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Assessment of lead bioaccessibility in peri-urban contaminated soils

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ABSTRACT

Lead (Pb) bioaccessibility was assessed in a range of peri-urban soils ($n = 31$) with differing sources of Pb contamination, including shooting range soils, and soils affected by incinerator, historical fill, mining/smelting, and gasworks activities. A gossan soil sample was also included. Lead bioaccessibility was determined using both gastric and intestinal phases of the SBRC in vitro assay and in vitro data was then incorporated into in vivo–in vitro regression equations to calculate Pb relative bioavailability. Lead bioaccessibility ranged from 26.8–105.2% to 5.5–102.6% for gastric and intestinal phase extractions respectively. Generally, Pb bioaccessibility was highest in the shooting range soils and lowest in the gossan soil. Predictions of relative Pb bioavailability derived from in vitro data were comparable for shooting ranges soils, but highly variable for the other soils examined. For incinerator, historical fill, gasworks and gossan soils, incorporating in vitro gastric data into the in vivo–in vitro regression equation resulting in more conservative Pb relative bioavailability values than those derived using the intestinal in vitro data.

1. Introduction

Although lead (Pb) is ubiquitous in the soil environment, concentrations vary widely and may be locally elevated due to a range of anthropogenic activities (e.g. mining and smelting, combustion of leaded fuels). Indeed, the National Priority List of Sites in the United States ranks Pb as the most common inorganic soil contaminant [1]. Due to the negative effects associated with Pb exposure, particularly with respect to neurological development in young children [2,3], there is considerable concern regarding human exposure to soil-borne Pb. Human Pb exposure may occur via a number of pathways, such as inhalation or the consumption of contaminated food and water, and is likely to differ for adults and children due to differences in typical daily activities and behaviour. For example, the incidental ingestion of contaminated soil and dust is a major exposure pathway for young children but is of lesser relevance for adults. This is because common activities, such as playing on floors and in gardens, and mouthing of hands, toys and other objects can bring children into greater contact with Pb contaminated soil [4]. Nevertheless, uptake of Pb following soil ingestion is not easily predicted as the amount of Pb actually absorbed into systemic circulation (i.e. the bioavailable fraction) is dependent on factors such as the nature and solubility of Pb in the soil/dust matrix and the child's nutritional status [5,6].

The relative bioavailability of Pb in contaminated soil may be determined using in vivo assays [4,7–12], but these methods are complicated, time consuming and prohibitively expensive. An alternative to in vivo assays are in vitro methods that simulate conditions in the human gastrointestinal tract to provide an estimate of contaminant bioaccessibility (i.e. the fraction that is soluble and therefore available for absorption). Recently, the USEPA [4], Drexler and Brattin [10] and Bannon et al. [11] determined that dissolution of Pb phases in the in vitro gastric phase provided a good prediction of Pb relative bioavailability for mining and shooting range soils. In addition, Juhasz et al. [12] and Smith et al. [13] determined that Pb relative bioavailability could also be estimated using the intestinal phase of the SBRC in vitro assay by adjusting the dissolution of Pb from contaminated soil by the solubility of Pb acetate at pH 6.5 (in vitro intestinal phase pH). Relative Pb bioavailability and bioaccessibility studies have reported that Pb relative bioavailability and bioaccessibility varies considerably and may range from 1% to 100% depending on factors including Pb mineralogy and soil physicochemical properties. However, the majority of Pb-contaminated soils which have been assessed have been limited to those sourced from mining/smelting and shooting range locations which may not be representative of soils contaminated through other anthropogenic activities commonly encountered in peri-urban environments. Consequently, the aim of this study was to assess Pb bioaccessibility using both gastric and intestinal phase

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in vitro methods in soils contaminated by a wide variety of anthropogenic activities.

2. Materials and methods

2.1. Pb contaminated soil

Soils used in this study were collected from a variety of peri-urban locations in Australia and New Zealand where elevated soil-Pb concentrations were due either to anthropogenic activities (i.e. mining/smelting, gasworks, use of contaminated fill, shooting range activities, waste incineration), or to geogenic processes where elevated Pb concentrations in soils are the result of weathering of sulphide bearing rock (gossans). Soils were air dried and sieved using stainless steel sieves to <2 mm and <250 μm. The <2 mm fraction was used for soil characterisation, whilst the <250 μm soil fraction was retained for bioaccessibility assessment. Soil physico-chemical properties were determined in duplicate for each soil. Soil pH was determined using 1:5 soil:water extracts and organic carbon content was determined by oxidation/combustion [14]. Total metal concentrations were determined using the USEPA 3052 aqua regia dissolution procedure [15] and a CEM MarsX microwave. Total metals in digest solutions were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). A certified reference material (GBW 07411; China National Analysis Centre for Iron and Steel, Beijing, China) was included in the analysis to ensure internal quality assurance/quality control (QA/QC) practices. The measurement trueness of the aqua regia digestion method was confirmed by a quantitative average Pb recovery of $2688 \pm 84\,mg\,kg^{-1}$ ($n = 6$) from GBW 07411 ($2700 \pm 100\,Pb\,mg\,kg^{-1}$). During the determination of Pb concentration in soil digests and in vitro extracts, duplicate sample analysis, spiked sample recoveries and continuing calibration verification standards (CCV) were included. The average deviation between duplicate samples ($n = 12$) was 1.4%, the average recovery from spiked samples ($n = 12$) was 98.9% whereas CCV recoveries ($n = 14$) ranged from 95.4% to 101.4% (99.1% average recovery).

2.2. Determination of Pb bioaccessibility

The Solubility Bioavailability Research Consortium (SBRC) in vitro assay [16], including both gastric and intestinal phases, was utilised for the assessment of Pb bioaccessibility. Lead contaminated soil was combined with gastric phase solution ($30.03\,g\,l^{-1}$ glycine adjusted to pH 1.5 with concentrated HCl) in polyethylene screw cap flasks to achieve a soil:solution ratio of 1:100. The pH was recorded, then the flasks were incubated at 37 °C and agitated at 40 rpm using a Ratek suspension mixer. After 1 h, the pH was determined again and gastric phase samples (10 ml) were collected and filtered through 0.45 μm filters for analysis by ICP-AES. Following gastric phase dissolution, the gastric solution was modified to the intestinal phase by adjusting the pH to 6.5 with either 5 or 50% NaOH and by the addition of bovine bile ($1750\,mg\,l^{-1}$) and porcine pancreatin ($500\,mg\,l^{-1}$). After 4 h, intestinal phase samples (10 ml) were collected and filtered through 0.45 μm filters for analysis by ICP-AES or ICP-MS. The solubility of Pb acetate ($1–10\,mg\,Pb\,l^{-1}$) was also determined in gastric and intestinal phases. All gastric and intestinal phase extractions were performed in triplicate for both Pb acetate and soil samples.

Absolute Pb bioaccessibility was calculated by dividing the gastric phase extractable Pb (termed SBRC-G) and intestinal phase extractable Pb (termed SBRC-I) by the total Pb acetate or soil Pb concentration (Eq. (1)).

$$\text{Absolute Pb bioaccessibility, \%} = \left[\frac{\text{In vitro Pb}}{\text{Total Pb}}\right] \times 100 \quad (1)$$

where: In vitro Pb = Pb (μg) extracted from soil following gastric phase (SBRC-G) or intestinal phase (SBRC-I) treatment, and Total Pb = Pb (μg) present in contaminated soil or Pb acetate added to the in vitro assay prior to treatment [17].

Relative Pb bioaccessibility (termed Rel-SBRC-I) was determined by adjusting the dissolution of Pb from contaminated soils by the solubility of Pb acetate at the corresponding pH value (Eq. (2)).

$$\text{Relative Pb bioaccessibility, \%} = \left[\frac{\left[\frac{\text{SBRC}-I_{\text{Soil Pb}}}{\text{Total Soil Pb}}\right]}{\left[\frac{\text{SbRC}-I_{\text{Pb acetate}}}{\text{Total Pb acetate}}\right]}\right] \times 100 \quad (2)$$

where: SBRC-$I_{\text{Soil Pb}}$ = Pb (μg) extracted from soil following intestinal phase (SBRC-I) treatment of Pb-contaminated soil at an intestinal pH of 6.5, Total soil Pb = Pb (μg) present in contaminated soil prior to treatment, SBRC-$I_{\text{Pb acetate}}$ = Pb (μg) solubilised following intestinal phase (SBRC-I) treatment of Pb acetate at an intestinal pH of 6.5, and Total Pb acetate = Pb acetate (μg) added to the in vitro assay prior to treatment [12].

3. Results and discussion

3.1. Soil properties

Lead concentration in the 31 soil samples ranged from 86 to $6840\,mg\,kg^{-1}$ in the <2 mm soil particle size fraction. Twenty eight soils exceeded the Australian National Environmental Protection Measure for the Assessment of Site Contamination (NEPM-ASC) Pb health investigation level ($300\,mg\,kg^{-1}$) for 'standard' residential garden/accessible soil and children's day care centres, kindergartens, preschools and primary schools [18] by 1.6–22.8-fold. Other physicochemical properties varied between soils with Fe, OC and pH ranging from 9.7–263 $g\,kg^{-1}$, 0.2–10.6% and 4.7–9.0 respectively (Table 1).

The concentration of Pb in the <250 μm soil particle size fraction was also determined as this particle size fraction was utilised for bioaccessibility assays. Utilisation of the <250 μm soil particle size fraction is based on the premise that this fraction adheres to the hands of children and is available for hand-to-mouth transfer [5]. A linear relationship existed between Pb concentration in the <2 mm and <250 μm soil particle size fraction (Fig. 1). For the 31 soil studied, the Pb concentration in the <250 μm soil particle size fraction was greater than that observed in the <2 mm soil particle size fraction ($y = 1.26x + 11.87$) with a variance of 0.86 compared to the model equation. In some soils, however, Pb concentrations in the <250 μm soil particle size fraction were substantially greater with enrichment factors ranging from 1.7 to 3.6 for incinerator soils (#10–12) and 3.8 for the gossan soil (#31). Previous studies have demonstrated the variability in Pb concentration in different soil particle size fractions [19–21] with Pb distribution varying depending on contaminant source and soil type.

3.2. Pb bioaccessibility

Lead bioaccessibility in the <250 μm soil particle size fraction was determined using both gastric and intestinal phases of the SBRC assay. As outlined in Table 2, Pb bioaccessibility varied considerably depending on whether gastric or intestinal phase extraction was used for its assessment. Following gastric phase extraction, Pb bioaccessibility ranged from 26.8% to 105.2% depending on the Pb source. In shooting range soils, Pb bioaccessibility was >75% in 8 of the 9 soils tested, the exception being soil #9 where gastric phase Pb bioaccessibility was 50% (mean Pb bioaccessibility = 89.0 ± 18.3%, $n = 9$). In a previous study undertaken on small arms range soils [11], Pb bioaccessibility ranged from 83% to 100% (mean = 95 ± 6%, $n = 8$)