



**Assessment of the environmental impact of metals and metalloids
contamination in rural soils in the vicinity of some abandoned
Portuguese mines**

***Avaliação do impacte ambiental da contaminação com metais e metalóides
em solos rurais na envolvente de algumas minas Portuguesas abandonadas***

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Abstract

A comparative assessment of the environmental impacts in the vicinity of three abandoned Portuguese mines was intended with this study. The mines of Jales, Vale das Gatas and Argoselo were selected for this purpose. Mining and mine tailings dumped on these sites originated progressively acid mine drainage and soil contamination. A simple visual inspection on the mine sites indicated that all the tailings are being considerably eroded due to the action of water, particularly during rainfall events. Significant concentrations of As and also of Cu, Cd, Pb and Zn occur in soils collected near the tailing deposits, with contents commonly exceeding the permissible levels determined by the National Public Health laws. Close to the mine sites it was noticed the existence of acid mine drainage (AMD) associated with the presence (and leaching) of sulphides. Such waters show values of pH around 3 and high concentrations of metals and metalloids. Meanwhile, the acid effluents and the resulting mixed stream waters also carry high contents of sulphate and metals. Surprisingly, stream waters (namely in the Vale das Gatas mine) do not have As, probably due to the co-precipitation with iron oxyhydroxides and to the formation of scorodite. The conditions of pH and Eh (oxidizing environment) existing in these waters, as well as microbiological mechanisms, appear to be the main cause for the precipitation of iron oxyhydroxides with co-precipitation of arsenic. The results of the investigation reveal the important role played by secondary minerals in the control of the metal migration to downstream waters.

Keywords: Abandoned mines, Acid mine drainage, Arsenic, Soil contamination, Environmental assessment

Resumo

Uma avaliação comparativa do impacte ambiental nas proximidades de três minas Portuguesas abandonadas foi efectuada neste estudo. As minas de Jales, Vale das Gatas e Argoselo foram seleccionadas para esta finalidade. Os materiais rejeitados da exploração mineira foram depositados nestes locais originando progressivamente drenagens ácidas e contaminação dos solos vizinhos. Uma simples inspecção visual nos locais indicou que os materiais depositados nas escombreiras estão a sofrer erosão considerável devido à acção da água, principalmente durante os períodos de chuva. Concentrações significativas de As e também de Cu, Cd, Pb e Zn ocorrem em solos amostrados perto das escombreiras, com teores que ultrapassavam os níveis admissíveis determinados pelas leis Nacionais de Saúde Pública. Perto das minas notou-se a existência de drenagem ácida de mina (DAM), associada à presença (e lixiviação) de sulfuretos. Essas águas apresentavam valores de pH à volta de 3 e elevadas concentrações de metais e metalóides. Entretanto, os efluentes ácidos e águas resultantes do fluxo misto com as águas das ribeiras também apresentam altos teores de sulfato e de metais. Surpreendentemente, as águas das ribeiras (nomeadamente na mina de Vale das Gatas) não possuem teores elevados em As, provavelmente, devido à co-precipitação com oxihidróxidos de ferro e à formação de escorodite. As condições de pH e Eh (ambiente oxidante) existentes nestas águas, bem como os mecanismos microbiológicos, parecem ser a principal causa para a precipitação dos oxihidróxidos de ferro com a co-precipitação do arsénio. Os resultados desta investigação revelaram o importante papel desempenhado pelos minerais secundários no controlo da migração de metais nas águas a jusante das áreas mineiras

Palavras chave: Minas abandonadas, Águas ácidas de drenagem, Arsénio, Contaminação de solos, Avaliação ambiental

1. Introduction

The key to understand the mining influence in the surrounding environment depends directly on knowing the processes that produce acid mine drainage (AMD) and contribute to the deposition of high concentrations of metals in the local soils. Although acid drainage is commonly associated with the extraction and processing of sulphide-bearing ore deposits, chemical reactions of oxidation can easily occur wherever sulphide minerals are mined and exposed to atmospheric oxygen (Blowes et al. 2003). Sulphide ore extraction and processing enhance the rate of pyrite oxidation increasing the rate of acid production. As result of this, severe environmental damage can occur (Plumlee and Logsdon, 1999; Jambor et al., 2003; Nordstrom et al., 2007). The generation of AMD with low pH and containing high concentrations of dissolved metals from mine wastes represents an environmental problem of international scale. Studies concerning AMD are increasing throughout the world, including in Portugal.

Aware of the great liabilities of the mining industry in Portugal and in order to characterize abandoned mines without owner or property rights, the Portuguese Government took the responsibility to carry out the inventory and characterization of the main abandoned mine sites dispersed over the country. To achieve this, the National Laboratory of Energy and Geology (LNEG) developed a comprehensive program of studies aiming: (a) to characterize those main mine sites; (b) to assess the symptoms of risks inherent to former mining operations; (c) to promote measures that best fit to the rehabilitation of the environmentally affected areas (Santos Oliveira, 1997). The results of this program led to the identification of more than 100 abandoned mines scattered around the country (Santos Oliveira et al., 2002) according to their hazardousness. These old mines were classified and hierarchized according to the following general criteria: type and magnitude of the chemical anomalies in soils, stream sediments and waters; actual conditions of mining safety; size and stability of the mine landfills (tailings); visual impact; degree of land and water use; archaeological (museum) relevance of the mine structures. Three of these abandoned mine sites, showing different ore paragenesis, but all of them exhibiting some potential environmental risk were selected to carry out a comparative assessment of the geochemistry of soils existing in their vicinities. Among others, two main criteria were followed: a) existence of mining activity with some significance until recent past, where huge tailings and other rejected "sterile" materials were generated and b) presence of local populations living close to the mine who, in some extent, use the land and soil. The mines of **Jales** (Au-Ag), **Vale das Gatas** (W-Sn) and **Argoselo** (Sn-W) located in the north of Portugal were chosen for this purpose.

2. Objectives of the study

The objectives of this study were a) to achieve the chemical characterization of the mine sites, b) to evaluate the extent of pollution in soils impacted by mining activities and by erosion of the tailings and c) to identify the geochemical characteristics of the AMD formed in the abandoned mines and on its tailing deposits. Arsenic was chosen as one of the main targets for this research due to the following reasons: a) arsenopyrite is one sulphide extensively present in the paragenesis of the three mines b) soils downstream of the tailings are a major repository for As released by mining and plants easily absorb As, so that high-ranking concentrations may be present in food (Walsh et al., 1977) and c) arsenic is considered a priority harmful pollutant element above certain levels both for humans and for ecosystems (Glanzman and Closs, 1993).

In recent past years arsenic has gained an increased attention mainly because high natural concentrations have been commonly found in geological materials of many countries (Smith et al., 1998; Smedley and Kinniburgh, 2002; Nickson et al., 2000; McArthur et al., 2001; Chakraborti et al., 2002; Bose and Sharma, 2002, among others). Moreover, arsenic occurrences related to anthropic activities are also an important source of As to the environment. From these, mining and ore dressing processes carried out on the metallic ore mines (which commonly contain sulphides) produce arsenic-rich wastes that are greatly responsible for high levels of this element in tailings and open-air impoundments. These tailings are exposed to the atmospheric conditions for long periods of time in places where the surface runoff and water percolation may easily cause the leaching of most of their minerals, being the main source of AMD. This process can lead to the contamination of the surrounding topsoils,

being the consequences particularly worrisome when mining and ore treatment operations take place nearby of populated areas.

Inorganic arsenic is a recognized human carcinogen causing urinary bladder, lung and skin cancers (IARC, 1987). Moreover, epidemiological data have shown a link between environmental As exposure and an increased risk of cancer in human populations (ATSDR, 1993). Chronic long-term exposure to As has been associated with other human health effects including, hyperkeratosis, spotted melanosis, skin pigmentation and lung cancer (Tokonaga et al., 2002). It is also thought that inorganic arsenic can damage DNA.

3. Geology and mining

According to the palaeogeographic and tectonic zonography established for the Hercynian Chain of the Hesperic massif, the study area is located in the Central Iberian Zone (Lotze, 1945 and Julivert et al., 1974). From the geological point of view these mines are accommodated in Cambrian and Silurian formations lithologically constituted mainly of schists, greywackes and quartzites which coexist with different types of granites (Figure 1).

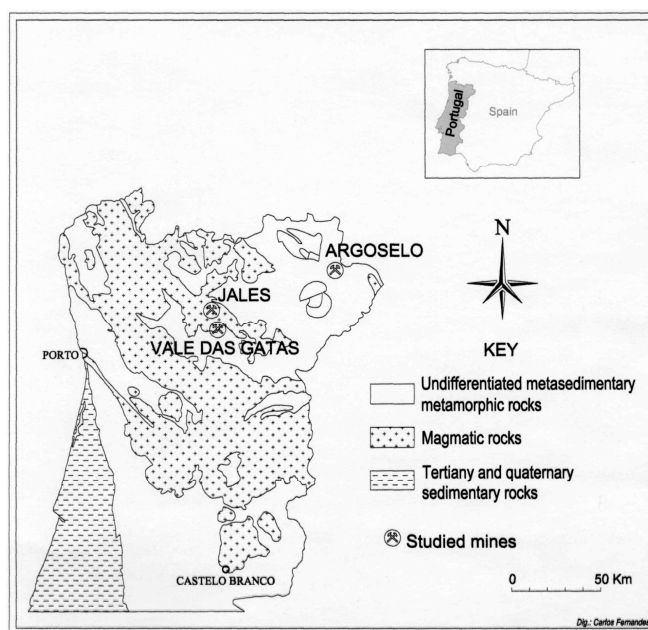


Figure 1 – Geology of the north of Portugal including the studied mines (sampling grid in Santos Oliveira and Ávila, 1995, 2003)

The mineralization of Jales is constituted of arsenopyrite, pyrite, galena, sphalerite, among other sulphides, sulphosalts and gold. The mineralization of Argoselo is mainly constituted of cassiterite, wolframite, scheelite and sulphides. Regarding the Vale das Gatas mine, the mineralization is mainly composed of wolframite (hubnerite, but also ferberite), cassiterite and schellite. Gold and silver were extensively exploited in the Jales mine, being the concentration of gold and sulphides obtained by flotation, whilst tin-tungsten ores were recovered in the Vale das Gatas and Argoselo mines using hydrogravitic procedures followed by froth flotation, magnetic and electrostatic separation in order to obtain a final wolframite–cassiterite–scheelite concentrate.

Huge amounts of tailings resulting from the mining operations carried out during many years are disposed at surface today (3 to 4 millions of tons in Jales, 0.5 millions of tons in Vale das Gatas and 0.8 millions of tons in Argoselo; see Table 1). These materials roughly have the same composition of the mineralization being mainly composed of (usually fine) inert and “sterile” minerals together with significant amounts of sulphides (pyrite, FeS_2 ; arsenopyrite, FeAsS ; pyrrhotite, FeS ; galena, PbS ; sphalerite, ZnS ; chalcopyrite, CuFeS_2) and some other minerals hosting trace metals (and metalloids).

Table 1- Characteristics of the Jales, Vale das Gatas and Argoselo tailings: tonnage, grain size and mineral paragenesis.

Mines	MTons	Grain size	Mineral Paragenesis
Jales	~3-4	Clay, silt	Arsenopyrite, pyrite, galena, sphalerite, chalcocopyrite, Ag sulphosalts and Au.
V.Gatas	~0.5	Silt, sand, some clay	Cassiterite, wolframite, scheelite arsenopyrite, pyrite, pyrrothite, chalcocopyrite, sphalerite, galena, stannite and sulphosalts.
Argoselo	~0.8	Clay, silt, some sand	Cassiterite, wolframite, scheelite, pyrite, arsenopyrite, chalcocopyrite and sphalerite.

When these mines ceased their activity no environmental remediation measures were taken till present time. The degree of soil and land use by the local populations, particularly of those who live nearby the old mines is appreciable taking in account that soils surrounding the mine sites have some agricultural aptitude (fruit-growing, horticulture, cultivation of cereals and, in places, grape cultivation for Oporto wine) and are incorporated in areas of cattle pasturing.

4. Materials and Methods

To investigate the impact caused by tailings in the surrounding soils of the mine sites 94 tailing, 203 soil and seepage water samples were collected in their surroundings. Tailing and soil samples were oven dried at 40°C, mixed, homogenized, and sieved through a < 200 mesh screen for chemical analysis. The fine-grained (<200 mesh) fraction of the Vale das Gatas samples was submitted to multielement analysis in an accredited Canadian lab (ACME Anal. ISO 9002 Accredited Lab—Canada). A 0.5 g split was leached in hot (95 °C) aqua regia (HCl–HNO₃–H₂O) for 1 h. After dilution to 10 ml with water, the solutions were analysed by ICP-ES for a high number of chemical elements, which included Ag, Al, As, Au, Ba, Bi, Ca, Co, Cr, Cu, Fe, Ga, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Sr, Th, Ti, U, V and Zn.

Tailing and soil samples from Argoselo and Jales were analysed in the S. Mamede de Infesta LNEG accredited lab. For trace metal analysis, a 0.5 g split was leached in hot (95°C) aqua regia (HCl–HNO₃–H₂O) for 1 hour. Although not all minerals are decomposed during aqua regia digestion, for the purposes of the study the results obtained for heavy metals with this extraction are considered as total concentrations due to the fact that hot aqua regia totally decomposes sulphides. After dilution to 10 mL with deionized water, the solutions were analysed for Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ni, P, Pb, Sb, V, Y, and Zn by DCP (conductive plasma emission spectrometry). Tin and W were analysed separately by X-ray fluorescence (XRF). Mineral constituents of selected solid materials were submitted to mineralogical and microanalytical studies with a Camebax microprobe.

Water samples were analysed without pre-concentration. Unacidified samples were analysed using a Dionex 1000i ion chromatography (IC) Work33 station to determine chloride, nitrate and sulphate concentrations. The concentrations of major cations and trace elements in acidified waters were determined by ICP-MS in the LNEG accredited lab. Reagent blanks and duplicate samples were inserted into each batch for quality control (Ramsey et al., 1987). The detection limit for the analysed trace metals was about 0.05-10 mgL⁻¹.

A Sequential Selective Chemical Extraction (SSCE) scheme was used to define the metal-bearing phases of metals in some selected solid samples followed six steps according to Cardoso Fonseca and Ferreira da Silva (1998). The reagents used in this procedure and the mineralogical phases extracted in each step were: Step 1- Ammonium acetate: water soluble and cations adsorbed by clay and elements co-precipitated with carbonates; Step 2- Hydroxylamine hydrochloride: Mn oxyhydroxides; Step 3- Ammonium oxalate (dark): amorphous Fe oxides; Step 4 - H₂O₂ 35%: organic matter and sulphides (primary sulphide minerals cannot be totally leached out in this step); Step 5- Ammonium oxalate under U.V. radiation: related to crystalline Fe oxides; Step 6- Three-acid mixture (HCl+HNO₃+HF): residual fraction and also resistant oxides and sulphides.

The methodology of the geochemical data interpretation involved one approach of comparison of metal concentrations which was based on the calculation of an index that

averages the accumulation of each metal in a sample. To evaluate the degree of trace metal contamination, an Enrichment Index (EI) (Chon et al., 1995; Ferreira da Silva et al., 2005; Kim et al., 1998; Lee et al., 1998; Nishida et al., 1982) was computed averaging the ratios of the element concentration (mg kg^{-1}) to the permissible level for each element based on hazard criteria. In this study, six elements (As, Cd, Cu, Pb, Zn and Sb) were selected to calculate the enrichment factor in each sample. The permissible level is the element concentration in the soil, from which crops produced are considered as unsafe for human health (As 20 mg kg^{-1} ; Cd 3 mg kg^{-1} ; Cu 100 mg kg^{-1} ; Pb 100 mg kg^{-1} ; Zn 300 mg kg^{-1} and Sb 5 mg kg^{-1} (Kloke, 1979; Reimann and Caritat, 1998). This index is useful to assess to the degree of multiple element enrichment. An enrichment index over 1.0 indicates that, on average, metal concentrations are above of the permissible level, though the element enrichment may result from anthropogenic inputs and/or natural geological sources (Nimick and Moore, 1991).

5. Results and discussion

5.1. Assessment of the extension of pollution.

Table 2 shows the mean contents determined for selected metals in the tailings. From these, As, Pb, Zn, Cu, Cd, Sn, (Sb), (Bi) and (Ag) exhibits concentrations of significant magnitude (from hundreds to tens of thousands of mg Kg^{-1}). It is interesting to note that basophile elements, like Cr, Ni and Co stand with background concentrations indicating that the ore structures do not contain significant amounts of minerals hosting these deleterious elements.

The Argoselo tailings seem to constitute the most harmful situation if one reports to the total concentrations determined and to the diversity of anomalous elements. However, the Jales site must be also emphasised due to the huge size of its tailings and to the very fine grain of its materials (see Table 1), being this a characteristic that facilitates mineral weathering and metal leaching.

Geochemical data appear to be highly correlated with the tailing mineralogy, being particularly noted the influence of the formation of secondary minerals. From microprobe analyses, Fe arsenates (scorodite), hydrated Fe–As oxides, hydrated Fe oxides, Pb–Fe arsenates, Mn hydroxides and Fe sulphates were identified in Vale das Gatas whilst Fe oxides, scorodite, covellite, Ca, Pb and Fe sulphates and argentite were determined in Argoselo.

Table 2 - Average contents of selected chemical elements in the Jales, Vale das Gatas and Argoselo tailings. Element contents in mg Kg^{-1} unless stated.

Mines	As	Pb	Zn	Cu	Cd	Ag	Sb
Jales	2960	810	1150	67	29	3	<10
V.Gatas	7857	5435	1615	1217	20	139	<10
Argoselo	14434	629	8543	15757	926	146	743
Mines	Cr	Ni	Co	Bi	Sn	Fe(%)	Mn
Jales	181	13	5	nd	nd	2.0	434
V.Gatas	23	11	5	688	3098	4.0	647
Argoselo	124	nd	nd	nd	2867	9.0	676

nd- No values determined

Chemical data found for *soils* are shown in Table 3. These results show evidences of chemical contamination which are assigned to the influence of the mine tailings and other mine residua disposed nearby. It also can be seen that the chemical element associations and the total concentrations are slightly different in each case, depending on the mineral paragenesis that exist in the ore.

Table 3 - Contents of selected elements in soils from the Jales, Vale das Gatas and Argoselo mining areas related to the tailing location (contents in mg Kg⁻¹).

Approximate distance from the tailing to soil samples	As	Pb	Zn	Cu	Cd	Cr	Ni	Co	Sn	Ag
Jales <600 meters	440	170	161	39	3.3	31	25	10	nd	<0.2
Jales 600-800 meters	258	114	134	32	0.9	124	25	8	nd	<0.2
Jales >800 meters	74	70	94	18	0.7	165	15	6	nd	<0.2
Vale das Gatas <200 meters	173	212	161	77	1.2	46	21	10	72	3.9
Argoselo <200 meters	1634	11	445	32	~3	59	25	8	nd	~1
Argoselo 200-500 meters	423	<10	301	14	<1	83	22	11	nd	<0.2
Argoselo 500-700 meters	102	24	128	53	<1	107	30	11	nd	<0.2
Argoselo >700 meters	80	23	112	38	<1	94	26	13	nd	<0.2
Background reference values for soils (medians)										
Non agricultural soils (Rose et al,1979)	8	17	36	15	0.5	43	17	10	10	nd
	5	17	70	25	0.3	80	20	10	4	0.07
World soils (Reimann and Caritat, 1998)										
nd- No values determined										

Metal concentrations are usually very high in soils nearby the mine sites but they tend to decrease rapidly with the distance to the polluting source (tailing). The geochemical aureoles are, in general, less than 1 km (Table 3) but some anomalous results beyond this distance were found in Jales. This behaviour is greatly related with the action of strong winds that frequently affect the area which easily remove and transport the very fine materials (minerals) away from the tailing surface to the surrounding soils. Arsenic, Pb, Zn, Cu and Cd are the most critical elements taking in account the magnitude of contents determined and the extension and gradients of dispersion in the soils.

The estimated EI values for the soils samples are high for all case studies (Table 4). As expected, the highest values occur in eroded soils collected in the proximity of the tailings indicating that these residual mineral deposits are the main source of chemical contamination. In Argoselo, the EI calculated for representative samples being distant < 200 m from de tailing varies from 1.62 to 69.9 showing that soils are metal enriched at a level likely to be toxic, as defined by Nimick and Moore (1991). Even for samples taken definitely away from the tailings site values are >1 (1.25<samples 200-500m<8.06 and 0.51<samples distant more 500m<4.21). In the Jales mine EI varies between 0.61 and 11.75 and in Vale das Gatas ranges between 0.67 and 6.47. Sulphides are still abundant at surface around the mine and its oxidation gives rise to a variety of neoformed secondary minerals on these sites.

Table 4 - EI (Enrichment Index) for soils in the study areas.

Approximate distance from the tailing to soil samples	EI
Jales <600 meters	0.61 to 11.75
Vale das Gatas <200 meters	0.67 to 6.47
Argoselo <200 meters	1.62 to 69.9
Argoselo 200-500 meters	1.25 to 8.06
Argoselo > 500 meters	0.51 to 4.21

Most trace elements appear to be associated in soils, in great extent also with secondary mineralogical phases as above (in general, of low chemical stability) which, in turn, can facilitate the secondary chemical element mobility and dispersion. This trend was supported by the application of techniques of sequential selective chemical extraction (SSCE) to some soil samples of the Jales and Vale das Gatas mines. In the first case, the results show that significant proportions of As are easily separated during the initial steps of the procedure, with

40% being liberated during the ammonium acetate and hydroxylamine chloridrate steps (in association with mineralogical phases related to ion-exchange positions, carbonates and to Mn oxides). In Vale das Gatas the chemical data show that As is mainly extracted by ammonium oxalate dark (64%) which corresponds to a mineralogical phase related to hydrated Fe-As oxides and hydrated Fe oxyhydroxides. In addition to this, 21% of the total As is extracted by ammonium oxalate U.V., which is the mineralogical phase corresponding to the Fe arsenates or Fe oxyhydroxides; only 15% As is extracted by hot mixed acid attack, this amount being associated to the presence of arsenopyrite in the sample.

However, it must be stressed that chemical mechanisms linked to AMD also contribute to the secondary dispersion of the metals with subsequent precipitation of hydroxide, oxyhydroxide and hydroxysulphate phases from aqueous species, as pH increases and to the adsorption of metals onto neoformed mineral surfaces (iron and manganese coatings, for example), according to Nordstrom (1982) and Chapman et al. (1983). For this, rain water together with moisture are powerful metal dispersive agents in soils as they percolate within the tailings causing weathering of sulphide-rich minerals, with generation of AMD. The chemical composition of the acid effluents is reported in Table 5. The high SO_4^{2-} and metal concentrations found in the acidic leachate from the huge waste piles of the three case studies are indicative of oxidation and solubilisation of pyrite and the accompanying sulphides (chalcopyrite, sphalerite, and arsenopyrite).

Table 5 - Hydrochemistry of the seepage waters from the Jales, Vale das Gatas and Argoselo sites.

	pH	Cond. ms cm^{-1}	SO_4^{2-} mg L^{-1}	Ca mg L^{-1}	Mn $\mu\text{g L}^{-1}$	Pb $\mu\text{g L}^{-1}$	Zn $\mu\text{g L}^{-1}$	Cd $\mu\text{g L}^{-1}$	Cu $\mu\text{g L}^{-1}$	As $\mu\text{g L}^{-1}$
Jales	3.4	nd	393	63	12620	20	15070	194	6	bdl
V.Gatas	3.2	1285	694	76	10700	0	46500	1000	12300	946
Argoselo	3.7	1857	1465	198	8700	61	159000	2700	60000	nd

nd- No values determined
bdl – below detection limits

An excellent correlation was found between the electrical conductivity and the dissolved SO_4^{2-} ($r = 0.999$, $p < 0.05$) for Argoselo and Vale das Gatas waters, which confirms conductivity as a good indicator of the dissolved ions of the stream waters caused by AMD. Seepage samples have pH values typical of AMD waters (around 3), high concentrations of dissolved sulphate and of most of metals. However, it is interesting to emphasize the high As contents found for the case of the Vale das Gatas waters. The low pH determined in these seepage waters keeps As in solution, facilitating its remobilization and increasing its spatial distribution. However samples taken in the main stream, in the place where the seepage waters mix with the more oxygenated stream waters, do not reveal high As concentrations (pH 5; 98 mg L^{-1} SO_4^{2-} and 1 $\mu\text{g L}^{-1}$ As), mainly due to the co-precipitation with Fe (III) oxyhydroxides in the tailing basement and also due to the scorodite formation (determined by microprobe analysis). It was shown that this secondary As mineral is the most environmentally important secondary phase associated to arsenopyrite oxidation in the Vale das Gatas site. This result agrees with conclusions of other authors (Boyle and Jonasson 1973; Dove and Rimstidt 1985) who state that arsenopyrite breaks down through the action of oxygen, water and catalytic bacteria (e.g. *Ferrooxidans* sp.) in the supergene environment, with scorodite being one of the major products of arsenopyrite oxidation. Meanwhile, Valente and Leal Gomes (1998) state that these neoformation mechanisms limit the downstream effects of the acid drainage since they fixate efficiently some of the contaminant elements.

A ferruginous crust collected on the base of the Vale das Gatas tailing revealed high levels of metals and As (As = 11500 mg kg^{-1} ; Cu = 1030 mg kg^{-1} ; Cd = 7.8 mg kg^{-1} ; Fe = 25.1%; Pb = 1902 mg kg^{-1} and Zn = 836 mg kg^{-1}) confirming the transference of these elements from the tailing. In the Vale das Gatas stream, to where the tailing drains, one iron coating was sampled. The comparison of the coating chemistry (26.6% Fe; 904 mg kg^{-1} Cu; 4193 mg kg^{-1} Pb; 172 mg kg^{-1} Zn; 182 mg kg^{-1} Mn and 61600 mg kg^{-1} As) with that of a water sample collected in the same place (pH 5; 98 mg L^{-1} SO_4^{2-} ; 30 mg L^{-1} Ca; 1075 $\mu\text{g L}^{-1}$ Fe; 1175 $\mu\text{g L}^{-1}$ Cu; 24 $\mu\text{g L}^{-1}$ Pb;

7650 $\mu\text{g L}^{-1}$ Zn; 1075 $\mu\text{g L}^{-1}$ Mn; 100 $\mu\text{g L}^{-1}$ Cd and 1 $\mu\text{g L}^{-1}$ As) suggests that the decrease of metals is mostly related to the co-precipitation of these elements with iron (Fe–As oxides and Fe arsenates) and manganese due to pH increment. This strongly supports that chemical reactions of leaching and chemical precipitation are taking place in areas surrounding the Vale das Gatas mine.

From an environmental point of view, reference values for arsenic in soils have been proposed elsewhere by some authors, either for toxic limits of polluted soils (Alloway, 1993; Canadian Environmental Quality Guidelines, 2002), or for contents exceeding admissible concentrations in agricultural soils (Salomons et al., 1995), as it can be seen in Tables 6 and 7. Contents above these limits were found in some places of soils around the Jales, Vale das Gatas and Argoselo mines (compare these values achieved with those of Tables 6 and 7).

Table 6 - Metals in polluted soils according to some authors (contents in mg Kg^{-1}).

	Canadian Enviro. Quality Guidelines	Slight contamination (UK) (Alloway, 1993)	Effective contamination (UK) (Alloway, 1993)	Tolerable limits (Germany) (Alloway, 1993)
As	12*	30-50	50-100	20

* all kind of soils (agricultural, residential, industrial and commercial land use)

Table 7 - Proposal of acceptable maximal concentrations for trace elements considered as phytotoxic in world agricultural soils (Salomons et al., 1995).

Element	Austria mg Kg^{-1}	Canada mg Kg^{-1}	Poland mg Kg^{-1}	Japan mg Kg^{-1}	UK mg Kg^{-1}	Germany mg Kg^{-1}
As	50	25	30	15	20	40(50)

6. Conclusions

With the present study it was intended to investigate and quantify the impact in the surrounding environment of some abandoned mines in Portugal. This was achieved with basis on the geochemical analysis of (mineral) tailing materials, soils and surface and seepage waters. Soils under the influence of the mining areas occur, in general, contaminated in metals and metalloids, (mainly arsenic), on close dependence of the ore paragenesis.

The controlling factors of the metal geochemical dispersion in this kind of soils are mainly related to the: a) grain size and mineralogical-chemical composition of the tailing materials (presence of sulphides and other "polluting" minerals); b) physical and geotechnical stability of the tailings; c) erosion agents, with predominance of the wind which can transport and disperse fine materials from the tailings surface (in particular, this is the case of Jales and Argoselo); d) action of surface acid percolating tailing waters which can leach, mobilise and transport metals in solution and in colloidal forms and e) mineralogical and physical-chemical characteristics of the soil (organic matter, clays, Fe-Mn oxides, pH, Eh, etc).

Many of the leached chemical elements co-precipitate with, or adsorb to, the iron rich precipitates. An approach based on chemical sequential extraction demonstrates that the distribution and accumulation of trace metals is related to sulphides but also to amorphous or poorly crystalline iron oxide geochemical phases. However, it was also noticed that a significant proportion of the trace metals is linked to exchangeable and acid-soluble species, upon which desorption and ion-exchange reactions may originate the release of these readily mobile phases. Metals contained in these phases can be explained with some probability by the precipitation of hydrated metal sulphates. Solubilisation of these salts appears to be one of the main sources for most of the metals in solution, being related with strong acidity of the tailing leachates. These salts may degrade water quality, particularly during severe winters which are not rare in the mountainous mine areas. Geochemical and hydrochemical results clearly indicate that acid mine drainage generated around the mines is the main agent of chemical contamination of the soils around the Jales, Argoselo and Vale das Gatas mines.

The degree of soil and land use by the local populations, particularly of those who live nearby the old mines is appreciable taking in account that these soils have some agricultural aptitude (fruit-growing, horticulture, cultivation of cereals) and are incorporated in areas with cattle pasturing. These conditions of man subsistence versus the results obtained with this study recommend that soils (and waters) of mining areas should be carefully surveyed in the country

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