Geochemical mapping of arsenic in surface waters and stream sediments of the Quadrilátero Ferrífero, Brazil

Mapeamento geoquímico do arsênio em águas superficiais e sedimentos fluviais no Quadrilátero Ferrífero, Brasil

http://dx.doi.org/10.1590/0370-44672015680077

Raphael de Vicq Ferreira da Costa
Doutorando
Universidade Federal de Ouro Preto.
Escola de Minas - Departamento de Geologia
Ouro Preto - Minas Gerais - Brazil
raphaelvicq@gmail.com

Mariangela Garcia Praça Leite
Professora Associada
Universidade Federal de Ouro Preto,
Escola de Minas - Departamento de Geologia
Ouro Preto - Minas Gerais - Brazil
mgpleite@gmail.com

Fellipe Pinheiro Chagas Mendonça
Doutorando
Universidade Federal de Ouro Preto,
Escola de Minas - Departamento de Geologia
Ouro Preto - Minas Gerais - Brazil
fellipe.chagas@gmail.com

Hermínio Arias Nalini Jr.
Professor Associado IV
Universidade Federal de Ouro Preto,
Escola de Minas - Departamento de Geologia
Ouro Preto - Minas Gerais - Brazil
herminio.nalini@gmail.com

Abstract

A regional study on the arsenic concentration in surface waters and stream sediments, with a density of one sample every 13 km^2, was carried out for the first time in the Quadrilátero Ferrífero (Brazil). The region was divided into 3rd order catchment basins, in which 512 areas were sampled. The arsenic concentration was determined in waters and stream sediments after partial digestion with the aid of ICP-OES. The arsenic values found in surface waters ranged from 57.70 to 414 µg.L^{-1}, while for stream sediments, arsenic concentrations ranged from 0.63 to 1691 mg.kg^{-1}, and from the 512 sampling points, 135 (26%) had arsenic concentrations above the limit of detection, which was 0.63 mg.kg^{-1}. It was also found that 106 3rd order catchment basins had values above the third quartile, (5.09 mg.kg^{-1}). The results show that high concentrations of this element are strongly related to the presence of Nova Lima rocks that contain minerals rich in arsenic. However, the anthropogenic influence in such high concentrations cannot be ruled out, as the region has a history of over 300 years of gold mining.

Keywords: Geochemical Mapping, Arsenic, Surface water, Stream sediments, Quadrilátero Ferrífero

Resumo

Um estudo regional da concentração do arsênio em águas superficiais e sedimentos fluviais com uma alta densidade de amostragem de uma amostra para cada 13 km^2 foi conduzido pela primeira vez no Quadrilátero Ferrífero (Brasil). A região foi dividida em bacias de 3ª ordem, sendo amostrados 512 trechos nessas bacias. A concentração de As foi determinada nas águas e nos sedimentos, após digestão parcial, com o auxílio de um ICP-OES. Os valores de arsênio encontrados nas águas superficiais variaram entre 57.70 e 414 µg.L^{-1}. Já para os sedimentos de corrente, as concentrações oscilaram entre 0.63 e 1691 mg.kg^{-1}, sendo que dos 512 pontos de amostragem 135 (26%) apresentaram concentrações de arsênio acima do limite de detecção, que é de 0,63 mg.kg^{-1}. Também foram encontradas 106 bacias de 3ª ordem com valores acima do 3º quartil (5.09 mg.kg^{-1}). Os resultados mostram que as elevadas concentrações deste elemento estão fortemente relacionadas com a presença de rochas do grupo Nova Lima, que contém minerais ricos em arsênio. Porém, a influência antrópica na existência destas elevadas concentrações não pode ser descartada, já que a região apresenta um histórico de mais de 300 anos de exploração de ouro.

Palavras-chave: mapeamento geoquímico, arsênio, águas superficiais, sedimentos de *corrente, Quadrilátero Ferrífero.*

1. Introduction

Arsenic is a trace element, whose average concentration in the earth's crust has been set to values between 1.0 (Taylor and McLennan 1995) and 4.8 ppm (Rudnick and Gao 2003). Its occurrence is associated with certain types of minerals, mainly arsenopyrite (FeAsS), loellingite (FeAs2), realgar (As4S4) and arsenian pyrite (FeS2), which can be released to waters, soils and sediments by oxidation processes of these sulfides, and immobilized via adsorption into iron, aluminum and manganese oxides/hydroxides or into clay minerals (Deschamps *et al.* 2003). These processes occur naturally but can be intensified by the action of mining activities, with the exposure of large volumes of rocks.

The occurrence of high arsenic concentrations in various environmental compartments, whether natural or amplified by human activities, has become a public health problem, greatly increasing the concern of society and the scientific community regarding human contamination by this element (Fewtrell *et al.* 2005; Ravenscroft, 2009). According to Reimann *et al.* (2009), this was the first chemical element to be recognized for its carcinogenic properties, being used as a poison since the times of the Romans. The inorganic form is recognized as the most harmful to humans, and chronic exposure can cause serious metabolic problems, including hyperkeratosis, skin cancer, lung cancer, nervous system disorders, increased frequency of miscarriages and other serious diseases (Abernathy *et al.* 1998).

However, the most common form of human exposure is through consumption of contaminated water (Matschullat et al. 2000; Nordstrom, 2002). Not surprisingly, the interest in arsenic exponentially increased after incidents occurred in Bangladesh, West Bengal, India and Mexico caused by consumption of contaminated ground water extracted from aquifers located in arsenic geological formations (Matschullat, 2000, Smith *et al.* 2002; Neumann *et al.* 2010).

Despite dozens of published articles, particularly at the end of the last century, the anthropogenic contribution to the high arsenic concentrations in various environmental compartments is not well defined, being a source of much debate. However, determining the natural abundance of arsenic is essential not only to support the analysis and environmental monitoring, but also to support actions to combat pollution (Deschamps *et al.* 2003). In this sense, with the introduction of new digital mapping technologies, geochemical maps have assumed an increasing relevance in recent years (Gielen 1998). These georeferenced maps allow observing the variation of the abundance of some chemical element in a specific area, thus contributing to the recognition of regions with anomalous values and contributing to the identification of its main sources, whether natural or linked to human activities (Plant *et al.* 2001).

In this context, the present study aimed to perform the mapping of arsenic concentrations in water and stream sediments of the Quadrilátero Ferrífero using data of 512 sampling points distributed over its 7,000 km^2.

Study Area
The Quadrilátero Ferrífero

The Quadrilátero Ferrífero is one of the richest regions in economic minerals in the world, covering an area of approximately 7,000 km^2, whose exploration history dates back to the last decades of the seventeenth century.

The region includes fully or partly 35 municipalities in the mid region of the state of Minas Gerais, Brazil (Figure 1), with a population of over 4,135,000 inhabitants (IBGE, 2010).

Mining is still among the productive activities that support the region's economy, highlighting the current iron exploitation, which contributes with 26.8% of the GDP(Gross domestic product) of Minas Gerais (IBGE, 2010).

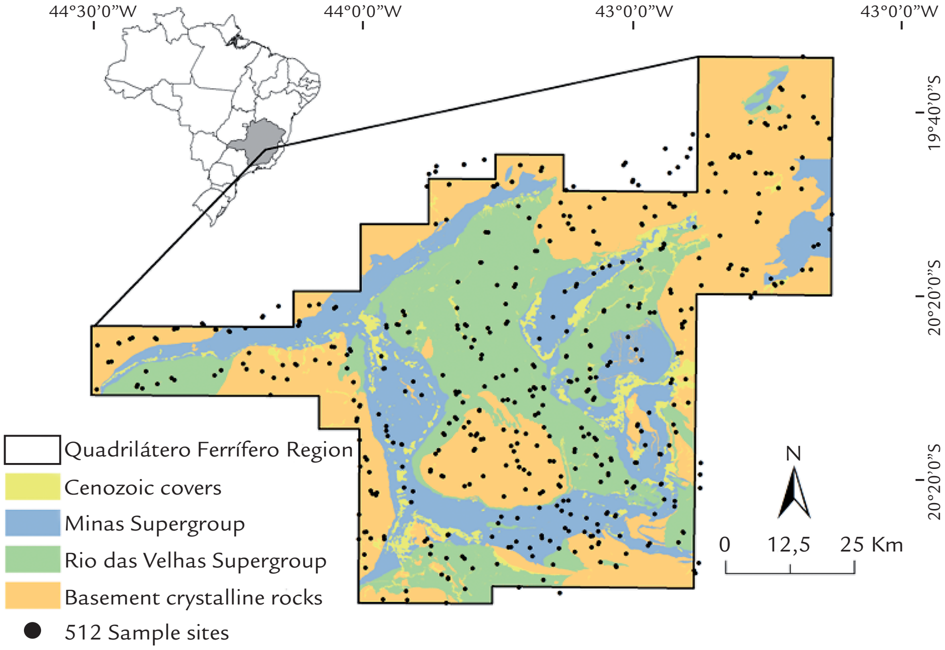

Figure 1
Geologic map of the QF region, showing the distribution of basement crystalline rocks, Rio das Velhas Supergroup, Minas Supergroup Cenozoic Covers and the location of the sample points.

References	Basin	Number of Sampling Points	As concentration					
			Water (µg.l^{-1})			Stream Sediments (mg.kg^{-1})		
			Min	Mean	Max	Min	Mean	Max
Borba *et al.* 2000	Velhas River Basin – Nova Lima	11	2	-	160	20	-	2830
	Carmo River Basin – Ouro Preto e Mariana	8		-	30		-	860
	Conceição River Basin – Santa Bárbara	7		-	8		-	135
Matschullat *et al*. 2000	Nova Lima and Santa Bárbara	18 (water) and 15 (stream sediments)	0.4	30.5	350	22	350	3200
Deschamps *et al*. 2002	Nova Lima	24	-	-	-	47	-	3300
	Santa Bárbara	18	-	-	-	22	-	160
	Mariana	9	-	-	-	22	-	860
Borba *et al.* 2003	Velhas River Basin– Nova Lima	9	3	67.2	349	34	583.5	2830
	Carmo River Basin – Ouro Preto and Mariana	8 (water) and 7 (stream sediments)	1.7	116.7	830	105	819.8	4709
	Conceição River Basin– Santa Bárbara	13 (water) and 6 (stream sediments)	1	7.7	74	29.5	73.2	153
Pimentel et al. 2003	Municipalities of Ouro Preto and Mariana	22 (water) and 4 (rocks)	0.05	0.36	2.3	0.11	60	139
Matschullat et al. 2007	Nova Lima	69 (water) and 39 (stream sediments)	2.2	49	350	40	140	3300
	Santa Bárbara		0.4	1.8	3.1	15	47	170
Parra et al. 2007	Conceição River Basin	25	-	-	-	4.91	51.0	89.0
Varejão et al. 2010	Carmo River Basin – Ouro Preto and Mariana	4	36.7	54.6	68.3	68.8	1773.9	3939

Table 1
Summary of the main studies on arsenic in waters and sediments sampled in the Quadrilátero Ferrífero.

Five main lithostratigraphic units are found in the Quadrilátero Ferrífero with ages ranging from the Archean: Metamorphic Complex (Noce, 1995; Alkmim and Marshak, 1998) and Rio das Velhas Supergroup (Alkmim and Marshak , 1998), to the Proterozoic: Minas Supergroup and Itacolomi Group (Dorr II, 1969; Alkmim and Marshak, 1998), and occurrences of mafic and granitic intrusions of several generations (Dorr II, 1969; Marshak and Alkmim, 1998). Its richness in mineral resources and enormous structural and lithological variability directly influence the distribution and geochemical characteristics of its waters, soils and sediments.

In the Quadrilátero Ferrífero, arsenic has a close relationship with gold deposits present in minerals such as arsenopyrite, löllingite or as an impurity in arsenopyrite (Borba *et al.* 2000; Figueiredo *et al.* 2006).

These gold deposits are associated with shear zones that cross rocks from the Nova Lima Group, base of the Rio das Velhas Supergroup, or are located at the base of the Minas Supergroup, near the contact with the Nova Lima Group, in quartz and carbonate veins (Borba *et al.* 2000; Matschullat *et al.* 2000; Mello *et al.* 2006).

Its genesis is related to hydrothermal processes that follow successive deformation phases recorded in the geologic history of the Quadrilátero Ferrífero (Barbosa and Sabaté, 2004)

Although the presence of arsenic in waters and sediments of the Quadrilátero Ferrífero has been long recognized, there are few studies that specifically address this issue.

Table 1 shows a summary of the most important studies. As observed, the works developed so far have focused on only 3 regions of the Quadrilátero Ferrífero: in the municipality of Nova Lima, the Velhas River Basin; in the municipalities of Ouro Preto and Mariana, the Carmo River Basin, and in the municipality of Santa Barbara, the Conceição River Basin.

On average, these studies relied on only 17 water sampling points and 13 points for the collection of sediments, featuring local studies.

2. Methodology

2.1 - Sampling points

The choice of the sampling points was based on methodology proposed by Bolviken *et al.* (1996), with water and sediment collection carried out in 3rd order stretches (Strahler, 1952) of catchment basins. In the present work, these stretches were determined based on the hydrographic map of the region on a 1:25,000 scale, provided by the Institute of Water Management of the State of Minas Gerais (IGAM), totaling 512 sampling points (Figure 1).

2.2 - Sample collection and treatment

Water samples were collected at the center of each stretch, filtered with the aid of a cellulose acetate membrane (Millipore 0.45 µm) and acidified with three drops of nitric acid (USEPA, 2001).

Then, they were sent for reading in Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), label SPECTRO / MODEL Ciros CCD at the Laboratory of Geochemistry of the Federal University of Ouro Preto, where the As concentration was analyzed.

As there is no standard methodology for sediment collection aimed at geochemical characterization, the adopted methodological procedures aimed to be as representative as possible, based on the characteristics of stream sediments sampled.

Thus, nine samples were obtained from each stretch. Thus, three subsamples were collected from a region of riffles, 3 subsamples from a region of pools and 3 subsamples from an area of transition between these two morphologies.

For each morphological area, samples were collected at the right bank, left bank and center of the river, and samples collected at the banks were collected at a distance of 0.50 m from the riverbed.

Also in the field, the subsamples were mixed so as to obtain a representative sample of the stretch. After complete homogenization, quartering was performed to obtain a sample of 500 g, which was packed in plastic bags, according to recommendations of EPA (Environmental Protection Agency) (USEPA, 2001).

In the laboratory, samples were dried under a controlled temperature at 40 ± 5°C, crushed, sieved and the sieve fraction smaller than 0.063 µm was digested in aqua regia (Calmano and Forstner 1996). Once digested, the final product was analyzed in ICP-OES, where the arsenic content of each sample was determined.

2.3 - Statistical processing and map presentation

With the aid of the ArcMap® 9.3 software and based on the geological map of the Quadrilátero Ferrífero on a 1:25,000 scale (Lobato *et al.* 2005), the percentage of all lithologies and geological formations that make up each of the 3rd order catchment basins sampled was calculated.

With the results, basic statistical parameters were determined and data normality was evaluated by the Komolgorov-Smirnov test.

The methodology defined by Reimann *et al.* (2005) was used to determine the background values, with the construction of boxplot-type curves and cumulative frequency histograms. Based on the geochemical analysis results and using the ArcMap® 9.3 software, maps showing the arsenic concentration in waters and stream sediments were constructed using a 1:150,000 scale and the IDW (inverse distance weight) method for interpolation.

3. Results and Discussion

Figures 2 and 3 respectively show the geochemical maps with the arsenic distribution in waters (Figure 2) and stream sediments (Figure 3) of the Quadrilátero Ferrífero.

Figure 4 shows the combined graphic representation of histograms, data density and boxplots for the same results.

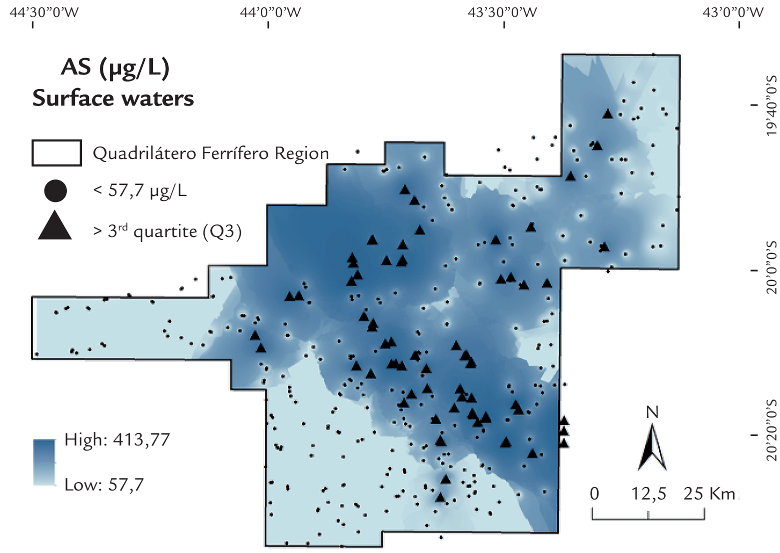

Figure 2
Geochemical map showing the variation of As concentrations found in surface waters of the Quadrilátero Ferrífero.

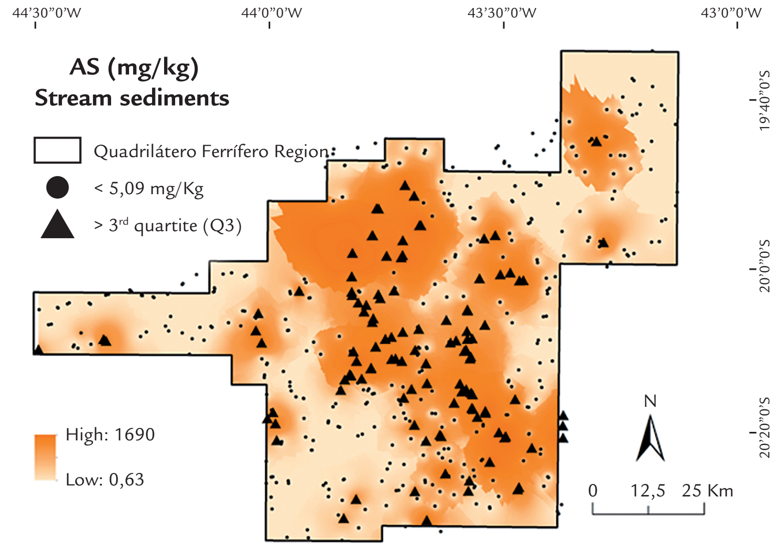

Figure 3
Geochemical map showing the variation of As concentrations found in stream sediments of the Quadrilátero Ferrífero.

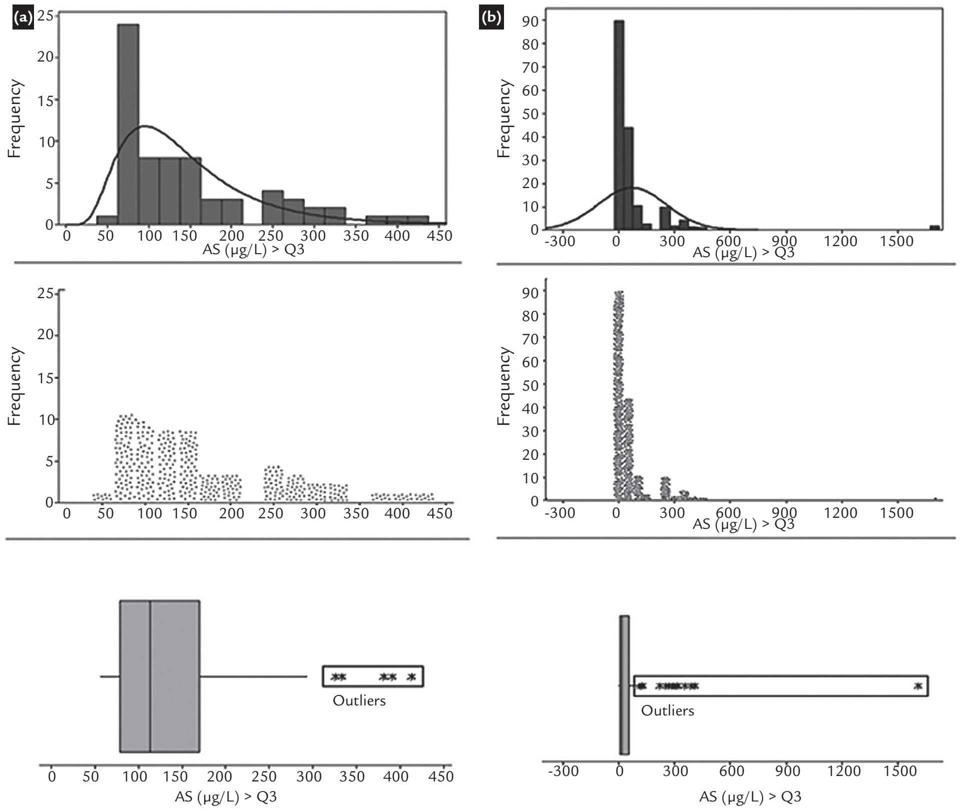

Figure 4
Combined graphic representation showing histogram, data density and boxplot to determine the background of water samples (A) and stream sediments (B) of the Quadrilátero Ferrífero.

The arsenic values in surface water ranged from < 57.70 to 414 μg. L^{-1}. A number of 70 sampling points (13.7%), have values of arsenic above the quantification limit of 57.7 μg. L^{-1}, which in this case was considered as the background value, because most of the sample points (86.7%) showed concentrations up to this level. As surface waters can have arsenic concentrations ranging from 0.5 μg L^{-1} to more than 5000 μg L^{-1}, with the most common values below 10 μg L^{-1}, and often less than 1 μg L^{-1} (Smedley and Kinniburgh, 2002), the obtained high limit of quantification value did not allow a more detailed statistical analysis of water samples. However, the distribution of points with values above the limit of quantification show important trends, with waters rich in As occurring not only in the Carmo River (Borba *et al.* 2000; Deschamps *et al.* 2002; Borba *et al.* 2003; Varejão *et al.* 2011), Velhas River (Borba *et al.* 2000; Matschullat *et al.* 2000; Deschamps *et al.* 2002; Borba *et al.* 2003, Matschullat *et al.* 2007) and Conceição River basins (Borba *et al.* 2000; Matschullat *et al.* 2000; Deschamps *et al.* 2002; Borba *et al.* 2003, Matschullat *et al.* 2007), but also in the Paraopeba and Piracicaba River basins.

For stream sediments, arsenic concentrations ranged from < 0.63 to 1691 mg.kg^{-1}, and from the 512 sampling points, 135 (26%) had arsenic concentrations above the limit of quantification, which was 0.63 mg.kg^{-1}. It was also found that 106 3rd order catchment basins had values above 5.09 mg.kg^{-1}, considered the background value. These sampling points are mostly composed of tributaries of the main local rivers, and another 35 in rural communities or suburban localities. These locations often have low-income and low-education populations, which are not aware of the risk they are being exposed to.

The highest values found in stream sediments (between 33 and 1691 mg.kg^{-1}) are related to a substratum composed of sericite- chlorite-quartz schist, sericite schist, carbonaceous schist, quartz-mica-chlorite schist and chlorite schist, rocks that compose the Rio das Velhas Supergroup, Nova Lima Group (Figure 5).

Among the sixteen 3rd order catchment basins with the highest concentrations (101.7 to 1691 mg.kg^{-1}), fourteen have an area greater than 60% draining on the above mentioned rocks (Table 2), which indicates a strong relationship between the lithological type and the presence of arsenic in the sediment (Figure 5 and Table 2).

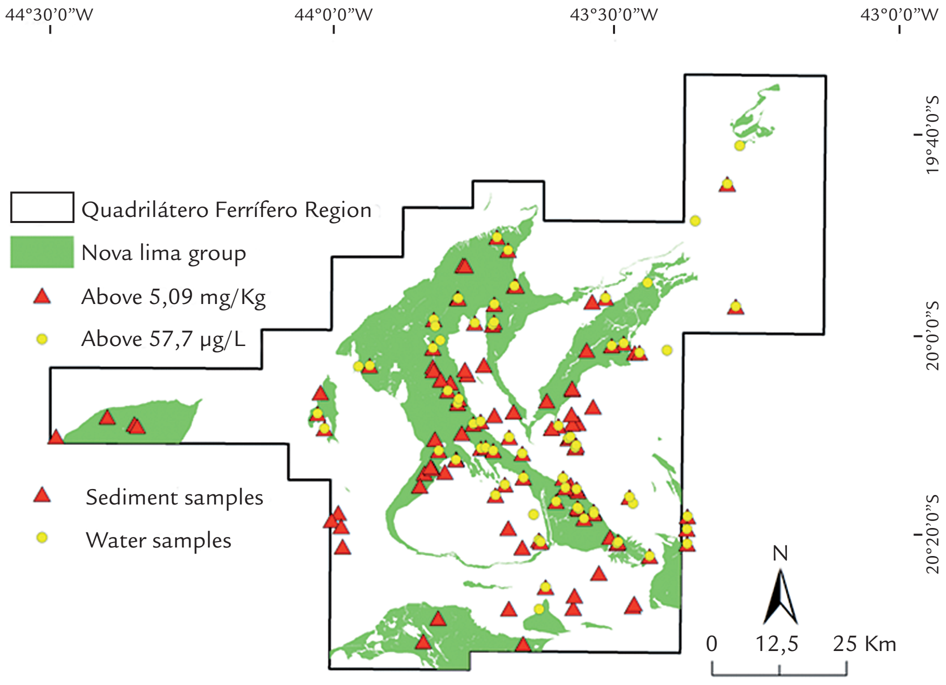

Figure 5
Map showing the distribution of the Nova Lima Group and the sampling points with the highest As concentrations in stream sediments.

Table 2
Relationship between the percentage of occurrence of rocks from the Nova Lima Group in 3rd order catchment basins of the Quadrilátero Ferrífero and as values found in the sediments analyzed.

Rocks from the Nova Lima Group	As concentration (mg.kg^{-1})						
	Mean	Standard deviation	Minimum	Q1 (25%)	Median (50%)	Q3 (75%)	Maximum
≤ 20	19.63	24.52	0.63	0.63	5.37	8.71	83.70
20 < x ≤ 30	21.87	29.86	0.63	0.63	5.37	8.71	83.70
30 < x ≤ 40	56.2	87.2	0.63	0.63	13.68	26.82	122.6
40 < x ≤ 50	73.8	116	0.63	3.8	17.60	32.27	374.1
50 < x ≤ 60	79.38	105.6	0.63	5.6	21.46	48.35	374.1
60 < x ≤ 70	90.4	128	3.45	7.1	30.83	62.91	407.4
> 70	179	267	5.87	9.32	90.71	104	1691

Analyzing the relationship between geology and the arsenic values obtained (Table 2), it appears that the basins with the highest percentages of rocks from the Nova Lima Group had Q3 values far greater than any other rock type. When considering the rock types outcropping in these basins, basins with more than 50% of their area on sericite-chlorite-quartz schist have 75% of rivers with arsenic concentrations up to 48.35 mg.kg $^{-1}$. On the other hand, basins with more than 60% of their area draining on sericite schist and carbonaceous schist showed Q3 value equal to 62.91 mg.kg^{-1}, and finally, rivers that cross basins with over 70% of quartz- mica-chlorite schists and chlorite schists have Q3 value of 104 mg.kg^{-1}. This analysis is particularly interesting when these values are compared to data obtained from other lithologies predominating in the IQ such as itabirites and hematites, dolomites and limestones, gneisses and granites, ferruginous quartzites, and various types of phyllites, which showed significantly lower arsenic concentrations, with Q3 values near zero.

Most of the high As concentrations found in Quadrilátero Ferrífero, either in waters or in stream sediments, are derived from rocks rich in this element. Confirming this hypothesis, it was found that several points considered anomalous were within Conservation Units (CUs) or Permanent Preservation Areas (PPAs), in which, theoretically, human interference is minimized. Examples are OP 23 (306.2 mg.kg^{-1}), OP 24 (130 mg.kg^{-1}), OP 30 (374.1 mg.kg^{-1}) and OP 31 (101.7 mg.kg $^{-1}$), located in the PPA of Cachoeira das Andorinhas, and OP 35, OP 36 and OP 38 that are within the Uaimii forest, which have As values in the sediments above 49.7 mg.kg^{-1}.

According to the map shown in Figure 5, it appears that most of the anomalies are located within the mid-northern region of the IQ, which despite having geological substratum rich in arsenic, is also characterized as having a high concentration of mining companies exploiting gold in Nova Lima, Sabará and Caeté, and iron in Nova Lima, Ouro Preto, Itabirito, Sabará, Santa Barbara and Caeté. Furthermore, much of the Quadrilátero Ferrífero region was intensively exploited for the removal of gold between the seventeenth and nineteenth centuries, showing evidence of extraction processes in this period, including mines and waste dumps (Fonseca *et al.* 2001). The presence of mining activity for the removal of gold, in the current or past centuries, can accelerate the availability of elements for the environment, including As (Ripley et al. 1996; Matschullat ***et al.*** 2007, Espinosa *et al.* 2009).

4. Conclusions

A regional study on the arsenic concentration in surface waters and stream sediments, with a robust density of one sample every 13 km^2, was carried out for the first time in Quadrilátero Ferrífero (Brazil). This enabled the construction of geochemical maps with the spatial distribution of this element, not available so far.

High arsenic concentrations, potentially harmful to human health, were found in both waters and stream sediments. In the case of waters, values greater than 57.70 µg. L^{-1} were found in all three major basins that cross the Quadrilátero Ferrífero: Velhas River, Doce River and Paraopeba River, and this is the first time that such concentrations have been reported in the Paraopeba River Basin.

In relationship to stream sediments, one fifth of the sampling points showed values above 5.09 mg.kg^{-1}. Points whose concentrations were above 101 mg.kg^{-1} occurred in basins with 60% or more of their area formed by rocks that compose the Nova Lima Group, Rio das Velhas Supergroup.

Although data have shown that arsenic occurs naturally in the Quadrilátero Ferrífero, the possibility that human action has contributed to increase these concentrations cannot be ruled out, particularly in areas where there are still caves and waste dumps from gold mining of ancient centuries.

5. Acknowledgements

The authors thankfully and gladly acknowledge the financial support of the institutions CNPq, FAPEMIG and mainly CAPES for the scholarship Proc. no 10228/13-6.

6. References

ABERNATHY, C. O., CALDERON, R. L., CHAPPELL, W. R. ***Arsenic exposure and health effects.*** San Diego, California: Elsevier, 1998.

ALKMIM, F. F., MARSHAK, S. Transamazonian Orogeny in the Southern São Francisco Craton Region, Minas Gerais, Brazil: evidence for Paleoproterozoic collision and collapse in the Quadrilátero Ferrífero. ***Precambrian Research***, v. 90, p. 29–58, 1998.

BARBOSA, J. S. F., SABATÉ, P. Archean Paleoproterozoic crust of the São Francisco Craton, Bahia, Brazil: geodynamic features. ***Precambrian Research***, v. 133, p. 1-27, 2004.

BERNASCONI, A. Archaean gold mineralization in central Brazil: a review. **Mineralium Deposita**, v. 20, p. 277-283, 1985.

BÖLVIKEN, B., BOGEN, J., DEMETRIADES, A., DE VOS, W., EBBING, J., HINDEL, R., LANGEDAL, M., LOCUTURA, J., O'CONNOR, P., OTTESEN, R. T., PULKKINEN, E., SALMINEN, R., SCHERMAN, O., SWENNEN, R., VAN DER SLUYS, J., VOLDEN, T. Regional geochemical mapping of Western Europe towards the year 2000. **Journal of Geochemical Exploration**, v. 56, p. 141-

166, 1996.

BORBA, R. P., FIGUEIREDO, B. R., RAWLINS, B., MATSCHULLAT, J. Arsenic in Water and Sediment in the Quadrilátero Ferrífero, State of Minas Gerais, Brazil. **Applied Geochemistry**, v. 15, n. 2, p. 181-190, 2000.

BORBA, R. P., FIGUEIREDO, B. R., MATSCHULLAT, J. Geochemical distribution of arsenic in waters, sediments and weathered gold mineralized rocks from Quadrilátero Ferrífero, Brazil. **Environmental Geology**, v. 44, n. 1, p. 39-52, 2003.

BORBA, R. P., FIGUEIREDO, B. R. A influência das condições geoquímicas na oxidação da arsenopirita e na mobilidade do arsênio em ambientes superficiais tropicais. **Revista Brasileira de Geociências**, v. 34, n. 4, p. 489-500, 2004.

CALMANO, W., FÖRSTNER, U., SALOMONS, W., ALLAN, R. **Sediments and toxic substances: environmental effects and ecotoxicity**. New York: Springer, 1996.

COSTA, A. T. **Registro histórico de contaminação por metais pesados, associadas à exploração aurífera no alto e médio curso da bacia do Ribeirão do Carmo, QF: um estudo de sedimentos de planícies de inundação e terraços aluviais.** Ouro Preto: Departamento de Geologia, Universidade Federal de Ouro Preto, 2007. 257 p. (Tese de Doutorado).

DESCHAMPS, E., CARNEIRO, M. E. D. P., CIMINELLI, V. S. T., PETER, W., RAMOS, A. Arsenic sorption onto soils enriched in Mn and Fe minerals. **Clays and Clay Minerals**, v. 51, p. 198–205, 2003.

DORR, J. N. Physiographic, stratigraphic, and structural development of the Quadrilátero Ferrífero, Minas Gerais. **USGS Professional Paper**: 641-A, 1969.

FEWTRELL, L., FUGE, R., KAY, D. An estimation of the global burden of disease due to skin lesions caused by arsenic in drinking water. **Journal of Water and Health**, v. 3, n. 2, p. 101–107, 2005.

FIGUEIREDO, B. R., BORBA, R. P., ANGÉLICA, R. S. Arsênio no Brasil e exposição humana. In: SILVA, C. R. da et al. **Geologia médica no Brasil - efeitos dos materiais e fatores geológicos na saúde humana e meio ambiente**. Rio de Janeiro: CPRM, 2006.

FONSECA M., SOBREIRA F., RAINHO M. E., OLIVEIRA M. Unbridled development of urban space and its implications on the preservation of landmarks – the Morro da Queimada archeological site, Ouro Preto, Brazil. **Cities**, v. 18, n. 6, p. 381–389, 2001.

GIELEN, E. Los SIG en el estudio de los humedales. **Boletín SEHUMED**. Valência, n. 5, marzo 1998.

INSTITUTO BRASILEIRO DE GEOGRAFIA E ESTATÍSTICA. **IBGE: Censo Nacional de 2010**. Available: <http://www.censo2010.ibge.gov.br/>. Acessed: 15 may 2013.

LOBATO, L., BALTAZAR, O. F., REIS, L. B. Projeto geologia do quadrilátero ferrífero - integração e correção cartográfica em SIG com nota explicativa. Belo Horizonte: CODEMIG, 2005. 1 CD-ROM.

MACHADO, N., NOCE, C. M., OLIVEIRA, O. A. B., LADEIRA, E. A. Evolução geológica do Quadrilátero Ferrífero no Arqueano e Proterozóico Inferior, com base em geocronologia U-Pb. In: SIMPÓSIO DE GEOLOGIA DE MINAS GERAIS, 5, SIMPÓSIO DE GEOLOGIA DE BRASILIA, 1. **Anais...** Belo Horizonte: SBG/Núcleo MG, 1989. p. 1-5.

MATSCHULLAT, J., DESCHAMPS E. **Arsênio antropogênico e natural: um estudo em regiões do Quadrilátero Ferrífero.** Belo Horizonte: Fundação Estadual do Meio Ambiente, 2007.

MATSCHULLAT, J., BORBA, R. P., DESCHAMPS, E., FIGUEIREDO, B. F., GABRIO, T., SCHWENK, M. Human and environmental contamination in the Quadrilátero Ferrífero, Brazil. **Applied Geochemistry**, v. 15, p. 181-190, 2000.

MELLO, J. W. V., ROY, W. R., TALBOTT, J. L., STUCKI, J. W. Mineralogy and arsenic mobility in arsenic rich Brazilian soils and sediments. **Journal of Soils and Sediments**, v. 6, p. 9–19, 2006.

NEUMANN, R. B., ASHFAQUE, K. N., BADRUZZAMAN, A. B. M., ALI, M. A., SHOEMAKER, J. K., HARVEY, C. F. Anthropogenic influences on groundwater arsenic concentrations in Bangladesh. **Nature Geoscience Journal**, v. 3, p. 46–53, 2010.

NOCE, C. M. **Geocronologia dos eventos magmáticos, sedimentares e metamórficos da região do Quadrilátero Ferrífero, Minas Gerais.** São Paulo: Instituto de Goeciências, Universidade de São Paulo, 1995. 127 p. (Tese de Doutorado).

NORDSTROM, D. K. Worldwide occurrences of arsenic in groundwater. **Science**, v. 296, p. 2143–2145, 2002.

PARRA, R.R., ROESER, H. M. P, LEITE, M. G. P, NALINI JR., H. A., GUIMARÃES, A. T. A., PEREIRA, J. C., FRIESE, K. Influência antrópica na geoquímica de água e sedimentos do rio Conceição, Quadrilátero Ferrífero, Minas Gerais – Brasil. **Geochimica Brasiliensis**, v. 21, n. 1, p. 36 – 49, 2007.

PIMENTEL, H.S., DE LENA, J.C., NALINI JR. H. A. Studies of water quality in the Ouro Preto region, Minas Gerais, Brazil: the release of arsenic to the hydrological system. **Environmental Geology**, v. 43, p. 725–730, 2003.

PLANT, J., SMITH, D., SMITH, B., WILLIAMS, L. Environmental geochemistry at the global scale. **Applied Geochemistry**, v. 16, p. 1291–1308, 2001.

RAVENSCROFT, P., BRAMMER, H. Arsenic in groundwater: A threat to sustainable agriculture in South and South-east Asia. ***Environment International***, v. 35, p. 647–654, 2009.

REIMANN, C., GARRET, R. G. Geochemical background - concept and reality. ***Science of the Total Environment***, v. 350, p. 12-27, 2005.

REIMANN, C., MATSCHULLAT, J., BIRKE, M., SALMINEN, R. Arsenic distribution in the environment: The effects of scale. **Applied Geochemistry**, v. 24, p. 1147–1167, 2009.

RIPLEY, E. A. REDMANN, R. E, CROWDER, A. A. **Environmental effects of mining.** Florida: St. Lucie Press, 1996.

RODRÍGUES. R., RAMOS, J. A., ARMIENTA, A. Groundwater arsenic variations: the role of local geology and rainfall. **Applied Geochemistry**, v. 19, p. 245–250, 2004.

RUDNICK, R. L., GAO, S. Composition of the continental crust. In: HEINRICH, H. D., TUREKIAN, K. K. (Org.). **Treatise on Geochemistry.** Elsevier: v. 3, p. 1-64, 2003.

SMITH, A. H., LOPIPERO, P. A., BATES, M.N., STEINMAUS, C. M. Arsenic epidemiology and drinking water standards. **Science**, v. 296, p. 2145–2146, 2002.

STRAHLER, A. N. Dynamic basis of Geomorphology, Geological Society. ***America Bulletin***, v. 63, p 923-938, 1952.

TAYLOR S.R &, MCLENNAN S.M. The geochemical evolution of the continental crust. **Geophysics**, v. 33, p. 241-265, 1995.

USEPA - UNITED STATES ENVIRONMENTAL PROTECTION AGENCY – USEPA. **Sediment Sampling Guide and Methodologies.** Division of Surface Water. Columbus, 2001. 36 p.

VAREJÃO, E. V., BELLATO, C. R., FONTES, M. P. F., MELLO, J. W. V. Arsenic and trace metals in river water and sediments from southeast portion of Quadrilátero Ferrífero, Brazil. **Environmental Monitoring Assessment**, v. 172, p. 631-642, 2010.

Received: 02 May 2014 - Accepted: 22 October 2014