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Lung bioaccessibility of As, Cu, Fe, Mn, Ni, Pb, and Zn in fine fraction (<20 μm) from contaminated soils and mine tailings

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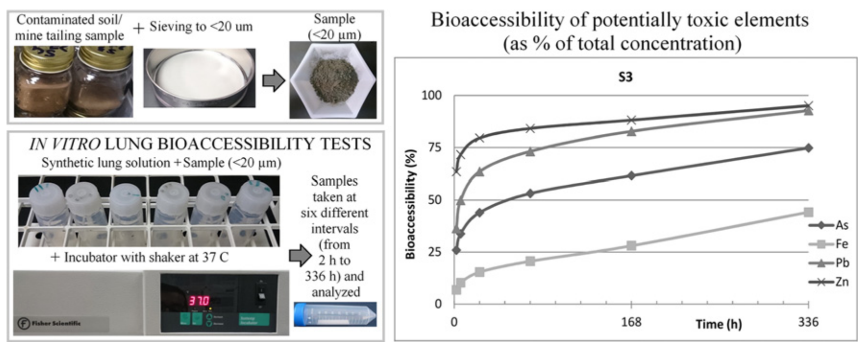
HIGHLIGHTS

- Fine fraction from samples had high levels of potentially toxic elements (PTEs).
- In vitro tests with ALF yielded higher bioaccessibility than Gamble's solution.
- Bioaccessibility in ALF after 2 weeks was high for all PTEs (in % and in $mg \cdot kg^{-1}$).
- PTE bioaccessibility typically increased rapidly, then tended to stabilize over time.
- PTE solubilization pattern was highly element- and sample-specific.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study aims (1) to characterize contaminated soils (n = 6) and mine tailings samples (n = 3) for As, Cu, Fe, Mn, Ni, Pb, and Zn content; and (2) to assess elemental lung bioaccessibility in fine fraction (d < 20 μm which might contribute to airborne particulate matter (PM) and thus be inhaled) by means of in vitro tests using Gamble's solution (GS) and an artificial lysosomal fluid (ALF). Elemental concentrations were high in the majority of samples, particularly for As (up to 2040 $mg \cdot kg^{-1}$), Fe (up to 30.7%), Mn (up to 4360 $mg \cdot kg^{-1}$), and Zn (up to 4060 $mg \cdot kg^{-1}$); and elemental concentrations (As, Cu, and Ni) in the sieved fraction (d < 20 μm) obtained from contaminated soils were significantly higher than in the bulk fraction (<160 μm). In vitro tests with ALF yielded much higher bioaccessibility than tests with GS, and the use of ALF in addition to GS is recommended to assess lung bioaccessibility. Bioaccessibility in ALF was high for all elements after 2 weeks of testing both in terms of concentration (e.g. up to 1730 $mg \cdot kg^{-1}$ for As) and percentages (e.g. up to 81% for Pb). The elemental solubilization rate generally declined rapidly and continuously with time. Similarly, bioaccessibility increased rapidly and tended to reach a plateau with time for most samples and metals. However, it is not possible to recommend a general testing duration as the solubilization behavior was highly element and sample-specific.

1. Introduction

Human exposure to potentially toxic elements (PTEs: harmful elements causing a potential occurrence of an adverse effect following exposure) in geological media can occur via ingestion, inhalation, and

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dermal pathways; and exposure to contaminated media constitutes a risk for human health (U.K.EA, 2009a). Air pollution is an important global environmental concern. Particulate matter (PM) is an air pollutant, which may affect human and ecosystem health (IPCC, 2013). Finer fractions of PM can penetrate deep into lungs and their clearance is difficult, and fine (PM2.5) and ultra-fine (PM0.1) are more closely linked with toxic effects (Schlesinger et al., 2006). Considering inhalation, particles generated from soil or soil-like material can be suspended via wind and human activities, contribute to air particulates, and therefore have the potential to add to human exposure (Wang et al., 2013; Zahran et al., 2013). More specifically, particles having an aerodynamic diameter (d) < 100 μm can be more easily suspended via wind or human activities, and stay in air for prolonged periods. As coarser fractions PM settle down more quickly, PM having smaller diameter can stay in air and thus can be more easily inhaled by humans i.e. workers on a contaminated site, or residents living nearby mining sites.

Following inhalation, larger particles (d > 10 μm) will be more probably deposited in the upper respiratory tract, while smaller particles (d < 10 μm [PM10]) reach tracheobronchial region (in lower respiratory tract), and particles with d < 4 μm will mainly deposit in the alveolar region of the human lung (Merget and Rosner, 2001). PM can then be trapped in two compartments: the extracellular environment of the deep lung (alveoli) which is neutral in pH, or the intracellular acidic environment of the macrophage where PM is chemically attacked and/or transported out of the lung (Zoitos et al., 1997). It is generally assumed that finer fractions of airborne PM (PM2.5) are mainly responsible for adverse health effects. Therefore, because of their assumed inherently inferior respirability, fraction larger than PM10 is generally excluded from such considerations (Hoare, 2014). However, all air-borne particles are susceptible to inhalation, hence, it is possible for any sorbed harmful substances to be subsequently desorbed in vivo which may facilitate their transport deeper into the lungs (Hoare, 2014).

Fine fraction from contaminated soils and mine tailings may contain different contaminants, including various elements. Some of these elements are relatively well studied and documented, such as As, Hg, Cd, and Pb for which ingestion remains the most problematic exposure route (e.g. Abrahams, 2012; Hur et al., 2009; Intawongse and Dean, 2006; Oomen et al., 2002; Ruby et al., 1999; and, Wragg and Cave, 2003). For other elements such as Ni, the inhalation pathway reveals high risk (U.K.EA, 2009b). Fe is also likely to form toxic complexes in the lungs (Goldstein et al., 2013). In general, transition metals seem important for lung exposure because of their ability to generate reactive oxygen species (ROS) in biological tissues via Fenton-type reactions (Chen and Lippmann, 2009). Among PTEs, Co, Cu, Fe, Mn, Ni, V, and Zn can be considered as particularly important for inhalation pathway.

Bioaccessibility may be defined as the availability of a metal for absorption when dissolved in vitro in a body fluid e.g. gastrointestinal or lung fluids (Ellickson et al., 2001; Guney et al., 2016). In vitro lung bioaccessibility tests can be used to estimate bioavailability of contaminants in human lungs. These in vitro tests were used in the last decades in order to assess the bioavailability of metal compounds in artificial fluids while avoiding higher cost and ethical considerations associated to in vivo tests (e.g. Stopford et al., 2003). Two types of synthetic lung fluid solution are mainly used with slight variations in these in vitro tests: Gamble's solution (GS) is representative of the extracellular environment of the deep lung (alveoli), which is neutral in pH; and, artificial lysosomal fluid (ALF) corresponds to the intracellular environment of the macrophage, which is acidic (Zoitos et al., 1997).

Studies on the inhalation of PM from different origins are numerous in the literature, including Pt, Pd, and Rh in urban airborne PM10 from catalytic origin (Zereini et al., 2012); common austenitic metal alloys and metal powders (Hillwalker and Anderson, 2014); various grades of stainless steel (Herting et al., 2007); Co metal alloys (Stopford et al., 2003); and, Pb, Cu, and Zn from power plant fly ash (Twining et al., 2005). Particularly for airborne PM, a detailed discussion of studies on the assessment of metal bioaccessibility can be found in the scoping review of Wiseman (2015). Briefly, although numerous studies were conducted on the subject, few among them used methods incorporating biologically-relevant parameters. Also, this review highlighted a critical need for a standardized in vitro bioaccessibility method. During the last decade, only a limited number of studies focused on the development of in vitro method to estimate the lung bioaccessibility of metals (Boisa et al., 2014; Caboche et al., 2011; Midander et al., 2006; Wragg and Klinck, 2007).

Lung bioaccessibility studies specifically based on fine fractions of samples of geological origin or on PM of geological origin are limited in the literature (e.g. Hg of airborne calcite particulates from mining residues (Gray et al., 2010), Pb from mine wastes (Wragg and Klinck, 2007), platinum group elements from exhaust catalysts and road dust (Colombo et al., 2008), inhalation of Cr(VI)-containing dust from soil (Broadway et al. (2010)); please refer to Guney et al. (2016) for a complete list and a detailed discussion of studies on PM of geological origin). Human exposure to fine particulates contributing to PM from contaminated soil or mine tailings via inhalation may constitute an important pathway as few existing studies demonstrate a high potential for PTE lung bioaccessibility in PM. The objectives of the present study are (1) to characterize the sieved fraction (d < 20 μm) obtained from contaminated soils and mine tailings samples (n = 9) for their As, Cu, Fe, Mn, Ni, Pb and Zn content, and (2) to measure the lung bioaccessibility of the PTEs associated to this fraction (n = 7) via in vitro tests using two different synthetic lung fluids (ALF and GS). In addition, a reference material was tested (BGS 102), and experiments with spiked samples were performed. In the present study, bioaccessibility is discussed in terms of concentrations and percentages.

2. Materials and methods

2.1. Sample handling and preparation

A total of nine samples from contaminated sites (n = 6, S1–S6) and mine tailings sites (n = 3, S7–S9) were investigated. Contaminated soil samples originate from petroleum-contaminated industrial sites in France and had been sieved (d < 160 μm) prior to reception. They contain PTEs in addition to organic contaminants (mainly aliphatic, alicyclic, and polyaromatic hydrocarbons). Mine tailing samples had been collected from mine waste sites in Northern Quebec (Canada) containing crushed and processed ores (d < 160 μm). Contaminated soil samples were taken from the surface (0–20 cm) by using a plastic shovel and were placed in pre-cleaned 250-mL plastic containers after removal of vegetation (if present). After sampling, soil samples were immediately transported to the laboratory where they were air-dried, homogenized, and then sieved to 160 μm. Similarly, surface (0–20 cm) mine tailing samples were collected by using a plastic shovel. The samples were also placed in pre-cleaned plastic containers. The reference material BGS 102 (ironstone soil, d < 40 μm) from British Geological Survey was also tested. This reference material was selected because it includes certified values for all PTEs tested in the present study. Since there is no certified reference material available for lung bioaccessibility assessment, BGS 102 was selected in order to obtain lung bioaccessibility results which can be compared to Boisa et al. (2014) values, and to provide reference for future research.

Soils and mine tailings samples were sieved to <20 μm by using a set of micromesh sieves of 75, 50, and 20 μm openings, with the aid of a vibrational shaker (Retsch AS-200). This fraction was selected because it approximates the fraction to be exposed following lung deposition, but more importantly, it could be separated from the original samples via dry sieving with relative ease. The fraction <10 μm was the original desired fraction to be separated; however, it was not possible to obtain sufficient sample quantity for sample characterization and bioaccessibility tests using a 10-μm micromesh sieve. The sieving was successively performed in 30 min sequences using discontinuous pulse until it was not possible to recover significant quantities of <20 μm fraction. The