Geochemical distribution of arsenic in waters, sediments and weathered gold mineralized rocks from Iron Quadrangle, Brazil

R.P. Borba · B.R. Figueiredo · J. Matschullat

Abstract The Iron Quadrangle has been the scenery of the most important gold production in Brazil. It is estimated that during the three centuries of gold mining in the Iron Quadrangle, at least 390,000 t of arsenic was discharged into the drainage system. This study presents geochemical data for the three river basins in the region, with focus on surface water and stream sediment monitoring. Samples of primary and oxidized sulfide ores as well as of tailings and groundwater from the major gold mines were also studied. The highest As concentrations in water and stream sediments occur in the vicinity of mining areas. In surface water, up to 300 μg As/l were found whereas the As contents in stream sediments were in the range of 20 to 4,000 mg/kg. The As^{3+}/As^{5+} concentration ratios obtained for some water samples range from 1.10^{-1} to 4.10^{-2}. The As mobility associated with ore-deposit weathering could be traced in some closed gold mines by observation of in-situ pyrite and arsenopyrite oxida-tion, precipitation of scorodite and gippsite, As adsorption onto goethite, and final liberation of As into underground and surface waters. This process is likely to produce large volumes of mine effluents containing total As and trivalent As up to 1,960 and 60 μg/l, respectively. River sediments and tailings pile samples were submitted to a leaching procedure showing maximal arsenic release from 1 to 4% of the original total As in the samples. There are potential risks for As hazards in some areas induced by, for instance, the dispersion of old tailings by flooding, occupation of poisoned soils for settlements, and occasional consumption of contaminated surface and groundwater.

Keywords Arsenic · Water · Sediment · Gold mining · Brazil

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Introduction

Since the end of the 17th century, the Iron Quadrangle in the State of Minas Gerais, Brazil (Fig. 1a), has been the most important gold producing region in Brazil. Gold was initially produced from alluvial placers and oxidation zones and in modern times from primary ores. Total gold production must have exceeded 1,300 t in all history. In the world-famous Morro Velho mine alone, around 600 t gold has been produced since 1834. In this ore deposit as well as in the other Iron Quadrangle gold deposits, the ore is rich in As, with As/Au ratios ranging from 300 to 3,000 (Vial 1988; Abreu and others 1988). Since the tailings produced in the past were mostly discharged into or nearby the drainage systems, the amount of arsenic which was released to the environment must have exceeded 390,000 t in the whole region.

In the southeastern portion of the São Francisco Craton, the Iron Quadrangle encompasses four main lithostratigraphic units (Dorr 1969): (1) the granite-gneissic metamorphic complexes; (2) the Archean greenstone belt sequence, known as the Rio das Velhas Supergroup; (3) the Paleoproterozoic metasedimentary and metavolcanic rocks of the Minas Supergroup; and (4) the metasedimentary rocks of the Itacolomi Group. The main gold deposits are found along shear zones which cut the basic volcanic rocks and banded iron formations of the Nova Lima Group, in the lower Rio das Velhas Supergroup. Examples of those are the Morro Velho, Raposos and Cuiabá gold deposits (Nova Lima district) and the São Bento ore deposit (Santa Bárbara district) which

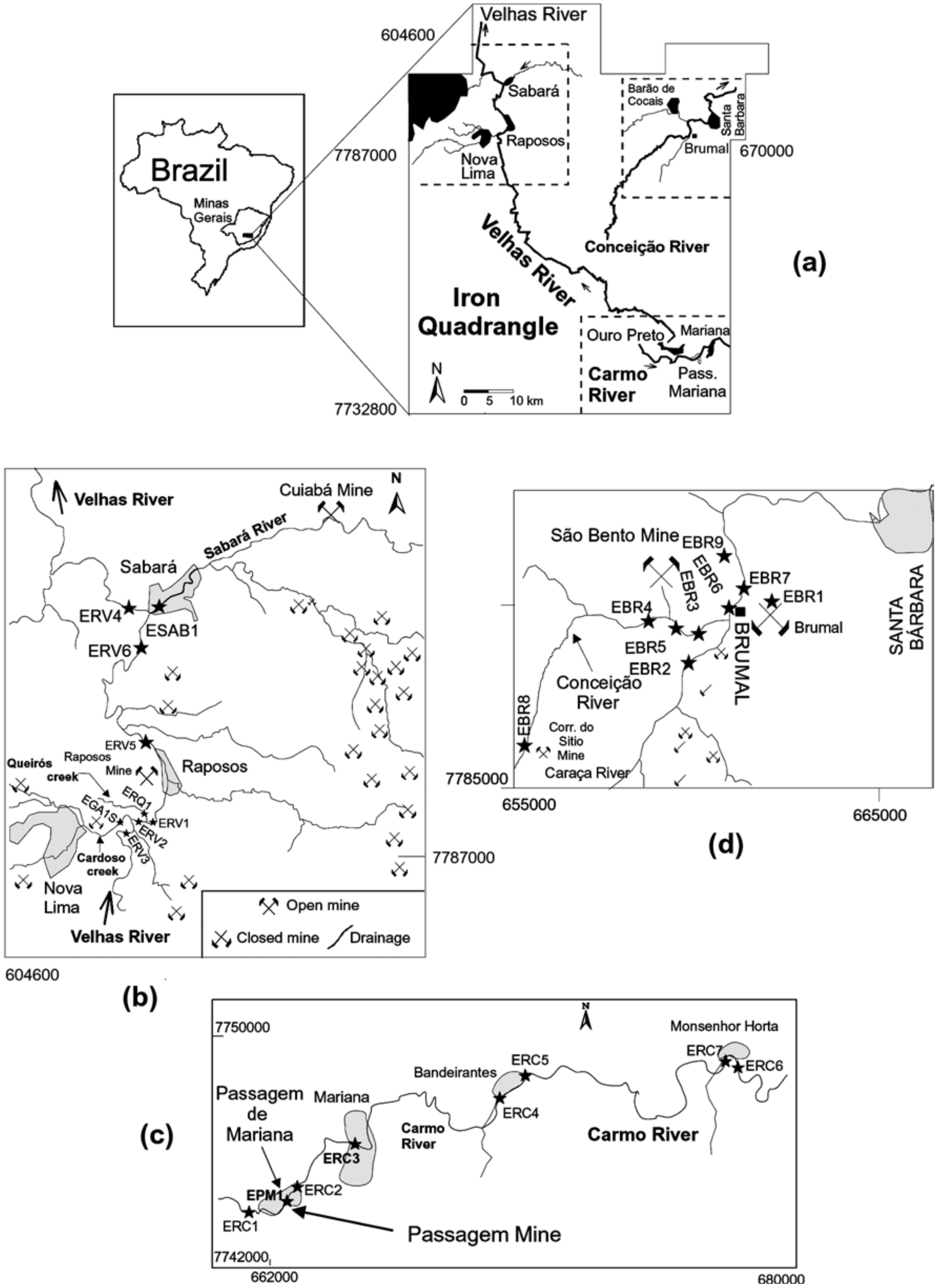

Fig. 1
a The Iron Quadrangle and study areas localization map. **b** Maps of the Velhas River basin, **c** the Carmo River basin, and **d** the Conceção River basin, with sampling sites indicated

contain appreciable amounts of pyrite, pyrrhotite and arsenopyrite mainly associated with banded iron formations (Vieira 1988, 1991; Ribeiro-Rodrigues 1998). Another situation is exemplified by the Passagem de Mariana gold deposit (Ouro Preto-Mariana district), close to the contact between the rocks of the Nova Lima Group and those of the Minas Supergroup. This ore deposit contains major amounts of arsenopyrite, either in quartz and carbonate veins or disseminated in banded iron formation, tourmalinite, phyllite and quartzite (Vial 1988; Oliveira 1998). A number of ancient gold mines can be found in the Ouro Preto-Mariana district, among these the Chico Rei, Scliar and Lajes ore deposits where gold mineralization looks like that of the Passagem mine, although in the former the arsenopyrite-bearing quartz veins without carbonate are more important and frequent than in the latter (Cavalcanti 1999).

Only a few geochemical studies, focusing on arsenic, were carried out so far in the Iron Quadrangle. Among these previous studies, most of them specifically designed for mineral prospecting, is the excellent stream sediment geochemical survey sponsored by the Brazilian Research Company of Mineral Resources in the late 1970s (Oliveira and others 1979). More recently, some information on As distribution in the region has been made available for environmental evaluation (Eleutério 1997; Rawlins and others 1997; Borba and others 2000) and for human biomonitoring (Matschullat and others 2000) in certain places.

The paper aims to contribute to a better understanding of the geochemical distribution of As in the most important Brazilian gold province. The three fluvial basins are of interest because of their proximity to the most important gold mining districts: the Velhas River basin within the limits of the Nova Lima district (Fig. 1b), the Carmo River basin (Ouro Preto-Mariana district, Fig. 1c), and the Conceição River basin (Santa Bárbara district, Fig. 1d). The potential risks of environmental and human As contamination in the Iron Quadrangle are discussed by comparing the analytical data with the observed geochemical processes which are responsible for As mobility in surface and near-surface environments in tropical regions.

Materials and methods

Surface water and stream sediments were collected at the previously selected sites during two different sampling campaigns carried out in April 1998 (summer) and in July 1999 (winter). In addition, samples of primary and oxidized ores as well as of the tailings and groundwater were studied to assess the environmental risks at specific pollution point sources.

At every sampling station, along the main rivers and some tributaries, membrane filtered (0.45 μm) and non-filtered water samples were collected and the physico-chemical parameters for water, pH, Eh, electrical conductivity, dissolved oxygen (DO), turbidity and temperature were measured in situ. The total alkalinity of the bicarbonate of the unfiltered water was determined by titration using 0.1 N sulfuric acid and bromocresol green indicator. Filtered water samples were analyzed by ICP-OES (cations) and ion chromatography (anions), whereas the dissolved total As as well the As^{3+} concentrations in filtered water were determined by AAS with a coupled hydride generator (HG-AAS). The required speciation method was improved by one of the authors (R.P.B.) based on the analytical procedure suggested by Shraim and others (1999). The As^{3+} determination was performed using the HG-AAS method and consisted in modifying the concentrations of HCl and $NaBH_4$ solutions in such a way that only As^{3+} present in the water sample reacted with the solutions to produce arsine (AsH_3).

The sediment samples were dried naturally and passed through nylon sieves to separate the granulometric fractions below 63 μm which were then analyzed by X-ray diffraction for mineral determination, and by X-ray fluorescence spectrometry for their major-, minor- and trace-element contents. A number of samples collected from recent and old tailings were also analyzed by these methods. At Unicamp's laboratory the lowest detection limits for trace-element analysis by XRF lie in the interval of 1–8 mg/kg. A variant of the "toxicity characteristic leaching procedure" (TCLP) by U.S. EPA (Anon 1986) was applied to estimate the As bioavailability in river sediments and tailings. The method adaptation consisted in taking a lesser amount of sample (5 g of <63 μm material) for weak acid attack, maintaining, however, the recommended solid/solution relation as well as the reaction time. Extraction solutions were analyzed by HG-AAS and the lowest detection limit was 1 μg/l.

Finally, a selected number of thin and polished sections of primary gold-sulfide ores and oxidized products were examined under the petrographic microscope and the scanning electronic microscope (SEM) with coupled EDS detector in order to characterize the mode of occurrence of As in these materials as well as to access the meaningful mineral reactions associated with the weathering of the ore deposits.

Results

The composition of surface water and stream sediments for each river basin is presented in this section. For some localities, the chemical compositions of groundwater have also been determined and discussed. In addition, information about the As speciation in water and on the bioavailability of As in stream sediments is given. Finally, the As release into aqueous media in the Ouro Preto-Mariana area is described in terms of in-situ arsenopyrite and pyrite oxidation phenomena assessed by petrographic and SEM studies.

River water and sediments

The hydrogeochemistry and the chemical composition of river sediments in the Iron Quadrangle are presented below for the three main river basins: (1) the segment of the Velhas River under the influence of the Morro Velho, Raposos and Cuiabá gold mines, and of the Queirós ore beneficiation and smelter complex; (2) the Carmo River which has been affected in the past by the activities of the Passagem gold mine and of the old mine works (e.g., Chico Rei, Scliar, Quartzito and Lajes) in the Ouro Preto area; (3) the Conceição River which has been influenced by the São Bento and Córrego do Sítio gold mines and, to a lesser extent, by the surveys at the Brumal mineral prospect.

The Velhas River basin

In the Velhas River basin (Fig. 1b), water and sediment samples were collected at stations along the Velhas River (ERV1 to 6), and at the tributaries Cardoso and Queirós creeks (EGA1 and ERQ1) which run from the Morro Velho mine and from the Queirós beneficiation and smelter plant, respectively, towards the Velhas River. Another station was at the Sabará River which drains the Cuiabá mining area and also runs towards the Velhas River. The chemical composition of water and sediments are presented in Tables 1 and 2.

At the time of sampling, the river waters were circumneutral and oxidized, showing a minimum pH of 6.3 (EGA1) and Eh values varying between 85 (EGA1) and 230 mV (ERV1). The conductivity ranged from 65 to 150 µS/cm in the Velhas River and the Cardoso Creek but reached 2,140 µS/cm in the Queirós Creek (ERQ1).

A general feature is the predominance of HCO_3^- in relation to SO_4^{2-} and of Ca and Mg in comparison with other cations. This can be explained by the occurrence of extensive carbonate alteration associated with the gold deposits, which has prevented the generation of acid mine drainage in the area. An exception is represented by the Queirós Creek where the concentrations of SO_4^{2-} and Ca exceed many times those of other anions and cations due to the influence of runoff waters from the Queirós tailings ponds.

The heavy-metal concentrations in water are low. Only As exceeds its threshold value of 50 µg/l as established by the Brazilian environmental regulations (CONAMA 1986), and this only at the Cardoso (349 µg/l) and Queirós creeks (112 µg/l; Fig. 2a).

The stream sediment samples exhibited elevated concentrations for As and some other trace metals. Arsenic concentrations exceeding 1,000 mg/kg were obtained in samples ERV3, EGA1 and ERQ1 (Fig. 2b) whereas Pb, Zn and Cu reached maximum concentrations of 35 mg/kg (EGA1), 167 mg/kg (ESAB1) and 126 mg/kg (ERQ1), respectively. The fluvial sediments collected closer to the Morro Velho mine area showed elevated contents of Fe, S and base metals, probably due to the influence of the Galo tailings pile (Fig. 1b), an old As-rich waste deposit at the margin of the Cardoso Creek. Two samples of this exposed material yielded As concentrations exceeding 5,000 mg/kg as well as 590–1,070 mg/kg Cu, 120–145 mg/kg Zn, and 50–60 mg/kg Pb. The occurrence of goethite, iron hydroxide, gypsum, epsomite, hydroniumjarosite and arsenolite was indicated in those samples by XRD determinations.

Thus, the following main As and metal point sources for water and stream sediment were identified: (1) the old tailings piles of the Morro Velho and the Raposos mines at the Cardoso Creek and the Velhas River, and (2) the Queirós Creek which drains the Queirós mining waste ponds also in the Nova Lima district. On the other hand,

Table 1
Water chemical composition of the Velhas river basin (concentrationsin mg/l, except for As in ö¥g/l; *w* winter, *s* summer, *d.l.* detection limits)

Stations	D.l.	EGA1		ERQ1		ERV1		ERV2		ERV3	ERV4	ERV5	ERV6	ESAB1
		W	S	W	S	W	S	W	S	W	W	W	W	W
pH		6.3	7.5	6.7	7.6	6.6	7.9	6.6	7.9	6.2	7.2	6.4	6.7	7
Eh (mV)		85	115	112	185	190	230	190	126	210	214	212	225	177
Cond (µS/cm)		184	151	2,140	1,400	124	90	83	70	65	130	116	128	98
T (°C)		18	20	20	21	19	18.8	18.3	18.5	18	19.2	19.5	20	19.7
Ca	0.05	13	11	381	256	14	9	8	6	7	15	7	14	9
Mg	0.3	6	5	46	45	4	3	3	3	3	5	2	5	4
Na	0.1	8	7	70	38	4	4	3	3	2	4	3	3	5
K	0.1	2	3	10	8	1	1	1	0.7	0.6	1	0.8	0.8	1
HCO_3		74	33	12	15	35	18	35	17	31	31	39	31	35
Cl	0.1	2	8	2	5	16	1	2	1	5	7	1	2	2
SO_4	0.2	26	16	1,046	758	63	16	8	7	3	6	1	28	20
NO_3	0.2	1	2	9	13	12	1	1	1	1	7	1	8	2
F	0.005	<d.l.	0.2	0.1	1	<d.l.	0.1	0.1	0.1	<d.l.	<d.l.	1	<d.l.	<d.l.
PO_4	0.05	0.1	0.2	0.1	<d.l.	0.1	<d.l.	0.1	<d.l.	0.1	0.1	1	0.1	0.1
Mn	0.001	0.4	0.4	0.9	1.8	0.2	0.1	0.1	0.1	0.1	0.2	0.1	0.2	<d.l.
Fe	0.006	0.5	0.7	0.1	<d.l.	0.1	0.2	0.1	0.2	0.1	<d.l.	<d.l.	0.1	0.2
As Total	0.8	349	160	112	39	64	12	50	13	3	34	34	<d.l.	4

Table 2
Chemical composition of Velhas basin sediments (units:oxides in %, elements in mg/kg; *w* winter, *s* summer, *d.l.* detection limits)

Stations	D.l.	ERV3		EGA1		ERV2		ERQ1		ERV1		ERV5		ERV6	ESAB1		ERV4	
		W	S	W	S	W	S	W	S	W	S	W	S	W	W	S	W	S
SiO_2		44	50	55	49	54	47	66	62	51	43	46	55	41	59	58	42	44
TiO_2		1.1	0.9	0.8	1	1	1	0.7	0.6	1	1	1	0.8	1	1	1	1	1
Al_2O_3		26	23	13	22	22	18	14	11	19	26	22	19	20	12	17	26	26
Fe_2O_3		18	20	16	20	22	20	10	9	17	20	18	16	22	16	24	19	19
MgO		0.8	1.2	1	1	0.8	0.8	0.8	1.2	0.7	0.9	0.8	1.1	0.9	0.7	0.8	0.8	0.9
CaO		0.2	0.2	0.6	0.4	0.2	0.3	0.3	0.3	0.2	0.2	0.3	0.5	0.3	0.3	0.4	0.3	0.2
Na_2O		0.1	0.2	0.2	0.1	0.1	0.2	0.2	0.2	0.1	0.2	0.1	0.2	0.2	0.2	0.1	0.1	0.1
K_2O		4	2	2	2	2	3	2	1	3	4	4	2	3	2	2	4	3
P_2O_5		0.2	0.2	1	0.1	0.1	0.3	0.2	0.05	0.2	0	0.2	0.2	0.5	0.3	0.1	0.2	0.2
Total		94.5	97.4	90.9	95.9	101.7	91.2	95	84.9	93	94.1	93.4	94.2	89.8	91.1	101.6	94.2	94.5
As	1	34	1,143	2,113	2,830	81	194	1,064	1,264	103	68	121	190	360	64	47	133	111
Cr	2	250	308	366	640	248	285	397	625	240	299	239	421	308	265	308	274	341
Cu	1	66	63	116	75	57	84	126	69	52	71	70	82	95	54	53	74	72
Mn		3,272	2,280	848	2,261	1,844	2,168	736	954	2,616	583	2,920	1,620	2,600	896	1,522	3,176	4,391
Pb	2	19	32	35	21	19	22	25	9	15	31	19	21	23	18	14	21	32
S	8	403	1,077	4,159	762	266	842	1,290	768	711	403	385	847	1,232	1,034	365	497	342
Zn	1	99	101	122	98	90	131	63	51	83	126	112	100	164	167	108	113	125

the highest concentrations of As and metals in water were found in the dry season (winter), whereas the highest metal concentrations in sediments were favored in the summer probably by the erosion of poisoned soils and tailings and the reworking of stream sediments by flooding.

The Carmo River basin

The water at the Carmo River (Fig. 1c) yielded pH values in the interval 7–8 and Eh ranging from 170 to 240 mV. Electric conductivity in the water varied from 117 to 570 μS/cm, the major electrolytes being Ca, Na, HCO_3^- and SO_4^{2-} (Table 3).

Water samples collected in the interior of the Passagem gold mine (EPM1) and from a lateral mine adit were slightly more alkaline, with pH in the interval 7–8.3, Eh of 128–220 mV, and conductivity oscillating between 240–280 μS/cm at EPM1 and 82–430 μS/cm at the adit. These mine waters are rich in Ca and Mg, and HCO_3^- and SO_4^{2-} are the predominant anions. In the mines in Ouro Preto (Chico Rei, Scliar, Quartzito and Lajes), the water yields a pH slightly more acidic in the interval 5.5 to 7.3, Eh varying from 130 to 215 mV and a low electric conductivity oscillating from 15 to 70 μS/cm.

The river waters are extraordinarily enriched in Na, probably due to seepage discharge, and display two groups of samples, one carbonate rich and another with equivalent concentrations of HCO_3^- and SO_4^{2-}, whereas in natural groundwater a predominance of Ca and Mg and homogeneous compositions for HCO_3^- and SO_4^{2-} were found.

The contents of Cu, Pb and Zn in filtered surface water and mine groundwater were lower than the concentrations established by CONAMA (1986) for non-treated drinking water, whereas the As concentration in surface water reached a maximum of 43 μg/l along the Carmo River (Fig. 2c).

Running water in the interior of gold mines were also sampled. In the Passagem mine (EPM1) and in the lateral adit, elevated As concentrations as high as 2,980 μg/l were found whereas in the Ouro Preto mines the As contents varied from 12 to 260 μg/l. However, some water samples from the Passagem mine yielded extremely low As concentrations (4 to 20 μg/l) because they have been collected at certain sites, very rich in carbonate espeleothemes, where the descending water did not percolate the mineralized rocks. By contrast, the highest As concentration (2,980 μg/l) was found in water running from a mineralized vein. Between these two extremes are the As contents in water from a lake (around 1,800 μg/l) which represents the water-table level in the mine and from the adit (800 μg/l) which runs directly into the Carmo River (Fig. 2c).

The stream sediments along the Carmo River showed extremely high As contents, reaching 4,700 mg/kg in the vicinity of the Passagem gold mine (ERC2 in Figs. 1c, 2d). The highest concentrations for other metals, as shown in Table 4, are 104 mg/kg Cu, 36 mg/kg Pb and 151 mg/kg Zn also at station ERC2.

The highest metal concentrations were found in samples collected in the winter when the dilution effect is less pronounced. Although the volume of running

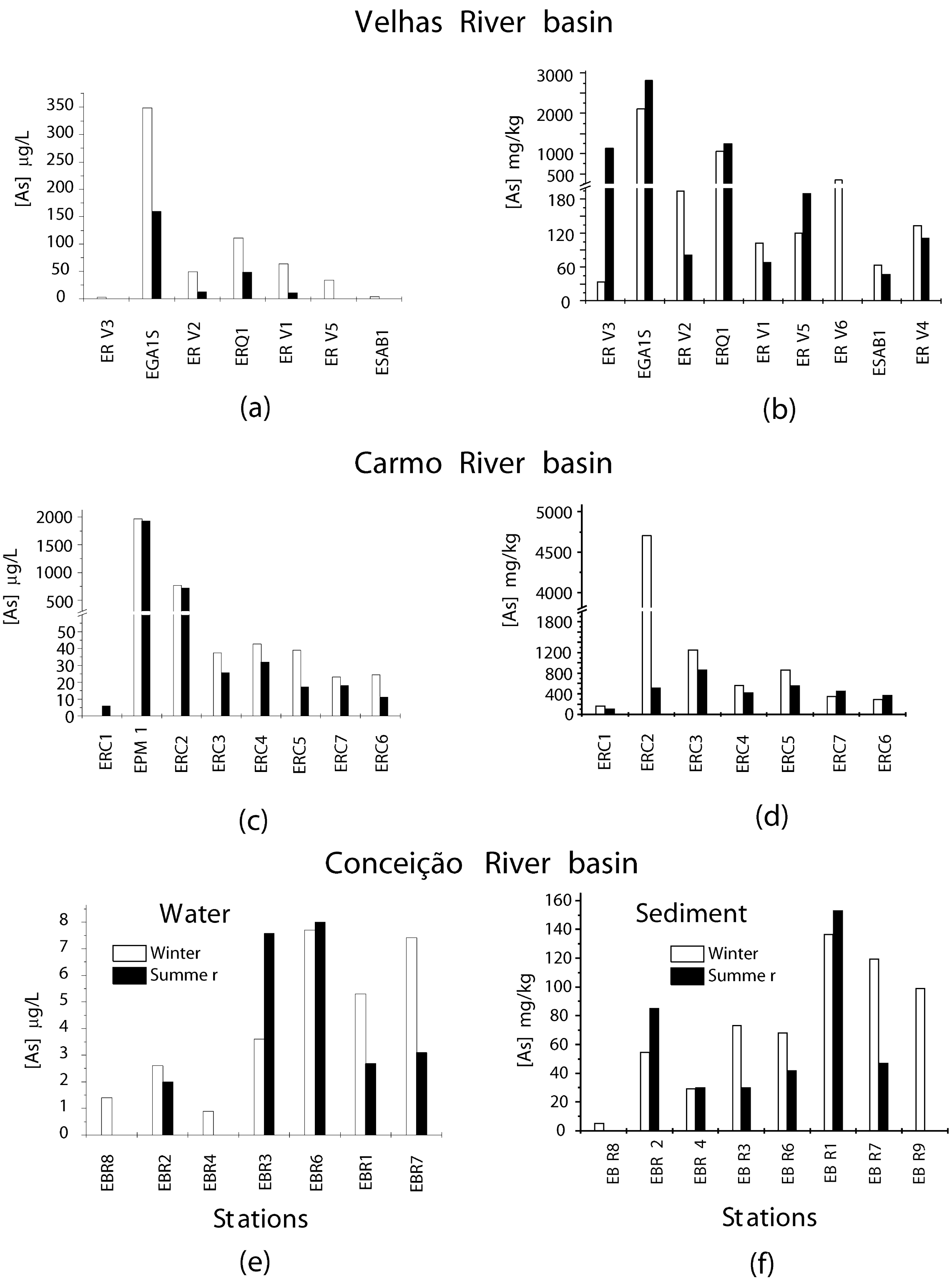

Fig. 2a–f
As concentrations in filtered water and stream sediments from the Velhas River basin (**a**, **b**), the Carmo River basin (**c**, **d**) and the Conceição River basin (**e**, **f**)

groundwater in the interior of the Passagem mine is also influenced by seasonal variation, no related significant change in As concentration was detected in the groundwater.

The running waters from the Ouro Preto mines and from the Passagem mine are As point sources to the Carmo River and, of these, the adit of the Passagem mine is the most noticeable in the area.

At the sampling stations closer to the Passagem mine, the river sediments yielded the highest metal concentrations in the winter, which suggests that deposition of fine-grained material is being favored by the low water flow at

Table 3
Water chemical composition of the Carmo river basin surface water and groundwater (concentrations in mg/l, except for As in µg/l; *w* winter, *s* summer, *d.l.* detection limits, *n.d.* not determined)

	Stations for surface water												Stations for groundwater[a]										
													Passagem Mine							Ouro Preto mines			
	ERC1		ERC3		ERC4		ERC5		ERC6		ERC7		EPM1		EPM2		EPM3	EPM4	EPM5	EOP1	EOP2	EOP3	EOP4
	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	W	W	W	W	W	W
pH	7.4	7.8	7.5	7.6	6.9	7.4	7.8	7.4	7.4	7.3	7.2	7.4	7.7	7.7	7.7	8	7.2	7.4	7.9	7.3	6.96	5.56	6
Eh (mV)	205	186	228	189	172	173	173	202	212	194	240	194	189	128	180	158	160	180	170	230	281	315	130
Cond (µS/cm)	570	362	n.d.	287	284	173	283	193	231	117	227	151	372	430	240	253	180	371	490	70	17	51	15
T (°C)	20.3	24	19	23.2	21	24.5	22.9	29.4	18.5	24.9	24.4	26.7	20.6	22	19	23.1	21.0	20.0	19	19.0	15.3	15	18
Ca	15	12	29	11	10	8	5	8	9	7	8	7	41	40	24	22	21	47	51	6	2	3	2
Mg	4	4	13	4	4	3	1	3	3	3	3	3	22	23	14	12	14	30	32	4	1	2	1
Na	75	49	50	36	23	20	23	18	30	16	35	15	2	4	6	2	0.5	3	4	0.5	0.6	2	0.2
K	3	3	4	2	2	2	1	2	2	2	2	2	3	10	3	3	1	1	6	1	0.4	1	0.2
HCO_3	66	47	63	34	47	37	39	28	35	23	35	38	121	90	94	55	74	234	381	12	8	4	12
Cl	4	7	5	4	9	3	8	3	5	11	<d.l.	3	11	5	5	2	1	4	3	3	1	4	1
SO_4	179	81	6	64	92	35	41	31	59	30	1	27	52	70	42	33	38	10	10	19	2	10	1
NO_3	4	9	8	5	6	2	3	3	5	4	1	4	4	9	3	2	1	0.3	0.1	3	2	5	1
F	0.3	0.4	<d.l.	0.4	<d.l.	0.3	<d.l.	0.2	<d.l.	0.2	<d.l.	0.3	0.1	0.3	<d.l.	0.2	0.1	0.1	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
PO_4	0.1	0.3	0.4	0.1	0.1	0.1	0.1	0.1	0.1	<d.l.	0.2	<d.l.	0.1	<d.l.	0.1	<d.l.	<d.l.	<d.l.	<d.l.	0.2	<d.l.	<d.l.	<d.l.
Mn	0.8	0.4	6	0.6	1.2	0.3	0.1	0.6	0.4	0.2	0.3	0.1	<d.l.	<d.l.	<d.l.	<d.l.	0.01	0.01	<d.l.	0.2	<d.l.	<d.l.	<d.l.
Fe	0.1	0.1	<0.1	0.1	0.2	0.1	<0.1	0.1	0.1	0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.1	<d.l.	0.1	<d.l.	<d.l.	<d.l.
As_{Total}	12	7	22	26	43	32	39	17	24	18	23	11	830	757	1,760	1,932	2,980	4	20	260	24	32	12
As^{3+}	–	–	2.5	–	–	–	–	–	–	–	–	–	35	–	59	–	86	1	–	12	–	–	–
As^{5+}	–	–	19.5	–	–	–	–	–	–	–	–	–	795	–	1,701	–	2,894	3	–	248	–	–	–

[a] Stations: EPM1, adit; EPM2, lake; EPM3, water from mineralized vein; EPM4, water from mine roof; EPM5, water from mine wall; EOP1, Chico Rei mine; EOP2, Quartzito mine; EOP3, Scliar mine; EOP4, Lajes mine

Table 4
Chemical composition of Carmo basin sediments (units: oxides in %, elements in mg/kg; *n.d.* not determined, *w* winter, *s* summer)

Stations	ERC1		ERC2		ERC3		ERC4		ERC5		ERC7		ERC6	
	W	S	W	S	W	S	W	S	W	S	W	S	W	S
SiO_2	28	62	32	63	34	74	42	28	28	14	31	45	33	38
TiO_2	1.6	0.7	1.5	0.8	1.5	0.5	1.4	0.7	1.5	0.6	1.1	1	1	1
Al_2O_3	13	3	17	4	12	4	18	3	30	1	12	2	11	2
Fe_2O_3	28	31	30	30	34	16	23	65	22	83	47	49	45	56
MgO	1	0.2	1	0.2	1	0.5	1	0.3	1	0.2	1	0.2	1	0.2
CaO	0.5	0.2	0.6	0.2	1	0.4	0.4	0.1	0.3	0.1	0.3	0.1	0.3	0.1
Na_2O	0.04	0.1	0.04	0.1	0.2	0.1	0.2	0.1	0.04	0	0.3	0.1	0.3	0.1
K_2O	2	0.4	2.1	0.5	1.3	0.4	2.7	0.4	3	0.1	1.7	0.3	1.7	0.2
P_2O_5	0.7	0.1	2	0.1	0.5	0.1	0.4	0.1	0.5	0.1	0.2	0.1	0.2	0.1
Total	74.8	99.5	87.9	99.7	87	99.7	89.5	99.4	84.9	99.7	94.8	98.7	94.6	99.4
As	161	105	4,709	518	1247	858	568	420	862	558	355	457	291	368
Cr	129	72	185	105	262	107	213	118	231	92	230	91	145	102
Cu	57	31	105	30	67	27	59	38	49	36	51	28	42	36
Mn	5,600	3,500	3,864	2,520	5,216	2,556	3,992	2,468	3	2,468	3,304	1,621	3,672	1,470
Pb	6	10	36	8	13	8	15	6	4	6	15	5	12	6
S	2,586	n.d.	2,803	n.d.	3,428	800	1,997	800	1,931	800	540	400	975	400
Zn	131	40	151	44	69	31	63	39	63	38	47	35	44	37

that season. The very high As concentrations in these sediments point to the occurrence of sulfide phases among the clay and oxihydroxide particulates and, to a certain extent, to the occurrence of alluvial gold which is responsible for the activity of "garimpeiros" still observed in this period of the year at that river segment.

The Conceição River basin

The surface water in the Conceição River basin (stations EBR1 to 8) yielded pH values in the range 5.7 to 7.5, Eh of 130–280 mV, and electric conductivity between 21 and 112 µS/cm (Table 5). At station EBR9 in the Carrapato Creek which drains the São Bento mining area, a more acidic water was found with pH 4, Eh 280 mV and a conductivity of 220 µS/cm. In the upper segment of the Caraça River, which runs through the Caraça ecological park (station ECAR1), the low pH (4.6) and conductivity (10 µS/cm) may be related to the contribution of organic acids produced by the rich vegetation of the area as suggested elsewhere by Drever (1997), and to the low buffer capacity of the quartzite bedrock.

In the Brumal area, groundwater was sampled at five sites where the water is collected from springs or wells for domestic use (stations EBR10 to 14). These waters have pH, Eh and conductivity values in the intervals 4–7, 130–270 mV, and 6–67 µS/cm, respectively.

For the whole region, total As concentrations in river water and groundwater were low and do not exceed 8 µg/l in surface and 3 µg/l in subsurface waters. The only exception was the water sampled at the Carrapato Creek (station EBR9) which contained 74 µg/l As (Fig. 2e).

Ca and Mg, present in equal proportions, are the major cations in surface and groundwater with the exception of two groundwater samples in which Na is also an important component. Concerning the anions, the HCO_3^- is the principal component in groundwater whereas in surface water there are samples collected closer to the mine's runoff (EBR3, 6, 7, 9) which are sulfate rich, and other samples collected far from the mine's effluents which are carbonate rich (Table 5). The highest metal concentrations in groundwater are found in samples collected in the summer whereas in surface water the cationic concentrations increase in wintertime in the presence of smaller volumes of water.

Stream sediments of the Conceição River yielded maximum concentrations for As, Cu, Pb and Zn of 119, 99, 25 and 104 mg/kg, respectively (Table 6). The highest As contents (136–153 mg/kg) were found in sediment samples collected from one tributary of the Conceição River in the gold prospecting area of the Brumal district (Fig. 2f). In general, the highest As contents in stream sediments were found in samples collected in wintertime, which suggests predominance of fine particulate deposition phenomena.

In the Conceição River basin, the point As sources, such as the exposed soils at the Brumal prospect, the São Bento tailings dam runoff and the Carrapato Creek, are not as prominent as those are in the other studied basins. This must be due to the fact that mining activities which started in the 1860s were less intense than those in the Nova Lima

Table 5
Water chemical composition of the Conceição river basin (concentrations in mg/l, except for As in μg/l; *n.d.* not determined, *d.l.* detection limits, *w* winter, *s* summer)

Stations[a]	EBR1		EBR2		EBR3		EBR4	EBR6		EBR7		EBR8	EBR9	EBR10	EBR11	EBR12	EBR13	EBR14
	W	S	W	S	W	S	W	W	S	W	S	W	W	W	W	W	W	W
pH	6	7	5.7	7	6.6	7.5	6	6	7.5	6	7	5.8	4	4.8	4	6.1	5	6.5
Eh (mV)	130	n.d.	245	n.d.	245	n.d.	230	251	n.d.	245	n.d.	280	280	230	250	210	270	255
Cond (μS/cm)	43	12	15	10	68	112	21	65	66	89	67	20	220	13	10	41	6	67
T (°C)	15	22	18	23	19	24	19	19	22	16	23	19	17	18	19	18	18	21
Ca	4	2	1	1	6	6	2	6	3	8	2	2	16	0.8	0.2	3	0.2	6
Mg	3	1	1	0.4	3	2	2	3	1	5	1	2	4	1	1	5	0.4	4
Na	2	1	0.2	0.3	1	0.4	0.3	1	0.2	1	0.2	0.2	5	0.4	0.5	1	0.3	2
K	0.1	0.1	0.2	0.4	0.2	0.2	0.1	0.2	0.1	0.3	0.1	0.1	10	0.3	0.3	0.1	0.2	0.2
HCO_3	35	n.d.	20	n.d.	20	n.d.	20	20	n.d.	20	n.d.	20	4	16	8	39	8	51
Cl	0.1	0.5	0.3	0.3	0.4	0.2	0.2	0.3	0.3	0.4	1	0.2	3.1	0.3	0.2	0.1	0.2	0.2
SO_4	1	0.3	0.6	0.3	25	20	1	23	13	33	10	1	95	0.4	0.2	0.5	0.3	2
NO_3	0.3	n.d.	1	0.2	1	0.3	0.4	1	n.d.	1	0.5	0.4	33	2	0.5	1	0.5	1
F	<d.l.	0.9	<d.l.	0.3	<d.l.	0.2	<d.l.	<d.l.	0.2	<d.l.	1	<d.l.	0.1	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
PO_4	0.1	n.d.	0.1	n.d.	0.1	n.d.	0.2	0.1	n.d.	0.1	n.d.	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Mn	<d.l.	<d.l.	0.1	0.1	0.1	<d.l.	<d.l.	0.1	<d.l.	0.1	<d.l.	<d.l.	1.9	<d.l.	0.1	<d.l.	<d.l.	<d.l.
Fe	0.2	0.2	0.2	0.2	0.1	<d.l.	<d.l.	0.1	0.1	0.1	0.1	<d.l.	0.1	<d.l.	0.1	<d.l.	<d.l.	<d.l.
As_{Total}	5	3	3	2	4	8	3	8	8	7	3	2	74	1	1	2	2	3

[a] Stations EBR1 – EBR9, surface water; stations EBR10–EBR14, groundwater

Table 6
Chemical composition of Conceição basin sediments (units: oxides in %, elements in mg/kg; *n.d.* not determined, *w* winter, *s* summer)

Stations	EBR2		EBR4	EBR3		EBR6		EBR1		EBR7	
	W	S	W	W	S	W	S	W	S	W	S
SiO_2	48	53	44	42	n.d.	44	n.d.	45	54	35	38
TiO_2	0.6	1	0.6	0.6	n.d.	0.7	n.d.	2	1	1	0.4
Al_2O_3	17	15	6	7	n.d.	8	n.d.	17	13	13	13
Fe_2O_3	12	11	36	41	n.d.	35	n.d.	16	11	41	59
MgO	6	7	0.4	0.4	n.d.	0.5	n.d.	2	5	1	0.4
CaO	0.3	0.3	0.1	0.1	n.d.	0.1	n.d.	0.2	0.2	0.1	0.1
Na_2O	0.3	n.d.	0.3	0.4	n.d.	0.2	n.d.	0.1	0.2	0.4	n.d.
K_2O	0.6	1	1	1	n.d.	1	n.d.	1	1	2	1
P_2O_5	0.1	0.1	0.1	0.1	n.d.	0.1	n.d.	0.2	0.1	0.2	0.1
Total	85.1	88.5	88.6	93.4	0	89.6	0	83.7	85.7	94.1	112
As	54.7	85	29.5	73.2	30	68.1	42	136.5	153	119.6	47
Cr	1,152	1,153	181	160	40	163	51	530	1,120	321	98
Cu	40	47	32	87	41	87	48	73	43	100	47
Mn	656	822	2,800	2,344	n.d.	3,912	n.d.	928	2,851	3,384	2,628
Pb	25	12	12	11	7	12	11	18	12	17	n.d.
S	220	345	185	220	n.d.	262	n.d.	707	364	433	343
Zn	104	73	39	46	27	45	35	125	73	66	48

and Passagem-Ouro Preto districts where major environmental effects can be noticed.

Arsenic speciation and bioavailability

In some water samples from the Carmo River basin, collected in the Passagem and Chico Rei mines as well as from the Carmo River, the As inorganic species were determined by a highly reproducible analytical procedure. In these samples significant concentrations of As^{3+} species were detected, with the concentration ratios $(As^{3+})/(As^{5+})$ ranging from 1.10^{-1} to 4.10^{-2}.

The As^{3+} concentrations found in those samples were unexpected because, at equilibrium conditions(Vink 1996), the As^{5+} oxianions ($H_2AsO_4^-$ and $HAsO_4^{2-}$) are expected to be dominant at the prevailing pH and Eh conditions of the surface and groundwater samples from the Iron Quadrangle (Fig. 3). Using a chemical speciation model for the chemical compositions of water (PHREEQC, version 2.3, and data bank wateqf4.dat from Parkhurst and Appelo 1999), not only the predominance of the As^{5+} species was theoretically confirmed as the concentration ratios $(As^{3+})/(As^{5+})$ could be calculated in the interval 2.10^{-7} to 1.10^{-12}. These As inorganic species ratios are at least 6 orders of magnitude lower than those obtained by the analytical procedure. However, it is suggested that the presence of As^{3+} in surface waters of the Velhas and Conceição basins must be less significant than in the Carmo River water.

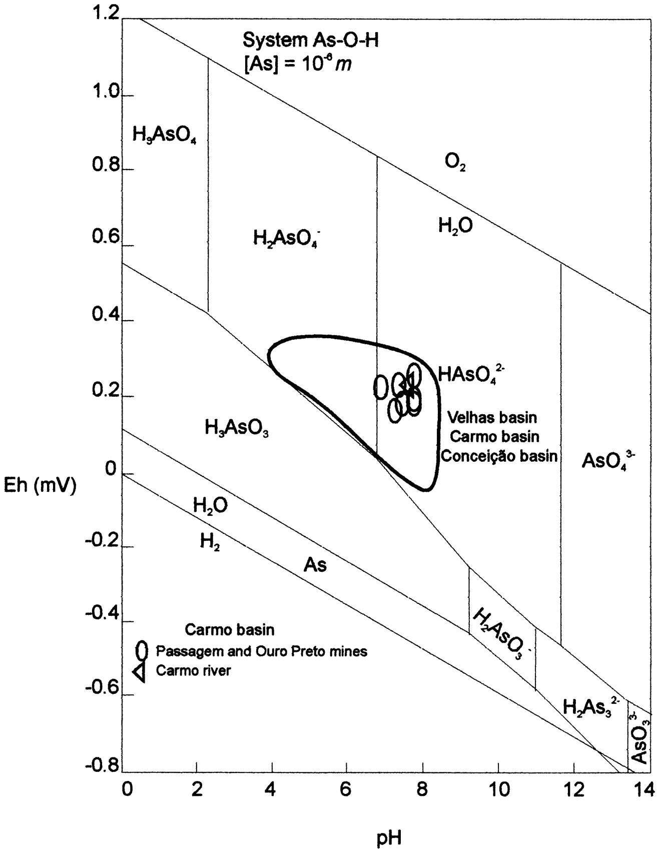

Fig. 3
The As–O–H system as a function of pH and Eh, according to Vink (1996) for As=10^{-6} *m* at 25 °C and 1 bar. The *field* indicates the Iron Quadrangle waters plot in relation to the stability fields of As-hydroxianions. The *symbols* are the samples subjected to As speciation tests

Some lixiviation tests were developed for a number of sediment samples. In all basins the most common minerals found in the stream sediment samples were quartz, Fe-oxihydroxides (mainly hematite and goethite) and kaolinite, as well as minor illite and other minerals not detected by X-ray diffractometry analyses (Table 7). Three samples collected from the Velhas River (EGA1, ERV6 and ERV3) with variable metal contents (Table 2) were preliminarily tested for As by the sequential extraction method developed by Terashima and Taniguchi (1998), which includes the analysis of the exchangeable, EDTA (carbonate), organic, oxidic, sulfidic, and residual (silicate) fractions. A similar trend of As release was

Table 7
Minerals related with As occurrence

Gold mineralized rocks	Weathered mineralized rocks	Sediments	Tailings
Arsenopyrite[a], pyrite[b], carbonates (calcite, dolomite), quartz	Scorodite[a], goethite[b], Fe-oxihydroxides[b], gypsum	Quartz, Fe-oxihydroxides (mainly hematite and goethite)[b], kaolinite, illite, sulfides (?)[a]	Arsenolite[a], goethite[b], iron hydroxide[b], gypsum, epsomite, hydroniumjarosite

[a] As minerals
[b] Minerals which have As as impurity or adsorbed/sorbed (see text for details)

obtained for all samples, indicating that most of the As was preferentially bonded to oxihydroxide phases. The As exchange fraction was less than 4% of total As content in the samples, which may represent a maximum concentration of 84 mg/kg for the As-richest sediment. A variant of the extraction method TCLP (toxicity characteristic leaching procedure) developed by the U.S. EPA (Anon 1986) was applied to one sample of mining waste collected from the Galo tailings pile (EGA1S, Fig. 1b), one from the Queirós creek (ERQ1), and three sediment samples from the Carmo River (ERC2, ERC5, ERC6). The As release during the weak acid attack reached 1 to 4% (2 to 196 mg/kg) of the original total As content of the samples. These results are quite similar to those obtained in the sequential extraction experiments.

Arsenic mobility related to ore-deposit weathering

Arsenic occurs in the Iron Quadrangle primary gold ores mainly in arsenopyrite and arseniferous pyrite (Table 7). Ore petrographical studies from the Morro Velho, Raposos and Cuiabá gold mines (Fig. 1b) reveal the presence of major amounts of pyrite and, to a lesser degree, of arsenopyrite and pyrrhotite. Arsenic is present as an impurity in these pyrite-rich ores with concentrations up to 2 wt%. The auriferous ores of the São Bento mine contain significant amounts of arsenopyrite which also is the major phase in sulfide ores of the Passagem and Chico Rei mines.

In all those ore deposits, both sulfides and arsenides undergo oxidation during weathering. This is responsible for the partial release of As into the environment as dissolved arsenate and arsenite species, and it explains the elevated As concentrations found in some water samples (EPM1 and EOP1 in the Passagem-Ouro Preto mines), while some As is precipitated in newly formed minerals or adsorbed onto other phases. This latter phenomenon was studied in several samples collected from the oxidation zones of the ore deposits using an EDS microanalyser coupled to a scanning electronic microscope. At least two As-retention mechanisms were identified. At the Passagem and Ouro Preto mines, the As is retained through precipitation of secondary phases as scorodite ($FeAsO_4{\cdot}2H_2O$) and goethite, the latter containing up to 8 wt% As (Table 7). On the other hand, in a more advanced stage of weathering, mixtures of iron oxides and hydroxides including remains of magnetite and hematite are formed. In a sample collected from the oxidation zone of the Raposos gold deposit, the Fe-rich material yielded As above 10,000 mg/kg, well above the detection limit of the equipment (SEM-EDS).

Discussion and conclusions

In Archean greenstone belts hosting meso-thermal gold deposits, the enrichment of the rocks with As and other elements such as Ag, Sb, B and, to a lesser extent, Cu, Pb, and Zn is a common geochemical feature, as observed in the Rio das Velhas Supergroup. In the Iron Quadrangle, As contents up to 4,800 mg/kg were found in gold deposits hosted by iron formations (BIF) of the Nova Lima Group, exceeding to about 40 times the average As concentration in non-mineralized iron formations (Raposo and Ladeira 1995). These rocks generate soils enriched in arsenic and other metals and give rise to natural geochemical anomalies similar to those found, for instance, in Ghana (Africa) and in the Barents region (northern Europe) where natural As anomalies were revealed in soils in the vicinity of gold mineralizations (Bowell 1994; Reimann and others 1998). In the case of some places in the Iron Quadrangle, soil contamination was enhanced by anthropogenic activities. In the Nova Lima district, As concentrations exceeding 2,000 mg/kg were determined by Rawlins and others (1997) in the Galo Hill soil where an industrial plant has processed the local mining waste for As_2O_3 production until its closure in 1976. There are also indications about As oxide production in the Passagem mine until the first decades of the last century. An attempt to integrate the sediment geochemical data generated in this study with results obtained in previous studies, particularly to the CPRM geochemical survey reported by Oliveira and others (1979), is shown in Fig. 4. The As concentrations in stream sediments have arbitrarily been grouped in four classes to clarify the widespread distribution of As in sediments collected even in upland regions, mainly dominated by metasedimentary rocks of the Minas Supergroup where large gold deposits are not known. It is clearly indicated that the Iron Quadrangle is the largest geochemical As anomaly so far described in Brazil. The highest As concentrations in sediments are found in the vicinity of the largest secular gold mines of the Nova Lima, Passagem-Ouro Preto and Santa Bárbara districts which have been the focus of the present study.

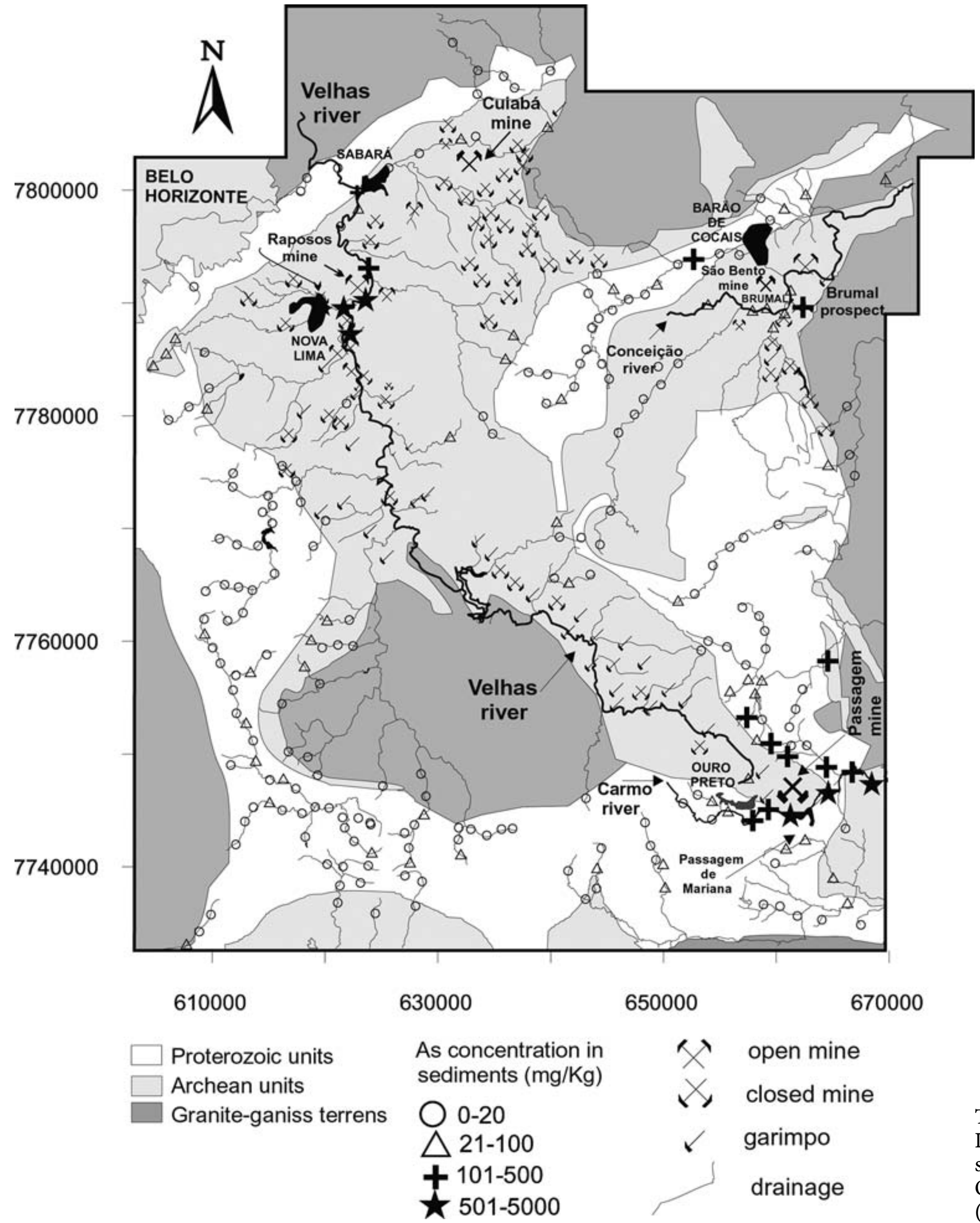

Fig. 4
The As geochemistry map of the Iron Quadrangle based on stream sediment analyses, according to Oliveira and others (1979), Eleutério (1997), and this study

Currently, the main sources of As, local and regional, are anthropogenic in origin and related to environmental heritage (contaminated soil, old tailings piles, old mines) as well as to the presence of As-enriched sediments in the water courses.

Natural As release to the environment in the Iron Quadrangle also occurs from weathering of ore deposits. Particularly, the weathering of arsenopyrite and pyrite is being followed by formation of new As-bearing minerals, As adsorption onto surfaces of other minerals or solubilization in aqueous media, as observed in the Passagem and other mines. The oxidation products formed at arsenopyrite surface include As^{3+} and As^{5+} hydroxianions which can be readily leached by diluted solution (Nesbitt and others 1995). Below pH 4 and oxidizing conditions, precipitation of scorodite from As^{5+} and Fe^{3+} oxianions reaction may occur (Dove and Rimdstidt 1985), whereas at pH>4 the incongruent solubilization of scorodite is likely to take place, yielding goethite, Fe-oxihydroxide and $H_2AsO_4^-$ as products (Dove and Rimdstidt 1985; Krause and Ettel 1988; Robins 1987). The amount of As adsorbed/sorbed to goethite can be as high as 8%, as previously described in the oxidation zone of the Chico Rei ore deposit.

It is well known that the oxidation of sulfides generates acid drainage in many mining areas. Due to the extensive carbonate alteration in the ore deposits of this study, these acid solutions have been buffered effectively. In the Passagem and other gold mines in the Ouro Preto region, the pH values are above 7.5. At these conditions, a release of adsorbed As oxianions is likely to occur, considering that the characteristic zero point of charge (pH_{zpc}) is 8 for

Fe-oxihydroxides (Dzombak and Morel 1990) and 6–7 for goethite (Smith 1999).

It is expected that the oxidation of arsenopyrite promotes the release of As^{3+} and As^{5+} hydroxianions into solution whereas part of As^{5+} is retained by precipitation of iron arsenate (scorodite), as demonstrated at the Passagem and Chico Rei mines, or by adsorption onto or co-preciptation with Fe-Mn oxihydroxides, as observed in the oxidation zone of the Raposos, Passagem and Chico Rei mines. Finally, the carbonate-induced pH increase of mine drainage favors a solubilization of scorodite as well as the As desorption from goethite which may contribute to As release to the underground and surface waters.

The old and present tailings are As reservoirs and point release sources for As in the Iron Quadrangle. The Galo tailings piles disposed along the Cardoso Creek (Nova Lima district) contain arsenolite, As-bearing Fe-oxihydroxides and, probably, amorphic Fe-arsenate, along with Ca and Mg sulfates, gibbsite and epsomite, like the mineral assemblage found in the Passagem mine oxidation zone. Similarly, percolating solutions with pH>7 promote the solubilization of adsorbed As and of arsenolite. The latter occurs at any pH–Eh conditions, whenever in contact with solutions in which the activity of H_3AsO_3 is less than $10^{-0.8}$ *m* (Vink 1996). Solubilization of As combined with the erosion of the tailings pile give rise to the highest known As concentrations found in water and sediment samples in the Velhas River basin.

Despite the high As contents in stream sediments and the occurrence of sulfur in samples from the Carmo River, the presence of As minerals could not be detected by X-ray diffractometry. Adsorption of As onto surfaces of goethite, hematite and kaolinite grains commonly found in the sediments is the most likely mode of As occurrence. However, since the zero point charges (pH_{pzc}) for these minerals are 6–7, 4–7 and pH_{pzc}>4.6, respectively, As adorption onto goethite and hematite is favored by the current pH conditions (6–8) of surface water in the Iron Quadrangle. This preference for oxihydroxides phases has been confirmed by the sequential extraction and leaching experiments reported above. The bioavailability of As in sediments, i.e., the weakly adsorbed As in the sediment fraction <63 μm, was estimated to be less than 4% of the total As content, which can be of great concern where some As-rich sediments are found, especially in the vicinity of mines.

The Carmo River receives the As-rich water which percolates the Passagem and other gold deposits in the Ouro Preto area. It seems, however, that the volume of mine groundwater reaching the main river can not explain the high As contents found in the surface water. Additional release of As from the sediments into the water is likely to be another relevant process in both the Carmo and Velhas rivers where great amounts of mining waste have been discharged in the past.

The elevated As concentration in groundwater in the mining areas may be due to oscillation of the water table and exposition of sulfide ore to oxidation. Partial solubilization of As recalls here the geogenic process described by Schreiber and others (2000) for the aquifer hosted by sulfide-bearing sandstone in Wisconsin, USA. An estimation of As^{3+}/As^{5+} ratios in water is of particular importance because the toxicity of As^{3+} is known to be many orders of magnitude greater than that of As^{5+}. The characterization of arsenic species is also mandatory for the success of water treatment, since As removal from water is dependent of the As oxidation state (Kim and Nriagu 2000; USEPA 2000). As^{5+} hydroxianions are partially consumed during the formation of scorodite and other sulfo- arsenates. Additionally, As^{5+} hydroxianions are more easily adorbed onto goethite and clay minerals surfaces than As^{3+} hydroxianions (Bowell 1994; Ladeira and Ciminelli 2000). This may lead to a partial As^{3+} enrichment via percolating water at the Passagem and Chico Rei mines even under incompatible pH–Eh conditions. Hence, the As^{3+}/As^{5+} ratios found for these groundwaters and for surface waters of the Carmo River (in the range of 1.10^{-1} to 4.10^{-2}) have been shown to be much higher than those calculated by the PHREEQC geochemical model (10^{-7} to 10^{-12}). The contrasting results between experimental and theoretic As^{3+}/As^{5+} values can be attributed to (1) the slow kinetics of redox transformations involving As in natural waters (Daus and others 2000), i.e., chemical equilibrium was not achieved in these waters; and (2) the selective retention of arsenate hydroxianions at solid phases in relation to As^{3+}, as explained above. Since the PHREEQC program works with solutions at equilibrium, the observed discrepancy is not surprising but at the same time suggests that the use of modeling programs to environmental approach has to be done with care, and needs to be supported by analytical work.

Summarizing the main conclusions arising from this study, it is worth recalling that the Iron Quadrangle comprises an extensive natural anomaly of arsenic related to the occurrence of mesothermal gold deposits hosted in the Rio das Velhas greenstone belt. Weathering of the As-rich rocks and of ore deposits brings about the release of this element into soils, sediments, groundwater and surface drainages. It is estimated that during the three centuries of gold mining production in the Iron Quadrangle, at least 390,000 t of arsenic was discharged into the drainage system.

The main recommendation arising from this study is that it is necessary to carry out an inventory of the point-As release sources in the region to give guidance to the local population about potential hazards of certain habits and to implement low-cost programs of environmental mitigation and countermeasures. Since the toxic effects of arsenic can take many years to become apparent and the conventional treatment of water is not designed for removal of dissolved arsenic, a broader geochemical monitoring of water quality in the region must be carried out, including the determination of arsenic species dissolved in water and the arsenic bioavailability in soils and sediments.

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