

# Dust from Zambian smelters: mineralogy and contaminant bioaccessibility

Vojtěch Ettler · Martina Vítková · Martin Mihaljevič ·  
Ondřej Šebek · Mariana Klementová · František Veselovský ·  
Pavel Vybíral · Bohdan Kříbek

Received: 26 September 2013 / Accepted: 19 February 2014 / Published online: 12 April 2014  
© Springer Science+Business Media Dordrecht 2014

**Abstract** Metal smelting is often responsible for local contamination of environmental compartments. Dust materials escaping from the smelting facilities not only settle in the soil, but can also have direct effects on populations living close to these operations (by ingestion or inhalation). In this particular study, we investigate dusts from Cu–Co metal smelters in the Zambian Copperbelt, using a combination of mineralogical techniques (XRD, SEM/EDS, and TEM/EDS), in order to understand the solid speciation of the contaminants, as well as their bioaccessibility using *in vitro* tests in simulated gastric and lung fluids

to assess the exposure risk for humans. The leaching of metals was mainly dependent on the contaminant mineralogy. Based on our results, a potential risk can be recognized, particularly from ingestion of the dust, with bioaccessible fractions ranging from 21 to 89 % of the total contaminant concentrations. In contrast, relatively low bioaccessible fractions were observed for simulated lung fluid extracts, with values ranging from 0.01 % (Pb) up to 16.5 % (Co) of total contaminant concentrations. Daily intakes via oral exposure, calculated for an adult (70 kg, ingestion rate 50 mg dust per day), slightly exceeded the tolerable daily intake limits for Co (1.66× for fly ash and 1.19× for slag dust) and occasionally also for Pb (1.49×, fly ash) and As (1.64×, electrostatic precipitator dust). Cobalt

**Electronic supplementary material** The online version of this article (doi:10.1007/s10653-014-9609-4) contains supplementary material, which is available to authorized users.

V. Ettler (✉) · M. Vítková · M. Mihaljevič  
Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague, Albertov 6, 128 43 Prague 2, Czech Republic  
e-mail: ettler@natur.cuni.cz

*Present Address:*

M. Vítková  
Department of Environmental Geosciences, Faculty of Environmental Sciences, Czech University of Life Sciences Prague, Kamýcká 129, 165 21 Prague 6, Czech Republic

O. Šebek  
Laboratories of the Geological Institutes, Faculty of Science, Charles University in Prague, Albertov 6, 128 43 Prague 2, Czech Republic

M. Klementová  
Institute of Inorganic Chemistry of the AS CR, v.v.i.,  
250 68 Husinec-Řež, Czech Republic

F. Veselovský · B. Kříbek  
Czech Geological Survey, Geologická 6, 152 00 Prague 5, Czech Republic

P. Vybíral  
Department of Environmental Engineering, Faculty of Mechanical Engineering, Czech Technical University, Technická 4, 166 07 Prague 6, Czech Republic

has been suggested as the most important pollutant, and the direct pathways of the population's exposures to dust particles in the industrial parts of the Zambian Copperbelt should be further studied in interdisciplinary investigations.

**Keywords** Dust · Metal smelting · Copper · Cobalt · Solid speciation · Bioaccessibility · Zambian Copperbelt

## Introduction

Mining and smelting activities are responsible for the extensive generation of dust particles, which can have a negative effect on various compartments of the environment, especially in dry and semi-dry areas (Castillo et al. 2013; Csavina et al. 2012; Křibek et al. 2010). Soils are mainly influenced by the dust emissions from these operations (Ettler et al. 2011, 2014; Křibek et al. 2010). Wind dispersion of the soil and industrial dusts can have direct effects on the population (through dust ingestion or inhalation, hand-to-mouth behaviours) (Ettler et al. 2012; Pelfrène et al. 2011) or effects via the food chain (due to consumption of foods grown in the contaminated soils, consumption of improperly washed vegetables) (e.g., Schreck et al. 2012).

The approaches and models often used in the estimation of human exposures to toxic compounds from various environmental compartments (soils, dust, water, food) can be affected by considerable uncertainties (Hursthouse and Kowalczyk 2009). However, for the last two decades, efforts have been made to develop numerous *in vitro* extraction tests designed to simulate the dissolution of geomaterials (dusts, soils) or industrial dusts in human body fluids in order to (1) estimate the “bioaccessible” fraction of these contaminants and (2) validate the extraction tests using *in vivo* approaches (Oomen et al. 2002; Ruby et al. 1993, 1996). These developments have resulted in several standardized tests, such as the relative bioaccessibility leaching procedure (RBALP), suggested as the most reliable method in a recent review by Deshommes et al. (2012), due to previous validation for Pb and As by *in vivo* tests on piglets. This method has also been adopted by the US Environmental Protection Agency (US EPA 2007). More recently, BARGE (the BioAccessability Research

Group of Europe) validated and published a new *in vitro* protocol to simulate conditions in the gastrointestinal tract and helps to understand the potentially bioaccessible fraction of metals/metalloids from polluted soils (Denys et al. 2012; Wragg et al. 2011). This method entitled UBM (Unified BARGE Method) has been frequently applied, primarily to contaminated soils (e.g., Gbafa et al. 2011; Pelfrène et al. 2011) but also to dust materials (Okorie et al. 2012; Reis et al. 2014).

Contaminant bioaccessibility and health studies related to mining-/smelter-polluted sites in African countries are still rare. Křibek et al. (2010) investigated dust materials collected using portable filters in the mining/smelting districts of the Zambian Copperbelt Province and found that numerous particles are <10 µm (i.e., easily respirable) and are rich in metals. High exposures to metal contaminants have also been reported from another site in the Copperbelt mining and smelting district, located in the Democratic Republic of Congo, where particularly high levels of Co were detected in urine (Banza et al. 2009). A few studies in Africa have already focused on the risks related to general geophagy (i.e., intentional soil consumption, commonly observed in many African cultures) (Kutalek et al. 2010; Momoh et al. 2013), as well as unintentional soil ingestion (e.g., via hand-to-mouth behaviours) (Ettler et al. 2012). These papers demonstrated that the intake of high levels of contaminants can be expected. Despite substantial variations and the lack of relevant datasets, it is generally estimated that <100 mg of soil is ingested daily in developed countries (e.g., in Europe) (Swartjes 2002; Bierkens et al. 2011). For calculation of the exposure to chemicals via dust, generally a conservative but realistic estimate of dust ingestion 100 mg/day for children and 50 mg/day for adults is used (Oomen et al. 2008). However, we suggest that the unintentional ingestion rates of dust might be significantly higher in some locations (e.g., in African countries). Whereas National Ambient Air Quality Standards (NAAQS) of USEPA state that the 24-h limit value for PM<sub>10</sub> particle pollution is 150 µg/m<sup>3</sup> (US EPA 2011a), Ojelede et al. (2012) reported that the concentration of aerosols near a mine tailing site in South Africa reached 2,160 µg/m<sup>3</sup> at wind speeds exceeding 7 m/s.

Smelter emissions as well as wind-blown dust from mine tailings and smelter slag dumps are generally the

main point sources of soil pollution in the Zambian Copperbelt. Following in the footsteps of previous geochemical investigations on waste materials from Cu–Co smelters (Vítková et al. 2010, 2011a, b, 2013) and smelter-affected soils in this area (Ettler et al. 2011, 2012, 2014; Kříbek et al. 2010), the aim of this study was to determine the potential bioaccessibility of inorganic contaminants (metals, As) and to estimate possible occupational exposure related to the ingestion/inhalation of three representative smelter dust samples by comparison with toxicological reference values.

## Materials and methods

### Smelter dusts

We collected three types of samples inside and from the near vicinity of Cu–Co smelters in the Zambian Copperbelt: (1) slag dust generated by slag crushers, sampled at the slag dust deposit site (slag crushing prior to further re-smelting and metal recovery in the Chambishi smelter); (2) fly ash from the Co smelter in Chambishi, sampled at the level of flue gas-cleaning facilities (filters); (3) dust from the Cu smelter in Mufulira, sampled at the electrostatic precipitator (denoted further as ESP dust). Further details on dust sampling are given in Vítková et al. (2010, 2011a, 2013).

The original dust samples were subsequently used for the bioaccessibility testing in simulated gastric fluid (SGF). The nominal <10 µm fraction of the dusts was separated using a BAHCO centrifugal separator (BAHCO AB, Sweden) to obtain only respirable particles (i.e., those that could potentially enter lung compartments), which were subsequently used for bioaccessibility testing in simulated lung fluid (SLF). The granulometry of the original and separated dust samples was characterized using a Sympatec particle size analyser equipped with a HELOS laser diffraction sensor and ultrasound sample treatment (Sympatec GmbH, Germany).

An aliquot of each dust sample was finely ground in an agate mortar (Fritsch Pulverisette, Germany) and used for the subsequent bulk chemical analysis. Heavy fractions of the original samples were obtained after separation in 1,1,2,2-tetrabromethane (density of 2.96 g/cm<sup>3</sup>) or in Clerici solution (Tl organic salts

with a density of 4.05 g/cm<sup>3</sup>). Both the original samples and the heavy mineral fractions were subsequently used for mineralogical investigations.

### Analytical determination

The bulk chemical composition of the samples was determined after dissolution in mineral acids (HF–HClO<sub>4</sub>–HNO<sub>3</sub>) and/or sintering, according to Ettler et al. (2009). The major elements were determined using gravimetric and volumetric analyses as well as photometry. The concentrations of the trace elements were determined using either inductively coupled plasma optical emission spectrometry (ICP-OES, ThermoScientific iCAP 6500 radial, UK) or inductively coupled plasma mass spectrometry (ICP-MS, ThermoScientific, Xseries<sup>II</sup>, UK). Total carbon (C<sub>tot</sub>) and total sulphur (S<sub>tot</sub>) were determined on Eltra CS 500 and Eltra CS 530 elemental analyzers (Eltra, Germany).

The bulk samples, as well as the heavy fractions of the samples, were investigated for their mineralogical compositions. The X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert Pro diffractometer (PANalytical B.V., the Netherlands). The conditions were: Cu–K $\alpha$  radiation, 40 kV and 30 mA, 2 $\theta$  range 5–80°, step 0.02, counting time of 300 s, using an X'Celerator detector. The qualitative analysis of the XRD patterns was performed using PANalytical X'Pert HighScore software (version 1.0d) and an ICDD PDF-2 database (ICDD 2003). The dust samples were prepared as polished sections and studied using a TESCAN VEGA scanning electron microscope (SEM; TESCAN Ltd., Czech Republic) equipped with an Oxford Link X-Max 50 energy dispersive X-ray spectrometer (EDS). The spectrometer was calibrated against a SPI set of standards (SPI supplies, USA) for quantitative microanalyses. The TEM investigations of the dust samples were carried out on a JEOL JEM 3010 microscope (JEOL Ltd., Japan), operated at 300 kV (LaB<sub>6</sub> cathode, point resolution 1.7 Å), with an attached Oxford Instruments EDS (Oxford Instruments plc., UK). The images were recorded on a CCD camera with a resolution of 1,024 × 1,024 pixels, using a Digital Micrograph software package (Gatan Inc., UK). The EDS analyses were acquired and treated with an INCA software package (Oxford Instruments plc., UK). Selected area electron diffraction patterns (SAED)

were evaluated using a Process Diffraction software package (Lábár 2005).

### Bioaccessibility testing

The oral bioaccessibility test was performed on the original dust fraction according to the US EPA's (2007) protocol, mainly due to its simplicity and reliability with *in vivo* tests (Deshommes et al. 2012), in order to investigate the amounts of contaminants that can be extracted in simulated gastric fluid (SGF). The extraction represents the “worst-case” scenario, and the simulated conditions correspond to a fasting human being. The extraction fluid contained 0.4 M glycine (30.028 g glycine dissolved in 800 ml of deionised water), adjusted to pH  $1.5 \pm 0.05$  by reagent grade HCl (Merck, Germany), finalised by diluting to 1 l with deionised water (MilliQ+, Millipore Academic, USA) and pH verification. A liquid-to-solid (*L/S*) ratio of 100 was used for the extraction. A mass corresponding to 0.1 g of the original dust sample was placed in PP centrifuge tubes (P-lab, Czech Republic), 10 ml of extraction fluid was then added, and the mixture was agitated occasionally for 2 h at 37 °C. All extractions were performed in triplicate with procedural blanks.

Numerous protocols have been suggested for estimates of lung bioaccessibility with variable solutions (e.g., so-called Gamble's salt solution with pH 7.4, whose exact composition changes substantially in the literature), with the *L/S* ratio varying from 10 to 50 000, and the extraction time varying from 5 min to 26 days (Berlinger et al. 2008; Caboche et al. 2011; Drysdale et al. 2012; Twining et al. 2005 and references therein). The extraction in simulated lung fluid (SLF) was performed according to the experimental fluid of Twining et al. (2005), with a salt solution having the pH adjusted to  $7.4 \pm 0.2$ , which roughly corresponds to Gamble's solution, simulating pulmonary surfactants. The exact composition of the SLF is reported in Table S1 in the Supplementary Material. The  $<10 \mu\text{m}$  fractions of the dust samples were used for the extraction. Samples were placed in PP centrifuge tubes (P-lab, Czech Republic), mixed with fresh SLF at a *L/S* ratio of 100 (0.1 g dust to 10 ml of extraction fluid), and then maintained at 37 °C with occasional agitation. Caboche et al. (2011) recently showed that *L/S* ratios of  $>50$  are suitable for bioaccessibility testing, so we opted for an *L/S* of 100 to be consistent with the oral bioaccessibility

test, despite the fact that Twining et al.'s protocol used an *L/S* of 20. Berlinger et al. (2008) and Caboche et al. (2011) reported that industrial aerosols and dust reference materials leached in simulated lung fluid attained equilibrium after 24 h. Assuming that the dissolution reactions will be relatively quick, due to the fine-grained characteristic of the studied materials, and in order to understand the initial kinetics of the dust digestion in SLF, each sample was subjected to 2, 6, 12, and 24 h of leaching and run in triplicate with procedural blanks. During the experiment, the pH was adjusted using dilute HCl or NaOH if necessary (Caboche et al. 2011).

After the extraction procedures, each extract was filtered through a  $0.45\text{-}\mu\text{m}$  nitrocellulose membrane filter (Millipore<sup>®</sup>, USA), diluted and analysed for As, Co, Cu, Pb, and Zn (these being the main contaminants) by ICP-MS. A CertiPUR<sup>®</sup> reference material was used for quality control of the measurements, and recoveries were always better than 10 % relative standard deviation (RSD) with respect to the certified values. Subsequently, the bioaccessible concentrations of the metals and As were expressed in mg/kg and converted to the % amount of the total contents (i.e., the bioaccessible fraction, BAF). The solid residue was dried at room temperature and analysed using XRD to determine possible changes in the mineralogical composition during the extraction.

### Exposure assessment

The oral exposure was calculated using bioaccessible concentrations and the dust ingestion rate for an adult corresponding to 50 mg/day. Adults were suggested to be the most exposed target in and near the smelter facilities, despite the fact that generally children, who have much higher ingestion rates, are used for similar calculations in other studies (e.g., Reis et al. 2014). The obtained daily intakes of individual metals and As were then compared with the tolerable daily intake (TDI) limits taken from Baars et al. (2001) and calculated for an adult weighing 70 kg. The hazard quotient for oral ingestion ( $HQ_{\text{ingestion}}$ ) was subsequently calculated as the ratio of the potential exposure of each contaminant (daily intake) and the level at which no adverse effects are expected as a result of exposure (TDI), suggesting that if  $HQ > 1$ , adverse health effects are possible (US EPA 2011b). It is important to note that our calculation corresponds to an estimate of occupational oral exposure of workers

and people working in the vicinity of the smelters. However, we are aware that the dust ingestion rate of 50 mg/day is highly conservative and can be much higher in the dusty environments of smelter areas.

The inhalation exposure is generally calculated using the concentrations of the individual contaminants in the aerosols or total suspended particles in the air. Unfortunately, no in situ measurements of total aerosols (particulate matter <10 µm; PM<sub>10</sub>) were carried out in our study. Relatively few studies reported PM concentrations in and near smelters, but all these studies indicated the highest levels in the facility itself, with a decreasing trend as a function of distance and prevailing wind direction (Csavina et al. 2012; Nikolić et al. 2010; Uzu et al. 2011). For example, Nikolić et al. (2010) reported that PM<sub>10</sub> concentrations in the urban air near a copper smelter in Serbia were generally below the European Union limit of 50 µg/m<sup>3</sup> (EC 1999), but occasionally rose up to 78 µg/m<sup>3</sup>. Recently, Uzu et al. (2011) reported that the total PM concentrations in the ambient air of various workplaces in a Pb smelter varied in the range of 70–700 µg/m<sup>3</sup>. Moreover, the role of storage facilities (mine tailing, smelter dust and slags) in the dust dispersion cannot be neglected; Ojelede et al. (2012) recently demonstrated that, during windy periods, PM<sub>10</sub> can reach 2,160 µg/m<sup>3</sup> near mine tailing storage facilities in South Africa. Thus, for our exposure estimates, we used an ad hoc PM<sub>10</sub> concentration 50 µg/m<sup>3</sup> (as a conservative value) and assumed that PM<sub>10</sub> can be composed of <10 µm dust fractions investigated in this study. The contaminant concentrations for individual dusts expressed in µg/m<sup>3</sup> were calculated and compared with the limits for tolerable concentration in the air (TCA) taken from Baars et al. (2001). As a result, the hazard quotient related to inhalation (HQ<sub>inhalation</sub>) was calculated as the ratio of the calculated contaminant concentration in the air and TCA to determine whether there was a risk of adverse health effects.

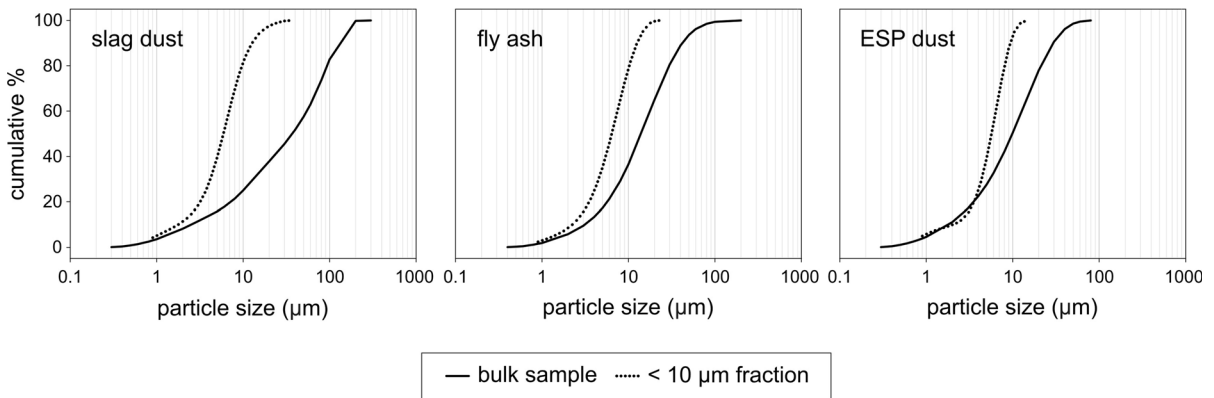
## Results

### Physico-chemical properties and mineralogical compositions of the dust samples

Granulometric measurements of the original dusts (Fig. 1; Table S2 in the Supplementary Material)

indicated that slag dust contained a larger fraction of coarser particles than fly ash and ESP dust. The proportion of the <50 µm fraction was as follows: slag dust, 57.5 %; fly ash, 93.6 %; and ESP dust, 98.6 %. Separation to the nominal <10 µm fraction, which was subsequently used for extractions in SLF, led to a significant shift towards desired particles smaller than 10 µm. However, the separation was not fully effective because some amount of the fractions in the range 10–30 µm was still present, namely slag dust, 18.5 %; fly ash, 21 %; and ESP dust, 6.5 % (Fig. 1; Table S2). The bulk chemical compositions (Table 1) indicated that practically little or no changes were observed in the major elements between the original dusts and the <10 µm fraction (except a significant C<sub>tot</sub> increase for slag dust and decrease for fly ash, probably related to the different size of possible carbonaceous fragments from the smelter furnace feed, e.g., coal residues and soot particles). In contrast, an increase in contaminant concentration was generally observed in the separated <10 µm fraction, indicating that metals/metalloids are predominantly concentrated in the finest dust fractions. The only exception is Co, which occurred in slightly lower concentrations in the <10 µm fraction than in the original dust. This phenomenon can be related to its partial binding in the silicate phases (e.g., olivine and glass, see Vítková et al. 2010), which can predominantly form larger fragments.

The three dust samples have very different chemical compositions (Table 1). Whereas slag dust and fly ash are mainly composed of Si, Fe, Ca, Al, and Mg, ESP dust is composed of Fe, S, and Si and contains high levels of Cu (up to 273 g/kg). The differences in the chemical composition also reflect the differences in mineralogy as revealed by a combination of XRD and microscopic techniques (Table 2; XRD patterns are reported in Figures S1–S3 in the Supplementary Material). Representative SEM and TEM images with corresponding EDS analyses and SAED patterns are depicted in Fig. 2. As the slag dust and fly ash were predominantly Si-rich materials, they are composed of high-temperature Ca–Fe aluminosilicates and amorphous glass associated with oxides (spinel series) (Table 2). The main metal- and metalloid-bearing species were oxides (Cu spinel, CuFe<sub>2</sub>O<sub>4</sub>), various sulphides (ZnS, Cu(Fe,Co)S, Co<sub>9</sub>S<sub>8</sub>), metallic copper, and to a lesser extent complex intermetallic phases and alloys (Table 2; Fig. 2a, b). Unfortunately, some of sulphide particles smaller than 200 nm and observed



**Fig. 1** Granulometry of the bulk dust samples and <10  $\mu\text{m}$  fractions

**Table 1** Bulk chemical composition of the dust samples

Element	Units	Original dust			<10 $\mu\text{m}$ fraction		
		Slag dust	Fly ash	ESP dust	Slag dust	Fly ash	ESP dust
Si	g/kg	191 <sup>a</sup>	108	42.6	136	93.7	31.8
Ti	g/kg	2.69	1.50	0.47	2.35	0.68	<0.005
Al	g/kg	39.3	25.7	9.72	50.7	22.9	10.3
Fe	g/kg	178	86.5	194	165	76.9	148
Mn	g/kg	0.77	1.50	0.24	0.82	1.47	0.31
Mg	g/kg	14.9	43.9	4.85	16.7	47.1	5.79
Ca	g/kg	65.4	79.6	10.8	65.8	71.8	11.6
Na	g/kg	0.91	1.75	2.07	0.81	2.00	2.90
K	g/kg	18.6	39.1	6.65	18.0	33.8	8.79
P	g/kg	1.22	1.40	0.24	0.94	1.60	0.46
C <sub>tot</sub>	g/kg	15.8	111	1.45	102	39.4	5.50
S <sub>tot</sub>	g/kg	10.4	35.5	85.0	22.3	26.5	78.8
As	mg/kg	65.0	523	2,790	257	233	5,380
Ba	mg/kg	659	327	113	645	256	134
Bi	mg/kg	44.6	836	15,000	353	895	17,500
Cd	mg/kg	<1.10	20.3	195	10.7	13.7	278
Co	mg/kg	8,940	4,060	992	8,380	3,770	963
Cr	mg/kg	487	227	52.1	1,296	430	241
Cu	mg/kg	32,200	41,000	273,000	51,700	50,500	232,000
Mo	mg/kg	40.9	48.5	1,150	137	51.3	2,320
Ni	mg/kg	69.7	39.0	576	236	68.9	638
Pb	mg/kg	144	8,420	2,160	323	12,000	4,870
Sr	mg/kg	334	332	56.6	487	296	69.5
Zn	mg/kg	279	21,500	2,140	556	37,800	4,590

<sup>a</sup> Mean values ( $n = 2$ )

by TEM were mixed Cu–Zn sulphides according to EDS analyses, yielding relatively reasonable SAED patterns, which could not, however, be attributed to

any of the phases in the diffraction database (Fig. 2b). This observation confirms the fact that during smelting of ores, phases unlike natural ones often can be formed

**Table 2** Phases occurring in the dust samples<sup>a</sup> as determined using XRD, SEM/EDS, and/or TEM/EDS

Phase	Formula	Original sample <sup>b</sup>	<10 μm fraction	SGF residue	SLF residue
<b>Slag dust</b>					
Diopside-hedenbergite	Ca(Fe,Mg)Si <sub>2</sub> O <sub>6</sub>	***	***	***	***
Fayalite	Fe <sub>2</sub> SiO <sub>4</sub>	**	–	**	–
Quartz	SiO <sub>2</sub>	***	**	***	**
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	**	***	–	–
<i>Magnetite</i>	<i>Fe<sub>3</sub>O<sub>4</sub></i>	**	–	–	–
Haematite	Fe <sub>2</sub> O <sub>3</sub>	–	**	**	**
Copper iron oxide	CuFe <sub>2</sub> O <sub>4</sub>	**	**	**	**
<i>Pyrite</i>	<i>FeS<sub>2</sub></i>	*	–	–	–
<i>Cu sulphides<sup>d</sup></i>	<i>Cu(Fe,Co)S</i>	*	–	–	–
<i>Co-pentlandite</i>	<i>Co<sub>9</sub>S<sub>8</sub></i>	*	–	–	–
<i>Copper</i>	<i>Cu</i>	*	–	–	–
Silicate glass		**	**	**	**
<b>Fly ash</b>					
Augite	Ca(Fe,Mg)Si <sub>2</sub> O <sub>6</sub>	***	***	***	***
Leucite	KAlSi <sub>2</sub> O <sub>6</sub>	*	–	**	–
Quartz	SiO <sub>2</sub>	***	**	***	**
Calcite	CaCO <sub>3</sub>	***	***	–	***
<i>Magnetite</i>	<i>Fe<sub>3</sub>O<sub>4</sub></i>	**	–	–	–
<i>Rutile</i>	<i>TiO<sub>2</sub></i>	*	–	–	–
Zinc sulphide <sup>c</sup>	ZnS	**	**	–	**
<i>Cu sulphides<sup>d</sup></i>	<i>Cu(Fe,Co)S</i>	*	–	–	–
<i>Copper</i>	<i>Cu</i>	*	–	–	–
<i>Alloys</i>	<i>Fe–Cu–Co</i>	*	–	–	–
Silicate glass		***	***	***	***
<b>ESP dust</b>					
Quartz	SiO <sub>2</sub>	*	*	***	*
Chalcanthite	CuSO <sub>4</sub> ·5H <sub>2</sub> O	***	***	–	–
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	**	**	–	–
Antlerite	Cu <sub>3</sub> (SO <sub>4</sub> )(OH) <sub>4</sub>	–	–	–	**
<i>Calcite</i>	<i>CaCO<sub>3</sub></i>	*	–	–	–
<i>Magnetite</i>	<i>Fe<sub>3</sub>O<sub>4</sub></i>	***	***	***	***
<i>Copper iron oxide</i>	<i>CuFe<sub>2</sub>O<sub>4</sub></i>	**	–	–	–
Delafossite	CuFeO <sub>2</sub>	***	***	***	***
<i>Cu sulphides<sup>d</sup></i>	<i>Cu(Fe)S</i>	*	–	–	–
<i>Alloys</i>	<i>Fe–Cu–Co–(As)</i>	*	–	–	–
Silicate glass		***	***	***	***

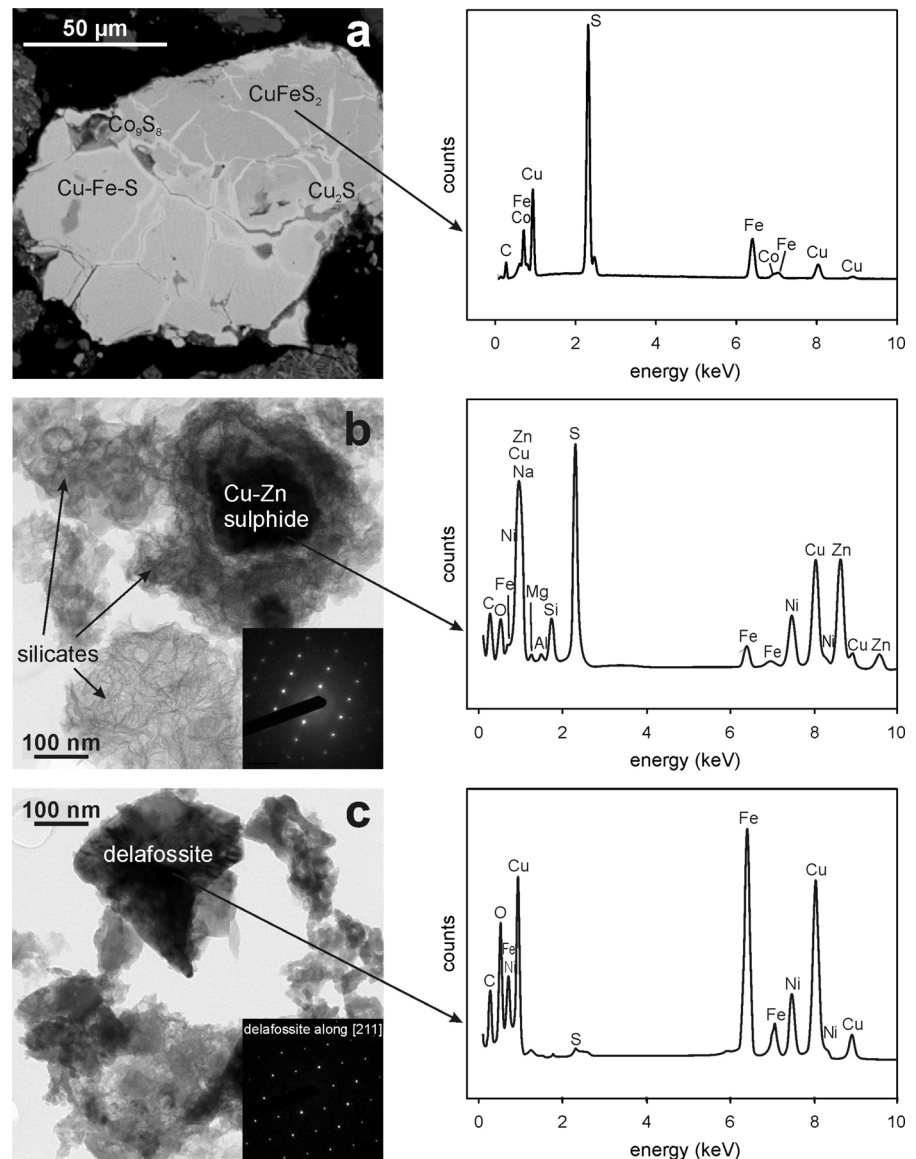
<sup>a</sup> Relative abundance: \*\*\* dominant or common phases, \*\* minor phases, \* trace phases, – not determined

<sup>b</sup> Phases determined by SEM/EDS or TEM/EDS are given in italics

<sup>c</sup> ZnS suggested by XRD, possible substitution with Cu suggested by SEM/EDS and TEM/EDS

<sup>d</sup> Non-stoichiometric compounds of various compositions; traces of chalcocite Cu<sub>2</sub>S, chalcopyrite CuFeS<sub>2</sub>, bornite Cu<sub>5</sub>FeS<sub>4</sub> or digenite Cu<sub>9</sub>S<sub>5</sub> were detected by SEM/EDS or TEM/EDS

**Fig. 2** SEM (a) and TEM (b, c) images of selected phases identified in the dust samples with corresponding EDS spectra and/or SAED. **a** Particle of slag dust; **b** fly ash; **c** ESP dust. Annotation: Cu–Fe–S—non-stoichiometric Cu–Fe sulphide,  $\text{Co}_9\text{S}_8$ —Co-sulphide corresponding to  $(\text{Co,Fe,Ni})_9\text{S}_8$ ,  $\text{CuFeS}_2$ —chalcocypite,  $\text{Cu}_2\text{S}$ —chalcocite



with a stoichiometry indicating non-equilibrium conditions of formation (e.g., quenching of the melt) (Vítková et al. 2010). In contrast to other dust samples, the ESP dust was predominantly composed of sulphates (chalcocypite,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ; and minor gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and oxides (magnetite,  $\text{Fe}_3\text{O}_4$ ; Cu spinel,  $\text{CuFe}_2\text{O}_4$ ; delafossite,  $\text{CuFeO}_2$ ) associated with amorphous silicate glass (Table 2; Fig. 2c). The proportion of Cu-sulphides and complex intermetallic compounds and alloys in the ESP dust was lower than for the other dust samples (Table 2).

X-ray diffraction revealed minor changes between the original dust samples and the corresponding separated fractions (nominally  $<10 \mu\text{m}$ ) (Table 2). In the slag dust, olivine disappeared from the  $<10 \mu\text{m}$  fraction and was probably predominantly bound in the larger slag fragments; in contrast, the proportion of gypsum increased in the  $<10 \mu\text{m}$  fraction (Table 2; Figure S1). In comparison with the original fly ash, leucite was not detected and quartz was present in smaller amounts in the  $<10 \mu\text{m}$  fraction (Table 2; Figure S2). In contrast, XRD data indicated that



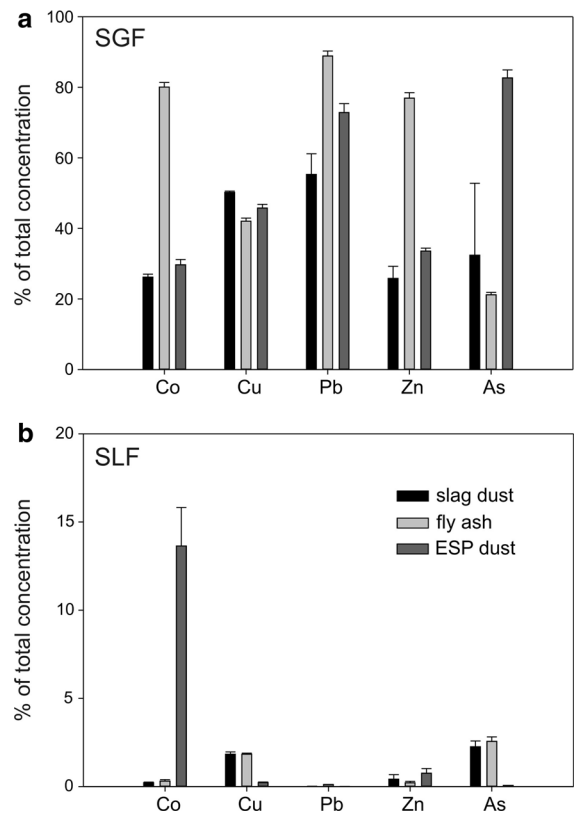
mineralogical compositions of the original ESP dust and <10 µm fraction were identical (Table 2; Figure S3).

Contaminant extractability in simulated body fluids and solubility controls

The bioaccessible concentrations of contaminants in SGF varied widely for the dust samples studied: Co (294–3,250 mg/kg), Cu (16.2–125 g/kg), Pb (80–7,490 mg/kg), Zn (72–16,500 mg/kg), and As (21–2,300 mg/kg) (Table S3). These values indicated that the bioaccessibilities in SGF, expressed as % of the total element concentration, were as follows: Co (26–80 %), Cu (42–50 %), Pb (55–89 %), Zn (26–77 %), and As (21–83 %) (Fig. 3a).

The XRD investigation of dust samples after the extraction in SGF indicated that, for slag dust, only gypsum was completely dissolved and the overall mineralogical composition remained the same (unfortunately, changes in the proportions of the trace metallic phases and sulphides could not be detected by XRD) (Table 2; Figure S1). During the fly ash extraction in SGF, calcite and ZnS completely dissolved, whereas silicates were still present in the same proportion as in the original sample (Table 2; Figure S2). The largest changes in mineralogical composition during extraction in SGF occurred for ESP dust: chalcantite and gypsum completely dissolved and silicates and oxides remained in the same proportion (except quartz which, after complete dissolution of the dominant sulphates, also became a major phase) (Table 2; Figure S3).

The bioaccessible concentrations obtained after leaching in SLF were significantly lower than that for SGF: Co (8.29–159 mg/kg), Cu (428–1,017 mg/kg), Pb (0.03–13.7 mg/kg), Zn (0.76–137), and As (2.91–6.76). The bioaccessible fractions (BAF, in % of total concentrations) were thus significantly lower than that for SGF: Co (0.17–16.5 %), Cu (0.18–1.97 %), Pb (0.01–0.11 %), Zn (0.14–1.15 %), and As (0.05–2.88 %) (Fig. 3b). Similar to the SGF, the release of individual contaminants in SLF was largely variable between samples, in relationship with their total concentration and solid speciation. The time-dependent bioaccessible concentration patterns for individual contaminants indicate that their release was relatively rapid and a steady state was generally attained within 6 h (Fig. 4). A slight decrease in the



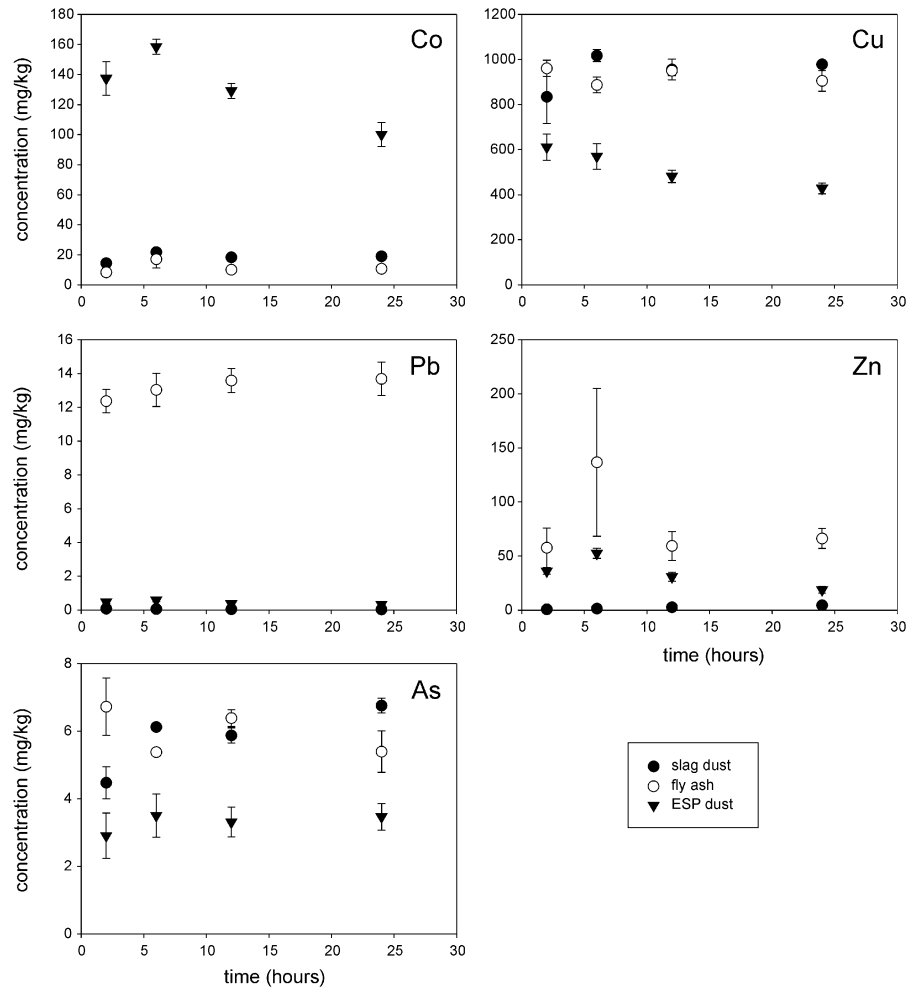
**Fig. 3** Bioaccessible fraction of metals and As in **a** simulated gastric fluid (SGF) and **b** simulated lung fluid (SLF) for the smelter dust samples (note different scales on the y-axis)

bioaccessible concentration after 6 h was observed for Co and Cu leaching from the ESP dust, and this could result from possible solubility controls by the precipitation of newly formed phases. Indeed, mineralogical investigation of dust after the extraction in SLF confirmed that dissolution of chalcantite and gypsum occurred and newly formed antlerite (Cu<sub>3</sub>(SO<sub>4</sub>)(OH)<sub>4</sub>) precipitated in the ESP dust (Table 2; Figure S3). Whereas no changes in the mineralogical composition were detected for fly ash, gypsum completely disappeared from the slag dust after the SLF leaching (Table 2; Figures S1 and S2).

Exposure estimations

Assuming daily intake of 50 mg/day (which is probably highly underestimated for dusty environments in and near the metal smelters in African countries), the calculated oral exposure via individual dusts and comparisons with reference doses (TDI) for a 70-kg-

**Fig. 4** Time-dependent patterns of bioaccessible concentrations of metals and As for the <10  $\mu\text{m}$  fraction of the smelter dust samples as obtained by extraction in simulated lung fluid (SLF)



**Table 3** Daily intake of metals and As in  $\mu\text{g}/\text{day}$  and hazard quotients for oral ingestion exposure ( $\text{HQ}_{\text{ingestion}}$ ) calculated in comparison with TDI

Code	Slag dust		Fly ash		ESP dust		TDI <sup>a</sup> ( $\mu\text{g}/\text{day}$ )
	Intake ( $\mu\text{g}/\text{day}$ )	$\text{HQ}_{\text{ingestion}}$	Intake ( $\mu\text{g}/\text{day}$ )	$\text{HQ}_{\text{ingestion}}$	Intake ( $\mu\text{g}/\text{day}$ )	$\text{HQ}_{\text{ingestion}}$	
Co	<b>117 <math>\pm</math> 4<sup>b</sup></b>	<b>1.19</b>	<b>163 <math>\pm</math> 3</b>	<b>1.66</b>	14.7 $\pm$ 0.7	0.15	98
Cu	810 $\pm$ 5	0.08	862 $\pm$ 18	0.09	6,240 $\pm$ 143	0.64	9,800
Pb	3.99 $\pm$ 0.42	0.02	<b>374 <math>\pm</math> 6</b>	<b>1.49</b>	78 $\pm$ 3	0.31	252
Zn	3.60 $\pm$ 0.48	0.00	826 $\pm$ 17	0.02	36 $\pm$ 1	0.00	35,000
As	1.05 $\pm$ 0.66	0.02	5.54 $\pm$ 0.17	0.08	<b>115 <math>\pm</math> 3</b>	<b>1.64</b>	70

Values calculated from data obtained by extraction in SGF and assuming the dust intake of 50 mg/day

<sup>a</sup> Baars et al. (2001), TDI values calculated for an adult, 70 kg body weight

<sup>b</sup> Values exceeding TDI limits ( $\text{HQ} > 1$ ) indicated in bold

weighting adult are reported in Table 3. The cobalt daily intake exceeded the TDI limit for the slag dust (1.19 $\times$ ) and fly ash (1.66 $\times$ ), Pb had high values only

in the fly ash (1.49 $\times$ ), and As in the ESP dust (1.64 $\times$ ). Zinc and Cu were not indicated as problematic contaminants.

**Table 4** Total amounts of contaminants in the air (in  $\mu\text{g}/\text{m}^3$ ) calculated from the  $<10\ \mu\text{m}$  fraction for the total  $\text{PM}_{10}$  concentration of  $50\ \mu\text{g}/\text{m}^3$  and hazard quotients for inhalation ( $\text{HQ}_{\text{inhalation}}$ ) calculated in comparison with tolerable concentrations in air (TCA)

Code	Slag dust		Fly ash		ESP dust		TCA <sup>a</sup> ( $\mu\text{g}/\text{m}^3$ )
	Conc. ( $\mu\text{g}/\text{m}^3$ )	$\text{HQ}_{\text{inhalation}}$	Conc. ( $\mu\text{g}/\text{m}^3$ )	$\text{HQ}_{\text{inhalation}}$	Conc. ( $\mu\text{g}/\text{m}^3$ )	$\text{HQ}_{\text{inhalation}}$	
Co	<b>4.19<sup>b</sup></b>	<b>8.38</b>	<b>1.88</b>	<b>3.77</b>	0.48	0.96	0.5
Cu	<b>26</b>	<b>25.9</b>	<b>25</b>	<b>25.3</b>	<b>116</b>	<b>116</b>	1
Pb	0.16	0.27	<b>6.02</b>	<b>10.0</b>	<b>2.44</b>	<b>4.06</b>	0.6
Zn	0.28	nd <sup>c</sup>	18.9	nd	2.29	nd	nd
As	0.13	0.13	0.12	0.12	<b>2.69</b>	<b>2.69</b>	1

<sup>a</sup> Baars et al. (2001)

<sup>b</sup> Values exceeding TCA limits ( $\text{HQ} > 1$ ) indicated in bold

<sup>c</sup> nd not defined for TCA, not determined for HQ

Table 4 reports the calculated total concentrations of contaminants in the  $<10\ \mu\text{m}$  dust fractions (assuming smelter dust dispersed in the air generating a  $\text{PM}_{10}$  concentration of  $50\ \mu\text{g}/\text{m}^3$ ) and comparisons with the tolerable concentrations in the air (TCA) used as reference concentrations for the inhalation exposure. The data show that some of the contaminants exceeded the TCA limits: Co 3.8–8.4× the value for slag dust and fly ash, Cu 25–116× for all three samples, Pb 4.3–10× for fly ash and ESP dust, and As 2.7× only for ESP dust. As no limit was set for Zn (Baars et al. 2001), the comparisons could not have been performed for this contaminant. However, as revealed by the extraction in SLF, the bioaccessible fraction of contaminants is relatively low (Fig. 3b). We attempted to calculate the amount of metals that could be potentially bioaccessible via inhalation exposure using the bioaccessible concentrations (in  $\text{mg}/\text{kg}$ ) and assuming a  $\text{PM}_{10}$  concentration of  $50\ \mu\text{g}/\text{m}^3$  and mean daily inhalation volume for an adult of  $16\ \text{m}^3$  (US EPA 2011c). Compared with the ingestion exposure, the calculated ranges of the daily bioaccessible levels of contaminant were very low (in  $\mu\text{g}/\text{day}$ ): Co (0.007–0.13), Cu (0.34–0.81), Pb (0.0003–0.011), Zn (0.0006–0.11), and As (0.002–0.005).

## Discussion

The chemical and mineralogical compositions of metallurgical dusts from the Zambian Copperbelt reflect processes related to the high-temperature smelting of Cu–Co ore. Slag dusts are mainly

composed of silicates, oxides, and metal-bearing phases, which were also observed in the slags studied previously by Vítková et al. (2010) and Ettler et al. (2009). Using portable air filters, Křibek et al. (2010) were able to trap dust particles in the vicinity of the Zambian smelters, and some of the  $<20\ \mu\text{m}$  particles were identified as a silicate slag material enriched in metallic elements (e.g., Cu). The fly ash also consisted of high-temperature silicates (clinopyroxenes, quartz) and sulphides, but it contained larger amounts of silicate glass, metallic copper, and various intermetallic compounds compared to the slag dust.

In relation to the leaching behaviour, granulometry could represent an important factor as the effect of the grain size on the leaching was observed, for example, by Morrison and Gulson (2007) on differently crushed Pb slag samples. If the influence of the granulometry were crucial, the contaminant leaching in SGF would be substantially higher for fly ash and ESP dust, which were significantly more fine-grained than the slag dust and thus presumably more reactive during the extraction. However, this was not ascertained (see Table S3). For this reason, we are convinced that the chemical and mineralogical differences among the individual dusts represent a key factor that affected the contaminant release and subsequent value of BAF. In SGF, the largest amounts of Co were leached from slag dust and fly ash due to the higher total Co concentrations in these dust samples and its binding in Co-bearing sulphides, which were probably more reactive than Co-bearing alloys (the only Co-bearing phases detected in ESP dust) (Tables 1, 2, S3). In contrast, the highest Co leaching was observed for ESP dust in

SLF, most likely due to precipitation of Co-bearing carbonates in the leachates of slag dust and fly ash. Although the occurrence of these newly formed phases could not have been detected by XRD analysis of the leached residues, it is important to stress that sphaerocobaltite ( $\text{CoCO}_3$ ) was commonly observed as one of the weathering products on the surfaces of Co-bearing slags from Zambia (Vítková et al. 2010). Copper leaching in SGF was similar for slag dust and fly ash, but yielded one order of magnitude higher concentrations for ESP dust (Table S3). This clearly reflects the differences in the solid speciation of Cu in the individual dusts. Whereas Cu is present in sulphides, alloys, and metallic forms in all the studied samples, a highly soluble Cu sulphate (chalcantite;  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) predominates in ESP dust and is completely dissolved in SGF (Table 2). Surprisingly, the release of Cu from ESP dust in SLF is smaller than for other dust samples (Fig. 4), because it is efficiently controlled by the precipitation of secondary antlerite ( $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$ ); Table 2). These results are in agreement with the previously reported pH-dependent leaching behaviours of dusts/slags from the Zambian smelters (Vítková et al. 2011a, b, 2013) displaying higher Cu and Co releases under acidic conditions and efficient controlling mechanisms leading to precipitation of newly formed carbonates and sulphates under circumneutral conditions. It is nevertheless important to emphasize that the calculated BAF values (and related exposure risks) are similar for all the studied dust samples (Fig. 3).

The extractions in SGF and SLF showed that Pb and Zn were released to a much greater extent from the fly ash than from the slag material and ESP dust (Table S3; Fig. 4). This observation can be partly explained by the higher total concentrations in the solids (Table 1). Unfortunately, no Pb-bearing phase was detected in any of the studied dusts. However, ZnS, as the dominant Zn-bearing phase in fly ash (Table 2), could be responsible for the particularly high release of Zn during the extractions in simulated biofluids. Contrasting leaching of these two metals is also reflected in the proportion of BAF displaying the highest values for fly ash (Fig. 3). In agreement with our results, generally high bioaccessible fractions in SGF (varying roughly between 70 and 90 % of the total concentration) were observed for Pb slags and other Pb smelting wastes at an old mining/smelting site in Brazil (Bosso and Enzweiler 2008). Slightly

lower releases of Pb were observed for Pb slags from Australia, strictly related to the grain size of the samples: varying between  $\sim 20$  % for fractions around  $210 \mu\text{m}$  and up to 100 % for fractions  $< 20 \mu\text{m}$  (Morrison and Gulson 2007). Whereas the highest As leaching in SGF was reported for ESP dust (in accordance with the highest total As concentrations and reported presence of As in complex alloys; Tables 1, 2, S3), the release in SLF was significantly lower compared to the slag dust and the fly ash (Fig. 4). Despite the fact that some elements were not analysed in the extracts (e.g., Fe, Al, Mn), we suggest that newly formed Fe-oxides, for example, could be responsible for As scavenging from the leachate, as has been previously suggested for these systems (Vítková et al. 2011b, 2013).

Contaminant solid speciation in smelting waste can be extremely complex. Vítková et al. (2010) previously showed that metals can be partly bound as admixtures in silicates and silicate glass and the contribution of these phases to release of the contaminants during the above-mentioned extractions cannot be fully discerned or quantified using the available mineralogical methods. Moreover, contaminants can be potentially bound to residual organic matter ( $C_{\text{tot}}$  up to  $111 \text{ g/kg}$ ; Table 1). Thus, it is extremely difficult to measure the release of contaminants from these compounds, because they can be “masked” by the significantly higher reactivity of the dominant metal- and metalloid-bearing phases.

In terms of exposure risk, our data indicate that total contaminant concentrations exceeded the TCA limits if the dust concentration in the air is assumed to be  $50 \mu\text{g/m}^3$  (Table 4). However, the SLF extraction showed that the bioaccessible fraction of contaminants is very low. The inhalation route of exposure will thus be relatively negligible compared to the oral ingestion route of exposure. Moreover, if dusts are inhaled, it is probable that the majority of particles will be transported out of the pulmonary tract via the “mucociliary escalator” (which is an efficient process of clearance of the airways) (Asgharian et al. 2001) and will subsequently be ingested orally.

The literature contains relatively little data related to metals released from various fly ash materials in SGF combined with any subsequent exposure risk calculations. For example, Twining et al. (2005) reported that extremely high bioaccessible fractions of metals, similar to those observed for our dusts, were

found in fly ash from coal-fired power plants, as well as fly ash from tire and coal co-combustion (varying between 7 % for Pb to 100 % for Cu); however, only Al, Pb, and Ni exceeded the health thresholds compiled from various sources (US EPA, Australian Ambient Air Quality, American Conference of Governmental Industrial Hygienists). Our exposure risk calculations for ingestion were conducted to demonstrate the occupational exposure of an adult worker in the Cu–Co smelter (being in direct contact with the dust). The calculated daily intakes of contaminants only slightly exceeded TDI limits. However, we are aware that our calculations were carried out using a very conservative value for the dust ingestion rate (50 mg/day), which can actually be much higher in a dusty environment in and near the smelter.

The major exposure risk is probably related to Co intake via dust ingestion (TDI values exceeded for two of the dust samples studied; Table 3). Despite the fact that Co is bound in vitamin B12, its daily intake recommended by the World Health Organization (WHO) in the adult diet is 0.1 g/day (for further explanations see Gál et al. 2008). These results are in accord with the recent investigation of human health impacts of mines/smelters at the other site of the Copperbelt in the Democratic Republic of Congo, where Co was greatly elevated mainly in urine samples of the local population living close to the polluted areas, especially children (Banza et al. 2009). Our data indicate that a potential risk for human health can be expected in the smelters (i.e., occupational exposure) and safety measures such as using mouth filters should be taken to prevent dust inhalation/ingestion in the factories. It is known that the amount of metals and metalloids in the air and in dust generally rapidly decreases with the distance from the smelter operations (Csavina et al. 2012; Nikolić et al. 2010). However, the strong winds occurring in the Zambian Copperbelt can cause smelter-derived particles to be transported over larger distances from the smelter operations (tens of km; Ettler et al. 2014; Kříbek et al. 2010) and the population will be mainly exposed to re-suspended contaminated soil dust. The first investigations in the Zambian Copperbelt indicated that a higher exposure risk via oral ingestion can be assumed for smelter-affected soils than for mine-affected soils and children represent the most vulnerable targets (Ettler et al. 2012). The direct exposure pathways in the Zambian part of the Copperbelt will

have to be studied in detail to perform a human health risk assessment using accurate methodology (Swartjes and Cornelis 2011); however, this will necessitate close interdisciplinary collaboration among geoscientists, atmospheric scientists, and medical doctors.

## Conclusions

The dusts from Cu to Co smelters located in the Zambian Copperbelt were subjected to extraction procedures using simulated gastric fluid (SGF) and simulated lung fluid (SLF) to assess the bioaccessibility of metals (Co, Cu, Pb, Zn) and As. The contaminant releases were corroborated with changes in mineralogical compositions. Slag dust and fly ash were composed of predominant high-temperature silicates, oxides, and trace sulphides/metallic alloys; the latter being the main source of contaminants during the leaching. In contrast, the leaching of contaminants from the electrostatic precipitator (ESP) dust was not related only to sulphides and alloys but mainly to highly soluble sulphates, which are the predominant component of the dust. Bioaccessible fractions (BAFs) for extraction in SGF varied between 21 and 89 % of the total contaminant concentrations. In contrast, relatively low BAF values were observed for SLF extractions (0.01–16.5 % of the total contaminant concentrations). Daily intakes via dust ingestion were calculated for an adult weighing 70 kg assuming the exposure to 50 mg dust per day slightly exceeded the TDI limits for Co (1.66× for fly ash and 1.19× for slag dust) and occasionally also for Pb (1.49×, fly ash) and As (1.64×, ESP dust). Our study highlights potential risks related to occupational exposure to dust in and near the smelter operations and indicated the need for accurate determination of possible exposure pathways in industrial areas in developing countries where higher unintentional dust ingestion rates can be assumed compared to the EU.

**Acknowledgments** This study was supported by the Czech Science Foundation (GAČR 210/12/1413 and 13-17501S), and the Ministry of Education, Youth and Sports of the Czech Republic (MSM 0021620855) and was carried out within the framework of IGCP Project No. 594 (“Assessment of impact of mining and mineral processing on the environment and human health in Africa”). Peter Lemkin and Madeleine Štulíková are thanked for review of the English in the manuscript.

## References

- Asgharian, B., Hofmann, W., & Miller, F. J. (2001). Mucociliary clearance of insoluble particles from the tracheobronchial airways of the human lung. *Journal of Aerosol Science*, *32*, 817–832.
- Baars, A. J., Theelen, R. M. C., Janssen, P. J. C. M., Hesse, J. M., van Apeldoorn, M. E., Meijerink, M. C. M., et al. (2001). *Re-evaluation of human-toxicological maximum permissible risk levels*. RIVM report 711701025, Bilthoven, The Netherlands.
- Banza, C. L. N., Nawrot, T. S., Haufroid, V., Decrée, S., De Putter, T., Smolders, E., et al. (2009). High human exposure to cobalt and other metals in Katanga, a mining area of the Democratic Republic of Congo. *Environmental Research*, *109*, 745–752.
- Berlinger, B., Ellingsen, D. G., Náray, M., Záray, G., & Thomassen, Y. (2008). A study of bio-accessibility of welding fumes. *Journal of Environmental Monitoring*, *10*, 1448–1453.
- Bierkens, J., Van Holderbeke, M., Cornelis, C., & Torfs, R. (2011). Exposure through soil and dust ingestion. In F. A. Swartjes (Ed.), *Dealing with contaminated sites* (pp. 261–286). Berlin: Springer.
- Bosso, S. T., & Enzweiler, J. (2008). Bioaccessible lead in soils, slags, and mine waste from an abandoned mining district in Brazil. *Environmental Geochemistry and Health*, *30*, 219–229.
- Caboche, J., Perdrix, E., Malet, B., & Alleman, L. Y. (2011). Development of an in vitro method to estimate lung bio-accessibility of metals from atmospheric particles. *Journal of Environmental Monitoring*, *13*, 621–630.
- Castillo, S., de la Rosa, J. D., de la Campa, A. M. S., González-Castanedo, Y., Fernández-Caliani, J. C., González, I., et al. (2013). Contribution of mine wastes to atmospheric metal deposition in the surrounding area of an abandoned heavily polluted mining district (Rio Tinto mines, Spain). *Science of the Total Environment*, *449*, 363–372.
- Csavina, J., Field, J., Taylor, M. P., Gao, S., Landázuli, A., Betterton, E. A., et al. (2012). A review on the importance of metals and metalloids in atmospheric dust and aerosol from mining operations. *Science of the Total Environment*, *433*, 58–73.
- Denys, S., Caboche, J., Tack, K., Rychen, G., Wragg, J., Cave, M., et al. (2012). In vivo validation of the Unified BARGE Method to assess the bioaccessibility of arsenic, antimony, cadmium, and lead in soils. *Environmental Science and Technology*, *46*, 6252–6260.
- Deshommes, E., Tardif, R., Edwards, M., Sauvé, S., & Prévost, M. (2012). Experimental determination of oral bioavailability and bioaccessibility of lead particles. *Chemistry Central Journal*, *6*, 138.
- Drysdale, M., Bjorklund, K. L., Jamieson, H. E., Weinstein, P., Cook, A., & Watkins, R. T. (2012). Calculating the respiratory bioaccessibility of nickel in soil through the use of simulated lung fluid. *Environmental Geochemistry and Health*, *34*, 279–288.
- EC. (1999). Council directive of 1999/30/EC of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air. *Official Journal of the European Communities*, *L163*, 41–60.
- Ettler, V., Johan, Z., Křibek, B., Šebek, O., & Mihaljevič, M. (2009). Mineralogy and environmental stability of slags from the Tsumeb smelter, Namibia. *Applied Geochemistry*, *24*, 1–15.
- Ettler, V., Konečný, L., Kovářová, L., Mihaljevič, M., Šebek, O., Křibek, B., et al. (2014). Surprisingly contrasting metal distribution and fractionation patterns in copper smelter-affected tropical soils in forested and grassland areas (Mufulira, Zambian Copperbelt). *Science of the Total Environment*, *473–474*, 117–124.
- Ettler, V., Křibek, B., Majer, V., Kněsl, I., & Mihaljevič, M. (2012). Differences in the bioaccessibility of metals/metalloids in soils from mining and smelting areas (Copperbelt, Zambia). *Journal of Geochemical Exploration*, *113*, 68–75.
- Ettler, V., Mihaljevič, M., Křibek, 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.
- Gál, J., Hursthouse, A., Tatner, P., Stewart, F., & Welton, R. (2008). Cobalt and secondary poisoning in the terrestrial food chain: Data review and research gaps to support risk assessment. *Environment International*, *34*, 821–838.
- Gbefa, B. K., Entwistle, J. A., & Dean, J. R. (2011). Oral bioaccessibility of metals in an urban catchment, Newcastle upon Tyne. *Environmental Geochemistry and Health*, *33*, 167–181.
- Hursthouse, A., & Kowalczyk, G. (2009). Transport and dynamics of toxic pollutants in the natural environment and their effect on human health: Research gaps and challenge. *Environmental Science and Technology*, *31*, 165–187.
- ICDD. (2003). *PDF-2 database, release 2003*. Newton Square, PA: International Centre for Diffraction Data.
- Křibek, 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. *Journal of Geochemical Exploration*, *104*, 69–89.
- Kutalek, R., Wewalka, G., Gundacker, C., Auer, H., Wilson, J., Haluza, D., et al. (2010). Geophagy and potential health implications: Geohelminths, microbes and heavy metals. *Transactions of the Royal Society of Tropical Medicine and Hygiene*, *104*, 787–795.
- Lábár, J. L. (2005). Consistent indexing of a (set of) SAED pattern(s) with the Process Diffraction program. *Ultramicroscopy*, *103*, 237–249.
- Momoh, A., Davies, T., Akinsola, H., Akinyemi, S. A., Mhlongo, S., Gitari, W., et al. (2013). Human bioaccessibility of Fe, Mn, Zn and Cu from consumed earth materials in Vhembe District, South Africa. *Transactions of the Royal Society of South Africa*, *68*, 33–39.
- Morrison, A. L., & Gulson, B. L. (2007). Preliminary findings of chemistry and bioaccessibility in base metal smelter slags. *Science of the Total Environment*, *382*, 30–42.
- Nikolić, D., Milošević, N., Mihajlović, I., Živković, Ž., Tasić, V., Kovačević, R., et al. (2010). Multi-criteria analysis of air pollution with SO<sub>2</sub> and PM<sub>10</sub> in urban area around the

- copper smelter in Bor, Serbia. *Water, Air, and Soil pollution*, 206, 369–383.
- Ojelede, M. E., Annegarn, H. J., & Kneen, M. A. (2012). Evaluation of aeolian emissions from gold mine tailings on the Witwatersrand. *Aeolian Research*, 3, 477–486.
- Okorie, A., Entwistle, J., & Dean, J. R. (2012). Estimation of daily intake of potentially toxic elements from urban street dust and the role of oral bioaccessibility testing. *Chemosphere*, 86, 460–467.
- Oomen, A. G., Hack, A., Minekus, M., Zeijdner, E., Cornelis, C., Verstaete, W., et al. (2002). Comparison of five in vitro digestion models to study the bioaccessibility of soil contaminants. *Environmental Science and Technology*, 36, 3326–3334.
- Oomen, A. G., Janssen, P. J. C. M., Dusseldorp, A., & Noorlander, C. W. (2008). *Exposure to chemicals via house dust*. RIVM Report 609021064, Bilthoven, the Netherlands.
- Pelfrène, A., Waterlot, C., Mazzuca, M., Nisse, C., Bidar, G., & Douay, F. (2011). Assessing Cd, Pb, Zn human bioaccessibility in smelter-contaminated agricultural topsoils (northern France). *Environmental Geochemistry and Health*, 33, 477–493.
- Reis, A. P., Patinha, C., Noack, Y., Robert S., Dias, A. C., & Ferreira da Silva, E. (2014). Assessing the human health risk for aluminium, zinc and lead in outdoor dusts collected in recreational sites used by children at an industrial area in the western part of the Bassin Minier de Provence, France. *Journal of African Earth Sciences*. doi:10.1016/j.afrearsci.2013.08.001.
- Ruby, M. V., Davis, A., Link, T. E., Schoof, R., Chaney, R. L., Freeman, G. B., et al. (1993). Development of an in vitro screening test to evaluate the in vivo bioaccessibility of ingested mine-waste lead. *Environmental Science and Technology*, 27, 2870–2877.
- Ruby, M. V., Davis, A., Schoof, R., Eberle, S., & Sellstone, C. M. (1996). Estimation of lead and arsenic bioavailability using a physiologically based extraction test. *Environmental Science and Technology*, 30, 422–430.
- Schreck, E., Foucault, Y., Sarret, G., Sobanska, S., Cécillon, L., Cestrec-Rouelle, M., et al. (2012). Metal and metalloid foliar uptake by various plant species exposed to atmospheric industrial fallout: Mechanisms involved for lead. *Science of the Total Environment*, 427–428, 253–262.
- Swartjes, F. A. (2002). *Variation in calculated human exposure. Comparison of calculations with seven European human exposure models*. RIVM report 711701030, Bilthoven, the Netherlands.
- Swartjes, F. A., & Cornelis, C. (2011). Human health risk assessment. In F. A. Swartjes (Ed.), *Dealing with contaminated sites* (pp. 209–259). Berlin: Springer.
- Twining, J., McGlenn, P., Loi, E., Smith, K., & Gieré, R. (2005). Risk ranking of bioaccessible metals from fly ash dissolved in simulated lung and gut fluids. *Environmental Science and Technology*, 39, 7749–7756.
- 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. OSWER 9285 (pp. 7–77). Washington, DC: US EPA.
- US EPA. (2011a). *National ambient air quality standards (NAAQS)*. Washington, DC: US EPA. <http://www.epa.gov/air/criteria.html>.
- US EPA. (2011b). *Glossary of key terms*. Washington, DC: US EPA. <http://www.epa.gov/nata/gloss1.html>.
- US EPA. (2011c). *Exposure factors handbook (EFH)*. Washington, DC: US EPA. EPA/600/R-09/052F.
- Uzu, G., Sobanska, S., Sarret, G., Sauvain, J. J., Pradère, P., & Dumat, C. (2011). Characterization of lead-recycling facility emissions at various workplaces: Major insights for sanitary risks assessment. *Journal of Hazardous Materials*, 186, 1018–1027.
- Vítková, M., Ettler, V., Hyks, J., Astrup, T., & Kříbek, B. (2011a). Leaching of metals from copper smelter flue dust (Mufulira, Zambian Copperbelt). *Applied Geochemistry*, 26, S263–S266.
- Vítková, M., Ettler, V., Johan, Z., Kříbek, B., Šebek, O., & Mihaljevič, M. (2010). Primary and secondary phases in copper-cobalt smelting slags from the Copperbelt Province, Zambia. *Mineralogical Magazine*, 74, 581–600.
- Vítková, M., Ettler, V., Mihaljevič, M., & Šebek, O. (2011b). Effect of sample preparation on contaminant leaching from copper smelting slag. *Journal of Hazardous Materials*, 197, 417–423.
- Vítková, M., Hyks, J., Ettler, V., & Astrup, T. (2013). Stability and leaching of cobalt smelter fly ash. *Applied Geochemistry*, 29, 117–125.
- Wragg, J., Cave, M., Basta, N., Brandon, E., Casteel, S., Denys, S., et al. (2011). An inter-laboratory trial of the unified BARGE bioaccessibility method for arsenic, cadmium and lead in soil. *Science of the Total Environment*, 409, 4016–4030.