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Soil contamination near the Kabwe Pb-Zn smelter in Zambia: Environmental impacts and remediation measures proposal

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ABSTRACT

Kabwe Town and its surroundings (central Zambia) belong to the most contaminated districts in Africa due to mining and smelting of local Pb-Zn ores. To assess the extent and intensity of this anthropogenic contamination, samples of topsoil (from a depth of 0 to 3 cm), together with reference subsurface soil from a depth of 70–90 cm, were collected in the area. In the Kitwe Town and downwind, the Pb and Zn contents in topsoils were found to be significantly higher compared to the permissible ecological limits used in Canada with regard to various land uses. Other elements (Cu, Fe, Mn, Cr, Ni and Ba) in topsoil demarcate only a small area of the former ore processing and smelter grounds.

The gastric bioaccessibility of metals in topsoils was tested by a US EPA-adopted in vitro method using a simulated gastric fluid. The results revealed that the intake of Cd, Cu, Zn, Co, and As does not exceed the tolerable daily intake (TDI) values for children but, for Pb, almost 50% of the samples exceeded TDI. Therefore, the concentrations of gastric bioaccessible Pb in highly contaminated topsoils or in resuspended soil-derived dust particles may be considered to be an important health risk in the Kabwe area.

The amounts of plant-available metals in topsoils were established by extraction with a diethylentriaminopentanacetic acid (DTPA) and triethanolamine (TEA) solution. These tests showed that the amounts of plant-available metals increase (median values, in mg kg^{-1}) in the sequence: Cd (0.7) → Cu (3.9) → Mn (76) → Fe (79) → Zn (110) → Pb (126). Chemical stabilization of the pollutants in soils using a phosphate amendment caused a significant reduction of the plant-available fraction of Pb and Cd, but did not suppress their gastric bioaccessibility. Based on our results, various measures were suggested to reduce the impact of the pollution on the Kabwe Town population.

1. Introduction

The mining and ore processing industries, in particular, are responsible for the generation of large amounts of metal(loid)-rich fine dust particles, which become the source of air and soil pollution (Newhook et al., 2003; Zota et al., 2009; Castillo et al., 2013; Ettler et al., 2009, 2016; Ettler, 2016). The issue of dust fallout from smelters and soil contamination has been discussed in numerous reports and papers (e.g., Dudka and Adriano, 1997; Barcan, 2002; Goodarzi et al., 2002; Krzaklewski et al., 2004; Beavington et al., 2004; Kříbek et al., 2010, 2014a, 2018; Csavina et al., 2012; Ettler et al., 2012; Shukurov et al., 2014). The extent of the environmental impact of ore smelting depends on the mineralogy and chemical composition of dust fallout (Castellano et al., 2004; Ettler et al., 2011, 2016) and other factors affecting the mobility of pollutants in the environment, such as their bonding to individual components in soils, the physical and chemical properties of soils or the chemical alteration of metalliferous dust particles during weathering processes (Li and Thornton, 2001; Kabala and Singh, 2001; Chatain et al., 2005; Luo et al., 2006; Ettler et al., 2011). The risk of dust generation is high, especially in dry or semi-arid areas (Ghorbel et al., 2010, 2014; Turner and Hefzi, 2010; Csavina et al., 2012; Albanese et al., 2014; Thomas et al., 2018).

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The health effects related to dust materials which can be inhaled or ingested are a known phenomenon (Csavina et al., 2012; Plumlee and Morman, 2011; Morman and Plumlee, 2013; Martin et al., 2014; Kim et al., 2015). Studies dealing with human exposure to potentially harmful elements (PHE) have traditionally been based on their analysis in blood (Yabe et al., 2015; Bose-O'Reilly et al., 2018) or urine (Cheyns et al., 2014; Yabe et al., 2018). However, these approaches are generally expensive and need the approval of the ethics committees of health organizations, institutions or ministries. To overcome these difficulties, numerous in vitro bioaccessibility methods (often called physiologically-based extraction tests, PBET) have been developed/validated by in vivo tests (generally using swine models) to evaluate the risk related to the ingestion of potentially harmful elements (PHE) (e.g., Ruby et al., 1999; US EPA, 2007). The bioaccessible fraction is defined as the amount of the PHE that is mobilized from the solid matrix (e.g. soil or dust) and becomes available for dust and/or soil incidental ingestion (e.g., Deshommes et al., 2012; Li et al., 2017) or inhalation (Molina et al., 2013; Alpofead et al., 2016, 2017; Kastury et al., 2018). Although bioacessibility methods have been used at numerous mining sites to assess human exposure to contaminants from soils, only a few investigations were carried out in the arid or semiarid regions of sub-Saharan Africa (Banza et al., 2009; Ettler et al., 2012; Kříbek et al., 2014a; Mileusnic et al., 2014).

Moreover, the consumption of vegetables growing on contaminated soils can pose a risk to human health in many mining areas (Hutchinson and Whitby, 1974; Fonkou et al., 2002; Kachenko and Singh, 2006; Yruela, 2009; Kříbek et al., 2014b). The metal/metalloid uptake by plants is not determined by the total amount of the elements in the soil, but by the amount which is available for plant metabolism. Plant availability of metals/metalloids is determined by a range of factors, for example the physical and chemical properties of soils, such as grain-size distribution, amount of organic carbon, cation exchange capacity, amount of Fe and Mn (hydr)oxides, volume and mineralogical composition of the clay fraction. Climatic factors obviously also play an important role (Li and Thornton, 2001; Kabata-Pendias, 2004; Kříbek et al., 2011). The uptake of PHE by plants growing on contaminated soils can be efficiently reduced by using immobilizing amendments, such as phosphate compounds, liming materials, organic matter, metal oxides and zeolites or their combinations (Wang et al., 2017) In-situ remediation of Pb-contaminated soils with P-based amendments has been proposed as an alternative to soil removal (US EPA, 1996).

Based on previous screening study of the soil contamination in the Kabwe area (Kříbek and Nyambe, 2005), this paper is focused (1) on assessment of the extent and intensity of soil contamination in the Kabwe area using the field portable X-ray fluorescence spectrometer (FP-XRF) and (2) on the assessment of gastric bioaccessibility of PHE in topsoil. As local agriculture is oriented towards the production of vegetables (lettuce, rape, cassava, sweet potato), (3) an important part of this project consisted in evaluation of the plant-available amount of PHE in contaminated soils and the possibility of reducing this amount using humate and triple superphosphate (TSP) amendments.

2. General information on the Kabwe area

2.1. Climatic conditions

The rainfall in the studied area occurs especially between September and May. Average precipitation in the area varies from 900 to 1000 mm, directly in the Kabwe area it corresponds to 900 mm. The maximum precipitation equals to 67 mm over 24 h, while the evaporation ranges between 48 and 295 mm, on an average 90 mm per year. The temperature measured in Kabwe since 1950 has fluctuated from 14.2 to 26.8 °C. The mean annual temperature corresponds to 20.2 °C. Southeasterly to easterly winds prevail in the area, with an average wind speed of 52 $m\,s^{-1}$ (cf. http://weatherspark.com/Average-Weather-in-Kabwe-Year-Round).

2.2. Soils

Soil cover in the Kabwe area consists of a range of soils formed on different geological bedrocks and under variable moisture regimes conditioned by topography and the human influence. According to the Soil World Reference Base for Soil Resources (IUSS, 2015) an important part of the soil cover is formed by Ferralsols that represent soil of the highest stage of parent material weathering and exhibit rather a thin humus layer at the top. The ferralic horizon is often underlain by plinthic, pisoplinthic, or petroplinthic horizons. Plinthosols are also present, forming the soil mosaic in terrain depressions where iron accumulation under stagnant water conditions occurs. Vertisols and Phaeozems developed at places with accumulation of fine materials accompanied by high moisture contents. These soils are characterized by a rather thick humus horizon, high base saturation and the presence of secondary calcium carbonates in the soil profile. Due to intensive human activity in the area, an important part of the soil cover is represented by Technosols formed on mine waste dumps. These soils are highly variable in their properties and morphology due to the heterogeneity of the mine waste materials.

2.3. The Kabwe base metal deposit

The mining and mineral processing complex and facilities at Kabwe began operating in 1904 and were closed in 1984 due to exhaustion of the rich "massive" ores (Kamona and Friedrich, 2007). A few open cast and underground mines were later gradually opened. The ore bodies are mostly confined to massive dolomites of the Neoproterozoic Nyama Formation. The major ore minerals included pyrite [FeS_2], sphalerite [ZnS], and chalcopyrite [$CuFeS_2$], while bornite [Cu_5FeS_4], covellite [CuS], chalcocite [Cu_2S], and tetrahedrite [$(Cu,Fe,Ag,Zn)_{12}Sb_4S_{13}$] were of minor importance. Non-sulfide ores are represented by cerussite [$PbCO_3$], willemite [Zn_2SiO_4], smithsonite [$ZnCO_3$] and V, As, Mo and Cu minerals. Over the 90 years of mining 1.8 Mt of Zn, 0.8 Mt of Pb and smaller amounts of Ag (79 t), V_2O_5 (7820 t), Cd (235 t) and Cu (64 t) were extracted.

2.4. Ore processing

Zinc silicate and carbonate concentrates were treated in a flash roasting plant to produce Zn-rich calcine, which was subsequently acid-leached and a feed solution was subjected to electrowinning. The stripped Zn was transferred to the smelter, slag was skimmed off and ingots of crude metal were produced (Barlin, 1970).

Sulfidic Pb-Zn concentrate from the concentrator unit was sintered, crushed and the resulting sinter, together with pre-heated coke, was transferred into a smelting furnace plant. The furnace operated at 1020 °C and the furnace gasses entered the condenser and were shock-cooled by a Pb spray. The mixture of gasses leaving the condenser passed to a wet scrubbing system which recovered solids (principally oxides of Zn and Pb) as "blue powder", which was filtered and the cake was added to the sinter plant feed. Liquid Zn was separated from the melt in a liquation bath maintained at a temperature close to the freezing point of Zn (419 °C) to ensure maximum removal of Pb, and was cast (Barlin, 1972). After the processing plants were closed in 1984, the Sable Zinc Plc., took over local dumps, including the settling pond containing leach tailings from the former ore treatment plant. The local dumps are currently owned by Enviro Processing Limited.

2.5. Environmental issues

High contamination of soils as a result of base metal ore smelting during 1904–1984 is a major problem faced by the local population of this area today. The contents of Pb in the soils of the Kabwe Town reach 2.6 wt%, and those of Zn attain a maximum of 3 wt%, but on an average do not exceed 0.5 wt% (Tembo et al., 2006). High contents of Pb were also found in agricultural products, particularly in rape (*Brassica napus*), which is an important crop grown in the local vegetable gardens (ZCCM-IH, 1996, 2002). High concentrations of Pb in soils, consumption of contaminated vegetables and inhalation/ingestion of dust enriched in Pb and other contaminants has resulted in high blood Pb levels of people living in the most affected areas of the Kabwe settlements. According to the standards issued by the World Health Organization (WHO, 2007), the maximum permissible value for the lead concentration in human blood is 10 µg/dl for children. In 1994, altogether 866 people living in the Kabwe Town were tested for blood Pb and the mean values ranged from 13.1 to 45 µg/dl for adults (Herzman, 1995). The highest blood Pb values were found in the youngest group of the population (age 6–16 years; 17.7 to 52 µg/dl). This is ascribed to the fact that children are generally shorter, closer to the contaminated ground and therefore tend to inhale and digest larger volumes of contaminated dust particles, particularly when playing outdoors. In addition to the decommissioned Pb-Zn smelter, the ferro-manganese smelters are still in operation in Kabwe and old tailings, slag deposits and residues left from base metal leaching represent potential sources for metalliferous dust re-suspension.

3. Materials and methods

3.1. Samples collection and processing

Regional environmental geochemical mapping of soils at the Kabwe area was carried out using the methodology recommended for regional geochemical mapping by the FOREGS Geochemistry Working Group (Salminen et al., 1998). The sampling site locations are presented in Fig. 1. Samples of the topsoil were prepared by mixing 5 individual topsoil sub-samples taken from the edges and the center of a sampling square 25 m by 25 m in size. If present, the litter was removed and individual topsoil samples were collected from a depth ranging from 0 to 3 cm. The weight of the composite topsoil samples was 0.6 to 1.7 kg. The sampling density was set to 1–2 samples per km^2 in Kabwe Town and to 1 sample per km^2 outside the town, but varied slightly according to the accessibility of individual parts of the surveyed area. Altogether, 116 topsoil samples were collected.

In arid or semi-arid areas, contamination related to emissions from mining operations and smelters are bound to thin, surficial parts of the soil profile (for a discussion, see Kříbek et al., 2010). To verified this concept, in addition to topsoil samples, subsurface (reference) soil samples (40 samples; from 0.3 to 0.4 kg in weight) were taken from a depth of 70 to 90 cm using a soil probe. Individual samples were prepared by blending 5 sub-samples. Sampling density varied between 1 and 2 subsurface samples per 4 km^2. All the samples were air-dried and sieved through a 2 mm mesh sieve.

Moreover, the distribution of the contaminants was studied in two soil profiles. Profile SP-1 was sampled in an area NW of the Mukobeko quarter of Kabwe (Fig. 1). The area is unaffected by dust fallout from the Kabwe industrial zone. The soil is classed as Pisoplinthic Plinthosol (IUSS, 2015). The soil of dark grey color and rich in clay material contains disseminated ferro-manganese nodules up to 0.5 mm in diameter. A highly contaminated profile SP-2 (Fig. 1) was located 50 m east of the Lusaka–Kabwe highway, at the periphery of Kasanda quarter of Kabwe, adjacent to the Kabwe industrial zone. The soil can be classed as Haplic Vertisol according to IUSS (2015). In both profiles, samples were taken from the surface down to a depth of 85 cm. Altogether 17

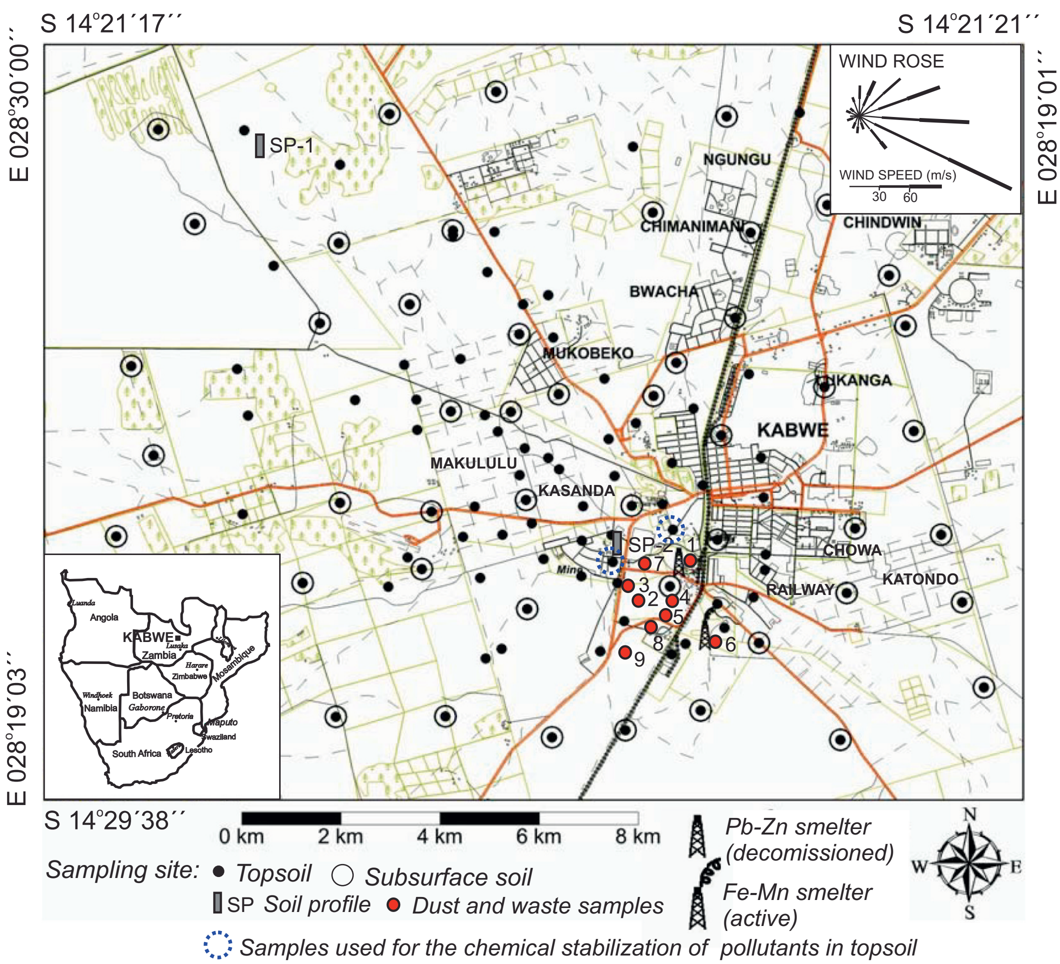

Fig. 1. Sketch map of the Kabwe area and the location of soil and mine and smelter wastes sampling sites.

samples were collected. All the samples were dried in the air and sieved through a 2 mm mesh sieve.

For the PHE in vitro gastric accessibility study, 25 topsoil samples collected in the most contaminated part of the surveyed area (former smelter area and the Kasanda quarter of Kitwe) were selected. The samples were air-dried and sieved through a 0.2 mm mesh sieve.

The plant-available contents of elements were studied in the same topsoil samples. Moreover, two highly contaminated topsoil samples (for the locations, see Fig. 1) from the former smelter area were dried, sieved through a 2 mm mesh sieve and prepared for experimental study of the chemical stabilization of PHE in contaminated soils. In addition to the soil samples, 7 representative samples of mine and smelter wastes (1 kg each) and 4 samples of dust from processing plants (20 g each) were collected.

3.2. Chemical analyses

3.2.1. X-ray fluorescence analysis (FP-XRF)

The concentration of elements in 173 samples of topsoil and subsurface soil, 17 soil samples from two soil profiles, and 7 samples of mine and smelter wastes were determined using a field portable X-ray fluorescence spectrometer (FP-XRF; Alpha, Innov-X, Woburn, USA). The equipment enables determination of the concentrations of 22 chemical elements (Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Zr, Mo, Ag, Cd, Sn, Sb, Ba, Hg, Pb and U). The FP-XFR measurements were carried out in the analytical mode and the measurement time was 2 min. The spectrometer was calibrated using an external standard supplied by the manufacturer.

The accuracy assessment (Relative Percent Difference; RPD) and measurement precision (Relative Standard Deviation; RSD) were carried out using SO-1 and SO-4 soil standards (Regosolic clay soil, Quebec, Canada and Chermozemic A horizon soil, Saskatchewan; Land Resource Research Institute, Agriculture Canada). The data, together with detection limits for each selected element are summarized in Table S1.

3.2.2. Flame atomic absorption spectroscopy (FAAS) and hydride-generation atomic absorption spectrometry (HGAAS)

3.2.2.1. Total concentrations of elements. The concentrations of elements in soil samples were determined after pseudo-total digestion in *aqua regia* in accordance with ISO 11466 (1995). This digestion method may not be efficient enough to attack the most resistant silicates, but for the purposes of this study the environmentally important metals were considered as their total concentrations. The contents of Cu, Fe, Mn, Pb, Cd, Co and Zn in the digests were established using Flame Atomic Absorption Spectroscopy (FAAS, Perkin Elmer 4000). Arsenic was determined by a Hydride-Generation Atomic Absorption Spectrometry (HGAAS, Perkin Elmer 503). All the samples were analyzed at the accredited Central Geochemical Laboratories of the Czech Geological Survey. The quality control procedure involved analysis of reagent blanks, duplicate samples and several reference soils. The analytical precision was determined by 10% analysis (in duplicate) of randomly chosen samples and reference samples. The reliability of the analyses was determined using the certified reference material (CRM) BCR-483 (sewage sludge-amended soil) and standard reference material (SRM) NIST 2711, Montana soil. The reliability was ± 5% for Co, Cu, Pb, Zn, ± 12% for Fe and Mn, and ± 22% for Cd due to the large number of samples in which the concentrations of Cd were near the analytical detection limits. The details of the analytical procedure are given in Ettler et al. (2012).

Very good correlation was found between FP-XRF and flame atomic absorption spectroscopy (FAAS) as well as hydride-generation atomic absorption spectrometry (HGAAS) data: For Pb ($r^2 = 0.99$), Zn ($r^2 = 0.98$) Cu ($r^2 = 0.97$), Fe ($r^2 = 0.96$), Mn ($r^2 = 0.98$, Fig. S1). The correlation for As was poor ($r^2 = 0.43$).

3.2.2.2. Bioaccessibility testing in simulated gastric fluids. The gastric bioaccessibility test was performed on the selected topsoil samples according to the US EPA (2007) protocol in order to establish the amounts of metal(loid)s that can be extracted in simulated gastric fluid (SGF). In the literature, this experimental protocol is known as SBRC-G, i.e., gastric phase extraction using the Solubility Bioaccessibility Research Consortium assay. This test was selected because of its simplicity and reliability for in vivo tests for Pb (US EPA, 2007; Deshommes et al., 2012) and As (Juhasz et al., 2014a, 2014b). The soil samples were air-dried and each sample was passed through a 0.2 mm mesh sieve and homogenized in an agate ball mill, below 0.063 mm. The samples were placed in 100-ml high-density polyethylene (HDPE) bottles (P-lab, Czech Republic) and extracted with a 0.4 M solution of glycine adjusted to pH 1.5 ± 0.05 using reagent grade HCl (Merck, Germany) at a L/S ratio of 100. The mixture was gently agitated for 2 h at 37 °C in a laboratory drying kiln. After the extraction procedure, the extract was filtered through 0.45 μm nitrocellulose membrane filters (Millipore, USA), diluted and analyzed for Mn, Fe, Co, Cu, Zn, As, Cd and Pb by HGAAS, and/or FAAS. The extraction was carried out in duplicate for six randomly selected samples and indicated that the reproducibility of the procedure was generally below 10%, but never exceeded 20% RSD (higher standard deviations were observed in some samples with bioaccessible concentrations below 5 $mg\,kg^{-1}$).

3.2.2.3. Plant-available concentration of contaminants. Selected topsoil samples ($n = 25$) for the determination of plant-available elements were extracted with a solution of diethylentriaminopentanacetic acid (DTPA; 0.5 M) and triethanolamine (TEA; 0.1 M) according to the method of Norvell and Lindsay (1972). The digests were filtered through a 0.45 μm membrane filter and the concentrations of inorganic contaminants were determined by FAAS.

3.2.3. Chemical stabilization of contaminated soils

To assess the ability to reduce the plant-available Zn, Cd and Pb in contaminated soil from the Kabwe area, two the most contaminated topsoil samples were collected from the former lead and zinc smelter area (for the sample locations, see Fig. 1). The total concentrations of analyzed elements in sample 1 (mean value) were: Zn: 6352 $mg\,kg^{-1}$, Cd: 21 $mg\,kg^{-1}$ and Pb: 5695 $mg\,kg^{-1}$, in sample 2 Zn: 49,575 $mg\,kg^{-1}$, Cd: 3 $mg\,kg^{-1}$, Pb: 1725 $mg\,kg^{-1}$ (*aqua regia* digest, FAAS data). Both samples were treated with a triple superphosphate (TSP) solution, humate solution and their mixture. Analyses of both samples were performed in duplicate. Because soils of the Kabwe area are usually carbonate-deficient and their pH ranges from 4.6 to 6.7, distilled water saturated with calcium carbonate (calcite) was used to prepare the aqueous suspensions of soil samples for batch-type experiments. For the experiments, 60 g of soil suspended in 200 ml of carbonate-saturated aqueous solution (pH 8.2) was distributed into Petri dishes and stirred for 2 min. Sixty milliliters of filtered TSP solution or 60 ml of the solution of Na-humate or a 1:1 mixture of both was added to the suspension. The solution of TSP was prepared from commercial grade triple superphosphate. The concentration of PO_4^{3-} in the solution saturated with commercial grade TSP was 9.55 g PO_4^{3-} per liter. The solution of humate was prepared from commercial grade Na-humate prepared by the Humeco Ltd., Czech Republic. One hundred milligrams of humate per liter was employed to prepare the humate solution. The samples were left to dry up at a temperature of 25 °C for six days. Dry soil samples were gently pulverized in an agate dish and Zn, Cd and Pb were extracted with (1) *aqua regia* solution (pseudo-total concentration of metals), (2) with glycine solution at pH 1.5 (gastric bioaccessible metals) and (3) with DTPA and TEA solutions (plant-available metals). Subsequently, the samples were filtered through a 0.45-μm Millipore membrane filter and the metals in all the types of extracts were analyzed by FAAS. The untreated soil sample, i.e., the suspension of soil in calcite-saturated distilled water was analyzed as a

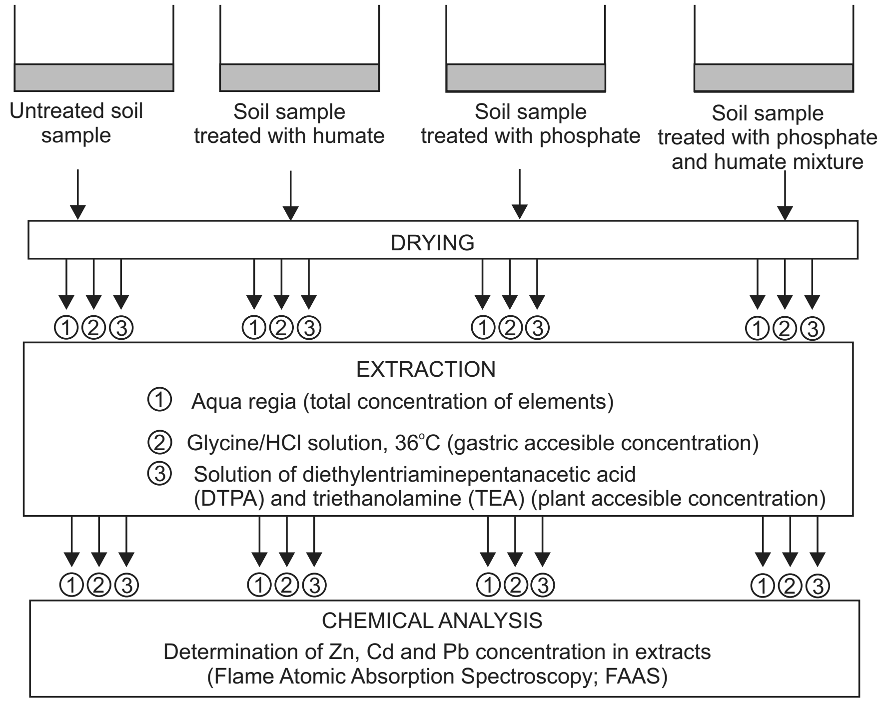

Fig. 2. The flow chart of the experimental assessment of the (1) triple superphosphate (TSP), (2) humate and (3) a mixture of the TSP and humate treatment on the gastric availability and plant availability of Zn, Cd and Pb in the contaminated soils in the Kabwe area.

"blank". The experiment flow sheet is shown in Fig. 2.

3.2.4. Statistical data treatment and map construction

Because the statistical distribution of most variables determined by FP-XRF analyses was not normal, a non-parametric statistics program (S-PLUS, MathSoft, USA) was used to assess the main statistic characteristics of individual data populations. For statistical treatment, data from FP-XRF analyses lower than the detection limit were replaced by values equal to the 2/5 of the limit. A data population with > 60% of values below detection limit was excluded from statistical treatment. Data for compilation of contour maps were transformed to a regular grid using the kriging method. The distance between grid nodes was 250 m. To calculate the grid node, values of up to 10 adjacent data points in the "search area" were taken into account. The search area with a radius of 5 km was finally divided into 4 sectors. In each of them, up to 10 adjacent data points were taken into account. A minimum condition for the retrieval of the grid node value was the presence of at least one sampling site in any sector of the search area. All the data sets displayed statistical distribution close to lognormal; therefore, logarithmic values were used for map construction. Concentration categories in the contour maps were selected as the 10%, 25%, 50% (median) 75% and 90% percentiles for the individual data sets. The last category represents extreme data. The statistical significance of differences between untreated and humate or TSP treated samples was evaluated using multifactor ANOVA and the significance of differences among individual variables was tested by a Scheffé post-hoc test (Winer et al., 1991).

4. Results

4.1. Sources of soil contamination

The emissions from the Pb and Zn smelter in Kabwe were potentially the most important source of contamination of local soils. In addition to dust from the Pb-Zn smelter, other sources of PHE in the Kabwe area contribute to various degrees to the current soil contamination: dust from (1) wastes after chemical leaching of silicate Pb-Zn ores, (2) the flash roasting plant residue, (3) settling ponds of flotation tailings of Pb-Zn ores, (4) granulated slag dumps, (4) a ferromanganese smelter of the Chiman Manufacturing Company Ltd. that is still in operation, (5) a local plant for production of aggregates and (6) a tailings pond following chemical treatment of base metal ores of Sable Zinc Plc. (Fig. S2). The location of the individual samples is shown in Fig. 1 and the chemical analyses of the samples are summarized in Table S2. As follows from this Table, the mining and ore-processing wastes and re-suspended dust particles contain very high concentrations of Cu, Zn, Pb and Ba (± Co, As and Se), depending on the source material and type of technological processing.

4.2. Soil contamination

4.2.1. Basic statistical characteristics of the distribution of selected chemical elements in topsoil and subsurface soil horizon in the Kabwe area

The basic statistical characteristics of individual data sets of chemical elements in the topsoil (depth 0–3 cm) and in the reference subsurface soil horizon (depth 70–90 cm, in brackets) are shown in Table 1.

As emerges from comparison of the topsoil and subsurface soil, the medians of the Zn and Pb concentrations are one order or magnitude higher in the topsoil relative to the deeper soil horizon. The enhanced contents of Zn and Pb in the topsoil are interpreted as being a result of dust fallout from the former Pb-Zn smelter or from tailings ponds left following mineral processing of local ores. For Cu, the median concentration in topsoils is similar to that in the subsurface soil, except the anomalously high concentration in the part of the Kabwe Region close to the Sable Zinc Plc. Tailings Dam.

In subsurface soil, the concentrations of Cr, Fe, Ni and Ba are usually higher compared to Zn and Pb. This indicates that their concentrations are mostly controlled by geogenic (soil-forming) processes. The characteristic distribution of values for selected elements in topsoil and in the subsurface soil in the surveyed area is shown in Fig. S3. Strong contamination is manifested by the very high topsoil to lower soil horizon ratio for the studied elements. The concentrations of Se and As in the topsoil as well as in the subsurface soil samples were below the

Table 1
Basic statistical characteristics of the data set of selected chemical elements (mg kg^{-1}) in topsoil (depth 0–3 cm) and in subsurface soil (depth 70–80 cm; in brackets) in the Kabwe area. Analyzed by FP-XRF. Number of topsoil samples: 116, subsurface soil samples: 40.

Element	Min.	Percentiles					Max.	Curt.[a]	Skew.[b]
		5%	25%	50% (median)	75%	95%			
Cr	12	13	15	17	25	146	293	4.37	2.11
	(13)	(14)	(18)	(93)	(120)	(271)	(965)	(23.2)	(4.19)
Mn	3	58	123	225	444	1677	4301	14.2	3.62
	(7)	(9)	(15)	(122)	(501)	(8608)	(15,328)	(10.7)	(3.32)
Fe	1531	3087	9871	16,318	26,048	49,059	215,059	38.9	5.21
	(2535)	(6961)	(15,740)	(26,565)	(48,343)	(114,764)	(288,489)	(14.8)	(3.31)
Ni	4	4	6	7	17	54	85	3.41	1.97
	(4)	(6)	(9)	(32)	(51)	(86)	(104)	(−0.19)	(0.82)
Cu	3	3	21	30	47	139	7121	114	10.8
	(3)	(3)	(22)	(29)	(35)	(74)	(1935)	(51.5)	(4.16)
Zn	7	17	70	230	705	6635	67,887	92.2	9.21
	(8)	(21)	(44)	(67)	(125)	(1796)	(90,161)	(51.3)	(7.21)
Ba	37	41	52	313	424	763	4783	57.9	6.69
	(40)	(56)	(326)	(432)	(655)	(1339)	(5884)	(32.8)	(7.21)
Pb	10	17	55	199	572	5385	40,692	47.7	6.42
	(9)	(14)	(17)	(28)	(72)	(791)	(39,529)	(51.5)	(7.16)

[a] Curtosis.
[b] Skewness.

detection limit of the FP-XRF method. However, a few topsoil samples collected in the former smelter area revealed concentrations up to 148 mg kg^{-1} Se, and up to 641 mg kg^{-1} As.

4.2.2. Distribution of elements in soils on a regional scale

The spatial distribution of selected elements in the Kabwe area is shown in Fig. 3. Individual maps depict data on the concentrations of variables in the topsoil and in the subsurface soil horizon. The concentrations of single elements in the topsoils (at a depth of 0–3 cm) are expressed as contours and the sampling sites are shown as black dots. Samples from the subsurface soil horizon are depicted by classed points. This graphic presentation enables correlation of the content of the given element in the topsoil with the concentration of the same element in the deeper soil horizon. It is assumed that high contents of elements in the topsoil relative to the deeper soil horizon indicate anthropogenic contamination. On the other hand, the same or even higher contents of a certain element in the deeper horizon indicate a geogenic origin of the element. This concept was verified during the pilot stage of environmental-geochemical survey undertaken in Zambia and Namibia between 2002 and 2017 (Kříbek and Nyambe, 2005; Kříbek et al., 2010, 2014a, 2016).

The highest Pb concentrations in topsoils (> 20,000 mg kg^{-1}) were recorded in the area of the former smelter and processing plant for Zn and Pb ores and in the area with industrial wastes (Fig. 3A). The source of contamination in this area probably corresponds to the dust fallout from former mining and processing operations. However, dust fallout from industrial waste deposits (residues from chemical leaching, slags and tailings) and from other industrial sources (production of aggregate) can also contribute to the topsoil contamination.

The highest Zn concentrations in the topsoils were recorded, similarly as for Pb, in the area of the former smelter and processing plant (Fig. 3B). Downwind, to the WNW direction, the concentrations of zinc in the topsoil gradually decrease. Compared with the Pb and Zn contents in the topsoils, the concentrations of Cu are substantially lower (Fig. 3C), except in the Kabwe industrial area. The highest concentrations of Ba were recorded in the area of the former processing plant (Fig. 3D) and correspond to relatively high amounts of barite in the Zn and Pb ores extracted in the past. At many sampling sites outside this area, however, the concentrations of Ba are higher in the subsurface soil horizon compared to the topsoil. In this case, the elevated Ba concentrations may indicate primary mineralization confined to the bedrock.

The concentrations of Fe and Mn outside the Kabwe industrial zone are usually higher in the subsoil compared with the topsoil, most probably due to the formation of ferromanganese cementation horizons (ferricrete) in the local soils. In the industrial area, however, the concentrations of both metals is very high in the topsoil, which can be attributed to emissions from the local ferromanganese plant (Fig. 3E, F). The concentrations of Cr and Ni (Fig. 3G, H) are usually higher in the subsurface soil layer and generally correlate with the Fe contents. Therefore, the principal factor which governs the distribution of Cr and Ni is the geochemical composition of the soil and bedrock.

4.2.3. Depth-related contamination patterns

For comparison purposes, the distribution of the elements was studied along two profiles affected and not affected by contamination (profiles SP-2 and SP-1, respectively). The uncontaminated profile SP-1 was sampled in the area NW of the Mukobeko quarter of Kabwe. The concentrations of Cu, Zn and Pb are very low in the upper part of this uncontaminated profile. The concentrations of Ni, Ba and Cr are low in the topsoil, but increase in the subsurface part of the soil profile. This indicates that the contents of Ni, Ba and Cr in the soils are mostly controlled by the geochemistry of the bedrock and/or by geogenic (soil-forming) processes. The concentrations of Cu, Zn and Pb in the contaminated SP-2 profile are very high in the upper part of the profile to a depth of approx. 7 cm (Fig. 4). Moreover, the surficial part of the profile is enriched with Se (up to 19 mg kg^{-1}) and As (up to 157 mg kg^{-1}; not shown in Fig. 4). Therefore it is concluded that anthropogenic contamination affects only the upper 5–10 cm thick surficial layer of soils.

4.3. Gastric bioaccessibility of contaminants in topsoils

The bioaccessible concentrations of selected contaminants (median values, in mg kg^{-1}) are summarized in Table 2. The gastric bioaccessible concentrations in the topsoil increase (median values, in % of their total contents in the topsoil; Table 2) in the following sequence: Fe (2.3) → As (8.3) → Cu (40) → Mn (50) → Co (54) → Zn (55) → Cd (78) → Pb (82). This indicates that Pb and Cd pose a serious environmental hazard when dust particles are swallowed.

4.4. Plant-available concentrations of contaminants in topsoils

The plant-available element concentrations are summarized in Table 3. The extraction tests indicated that the amounts of plant-

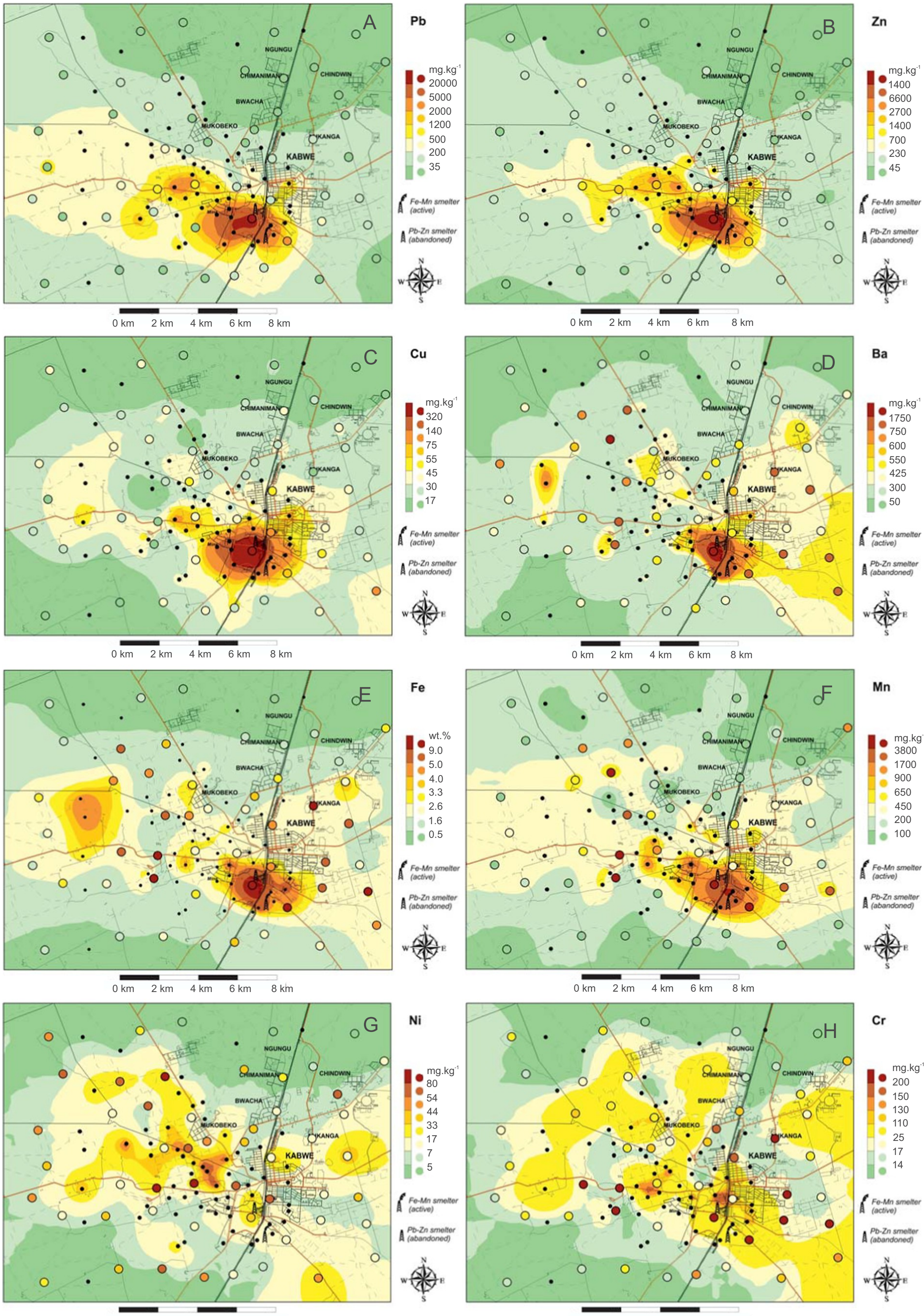

Fig. 3. Contour maps of the Pb (A), Zn (B), Cu (C), Ba (D), Fe (E), Mn (F), Ni (G) and Cr (H) concentrations (in mg kg^{-1}) in topsoil (0–3 cm depth) and classed point maps of the same elements in subsurface soils (70–80 cm depth) in the Kabwe area, Zambia.

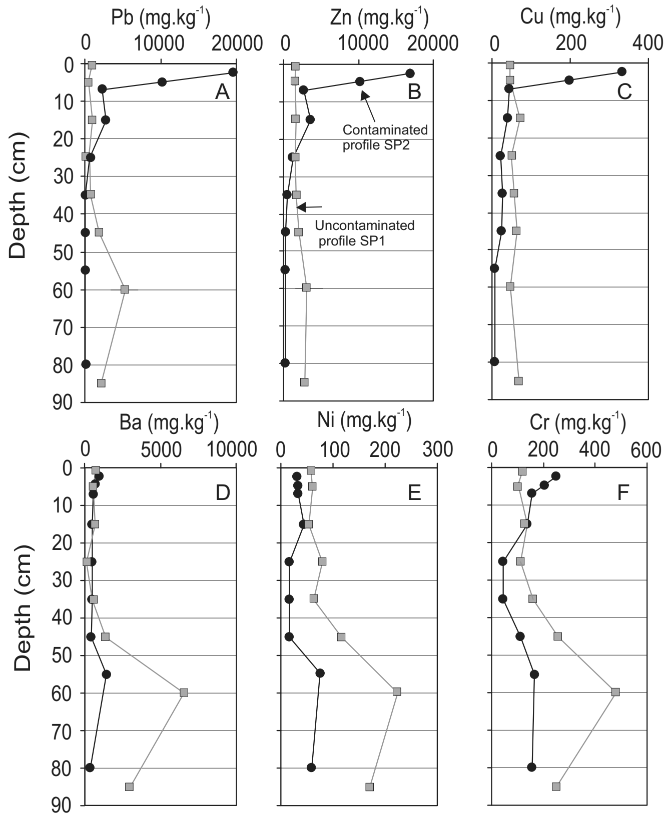

Fig. 4. Distribution of Pb (A), Zn (B), Cu (C), Ba (D), Ni (E) and Cr (F) in an uncontaminated soil profile SP-1 and contaminated profile SP-2. FP-XRF data. For the profiles location see Fig. 1.

available metals increase (median values, in % of their total contents in topsoil) in the following sequence: Fe (2.3) → Mn (15) → Zn (18) → Pb (37) → Cu (45) → Cd (56). Arsenic was below the detection limit of the analytical method used (HGAAS).

4.5. Immobilization of metals in soils using phosphate- and humate-based amendments

Determination of metals (Zn, Cu, Pb) in untreated and treated samples in all types of extracts is summarized in Table S3 and the average amount of elements established in the individual digests (in % of their concentration in the digests from an untreated sample) are shown in Fig. 5.

The amounts of elements extracted with the glycine extractant (gastric bioaccessible fraction) are the same in the treated and untreated samples. Therefore, the addition of a humate (HU) or phosphate (TSP) solution does not reduce the dissolution of Pb and Cd in the human stomach if soil dust is swallowed or unwashed vegetables with adhered dust particles are consumed. However, compared with the dissolution of elements in the *aqua regia* solution or in the glycine, the concentration of Pb and Cd extracted with the DTPA/TEA extractant (plant-available metals) decreased when samples were treated with a TSP or TSP-HU mixture. Compared with Pb and Cd, the concentration of DTPA/TEA-extracted Zn was essentially the same in the untreated and treated samples. Statistically significant differences between the plant available concentrations of Pb and Cd in the untreated and phosphate-treated soils were confirmed using multiparametric ANOVA and Scheffé post-hoc tests (Table S4).

5. Discussion

5.1. Assessment of soil contamination

No criteria for the assessment of soil contamination are available in the Republic of Zambia. Therefore, the concentrations of PHE in topsoil in the Kabwe area were compared with the permissible ecological limits for PHE used in Canada with regard to various land-uses (CCME, 2007; Table 4). Areas exceeding the Canadian limits for various land uses are shown in Fig. 6 by different color hatching. Where the quality guidelines do not differ for various land-uses, the same hatching is used in individual maps.

As indicated in Fig. 5, the Canadian soil quality limits are exceeded in the Kabwe area particularly for Zn and Pb, which are related to historical mining and smelting of local Pb-Zn ores. The Pb contamination of the topsoil affects the central part of Kabwe and extends from the former mining and processing area downwind, WNW of the Kabwe Town.

For Cu, the limits are exceeded in the industrial area of Kabwe, probably due to dispersion of dust from the Sable Zinc Plc. dry tailings pond. Barium levels exceed Canadian limits only in the Kabwe industrial area probably caused by former mining and crushing of ore or by dust fallout from the local plant for construction aggregate

Table 2

Gastric bioaccessible contents of elements in topsoils (in mg kg^{-1} and in % of their total concentration in topsoils). Number of samples: 25.

	Mn (mg kg^{-1})	Fe (mg kg^{-1})	Co (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})	As (mg kg^{-1})	Cd (mg kg^{-1})	Pb (mg kg^{-1})
Min.	93	200	2.5	2.0	14	0.05	0.3	18
Max.	731	2100	10	128	5152	7.4	19.8	5656
Mean	316	554	4.5	18	715	0.8	2.1	770
Percentile 10	134	300	2.5	4.6	34	0.05	0.3	49
Percentile 25	150	300	2.5	6.0	85	0.05	0.3	158
Percentile 50 (median)	307	400	2.5	10	228	0.34	0.8	298
Percentile 75	437	625	6.0	20	829	0.91	1.9	715
Percentile 90	562	970	8.0	37	1789	1.3	3.4	1692

	Mn %	Fe %	Co (%)	Cu (%)	Zn (%)	As (%)	Cd (%)	Pb (%)
Min	25	0.5	13	19	36	1.4	57	60
Max	83	9.2	100	75	81	53	97	97
Mean	52	3.0	57	43	57	13	82	82
Percentile 10	35	1.4	20	29	39	3.7	75	75
Percentile 25	45	2.0	35	35	47	5.5	75	77
Percentile 50 (median)	51	2.3	54	40	55	8.3	78	82
Percentile 75	57	3.4	85	51	69	15	92	89
Percentile 90	76	5.5	100	61	77	27	96	92

Table 3
Plant available contents of elements in topsoils (in $mg\,kg^{-1}$ and in % of their total concentration in topsoils). Number of samples: 25.

	Mn ($mg\,kg^{-1}$)	Fe ($mg\,kg^{-1}$)	Cu ($mg\,kg^{-1}$)	Zn ($mg\,kg^{-1}$)	Cd (mg kg–1)	Pb ($mg\,kg^{-1}$)
Min.	33	39	1	4	0.1	4
Max.	207	319	57	1900	14.5	2590
Mean	80	105	8	251	1.5	354
Percentile 10	41	55	2	13	0.1	16
Percentile 25	57	63	3	28	0.3	69
Percentile 50 (median)	76	79	4	111	0.7	126
Percentile 75	99	101	7	292	1.2	269
Percentile 90	112	199	15	359	2.3	853

	Mn (%)	Fe (%)	Cu (%)	Zn (%)	Cd (%)	Pb (%)
Min.	5.4	0.5	18	8.9	25	17
Max.	34	9.2	85	54	100	56
Mean	15	3.0	45	22	60	35
Percentile 10	6.5	1.4	29	12	25	18
Percentile 25	12	2.0	39	15	47	22
Percentile 50 (median)	14	2.3	45	18	60	39
Percentile 75	19	3.4	49	25	75	44
Percentile 90	20.4	5.5	59.5	40.1	83.9	45.7

production. For Cr or Ni, their concentration values that exceed the Canadian limits are difficult to interpret. They may represent both anthropogenic pollution and natural variations of Cr and Ni concentrations in topsoils. It is generally known that the concentrations of Cr and Ni are high in lateritic soils (i.e., Ferrasols) (McQueen, 2008). These "immobile" elements are usually adsorbed on iron oxides or even bound into their structure (Schwertmann and Pfab, 1996; Oliveira et al., 2001).

As a concluding remark, it should be pointed out that the soil quality guideline values for PHE differ significantly in Canada and in other countries (ESDAT, 2013) and therefore a certain amount of caution is necessary when applying the environmental standards of other countries for subtropical soils of the Kabwe area.

5.2. Gastric bioaccessibility of metals in topsoil

Although the simple simulations of gastric conditions (similar to the model used in this study) are thought to overestimate the total accessibility of metals/metalloids due to the aggressive pH of ~1.5 (corresponding to fasting conditions), these bioaccessibility models represent very suitable tools for human risk assessment in areas with high levels of metals/metalloids in soils and dust particles (Ruby et al., 1999; Oomen et al., 2002, 2003a, 2003b; Wragg and Cave, 2003; Wragg et al., 2011). Generally, studies revealed that samples with higher total concentrations of As, Cu, Pb and Zn also exhibit larger gastric bioaccessible fractions (Kříbek et al., 2016). Li and Thornton (2001) and Ettler et al. (2012) state that the gastric accessibility of lead in soils is mainly determined by the granulometric composition of dust fallout, which has a fine-grained nature in metallurgical operations. This corresponds to the findings of Csavina et al. (2012), who found that submicroscopic (0.05 to 18 μm) particles occur in smelting fumes and can be deposited onto adjacent soils. In contrast, the coarser character of dust from mining operations and tailings dams and the bonding of PHE in sulfides or insoluble sulfates reduce their bioaccessibility. The very high gastric accessibility of Pb (in % of the total Pb concentration in soils) in the Kabwe topsoils corresponds to the findings of other authors (Morrison and Gulson, 2007; Bosso and Enzweiler, 2008; Roussel et al., 2010; Reis et al., 2013).

In contrast to the high gastric bioaccessibility of Pb (and Cd), that of As is quite low in the Kabwe soils. This corresponds to the similarly low accessibility of As that was established in contaminated soils by Kim et al. (2002) and in the mine tailings of Namibia (Nejeschlebová et al., 2015). It is generally agreed that As in soils is mostly bound in amorphous, poorly or well crystallized forms of iron (goethite, FeOOH; hematite, Fe_2O_3; Doušová et al., 2008). Therefore, very low gastric accessibility of arsenic may be related to the very low accessibility (i.e., solubility) of iron phases such as hematite.

The calculations of the daily amount of ingested contaminants are related to children, who are considered to be the entity most exposed to contamination in and near the mining sites and smelter facilities. Data from Kabwe topsoil were compared to the tolerable daily intake (TDI) values calculated for a child weighing 10 kg and using the human-toxicity maximum permissible levels published by Baars et al. (2001; Table 5). For the calculation, a soil ingestion rate of 100 mg per day for children was used (Bierkens et al., 2011). The obtained daily intakes of PHE were then compared to the tolerable daily intake (TDI) limits taken from Baars et al. (2001). The results of the calculation revealed that the intake of Cd, Cu, Zn, Co, and As does not exceed the TDI values, but for Pb almost 50% of samples exceeded the TDI limit values and at least 10% of the values exceed the TDI by one order of magnitude. Therefore, the concentrations of gastric bioaccessible Pb in highly contaminated soils or in dust fallout may be considered to be an important health risk in the Kabwe area.

It should be noted that, for determination of the gastric bioaccessible fraction of PHE, a granulometric fraction of topsoils of < 0.2 mm in size was used, but not their PM_{10} fraction (i.e. fraction < 10 μm), which is more easily inhaled, ingested and dissolved (more bioaccessible) in the gastrointestinal tract (Juhasz et al., 2011; Csavina et al., 2012; Ettler et al., 2014 and references therein). This means that the actual intake of Pb in the studied area may be somewhat higher than that given in this study.

5.3. Plant-available metals and the application of phosphate and humate as soil amendments

The addition of phosphate can significantly reduce Pb plant-availability because of the limited solubility of Pb-phosphates, such as pyromorphite [$Pb_5(PO_4)_3Cl$] (Mahar et al., 2015). Moreover, Pb and, to a lesser degree, Cd can substitute Ca in carbonate–fluorapatite [$Ca_5(PO_4,CO_3)F$] or in carbonate-hydroxylapatite [$Ca_5(PO_4CO_3)_3(OH)$] (Ma et al., 1995; Chrysochoou et al., 2007). Three main mechanisms have been proposed for the entry of metal cations into phosphate minerals (Trueman and Tuross, 2002): (1) adsorption of metal cations onto crystal surfaces (presumably displacing surface calcium), (2) direct ion substitution (or coupled substitution) in the apatite structure and (3) growth of discrete trace metal-phosphate phases disseminated

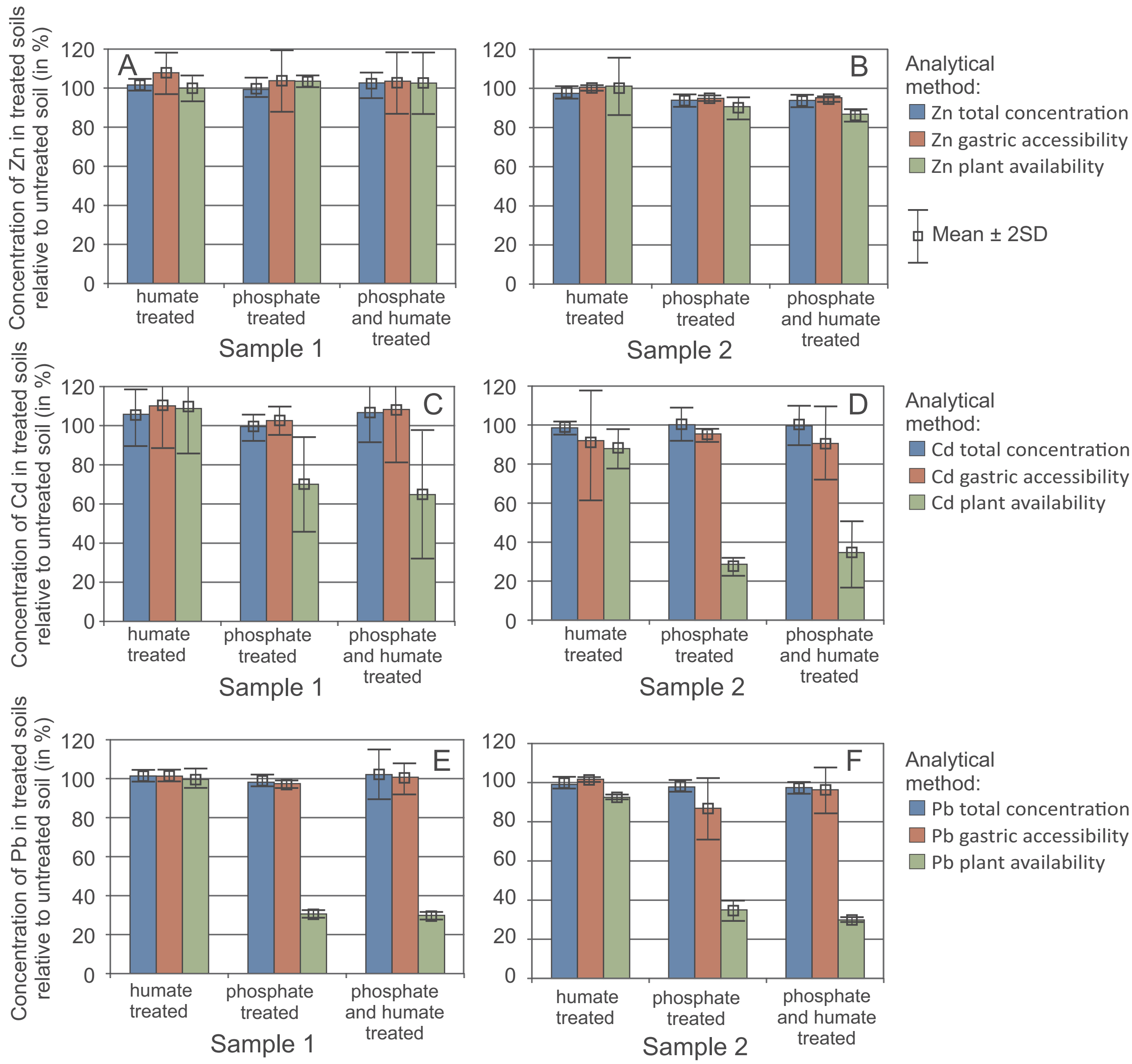

Fig. 5. Concentrations of Zn (A, B), Cd (C, D) and Pb (E, F) in two contaminated samples of topsoil from the Kabwe area, treated with humate (HU), triple superphosphate (TSP) and a mixture of TSP and humate. The concentrations are presented in % relative to untreated samples. Untreated and treated samples were digested with *aqua regia* (total concentration), in an acidified solution of glycine (gastric accessible metals) and in a mixture of DTPA and TEA (plant available metals). The experimental results indicate that the concentrations of plant-available Pb and, to a lesser degree, also Cd decrease in the TSP- and in the TSP and humate-treated samples compared with untreated samples. The addition of only humate does not affect the plant availability of Zn. The gastric accessibility of Zn, Cd and Pb is not affected by addition of phosphate or humate solutions.

Table 4
Maximum permissible ecological concentration limits for inorganic contaminants in soils used in Canada with regard to various land uses (CCME, 2007; in mg kg^{-1}, dry weight).

Element	Land use			
	Agricultural	Residential	Commercial	Industrial
Cr	64	64	87	87
Ni	50	50	50	50
Cu	63	63	91	91
Zn	200	200	360	360
Ba	750	500	2000	2000
Pb	70	140	260	600

within the apatite lattice. The latter mechanism has been confirmed experimentally (Valsami-Jones et al., 1996) for Pb and Cd. However, Molleson et al. (1998) gave a unique example of extensive replacement of carbonate-bearing hydroxylapatite with the Pb phosphate mineral pyromorphite, apparently through diffusive-substitution of apatite lattice-bound Ca with Pb. Other divalent cations which substitute for Ca^{2+} in apatites include Ni^{2+}, Co^{2+}, Cu^{2+}, and Cd^{2+} (Pan and Fleet, 2002). Direct evidence that Cd can occupy Ca crystallographic sites has been demonstrated using extended X-ray absorption fine structure (EXAFS spectroscopy; Sery et al., 1996).

The results of our experiments, summarized in Fig. 5 and Table S3, confirmed that the addition of TSP can significantly reduce the plant availability of Pb and, to a lesser extent, also Cd. Therefore, the amount of Pb and Cd in plant tissues, especially in vegetables, can be suppressed by this soil amendment. However, this conclusion should be considered preliminary because the results will have to be tested directly on farmlands and long-term monitoring is needed to ensure the efficiency of metal immobilization during a prolonged period of time. The possible release of metal ions from the fixed complexation under different environmental stresses, such as acidity and temperature fluctuations

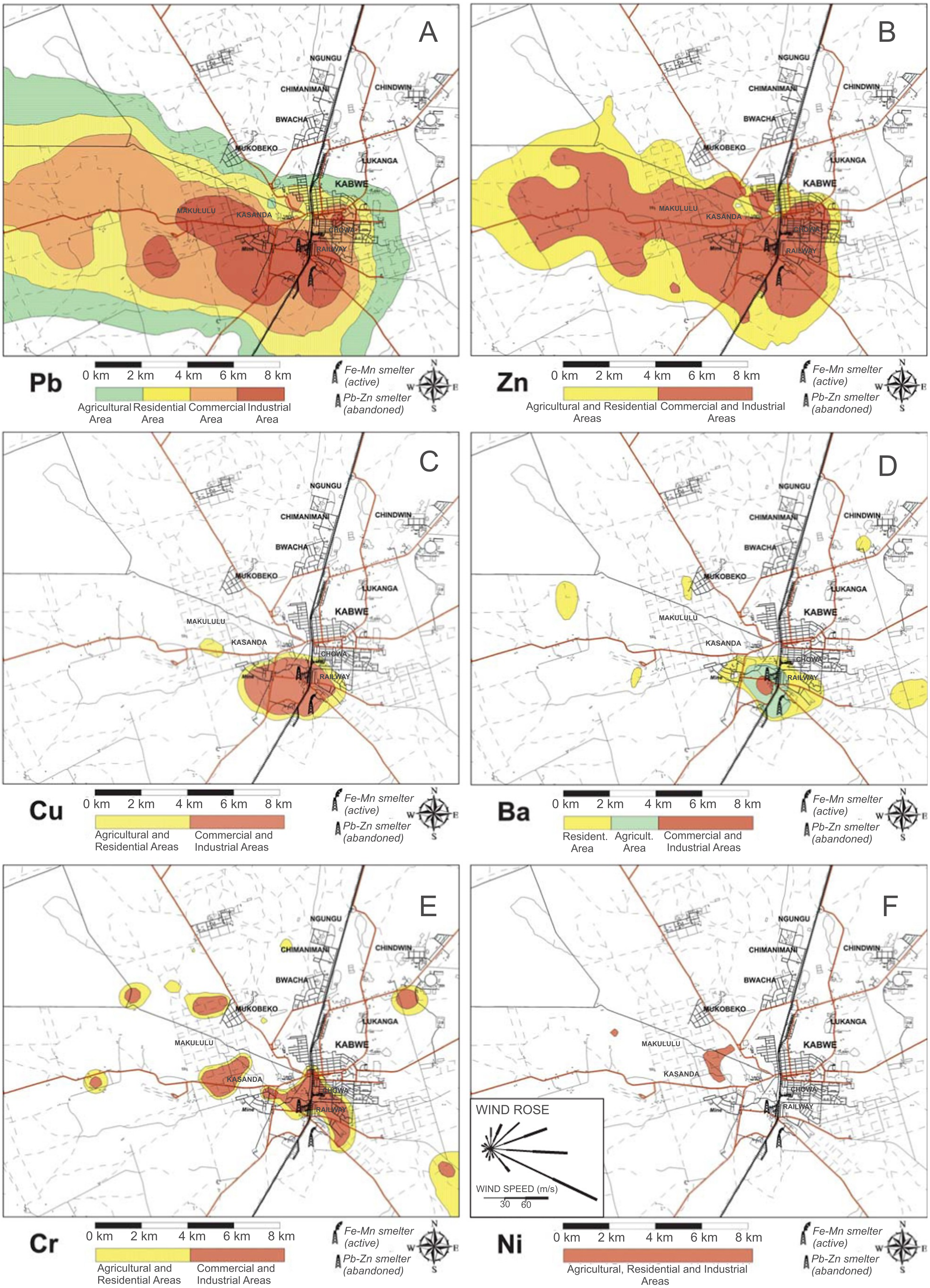

Fig. 6. Areas exceeding the permissible ecological limits for Pb (A), Zn (B), Cu (C) Ba (D), Cr (E) and Ni (F) in soil used in Canada with regard to various land uses (CCME, 2007). The Canadian limit values are summarized in Table 4.

Table 5
Calculated amounts of gastrically accessible elements (μg) assuming a soil ingestion rate of 100 mg per day for studied topsoils in the Kabwe area. Number of samples: 25.

	Pb	Cd	Cu	Zn	Co	As
Min	1.8	0.04	0.2	1.41	0.25	0.01
Max	565	1.98	12.8	515	1.00	0.74
Mean	77	0.23	1.81	71.4	0.45	0.08
Percentiles						
10%	4.92	0.04	0.46	3.42	0.25	0.01
25%	15.8	0.04	0.6	8.51	0.25	0.01
50% (median)	29.8	0.11	1.11	22.8	0.25	0.03
75%	71.5	0.22	2.02	82.9	0.60	0.09
90%	240	0.57	5.74	262	1.40	0.23
TDI* (10 kg)	36	5	1400	5000	14	10

TDI* = Tolerable daily intake of elements calculated from the human-toxicity maximum permissible levels of Baars et al. (2001) in micrograms per day for a child weighing 10 kg.

and other accelerated weathering processes could be simulated kinetically in order to obtain detailed information on environmental risk assessment (Guo et al., 2006).

Unlike Pb and Cd, which in our experiments of TSP treated samples exhibited a decrease in plant availability of both elements, the Zn concentration in untreated and treated samples was found to be virtually identical. This corresponds to the results of Cao et al. (2003), who concluded that phosphate is more effective in reducing Pb plant availability than Zn and Cu availability, because Pb is immobilized by P via the formation of an insoluble pyromorphite-like mineral in the soil, whereas Zn or Cu phosphate minerals are more soluble. In their study of the remediation of contaminated agricultural soils near a former Pb/Zn smelter in Austria, Friesl et al. (2006) found that the immobilization of Pb and Cd in soil using phosphate was very successful, whereas the immobilization of Zn was inefficient.

Wang et al. (2017) found that natural minerals and humic acids each have positive effects on the remediation of metal-contaminated soils. They proposed that the co-remediation of hydroxyapatite with humic acid showed the best effect in reducing the amount of Pb, Cd and Zn taken up by the plant. In our experiments, the treatment of contaminated soil samples with a mixture of phosphate and humate did not reduce the plant availability of Pb, Cd and Zn relative to the treatment with phosphate alone. This corresponds to conclusions of Kumpiene et al. (2008) who deduced that it is very effective to add P to soils contaminated with Pb and Cd, while the application of organic matter alone leads to only a slight improvement in metal immobilization. However, an organic amendment could improve the soil properties, nutritional status, water infiltration and water-holding capacity of the contaminated soils (Tordoff et al., 2000).

The impact of amendment with phosphates or humates on the gastric bioaccessibility of Pb, Cd and Zn was studied by Xu et al. (2016). They concluded that the gastric bioaccessibility of Cd can be reduced by 54% using a mixture of biochar and phosphate. However, estimation of the gastric bioaccessibility depends on an evaluation method, notably on the acidification of a glycine solution (Adamo and Zampella, 2008). In their study, Xu et al. (2016) followed the procedures introduced by Kelley et al. (2002) and the glycine solution was acidified only to pH 2.5. Our gastric bioaccessibility tests were carried out according to the US EPA (2007) protocol and glycine was acidified to pH 1.5, corresponding to fasting conditions. Therefore, the very low pH used in our tests could probably have been the reason, why we did not find any decrease in the gastric available amount of the analyzed elements in either TSP or humate treated samples.

5.4. Measures proposed to reduce the health risks in the Kabwe area

Based on the results of this study and earlier investigations (Kříbek and Nyambe, 2005) it is suggested that the following measures be taken to reduce the health risks to the population in the Kabwe area:

(1) This highly contaminated area is actually a playground for children and local residents also pick up mineral samples from industrial wastes. This industrial zone contains very high concentrations of potentially harmful elements and consequently it should be permanently guarded by a security agency.
(2) The crushers of the Kabwe Earth Movers Company, if still in operation, should be equipped with dust collectors and covered with a sheet metal shelter, and dust filters should be installed at the ferromanganese smelter of the Chiman Manufacturing Company. Dust fallout in the environs of the smelter should be regularly monitored.
(3) The tailings dam operated and owned by the Zinc Sable Plc. should be raised and safely sealed and a drainage canal should be constructed around the settling pond. The site should be fenced off in order to prevent children from entering. This high-risk waste storage area should be covered with a layer of earth or inert granulated slag.
(4) Special attention should to be paid during reclamation works to create playing fields, particularly playgrounds and sports grounds or lawns adjacent to schools. Reclaiming of these areas should be treated as a priority. Irrigation systems should be constructed and these areas covered with uncontaminated earth.
(5) The surface of unpaved and dusty roads inside residential areas can be simply modified by rolling and wetting of imported laterite blended with a small amount of cement. Spraying of public areas and roads during the dry season would contribute significantly to reducing dust levels. Addition of calcium chloride to the wetting solutions should be also considered, because it is a strongly hygroscopic substance which will cause aggregation of dust particles and prevent them from being dispersed by turbulence.
(6) Reduction of dust fallout can be achieved by planting trees. The following species are most suitable for this purpose: *Eucalyptus hybrid*, *Toona ciliata* (Cedrella), *Achrocarpus frazinifolia* and *Acacia* spp.
(7) On plots of land used for cultivation of vegetables, contaminated soil should be removed to a minimum depth of 30 cm. As it is costly, cheaper methods of reclamation, for example liming to increase the pH or spraying with superphosphate solution to achieve immobilization of plant-available Pb and Cd in soils are recommended in highly contaminated areas. The concentrations of Pb and Cd in vegetables grown in contaminated areas should be monitored regularly.
(8) The development of a program of health care involving long-term monitoring of lead contents in the blood of groups at high risk (especially pregnant women and children) is of utmost importance in contaminated areas, especially in the Kabwe Town districts of Kasanda, Makululu, Katondo, Railway, and Chowa. The monitoring undertaken in the past was based on random measurements, the analyses were carried out in various laboratories and the results cannot be reliably compared. This problem could be resolved by increasing support for equipping the constructed clinics and Kabwe General Hospital with permanent laboratories for monitoring and treatment.

6. Conclusions

Monitoring of the regional extent of topsoil contamination has shown that emissions from the abandoned Pb-Zn smelter play a major role in the large-scale pollution of the local environment. However, resuspended dust from other sources (tailing ponds, slag deposits) and emissions from the active ferromanganese smelter also probably participate in the pollution. Strong contamination of the topsoil was found especially in for Pb and Zn. The concentrations of both elements exceed Canadian soil quality limits in several Kabwe Town districts. The distribution in the topsoil of the other monitored elements (Cu, Fe, Mn, Cr, Ni), d by both anthropogenic and geogenic factors.

The tests undertaken demonstrated the very high gastric accessibility of Pb and Cd in the topsoils. However, the tolerable daily intake (TDI) values calculated for a child weighing 10 kg, using the human-toxic maximum permissible levels, are exceeded for a large number of the studied samples only for Pb.

The results of plant-availability studies of PHE in the topsoil showed that a significant proportion of the contaminants are present in a plant-available fraction. To suppress the plant availability of Pb, Zn and Cd, the samples of strongly contaminated topsoil were treated with phosphate or humate solution. Application of phosphate showed that the plant availability of Pb and Cd decreased significantly. The plant-availability of Zn was not affected by the phosphate treatment.

Based on these results, a range of measures has been formulated and suggested to improve the quality of the Kabwe environment. These include, for example, proposals to restrict the free movement of people and, in particular, children in the former technological grounds. Dust control can be achieved by planting greenery and sprinkling water on dusty roads, particularly in the dry season (May–October). Special attention should be paid to playgrounds and lawns adjacent to schools. These areas should be covered with uncontaminated soil and grass. Rehabilitation of these areas should be treated as a priority. The efficiency of these measures should be controlled by long-term monitoring of the amounts of lead in the blood of the population living in vulnerable areas, especially children and pregnant women. The amounts of plant-accessible Pb and Cd in heavily polluted soils can be reduced by phosphate amendment and the content of toxic elements in vegetables grown in phosphate-treated grounds should also be monitored regularly to verify the efficiency of phosphate treatment.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gexplo.2018.11.018.

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References

Adamo, P., Zampella, M., 2008. Chemical speciation to assess potentially toxic metals (PTMs') bioavailability and geochemical forms in polluted soils. In: de Vivo, B., Belkin, H.E., Lima, A. (Eds.), Environmental Geochemistry: Site Characterization, Data Analysis and Case Histories. Elsevier, Amsterdam, pp. 175–212.

Albanese, S., De Vivo, B., Lima, A., Frattasio, G., Kříbek, B., Nyambe, I., Majer, V., 2014. Prioritising environmental risk at the regional scale by a GIS aided technique: the Zambian Copperbelt Province case study. J. Geochem. Explor. 144, 433–442. https://doi.org/10.1016/j.explo2014.03.014.

Alpofead, J.A.H., Davidson, C.M., Littlejohn, D., 2016. Oral bioaccessibility tests to measure potentially toxic elements in inhalable particulate matter collected during routine air quality monitoring. Anal. Methods 8, 5466–5474. https://doi.org/10.1039/c6ay01403h.

Alpofead, J.A.H., Davidson, C.M., Littlejohn, D., 2017. A novel two-step sequential bioaccessibility test for potentially toxic elements in inhaled particulate matter transported into the gastrointestinal tract by mucociliary clearance. Anal. Bioanal. Chem. 409, 3165–3174. https://doi.org/10.1007/s00216-017-0257-2.

Baars, A.J., Theelen, R.M.C., Janssen, P.J.C.M., Hesse, J.M., van Apeldoorn, M.E., Meijerink, M.C.M., Verdam, L., Zeilmaker, M.J., 2001. Re-evaluation of human-toxicological maximum permissible risk levels. In: RIVM Report 711701 025, (Bilthoven, The Netherlands. 297 pp.).

Banza, C.L.N., Nawrot, T.S., Haufroid, V., Decrée, S., De Putter, T., Smolders, E., Kabyla, B.I., Luboya, O.N., Ilunga, A.N., Mutombo, A.M., Nemery, B., 2009. High human exposure to cobalt and other metals in Katanga, a mining area of the Democratic Republic of Congo. Environ. Res. 109, 745–752. https://doi.org/10.1016/j.envres.2009.04.012.

Barcan, V., 2002. Nature and origin of multicomponent aerial emissions of the copper-nickel smelter complex. Environ. Int. 28, 451–456. https://doi.org/10.1016/S0160-4120(02)00064-8.

Barlin, B., 1970. The Evolution of Lead Smelting Practice at the Zambia Brooken Hill Development Co. Ltd. A.I.M.E. Symposium on Mining and Metallury of Lead and Zinc, St. Louis, U.S.A., October 1970.

Barlin, B., 1972. Metallurgical practice at the Broken Hill division of Nchanga consolidated copper mines limited. Geol. Mijnb. 51, 423–448.

Beavington, F., Cawse, P.A., Wakenshaw, A., 2004. Comparative studies of atmospheric trace elements: improvements in air quality near a copper smelter. Sci. Total Environ. 332, 39–49. https://doi.org/10.1016/j.scitotenv.2004.04.016.

Bierkens, J., Van Holderbeke, M., Cornelis, C., Torfs, R., 2011. Exposure through soil and dust ingestion. In: Swartjes, F.A. (Ed.), Dealing with Contaminated Sites. Springer Science + Business Media B.V, Berlin, pp. 261–286.

Bose-O'Reilly, S., Yabe, J., Makumba, J., Schutzmeier, P., Ericson, B., Caravanos, J., 2018. Lead intoxicated children in Kabwe, Zambia. Environ. Res. 165, 420–424. https://doi.org/10.1016/j.envres.2017.10.024.

Bosso, S.T., Enzweiler, J., 2008. Bioaccessible lead in soils, slag, and mine wastes from an abandoned mining district in Brazil. Environ. Geochem. Health 30, 219–229. https://doi.org/10.1007/s10653-007-9110-4.

Cao, R.X., Ma, L.Q., Chen, M., Singh, S.P., Harris, W.G., 2003. Phosphate-induced metal immobilization in a contaminated site. Environ. Pollut. 122, 19–28. https://doi.org/10.1016/S0269-7491(02)00283-X.

Castellano, A.V., Cancio, J.A.L., Martin, S.S., Sanchez, A.D., 2004. Metallic water-soluble species present in atmospheric particles. Afinidad 61, 286–293.

Castillo, S., de la Rosa, J.D., Sánchez de la Campa, A.M., González-Castanedo, Y., Fernández-Caliani, J.C., Gonzalez, I., Romero, A., 2013. Contribution of mine waste to atmospheric metal deposition in the surrounding area of an abandoned heavily polluted mining district (Rio Tinto mines, Spain). Sci. Total Environ. 449, 363–372. https://doi.org/10.1016/j.scitotenv.2013.01.076.

CCME, 2007. Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health Summary Tables, Update 7.0. http://st-ts.ccme.ca/, Accessed date: 4 October 2018.

Chatain, V., Sanchez, F., Bayard, R., Moszkowicz, P., Gourdon, R., 2005. Effect of experimentally induced reducing conditions on the mobility of arsenic from a mining soil. J. Hazard. Mater. 122, 119–128. https://doi.org/10.1016/j.jhazmat.2005.03.026.

Cheyns, K., Banza, C.L.N., Ngombe, L.K., Asosa, J.A., Haufroid, V., De Putter, T., Nawrot, T., Kimpanga, C.M., Numbi, O.L., Ilunga, B.K., Nemery, B., Smolders, E., 2014. Pathways of human exposure to cobalt in Katanga, a mining area of the D. R. Congo. Sci. Total Environ. 490, 313–321. https://doi.org/10.1016/j.scitotenv.2014.05.014.

Chrysochoou, M., Dermatas, D., Grubb, D.G., 2007. Phosphate application to firing range soils for Pb immobilization: the unclear role of phosphate. J. Hazard. Mater. 144, 1–14. https://doi.org/10.1016/j.jhazmat.2007.02.008.

Csavina, J., Field, J., Taylor, M.P., Gao, S., Landázuri, A., Betterton, E.A., Sáez, A.E., 2012. A review on the importance of metals and metalloids in atmospheric dust and aerosol from mining operations. Sci. Total Environ. 433, 58–73. https://doi.org/10.1016/j.scitotenv.2012.06.013.

Deshommes, E., Tardif, R., Edwards, R., Sauvé, S., Prévost, M., 2012. Experimental determination of the oral bioavailability and bioaccessibility of lead particles. Chem. Cent. J. 6, 138. https://doi.org/10.1186/1752-153X-6-138.

Doušová, B., Martaus, A., Filippi, M., Koloušek, D., 2008. Stability of arsenic species in soils contaminated naturally and in an anthropogenic manner. Water Air Soil Pollut. 187, 233–241. https://doi.org/10.1007/s11270-007-9511-0.

Dudka, S., Adriano, D.C., 1997. Environmental impacts of metal ore mining and processing: a review. J. Environ. Qual. 26, 590–602. https://doi.org/10.2134/jeq1997.00472425002600030003x.

ESDAT, 2013. Environmental Data Management System. Earth Science Information System Inc., Melbourne. http://www.esdat.com.au, Accessed date: 6 October 2017.

Ettler, V., 2016. Soil contamination near non-ferrous metal smelters: a review. Appl. Geochem. 64, 56–74. https://doi.org/10.1016/j.apgeochem.2015.09.020.

Ettler, V., Johan, Z., Kříbek, B., Šebek, O., Mihaljevič, M., 2009. Mineralogy and environmental stability of slags from the Tsumeb smelter, Namibia. Appl. Geochem. 24, 1–15. https://doi.org/10.1016/j.apgeochem.2008.10.003.

Ettler, V., Mihaljevič, M., Kříbek, B., Majer, V., Šebek, O., 2011. Tracing the spatial distribution and mobility of metal/metalloid contaminants in Oxisols in the vicinity of the Nkana copper smelter, Copperbelt Province, Zambia. Geoderma 164, 73–84. https://doi.org/10.1016/j.geoderma.2011.05.014.

Ettler, V., Kříbek, B., Majer, V., Knésl, I., Mihaljevič, M., 2012. Differences in the bioaccessibility of metals/metalloids in soils from mining and smelting areas (Copperbelt, Zambia). J. Geochem. Explor. 113, 68–75. https://doi.org/10.1016/j.gexplo.2011.08.001.

Ettler, V., Vítková, M., Mihaljevič, M., Šebek, O., Klementová, M., Veselovský, F., Vybíral, P., Kříbek, B., 2014. Dust from Zambian smelters: mineralogy and contaminant bioaccessibility. Environ. Geochem. Health 36, 919–933. https://doi.org/10.1007/s10653-014-9609-4.

Ettler, V., Johan, Z., Kříbek, B., Veselovský, F., Mihaljevič, M., Vaněk, A., Penížek, V., Majer, V., Sracek, O., Mapani, B., Kamona, F., Nyambe, I., 2016. Composition and fate of mine- and smelter-derived particles in soils of humid subtropical and hot semi-arid areas. Sci. Total Environ. 563–564, 329–339. https://doi.org/10.1016/j.scitotenv.2016.04.133.

Fonkou, T., Agendia, P., Kengne, I., Akoa, A., Nya, J., 2002. The accumulation of heavy metals in biotic and abiotic components of the Olezoa wetland complex in Yaounde, Cameroon (West Africa). In: Kenge, I. (Ed.), Proceedings of International Symposium on Environmental Pollution Control and Waste Management, 7–10 January 2002, Tunis (EPCOWM'2002), pp. 29–33.

Friesl, W., Friedl, J., Platzer, K., Horak, O., Gerzabek, M.H., 2006. Remediation of contaminated agricultural soils near a former Pb/Zn smelter in Austria: batch, pot and field experiments. Environ. Pollut. 144, 40–50. https://doi.org/10.1016/j.envpol.2006.01.012.

Ghorbel, M., Munoz, M., Courjault-Radé, P., Destigneville, C., de Perseval, P., Souissi, R., Souissi, F., Ben Mammou, A., Abdeljaouad, S., 2010. Health risk assessment for human exposure by direct ingestion of Pb, Cd, Zn bearing dust in the former miners'village of Jebel Ressas (NE Tunisia). Eur. J. Mineral. 22, 639–649. https://doi.org/10.1127/0935-1221/2010/0022-2037.

Ghorbel, M., Munoz, M., Solmon, F., 2014. Health hazard prospecting by modelling wind transfer of metal-bearing dust from mining waste dumps: application to Jebel Ressas Pb-Zn-Cd abandoned mining site (Tunisia). Environ. Geochem. Health 36, 935–951. https://doi.org/10.1007/s10653-014-9610-y.

Goodarzi, F., Sanei, H., Garrett, R.G., Duncan, W.F., 2002. Accumulation of trace elements on the surface soil around the trail smelter, British Columbia, Canada. Environ. Geol. 43, 29–38. https://doi.org/10.1007/s00254-002-0634-8.

Guo, G., Zhou, Q., Ma, Q., 2006. Availability and assessment of fixing additives for the in situ remediation of heavy metal contaminated soils: a review. Environ. Monit. Assess. 116, 513–528. https://doi.org/10.1007/s10661-006-7668-4.

Herzman, C., 1995. Monitoring of Lead Concentration in the Kasanda, Railway and Katonndo Townships in Kabwe. MS. University of British, Columbia, Canada (42 pp.).

Hutchinson, T.C., Whitby, L.M., 1974. Heavy metal pollution in the Sudbury mining and smelting region of Canada. I. Soil and vegetation contamination by nickel, copper and other metals. Environ. Conserv. 1, 123–132. https://doi.org/10.1017/s0376892900004240.

ISO 11466, 1995. Soil Quality: Extraction of Trace Elements Soluble in Aqua Regia. International Organization for Standardization, Geneva.

IUSS, 2015. World Reference Base for Soil Resources 2014, Update 2015. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps. World Soil Resources Reports No. 106. FAO, Rome.

Juhasz, A.L., Weber, J., Smith, E., 2011. Impact of soil particle size and bioaccessibility on children and adult lead exposure in peri-urban contaminated soils. J. Hazard. Mater. 186, 1870–1879. https://doi.org/10.1016/j.hazmat.2010.12.095.

Juhasz, A.L., Smith, E., Nelson, C., Thomas, D.J., Bradham, K., 2014a. Variability associated with As in vivo-in vitro correlations when using different bioaccessibility methodologies. Environ. Sci. Technol. 48, 11646–11653. https://doi.org/10.1021/es502751z.

Juhasz, A.L., Herde, P., Herde, C., Boland, J., Smith, E., 2014b. Validation of the predictive capabilities of the Sbrc-G in vitro assay for estimating arsenic relative bioavailability in contaminated soils. Environ. Sci. Technol. 48, 12962–12969. https://doi.org/10.1021/es503695g.

Kabala, C., Singh, B.R., 2001. Fractionation and mobility of copper lead, zinc in soil profiles in the vicinity of a copper smelter. J. Environ. Qual. 30, 485–492. https://doi.org/10.2134/jeq2001.302485x.

Kabata-Pendias, A., 2004. Soil-plant transfer of trace elements - an environmental issue. Geoderma 122, 143–149. https://doi.org/10.1016/j.geoderma.2004.01.004.

Kachenko, A.G., Singh, B., 2006. Heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia. Water Air Soil Pollut. 169, 101–123. https://doi.org/10.1007/s11270-006-2027-1.

Kamona, A.F., Friedrich, G.H., 2007. Geology, mineralogy and stable isotope geochemistry of the Kabwe carbonate-hosted Pb-Zn deposit, Central Zambia. Ore Geol. Rev. 30, 217–243. https://doi.org/10.1016/j.oregeorev.2006.02.003.

Kastury, F., Smith, E., Karna, R.R., Scheckel, K.G., Juhasz, A.L., 2018. An inhalation-ingestion bioaccessibility assay (IIBA) for the assessment of exposure to metal(loid)s in PM10. Sci. Total Environ. 631-632, 92–104. https://doi.org/10.1016/j.scitotenv.2018.02.337.

Kelley, M.E., Brauning, S.E., Schoof, R.A., Ruby, M.V., 2002. Assessing Oral Bioavailability of Metals in Soil. Battelle Press, USA (48 pp.).

Kim, J.Y., Kim, K.W., Lee, J.U., Lee, J.S., Cook, L., 2002. Assessment of As and heavy metal contamination in the vicinity of the Duckum Au–Ag mine, Korea. Environ. Geochem. Health 24, 213–225. https://doi.org/10.1023/A:1016096017050.

Kim, K.H., Kabir, E., Kabir, S., 2015. A review on the human health impact of airborne particulate matter. Environ. Int. 74, 136–143. https://doi.org/10.1016/j.envint.2014.10.005.

Kříbek, B., Nyambe, I. (Eds.), 2005. Impact Assessment of Mining and Processing of Copper and Cobalt Ores on the Environment in the Copperbelt, Zambia. — The Kitwe and Mufulira Areas. Project of the Development Assistance Programme of the Czech Republic for the Years 2004–2006. Final Report for Year 2004. MS., Czech Geological Survey, Prague (196 pp.).

Kříbek, B., Majer, V., Veselovský, F., Nyambe, I., 2010. Discrimination of lithogenic and anthropogenic sources of metals and sulphur in soils of the central-northern part of the Zambian Copperbelt Mining District: a topsoil vs. subsurface soil concept. J. Geochem. Explor. 104, 69–86. https://doi.org/10.1016/j.gexplo.2009.12.005.

Kříbek, B., Mihaljevič, M., Sracek, O., Knésl, I., Ettler, V., Nyambe, I., 2011. The extent of arsenic and of metal uptake by aboveground tissues of Pteris vittata and Cyperus involucratus growing in copper- and cobalt-rich tailings of the Zambian Copperbelt. Arch. Environ. Contam. Toxicol. 61, 228–242. https://doi.org/10.1007/s00244-010-9604-4.

Kříbek, B., Majer, V., Pašava, J., Kamona, F., Mapani, B., Keder, J., Ettler, V., 2014a. Contamination of soils with dust fallout from the tailings dam at the Rosh Pinah area, Namibia: regional assessment, dust dispersion modeling and environmental consequences. J. Geochem. Explor. 144, 391–408. https://doi.org/10.1016/j.gexplo.2014.01.010.

Kříbek, B., Majer, V., Knésl, I., Nyambe, I., Mihaljevič, M., Ettler, V., Sracek, O., 2014b. Concentrations of arsenic, copper, cobalt, lead and zinc in cassava (*Manihot esculenta* Crantz) growing on uncontaminated and contaminated soils of the Zambian Copperbelt. J. Afr. Earth Sci. 99, 713–723. https://doi.org/10.1016/j.jafrearsci.2014.02.009.

Kříbek, B., Majer, V., Knésl, I., Keder, J., Mapani, B., Kamona, F., Mihaljevič, M., Ettler, V., Penížek, V., Vaněk, A., Sracek, O., 2016. Contamination of soil and grass in the Tsumeb smelter area, Namibia: modeling of contaminants dispersion and ground geochemical verification. Appl. Geochem. 64, 75–91. https://doi.org/10.1016/j.apgeochem.2015.07.006.

Kříbek, B., Šípková, A., Ettler, V., Mihaljevic, M., Majer, V., Knésl, I., Mapani, B., Penízek, V., Vaněk, A., Sracek, O., 2018. Variability of the copper isotopic composition in soil and grass affected by mining and smelting in Tsumeb, Namibia. Chem. Geol. 493, 121–135. https://doi.org/10.1016/j.chemgeo.2018.05.035.

Krzaklewski, W., Barszcz, J., Małek, S., Kozioł, K., Pietrzykowski, M., 2004. Contamination of forest soils in the vicinity of the sedimentation pond after zinc and lead ore flotation (in the region of Olkusz, Southern Poland). Water Air Soil Pollut. 159, 151–164. https://doi.org/10.1023/B:WATE.0000049173.18935.71.

Kumpiene, J., Lagerkvist, A., Maurice, C., 2008. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments - a review. Waste Manag. 28, 215–225. https://doi.org/10.1016/j.wasman.2006.12.012.

Li, X., Thornton, I., 2001. Chemical partitioning of trace and major elements in soils contaminated bymining and smelting activities. Appl. Geochem. 16, 1693–1706. https://doi.org/10.1016/S0883-2927(01)00065-8.

Li, W., Ji, B., Hu, Y., Liu, R.Sun, 2017. A review on in situ phytoremediation of mine tailings. Chemosphere 184, 594–600. https://doi.org/10.1016/j.chemosphere.2017.06.025.

Luo, X.S., Zhou, D.M., Liu, X.H., Wang, Y.J., 2006. Solid/solution partitioning and speciation of heavy metals in the contaminated agricultural soils around a copper mine in eastern Nanjing city, China. J. Hazard. Mater. 131, 19–27. https://doi.org/10.1016/j.jhazmat.2005.09.033.

Ma, Q.Y., Logan, T.J., Traina, S.J., 1995. Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. Environ. Sci. Technol. 29, 1118–1126. https://doi.org/10.1021/es00004a034.

Mahar, A., Wang, P., Li, R., Zhang, Z., 2015. Immobilization of lead and cadmium in contaminated soil using amendments: a review. Pedosphere 25, 555–568. https://doi.org/10.1016/S1002-0160(15)30036-9.

Martin, R., Dowling, K., Pearce, D., Sillitoe, J., Florentine, S., 2014. Health effects associated with inhalation of airborne arsenic arising from mining operations. Geosciences 4, 128–175. https://doi.org/10.3390/geosciences4030128.

McQueen, K., 2008. Regolith geochemistry. In: Scott, K.M., Pain, C. (Eds.), Regolith Science. Co-publisked by Springer Science Dordrecht, the Netherlands with CSIRO PUBLISHING, Collingwood, Australia, pp. 105–126.

Mileusnic, M., Mapani, B.S., Kamona, A.F., Ružičic, S., Mapaure, I., Chimwamurombe, P.M., 2014. Assessment of agricultural soil contamination by potentially toxic metals dispersed from improperly disposed tailings, Kombat mine, Namibia. J. Geochem. Explor. 144, 409–420. https://doi.org/10.1016/j.gexplo.2014.01.009.

Molina, R.M., Schaider, L.A., Donaghey, T.C., Shine, J.P., Brain, J.D., 2013. Mineralogy affects geoavailability, bioaccessibility and bioavailability of zinc. Environ. Pollut. 182, 217–224. https://doi.org/10.1016/j.envpol.2013.07.013.

Molleson, T.I., Williams, C.T., Cressey, G., Din, V.K., 1998. Radiographically opaque bones from lead-lined coffins at Christ Church, Spitalfields, London – an extreme example of diagenesis. Bull. Soc. Geol. Fr. 169, 425–432.

Morman, S.A., Plumlee, G.S., 2013. The role of airborne mineral dusts in human disease. Aeolian Res. 9, 203–212. https://doi.org/10.1016/j.aeolia.2012.12.001.

Morrison, A.L., Gulson, B.L., 2007. Preliminary findings of chemistry and bioaccessibility in base metal smelter slags. Sci. Total Environ. 382, 30–42. https://doi.org/10.1016/j.scitotenv.2007.03.034.

Nejeschlebová, L., Sracek, O., Mihaljevič, M., Ettler, V., Kříbek, B., Knésl, I., Vaněk, A., Penížek, V., Dolníček, Z., Mapani, B., 2015. Geochemistry and potential environmental impact of the mine tailings at Rosh Pinah, southern Namibia. J. Afr. Earth Sci. 105. https://doi.org/10.1016/j.jafrearsci.2015.02.005.

Newhook, R., Hirtle, H., Byrne, K., Meek, M.E., 2003. Releases from copper smelters and refineries and zinc plants in Canada: human health exposure and risk characterization. Sci. Total Environ. 301, 23–41. https://doi.org/10.1016/S0048-9697(02)00229-2.

Norvell, W.A., Lindsay, W.L., 1972. Reactions of DTPA chelates of iron, zinc, copper and manganese with soils. Soil Sci. Soc. Am. Proc. 36, 778–783. https://doi.org/10.2136/sssaj1972.03615995003600050027x.

Oliveira, S.M.B., de Moya Partiti, C.S., Enzweiler, J., 2001. Ochreous laterite: a nickel ore from Punta Gorda, Cuba. J. S. Am. Earth Sci. 14, 307–317.

Oomen, A.G., Hack, A., Minekus, M., Zeijdner, E., Cornelis, C., Verstaete, W., Van de Wiele, T., Wragg, J., Rompelberg, C.J.M., Sips, A.J.A.M., van Wijnen, J.H., 2002. Comparison of five in vitro digestion models to study the bioaccessibility of soil contaminants. Environ. Sci. Technol. 36, 3326–3334. https://doi.org/10.1021/es010204v.

Oomen, A.G., Rompelberg, C.J.M., Bruil, M.A., Dobbe, C.J.G., Pereboom, D.P.K.H., Sips, A.J.A.M., 2003a. Development of an in vitro digestion model for estimating the bioaccessibility of soil contaminants. Arch. Environ. Contam. Toxicol. 44, 281–287.

https://doi.org/10.1007/s00244-002-1278-0.
Oomen, A.G., Tolls, J., Sips, A.J.A.M., Groten, J.P., 2003b. In vitro intestinal lead uptake and transport in relation to speciation. Arch. Environ. Contam. Toxicol. 44, 116–124. https://doi.org/10.1007/s00244-002-1226-z.
Pan, Y., Fleet, M.E., 2002. Compositions of the apatite-group minerals: substitution mechanisms and controlling factors. In: Kohn, J., Rakovan, J. (Eds.), Phosphates. Geochemical, Geobiological and Materials Importance. Reviews in Mineralogy and Geochemistry 48. Mineralogical Society of America, pp. 13–49.
Plumlee, G.S., Morman, S.A., 2011. Mine wastes and human health. Elements 7, 399–404. https://doi.org/10.2113/gselements.7.6.399.
Reis, A., Patinha, C., Noack, Y., Robert, S., Dias, A.C., Ferreira da Silva, E., 2013. Assessing human exposure to potentially harmful elements through dust ingestion in the Basin Minier de Provence (France). In: Asrat, A. (Ed.), Abstracts of the 24th Colloquium of African Geology (CAG 24). Addis Ababa University Press, Addis Ababa, Ethiopia (325 pp.).
Roussel, H., Waterlot, C., Pelfrêne, A., Pruvot, C., Mazzuca, M., Douay, F., 2010. Cd, Pb and Zn oral bioaccessibility of urban soils contaminated in the past by atmospheric emissions from two lead and zinc smelters. Arch. Environ. Contam. Toxicol. 58, 945–954. https://doi.org/10.1007/s00244-009-9425-5.
Ruby, M.V., Schoof, R., Brattin, W., Goldade, M., Post, G., Hranois, M., Mosby, D.E., Casteel, S.W., Berti, W., Carpenter, M., Edwards, D., Cragin, D., Chappell, W., 1999. Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment. Environ. Sci. Technol. 33, 3697–3705. https://doi.org/10.1021/es990479z.
Salminen, R., Tarvainen, T., Demetriades, A., Duriš, M., Fordyce, F.M., Gregorauskiene, V., Kahelin, H., Kivisilla, J., Klaver, G., Klein, H., Larson, J.O., Lis, J., Locutura, J., Marsina, K., Mjartanova, H., Mouvet, C., O'Connor, P., Odor, L., Ottonello, G., Paukola, T., Plant, J.A., Reimann, C., Schermann, O., Siewers, U., Steenfelt, A., van der Sluys, J., Devivo, B., Williams, L., 1998. FOREGS Geochemical Mapping Field Manual. Geological Survey of Finland (168 pp.).
Schwertmann, U., Pfab, G., 1996. Structural vanadium and chromium in lateritic iron oxides: genetic implications. Geochim. Cosmochim. Acta 60, 4279–4283. https://doi.org/10.1016/S0016-7037(96)00259-1.
Sery, A., Manceau, A., Greaves, G.N., 1996. Chemical state of Cd in apatite phosphate ores as determined by EXAFS spectroscopy. Am. Mineral. 81, 864–873. https://doi.org/10.2138/am-1996-7-809.
Shukurov, N., Kodirov, O., Peitzsch, M., Kersten, M., Pen-Mouratov, S., Steinberger, Y., 2014. Coupling geochemical, mineralogical and microbiological approaches to assess the health of contaminated soil around the Almalyk mining and smelter complex, Uzbekistan. Sci. Total Environ. 476–477, 447–459. https://doi.org/10.1016/j.scitotenv.2014.01.031.
Tembo, B.D., Sichilongo, K., Cernak, J., 2006. Distribution of copper, lead, cadmium and zinc concentrations in soils around Kabwe town in Zambia. Chemosphere 63, 497–501. https://doi.org/10.1016/j.chemosphere.2005.08.002.
Thomas, A.N., Root, R.A., Lantz, R.C., Sáez, A.E., Chorover, J., 2018. Oxidative weathering decreases bioaccessibility of toxic metal(loid)s in PM_{10} emissions from sulphide mine tailings. GeoHealth 2, 118–138. https://doi.org/10.1002/2017GH000118.
Tordoff, G.M., Baker, A.J.M., Willis, A.J., 2000. Current approaches to the revegetation and reclamation of metalliferous mine wastes. Chemosphere 41, 219–228. https://doi.org/10.1016/S0045-6535(99)00414-2.
Trueman, C.N., Tuross, N., 2002. Trace elements in recent and fossil bone apatite. In: Kohn, J., Rakovan, J. (Eds.), Phosphates. Geochemical, Geobiological and Materials Importance. Reviews in Mineralogy and Geochemistry 48. Mineralogical Society of America, pp. 489–519.
Turner, A., Hefzi, B., 2010. Levels and bioaccessibilities of metals in dusts from an arid environment. Water Air Soil Pollut. 210, 483–491. https://doi.org/10.1007/s11270-009-0274-7.
US EPA, 1996. Proposed Plan: Residential Yard Soil, Oronogo-Duenweg Mining Belt Site, Jasper County, Missouri, USEPA, Kansas City, KS. United States Environmental Protection Agency, Washington (56 pp.).
US EPA, 2007. Estimation of Relative Bioavailability of Lead in Soil and Soil-like Materials Using In Vivo and In Vitro Methods. Office of Solid Waste and Emergency Response, US EPA, Washington, OSWER 9285 (77 pp.).
Valsami-Jones, E., Ragnarsdottir, K.V., Crewe-Read, N.O., Mann, T., Kemp, A.J., Allen, G.C., 1996. An experimental investigation of the potential of apatite as radioactive and industrial waste scavenger. In: Bottrells, S.H. (Ed.), Fourth Intl Symp Geochemistry of the Earth's Surface. Yorkshire, UK. University of Leeds, Leeds, UK, pp. 686–689.
Wang, L., Ji, B., Hu, Y., Liu, R., Sun, W., 2017. A review on in situ phytoremediation of mine tailings. Chemosphere 184, 594–600. https://doi.org/10.1016/j.chemosphere.2017.06.025.
WHO, 2007. Blood Lead Levels in Children. World Health Organization Regional Office for Europe, European Environment and Health Information System (Fact Sheet No. 4.5).
Winer, B.J., Brown, D.R., Michels, K.M., 1991. Statistical Principals in Experimental Design, 3rd ed. McGraw-Hill, New York, pp. 298.
Wragg, J., Cave, M.R., 2003. Factors Controlling the Bioaccesibility of Selected Metals and Metalloids in Soil: A Critical Review. P5-062/TR/01, British Geological Survey (35 pp.).
Wragg, J., Cave, M., Basta, N., Brandon, E., Casteel, S., Denys, S., Gron, C., Oomen, A., Reimer, K., Tack, K., Van de Wiele, T., 2011. An inter-laboratory trial of the unified BARGE bioaccessibility method for arsenic, cadmium and lead in soil. Sci. Total Environ. 409, 4016–4030. https://doi.org/10.1016/j.scitotenv.2011.05.019.
Xu, Y., Fang, Z., Tsang, E.P., 2016. In situ immobilization of cadmium in soil by stabilized biochar-supported iron phosphate nanoparticles. Environ. Sci. Pollut. Res. 23, 19164–19172. https://doi.org/10.1007/s11356-016-7117-z.
Yabe, J., Nakayama, S.M.M., Ikenaka, Y., Yohannes, Y.B., Bortey-Sam, N., Orostlany, B., Muzandu, K., Choongo, K., Kabalo, A.N., Ntapisha, J., Mweene, A., Umemura, T., Ishizuka, M., 2015. Lead poisoning in children from townships in the vicinity of a lead-zinc mine in Kabwe, Zambia. Chemosphere 119, 941–947. https://doi.org/10.1016/j.chemosphere.2014.09.028.
Yabe, J., Nakayama, S.M.M., Ikenaka, Y., Yohannes, Y.B., Bortey-Sam, N., Kabalo, A.N., Ntapisha, J., Mizukawa, H., Umemura, T., Ishizuka, M., 2018. Lead and cadmium excretion in feces and urine of children from polluted townships near a lead-zinc mine in Kabwe, Zambia. Chemosphere 202, 48–55. https://doi.org/10.1016/j.chemosphere.2018.03.079.
Yruela, I., 2009. Copper in plants: acquisition, transport and interactions. Funct. Plant Biol. 12, 409–430. https://doi.org/10.1071/FP08288.
ZCCM-IH, 1996. Rehabilitation and Decommissioning Plan for Kabwe, Zambia. MS., Zambia Copper and Cobalt Mining-Investment Holding Plc, Kitwe (72 pp.).
ZCCM-IH, 2002. Environmental Assessment of the Copperbelt and Kabwe Area. MS., Zambia Copper and Cobalt Mining-Investment Holding Plc, Nkana, Zambia (126 pp.).
Zota, A.R., Willis, R., Jim, R., Norris, G.A., Shine, J.P., Duvall, R.M., Schaider, L.A., Spenger, J.D., 2009. Impact of mine waste on airborne respirable particulates in northeastern Oklahoma, United States. J. Air Waste Manage. Assoc. 59, 1347–1357. https://doi.org/10.3155/1047-3289.59.11.1347.