GeoHealth

Contaminant Binding and Bioaccessibility in the Dust From the Ni-Cu Mining/Smelting District of Selebi-Phikwe (Botswana)

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Abstract We studied the dust fractions of the smelting slag, mine tailings, and soil from the former Ni-Cu mining and processing district in Selebi-Phikwe (eastern Botswana). Multi-method chemical and mineralogical investigations were combined with oral bioaccessibility testing of the fine dust fractions (<48 and <10 μm) in a simulated gastric fluid to assess the potential risk of the intake of metal(loid)s contaminants. The total concentrations of the major contaminants varied significantly (Cu: 301–9,600 mg/kg, Ni: 850–7,000 mg/kg, Co: 48–791 mg/kg) but were generally higher in the finer dust fractions. The highest bioaccessible concentrations of Co, Cu, and Ni were found in the slag and mine tailing dusts, where these metals were mostly bound in sulfides (pentlandite, pyrrhotite, chalcopyrite). On the contrary, the soil dusts exhibited substantially lower bioaccessible fractions of these metals due to their binding in less soluble spinel-group oxides. The results indicate that slag dusts are assumed to be risk materials, especially when children are considered as a target group. Still, this exposure scenario seems unrealistic due to (a) the fencing of the former mine area and its inaccessibility to the local community and (b) the low proportion of the fine particles in the granulated slag dump and improbability of their transport by wind. The human health risk related to the incidental ingestion of the soil dust, the most accessible to the local population, seems to be quite limited in the Selebi-Phikwe area, even when a higher dust ingestion rate (280 mg/d) is considered.

Plain Language Summary The mining and processing of nickel-copper ores in Selebi-Phikwe (semi-arid east of Botswana) left a legacy of various waste materials (mine tailings, slags) and contaminated soils. This study examines the forms of inorganic contaminants and their gastric bioaccessibility (defined as their fraction, which is soluble under the simulated gastric conditions) in the fine dust fractions, which could be wind-eroded from the waste disposal sites or unvegetated topsoil. The bioaccessible concentrations of cobalt, copper, and nickel were higher for the slag and tailing dusts. In contrast, their bioaccessibility from the soil dusts was relatively low due to their binding in less soluble minerals. The exposure estimates were calculated for children and adults, assuming variable dust ingestion rates. Still, the daily intakes exceeded the guidelines only for the slag dust and, in the case of nickel, also for the tailing dust when children are considered as the target population. However, this exposure scenario seems improbable due to the fencing of the former mine area and its inaccessibility to the local community. Our findings demonstrate that the overall human health risk related to the contaminated dust ingestion seems quite limited in the Selebi-Phikwe area.

1. Introduction

Dust particles emitted from active and abandoned mining and ore processing sites cause soil and crop contamination (Ettler, 2016 and references therein) and represent a risk for the populations living in adjacent areas due to incidental dust ingestion and inhalation (Entwistle et al., 2019; Ghorbel et al., 2010; Landes et al., 2019; Li & McDonald-Gillespie, 2020; Morman & Plumlee, 2013; Plumlee & Morman, 2011; Thomas et al., 2018). This problem is especially accentuated in semi-arid or arid areas, where dust is generated in large amounts (Csavina et al., 2012; Ettler et al., 2019; Plumlee & Morman, 2011).

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Numerous in vitro bioaccessibility tests have been developed and validated using in vivo experiments to assess the health risks related to the transfer of contaminants due to dust ingestion/inhalation (e.g., Denys et al., 2012; Drexler & Brattin, 2007; Kastury et al., 2018; US EPA, 2007). They have been widely applied to indoor and outdoor dusts and soils in urban areas (Harvey et al., 2016; Patinha et al., 2015; Reis et al., 2018) or industrial areas affected by emissions from the mining and processing industries (Argyraki, 2014; Boisa et al., 2013; Ettler et al., 2018, 2019, 2020; Ghorbel et al., 2010; Pelfrêne & Douay, 2018; Pelfrêne et al., 2011; Reis et al., 2014; Thomas et al., 2018).

Whereas many bioaccessibility studies have been conducted in developed parts of the world, similar investigations are still relatively rare in the sub-Saharan Africa, where direct exposure to (contaminated) dust is expected to be significantly higher than in high-income countries. The high risks of metal(loid) contaminant intake through dust ingestion and inhalation have been demonstrated in pioneering biomonitoring and bioaccessibility studies from the ore mining and processing areas of DR Congo (Banza et al., 2009; Cheyns et al., 2014), Namibia (Ettler et al., 2019; Kříbek et al., 2014; Mapani et al., 2010; Nejeschlebová et al., 2015), Zambia (Ettler et al., 2012, 2014, 2020; Kříbek et al., 2019; Yabe et al., 2018) and Uganda (Mwesigye et al., 2016).

This study deals with dust fractions of waste materials and soil collected in and near the mining district of Selebi-Phikwe, located in the semi-arid east of Botswana, where Ni-Cu ores were mined and processed by a pyrometallurgical operation. Previous studies in this area were focused on the distribution of the metals in the soils and vegetation (Ekosse, 2005; Ekosse et al., 2003; Manyiwa et al., 2022; Motswaiso et al., 2019; Ultra & Manyiwa, 2021), and on the geochemistry, environmental impacts, and potential rehabilitation of the contaminated mine tailing sites (Schippers et al., 2007; Schwartz & kgomanyane, 2008; Sracek et al., 2018; Ultra, 2020; Ultra & Manyiwa, 2021). The human health issues in the Selebi-Phikwe area were only evaluated using the old statistical data from the 1990 s and the statistical processing of questionnaires acquired during the early 2000 s, when the mine and smelter were still in operation, and indicated that mine workers suffered from different symptoms and illnesses such as influenza, headaches, chest pain, and coughing (Asare & Darkoh, 2001; Ekosse, 2008). However, apart from the chemistry and mineralogy of the particulate air matter (Ekosse et al., 2004), the potential health effects of the contaminated dust dispersed from the mining and smelting area in Selebi-Phikwe, including a bioaccessibility investigation (considering the local inhabitants as the potential receptors), have never been studied. To fill this gap, we conducted a multi-method study on the contaminant-bearing dust materials from this site (slag, tailings, and soil) because we hypothesize that they can still represent a risk to human health even though the mine and smelter were closed in 2016. The specific objectives were to perform a detailed (geo)chemical and mineralogical characterization of the dust materials combined with an assessment of the potential risk of the dust ingestion and exposure to metal(loid) contaminants.

2. Materials and Methods

2.1. Site Description

The Selebi-Phikwe town is located in eastern Botswana (Figure 1). The climate corresponds to a mid-latitude steppe and desert climate subtype ("Bsh") according to the Köppen Climate Classification, with an average temperature of 21.5°C (warmest month: January; coldest month: July) and average precipitation of ∼410 mm (weatherbase.com). There is a strong seasonality when more than 90% of the precipitation falls in the period of November-March.

The Selebi-Phikwe Ni-Cu sulfide deposit is an Archean stratabound massive sulfide deposit associated with amphibolite host rocks, with pyrrhotite ($Fe_{1-x}S$), chalcopyrite ($CuFeS_2$), and pentlandite [$(Fe, Ni)_9S_8$] being the most important ore minerals (Baldock et al., 1976; Wakefield, 1976). The mining of sulfide Ni-Cu-Co ores started in 1973. In mid-October 2014, Norilsk Nikel of Russia sold its 85% interest in Tati Nickel Mining Co (Pty) Ltd. To the government-owned Bamangwato Concessions Ltd. (BCL), and the mine production significantly decreased due to the difficulty of mining at greater depths. The mining and ore processing operation closed in 2016 due to the high costs and reduced Cu prices on the world markets (Yager, 2019, 2021). Over 100 million tons of tailings and 45 million tons of metallurgical slag were left in the Selebi-Phikwe mine area (https://www.mmegi.bw/business/bcl-to-commission-p28bn-tailings-plant/news; Figure 1).
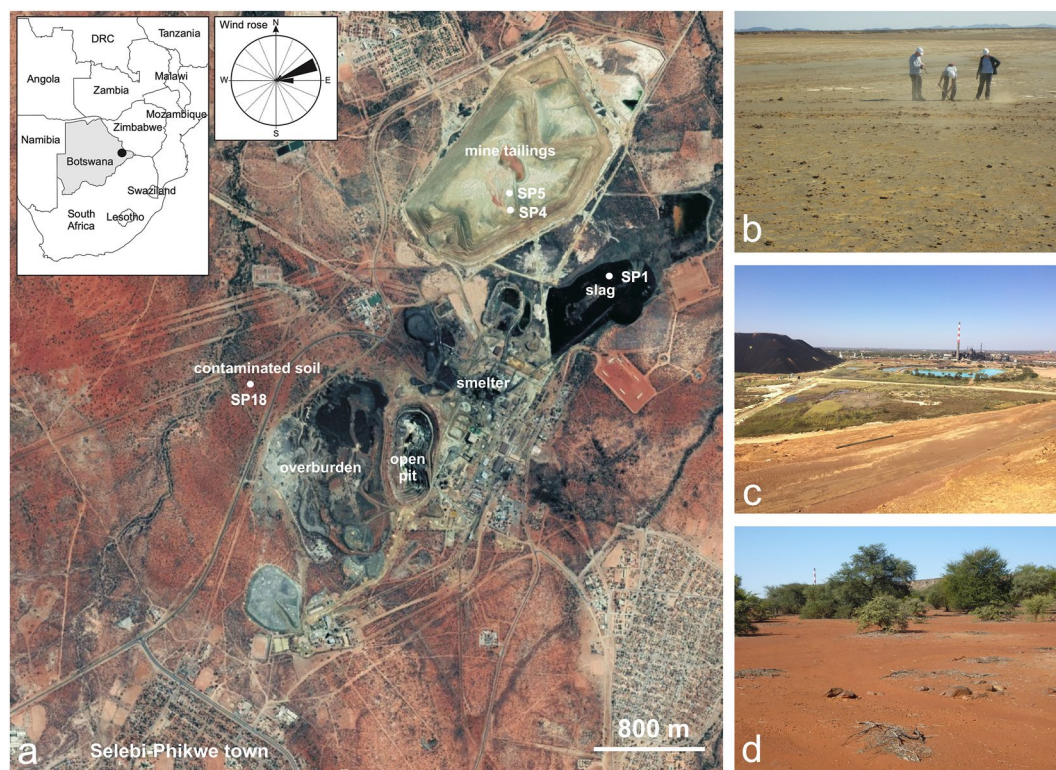
Figure 1. The Selebi-Phikwe mining and smelting area, northeastern Botswana. (a) Aerial view of the site (based on Google Earth™) with the location of the sampling points indicated by white dots and a wind rose (according to Meteoblue.com); photos showing the sampling areas on the surface of the tailings dams (b), on a granulated slag dump (c) near the former smelter, and in the contaminated soil downwind of the mining/smelting area (d).

2.2. Sample Collection and Processing

Composite grab samples of granular materials weighing up to 2 kg were collected in June 2017 using a plastic shovel at the following sites: granulated slag dump ($n = 1$; sample SP1), mine tailing dams ($n = 2$; samples SP4 and SP5), polluted soil downwind of the mine and smelter area, located in a pollution hotspot according to the contaminant spatial distribution performed by Motswaiso et al. (2019) ($n = 1$; sample SP18) (for location, GPS coordinates, and sample description see Table 1 and Figure 1). Each composite sample was prepared by blending subsamples taken on the edges and in the central point of a square 25 × 25 m in size (Kříbek et al., 2010). These samples were considered as representative contaminant-rich materials, which can be windblown. They could represent a risk of ingestion/inhalation for workers in the mine area and the nearby population (note the vicinity of the Selebi-Phikwe town in Figure 1). The Selebi-Phikwe mining town has a population of ~54,000 (2022 data; https://worldpopulationreview.com/countries/botswana-population). The local population is relatively young, with 70.5% of the inhabitants younger than 29 years in age and small children (0–4 years old) accounting for 12.2% of the inhabitants (Asare & Darkoh, 2001).

The samples were first sieved to <2 mm to remove large debris. The obtained samples were further sieved to obtain fine-grained fractions before the subsequent bioaccessibility testing in a simulated gastric fluid (SGF). The dust fractions <48 μm (corresponding to material vulnerable to accidental dust ingestion via hand-to-mouth transfer) and <10 μm (representing particles that can be inhaled and subsequently removed from the airways by clearance and swallowed) were obtained by dry sieving using polyamide sieves (details see below). The rationale for the selection of these particle size fractions for the bioaccessibility testing is given below in subchapter 2.4. The fraction <48 μm, determined by weighing, accounted for 1.5% (slag), 6.6%–9.5% (tailings) and 7.0% (soil) of the total sample mass. The fraction <10 μm corresponded to 0.4% (slag), 2.3%–4.8% (tailings) and 3.3% of the total sample mass.

Table 1
Chemical and Mineralogical Composition of the Dust Fractions From the Selebi-Phikwe Mining and Smelting Area

Code		SP1		SP4		SP5		SP18	
Type		Slag		Tailing		Tailing		Contaminated soil	
GPS coordinates		S21.93776, E27.86869		S21.93341, E27.86201		S21.93245, E27.86183		S21.94459, E27.84341	
Fraction		<48 μm	<10 μm	<48 μm	<10 μm	<48 μm	<10 μm	<48 μm	<10 μm
Chemistry									
Element	**Units**								
As	mg/kg	5.63	9.63	3.31	3.88	8.29	32.3	21.1	53.8
Cd	mg/kg	6.30	7.45	2.50	3.00	2.95	5.20	6.16	28.0
Co	mg/kg	791	738	47.7	62.1	64.8	134	134	162
Cr	mg/kg	426	405	250	329	286	441	123	171
Cu	mg/kg	5240	9600	301	565	1140	4110	3800	3810
Ni	mg/kg	3950	7000	850	1450	1200	3000	1570	2790
Pb	mg/kg	27.3	44.2	17.8	26.9	22.7	60.1	70.2	181
V	mg/kg	125	94.0	164	126	205	157	99.1	92.5
Zn	mg/kg	480	690	99.7	116	108	156	116	207
Mineralogy									
Phase	**Composition**								
Glass	Si-Ca-Fe-O	***	***						
Olivine	Fe_2SiO_4	**	**						
Mica/clay	Complex[a]	*	**	**	**	**	*	*	***
Quartz	SiO_2	tr	tr	*	tr	tr		tr	
Feldspar	Complex[b]			***	***	**	***	**	
Amphibole	Complex[c]			**	***	**	**	**	
Gypsum	$CaSO_4 \cdot 2H_2O$			tr	*	*	*		
Grossular	$Ca_3Al_2Si_3O_{12}$							*	*
Pentlandite	$(Fe,Ni)_9S_8$	*	tr						
Spinel	$(Fe,Ni)(Fe,Al,Cr)_2O_4$	*	*					tr	*
Hematite	Fe_2O_3							tr	*
Goethite	FeOOH	tr	tr					tr	tr
Jarosite	$KFe_3(SO_4)_2(OH)_6$							tr	tr

Note. Relative abundances of the phases were estimated according to the XRD patterns using the relative intensity ratio (RIR) method.
***abundant.**common.*minor, tr trace.[a]mainly corresponding to phlogopite [$KMg_3AlSi_3O_{10}(OH)_2$], kaolinite [$Al_2Si_2O_5(OH)_4$] and clinochlore [$(Mg,Fe)_5Al[AlSi_3O_{10}](OH)_8$]. [b]dominant proportion of anorthite ($CaAl_2Si_2O_8$). [c]corresponding to hornblende-group amphiboles, such as pargasite [$(Na,K)Ca_2(Mg)_4Al(Si_6Al_2O_{22})(OH)_2$].

2.3. Chemical and Mineralogical Investigations

Aliquots of <48 μm and <10 μm dust fractions were used to determine the bulk chemical compositions. A mass of 0.2 g was placed in a platinum (Pt) dish and heated in a muffle furnace to 450°C (Linn Elektro Therm GmbH, Germany; step: 1°C per min) to remove the organic matter. The obtained residue was dissolved in a mixture of 10 ml of HF (49% v/v) and 0.5 ml of $HClO_4$ (70% v/v) on a hot plate (130°C) and evaporated to near dryness. This procedure was repeated, and the residue was dissolved in 2% HNO_3 (v/v) and diluted to 100 mL before the analysis. The concentrations of As, Cd, Co, Cr, Cu, Ni, Pb, and Zn in the digests were determined using either inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 5110, USA) or inductively coupled plasma mass spectrometry (ICP-MS, ThermoScientific, iCAP-Q™, Germany).

The bulk mineralogy was determined by X-ray diffraction analysis (XRD) using a PANalytical X'Pert Pro diffractometer (PANalytical, the Netherlands) with an X'Celerator detector (CuKα radiation at 40 kV and 30 mA, 2 theta

range of 2–80°, a step of 0.02°, counting time of 150 s per step). The diffraction patterns were analyzed using the X'Pert High Score Plus 3.0 software coupled with the Crystallography Open Database (Gražulis et al., 2012).

Dust samples (fraction <48 μm) were prepared as polished sections and examined using an electron probe micro-analyzer (EPMA; JEOL JXA-8530F, Japan) equipped with a field emission gun electron source for the scanning electron microscopic (SEM) imaging and the energy dispersion spectroscopic (EDS) analyses (spectrometer JEOL JED-2300F). We used the same instrument for the quantitative chemical analyses of the individual minerals and phases. The analytical conditions, standards, and detection limits are given in Table S1 in Supporting Information S1. A Renishaw InVia Reflex Raman microspectrometer was used for the Raman spectroscopic analyses of the selected phases and minerals (50 × objective, laser spot diameter 2–3 μm, 514.5 nm argon laser, spectral range 100–1,600 cm^{-1}, spectral resolution <2 cm^{-1}, laser power of ~2 mW, 10 s exposure time, 1–5 accumulations). Spectral manipulations (baseline corrections) were performed using the GRAMS/AI spectroscopy software suite (9.1, Thermo Fisher Scientific Inc, Waltham, MA, USA).

2.4. Bioaccessibility Testing and Exposure Calculations

For investigation into the hand-to-mouth incidental soil ingestion, a <250-μm fraction has been traditionally used (e.g., Cave et al., 2011; Pelfrêne et al., 2011; US EPA, 2007). Based on a literature review by Ruby and Lowney (2012), the United Sates Environmental Protection Agency (US EPA) decided to lower the particle size fraction to <150 μm for the bioaccessibility testing (Test Method 1340; US EPA, 2017). However, other studies demonstrated that much smaller size fractions of the dust adhere to hands (e.g., Siciliano et al., 2009; Yamamoto et al., 2006), and it has been suggested that a ~45-μm sieve should be used as a cut-off mesh size for the sample preparation before the bioaccessibility testing in a SGF (Siciliano et al., 2009). Thus, we used a polyamide sieve with the closest nominal mesh of 48 μm (UHELON 120T, Silk & Progress, s.r.o, Brněnec) for the preparation of the <48 μm dust fraction. Moreover, the <10 μm fraction (PM10) of the dusts was obtained by dry sieving through a SEFAR NITEX 03–10/2 polyamide sieve (SEFAR AG, Switzerland; nominal mesh of 10 μm) to only obtain particles that could potentially enter the upper respiratory compartments. However, it is assumed that larger inhaled particles (2.5–10 μm) are cleared from the airways by the mucociliary escalator, swallowed, and transported into the gastrointestinal tract so that only particles <2.5 μm can access the deep lung (e.g., Kastury et al., 2017; Meza-Figueroa et al., 2020; Morman & Plumlee, 2013 and references therein). It is also known that the release of contaminants in a simulated lung fluid (SLF) is substantially lower compared to the highly acidic SGF, especially because of the near-neutral pH of the SLF (see, e.g., Ettler et al., 2014; Plumlee & Morman, 2011; Thomas et al., 2018). For this reason, we decided to perform oral bioaccessibility tests only, which correspond to the "worst-case scenario." The bioaccessibility extractions were carried out according to the experimental protocol called SBRC-G (gastric phase extraction using the Solubility Bioaccessibility Research Consortium assay) adopted by US EPA (2007, 2017). The sample was extracted in a 0.4 mol/L glycine solution adjusted to pH 1.5 ± 0.05 by HCl (reagent grade, Merck, Germany) at a liquid-to-solid (L/S) ratio of 100. The mixture was gently agitated for 1 hr at 37°C in a GFL 3032 incubator (GFL, Germany). All the extractions were performed in duplicate and with procedural blanks. The extracts were filtered through a 0.45-μm membrane filter (Millex-HV PVDF Durapore, Millipore, USA), diluted, and analyzed for As, Cd, Co, Cr, Cu, Ni, Pb, V, and Zn by a combination of ICP-OES and/or ICP-MS. The bioaccessible concentrations of the metal(loid)s were expressed in mg/kg and converted to a bioaccessible fraction (BAF; percent amount of the total contents).

The daily contaminant intakes have been calculated using the following equation:

$$DI = (BC/1000) * DIR \tag{1}$$

Where DI is the daily intake of the given contaminant (in μg/d), BC is the bioaccessible concentration obtained by the gastric bioaccessibility extraction test (in mg/kg), and DIR is the dust ingestion rate (in mg/d) and 1,000 is the unit conversion factor.

The exposure calculations were based on adults (weighing 70 kg) and children (weighing 10 kg, corresponding to a ~1 year-old child according to the US EPA, 2011) who are considered as potential targets in the Selebi-Phikwe area. Recent data from a mining district in the Democratic Republic of Congo (Smolders et al., 2019) reported that the daily dust intake generally used in this kind of exposure assessment corresponded to 50 mg/d for adults

and 100 mg/d for children (Bierkens et al., 2011; Ghorbel et al., 2010) is too conservative compared to the real situations in sub-Saharan Africa. Given the fact that Selebi-Phikwe corresponds to a semi-arid area with a higher dust generation potential, for the basic exposure estimates, we used the daily ingestion rates corresponding to (a) a conservative value of 100 mg/d and (b) 280 mg/d corresponding to the geometric mean obtained in a Congolese Katanga mining district by Smolders et al. (2019). Both these values have recently been adopted for exposure calculations in a highly polluted mining area of Kabwe, Zambia (Ettler et al., 2020).

For the sake of consistency with other studies, the obtained daily intakes of the metal(loid)s were compared to the tolerable daily intake (TDI) limits taken from Baars et al. (2001) and Tiesjema and Baars (2009) ($\mu g/kg_{bw}$/d): As (1), Cd (0.5), Co (1.4), Cr (5), Cu (140), Ni (50), Pb (3.6), V (2), Zn (500) (bw = body weight). This has been performed despite the fact that the European Food Safety Authority (EFSA) has recently lowered the TDI for Cd to 0.36 $\mu g/kg_{bw}$ (EFSA, 2009) and suggested that the provisional TDI limits for Pb (3.57 $\mu g/kg_{bw}$) and As (2.14 $\mu g/kg_{bw}$) are no longer appropriate (EFSA, 2010; EFSA, 2014a). For comparison purposes, we notice that the EFSA Panel on Contaminants in the Food Chain recently derived a TDI value of 2.8 $\mu g/kg_{bw}$/d for Ni (EFSA, 2015), which is substantially lower than those compiled by Baars et al. (2001). Moreover, the minimal risk levels defined by the US Agency for Toxic Substances and Disease Registry (ATSDR, 2022) were used for comparison purposes ($\mu g/kg_{bw}$/d, exposure duration): As (5, acute), Cd (0.5, acute), Co (10, intermediate), Cr(VI) (5, acute), Cu (10, acute), V (10, intermediate), Zn (300, intermediate).

2.5. Data Processing and QC/QA

The data were plotted using the Prism 9 (GraphPad, USA) and Graphic for Mac (Picta, USA) software packages. Certified reference materials (CRMs) were used to ensure the accuracy of the digestion procedure and the subsequent analysis of the digests and leachates. The SU-1b Nickel-Copper-Cobalt Ore ($n = 3$), certified by Natural Resources Canada (Canadian Certified Reference Materials Project), and the standard reference material (SRM) 2710a Montana I Soil ($n = 5$), released by the National Institute of Standards and Technology (NIST), USA, were used for the accuracy check of the bulk concentration determinations in the solid sample. The accuracy of the analytical determinations in the digests and extracts obtained from the bioaccessibility testing was controlled by the parallel analyses of SRM 1640a (Trace elements in natural water, NIST, USA; $n = 2$). We report the quality control/quality assurance (QC/QA) results in Table S2 in Supporting Information S1; they indicate good agreement between the measured and certified values.

3. Results

3.1. Dust Chemistry

Table 1 reports the total metal(loid) concentrations in the <48 and <10-μm fractions of the individual samples. As expected, the total concentrations of Cu (301–9,600 mg/kg), Ni (850–7,000 mg/kg), Cr (123–441 mg/kg), and Co (48–791 mg/kg) were substantially higher than those of As, Cd, Pb, and Zn, which ranged from units to lower hundreds of mg/kg (Table 1). The slag dusts were enriched in Co, Cu, Ni, Pb, V, and Zn as compared to other types of samples; in contrast, more volatile elements such as As and Cd were found in higher concentrations in the soils dust, probably due to downwind deposition of the historical smelter emissions (note that the Selebi-Phikwe smelter was closed in 2016) (Table 1). With a few exceptions (e.g., Co and Cr in slag dust and V in all the samples), the bulk concentrations of the metal(loid) contaminants are substantially higher in the finer dust fractions; a common phenomenon observed in other areas (Table 1; e.g., Ettler et al., 2019).

3.2. Dust Mineralogy and Solid Speciation of Metallic Contaminants

The mineralogical investigation indicated that there are substantial differences in the phase compositions of the three types of dust samples. The slag dusts are mainly composed of amorphous glass, olivine, and phyllosilicates with a trace to a minor proportion of spinel-group phases, pentlandite [(Fe, Ni)$_9$S$_8$], (windblown) quartz, and goethite (FeOOH), forming secondary weathering rims (Table 1; Figure 2). The SEM observations also indicated that pyrrhotite (Fe$_{1-x}$S) and complex Fe-Ni-Cu sulfides occur in the slag dust (Figure 2a). The tailings are composed of primary gangue silicates such as feldspar, amphibole, and phyllosilicates with trace amounts of quartz and gypsum (CaSO$_4$·2H$_2$O) (Table 1; Figures 2b–2d). According to the SEM observations, the
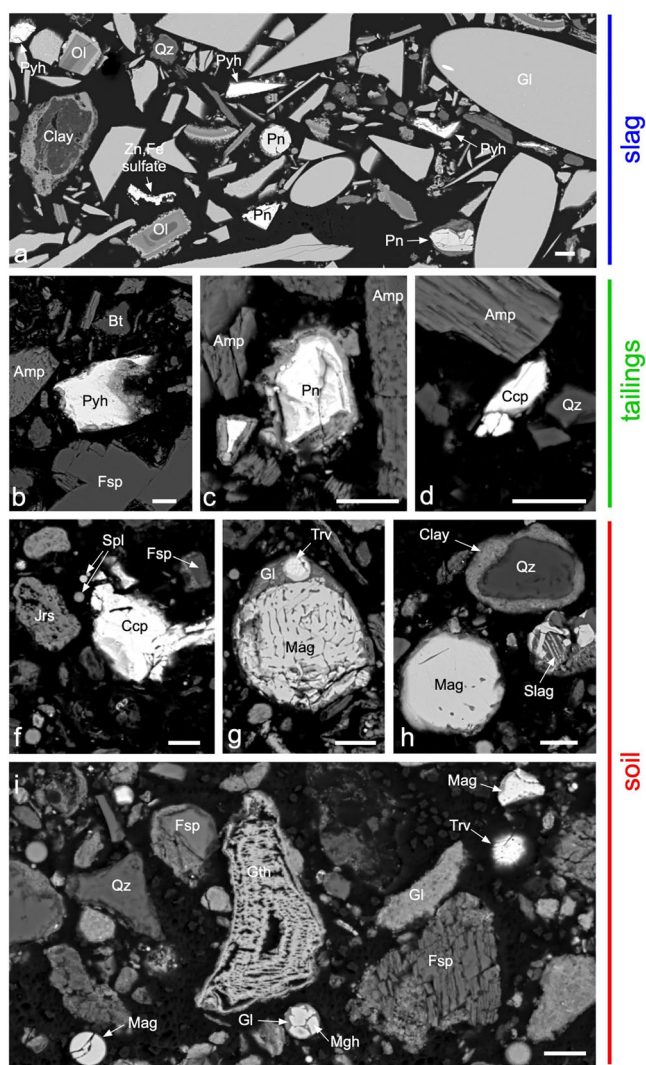
Figure 2. Scanning electron micrographs (SEM) in back-scattered electrons (BSEs) of the <48 µm fractions of the slag dust (a), tailings (b–d) and contaminated soil (f–i) (scale bar corresponds to 10 µm). (a) Slag glassy fragments of irregular shapes, some with crystals of olivine, crystallizing from the slag melt, associated with metal-bearing pentlandite and pyrrhotite grains, Zn, Fe-sulfate, and geogenic phases such as quartz and clay minerals; (b–d) Irregular grains of ore minerals (pyrrhotite, pentlandite, chalcopyrite) associated to the gangue minerals amphibole, biotite, feldspar and quartz in the mine tailing dusts; (f) Soil dust containing an irregular grain of the ore-derived chalcopyrite associated with pedogenic jarosite, geogenic feldspar and spherical spinel particles originating from the smelter emissions; (g) Spherical particle composed of magnetite, trevorite and glass derived from the smelter emissions; (h) Spherical magnetite and slag particles associated with geogenic quartz and clay mineral; (g) Grains of geogenic minerals (feldspar, quartz) and spherical and angular particles composed of magnetite, trevorite, maghemite, and slag-like glass and pedogenic goethite. Abbreviations: Amp—amphibole, Bt—biotite, Ccp—chalcopyrite, Fsp—feldspar, Gl—glass, Gth—goethite, Jrs—jarosite, Mag—magnetite, Mgh—maghemite, Ol—olivine, Pn—pentlandite, Pyh—pyrrhotite, Qz—quartz, Spl—spinel, Trv—trevorite.

residual sulfides in the tailings are pyrrhotite, pentlandite, and chalcopyrite ($CuFeS_2$) (Figures 2b–2d). The mineralogical composition of the soil dust is very complex and is, in the case of the major phases, different for the two granulometric fractions. Whereas the <48 µm fraction is mostly composed of silicates originating from the local geological environment (feldspar, amphibole, grossular, quartz), the <10 µm fraction contains predominantly phyllosilicates (Table 1). Both samples contain trace to minor proportions of Fe oxides and hydroxides (spinels, hematite [α-Fe_2O_3], goethite), and jarosite [$KFe_3(SO_4)_2(OH)_6$] (Table 1; Figures 2f–2i). The SEM observations also confirmed the occurrence of sulfides (chalcopyrite) originating from the crushed ore/tailings (Figure 2f). The rounded slag-like particles composed of glass and spinels (Figures 2g–2i) presumably resulted from the smelter emissions.

The electron probe microanalyses indicated that the key hosts of Cu and Ni are sulfides (Table S3 in Supporting Information S1). Moreover, Co was only detected in some of these sulfides, especially in pentlandite (0.17–1.65 wt%) in the tailing dusts and also rarely in the complex Fe-Ni-Cu sulfides reported from slag dusts (up to 0.33 wt%) (Table S3 in Supporting Information S1). Low concentrations of Ni were detected in geogenic amphiboles (tailing dusts; 0.03–0.07 wt.% NiO), but Ni and Cu are also present in the olivine-group phases in the slag dusts (0.11–0.22 wt% NiO; 0.03–0.06 wt% CuO) (Table S4 in Supporting Information S1). Oxides are particularly enriched in the contaminants. Spinel-group oxides are common in all the studied dusts and contain quite variable Ni contents. Whereas the magnetite-dominated spinels are generally Ni-poor (0.02–7.63 wt%), the trevorite-dominated spinels are Ni-rich (up to 68.00 wt% NiO) (Table S5 in Supporting Information S1). Nickel-bearing spinels are mostly observed in the soil dusts. The Cu concentrations in spinels are also quite elevated, especially in the soil dust samples (0.02–10.99 wt% CuO) (Table S5 in Supporting Information S1). Apart from spinels, other Fe oxides and oxyhydroxides such as hematite, goethite and maghemite (γ-Fe_2O_3) were distinguished by the Raman spectroscopy, especially in the soil dusts (Figures S1 in Supporting Information S1 and Figure 2). The EPMA indicated that some of them are also rich in Ni and Cu (e.g., up to 8.06 wt% NiO and 3.74 wt% CuO in maghemite; Table S6 in Supporting Information S1). Similarly, the glassy phase from the slag dusts and slag-like particles emitted from the smelter stack and deposited in the soil also contain some Ni (up to 3.32 wt% NiO) and Cu (up to 5.33 wt% CuO) (Table S6 in Supporting Information S1). Jarosite found in the soil dusts contains 0.1 wt% NiO and 0.51 wt% CuO (Table S6 in Supporting Information S1). Interestingly, no Co was detected in the silicate and oxide phases, and the Cr contents (apart from some spinels, e.g., hercynite, analysis SP1_76 in Table S5 in Supporting Information S1) were relatively low (<1 wt% Cr_2O_3). Zinc was not detected in any of the sulfides, oxides and silicates, but rare grains of Zn-rich sulfates similar to gunningite [(Zn,Mn)$SO_4 \cdot H_2O$] or goslarite ($ZnSO_4 \cdot 7H_2O$) were found in the slag dusts (Figure 2a; Table S6 in Supporting Information S1). Other studied contaminants, such as As, Cd, Pb, and V, occurring in the dusts in substantially lower concentrations, were not detected in any of the phases using the combination of SEM/EDS and EPMA.

3.3. Metal(loid) Bioaccessibility and Exposure Assessment

The bioaccessible concentrations of the metal(loid)s and BAFs in the studied dusts are reported in Table S7 in Supporting Information S1 and plotted for
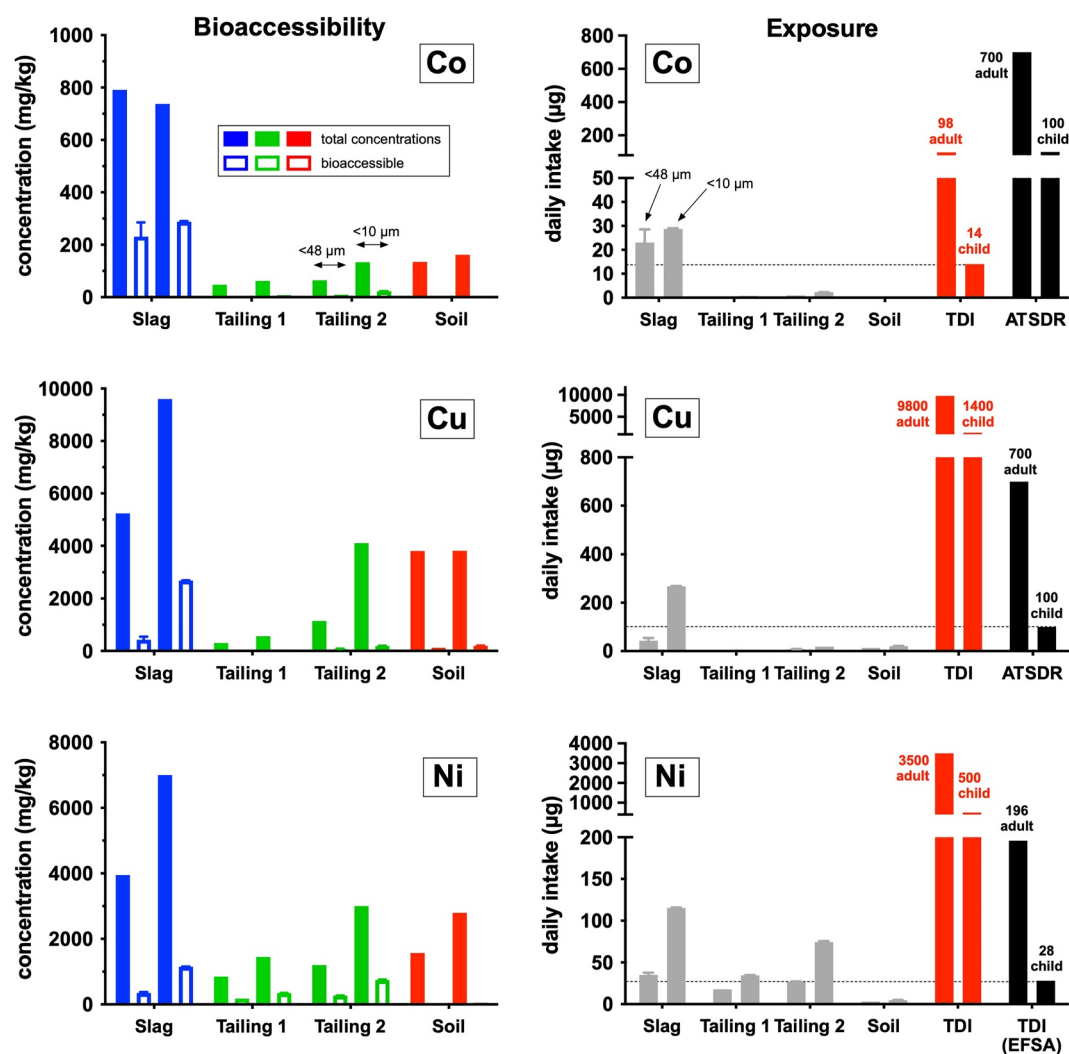
Figure 3. Total and bioaccessible concentrations and calculated daily intakes of Co, Cu, and Ni in μg/d, assuming a dust intake of 100 mg/d. Comparisons with the tolerable daily intake limits (μg/kg$_{bw}$/d) taken from Baars et al. (2001) (marked as TDI), European Food Safety Authority (marked as TDI(EFSA)), and the Agency for Toxic Substances and Disease Registry (2022; marked as ATSDR) are indicated for a 70-kg adult and a 10-kg child. Values obtained for the dust fractions <48 μm and <10 μm are plotted. The dotted lines in the right-hand panels correspond to the lowest regulation limit values calculated for children.

the major contaminants (Co, Cu, Ni) in Figure 3. The average bioaccessible concentrations are generally higher for the <10-μm fraction than for the <48-μm fraction, except for As in several samples (slag dust and tailing dust SP4), and Cr in the soil dust. For the slag samples, which are the most enriched in all the studied contaminants (except As and Cd) (Table 1), the bioaccessible concentrations are one order of magnitude higher than in the other dust samples (Table S7 in Supporting Information S1). Except for Ni, exhibiting the highest BAF values in the case of the tailing dusts (21.0%–24.9%), the BAF values for most of the metal(loid)s are substantially higher for the slag dusts when compared to the other sample types: As (8.4%–24.5%), Co (29.2%–39.0%), Cu (8.3%–28.0%), Pb (17.5%–22.3%), V (14.9%–28.3%), Zn (66.8%–73.8%).

Comparisons of the daily intakes of the individual contaminants with the limit values for two scenarios assuming dust intakes of 100 mg/d and 280 mg/d are reported in Table S8 in Supporting Information S1. Arsenic, Cd, Cr, Pb, V and Zn are far below the TDI limits. The data for the principal contaminants (Co, Cu, Ni), assuming the conservative dust intake of 100 mg/d, are plotted in Figure 3 and compared with the TDI and ATSDR limit values.

The daily intakes of Co exceeded the TDI value by 2.1 times only for children in the case of both granulometric fractions of the slag dust (Figure 3, Table S8 in Supporting Information S1). The daily intake of Cu exceeded the limit value calculated for children using the ATSDR data only in the case of the <10-μm fraction of the slag dust (2.7 times; Figure 3, Table S8 in Supporting Information S1). It is nevertheless important to note that the ATSDR limit value is substantially lower than the TDI value (10 and 140 $\mu g/kg_{bw}/d$, respectively, Table S8 in Supporting Information S1), which indicates that the daily intake limit for Cu would not be exceeded when the TDI value by Baars et al. (2001) is considered. In the case of the slag and tailing dusts (particularly the <10-μm fractions), the TDI value stipulated by the EFSA in 2015 is exceeded by up to 4.1 times if children are considered as the targets (Figure 3). When a higher dust ingestion rate is considered in the model calculations (i.e., 280 mg/d), the limit values calculated would also be exceeded even for adults in the case of Cu (slag dust <10 μm) and Ni (<10-μm fraction of the slag dust and tailing SP5) (Table S8 in Supporting Information S1). Surprisingly, in the case of the soil dusts, the daily intake of all the studied contaminants were far below the limit values, indicating that the health risk related to soil ingestion seems quite limited.

4. Discussion

4.1. Contaminant Solid-Phase Speciation and Relationship to Bioaccessibility

The bulk concentrations and especially the mineralogical forms of contaminants in the dust particles emitted from the active and former mining sites are the key determinants affecting their environmental fate, including the leaching in biofluids when incidental inhalation or ingestion are considered (Argyraki, 2014; Boisa et al., 2013; Bosso & Enzweiler, 2008; Ettler et al., 2018, 2020; Ettler & Kierczak, 2021; Lanteigne et al., 2012; Romero et al., 2008; Thomas et al., 2018; Vítková et al., 2010).

Many of the contaminants in the studied dust materials were found in relatively low concentrations (units to lower hundreds of mg/kg; e.g., As, Cd, Pb, V, Zn) and were not detected in any of the phases and minerals analyzed by the conventional mineralogical methods (SEM/EDS, EPMA). From these elements, only Zn exhibited elevated concentrations in the slag dusts (480–690 mg/kg) and was found in a relatively soluble form (Zn-bearing sulfate goslarite; Table S6 in Supporting Information S1), which was also probably responsible for the higher Zn bioaccessibility compared to the other dusts (BAFs in the slag dust: 57%–74%; BAFs in the other samples: 2%–16%) (Table S7 in Supporting Information S1).

The major contaminants in the studied dusts are thus Cu, Ni, and Co, but their concentrations vary as a function of the dust origin. In agreement with other studies dealing with slags and mining waste from Ni and Cu mining districts, Co exhibited elevated concentrations mainly in the slag dusts (up to 791 mg/kg), where it was only detected in various forms of sulfides. Similarly, Vítková et al. (2010) and Ettler et al. (2022) found that, in the slags from the Zambian Copperbelt, Co is hosted in cobalt pentlandite, $(Co,Fe,Ni)_9S_8$, and Fe sulfides (troilite, FeS or pyrrhotite). Cobalt-bearing pentlandite was also found in the emissions from the Ni-Cu mining and smelting of the Pechenga ores from the Kola Peninsula, Russia, by Gregurek et al. (1998). Our observations are not surprising because historical geological studies have indicated that ore-derived pentlandite is the key Co carrier in the Selebi-Phikwe mining district, with 2–3 wt% Co measured by an electron microprobe (Wakefield, 1976). Ettler et al. (2014) studied contaminant leaching from various smelter dusts. They found that significantly higher Co gastric bioaccessibility is typical for samples with Co-bearing sulfides, which are probably more reactive in the SGF than Co alloys. Given that Co was mostly detected in relatively non-weathered sulfide grains in slags, this may explain the substantially higher absolute and relative Co bioaccessibility from this type of dust compared to the other samples (Figure 3; Table S7 in Supporting Information S1). Sulfides occurring in various forms in all the studied dust samples are the main carriers for Ni and Cu (Figure 2; Table S3 in Supporting Information S1). This was also observed in the dust and soils from the Selebi-Phikwe area (Ekosse et al., 2003, 2004) and soils and waste materials from other similar mining sites such as Sudbury, Canada (Lanteigne et al., 2012), the Kola Peninsula, Russia (Gregurek et al., 1998) and the Zambian Copperbelt (Ettler et al., 2014, 2022; Vítková et al., 2010). Dutton et al. (2021) recently compared the Ni bioaccessibilities in soils with variable Ni mineralogy. They found that, in samples with pentlandite, a primary Ni carrier (79%–80% of the total Ni speciation) in some soils, the BAF values varied in the range of 24.9%–34.6% (Dutton et al., 2021). Similar BAFs were also observed for our tailing dusts, where sulfides are the dominant Ni-hosting phases (BAF: 21%–25%). Interestingly, a lower relative Ni bioaccessibility was found for the slag dusts (9%–17%) compared to the tailings despite the opposite trend observed for Co and similarities in the solid-phase speciation

of both these elements (Table S7 in Supporting Information S1). To explain this phenomenon, it would be useful to perform a quantitative mineralogical investigation and calculate the contaminant deportment within the individual phases of the dust materials using an automated SEM (e.g., Tuhý et al., 2020). It is nevertheless possible that the formation of Ni-bearing secondary phases, such as highly soluble Ni sulfates (e.g., Lau et al., 2022; Vasiluk et al., 2011), which were not found by our mineralogical investigations, might be responsible for the higher relative Ni bioaccessibility in the weathered tailing dusts (Figure 2a).

We assume that the relatively low Ni bioaccessibility in the soil dusts (1.8%–2.1%) originates from the different Ni speciation in the solid phase, which is dominated by oxides and hydroxides. The EPMA identified all these phases as important hosts of Ni (and Cu) (Tables S5 and S6 in Supporting Information S1). Iron spinels, such as magnetite, either crystallize from the slag melt or form metal-rich spheres emitted by the high-temperature industrial processes and deposited in the topsoils (Ettler et al., 2016; Gregurek et al., 1998; Kelepertzis et al., 2021; Lanteigne et al., 2012). Lanteigne et al. (2012) suggested that the transformation of magnetite derived from smelter emissions and deposited into soils occurs via the formation of maghemite, followed by its transformation to hematite under temperate climatic conditions. This process can also be accompanied by a partial release of the divalent cations, such as Co, Ni, Zn, and Cu, originally present in the magnetite structure. They also suggested that this phenomenon can explain why hematite is generally depleted in Cu and Ni relative to the primary magnetite (Lanteigne et al., 2012). All these primary and secondary Fe oxides were also detected in our soil dust samples, and we observed the same phenomenon: whereas magnetite can host up to 7.63 wt% NiO and 6.62 wt% CuO, the Ni and Cu concentrations in the secondary hematite decreased by half (Tables S5 and S6 in Supporting Information S1). In addition, the occurrence of Fe oxyhydroxides (goethite) and Fe oxysulfates (jarosite), which also contain some of these contaminants, is reported in our soils (Figure 2; Table S6 in Supporting Information S1). The presence of jarosite, a typical phase for the acidic environments of the Selebi-Phikwe tailings (Sracek et al., 2018), agrees with the high soil acidity (pH = 3.2) and high sulfur content (up to 0.45 wt%) (unpublished results). In contrast, goethite (Figure 2i) preferentially precipitates under slightly acidic-to-circumneutral conditions (Majzlan & Myneni, 2005), but there are indications that goethite can also form under acidic conditions with a pH around three in many mining-affected environments (Murad & Rojík, 2005; Sracek et al., 2018). Also, precipitated jarosite can be transformed to goethite during the process of aging and release co-precipitated and adsorbed contaminants (Baleeiro et al., 2018; Fukushi et al., 2003) relatively weakly bound as bidentate surface complexes (Gräfe et al., 2008). At Selebi Phikwe, large contents of Ni (up to 2,681.5 mg/kg) and especially Cu (up to 8,101 mg/kg) were found in jarosite in the sediments of the stream flowing from the base of the mine tailings (Sracek et al., 2018).

Very high Ni bioaccessibilities (32%–99%) were found in soils spiked with soluble Ni hydroxides and Ni sulfates, however, such species are scarce in mining- and smelter-affected environments (Dutton et al., 2021). Studies dealing with Ni smelter polluted soils, where Ni is mainly bound to various oxides phases, indicate much lower BAFs. For instance, in soils from Port Colborne, Ontario, Canada, polluted by a Ni refinery, Dutton et al. (2019) found Ni hosted in the form of NiO (bunsenite) and other oxidic phases (spinels). They demonstrated that the BAFs were relatively low and varied in the range of 5.8%–19%; moreover, it was generally lower in samples with a higher proportion of Ni-bearing spinels (Dutton et al., 2019). Vasiluk et al. (2011) also found that Ni is mainly bound to Fe oxides in smelter-affected soils from Sudbury, Canada. For both these Canadian sites, the relatively low Ni bioaccessibility was explained by the low solubility of the NiO and spinels in the acidic media. Moreover, even though metal oxides were generally supposed to be more soluble than sulfides in the SGF (e.g., Bosso & Enzweiler, 2008), many recent studies confirmed that even pedogenic Fe oxides (hematite) and oxyhydroxides (goethite) are relatively stable under these acidic conditions and were still detected in the residue after the extraction (e.g., Ettler et al., 2020). Thus, these facts clearly explain the relatively low Ni bioaccessibilities in our soil dusts (Figure 3; Table S8 in Supporting Information S1).

Geogenic phases also contain trace amounts of Ni (e.g., amphibole in tailings; up to 0.07 wt% NiO). Similar findings were reported by Vasiluk et al. (2019), who studied solid-phase speciation and Ni bioaccessibility in ultramafic soils, where Ni was suggested to be accommodated in the crystal structures of naturally occurring silicates and oxides. Both Ni and Cu are also found in the silicate glass and olivine in our slag dusts (Tables S4 and S6 in Supporting Information S1). However, recent comparative investigations of Ni bioaccessibility in soils with different Ni solid speciation indicate that the BAF fractions in soils where Ni is predominantly speciated in slag particles and silicates are quite low (0%–15%) due to their low solubility (Dutton et al., 2021) and this seems to be similar for our samples.

4.2. Exposure Estimates and Human Health Implications

Dust generated by mining and ore processing activities seriously impacts human health in mining communities (Entwistle et al., 2019; Ettler et al., 2020; Landes et al., 2019; Reis et al., 2014 and references therein). It is nevertheless important to stress that the toxicity of the studied metal(loid)s strikingly varies as also reflected by the definition of the risk levels. For instance, Cu and Zn are essential components of various enzymes and are toxic only at high levels (Goldhaber, 2003). Their importance in the biological function of organisms is also reflected by the relatively high TDIs (ATSDR, 2022; Baars et al., 2001; Goldhaber, 2003). In contrast, As, Cd, and Pb are known to be toxic elements with no biological function in living organisms (Jaishankar et al., 2014; Wu et al., 2016).

Our bioaccessibility data show that risk contaminants in the dust from the mining area of Selebi-Phikwe are not toxic elements like As, Cd, and Pb. The main risk contaminants are Co, Cu, and Ni, but the calculated daily intake of these elements remains relatively low (Table S8 in Supporting Information S1; Figure 3). Our results agree with the data from a Ni ore smelting area in Brazil, where similarly low risk for human health was observed due to the low bioaccessibility of the metals from the slag dusts and fly ashes generated by the Ni ore processing (Ettler et al., 2018). In Selebi-Phikwe, the most hazardous material seems to be slag dust (especially the finer dust fraction), for which some of the regulation limits were exceeded when a 10-kg child is considered as a target. However, this exposure scenario is improbable, given the fact that (a) the former mine and smelter area is fenced and inaccessible to the local population (direct contact with the slag material and the "hand-to-mouth" behavior, typical for children, is, thus, unlikely) and that (b) compared to the tailings and soils, the amount of dust from the slag dump, which can potentially be windblown and transported by air is substantially lower (4–6 times for the <48 µm fraction and 6 to 12 times for the <10 µm fraction; see the particle size distribution in chapter 2.2). Due to its higher density and larger particles, the granulated slag is often used to cover the mine tailing disposal sites to limit the dust dispersion in the mining areas such as Tsumeb in Namibia (see Ettler et al., 2019). Thus, we assume that the wind transport of the slag particles to more considerable distances is unlikely in the Selebi-Phikwe area. The "halo" of soil contamination located W-NW of the mine and smelter area recorded by Motswaiso et al. (2019) is likely caused by historical smelter emissions, which also corroborates our mineralogical data. For this reason, the soil dusts represent the material, to which the local population can be most exposed. Nevertheless, our data show that all the studied contaminants exhibit very low bioaccessibility in the soil dusts. Their intakes are far below the limit values even when a higher dust intake (280 mg/d) is considered. Based on our results, there seems to be limited human health risk in the Selebi-Phikwe area. However, a more complex exposure calculation using the human exposure assessment guidelines adopted by the US EPA (US EPA, 2019 and previous document versions), and successfully used in many mining areas worldwide (e.g., Reis et al., 2014), could be used to calculate the combined ingestion, inhalation, and dermal exposure. A more detailed and holistic approach via biological indicators (urine, blood) would be even better in the local community (like Banza et al., 2009 and Cheyns et al., 2014 conducted in the Co mining areas of Katanga in the DR Congo) and is needed to accurately determine the human exposure, and to assess the incidental dust ingestion and inhalation and to depict the role of food and water contamination as well.

5. Conclusions

The multi-method characterization and oral bioaccessibility testing of dusts (slag, tailings, soil) from the former Ni-Cu mining and smelting area in Selebi-Phikwe, eastern Botswana, showed large variability in the bulk concentrations and solid speciation of metal(loid) contaminants and their extractability in a SGF. The bioaccessibility of the major contaminants (Co, Cu, Ni) was higher for the finer dust fractions (<10 µm) and was strictly dependent on the bulk concentrations and the mineralogy of the dust samples. Higher bioaccessibilities were observed for the slag dusts and tailings, where the contaminants are primarily bound in sulfides, compared to the soils, where the major carriers for Ni and Cu are less soluble oxides (e.g., spinels). The exposure estimates indicate that slag dusts are the main risk materials (high Co, Cu, and Ni intake), especially when children are considered as the target population. However, given the fact that the waste disposal sites in former mine area are fenced, such an exposure scenario seems improbable. Even when calculating higher dust ingestion rates (280 mg/d), the human health risk related to incidental ingestion of the soil dust, which is the most accessible to the local community, seems quite limited.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The complete dataset related to this paper is present in the Supporting Information and is also freely accessible from the Research Gate repository: https://doi.org/10.13140/RG.2.2.23903.12961.

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