA, S. P.; CAVAGNOLI, A. R.; MARTINS, V. J. 2009. Avaliação da distribuição de Cr, Pb e Cu em sedimentos superficiais. **Revista Ciências Exatas e Naturais**, **11**(1):49-66.

REZENDE, P. S. et al. Arsenic and Mercury mobility in Brazilian sediments from the São Francisco river basin. **Journal of the Brazilian Chemical Society**, **22**(5):910-918.

ROESER, H. M. P.; ROESER, P. A. 2010.O Quadrilátero Ferrífero - MG, Brasil: aspectos sobre sua história, seus recursos minerais e problemas ambientais relacionados. **Revista Geonomos**, **18**(1):33-37.

SEDDIQUE, A. A. et al. 2011. Mineralogy and geochemistry of shallow sediments of Sonargaon, Bangladesh and implications for arsenic dynamics: focusing on the role of organic matter. **Applied Geochemistry**, **26(1**):587-599.

SHARIF, M. S. U. et al. 2011. Surface complexation modeling for predicting solid phase arsenic concentrations in the sediments of the Mississippi River Valley alluvial aquifer, Arkansas, USA. **Applied Geochemistry**, **26**(1):496-504.

VAREJÃO, E. V. V. et al. 2011. Arsenic and trace metals in river water and sediments from the southeast portion of the Iron Quadrangle, Brazil.**Environmental Monitoring and Assessment**, **172**(1-4):631-642.

ZABETOGLOU, K.; VOUTSA, D.; SAMARA, C. 2002. Toxicity and heavy metal contamination of surficial sediments from the Bay of Thessaloniki (Northwestern Aegean Sea) Greece. **Chemosphere**, **49**(1):17-26.

ZIMMERMAN, A. J.; WEINDORF, D. C. 2010. Heavy metal and trace metal analysis in soil by sequential extraction: a review of procedures. **International Journal of Analytical Chemistry**, 2010(1):1-7.