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Bioaccessibility of As, Cu, Pb, and Zn in mine waste, urban soil, and road dust in the historical mining village of Kaňk, Czech Republic

Petr Drahota · **Karel Raus** · **Eva Rychlíková** · **Jan Rohovec**

Abstract Historical mining activities in the village of Kaňk (in the northern part of the Kutná Hora ore district, Czech Republic) produced large amounts of mine wastes which contain significant amounts of metal(loid) contaminants such as As, Cu, Pb, and Zn. Given the proximity of residential communities to these mining residues, we investigated samples of mine waste ($n = 5$), urban soil ($n = 6$), and road dust ($n = 5$) with a special focus on the solid speciation of As, Cu, Pb, and Zn using a combination of methods (XRD, SEM/EDS, oxalate extractions), as well as on in vitro bioaccessibility in simulated gastric and lung fluids to assess the potential exposure risks for humans. Bulk chemical analyses indicated that As is the most important contaminant in the mine wastes

(~ 1.15 wt%), urban soils (~ 2900 mg/kg) and road dusts (~ 440 mg/kg). Bioaccessible fractions of As were quite low (4–13%) in both the simulated gastric and lung fluids, while the bioaccessibility of metals ranged between <0.01% (Pb) and 68% (Zn). The bioaccessibilities of the metal(loid)s were dependent on the mineralogy and different adsorption properties of the metal(loid)s. Based on our results, a potential health risk, especially for children, was recognized from the ingestion of mine waste materials and highly contaminated urban soil. Based on the risk assessment, arsenic was found to be the element posing the greatest risk.

Keywords Metal(oid)s · Bioaccessibility · Mineralogy · Topsoil · Street dust · Mine waste

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Introduction

Gold and silver mining conducted during the Middle Ages throughout the Kingdom of Bohemia (predecessor of the modern Czech Republic) has left an environmental legacy of mine waste dumps containing elevated levels of potentially toxic metals and metalloids. Chief among these in the world-renowned Kutná Hora silver ore district, arsenic (As), a well-known carcinogen to humans (IARC 2012), occurs at higher levels and to a greater spatial extent than anywhere else in the contiguous central Czech Republic (Kocourková-Víšková et al. 2015; Horák and Hejcman

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2016). Centuries of exposure to, and weathering of, the abundant mine waste dumps has resulted in the mobilization and increased spatial distribution of metal(loid)-bearing mine wastes in this region; mobilized by erosion (rainwater runoff, streams, and eolian transport of windblown fine-grained mine waste particles), as well as by uncontrolled anthropogenic dispersion of the historical mine waste materials (Bílek et al. 1965; Horák and Hejcman 2016).

The proximity of residential communities to the wastes of this historical mining and processing, such as in the Kutná Hora region, presents potential health risks for residents, especially via the incidental ingestion and/or inhalation of contaminant-bearing particles. Samples of urban soil collected in the historical mining village of Kaňk, located in the northern part of the Kutná Hora ore district, have As concentrations ranging from 34 to 20,300 mg/kg ($n = 33$, mean 3200 mg/kg) (Rychlíková et al. 2015); most of these exceeding the local regulatory level of 70 mg/kg (Metodický pokyn MŽP 1996). The concentrations of metal contaminants are much lower (Horák and Hejcman 2016). That study and several unpublished technical reports show that Cu, Pb, and Zn in the urban soils of Kaňk do not usually exceed the local regulatory levels of: 600 mg/kg for Cu, 300 mg/kg for Pb, and 2500 mg/kg for Zn (Metodický pokyn MŽP 1996).

Concentrations of As and Pb in the dust collected in four households at Kaňk, ranged from 92 to 494 mg/kg (mean 182 mg/kg) for As, and from 19 to 112 mg/kg (mean 47 mg/kg) for Pb, demonstrating the migration of contaminated soil and/or As, Pb-bearing airborne particulates into indoor dust (Rychlíková et al. 2015). Once ingested or inhaled, a portion of the metal(loid) contaminant may solubilize (i.e., become bioaccessible) in the gastrointestinal tract or lung, respectively; and some of this may be absorbed (i.e., be bioavailable) in the systemic circulation (Basta and Juhasz 2014; Wiseman 2015). For example, arsenic relative bioavailability (RBA) in the gastrointestinal tract has been reported to vary from 3 to 100%, but most As-bearing soils and wastes have an As RBA of <50% (Basta and Juhasz 2014). Metal(loid) RBA may be influenced by a number of physiological parameters in addition to the physicochemical properties and effects of the mineralogical compositions of metal(loid)-bearing soil/waste (Davis et al. 1993; Ruby et al. 1999; Beak et al. 2006; Meunier et al. 2010; Ettler

et al. 2014). Thus, estimating the bioaccessibility of As and metal pollutants from site-specific samples provides a more accurate approximation of the relevant dose, and as such is an important component of the risk assessment.

The present study focused on the multiple As, Cu, Pb, and Zn mineral forms present in the As-enriched mine wastes, urban soils, and road dusts of this historical mining village. The objectives were to determine: (1) the bioaccessibility of the contaminants for risk assessment purposes, and (2) the extent to which sample chemical properties (pH, elemental composition) and mineralogical composition affect the bioaccessibility of the As, Cu, Pb, and Zn.

Methods

Site description

The Central Bohemian village of Kaňk, with a population of around 800, is located in the northern periphery of the Kutná Hora ore district, one of the best known European mining centers of the Middle Ages. The Kaňk mining village sprouted up along one of the most important Ag–Cu ore zones (called the "Staročeský" ore zone) of the district, which was exploited from the end of fourteenth century until the beginning of seventeenth century (Bílek et al. 1965). The intensive mining and processing activities of that time left a legacy of large waste dumps (average areas of 3000 m^2, with heights up to 20 m, individually; totaling a few hundred thousand tons), which are concentrated in an elongated north–south area of $\sim 1500 \times 200$ m (from the northern to the southern borders of Kaňk village) (Fig. 1). The waste dumps are currently covered by a thin soil layer and vegetated; nevertheless, building operations and erosion have locally bared the waste dump materials near various residential locations. In addition, two permanent outcrops of waste materials occur in a forested area northwest of Kaňk.

The waste dump materials are heterogeneous, with particles ranging from very fine (clay) to coarse (tens of cm), including barren gneiss host rock and hydrothermally altered and mineralized materials. Composition of the waste dumps is characterized by high to extreme levels of As (up to 2.68 wt%), while the contents of Cu (up to 0.1 wt%), Pb (up to
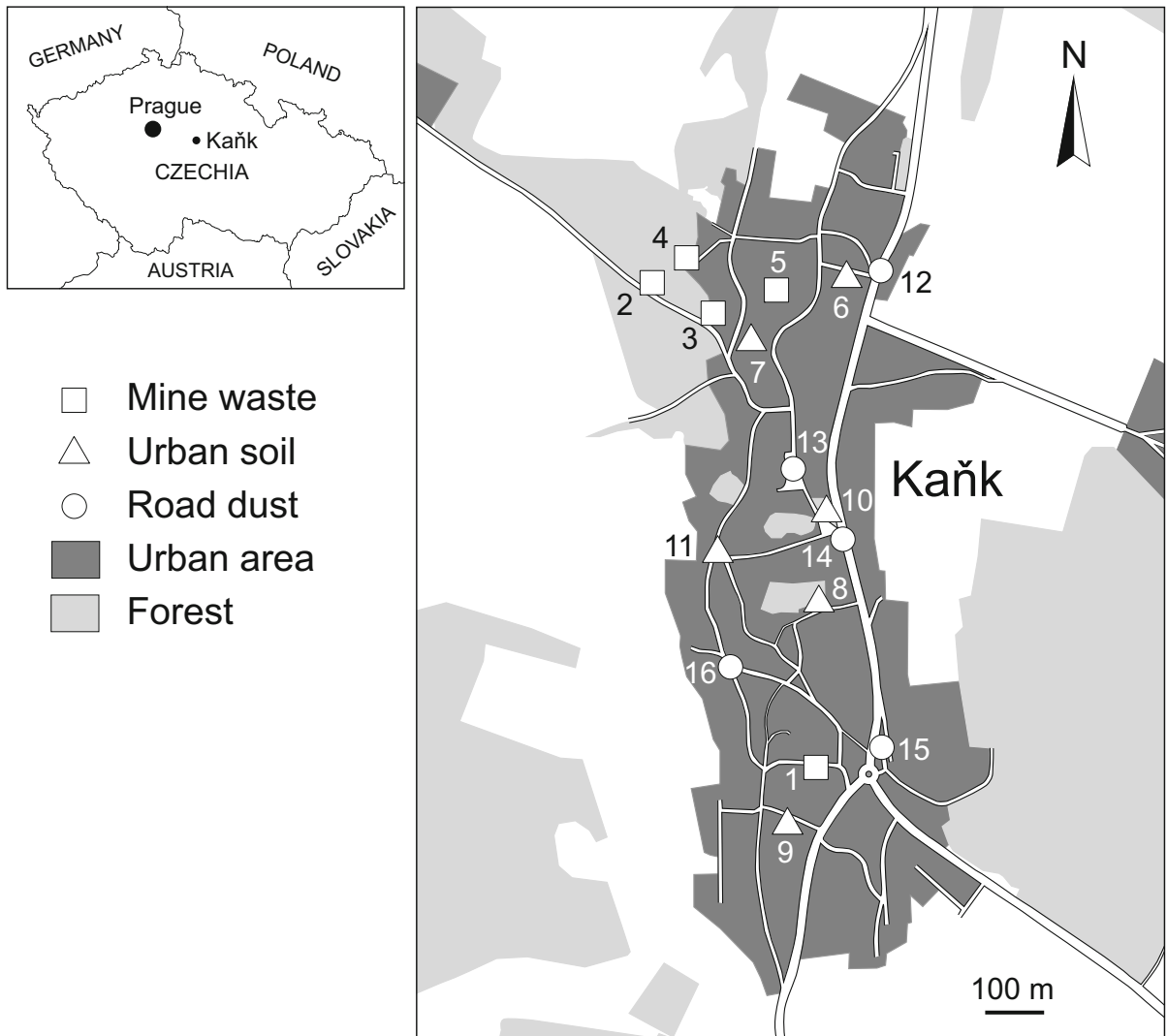
Fig. 1 Sampling sites of mine waste, urban soil, and road dust in the historical mining village of Kaňk

0.03 wt%), and Zn (up to 0.1 wt%) are typically 1–2 orders of magnitude lower (Kocourková-Víšková et al. 2015). The mineralized waste materials are heavily weathered, and primary ore minerals such as pyrite (FeS_2), pyrrhotite (FeS), arsenopyrite ($FeAsS$), sphalerite (ZnS), galena (PbS), chalcopyrite ($CuFeS_2$), and stannite (Cu_2FeSnS_4) are mostly only now present as highly weathered remains (Kocourková-Víšková et al. 2015). Most of the arsenic and metals are bound to secondary mineral phases belonging to the groups of ferric (hydr)oxides, hydroxosulfates, arsenates, and sulfoarsenates. Probably the most common secondary phases in the waste material include different species

of Fe (hydr)oxides, jarosite ($KFe_3(SO_4)_2(OH)_6$), gypsum ($CaSO_4 \cdot 2H_2O$), scorodite ($FeAsO_4 \cdot 2H_2O$), schwertmannite ($Fe_{16}O_{16}(SO_4)_2(OH)_{12} \cdot nH_2O$), and amorphous ferric arsenate. Other secondary minerals phases such as bukovskýite ($Fe_2(AsO_4)(SO_4)$ $(OH) \cdot 9H_2O$) and kaňkite ($FeAsO_4 \cdot 3.5H_2O$) are only common locally (Pauliš 1998; Drahota et al. 2014; Kocourková-Víšková et al. 2015). Except for rare chalcanthite ($CuSO_4 \cdot 5H_2O$), secondary Cu and Zn mineral phases were not found in the mine wastes (Pauliš 1998). Lead is exclusively incorporated into the jarosite group of minerals (Kocourková-Víšková et al. 2015).

Sample collection and preparation

In 2015, three types of samples were collected within the urbanized area of Kaňk (Fig. 1): (1) mine waste ($n = 5$), (2) soil ($n = 6$), and (3) road dust ($n = 5$). The mine waste samples were collected from bare walls of the dumps, lacking any soil cover or vegetation. The urban soil samples were collected from undeveloped lands in residential parks, playgrounds, or other areas where Kaňk citizens might easily be exposed. The soil and mine waste samples were collected using a plastic trowel from the top 2 cm, as this is the portion most likely to become ingested and airborne. Road dust was collected from both the main road ($n = 3$) and local roads ($n = 2$) by sweeping, using a polyethylene (PE) brush on a road surface area of approx. 1 m². The samples were stored in PE bags, air-dried under ambient conditions, and sieved to collect the <250 μm particle size fraction (which can adhere to fingers and thus is potentially available for incidental ingestion). The <250 μm fraction was used for pH determination, elemental and mineralogy analyses, as well as for bioaccessibility testing using an in vitro solubility bioaccessibility research consortium method (SBRC) (Kelley et al. 2002). Using a dry-sieving method, the remaining samples were separated into finer size fractions. The finest size fraction obtained (<50 μm) was gently kneaded by hand through an 11-μm polyamide mesh sieve (SEFAR PETEX 07-11/5, Switzerland) until at least 0.5 g of the respirable fraction of each sample was isolated. This material was subjected to elemental and mineralogical analyses, as well as to the simulated lung fluid analysis using a modified Gamble's solution (Moss 1979).

Analytical determination

Sample pH was measured in a 1:2.5 (w/v) solid-deionized water suspension after 1 h of agitation, using a combined pH electrode and WTW multimeter. An aliquot sample was milled to analytical fineness in an agate mortar (Fritsch Pulverisette, Germany) and then used for bulk chemical analysis. Total organic carbon (TOC), total inorganic carbon (TIC), and total sulfur were determined using Eltra CS 500 and Eltra CS 530 analyzers (Eltra, Germany). The pseudo-total digests of the solid samples were obtained by a standardized *aqua regia* extraction protocol according to ISO Standard 11466 (ISO 1995). The digests were analyzed for concentrations of As, Cu, Fe, Pb, and Zn by inductively coupled plasma optical emission spectrometry (ICP OES; Agilent 5100, USA) under standard analytical conditions.

The X-ray diffraction analyses (XRD) of the samples were employed to identify the principal and potential metal(loid)-bearing phases. XRD analyses were performed using a PANalytical X'Pert Pro diffractometer, Netherlands (settings: Cu Kα radiation, 40 kV and 30 mA, 2θ range 3°–70°, step 0.02, 150 s counting time, using an X'Celerator multi-channel detector). The qualitative analysis of the XRD patterns was performed using PANalytical X'Pert HighScore software (version 3.0e) and ICDD PDF-2 database (ICDD 2003). Semiquantitative estimates of the abundances of major minerals were obtained by comparing the integrated intensities of diffraction peaks. The <250 μm fraction of six samples (two of each type) was prepared as polished sections and studied using a TESCAN VEGA (TESCAN Ltd., Czech Republic) scanning electron microscope (SEM) equipped with an Oxford Link X-Max 50 (UK) energy-dispersive X-ray spectrometer (EDS). Subsamples of both particle size fractions were extracted in pH 3, 0.2 M NH_4-oxalate/oxalic acid for 2 h in the dark. This method is fairly selective for dissolving amorphous or poorly crystalline Fe (hydr)oxides and Fe arsenates (Dold 2003; Drahota et al. 2014). The concentration of As, Cu, Fe, Pb, S, and Zn in the leachate was determined by ICP OES.

Bioaccessibility testing

The oral bioaccessibility test was performed on the <250 μm particle size fraction using the gastric phase of the SBRC method, which was primarily chosen for its simplicity and reliability with in vivo bioassays (Bradham et al. 2011; Deshommes et al. 2012; Juhasz et al. 2014a). Thus, gastrointestinal phase extraction was not tested. A recent comparative study evaluating the correlation between the mouse model and five commonly employed in vitro methods for As (which varied from simplified gastric methods to complex physiological methods) reported that the strongest correlation was found between the result obtained with a mouse model and the SBRC-G method (Juhasz et al. 2014b). Briefly, the sample was added to the gastric

phase of the SBRC (0.4 M glycine, pH 1.5) at a solid/solution ratio of 1:100. Suspensions were incubated at 37 °C, in a shaking incubator (GFL, Germany) at 40 rpm for 1 h.

The bioaccessible lung test was performed on the potentially inhalable particle size fraction (<11 µm) using Gamble's solution (Moss 1979), which mimics the interstitial fluid within the lung (Davies and Feddah 2003). Many studies have modified the original composition of Gamble's solution in terms of the specific chemicals included, the amount added to solution, as well as the extraction conditions (e.g., extraction temperature and time, sample shaking, solid/solution ratio) (Wiseman 2015). In addition, elements which typically occur at a low ambient concentration in the environment (such as As) were usually not focused upon, except in a few studies (Ettler et al. 2014; Huang et al. 2014; Wiseman and Zereini 2014). For that reason, the lung simulating solution in this study was prepared according to the Ettler et al. (2014) adaptation of the original fluid as reported by Twining et al. (2005), because only that study enables a comparison of two mining sites in terms of their metal(loid)'s bioaccessibility. Briefly, the <11 µm fraction of the samples was added to the extraction solution (pH 7.4 $\pm$ 0.1) at a solid/solution ratio of 1:100 (0.1 g to 10 mL) and then maintained for 24 h at 37 °C with occasional agitation. The pH of the leachates was monitored and adjusted to pH 7.4 with dilute NaOH as necessary.

After the extraction procedures, the extracts were collected, filtered through 0.2 µm membrane filters (nylon, Profill), and stabilized by diluted HNO_3 prior to analysis of As, Cu, Fe, Pb, S, and Zn by ICP OES. The bioaccessible concentrations of metal(loid)s (mg/kg) were converted to a % of the total content.

Quality assurance and quality control

The reproducibility and accuracy of the *aqua regia* digestion method were determined by duplicates for six randomly selected samples and confirmed by the quantitative average of As, Cu, Fe, Pb, and Zn recovery analysis from NIST 2710a Montana I soil standard reference material, respectively, which yielded good agreements with the certified values (90–98%). The lower recoveries of the pseudo-total digests were consistent with the results of other authors (Karadaş and Kara 2011; Ettler et al. 2012)

and may imply an incomplete dissolution of the metal(loid)-bearing phases.

The extractions were performed in duplicate for three samples of each particle size fraction, which indicated that the reproducibility of the oral and lung bioaccessibility tests was always below 5% (0.2–4.1%) and 6% (0.1–6.0%; only for As and Cu), respectively. The reproducibility of the oxalate extractions was always below 9% (0.1–9.4%).

Exposure assessments

The bioaccessible concentrations of metal(loid)s were used to make both an exposure assessment and risk characterization for the local population according to the methodology described by the U.S. Environmental Protection Agency (US EPA 2004, 2011). A fully integrated risk assessment was not carried out. In order to perform a comparative study between the three types of solid samples (mine waste, urban soil, road dust), only two exposure routes (incidental ingestion and inhalation) were considered. The average daily dose of the metal(loid)s was quantified for two population groups: children (from birth to 6 years—this being the most sensitive life stage) and adults.

Inhalation exposure is generally calculated using concentrations of the individual metal(loid)s in the aerosols or the total suspended particles in the air. Unfortunately, no in situ measurement of total aerosols (particulate matter <10 µm; PM_{10}) was carried out in our study. Thus, the concentrations of metal(loid)s for individual dusts (ng/m³) were calculated using an *ad hoc* PM_{10} concentration of 50 µg/m³ (as a conservative value), and by assuming that PM_{10} could be composed of the <11 µm fraction observed in this study.

The calculated average daily doses were subsequently divided by a reference dose to yield a noncancer hazard quotient (HQ) for each element. The HQs were compared with the non-cancer target risk of 1. If the HQ exceeded 1, there would be concern over potential non-carcinogenic effects. Most of the toxicity values used in the analysis were taken from the Agency for Toxic Substances and Disease Registry, U.S. (As: 0.3 µg/kg/day, Cu: 10 µg/kg/day, Zn: 300 µg/kg/day; ATSDR 2015). The only exception was for Pb, whose reference dose was taken from the Joint FAO/WHO Expert Committee on Food Additives (JECFA 1999). No reference concentrations for

chronic inhalation exposures to As, Cu, Pb, and Zn were reported; therefore, no calculation of their respective HQs was conducted.

Results

Chemistry of samples

The 16 samples have distinct physicochemical and mineralogical characteristics that represent the variability in the near-surface mine wastes, urban soils, and road dusts encountered within the historical mining site (Table 1). The pH of the samples was generally moderately acidic to slightly alkaline (ranging from 5.4 to 7.7), with the exception of three extremely acidic mine waste samples (pH < 3.5) collected from the walls of a large and undisturbed dump in the northern part of the former mining area (samples 2–4, Fig. 1). Of the three substrates, the < 250 μm particle size fraction of the mine wastes contains the highest concentration of Fe (6.4–9.2 wt%), S (0.9–4.0 wt%), and As (9250–15,500 mg/kg). Concentrations of As in the urban soils and road dusts were also high (>87 mg/kg), but generally displayed values 1–2 orders lower than those in the mine wastes. Notable exceptions were urban soil samples 8 and 9, which represent the only soil samples collected on the mine waste dump, and contained very high concentrations of Fe, S, and As (Table 1). In contrast, concentrations of Cu, Pb, and Zn in the mine waste samples did not show a significant increase compared to the urban soil; nevertheless, decreased concentrations of these metals were generally observed for the road dust. A similar distributional trend of the metal(loid)s in those samples was found in the <11 μm particle size fraction (which, on average, makes up 5 wt% of the <250 μm sample fraction). The bulk chemical compositions (Table 1) indicated that the concentration of all metal(loid)s in the <11 μm fraction displayed 20–150% higher average values in all sample types, indicating that the contaminants are concentrated in the finest particle fraction. The greatest increase in contaminant concentration was observed for Pb (129, 86, and 121% in the mine waste, urban soil, and road dust, respectively) as well as in the road dust (84, 117, 121, and 150% higher for As, Cu, Pb, and Zn, respectively).

Mineralogy of samples

The major crystalline mineral phases in the samples were identified by bulk XRD analyses; the summary can be found in Table 1. The dominant crystalline phases in all substrates were quartz, illite and/or muscovite (the latter two both referred to as mica in Table 1), as well as less common feldspar. Minor amphibole and chlorite were detected in the road dust and in some of the soil samples; calcite was only detected in near-neutral samples. The mine waste samples are characterized by common gypsum and jarosite; the latter phase was also identified in two soil samples (samples 8 and 9) that were collected from sites in the immediate vicinity of mine waste dumps. The only contaminant-bearing phase identified using bulk XRD analysis includes the crystalline ferric arsenate, scorodite, which was detected at trace amounts in samples 3, 4, and 5. A similar mineral composition was found in the < 11 μm particle size fraction of the corresponding samples. Comparison of the XRD patterns of both particle size fractions suggests an increased proportion of chlorite, illite/smectite, jarosite, and kaolinite, with respect to feldspar and quartz in the finer particle size fraction.

Although bulk XRD analysis provides useful information on the dominant mineralogical characteristics, the metal(loid)-bearing phases are also present in quantities or proportions so small that they could not be identified by this method. For this reason, the < 250 μm particle size fraction of the two mine wastes (samples 1 and 5), two urban soils (samples 7 and 9), and two road dusts (samples 14 and 16) were studied by SEM/EDS. Arsenic mineralogy in the mine waste samples was dominated by Fe arsenates and As-bearing Fe (hydr)oxides, with the latter phases dominating in the urban soil and the road dust samples (Fig. 2). Minor metal(loid)-bearing minerals identified in the mine waste samples include sulfides (pyrite, arsenopyrite, chalcopyrite, sphalerite, and stannite) (Fig. 2a, f, h), as well as minerals of the jarosite subgroup (Fig. 2e). These mineral phases were also rarely detected in the soil (sample 9) and road dust (sample 16). Iron arsenates ranged in their chemical compositions from almost pure Fe arsenate (e.g., pure Fe arsenate in Fig. 2b, resembling the specific appearance of kaňkite on the micro scale; Majzlan et al. 2012) to a mixture of As, Fe, and Ca oxides (up to

Table 1 Bulk mineralogical and chemical composition of the mine waste, urban soil, and road dust samples

Sample	Type	Mineralogy (XRD)[a]	pH	TIC (wt%)	TOC (wt%)	S (wt%)	Fe (wt%)	As (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
<250 μm fraction											
1	Mine waste	**Qtz, Mca,** Fsp, *Jrs, Gp, Kal*	6.46	0.02	0.59	0.89	7.398	9250	877	104	7050
2	Mine waste	**Qtz, Mca,** Fsp, *Jrs, Kal*	2.86	nd	1.19	1.80	9.200	15,500	288	204	280
3	Mine waste	**Qtz, Mca,** Fsp, *Jrs, Gp, Kal, Sc*	3.36	nd	1.05	2.22	6.770	9700	416	219	808
4	Mine waste	**Qtz, Mca,** Fsp, *Jrs, Gp, Sc*	3.50	nd	0.90	4.00	7.683	11,800	498	81	195
5	Mine waste	**Qtz, Mca,** Fsp, *Jrs, Gp, Kal, Sc, Cal*	6.78	0.16	2.33	1.63	6.395	11,030	189	131	359
6	Urban soil	**Qtz, Mca,** Fsp, *Cal, Am, Chl, Kal*	7.33	0.04	12.06	0.30	2.215	335	80	90	454
7	Urban soil	**Qtz, Mca,** Fsp, *Am, Cal, Kal*	7.60	0.31	6.48	0.34	2.855	1325	183	109	2075
8	Urban soil	**Qtz, Mca,** Fsp, *Jrs, Kal*	5.35	<0.01	9.12	0.78	6.538	10,350	1393	174	3750
9	Urban soil	**Qtz, Mca,** Fsp, *Jrs, Cal, Chl, Kal*	7.29	0.22	4.78	0.49	4.138	4275	187	142	623
10	Urban soil	**Qtz, Mca,** Fsp, *Am, Cal, Chl, Kal*	7.51	0.21	9.69	0.22	2.050	164	68	37	220
11	Urban soil	**Qtz, Mca,** Fsp, *Kal, Am, Chl*	6.66	<0.01	12.00	0.41	2.710	992	140	61	262
12	Road dust	**Qtz, Mca,** Fsp, *Am, Kal, Cal, Chl*	7.59	0.38	3.25	0.71	2.751	125	116	55	266
13	Road dust	**Qtz, Mca,** Fsp, *Am, Chl, Kal, Cal*	7.62	0.08	3.19	0.28	2.965	393	111	58	138
14	Road dust	**Qtz, Mca,** Fsp, *Am, Chl, Kal, Cal*	7.72	0.34	2.51	0.83	2.628	174	96	34	214
15	Road dust	**Qtz, Mca,** Fsp, *Am, Chl, Kal, Cal*	7.56	0.24	6.24	0.33	2.890	87	89	28	206
16	Road dust	**Qtz, Mca,** Fsp, *Am, Cal, Kal, Chl*	7.41	0.16	2.95	0.35	2.980	1402	114	46	96

Sample	Type	Fe (wt%)	As (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
<11 μm fraction						
1	Mine waste	10.77	11,630	1284	214	11,086
2	Mine waste	13.75	17,590	395	462	353
3	Mine waste	10.74	13,520	681	541	1198
4	Mine waste	13.50	14,010	830	202	332
5	Mine waste	10.07	13,780	267	281	522
6	Urban soil	2.164	474	99	176	730
7	Urban soil	3.900	1953	121	194	1400
8	Urban soil	7.170	8895	1339	252	4199
9	Urban soil	5.543	4414	253	247	849
10	Urban soil	2.467	401	119	85	427
11	Urban soil	3.519	1498	199	120	385
12	Road dust	3.968	162	211	107	565
13	Road dust	4.090	719	323	94	346

Table 1 continued

Sample	Type	Fe (wt%)	As (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
14	Road dust	3.610	351	183	92	522
15	Road dust	4.130	157	176	73	474
16	Road dust	5.010	3116	254	101	300

Am amphibole, *Cal* calcite, *Chl* chlorite, *Fsp* feldspar, *Gp* gypsum, *Jrs* jarosite, *Kal* kaolinite, *Mca* mica, *Qtz* quartz, *Sc* scorodite, *nd*: not determined

[a] Relative abundance: dominant phases in bold type, common phases in normal type, minor phases in italics

8.0 wt% CaO) (Fig. 2h, i). The Fe (hydr)oxides act as scavengers of As (up to 13.2 wt% As_2O_5), Cu (up to 10.2 wt% CuO), and Zn (up to 17.1 wt% ZnO). Less abundant minerals of the jarosite subgroup sporadically contained Pb and As, with up to 8.3 wt% PbO and 14.3 wt% As_2O_5.

Oxalate extraction

Arsenic extracted by pH 3 NH_4-oxalate in the dark is usually associated with both amorphous Fe(III) (hydr)oxides and reactive Fe(III) arsenates such as kaňkite and amorphous ferric arsenate (Dold 2003; Drahota et al. 2014). The extraction results indicate that the proportion of As in the <250 μm particle size fraction associated with these phases was $62 \pm 9\%$ in the mine wastes, $65 \pm 9\%$ in the urban soils, and $49 \pm 9\%$ in the road dusts (Table S1). In contrast, the proportion of oxalate-extractable As in the <11 μm particle size fraction is significantly higher (approximately 90% for all sample types), suggesting that As in the finer particle size fraction is exclusively bound to the amorphous and poorly crystalline Fe phases. To overcome the problem of extraction selectivity between (hydr)oxides and arsenates, the molar ratio of Fe/As in the oxalate fraction was calculated (Table S1). Congruent dissolution of Fe arsenates theoretically provides approximately equimolar Fe and As, whereas congruent dissolution of As-bearing Fe (hydr)oxides provides several tens or hundreds of mols of Fe per 1 mol of As (based on EDS data). The Fe/As molar ratio in the oxalate extraction varied from 3 to 5 in the <250 μm particle size fraction of the mine waste, whereas this ratio was significantly higher in the urban soil (up to 44) and the road dust (up to 155). The notable exceptions of soil and road dust samples, with low Fe/As molar ratios, included samples 8, 9, and 16 (with molar ratios of 5 or 6). These samples represent soils associated with mine waste, and dust from a local dirt road developed on a basement of mine waste/soil. These findings and assumptions led us to the following conclusions: (1) As in the mine waste samples is significantly contained in reactive Fe(III) arsenates (amorphous ferric arsenates kaňkite, bukovskýite), whereas As association with these arsenates in most soil and road dust samples is negligible; and (2) in the <11 μm particle size fraction of all substrates, arsenic is almost exclusively bound to reactive Fe phases, which are predominantly
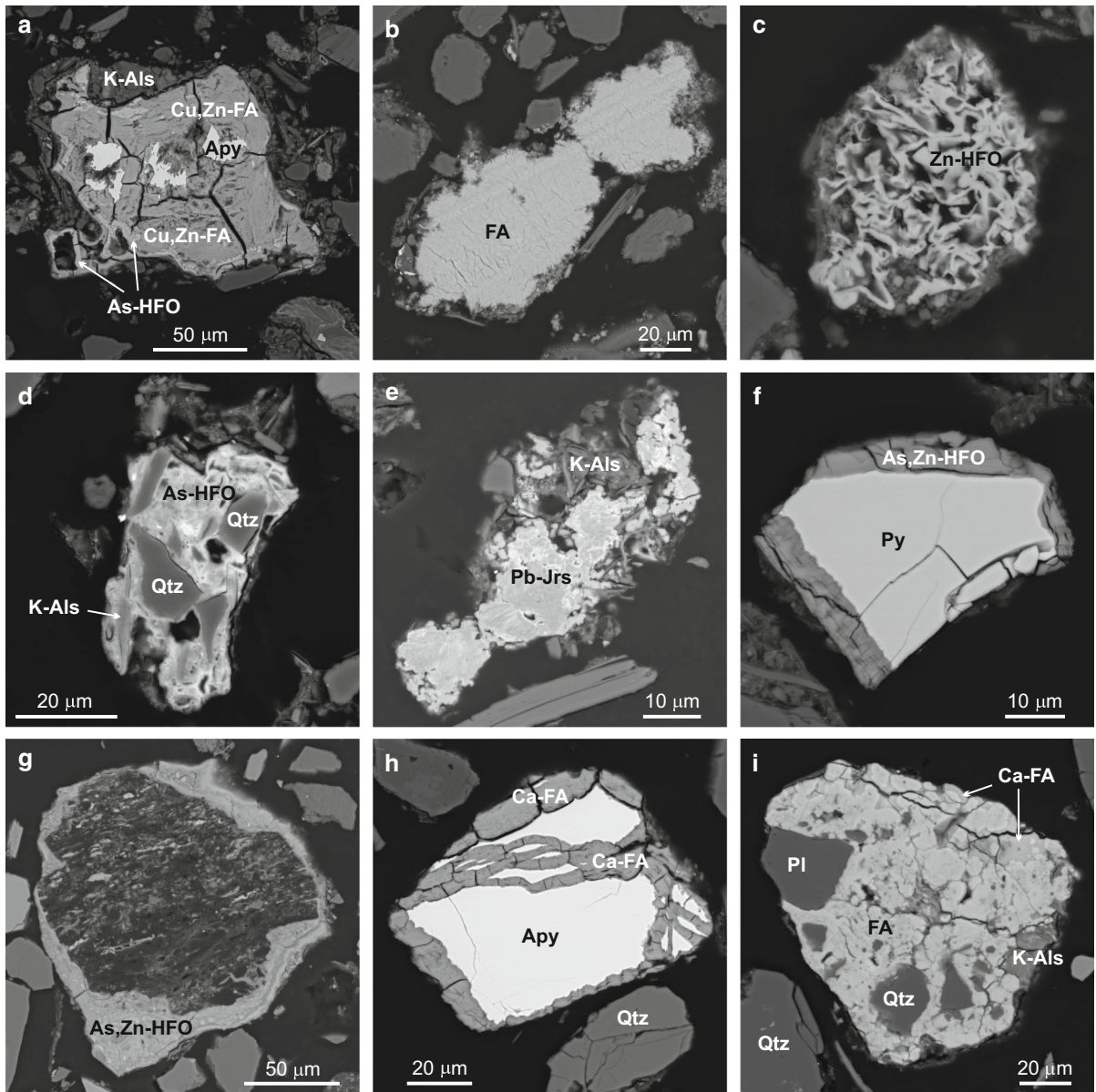
Fig. 2 Selected back-scattered electron images of the mineral phases from mine wastes (**a**–**c**), urban soils (**d**–**f**), and road dusts (**g**–**i**) at the historical mining village of Kaňk. Identification of the phases is based on EDS analyses. *Apy* arsenopyrite, *Ca-FA* calcium-iron arsenate, *FA* iron arsenate, *HFO* iron (hydr)oxide, *K-Als* potassium aluminosilicate, *As,Pb-Jrs* arsenic- and lead-rich jarosite, *Py* pyrite, *Qtz* quartz

represented by amorphous and poorly crystalline Fe (hydr)oxides. The average proportions of oxalate-extractable Cu and Zn were in the range of 38–64% in the <250 μm particle size fraction and 49–90% in the <11 μm particle size fraction. Similarly, as with As, enrichment of these metals in the <11 μm particle size fraction was likely due to their exclusive association with Fe (hydr)oxides. In contrast, oxalate-extractable Pb was very low (6–17%) in all substrates and in both particle size fractions (Table S1). This indicates that the majority of Pb exhibits a different mode of binding, which is most likely represented by

structurally incorporated Pb in highly oxalate-insoluble minerals of the jarosite subgroup (Drahota et al. 2014).

Bioaccessibility results

The measured bioaccessible As concentrations from all samples are much lower than the total As concentrations ranging from 7 to 795 mg/kg in the gastric phase (<250 μm particle size fraction) and from 9 to 1010 mg/kg in the lung test (<11 μm particle size fractions). A similar situation was found for the metal contaminants: bioaccessible Cu, Pb, and Zn ranged from 6 to 160, <0.5 to 23, and 6 to 3260 mg/kg in the gastric phase, respectively, whereas their bioaccessible concentrations in the lung test were very low (Cu: up to 51 mg/kg, Pb: up to 0.5 mg/kg, Zn: up to 8 mg/kg). The bioaccessibility results are summarized in Fig. 3 and Table S2. The average percent of As bioaccessibility in the gastric phase was relatively low at $5.1 \pm 1.5\%$ in the mine waste, $8.2 \pm 2.9\%$ in the urban soil, and $7.5 \pm 2.9\%$ in the road dust, being relatively similar to the average proportions of the bioaccessible As in the lung solution (5.3–5.9%). The relative bioaccessibility of metal contaminants in the gastric phase was usually higher (17–47%), but their maximum average bioaccessibility fractions in the lung test were only 3.8% (Cu in the urban soils), with the maximum bioaccessible fractions of Pb and Zn in all samples being lower than 0.5%. The only exception to a low bioaccessible fraction in the gastric fluid was for Pb in the mine waste samples (averaging 3.4%).

Exposure estimations

Assuming a daily intake of 100 mg/kg for a 70-kg adult, and 200 mg/kg for a 16.2-kg child (representing one of the most conservative ingestion rate values with respect to human health; Reis et al. 2014), the calculated oral and inhalation exposures via individual dusts, compared with guideline doses, can be found in Table 2. Due to the very high concentrations of As in the mine wastes, soils, and road dust (usually exceeding the local regulatory level of 70 mg/kg in soil by 2 or 3 orders of magnitude), As seems to be the most problematic contaminant at the site. The arsenic daily oral intake by children exceeded the health risk guideline limit for mine waste (HQ ∼ 22.3), urban soil (HQ ∼ 7.3), and road dust (HQ ∼ 1.5); the daily
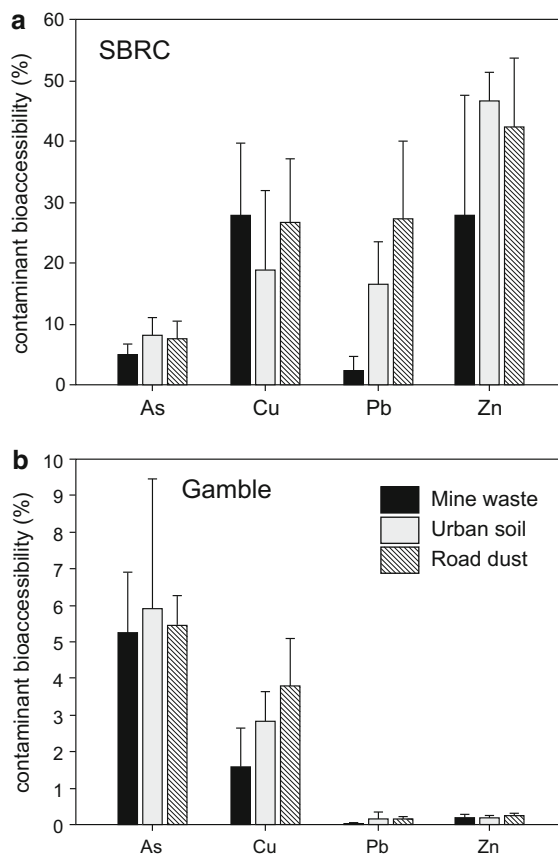

Fig. 3 Percentage of As, Cu, Pb, and Zn in mine waste, urban soil, and road dust dissolved in: **a** simulated gastric fluid using the SBRC method, and **b** simulated lung fluid using Gamble's solution. Values represent the mean and SD of different substrates (mine wastes 1–5, urban soils 6–11, road dusts 12–16)

oral intake of arsenic by adults only exceeded the guideline limit for mine waste (HQ ∼ 2.6). Cu, Pb, and Zn were not indicated as problematic contaminants (Fig. 4).

The daily intake of the metal(loid)s by inhalation was not compared with guideline doses, because the EPA has not yet determined the respective inhalation reference concentrations. If the toxicity values considered by the inhalation route would be equal to the corresponding oral reference doses (based on the conservative assumption that, after inhalation, the absorption of the particle-bound metal(loid)s will result in similar non-carcinogenic health effect as when the particles had been ingested), then the daily inhalation intake by children would not exceed the guideline limit for As (<0.4×), and the inhalation intake of the metals would be negligible. This is due to

Table 2 Summary of average exposures via dust ingestion (min–max) for adults and children

	Guideline[a]	(ng/kg/day)	Adults			Children		
			Mine waste	Urban soil	Road dust	Mine waste	Urban soil	Road dust
As	300 (ATSDR 2015)	Oral intake	**770 (550–1100)**	250 (16–**600**)	53 (8.2–200)	**6700 (4700–9400)**	**2200 (140–5200)**	**450 (71–1700)**
	na	Inhalation intake	67 (43–96)	15 (1.7–36)	4.2 (0.82–15)	110 (68–150)	23 (2.7–57)	8.1 (1.4–24)
Cu	10,000 (ATSDR 2015)	Oral intake	190 (29–460)	160 (8.2–840)	38 (25–55)	1700 (250–3900)	1400 (71–7300)	330 (210–570)
	na	Inhalation intake	0.91 (0.0.28–2.1)	1.1 (0.18–4.5)	0.79 (0.42–1.5)	1.5 (0.44–3.3)	1.7 (0.29–7.2)	1.3 (0.67–2.5)
Pb	3500 (JECFA 1999)	Oral intake	3.4 (0.34–8.2)	20 (11–31)	15 (10–25)	30 (3.0–71)	170 (95.270)	130 (93–210)
	na	Inhalation intake	<0.004	0.02 (<0.004–0.05)	0.01 (<0.004–0.02)	<0.007	0.03 (<0.007–0.07)	0.02 (<0.007–0.03)
Zn	300,000 (ATSDR 2015)	Oral intake	1000 (8.2–4500)	810 (130–2600)	110 (44–160)	8900 (71–39,000)	7000 (1100–23,000)	960 (380–1400)
	na	Inhalation intake	0.08 (<0.004–0.36)	0.18 (<0.004–0.72)	<0.004	0.12 (<0.007–0.58)	0.29 (<0.007–1.1)	<0.007

na not available

[a] As, Cu, Zn: ATSDR (2015), Pb: JECFA (1999); (exceeded guidelines are indicated in bold)

Fig. 4 Hazard quotients (HQs) for adults and children calculated from the ingestion of mine waste, urban soil, and road dust at the mining village of Kaňk. Note different scales for adults and children. The mean is represented by a *black circle*, and the median is a *solid line* through the *box*
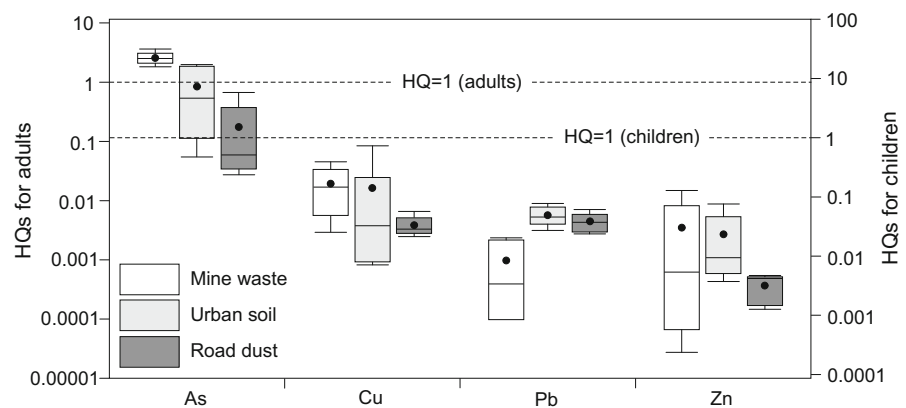

Table 3 Metal(loid)s average concentrations (min–max) in the PM_{11} or PM_{10} fraction (ng/m^3) of potentially inhalable particles or aerosol, respectively

	Guidelines[a]	Mine waste[b]	Urban soil[b]	Road dust[b]	Indoor[c]	Outdoor[d]
As	6 (European Council 2005)	**705 (582–880)**	**147 (24–445)**	**45 (8–156)**	**8.6** (4.1–**12**)	**6.3** (2.2–**12**)
Cu	na	35 (13–64)	18 (5–67)	11 (9–16)	nd	3.2 (2.9–3.8)
Pb	500 (European Council 1999)	17 (10–27)	9 (4–13)	4.7 (3.7–5.4)	19 (<1–24)	10 (8.1–12.1)
Zn	na	135 (18–554)	67 (19–210)	22 (15–28)	nd	23 (18–27)

na not available; *nd* not determined

[a] As: European Council (2005), Pb: European Council (1999); (exceeded guidelines are indicated in bold)

[b] This study; total amounts of metal(loid)s in the air (ng/m^3) calculated from the <11 μm fraction for the PM_{10} concentration of 50 mg/m^3

[c] $n = 5$; concentrations in PM_{10} measured in five households in Kaňk (Rychlíková et al. 2015)

[d] $n = 3$; concentrations in PM_{10} measured in Kaňk (Sáňka et al. 2003)

the very low daily inhalation exposures of metal(loid)s with respect to the respective oral exposures: As (two orders of magnitude lower), Cu (three orders of magnitude lower), Pb (four orders of magnitude lower), Zn (usually five orders of magnitude lower) (Table 2). Table 3 reports the calculated total concentrations of metal(loid)s in the 11 μm dust fractions (assuming mine waste, soil, and road dust samples dispersed in the air generating a PM_{10} concentration of 50 $μg/m^3$) as well as comparisons with the guideline reference concentrations in the air. These data show that only arsenic exceeded the reference concentration limit (7–121×) for all three types of substrates. However, comparisons of the calculated concentrations with the measured concentration in the indoor and outdoor PM_{10} aerosols at Kaňk (Sáňka et al. 2003;

Rychlíková et al. 2015) revealed a significant overestimation (e.g., a hundred times higher for mine wastes, and twenty times higher for soil) of our calculated values. These indicate that As-rich substrates such as mine wastes and highly contaminated soils are not blown into the air and/or that the heavy As-bearing mineral phases preferentially remain in the parental substrates during eolian erosion.

Discussion

Distribution patterns of metal(loid)s

The Czech guideline values for soil As, Cu, Pb, and Zn at urban sites correspond to 70, 600, 300 and 2500 mg/

kg, respectively (Metodický pokyn MŽP 1996). In all of the samples collected from the historical mining village, arsenic exceeds the Czech guideline value by up to 2 orders of magnitude. As expected, the highest As concentrations were found in the mine wastes, but similar concentrations of As have been detected in the topsoils located on the surface of vegetated mine waste dumps as well as in the areas surrounding the mine waste dumps. In all of the samples, and in both size fractions, total As was substantially explained by Fe ($R^2 > 0.95$, $p < 0.001$) and S ($R^2 = 0.54$, $p < 0.001$), which reflects the contamination of the urban soil and road dust by sulfide- and sulfoarsenide-bearing mine wastes. This is in agreement with the observation of Horák and Hejcman (2016), who attributed As accumulation in the soils of the Kutná Hora ore district to the past mining activity. The dispersion of mine wastes into the soil was probably very high during the mining and processing period, but also continued to take place after the closure of the mines. The latter consideration is supported by the facts that: (1) the rate of revegetation of the bare mine waste dumps was slow, and some medieval waste dumps in the 40 and 50 s of the last century still only had a sparse vegetation cover (Kořan 1950; Bílek et al. 1965), and (2) environmental management with proper waste handling and disposal during urban development of the village has still not occurred. Arsenic mineralogy in the topsoil also supports the hypothesis of historical contamination by mine waste materials. Near-neutral soil samples contain minerals from the sulfide-rich mine waste, and some of the secondary mineral phases that have formed under acidic conditions of mine wastes, such as Fe(III) arsenates and minerals of the jarosite subgroup (Baron and Palmer 1996; Majzlan et al. 2012), display dissolution patterns and replacement by Ca–Fe arsenates and Fe (hydr)oxides (Fig. 2e, i) of the stable secondary As mineral phases under near-neutral conditions (Paktunc et al. 2015).

The concentrations of Cu, Pb, and Zn do not exceed the local regulatory levels in most of the mine waste or soil samples, and in none of the road dust samples. Similar concentrations of Cu, Pb, and Zn in the mine waste and top soil did not support the hypothesis that mining is the major source of the metals in the topsoil. In accordance with Horák and Hejcman (2016), their distribution in the topsoil was instead related to emissions from historic non-ferrous metal smelters.

Effect of geochemistry and mineralogy on bioaccessibility of contaminants in solution

The bioaccessibility of metal(loid)s in the samples have been reported in the range of <0.1–68%. The reasons for this wide range of these values may include differences in the metal(loid)'s speciation and mineralogy; additionally to the variability in other sample constituents, which may influence metal(loid) dissolution or precipitation in the gastric and lung solutions (Ruby et al. 1999).

In accordance with previous studies (e.g., Juhasz et al. 2007; Mikutta et al. 2014), the absolute bioaccessible gastric As was best predicted by total As ($R^2 = 0.84$, $p < 0.001$). Bioaccessible As was also positively correlated with the oxalate-extractable As and Fe concentrations ($R^2 = 0.77$, $p < 0.001$, and $R^2 = 0.74$, $p < 0.01$, respectively); implying that reactive Fe(III) arsenates and (hydr)oxides are the major source for soluble As in the gastric solution (Mikutta et al. 2014; Palumbo-Roe et al. 2015). Meunier et al. (2010), Kim et al. (2014) and Ollson et al. (2016) reported a wide range of gastric As bioaccessibility for mine-impacted samples that had different As mineralogy. In general, samples rich in As sulfides and scorodite displayed the lowest bioaccessibility percentages (up to 0.6%). The presence of Fe arsenates other than scorodite (e.g., amorphous ferric arsenate and kaňkite) and Fe (hydr)oxides increased the bioaccessibility to between 2 and 7%; but the highest percentage bioaccessibility (>20%) was attributed to the presence of Ca–Fe arsenates such as arseniosiderite ($Ca_3Fe_4(OH)_6(AsO_4)_4 \cdot 3H_2O$) and yukonite ($Ca_2Fe_3(AsO_4)_3(OH)_4 \cdot 4H_2O$). These findings are in accordance with our mineralogical observations and the relative As bioaccessibility values (between 4 and 13%) documented in the Kaňk mine waste, soil, and road dust samples. The lowest relative bioaccessibility was found in the mine waste samples (4–7%) that were rich in amorphous and reactive ferric arsenates and (hydr)oxides, and which also containing poorly-soluble scorodite and rarely arsenopyrite. The higher relative bioaccessibilities in mine waste samples 1 and 5 can be attributed to the presence of Ca–Fe arsenates that replace the assemblage of ferric arsenates, unstable under the near-neutral conditions of the soil. This could mean that the higher pH in the mine waste samples coincides with a greater fraction of As being bound to Ca–Fe arsenates and other mineral phases easily soluble in the low pH of a gastric solution. This

suggestion is supported by the positive correlation of the relative As bioaccessibilities and the pH of the mine waste samples ($R^2 = 0.94$, $p < 0.5$). A slightly lower positive correlation between pH and relative As bioaccessibility ($R^2 = 0.65$, $p < 0.5$) was found in the soil. The explanation for this relationship would be similar to that in the mine wastes, because high levels of As in the soil samples are bound in the mineral phases typical for the mine wastes. In the soil and road dust samples, with low amounts of arsenates and sulfides, chemical dissolution is probably limited by the slow dissolution kinetics of As-bearing Fe (hydr)oxides (Mikutta et al. 2014) and/or desorption of the surficially adsorbed As (Davis et al. 1996).

Corresponding to the As, bioaccessible concentrations of Cu and Zn in the simulated gastric solution strongly correlated with total and oxalate-soluble concentrations of the corresponding metal (Cu: $R^2 > 0.97$, $p < 0.001$, and Zn $R^2 > 0.99$, $p < 0.001$), implying that reactive Fe(III) (hydr)oxides are the major source for soluble Cu and Zn in the gastric solution. In contrast, bioaccessible Pb cannot be predicted by its total nor oxalate-soluble concentrations ($R^2 < 0.23$, $p < 0.05$). This is in accord with the finding that oxalate-insoluble minerals of the jarosite subgroup play an important role in the scavenging of Pb in mine wastes and soils contaminated by mine waste materials. The relatively large fractions of bioaccessible Cu, Pb, and Zn (Fig. 3a) observed in the samples cannot be explained by the complete dissolution of discrete Fe (hydr)oxides and jarosite because both phases display slow dissolution kinetics at the pH of the gastric solution (Beak et al. 2006; Smith et al. 2006; Mikutta et al. 2014). Thus, the data suggest that bioaccessible metals from our samples primarily originated from the dissolution of either the surface-bound metal fractions or from the exterior portion of individual metal-bearing mineral particles. High aqueous concentrations of metals in the gastric solution could then be controlled by their ineffective adsorption at low pH. This finding is supported by the fact that the order of bioaccessible metal concentrations in the samples (excluding the jarosite-bearing samples) decrease in accordance with the adsorption edge for Cu, Pb, and Zn onto Fe (hydr)oxides and hydroxosulfates (Webster et al. 1998). Significantly lower Pb bioaccessibilities in the samples rich in jarosite (i.e., mine wastes, and soil samples 8 and 9) suggest that the dissolution kinetic of Pb-bearing jarosite at low pH is significantly lower than for Fe (hydr)oxides.

Soluble As concentrations in the simulated lung solution correlated with the total As ($R^2 = 0.87$, $p < 0.01$), and displayed a relationship with both oxalate-extractable As ($R^2 = 0.92$, $p < 0.001$) and Fe ($R^2 = 0.72$, $p < 0.001$). The mineralogical differences among the substrates and individual samples of the <11 μm particle size fraction are relatively low, since the As is almost entirely bound to amorphous and poorly crystalline Fe (hydr)oxides (Table S1). These phases are stable and highly insoluble under the slightly alkaline conditions of Gamble's solution. Therefore, the chemical dissolution of As occurs particularly as a result of the desorption of surficially adsorbed As. Many studies have shown that even a low concentration of major anions may mobilize As from Fe (hydr)oxide-bearing soil by competitive desorption (Wenzel et al. 2001; Goh and Lim 2005; Frau et al. 2008). Goh and Lim (2005) found that a solution as dilute as 5 mM PO_4^{3-} could mobilize more than 45% of the As from the soil within 180 min. From the anions present in the Gamble's solution (112 mM Cl^-, 2 mM PO_4^{3-}, 1 mM SO_4^{2-}), phosphate would probably be the most efficient in extracting As from the different types of the samples because high chloride concentrations as well as similar sulfate concentrations have a negligible effect on the As(V) desorption reactions (Goh and Lim 2005; Frau et al. 2008).

The solubilities of the metals in the simulated lung solution were almost negligible, with the exception of the slightly higher solubility of Cu (Fig. 3b), indicating the efficient sorption of Pb and Zn onto Fe (hydr)oxides and other substrates at pH 7.4. This finding is supported by both Ettler et al. (2014) and Wiseman and Zereini (2014), who documented that Cu in the inhalable fraction is much more soluble than Pb and Zn in Gamble's solution. The bioaccessible Cu in the lung solution was positively correlated with bioaccessible Cu in the gastric fluids ($R^2 = 0.72$, $p < 0.01$), suggesting that a similar mechanism (i.e., adsorption/desorption reactions onto Fe (hydr)oxides) control the level of bioaccessible Cu in the lung solution.

Exposure estimates and implications for human health

The daily oral intake of As surpasses the Czech guidelines set for children and adults by up to 22 fold and sevenfold, respectively; thus highlighting the importance of foremost preventing the exposure of

children in the area to the uncovered mine wastes and highly contaminated urban soil (Fig. 4). The calculated contribution by aerosol inhalation to the total exposures is less important than is the contribution by dust ingestion (Table 2). Moreover, the remarkable overestimation of the calculated metal(loid) concentrations in the air, with respect to the measured concentrations of contaminants in the indoor and outdoor PM_{10} fraction of aerosols at Kaňk (Table 3), indicates that real daily inhalation intakes would be significantly lower than those calculated in Table 2. Therefore, inhalation is an almost negligible pathway when compared to ingestion, and it is unlikely that this exposure pathway would pose a higher non-carcinogenic risk than by ingestion. This matches the results of previous studies, which showed inhalation as a minor pathway when compared to the ingestion of mine waste, soil, or road dust (Zheng et al. 2010; Goix et al. 2016).

The results of a previous epidemiologic study at the same locality (Rychlíková et al. 2015) documented that the concentration of As in hair ranged from 0.05 to 3.77 μg/g (median 0.25 μg/g), with 85% of the samples similar to the normal concentration range for humans (0.02–1 μg/g) as reported by Hindmarsh et al. (1999). Total urinary As concentrations were below 50 μg/g creatinine (the legal standard in the Czech Republic; Vyhláška č. 432 2003), with the exception of two adults and one child out of a total of 39 respondents (Rychlíková et al. 2015). The median value of 10 μg/g creatinine found in that study was lower than the 27.9 μg/g creatinine reported by Gamiño-Guitérrez et al. (2013) in a Mexican urban area affected by historical mining, slightly higher than the 7.2 μg/g creatinine in the vicinity of mining sites in South Korea (Cho et al. 2013), and remarkably higher than the median of 3.5 μg/g creatinine in the general Czech population (Spěváčková et al. 2002).

It seems that the low As concentrations in aerosols, associated with the low As gastric bioaccessibility from different types of substrates, is one of the factors that might explain the surprisingly low level of As found in human hair and urine from the historical mining area at Kaňk observed in a recent epidemiological study (Rychlíková et al. 2015), despite As concentrations in mine waste, urban soil, and road dust greatly exceeding the guidelines. However, only outdoor substrates were collected, and people spend most of their time indoors in the

home environment or at their school or office. In this regard, a more detailed risk assessment study also including indoor dusts (Liu et al. 2016) and all potential pathways (ingestion, inhalation, dermal contact, and consumption of domestic food) for any area under study would be highly desirable. In this case, the results of a full risk analysis, including carcinogenic health risk assessment, should be discussed in conjunction with a deeper analysis of the local population's health status.

Conclusion

The findings of this study indicated that the historical mining village of Kaňk is highly contaminated by metal(loid)s (As, Cu, Pb, Zn), of which arsenic is the most significant contaminant. In vitro bioaccessibility leaching behavior in a simulated gastric fluid indicated that the bioaccessible fraction of arsenic was quite low in the mine wastes (∼5.1% of total concentration) and slightly higher in the road dusts (∼7.5%) and urban soils (∼8.2%). In contrast, the gastric bioaccessibility of metals (Cu, Pb, and Zn) was relatively high (17–47%) in all types of substrates, with the exception of Pb in the mine wastes (∼3.4%). The observed differences in gastric bioaccessibilities between these elements and the different types of samples are related to the differences in their mineralogical compositions. In contrast, differences in metal(loid) bioaccessibilities in the lung fluid are attributed to the variable effectiveness of different metal(loid) sorption onto Fe (hydr)oxides.

The obtained bioaccessibility data were used for the calculation of daily intakes of metal(loid)s, assuming oral and inhalation exposure pathways. The results indicated that the inhalation of dust particles is an insignificant exposure pathway compared with the oral pathway. Risk was only associated with mine waste and contaminated soil materials via oral exposures to arsenic (especially for children). Nevertheless, some factors might cause either an overestimation (use of only outdoor materials) or an underestimation (absence of other exposure pathways) of the potential human health effects. In order to intelligibly estimate the health risk, there is the need for further research of the exposure parameters and transport factors that would help reduce the uncertainties associated with the calculation of risk.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interests.

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