1 Bioaccessibility of Ba, Cu, Pb, and Zn in urban garden and orchard soils

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Abstract

Exposure of young children to toxic metals in urban environments is largely due to soil and dust ingestion. Thus, soil particle size distribution and concentrations of toxic metals in different particle sizes are important risk factors in addition to bioaccessibility of these metals in the particles. Analysis of particle size distribution and metals concentrations for 13 soils, 12 sampled from urban gardens and 1 from orchard found that fine particles ($<105\ \mu\text{m}$) comprised from 22 to 66% by weight of the tested soils, with Ba, Cu, Pb and Zn generally at higher concentrations in the finer particles. However, metal bioaccessibility was generally lower in finer particles, a trend most pronounced for Ba and Pb. Gastric was higher than gastrointestinal bioaccessibility for all metals except Cu. The lower bioaccessibility of Pb in urban garden soils compared to orchard soil is attributable to the higher organic matter content of the garden soils.

Capsule

Pb and other trace metals (Ba, Cu, Zn) were concentrated in fine particles of urban and orchard soils, but the bioaccessibility of Ba and Pb was generally lower in finer particles.

Keywords: Soil particle size distribution; Metal bioaccessibility; Urban soil; Orchard soil

1. Introduction

Urban soils are commonly contaminated with a number of toxic metals, with Pb perhaps being the metal presenting the most pervasive and persistent risk to human health in the urban environment (Laidlaw and Filippelli, 2008; Mitchell et al., 2014; Zahran et al., 2013). The most at-risk population in urban centers for Pb exposure and poisoning is very young children (Laidlaw et al., 2005; Mielke et al., 1999). Soil ingestion is a major route of exposure of children to Pb in urban centers (Mielke et al., 1999; Zahran et al., 2013), with seasonal fluctuation in children's blood lead levels implicating soil dust as an important contributor to children's exposure.

The most common measure of Pb exposure risk from soil is total Pb concentration in the soil. However, for several reasons, this parameter is inadequate for estimating Pb poisoning risk in children. Firstly, soils vary in texture, so that some soils have a higher percentage of finer particles. Soil particle size distribution is important because finer particles adhere most efficiently to children's hands (Ikegami et al., 2014). It is common to use the <250 μm particle size for exposure assessment, but this may underestimate Pb exposure due to preferential adhesion of smaller particles (<100 μm) that may have substantially higher Pb concentrations (Ikegami et al., 2014; Juhasz et al., 2011; Madrid et al., 2008). Secondly, the forms and chemical lability of Pb in different soils and particle sizes of soils can vary, which affects the rate and extent of Pb dissolution into absorbable forms in the gastrointestinal tract. Thus, the fraction of soil Pb that is bioaccessible can vary due to differences in soil properties (pH, organic matter, reactive Fe, particle size,

etc.) (Madrid et al., 2008; Sialleli et al., 2011) and form and severity of Pb contamination (Lamb et al., 2009). Consequently, total soil Pb in itself does not predict % bioaccessibility reliably (Walraven et al., 2015). Within a given soil, an increase in % Pb bioaccessibility is commonly observed with decreasing particle size (Juhasz et al., 2011; Madrid et al., 2008). Nevertheless, the only independent soil parameter that is correlated to the magnitude of bioaccessible Pb in soils with a high level of statistical significance overall is total soil Pb (Appleton et al., 2012).

A number of in vitro assays such as the physiologically based extraction test (PBET) described by Ruby et al. (1996) have been used to measure gastric phase and intestinal phase bioaccessibility of Pb and other toxic metals in contaminated soils (Juhasz et al., 2011; Oomen et al., 2002). The Pb bioaccessibility is calculated as:

$$\text{In vitro bioaccessibility (\%)} = (\text{in vitro Pb} / \text{total Pb}) \times 100$$

By the PBET assay, gastric bioaccessibility of Pb (typically 40-100%) is much greater than intestinal bioaccessibility (usually < 10%), owing to the much more acidic nature of the gastric extractant (Juhasz et al., 2011). However, different in vitro assays can give quite different bioaccessibility of soil metals largely due to different gastric pH values used in these tests (Oomen et al., 2002).

In addition to Pb, urban soils and brownfields commonly contain concentrations of Ba, Cu and Zn as well as a number of other metals, which are higher than concentrations in rural soils of the same geographical region. The New York State Department of Environmental Conservation has set soil cleanup objectives (SCOs) for concentrations of

potentially toxic metals based on an assessment of human exposure (NYDEC, 2006). These SCOs are 400, 270, 400 and 2200 mg kg⁻¹ for Ba, Cu, Pb and Zn, respectively, for protection of human health under a restricted use designation.

Contamination in urban areas is attributable to various sources such as galvanized steel, engine emissions, and wear or abrasion of vehicle components such as tires, brake pads and metal body parts, with generally higher concentrations of these metals near high-traffic density roads (Apeagyei et al., 2011; Harrison et al., 1981; Hjortenkrans et al., 2007; Nabulo et al., 2006; Ozaki et al., 2004). The use of high levels of Cu and Zn in brake components in recent decades has led to concerns about Cu and Zn dust emitted along high-traffic density roads (Hjortenkrans et al., 2007), suggesting that the accumulation of these two metals is likely to continue in areas with heavy vehicle traffic. Brake wear debris can contain extremely high concentrations of Cu, with one study measuring an average Cu content of 10.8% in the debris (Hur et al., 2003). A study in the Puget Sound basin of Washington State, USA, estimated Zn (from tire wear) and Cu (from brake pad wear) loading to road surfaces of 914 g/ km-yr Zn and 425 g/km-yr (Whiley, 2011). The concern for urban watershed contamination by Cu (and other metals) resulted in legislation in California and Washington State in 2010 to prohibit the sale of brake pads containing high concentrations of Cu and a number of other potentially toxic metals such as Cd and Pb; in 2015, the USEPA reached an agreement with the automotive industry to reduce Cu levels in brake pads to 0.5% by 2025.

The bioaccessibility of Cu and Zn have been reported for contaminated soils, although

these have frequently used the simplified gastric (SBET) extraction (Lamb et al., 2009; Madrid et al., 2008). Sialelli et al (2010, 2011) used the PBET assay for urban soils of Glasgow, UK and Torino, Italy, and determined in both studies that % Cu accessibility increased from the gastric to the intestinal phase, in contrast to the tendency of Pb and Zn to become substantially less soluble in the intestinal phase. Cu intestinal bioaccessibility in roadside soils averaged 46% compared to 39% and 48 % (gastric) for Zn and Pb, respectively. Roussel et al. (2010) measured in vitro PBET bioaccessibility of Zn as well as Cd and Pb in smelter-contaminated soils, with Zn averaging lower gastric bioaccessibility (47%) than Pb (62%). In the gastro-intestinal phase, Pb and Zn bioaccessibility reduced on average to 23% and 32%, respectively.

Ba concentrations in urban soils tend to be greater than rural background levels (Mitchell et al., 2014), with research indicating that Ba is a reliable tracer for vehicular emissions, specifically brake pad wear (Apeagyei et al., 2011; Gietl et al., 2010; Monaci and Bargagli, 1997). However, because Ba is relatively abundant in many uncontaminated soils, and has a low presumed bioavailability, it has not usually been considered a heavy metal of concern. Consequently, there is little research published on “in vitro” Ba bioaccessibility in soils; one study indicates that Ba bioavailability in soils contaminated by mining activity is limited by the low solubility of BaSO₄ (Lamb et al., 2013). This suggests that gastric bioaccessibility of soil Ba should be relatively low. Shock et al. (2007) reported, using an “in vitro” assay (0.4 M glycine at pH 1.5 to simulate gastric extraction), that extractable Ba in a mine-dust contaminated soil ranged

from 11 to 47 %. However, the measured extractability was strongly affected by both particle size and soil/extractant ratio.

In summary, in addition to the particular “in vitro” assay chosen to assess either gastric or intestinal bioaccessibility of toxic metals in soils, other variables that affect bioaccessibility are soil properties, chemical nature of the metal contaminant, particle size and soil/extractant ratio. The present study was undertaken to measure Ba, Cu, Pb, and Zn bioaccessibility in urban garden and orchard soils with one widely-used assay, the PBET (Ruby et al., 1996). The goals of this study were to establish relationships between soil particle size and both total metal concentration and metal bioaccessibility in the gastric and intestinal phase for soils known to be anthropogenically contaminated with Pb and other potentially toxic metals. Because forms of historical contamination likely to be present in the soils collected from the urban gardens are diverse and include Pb from paint and vehicle emissions (Mitchell et al., 2014), whereas lead arsenate pesticide is the only significant source of Pb contamination in the orchard (McBride et al., 2015), a second objective of this study was to assess the effect of Pb source on bioaccessibility. However, we decided that the much greater measured variability in soil properties (organic matter content, pH, metal and nutrient concentrations) of the urban gardens compared to the orchard required that a number of garden soils be included in the study to give some representation of the expected variability among soils in metal distribution and extractability.

2. Materials and methods

2.1 Soil samples

Soil samples (0-15 cm depth) were collected in 2012 from specific vegetable planting locations within community gardens and urban farms in NYC and Buffalo, NY as described in McBride et al. (2014). The samples were processed by air-drying in a laboratory hood for several days, passed through a 2 mm plastic sieve, and subsequently stored in closed cardboard containers. Soil pH values were measured by weighing 10 g of dry soil into 20 ml deionized water, equilibrating 30 minutes, and measuring pH with a combination glass electrode pre-calibrated with buffers at pH 4 and 7.

2.2 Separation of soils into particle size fractions

Twelve soil samples from the urban garden soils and one from an old apple orchard in Ithaca, NY contaminated by Pb arsenate, were chosen for particle size fractionation and analysis of size fractions for Pb, Ba and other metals of concern. The soils were selected to represent a range of Pb and Ba concentrations, based on pseudo-total determination of metals by acid digestion of the soils, and analysis by ICP-AES, and are listed in Table 1, with “G” and “O” signifying garden and orchard soils, respectively. They were sieved to 4 different particle size fractions ($<53\mu\text{m}$, $<105\mu\text{m}$, $<212\mu\text{m}$ and $>212\mu\text{m}$) by dispersing in polyethylene bottles with deionized water (soil:water = 1:2), shaking at high speed on a horizontal shaker for 1h, and then passing through sieves in sequence from larger to smaller sieve size. All particle size fractions obtained were dried at 65°C and weighed prior to analysis of total heavy metals by ICP-AES. The percentage of soil

composed of these 4 size fractions was then determined for all 13 soils listed in Table 1.

These weight percentages of the size fractions are presented in Table 2.

2.3 Determination of total metals in different size fractions of soils

Weighed subsamples of the various soil particle size fractions were digested with 60% nitric-40% perchloric acid at 180°C for 30 minutes on an automated hot-plate before determination of metals in the digests by ICP-AES. The soil concentrations determined in this way are not true total concentrations, which generally require HF to be used to obtain complete dissolution of the soil mineral fraction, and are referred to as “pseudo-total” metals. Standard reference soil materials (NIST 2702 and 2709) were digested by the same method and analyzed by ICP-AES to determine recoveries of Ba, Cu, Pb and Zn. Recoveries of Cu, Pb and Zn were generally acceptable (>72%), but those for Ba were not. Low Ba recoveries using standard nitric or hydrochloric acid digestion methods that do not utilize HF (such as EPA 3050) have been documented in other studies (Medved’ et al., 1998; Shock et al., 2007). Ba recovery for the high-Ba San Joaquin soil (NIST 2709) was 40% using our nitric-perchloric acid digestion method. Therefore, the pseudo-total soil Ba concentrations reported in this study should be interpreted as representing the strong acid-labile quantities of Ba in the soils, rather than the actual total quantities.

Twenty-six elements, including heavy metals and trace elements were analyzed by ICP-AES, but only Ba, Cu, Pb, and Zn were chosen for further study. Table 1 reports the

concentrations of these metals in all of the soils selected for study. Pb and Ba exceeded NY State SCO of 400 mg kg⁻¹ for both metals (NYDEC, 2006) in some soils, and therefore represented a possible concern for human health. However, the SCOs for Cd, Cu and Zn were not exceeded in any of the soils.

2.4 Bioaccessibility of Ba, Cu, Pb, and Zn in soils

Based on the results of the measured Ba and Pb concentrations in the soils, 5 soil samples representing a range of Pb and Ba were selected for the PBET test. Because Cu and Zn also tended to be higher in the urban garden soils than in uncontaminated rural soils, bioaccessibility assays were conducted for these metals as well. For each soil sample selected, the 4 subsample size fractions were subjected to the PBET test in duplicate. The PBET method used was based on that described by Ruby et al. (1996) and involved a first extraction step with simulated gastric solution at pH 2.5 for 1h and a second extraction step at pH 7 to simulate intestinal digestion for another 3h by the addition of bile salts and pancreatin. Specifically, 50 mL gastric solution (1L gastric solution contains 1.25g pepsin (from porcine gastric mucosa, Sigma), 0.5g sodium citrate, 0.5g malic acid, 0.42ml lactic acid, 0.5ml acetic acid and 0.8ml concentrated HCl) was combined with 0.5g soil in a 125 mL Erlenmeyer flask, then put in an incubator-rotary shaker at 180 rpm for 1 h at 37°C. After 1h, gastric digestion was stopped by filtration with Whatman No. 42 paper, Pb and other metals (Ba, Cu, Zn,) in the filtrate were analyzed by ICP-AES. For gastrointestinal digestion, 50 mL gastric solution was

combined with 0.5 g soil in a 125 mL Erlenmeyer flask, then put in an incubator-rotary shaker at 180 rpm for 1 h at 37°C. After 1h, the suspension was titrated to pH 7 with 3 mL saturated NaHCO₃ solution, then 87.5 mg bile salts (bile extract porcine, Sigma) and 25 mg of pancreatin (from porcine pancreas, Sigma) were added. After another 3h, the gastrointestinal digestion was stopped by filtration with Whatman No. 42 paper, and Ba, Cu, Pb, and Zn in the filtrates were analyzed by ICP-AES.

2.5 Organic carbon in soil particle size fractions

The Walkley-Black method was used to determine organic carbon contents of the separated particle size fractions of the 5 soils selected for the PBET assay. An appropriate amount of each size fraction (containing 5 to 12 mg of organic carbon) was weighed into a 125 ml Erlenmeyer flask before adding 5 ml of 0.167 M K₂Cr₂O₇ and 10 ml of concentrated H₂SO₄, then the flask was swirled for 1 minute and let stand on a hot plate for 30 minutes. Finally, 15 ml of deionized water was added and the flask was cooled in a water bath before adding 8 drops of Ferroin and titrating with 0.5 M FeSO₄ solution until the color flashed from dark green to reddish-brown. The Walkley-Black method used here (without a supplemental heating step) does not completely oxidize soil organic carbon, and a correction factor of 1.33 has been recommended to scale the measured values to total organic carbon contents of samples (Allison, 1965). We used a reference sediment (SRM 2702) with known total organic carbon (3.36%, based on combustion methods) to calibrate the method. The uncorrected Walkley-Black C content

of SRM 2702 averaged 70.0 % of the known total C value, so the correction factor for our organic carbon determinations of soils was taken to be 1.43.

3. Results and discussion

3.1 Metal concentrations in different soil particle sizes

The particle size distributions of all 13 soils, based on sequential sieving of the water-dispersed soils, are given in Table 2. Most of the urban garden soils were composed of at least 40% coarse ($>212\ \mu\text{m}$) particles, whereas the orchard soil was lower in coarse and higher in fine ($<53\ \mu\text{m}$) particles. Only one urban garden soil (66G) had as high a percentage of fine particles (37.5%) as the fine-textured orchard soil.

The concentrations of Ba, Cu, Pb and Zn in the different particle size fractions of each of the 13 soils are presented in Table 3. These results show that, with few exceptions, the highest Ba, Cu, Pb and Zn concentrations are found in the finer grain sizes of the urban garden soils. The orchard soil (O2) had a more even distribution of metal concentrations in different particle size fractions than the urban soils. As illustrated in Figure 1, soil organic matter was not evenly distributed in the particle size fractions of the urban garden soils, but was more concentrated in the 53-212 μm fractions. Other studies have found the highest organic matter content in the finest soil fractions, but these typically studied low-organic matter soils using aggressive dispersing techniques such as ultrasonication or chemical dispersants (Li and Pang, 2014; Schmidt and Kögel-Knabner, 2002). It is possible that the “natural” particle size of aggregated organic matter of the garden soils containing high organic matter contents tended to be in the 53-212 μm size

range (no dispersing agents were used to disaggregate organic and mineral matter in the soil shaking step of this study). Clay minerals ($< 2 \mu\text{m}$ particle size) could have dominated the smallest sieve size ($< 53 \mu\text{m}$) fraction, possibly accounting for the lower organic matter content of this fraction. Therefore, the higher metal concentrations in the finest particle size fractions of the garden soils is not explained fully by metal bonding to organic matter. The orchard soil was unlike the urban garden soils in that it contained much lower total organic matter, with both organic matter and metal (Ba, Cu, Pb and Zn) concentrations distributed fairly evenly among the 4 particle size fractions (Figure 1, Tables 1, 2, 3).

3.2 Bioaccessibility of Ba, Cu, Pb and Zn in particle size fractions

Bioaccessibility (GB and GIB) of the tested metals were calculated by multiplying the measured concentrations of the metals in the filtered gastric and intestinal phase extracts by the extract volume (50 ml) to determine mg of dissolved metal, and dividing this value by the total mg of metal initially present in 0.5 g of the extracted soil particle-size fraction based on the pseudo-total measurement of metal concentration in each soil fraction. This final ratio of dissolved to total metal is multiplied by 100 to represent bioaccessibility on a percent basis. The bioaccessibility for the four metals are presented below.

Barium

The % bioaccessibility of Ba was relatively low, with GB and GIB generally less than 25% and 10%, respectively, in the urban garden soils (see Figure 2). The %

bioaccessibility tended to be higher in the coarser particle size fractions. The % bioaccessibility of 109G and 2G, which had the highest Ba concentrations (see Table 1) were lower than those of the other soils. Conversely, the % bioaccessibility of Ba in the orchard soil (2O), which contained the lowest total Ba, was higher than that of the urban garden soils.

Overall, regression analysis showed that the % GB and GIB both decreased as total Ba in the soil fractions increased (r^2 of 0.754 and 0.809, respectively). These trends in % bioaccessibility dependence on soil Ba content suggests that more Ba-contaminated soils or soil fractions may contain a higher fraction of insoluble mineral forms such as barite. However, it is also possible that, because greater dilution of soil in extractants has been shown to dissolve a greater fraction of Ba (Shock et al., 2007), soil fractions with lower Ba in the form of barite would tend to release Ba more efficiently into solution during extraction by the PBET method in accordance with the solubility product.

Copper

Cu was unlike all other metals tested in consistently having GIB higher than GB for all particle size fractions of all soils (see Figure 3). For the urban garden soils, GB was well below 20% in nearly every particle size fraction, perhaps attributable to the ability of Cu to bind to organic matter in these high-OM soils under strongly acidic conditions (Manceau and Matynia, 2010). Conversely, the GIB values were higher than for any of the other metals, ranging from 30 to 70%. These results are consistent with those reported by Sialelli et al. (2010, 2011), who determined that % Cu bioaccessibility

increased from the gastric to the intestinal phase, unlike Pb and Zn which became less soluble in the intestinal phase. The behavior of Cu suggests that certain organic compounds in the PBET assay (e.g., malate, citrate, lactate, pepsin, pancreatin) complex Cu at the near-neutral pH of the GIB extraction, bringing a large fraction of soil Cu into the dissolved phase.

Regression analysis revealed no significant correlation between either % GB or % GIB and total Cu in the soil fractions (n=20, data not shown).

Lead

The gastric (GB) and gastrointestinal (GIB) bioaccessibilities of Pb for the particle size fractions of the 5 soils selected in the assay are presented in Figure 4. The GB was less than 20% in most particle size fractions of the urban garden soils, with a tendency to be higher in the larger particles. Thus, GB was close to 30% in the coarse fractions of soils 47G and 109G (Figure 4). GIB was generally lower than GB for all soils tested, and was usually well below 15% for all urban garden soils. As with GB, there was a trend of increasing GIB with increasing particle size. The orchard field soil (2O) was unique in having substantially higher GB and GIB than the urban garden soils. It is important to note that the organic matter content of the orchard soil was much lower in all but the coarsest particle size fraction than the 4 urban garden soils (see Figure 1).

In summary, the bioaccessibilities reported for the urban garden soils tested here are lower than those usually reported for other Pb-contaminated urban and industrially contaminated soils (Lamb et al., 2009; Roussel et al., 2010; Sialelli et al., 2011). The

generally lower GB and GIB in the finer particle size fractions of the urban garden soils is consistent with other studies which have shown that clay particles have the lowest Pb bioaccessibility, possibly due to the formation of stable Pb-humic complexes attached to clays (Madrid et al., 2008).

There was no overall significant relationship of % bioaccessibility to total Pb content of the various soil particle fractions (data not shown). This observation is different from that of Lamb et al. (2009), who found that % Pb bioaccessibility in severely contaminated soils tended to be higher than that in less contaminated soils. However, the contaminated soils in that study were collected near smelters and contained quite low organic matter in most cases.

Zinc

The GB and GIB assays gave Zn bioaccessibility in the urban garden soils in the 25-60% and 5-20% range, respectively, with the orchard soil (2O) having lower bioaccessibility for both assays (see Figure 5). The lower extractability of Zn in 2O is probably a consequence of the low total Zn concentration in this soil and consequently strong bonding to minerals and organic matter. As with Ba and Pb, there was some tendency for the GIB to give lower % bioaccessibility of Zn in the finer particle fraction of soil. The % bioaccessibilities for the urban garden soils shown in Figure 5 are fairly similar to those reported by Roussel et al. (2010) but higher than those reported by Sialleli et al. (2011) for urban roadsides and, especially, urban parks.

Overall, Zn bioaccessibility (%) was not significantly correlated to total Zn

concentration in the soil fractions (n=20, regression not shown). Thus, as with Cu, Zn % bioaccessibility was not a function of total Zn in the soil fraction.

3.3 Effect of soil organic matter on metal bioaccessibility

Table 4 presents the best-fit linear functions describing the relationships of Ba, Cu, Pb, and Zn % bioaccessibility to measured organic carbon in the particle size fractions (data from all size fractions pooled together), both gastric and intestinal phases.

For Ba, Cu and Pb, gastric bioaccessibility (% GB) was significantly lower in soil particle fractions with higher OM content; however, soil OM was not significantly correlated to the GB of Zn. These trends are consistent with the known high affinity of soil organic matter with Cu and Pb, and suggest that Ba is also retained strongly by organic matter in the acidic gastric extraction assay. Intestinal bioaccessibility (% GIB) was also lower in soil fractions with higher OM in the cases of Ba, Pb, and (to a lesser extent) Zn. However, it seems likely that Cu was solubilized in the gastrointestinal extraction phase by the combination of neutral pH and presence of organic ligands with high affinity for Cu, counteracting the ability of soil organic matter to inhibit Cu extraction by the gastric phase.

In summary, the organic matter content of the soils tested using the PBET assay had an important effect in reducing the gastric bioaccessibility (GB) of Ba, Cu and Pb, with less clear effects on Zn. The beneficial effect of organic matter carried over to gastrointestinal bioaccessibility (GIB) for Ba and Pb, but not for Cu.

4. Conclusions

Using physical agitation (without chemical dispersants) to disperse soil aggregates in water, it was found that urban garden soils averaged about 34% (ranging from 22 to 53%) by weight particles of size $< 105 \mu\text{m}$, the size of particles most likely to adhere to children's hands and possibly other surfaces. A high-Pb fine-textured orchard soil contained an even higher percentage (66%) of particles $< 105 \mu\text{m}$. The metals measured in the urban garden soils (Ba, Cu, Pb, Zn) were generally at higher concentrations in the finer size fractions ($<105 \mu\text{m}$); however, this tendency was less evident in the orchard soil.

Gastric and gastrointestinal bioaccessibility (% GB and GIB) of urban soil Ba and Pb tended to be lower in finer particles. Although Zn showed less consistent trends in bioaccessibility, Zn had lower % GIB in smaller particle size fractions. Cu had no consistent pattern of % GIB dependence on particle size. The relationships of % GB and GIB to particle size may be due to the effects of strong metal bonding to organic matter, as there were overall significant negative relationships between organic carbon content of particle size fractions and % bioaccessibility, at least for Ba, Cu and Pb. This relationship was weaker or insignificant for Zn. Because organic carbon content of the urban garden soils was generally higher in the finer ($<105 \mu\text{m}$) than in the coarse ($>212 \mu\text{m}$) fractions, the lower % bioaccessibility of Ba, Cu and Pb in the fine fractions is attributable at least in part to metal bonding to organic matter. The higher clay mineral content of the fine fractions also may be important in specific adsorption and reduced bioaccessibility of

metals.

The orchard soil did not follow the pattern of lower % bioaccessibility in smaller particle size fractions described above for the urban garden soils. Furthermore, this soil had a much higher % GB and GIB for Ba, Pb and to some extent, Cu. The clear contrasts in behavior to the garden soils can be attributed to the much lower and more evenly distributed organic carbon in the particle size fractions compared to the urban soils and the likelihood that the chemical form of Pb contamination in this soil is different from that in the urban soils.

For all soils tested, the % GB was higher than GIB for every metal except Cu. This trend is consistent with other studies, and reflects the much lower pH of the simulated gastric extraction. It is noteworthy that the % Pb bioaccessibility reported here for urban garden soils is lower than values reported for other severely Pb-contaminated soils. It is suggested that the high organic carbon contents of these garden soils, many of which have been amended with composts, provides a significant protection against Pb absorption for exposed individuals.

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Table 1. Properties and pseudo-total metal concentrations of urban garden (G) and
 orchard (O) soils selected for particle size fractionation.

Soil ID	pH	OM (%)	Ba (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Zn (mg kg ⁻¹)
2G	7.28	4.58	446	67.2	994	510
4G	6.61	3.85	120	42.4	218	136
5G	7.13	4.81	414	46.4	384	284
13G	6.82	6.82	200	39.8	369	223
47G	7.69	4.22	217	40.2	280	238
66G	7.24	4.77	177	82.9	676	430
87G	6.75	3.09	294	73.0	1400	295
109G	7.36	6.78	553	58.7	673	490
116G	6.54	8.20	204	58.5	1620	652
129G	6.82	7.65	188	63.4	1210	548
133G	7.08	3.74	306	46.6	3620	1060
150G	7.13	8.69	124	65.8	232	221
2O	5.24	4.34	50.9	41.4	826	74.1

Table 2. Weight percentages (%) of different particle size fractions determined by sequential sieving of the urban garden and orchard soils

Soil ID	<53µm	53-105µm	105-212µm	>212µm
2G	14.0	10.1	17.4	58.5
4G	23.5	13.7	17.8	45.1
5G	20.8	7.92	15.6	55.7
13G	15.8	8.88	13.4	61.9
47G	13.6	8.60	14.4	63.4
66G	37.5	15.6	22.1	24.8
87G	17.0	12.1	19.2	51.7
109G	17.0	11.2	16.8	55.0
116G	20.3	16.0	23.4	40.3
129G	17.3	16.2	21.9	44.5
133G	24.9	22.0	24.7	28.4
150G	28.8	11.9	17.3	41.9
2O	37.4	29.0	17.0	16.6

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527 **Table 3.** Heavy metal concentrations (mg kg⁻¹) in different size fractions of soils

Particle size (μm)		2G	4G	5G	13G	47G	66G	87G	109G	116G	129G	133G	150G	2O
Ba	<53	945	219	724	346	521	219	573	1060	290	258	357	137	59.3
	53-105	748	162	628	325	376	170	438	902	185	189	269	116	47.4
	105-212	643	141	590	267	285	132	286	719	183	168	285	105	46.3
	>212	216	47.9	219	131	115	159	172	277	180	171	306	124	43.0
Cu	<53	171	80.4	96.3	87.0	90.1	113	151	122	95.8	111	69.3	89.9	62.8
	53-105	104	55.8	68.7	68.6	71.8	82.5	132	96.5	52.6	50.3	42.8	64.5	29.2
	105-212	84.1	46.9	61.5	54.3	53.9	57.2	79.4	69.9	52.6	66.7	47.0	59.3	36.3
	>212	31.0	16.9	20.4	20.6	22.1	60.7	31.2	28.0	45.5	47.8	29.4	52.3	19.7
Pb	<53	1570	378	741	556	700	764	2610	1310	2030	1670	4140	298	783
	53-105	1220	299	647	558	561	648	2000	1180	1410	1170	3100	277	846
	105-212	919	257	600	483	398	516	1200	839	1390	1080	3480	231	929
	>212	838	94.1	152	270	125	703	942	321	1620	1110	3690	175	779
Zn	<53	1100	243	536	408	551	570	643	970	938	819	1400	285	92.0
	53-105	838	180	423	385	424	442	504	799	591	526	936	219	62.7
	105-212	680	159	419	315	294	324	306	606	567	492	1030	193	68.0
	>212	261	58.4	132	132	133	307	128	243	582	479	873	189	59.8

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Table 4. Linear regression functions relating % bioaccessibility (GB and GIB) to measured soil organic matter (% OM)

Metal	Gastric Bioaccessibility (GB)		Gastrointestinal Bioaccessibility (GIB)	
	equation	R ²	equation	R ²
Ba	50.6 – 2.70×OM	0.302 s	16.4 – 0.962×OM	0.556 s
Cu	26.4 – 1.36×OM	0.489 s	49.0 – 0.0565×OM	0.0008 ns
Pb	47.8 – 2.78×OM	0.528 s	17.6 – 0.994×OM	0.524 s
Zn	32.2 + 0.687×OM	0.051 ns	14.1 – 0.556×OM	0.149 ns

* All soil size fractions pooled (n =20), with significant correlation coefficients (p < 0.05) denoted by “s”.

Fig. 1. Organic matter in different fractions of soil as determined by the Walkley-Black method

Fig. 2. Ba bioaccessibility in size fractions of the 5 soils subjected to the PBET assay

Fig. 3. Cu bioaccessibility in size fractions of the 5 soils selected for the PBET assay

Fig. 4. Pb bioaccessibility in size fractions of the 5 soils selected for the PBET assay

Fig. 5. Zn bioaccessibility in size fractions of the 5 soils selected for the PBET assay