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ORIGINAL PAPER

Health risk assessment through consumption of vegetables rich in heavy metals: the case study of the surrounding villages from Panasqueira mine, Central Portugal

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Abstract Panasqueira mine is a tin–tungsten mineralization hosted by metasediments with quartz veins rich in ferberite. The mineralization also comprises wolframite, cassiterite, chalcopyrite, several sulfides, carbonates and silver sulfosalts. The mining and beneficiation processes produce arsenic-rich mine wastes laid up in huge tailings (Barroca Grande and Rio tailings). The contents of As, Cd, Cr, Cu, Pb and Zn were estimated in rhizosphere soils, irrigation waters, road dusts and in potatoes, cabbages, lettuces and beans, collected on local gardens of four neighborhood Panasqueira mine villages: S. Francisco de Assis (SFA) and Barroca suffering the influence of tailings; Unhais-o-Velho and Casegas considered as non-polluted areas. The mean concentrations of metals in rhizosphere soils and vegetables exceed the reference guidelines values and seem to be linked to the sulfides. The rhizosphere ecological risks were ranked in the order of Cd > As > Cu > Pb > Zn > Cr and SFA > Barroca > Casegas > Unhais-o-Velho. Metal concentrations, in vegetables, were found in the order of lettuce > cabbage > potatoes and SFA > Barroca > Casegas > Unhais-o-Velho. For cabbages and lettuces, the tendency of contamination is roots > leaves and for potatoes is roots > leaves > tubers. The risk for residents, due to ingesting of metals/metalloid, by consuming vegetables grown around the sampling area, was calculated and the result indicates that the inhabitants of these villages are probably exposed to some potential health risks through the intake of heavy metals and metalloids via consuming their vegetables.

Keywords Mining activity · Heavy metals/metalloids · Vegetables · Exposure · Hazard

Introduction

Mining is one of the oldest activities in human civilization and is a vital economic sector for many countries. It is also one of the most hazardous activities. Metal mining processing and smelting can negatively affect the surrounding environment and are a major contributor to environmental pollution. After the extraction of economic elements, mine sites contain large amounts of waste material characterized by high concentrations of metals and metalloids such

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as As, Cd, Cr, Pb, Ni, Sb and Zn, increasing the abundance of these elements at the Earth crust (e.g., Rodríguez et al. 2009; Wanat et al. 2014) and providing sources of heavy metals that may lead to the surrounding environment contamination. There is extensive literature devoted to studies of soils contaminated by metals and metalloids around mine sites (e.g., Bech et al. 2012; Boussen et al. 2013; Wanat et al. 2014), with studies focusing on methods for evaluating the factors controlling the distribution, behavior and environmental impact of these pollutants with respect to both vegetation and human health. Mineral extraction and processing produce crushed and milled waste rock and tailings that cause a potential risk to the environment when exposed to weathering (Dold and Fontboté 2001). The dispersion of these pollutants into the environment around mine tailings, through wind and water, is an important type of anthropogenic contamination. 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 (Bes et al. 2014; Kříbek et al. 2014). In particular, mine wastes containing high sulfide concentrations are notorious for their potential production of acid mine drainage (AMD) and leaching of contaminants during and after mining. These consequences can be particularly problematic when the mining and ore treatment occur in populated areas once soil and water can be easily contaminated by metals (and metalloids) (Alloway 1993) leading eventually to a loss of biodiversity and acting like a potential health risk to residents in the vicinity of the mining area (Wong et al. 2002; Galán et al. 2003).

Heavy metal pollution of agricultural soils and vegetables is one of the most severe ecological problems on a world scale. The food chain contamination is the major pathway of heavy metal exposure for humans (Khan et al. 2008). Some trace elements are essential in plant nutrition, but plants growing in the nearby zone of industrial areas display increased concentration of heavy metals serving in many cases as biomonitors of pollution loads (Mingorance et al. 2007). The rhizosphere soil is directly influenced by root activity. For decades, the investigations of chemical elements in the rhizosphere had focused on the macronutrients N, P and K, and the essential micronutrient Fe and little work was done on the impact of root-induced processes on the solubility, speciation, bioavailability and mobility (including leaching) of heavy metals in the root zones (Wenzel et al. 2003). The understanding of heavy metal behavior in the rhizosphere is essential because rhizosphere is a focal point of entry of heavy metals into the food chain. Water uptake by plant roots induces convective transport of solutes toward the root. Depending on how this flux of solutes matches with its uptake by the roots from the soil solution, solutes will either accumulate or be depleted in the rhizosphere (Lorenz et al. 1994).

Vegetables cultivated in soils polluted with toxic metals take up heavy metals and accumulate them in their edible and non-edible parts in quantities high enough to cause clinical problems both to animals and human beings by consuming these metal-rich plants because there is no good mechanism for their elimination from the human body (Naser et al. 2012). Better understandings of heavy metal sources, the effect of their presence in water, accumulation in soil and on plant systems are important issues on risk assessment studies, since the toxic heavy metals entering the ecosystem may be geoaccumulated and bioaccumulated (Prabu 2009).

Heavy metals such as Cu, Fe, Mn and Zn and other trace elements are important for proper functioning of biological systems and their deficiency or excess could lead to a number of disorders (Finkelman et al. 2005). The remarkable increase in exposure to metals and metalloids in several environmental settings represents a worldwide pattern, affecting a significant number of individuals. Most metals and metalloids have toxic properties and can represent an important threat for human health. Major health effects include development retardation, endocrine disruption, kidney damage, immunological and neurologic effects and several types of cancer (Mudgal et al. 2010).

The Panasqueira hydrothermal mineralization located in Central Portugal (40°9′57″N, 7°45′37″W—Fig. 1) is the biggest Sn–W deposit of Western Europe and has been in operation since 1896 to the present date, being one of the largest economic vein deposits in the world (Smith 2006).

The aim of the present study was: (a) to highlight the accumulation status of essential and non-essential heavy metals in vegetables and respective rhizospheres; (b) to compare the essential and non-essential heavy metal status of vegetables and rhizosphere soils in polluted and supposedly non-polluted areas; (c) to estimate dietary

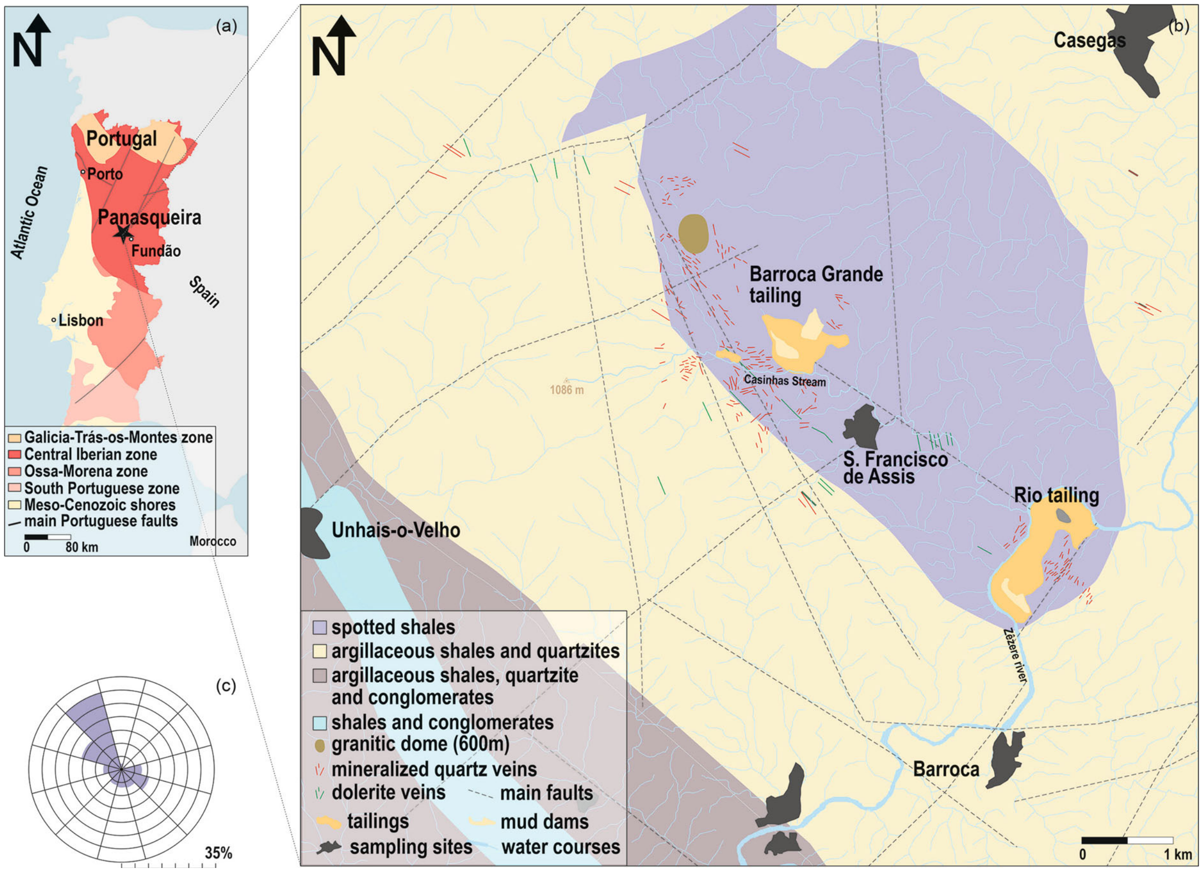

Fig. 1 **a** Location of the study area, **b** Panasqueira mine, sampling sites and the main geological units, **c** wind rose of the prevailing winds on the *top* of the mine, on Barroca Grande tailing (extracted from CD-ROM “Atlas do Potencial Eólico para Portugal Continental—version 1.0”)

intake and identify the risk to local populations through the ingestion of metal-rich vegetable that grow in their yards located in the mine vicinity; and (d) to highlight that the combination of environmental and human biomonitoring studies may synergistically increase the knowledge about the bioaccessibility and bioavailability of toxic elements, which is essential to assess the potential risks to human health.

The study area

Site description

The Panasqueira mine, active for over 110 years, is located in Central Portugal in the municipalities of Covilhã and Fundão (Castelo Branco district, Central Portugal). The mining district is situated between the S. Pedro de Açor, Estrela and Gardunha mountains, to the W of the Cova da Beira central Portuguese depression (Beira Baixa Province) 20 km SW from the Serra da Estrela Mountain, the highest mountain of Portugal mainland (1993 m high). 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 average annual rain precipitation in the region is 1200–1400 mm; snow fall is frequent, particularly above the altitude of 700 m. The average annual temperature is ≈12 °C, ranging from ≈0 °C during the winter to about ≈30 °C in summer (Ávila et al. 2008). The evapotranspiration in this region is around 1080 mm (source: inag 2016).

The mine is a group of interconnected room and pillar underground mines where several decades of mineral extraction and processing produced crushed and milled wastes stored in large tailings and open-air impoundments (Ávila et al. 2008; Ferreira da Silva et al. 2013). Between 2002 and 2007, the physical, chemical and mineralogical characterization of the stored mining leftovers in the Panasqueira tailings and the affected surrounding area were studied in the scope of the e-Ecorisk project, an EU 5th Framework Programme (e-Ecorisk 2007) that was designed to identify, characterize and quantify the threat and potential environmental and social impacts (harm) of a catastrophic disruption of an impoundment which would lead to the uncontrolled release of effluent into the environment. In Panasqueira mine this study was centered in the arsenopyrite-rich mining leftovers that are disposed into two large tailing sites (Rio Tailings ≈5MT and Barroca Grande tailing ≈17MT) and in the ore processing materials stored in open-air impoundments which are responsible for the continuous generation of acid drainage.

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).

Mining activity and origin of the soil pollution

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. Detailed descriptions of the mining activity history and ore treatment process were presented in Ávila et al. (2008) and Candeias et al. (2014a). Until 1996, the pre-concentrates from ore treatment processes were transported to the Rio plant. The Rio tailing site, located near and draining directly to the Zêzere River, is a large site where tailings have been disposed of for approximately 90 years (Ávila et al. 2008). Nowadays the economic exploitation is located in Barroca Grande as well as the beneficiation plant. The waste rock is placed in a huge tailing pile and the rejected materials from the ore processing in two tailing pounds, one 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 sulfides, arsenopyrite is the main sulfide present) obtained from the ore dressing operations. 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. Soils, downstream both tailings deposits, are a major repository for the heavy metals released from these piles of rejected materials.

Materials and methods

Field sampling

Sampling sites were chosen taking into account its location concerning the mine (Fig. S1) and different degrees of environmental pollution exposure: (1) S. Francisco de Assis (SFA), 4 km downstream Barroca Grande tailing, is a little village with 16.08 km^2 and 632 inhabitants, (2) Barroca is a village located downstream Rio tailing, with 23.1 km^2 and 496 inhabitants, and suffers the contribution of both tailings (Barroca Grande and Rio tailings), (3) Unhais-o-Velho, 40.1 km^2 and 458 inhabitants, lies around 12 km west from the mine, supposedly is a non-polluted area and (4) Casegas, 41.2 km^2 and 425 inhabitants, is an area upstream Barroca Grande also considered as a non-polluted area.

To investigate the possible environmental contamination on agricultural and residential soils of the surrounding villages due to the mining activities, four sampling media were selected, rhizosphere soils, vegetables, irrigation water and outdoor dusts. In each site of sampling (private houses), a questionnaire was filled, characterizing the family habits and agricultural behaviors (Candeias 2013). These media are important to assess the impact of the anthropogenic activities both on the surrounding ecosystems and human health of the inhabitants. Samples of rhizosphere, waters and vegetables were collected by a random process from particular backyards in all four selected villages.

Vegetables and rhizosphere soil samples will define the extent of local soil contamination and will also allow to understand the metals transfer processes from soils to the different part of the plants once the plant root system removes nutrients from the soil mineral phases. The sampling campaign started in SFA, village with a large exposure to the tailing materials and suffering directly the impact of environmental contamination on their agricultural and residential soils due to the mining activities (Fig. 2). The selected vegetables for this study in SFA, once they grow extensively in this village, were potatoes (*Solanum tuberosum* L.) and cabbages (*Brassica olerácea* L.). Potatoes, cabbages, lettuces (*Lactuca sativa* L.) and beans (*Phaseolus vulgaris* L.) were the sampled vegetables in Barroca village. In Casegas, as in SFA, the collected vegetables were potatoes and cabbages and in Unhais-o-Velho, potatoes, cabbages and lettuces. The plant samples represent whole parts of the vegetable (fruits, leaves, stems and roots whenever possible). The edible part of each vegetable is as follows: potatoes—tubers; cabbages—leaves and stems; lettuces—leaves; and beans—dry seed or unripe fruit. Its leaf is also used as a vegetable. Soil samples from rhizosphere of the respective vegetable were collected simultaneously with the vegetables.

Water samples will define the influence of soils and human activities in the quality of the water used by the local populations for consumption and for irrigation. In all the above sites, waters were collected in private wells but also in the river and streams whenever their waters are used to irrigate the vegetables. The outdoor dust allows the quantification of the contaminants from tailings through wind transport and its influence in local soils, vegetables and water bodies (Candeias 2013). According to Costa (2004) and Costa and Estanqueiro (2006a, b) the wind speed in Barroca Grande at an elevation of 80 m reveals that NNW is the preferential wind direction in this area, and the wind that blows from NW goes to SE, and that is precisely the direction of SFA and Barroca regarding the Barroca Grande tailing position (Fig. 1). This fact was the reason that at each sampling point, in addition

Fig. 2 View of S. Francisco de Assis (SFA), located downstream Barroca tailing

to vegetables, rhizosphere and irrigation water, also dust samples, accumulated on the roads nearby the backyard were collected.

Rhizosphere soil, dusts and vegetables

Fifty-four rhizosphere soil samples and 54 edible vegetables, distributed as follows: 14 potatoes (*Solanum tubersum* sava), 29 cabbages (*B. olerácea* L.), 7 lettuces (*L. sativa* L.) and 4 beans (*P. vulgaris* L.) were collected (Fig. S1) in polyethylene bags and brought to the laboratory. In this study, 40 road dusts were collected, whenever it was possible, 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 2 mm aperture sieve and milled for chemical analysis. The vegetables samples were cleaned from any soil particles, oven-dried also at a temperature of 40 °C and finely milled.

Waters

A total of 44 irrigation waters samples were collected in private houses of the four villages (Fig. S1), picked from public water supply network, private wells, small water courses, spring waters and Zêzere River. The samples were collected using a clean 1-L acid-washed polyethylene bottle and stored at 4 °C until analysis. Values of pH, electric conductivity (EC), oxidation–reduction potential (ORP) of the waters were recorded at each site using a multiparametric probe HI9828 with GPS from HANNA Instruments©. Samples were filtered onsite through 0.45-µm Millipore© membrane filters using an all-plastic pressurized filtering system. The concentrations of HCO_3 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_3, avoiding Fe hydroxide precipitation. All the water samples were stored at 4 °C pending further analysis.

At the same time, a biological survey was conducted, being also a questionnaire filled, by the inhabitants in each sampling point to characterize the family uses and habits, as also the agricultural practices and behaviors. The study conducted by Coelho (2013) was undertaken in 121 individuals: 40 male workers from the Panasqueira mine represented the group of occupationally exposed, 41 individuals from SFA and Barroca living in the vicinity of the mine and considered as environmentally exposed; and 40 individuals without environmental and/or occupational exposition living in areas considering non-contaminated (Casegas and Unhais-o-Velho villages).

Sample preparation and chemical analysis

Sample preparation and chemical analysis procedure were the same described in detail in Candeias et al. (2014a). Rhizosphere soil, dusts and vegetable samples were analyzed by inductively coupled plasma emission spectrometry (ICP-MS) for 35 chemical elements. 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 procedure was modified from ISO 10390:1994 Soil; the pH was determined with samples in diluted $CaCl_2$, and measures were taken 24 h after. Soil organic matter (SOM) were determined in 5 g dried samples, after 20 h in a 430 °C muffle as described in Candeias et al. (2014a). Waters samples were analyzed for major cations by ion chromatography using a Dionex© 2000i and a Spectraphysics integrator and for trace elements by ICP-MS. Reagent blanks and duplicate samples were inserted into each batch for quality control. Depending on the concentration levels, typical uncertainties, including all error sources, are <6 % for the trace elements, and between 2 and 7 % for the major anions (Candeias et al. 2014a). Arsenic [As(III) and As(V)] and iron [Fe(III) and Fe(II)] speciation were determined, respectively, by cathodic stripping voltammetry (CSV) and a color spectrophotometric–Vis method using ferrozine iron reagent (Candeias et al. 2014a).

Data analysis

Enrichment factors

According to Wu et al. (2015), the enrichment factors (EFs) of heavy metals were designed to quantitatively assess the contributions of anthropogenic sources to the concentrations observed in the surface soils, and they can reflect the soil evolution through time and were calculated, as indicated in Eq. (1), to determine the metal enrichment in the rhizosphere soils and dusts and the natural or anthropogenic sources.

$$\mathrm{EF} = \frac{(C_x/C_{\mathrm{ref}})_{\mathrm{sample}}}{(C_x/C_{\mathrm{ref}})_{\mathrm{background}}} \tag{1}$$

where EF is the enrichment factor of the heavy metal x and C_x is the concentration of element x. C_{ref} is the concentration of a reference element, usually a heavy metal mainly originated from soil parent material that are neither likely to be affected or suffered little contamination by anthropogenic activities nor correlated with heavy metal pollutants (Wu et al. 2015). In environmental sciences, the background, according Reimann and Garrett (2005), is the concentration of an element in a sample faraway enough from an eventual contaminant source so that it can be proved that this concentration does not originate from that source. In this study, the background values of elements in soils were obtained from Ferreira (2004), As = 11 mg kg^{-1}, Cd = 0.1 mg kg^{-1}, Cr = 21 mg kg^{-1}, Cu = 16 mg kg^{-1}, Pb = 21 mg kg^{-1}, Zn = 55 mg kg^{-1}; and the background values for dusts soils were obtained from the maximum limit of the reference value range (RVR) according to Sezgin et al. (2003), As = 20 mg kg^{-1}, Cd = 1 mg kg^{-1}, Cr = 50 mg kg^{-1}, Cu = 20 mg kg^{-1}, Pb = 20 mg kg^{-1}, Zn = 50 mg kg^{-1}. Han et al. (2006) defined five different EF classes: (1) EF <2—deficiency to minimal enrichment; (2) $2 \leq \mathrm{EF} < 5$—moderate enrichment; (3) $5 \leq \mathrm{EF} < 20$—significant enrichment; (4) $20 \leq \mathrm{EF} < 40$—very high enrichment; and (5) EF ≥40—extremely enrichment.

Pollution evaluation of heavy metals

The pollution index (Pl) by a given heavy metal i was evaluated with the single pollution index (PI$_i$), calculated as the ratio between the metal concentration (C_i) in a soil sample and its reference value (S_i) according to Eq. (2) (Wu et al. 2015):

$$\mathrm{PI}_i = \frac{C_i}{S_i} \tag{2}$$

The S_i values for As, Cd, Cr, Cu, Pb and Zn were based on the criteria (agricultural soil) specified in the Standards for Soil Environmental Quality of Portugal proposed by Ferreira (2004) As = 22 mg kg^{-1}, Cd = 0.6 mg kg^{-1}, Cr = 43 mg kg^{-1}, Cu = 35 mg kg^{-1}, Pb = 34 mg kg^{-1}, Zn = 85 mg kg^{-1}. Contamination classes based on pollution index values (Wu et al. 2015) are: (a) PI ≤1—no contamination; (b) $1 < \mathrm{PI} \leq 3$—slight contamination; (c) $3 < \mathrm{PI} \leq 5$—moderate contamination; and (d) PI >5—severe contamination.

Ecological risk

The method to determine ecological risk of heavy metals, originally introduced by Hakanson (1980) and recently used in soil contamination studies (Candeias et al. 2014b), integrates the concentration of heavy metals with ecological effect, environmental effect and toxicology, and was used to assess degree of metal pollution in the rhizosphere soils surrounding Panasqueira mine based on Eq. (3):

$$\mathrm{RI} = \sum_{i=1}^{m} E_{\mathrm{r}} \tag{3}$$

with

$$E_{\mathrm{r}} = T_{\mathrm{r}} \times C_{\mathrm{f}} \quad \text{and} \quad C_{\mathrm{f}} = \frac{C_{\mathrm{s}}}{C_{\mathrm{n}}}$$

where C_{s} is the heavy metal sample concentration and C_{n} the background concentration. E_{r} is the ecological risk of each element and RI the ecological risk of multiple elements. Hakanson (1980) defined T_{r} as a toxic response factor for a given substance and calculated it for a set of elements: 30 for Cd, 10 for As, 5 for Cu and Pb, 40 for Hg, 2 for Cr and 1 for Zn. Different RI classifications are: (a) RI <150—low ecological risk; (b) $150 \leq \mathrm{RI} < 300$—moderate ecological risk; (c) $300 \leq \mathrm{RI} < 600$—considered ecological risk; and (d) RI ≥600—very high ecological risk.

The potential ecological hazard index, proposed by Hakanson (1980), integrates the concentration of heavy metals with ecological effect, environmental effect and toxicology, and was used to assess the heavy metals pollution and ecological hazard in soils. The risk indexes of heavy metals in rhizosphere soils were calculated based on Eq. (3) where to quantitatively express the potential ecological risk of a contaminant it is necessary to determinate the ecological risk E_{r} of each element and describe this factor. The following terminology is used: E_r <40—low potential ecological risk; $40 \leq E_r < 80$—moderate potential ecological risk; $80 \leq E_r < 160$—considerable potential ecological risk; $160 \leq E_r < 320$—high potential ecological risk; $E_r \geq 320$—very high potential ecological risk.

Bioconcentration and translocation factors in vegetables

The mobility of the heavy metals from the rhizosphere soils into the parts of the plant and the ability to translocate the metals from roots to aerial part were assessed by bioconcentration factor (BCF) and translocation factor (TF), respectively (Antonijević et al. 2012). BCF was calculated for different plant parts (root, rhizome and middle leaf part) by the following equation: BCF = metal in plant part/metal in soil. The BCF was ordered as: BCF <1—there is no metal accumulation in the plant; $1 \leq \text{BCF} < 10$—metal accumulation; and ≥10—hyperaccumulator (Pandey et al. 2014). TF was estimated by the ratio of metal concentration in rhizome as compared to that of the plant root (Pandey et al. 2014). If TF values are higher than one, plants are classified as hypermetal accumulators, whereas if they are lower than one, they are considered as metal tolerant plants.

Daily intake of metals

According to Khan et al. (2008) and Mahmood and Malik (2014), the daily intake of metals (DIM) was determined by the following equation

$$\text{DIM} = \frac{C_{\text{metal}} \times C_{\text{factor}} \times D_{\text{food intake}}}{B_{\text{average weight}}} \tag{4}$$

where C_{metal}, C_{factor}, $D_{\text{food intake}}$ and $B_{\text{average weight}}$ represent the heavy metal concentrations in plants (mg kg^{-1}), conversion factor, daily intake of vegetables and average body weight, respectively. The conversion factor 0.085 was used to convert fresh green vegetable weight to dry weight, as described by Rattan et al. (2005). The average daily vegetable intakes for adults and children were considered to be 0.345 and 0.232 kg person^{-1} day^{-1}, respectively, while the average adult and child body weights were considered to be 60 and 32.7 kg, respectively, as used in previous studies (Wang et al. 2005).

Health risk index

To assess the human health risk of heavy metals, it is necessary to calculate the level of human exposure to that metal by tracing the route of exposure of pollutant to human body. Receptor population use the vegetables enriched with higher concentration of heavy metals which enters the human body leading to health risks (Mahmood and Malik 2014). The health risk index (HRI) (Eq. 5) for the locals through the consumption of contaminated vegetables was assessed based on the food chain and the reference oral dose (RfD) for each metal in mg kg^{-1} of body weight day^{-1} (Guerra et al. 2012). Values of RfD for As (0.0003 mg kg^{-1} day^{-1}), Cd (0.001 mg kg^{-1} day^{-1}), Cr (0.003 mg kg^{-1} day^{-1}) and Zn (0.3 mg kg^{-1} day^{-1}) were taken from Integrated Risk Information System (US EPA 2010). The value of RfD for Pb (0.0035 mg kg^{-1} day^{-1}) was taken from WHO (1993) and the RfD for Cu (0.04 mg kg^{-1} day^{-1}) from US EPA (1997). The HRI <1 means the exposed population is assumed to be safe.

$$\text{HRI} = \frac{\text{DIM}}{\text{RfD}} \tag{5}$$

Results and discussion

Status of rhizosphere soil pollution by heavy metals

Sampling sites were chosen taking into account its location concerning the mine (Fig. S1) and different degrees of environmental pollution exposure as stated in "Field sampling" section. Soil pH and SOM strongly affect soil functions and plant nutrient availability (McCauley et al. 2009). Table 1 summarizes the mean, minimum and maximum concentration of some trace elements as well pH and SOM in rhizosphere soils (mg kg^{-1}) from SFA, Barroca, Casegas and Unhais-o-Velho villages. The rhizosphere soils show a mean pH values between 4.1 and 6.3. According to the US Department of Agriculture (nrcs 2016), the rhizosphere soils collected in SFA and Casegas are classified as slightly acid with a mean value around 6; nevertheless, the rhizosphere soil

Table 1 Mean, minimum and maximum concentration (mg kg^{-1}) of pH, SOM (%) and also selected trace metals in rhizosphere soils from S. Francisco de Assis (SFA), Barroca (B), Casegas (C) and Unhais-o-Velho (UV) villages

	pH		SOM		As		Cd	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Cabbage ($n = 29$)								
SFA	6.2	5.1–6.9	15.4	6.7–27	262	84–919	0.9	0.4–1.4
B	6.0	5.3–70	9.1	6.2–13	62	18–171	0.5	0.2–2.0
C	6.1	5.3–6.8	10.5	5.9–16	31	20–59	0.4	0.2–0.7
UV	5.6	4.1–6.4	15.8	5.8–21	24	11–35	0.4	0.01–1
Potato ($n = 14$)								
SFA	6.3	5.9–6.6	14.6	11–21	201	71–497	1.7	0.8–2.8
B	5.6	4.6–6.5	8.3	4.0–13	46	15–86	0.7	0.1–1.5
C	6.1	5.8–6.4	11.6	11–13	36	32–40	0.3	0.2–0.3
UV	4.1	na	20.7	na	27	na	1	na
Lettuce ($n = 7$)								
SFA	na	na	na	na	na	na	na	na
B	5.5	5.4–5.7	10.5	5.5–17	31	15–58	0.4	0.01–1.1
C	na	na	na	na	na	na	na	na
UV	5.8	5.0–6.4	19.2	18.6–20	27	21–35	0.4	0.3–0.4
Bean ($n = 4$)								
SFA	na	na	na	na	na	na	na	na
B	5.6	4.8–6.2	8.4	8.1–8.9	40	23–65	0.6	0.3–0.9
C	na	na	na	na	na	na	na	na
UV	na	na	na	na	na	na	na	na
Guidelines								
(a)	na	na	na	na	11	na	1	na
(b)	na	na	na	na	22	na	0.6	na
(c)	na	na	na	na	11	na	0.1	na

	Cr		Cu		Pb		Zn	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Cabbage ($n = 29$)								
SFA	39	27–45	103	67–139	62	28–146	369	128–911
B	30	27–32	49	32–66	26	20–35	135	97–205
C	32	23–46	62	29–140	49	20–96	222	65–683
UV	25	15–30	43	18–63	41	12–108	126	79–202
Potato ($n = 14$)								
SFA	36	23–47	263	57–758	61	24–95	297	236–374
B	29	20–34	48	30–56	25	17–38	133	70–205
C	32	29–35	42	30–54	42	27–58	94	84–103
UV	30	na	42	na	40	na	152	na
Lettuce ($n = 7$)								
SFA	na	na	na	na	na	na	na	na
B	28	27–29	85	29–139	28	25–30	109	71–185
C	na	na	na	na	na	na	na	na
UV	26	21–30	54	39–63	54	21–108	141	103–202

Table 1 continued

	Cr		Cu		Pb		Zn	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Bean ($n = 4$)								
SFA	na	na	na	na	na	na	na	na
B	29	23–30	50	32–73	26	22–33	133	92–193
C	na	na	na	na	na	na	na	na
UV	na	na	na	na	na	na	na	na
Guidelines								
(a)	67	na	62	na	45	na	290	na
(b)	43	na	35	na	34	na	85	na
(c)	21	na	16	na	21	na	55	na

(a) Canadian Guidelines, Ministry of the Environment (2011); (b) Portuguese Guidelines, Ferreira (2004); (c) Portuguese background, Ferreira (2004)

n number of rhizosphere soils samples, *na* not applicable

samples range, in SFA, from 5.1 (strongly acid) to 6.9 (neutral) and, in Casegas, from 5.9 (moderately acid) to 6.6 (neutral). Soils from Barroca are moderate to slightly acid, while Unhais-o-Velho ranges from 4.1 to 6.4, meaning that there are samples classified as extremely acidic (pH $4.5 < \text{pH} < 5.0$). Soil pH is considered a master variable in soils as it controls many chemical processes that take place. It specifically affects plant nutrient availability by controlling the chemical forms of the nutrient. The optimum pH range for most plants and vegetables is between 5.5 and 7.0. According to McCauley et al. (2009), soil pH is influenced by both acid and basic forming cations, being H^+, Al^{3+} and Fe^{2+} or Fe^{3+} the common acid forming cations whereas the base forming cations include Ca^{2+}, Mg^{2+}, K^+ and Na^+. Acid conditions occur in soil having parent material high in elements such as silica and in regions with high amount of precipitation because an increase in precipitation causes increased leaching of base cations and the pH lowered (McCauley et al. 2009). In this region, acidic soils are commonly found in areas with high precipitation (average annual rain precipitation in the region is 1200–1400 mm) where soils were formed from acid forming parent material with mining contribution.

The cation and anion exchange capacity is the soil ability to retain and supply nutrients to crops, so when soil pH is high (more basic, low concentration of H^+) more base cations will be on the particle exchange sites and thus be less susceptible to leaching. However, according to McCauley et al. (2009) when pH lower (less basic, higher concentration of H^+) more base cations are available to exchange removing them from exchange sites and releasing them to the soil solution and either they are taken by the plants or lost through leaching or erosion. Metals are very tightly bound to the soil at high pH and are therefore more available at low pH levels than high pH levels, and this can cause potential metal toxicities for vegetables in acid soils. From Table 1 observation, it is possible to verify that the majority of the cabbages (*B. olerácea* L.) soils follow in the ideal pH for this vegetable ($5.6 < \text{pH} < 6.6$), according to Havlin et al. (1999). Regarding the potatoes (*S. tuberosum* L.) soil samples, they also present pH values within the recommended ranges ($5.8 < \text{pH} < 6.5$), as for lettuce (*L. sativa* L.) the ideal soil pH for this vegetables is $6.5 < \text{pH} < 7.0$ (Havlin et al. 1999), meaning that the rhizosphere soils from the lettuces sampled were more acidic than the ideal for this vegetable. Finally, the beans (*P. vulgaris* L.) from Barroca grow in a moderate acidic soil, being the level considered ideal by Havlin et al. (1999) for beans, $6 < \text{pH} < 7$. Some of these specific drops, as for example the *S. tuberosum* L., grows in a soil pH acidic ideally because the risk of infections is minimized at lower pH due to lower microbial activity (McCauley et al. 2009).

SOM serves multiple functions in the soil, including nutrient storage and soil aggregation and is a key indicator of soil quality (McCauley et al. 2009). The mean values of SFA rhizospheres SOM ranges between 14.6 and 15.4 %; for Barroca from 8.3 to

10.4 %; for Casegas samples varies from 10.5 to 11.6 %; and Unhais-o-Velho from 15.8 to 20.7 %. In general, the rhizosphere soils on the villages surrounding Panasqueira mine are classified, according to the System of Classification of Organic Soils (Perrin 1974), as medium organic soils, with 10 % $<$ SOM $<$ 30 %, except the Barroca rhizosphere samples which corresponds to low organic soils (3 % $<$ SOM $\leq$ 10 %).

Analyzing Table 1, it is possible to conclude that the mean concentrations for As, Cu and Zn of the rhizosphere soils in all sites and considered vegetables in this study, exceed the reference values proposed by the Ontario Soil Quality Guidelines (Ministry of the Environment 2011) and also the Portuguese guidelines proposed by Ferreira (2004). According to these values, soils from SFA, for example, exceed for As 20 times the Ontario reference value for agricultural soils (11 mg kg^{-1}) and ten times the Portuguese guidelines (22 mg kg^{-1}). Heavy metal concentration in most rhizosphere soils samples warranted a pollution warning, especially those nearest to the mine. The results achieved demonstrate that, according to the quality soil standard for Portugal proposed by Ferreira (2004), 100 % of the cabbage rhizosphere soils of SFA are contaminated in As, Cu and Zn; 87.5 % in Cd; 12.5 % in Cr; and 50 % in Pb. For the potatoes rhizosphere, 100 % of the samples have concentrations higher than de Portuguese adopted guidelines for As, Cd, Cu and Zn; 16.7 % of the samples are contaminated in Cr and 83.3 % in Pb. Regarding Barroca rhizospheres, for cabbage soils 100 % of the samples have concentrations higher than the guideline for As and Zn, 80 % for Cu and 20 % for Cd and Pb, Cr has all samples below the proposed Portuguese standards. The Barroca potatoes rhizosphere are contaminated in As and Zn (80 %), Cu (100 %), Cd (60 %) and for Pb 20 % of the samples are considered contaminated. For lettuce, 64 % for As and Cu, 33 % for Cd and Zn and neither Pb nor Cr have revealed high concentration in these rhizospheres. For beans, these soils have 100 % of the samples with higher contents in As and Zn regarding the guideline for these elements, 75 and 50 %, respectively, for Cu and Cd, no problems with Pb and Cr. Casegas rhizospheres cabbages have around 90 % of samples contaminated in As, Cu and Zn, 33 % in Cd, 11 % in Cr and 67 % in Pb and for potatoes soils, As and Zn reveal a percentage of 80 % of the samples contaminated in those two elements, 100 % for Cu, 60 % for Cd and 20 % for Pb. At last, Unhais-o-Velho has for cabbages rhizospheres around 86 % of the samples contaminated in As and Zn, 70 % in Cu, around 60 % in Pb and 14 % in Cd, the lettuce soils reveals 100 % in contamination for Cu and Zn, 75 % in As, 50 % in Pb and no problem with Cd and Cr.

These high levels of As, Cu, Zn and Cd in soils seems to be linked to the sulfides, existing in the Panasqueira paragenesis and also in the open-air impoundment material located in Barroca Grande and Rio tailing areas, namely arsenopyrite, calcophyrite and spharelite. Analysis of the impoundment material revealed the presence of scorodite, arsenopyrite, quartz, sphalerite, hematite and muscovite. These materials are metal-enriched at a level likely to be toxic to the ecosystem (Ávila et al. 2008). As for the other metals and taking into account the Portuguese guidelines (Ferreira 2004), Cd reveals higher values than the references in cabbages and potatoes soils of SFA, in potatoes soils of Unhais-o-Velho and bean soils of Barroca. Lead exceeds the 34 mg kg^{-1} Portuguese guideline in the following rhizosphere soils: SFA and Casegas cabbages and potatoes, also Unhais-o-Velho potatoes and lettuces. These findings indicate that even villages that were considered as outside of the mine impact—not polluted, reveal high concentrations of toxic elements in rhizosphere soils, possibly due to wind dispersion. The prevailing wind in the area is NW–SE, with mean wind speeds of 4.22 m s^{-1} ($h = 10$ m), 5.55 m s^{-1} ($h = 40$ m) and 6.21 m/s ($h = 80$ m) according to Costa (2004) and Costa and Estanqueiro (2006a, b).

Uptake, from the rhizosphere, and accumulation by crop plants represent the main entry pathway for potentially health-threatening toxic metals into human and animal food (Clemens 2006). Two elements of major concern, in the study area, are the metalloid As and the metal Cd. Cadmium is a relevant pollutant because it is a non-essential and toxic metal and has a bioavailability far greater than that of arsenic, for example (Kirkham 2006). The mobility of the metals in soils and its toxicity are related to its association with various soil constituents rather than to its total concentration. One approach to the study of the solid-phase association of elements that has applied in soil samples of SFA area by Ferreira da Silva et al. (2013) is the selective chemical extraction procedure. According the results obtained in this study, the high levels of As in soils seems to be linked to sulfides, since a considerable proportion is extracted by aqua regia (66.7–68.4 %). This high percentage associated with sulfides reflects the presence of arsenopyrite in the samples. Amorphous and crystalline Fe and Mn oxyhydroxides 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 mg kg^{-1}) may be considered very high. Cadmium show high partitioning patterns in the studied soil samples, 64.8–74.4 % of extraction by hydroxylamine leach cold, suggesting that these may be linked, to some extent, to amorphous Fe/Mn oxyhydroxides. Moreover, part of these elements was extracted with aqua region, suggesting that these elements may also be linked, to some extent, to sulfide or clay minerals. It was also shown that Cd (10.3–13.9 % of extraction, 1.9–4 mg kg^{-1} for Cd) was also extracted with sodium acetate indicating that the soluble/exchangeable/carbonate fraction is probably a preferential sink for Cd (Ferreira da Silva et al. 2013).

In this study, vanadium was selected as a reference element to calculate the EFs of the other elements. This element was selected because of its very weak relation with elements originated from anthropogenic activities; additionally, V usually originates from parent materials of soils (Wu et al. 2015). The V background value, for Portuguese soils, proposed by Ferreira (2004) is 27 mg kg^{-1}. According to Table S1, the rhizosphere soils of SFA have the higher EF for As, Cd and Cu both in cabbages and potatoes, in levels considered as a significant enrichment. Nevertheless, it should be noted that two samples from rhizosphere potatoes (SFA-9A and SFA-11) have EF values in the very high enrichment category, and two different samples from cabbage rhizosphere also have high As concentration; SFA-3B reveals an EF value in the very high enrichment category and SFA-13 with an EF = 53.7 is classified as an extremely enriched rhizosphere soil. It could be observed, in Table S2, that the heavy metals most likely to cause some kind of risk in SFA rhizosphere are in order As > Cd > Cu > Zn > Pb > Cr. For As, Cd and Cu concentrations in SFA potatoes (mean $EF_{As} = 13.7$; $EF_{Cd} = 12.7$ and $EF_{Cd} = 11.2$), these EFs > 10 indicate that the area has been strongly impacted by anthropogenic sources of heavy metals (Liu et al. 2003) and clearly reveal that the sulfide lixiviation (arsenopyrite, sphalerite and chalcopyrite) from Barroca Grande tailings and open-air impoundment to the soils downstream is continuous, being SFA soils a major repository for the heavy metals released from the tailing and the rejected materials from milling. In average, potatoes rhizosphere has EF values higher than cabbage rhizospheres. Soils from Barroca have the highest As and Cd EFs for cabbages, potatoes and beans while for lettuce the higher EF's were revealed in Cd and Cu, so the heavy metals in the rhizosphere soils from Barroca are ordered as follow: Cd > As > Cu > Zn > Cr > Pb and regarding EF rhizospheres according to the planted vegetable the order is: EF potatoes > EF lettuce = EF beans > EF cabbages. These soils suffer the influence of both tailings, Barroca Grande and Rio (Fig. 1). Casegas samples present the heavy metals ordered as Cd = Cu > As > Zn > Pb > Cr and the vegetables according the metal concentration of their rhizosphere are ordered as follow: EF cabbages > EF potatoes. Finally for Unhais-o-Velho rhizosphere soil samples the heavy metals are ordered as Cd > Cu > Zn > As > Pb > Cr and the EF's as EF potatoes > EF Lettuce > EF cabbages. The EF values less than or close to 2, indicating that these metals were originated predominantly from natural sources (Liu et al. 2003).

The evaluation of pollution indexes (PI) of heavy metals in rhizospheres was carried for the six heavy metals (metalloid) in study, As, Cd, Cr, Cu, Pb and Zn based on soil environment quality standards of Portugal proposed by Ferreira (2004). The PI results (Table S2) demonstrate that the degree of contamination of the rhizospheres soils reveals different levels as follow: in SFA the contamination is severe (PI >5) for As and Zn in cabbages, and slight ($1 < PI \leq 3$) for Cd, Pb and Cu; regarding SFA potatoes rhizospheres, they are severely contaminated in As and Cu, moderately contaminated ($3 < PI \leq 5$) in Cd and Zn and slightly in Pb. The Barroca and Casegas rhizospheres have slight contamination in As, Cu and Zn and occasionally in Cd; nevertheless, there are samples, in both villages, with individual pollution indexes classified as moderate to severe contamination. Unhais-o-Velho revealed, in general, slightly contamination. The degree of contamination of the rhizosphere soils in the majority of the samples is low, except for SFA, being the proportion of samples which have moderate ($3 < PI \leq 5$) and high (PI >5) contamination, respectively, 7.4 and 5.5 %. These results indicate that the rhizosphere soils from the selected four villages surrounding the Panasqueira mine are contaminated, mainly, by As, Cd, Cu and Zn, but in average the contamination is minimal for all metals analyzed in samples from Barroca, Casegas and Unhais-o-Velho while the samples from SFA are severely polluted in As and Cu and moderately in Zn.

The average ecological risk (E_r) of Cd in the studied area was 202.3, indicating that Cd, individually, posed a high risk to local ecosystem ($160 < E_r < 320$). Generally, metal mining and refining, manufacture and application of phosphate fertilizers and waste disposal are the main anthropogenic sources of Cd in the environment. Metal mining is the source of Cd in the studied soils and very high risk to local environment posed by Cd should be widely concerned. It was found that the E_r of heavy metals were ranked in the order of Cd > As > Cu > Pb > Zn > Cr.

In order to quantify the overall potential ecological risk of heavy metals in the rhizosphere soils, the values of RI (risk index) were computed (Table S3). RI results for rhizosphere soils in SFA ranged from 244 to 1284, with an average of 558 in cabbages and from 357 to 1391, with an average of 798 in potatoes. The lower ecological risk values were observed in rhizosphere soils of cabbages and lettuces from Unhais-o-Velho and potatoes from Casegas. The selected heavy metals in 12.9 % of the sampling sites posed very high ecological risk, 27.7 % of the samples have a considered ecological risk, 35.2 % moderate risk and 24.1 % low risk. The heavy metals pollution was ordered according to the mean RI calculated for the rhizosphere soils for each village as following: SFA > Barroca > Casegas > Unhais-o-Velho. With the distance increasing to the mine, the RI values decreases in the order of approximately <400.

Heavy metals present an environmental hazard in the vicinity of mines and their uptake by vegetables depend upon soil characteristics, both chemical and physical, as well the specie of vegetables growing in this type of substrate. The heavy metals that indicate a pollution warning in the studied rhizospheres were, mainly, As, Cu, Zn and Cd. Arsenic and Cd are the most toxic for animals and humans due to their non-biodegradable and persistent nature potentially leading, if ingested in large doses or over a long period of time, to death. Exposure to hazardous elements may have different pathways, being one of them the ingestion of vegetables grown on contaminated soils and irrigated with contaminated waters. The low pH values determined in some of the rhizosphere samples (Table 1) may be due to the irrigation with waters from the river and streams located downstream of the mining activities. Despite SFA location, immediately downstream of the Barroca tailing (Fig. 2), being expected that the pH of the rhizosphere remained more acidic due to the proximity of the mine, it was verified the contrary, probably, due to the fact that the vegetables cultivated in these rhizosphere soils were mainly, according to the owners of the sampled gardens, irrigated with waters from the public water supply network.

The chemical properties of soils depend primarily on the type of weathered rocks of the area. Particularly, the mafic rocks usually contain high concentrations of heavy metals, which contaminate the agricultural soil as well as the growing vegetables (Shah et al. 2010). The Panasqueira deposit lies in a folded metasedimentary sequence, the Beira-Schist Formation of upper Precambrian–Cambrian age, which was subjected to lower greenschist grade regional metamorphism during the early compressive stages of the Hercynian Orogeny, being composed of a several 1000 m thick sequence of lower marine flyschoid schists, graywackes, lenticular, thinly bedded mudstones, shales and arenites. Brown argillaceous schists and dark gray siliceous schists interbedded with graywackes were also identified in the area and mafic rocks as dolerites were also observed (Ávila et al. 2008). The levels of heavy metals in the rhizosphere soil samples collected from the four villages were high, probably, due to the presence of mafic bed rocks in the study area with high level of metal contents; possibly the use of different fertilizers and pesticides also brings changes in the level of heavy metals in soil; and thirdly the downstream river erosion, river irrigation and wind transportation may also effect the level of heavy metals in the studied locations.

Road dusts characterization

Road dusts, which generally are formed from several sources including natural materials (e.g., re-suspended soil and weathered materials) and anthropogenic matters (e.g., mining industry rejected materials), contribute significantly to the local environmental pollution. Road dusts carry a high loading of contaminant species including metals and were recognized as a significant pollution source itself (Bourliva et al. 2011). Road dusts are relatively complex materials, the compositions of which are seldom constant. This is because of changes during weathering, the relatively short residence time in the environment, and because the residence time is directly related to climate. Re-suspension of road dust and inadvertent ingestion of the dust adversely affect human health (Bourliva et al. 2011).

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. On the top of Barroca Grande tailing, there is a 24 h movement of dumpers in order to deposit the coarse rejected materials from the mining exploration. The dumpers tires roll cause the release of large amounts of dusts to the surrounding environment (Fig. S2). When the truck tires roll on the tailing, a large amount of dust is produced and accumulated and when lacks moisture, the dust is kicked up easily under the mechanical wind, the centrifugation of wheels and the shear flow of the truck and the natural flow. Being SFA located downstream the tailing these dusts poses serious threats to the environment and human health.

Regarding the most critical and potential hazardous elements in road dusts, arsenic for example, ranges between 62–3565, 35–519, 12–2288 and 29–1777 mg kg^{-1}, respectively, for SFA, Barroca, Casegas and Unhais-o-Velho; Cd is between a minimum of 0.3, 0.2, 0.1 and 0.2 mg kg^{-1} and a maximum of 19.4, 2.3, 10 and 15 mg kg^{-1}, while for Cu the concentrations ranges between 52, 33, 27 and 62 mg kg^{-1} and a maximum of 766, 243, 876 and 2379 mg kg^{-1} (Table 2). Comparing these concentrations with the reference values range, acceptable risk values (ARVs) and maximum acceptable values (MAVs) (Sezgin et al. 2003, Table 2), it is obvious that the dusts from SFA exceeded the RVR, ARV as also the MAV for As, Cd, Cu and Zn and the RVR for Pb. Dusts from Barroca exceeded RVR and AVR for As and Cu and ARV for Zn, as for Cd and Pb the mean values are less than RVR. Casegas samples exceeded RVR, ARV and MAV for As, Cu and Zn and RVR for Cd and Pb and for Unhais-o-Velho RVR, AVR and MAV for As, Cd, Cu and Zn. Chromium does not reveal any contamination in dust samples.

The concentrations of these heavy metals in dusts, caused by the wind dispersion mechanism, pose a severe danger for the village inhabitants affecting their health once the dusts are deposited in soils, vegetables and irrigation and animals drinking water. Heavy metals are kept under environmental pollutant category due to their toxic effects in plants, human and food. Some elements like As, Cd and Pb, for example, are cumulative. These heavy metals are persistent, accumulate and not metabolize in other intermediate compounds and do not easily breakdown in environment. These metals are accumulating in the food chain through uptake at primary producer level and then through consumption at consumer level. In the animal body, metals are entering through animal feeds, green fodder and drinking water (Raikwar et al. 2008). Cadmium is almost absent in the human body at birth and, however, accumulates with age, once is not recognized by the human system and, consequently, not excreted. Refined foods, water foods, water pipes, coffee, tea and coal burning are all the most important source of Cd with a daily dietary intake of 40–50 µg day^{-1} (WHO 2000). Cadmium interacts with some of the essential elements mainly Zn, Fe, Cu and Se due to chemical similarities and competition for binding stage. It is also reported that Cd can affected Ca, P and bone metabolism, both in industrial workers and people exposed to Cd in general environment (Jarup et al. 1998). The general population is exposed to cadmium via ingestion of food and drinking water, but also via inhalation of contaminated dusts present in the ambient air. Cadmium is classified, like arsenic, carcinogenic to humans, and studies reveal that when these two elements are associated there is an increase in the lung cancer risk in humans (iarc 2016). Arsenic, by its toxicity, may have chronic health effects that may be local or systemic. Such effects generally occur at the levels of exposure equal to 50 µg kg^{-1} weight day^{-1}. However, chronic poisoning of As includes anemia, liver and kidney damage, hyperpigmentation and keratosis, i.e., skin damage. The lung cancer is regarded as the most critical effect that results from inhalation of As particles (WHO 2000).

In road dusts, V was also selected as the reference element to calculate the EFs of the other elements (Table S4). The references values used to calculate EF's for dusts can be found in Table 2, for V the background value used was 100 mg kg^{-1} (Sezgin

Table 2 Mean, minimum and maximum concentration of trace elements in road dusts (mg kg^{-1}) from S. Francisco de Assis (SFA), Barroca (B), Casegas (C) and Unhais-o-Velho (UV) villages

	As		Cd		Cr		Cu		Pb		Zn	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
SFA (*n* = 12)	827	62–3565	5.5	0.3–19	20	9–30	346	52–766	45	14–128	462	110–1262
B (*n* = 7)	174	35–519	1.0	0.2–2.3	14	8–21	135	33–243	17	10–23	157	101–267
C (*n* = 8)	513	12–2288	2.5	0.1–10	17	9–31	269	27–879	46	12–153	320	73–707
UV (*n* = 8)	614	29–1777	4.8	0.2–15	13	9–20	590	62–2379	15	6–25	448	45–1028
RVR	2–20		0.1–1		10–50		5–20		0.1–20		10–50	
ARV	20		3		100		50		100		300	
MAV	na		3		100		100		100		300	

n number of road dusts samples, *na* not applicable, *RVR* reference value range (Sezgin et al. 2003), *ARV* acceptable risk value (Sezgin et al. 2003), *MAV* maximum acceptable values (Sezgin et al. 2003)

et al. 2003). The heavy metals analyzed in the dust samples, in all of the four studied villages, and most likely to cause risk are in descending order As > Cu > Zn > Cd > Pb > Cr. The EF values for As are substantially higher than for the other metals and to same extent EF values also for Cu too. Heavy metals with EF values >10 are believed to derive from human activities (Yongming et al. 2006). Substantially higher values indicate high enrichments and probable higher risk of the corresponding metals. According to results (Table S4) and the enrichment criteria, EFs of As, Cu and partially Zn, of the street dusts surrounding Panasqueira mine, are very high to extremely enriched by these metals. Cadmium shows EF values in SFA and Unhais-o-Velho classified as very high enrichment, Pb presents significant levels of enrichment in all sites and Cr with lower levels of EFs shows enrichment levels from moderate to minimal. Overall, the studied dusts are highly contaminated with As, Cu and Zn and although Cd and Pb are derived mostly from the same source they are not highly enriched in dust indicating that, probably, their emissions are less than for the other metals. Chromium with minimal to moderate values, possibly, arises from natural sources.

Waters characterization

The local populations strongly depend on the use of the water for supply, agriculture and cattle beverage. Most of the inhabitants have private wells; nevertheless, some use the public water supply network and waters from the streams and the Zêzere River for irrigation. According to the results, presented in Table 3, the lowest pH values were recorded in waters from wells which present a slightly acidic character (mean value from the 12 collected wells is 6.3) giving the parametric values set out in the Portuguese Decree-Law 306/2007. The other samples from streams, river, local fountains and the public water supply network have circumneutral pH. The mean values of EC ranging from 71 to 400 µS cm^{-1} classify them as waters with low mineralization, according to the parametric values of the Decree-Law 306/2007 with values up to 2500 µS cm^{-1}. These samples have low SO_4^{2-} and Cl^- concentrations and low metal concentrations, and although some concentrations occasionally have significant values, the average concentrations are below the parametric and legally acceptable standard (Table 3). Comparing the results obtained 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 the neighborhood villages of Panasqueira mine are in conditions to be used by the population. Nevertheless, and because As is a toxic element and arsenopyrite is the main sulfide rejected from the Panasqueira mine, As and Fe have been object of chemical speciation according to the methodologies described in (Ferreira and Barros 2002). The results in Table 4 show that As is present only in a very few samples, one of them in the form of As(V) and the others in the form of As(III), nevertheless far below the parametric water values for human consumption according to the Portuguese Law. The results also show that Fe(III) is dominant in the majority of the samples.

Table 3 Mean, minimum and maximum concentration of trace elements (μg L^{-1}), major ions (mg L^{-1}), pH, electrical conductivity (EC in μS cm^{-1}) and ORP (mV) collected in irrigation water from S. Francisco de Assis (SFA), Barroca (B), Casegas (C) and Unhais-o-Velho (UV) villages

	pH		EC		ORP		As		Cd	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Cabbage										
SFA ($n = 3$)	6.4	5.6–6.8	71	18–122	223	156–287	3.2	0.25–8.0	0.10	0.25–0.14
B ($n = 5$)	7.0	5.5–9.2	205	99–483	161	64–251	5.1	0.8–18	0.90	0.03–4.0
C ($n = 8$)	7.0	6.0–8.3	324	38–914	76	12–119	3.2	0.6–6.0	na	na
UV ($n = 5$)	6.7	6.3–7.2	400	210–709	43	5.0–137	0.3	0.03–1.0	0.03	0.03–0.07
Potato										
SFA ($n = 3$)	6.0	5.3–6.7	112	35–161	195	187–207	3.6	1.0–7.8	0.20	0.1–0.4
B ($n = 5$)	7.6	6.1–9.4	245	78–521	174	19–270	5.9	0.8–18	0.10	0.03–0.3
C ($n = 4$)	6.7	6.0–7.5	268	95–641	74	33–130	1.3	0.6–1.8	na	na
UV ($n = 1$)	5.4	na	334	na	250	na	2.2	na	0.24	na
Lettuce										
B ($n = 2$)	6.2	0.06–6.5	262	172–352	204	144–264	0.7	0.6–0.8	0.04	0.03–0.1
UV ($n = 4$)	6.9	6.3–7.5	220	59–355	67	5.0–137	0.4	0.03–1	0.03	na
Bean										
B ($n = 4$)	6.1	5.4–7.0	257	100–337	218	172–250	3.6	1.8–6.7	0.40	0.03–0.8
Guidelines (a)	$6.5 < \mathrm{pH} < 9.0$		2500		na		10		5	

	Cr		Cu		Pb		Zn	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Cabbage								
SFA ($n = 3$)	0.3	0.3–0.3	5.7	2.5–10	1.2	0.3–1.9	1082	5.0–4217
B ($n = 5$)	0.7	0.5–0.9	11	1.9–24	0.5	0.1–1.0	132	3.8–486
C ($n = 8$)	0.5	0.03–0.8	8.0	0.7–34	0.8	0.05–3.8	32	1.1–149
UV ($n = 5$)	0.6	0.5–0.7	3.5	1.2–7.5	0.5	0.3–0.7	76	2.0–214
Potato								
SFA ($n = 3$)	0.4	0.3–0.7	4.8	3.2–7.3	7.8	0.2–23	124	13–319
B ($n = 5$)	0.7	0.5–0.9	7.5	1.2–17	0.8	0.1–2.0	70	2.3–256
C ($n = 4$)	0.7	0.6–0.8	1.5	0.7–2.1	1.4	0.1–3.8	21	3.2–40
UV ($n = 1$)	0.9	na	24	na	1.6	na	145	na
Lettuce								
B ($n = 2$)	0.6	na	8.9	2.2–16	0.3	0.2–0.4	185	115–256
UV ($n = 4$)	5.1	0.5–19	3.6	1.7–7.5	0.5	0.3–0.7	39	1.9–136
Bean								
B ($n = 4$)	0.7	0.5–0.9	13	Fev/24	0.9	0.2-1.6	89	4-145
Guidelines (a)	50		2000		25		5000	

	Ca		K		Mg		Na	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Cabbage								
SFA ($n = 3$)	5.8	4.9–6.3	1.0	0.4–6.3	3.3	0.6–7.6	6.3	3.6–10
B ($n = 5$)	6.7	2.1–15	1.2	0.4–2.3	3.7	3.0–5.0	11	7.6–14
C ($n = 8$)	5.7	1.0–17	2.5	0.2–16	3.2	1.2–5.6	15	5.2–55

Table 3 continued

	Ca		K		Mg		Na	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
UV ($n = 5$)	6.8	2.1–16.4	0.4	0.2–0.5	5.5	1.0–12	5.7	4.2–9.7
Potato								
SFA ($n = 3$)	4.4	2.6–5.9	1.1	0.3–2.4	4.2	1.6–7.4	8.2	6.0–12
B ($n = 5$)	4.8	2.1–9.3	0.8	0.4–2.1	3.2	2.6–4.0	8.5	7–.0
C ($n = 4$)	5.4	1.5–15	0.6	0.3–0.8	4.2	2.1–5.7	20.5	6.7–55
UV ($n = 1$)	3.2	na	0.7	na	5.5	na	15.3	na
Lettuce								
B ($n = 2$)	2.4	2.3–2.5	0.5	0.4–0.5	4.0	2.8–5.2	9.8	7.0–13
UV ($n = 4$)	3.7	1.7–6.3	0.4	0.2–0.5	4.5	1.4–12	5.2	4.2–6.2
Bean								
B ($n = 4$)	4.8	3.0–8.4	1.1	0.6–2.0	5	4.6–5.5	13	10–15
Guidelines (a)	100		10		30		200	

	Na		Cl		NO_3		SO_4		HCO_3	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Cabbage										
SFA ($n = 3$)	6.3	3.6–10	5.0	2.0–11	8.0	1.0–21	7.0	1.0–20	30	20–39
B ($n = 5$)	11	7.6–14	6.8	3.2–9.0	7.9	0.8–17	9.2	1.7–28	47	39–59
C ($n = 8$)	15	5.2–55	8.3	4.0–21	7.6	0.3–31	9.6	0.2–35	na	na
UV ($n = 5$)	5.7	4.2–9.7	4.2	3.3–6.0	5.0	3.3–7.0	4.0	2.0–8.0	35	30–39
Potato										
SFA ($n = 3$)	8.2	6.0–12	3.7	2.0–7.0	7.0	2.0–15	5.0	1.0–9.0	26	10–49
B ($n = 5$)	8.5	7–.0	6.8	4.8–7.8	7.0	1.4–12.	8.4	3.0–28	142	39–493
C ($n = 4$)	20.5	6.7–55	11	4.3–21	12	1.7–27	11	1.7–35	na	na
UV ($n = 1$)	15.3	na	8.2	na	15	na	15	na	20	na
Lettuce										
B ($n = 2$)	9.8	7.0–13	6.9	6.2–7.6	6.9	3.0–11	4.5	3.2–5.7	49	39–59
UV ($n = 4$)	5.2	4.2–6.2	4.0	2.7–6.0	3.6	1.5–6.0	2.3	1.3–3.4	36	30–39
Bean										
B ($n = 4$)	13	10–15	7.2	5.3–8.2	8.9	0.8–15	17	1.7–33	26	20–39
Guidelines (a)	200		250		50		250		na	

(a) Portuguese Guidelines, Decree-Law 306/2007

n number of irrigation water samples, *na* not applicable

Heavy metals concentration in vegetables

The consumption of plants produced in contaminated areas and the ingestion or inhalation of contaminated particles are the two main factors contributing to human exposure to metals. Potential health risks to humans and animals from consumption of crops can be due to heavy metal uptake from contaminated soils via plant roots as well as direct deposition of contaminants from the atmosphere onto plant surfaces (McBride 2003). Cultivation of crops for human or livestock consumption on contaminated soil can potentially lead to the uptake and accumulation of trace metals in the edible parts of the vegetables with a resulting risk to human and animal health (McBride 2007). Increasing evidence shows that heavy metal pollution of mined areas caused health damage to the local inhabitants (Kachenko and Singh 2006). Serious

Table 4 Arsenic and iron speciation results (μg L^{-1}) from S. Francisco de Assis (SFA), Barroca (B), Casegas (C) and Unhais-o-Velho (UV) villages irrigation waters

ID	As(III)	As (total)	Fe(II)	Fe (total)
SFA-01	<0.6	<4.5	<0.015	0.041
SFA-04	<0.6	<4.5	<0.015	0.031
SFA-05	<0.6	**5.6**	<0.015	0.023
SFA-06	<0.6	<4.5	<0.015	0.047
SFA-07	<0.6	<4.5	<0.015	0.035
SFA-08	<0.6	<4.5	0.0017	0.064
B-01	<1	<4	<0.018	<0.018
B-4A	<1	<4	<0.018	0.045
B-04B	<1	<4	<0.018	0.025
B-07	<1	<4	<0.018	0.041
B-08	<1	<4	<0.018	0.02
B-09	**1.3**	<4	0.136	0.178
B-10	<1	<4	0.026	0.124
B-11	**1.3**	<4	0.048	0.187
B-12	<1	<4	<0.018	0.045
B-13A	<1	<4	<0.018	0.048
B-13B	<1	<4	<0.018	<0.018
B-15	<1	<4	<0.018	0.031
C-01	<1	<4	<0.018	0.026
C-03A	**1.3**	<4	1.07	1.19
C-03B	<1	<4	0.031	0.074
C-04	1	<4	0.391	0.484
C-05	<1	<4	0.031	0.078
C-06	<1	<4	<0.018	0.054
C-07	<1	<4	<0.018	0.025
C-08	<1	<4	<0.018	0.021
C-10	<1	<4	<0.018	0.043
C-11	<1	4.5	<0.018	0.041
C-13	<1	<4	0.021	0.054
C-16A	<1	<4	<0.018	0.064
C-16B	<1	<4	<0.018	0.03
UV-01	<1	<4	0.025	0.043
UV-02	<1	<4	<0.018	0.026
UV-03	<1	<4	<0.018	0.038
UV-04	<1	<4	<0.018	0.025
UV-06	<1	<4	<0.018	0.028
UV-09	<1	<4	<0.018	0.043
UV-10	<1	<4	1.22	1.31

The considered high contents are in bold

systemic health problems can develop as a result of excessive dietary accumulation of heavy metals such as As, Cd and Pb in the human body. Although Zn and Cu are essential elements, their excessive concentration in food and feed plants are of great concern because of their toxicity to humans and animals (Kabata-Pendias and Mukherjee 2007). Dietary intake is the main route of exposure for most people, although inhalation can play an important role in very contaminated sites. Knowledge about heavy metal concentrations in vegetables and the dietary intake, from the local population, is very important for assessing the risk to human health. Coelho (2013) have performed a study in the local population with 122 individuals living in the area of the Panasqueira mine where health conditions, medical history, medication, diagnostic tests (X-rays, etc.) and lifestyle factors were assessed by means of questionnaires. Subjects also provided information about drinking and agricultural water source, agricultural practices including pesticides usage and their diet.

The average concentrations and range of heavy metals (mg kg^{-1}) in the selected vegetables: *S. tuberosum* L. (potato), *B. olerácea* L. (cabbage), *L. sativa* L. (lettuce) and *P. vulgaris* L. (beans) growing in the four selected villages are listed in Table 5. The concentrations of heavy metals were highest for As followed by Cd, Zn and Pb, being Cr the element with the lowest concentrations. The cabbages exhibit in their edible parts (leaves) an average concentration for As, Cd and Zn higher than the recommended levels of FAO/WHO (2001) ($As = 0.1$ mg kg^{-1}, $Cd = 0.1$ mg kg^{-1} and $Zn = 40$ mg kg^{-1}). For Cu ($Cu = 0.1$ mg kg^{-1} FAO/WHO 2001) and Cr ($Cr = 2.3$ mg kg^{-1} DHFCD 2003), the average concentrations are below the recommended levels except for the average content of Cr in SFA cabbages leaves.

For potatoes tuber (the edible part of this vegetable), As contents are higher than the recommended levels of FAO/WHO (2001) in SFA, Barroca and Casegas samples; Cd in all villages is in the limit values of FAO guidelines (0.1 mg kg^{-1}), and for Cr, Cu, Pb and Zn the average concentrations are below the recommended levels except for the average content of Pb in SFA potatoes tubers. The lettuce leaves shows As, Cd, Pb and Zn values higher than the recommended levels of FAO/WHO (2001) in both Barroca and Unhais-o-Velho villages; for Cr and Cu, the average concentrations are below the recommended levels except for the average content of Cu in Barroca lettuce leaves. As for beans As, Cu, Pb and Zn concentrations are higher than the considered

Table 5 Mean, minimum and maximum concentration of trace elements in vegetables (mg kg^{-1}) from S. Francisco de Assis (SFA), Barroca (B), Casegas (C) and Unhais-o-Velho (UV) villages

	As		Cd		Cr		Cu		Pb		Zn	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Cabbage												
Roots ($n = 29$)												
SFA	20	1.6–52	0.4	0.1–0.7	56	2.2–244	23	8.8–43	6.1	0.9–11.4	134	62–237
B	0.6	0.3–1.1	0.1	0.03–0.3	2.1	1.0–4.4	105	2–508	6.5	0.1–31.8	95	10–369
C	0.4	0.01–0.8	0.1	0.01–0.1	2.0	1.1–3.9	32	2.1–264	2.1	0.03–17.5	55	17–249
UV	0.4	0.1–0.9	0.1	0.01–0.3	2.6	1.3–5.7	3.4	1.6–4.9	0.7	0.1–3.1	50	5.3–79
Stems ($n = 28$)												
SFA	0.5	0.2–1.3	0.2	0.1–0.4	1.7	1.1–2.4	3.8	2.5–4.5	0.3	0.1–0.4	84	29–237
B	0.2	0.001–0.5	0.2	0.02–0.5	1.0	0.8–1.2	2.4	2.0–2.7	0.1	0.001–0.1	18	0.01–38
C	0.4	0.2–1.0	0.1	0.01–0.1	1.0	0.7–1.1	2.4	1.3–3.8	0.000	0.001–0.1	36	13–92
UV	0.2	0.01–0.3	0.1	0.01–0.5	1.0	0.8–1.1	2.3	1.6–3.0	0.1	0.001–0.1	44	10–64
Leaves ($n = 29$)												
SFA	1.4	0.2–2.9	0.2	0.1–0.4	2.4	1.6–3.7	5.1	3.7–7.7	0.4	0.1–1.5	64	25–115
B	0.4	0.3–0.6	0.4	0.1–0.8	1.2	1.0–1.4	18	3.4–51	0.7	0.2–2.0	53	24–102
C	0.2	0.1–0.4	0.1	0.02–0.1	1.2	0.8–1.5	7.4	2.3–41	0.4	0.1–1.6	41	16–108
UV	0.2	0.01–0.4	0.2	0.001–0.7	1.2	0.9–1.5	3.4	1.2–4.7	0.2	0.03–0.5	60	13–111
Potato												
Roots ($n = 11$)												
SFA	15	4.4–22	2.1	0.3–4.7	7.1	3.0–15	20	12–28	2.4	1.1–3.1	71	49–92
B	2.4	0.7–2.5	1.1	0.1–3.7	1.9	1.4–3.0	17	11–30	1.5	0.8–2.4	120	14–246
C	1.7	1.3–2	0.7	0.4–1.0	1.9	1.8–1.9	21	19–23	1.3	0.9–1.7	132	778–185
UV	1.3	na	0.8	na	1.8	na	10	na	1.0	na	241	na
Stems ($n = 11$)												
SFA	0.8	0.7–0.9	0.2	0.1–0.3	2.0	0.9–2.1	12	9.2–14	1.6	1.5–1.7	119	88–150
B	0.4	0.2–1.4	1.3	0.2–5.2	0.9	0.8–2.3	16	5.9–66	0.3	0.1–0.9	138	0.02–599
C	0.6	0.6–0.6	0.6	0.4–0.8	1.2	1.1–1.2	18	12–24	0.2	0.2–0.2	163	149–179
UV	0.4	na	0.9	na	1.0	na	5.6	na	0.000	na	297	na
Leaves ($n = 14$)												
SFA	5.7	41,334	0.3	0.2–0.5	6.0	2.8–14	16	12–20	2.1	0.7–3.7	49	36–64
B	1.1	0.5–1.8	1.4	0.2–4.2	1.6	0.9–2.9	20	13–29	0.6	0.1–1.6	52	27–103
C	0.7	0.8–1.1	0.4	0.1–0.7	2.4	1.1–3.8	12	3.0–20	0.6	0.2–0.9	44	23–62

Table 5 continued

	As		Cd		Cr		Cu		Pb		Zn	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
UV	0.7	na	0.6	na	1.9	na	11	na	0.6	na	31	na
Tubers ($n = 11$)												
SFA	0.8	0.2–1.4	0.1	0.04–0.13	1.8	1.4–2.5	8.9	7.8–9.9	0.5	0.1–1.5	23	17–30
B	0.1	0.002–0.2	0.1	0.03–0.3	1.1	0.9–1.3	6.9	4.0–10	0.001	0.001–0.001	21	14–33
C	0.2	0.1–0.2	0.1	0.03–0.13	0.9	0.8–0.9	6.9	6.8–6.9	0.001	0.001–0.002	25	23–26
UV	0.01	na	0.1	na	0.9	na	5.6	na	0.001	na	26	na
Lettuce												
Roots ($n = 7$)												
B	1.8	0.4–1.2	2	0.8–4.6	2.7	2.5–2.6	12	9.6–13	2.1	1.6–2.4	58	38–78
UV	2.1	0.6–5.0	0.2	0.1–0.3	5.7	2.1–12	9.7	6.1–16	1.5	0.5–2.3	42	28–55
Leaves ($n = 7$)												
B	0.6	0.6–0.7	1.3	0.6–2.3	1.8	1.1–2.4	38	6.9–92	1.4	0.2–3.6	92	48–145
UV	0.4	0.2–0.6	0.2	0.2–0.4	1.3	1.1–1.7	14	Jun/26	0.5	0.3–0.7	43	20–54
Bean												
Stems ($n = 4$)												
B	0.3	0.2–0.5	0.1	0.1–0.1	1.1	0.9–1.3	11	6.3–19	0.4	0.001–1.3	68	44–121
Leaves ($n = 4$)												
B	1.2	0.4–1.8	0.1	0.1–0.1	1.5	0.9–2.1	89	8–324	3.8	0.1–15	106	28–259
Guidelines	0.1 (a)		0.1 (a)		2.3 (b)		30 (a)		0.3 (a)		40 (a)	

(a) FAO/WHO (2001); (b) DHFCD (2003)

n number of vegetables samples components, *na* not applicable guideline values while Cd is equal to the guideline value and Cr is lowest.

According to the recommended levels of FAO/WHO, the cabbage leaves were found with 90 % of the samples above the recommended level for As, 41.4 % for Cd, 58.6 % for Zn, 41.4 % for Pb, 10.3 % for Cr and 6.9 % for Cu; the potato tubers, the edible part of the vegetable, have 64, 45, 18 and 9 % of the samples above the recommended level for As, Cd, Pb and Cr, as for Cu and Zn they were below the recommended level; the lettuce leaves were found with 100 % of the samples above the FAO guidelines for As and Cd, 86 and 71 % for Pb and Zn, while for Cu and Cr only 14 % of the samples were higher than the recommended levels. Arsenic, Cd, Zn and Pb concentrations were found in the order of lettuce > cabbage > potatoes. Mean concentration of Cr and Cu in all vegetables was below the recommended level. In vegetables, the trend in heavy metal concentrations was observed as follows: SFA > Barroca > Casegas > Unhais. For cabbages and lettuces, the tendency of contamination is roots > leaves and for potatoes is roots > leaves > tubers. The contamination and accumulation of metals in the edible parts of the vegetables in the vicinity of the mine, as it was possible to verify, could have a direct impact on the health of nearby inhabitants, especially in people living downstream of the mine, since vegetables produced from gardens are mostly consumed locally. It is therefore important to control and limit the accumulation of heavy metals in food crops.

Bioconcentration (BCF) and translocation (TF) factors in vegetables

The ability of plants to accumulate metals from soil is determined on the basis of the values of BCF and TF. If BCF values are higher than one, vegetables are classified as tolerant or even hyperaccumulators, whereas if they are lower than one, they are considered as no contaminated vegetable, as for TF if the values are higher than one vegetables are classified as hyperaccumulators and if TF <1 they are classified as tolerant plants. Based on this criterion and on BCF and TF values which were determined in this study (Tables S5, S6) and considered only the edible part of the selected and studied vegetables, the leaves of cabbages from Unhais-o-Velho and the leaves of lettuce from Barroca show high BCF mean values (10 and 39, respectively) (Table S5) and can be considered potential hyperaccumulators of these metals. Barroca samples of lettuces besides high BCF values for Cd present also BCF values of 1.1 to Cu and Zn being considered as tolerance to these metals and the beans from Barroca are also tolerant to Cu with BCF value equal to 1.31. The potatoes tubers (edible part) did not accumulate sufficient amounts and they cannot be classified as hyperaccumulators. Regarding the TF (Table S6), Barroca and Casegas cabbages have TF values higher than 1 for As, Cd, Cu, Pb and Zn and Unhais-o-Velho show TR >1 for Cd, Cu and Zn. As for potatoes tubers all samples in all selected villages have TR <1. Lettuces and beans leaves from Barroca also have TR >1 for Cu and Zn and Unhais-o-Velho have TR values >1 for Cd and Cu. TF values >1 means that these vegetables have high translocation efficiency of metals from root to leaves and considered the TR values for cabbages, lettuces and beans this mean that it is not safe to consume them. Poor translocation of heavy metals to the above ground parts may be attributed to metal sequestration in the root cell vacuoles to render it non-toxic (Shanker et al. 2005). The results also show that the metals accumulated by these vegetables were mainly retained in roots except for Cd and occasionally for Cu and Zn which also accumulate in stems and leaves.

Daily intake and health risk index of heavy metals

Soil pollution with heavy metals due to the discharge of untreated mining wastes is a major threat to ecological integrity and human well-being. In this study, we aim to determine human health risks associated, via food chain, to the contamination by heavy metals from mine extraction. Health risk assessment of heavy metals in contaminated vegetables is an important issue that it is worth being studied.

Values of DIM calculated for adults and children are presented in Table S7. These data revealed that the values of daily intake of metal were high for vegetables grown at SFA followed by Barroca, Casegas and Unhais-o-Velho. The vegetables of the studied villages, have the highest DIM, both for adults and children, for Zn followed by the same trend for all sites Cu > Cr > As ≈ Cd ≈ Pb. The DIM by the inhabitants follows the trend SFA > Barroca > Casegas ≈ Unhais-o-Velho, and regarding the vegetables the trend beans > lettuce > cabbage > potato for As, Cu, Pb and Zn and lettuce > beans > cabbage > potato for Cd and Cr.

The HRI for heavy metals by consumption of vegetables grown on the four selected sites for this study both for adults and children were calculated and values are given in Table S8. The maximum HRI was found for As determined in cabbages, 2.72 for children and 2.22 for adults grown at SFA. Values of HRI >1 mean that it is assumed that the exposed populations are not safe. The HRI values for cabbages follows the trend: As > Cr > Cu > Cd > Zn > Pb and SFA > Barroca > Casegas > Unhais-o-Velho; for potatoes As > Cr > Cu > Cd > Zn > Pb and SFA > Casegas > Barroca > Unhais-o-Velho; for lettuces As > Cd > Cu > Cr > Pb > Zn and Barroca > Unhais-o-Velho and for the Barroca beans the observed metal trend is As > Cr > Cu > Cd > Zn > Pb.

These results indicate that the inhabitants of the four villages probably are exposed to some potential health risks, mainly, through the intake of As via consuming their vegetables. The accumulation of arsenic in the edible parts of the vegetables could have a direct impact on the health of nearby inhabitants, because vegetables produced from gardens are mostly consumed locally. Consequently, some effective measures may be necessary to eliminate heavy metal contamination in soil and to reduce metal translocation from soil to edible vegetables in order to avoid an increased risk of developing cancer and other diseases.

Biomonitoring of environmental exposure of the local populations

Coelho (2013) conducted a biomonitoring study of metals and metalloids in different biological matrices from Panasqueira mine environmentally and occupationally exposed populations. The goal was to evaluate the impact of heavy metal contamination in the populations living nearby and working in Panasqueira mine, through a multistage approach that integrates information obtained with biomarkers of exposure and environmental geochemical studies. The possible health effects caused by this environmental contamination were also assessed. The study population consisted of 122 individuals living in the vicinities of Panasqueira mine. Forty-one individuals were classified as environmentally exposed (16 males and 25 females), 41 male workers from the Panasqueira mine represented the group of occupationally exposed and 40 additional subjects without environmental and/or occupational exposure to mining activities, or other known toxic exposure, were the controls. This latter group included individuals living in non-contaminated areas, working mainly in administrative offices and matched with the environmentally exposed group by age, gender, lifestyle and smoking habits (17 males and 23 females and only individuals aged over 18 years and living in the same village for at least 5 years before the study were selected). Health conditions, medical history, medication, diagnostic tests (X-rays, etc.), and lifestyle factors were assessed by means of questionnaires. Subjects also provided information about the presence of specific symptoms related to metal exposure and chronic respiratory diseases, such as bronchitis and others; drinking and agricultural water source; agricultural practices, including pesticides usage; diet.

According to Coelho (2013), biomarkers of exposure included quantification of several metals (As, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Se, S, Si and Zn) in blood, urine, nail (finger and toe) and hair samples and the results agree with those obtained in the environmental studies performed in Panasqueira mine area, pointing out to the fact that the populations who live and work near the mine are exposed to these harmful elements some of them potentially toxic. In environmentally exposed populations, arsenic revealed the highest concentrations Nevertheless, concentration of other elements such as Cr, Mg, Mn, Ni, Pb, S, Se and Zn were also high, although at a lesser extent, especially in individuals with environmental exposure. Regarding the effect of gender on the metals and metalloid levels in the different matrices, the females have higher concentrations of As, Cr, Mg, Mn and Se in urine, fingernails and toenails, while males have higher levels of Fe, Hg, Mg, Pb, S and Zn in blood and hair samples (Coelho 2013).

A greater understanding of the relationship between exposure, individual susceptibility and biological effect enables the development of preventive measures, leading to a reduction in cancer risks for humans exposed to similar conditions. The combination of environmental and human biomonitoring studies may synergistically increase the knowledge about the bioaccessibility and bioavailability of toxic elements, which is essential to assess the potential risks to human health.

Conclusions

A field survey was carried out, in Panasqueira mine, to investigate the trace elements contents in rhizosphere soils and vegetables collected in areas under mining influence and in non-polluted neighborhood areas. The metal assemblage identified in the rhizosphere soils 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. The rhizosphere soils EFs are generally ordered as Cd > As > Cu > Zn > Pb > Cr and the trend for vegetables is EF potatoes > EF lettuce = EF beans > EF cabbages. The cabbage leaves, potato tubers and lettuce leaves were found above the recommended FAO guidelines for As and Cd and for cabbages and lettuces the tendency of contamination is roots > leaves and for potatoes is roots > leaves > tubers. The BCF for cabbages and lettuce reveal that they are potential hyperaccumulators of Cd.

The DIM and the index of the risk for residents were calculated and the results indicate that the inhabitants of these villages, probably, are exposed to some potential health risks through the intake of heavy metals via consuming their vegetables. The accumulation of these elements in the edible parts of the vegetables could have a direct impact on the health of nearby inhabitants, because vegetables produced from gardens are mostly consumed locally. Biomarkers of exposure determined in the local populations indicated that they were experiencing severe health effects derived from exposure to the environmental and occupational contamination to harmful elements, some of them potentially toxic, resulting from the mining activities. In these environmentally exposed populations, As was revealed as the element with the highest concentrations specialty in females as they presented significantly higher values of the most toxic elements, i.e., As, Cr, Mn and Ni. Consequently, some effective measures may be necessary to eliminate heavy metal contamination in soil and to reduce metal translocation from soil to edible vegetables in order to avoid an increased risk of developing cancer and other diseases. The ongoing step in this research is the identification of bioavailability and bioaccumulation patters of these elements through biological absorption coefficients for each element.

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References

Alloway, B. J. (1993). *Heavy metals in soils*. New York: Wiley.

Antonijević, M. M., Dimitrijević, M. D., Milić, S. M., & Nujkić, M. M. (2012). Metal concentrations in the soils and native plants surrounding the old flotation tailings pond of the copper mining and smelting complex Bor (Serbia). *Journal of Environmental Monitoring, 14*, 866–877.

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. *Journal of International Mine Water Association, 27*(4), 210–224.

Bech, J., Duran, P., Roca, N., Poma, W., Sánchez, I., Roca-Pérez, L., et al. (2012). Accumulation of Pb and Zn in *Bidens triplinervia* and *Senecio* sp. spontaneous species from mine spoils in Peru and their potential use in phytoremediation. *Journal of Geochemical Exploration, 123*, 109–113.

Bes, C. M., Pardo, T., Pilar Bernal, M., & Clemente, R. (2014). Assessment of the environmental risks associated with two mine tailing soils from the La Unión-Cartagena (Spain) mining district. *Journal of Geochemical Exploration*. doi:10.1016/j.gexplo.2014.05.020.

Bourliva, A., Kantiranis, N., Papadopoulou, L, Aidona, E., Christoforidis, C., & Kollias, P. (2011). On the morphology, geochemical characteristics and magnetic properties of urban road dust particles from the historic center of the city of Thessaloniki, Greece. In *Proceedings of the 12th international conference on environmental science and technology, Rhodes, Greece*.

Boussen, S., Soubrand, M., Bril, H., Ouerfelli, K., & Abdeljaouad, S. (2013). Transfer of lead, zinc and cadmium from mine tailings to wheat (*Triticum aestivum*) in carbonated Mediterranean (Northern Tunisia) soils. *Geoderma, 192*, 227–236.

Candeias, C. M. L. (2013). *Modelling the impact of Panasqueira mine in the ecosystems and human health: A multidisciplinary approach*. Ph.D. thesis, Universidade de Aveiro, Aveiro, Portugal.

Candeias, C., Ferreira da Silva, E., Ávila, P. F., & Teixeira, J.P. (2014b). Identifying sources and assessing potential risk of exposure to heavy metals and hazardous materials in mining areas: The case study of Panasqueira mine (Central Portugal) as an example. *Geosciences*. doi:10.3390/geosciences4040240.

Candeias, C., Melo, R., Ávila, P. F., Ferreira da Silva, E., Salgueiro, A. R., & Teixeira, J. P. (2014a). Heavy metal pollution in mine–soil–plant system in S. Francisco de Assis—Panasqueira mine (Portugal). *Applied Geochemistry, 44*, 12–26.

Clemens, S. (2006). Toxic metal accumulation, responses to exposure and mechanisms of tolerance in plants. *Biochimie, 88*, 1707–1719.

Coelho, P. (2013). *Biomonitoring of environmental contamination resulting from mining activities on exposed populations*. Ph.D. thesis, UP/ICBAS/INSA, Porto, Portugal.

Costa, P. (2004). Atlas do Potencial Eólico para Portugal Continental. Master thesis, Faculdade de Ciências da Universidade de Lisboa, Lisbon, Portugal **(in Portuguese)**.

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, Greece*.

Costa, P., & Estanqueiro, A. (2006b). Development and validation of the Portuguese wind atlas. In *Proceedings of the European wind energy conference (EWEC), Athens, Greece*.

Decree-Law 306/2007. (2007). Portuguese Republic Diary, Ministry for Environment, Spatial Planning and Regional Development. Diário da Republica, 1.^{a} serie—N° 164—27 August **(in Portuguese)**.

DHFCD. (2003). Department of Health, Foodstuffs, Cosmetics and Disinfectants Act. 1972 (Act 54 of 1972); Regulation relating to maximum levels in foodstuffs: Amendment. Pretoria: DoH.

Dold, B., & Fontboté, L. (2001). Element cycling and secondary mineralogyin porphyry copper tailings as a function of climate, primary mineralogy and mineral processing. Special issue: Geochemical studies of mining and the environment. *Journal of Geochemical Exploration, 74*(1–3), 3–55.

e-Ecorisk. (2007). A *regional enterprise network decision-support system for environmental risk and disaster management of large-scale industrial soils*. Contract No. EGV1-CT-2002-00068, WP3—case study site characterization. Deliverable 3.1—Project Management Report for the Reporting Period.

FAO/WHO. (2001). Joint Codex Alimentarius Commission. Food additives and contaminants. Food Standards Programme; ALINORM 01/12A:1-289.

Ferreira, M. M. S. I. (2004). Dados geoquímicos de base de solos de Portugal Continental, utilizando amostragem de baixa densidade. Ph.D. thesis, Universidade de Aveiro, Aveiro, Greece **(in portuguese)**.

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. *Analytica Chimica Acta, 459*, 151–159.

Ferreira da Silva, E., Ávila, P. F., Salgueiro, A. R., Candeias, C., & Pereira, H. G. (2013). Quantitative–spatial assessment of soil contamination in S. Francisco de Assis due to mining activity of the Panasqueira mine (Portugal). *Environmental Science and Pollution Research, 20*, 7534–7549.

Finkelman, R., Centeno, J., & Selenius, O. (2005). The emerging medical and geological association. *Transactions of the American Clinical and Climatological Association, 116*, 155–165.

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. *Applied Geochemistry, 18*, 409–421.

Guerra, F., Trevizam, A. R., Muraoka, T., Marcante, N. C., & Canniatti-Brazaca, S. G. (2012). Heavy metals in vegetables and potential risk for human health. *Scientia Agricola, 69*(1), 54–60.

Hakanson, L. (1980). Ecological risk index for aquatic pollution control, a sedimentological approach. *Water Research, 14*, 975–1001.

Han, Y. M., Du, P. X., Cao, J. J., & Posmentier, E. S. (2006). Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. *The Science of Total Environment, 355*, 176–186.

Havlin, J. L., Beaton, J. D., Tisdale, S. L., & Nelson, W. R. (1999). *Soil fertility and fertilizers: An introduction to nutrient management* (6th ed.). Upper Saddle River, NJ: Prentice Hall.

http://www.inag.pt.

Jarup, L., Bergluud, M., & Elinder, C. G. (1998). Scandian. *Journal of Work Environmental Health, 24*, 1–51.

Kabata-Pendias, A., & Mukherjee, A. B. (2007). *Trace elements from soil to human*. New York: Springer.

Kachenko, A. G., & Singh, B. (2006). Heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia. *Water, Air, and Soil Pollution, 169*, 101–123.

Khan, S., Cao, Q., Zheng, Y. M., Huang, Y. Z., & Zhu, Y. G. (2008). Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environmental Pollution*. doi:10.1016/j.envpol.2007.06.056.

Kirkham, M. B. (2006). Cadmium in plants on polluted soils: Effects of soil factors, hyperaccumulation, and amendments. *Geoderma, 137*, 19–32.

Křı́bek, B., Majer, V., Pašava, J., Kamona, F., Mapani, B., Keder, J., & Ettler, V. (2014). Contamination of soils with dust fallout from the tailings dam at the Rosh Pinah area, Namibia: Regional assessment, dust dispersion modeling and environmental consequences. *Journal of Geochemical Exploration, 144*, 391–408.

Liu, Q., Diamond, M. L., Gingrich, S. E., Ondov, J. M., Maciejczyk, P., & Stern, G. A. (2003). Accumulation of metals, trace elements and semivolatile organic compounds on exterior window surfaces in Baltimore. *Environmental Pollution, 122*(1), 51–61.

Lorenz, S. E., Hamon, R. E., & McGrath, S. P. (1994). Differences between soil solutions obtained from rhizosphere and non-rhizosphere soils by water displacement and soil centrifugation. *European Journal of Soil Science, 45*, 431–438.

Mahmood, A., & Malik, R. N. (2014). Human health risk assessment of heavy metals via consumption of contaminated vegetables collected from different irrigation sources in Lahore, Pakistan. *Arabian Journal of Chemistry, 7*, 91–99.

McBride, M. B. (2003). Toxic metals in sewage sludge-amended soils: Has promotion of beneficial use discounted the risks? *Advances in Environmental Research, 8*, 5–19.

McBride, M. B. (2007). Trace metals and sulfur in soils and forage of a chronic wasting disease locus. *Environmental Chemistry, 4*, 134–139.

McCauley, A., Jones, C., & Jacobsen, J. (2009). Soil pH and organic matter. *Nutrient Management Module*, *8*, 1–12.

Mingorance, M.D., Valdes, B., & Rossini, S.O. (2007). Strategies of heavy metal uptake by plants growing under industrial emissions. *Environment International*. doi:10.1016/j.envint.2007.01.005.

Ministry of the Environment. (2011). *Soil. GroundWater and sediment standards for the use under part XV.1*. Ontario: Environmental Protection Action.

Mudgal, V., Madaan, N., Mudgal, A., Singh, R., & Mishra, S. (2010). Toxic metals on human health. *The Open Nutraceuticals Journal, 3*, 94–99.

Naser, H. M., Mahmud, N. U., Sultana, S., Gomes, R., & Rahman, M. (2012). Trace elements content in vegetables grown in industrially polluted and non-polluted areas. *Bangladesh Journal of Agricultural Research, 37*(3), 515–527.

Pandey, V. C., Singh, N., Singh, R. P., & Singh, D. P. (2014). Rhizoremediation potential of spontaneously grown *Typha latifolia* on fly ash basins: Study from the field. *Ecological Engineering, 71*, 722–727.

Perrin, J. (1974). Classification des sols organiques. *Bull Liaison de LCPC*, *69*, 36–47 **(in French)**.

Prabu, P. C. (2009). Impact of heavy metal contamination of Akaki River of Ethiopia on soil and metal toxicity on cultivated vegetable crops. *Electronic Journal of Environmental, Agricultural and food Chemistry, 8*(9), 818–827.

Raikwar, M. K., Kumar, P., Singh, M., & Singh, A. (2008). Toxic effect of heavy metals in livestock health. *Veterinary World, 1*(1), 28–30.

Rattan, R. K., Datta, S. P., Chhonkar, P. K., Suribabu, K., & Singh, A. K. (2005). Long-term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater—A case study. *Agriculture, Ecosystem and Environment, 109*, 310–322.

Reimann, C., & Garrett, R. G. (2005). Geochemical background: Concept and reality. *The Science of Total Environment, 350*, 12–27.

Reis, A. C. (1971). As Minas da Panasqueira. *Boletim de Minas, 8*(1), 3–34 **(in Portuguese)**.

Rodríguez, L., Ruiz, E., Alonso-Azcárate, J., & Rincón, J. (2009). Heavy metal distribution and chemical speciation in tailings and soils around a Pb–Zn mine in Spain. *Journal of Environmental Management, 90*, 1106–1116.

Sezgin, N., Ozcan, H. K., Demir, G., Nemlioglu, S., & Bayat, C. (2003). Determination of heavy metal concentrations in street dusts in Istanbul E-5 highway. *Environment International, 29*, 979–985.

Shah, M. T., Shaheen, B., & Khan, S. (2010). Pedo and biogeochemical studies of mafic and ultramafic rocks in the Mingora and Kabal areas, Swat, Pakistan. *Environmental Earth Sciences, 60*, 1091–1102.

Shanker, A. K., Carlos, C., Loza-Tavera, H., & Avudainayagam, S. (2005). Chromium toxicity in plants. *Environment International, 31*, 739–753.

Smith, M. (2006). Panasqueira the tungsten giant at 100+. *Operation Focus International Mining, 2*, 10–14.

US EPA Environmental Protection Agency. (1997). *Health effects assessment summary tables (HEAST)*. Washington, D.C: U.S. Environmental Protection Agency.

US EPA Environmental Protection Agency. (2010). *IRIS-integrated risk information system*. http://cfpub.epa.gov/ncea/iris/compare.cfm (January 2015).

Wanat, N., Joussein, E., Soubrand, M., & Lenain, J. F. (2014). Arsenic (As), antimony (Sb), and lead (Pb) availability from Au-mine technosols: A case study of transfer to natural vegetation cover in temperate climates. *Environmental Geochemistry and Health*. doi:10.1007/s10653-014-9596-5.

Wang, X., Sato, T., Xing, B., & Tao, S. (2005). Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish. *The Science of the Total Environment, 350*, 28–37.

Wenzel, W. W., Unterbrunner, R., Sommer, P., & Sacco, P. (2003). Chelate-assisted phytoextraction using canola (*Brassica napus* L.) in outdoors pot and lysimeter experiments. *Plant and Soil, 249*, 83–96.

WHO. (1993). Evaluation of certain food additives and contaminants. In *41st report of the Joint FAO/WHO Expert Committee on Food Additives (WHO Technical Series, 837)*. Geneva: World Health Organization.

WHO. (2000). *Air quality guidelines for Europe*. WHO Regional Publications, European Series N° 91 (2nd ed.). Copenhagen: World Health Organization.

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. *Environmental Pollution, 119*, 33–44.

Wu, S., Peng, S., Zhang, X., Wu, D., Luo, W., Zhang, T., et al. (2015). Levels and risk assessments of heavy metals in urban soils in Dongguan, China. *Journal of Geochemical Exploration, 148*, 71–78.

www.iarc.fr.

www.nrcs.usda.gov.

Yongming, H., Peixuan, D., Junji, C., & Posmentier, E. S. (2006). Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. *The Science of Total Environment, 335*, 176–186.