Environ Monit Assess (2011) 172:631–642
DOI 10.1007/s10661-010-1361-3

Arsenic and trace metals in river water and sediments from the southeast portion of the Iron Quadrangle, Brazil

**Eduardo V. V. Varejão · Carlos R. Bellato ·
Maurício P. F. Fontes · Jaime W. V. Mello**

Received: 29 April 2009 / Accepted: 11 February 2010 / Published online: 18 March 2010

Abstract The Iron Quadrangle has been one of the most important gold production regions in Brazil since the end of the seventeenth century. There, arsenic occurs in close association with sulfide-rich auriferous rocks. The most abundant sulfide minerals are pyrite and arsenopyrite, yet trace metal sulfides occur in subordinate phases as well. Historical mining activities have been responsible for the release of As and trace metals to both aquatic and terrestrial environments close to mining sites in the region. Therefore, this study was aimed to evaluate the distribution and mobility of As, Cd, Co, Cr, Cu, Ni, Pb, and Zn in streams in the southeast portion of the Iron Quadrangle between the municipalities of Ouro Preto and Mariana, the oldest Brazilian Au mining province. Total concentrations of some trace metals and arsenic in water were determined. The four-stage sequential extraction procedure proposed by the commission of the European Communities Bureau of Reference (BCR) was used to investigate the distribution of these elements in stream sediments. Arsenic concentration in water was >10 μg L^{-1} (maximum limit permitted by Brazilian environmental regulations for water destined for human consumption) at all sampling sites, varying between 36.7 and 68.3 μg L^{-1}. Sequential extraction in sediments showed high concentrations of As and trace metals associated with easily mobilized fractions.

Keywords Fractionation · Sequential extraction · Bioavailability

Introduction

The Iron Quadrangle (IQ) is one of the largest and most well-known mineral deposits in the world (Deschamps et al. 2002). Not only extensive iron deposits but also hydrothermal gold deposits are found in this region. The area has been the most important gold producing region in Brazil since the end of the seventeenth century, with a total production exceeding 1,300 tons (Borba et al. 2003). In IQ mineral deposits, As is found in close association with sulfide-rich gold-bearing rocks (Matschullat et al. 2000; Mello et al. 2006). The most abundant sulfide minerals are pyrite (FeS_2), arsenopyrite (FeAsS), and pyrrhotite ($Fe_{1-x}S$) (Matschullat et al. 2000; Vial et al. 2007), yet trace metal sulfides occur in subordinate phases as

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E. V. V. Varejão · C. R. Bellato (✉)
Departamento de Química, Universidade Federal
de Viçosa, Av. P.H. Rolfs, s/n, 36571-000, Viçosa,
Minas Gerais, Brazil
e-mail: bellato@ufv.br

M. P. F. Fontes · J. W. V. Mello
Departamento de Solos, Universidade Federal
de Viçosa, Av. P.H. Rolfs, s/n, 36571-000, Viçosa,
Minas Gerais, Brazil

well (Gonçalves et al. 2007). Previous studies have revealed high levels of arsenic (Matschullat et al. 2000; Deschamps et al. 2002; Borba et al. 2003; Veado et al. 2006; Deschamps and Matschullat 2007; Gonçalves et al. 2007; Pereira et al. 2007) in aquatic and terrestrial environments in different regions of the IQ. According to Deschamps et al. (2002), such high amounts of arsenic in water, soils, and sediments in the IQ is related to both natural causes as well as past and recent mining activities. Matschullat et al. (2000) reported high concentrations of As in surface water, soils, sediments, and waste in the districts of Nova Lima and Santa Barbara. The same study evaluated the potential health risks to the local population through the analysis of urine samples from school children. Concentrations between 2.2 and 105 $\mu g\ L^{-1}$ were found, and according to the authors, the principal form of human contamination in the region is likely due to the ingestion of contaminated dust, fish, and water (Matschullat et al. 2000; Deschamps and Matschullat 2007). The presence of toxic metals in water and sediments has also been reported by Veado et al. (2006) and Pereira et al. (2007).

In the southeast portion of the IQ, the municipalities of Ouro Preto and Mariana are known as the oldest auriferous provinces in Brazil. High amounts of arsenic in soil, sediments, groundwater, and stream water have also been found in this region (Matschullat et al. 2000; Borba et al. 2003; Gonçalves et al. 2007). Small-scale Au mining activities (namely, *garimpos*) have also been historically performed during nearly 300 years of mineral exploration. Such activities typically involve the use of Hg to improve gold recovery by amalgamation. Therefore, the presence of high amounts of Hg in sediment samples from this region has also been reported (Varejão et al. 2009a). Despite previous reports concerning total arsenic contents in sediments from the southeast region of the IQ, none of them have dealt with the partitioning of arsenic and trace metals in sediments. It is well-known that total concentration is not the best criterion to determine the potential toxicological effects of sediment contamination by trace elements. It assumes that all forms of an element present in the sediment present equal impact on the medium, providing limited information on its mobility (Tessier et al. 1979). Arsenic and trace metals can be distributed in different mineralogical phases in sediments (Gismera et al. 2004); thus, mobility and bioavailability of these elements depend on the different forms with which they are associated within sediment fractions (Filgueiras et al. 2004). Sequential extraction methods provide more detailed information on the association of trace elements with different sediment fractions (Davidson et al. 1998; Žemberyová et al. 2006; Raposo et al. 2006). Sequential extraction (or fractionation as defined by the International Union of Pure and Applied Chemistry) methods assume the selective extraction of trace elements in defined fractions of the sediments (Templeton et al. 2000; Pueyo et al. 2003). These procedures are based on the application of chemical extractions in a rational sequence, using selected reagents to solubilize different mineralogical fractions responsible for the retention of trace elements (Gleyzes et al. 2002).

The objective of this work was to estimate the distribution of As, Cd, Co, Cr, Cu, Ni, Pb, and Zn in stream sediment samples and determine their concentrations in surface waters of the southeast portion of the IQ region. The results are expected to be useful for understanding the distribution and mobility of these elements and assessing ecotoxicological risks related to past mining in the area.

Description of the sampling sites

The Carmo River Basin is part of the Doce River Basin, which makes up a drainage area of 83,400 km^2, 222 municipalities, and 461 districts. The Carmo River is formed by the union of the Tripui and Funil creeks in the municipality of Ouro Preto. It has been affected by various gold mining activities (e.g., Passagem de Mariana, Chico Rei, Sciliar, Quartzito, and Lajes). It is estimated that only the Passagem mine, located 7 km east of Ouro Preto, produced at least 60 tons of gold from the end of the seventeenth century to 1954. Along the Tripui creek and Carmo river, exploration of Al and gemstones remains active, and some small-scale gold mining can be found. Diverse abandoned gold mines are also encountered. An abandoned cinnabar (HgS) mine was

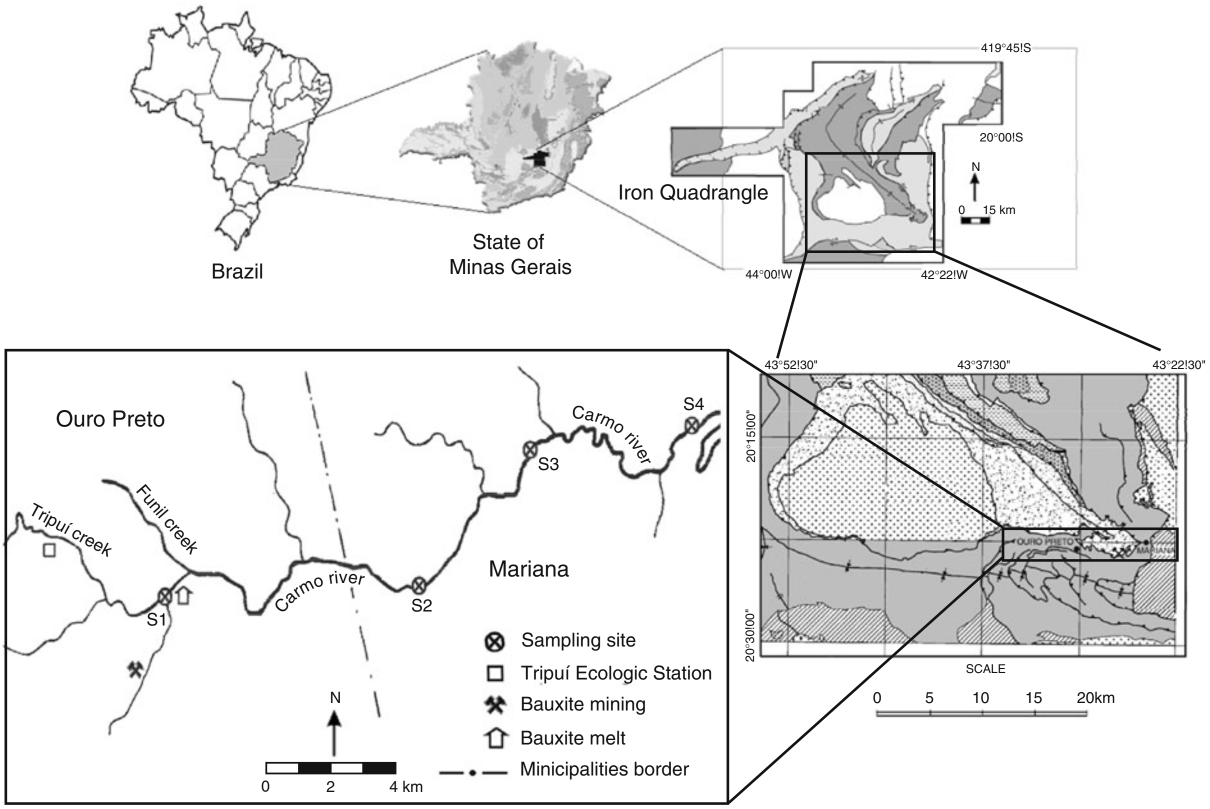

Fig. 1 Region under study (adapted from Vial et al. 2007; Figueiredo et al. 2004)

also found near the Botafogo Creek, a tributary of the Tripui Creek.

Water and stream sediment samples were collected at four sites (S1 to S4) along the Tripui Creek and Carmo River in March, 2006 (Fig. 1).

Materials and methods

Reagents, solutions, and flasks

Flasks and glassware were rigorously washed with distilled water, immersed in nitric acid 10% (*v*/*v*) for 48 h, and thoroughly rinsed with distilled deionized water. Only analytical grade reagents were used (VETEC and MERCK), and all solutions were prepared with distilled deionized water.

Sampling, pretreatment, and storage of the samples

Five water subsamples were collected at each sampling site using 1,000-ml polytetrafluoroethylene flasks, previously washed and rinsed with the water to be collected. The samples were filtered using a cellulose acetate membrane (MILLIPORE, 0.45 μm), acidified to pH 2 with nitric acid, stored in coolers, and immediately transported. In the laboratory, water samples were kept refrigerated at 4°C until analysis.

At each sampling sites, three to five sediment subsamples were collected (depth of 0–20 cm) using a plastic shovel. Sediment samples were transferred to plastic bags and transported in coolers to the laboratory where they were naturally dried, sieved (<2 mm), carefully ground, and homogenized. No preservatives were added to the sediments. Part of the samples (<2 mm) was submitted to physical and chemical characterization and part was sieved to <1 mm for sequential extraction analyses.

Sediment analyses

Sediment samples were submitted to physical–chemical characterization. Mineralogical analyses were carried out by powder X-ray diffraction in a Rigaku D-Max diffractometer equipped with a cobalt tube (Co-Kα radiation, $\lambda = 1.790269$), graphite curved crystal monochromator and operated at 40 kV and 30 mA. Scans were performed in a step-by-step mode from 4° to 50° 2θ with 0.05° increments per 1 s.

Cation exchange capacity (CEC), organic matter content, and granulometry of the sediments were determined by current methods reported by EMBRAPA (1997).

The BCR sequential extraction method was applied for element fractionation. Approximately 0.8000 g of sediment sample sieved to <1 mm was transferred to 50-ml centrifuge tubes and submitted to the BCR sequential extraction procedure (Table 1) as reported by Ure et al. (1993) and Rauret et al. (1999). All analyses were done in triplicate.

At the end of each stage, the extracts were separated from the residual solids by centrifuging for 20 min at 3,000 rpm. The residue was washed by adding 16 ml of water, shaking for 15 min, and finally centrifuging the resulting suspension. The supernatant was decanted and discarded, taking care not to discard any of the solid residue. The "cake" obtained upon centrifugation was disrupted by using a vibrating rod before the next step. In the fourth step, the residue was digested with aqua regia in a microwave oven, increasing the temperature to 200°C in 10 min (1,000 W) and maintaining these conditions for 15 min. This same digestion process was applied to 0.5000 g of integral sediment (not submitted to the extraction steps) for the determination of pseudototal contents.

Heavy metal concentrations were determined by Atomic Absorption Spectrometry (AAS) with a Varian SpectrAA200 spectrometer. Quantification of arsenic was performed by hydride generation–atomic absorption spectrometry (HG-AAS) using a Varian VGA77 hydride generator. Formation of hydrides was obtained using $NaBH_4$ 0.4% (w/v) in NaOH 0.6% (w/v) and 6 mol L^{-1} HCl after prereducing As(V) to As(III) using KI 1% (w/v) in the final extracts. The interference of oxidizing agents in the extracts from stages 3 and 4 was avoided by addition of ascorbic acid during the prereduction of arsenate in the samples. Previous studies showed that the addition of ascorbic acid at final concentrations of 3% and 2% (w/v) to the extracts obtained in steps 3 and 4, respectively, was sufficient to avoid the reduction of iodide to iodine, and allowed the reduction of As(V) and the quantitative detection of As (Varejão et al. 2009b).

Reference material SRM 2704 National Institute of Standards and Technology (NIST; Buffalo River Sediment) was submitted to the three initial steps of the BCR extraction method. The method's recovery capability was evaluated by the relation between the sum of the extracted content in the three initial steps and the certified values.

Table 1 BCR protocol

Shaking	Time (h)	Temp. (°C)	Vol. (ml)[a]	Extractants	Fraction	Step
40 rpm	16	22 ± 5	32	CH_3COOH 0.11 mol L^{-1}	Exchangeable and acid-soluble	1
40 rpm	16	22 ± 5	32	$NH_2OH{\cdot}HCl$ 0.5 mol L^{-1} (pH 1.5)[b]	Reducible	2
Occasional	1	22 ± 5	8	H_2O_2 8.8 mol L^{-1} (pH 2)[b]	Oxidizable	3
Occasional	1	80 ± 5				
Occasional	1	80 ± 5	8	H_2O_2 8.8 mol L^{-1} (pH 2)[b]		
40 rpm	16	22 ± 5	40	NH_4OAc 1 mol L^{-1} (pH 2)[b]		
Microwave digestion			12	Aqua regia (HCl/HNO_3, 3:1)	Residual	4

[a] Related to sample weight of 0.8 g

[b] pH values adjusted with concentrated nitric acid

Table 2 As (in micrograms per kilogram; average of three repetitions ± SD) and heavy metal (in milligrams per kilogram; average of three repetitions ± SD) quantities recovered from the sediments by application of the BCR sequential extraction method

	S1					
	Steps				PT	(%)[a]
	1	2	3	Residual		
As	188.7 ± 11.2	68.8 ± 5.9	22.5 ± 1.6	21,868 ± 1,478	23,472 ± 1,307	94
Cd	1.12 ± 0.11	1.97 ± 0.1	<DL	3.11 ± 0.22	5.92 ± 0.2	105
Co	1.58 ± 0.02	9.53 ± 0.60	<DL	31.12 ± 2.16	43.7 ± 2.9	97
Cr	0.97 ± 0.09	2.18 ± 0.17	4.15 ± 0.33	64.72 ± 4.10	75.8 ± 4.2	95
Cu	1.89 ± 0.11	5.11 ± 0.44	<DL	30.91 ± 2.01	34.8 ± 2.9	109
Ni	<DL	2.96 ± 0.21	<DL	40.96 ± 3.14	47.7 ± 3.0	92
Pb	1.96 ± 0.10	7.29 ± 0.56	2.53 ± 0,19	15.76 ± 1.13	29.4 ± 1.8	94
Zn	2.94 ± 0.19	4.42 ± 0.29	1.76 ± 0.09	48.32 ± 4.11	58.7 ± 2.6	98
	S2					
	Steps				PT	(%)
	1	2	3	Residual		
As	201.4 ± 14.9	435.0 ± 39.6	324.7 ± 28.3	66,228 ± 4,288	69,541 ± 3,182	97
Cd	1.24 ± 0.08	2.25 ± 0,13	<DL	3.53 ± 0.27	6.75 ± 0.42	104
Co	1.63 ± 0.09	1.83 ± 0.07	2.90 ± 0.18	43.8 ± 2.0	48.4 ± 3.8	104
Cr	<DL	2.09 ± 0.13	3.65 ± 0.23	64.3 ± 4.0	73.3 ± 4.6	96
Cu	2.07 ± 0.12	5.18 ± 0.33	1.82 ± 0.13	24.6 ± 1.8	31.7 ± 2.5	106
Ni	<DL	4.01 ± 0.29	4.44 ± 0.24	56.1 ± 3.7	69.0 ± 3.5	94
Pb	4.46 ± 0.29	8.73 ± 0.52	2.60 ± 0.19	16,9 ± 1.3	37.1 ± 1.2	88
Zn	4.64 ± 0.32	7.14 ± 0.50	3.71 ± 0.26	52.8 ± 3.8	77.7 ± 4.3	88
	S3					
	Steps				PT	(%)[a]
	1	2	3	Residual		
As	336.1 ± 29.61	2,653 ± 177.1	40,354 ± 3,796	221,398 ± 14,535	281,805 ± 17,861	94
Cd	1.32 ± 0.11	2.21 ± 0.13	<DL	3.46 ± 0.31	6.50 ± 0.54	107
Co	1.89 ± 0.14	7.50 ± 0.54	1.39 ± 0.07	34.06 ± 2.16	42.12 ± 3.11	106
Cr	1.04 ± 0.06	2.88 ± 0.17	5.90 ± 0.34	85.90 ± 6.02	102.5 ± 6.87	93
Cu	1.08 ± 0.05	4.61 ± 0.30	<DL	24.39 ± 1.99	28.56 ± 1.65	105
Ni	<DL	2.50 ± 0,18	2.65 ± 0.18	49.68 ± 3.18	56.40 ± 3.43	97
Pb	3.13 ± 0.21	8.65 ± 0.59	3.46 ± 0.25	16.27 ± 1.50	29.39 ± 1.23	107
Zn	3.10 ± 0.17	5.34 ± 0.44	1.55 ± 0.16	52.00 ± 3.69	63.46 ± 2.99	98
	S4					
	Steps				PT	(%)
	1	2	3	Residual		
As	521.3 ± 38.7	3,939 ± 245.9	40,710 ± 2,987	128,620 ± 9,858	189,295 ± 12,746	92
Cd	1.67 ± 0.17	2.39 ± 0.14	<DL	2.27 ± 0.21	6.90 ± 0.41	92
Co	2.01 ± 0.13	5.92 ± 0.36	1.46 ± 0.12	16.28 ± 0.99	29.92 ± 2.42	86
Cr	<DL	2.78 ± 0.19	4.68 ± 0.35	49.76 ± 2.89	61.75 ± 4.26	93
Cu	<DL	1.26 ± 0.14	<DL	23.43 ± 1.68	24.39 ± 2.10	101
Ni	<DL	<DL	<DL	21.83 ± 1.39	22.02 ± 1.88	99
Pb	3.78 ± 0.22	4.93 ± 0,27	4.35 ± 0.31	10.89 ± 0.76	21.95 ± 1.56	109
Zn	1.79 ± 0.11	3.13 ± 0.21	1.21 ± 0.09	27.97 ± 1.77	33.13 ± 1.91	103

DL detection limits, *PT* pseudototal digestion

[a] Recuperation in percentage

Water analyses

In situ measurements of pH, redox potential, and dissolved oxygen content of the water were carried out in all of the sampling sites. Values of pH were determined using a digital pH meter (WTW, model 340i). Dissolved oxygen concentrations were determined using an oxygen-sensitive membrane electrode (HANNA, model HI-9142), and the redox potential was determined using a SCHOTT handylab LF1 portable device.

Chemical oxygen demand (COD) was determined by the $K_2Cr_2O_7/H_2SO_4$ method using a MERCK (TR 300 model) thermoreactor and a Varian (CARY 50 Conc. model) spectrophotometer. Heavy metal concentrations were determined by atomic absorption spectrometry (AAS) with a Varian SpectrAA200 spectrometer. Quantification of arsenic was performed by HG-AAS using a Varian VGA77 hydride generator. The formation of hydrides was obtained using $NaBH_4$ 0.4% (*w*/*v*) in NaOH 0.6% (*w*/*v*) and 6 mol L^{-1} HCl. As(V)/As(III) prereduction was obtained using KI 1% (*w*/*v*) in the final solutions.

Results and discussion

Sediment analyses

Although the BCR method was initially developed and proposed for the sequential extraction of metals, it has also been applied for arsenic fractionation (Dhoum and Evans 1998; Rauret et al. 1999; Weisz et al. 2000; Marguí et al. 2004; Basílio et al. 2005; Pereira et al. 2007; Pertsemli and Voutsa 2007). In accordance, our results showed recoveries >90%, including arsenic. Only Pb and Zn presented lower recoveries (88%) for sampling site S3, and Co (86%) for sampling site S4 (Table 2).

The results also revealed adequate reproducibility, with SDs <10% in all steps of the sequential extraction procedure (Table 2). Results for detection limits (DL), calculated according to the 3σ criteria (Long and Winefordner 1983), can be considered quite low (Table 3), corroborating the sensitivity of the BCR procedure followed by the AAS or HG-AAS method to evaluate contamination of sediments by trace elements.

Table 3 DL obtained for arsenic (in micrograms per kilogram) and metals (in milligrams per kilogram) in the sequential extraction analysis

	Step			
	1	2	3	4
As	1.35	1.83	1.86	1.42
Cd	0.41	0.39	0.50	0.37
Co	0.88	0.83	1.01	0.82
Cr	0.94	0.98	1.12	0.89
Cu	0.52	0.54	0.67	0.50
Ni	1.56	1.58	1.62	1.55
Pb	1.89	1.76	2.02	1.52
Zn	0.36	0.41	0.49	0.39

The residual fraction corresponds to the arsenic and metals occluded in nonsilicate mineral extracted during the final step of the chemical extraction sequence by means of digestion with aqua regia. The largest portion of the studied elements was encountered in association with this fraction (Fig. 2) and is considered unavailable since its mobility to the aquatic medium is unlikely to occur. On the other hand, trace elements associated with the acid-soluble, reducible, and oxidizable fractions are considered bioavailable. It is recognized that environmental variations in pH, ionic strength, and redox potential (Eh) may cause remobilization of these elements to the water (Gleyzes et al. 2002; Jain et al. 2008).

The exchangeable and acid-soluble fraction extracted in the first step of the sequential chemical procedure corresponds to trace elements bound to sediment particles by weak adsorption and elements associated to carbonates. Since the sediments showed low levels of clay minerals and consequently a relatively low adsorptive capacity (Table 4), extraction of As and trace metals in step 1 as part of the acid-soluble fraction can be ascribed mainly to its association with carbonates present in the sediments due to extensive carbonate alteration in the ore deposits of this region (Vial 1988; Oliveira 1998; Vial et al. 2007). High levels of carbonates in water ways of the studied area have been reported (Borba et al. 2003).

Less than 1% of total As was found associated to the acid-soluble fraction in all sampling sites. The risk assessment code (RAC; Table 5)

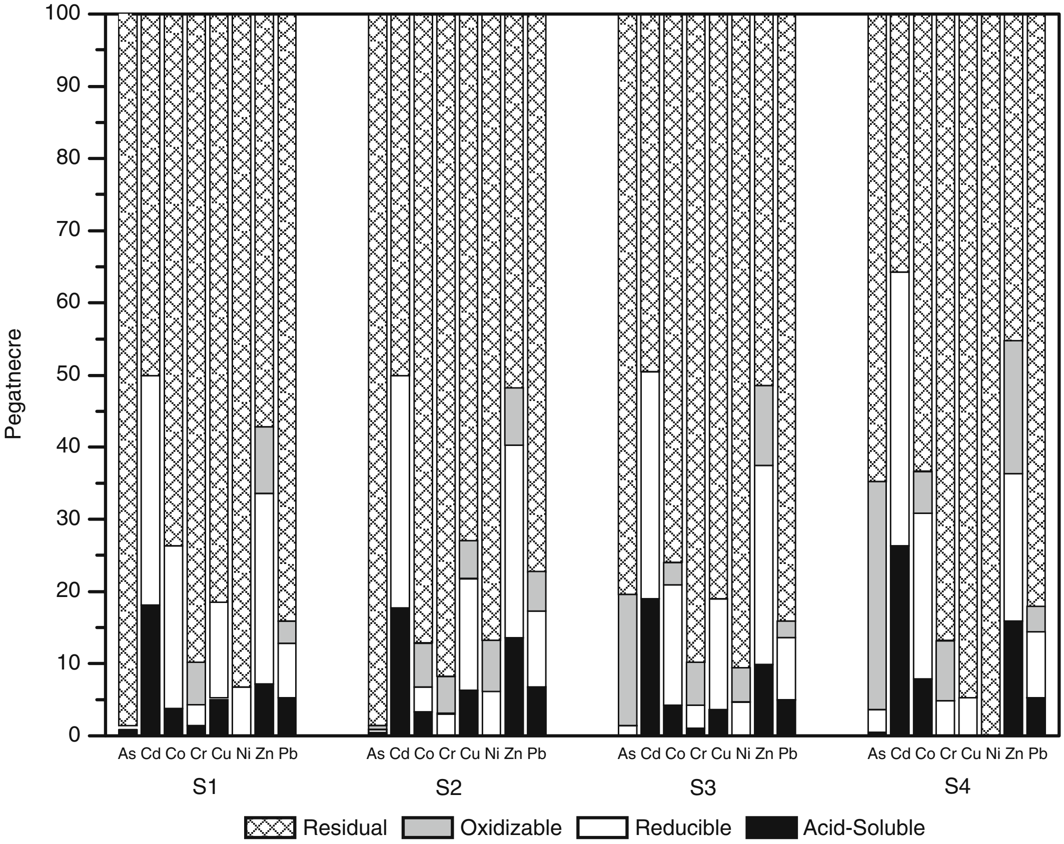

Fig. 2 Arsenic and trace metals (in percentage) in the different sediment fractions. Sampling sites S1 to S4

indicates the potential ecotoxicological risk related to the presence of metals in the carbonate fraction, which are sensitive to pH changes, with the lowering of pH being associated with the release of metal cations (Jain et al. 2008). It can be assumed that Cd is classified in the medium risk category for all of the sampling sites, Pb of low to medium risk, and the other metals are present at <10% of the total, being considered of low risk.

The presence of secondary minerals such as goethite and hematite in the silt fraction as revealed by X-ray diffraction analyses (Fig. 3) explain the presence of As and trace metals in the reducible fraction. Besides the charge generated due to the amphoteric surfaces of these minerals, the possibility of chemisorption of As and trace metals by iron oxides is well documented (Wilkie and Hering 1996; Gomes et al. 2001; Deschamps 2003; Fontes and Gomes 2003; Lakshmipathiraj 2006; Giménez et al. 2007). The release of trace elements from these matrices is most likely to be affected by the redox potential and pH. Mello

Table 4 Characterization of the sediments collected along the Tripuí Creek and Carmo River

	Organic matter	Total	Effective	Granulometry (%)			
	(mg kg^{-1})	CEC	CEC	Coarse sand	Fine sand	Silt	Clay
S1	3.10	0.80	0.71	50	41	4	5
S2	9.83	0.65	0.50	80	12	4	4
S3	7.93	0.76	0.47	65	24	8	3
S4	5.84	0.88	0.39	53	44	2	1

CEC cation exchange capacity

Table 5 The RAC

RAC	Criteria
No risk	<1%
Low risk	1–10%
Medium risk	11–30%
High risk	31–50%
Very high risk	>50%

et al. (2007) showed that As can be released by reductive dissolution of Fe oxyhydroxides in contaminated soils from the IQ region.

Arsenic and trace metals can be regarded as mainly associated with sulfide minerals in the oxidizable fraction (step 3). The greater amounts of As in the oxidizable fraction of sediments from sampling sites S3 and S4 may be related to the contribution of oxidative dissolution of arsenic-rich sulfide minerals from the Passagem Mine (Mariana municipality), the most important ancient gold mine of the region located upstream of S3 and S4.

Pseudototal digestion with aqua regia is used as a tool for the internal evaluation of the method's recovery capability. The relation between the sum of quantities obtained from the sequential extraction (including residual fraction) and pseudototal content allows for calculation of recovery. Results showed acceptable recovery percentages for the BCR method, varying from 86% to 109%. Application of this method for the SRM 2704 NIST reference material also showed satisfactory recoveries in relation to certified values: As (91%), Cd (86%), Co (86%), Cr (92%), Cu (88%), Ni (89%), Pb (86%), and Zn (84%). Such results are in agreement with previous studies using the BCR method (Davidson et al. 1994, 1998; Tokalioglu et al. 2000; Marguí et al. 2004; Pertsemli and Voutsa 2007).

Although the largest portion of the studied elements was encountered in association with the residual fraction considered unavailable under normal conditions encountered in nature, all of

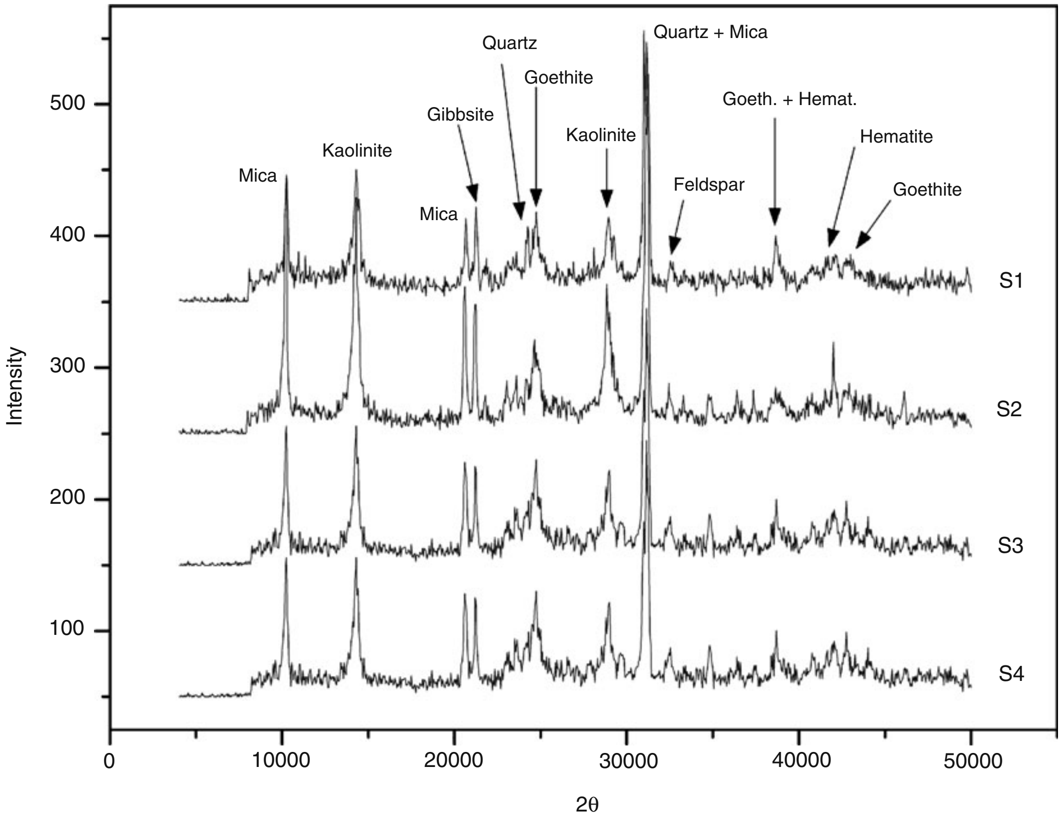

Fig. 3 X-ray diffraction spectra of the sediment samples. Sampling sites S1 to S4

Table 6 Total As level and physical–chemical parameters related to water quality

	Sampling sites				BES[a]
	S1	S2	S3	S4	
Total As ($\mu g\ L^{-1}$)	36.7 ± 2.1	51.6 ± 3.8	61.7 ± 3.1	68.3 ± 1.8	<10
pH	7.6	7.5	7.3	6.9	6.0–9.0
Redox potential (Eh), mV	281	210	233	184	
Temperature, °C	15.6	18.1	20.8	20.4	
Dissolved oxygen (DO), mg $O_2\ L^{-1}$	14.9	9.3	8.4	11.3	>5

[a] Values established by Brazilian environmental standards (BES) to human supply-destined waters (CONAMA 2005)

them were also found in easily mobilized fractions. For some of the sampling sites, the sum of the amounts extracted in acid-soluble, reducible, and oxidizable fractions reached values >30% for As and Co, 50% for Pb, and 60% for Cd. Therefore, the potential for remobilization from sediments to aquatic media must be considered.

Water analyses

Physical–chemical parameters and total dissolved arsenic are reported in Table 6. It is well-known that mining activities not only produce residues but also increase the surface area of minerals in contact with water and atmospheric oxygen. Under these conditions, minerals such as arsenopyrite and pyrite become unstable. The dissolution of these minerals, expressed in Eqs. 1 and 2 (Craw et al. 2003; Rimstidt and Vaughan 2003; Sracek et al. 2004) can cause the production of acidic wastes, making lower pH values expected (Smedley and Kinniburgh 2002):

$$\mathrm{FeAsS} + 7\mathrm{H_2O} \rightleftharpoons \mathrm{Fe^{2+}_{(aq)}} + \mathrm{H_3AsO_{3(aq)}} + 11\mathrm{H^+} + 11\mathrm{e^-} + \mathrm{SO_4^{2-}}, \tag{1}$$

$$\mathrm{FeS_2} + 3.5\mathrm{O_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{Fe^{2+}_{(aq)}} + 2\mathrm{H^+} + 2\mathrm{SO_4^{2-}}. \tag{2}$$

However, the presence of dolomite in ores found in the region (Vial et al. 2007) can neutralize the produced acids, buffering pH at higher values (Thomas et al. 2000). Borba et al. (2003) reported elevated concentrations of carbonates in stream water in this region. Carbonate rocks neutralizing water acidification brought about by the oxidation of sulfide minerals have also been reported (Cidu et al. 2009).

All samples presented As contents >10 $\mu g\ L^{-1}$, the maximum limit established by Brazilian environmental regulations (CONAMA 2005) for water sources of human uses (e.g., human consumption, irrigation). Such results are in line with values verified by previous studies on As concentration in surface water samples from the Carmo River Basin (Borba et al. 2003) and within the range observed in other regions of the IQ (Matschullat et al. 2000). Values greater than the recommended limit by local regulatory agencies confirm the potential risk to the local population.

Although above the maximum limit, As contents in water samples were relatively low as compared with high values in sediments. As discussed earlier, the largest portion of trace elements in sediments was associated with the residual fraction and considered unavailable to aquatic medium. Furthermore, in situ measurements showed values of pH varying from 6.9 to 7.6, and redox potential (Eh) ranging from 184 to 281 mV, indicating oxidative conditions as expected for well-oxygenated surface waters (Table 2). This observation is confirmed by the dissolved oxygen (DO) values, which varied from 8.4 to 14.9 mg $O_2\ L^{-1}$. In such conditions, prevalence of the As(V) anionic species was expected, which are more strongly adsorbed onto mineral oxyhydroxides in comparison with the neutral As(III) species (Vink 1996; Kumaresan and

Table 7 DL for water analysis and limits established by the BES for water destined for public usage (in micrograms per liter)

	As	Cd	Co	Cr	Cu	Ni	Pb	Zn
DL	0.04	4.25	5.60	7.55	13.0	20.0	2.15	21.5
BES	10	1	50	50	9	25	10	180

Riyazuddin 2001; Smedley and Kinniburgh 2002; Terlecka 2005).

When As levels in water are compared to the distribution of arsenic among the different fractions of the sediments at each of the sampling sites, a correlation between the amounts of arsenic in the oxidizable fraction of the sediments and the As concentration in water samples can be observed. Since the in situ measurements of redox potential (Eh) indicate oxidizing conditions, the greater the As concentration present in the oxidizable fraction the higher the As mobilized into the aquatic media.

The elements Cd, Co, Cr, Cu, Ni, Pb, and Zn were all found in concentrations less than the maximum limit established by the Brazilian Environmental Regulation and the DL of the analytical techniques used here (Table 7).

Conclusions

Total arsenic and heavy metal contents in water and its partitioning in sediment samples collected from the Tripui Creek and Carmo River were evaluated in the southeast region of the IQ, Brazil. Results showed concentrations of As in water varying from 36.7 to 68.3 $\mu g\ L^{-1}$, well above the limit defined by Brazilian environmental regulations. Based on water analyses, all the trace metals studied were below the DL of the analytical techniques utilized and the maximum limit established by Brazilian Standards.

Analyses of the sediments showed that the greatest portion of extracted As and trace metals was associated with the residual fraction. Nevertheless, considerable amounts were extracted as easily remobilizable fractions indicating the potential for remobilization of these elements from sediments to the aquatic medium.

It is also important to considerer that local waterways are utilized as water sources for both human and agricultural supply, and the potential risk to human health due to the presence of As and toxic metals in the sediment fractions considered easily remobilizable cannot be ignored.

Acknowledgements The authors are very grateful to Dr Jörg Matschullat of the Interdisciplinary Environmental Research Centre (IÖZ, IERC), Germany, for his kind assistance. The authors also thank the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG) and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Brazil for their financial support.

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