Research Articles

Soil and Sediment Geochemistry of the Iron Quadrangle, Brazil

The Case of Arsenic

Eleonora Deschamps[1]*, Virginia S.T. Ciminelli[1], Frank Thomas Lange[2], Jörg Matschullat[3], Brigitte Raue[2] and Hanka Schmidt[3]

[1] Universidade Federal de Minas Gerais, Rua Espírito Santo 35/217, 30160-030 Belo Horizonte, M.G., Brazil
[2] TZW Technologiezentrum Wasser, Karlsruherstr. 84, D-76139 Karlsruhe, Germany
[3] Interdisciplinary Environmental Research Centre, Freiberg University of Mining and Technology, Brennhausgasse 14, D-09599 Freiberg, Germany

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* **Corresponding author** (eleonora.deschamps@terra.com.br)

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Abstract. Soils and sediments around gold ore deposit and mining sites in the Iron Quadrangle present positive As anomalies (median concentrations > 100 mg kg^{-1}) and wide ranges (< 20 to > 2000 mg kg^{-1}) even in densely populated areas. These anomalies can be related to geological structures, to hydrothermal ore deposits and to their continuous exploitation over the past three centuries. The paper presents new data on both As geochemistry and soil and sediment geochemistry in general, and discusses consequences of the encountered anomalies, their reasons and potential effects and how they compare with current screening and threshold values. While surface soil As-values are reproducible at a given site, sediment anomalies show a strong seasonal variation that can be explained by tropical hydrological variances. Suggestions are presented on how to minimize the As-load in densely populated areas that might otherwise pose a potential health risk.

Keywords: Arsenic; arsenopyrite; Brazil; gold-mining; Iron Quadrangle; Minas Gerais; sediments; soil; subtropical climate

Introduction

There is much debate on what is natural in element concentrations in soils and sediments. Answers are crucial when human health and ecological risks are to be assessed. The natural abundance of arsenic is of great importance both for the assessment of environmental quality and for devising counter measures against soil and sediment pollution. An attempt to understand the biogeochemistry of arsenic (As) under subtropical conditions led to a series of works in the Iron Quadrangle that revealed positive As-anomalies in several environmental media (Borba et al. 2000, 2002, Eleuterio 1997, Haßler 2002, Rawlins et al. 1997, Schmidt 2001). The size and quantity of these As anomalies gave rise to concern regarding their environmental impact, and particularly with regard to aspects associated with human health. A human biomonitoring study in the area revealed that As found its way into the human body (Matschullat et al. 2000) and that children seem to be particularly affected (Matschullat et al. 2002). Based on these results, this work presents a more detailed study of surface soil material to assess the hypothesis that air-borne fine-soil dust may be a decisive factor in the As supplies to the human body. The sediment analysis tries to answer additional questions related to As-mobility in the target area.

The Iron Quadrangle is one of the richest and best-known mineral deposit structures worldwide. Its wealth has shaped the modern state of Brazil and still provides a major part of the national income and the economic strength of Minas Gerais. Occupying the southeastern part of the São Francisco craton, with an area of about 7,000 km^2, the Iron Quadrangle consists of four major lithostratigraphic units: 1) granite-gneiss metamorphic terrains, basement, 2) the Archaean greenstone belt sequence, the Rio das Velhas Supergroup, 3) palaeoproterozoic metasediments and metavolcanics of the Minas Supergroup, and 4) metasediments of the Itacolomi Group (Dorr 1969, **Fig. 1a**). The dominating products of this traditional mining region are iron, aluminum, topaz, and gold (Vial 1991). Gold was first discovered in the Rio das Velhas valley in 1680 AD, with the richest gold deposits situated along shear zones that cut rocks of the Nova Lima group at the base of the Rio das Velhas Supergroup and the Minas Supergroup (Fig. 1a).

There are four principal gold deposits in the Nova Lima Group: Morro Velho, Raposos, Cuiabá and São Bento, located in the districts of Nova Lima and Santa Bárbara (**Fig. 1b**). In the Morro Velho mine, gold is associated with sulfides and localized in quartz-ankerite-dolomite rocks. The dominant sulfides are pyrrhotite, arsenopyrite, pyrite, and chalcopyrite. From at least 1962 to 1975 AD, arsenic was a by-product of gold production with an output of about 100 tons of As_2O_3 per month (As-trioxide factory in Galo, Nova Lima). In the Raposos mine, gold and sulfides are localized in a siderite carbonate iron formation. Pyrrhotite evidently is the principal sulfide in the ore, although arsenopyrite and pyrite are present. In the Cuiabá mine, the ore bodies are essentially sulfides (pyrite and locally arsenopyrite) hosted in the banded iron formation (BIF). Pyrrhotite in the shear zone is rare. The São Bento gold deposits are sulfide replacements in iron formations of the Nova Lima group. Most of the gold is associated with arsenopyrite and to a lesser extend with py-

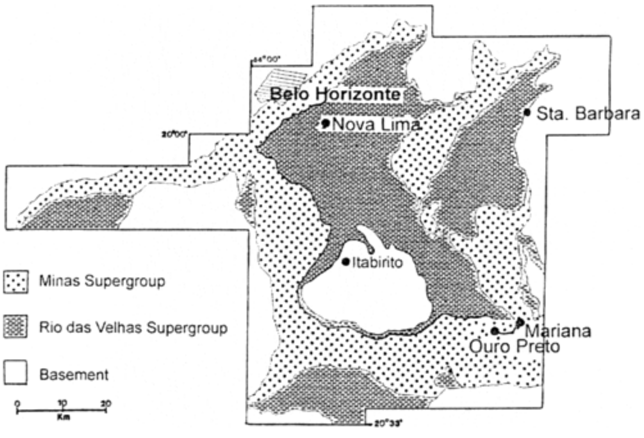

Fig. 1a: Simplified geology of the Iron Quadrangle (after Dorr 1969)

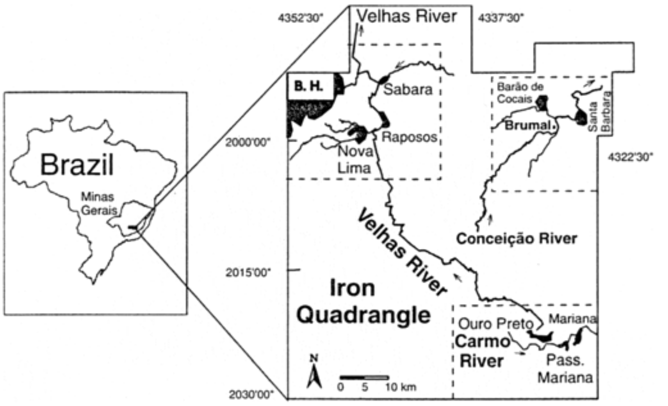

Fig. 1b: Location of the districts of Nova Lima, Santa Barbara, and Mariana, and the river basins

rite and pyrrhotite (Vieira et al. 1991, Gair 1962). Another important gold deposit, the Passagem de Mariana deposit in the district of Ouro Preto-Mariana, is located close to the contact between the rocks of the Nova Lima Group and the Minas Supergroup (Fig. 1b). The gold ore, very rich in arsenopyrite, occurs in quartz and carbonate veins, hosted in BIF, tourmalinite, phyllite and quartzite (Oliveira 1998, Vial 1988). Here, As-trioxide was also being produced in the past, but precise production data are not yet available.

The As enrichment yields consequences for all environmental compartments including that of human health. Considering the relatively low average As concentrations in most natural media (Matschullat 2000), and the sensitivity of many biota towards this element, many countries have introduced rather low threshold values for As in soils and sediments. In this work, the relatively high value of 100 mg As kg^{-1} in soils and sediments is taken as the uppermost tolerable limit for total As in respective media (**Table 1**). Older geochemical studies in the Iron Quadrangle were primarily oriented towards mineral prospecting (e.g. Oliveira et al. 1979). Their work presented a major geochemical mapping program on grid points covering the area. 76% of the 1,297 samples revealed As-concentrations between 20 and 100 mg kg^{-1}. Only 3.7% or 48 samples yielded high As-concentrations between 101 and 5,000 mg kg^{-1}. All of these samples, and quite a few from the second subcollective, were from material over Nova Lima group rocks – the area where gold mining has been active for the past 300 years. Environmental studies that take more media into account were published only recently and highlight the need for further studies (Eleutério 1997, Rawlins et al. 1997, Matschullat et al. 2000, Borba et al. 2000, 2002).

This work presents new data on the geochemistry of surface soils and sediments in the Iron Quadrangle, based on recent sampling, masters and dissertation material (e.g. Ladeira 1999, Schmidt 2001), since hardly any systematic studies have been performed so far. A completely new aspect is also the use of fine topsoil material (surface soil) – the material from the immediate interface between pedosphere and atmosphere. Although As is seen as the most relevant element in respect to environmental impact, new geochemical data from major, minor and other trace elements are presented to allow a more comprehensive discussion. Although the present mining operations may no longer contribute significantly to the contamination of soils and sediments, there are many potential risks for As intoxication induced by the dispersion of old tailings, human occupation of polluted soils, and the consumption of contaminated surface and groundwater.

1 Materials and Methods

Soils. Under subtropical and tropical conditions, the climate-related, higher average temperatures, together with high precipitation, favor intense chemical weathering and erosion. All rocks of the region are intensely weathered, often to depths exceeding 50 m (Dorr 1969). In Brazil, oxisols represent approximately 40% of all surface soils (Neto et al. 1981). In the Iron Quadrangle, the different types of neosols and cambisols prevail, and to a lesser extent, latosols (EMBRAPA 1999, CETEC 1983). Due to the high amount of iron oxihydroxides, the soils are reddish, yellowish and sandy. While quartz dominates, muscovite and kaolinite are commonly present, feldspar, hematite, and goethite may occur, and sometimes gibbsite (Ladeira 1999). Specific surface areas lie between 16 and 36 $m^2 g^{-1}$ (Ladeira 1999) – at the lower end of kaolinite values. These low values may not be representative, however, since they are based on individual

Table 1: International soil threshold values for arsenic in comparison with median values from the investigated areas in Minas Gerais, Brazil. All concentration values in mg kg^{-1}

	BR	CAN	D	DK	NL	USA
Soil	15–100	19	5–50	10	34–50	10–100

BR: Threshold values for soils in São Paulo state (CETESB 2001; EMBRAPA 1999); **CAN**: Soil Quality Guideline for Agriculture (CCME 1997); **D**: German Soil Quality Criteria (Throl 2000); **DK**: Danish Soil Quality Criteria (Jensen et al. 1997); **NL**: Dutch value for maximum permissible concentration (Crommentuijn et al. (1997); **USA**: Screening benchmark concentrations (Efroymson et al. 1997a, b) samples alone. And the topsoil material is much finer than material from deeper soil horizons due to enhanced physical and chemical weathering. The fast turnover of organic material generally prevents the formation of humic A-horizons; total C and N-concentrations are low to very low (always below 1.0 wt-% for C, and below 0.1 wt-% for N). Consequently, element turnover times are relatively fast and the fine topsoil material is an ideal tool to assess geochemical anomalies from allochthonous sources.

Composite surface soil samples (easily mobile material) have been gathered in settled areas of at least 10,000 m^2 in the districts of Nova Lima and Santa Barbara, and in smaller areas (<1,000 m^2) near Mariana. The samples were taken either with a stainless steel blade (scratching of top layer of hard surface) or with a polyethylene blade. Avoiding larger mineral and plant compounds, finer material (150 ± 50 g) was filled directly into 180 mL PE bags (Whirl-Pak), marked and sealed. The material was air-dried in the field, and subsequently freeze-dried in the laboratory to constant weight (Alpha I, Christ, Germany). After dry sieving (nylon mesh 63 µm), the fine fraction (usually >90 wt-%) was used for subsequent analyses, while coarser material (if present) was discarded.

Sediments. Due to the vast hydrological variances in surface flow (level changes of 5 m and more), sediment accumulation is a lot more dynamic as compared to moderate climate zones. Thus, single sediment sampling campaigns may not yield reliable information on the distribution and accumulation of sediment compounds. Therefore, several sampling campaigns were performed in different seasons (April and August). The sediments were manually sampled in streams and creeks during low-flow conditions. Very coarse sediments were already avoided during sampling. Fresh, unconsolidated material was taken up with PE cups from the benthic surface and each sample (ca. 500 mL) represents an area of ca. 100 m^2 sediment surface. The bulk sample was freeze-dried to constant weight, and subsequently dry-sieved in nylon sieves. Material <63 µm was used for the subsequent analysis, while more coarse material was discarded.

Sample preparation. From the beginning, it was planned to analyze the material with different and independent methods (over-determination) to ensure maximum data quality and to gather more experience with the Fe-rich matrices of both soils and sediments. Thus, sub-samples were directly used for solid-sampling (SS) analysis by GF-AAS for As after digestion by ICP-MS for multi-element determinations, and by ED and WD-XRF, after pellet pressing for the independent determination of major, minor, and trace compounds.

For SS-GF-AAS, no further sample preparation was needed. The fine material was directly used for analysis. For ICP-MS, the samples were digested in a microwave oven (MWS1, Maasen, Germany) in 80 mL PTFE vessels. The temperature was held for 20 min at 175°C. The resulting pressure was approximately 25 bar ($2.5 * 10^6$ Pa). After cooling, the digested samples were transferred to 25 or 50 mL flasks, respectively, and filled up with de-ionized water. The samples were stored in 50 mL PP bottles until measurement. For XRF (ED and WD), aliquots of both homogenized soil and sediment material were pressed to powder discs for subsequent analysis. Ca. 5 g of sample powder were homogenized with ca. 1 g of Hoechst wax and pressed with 20 t for 30 sec.

Analysis and quality control. Pyrolysis at 400°C and atomization at 2100°C allowed for a reproducible and accurate As-determination at 193.7 nm by SS-GF-AAS (5EA, Analytik Jena, Germany). The calibration was done with diluted, pure As standard solutions (Merck, Germany). Compared with certified standard reference material (STSD-2, Canada), 40 ± 1.5 instead of 42 mg As kg^{-1} were found (6 replicates).

For ICP-MS analysis, the calibration was carried out with reference solutions containing arsenic at 1, 20, 50 and 100 µg L^{-1}, prepared from a 1 mg L^{-1} As stock solution (ICP-MS standard, Merck) by dilution with 1% nitric acid. Rhodium was used as an internal standard (ICP-MS standard, 1 g L^{-1}, Merck). The Rh concentration was 10 µg L^{-1}, both in the samples and in the reference solutions. For acidification and digestion, nitric acid (Suprapur®, Merck), hydrogen peroxide (30%, Suprapur®, Merck) and hydrochloric acid (Instra-Analyzed®, Baker) were used. The certified reference material, NIST Standard Reference Material 1643d "Trace Elements in Water", was regularly measured for quality control. Errors were always below 5% RSD.

The XRF measurements were performed using the program UniQuant® (Philips, Netherlands) and certified reference materials as unknown samples. Low As values led to positive errors of 21% RSD (below 100 mg kg^{-1}), while higher As values and all other compounds shown in this paper yielded errors below 3% RSD.

2 Results and Discussion

Soils. The principal processes influencing element concentrations in soils are the parent rock material and human activities. Pedogenesis determines the behavior of elements from different parent rock and climate, organic and inorganic soil components, and redox status affects the elemental concentration in soils. The parent rock is supposedly a much more important parameter affecting soil metal contents than soil type (Tang 1985, 1987). In the Iron Quadrangle, comparatively low humus content, generally hard to very hard surfaces due to baking of very fine-grained topsoil material, intense and deep weathering, and yellowish and reddish colors characterize the oxisols (ferralsols) of subtropical and tropical regions. The hard crusts that form at the surface are being mechanically eroded and form a fine oxic soil dust. This dust is being blown off by wind and washed down by precipitation, thus feeding the local drainage system and its sediments. At the same time, the soils are receptors for atmospheric deposition and may accumulate atmosphere-derived particles. The analysis of soil material thus delivers potentially mixed signals of soil geochemistry from in-situ weathering, from atmospheric deposition and/or local contamination.

An overview of the soil geochemistry (**Table 2**) and the As-anomalies (**Fig. 2**) from the Nova Lima, Santa Barbara and Mariana areas demonstrates the high variance and unusually high average values in the region. These data are fully compatible with other individual data sets – so far available

Table 2: Median (rounded) soil geochemical composition and ranges* in the Iron Quadrangle in comparison with the estimated world soil averages**. Major and minor compounds in weight-%, trace elements in mg kg^{-1}

	Nova Lima n = 21	**Santa Bárbara** n = 13	**Mariana** n = 4***	**World soil averages****
SiO_2	59 (49.7–68.1)	39 (12.9–59.4)	54 (42.0–63.8)	60
Al_2O_3	24 (19.3–28.6)	28 (17.8–36.4)	9 (1.5–19.4)	15
Fe_2O_3	13 (3.2–21.0)	27 (7.8–54.7)	29 (13.2–43.5)	5
CaO	0.9 (0.01–3.8)	1.1 (0.09–5.1)	0.07 (0.05–0.09)	1.9
Na_2O	0.2 (0.03–1.0)	0.3 (<0.03–0.74)	0.09 (0.01–0.16)	1.3
K_2O	2.4 (1.14–3.39)	1.8 (0.39–3.44)	0.9 (0.17–1.52)	1.7
MnO	0.09 (0.02–0.18)	0.16 (0.01–0.39)	0.7 (0.09–1,0)	0.07
MgO	0.6 (0.30–1.50)	0.6 (0.28–1.24)	0.3 (0.12–0.47)	1.5
TiO_2	0.9 (0.56–1.22)	1.2 (0.69–1.66)	0.5 (0.23–0.65)	0.7
As	960 (16–13400)	100 (13–467)	53 (16–80)	5
Co	71 (13–102)	117 (32–160)	27 (23–30)	10
Cr	410 (190–680)	435 (150–730)	88 (22–180)	80
Cu	44 (22–90)	53 (18–92)	25 (17–35)	25
Ni	163 (63–300)	93 (20–220)	46 (25–68)	20
Pb	23 (11–32)	33 (19–51)	15 (4–32)	17
Zn	71 (12–240)	93 (38–170)	33 (17–58)	70

* Individual samples yielded trace element concentrations below the detection limit of the respective element
** Data from compilation in Reimann and Caritat (1998)
*** Mariana data may not be as representative as the others, since they are derived from individual soil profiles close to active streams

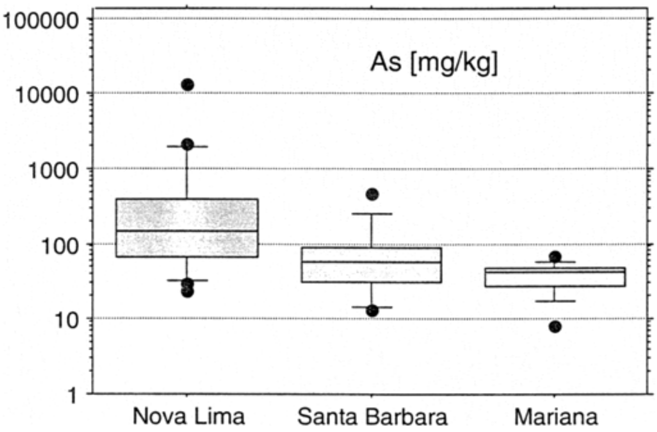

Fig. 2: As-concentrations in topsoil material from Nova Lima (**NL**), Santa Bárbara (**SB**) and Mariana (**M**)

(e.g. Ladeira 1999). Average global soil As-values are given for comparison. The enrichment of Al and Fe, and the depletion of Ca, Na, and Mg, clearly demonstrate the tropical/subtropical origin of the soils from Minas Gerais. Except for Zn and Pb, and to some extent Cu, the trace elements As, Co, Cr, and Ni show relative enrichments as compared to world soil averages. This reflects both the lithological situation in the Iron Quadrangle and, particularly for As, the additional dissipation due to centuries of mining and smelting activities.

Soil As may originate from the bedrock material. Natural As concentrations in soils and rocks are usually fairly low (Riedel and Eikmann 1986, Tanaka 1988, Matschullat 2000). Higher As-concentrations occur in magmatic sulfides and iron ores. Soils in such areas often exceed 'normal' As levels (Huang 1994). In regions with active volcanism (e.g. Italy, Japan, Mexico), average soil As contents may reach 20 mg kg^{-1}, while soils further away from these localities contain an average of 2 mg kg^{-1} (Vinogradov 1959). In the Iron Quadrangle, As occurs within the primary gold ore either as discrete minerals, such as arsenopyrite and loellingite, or as an impurity in the remaining sulfides, mainly in pyrite. The As/Au ratio in these ores varies from 300 to 3000 between the deposits. Total Au-production must have exceeded 1300 t throughout history (Abreu et al. 1988). In the famous Morro Velho Mine alone, around 600 t gold have been produced since 1834 (Pires et al. 1996). **Fig. 2** shows the As-distribution in the adjacent soils. Minima are below 20 mg kg^{-1} and certainly represent a local background. The lower As-concentrations (<60 mg kg^{-1}) of the Iron Quadrangle occur far (>1 km) from the gold mining and smelting sites, and may represent natural anomalies, while concentrations of 150–390 mg kg^{-1} were found close to the big gold mines. The highest concentrations (>1000 mg kg^{-1}) regularly occur close to or on old tailing deposits. The main difference between the samples from Nova Lima and Santa Bárbara can be explained by the prevalence of long-term mining and smelting activities in the Nova Lima district, while these activities took and take place on a much smaller scale in the Santa Bárbara district. These results confirm the hypothesis that As in rocks and ores oxidizes during weathering and part of the As is naturally liberated into the environment, while human activities related to mining enhance the As mobilization into the environment by at least an order of magnitude.

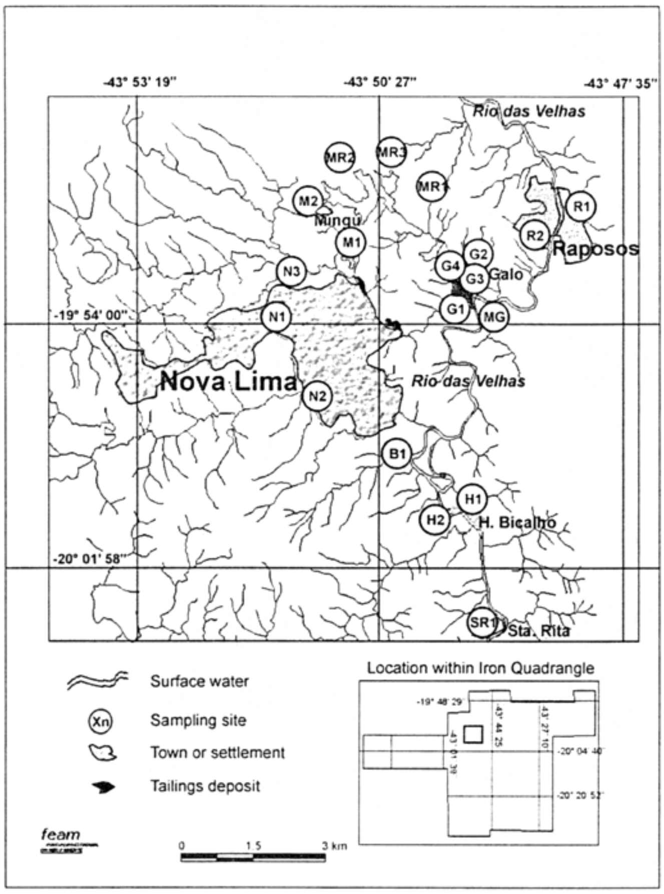

Fig. 3: Soil sampling points in the Nova Lima district with its position in the Iron Quadrangle

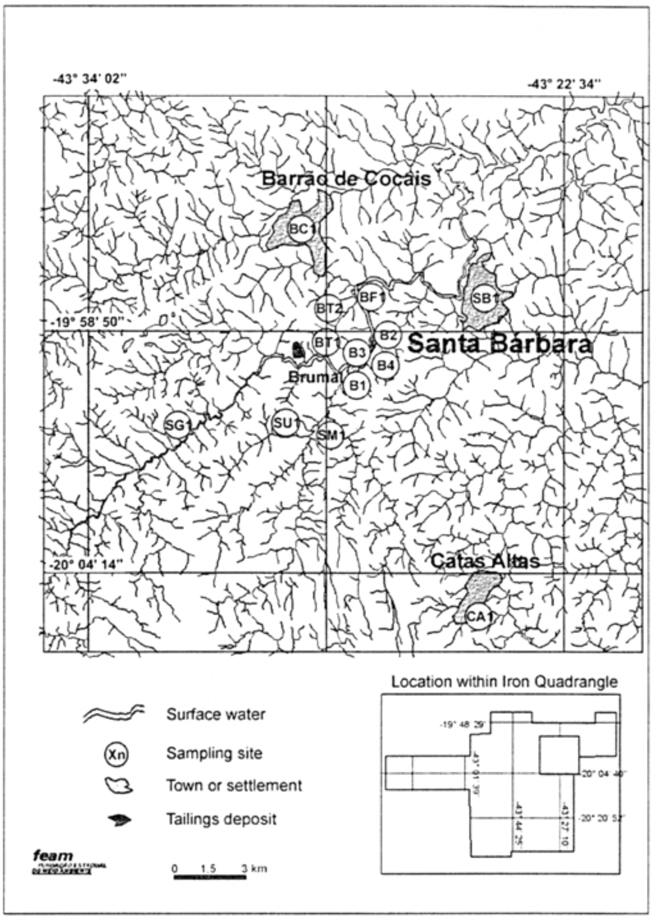

Fig. 4: Soil sampling points in the Santa Barbara district with its position in the Iron Quadrangle

From 1900 to 1940 AD, about 3 million tons of tailing materials were disposed alongside the valleys of the Cardoso stream in the Nova Lima district. This method represented advanced engineering techniques for that time and assured that these residues, still rich in gold (consequently rich in arsenic, too), would be available for secondary processing in the future. Once the tailing deposit capacity along the Cardoso stream had been exhausted, the tailings were discharged directly into the Cardoso stream until 1983 AD, darkening the water and polluting it to the point where its name – even on official maps – was changed to Dark Water Stream (Pires et al. 1996). The total As amount that entered the drainage system until the 1980s must have exceeded 390,000 t in the whole region. As a result, elevated As concentrations have to be expected in environmental compartments near mining areas. By sampling the area, several hitherto unknown anomalies were detected – and all could be related to historical mining and/or smelting activities (**Figs.** 3 and 4).

Sediments. From the environmental point of view, fine-grained sediments (<63 µm) are particularly well-suited to assess the environmental quality of a source catchment. Due to its large surface area, this material offers high sorption capacities, and is much more homogenous than coarser particles that may represent, for example, weakly weathered mineral grains. The high turnover rates for weathered material and subsequent transport into drainage channels should lead to sediment geochemical concentrations that are somewhat similar to those in soils. The results of the sediment samples from the Nova Lima, Santa Bárbara and Mariana districts confirm this hypothesis (**Table** 3). The rounded average grain size was 45% of fine-grained material (7–77%) and 55% of larger-grained sizes (23–93%).

The high As-concentrations are obvious, but elements like Cd (not shown in this paper), Pb, and Zn reveal rather low concentrations when compared to a multitude of results from all over the world – primarily from the northern hemisphere. The authors assume that this result reflects the still comparatively low amount of car traffic in the area investigated, and the extensive use of alcohol for car engines in Brazil. To test this hypothesis, additional work should be performed in urban centers.

The highest As-concentrations were again found in the Nova Lima district (median 190 mg kg^{-1}), while material from the Santa Bárbara district showed a median value of 86 mg kg^{-1}. In the Nova Lima district, maximum values were found next to large tailing deposits and downstream from secondary streams that drain mining and smelting grounds. The highest concentrations occurred in sediments from the Cardoso creek, draining an old tailing deposit in the community of Galo. In stream sediments of the area, As concentrations lie between 47 and 3300 mg kg^{-1}, with a mean of 547 mg kg^{-1}.

Table 3: Ranges for sediment geochemical composition in the Iron Quadrangle in comparison with the estimated world averages*. Major and minor compounds in weight-%, trace elements in mg kg^{-1}

	Nova Lima **n = 24**	**Santa Bárbara** **n = 18**	**Mariana** **n = 9**	**World sediment***
SiO_2	42.6–61.8	37.7–65.0	no data	61.3–63.8
Al_2O_3	10.8–26.2	6.6–19.3	1.6–4.0	1.2–16.6
Fe_2O_3	8.8–23.7	10.9–59.3	14.3–21.5	1.4–7.8
CaO	0.16–0.50	0.06–0.32	0.07–0.34	0.57–1.80
Na_2O	0.16–0.26	0.19–0.25	0.01**	0.04–2.0
K_2O	1.2–3.6	0.48–0.86	0.01–0.07	0.17–2.78
MnO	0.07–0.57	0.10–0.37	0.20–0.88	0.07–0.25
MgO	0.67–1.2	0.4–7.1	0.08–0.4	0.63–2.39
TiO_2	0.58–1.02	0.45–1.35	0.05–0.10	0.21–0.97
As	47–3,300	22–160	22–860	2–22
Co	11–62	3–86	3–30	7–32
Cr	24–640	17–1150	33–160	24–161
Cu	36–82	26–93	13–71	12–24
Ni	31–190	15–510	5–160	14–59
Pb	9–57	7–48	15–45	8–195
Zn	46–130	27–160	21–80	44–209

* Compiled from sediment data in Reimann and Caritat (1998). These data cannot be seriously considered representative as a global average, however, due to the very limited, reliable data sets

** Doubtful result, no explanation possible

In the district of Santa Bárbara, the highest As-concentrations occurred close to the São Jorge mine near the community of Brumal. The principal workings consisted of a large excavation about 100 meters long, 50 meters wide and 30 meters deep in rocks of the Nova Lima Group. Production apparently came from a ferruginous quartzite and a quartz vein, both of which contained pyrite, pyrrhotite, arsenopyrite, and probably very fine-grained, native gold. Since 1948, there has been no production (Prado et al. 1991). Arsenic that is not retained by the Fe-Mn oxihydroxides will be transported with the surface drainage to the streams.

In both districts, concentrations vary widely within the rivers' course and between individual sampling campaigns. While average values remain identical over longer time frames – indicating constant supply – individual sampling sites may show order of magnitude differences. In the Rio das Velhas, samples from April 1998 showed 3,300 mg As kg^{-1} prior to the inflow of Cardoso stream; the same sampling spot yielded 100 mg As kg^{-1} in August 1999. The Cardoso, upstream from its confluence with Rio das Velhas, showed similar changes: from 120 mg As kg^{-1} in April 1998 to 2400 mg As kg^{-1} in August 1999. Similar variances occur in the other rivers and creeks – certainly a result from sediment redistribution during high and very high run-off events.

3 Conclusions and Outlook

The vast majority of surface soil and sediment samples exceeded both global average values, and all threshold values recommended by national and international bodies (Table 1). This reflects the distribution of positive As anomalies in the Iron Quadrangle, related to both the lithology and to historical and recent gold mining and smelting activities in the Iron Quadrangle. At the same time, people living in the immediate vicinity of related sites are exposed to an elevated uptake of As through environmental media, particularly soil. Human biomonitoring in the area showed distinct As enrichments in urine from people living close to mining, smelting, and disposal sites in both the Nova Lima and the Santa Bárbara district (Matschullat et al. 2000, 2002). Since first investigations on the depth of As enrichments within the soils point at a serious contamination to greater soil depth (several dm, Haßler 2002), solutions have to be found to stabilize the soils against wind and water erosion. In the year 2000, some of the larger old tailing deposits have been covered and protected from direct human interaction by the responsible mining company. The related, hopefully positive effects will have to be studied in the future.

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