LUNG BIOACCESSIBILITY OF METALS IN PARTICULATE MATTER OBTAINED FROM GEOLOGICAL SAMPLES

Gerald J. Zagury, M. Guney, C. M.-J. Bourges, R. P. Chapuis

Polytechnique Montréal, Department of Civil Geological and Mining Engineering, Montréal, Canada
gerald.zagury@polymtl.ca

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Introduction

Particulate matter (PM) has the potential to affect human and ecosystem health (IPCC, 2013). Finer fractions of PM can penetrate into lungs and are closely linked with toxic effects (Schlesinger et al., 2006). For inhalation pathway, particles generated from soil and soil-like materials can be suspended (e.g. via wind, human activities), contributing to PM and adding to the potential for human exposure (Wang et al., 2013; Zahran et al., 2013). Bioaccessibility may be defined as the availability of an element 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 are used 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 synthetic lung fluid solutions are commonly used: Gamble's solution (GS) being representative of the extracellular environment of the deep lung (alveoli) with neutral pH, and artificial lysosomal fluid (ALF) corresponding to the intracellular environment of the macrophage with acidic pH (Zoitos et al., 1997). Lung bioaccessibility studies on PM from geological samples are limited (see the critical review of Guney et al., (2016)), and a few studies demonstrated a high potential for metals lung bioaccessibility in PM. The present study aims to (1) 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 PM by using GS and ALF.

Methods

Soils (samples S1-S6) and mine tailings (S7-S9) were repeatedly sieved to obtain PM20 (d<20 µm) by using a set of micromesh sieves of 75, 50, and 20 µm openings and a vibrational shaker (Retsch AS-200). Samples were then characterized for their metal content both as received and in <20 µm fraction via acid digestion. The *in vitro* tests were conducted on selected samples (n=7) by using GS and ALF (see Colombo et al. (2008) for chemical compositions) inside an incubator at 37 °C using an orbital shaker at 100 rpm. Solid:solution ratio was 1:100 and an initial test time of 2 h was followed by repeated sampling of extracts at 6 h, 1 d, 3 d, 1 w, and 2 w. The analyses for potentially toxic elements were performed via AAS (Perkin-Elmer A200) and by ICP-OES (Varian Vista). For each contaminant, total and bioaccessible concentrations ($mg.kg^{-1}$) as well as bioaccessible fractions (%) were determined. For QA/QC, procedure blanks were used, analyses were made in duplicate, a certified reference material was tested (BGS 102 for total and bioaccessible concentrations), and some bioaccessibility tests were conducted with spiked samples.

Results

Contamination in samples: Total concentrations of potentially toxic elements in soils and mine tailings were elevated in bulk samples, particularly for As (up to 2,040 $mg.kg^{-1}$), Fe (up to 30.7%), Mn (up to 4,360 $mg.kg^{-1}$), and Zn (up to 4,060 $mg.kg^{-1}$). Furthermore, total concentrations in PM20 were almost always higher than in the original samples (e.g. As up to 3,940 $mg.kg^{-1}$, Fe up to 41.6%, Mn up to 5,210 $mg.kg^{-1}$, and Zn up to 3,230 $mg.kg^{-1}$). Finally, contamination in mine tailings (S7-S9) were higher than in soil samples (S1-S6).

Comparison of tests with ALF and GS: For all elements and all samples, tests with ALF yielded higher bioaccessibility than the tests with GS. Moreover, bioaccessible concentrations in GS were below DLs for most elements (e.g. As, Cu, Fe, Ni, Pb, and Zn for S1; all seven elements for S7). The difference can be explained by the difference in chemical compositions of GS and ALF, with ALF having a pH of 4.5, which could favor metal solubilisation. For the determination of metal lung bioaccessibility, the use of ALF could be recommended over GS as it provides more conservative results.

Lung bioaccessibility of metals: For the *in vitro* tests using ALF, metal cumulative bioaccessible concentrations and percentages were elevated in numerous samples, especially for As, Fe, Mn, Pb, and Zn: e.g. 1,730 $mg.kg^{-1}$ after 2 weeks (43.9%) for As in PM20 for S8, 1.33×10^5 $mg.kg^{-1}$ (44.1%) for Fe for S3, and 728 mg,kg^{-1} (80.8%) for Pb for S7. Elevated bioaccessible concentrations as well as percentages of As, Fe, Mn, Pb, and Zn indicates a high potential for solubilisation in the case of inhalation exposure to PM, following the phagocytosis of the particles.

Bioaccessibility and test duration: The calculated solubilisation rates of elements were higher at 2 h, and then declined rapidly and continuously with time. Consequently, % bioaccessibility increased rapidly and tended to reach a plateau with time. For As, Mn, Pb, and Zn, high solubilisation rates rapidly dropped to around or below 1 $mg.kg^{-1}.h^{-1}$ after 6 h - 1 d. However, Fe was soluble at around 100 $mg.kg^{-1}.h^{-1}$ even after 1 d, which could be explained by its very high total concentrations in samples. At this stage, it is not possible to recommend a fixed testing time as the exact behavior was highly element- and sample-specific.

Conclusion

PM from soil and mine tailings samples can be potentially dangerous following inhalation due to contamination by As, Cu, Fe, Mn, Ni, Pb, and Zn. The use of ALF in *in vitro* bioaccessibility tests could be recommended as tests conducted on PM20 using ALF indicated more conservative lung bioaccessibility values than the tests using Gamble's solution. Elevated bioaccessible fractions (%) as well as concentrations ($mg.kg^{-1}$) especially for As, Fe, Mn, Pb, and Zn after 2 w of testing of various samples indicate potential concerns in case of human exposure. Additional research is recommended (1) on the bioaccessibility of metals in additional various samples from geological samples as existing studies are limited, (2) on the standardization of *in vitro* lung bioaccessibility tests, and (3) on the characterization of human health risks for different scenarios of potential inhalation exposure.

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