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Metal concentration and bioaccessibility in different particle sizes of dust and aerosols to refine metal exposure assessment

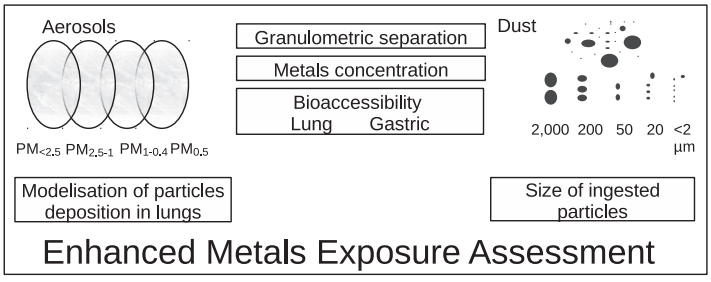
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HIGHLIGHTS

- Metal bioaccesibility and size distribution are different in smelting and mining area.
- Consider particles <50 μm to avoid underestimating exposure to children.
- Gastric bioaccessibility varies according to particle size but not linearly.
- Modelization of particles deposition in lungs refines exposure assessment.
- Contribution from oral or inhalation to internal exposures depends on the metal.

GRAPHICAL ABSTRACT



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ABSTRACT

Refined exposure assessments were realized for children, 7–9 yrs, in the mining/smelting city of Oruro, Bolivia. Aerosols ($PM_{>2.5}$, $PM_{1\text{-}2.5}$, $PM_{0.4\text{-}1}$ and $PM_{0.5}$) and dust (separated in different particle size fractions: 2000–200 μm, 200–50 μm, 50–20 μm, 20–2 μm and <2 μm) were sampled on football fields highly frequented by children in both the mining and smelting areas. Trace element concentrations (Ag, As, Cd, Cu, Pb, Sb, Sn and Zn) in each size fraction of dust and aerosols, lung bioaccessibility of metals in aerosols, and gastric bioaccessibility of metals in dust were measured. Exposure was assessed considering actual external exposure (*i.e.* exposure pathways: metals inhaled and ingested) and simulated internal exposure (*i.e.*, complex estimation using gastric and lung bioaccessibility, deposition and clearance of particles in lungs). Significant differences between external and simulated internal exposure were attributed to dissemblances in gastric and lung bioaccessibilities, as well as metal distribution within particle size range, revealing the importance of both parameters in exposure assessment.

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1. Introduction

Metals and metalloids are present in the environment both as natural compounds of the Earth's Crust and as anthropogenic con-

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taminants. Among human activities, mining and smelting play an important role in generating contaminated particulate matter (PM) and the transfer of trace elements (TE) [1]. Since numerous TE are known to be harmful, studying their sources, transference and potential human health effects in the vicinity of mining areas is of significant concern.

PM_{10} aerosols (*i.e.*, particles of diameter <10 μm) are used to assess inhalation exposure and are defined as the particle fractions that enter the respiratory tract and are usually subdivided in coarse ($PM_{10\text{-}2.5}$), fine ($PM_{2.5\text{-}0.1}$) and ultrafine particles ($PM_{0.1}$). Most epidemiological studies [2–4] have focused on PM_{10} and more recently on $PM_{2.5}$ as well [5–7]. Despite recent evidence of the health impact of ultrafine particles [8], almost no epidemiological studies have focused on this size fraction [9]. Existing guidelines for As, Cd and Pb in aerosols are given for PM_{10} [10–12] and consequently, numerous geochemical studies focus on TE concentrations in PM_{10} and $PM_{2.5}$ [13–16]. More recently, the impact on human health of metallic fine particles has been studied [17,18] highlighting the importance of fine metallic particles in metal exposure assessment.

Dust is defined as particles that have settled onto objects or surfaces due to either wet or dry deposition. Outdoor dust is often mixed with the uppermost surface layer of soil [19]. There are no environmental regulations about TE levels in dust, contrarily to their concentrations in agricultural or residential soils [20]. The sources of anthropogenic metallic particles in dust mainly encompass atmospheric depositions, contaminated soil erosion and/or direct anthropogenic inputs. For children, dust is a significant source of exposure to metals by ingestion due to hand-to-mouth behavior [19]. Particles that adhere to hands are <63 μm [21,22] in diameter, yet health risk calculations are based on soil samples sieved to <250 μm and there is little consideration of particle size in classic exposure assessment methodologies [23–26].

Metal bioaccessibility is defined as the total metal fraction that is accessible (or soluble) in the target organ, *i.e.* the gastro-intestinal tract for gastric bioaccessibility [27] and lungs for respiratory bioaccessibility. *In vitro* bioaccessibility is determined after the incubation of samples in solutions that mimic chemical conditions encountered successively in the human stomach and intestines [28], or in the lungs [29]. Metal bioaccessibility evaluation can thus be used to refine exposure assessment. One of the main *in vitro* methods for assessing the gastric bioaccessibility of inorganic elements (As, Cd and *Pb)* in soils is the Unified BARGE Method (UBM) [30] which was successfully benchmarked *versus in vivo* experiments [31]. To our knowledge, few studies have focused on metals bioavailability in different size fractions of contaminated soils [32–35]. Concerning lung bioaccessibility, there is no unified methodology, but most studies used Artificial Lysosomial Fluid (ALF) and Gamble solution to mimic cellular conditions and interstitial fluids between lung cells [29,36,37].

The present study focuses on the polymetallic mining city of Oruro (Bolivia), which has undergone intense research activity through the ANR ToxBol program around the sources and transfer of TE in the environment [13,38–41], and their impact on human health [42–46]. The city lies between a mining area in the west and a smelting area in the east. Oruro's aerosols and dust were previously shown to be highly contaminated with metal(loïds) related to mining and smelting activities (i.e., Ag, As, Cd, Cu, Pb, Sb, Sn and Zn). The present paper aims to (i) determine and discuss TE concentrations and distribution in different dust and aerosol particles size sampled in both the mining and smelting areas; (ii) study gastric and lung bioaccessibility of TE in different dust and aerosol particle sizes (iii) assess scenarios of health risk assessment for the Aymara-Quechua children population *via* dust ingestion and aerosols inhalation considering particle sizes, metal bioaccessibility and local conditions.

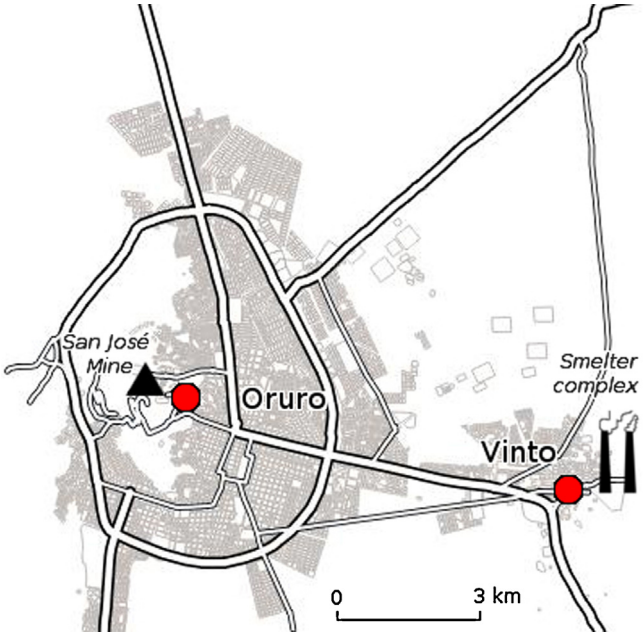


Fig. 1. Location of sampling points (red circles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Materials and methods

Table 1 describes analytical process for all samples.

2.1. Site description

Oruro is located on the Bolivian Altiplano (17° 58′ S-67° 06′ W) at 3750 m above sea level. Located on the "Bolivian Tin Belt", Oruro is one of the largest and oldest mining cities of Bolivia (250,000 inhabitants). The city lies around the San Pedro volcanic dome which hosts polymetallic ore deposits of Au, Ag, Cd, Cu, Pb, Sb, Sn, W and Zn [48] exploited from 2.5 t of Au up to 30,000 t per year of Zn [47]. Tailings accumulate on the southern (Itos tailings) and eastern (San José tailings) slopes. Eight kilometers east from downtown Oruro, Empresa Metalurgica Vinto (EMV) is the largest Sn-Sb smelter complex in Bolivia. It is in the immediate vicinity of Vinto agglomeration (30,000 inhabitants). The climate is cold and semi-arid with a short wet season (November-January). The environment is particularly dusty as a consequence of climate, strong substrate erosion due to wind and poor vegetation cover. More information on the study area is available elsewhere [13].

2.2. Sampling

Dust samples were taken from two football fields in the smelting zone (SmD sample, 17°S58′43.14″, 67°W2′43.454″) and in the mining zone (MinD sample, 17°S57′24.379″, 67°W7′20.834″, Fig. 1). Football fields were chosen because children often play here for several hours after school. Because of the high resuspension of dust during these kind of activities, it is thought to be a critical pathway for dust ingestion. At each location, a composite dust sample (center and side of the fields, at least a pool of 10 subsamples) was collected using a stainless steel spatula. Approximately 1000 g were sampled and stored in sealed polyethylene packaging to avoid contamination. Dust samples were dry-sieved on a 2000 μm nylon mesh before any analysis and will be referred as "bulk dust" in this study. Further analysis was done on bulk dust and on 5 granulometric fraction (2000–200 μm, 200–50 μm, 50–20 μm, 20–2 μm and

Table 1
Summary of all samples analysis.

Sampling area	Type	Sample	Granulometric separation		Physico-chemical composition		Distribution of particle sizes			Bioaccessbility			Exposure assessment	
			4 filters sampling	5 fractions from bulk (<2000 μm) (wet sieving/stokes law)	TE content (ICP-MS)	Mineralogy (X-Ray diffraction)	Dynamic light scattering (NanoZS zetasizer)	X-Ray difraction (Dusttrak)	Weighting	Gastric (UBM)	Lung (Gamble)	Lung (ALF)	External exposure	Simulated internal exposure
Smelting area	Aerosol	SmA	$PM_{>2.5}$ $PM_{2.5\text{-}1}$ $PM_{1\text{-}0.4}$ $PM_{0.5}$		All fractions		$PM_{0.5}$	TSP			$PM_{0.5}$	$PM_{0.5}$	E.exp.a	Si.exp.a
	Dust	SmD		2,000 200–50 50–20 20–2 <2 μm	All fractions + bulk	All fractions			All fractions + bulk	Bulk 200–50 50–20 20–2 <2 μm			E.exp.d	Si.exp.d
Mining area	Aerosol	MinA	$PM_{>2.5}$ $PM_{2.5\text{-}1}$ $PM_{1\text{-}0.4}$ $PM_{0.5}$		All fractions		$PM_{0.5}$	TSP			$PM_{0.5}$	$PM_{0.5}$	E.exp.a	Si.exp.a
	Dust	MinD		2000–200 200–50 50–20 20–2 <2 μm	All fractions + bulk	All fractions			All fractions + bulk	Bulk 200–50 50–20 20–2 <2 μm			E.exp.d	Si.exp.d

<2 μm). See supplementary material for granulometric separation methodology.

Aerosols were sampled from 23/06/2012 to 26/06/2012 by filtration and impaction for 48H (2 × 24H) on dust sampling zone at 2 m high (Fig. 1). Aerosols from mining and smelting area were named respectively MinA and SmA samples. An inertial cascade impactor (PM10 Dekati®) was operated at 10 L min^{-1} to collect $PM_{>2.5}$, $PM_{2.5\text{-}1}$, $PM_{1\text{-}0.4}$ on PVDF filters (Millipore®, 0.45 μm porosity and 47 mm diameter) and a high volume air sampler (Staplex®, TFIA series) was operated at 40 CFM (1133 L min^{-1}) to obtain $PM_{0.5}$ fraction in sufficient quantities for bioaccessibility tests on quartz fiber filters (TFAQ810 from Staplex®, 8"x10"). Filters were stored in a cool (4 °C) dark place with Merck desiccant until analyses.

2.3. Physical characterization

The granulometry of aerosols was measured by two complementary methods. A monitoring of the mass concentration of PM_{10}, $PM_{2.5}$ and PM_1 operated for 48 h using a Dusttrak 8533 (TSI) at both locations. The apparent hydrodynamic diameter and size distribution of ultrafine particles ($PM_{0.5}$) in ultrapure water after ultrasonics were measured by dynamic light scattering (DLS) using a NanoZS Zetasizer (Malvern Instruments—UK). For each suspension, the mean of 6 measurements was recorded.

Main minerals were identified in dust by powder X-ray diffraction (XRD) using CuKα radiation (λ = 1.788978 Å) on a X-ray goniometer (G3000, INEL). Bulk dust was finely crushed and analysed from 2° to 120° 2θ with a 0.02° step size.

2.4. Multi-elementary analysis

Dust samples (bulk and granulometric fractions) were crushed in an agate mortar. Dust was digested by microwave (Mars system, CEM) following USEPA analyses procedure 3052. Atmospheric particles deposited on filters were digested in PFA digestion vessels in 2 steps (cf Supplementary material) adapted from Goix et al. [13]. $PM_{0.5}$ filters were divided in 9 cm^2 sections to perform triplicates. Trace element (TE) concentrations were obtained by ICP-MS analyses (7500ce, Agilent Technologies) for dust and with a High Resolution ICP-MS (ELEMENT XR™, Thermo-Scientific) for aerosols. Both analyses were conducted using In and Re as internal standards. Quality control and measurement performance was checked using NIST SRM 2711a for dust and NIST SRM 1648 and CRM ERM CZ120 for aerosols.

2.5. Metal(loïd)s bioaccessibility

As, Cd, Pb, Sb, Sn and Zn gastric bioaccessibility was assessed using Unified Barge Method (UBM) on bulk dust (<2000 μm) and on the granulometric fractions 200–50 μm, 50–20 μm, 20–2 μm and <2 μm. This *in vitro* test was validated as a proxy of bioavailability [30] for As, Cd and Pb using mine waste and slag soils by comparison with an *in vivo* model of young swine. Recent studies extended UBM test to measure bioaccessibility of Cu, Sb and Zn in soils, vegetables or anthropogenic particles [17,49–51]. This procedure consists of consecutive steps of soil incubation in simulated human saliva and gastric juice (gastric bioaccessibility, 37 °C, 1 h) then in simulated bile and duodenal fluid (intestinal bioaccessibility, 37 °C, 4 h) fully described elsewhere [27,30]. Precipitates occurred in intestinal phase after centrifugation, preventing correct analysis. However, the two referent studies comparing *in vitro* UBM bioaccessibility and *in vivo* bioavailability showed that gastric bioaccessibility (GB) was a better proxy of bioavailability than intestinal bioaccessibility [30,52]. Thus, only GB was considered for this experiment and showed in the results. For each sample, 3–5 replicates were analysed to verify method repeatability. Analysis

was conducted using an ICP-MS (7700x, Agilent Technologies) and results were corrected by external calibration.

Lung bioaccessibility (LB) of TE in artificial lysosomal fluid (ALF, that mimic lung inflammation in harsh conditions) and simulated interstitial fluid within the deep lung (Gamble for pulmonary physiological condition) were prepared as listed in Supplementary material. Extraction consisted of intimate contact between PM filters and lung fluids with physiological conditions and for a given time. Solid/liquid ratio is critical: values 1/500 and 1/50,000 are acceptable physiological conditions allowing plausible inhalation scenario [29]. However, under 1/500, solutions could be saturated or could permit a competition between soluble elements. $PM_{0.5}$ filters (~516 cm^2) were divided in 36 cm^2 sections to get a minimal amount of 10 mg of PM and allow a ratio solid/liquid in between 1/500 and 1/5000. They were gently shaken with 20 mL of "lung fluids" in 50 mL tubes (Falcon) at 37 °C for 24H. The volume of lung fluids was chosen in accordance with physiological data for an adult [53]. Time of extraction was fixed at 24H to reach a maximum metal dissolution [29]. After extraction, solutions were filtrated at 0.45 μm before dilution and analysis by ICP-MS (7500ce, Agilent Technologies). Duplicate samples were prepared for each material in each artificial biological fluid. The accuracy of the analytical procedures was checked using the reference material ERM CZ 120 (PM-10 like).

2.6. Exposure assessments

Assessment of daily external exposures:

$$E.exp_d = (Ing\overline{R_d} \times \sum_{gf=<2\mu m}^{200\mu m} [C_{gf(outdoor)} \times MF_{gf<200}])/BW \quad (1)$$

$$E.exp_a = Inh\overline{R_a} \times \sum_{PM<0.5}^{PM>2.5} [C_{PM}]/BW \quad (2)$$

$$E.exp_t = E.exp_a + E.exp_d \quad (3)$$

where E.exp are daily external exposure assessment (ng kg^{-1} day^{-1}) for dust ingestion (d), aerosol inhalation (a) and both inhalation and ingestion (t). $IngR_d$ is the daily ingestion rate of dust (0.1 g day^{-1}, [19]), $InhR_a$ the daily inhalation rate of aerosols (m^3 day^{-1}, see Supplementary material), C_{gf} is the TE concentration in each granulometric fraction (ng g^{-1}), $MF_{gf<200}$ the massic percentage of each fraction in the <200 μm fraction, C_{PM} and C_{gf} the TE concentration in each aerosol fraction (ng m^{-3}) and dust fraction (ng g^{-1}) and BW the body weight considered (30 kg for 10 yrs old child [54]).

Assessment of daily simulated internal exposures:

$$SI.exp_{d(smelting\ area)} = (Ing\overline{R_d} \times \sum_{gf=<2\mu m}^{50\mu m} [C_{gf(outdoor)} \times GB_{gf} \times MF_{gf<50}])/BW \quad (4)$$

$$SI.exp_{d(mining\ area)} = \left[(0.5 \times Ing\overline{R_d} \times \sum_{gf=<2\mu m}^{50\mu m} [C_{gf(outdoor)} \times GB_{gf} \times MF_{gf<50}]) + (0.5 \times Ing\overline{R_d} \times C_{indoor} \times \sum_{gf=<2\mu m}^{50\mu m} [GB_{gf} \times MF_{gf<50}])\right]/BW \quad (5)$$

$$SI.exp_a = Inh\overline{R_a} \times \left[(GB_{<2} \times \sum_{PM<0.5}^{PM>2.5} [C_{PM} \times DFhead_{PM}]) + (LB \times \sum_{PM<0.5}^{PM>2.5} C_{PM} \times DFtrb_{PM}) + (GB_{<2} \times (1-LB) \times \sum_{PM<0.5}^{PM>2.5} [C_{PM} \times DFtrb_{PM}]) + \sum_{PM<0.5}^{PM>2.5} [C_{PM} \times DFpulm_{PM}]\right]/BW \quad (6)$$

$$Si.exp_t = Si.exp_a + Si.exp_d \quad (7)$$

where Si.exp are simulated as daily internal exposure assessments (ng kg^{-1} day^{-1}) for dust ingestion (d), aerosol inhalation (a) and both inhalation and ingestion (t). GB_{gf} is the gastric bioaccessibility in each granulometric fraction, LB is the lung bioaccessibility and DF is the deposited fraction of inhaled aerosols in the head, tracheobronchial and pulmonary region calculated with MPPD model v2.11 (see Supplementary material for details and numeric example).

All statistical analyses were carried out using the R statistical software 2.13.2.

3. Results and discussion

3.1. Chemical and physical properties of bulk dust and aerosols

3.1.1. Particles size distribution in dust and aerosols

The separation processes within dust samples are efficient as evidenced by the initial mass of the bulk dust compared to the sum of all fractions obtained (97–98%, Table 2). Losses can be attributed to mineral dissolution or mechanical loss during the different treatments (*e.g.*, centrifugation, sieving, quarting, drying). Dust from the mining area (MinD) is strictly sandy with 80% w/w of sands (2000–50 μm) and only 7% w/w of clay (<2 μm). Dust from the smelting area (SmD) has a sandy-clay texture with 56% w/w of sands and 15% w/w of clay. These sandy textures could be explained by possible anthropogenic origin as the football fields in Oruro can be partly composed by non-local building material.

The granulometric partition of Total Suspended Matter (TSP) measured by Dust Trak 8533 is stable over time, with PM_{10}, $PM_{2.5}$ and PM_1 contributing to TSP at 72 ± 10%, 42% ± 15% and 41% ± 15% respectively in the smelting area and 71 ± 8%, 33% ± 13% and 31% ± 13% respectively in the mining area. For both sampling sites, 2 peaks of higher particle concentration were observed during sampling days: (i) between the beginning of the sampling (~08:30) and 10:00 and (ii) between 17:00 and the end of the sampling (~18:00) which corresponds to the peaks of road traffic intensity. Granulometric analysis of ultrafine particles ($PM_{0.5}$ filters) indicate bimodal distributions, with a first mode at ~100 nm (100 nm for MinA and 80 nm for SmA) and a second mode at ~250 nm for both stations. Peak at 100 nm is higher in MinA than in the SmA (80% *vs* 60% of total particles respectively) whereas the peak at 250 nm is higher in SmA than in MinA (40% *vs* 20% of total particles respectively).

3.1.2. Trace elements concentrations

3.1.2.1. Dust. All TE elements are more concentrated in SmD than in MinD (Table 2). As, Cd, Cu, Pb, Sn and Zn concentrations in SmD bulk dust exceed Canadian guidelines for residential soils. Pb concentration reach 16,000 μg g^{-1} for a guideline at 140 ng g^{-1} and is higher than all other published values of Pb content in topsoils in the Vinto smelting area [55,56]. In MinD bulk dust, only As and Pb concentrations exceed guidelines.

The finer the granulometric fraction is, the greater TE concentrations are, with the exception of coarse sand, which is more enriched in TE than fine sand in both samples (Table 2). Such observation is attributed to the presence of residual fine particles in the coarse fractions. This hypothesis is confirmed by observation of illite in XRD patterns of coarse sand fractions. The geometric mean of indoor dust TE content [41] is 2–10 times higher than in MinD bulk dust. As the sampling methodology used for indoor dust collection was different from our sampling method (fine settled dust collected on top surfaces of furniture or windowsills with a clean brush), we hypothesized that indoor dust was exempt of coarse particles less enriched in TE. Indeed, TE concentrations in indoor

Table 2
Concentrations of major and trace elements in $\mu g\,g^{-1}$ in dust for bulk and granulometric fractions.

Site	Granulometric fraction	Size distribution (massic %)	Concentrations in $\mu g\,g^{-1}$ (gastric bioaccessibility in %)							
			As	Cd	Cu	Pb	Sb	Sn	W	Zn
Guideline[a]			12	10	63	140		50		200
Indoor dust in Oruro mining area (<50 μm)[b]			**90**	**11**	**89**	**619**	153	**76**		**443**
Smelting dust (SmD)		15%	**1060 (29)**	**66.3 (76)**	**1570 (84)**	**39503 (61)**	7863 (2)	**1173 (0.2)**	13.1	**3640 (63)**
	<2 μm	15%	**866 (13)**	**35.7 (36)**	**1064 (18)**	**24749 (27)**	7848 (2)	**1231 (0.3)**	15.0	**3811 (9)**
	2–20 μm	10%	**496 (25)**	**14.7 (70)**	**397 (43)**	**12302 (59)**	4683 (5)	**1126 (2)**	12.5	**2001 (25)**
	20–50 μm	33%	**182 (41)**	**6.5 (92)**	**185 (58)**	**5297 (77)**	1666 (6)	**212 (2)**	3.3	**678 (31)**
	50–200 μm	23%	**306**	**14.8**	**332**	**10291**	2121	**184**	3.9	**770**
	2000–200 μm	97%	**500 (30)**	**21.6 (86)**	**570 (72)**	**16000 (62)**	4210 (4)	**614 (1)**	8.5	**1746 (42)**
	Bulk (<2000 μm)									
Mining dust (MinD)		7%	**126 (14)**	7.1 **(86)**	**87 (21)**	**1004 (18)**	67 (1)	43 (0.4)	2.7	**515 (35)**
	<2 μm	6%	**79 (19)**	4.8 (82)	56 **(22)**	**645 (21)**	57 (1)	30 (1.2)	4.6	**252 (31)**
	2–20 μm	4%	**46 (12)**	1.5 (50)	26 **(6)**	**288 (15)**	36 (1)	18 (0.8)	5.9	116 (15)
	20–50 μm	33%	**30 (18)**	0.6 (73)	19 **(8)**	**168 (19)**	15 (2)	4 (4.7)	1.3	63 (23)
	50–200 μm	47%	**82**	1.2	19	**525**	48	11	2.1	100
	2000–200 μm	98%	**55 (15)**	1.7 (84)	18 **(33)**	**434 (13)**	34 (2)	12 (0.9)	1.9	118 (37)
	Bulk (<2000 μm)									

[a] Canadian guidelines for residential soils (exceeded guidelines are indicated in bold).
[b] Fonturbel et al. [41].

dust were close to TE MinD concentrations in fine loam and clay fractions (Table 2). We will thus assume indoor dust as <50 μm fraction in exposure assessment in the mining area.

3.1.2.2. Aerosols. TE concentrations in SmA and MinA are presented in Table 3. Triplicates of $PM_{0.5}$ show a good reproducibility (SD < 10%). TE concentrations in $PM_{2.5}$ (calculated as the sum of all size fractions of diameter inferior to 2.5 μm) vary from 0.22 to 334 ng m-3 in the following order: W < Ag < Cd < As ~ Cu ~ Sb ~ Pb < Sn < Zn in both areas. All TE contents are higher in SmA than in MinA. $PM_{2.5}$ As concentrations in both areas and Cd in SmA exceed PM_{10} air quality guidelines ($p < 0.05$) determined by WHO and European council [10,11]. Cd concentration in MinA $PM_{2.5}$ ($p = 0.008$) and Pb $PM_{2.5}$ concentrations in both areas ($p < 0.05$) are below the PM_{10} guidelines.

When comparing $PM_{2.5}$ TE concentrations calculated in the present study (sampling in 2012) with those calculated for a previous sampling (2008) [57] in the mining area, there are no differences between the two studies for the levels of Ag, As and Cd. Sb concentration was higher in 2008 ($p < 0.01$) whereas Pb and Zn concentrations were higher in 2012 ($p < 0.05$). This is surprising given the encapsulation of San José mining waste that took place in 2009 and was supposed to limit reemission of tailing particles in the atmosphere. In the smelting area, there were no statistical differences for Pb and Sb, but other TE concentrations were 2–8 times higher in 2012 than in 2008 ($p < 0.05$). This increase of metal(loïd) in the air of the smelting area could be related to the increase of tin production by EMV from ~9500 t in 2008 to ~12,000 t from 2009 to 2012 owing to the company's reactivation of at least one older rotary furnace, a reverberatory furnace, and an increase in the supply of tin concentrates [58].

TE concentrations ($ng\,m^{-3}$) increase when PM diameter decreases. Despite $PM_{2.5}$ only represent 33–41% of TSP in weight, their metallic concentrations represents 73% to 97% of the contents in TSP. This highlights the presence in TSP of particles of a diameter greater than 2.5 μm which are not metallic-rich, in both areas (*i.e.* terrigenous particles). In both areas, $PM_{0.5}$ contributed 60% to 80% of total element concentrations in TSP, except for Sn, Zn (~45%), and W (~15%) in the mining area which are mainly present in the 2.5–0.5 μm fraction. These particles could originate from residual tailings and contaminated dome erosion in the vicinity of the mine as previously shown [13].

3.1.3. Trace element bioaccessibility

3.1.3.1. Gastric bioaccessibility of TE in dust. Gastric bioaccessibility (GB) was measured in bulk dust and in each size fraction of both mining and smelting dust. In MinD bulk dust, GB varies from the most to the least bioaccessible element: Cd > Zn > Cu > As > Pb > Sb ~ Sn whereas in SmD bulk dust, GB ranges as: Cd > Cu > Pb > Zn > As > Sb ~ Sn (Fig. 2). Cd, Sb, Sn and Zn bioaccessibility are almost equal in the two areas (respectively ~85%, <5%, <5% and ~40%). For As, Cu and Pb, GB is higher in SmD than in MinD. The highest range is observed for Pb with 62% GB in the SmD compared with 13% GB in the MinD. These results are in agreement with previous GB assays on soils giving a range of 5–25% for As, 24–86% for Cd, 12–51% for Cu, 12–60% for Pb, 1.5–12% for Sb and 6.9–68.5% for Zn [30,50,59]. More specifically, Cd exhibits similar GB in both samples whereas a previous study showed significant lower cadmium GB in mining (average of 36%) than in smelting (average of 65%) soils [52].

Concerning size influence over GB, the smelting dust exhibits the same pattern for all elements, with a diminution of GB when particles diameter decreases between 200 and 2 μm and an increase of GB in the finest fraction. SmD shows a maximum GB in the 50–200 μm fraction for As, Cd, Pb, Sb and Sn whereas Cu and Zn are more bioaccessible in the finest fraction (Fig. 2). Maximum gaps

Table 3
Trace elements concentrations (±SD) in the different granulometric fractions of aerosols.

Site	Granulometric fractions	Average concentrations (ng m^{-3})								
		Ag	As	Cd	Cu	Pb	Sb	Sn	W	Zn
Guidelines	<10 μm		6[a]	5[b]		500[b]				
Oruro mining district aerosols (2008) [57]	PM_{10}	2.2 ± 1.1	65 ± 23	3.3 ± 1.2		118 ± 56	140 ± 44			75 ± 30
	$PM_{2.5}$	0.8 ± 0.5	**21 ± 8**	1.7 ± 0.9		39 ± 21	65 ± 27			38 ± 17
Mining area aerosols (MinA, 2012) This study	<0.5 μm	0.83 ± 0.03	**15.8 ± 2.3**	0.91 ± 0.03	32.2 ± 6.6	47.5 ± 2.2	9.9 ± 1.2	7.95 ± 1.19	0.04	90.5 ± 22.2
	0.4–1 μm	0.10	2.9	0.24	5.2	6.5	1.3	1.29	0.10	27.8
	1–2.5 μm	0.06 ± 0.05	2.8	0.12 ± 0.06	4.8 ± 1.3	13.3 ± 2.4	1.0 ± 0.4	1.01 ± 0.42	0.08 ± 0.09	26.8
	>2.5 μm	0.07 ± 0.02	5.2	0.06 ± 0.02	1.5 ± 0.9	5.3 ± 1.2	0.8 ± 0.2	0.76 ± 0.19	0.04 ± 0.02	51.1
	$PM_{2.5}$[d]	0.99	**21.5**	1.28	42.2	67.2	12.2	15.21	0.22	145.0
Oruro smelting district aerosols (2008) [57]	PM_{10}	1.8 ± 1.0	**259 ± 114**	**6.3 ± 2.1**		46 ± 24	215 ± 107			99 ± 41
	$PM_{2.5}$	0.6 ± 0.4	**82 ± 38**	3.3 ± 1.2		137 ± 64	101 ± 59			50 ± 24
Smelting area aerosols (SmA, 2012) This study	<0.5 μm	4.26 ± 0.35	**128.8 ± 10.5**	**5.20 ± 0.33**	88.2 ± 2.4	145.1 ± 14.4	114.3 ± 9.3	210.9 ± 52.6	0.93	228.2 ± 19.2
	0.4–1 μm	0.23	**37.0**	2.96	8.4	22.6	28.9	88.6	0.08	75.5
	1–2.5 μm	0.20 ± 0.05	**21.6 ± 6.3**	0.38 ± 0.03	6.4 ± 1.4	15.9 ± 1.9	15.2 ± 5.6	17.4 ± 1.6	0.09 ± 0.00	30.6 ± 7.6
	>2.5 μm	0.57 ± 0.28	5.3 ± 2.9	0.18 ± 0.08	4.4 ± 1.0	27.4 ± 10.5	13.4 ± 1.6	17.1 ± 1.6	0.33 ± 0.03	24.0 ± 9.6
	$PM_{2.5}$[c]	4.70	**187.4**	8.54	103.1	183.6	158.4	316.9	1.09	334.3

[a] [11].
[b] [12].
[c] $PM_{2.5} = PM_{1-2.5} + PM_{0.4-1} + PM_{0.5}$.

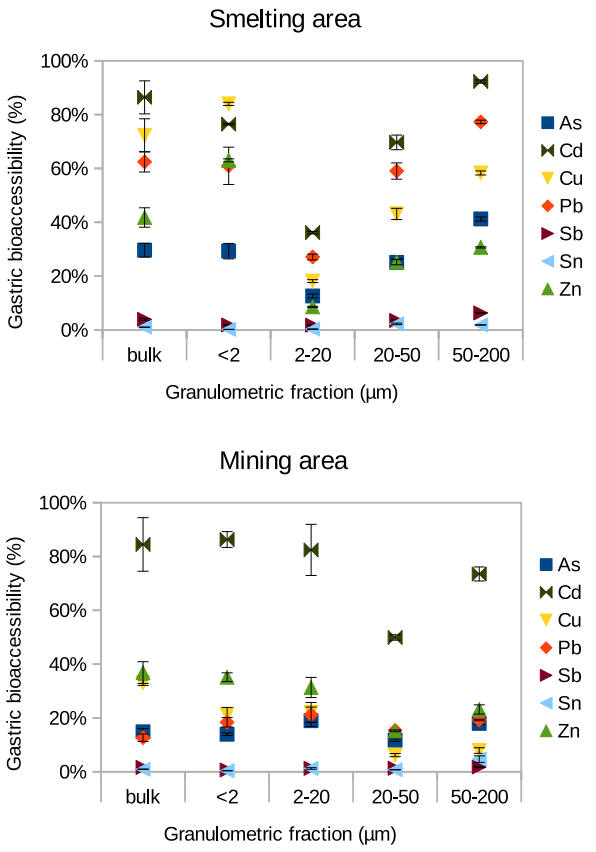


Fig. 2. Gastric bioaccessibility ± SD of TE in different dust granulometric fractions.

in values of bioaccessibility between the different granulometric fractions of SmD varied from 66% for Cu to 2% for Sn. The mining dust exhibits the same GB pattern for all TE, with a minimum of GB in the 20–50 μm fraction. The highest GB for all TE elements are found in the 2–20 μm and the <2 μm fractions, both fractions presenting similar results. Gap in values of GB among the granulometric fractions in MinD is maximal for Cu (36% between 2 and 20 and 20–50 μm fraction).

Previous studies have shown that TE bioaccessibility in soil was mainly controlled by total content and the granulometric properties of the soil [60,61]. In our work on dust, there are no correlations between concentration and bioaccessibility among the granulometric fractions of a single sample ($R^2 < 0.1$ for all TE). GB among granulometric fractions appears to be controlled by the element's physical and chemical speciation, (*i.e.*, its valence state, its adsorption onto clay minerals, oxides, or its presence as a constituent of minerals) and not by its concentration. According to published data, the smelting process seems to increase the GB of several metals, especially for Ac, Cd and Pb [52], highlighting the control of metal speciation on its GB.

3.1.3.2. Lung bioaccessibility of TE in aerosols. TE lung bioaccessibility in ALF and Gamble solutions (LB_{ALF} and LB_{Gamble}) in $PM_{0.5}$ were measured on both MinA and SmA (Fig. 3). In MinA, LB_{ALF} of the different elements varies from 1% to 74% in the following order: Ag < Sn < Sb ~ Pb < Zn < Cd < Cu < As whereas in SmA, LB_{ALF} varies from 1% to 97% in the following order: Ag < Sn < Cu ~ Sb < Zn < Pb ~ Cd < As. Except for Ag and Cu, LB_{ALF} is higher in the smelting than in the mining area (+23% ±3% for As, Cd, Sb, Sn and Zn; +39% for Pb, ~0% for Ag and −13% for Cu). In MinA, LB_{Gamble} varies from <limit of detection to 44% in the following order: Pb < Zn < Sb < Cd < As ~ Cu whereas in SmA, LB_{Gamble} varies from <limit of detection to 73% in the following order:

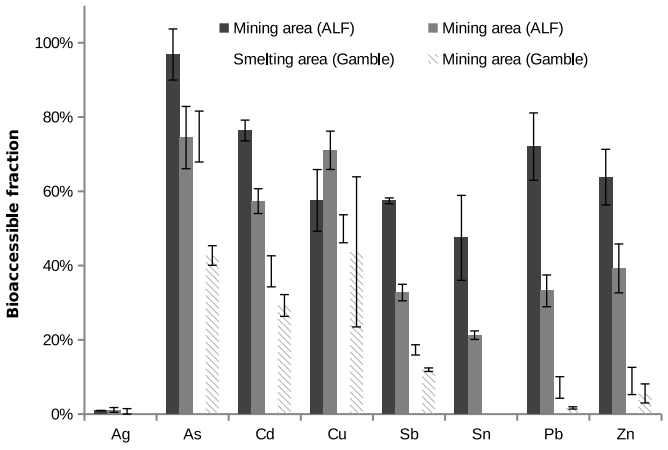


Fig. 3. Lung bioaccessibility (+/− SD) of metal(loïds) in $PM_{0.5}$ in artificial lysosomial fluid (ALF) and simulated interstitial fluid within the deep lung (Gamble).

Ag < Pb ~ Zn < Sb < Cd < Cu < As. In the same way, LB_{Gamble} is higher in the smelting than in the mining area': +6% ±2% for Cd, Cu, Sb, Pb, Zn and +32% for As. Differences between LB in mining and smelting aerosols are attributed to the physico-chemical speciation of TE as the granulometric distribution of particles is similar in both areas.

TE LB_{ALF} is systematically higher than LB_{Gamble} for both areas, except for Ag which is not bioaccessible whatever fluid is considered. InMinA, LB_{ALF} is +29% ± 5% greater than LB_{Gamble} for As, Cd, Cu, Sb, Pb and Zn. In SmA, the ranges between LB_{ALF} and LB_{Gamble} are more heterogeneous, varying from 8% to 65% in the following order: Cu < As < Cd ~ Sb < Zn < Pb. This is in agreement with previous studies on various metal(loïds) LB [36,37,62], showing that metal(loïd)s release is improved by acidic conditions during inflammation (ALF, pH 4.5 *versus* Gamble solution, pH 7.4).

3.2. Exposure assessment

3.2.1. Exposure via dust ingestion

Fig. 4 shows external and simulated internal exposure to TE via dust ingestion ($Si.Exp_d$ and $E.exp_d$) calculated by considering the ingestion of <2000 μm, <200 μm and <50 μm fractions (cf Supplementary material for these particle sizes choice). $Si.exp_d$ is calculated with mixed indoor/outdoor dust consideration for MinD <50 μm fraction. Results were compared to Minimal Risk Level [63] for As and Cd and Tolerable Daily Intake (TDI) for Pb [64]. Both $E.exp_d$ and $Si.exp_d$ in the smelting area exceeds up to 10 fold the guidelines for As and Pb (reaching respectively 2814 and 90427 ng kg^{-1} day^{-1}). Exposure in the mining area is lower than in the smelting area and exceeds guidelines only for As when considering $E.exp_d$ in the <50 μm fraction. Antimony $Si.exp_d$ in both areas is particularly lower than $E.exp_d$ as a consequence of a low GB (<5%). In the case of Cd and Sb, addition of indoor dusts to exposure assessment increased by 1.5 and 2 the final result. Finally, metal(loïd)s exposure assessment through dust/soil ingestion appears to be significantly sensitive to the granulometric fraction considered with exposures multiplied by a factor 1.5–3.6 when considering the finest fraction in regards with the bulk dust. We strongly recommend that dust/soil samples <50 μm be sieved before analysis for exposure assessment to be consistent with published data particles sizes that adhere to children hands (cf Supplementary material) and to avoid under estimating actual exposure.

3.2.2. Exposure via aerosol inhalation

Given that both TE concentrations and LB are higher in SmA than in MinA, the highest daily inhalation exposure to metals is found in the smelting area. About 60–70% of inhaled metals are deposited in the respiratory system (Fig. 5). The lowest expired fractions of TE are observed in the mining area for As, Sn and Zn (respectively 32, 32 and 29%), driven by high TE concentrations in finest particles (Section 3.1.2.2). $E.Exp_a$ considers the amount of TE which are inhaled while $SI.Exp_a$ is achieved by considering the maximum of fate particles parameters: regional deposition, lung bioaccessibility, mucociliary transport toward gastrointestinal tract and absorption in the deep lungs. The gap between $Si.Exp_{Gamble}$ and $Si.Exp_{ALF}$ vary between 0 and 10% depending of the considered metal (Table 4) despite high variations between TE LB_{Gamble} and LB_{ALF} (8–65%). This highlights the relatively low contribution of LB in $SI.Exp_a$ assessment in comparison with TE granulometric distribution and fate during regional deposition process in the human body. $SI.Exp_a$ represents 31%–69% of $E.Exp_a$. The main processes for TE excretion are the fraction released during expiration in a single breath (29–40%) and the remaining metals after transfer in the gastro-intestinal tract (unabsorbed, 3–38%) (Fig. 5). TE excretion during expiration is more important for metals coming from particles with a diameter corresponding to low deposition deep in deep the airways (*i.e.*, As, Cu, Sb): between 0.1 and 1 μm (entrance but low efficiency to deposit) or >10 μm (low entrance) (Fig. A, Supplementary material). TE excretion after transfer in GI tract is more important for metals with a low gastric bioaccessibility (*i.e.*, Sb and Sn).

3.2.3. Contribution of different pathways to total exposure

Total external and simulated internal exposures ($E.exp_t$ and $Si.exp_t$) were calculated for both inhalation and ingestion pathways (Table 4). Daily intake of As and Pb for children living in the smelting area surpass the guidelines up to 10 fold, highlighting the prime importance to prevent children's exposure in this area. The contribution of aerosol inhalation is less important than the contribution of dust ingestion in E. Exp_t to TE whatever the metal (Table 4). It varies from ~0% (Pb in smelting area) to 33% (Sn and Zn in mining area). This matches the results of previous studies showing inhalation as a minor pathway when compared to soil/dust ingestion, except in the case of volatile elements (*i.e.*, Hg) [65–68]. An evolution of contribution of inhalation and ingestion to exposure is observed between $E.exp_t$ and $Si.exp_t$, affected by gastric and lung bioaccessibilities or metal distribution among granulometric fractions. In our case, contribution of inhalation is globally higher in $SI.Exp_t$ than in $E.Exp_t$, varying from ~0% (Pb in smelting area) to ~100% (Sn in mining area). This increase is particularly high when considering Sb and Sn, which exhibit a GB close to 0% but a high LB associated to concentration ~10 times higher in the <0.5 μm than in other granulometric fractions of aerosols. The only element presenting a lower inhalation contribution in $SI.Exp_t$ than in $E.Exp_t$ is Cd in the smelting area. In this case, Cd presents higher GB than LB and its concentration in the finest fraction of aerosol is "only" 2 times higher than in the other fractions.

Our results match previous epidemiologic studies in the same area comparing TE elements found in children's hair in different areas of Oruro [45]. As, Pb, Sb and Sn concentrations in children's hair were higher in the smelting area than in the mining area (factor 1.5–6), but the differences monitored between both areas were lower than those calculated in our study (factor 12–99). This can easily be explained by the positive correlation recently observed between hair element concentration and element concentration in indoor dust in the mining district [44]. No data are available for indoor dust in the smelting area, but the high concentrations for mining indoor dust were previously related to the presence of a mine worker in the children house, and particularly to the habits of carrying work clothes at home [41], which should not be the case in the smelting area due to the large distance to the mining workplace (>10 km). Furthermore, low Pb concentrations in aerosols associated to a low Pb gastric bioaccessibility in mining dust could explain

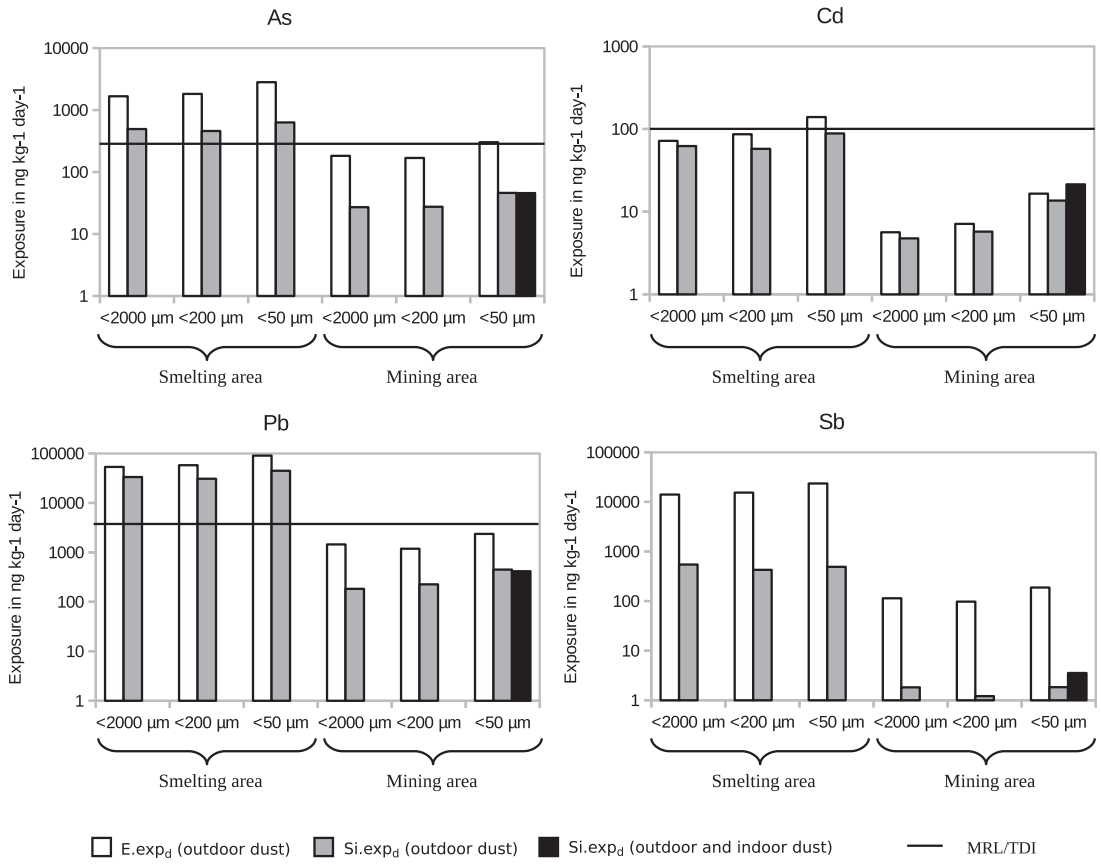


Fig. 4. Simulated (Si.exp$_d$) and external (E.exp$_d$) exposure assessment of children (7 years of age) to metals via dust ingestion (ng kg^{-1} day^{-1}). Different particle sizes for ingestion are considered (<2000 µm, <200 µm and <50 µm). Tolerable Daily Intake [64] or Minimal Risk Level [63] for chronic oral exposure (Table 4) are indicated.

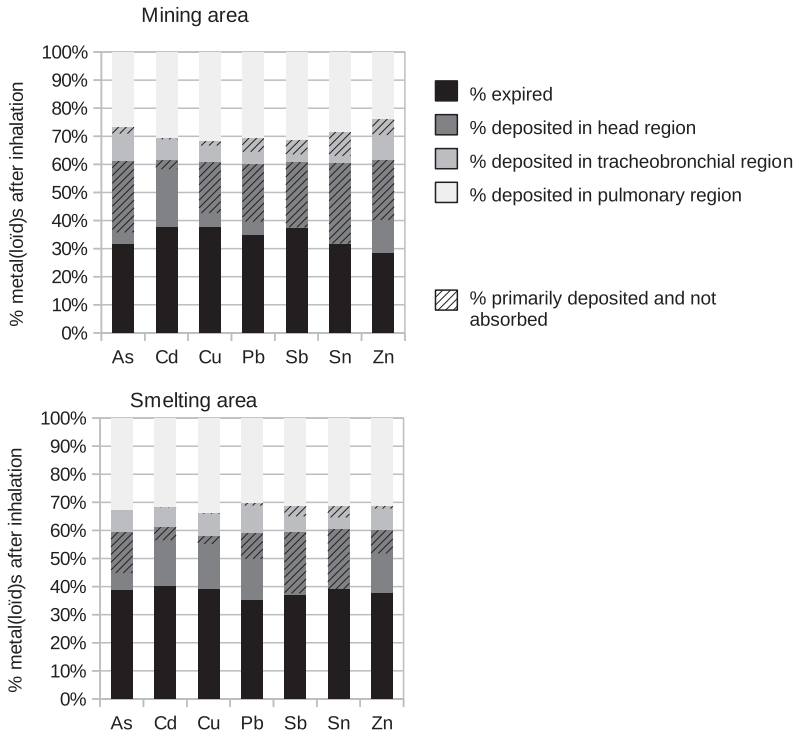


Fig. 5. Fate of TE after inhalation (%). Deposition rates are calculated after MPPD modelization and absorption rates as described in Eq. (6).

Table 4
Total external ($E.Exp_t$) and simulated internal ($Si.Exp_t$) exposure assessment (ng kg^{-1} day^{-1}) in mining and smelting areas for children, 7–9 yrs old, following aerosol inhalation ($E.Exp_a$ and $Si.Exp_a$) and dust ingestion ($E.Exp_d$ and $Si.Exp_d$).

		Exposure in ng kg^{-1} day^{-1}						
		As	Cd	Cu	Pb	Sb	Sn	Zn
mining area	$E.exp_a$	35	2	57	95	17	23	256
	$E.exp_d$	169	7	113	1183	97	46	516
	$E.exp_t$	204	9	170	1278	114	69	772
smelting area	$E.exp_a$	252	11	141	276	225	437	469
	$E.exp_d$	**1820**	86	2264	**57667**	**15406**	2485	7033
	$E.exp_t$	**2072**	98	2404	**57943**	**15630**	2922	7501
mining area	$Si.exp_a$[c]	14 (13)	1 (1)	24 (23)	37 (35)	6 (5)	7 (n.d)	113 (105)
	$Si.exp_d$	46	21	47	416	4	1	477
	$Si.exp_t$[c]	60 (59)	22 (22)	71 (70)	453 (451)	9 (9)	8 (n.d.)	591 (583)
smelting area	$Si.exp_a$[c]	117 (114)	6 (6)	80 (80)	149 (142)	83 (75)	153 (n.d.)	248 (239)
	$Si.exp_d$	**630**	88	2043	**44732**	489	0	3718
	$Si.exp_t$[c]	**747 (744)**	95 (94)	2123 (2123)	**44881 (44874)**	**572 (564)**	153 (n.d.)	3965 (3957)
Guideline (chronic oral intake MRL/TDI)		300[a]	100[a]	10000[a]	3500[b]			300000[a]

[a] Minimal risk level [63].
[b] TDI [64].
[c] Results for calculation with LB_{ALF}. Results for calculation with LB_{Gamble} are indicated within brackets.

the surprising low level of Pb found in women's blood samples coming from the mining area as previously observed in a recent epidemiological study [42,46] despite Pb concentrations in dusts exceeding the guidelines.

Three major uncertainties emerge from our work: (i) the representativeness of the samples, and particularly aerosols and outdoor dust which are only valuable at the precise sampling point and date, (ii) aerosol physical properties (*e.g.*, GSD, density) which could modify final simulated exposure, especially in the case of TE with high LB and low GB, and (iii) the rate of dust ingestion by children. The rate used in this study was 100 mg/day, as recommended by USEPA, but Oruro is a particularly dusty environment and a provisional rate of 350 mg/day, proposed by a local study [41], would have lead to multiply final results by a factor 3.5, and consequently to surpass the guidelines for Cd in the smelting area and for As and Pb in the mining area.

4. Conclusion

Our study shows that children from Oruro living in mining and smelting areas are highly exposed to metals via dust ingestion and PM inhalation. Significant differences between external and simulated internal exposure are attributed to differences in gastric and lung bioaccessibilities, as well as metal distribution among particle size range, revealing the importance of both parameters in exposure assessment. Bioaccessibility helps to significantly refine exposure assessment. The contribution of pathways (inhalation or ingestion) are different depending on the considered element. Inhalation is the main pathway of simulated internal exposure when considering elements with low gastric bioaccessibility but high lung bioaccessibility (*i.e.*, Sb and Sn). We strongly recommend to sieve dust/soil samples at <50 μm before analysis for health risk assessment to limit underestimation. It is furthermore essential for local authorities to take sanitary measures to limit exposure of young children to metal(loïds). In addition to limiting pollutants emission, football fields sampled in the present study should be promptly paved and regularly cleaned to prevent children's metal exposure through dust ingestion.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2016.05.083.

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