

Arsenic-Contaminated Soils in the Urban Area of Ouro Preto, Minas Gerais, Southeastern Brazil

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Abstract— Arsenic (As) is a toxic and carcinogenic element. Numerous As compounds are present in the environment and in biological systems. The most common exposure routes of humans to As are consumption of polluted water, gas inhalation or ingestion of soil dust, causing toxic and acute effects in tens of millions of victims all over the planet. In the Brazilian city of Ouro Preto, in the urban districts Piedade, Antônio Dias, Padre Faria, Taquaral and Alto da Cruz, 21 soil samples were collected at sites spaced about 200 m apart, in a 2 km² area, to analyze the physical properties, chemical constitution, mineralogy and presence of As. Of all samples, 15 had a predominantly clayey texture, and in 12 of these, As levels of > 250 mg.kg⁻¹ were detected. In general, the As levels ranged from 6 to 925 mg.kg⁻¹. No primary or secondary As minerals were found, suggesting that As had been retained and adsorbed by Fe, Al and oxides and hydroxides and by clay minerals. The predominant minerals were quartz, muscovite, kaolinite, goethite, hematite, illite and gibbsite.

Keywords—Arsenic, Contaminated Soil, Ouro Preto.

I. INTRODUCTION

The movement and mixture of different terrains as a result of anthropogenic activities may induce the development of new materials (soils, tailings, weathering rocks), which reflect characteristics of the underlying rock, but may lead to the formation of new compounds and substances in the environment, which can affect humans who get in touch with these materials.

In former, now abandoned, mining areas, tailing dumps were formed as a result of the extraction processes. They have the inherent characteristics of the ore and surrounding rock and are carriers of potentially hazardous chemical elements, at high concentrations. They may come to be a source of dispersion of these elements and, consequently, of environmental contamination, in particular in the case of trace elements such as heavy metals and metalloids. According to Kabata-Pendias et al. (2004), the transfer of chemical elements between the

various constituent soil phases can be considered the main process governing their solubility, mobility and availability in surface water, groundwater and living organisms.

The availability of heavy metals in soils depends on the presence of the elements in the soil solution, defined by the composition and reaction of the systems, oxidation conditions and reaction kinetics. These in turn depend on the soil properties and the tendency to form insoluble compounds, which are precipitated and coprecipitated with other minerals and form complexes with organic matter and adsorb other minerals.

Mining areas in particular are drastically altered zones and, in this context, the assessment of soil contamination is the first step in the characterization of degraded areas.

In Brazil, specifically in the region of the Quadrilátero Ferrífero (QF), previous studies report As-contamination of stream sediments in some rivers, surface waters and groundwater. In stream sediments of the Rio do Carmo, Eleutério (1997) reported As contents of 620.0 µg.g⁻¹ in the summer and 1.268 µg.g⁻¹ in the winter. In the counties of Nova Lima and Santa Bárbara, in the QF, Mattschullat et al. (2000) analyzed As concentrations in urine of 7 to 12-year-old children. These authors confirmed human As contamination at concentrations between 2 and 106 µg.L⁻¹, and concentrations of > 40 µg.g⁻¹ in 22% of the children. In Ouro Preto, Pimentel (2001) analyzed water from abandoned gold mines and springs and detected As contents between 0.07 and 2.30 mg.L⁻¹. In studies in the former gold-mining districts, Borba et al. (2002) analyzed the As concentrations of sediments in the hydrographic basins of the rivers do Carmo, Conceição and das Velhas. These authors reported As concentrations in sediments of up to 4000 mg.kg⁻¹ and of 350 µg.L⁻¹ in surface waters, while in the groundwater of mines in Ouro Preto and Mariana they found As concentrations of up to 2,800 µg.L⁻¹. In groundwater consumed by the population of Ouro Preto, Gonçalves et al. (2007) detected As levels of 224 µg.L⁻¹.

In this context, the objective of this study was to characterize the physical, chemical and mineralogical properties of the soils of five urban sectors of Ouro Preto, to deepen the understanding of the influence of the matrix rock on the genesis, evolution processes and soil properties, as well as to understand and evaluate the As concentrations they contain.

General characteristics of the study area

The studied area lies in the southeastern part of the QF. This region covers an area of 7.200 km² in the center-south part of the state of Minas Gerais.

The geology of Ouro Preto consists of a set of metasedimentary and metavolcanic rocks derived from the Supergroups Minas and Rio das Velhas (Figure 1). The Supergroup Minas consists of a Paleoproterozoic metasedimentary sequence grouped, from base to top, in: Caraça, Itabira and Piracicaba (Derby 1906; Harder &

Chamberlin 1915; Dorr 1969; Ladeira 1980; Alkmim & Marshak 1998).

The Supergroup Rio das Velhas consists of a volcanic-sedimentary sequence corresponding to a greenstone belt, divided by Dorr et al. (1957), from base to top, in the groups Nova Lima and Maquiné. The Group Nova Lima is divided into three units: metavolcanic (basal); chemical metasedimentary (intermediate) and chemical metastatic (at the top). The Group Maquiné is divided, from base to top, in the formations Palmital and Casa Forte. The stratigraphic section of the study area consists of the following units, from base to top: metapelitic sericitic; quartzitic; carbonaceous metapelitic, banded iron-rich and dolomitic carbonate sequences. These units correspond, respectively, to the Group Nova Lima, Moeda formation, Batatal formation, Cauê and Gandarela formation, Cercadinho formation, Group Sabará and lateritic covers (Dorr 1969). These units are distributed in continuous layers with vertical variations.

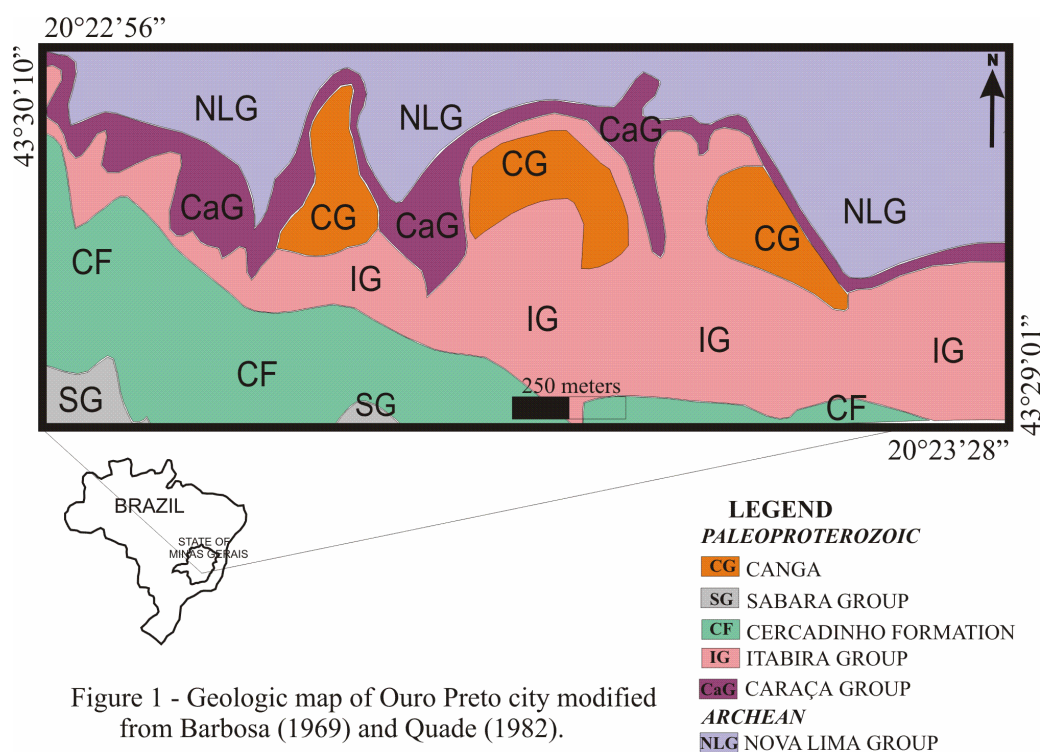


Figure 1 - Geologic map of Ouro Preto city modified from Barbosa (1969) and Quade (1982).

II. MATERIALS AND METHODS

Twenty-one soil samples were collected in the county of Ouro Preto, specifically in the urban districts Padre Faria,

Piedade, Antônio Dias, Morro Santana and Taquaral (Figure 2).

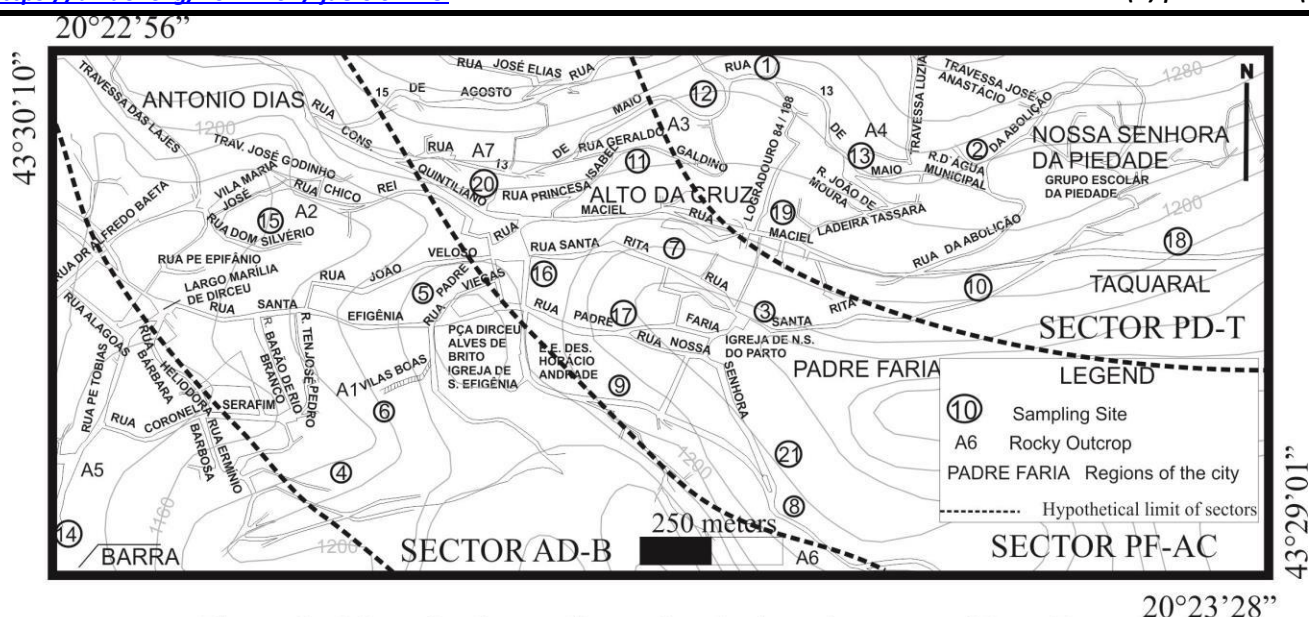


Figure 2 - Map of soil sampling points in the urban area of Ouro Preto

The soil was sampled systematically, at predetermined regular intervals. The distance between the sampling points was not more than 150 m. The points were localized by UTM coordinates and identified by the address of the nearest residences.

Each sample consisted of four sub-samples collected within a 5 m - diameter circle at each sampling point, using a stainless steel core, inserted to a depth of 10 cm. The composite samples (approximately 2.0 kg) were quartered, and sub-aliquots of approximately 100 g of each quarter were filled into labelled sample vials. The soil samples were air-dried, crumbled and sieved (2 mm plastic mesh). The particle size of the resulting air-dried fine soil (ADFS) was analyzed for the fractions sand (2-0.05 mm), silt (0.05-0.002 mm) and clay (<0.002 mm).

In the Laboratory of Mineralogy, of the Department of Soils of the Universidade Federal de Viçosa (UFV), the mineralogical composition was analyzed by X-ray diffraction using a Rigaku D-Max diffractometer equipped with a cobalt tube (Co-K α radiation, $\lambda = 1.79026 \text{ \AA}$), operated at 40 kV and 30 mA. The scanning

range was between 4° and $50^\circ 2\theta$, with a step size of 0.05° and 1 s per step. The chemical composition was determined by X-ray fluorescence (XRF79C - Lithium tetraborate fusion) and the total As content by the method of hydride generation (AAS/HAS14B). All chemical analyses were carried out in the laboratories of the company SGS - Geosol, in Belo Horizonte - MG.

III. RESULTS AND DISCUSSION

In the study area, covering five completely urbanized districts of the city of Ouro Preto, the observation of and access to exposed rocks were impaired. Table 1 shows the lithology of outcrops close to the sampling sites and Figure 2 their locations. Table 2 shows the results of the particle-size analysis of the clay, silt, and coarse and fine sand fractions. The mean and median values of all studied variables are close to each other and symmetrically distributed, which can be confirmed by the asymmetry and kurtosis values close to zero. For being field data, the fitting of the theoretical distribution was only approximate (Warrick & Nielsen 1980).

Table.1: Lithography of outcrops in the study area

Outcrop	Lithology
A1	Quartzite, iron-rich quartzite, and phyllite
A2	Iron-rich quartzite, sericitic and with coarser quartz grains
A3	Quartzite, metagrawacke and chlorite, phyllite
A4	Canga, quartzite, iron-rich quartzite, phyllite, dolomite, chlorite schist
A5	Canga, iron-rich quartzite, conglomerate, phyllite, dolomite, chlorite schist
A6	Canga, quartzite, iron-rich quartzite
A7	Conglomerate, phyllite, dolomite, chlorite schist

Table 2 - Descriptive statistics for the particle-size properties of 21 soil samples

Particle-size properties	Values					Coefficients	
	Mean	Median	Minimum	Maximum	SD	Variation	Kurtosis
Clay (g kg ⁻¹)	404.36	370.00	5.80	710.20	186.81	46.20	-0.52
Silt (g kg ⁻¹)	155.56	155.60	108.30	212.80	34.73	22.33	-1.38
Fine sand (g kg ⁻¹)	301.02	299.50	73.70	610.00	136.72	45.42	0.01
Coarse sand (g kg ⁻¹)	139.05	163.00	30.20	236.70	75.11	54.02	-1.35

Data normality is not a requirement, whereas it is relevant that the sample distribution does not have very long tails in these cases (Cressie 1991). Thus, based on the results of Table 2, it was assumed that the sample distributions of the particle-size properties were sufficiently symmetrical. In different parts of the world, studies reported the natural presence of arsenic or As contents as a result of some anthropogenic activity in soils. In Brazil, Curi and Franzmeir (1987) found As levels in Latossolo Vermelho férreo between 6 and 10 mg.kg⁻¹, whereas in Latossolo ferrífero, the concentration was 36 mg.kg⁻¹. In the Quadrilátero Ferrífero, Matschullat et al. (2000) found soil As concentrations between 200 and 860 mg.kg⁻¹, in the sub-basin of the Córrego do Manso, Andrade et al. (2009) detected As contents between 46.5 and 238.7 mg kg⁻¹, and in Latossolos of the Cerrado, Marques (2000) found As concentrations of the order of 38 mg.kg⁻¹. In 43 soil samples of the state of Paraná, Licht et al. (2005) found peak As concentrations of 29.40

mg.kg⁻¹ and an average value of 7.5 mg.kg⁻¹. In this study, soil As concentrations from 6 mg.kg⁻¹ to 925 mg.kg⁻¹ were found in the urban area of Ouro Preto (Table 3).

In the analyzed soils, a strong relation was observed between samples with predominantly clayey texture and high As levels (Table 4). Regarding the 10 major oxides, the results of the soil chemical analysis (Table 5) indicated a similar behavior of the samples 10, 11, 12, 13 and 20, as well as of 1 to 9, 14 to 19 and 21. This is a characteristic of tropical soils under high incidence of rainfall. The concentrations of water-soluble forms of the elements, such as [Si(OH)₄], Ca²⁺, Mg²⁺, Na⁺, K⁺, Mn²⁺, H₂PO₄⁻ decrease from rock to soil, whereas insoluble elements such as Al(OH)₃, Fe₂O₃ and FeOOH increase from rock to soil. The SiO₂ concentration in soils is higher, because a part of the silica released from rocks by weathering is fixed in the soil as a clay component or in the form of quartz, while another part is washed away by the water.

Table.3: Location of sampled points, As contents and textural classification of the 21 soil samples.

Samples	Longitude	Latitude	Texture	Total As (mg kg ⁻¹) **D.L. (1)
SOL 01	657496	7745330	Sandy clay loam	660
SOL 02	657878	7745156	Clayey loam	725
SOL 03	657510	7744899	Sandy clay loam	353
SOL 04	656764	7744758	Sandy loam	46
SOL 05	656897	7744955	Sandy loam	130
SOL 06	656832	7744824	Sand	6
SOL 07	657302	7745025	Clay	386
SOL 08	657523	7744640	Sandy clay loam	17
SOL 09	657300	7744790	Sandy loam	34
SOL 10	657856	7744943	Very fine clayey	22
SOL 11	657281	7745216	Clay	610
SOL 12	657468	7745281	Very fine clayey	925
SOL 13	657650	7745160	Very fine clayey	515
SOL 14	656451	7744678	Sandy loam	245
SOL 15	656639	7745085	Clay	910
SOL 16	657110	7744990	Sandy clay	686
SOL 17	657305	7744890	Sandy clay loam	61
SOL 18	658154	7745011	Clay	905
SOL 19	657458	7745064	Sandy clay loam	840

SOL 20	657022	7745165	Clay	925
SOL 21	657534	7744717	Sandy loam	186

Table.4: Arsenic contents and predominant textures of the soil samples.

As concentrations mg kg ⁻¹	Sandy soil texture	Clayey soil texture	Total
<50	3	2	5
50 – 150	1	1	2
151 -250	2	0	2
>250	0	12	12
Total	6	15	

Table.5: Results of semiquantitative analysis, by X-ray fluorescence.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	P ₂ O ₅	Na ₂ O	K ₂ O	MnO
Samples	%	%	%	%	%	%	%	%	%	%
**D.L.	0.10	0.10	0.01	0.01	0.10	0.01	0.010	0.10	0.01	0.01
SOL 01	57.70	14.60	17.60	0.23	0.65	0.47	0.127	0.28	2.24	0.11
SOL 02	47.30	9.02	32.80	1.01	0.56	0.71	0.166	<0.10	0.9	0.07
SOL 03	55.20	9.11	19.70	1.97	1.16	0.54	0.404	<0.10	0.98	0.18
SOL 04	76.20	6.53	11.10	0.68	0.51	0.46	0.091	0.14	1.05	0.25
SOL 05	66.50	7.38	17.60	1.06	0.94	0.45	0.106	0.13	1.45	0.54
SOL 06	97.90	0.47	1.50	0.04	0.11	0.03	0.013	<0.10	0.11	0.03
SOL 07	36.00	6.01	49.60	0.04	0.28	2.00	0.149	<0.10	0.42	0.12
SOL 08	62.40	9.82	18.10	0.11	0.31	0.98	0.086	0.16	1.08	0.50
SOL 09	60.70	14.40	11.60	1.48	1.16	0.76	0.068	0.20	2.17	0.05
SOL 10	24.90	1.05	70.80	0.87	0.34	0.09	0.164	<0.10	0.06	0.08
SOL 11	29.20	3.02	54.40	2.38	1.64	0.09	0.299	0.23	0.33	0.24
SOL 12	25.30	0.94	70.70	0.10	0.28	0.03	0.191	0.21	0.17	0.10
SOL 13	22.80	1.38	71.90	0.28	0.33	0.09	0.321	<0.10	0.04	0.07
SOL 14	67.40	6.89	12.60	2.50	1.80	0.90	0.172	0.24	1.14	0.54
SOL 15	43.00	1.77	49.50	0.12	1.12	0.09	0.179	<0.10	0.22	0.19
SOL 16	39.70	23.00	20.90	0.20	0.51	0.83	0.228	0.25	1.45	0.11
SOL 17	61.70	14.00	12.10	1.30	0.92	0.67	0.117	0.17	2.19	0.10
SOL 18	44.10	3.96	44.00	0.43	0.40	0.30	0.220	<0.10	0.52	0.09
SOL 19	44.50	3.47	33.80	3.95	2.08	0.26	0.165	<0.10	0.43	0.21
SOL 20	28.50	4.13	58.10	0.15	0.44	0.40	0.375	<0.10	0.31	0.82
SOL 21	62.00	12.10	14.40	0.42	0.53	0.83	0.113	0.18	1.85	0.17

The oxides CaO, MgO, Na₂O and K₂O are easily leached by the water, which explains the lower levels in the soil. The mobility of Al₂O₃, MnO and P₂O₅ is low, although they usually remain in the soil after release from the rocks. In oxidizing environments (as in the studied soils), the mobility of hematite (Fe₂O₃) is low, and it remains in the soil, which also contains Fe₃O₄, found in opaque minerals such as magnetite. Titanium oxide (TiO₂), once released from the rock, remains in the soil as ilmenite and rutile (Piccirilo & Melfi 1988). The arsenic enrichment in surface soils, compared to the concentrations of the parent

rock, seems to reflect the influence of external sources (Kabata - Pendias 1992). As and P are chemically similar. In soils, both form insoluble compounds with Al and Fe. Arsenic forms are dominant in most soils, although As has less affinity with Al oxides than phosphates. The As in the soil can behave similarly to phosphorus, being strongly adsorbed by the oxides, although its chemistry is far more complex, due to the different oxidation states (O'Neill 1990). In the studied soils, As can bind to total Fe oxides (crystalline and non-crystalline oxides), manganese oxides and organic matter. Iron

oxides are rather effective in immobilizing this metalloid (As), in particular non-crystalline As (El Khatib et al. 1984; Carbonell-Barrachina et al., 2004). The soil mineralogical analysis showed that the sand fraction consists mostly of quartz and hematite (Table 6). The mineralogy of the silt and clay fractions is practically the same, containing mainly goethite, gibbsite, mica, kaolinite

and talc. In general, the mineralogical analysis showed the disappearance of the less weathering-resistant minerals from altered rock samples, which may also be the result of the predominance of iron compounds in these samples. Little weathered soils, as in this case, tend to reflect the mineralogical composition of the parent material.

Table.6: Results of X-Ray Diffraction analysis

SAMPLES	CLAY	SILT	SAND
SOL 1	Il, Ct, Gt, Gb	Mu, Ct	Qz, Mu, Ct, Hm
SOL 2	Il, Ct, Gb	Mu, Ct, Gb	Qz
SOL 3	Il, Ct, Gb	Mu, Ct, Gb	Qz, Ct, Hm
SOL 4	Il, Ct, Gb	Mu, Ct, Gb	Qz, Um
Solo 5	Il, Ct, Gt, Gb, Ta	Mu, Ct, Gb, Ta	Qz, Mu, Ct, Hm
SOL 6	Il, Ct, Gt, Gb, Ta	Mu, Ct, Qz, Gt	Qz
SOL 7	Il, Ct, Gt, Gb, Ta	Mu, Gt, Ta	Qz, Mu, Hm
SOL 8	Il, Ct, Gt, Gb	Mu, Gt, Ta	Qz, Mu, Gb, Hm
SOL 9	Il, Ct, Gt, Gb, Ta	Mu, Gt, Gb, Ta	Qz, Hm
SOL 10	Gt	Mu, Gt, Gb, Ta	Qz, Gb, Hm
SOL 11	Gt	Mu, Gt, Qz	Qz, Mu, Gt, Hm
SOL 12	Il, Ct, Gt, Mh	Qz, Gt, Hm, Mh	Qz, Mu, Gt, Hm
SOL 13	Ct, Gt, Ru	Mu, Ct, Gt, Hm	Qz, Gt, Hm
SOL 14	Il, Ct, Gt	Mu, Ct, Gt, Gb, Ta	Qz
SOL 15	Il, Ct, Gt, Ta	Mu, Ct, Gt, Ta	Qz, Mu, Ta
SOL 16	Il, Ct, Gt	Mu, Ct, Gb, Gt	Mu, Ct, Gb, Gt
SOL 17	Ct, Il, Gt, Gb	Mu, Ct, Gb	Qz
SOL 18	Ct, Gt	Mu, Ct, Gt, Ta	Qz
SOL 19	Ct, Il	Mu, Ct, Gt, Ta	Qz
SOL 20	Ct, Gb	Mu, Ct, Gt, Ta	Qz, Hm
SOL 21	Il, Ct	Mu, Ct, Ta	Qz

The mineralogy of the soils selected for having maximum As contents is shown in Figure 3. Quartz was found in all studied soils, highlighting the marked presence of talc in sample SOL 15 and of iron oxides such as hematite and maghemite in sample SOL 12. Arsenic-containing primary minerals, e.g. arsenopyrite, scorodite, kolfanite or kraunite, were not detected. Talc and iron oxides may be As carriers, according to the ionic radius and valence (V) of As, facilitating the incorporation

in the tetrahedra as a substitute for the Si^{4+} of the talc mineral. The same does not apply to quartz, which does not assimilate As in its structure. The results of the mineralogical characterization of the silt fraction were similar to those of the sand fraction, with high proportions

of quartz and of the talc and hematite/maghemite minerals in the samples SOL 15 and SOL 12, respectively.

High As contents were found in talc-type minerals by Moen et al. (2010), which was attributed to the presence of these mineral in the crystalline structure, characterizing them as possible primary minerals containing As. Arsenic (III) can participate in the crystalline structure of Fe oxides due to the ease of As incorporation in this oxidation state into the crystalline structure of maghemite and hematite, the main As-containing minerals in mineralized former mining areas (Walker & Jamieson 2005). Arsenates coprecipitated with amorphous iron oxides can be stabilized and crystallized during the transformation of amorphous into crystalline oxides (Ford 2002).

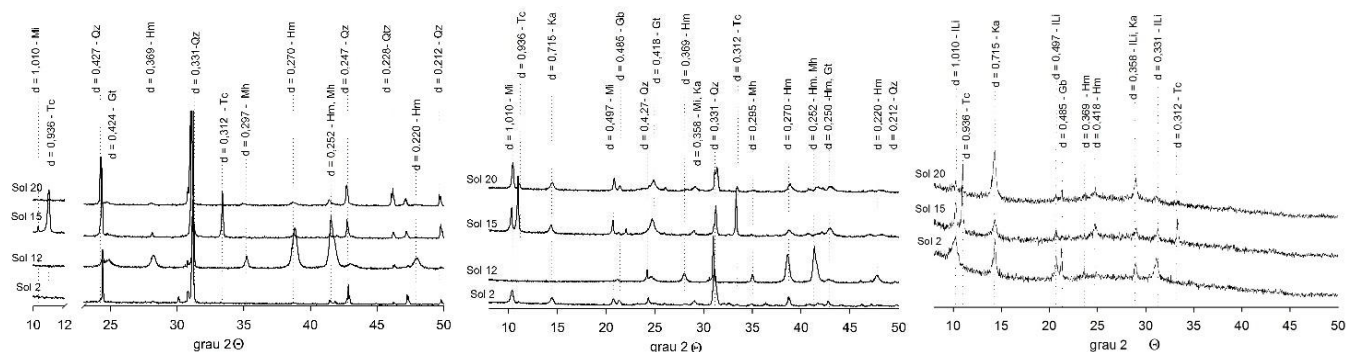


Fig3: Diffractograms of the sand, silt and clay fractions in the samples SOL 12,15,20.

In this study, Fe and clay contents were highest in sample SOL 12, suggesting hematite in the clay fraction as controllers of As availability. On the other hand, sample 2 contained high SiO₂ and lower clay contents, suggesting clay minerals (minerals 1:1 and 2:1) as possible controllers of As in soil. In this context, As availability can be higher under low oxide conditions and poor adsorption capacity of kaolinite. In the clay fraction, the minerals kaolinite, gibbsite and iron oxides were identified. Among these, the most efficient in terms of As adsorption in the soil solution are the Fe and Al (Pierce & Moore, 1982) and Mn oxides Oscarson et al. (1981).

These Al, Fe and Mn oxides and hydroxides are amphoteric minerals that occur as discrete phases and/or associated with other minerals in the form of coatings (Ax and Trivedi 2002). Importantly, these minerals have a large specific surface (>400 m² g⁻¹) and contain micropores and different adsorption sites, which makes them influential with regard to the mobility, distribution and attenuation of heavy metals (Axe & Trivedi 2002).

In cases of densely populated urban areas of Brazil and some other countries, it is relevant to reconsider the legislation with regard to the maximum admissible value for any type of land use. In Germany, the reference values of As in soils, for intervention established by environmental agencies for playgrounds, residential areas, parks/leisure areas, commercial and industrial areas are 25, 50, 125 and 140 mg.kg⁻¹, respectively.

In the state of Pernambuco, studies for the determination of soil As thresholds found mean As levels of 0.43 mg kg⁻¹, 0.36 mg kg⁻¹ and 0.52 mg kg⁻¹ in the surface horizons of the regions Zona da Mata, Agreste (sub-humid woodland) and Sertão (semi-arid region), respectively. A mean content close to that of the surface was found in the subsurface horizons of the Agreste, with a mean of 0.39 mg kg⁻¹, and lower values in the regions of Zona da Mata and Sertão (0.26 and 0.25 mg kg⁻¹) (Biondi 2010). For the soils of the state of Minas Gerais, the As reference values found ranged from 3.8 to 50.6 mg kg⁻¹ Caires (2009). In

the state of São Paulo, the reference soil As value was established at 3.5 mg kg⁻¹, the alert value is 15 mg.kg⁻¹, whereas the levels for intervention in agricultural, residential and industrial areas are 25, 50 and 100 mg.kg⁻¹, respectively CETESB (2005).

IV. CONCLUSIONS

1 - In the city of Ouro Preto, the soils of the urban sectors Santana, Padre Faria, Piedade, Antônio Dias contain high total As levels, which exceed the maximum admissible value for any type of use by far. Dust from contaminated soil may have toxic effects if inhaled or ingested by humans, particularly by children, who are most susceptible to this type of contamination as a result of their habits. Soil ingestion has been recognized as the most relevant source of heavy metal contamination.

2 - Among the criteria and guiding values of soil quality for the presence of chemical substances established by CONAMA, Resolution No. 420 (2009) determined a soil As content of 15 mg.kg⁻¹ for a given area as a situation requiring prevention and a content of 55 mg.kg⁻¹ in a residential area as requiring investigation. Averaged across the 21 soil samples studied, the mean As concentration was 437.47 mg.kg⁻¹.

3 -Soils with a clayey texture accounted for 71% of all samples, and of these, 80% contained As levels of > 250 mg.kg⁻¹.

4 - The mineralogical analyses identified silicates, predominantly in quartz, muscovite and kaolinite. A high proportion of a variety of iron and aluminum oxides and/or oxides-hydroxides, represented by goethite, hematite and gibbsite, was also found.

5 - The distribution of As in the soil throughout the study area varied according to the intrinsic characteristics of the parent material.

6 - No autigenic or secondary As minerals were detected in the studied soils. The absence of these minerals in the analyzed soils means that a greater amount of As is retained in the crystalline and noncrystalline iron oxides

(amorphous materials) formed during the meteorization processes of the bedrock.

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