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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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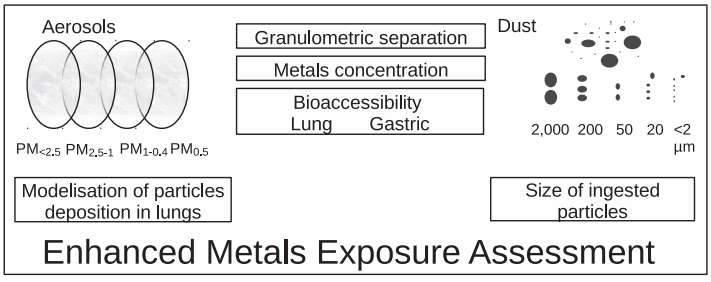
HIGHLIGHTS

- 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.

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.

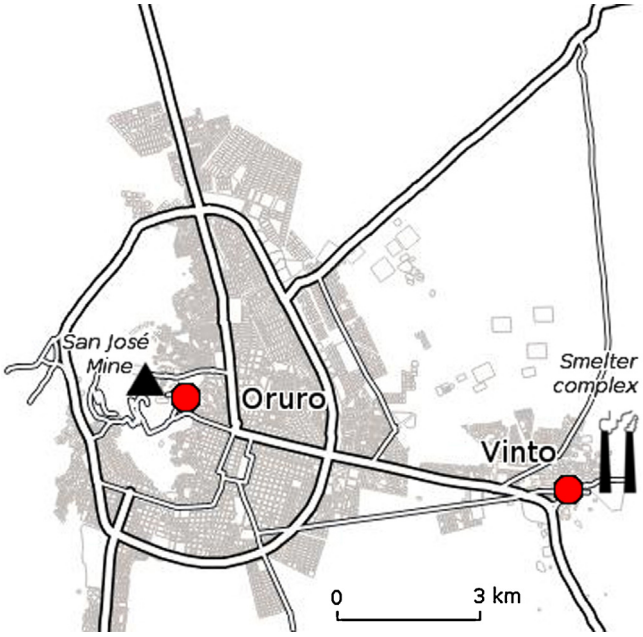

Fig. 1. Location of sampling points (red circles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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