



Assessment of lead bioaccessibility in peri-urban contaminated soils

Euan Smith^{a,b,*}, John Weber^{a,b}, Ravi Naidu^{a,b}, Ronald G. McLaren^c, Albert L. Juhasz^{a,b}

^a Centre for Environmental Risk Assessment and Remediation, University of South Australia, Mawson Lakes, SA 5095, Australia

^b Cooperative Research Centre for Contamination Assessment and Remediation of the Environment, Mawson Lakes, SA 5095, Australia

^c Faculty of Agriculture and Life Sciences, Lincoln University, Christchurch, New Zealand

ARTICLE INFO

Article history:

Received 30 August 2010

Received in revised form 28 October 2010

Accepted 30 October 2010

Available online 9 November 2010

Keywords:

Bioaccessibility

In vitro

Lead

Relative bioavailability

SBRC

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 range 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.

© 2010 Elsevier B.V. All rights reserved.

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

* Corresponding author at: Centre for Environmental Risk Assessment and Remediation, University of South Australia, Mawson Lakes, SA 5095, Australia. Tel.: +61 8 8302 5042; fax: +61 8 8302 3057.

E-mail address: Euan.Smith@unisa.edu.au (E. Smith).

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 $2688 \pm 84 \text{ mg kg}^{-1}$ ($n=6$) from GBW 07411 ($2700 \pm 100 \text{ Pb mg kg}^{-1}$). 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_{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_{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 = $89.0 \pm 18.3\%$, $n=9$). In a previous study undertaken on small arms range soils [11], Pb bioaccessibility ranged from 83% to 100% (mean = $95 \pm 6\%$, $n=8$)

Table 1
Source and physicochemical properties of soils used in bioaccessibility studies.

Soil #	Source	Physicochemical properties ^a			
		Pb (mg kg ⁻¹)	Fe (g kg ⁻¹)	OC (%)	pH
1	Shooting range	960	14.4	1.8	5.6
2	Shooting range	2009	14.8	2.6	5.7
3	Shooting range	576	13.3	1.7	6.2
4	Shooting range	3026	12.8	2.4	5.5
5	Shooting range	806	10.3	6.2	5.7
6	Shooting range	1801	15.0	4.7	4.7
7	Shooting range	719	17.2	1.6	6.0
8	Shooting range	1373	1.6	1.7	5.0
9	Shooting range	661	13.2	6.9	7.5
10	Incinerator	1140	41.6	0.2	6.9
11	Incinerator	835	44.8	0.2	7.7
12	Incinerator	2248	57.9	0.2	6.8
13	Historical fill	105	68.3	5.8	7.8
14	Historical fill	567	14.5	3.2	8.7
15	Historical fill	640	36.8	10.6	7.0
16	Historical fill	954	62.6	9.5	6.4
17	Mining/smelting	805	14.9	0.5	5.9
18	Mining/smelting	1004	189	0.5	6.1
19	Mining/smelting	881	245	0.2	9.0
20	Mining/smelting	820	263	0.3	6.6
21	Mining/smelting	489	7.3	0.4	8.6
22	Mining/smelting	6840	13.1	1.6	8.1
23	Mining/smelting	5101	15.3	1.7	8.7
24	Mining/smelting	736	13.8	3.0	8.9
25	Mining/smelting	1186	11.3	1.7	8.8
26	Mining/smelting	124	13.3	3.7	8.2
27	Mining/smelting	86	9.7	3.5	9.0
28	Mining/smelting	1274	33.0	2.3	8.3
29	Mining/smelting	1392	28.3	2.4	8.4
30	Gasworks	1343	27.8	5.0	7.0
31	Geogenic	142	42.7	2.8	6.9

^a Physicochemical properties were determined using the <2 mm soil particle size fraction.

for soils containing between 4503 and 23 409 mg Pb kg⁻¹. Bannon et al. [11] account for the high Pb bioaccessibility due to the presence of Pb carbonates and oxides in the soils. The presence of these Pb phases was attributed to the weathering of Pb shot remaining in the soil environment. Hydrocerrusite [Pb₃(CO₃)₂(OH)₂], cerrusite (PbCO₃) and masicot (PbO) have been identified as Pb shot weathering products [22–24] which are all highly soluble under acidic

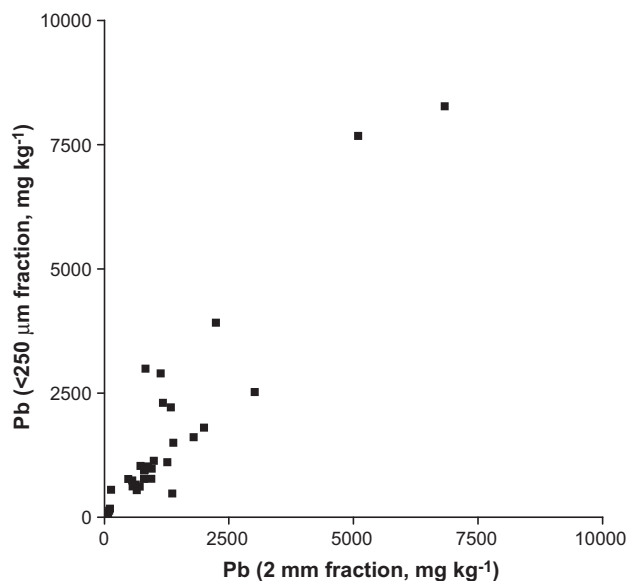


Fig. 1. Comparison of Pb concentration in the <2 mm and <250 μm soil particle size fractions.

Table 2
Determination of Pb bioaccessibility in contaminated soils using the SBRC assay.

Soil #	Pb (mg kg ⁻¹) ^a	Pb Bioaccessibility (%)		
		SBRC-G ^b	SBRC-I ^c	Rel-SBRC-I ^d
1	967	105.2	9.4	87.4
2	1795	100.7	6.8	63.3
3	611	100.2	8.2	75.6
4	2512	76.8	7.0	65.3
5	931	75.2	6.6	59.9
6	1602	99.1	6.0	64.0
7	606	103.1	8.9	83.2
8	469	90.4	11.1	102.6
9	536	50.0	2.2	21.3
10	2885	64.1	1.5	14.4
11	2980	64.1	2.3	22.5
12	3905	60.9	1.2	11.7
13	125	81.6	2.8	25.6
14	731	85.1	0.6	5.5
15	646	61.0	2.7	26.1
16	765	35.7	2.1	20.0
17	760	67.5	4.5	41.4
18	1125	26.8	1.7	15.5
19	1014	36.3	1.3	11.6
20	941	53.8	1.7	15.5
21	760	35.1	4.2	48.0
22	8261	40.8	8.9	82.9
23	7663	55.5	6.4	60.4
24	1021	41.6	8.8	82.5
25	2295	54.9	2.7	25.7
26	163	38.4	2.5	23.6
27	73	93.1	3.8	35.3
28	1096	95.0	3.3	30.8
29	1489	73.9	3.2	30.8
30	2200	45.2	2.9	27.2
31	545	35.2	1.3	12.5

^a Lead concentration in the <250 μm particle size fraction.

^b Lead bioaccessibility was determined using the gastric phase of the SBRC assay (SBRC-G).

^c Lead bioaccessibility was determined using the intestinal phase of the SBRC assay (SBRC-I).

^d Relative Pb bioaccessibility was calculated by adjusting the dissolution of Pb from contaminated soils by the solubility of Pb acetate at the intestinal phase pH (6.5) (Rel-SBRC-I).

conditions, such as those that occur in the gastric phase of the SBRC bioaccessibility assay.

In soils where Pb inputs occurred as a result of mining and smelting activities, mean Pb bioaccessibility was 54.8 ± 21.9% (n = 13), however, for soils #27 and #28, Pb bioaccessibility was >90% (93.1% and 95.0% respectively). Several studies have determined Pb bioaccessibility to be low in mine site soils due to the limited solubility of Pb species such as Pb sulphides, Pb phosphates, ferromanganese Pb oxides and iron Pb sulphates [8,25]. In contrast, high gastric phase Pb bioaccessibility has been reported for soils contaminated via smelter emissions due to the presence of highly soluble Pb oxides and carbonates [26]. Lead speciation studies conducted with soil #28 (collected downwind from a Pb smelter) using XRD and SEM-EDX was unable to identify Pb species, however, discrete amorphous particles (<20 μm) containing Pb associated with oxygen, calcium and magnesium were identified. Mean Pb bioaccessibility in soils containing incinerator waste and historical fill material were similar (63.0% and 65.8% respectively), however, Pb bioaccessibility ranged from 35.7% to 85.1% in soils sourced from a former landfill area. In contrast, Pb bioaccessibility in gasworks (45.2%) and gossan soils (35.2%) were low although it should be noted that only single soil samples were obtained from these Pb sources.

Following gastric phase extraction, adjustment of the solution pH to reflect intestinal phase conditions resulted in a significant decrease in soluble Pb (Fig. 2). Lead bioaccessibility in the intestinal phase was significantly less than that observed in the gastric

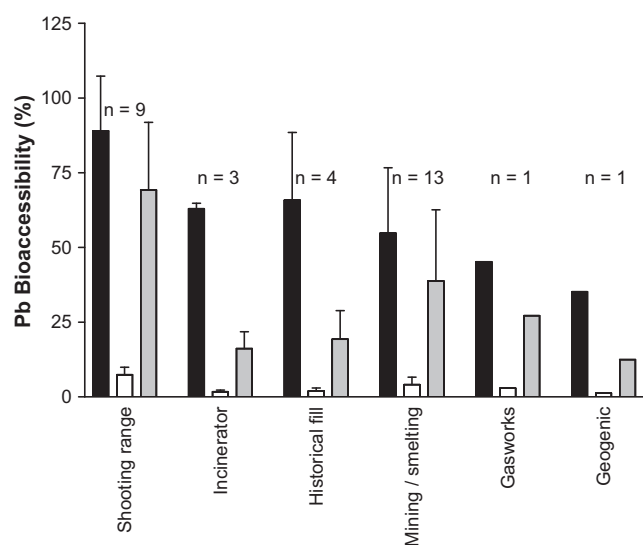


Fig. 2. Comparison of Pb bioaccessibility in contaminated soils based on Pb source. Lead bioaccessibility was determined following gastric (■) and intestinal (□) phase extraction using the SBRC assay. In addition relative Pb bioaccessibility (■) was calculated by adjusting the dissolution of Pb from contaminated soils in the intestinal phase by the solubility of Pb acetate at the corresponding pH value.

phase ranging from 0.6% for soil #14 to 11.1% for soil #8. Similar decreases in Pb bioaccessibility from gastric to intestinal phases have previously been reported by Ruby et al. [5], Schroder et al. [8] and Juhasz et al. [12] using PBET, IVG and SBRC assays. As pH strongly influences the solubility of Pb in solution [27] the decrease in Pb bioaccessibility at an intestinal phase pH of 6.5 compared to gastric phase conditions (pH 1.5) was not unexpected.

In order to account for the effect of pH on Pb solubility, relative Pb bioaccessibility (Rel-SBRC-I) was calculated by incorporating the solubility of Pb acetate at the intestinal phase pH (Eq. (2)). Previous studies have demonstrated that this approach may improve both gastric and intestinal phase estimates for predicting Pb relative bioavailability [12]. Lead relative bioavailability ranged from 5.5% to 102.6% with the highest values recorded for shooting range soils (#1–8; 59.9–102.6%) and soils #22 (82.9%), #23 (60.4%) and #24 (82.5%) impacted through mining and smelting activities (Fig. 2). As detailed in Table 2, Pb bioaccessibility values derived for contaminated soils are greatly influenced by the method employed (i.e. SBRC-G, SBRC-I, Rel-SBRC-I). For soils used in this study, extending the SBRC assay from the gastric to the intestinal phase resulted in a decrease in Pb bioaccessibility by 4–144-fold while calculating relative Pb bioaccessibility resulted in values approximately 10-fold greater than intestinal phase data alone.

The behaviour of Pb in the intestinal phase was of particular interest as metals are absorbed into the human body in the small intestine [28]. Therefore factors that influence metal bioavailability in the intestinal phase are particularly relevant in any bioavailability/bioaccessibility assessment. Fig. 3 illustrates the change in Pb and Fe solution concentrations in gastric and intestinal phases of the SBRC assay. Lead bioaccessibility was found to vary between these soils. Analysis of Fe solution concentrations following the transition of Fe from the gastric to the intestinal phase showed that the concentration of soluble Fe was reduced by 2.0–105-fold (Fig. 3). The change in Fe concentration following modification of the gastric phase to intestinal phase conditions occurred as a result of the precipitation of amorphous Fe phases due to the oversaturation of hydrolysed Fe species resulting from the increase in solution pH [29]. The corresponding decrease in soluble Pb in the intestinal versus gastric phase may occur as a result of a number of processes including Pb precipitation due to the increase in solution

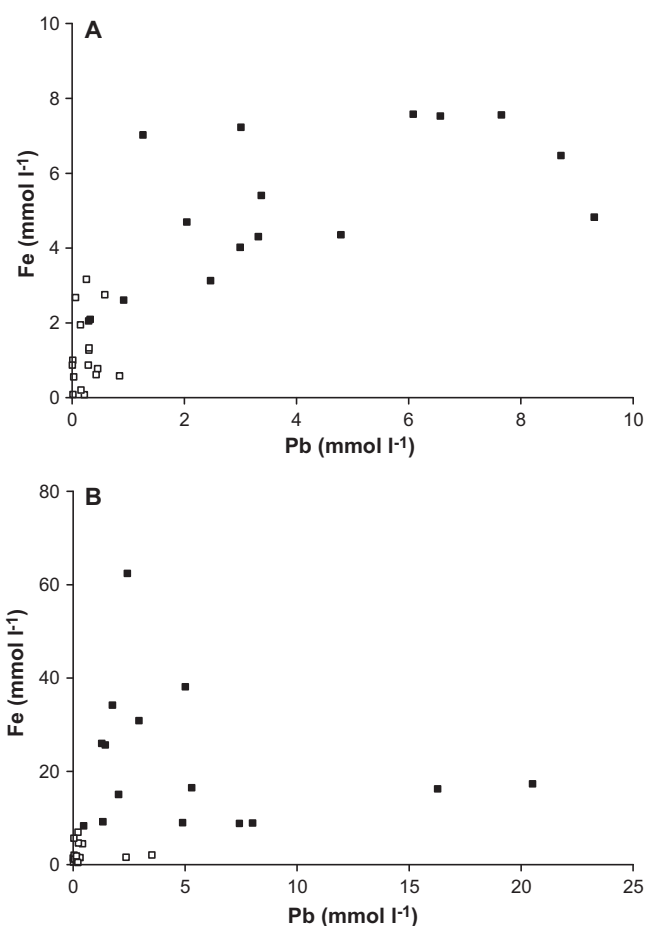


Fig. 3. Lead and Fe solution concentrations during gastric (■) and intestinal (□) phase extraction of soil samples. Panels represent data for soils with $<8 \text{ mmol l}^{-1}$ (A) and $>8 \text{ mmol l}^{-1}$ (B) of Fe in solution following gastric phase extraction.

pH, co-precipitation with amorphous Fe or re-adsorption onto the soil matrix [9,30–32]. Dissolved Pb may be sorbed to the amorphous Fe by surface complexation or may be incorporated into the amorphous Fe precipitate [13] which contributes to the reduction in dissolved Pb concentration in the intestinal phase.

3.3. Prediction of relative Pb bioavailability

The correlation between Pb bioaccessibility and Pb relative bioavailability has been determined by a limited number of researchers. The USEPA [4] and Drexler and Brattin [10] found that gastric phase extraction of Pb contaminated soils provided the best estimate of Pb relative bioavailability as determined using an in vivo swine model ($\text{Pb relative bioavailability} = 0.878 \times \text{SBRC-G} - 0.028$). However, the USEPA [4] cautioned that the in vivo–in vitro regression equation may not be suitable for all Pb contaminated soils as the model was developed predominantly using mining and smelting impacted soils. Further research by Bannon and Drexler [11] validated the use of gastric phase extraction for predicting Pb relative bioavailability using Pb contaminated soils sourced from small arms ranges. In contrast, Juhasz et al. [12] demonstrated that Pb relative bioavailability (swine model) could be predicted using the intestinal phase of the SBRC assay after the incorporation of Pb acetate solubility into calculation of Pb bioaccessibility (Eq. (2)). This approach was further validated by Smith et al. [13] using a larger number of soils impacted from a variety of Pb sources ($\text{Pb relative bioavailability} = 0.95 \times \text{Rel-SBRC-I} + 7.02$). In vivo–in vitro regression equations developed by the USEPA [4] and Smith et al.

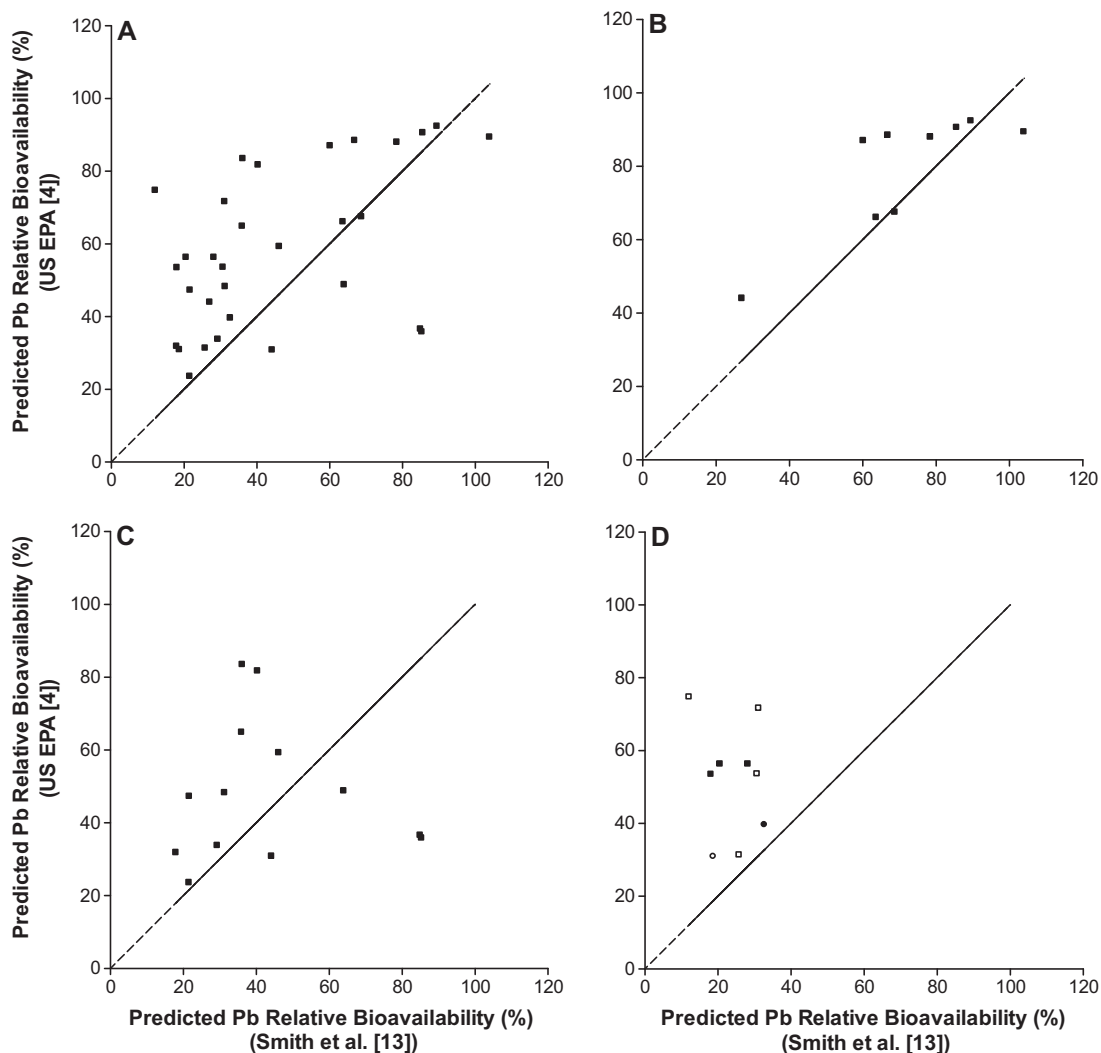


Fig. 4. Relationship between Pb relative bioavailability predicted using Rel-SBRC-I Pb bioaccessibility data and the in vivo–in vitro model (Relative bioavailability = $0.95x$ Rel-SBRC-I + 7.02) of Smith et al. [13] and SBRC-G Pb bioaccessibility data and the USEPA [4] in vivo–in vitro model (Relative bioavailability = $0.878x$ SBRC-G – 0.028). Panels represent data for all soils (A), shooting range soils (B), mining/smelting impacted soils (C) and incinerator (■), historical fill (□), gasworks (●) and geogenic (○) soils (D).

[13] were utilised to convert SBRC-G and Rel-SBRC-I in vitro data determined for the 31 soils used in this study (Table 2) into relative Pb bioavailability values. Both regression equations were utilised in order to determine whether different methodologies yield similar Pb relative bioavailability results.

A comparison of predicted Pb relative bioavailability values is shown in Fig. 4. While the relationship between predicted relative Pb bioavailability using the USEPA [4] and Smith et al. [13] in vivo–in vitro regression equations for all soils (Fig. 4a) was poor (Pearson correlation = 0.49), analysis of data based on the source of Pb contamination provided better relationships for some soils. For shooting range soils ($n=9$) relative Pb bioavailability values determined using SBRC-G and Rel-SBRC-I in vitro data were similar (Pearson correlation = 0.85) with a variance of 0.72 compared to the model equation (Fig. 4b; $y = 0.65x + 31.84$). In mining/smelting impacted soils, the relationship between predicted Pb relative bioavailability values fell into two distinct groups (Fig. 4c). For 9 of the 13 soils, predicted relative Pb bioavailability determined using SBRC-G in vitro data and the USEPA [4] in vivo–in vitro regression equation yielded values that were more conservative compared to those derived using the regression equation of Smith et al. [13] (Fig. 4c; $y = 1.70x - 0.40$; $r^2 = 0.56$; Pearson correlation = 0.75). In contrast, predicted relative Pb bioavailability using Rel-SBRC-I

in vitro data was 1.3–2.4-fold more conservative for the remaining 4 mining/smelting soils compared to values determined using gastric phase in vitro data. These soils were collected downwind from a Ag–Pb–Zn mine and the total Pb – concentrations in soil decreased with increasing distance from the mine. The total Fe concentrations in these soils were considerably lower compared to other soils studied where the Pb bioaccessibility was $<50\%$. As amorphous Fe precipitation influences dissolved Pb concentrations in the intestinal phase [9,29–31], the elevated Rel-SBRC-I Pb bioaccessibility values were derived for these soils compared to other mining/smelting soils with higher total Fe concentrations. For the remaining soils from incinerator, historical fill, gasworks and geogenic sources (Fig. 4d), the limited number of samples from each Pb source ($n=3, 4, 1$ and 1 respectively) prohibited an extensive analysis of the data, however, predicting Pb relative bioavailability using the USEPA [4] regression equation yielded more conservative values (1.2–6.1-fold) than those derived using the regression equation of Smith et al. [13].

4. Conclusions

The bioaccessibility of Pb in peri-urban contaminated soils was assessed using gastric and intestinal phases of the SBRC assay with

data incorporated into in vivo–in vitro regression equations for the calculation of Pb relative bioavailability. Lead bioaccessibility varied considerably ranging from 26.8% to 105.2% and 0.6–11.1% for gastric and intestinal phase extraction respectively. When Pb relative bioavailability was calculated using SBRC-G or Rel-SBRC-I in vitro data, similar values were derived for shooting range soils. However, the Fe content of the soil influenced the prediction of Pb relative bioavailability in mining/smelting impacted soils as this parameter affected Pb bioaccessibility particularly during intestinal phase extraction. For incinerator, historical fill, gasworks and gossan soils, incorporating SBRC-G data into the in vivo–in vitro regression equation resulted in more conservative Pb relative bioavailability values (1.2–6.1-fold) than those derived using Rel-SBRC-I in vitro data. This study highlights the impact of in vitro methodology on the assessment of Pb bioaccessibility in contaminated soils and the influence of in vivo–in vitro regression equations on the prediction of Pb relative bioavailability in soils contaminated from various Pb sources.

Acknowledgements

This research was funded by the Cooperative research Centre for Contamination Assessment and Remediation of the Environment (Grant number 1-3-01-05/6). The authors acknowledge the support of the Centre for Environmental Risk Assessment and Remediation, University of South Australia for this research.

References

- [1] H.E. Allen, C.P. Huang, G.W. Bailey, A.R. Bowers, Metal Speciation and Contamination of Soil, Lewis, Ann Arbor, MI, 1995.
- [2] B.P. Lanphear, R. Hornung, J. Khoury, K. Yolton, P. Baghurst, D.C. Bellinger, R.L. Canfield, K.N. Dietrich, R.L. Bornschein, T. Greene, S.J. Rothenberg, H.L. Needleman, L. Schnaas, G. Wasserman, J. Graziano, R. Roberts, Low level environmental lead exposure and children's intellectual function: an international pooled analysis, *Environ. Health Perspect.* 113 (2005) 894–899.
- [3] D.L. Simon, E.J. Maynard, K.D. Thomas, Living in a sea of lead – changes in blood- and hand-lead of infants living near a smelter, *J. Exposure Sci. Environ. Epidemiol.* 17 (2007) 248–259.
- [4] U.S. Environmental Protection Agency (USEPA), Estimation of relative bioavailability of lead in soil and soil-like material using in vivo and in vitro methods, OSWER 9285.7-77 (2007) EPA: Washington, DC.
- [5] M.V. Ruby, A. Davis, R. Schoof, S. Eberle, C.M. Sellstone, Estimation of lead and arsenic bioavailability using a physiologically based extraction test, *Environ. Sci. Technol.* 30 (1996) 422–430.
- [6] J.A. Ryan, K.G. Scheckel, W.R. Berti, S.L. Brown, S.W. Casteel, R.L. Chaney, J. Hallfrisch, M. Doolan, P. Grevatt, M. Maddaloni, D. Mosby, Reducing children's risk from lead in soil, *Environ. Sci. Technol.* 38 (2004) 19A–24A.
- [7] C.P. Weis, J.M. LaVelle, Characteristics to consider when choosing an animal model for the study of lead bioavailability, *Chem. Speciation Bioavailability* 3 (1991) 113–119.
- [8] J.L. Schroder, N.T. Basta, S.W. Casteel, T.J. Evans, M.E. Payton, J. Si, Validation of the in vitro gastrointestinal (IVG) method to estimate relative bioavailable lead in contaminated soils, *J. Environ. Qual.* 33 (2004) 513–521.
- [9] B. Marschner, P. Welge, A. Hack, J. Wittsiepe, M. Wilhelm, Comparison of soil Pb in vitro bioaccessibility and in vivo bioavailability with Pb pools from a sequential soil extraction, *Environ. Sci. Technol.* 40 (2006) 2812–2818.
- [10] J.W. Drexler, W.J. Brattin, An in vitro procedure for the estimation of lead relative bioavailability: with validation, *Hum. Ecol. Risk Assess.* 13 (2007) 383–401.
- [11] D. Bannon, J.W. Drexler, G.M. Fent, S.W. Casteel, P.J. Hunter, W.J. Brattin, M.A. Major, Evaluation of small arms range soils for metal contamination and lead bioavailability, *Environ. Sci. Technol.* 43 (2009) 9071–9076.
- [12] A.L. Juhasz, J. Weber, E. Smith, R. Naidu, B. Marschner, M. Rees, A. Rofe, T. Kuchel, L. Sansom, Evaluation of SBRC-gastric and SBRC-intestinal methods for the prediction of in vivo relative lead bioavailability in contaminated soils, *Environ. Sci. Technol.* 43 (2009) 4503–4509.
- [13] E. Smith, I. Kempson, A.L. Juhasz, J. Weber, A. Rofe, D. Gancarz, R. Naidu, R.G. McLaren, M. Gräfe, In vivo - in vitro and XANES spectroscopy assessments of lead bioavailability in contaminated peri-urban soils, (2010) *Environ. Sci. Technol.* Submitted for publication.
- [14] D.W. Nelson, L.E. Sommers, Total carbon, organic carbon, and organic matter, in: A.L. Page (Ed.), *Methods of Soil Analysis, Part 2*, 2nd ed., Agronomy, 9, Am. Soc. of Agron, Inc, Madison, WI, 1996, pp. 961–1010.
- [15] U.S. Environmental Protection Agency (USEPA) Method 3015A, Microwave assisted acid digestion of aqueous samples and extracts, In *USEPA Methods*, EPA: Washington, DC, (1998) pp 1–18.
- [16] M.E. Kelley, S.E. Brauning, R.A. Schoof, M.A. Ruby, *Assessing Oral Bioavailability Of Metals In Soil*, Battelle Press, Ohio, 2002.
- [17] T.R. Van de Wiele, A.G. Oomen, J. Wragg, M. Cave, M. Minekus, A. Hack, C. Cornelis, C.J.M. Rompelberg, L.L. de Zwart, B. Klinck, J. van Wijnen, W. Verstraete, A.J.A.M. Sips, Comparison of five in vitro digestion models to in vivo experimental results: lead bioaccessibility in the human gastrointestinal tract, *J. Environ. Sci. Health Part A* 42 (2007) 1203–1211.
- [18] National Environmental Protection Council, National environmental protection measure for the assessment of site contamination, National Environmental Protection Council Service Corporation, Adelaide, Australia, Schedule B1, (1999) pp. 1–12.
- [19] P.E. Rasmussen, K.S. Subramanian, B.J. Jessiman, A multi-element profile of housedust in relation to exterior dust and soil in the city of Ottawa, Canada, *Sci. Total Environ.* 267 (2001) 125–140.
- [20] D.A. Bright, G.M. Richardson, M. Dodd, Do current standards of practice in Canada measure what is relevant to human exposure at contaminated sites? I: a discussion of soil particle size and contaminant partitioning in soil, *Hum. Ecol. Risk Assess.* 12 (2006) 591–605.
- [21] K. Ljung, O. Selinus, E. Otabbong, M. Berglund, Metal and arsenic distribution in soil particle sizes relevant to soil ingestion by children, *Appl. Geochem.* 21 (2006) 1613–1624.
- [22] X. Cao, L.Q. Ma, M. Chen, D.W. Hardison, W.G. Harris, Weathering of lead bullets and their environmental effects at outdoor shooting ranges, *J. Environ. Qual.* 32 (2003) 526–534.
- [23] D.W. Hardison, L.Q. Ma, T. Luongo, W.G. Harris, Lead contamination in shooting range soils from abrasion of lead bullets and subsequent weathering, *Sci. Total Environ.* 328 (2004) 175–183.
- [24] C. Rooney, R.G. McLaren, L.M. Condron, Control of lead solubility in soil contaminated with lead shot: effect of pH, *Environ. Pollut.* 149 (2007) 149–157.
- [25] M.A. Ruby, A. Davis, T.E. Link, R. Schoof, R.L. Chaney, G.B. Freeman, P. Bergstrom, Development of an in vitro screening test to evaluate the in vivo bioaccessibility of ingested mine-waste lead, *Environ. Sci. Technol.* 27 (1993) 2870–2877.
- [26] R.A. Schoof, M.K. Butcher, C. Sellstone, R.W. Ball, J.R. Fricke, V. Keller, B. Keehn, An assessment of lead absorption from soil affected by smelter emissions, *Environ. Geochem. Health* 17 (1995) 189–199.
- [27] W. Stumm, J.J. Morgan, *Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters*, John Wiley & Sons: New York, 1996.
- [28] A.F. Hoffman, Regulation of metal absorption in the gastrointestinal tract, *Gut* 39 (1996) 625–628.
- [29] K.L. Mercer, J.E. Tobiasson, Removal of arsenic from high ionic strength solutions: effects of ionic strength, pH and preformed versus in situ formed HFO, *Environ. Sci. Technol.* 42 (2008) 3797–3802.
- [30] C.E. Martinez, M.B. McBride, Cd, Cu, Pb and Zn coprecipitates in Fe oxide formed at different pH: Ageing effects on metal solubility and extractability by citrate, *Environ. Toxicol. Chem.* 20 (2001) 122–126.
- [31] S.E. O'Reilly, M.F. Hochella Jr., Lead sorption efficiencies of natural and synthetic Mn and Fe-oxides, *Geochim. Cosmochim. Acta* 67 (2003) 4471–4487.
- [32] C.H. Yu, L.M. Yin, P.J. Liyo, The bioaccessibility of lead (Pb) from vacuumed house dust on carpets in urban residences, *Risk Anal.* 26 (2006) 125–134.