



## Heavy metal pollution in mine–soil–plant system in S. Francisco de Assis – Panasqueira mine (Portugal)



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### ABSTRACT

The active Panasqueira mine is a tin–tungsten (Sn–W) mineralization hosted by metasediments with quartz veins rich in ferberite. The economic exploitation has been focused on wolframite, cassiterite and chalcopyrite. The mineralization also comprises several sulphides, carbonates and silver sulphosalts. The mining and beneficiation processes produces arsenic-rich mine wastes laid up in huge tailings and open air impoundments that are the main source of pollution in the surrounding area, once the oxidation of sulphides can result in the mobilization and migration of trace metals/metalloids from the mining wastes into the environment, releasing contaminants into the ecosystem.

A geochemical survey was undertaken, in order to investigate the environmental contamination impact on agricultural and residential soils in S. Francisco de Assis village due to the mining activities. Rhizosphere samples, vegetables (*Solanum tuberosum* sava and *Brassica oleracea* L.) which constitute an important part of the local human diet, irrigation waters and road dusts were collected in private residences in S. Francisco de Assis village. According to the Ontario guidelines (Ministry of Environment, 2011), the Arsenic contents in the rhizosphere soils exceed 20 times the reference value for agricultural soils (11 mg kg<sup>-1</sup>). The result obtained showed that some edible plants frequently used in the region could be enriched in these metals/metalloids and may represent a serious hazard if consumed. The potatoes tend to have a preferential accumulation in the leaves and roots while in cabbages most elements have a preferential accumulation in the roots. An index of the risk for residents, due to ingesting of these metals/metalloids, by consuming vegetables grown around the sampling area, was calculated and the result indicates that the inhabitants of S. Francisco de Assis village are probably exposed to some potential health risks through the intake of arsenic, cadmium and also lead via consuming their vegetables.

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### 1. Introduction

The demand for ore comes from the beginning of the human existence and this activity plays a key role for human survival and development. Europe have an unquestionably importance in the world economy and mineral extraction plays an important role in the supply as also in the consumption of all groups of explored minerals. Portugal holds a rich and complex geology, which gives it a considerable mineral potential, although this sector only contributes with 1% for the Portuguese Gross Domestic Product (GDP).

The main mineral resources in Portugal are copper (Cu), tin (Sn), tungsten (W), lithium (Li), gold (Au), iron (Fe), zinc (Zn), lead (Pb), uranium (U), coal, raw materials for construction and ornamental stones. Portugal is a country with a long mining tradition; it had

in the past and still has a strong mining activity. Land pollution due to mining activities is a major issue in many European countries and Portugal is not an exception (Santos Oliveira and Ávila, 1995, 2003; Valente and Leal Gomes, 1998; Bobos et al., 2006; Luís et al., 2009; Santos Oliveira et al., 2002; Ávila et al., 2005, 2008; Salgueiro et al., 2008; Grangeia et al., 2011; Candeias et al., 2011a,b; Ferreira da Silva et al., 2005; Antunes et al., 2002; Pinto et al., 2004; Carvalho et al., 2009, 2012; Gomes et al., 2010).

The extraction of metals from sulphide minerals usually results in large amounts of waste materials, tailings, and acid mine drainages, which often contain high concentrations of potentially toxic elements (PTE – As, Cu, Zn, Cd as an example) (Moore and Luoma, 1990; Boulet and Larocque, 1998; Jung, 2001; Naicker et al., 2003). Metals/metalloids can be dispersed downstream due to the weathering and erosion process of tailings. Thus, the extent and degree of heavy metal contamination around the mines varies depending upon geochemical characteristics and mineralization of tailings.

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High concentrations of heavy metals can be found in and around abandoned and active mines due to the discharge and dispersion of mine waste materials into nearby soils, food crops and stream sediments (Lee et al., 2001; Jung, 2001; McKenzie and Pulford, 2002; Witte et al., 2004). This will “eventually” lead to a loss of biodiversity, amenity, and economic well-being as well as pose a potential health risk to residents in the vicinity of the mining area (Verner and Ramsey, 1996; Lee et al., 2001; Wong et al., 2002; Galán et al., 2003).

Soils are very prone to contamination from hydrological sources and also from atmospheric sources. When soils are the receptor of tailings drainage coming from metal mining and smelting this waste disposal causes a major impact, posing serious environmental concerns. The smelter emissions as well as wind-blown dust from mine tailings and smelter slag dumps are generally the main point sources of metal/metalloid (As, Cd, Cr . . .) soil pollution (Ettler et al., 2005, 2009, 2011, 2012; Kříbek et al., 2010; Šrámek et al., 2010; Vítková et al., 2010). Exposure to these hazardous elements may have different pathways, through the ingestion of vegetables grown on contaminated soils or through dust inhalation and dust adhering to plants. According to several authors (Bosso and Enzweiler, 2008; Chen et al., 2009; Douay et al., 2008; Juhasz et al., 2011; Roussel et al., 2010; Ettler et al., 2012) the studies dealing with the bioavailability and bioaccessibility of metals/metalloids contaminants in highly-polluted soils are extremely useful in understanding the possible effect on biota, and particularly on human health due to the exposure to those contaminants (Banza et al., 2009; Roussel et al., 2010; Coelho et al., 2007).

In a previous paper from the same authors (Ferreira da Silva et al., 2013) the environmental contamination impact on S. Francisco de Assis (SFA) agricultural and residential soils due to the mining activities has been investigated.

The objectives of this study are: (a) the assessment of the levels of soil contamination in respect to median concentrations of PTE in the region; (b) the determination of the associations between the different PTE and their spatial distribution; (c) the identification of possible sources of contamination that can explain the spatial patterns of soil pollution in the SFA area; (d) determine the associations between the different toxic elements and identify the possible contamination sources that can explain the risk to the SFA population by the ingestion of some metals/metalloids by consuming vegetables that grow in their yards located in the mine vicinity.

## 2. The study area

The Panasqueira mine is located in Central Portugal (Fig. 1a). Nowadays the economic exploitation is located in Barroca Grande as well as the beneficiation plant. S. Francisco de Assis is a little village, with 16.24 km<sup>2</sup> and 692 inhabitants, located downstream the Barroca Grande tailings deposit and impoundments. The topography ranges in altitude from 350 to 1080 m (Reis, 1971), with deep valleys. The streams are generally dry in the summer and flooded in the winter.

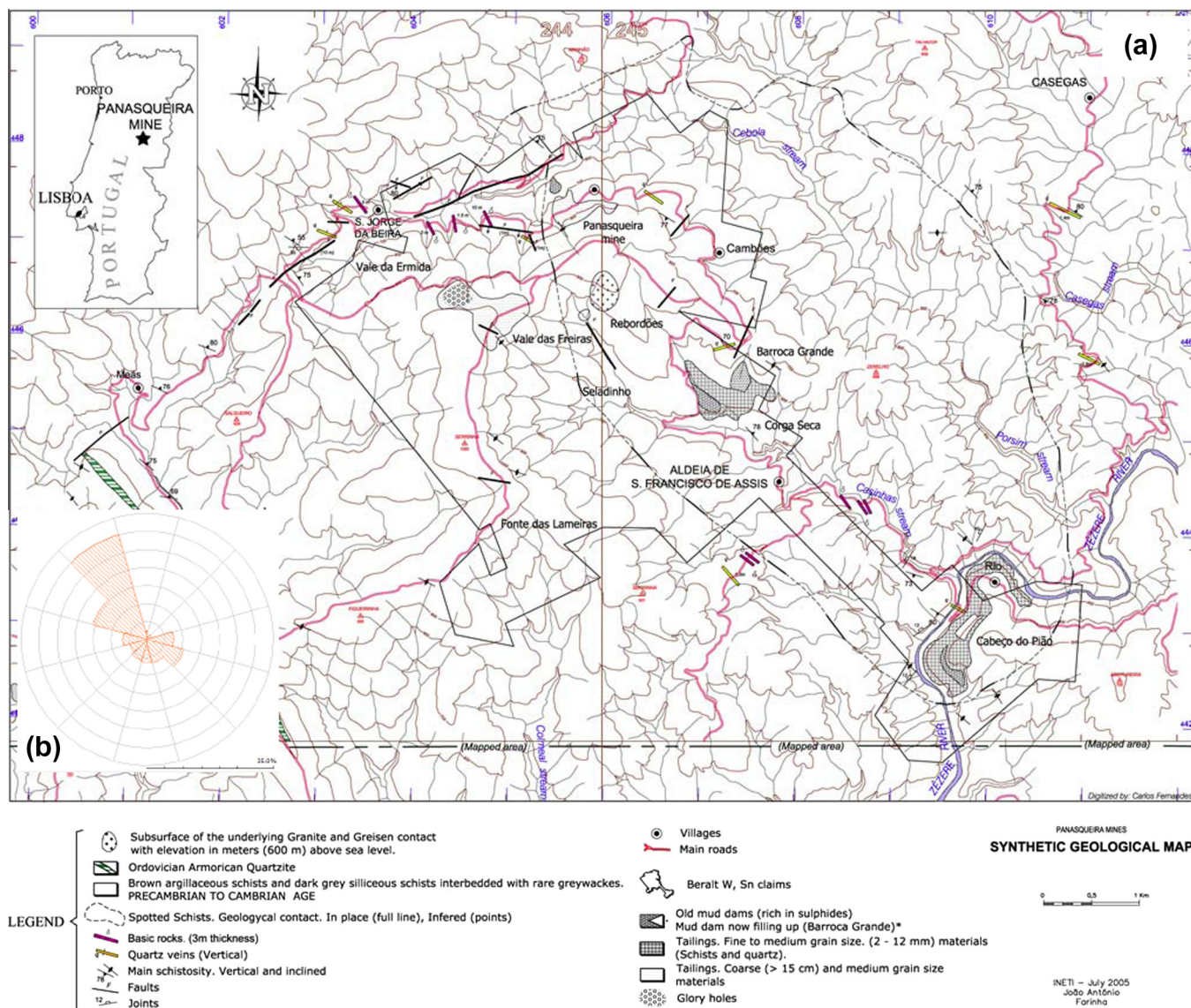
Climate, which can be an important instability factor, is aggressive in the Panasqueira region, with hot and dry conditions during the summer and very cold, rainy, and windy conditions in the winter. The mean annual rain precipitation in the region is 1200–1400 mm; snow fall is frequent, particularly above the altitude of 700 m. The annual mean temperature is ≈12 °C, ranging from ≈0 °C during the winter to about ≈30 °C in summer. The evapotranspiration in this region is around 1080 mm (Ávila et al., 2008). Table 1 shows the wind speed in Barroca Grande at an elevation of 80 m (Costa, 2004; Costa and Estanqueiro, 2006a,b). Results point out that NNW is the preferential wind direction in the area (Fig. 1b), and as we know the wind that blows from NW goes

to SE, and that is precisely the direction of S. Francisco de Assis regarding the Barroca Grande tailing position.

**Geology and Mineralization:** The Panasqueira ore deposit is a typical example of a Sn–W hydrothermal mineralization associated with the Hercynian plutonism. A detailed description of the local geology was presented in Ávila et al. (2008). The Panasqueira deposit consists of a series of stacked, sub-horizontal, hydrothermal quartz veins intruding into the Beira schists formation of upper Precambrian–Cambrian age and shales. The paragenesis is complex. Four stages of mineral formation are generally accepted by most of the authors who have studied this deposit: 1st stage: the oxide–silicate phase (quartz, wolframite; cassiterite); 2nd stage: the main sulphide phase (pyrite, arsenopyrite, pyrrhotite, sphalerite, chalcopyrite); 3rd stage: the pyrrhotite alteration phase (marcasite, siderite, galena, Pb–Bi–Ag sulphosalts); and 4th stage: the late carbonate phase (dolomite, calcite) (Breiter, 2001; Corrêa de Sá et al., 1999; Correa and Naique, 1998; Noronha et al., 1992). At Panasqueira, more than 65 minerals, including sulphides, sulphosalts, oxides, carbonates, silicates, phosphates, and tungstate minerals, have been identified (Kelly and Rye, 1979). In general, the most common minerals in addition to quartz are: wolframite, pyrite, pyrrhotite, arsenopyrite, chalcopyrite, cassiterite, beryl, mica, and fluorite. The Panasqueira mine has many rare minerals that can only be observed microscopically, making it a site of specific scientific importance.

**Mining Activity and Potential Environmental Considerations:** the Panasqueira hydrothermal mineralization is the biggest Sn–W deposit of the Western Europe, and has been in operation since 1896 to the present date. The economic exploitation mainly focused on wolframite, cassiterite, and chalcopyrite, the last two as by-products. On mean the “tout-venant” contains 0.3% WO<sub>3</sub>; the three final concentrates contain 75% WO<sub>3</sub>, 72% SnO<sub>2</sub>, and 22% Cu together with significant amounts of silver (Ag). At the present time, exploitation is focused at Barroca Grande. The long history of exploitation and ore treatment operations are testified by the presence of tailings and other debris (Cavey and Gunning, 2006; Ávila et al., 2008). Nowadays, the waste rock is still placed in the Barroca Grande tailings area. The mine wastes were and still are discharged in a huge tailings pile and in two mud dams, one is old and deactivated, although stabilized in geotechnical terms, while the other (smaller and disposed over the tailings) is still being fed with steriles (some rich in sulphides, arsenopyrite is the main sulphide present) obtained from the ore dressing operations. Mining exploitation and ore processing operations left and continue to leave behind huge tailings, being Barroca Grande ≈7 Mm<sup>3</sup> with two mud dams ≈1.2 Mm<sup>3</sup>, one of the main tailings deposit in the mine area. The mining and beneficiation processes at the site produces metal/metalloid rich mine wastes. According Ávila et al. (2008) the rejected materials from the ore processing, containing high concentrations of metals, stored in the open-air impoundments are responsible for the continuous generation of acid drainage. Barroca Grande impoundment shows high concentrations of As, Cd, Cu and Zn. The analysis of the fine grained materials existing in the two Barroca Grande open impoundments reveals the existence of arsenopyrite, ferberite, sphalerite, pyrite, chalcopyrite, natrojarosite, scorodite and hematite.

These tailings and impoundments are exposed to atmospheric conditions. Surface runoff and water percolation leach the tailings and form AMD. The tailings piles at Barroca Grande are adjacent to the small, but perennially flowing, Casinhas Stream, which drains to the Zêzere River. The unconfined tailings and open impoundments are the main source of pollution in the surrounding area once the oxidation of sulphides can result in the mobilization and migration of trace metals from the mining wastes into the environment, releasing contaminants into the ecosystem. The effect of Panasqueira mining activities and the metals release from



**Fig. 1.** (a) Synthetic map showing the location of Panasqueira mining area and the main geological units (Farinha, 2005); (b) Modeled windrose of Barroca Grande, extracted from the CD-ROM "Wind potential Atlas for Continental Portugal-Version 1.0". ISBN: 972-676-196-4. National Institute of Engineering, Technology and Innovation I.P. (INETI) production, September 2004.

**Table 1**  
Wind speed in Barroca Grande ( $\text{m s}^{-1}$ ) at 80 m.

Sector	0	30	60	90	120	150	180	210	240	270	300	330	Mean
Wind speed	3.55	1.75	3.66	4.93	4.48	3.05	3.28	4.03	5.89	7.93	8.19	8.07	6.21

acid mine waters to ground waters and stream sediments is dynamic and actual. Soils, downstream Barroca Grande tailings deposit, will be a major repository for the heavy metals released being the SFA village the most affected.

### 3. Materials and methods

#### 3.1. Field sampling

In order to investigate the environmental contamination impact on agricultural and residential soils of SFA due to the mining activities

and to understand the geochemical behaviour of a set of chemical elements in this mining region, we selected four sampling media (rhizosphere soils, irrigation waters, road dusts and horticultural plants – Fig. 2). These media constitute the most important means for the geochemical characterization of the studied area and also for assessment of the impact of anthropogenic activities on different ecosystems, including the public health of the inhabitants. Vegetables and rhizosphere soil samples will define the extent of soil contamination and the metals transfer process from soils to the different parts of the plants once the root system of the plants remove nutrients from the mineral phases





Fig. 2. Location of rhizosphere soils, waters, road dusts and vegetables sampling sites in SFA area (Google Earth image modified).

of the soils. Waters samples will define the influence of soils and human activities in the quality of potable water, for human consumption and for irrigation. Finally, the road dusts samples allow quantifying the wind transfer of the contaminants from tailings and its influence in local soil, vegetables and air quality.

**Rhizosphere soil, dusts and vegetables:** seventeen rhizosphere soil samples (RSS) and 14 edible vegetables (VEG), potatoes (*Solanum tuberosum sava*) and cabbage (*Brassica oleracea* L.), were collected (Fig. 2) in polyethylene bags and brought to the laboratory. In this campaign, thirteen road dusts (RDS) were also collected in the road, inside the village whenever it was possible in the same place where soils, vegetables and waters were taken, with a small broom and stored in polyethylene bags for further analyses. The soil and dust samples were oven dried, before dry sieving, at a temperature of 40 °C, until a constant weight was attained, disaggregated, passed through a 177 µm aperture plastic sieve and milled for chemical analysis. The vegetables samples were washed, dried at a temperature of 40 °C, disaggregated and finely milled.

**Waters:** a total of 6 waters samples (UW) were collected in private houses in S. Francisco de Assis village (Fig. 2). Two of them were picked from the public water supply network and the other four from wells used for irrigation. Samples were collected from each selected site using a clean 1-L acid-washed polyethylene bottle and stored at 4 °C until analyzed. Values of pH, electric conductivity (EC), oxidation–reduction potential (ORP), Dissolved Oxygen (DO), Total Dissolved Solids (TDS) and Salinity (SAL) of the waters were recorded at each site using a multiparametric probe HI9828 with GPS from HANNA Instruments. Samples were filtered on-site through 0.45-µm Millipore membrane filters using an all-plastic pressurized filtering system. The concentrations of HCO<sub>3</sub> were determined in situ by volumetric titration on filtered unacidified samples. Samples for metal analysis were immediately preserved after collection in the field, with pH reduction to 2.0 using HNO<sub>3</sub>, avoiding Fe hydroxide precipitation. All the water samples were stored at 4 °C pending further analysis.

### 3.2. Sample preparation and chemical analysis

**Rhizosphere soil, dusts and vegetable samples:** the fine grained fraction of rhizosphere soils dust and vegetables was submitted to multi-elemental analysis in ACME Anal. ISO 9002 Accredited Lab-Canada. A 0.5 g split was leached in hot (95 °C) aqua regia (HCl–HNO<sub>3</sub>–H<sub>2</sub>O) for 1 h. After dilution to 10 ml with demineralized water, the solutions were analyzed by Inductively Coupled Plasma-Emission Spectrometry (ICP-ES) for 35 chemical elements. Included in this analytical package were silver (Ag), aluminium (Al), arsenic (As), gold (Au), barium (Ba), bismuth (Bi), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), gallium (Ga), mercury (Hg), potassium (K), lanthanum (La), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), phosphorus (P), lead (Pb), sulphur (S), antimony (Sb), scandium (Sc), selenium (Se), strontium (Sr), thorium (Th), titanium (Ti), vanadium (V), tungsten (W) and zinc (Zn). The accuracy and analytical precision were determined using analyses of reference materials (standards C3 and G-2) and duplicate samples in each analytical set. The results were within the 95% confidence limits of the recommended values given for this certified material. The relative standard deviation was between 5% and 10%.

**Soil pH** the procedure adopted was modified from ISO 10390:1994 Soil.; the pH was determined with samples in diluted CaCl<sub>2</sub>, and measures taken 24 h after.

**Soil Organic Matter (SOM):** the procedure was adapted from Reeuwijk (2002); The SOM was quantified in 5 g dried samples, after 20 h in a 430 °C muffle.

**Mineralogy:** the mineral constituents in selected solid media samples were identified by X-ray diffraction (XRD) at LNEG. The mineralogical composition was determined using a Philips X'Pert MPD machine equipped with Cu K $\alpha$  radiation, graphite monochromator automatic divergence slit, and 0.5-receiving slit. A step size of 0.05–2 h, a scan setting of 2–70–2 h, and a 10 s counting time were chosen.

**Waters samples** samples were analyzed without pre-concentration. The analyzed elements include major anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>), major cations (Ca, K, Na, and Mg), as well as a suite of dissolved trace elements (Al, As, B, Cd, Cl, Cu, Fe, Mn, Pb, and Zn). Unacidified samples were analyzed using a Dionex 2000i ion chromatography and a SPECTRAPHYSICS integrator. The concentrations of major cations and trace elements in acidified waters were all determined by mass inductive plasma spectrometry (ICP-MS) in the ACME Anal. ISO 9002 Accredited Lab-Canada. Reagent blanks and duplicate samples were inserted into each batch for quality control (Ramsey et al., 1987). Depending on the concentration levels, typical uncertainties, including all error sources, are less than 6% for the trace elements, and between 2% and 7% for the major anions. The limit of detection for the analyzed trace metals is about 0.05–10 mg L<sup>-1</sup>. In this work As (III) and As (total) were determined by Cathodic Stripping Voltammetry (CSV) (Ferreira and Barros, 2002), using a hanging mercury drop electrode (HMDE). The method requires hydrogen chloride (HCl) 1 M as electrolyte support and the presence of Cu (II), as it involves the preconcentration of a copper–arsenic intermetallic compound at the mercury electrode. The determination of As (T) involves the reduction of As (V) with thiosulfate and the subsequent determination of As (III); As (V) is obtained by difference. The Fe (III) concentration is obtained by difference between the concentrations of Fe (T) and Fe (II), being Fe (II) determined by a colorimetric method and Fe (T) by another method such AEOS-ICP or AAS after reduction of Fe (III). In this work, Fe (III), Fe (II) and Fe (T) will be determined by a colour spectrophotometric-Vis method using FerroZine Iron Reagent. The method requires preservation of water samples by filtration through a 0.2  $\mu$ m membrane and acidification to pH 1 with HCl (0.4% HCl), and storage in the dark (To et al., 1999).

### 3.3. Data analysis

**Enrichment Index** one common approach to estimate metal concentrations is to compute an index that averages the accumulation of each metal in each sample. To evaluate the degree of trace metal contamination in soils the Enrichment Index (EI) (Ávila et al., 2008; Ferreira da Silva et al., 2005; Kim et al., 1998; Lee et al., 1998; Chon et al., 1995; Nishida et al., 1982) was calculated by averaging the ratios of the elements concentrations (mg kg<sup>-1</sup>) to the permissible level (PL). In this study eight elements (As, Cd, Cu, Mn, Pb, V, W, Zn) were selected to calculate the Ei in each sample. The PL is the element concentration in the soil, from which crops produced are considered as unsafe for human health (As = 20 mg kg<sup>-1</sup>; Cd = 3 mg kg<sup>-1</sup>; Cu = 100 mg kg<sup>-1</sup>; Mn = 394 mg kg<sup>-1</sup>; Pb = 85 mg kg<sup>-1</sup>; V = 50 mg kg<sup>-1</sup>; W = 1 mg kg<sup>-1</sup>; Zn = 140 mg.kg<sup>-1</sup>; Ferreira, 2004; Reimann and De Caritat, 1998; Kloke, 1979). This index is useful to evaluate the degree of multiple element contamination. An Enrichment Index over 1.0 indicates that, on average, metal concentrations are above the permissible level, though element enrichment may be from anthropogenic inputs or natural geological sources (Nimick and Moore, 1991).

**Total metal concentration in vegetables** the total metal content for each vegetable (TP) was calculated using the following formula:

$$TP = \frac{(Rdw * Rec) + (Sdw * Sec) + (Ldw * Lec) + (Tdw * Tec)}{Rdw + Sdw + Ldw + Tdw} \quad (1)$$

where Rdw – Root dry weight; Rec – Root element content; Sdw – Stem dry weight; Sec – Stem element content; Ldw – Leaves dry weight; Lec – Leaves element content; Tdw – Tubercle dry weight; Tec – Tubercle element content.

**Estimated daily intake of heavy metals from vegetables:** the estimated daily exposure to metals (EDEM) through vegetables is dependent on metal contents in vegetables, daily vegetable consumption, as well as the body weight. The EDEM was calculated according the formula.

$$EDEM = \frac{\text{daily intake of metals(DIM)}}{\text{body weight}} \quad (2)$$

$$\text{DIM} = \text{daily vegetable consumption} \\ \times \text{mean vegetable metal concentration} \quad (3)$$

considering the average daily intake of metals present in 345 g of vegetables per day for adult residents (Luo et al., 2011; JECFA, 1993); the body weight of an adult resident was set to 60 kg in the present study.

**Calculation of health risk:** in this study, the health risk associated with the consumption of vegetables was defined as the ratio of the estimated daily intake of metals to the reference dose oral (RfDo) for each metal (Luo et al., 2011; JECFA, 1993), as in the following equation.

$$\text{Risk index} = \frac{EDEM}{RfDo} \quad (4)$$

where RfDo represents safe levels of exposure by oral intake for a lifetime (JECFA, 1993). If the risk index was less than 1, no obvious risk is involved. If the risk index was equal to or higher than 1, there is a potential health risk, and related interventions and protective measurements should be taken. In the present study, metals/metalloids concerned were As, Cd, Cu, Pb, and Zn, and only the chronic risk RfDo was considered in the risk assessments (Luo et al., 2011).



## 4. Results and discussion

### 4.1. Geochemical characterization of S. Francisco de Assis village

#### 4.1.1. Rhizosphere soils

Previous study carried out in the area by the same team (Candeias et al., 2012), determined the contents of selected elements in soils samples, collected in two depths, from superficial soil (A) and from a depth of 15–20 cm (B). Superficial soil samples allowed the characterization of superficial contamination coming from the tailings, while B soil samples makes possible the establishment of the local geochemical background. To evaluate the presence of possible local anomalies, the mean, median and maximum contents of the rhizosphere soils were compared with the results obtained for the horizon B.

Table 2 presents the median values of pH and SOM in soil samples. The rhizosphere soils shows a median pH of 6.3 and are classified according to the United States Department of Agriculture ([www.nrcs.usda.gov](http://www.nrcs.usda.gov)) as slightly acid ( $6.1 < \text{pH} < 6.5$ ) while the geogenic soils from horizon B (median pH = 4.2) are classified as acidic soils ( $3.5 < \text{pH} < 4.4$ ). The SOM present median values of 12.2% in rhizosphere soils and 10.2% in horizon B soils, showing that these soils are medium organic soils with  $10\% < \text{SOM} < 30\%$  (Perrin, 1974).

Soil pH and SOM strongly affect soil functions and plant nutrient availability. Specifically, pH influences chemical solubility and availability of plant essential nutrients, pesticide performance, and organic matter decomposition. SOM serves multiple functions

in the soil, including nutrient storage and soil aggregation (McCauley et al., 2009).

From the analysis of Table 2, it is also possible to conclude that As, Ba, Cu, Mn, Sr, and Zn show large variations in mean, median and maximum values. For all these elements, the difference between both kinds of samples clearly shows that there are higher contents in rhizosphere soils when compared with local geochemical background. The behaviour of the elements in the rhizosphere soils may reflect the influence of the Barroca Grande tailings and open impoundments, due to wind dispersion and deposition.

According to Ávila et al. (2008), the Barroca Grande tailings and open impoundments have high As, Cd, Cu, Pb, Sn, W, and Zn concentrations (mean content in the more coarse tailings material As =  $7142 \text{ mg kg}^{-1}$ ; Cd =  $56 \text{ mg kg}^{-1}$ ; Cu =  $2501 \text{ mg kg}^{-1}$ ; Pb =  $172 \text{ mg kg}^{-1}$ ; Sn =  $679 \text{ mg kg}^{-1}$ ; W =  $5400 \text{ mg kg}^{-1}$  and Zn =  $1689 \text{ mg kg}^{-1}$  and mean content in the impoundment material (rejected from the mill operations) As =  $44,252 \text{ mg kg}^{-1}$ ; Cd =  $491 \text{ mg kg}^{-1}$ ; Cu =  $4029 \text{ mg kg}^{-1}$ ; Pb =  $166 \text{ mg kg}^{-1}$ ; Sn =  $454 \text{ mg kg}^{-1}$ ; W =  $3380 \text{ mg kg}^{-1}$  and Zn =  $3738 \text{ mg kg}^{-1}$ ). The mineralogy of these tailings is mainly quartz, muscovite, kaolinite, illite–montmorillonite, montmorillonite–vermiculite, and chlorite, and also arsenopyrite, wolframite, and natrojarosite. The dam in Barroca Grande may pose a significant potential threat due to the fine-grained nature of the materials and its location with respect to the Casinhas stream that cross SFA village. The XRD analysis of the impoundment material revealed the presence of scorodite, arsenopyrite, quartz, sphalerite, hematite, and muscovite. These

**Table 2**

Mean, median and maximum values and its difference (DF) from the SFA rhizosphere soils (RSS,  $n = 17$ ) and the geogenic soil from horizon B (GTB,  $n = 116$ ) (the considered high contents are in bold). Detection limits values (DL) of the method are also presented (according to <http://acmelab.com/>).

Var	Units	DL	Mean values			Median values			Maximum values		
			RSS	GTB	DF	RSS	GTB	DF	RSS	GTB	DF
pH			6.17	4.24	1.93	6.31	4.23	2.08	6.9	6.22	0.68
SOM	%		14.41	10.6	3.81	12.21	10.2	2.01	27.4	19.5	7.9
Ag	mg kg <sup>-1</sup>	0.1	0.7	0.2	0.5	0.6	0.1	0.5	1.2	0.5	0.7
Al	%	0.01	1.9	2.2	0.4	1.8	2.3	0.5	2.7	3.4	0.8
As	mg kg <sup>-1</sup>	0.5	223.6	97.8	<b>125.8</b>	133.0	68.3	<b>64.7</b>	918.6	350.4	<b>568.2</b>
Au	μg kg <sup>-1</sup>	0.5	14.5	8.2	6.2	13.8	4.9	8.9	28.4	112.2	<b>83.8</b>
Ba	mg kg <sup>-1</sup>	1	192.8	28.8	<b>164.0</b>	96.0	27.0	<b>69.0</b>	657.0	56.0	<b>601.0</b>
Bi	mg kg <sup>-1</sup>	0.1	3.7	1.6	2.2	3.3	0.8	2.5	10.0	15.4	5.4
Ca	%	0.01	1.1	0.0	1.1	1.1	0.0	1.1	3.1	0.3	2.9
Cd	mg kg <sup>-1</sup>	0.1	1.3	0.2	1.0	1.0	0.1	0.9	3.4	1.5	1.9
Co	mg kg <sup>-1</sup>	0.1	10.7	9.0	1.6	8.3	7.2	1.1	25.9	62.8	36.9
Cr	mg kg <sup>-1</sup>	1	37.8	34.9	2.9	39.0	34.0	5.0	47.0	71.0	24.0
Cu	mg kg <sup>-1</sup>	0.1	163.7	41.7	<b>121.9</b>	103.6	35.5	<b>68.1</b>	757.6	146.0	<b>611.6</b>
Fe	%	0.01	3.3	3.6	0.3	3.2	3.5	0.3	4.3	6.4	2.1
Ga	mg kg <sup>-1</sup>	1	5.8	6.0	0.2	6.0	6.0	0.0	8.0	8.0	0.0
Hg	mg kg <sup>-1</sup>	0.01	0.1	0.1	0.1	0.1	0.0	0.0	0.3	0.1	0.2
K	%	0.01	0.3	0.1	0.1	0.2	0.1	0.1	0.5	0.4	0.1
La	mg kg <sup>-1</sup>	1	14.6	21.1	6.5	15.0	20.0	5.0	25.0	35.0	10.0
Mg	mg kg <sup>-1</sup>	0.01	0.3	0.3	0.0	0.3	0.3	0.0	0.4	0.9	0.4
Mn	mg kg <sup>-1</sup>	1	531.3	170.0	<b>361.3</b>	457.0	114.0	<b>343.0</b>	1194.0	840.0	<b>354.0</b>
Mo	mg kg <sup>-1</sup>	0.1	0.6	0.6	0.0	0.6	0.6	0.0	0.9	2.2	1.3
Na	%	0.001	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1
Ni	mg kg <sup>-1</sup>	0.1	24.7	22.8	2.0	23.3	23.3	0.0	38.8	36.4	2.4
P	%	0.001	0.2	0.0	0.2	0.2	0.0	0.1	0.5	0.1	0.4
Pb	mg kg <sup>-1</sup>	0.1	58.6	26.7	32.0	45.8	21.7	24.1	146.1	78.4	67.7
S	%	0.05	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.1	0.0
Sb	mg kg <sup>-1</sup>	0.1	0.6	0.4	0.2	0.5	0.4	0.1	1.6	1.0	0.6
Sc	mg kg <sup>-1</sup>	0.1	2.5	2.4	0.1	2.4	2.3	0.1	4.2	6.4	2.2
Se	mg kg <sup>-1</sup>	0.5	0.6	0.6	0.0	0.6	0.5	0.1	1.0	1.8	0.8
Sr	mg kg <sup>-1</sup>	1	49.2	4.3	<b>44.9</b>	40.0	3.0	<b>37.0</b>	120.0	22.0	<b>98.0</b>
Th	mg kg <sup>-1</sup>	0.1	2.7	6.7	4.0	2.7	6.9	4.2	6.1	10.6	4.5
Ti	%	0.001	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0
Tl	mg kg <sup>-1</sup>	0.1	0.3	0.4	0.1	0.3	0.3	0.0	0.5	1.1	0.6
V	mg kg <sup>-1</sup>	2	39.3	34.3	5.0	40.0	34.0	6.0	53.0	52.0	1.0
W	mg kg <sup>-1</sup>	0.1	12.1	4.6	7.5	6.0	2.4	3.6	56.7	29.4	27.3
Zn	mg kg <sup>-1</sup>	1	323.2	85.7	<b>237.5</b>	256.0	79.0	<b>177.0</b>	911.0	192.0	<b>719.0</b>

tailings and impoundment material are metal-enriched at a level likely to be toxic to the ecosystem (Ávila et al., 2008).

The coexistence of wolframite, cassiterite, sulphides, carbonates, and silicates is responsible for the peculiar behaviour in the tailings surface environment. Weathering of sulphide-rich materials results in AMD at the Panasqueira mine. During runoff events, rain water infiltrates the tailings and dissolves secondary minerals, producing strongly acidic water (pH 3.0 Ávila et al., 2008). The low pH keeps the trace elements dissolved and increases remobilization and spatial distribution. This scenario leads to the high contents of metals verified in the village agricultural soils, some of them with acid pH and others near neutral pH ( $5.1 < \text{pH} < 6.9$ ). According to McCauley et al. (2009) acid conditions occur in soil having parent material high in silica, high levels of sand with low buffering capacities (ability to resist pH change), and in regions with high amounts of precipitation. An increase in precipitation causes increased leaching of base cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) and the soil pH is lowered. Acidic soils are most commonly found in areas where soils were formed from siliceous parental material, forest soils, mining sites containing pyrite (McCauley et al., 2009).

Considering that the sampling area is located in an inhabited village and that the local population strongly depends on the use of soil for their subsistence (agriculture, cattle breeding and forestry), it is useful to compare the As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Zn concentrations in soil with the reference values proposed by the Ontario Soil Quality Guidelines (Ministry of the Environment, 2011) and also with the national median concentrations proposed by Ferreira (2004) (Table 3).

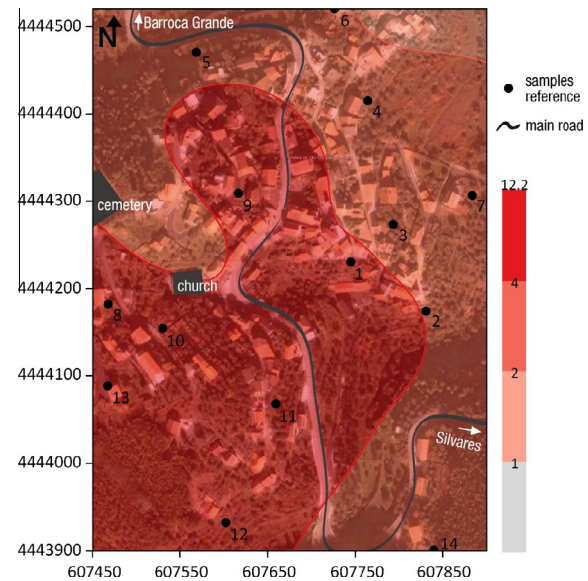
According to these values, the soils from SFA exceed, for example, for As twenty times the Ontario reference value for agricultural soils ( $11 \text{ mg kg}^{-1}$ ) and 10 times the national median concentrations ( $22 \text{ mg kg}^{-1}$ ) proposed by Ferreira (2004). The estimated EI values for soils are elevated ranging from 1.0 to 12.2 (Fig. 3), mainly due to the presence of significant contents of As, Cu and also Cd and Pb. Comparison to the Ontario guidelines indicates that the majority of the samples exceed the severe effect level for As and Cu (100% of samples), Cd (50% of samples), Pb (53% of samples) and Zn (47% of samples) and so are deemed “grossly polluted”.

According to Ferreira da Silva et al. (2013) the high levels of As in these soils seems to be linked to sulphides, since a considerable proportion is extracted by aqua regia (F4 – 66.7–68.4%). This high percentage associated with sulphides reflects the presence of arsenopyrite in the samples. Amorphous and crystalline Fe and Mn oxyhydroxides (F3) seems to be also important metal bearing-phases. The percentage of easily mobilized phases is very low (0.04–0.05%); however, the As concentrations associated with this extraction values (0.4–0.7  $\text{mg kg}^{-1}$ ) may be considered very high. Also according the same author Cd, Cu and Pb show high (and sim-

**Table 3**

Reference values proposed by the Ontario Soils Quality Guidelines (Ministry of the Environment, 2011) and Ferreira (2004).

	Ministry of the Environment (2011)	Ferreira (2004)	Rhizosphere mean
As	11	22	223.6
Ba	210	163	192.8
Cd	1.0	–	1.3
Co	19	19	10.7
Cr	67	43	37.8
Cu	62	35	163.7
Mn	–	–	531.3
Mo	0.6	–	0.6
Ni	37	43	24.7
Pb	45	34	58.6
Sb	1.0	–	0.6
Zn	290	85	323.2



**Fig. 3.** Enrichment Index (EI) mapping for soils in the study area.

ilar) partitioning patterns in the studied soil samples (64.8–74.4%, 49.5–54.9%, 46.2–56.3% of extraction by hydroxylamine leach cold, respectively), suggesting that these may be linked, to some extent, to amorphous Fe/Mn oxyhydroxides. Moreover, part of these ele-



(a)



(b)

**Fig. 4.** (a) Partial view of Barroca Grande tailings deposit with dust in the air due to the wind. (b) Vehicles ready to load the coarse material in Barroca Grande tailings deposit.

ments was extracted with aqua regia in both samples, suggesting that these elements may also be linked, to some extent, to sulphide or clay minerals. It was also shown that Cd (10.3–13.9% of extraction, 1.9–4 mg kg<sup>-1</sup> for Cd) was also extracted to a great extent with sodium acetate indicating that the soluble/exchangeable/carbonate fraction is probably a preferential sink for Cd.

These elements (As, Cd or Pb, for example) are the most toxic for humans, as well as for animals and can even lead to death if ingested in large doses, or over large periods of time. Exposure to hazardous elements may have different pathways, being one of them the ingestion of vegetables grown on contaminated soils.

#### 4.1.2. Road dusts

Road dust originated from the interaction of solid, liquid and gaseous materials are produced from different sources and deposited on a road. The composition and quantity of chemical matrix of road dust are indicators of environmental pollution (Banerjee, 2003). Road dust receives varying inputs of heavy metals from diversity of mobile or stationary sources such as vehicles emissions, industrial plants, power generation plants, oil burning, waste incineration, construction and demolition activities as well as resuspension of surrounding contaminated soils (Ahmed and Ishiga, 2006; Al-Khashman, 2007; Atiemo et al., 2011). These inputs contribute significantly to the pollution of urban environment. This makes the study of road dust important for determining the origin, distribution and level of heavy metal in urban surface environments. Elevated levels of heavy metal contents are the result of human activities and as a result, the adverse effects of poor environmental conditions on human health are most evident in the affected environments.

Exposure to heavy metals in road dust can occur by means of ingestion through vegetables that grow near roads, inhalation and dermal contact. The adverse effects of heavy metals in road dust include respiratory system disorders, nervous system interruptions, endocrine system malfunction, immune system suppression and the risk of cancer in later life (Ferreira-Baptista and De Miguel, 2005).

Most mining and quarrying wastes obtained from grinding of rocks are placed in deposits in specific locations/regions and can be reused in earthworks and construction, in particular the coarser fractions. Typical applications include use in asphalt pavements. In the SFA area, the main concern focuses on dust associated with mining operations due to vehicles moving at the top of the Barroca Grande tailings deposit to load the coarse rejected materials from the mining exploration (Fig. 4).

The statistical parameters calculated from the “total” contents of the road dust samples are shown in Table 4.

From Table 4 it was notice that some elements have a strong positive asymmetry, due to the presence of “outliers”, namely, Ag, As, Au, Ca, Cd, Hg, Mo, Na, Pb, S, Sb, Se and Zn (with values above 1.5). Most of these elements present mean values significantly higher than their median values. Nevertheless, it is important to emphasize the most critical elements in contamination terms and as potential hazardous elements. For example, As ranging between 61.9 mg kg<sup>-1</sup> and 3564.9 mg kg<sup>-1</sup>; Cd from a minimum of 0.3 mg kg<sup>-1</sup> and a maximum of 19.4 mg kg<sup>-1</sup> and Cu between 51.6 mg kg<sup>-1</sup> and 766.0 mg kg<sup>-1</sup>, poses a severe danger for the village inhabitants affecting their health once these dust lay down in soils, vegetables and animals drinking water.

Once again, it is useful to compare the dust contents with reference values and acceptable risk values. For a better understanding

**Table 4**

Mean, median, minimum, maximum, standard deviation (SD) and skewness values (SK) of the road dust samples (n = 13). Detections limits (DL) of the method are also presented (according to <http://acmelab.com/>).

Element	Units	DL	Mean	Median	Minimum	Maximum	SD	Asymmetry
Ag	mg kg <sup>-1</sup>	0.1	1.95	1.00	0.10	6.00	1.95	1.41
Al	%	0.01	1.10	1.15	0.57	1.49	0.25	-0.89
As	mg kg <sup>-1</sup>	0.5	810.15	469.90	61.90	3564.90	1007.92	2.16
Au	mg kg <sup>-1</sup>	0.5	10.58	3.60	1.40	73.00	19.43	3.23
Ba	mg kg <sup>-1</sup>	1	43.15	40.00	22.00	65.00	12.81	0.35
Bi	mg kg <sup>-1</sup>	0.1	9.86	6.30	0.90	26.30	8.29	1.15
Ca	%	0.01	0.57	0.40	0.13	2.46	0.60	2.95
Cd	mg kg <sup>-1</sup>	0.1	5.39	3.20	0.30	19.40	6.13	1.78
Co	mg kg <sup>-1</sup>	0.1	7.18	6.90	2.30	11.60	2.68	-0.03
Cr	mg kg <sup>-1</sup>	1	20.08	20.00	9.00	30.00	6.40	-0.10
Cu	mg kg <sup>-1</sup>	0.1	338.91	326.40	51.60	766.00	216.40	0.97
Fe	%	0.01	2.46	2.25	1.02	3.57	0.76	-0.21
Ga	mg kg <sup>-1</sup>	1	3.92	4.00	2.00	5.00	0.95	-1.19
Hg	mg kg <sup>-1</sup>	0.01	0.01	0.01	0.01	0.03	0.01	3.61
K	%	0.01	0.34	0.34	0.17	0.47	0.08	-0.47
La	mg kg <sup>-1</sup>	1	11.08	11.00	6.00	15.00	2.50	-0.44
Mg	%	0.01	0.37	0.38	0.17	0.48	0.08	-0.94
Mn	mg kg <sup>-1</sup>	1	258.15	224.00	115.00	469.00	100.66	1.13
Mo	mg kg <sup>-1</sup>	0.1	0.92	0.60	0.30	3.90	0.94	3.07
Na	%	0.001	0.02	0.02	0.01	0.08	0.02	2.33
Ni	mg kg <sup>-1</sup>	0.1	17.77	19.10	6.20	25.10	5.88	-0.66
P	%	0.001	0.08	0.07	0.04	0.12	0.02	0.04
Pb	mg kg <sup>-1</sup>	0.1	43.86	31.30	14.40	127.70	37.10	1.76
S	%	0.05	0.43	0.20	0.03	2.01	0.62	2.14
Sb	mg kg <sup>-1</sup>	0.1	1.02	0.70	0.30	2.60	0.77	1.30
Sc	mg kg <sup>-1</sup>	0.1	1.76	1.70	0.80	2.40	0.46	-0.56
Se	mg kg <sup>-1</sup>	0.5	0.57	0.25	0.25	1.70	0.49	1.72
Sr	mg kg <sup>-1</sup>	1	17.00	16.00	7.00	34.00	7.52	0.82
Th	mg kg <sup>-1</sup>	0.1	5.17	5.10	3.20	7.60	1.31	0.37
Ti	%	0.001	0.05	0.05	0.03	0.08	0.01	0.51
Tl	mg kg <sup>-1</sup>	0.1	0.71	0.60	0.20	1.40	0.35	0.63
V	mg kg <sup>-1</sup>	2	22.38	23.00	12.00	30.00	5.30	-0.58
W	mg kg <sup>-1</sup>	0.1	36.15	22.70	7.10	100.10	32.09	1.34
Zn	mg kg <sup>-1</sup>	1	464.38	370.00	110.00	1262.00	368.77	1.55



**Table 5**  
Reference Values Range (RVR), Acceptable Risk Values (ARV), Maximum Acceptable Values (MAV) (Sezgin et al., 2003) and mean, median and maximum values determined in SFA road dust samples (the considered RVR high contents are in bold).

Element	RVR	ARV	MAV	SFA road dust samples		
				Mean	Median	Maximum
As	2–20	20	no inf.	<b>810.2</b>	<b>469.9</b>	<b>3564.9</b>
Cd	0.1–1	3	3	<b>5.4</b>	<b>3.2</b>	<b>6.13</b>
Co	1–10	50	no inf.	7.2	6.9	11.6
Cr	10–50	100	100	20.1	20	30
Cu	5–20	50	100	<b>338.9</b>	<b>326.4</b>	<b>766</b>
Mo	1–5	5	no inf.	0.9	0.6	3.9
Ni	10–50	50	50	17.8	19.1	25.1
Pb	0.1–20	100	100	43.9	31.3	127.7
Zn	10–50	300	300	<b>464.4</b>	<b>370</b>	<b>1262</b>

of the metals behaviour in dust samples, this study only focuses on toxic elements. Table 5 shows, according to Sezgin et al. (2003), the reference values range, acceptable risk values, and maximum acceptable values and, for comparison, the mean, median and maximum value determined in S. Francisco de Assis (SFA) road dust samples.

From Table 5, it is obvious that the collected dusts, clearly, exceed the reference values range, acceptable risk values as also the maximum acceptable values for, at least, As, Cd, Cu and Zn. For a better visualization, Fig. 5 shows the cartography of the As, Cd and Cu road dust contents according the reference values presents in Table 5.

These high contents are caused by a great wind dispersion mechanism in this area (see Table 1). According to these results

it would be advisable the close monitoring of dust that are carried by the winds from the Barroca Grande tailing and implementing a form of mitigation to prevent its deposition in urban areas (in that case in SFA village). Indeed As, by its toxicity, may have chronic health effects that may be local or systemic. The lung cancer is regarded as the most critical effect that results from inhalation of particles of Arsenic (WHO, 2000). Cadmium when present in the atmosphere and in food can cause severe kidney problems. Moreover the dispersion of Pb existing in dust, if particles are at an inhaled size e.g. PM<sub>10</sub> and PM<sub>2.5</sub>, could be worrying, especially for children, primarily due to blood diseases which become frequent when humans are exposed to this element (WHO, 2000).

#### 4.1.3. Waters

In SFA the local population strongly depends on the use of water (water supply and agriculture), nevertheless most of the inhabitants use the public supply network. In the study area, we chose to perform the collection of water samples in private wells (UW4, UW6, UW7) one sample (UW5) was collected in a little stream (Barroco) and for comparison two samples (UW1, UW8) from public supply network, all of these waters are used for vegetable irrigation (Table 6).

According to the results, the lowest pH values were recorded in samples collected in wells (UW4, UW6 and UW7) having a slightly acidic character, according to the parametric values set out in the Decree-Law 306/2007 with values between 6.5 and 9.0. The other samples have circumneutral pH. The measured values electric conductivity ranging from 18 to 161  $\mu\text{S cm}^{-1}$  classifies them as waters with very low mineralization, according to the parametric values set out in the Decree-Law 306/2007 with values up to 2500  $\mu\text{S cm}^{-1}$ . These samples have lower  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  concentrations but major ions contents tend to increase with the decrease of pH. Have also low metal concentrations, sometimes Zn and Mn were present in significant concentrations though below the standard parametric values. The concentrations of other elements were all legally acceptable.

Fig. 6 shows the samples representation in a Piper's diagram. Two distinct hydrochemical facies were determined: (a) UW1, UW8 from public network supply, UW5 from Barroco stream and the well UW6 are Ca/Mg-HCO<sub>3</sub> waters, and (b) UW4 and UW7 collected in private wells have a closer facies to the type Ca/Mg-Cl/SO<sub>4</sub> waters.

Comparing the obtained results from the collected samples with the Portuguese criteria values of quality of surface fresh water for human consumption and irrigating waters (Decree-Law 306/2007), all the analyzed waters in SFA village are in perfect conditions to be used by the population.

Nevertheless, and because As is a toxic element and because arsenopyrite is the main sulphide rejected in Panasqueira mine, As and also Fe have been object of chemical speciation according



**Fig. 5.** Cartography of road dust contents for As, Cd and Cu (Google Earth image modified).

**Table 6**

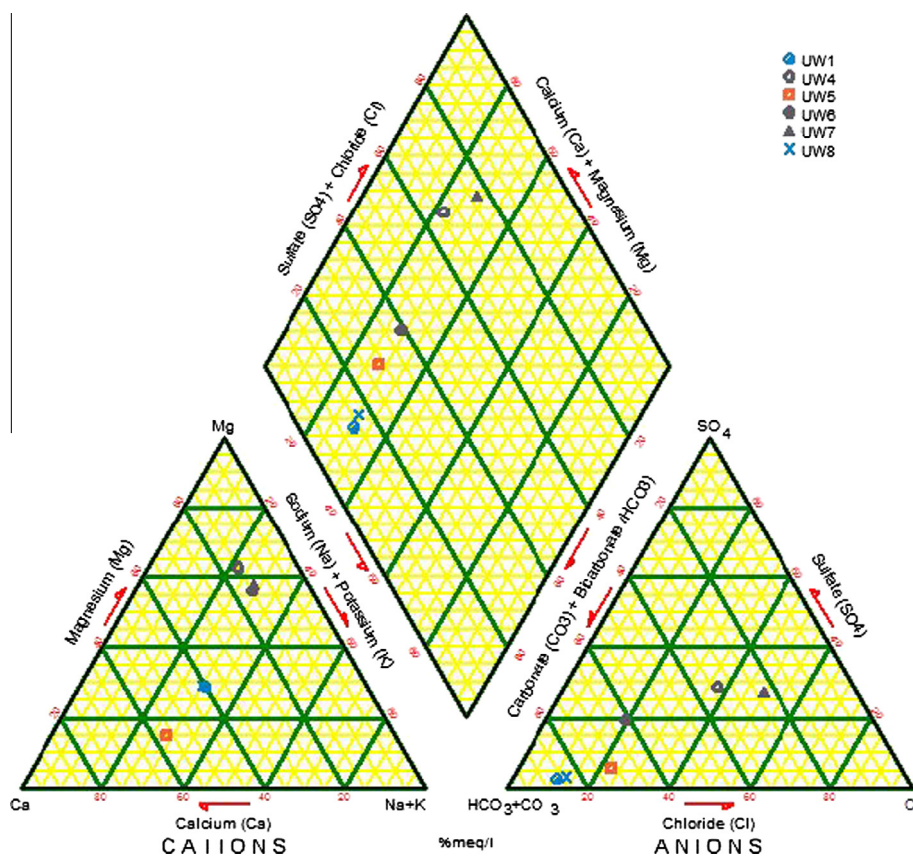
The water origin, pH, electrical conductivity (EC), Total Dissolved Solids (TDS), Salinity, ORP, Dissolved Oxygen (DO), major ions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) and trace elements in waters collected in SFA village – Panasqueira mine ( $n = 6$ ). Detections limits (DL) of the method are also presented (according to <http://acmelab.com/>).

Element	Units	DL	UW1	UW8	UW4	UW6	UW7	UW5	DWS
pH			6.7	6.7	5.6	6.1	5.3	6.8	$6.5 < \text{pH} < 9.0$
T	$^{\circ}\text{C}$		18.8	19.2	14.4	15.7	16.0	12.9	$12^{\circ} < T < 25^{\circ}$
EC	$\mu\text{S cm}^{-1}$		139	73	122	35	161	18	2500
TDS	$\text{mg L}^{-1}$		68	37	61	14	80	9	1500
Salinity			0.06	0.03	0.06	0.02	0.08	0.01	–
ORP	mV		192.0	155.5	287.4	187.3	206.5	226.4	–
DO	%		44.5	65.7	44.5	54.7	83.0	61.0	–
DO	$\text{mg L}^{-1}$		3.82	5.65	4.13	5.21	7.64	6.02	–
Cl	$\text{mg L}^{-1}$	1	2	2	11	2	7	2	250
$\text{NO}_3$	$\text{mg L}^{-1}$	1	2	2	21	4	15	1	50
$\text{SO}_4$	$\text{mg L}^{-1}$	1	1	1	20	5	9	1	250
$\text{HCO}_3$	$\text{mg L}^{-1}$	1	49	39	30	20	10	20	–
Na	$\text{mg L}^{-1}$	0.05	6	6	9	7	12	4	200
K	$\text{mg L}^{-1}$	0.05	0.3	0.4	1.3	0.7	2.4	1.4	10
Mg	$\text{mg L}^{-1}$	0.05	2	2	8	4	7	1	30
Ca	$\text{mg L}^{-1}$	0.05	6	6	5	3	5	6	100
Al	$\mu\text{g L}^{-1}$	1	7	18	51	139	21	24	200
As	$\mu\text{g L}^{-1}$	0.5	2.0	bdl	1.5	7.8	1.0	7.7	10
B	$\mu\text{g L}^{-1}$	5	4.5	4.5	5.0	4.5	8.0	4.5	1000
Cd	$\mu\text{g L}^{-1}$	0.05	0.06	0.14	0.10	0.36	0.27	bdl	5.0
Cu	$\mu\text{g L}^{-1}$	0.1	3.8	4.2	10.3	7.3	3.2	2.5	2000
Fe	$\mu\text{g L}^{-1}$	10	bdl	111	28	180	bdl	10	200
Mn	$\mu\text{g L}^{-1}$	0.05	1.6	66.4	5.7	15.6	8.4	1.7	50
Pb	$\mu\text{g L}^{-1}$	0.1	0.2	1.9	1.4	23.1	0.2	0.3	25
Zn	$\mu\text{g L}^{-1}$	0.5	13.3	4217.3	66.0	319.3	39.9	5.0	5000

DWS – Drinking water standards (Decree-Law 306/2007); UW1 and UW8 – Public network; UW4, UW6 and UW7 – Well; UW5 – Barroco stream.

to the methodologies described. According to the results of Table 7, it can be stated that As is present only in UW5 sample in the form of As (V), nevertheless below the parametric water values for human consumption according to the Portuguese Law. The toxicity

of As depends on its oxidation state and knowing that its reduced forms are the most toxic, it was of extremely importance its determination because it allowed the verification that the As in UW5, which is used for irrigation, is present in its oxidized form and



**Fig. 6.** Plot of data of water samples collected in S. Francisco de Assis village – Panasqueira mine in the Piper's diagram.



**Table 7**  
As and Fe speciation results.

Samples	As (III) ( $\mu\text{g L}^{-1}$ )	As (total) ( $\mu\text{g L}^{-1}$ )	Fe (II) ( $\mu\text{g L}^{-1}$ )	Fe (total) ( $\mu\text{g L}^{-1}$ )
UW1	<0.6	<4.5	<15	41.0
UW4	<0.6	<4.5	<15	31.0
UW5	<0.6	5.6	<15	23.0
UW6	<0.6	<4.5	<15	47.0
UW7	<0.6	<4.5	<15	35.0
UW8	<0.6	<4.5	1.7	64.0

hence with a lower degree of toxicity. The results also show that Fe (III) is dominant in all samples.

#### 4.1.4. Vegetables

Many heavy metals exist in minute amounts in natural agricultural soil, however when their amounts exceed a certain level due to pollutants brought from outside, soil contamination occurs and agricultural products become contaminated so the consumption of locally produced vegetables may be an important exposure pathway for soil contaminants due to agricultural land use. Prolonged exposure to heavy metals can cause deleterious health effects in humans. Hence, prediction of metal and metalloid uptake by vegetables from contaminated soils is an important part of the Human health risk assessment.

Given the high contents, of some metals/metalloids, that were recorded in the soils as well as in the road dusts and the fact that most inhabitants have a diet rich in vegetables, we attempted to

study the relationship between the metals/metalloids contents of the rhizosphere soils and vegetables. Two species were analyzed, *S. tuberosum sava* (potato) and *B. oleracea* L. (cabbage). For each sample it was calculated the total content of the elements according to equation (1), taking into consideration the different parts of each vegetable. Trace elements concentrations found in vegetables were summarized in Table 8.

Analysis of the results shows that the concentration of some potential hazardous elements ranges from 0.8–14.4  $\text{mg kg}^{-1}$  for As; 0.1–0.1  $\text{mg kg}^{-1}$  for Cd; 3.7–19.6  $\text{mg kg}^{-1}$  for Cu; 21–270.2  $\text{mg kg}^{-1}$  Mn, 0.2–4.2  $\text{mg kg}^{-1}$  Pb and 35–176.6  $\text{mg kg}^{-1}$  Zn. Data also show that element uptake is different in both studied species, the highest concentrations of As, Pb, Zn and Mn accumulation were found in cabbages, while potatoes concentrate more Cd and Cu.

Comparing the obtained results of the metal/metalloids contents in vegetables with the guidelines for vegetables proposed by FAO/WHO (As = 0.1  $\text{mg kg}^{-1}$ , Cd = 0.1  $\text{mg kg}^{-1}$ , Cu = 73  $\text{mg kg}^{-1}$ , Pb = 0.2  $\text{mg kg}^{-1}$ , Zn = 100  $\text{mg kg}^{-1}$ , Mn = 500  $\text{mg kg}^{-1}$ ) it is possible to say that As, Cd and Pb contents are above the maximum allowed level for vegetables while Cu, Zn and Mn contents are below the guidelines for maximum allowed metals in vegetables. On the whole, all vegetables that were studied were contaminated by arsenic, cadmium and lead and they are toxic if continually consumed. Consumption of heavy metals-contaminated food can seriously deplete some essential nutrients in the body causing a decrease in immunological protection, intrauterine growth retardation, impaired psycho-social behaviour, disabilities associated with malnutrition and a high prevalence of upper gastrointestinal cancer (Arora et al., 2008).

**Table 8**  
Comparison between total content of As, Cd, Cr, Cu, Mn, Ni, Pb and Zn in rhizosphere soils (S) and vegetables (V).

	DL	Site1 P	Site 2 P	Site7A P	Site 9 P	Site 10 P	Site 11 P	Site 3 C	Site 4 C	Site 5 C	Site 7B C	Site 8 C	Site 12 C	Site 13 C	Site 14 C	
As S	$\text{mg kg}^{-1}$	0.5	88.5	101.6	71.1	314.9	133	496.6	346.4	156.5	98.6	83.9	207.7	130.2	918.6	151.8
As V	$\text{mg kg}^{-1}$	0.1	5.9	2.8	2.8	2	1.5	2.8	12.8	14.4	8.7	0.8	4.7	0.8	4.1	0.9
Cd S	$\text{mg kg}^{-1}$	0.1	0.8	1.2	1.1	2.4	1.9	2.8	0.7	0.8	0.4	0.8	0.6	1.4	1.3	1
Cd V	$\text{mg kg}^{-1}$	0.01	0.2	0.2	0.2	0.3	0.2	0.3	0.1	0.4	0.3	0.2	0.3	0.2	0.4	0.1
Cr S	$\text{mg kg}^{-1}$	1	5.3	8	6.6	10.6	7.2	25.9	27	42	45	39	43	33	39	41
Cr V	$\text{mg kg}^{-1}$	0.1	0.4	0.4	0.1	0.1	0.1	0.2	2.2	17.7	87.9	3.4	18.7	3.2	2.0	2.2
Cu S	$\text{mg kg}^{-1}$	0.1	56.7	88.0	756.6	194.5	224.1	233.1	95.4	103.6	66.8	98.5	102.1	110.8	138.5	104.6
Cu V	$\text{mg kg}^{-1}$	0.01	12.3	11.6	19.6	11.0	17.0	10.4	6.7	20.2	18.3	6.3	8.3	5	6.2	3.7
Mn S	$\text{mg kg}^{-1}$	1	457	475	642	423	322	673	292	221	255	987	168	1194	826	895
Mn V	$\text{mg kg}^{-1}$	1	49.7	28.4	84	11.4	34	16.2	21.1	270.2	135.7	36.2	57.5	74.4	31.1	21
Ni S	$\text{mg kg}^{-1}$	0.1	13.9	20.3	21.9	19.9	23.3	28.6	13.2	30.6	36.4	20.6	27.9	23.7	27.7	32.5
Ni V	$\text{mg kg}^{-1}$	0.1	2.1	1.4	1.3	0.4	0.5	0.6	0.9	7.6	26.6	0.9	6.2	0.7	0.6	0.3
Pb S	$\text{mg kg}^{-1}$	0.1	49.0	94.5	93.5	38.1	24.4	66.5	146.1	31.3	29.4	48.2	27.8	134.5	32.1	44.3
Pb V	$\text{mg kg}^{-1}$	0.01	2.5	2.1	1.6	0.3	0.2	0.3	1.9	4.2	4.2	1.3	1.7	0.8	0.5	0.2
Zn S	$\text{mg kg}^{-1}$	1	244	236	364	309	254	374	551	188	128	439	179	911	256	300
Zn V	$\text{mg kg}^{-1}$	0.1	53.2	37.9	63.9	28.1	58.7	35	61.7	176.6	117.6	52.2	104.4	72	64.8	38.2

P – *Solanum tuberosum sava* (potato); C – cabbage.

**Table 9**  
Concentrations in the different components of *Solanum tuberosum sava* (potato) (T – tubers, L – leaves, S – stems and R – roots). The considered high contents are in bold.

Elem.	Units	S1			S2				S7A	S9			S10	S11		
		T	L	S	T	L	S	R	L	T	L	R	L	T	L	R
As	$\text{mg kg}^{-1}$	0.4	<b>12.5</b>	0.7	3.5	<b>4.5</b>	0.9	4.4	2.8	0.9	<b>5.1</b>	<b>21.9</b>	1.5	0.5	<b>3.8</b>	<b>18</b>
Cd	$\text{mg kg}^{-1}$	<b>0.39</b>	<b>0.23</b>	0.28	<b>0.52</b>	0.19	0.12	0.28	0.2	0.12	0.26	<b>4.66</b>	0.21	0.13	0.46	<b>1.26</b>
Cr	$\text{mg kg}^{-1}$	2.2	<b>13.7</b>	2.1	<b>7.3</b>	<b>7.2</b>	1.9	3.5	2.8	2.5	3.4	<b>14.9</b>	1.6	1.7	<b>3.1</b>	2.8
Cu	$\text{mg kg}^{-1}$	9.78	<b>15.59</b>	9.24	12.25	<b>15.31</b>	13.79	11.79	<b>19.56</b>	9.92	16.09	<b>27.71</b>	16.99	8.41	12.25	<b>19.96</b>
Mn	$\text{mg kg}^{-1}$	16	<b>92</b>	23	35	<b>57</b>	13	24	84	7	<b>45</b>	<b>60</b>	34	8	<b>33</b>	22
Ni	$\text{mg kg}^{-1}$	1	<b>4</b>	0.6	3	2.2	0.5	<b>0.9</b>	1.3	0.2	<b>1.1</b>	<b>2.8</b>	0.5	0.3	<b>1.1</b>	<b>1.1</b>
Pb	$\text{mg kg}^{-1}$	1.95	<b>3.6</b>	1.45	3.25	<b>3.68</b>	1.74	3.08	1.59	0.17	<b>0.69</b>	<b>3.13</b>	0.17	0.06	0.74	<b>1.08</b>
Zn	$\text{mg kg}^{-1}$	26.6	59.6	<b>149.8</b>	53	41.5	<b>87.7</b>	49.3	63.9	24.1	43.6	<b>91.6</b>	58.7	29.9	35.7	73.1

**Table 10**  
Concentrations in the different components of *B. oleracea* L. (cabbage) (L – leaves, S – stems and R – roots). The considered high contents are in bold.

Elem.	Units	S3			S4			S5			S7B			S8			S12			S13			S14		
		L	S	R	L	S	R	L	S	R	L	S	R	L	S	R	L	S	R	L	S	R	L	S	
As	mg kg <sup>-1</sup>	0.9	0.3	<b>52.3</b>	1.7	0.4	0.4	0.7	2.9	<b>31.7</b>	2.9	0.8	0.2	1.2	0.4	0.2	0.2	<b>22.5</b>	0.2	<b>3.6</b>	1.9	1.3	<b>8.8</b>	1.3	0.4
Cd	mg kg <sup>-1</sup>	0.07	0.09	<b>0.12</b>	0.25	0.27	<b>0.56</b>	0.21	0.28	<b>0.56</b>	0.28	0.16	0.14	0.35	0.16	0.32	0.08	<b>0.34</b>	0.08	<b>0.7</b>	<b>0.43</b>	0.39	0.34	0.06	0.06
Cr	mg kg <sup>-1</sup>	1.6	1.3	<b>4.7</b>	3.2	1.1	<b>37.9</b>	2.4	1.7	<b>37.9</b>	1.7	3.7	2	1.8	1.9	<b>3.2</b>	2.6	<b>96.6</b>	2.6	<b>5.9</b>	2.1	1.6	<b>2.2</b>	1.6	1.5
Cu	mg kg <sup>-1</sup>	5.73	4.1	<b>12.32</b>	7.69	3.77	<b>39</b>	4.48	5.47	<b>42.59</b>	4.57	4.07	4.07	3.66	4.18	<b>20.57</b>	3.73	<b>28.78</b>	3.73	<b>10.37</b>	5.37	3.58	<b>8.78</b>	3.58	2.46
Mn	mg kg <sup>-1</sup>	<b>32</b>	8	<b>21</b>	45	11	<b>586</b>	44	108	<b>253</b>	<b>39</b>	18	39	65	25	<b>115</b>	77	<b>63</b>	77	<b>36</b>	36	13	<b>34</b>	13	14
Ni	mg kg <sup>-1</sup>	0.8	0.6	<b>1.6</b>	1.7	0.9	<b>15.7</b>	1.5	3.4	<b>70.6</b>	1	0.6	0.9	1.7	1.8	<b>0.9</b>	0.5	<b>26.9</b>	0.5	<b>1.6</b>	0.6	0.4	<b>0.6</b>	0.4	0.005
Pb	mg kg <sup>-1</sup>	0.36	0.28	<b>7.09</b>	0.48	0.32	<b>9.1</b>	0.26	0.32	<b>11.43</b>	1.46	0.32	0.32	0.3	0.44	<b>1.79</b>	0.1	<b>7.99</b>	0.1	<b>4.09</b>	0.4	0.14	<b>0.86</b>	0.4	0.23
Zn	mg kg <sup>-1</sup>	43.2	71.2	<b>80.7</b>	76.4	236.5	<b>131.5</b>	106	115.4	<b>131.5</b>	51.8	45.6	45.6	96.5	55.1	<b>62.1</b>	68.7	<b>236.6</b>	68.7	<b>86.3</b>	25.3	28.5	<b>139.1</b>	28.5	44.6

Table 9 and 10 presents the concentrations distributed by the different components (T – tubercles, L – leaves, S – stems and R – Roots) of the two studied species *S. tubersum sava* and *B. oleracea* L.

The results obtained for the different component of the studied vegetable shows that: (a) for potatoes the roots contained maximum As (21.9 mg kg<sup>-1</sup>) followed by leaves (12.5 mg kg<sup>-1</sup>) and tubers (3.5 mg kg<sup>-1</sup>) (Table 9); (b) for cabbages the roots contained maximum As (52.3 mg kg<sup>-1</sup>) followed by leaves (2.9 mg kg<sup>-1</sup>) (Table 10). Despite the edible parts of vegetables, potatoes tubers and cabbage leaves have the lowest As contents, these contents are above the maximum permitted level for vegetables proposed by FAO/WHO (2012) guidelines (0.1 mg kg<sup>-1</sup>). As for Cd, the higher concentration in potatoes is found in roots (4.66 mg kg<sup>-1</sup>) and in tubers (0.52 mg kg<sup>-1</sup>) both above the FAO/WHO (2012) guidelines for Cd (0.1 mg kg<sup>-1</sup>) and for leaves cabbages Cd have a maximum concentration of 0.43 mg kg<sup>-1</sup> and for cabbages, the roots also have the highest Cd contents (0.56 mg kg<sup>-1</sup>), again both above the maximum limit considered by the FAO/WHO guidelines. Due to the high contents of exchangeable Cd in vegetable soils, the Cd in the edible parts of vegetables probably came from the root uptake from soils.

Copper is below the maximum limit regarding the FAO/WHO, 2012 guidelines (73 mg kg<sup>-1</sup>) in all parts of the plant of both vegetables, and the same pattern is observed for Zn (max limit permissible 100 mg kg<sup>-1</sup>) in the potatoes but some cabbages have concentrations above the permissible limit. Nevertheless Cu reveals a preferential accumulation in the leaves and roots in the potatoes and Zn cumulates in the stems, and in cabbages Cu prefers to cumulate in roots and Zn also in the roots.

Metals (Cu, Fe, Mn, Ni, and Zn) are very tightly bound to the soil at high pH and are therefore more available at low pH levels than high pH levels. In addition to the effects of pH on nutrient availability, individual plants and soil organisms also vary in their tolerance to alkaline and/or acid soil conditions. Neutral conditions appear to be best for crop growth. As it stated above in rhizosphere soils discussion, the pH of the sampled soils ranged 5.1 < pH < 6.9 which is the considered pH range more favourable for micronutrients availability.

According to Eqs. (2) and (3), an index of the risk for residents, due to the ingestion of these metals/metalloids, by consuming vegetables grown around the sampling area was calculated on the basis of the oral reference dose being 0.5 µg kg<sup>-1</sup> d<sup>-1</sup> for As, 0.5 µg kg<sup>-1</sup> d<sup>-1</sup> for Cd, 40 µg kg<sup>-1</sup> d<sup>-1</sup> for Cu, 3.5 µg kg<sup>-1</sup> d<sup>-1</sup> for Pb, and 300 µg kg<sup>-1</sup> d<sup>-1</sup> for Zn (Luo et al., 2011; JECFA, 1993).

According to Table 11 the risk index, in descending order is Cd < As < Pb < Cu < Zn, and for Cd, As and Pb is higher than 1, while the risk indexes for Cu, and Zn were less than 1. The result indicates that the inhabitants of SFA village probably are exposed to some potential health risks through the intake of As, Cd and also Pb via consuming their vegetables. The accumulation of metals in the edible parts of vegetables could have a direct impact on the health of nearby inhabitants, because vegetables produced from gardens are mostly consumed locally. For Cu and Zn, there is no significant risk from the intake of vegetables. According to Luo

**Table 11**  
Estimated mean and range daily intake for a 60 kg body weight adult.

Metals	DIM (mg d <sup>-1</sup> )	EDEM (mg kg <sup>-1</sup> d <sup>-1</sup> )	RfDo (mg kg <sup>-1</sup> d <sup>-1</sup> )	Risk index
As	74.30769	0.001238462	0.0005	2.476923
Cd	1401.6	0.023359375	0.0005	46.71875
Cu	31.06109	0.000517685	0.04	0.012942
Pb	221.5596	0.003692661	0.0035	1.055046
Zn	5.008815	8.34802E-05	0.3	0.000278



**Table 12**  
Concentrations (mg kg<sup>-1</sup>) in vegetables reported in other similar studies and comparison with data of the present study.

District (Country)	Sampling site description		As	Cd	Cu	Pb	Zn	References
Dabaoshan (China)	Pyrite mine	Range <b>Risk index</b>		0.001–0.71 <1	0.28–3.61 <0.2	0.01–0.39 <0.25	2.34–48.1 <0.2	Zhuang et al. (2009)
Enyigba (Nigeria)	Lead mine	Range	0.035–0.4	0.001–0.01	–	0.105–0.826	0.016–0.174	Oti Wilberforce and Nwabue (2013)
Cyöngyösoroszi (Hungary)	Abandoned Zn/Pb mine	Range <b>Risk index</b>		0.005–0.13 <b>0.033</b>		0.079–1.06 <b>0.087</b>	1.41–60.5 <b>0.049</b>	Sipter et al. (2008)
Guangdong	Waste incineration site	Range <b>Risk index</b>		0.04–0.38 <b>2.71</b>	0.59–3.99 <b>0.264</b>	0.11–1.3 <b>0.857</b>	3.69–21.9 <b>0.233</b>	Luo et al. (2011)
Harare (Zimbabwe)	Wastewater irrigated garden	Mean		0.15	0.2	0.35	9.1	Mapanda et al. (2007)
Huludao (China)	Zn plant	Range <b>Risk index</b>		0.011–4.58 <b>5.134</b>	0.405–2.13 <b>0.133</b>	0.067–5.45 <b>2.299</b>	2.93–66.9 <b>0.295</b>	Zheng et al. (2007)
Minas Gerais (Brasil)	Agricultural Soils	Range	–	0.0–0.48	0.44–37.4	0.0–331.6	8.84–115.36	Fernandes et al. (2007)
Mortagne du Nord (France)	Near a former Zn smelter	Range		0.01–0.46		0.02–0.35		Douay et al. (2007)
Panasqueira (Portugal)	Sn–W mine	Range <b>Risk index</b>	0.8–14.4 <b>2.477</b>	0.1–0.4 <b>46.7188</b>	3.7–20.2 <b>0.0129</b>	0.2–4.2 <b>1.0550</b>	28.1–176.6 <b>0.0003</b>	<b>Present Study</b>
Varanasi (India)	Urban area	Range		1.1–4.5	20.5–71.2	0.9–2.2	45.3–141	Sharma et al. (2008)
Zlatna (Romania)	Near a Cu smelter	Range		0.2–0.97	0.3–0.8	0.19–9.1	1.8–12.95	Pope et al. (2005)

et al. (2011), when determining the risk index, it was assumed that the intake is equal to the absorbed dose (USEPA, 1989), which may magnify the effect of the ingested contaminants to some extent, because part of the heavy metals that were ingested maybe egested. From this point of view, it is reasonable to think that no obvious adverse health effects from exposure to the heavy metals could be observed on those living in the village.

According to Luo et al. (2011) and comparing the results with other studies (Table 12), the health risk for adults from consuming vegetables in this region is comparable to, or even higher than those associated with the consumption of vegetables from gardens impacted by mining, wastewater, irrigation or smelting activities.

For soil–plant system, heavy metal toxicity threshold is the highest permissible content in the soil (total or bioavailable concentration) that does not pose any phytotoxic effects or heavy metals in the edible parts of the crops does not exceed food hygiene standards (Islam et al., 2007). The factors that affect the thresholds of heavy metal toxicity in soil–vegetable system include the soil type (soil pH, organic matter content, clay mineral and other soil chemical and biochemical properties) and the vegetable species, the transport and heavy metal accumulation in each plant. Also the interactions between soils, the plant roots and microbes play an important role regarding the heavy metal movement from soil to the edible parts of crops (Islam et al., 2007). These are issues that can affect bioavailability and heavy metals accumulation in vegetables, subject for a further investigation.

## 5. Conclusions

The mining and beneficiation process at Panasqueira mine produces mine wastes that are largely responsible for the high levels of metals/metalloids at the Barroca Grande tailings, releasing considerable amounts of heavy metals and metalloids in the surrounding soils and water. The metal assemblage identified in the rhizosphere soils collected in S. Francisco de Assis village, downstream Barroca Grande tailings deposit, and its behaviour may reflect the influence of the tailings and open impoundments materials, due to several dispersion agents, including the wind, and deposition in soils, vegetables and animals drinking water as also in little creeks used for irrigation. These soils exceed, for example, for As 20 times the Ontario reference value for agricultural soils (11 mg kg<sup>-1</sup>) and the estimated values for Enrichment

Index are elevated ranging (1.0 < EI < 12.2) mainly due to the presence of As, Cu and also Cd and Pb. The high levels of As in these soils seems to be linked to sulphides extracted by aqua regia and this association to sulphides reflects the presence of arsenopyrite in soils. The comparison to the Ontario guidelines indicates that these soils are deemed as “grossly polluted”. Also the road dusts analyzed exceed the reference acceptable risk and the maximum acceptable values for As, Cd, Cu and Zn and these contents results from a wind dispersion mechanism with a great expression in this area. If particles are at an inhaled size e.g. PM<sub>10</sub> and PM<sub>2.5</sub>, could be very worrying. Regarding the sampled waters, some have slightly acidic character and the others have circumneutral pH, they have very low mineralization (electric conductivity range from 18 to 161 μS cm<sup>-1</sup>) and low SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> concentrations but major ions contents tend to increase with the decrease of pH. Metal and metalloid concentrations are also low and, according the Portuguese law, legally acceptable.

Vegetables grown in the nearby sites were also contaminated, in one way, for potatoes there is a preferential accumulation in the roots and leaves while for the cabbage most elements have a preferential accumulation in the roots and, in another way, As, Cd and Pb concentrations are above the maximum permitted level for vegetables proposed by FAO/WHO, which could be a potential health concern to local residents. The risk index for residents determined, due to the ingestion of the metals and metalloids, reveal that Cd, As and Pb represents an hazard for the inhabitants of S. Francisco de Assis village, once they are probably exposed to some potential health risks through the intake of As, Cd and also Pb through the of ingesting these metals, by consuming vegetables grown in their yards.

This research requires further studies to establish the metals transfer process from soil to the different parts of the plants, to understand their bioavailability and to identify the bioaccumulation patterns based in indicators as Biological Absorption Coefficient for each element.

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## References

- Ahmed, F., Ishiga, H., 2006. Trace metal concentrations in street dusts of Dhaka city, Bangladesh. *Atmos. Environ.* 40, 3835–3844.
- Al-Khashman, O.A., 2007. The investigation of metal concentrations in street dust samples in Aqaba city, Jordan. *Environ. Geochem. Health* 29, 197–207.
- Antunes, I.M.H.R., Neiva, A.M.R., Silva, M.M.V.G., 2002. The mineralized veins and the impact of old mine workings on the environment at Segura, central Portugal. *Chem. Geol.* 190, 417–431.
- Arora, M., Kiran, B., Rani, S., Rani, A., Kaur, B., Mittal, N., 2008. Heavy metal accumulation in vegetables irrigated with water from different sources. *Food Chem.* 111, 811–815.
- Atiemo, M.S., Ofosu, G.F., Mensah, H.K., Tutu, A.O., Palm, N.D.M.L., Blankson, S.A., 2011. Contamination assessment of heavy metals in road dust from selected roads in Accra, Ghana. *Res. J. Environ. Earth Sci.* 3 (5), 473–480.
- Ávila, P.F., Santos Oliveira, J.M., Ferreira da Silva, E., Cardoso Fonseca, E., 2005. Geochemical signatures and mechanisms of trace elements dispersion in the area of the Vale das Gatas mine (Northern Portugal). *J. Geochem. Explor.* 85 (1), 17–29.
- Ávila, P.F., Ferreira da Silva, E., Salgueiro, A.R., Farinha, J.A., 2008. Geochemistry and mineralogy of mill tailings impoundments from the Panasqueira Mine (Portugal). Implications for the surrounding environment. *Mine Water Environ. J. Int. Mine Water Assoc.* 27 (4), 210–224.
- Banerjee, A.D.K., 2003. Heavy metal levels and solid phase speciation in street dusts of Delhi, India. *Environ. Pollut.* 123, 95–105.
- Banza, C.L.N., Nawrot, T.S., Hufroid, V., Decrée, S., De Putter, T., Smolders, E., Kabyła, B.I., Luboya, O.N., Ilunga, A.N., Mtombo, A.M., Nemery, B., 2009. High human exposure to cobalt and other metals in Katanga, a mining area of the Democratic Republic of Congo. *Environ. Res.* 109, 745–752.
- Bobos, I., Durães, N., Noronha, F., 2006. Mineralogy and geochemistry of mill tailings impoundments from Aljustrel (Aljustrel), Portugal. Implications for acid sulfate mine waters formation. *J. Geochem. Explor.* 88, 1–5.
- Bosso, S.T., Enzweiler, J., 2008. Bioaccessible lead in soils, slag, and mine wastes from an abandoned mining district in Brazil. *Environ. Geochem. Health* 30, 219–229.
- Boulet, M.P., Larocque, A.C.L., 1998. A comparative mineralogical and geochemical study of sulfide mine tailings at two sites in New Mexico, USA. *Environ. Geol.* 33, 130–142.
- Breiter, K., 2001. Report about Laboratory Investigations of Rock Samples from the Panasqueira Mine and Recommendations for Future Exploration.
- Candeias, C., Ferreira da Silva, E., Salgueiro, A.R., Pereira, H.G., Reis, A.P., Patinha, C., Matos, J.X., Ávila, P.H., 2011a. The use of multivariate statistical analysis of geochemical data for assessing the spatial distribution of soil contamination by potentially toxic elements in the Aljustrel mining area (Iberian Pyrite Belt, Portugal). *Environ. Earth Sci.* 62, 1461–1479.
- Candeias, C., Ferreira da Silva, E., Salgueiro, A.R., Pereira, H.G., Reis, A.P., Patinha, C., Matos, J.X., Ávila, P.H., 2011b. Assessment of the soil contamination by potentially toxic elements in Aljustrel mining area in order to implement soil reclamation strategies. *Land Degrad. Dev.* 22, 565–585.
- Candeias, C., Salgueiro, A.R., Ferreira da Silva, E., Ávila, P.F., 2012. Assessment of Panasqueira mine surrounding soils through a contamination factor. In: 9th International Symposium on Environmental Geochemistry. Book of Abstracts, pp. 27–28.
- Carvalho, P.C.S., Neiva, A.M.R., Silva, M.M.V.G., 2009. Geochemistry of soils, stream sediments and waters close to abandoned W–Au–Sb mines at Sarzedas, Castelo Branco, central Portugal. *Geochem.: Explor., Environ., Anal.* 9, 341–352.
- Carvalho, P.C.S., Neiva, A.M.R., Silva, M.M.V.G., 2012. Assessment of the potential mobility and toxicity of metals and metalloids in soils contaminated by old Sb–Au and As–Au mines (NW Portugal). *Environ. Earth Sci.* 65, 1215–1230.
- Cavey, G., Gunning, D., 2006. Updated Technical Report on the Panasqueira Mine, Distrito de Castelo Branco, Portugal. OREQUEST.
- Chen, S., Sun, L., Chao, L., Zhou, Q., Sun, T., 2009. Estimation of lead bioavailability in smelter-contaminated soils by single and sequential extraction procedure. *Bull. Environ. Contam. Toxicol.* 82, 43–47.
- Chon, H.T., Cho, C.H., Kim, K.W., Moon, H.S., 1995. The occurrence and dispersion of potentially toxic elements in areas covered with black shales and slates in Korea. *Appl. Geochem.* 11, 69–76.
- Coelho, P., Silva, S., Roma-Torres, J., Costa, C., Henriques, A., Teixeira, J., Gomes, M., Mayan, O., 2007. Health impact of living near an abandoned mine – case study: Jales mine. *Int. J. Hyg. Environ.-Health* 210, 399–402.
- Correa, A., Naique, R.A., 1998. Minas Panasqueira, 100 Years of Mining History. Paper Presented at the 1998 International Tungsten Industry Association (ITIA) Conference.
- Corrêa de Sá, A., Naique, R.A., Nobre, E., 1999. Minas da Panasqueira – 100 anos de História. *Bol. de Minas* 36 (1), 3–22.
- Costa, P., 2004. Atlas do Potencial Eólico para Portugal Continental. Dissertação de Mestrado, Faculdade de Ciências da Universidade de Lisboa.
- Costa, P., Estanqueiro, A., 2006a. Building a wind atlas for Mainland Portugal using a weather type classification. In: Proceedings of the European Wind Energy Conference, (EWEC), Athens.
- Costa, P., Estanqueiro, A., 2006b. Development and validation of the Portuguese wind atlas. In: Proceedings of the European Wind Energy Conference, (EWEC), Athens.
- Decree-Law 306/2007, 2007. Portuguese Republic Diary, Ministry for Environment, Spatial Planning and Regional Development. Diário da República, 1.ª série – N.º 164–27 de Agosto de 2007.
- Douay, F., Rousselet, H., Fourrier, H., Heyman, C., Chateau, G., 2007. Investigation of heavy metal concentrations on urban soils, dust and vegetables nearby a former smelter site in Mortagne du Nord, Northern France. *J. Soil Sediments* 7, 143–146.
- Douay, F., Roussel, H., Pruvot, C., Waterlot, C., 2008. Impact of a smelter closedown on metal contents of wheat cultivated in the neighborhood. *Environ. Sci. Pollut. Res.* 15, 162–169.
- Ettler, V., Vaněk, A., Mihaljevič, M., Bezdička, P., 2005. Contrasting lead speciation in forest and tilled soils heavily polluted by lead metallurgy. *Chemosphere* 58, 1449–1459.
- Ettler, V., Johan, Z., Kříbek, B., Šebek, O., Mihaljevič, M., 2009. Mineralogy and environmental stability of slags from the Tsumeb smelter, Namibia. *Appl. Geochem.* 24, 1–15.
- Ettler, V., Mihaljevič, M., Kříbek, B., Majer, V., Šebek, O., 2011. Tracing the spatial distribution and mobility of metal/metalloid contaminants in Oxisols in the vicinity of the Nkana copper smelter, Copperbelt province, Zambia. *Geoderma* 164, 73–84.
- Ettler, V., Kříbek, B., Majer, V., Knésl, I., Mihaljevič, M., 2012. Differences in the bioaccessibility of metals/metalloids in soils from mining and smelting areas (Copperbelt, Zambia). *J. Geochem. Explor.* 113, 68–75.
- FAO/WHO, 2012. Food Additives and Contaminants. Codex Alimentarius Commission. Joint FAO/WHO Food Standards Programme 2001, ALINORM 01/12A 1–289.
- Farinha, J.A., 2005. Packing and Sealing of the Sulphides Existing on Rio Tailing, Environmental Concerns. Internal Technical Note, 5 pages plus appendices.
- Fernandes, R.B.A., Luz, W.V., Fontes, Maurício, P.F., Fontes, L.E.F., 2007. Evaluation of heavy metal concentrations in vegetable crop cultivation areas in Minas Gerais, Brazil. *R. Bras. Eng. Agríc. Ambient.* 11 (1), 81–93.
- Ferreira, M.M.S.I., 2004. Dados geoquímicos de base de solos de Portugal Continental, utilizando amostragem de baixa densidade. Tese de Doutoramento da Universidade de Aveiro.
- Ferreira, M.A., Barros, A.A., 2002. Determination of As(III) and arsenic(V) in natural waters by cathodic stripping voltammetry at a hanging mercury drop electrode. *Anal. Chim. Acta* 459, 151–159.
- Ferreira da Silva, E., Cardoso Fonseca, E., Matos, J.X., Patinha, C., Reis, P., Santos Oliveira, J.M., 2005. The effect of unconfined mine tailings on the geochemistry of soils, sediments and surface waters of the Lousal area (Iberian Pyrite Belt, Southern Portugal). *Land Degrad. Dev.* 16, 213–228.
- Ferreira da Silva, E., Ávila, P.F., Salgueiro, A.R., Candeias, C., Garcia Pereira, H., 2013. Quantitative-spatial assessment of soil contamination in S. Francisco de Assis due to mining activity of the Panasqueira mine (Portugal). *Environ. Sci. Pollut. Res.* <http://dx.doi.org/10.1007/s11356-013-1495-2>.
- Ferreira-Baptista, L., De Miguel, E.D., 2005. Geochemistry and risk assessment of street dust in Luanda, Angola. A tropical urban environment. *Atmos. Environ.* 9, 4501–4531.
- Galán, E., Gómez-Ariza, J.L., González, I., Fernández-Caliani, J.C., Morales, E., Giráldez, I., 2003. Heavy metal partitioning in river sediments severely polluted by acid mine drainage in the Iberian Pyrite Belt. *Appl. Geochem.* 18, 409–421.
- Gomes, M.E.P., Antunes, I.M.H.R., Silva, P.B., Neiva, A.M.R., Pacheco, F.A.L., 2010. Geochemistry of waters associated with the old mine workings at Fonte Santa (NE of Portugal). *J. Geochem. Explor.* 105 (3), 153–165.
- Grangeia, C., Ávila, P.F., Matias, M., Ferreira da Silva, E., 2011. Mine tailings integrated investigations: the case of Rio Tailings (Panasqueira Mine – Centre Portugal). *Eng. Geol.* 123 (4), 359–372.
- Islam, Ejazul, Yang, Xiao-e, He, Zhen-li, Mahmood, Qaisar, 2007. Assessing potential dietary toxicity of heavy metals in selected vegetables and food crops. *J. Zhejiang Univ. Sci. B* 8 (1), 1–13.
- JECFA, 1993. Joint FAO/WHO Expert Committee on Food Additives Evaluation of Certain Food Additives and Contaminants. 41st Report of the Joint FAO/WHO expert Committee on Food Additives, World Health Organization, Geneva, Technical Reports Series No. 837.
- Juhász, A.L., Weber, J., Smith, E., 2011. Impact of soil particle size and bioaccessibility on children and adult lead exposure in peri-urban contaminated soils. *J. Hazard. Mater.* 186, 1870–1879.
- Jung, M.C., 2001. Heavy metal contamination of soils and waters in and around the Imcheon Au–Ag mine, Korea. *Appl. Geochem.* 16, 1369–1375.
- Kelly, W.C., Rye, R.O., 1979. Geologic, fluid inclusion and stable isotope studies of the tin–tungsten deposits of Panasqueira, Portugal. *Econ. Geol.* 74, 1721–1822.
- Kim, K.W., Lee, H.K., Yoo, B.C., 1998. The environmental impact of gold mines in the Yugu-Kwangcheon Au–Ag metallogenic province, Republic of Korea. *Environ. Technol.* 19, 291–298.
- Kloke, A., 1979. Contents of Arsenic, Cadmium, Chromium, Fluorine, Lead, Mercury, and Nickel in Plants Grown on Contaminated Soil. UNECE Symposium, Geneva.
- Kříbek, B., Majer, V., Veselovský, F., Nyambe, I., 2010. Discrimination of lithogenic and anthropogenic sources of metals and sulphur in soils of the central-northern part of the Zambian Copperbelt Mining District: a topsoil vs. subsurface soil concept. *J. Geochem. Explor.* 104, 69–86.
- Lee, J.S., Chon, H.T., Kim, J.S., Kim, K.W., Moon, H.S., 1998. Enrichment of potentially toxic elements in areas underlain by black shales and slates in Korea. *Environ. Geochem. Health* 20, 135–147.
- Lee, C.G., Chon, H.T., Jung, M.C., 2001. Heavy metal contamination in the vicinity of the Daduk Au–Ag–Pb–Zn mine in Korea. *Appl. Geochem.* 16, 1377–1386.



- Luís, A.T., Teixeira, P., Almeida, S.F.P., Ector, L., Matos, J.X., Ferreira da Silva, E.A., 2009. Impact of acid mine drainage (AMD) on water quality, stream sediments and periphytic diatom communities in the surrounding streams of Aljustrel mining area (Portugal). *Water Air Soil Pollut.* 200, 147–167.
- Luo, C., Liu, C., Wang, Y., Liu, X., Li, F., Zhang, G., Li, X., 2011. Heavy metal contamination in soils and vegetables near an e-waste processing site, south China. *J. Hazard. Mater.* 186, 481–490.
- Mapanda, P., Mangwayana, E.N., Nyamangara, J., Giller, K.E., 2007. Uptake of heavy metals by vegetables irrigated using wastewater and the subsequent risks in Harare, Zimbabwe. *Phys. Chem. Earth* 32, 1399–1405.
- McCauley, A., Jones, C., Jacobsen, J., 2009. Soil pH and Organic Matter. Nutrient Management Module No. 8. Montana State University.
- McKenzie, A.B., Pulford, I.D., 2002. Investigation of contaminant metal dispersal from a disused mine site at Tyndrum, Scotland, using concentration gradient and Pb isotope ratios. *Appl. Geochem.* 17, 1093–1103.
- Ministry of the Environment, 2011. Soil, Groundwater and Sediment Standards for the Use Under, Part XV.1 of the Environmental Protection Act. Ontario.
- Moore, J.N., Luoma, S.N., 1990. Hazardous wastes from large-scale metal extraction. *Environ. Sci. Technol.* 24, 1278–1285.
- Naicker, K., Cukrowska, E., McCarthy, T.S., 2003. Acid mine drainage arising from gold mining activity in Johannesburg, South Africa and environs. *Environ. Pollut.* 22 (1), 29–40.
- Nimick, D.A., Moore, J.M., 1991. Prediction of water-soluble metal concentrations in fluvially deposited tailing sediments, Upper Clark Fork Valley, Montana, USA. *Appl. Geochem.* 6, 635–646.
- Nishida, H., Miyai, M., Tada, F., Suzuki, S., 1982. Computation of the index of pollution caused by heavy metals in river sediment. *Environ. Pollut.* B4, 241–248.
- Noronha, F., Doria, A., Dubessy, J., Charoy, B., 1992. Characterization and timing of the different types of fluids present in the barren and ore veins of the W–Sn deposit of Panasqueira, Central Portugal. *Miner. Deposita* 27, 72–79.
- Oti Wilberforce, J.O., Nwabue, F.I., 2013. Heavy Metals Effect due to Contamination of Vegetables from Enyigba Lead Mine in Ebonyi State, Nigeria. *Environ. Pollut.* 2 (1), 19.
- Perrin, J., 1974. Classification des sols organiques. *Bull. Liaison de LCPC*, 69.
- Pinto, M.M.S.C., Silva, M.M.V.G., Neiva, A.M.R., 2004. Pollution of water and stream sediments associated with the Vale De Abrutiga uranium mine, Central Portugal. *Mine Water Environ.* 23, 66–75.
- Pope, J.M., Farago, M.E., Thornton, I., Cordos, E., 2005. Metal enrichment in Zlatna, a Romanian copper smelting town. *Water Air Soil Pollut.* 162, 1–18.
- Ramsey, M.H., Thompson, M., Banerjee, E.K., 1987. Realistic assessment of analytical data quality from inductively coupled plasma atomic emission spectrometry. *Anal. Proc.* 24, 260–265.
- Reeuwijk, L.P.V., 2002. Procedures for Soil Analysis, sixth ed. Technical Paper/International Soil Reference and Information Centre, Wageningen, The Netherlands.
- Reimann, C., De Caritat, P., 1998. Chemical elements in the environment: factsheets for the geochemist and environmental scientist. Springer Verlag, Berlin.
- Reis, A.C., 1971. As Minas da Panasqueira. *Bol Minas* 8 (1), 3–34.
- Roussel, H., Waterlot, C., Pelfrène, A., Pruvot, C., Mazzuca, M., Douay, F., 2010. Cd, Pb and Zn oral bioaccessibility of urban soils contaminated in the past by atmospheric emissions from two lead and zinc smelters. *Arch. Environ. Contam. Toxicol.* 58, 945–954.
- Salgueiro, A.R., Ávila, P.F., Pereira, H.G., Santos Oliveira, J.M., 2008. Geostatistical estimation of chemical contamination in stream sediments. The case study of Vale das Gatas mine (northern Portugal). *J. Geochem. Explor.* 98, 15–21.
- Santos Oliveira, J.M., Ávila, P.F., 1995. Avaliação do Impacte Ambiental provocado por uma exploração mineira. Um caso de estudo na mina de Jales. *Estudos, Notas e Trabalhos do IGM* 37, 25–50 (in Portuguese).
- Santos Oliveira, J.M., Ávila, P.F., 2003. Geoquímica e mineralogia ambientais na investigação de impactes resultantes da actividade mineira. Um caso de estudo. *Memórias e Notícias, No 2 (Nova série)*. Publ. Do Dep. Ciênc. Terra e do Mus, Univ. Coimbra. *Mineral. Geol.* 279–300 (in Portuguese).
- Santos Oliveira, J.M., Farinha, J., Matos, J.X., Ávila, P., Rosa, C., Canto Machado, M.J., Daniel, F.S., Martins, L., Machado Leite, M.R., 2002. Diagnóstico Ambiental das Principais Áreas Mineiras Degradadas do País. *Boletim de Minas. Publ. Inst. Geol. Min.* 39 (2), 67–85 (in Portuguese).
- Sezgin, N., Ozcan, H.K., Demir, G., Nemioglu, S., Bayat, C., 2003. Determination of heavy metal concentrations in street dusts in Istanbul E-5 highway. *Environ. Int.* 29, 979–985.
- Sharma, R.K., Agrawal, M., Marshall, F.M., 2008. Heavy metal (Cu, Zn, Cd and Pb) contamination of vegetables in urban India: a case study in Varanasi. *Environ. Pollut.* 154, 254–263.
- Sipter, E., Rózsa, E., Gruiz, K., Tátrai, E., Morvai, V., 2008. Site-specific risk assessment in contaminated vegetable gardens. *Chemosphere* 71, 1301–1307.
- Šrāček, O., Mihaljevič, M., Křibek, B., Majer, V., Veselovský, F., 2010. Geochemistry and mineralogy of Cu and Co in mine tailings at the Copperbelt, Zambia. *J. Afr. Earth Sc.* 57, 14–30.
- To, T.B., Nordstrom, D.K., Cunningham, K.M., Ball, J.W., McCleskey, R.B., 1999. New method for the direct determination of dissolved Fe(III) concentration in acid mine waters. *Environ. Sci. Technol.* 33 (5), 807–813.
- USEPA, 1989. Risk Assessment Guidance for Superfund, Human Health Evaluation Manual Part A, Interim Final, vol. I. 7 United States Environmental Protection Agency, Washington, DC, EPA/540/1-89/002.
- Valente, T., Leal Gomes, C., 1998. Tipologia e evolução dos materiais de neoformação supergênica detectados na escombreira da Mina de Valdearcas (Vila Nova de Cerveira – N Portugal) – Implicações ambientais. *Cadernos Lab. Xeológico de Laxe* 23, 43–58.
- Verner, J.F., Ramsey, M.H., 1996. Heavy metal contamination of soils around a Pb–Zn smelter in Bukowno, Poland. *Appl. Geochem.* 11 (1–2), 11–16.
- Vítková, M., Ettler, V., Johan, Z., Křibek, B., Šebek, O., Mihaljevič, M., 2010. Primary and secondary phases in copper–cobalt smelting slags from the Copperbelt Province, Zambia. *Mineral. Mag.* 74, 581–600.
- WHO, 2000. Air Quality Guidelines for Europe. WHO Regional Publications, European Series No. 91. Second Edition, World Health Organization, Copenhagen.
- Witte, K.M., Wanty, R.B., Ridley, W.I., 2004. Engelmann Spruce (*Picea engelmanni*) as a biological monitor of changes in soil metal loading related to pas mining activities. *Appl. Geochem.* 19, 1367–1376.
- Wong, S.C., Li, X.D., Zhang, G., Qi, S.H., Min, Y.S., 2002. Heavy metals in agricultural soils of Pearl River Delta, South China. *Environ. Pollut.* 119, 33–44.
- Zheng, N., Wang, Q., Zheng, D., 2007. Health risk of Hg, Pb, Cd, Zn, and Cu to the inhabitants around Huludao Zinc Plant in China via consumption of vegetables. *Sci. Total Environ.* 383, 81–89.
- Zhuang, P., McBride, M.B., Xia, H., Li, N., Li, Z., 2009. Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China. *Sci. Total Environ.* 407, 1551–1561.