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Lead and Arsenic Bioaccessibility and Speciation as a Function of Soil Particle Size

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Abstract

Bioavailability research of soil metals has advanced considerably from default values to validated *in-vitro* bioaccessibility (IVBA) assays for site-specific risk assessment. Previously, EPA determined the soil size fraction representative of dermal adherence and consequent soil ingestion was <250 μm . This size fraction was widely utilized in testing efforts for both *in-vivo* and *in-vitro* experiments. However, recent studies indicate the <150 μm size fraction better represents the particle size that adheres to skin for potential ingestion.

At issue is the relevance of validated *in-vivo* and *in-vitro* methods developed with <250 μm upon moving to the <150 μm fraction. The objectives of this study were to investigate <250 μm versus <150 μm particle size and particle size groups for evaluating lead and arsenic IVBA and speciation. Soils with different properties were homogenized, oven-dried, and sieved: <250 μm to >150 μm , <150 μm to >75 μm , <75 μm to >38 μm , and <38 μm . Sieved versus ground subsamples of <250 μm and <150 μm bulk soils were also used for IVBA and synchrotron-based lead and arsenic speciation. Although we observed increased in total and IVBA extractable lead and arsenic with decreased soil particle size, changes in %IVBA of Pb and As (dependent on the ratio of extractable to total) remained consistent in all the tested soils. No significant changes in Pb and As speciation were observed across the soil fractions. The results suggest utilizing the more relevant <150 μm fraction will not undermine currently validated IVBA protocols in future bioavailability studies.

Introduction

Exposure to lead (Pb) via inhalation and ingestion is a major public health hazard of global dimensions. Childhood (age < 6 yrs) Pb-poisoning via hand-to-mouth exposure is of

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particular concern (Canales and Leckie, 2007). Intake of Pb per unit body weight is higher for children, and they are vulnerable to the central nervous system and other effects of lead (National Toxicology Program 2012; U.S. EPA, 2013). At high levels of exposure, Pb causes spectrum of injury across multiple body systems, in particular affecting children's central nervous system and consequent behavioral and cognitive abnormalities. Lead exposure can also cause anaemia, hypertension, renal impairment, immunotoxicity and toxicity to reproductive organs (National Toxicology Program, 2012). Arsenic (As) is a naturally occurring metalloid with certain As-species being highly-toxic and is recognized as a carcinogen responsible for gastrointestinal, cardiovascular, and reproductive illnesses (ATSDR, 2016; Fowler, 2015; Ng et al., 2003; Nordberg and Fowler, 2015; Rossman et al., 2003; Selene et al. 2015; States et al., 2016 and Wang et al. 2003). Arsenic poses a public health risk either directly through incidental soils/dust ingestion or indirectly through translocation into groundwater used for drinking (USEPA, 2000).

Total metal content is a critical regulatory factor in the risk assessment of any contaminated site, however total metal content alone cannot predict the fate of metal contaminants, their mobility and bioavailability. Lead and As react with soil components to form sorbed or mineral phases that could be weakly bound and become bioaccessible (a specific measure of solubility designed to predict bioavailability) and enter the bloodstream. Oral bioavailability is defined as 'the fraction of an ingested dose that crosses the gastrointestinal epithelium and becomes available for distribution to internal target tissues and organs' (US EPA 2007a). Bioavailability research of soil metals has advanced considerably in the past two decades from default assumptions of 100% availability, to extensive *in-vivo* studies determining an upper bound prediction value, and to validated *in-vitro* bioaccessibility (IVBA) assays for extensive site-specific risk assessment at several major Superfund sites (USEPA, 2007a, b). However, the decision making process based on bioavailability measurements are gaining slow acceptance because bioavailability studies are based on different assumptions such as 'nature of the matrix' or 'the particle size fractions' of the soils that determines the metals' exposure level (USEPA, 2007a, b), as well as biological and physiological variables of the exposed individual (Scheckel et al., 2009). An assumption of equivalent bioavailabilities in two different matrices can over- or under-estimate associated risk and can significantly affect estimated risk and cleanup goals (Bradham et al. 2011). Therefore, it is very important to gain a better understanding, and validation on the approaches that have been in use in determining the bioavailability of metal to enhance regulatory acceptance in the use of bioavailability adjustments.

For bioavailability studies, the estimated dose should represent the exposure scenario, and soil particle size plays a significant role in exposure routes. In general, finer particles consist of higher concentrations of metal(loid)s as they have higher specific surface areas due to more exposed mineral surfaces, and contain clay minerals, organic matter, and oxides of Fe/Mn/Al oxides forming fine-sized aggregates (Cai et al., 2002; Ljung et al., 2006 and Semlali et al., 2001). Various soil size fractions may have different composition and properties that influence the behavior of pollutants in soil microenvironments (Acosta et al., 2011). Particle size influences soil adherence variability on children's hands as the estimation of exposure from hand to mouth activity (incidental ingestion). In the past, a wide variety of soil particle sizes ranging from <45 to <2000 µm has been used by different

research groups thereby making it difficult to directly compare reported results across studies (Bartrop and Meek, 1979 and Ruby et al., 2012). Although <150 µm size soil fraction tends to adhere more, <250 µm size soil fraction incorporates more particle size ranges that are capable of adhering to children's hand (Driver et al., 1989). Thus, early research determined the soil size fraction involved with soil ingestion was <250 µm, and this fraction has been widely utilized in testing efforts for both *in-vivo* and *in-vitro* experiments. Since the 1990s, USEPA utilized a swine model for the determination of relative Pb and As bioavailability from soil, which uses a <250 µm soil fraction (USEPA, 2005). Thereafter, most researchers have used the <250 µm particle size for oral bioavailability research models: Maddaloni et al., 1998 (Pb in humans); Roberts et al., 2007 (As in primates); Budinsky et al., 2008 (dioxins/furans in rats and swine); Finley et al., 2009 (dioxins/furans in rats); Casteel et al., 2006 and Bannon et al., 2007 (Pb and As in juvenile swine); Bradham et al., 2011, 2013, 2015 (As in mice).

The EPA's Technical Review Workgroup (TRW) Lead Committee initially recommended that Pb in <250 µm particle size fraction is more representative of ingestion exposure compared to unsieved (nominally < 2mm) soil (U.S. EPA, 2000). While this remains true, in July 2016, the TRW reviewed ten recent studies (Ruby and Lowney 2012; Bergstrom et al., 2011; Choate et al., 2006a; Gong et al., 2013; Juhasz et al., 2011; Siciliano et al., 2009; USEPA, 1995, 2000 and Yamamoto et al., 2006) reporting the relationship between dermal adherence of soil and dust as a function of particle size fractions (e.g., <150, <125, <40 µm) from a variety of samples, leading the TRW to recommend the <150 µm particle size for use in the assessment of human health risks for soil and dust exposures (USEPA, 2016). Reliable data on the particle size fraction and the contaminant enrichment that is most likely to adhere to children's hands improves the accuracy of exposure and consequent risk estimates. At issue is the relevance of previous research with the <250 µm soil fraction as new research increasingly transitions to <150 µm fraction pertaining to *in-vivo* – *in-vitro* correlations (IVIVC) predictive of relative bioavailability for site-specific risk assessment. To date, a tremendous amount of effort and expense has been put forth to develop and refine *in-vivo* and *in-vitro* methods utilizing the <250 µm soil fraction.

In concert with total concentration, particle size, and biological risks of soil contaminants, the form of the metal contaminant in soil, as influenced by soil physicochemical characteristics, impacts soil-metal bioavailability. Metal speciation is a strong modifier of bioavailability based on differences in solubility (Casteel et al., 2006 and Scheckel et al., 2009). For example, solubility of Pb minerals present in a test material may correlate with bioavailability results. Lead minerals have been classified based on their range of solubility as very high for Pb oxide (PbO); average for Pb-manganese (Pb-Mn) oxides, Pb-iron (Pb-Fe) oxides, and Pb carbonates; moderate for Pb sulfates and Pb arsenate; and minimal for Pb phosphates (Pb-P) (Schoof et al., 1995). Bioavailability testing (and subsequent bioaccessibility) for several *in-vivo* and *in-vitro* studies varies from high for cerussite PbCO₃ and Pb-Mn oxide (>75%), to medium for Pb-P and PbO (25 to 75%), to low for anglesite, galena, Fe-Pb species and remaining Pb-based oxides (<25%) (USEPA, 2007a, b). Similarly, soil minerals play an important role in determining As-retention and its solid-state speciation that further regulates the mobility and bioavailability of As in soil (Meunier et al., 2010; Niazi et al., 2011; Ruby et al., 1999). Meunier et al. (2010) reported the bioaccessibility of

As-speciation in the following order: high for calcium-iron arsenate (approx. 49%), medium for amorphous Fe arsenates and arsenic-bearing Fe hydr(oxides) (1 to 10%), and low for arsenopyrite or scorodite (<1%).

X-ray absorption spectroscopy (XAS) was used to determine Pb and As speciation with changes in soil size fractions in four soils used in this study. This technique provides the following advantages over wet chemical methods: lower detection limits, ability to identify more mineral phases information on metals in a variety of physical states, including amorphous or crystalline compounds as well as dissolved species, reduced subjectivity relative to microprobe, and has been successfully used over several years to speciate metals in heterogeneous and complex soils and sediments samples (Isaure et al., 2002, Karna et al., 2016; Manceau et al., 2004; Nachtegaal et al., 2005; Roberts et al., 2002; Scheckel and Ryan, 2004 and Scheinost et al., 2002). In addition, this technique combines the element specific, *in-situ* capabilities of XAS with the comprehensive statistical analysis of linear combination fittings (LCF) or principle component analysis (PCA) by examining unknown sample spectra relative to known reference compounds to identify the % components of each particular metal-species present in the sample. Information obtained via XAS measurement can be used to predict the long-term fate of the metal and its potential bioavailability based on known solubility products (Scheckel and Ryan, 2004). However, bulk XAS analysis demands a library of reference spectra to perform a linear combination fitting that estimates a single average spectrum collected from a large spot (i.e., relatively large soil volume) (Manceau et al., 2000a).

We hypothesized that a) while total and IVBA extractable Pb and As might congruently increase with decreasing particle size, the %IVBA (dependent on the ratio of extractable to total) may remain similar, b) pulverization (i.e., ground samples) may enhance IVBA with increased reactive mineral surfaces, and greater dissolution thereby enhancing metal release due to increase in surface oxidation forming products that are more readily absorbed, and c) while the percent composition for each Pb and As species may change, overall speciation should remain similar in different soil fractions. The objectives of this study were: a) to investigate <250 μm versus <150 μm particle size for evaluating IVBA of Pb and As from soils with respect to other soil fractions on IVBA estimation, b) to measure any variability in IVBA in sieved versus ground soils, c) to determine any changes in Pb and As speciation in different soil fractions and sieved versus ground in order to provide more confidence in selecting the soil particle size for a particular soil type that best represents oral exposure to human, and help make it widely acceptable in decision making process.

Materials and methods

Soil sampling and processing

Substrates evaluated for Pb and As IVBA included a variety of soils co-contaminated with both Pb and As such as BO (orchard, NC, USA), IKJ 583 (mining-impacted, AZ, USA), HSJ 583 (smelter-impacted, AZ, USA), and SOFc-1 (mining-impacted USGS standard reference material, MT, USA). More details are provided in SI (Figure S1, Table S1).

Physicochemical characterization of soils

Total extractable solid digestion (EPA Method 3051a) was conducted on each soil size fraction to measure the total contents of Pb, As, Mg, Ca, Fe, P and most of the transition metals by using Inductively Coupled Plasma– Optical Emission Spectroscopy (ICP- 6500 trace Analyzer). Triplicates of each sample were used to minimize the estimation error. The aqueous samples collected from total digestion were stored at 4 °C in the refrigerator until analyzed.

Bioaccessibility assays

Details on EPA Method 1340 at pH 1.5 is provided in SI. Statistical analysis was conducted using Excel 2016 Data Analysis Tool Pak.

Quality assurance and quality control (QA/QC) checks

Details on QA/QC checks are provided in table S2A, table S2A.

Synchrotron-based XAS data collection and analyses

XAS was performed on all size fractions of test soils including bulk versus ground at the Materials Research Collaborative Access Team 10-ID for Pb (Segre et al., 2000) and 10-BM for As (Kropf et al., 2010) beamlines, Advanced Photon Source (Argonne National Laboratory). For XAS data collection, the individual soil sample fractions (~100 mg) were mixed with 10 mg of polyvinylpyrrolidone (PVP), gently ground to homogenize with an agate mortar and pestle, pressed into a 1-cm pellet, and mounted on Kapton tape.

The beamline optics and setup parameters for the Pb L(III) edge XAS measurements were as follows: The energy of the incident X-rays was scanned by using the (111) reflection of a cryogenically-cooled Si double-crystal monochromator. The beam size was 750 µm by 750 µm. At least 10 quick scans (0.5 eV steps) of each sample were collected (–200 to 800 eV). Calibration was performed by assigning the first derivative inflection point of the absorption edge of a Pb-foil standard (13035 eV). Spectra were averaged, aligned, and merged. Backgrounds were subtracted using a linear fit to the pre-edge region (–155 to –55 eV below edge) that was extended through the spectrum. Spectral step heights were normalized using a post-edge. Once normalized, rebinning of Pb-XAS data were done by using IFEFFIT's rebin function. For rebinning, default value of 10 eV was used for pre-edge region. For edge region (–50 to 100 eV), the size of grid used varied from 0.5–0.75 eV, and 0.05–0.075 inverse angstroms were used for EXAFS region to move oversampled $\mu(E)$ data onto a sparser grid which is usually one quarter of a size of the oversampled grid. Oversampling usually occurs when the monochromator is slewed continuously during the measurement.

Arsenic XAS data collection at 10-BM was accomplished in triplicate for each sample at the As K edge (11867 eV) using a 4-element Vortex fluorescence detector with several layers of aluminum foil shield to suppress fluorescence from other elements (i.e., iron) in the samples. For each unknown sample, depending on the data quality, three to five As K α (11867 eV) spectra were collected in both transmission and fluorescence mode with a sodium arsenate as a reference sample. Calibration was performed by assigning the first derivative inflection point of the K-edge of sodium arsenate (11874 eV) (Beak et al., 2009) with simultaneous

collection of the reference for each scan for calibration of sample spectra. Data were then converted to k space if XAFS region were chosen to be analyzed. Based on the data quality, Pb-XAS data collected for IKJ 583 and BO soils were analyzed in k -space of (2 to 7 Å⁻¹), and (2 to 9 Å⁻¹), respectively, whereas for HSJ 583 and SOFc-1, first derivative Pb-XANES spectra were fit within -50 to +100 eV from E_0 using ATHENA software. Similarly, As-XAS spectra for IKJ 583 and HSJ 583 were analyzed in k -space of (1.5 to 8 Å⁻¹), and BO and SOFc-1 were fit in derivative XANES within -50 to +100 eV.

Pb- and As-XAS processed spectra were analyzed in a two-step process using SixPack software for principal component analysis (PCA), and the IFEFFIT software package for linear combination fitting (LCF) (Ravel, and Newville, 2005). A library of previously collected Pb and As reference spectra were utilized for linear combination fittings. Principal component analysis of the normalized sample spectra was used to determine the number of components (standards) that would most likely be present in the samples, while target transformation (TT) was used to identify the most suitable standards for linear combination fitting (LCF) of the sample spectra. Standards used for Pb and As-XAS LCF, along with SPOIL values, are provided in supplementary information (Table S4). The combination of standards with the lowest χ^2 , were considered the most likely set of components in our experimental spectra and were used for data interpretation.

Results and Discussion

All results of quality assurance and quality control were within acceptable limits based on the established criteria, and are described in the supplementary information (Table S 2A, 2B).

Soil characterization

Table S1 summarizes total content of Pb, As, Zn, Cd, Fe, Al, Mn, P, S, Mg, Ca, Cu, and Cr in the four test soils by using the microwave-assisted acid digestion, EPA Method 3051a (USEPA, 1997). The test soils used in this study were co-contaminated with Pb and As. Total Pb and As concentration in test soils ranged from 354–6262 mg kg⁻¹ with a median value of 3308 mg Pb kg⁻¹ (n=4), and 245–3958 mg kg⁻¹ with a median value of 2101 mg As kg⁻¹ (n=4), respectively. IKJ 583 and HSJ 583 were high in Fe and S, and varied considerably in total Pb and As contents, whereas BO soil was contaminated via Pb-arsenate pesticide, and had very high organic matter content (~7.2%). Despite elevated Pb and As contents, variation in IVBA may occur depending on the solubility of minerals present in soils (Schoof et al., 1995).

Soil mass as a function of soil particle size

Soil particle size strongly influences dermal adherence, and is inversely associated with metal concentrations, their mobility, and bioavailability (ATSDR, 2007; Beamer et al., 2012; Madrid et al., 2002, 2008; Ruby and Lowney 2012). The percentage of soil mass determined in all four soils, HSJ 583, IKJ 583, BO, and SOFc-1 varied as a function of tested soil particle sizes (<38 µm, <75 to >38 µm, <150 to >75 µm, <250 to >150 µm) ranging from 0.55 to 70%. There are two general assumptions regarding particle size distributions in soils:

1) fractions will decrease in mass as particle size decreases and 2) contaminant concentration will increase as particle size decreases. These assumptions are not always valid, but are met more often than not to provide guidelines to reduce uncertainties in risk assessment. For the soils in this study, HSJ 583 and SOFc-1 observed decreasing mass in successive fractions of <250 μm to >150 μm , <150 μm to >75 μm , <75 μm to >38 μm , and <38 μm . However, BO and IKJ 583 show an increase in mass for the <75 μm to >38 μm fraction compared to the <150 μm to >75 μm fraction. The <38 μm fraction was the smallest mass contribution for all soils ranging from 0.55 to 17% (Figure 1).

The <250 to >150 μm fraction of HSJ 583 contained about 70% of the total mass; whereas, the BO contained 32% of its mass in this fraction (Figure 1). This mass fraction is the difference in moving from <250 μm to <150 μm particle size for bioavailability testing. With a significant loss in mass contribution for the <250 to >150 μm fraction, additional bulk soil mass will need to be collected in the field (in some cases more than double) to amass suitable amounts of <150 μm soil necessary for laboratory testing.

Total metal contents as a function of soil particle size

The total Pb and As content increased from the larger (<250 to >150 μm) soil size fractions relative to the smaller (<38 μm) soil size fractions ranges, with minimum/maximum distributions of 13% (BO) to 124% (HSJ 583) for Pb, and -0.8% (BO) to 62% (HSJ 583) for As (Table S3). Similarly, higher Pb and As contents (16% max difference) were detected in <150 μm compared to <250 μm soil particle size in both bulk sieved and ground soils; however, not to the extreme observed for <250 μm vs <38 μm noted above. The trend is primarily attributed to surface area and the processes of sorption, coprecipitation and complexing of metals on particle surfaces and coatings. Larger surface area/volume ratios, presence of clay minerals, organic matter and Fe/Mn/Al oxides in the micro-aggregate also impute to higher concentrations of metals in smaller size fractions (Sutherland, 2003; Wang et al., 2006 and Zhang et al., 2007a). Therefore, exploring the partition of soil particle sizes is very important for the assessment of mobility and bioavailability of heavy metals in soil (Wang et al., 2006).

Extractable, and bioaccessible lead and arsenic as a function of soil particle size

Figure 2 and Table S3 summarizes extractable Pb and As, and *in-vitro* bioaccessibility test results obtained via IVBA extraction procedure (EPA Method 1340). Extractable Pb and As in gastric solution increased with decrease in soil particle size fractions along with bulk vs ground of <150 μm and <250 μm soil particle size, which follows a similar trend as total Pb and As content for each fraction (Table S3). Several factors determine the extent of dissolution of metals such as metal speciation, the soil matrix in which the metals are incorporated, and the composition of gastric solution used for IVBA extraction (Ellickson et al., 2001). Both IKJ 583 and HSJ 583 exhibited lower % IVBA Pb values for all sieved soil size fractions that ranged from <1 to 4%, whereas BO soil and SOFc-1 exhibited higher %IVBA Pb that ranged from 65.12 to 81.62%. Overall, HSJ 583 exhibited increasing trend ($p=0.012$) of %IVBA Pb with decrease in soil size fractions, whereas such trend was lacking in the remaining three tested soils, IKJ 583 ($p=0.08$), BO ($p=0.12$), and SOFc-1 ($p=0.23$). When comparing Pb versus As bioavailability, unlike %IVBA Pb, %IVBA As was higher

(approx. 65%) in HSJ 583, and (6 to 9%) in IKJ 583 across all soil size fractions. Among all, IKJ 583 with very high As_{Tot} (3958 mg/kg) exhibited decrease in %IVBA As with decrease in soil size fraction that was not statistically significant ($p=0.10$), whereas the other three soils (HSJ 583, BO, and SoFc-1) indicated increase in %IVBA As with decrease in soil particle size. Mikutta et al. (2014) reported As (% of total) decreased with decreasing particle size only in a highly As-contaminated soil and suggested the formation of As-rich hydrous ferric oxides in the gastric extracts, and vice versa in soils with lower As_{Tot} . However, this phenomenon for highly As-contaminated samples may be a saturation effect within the IVBA test vessel and should warrant further investigation. Lack of any noticeable trend in the results for %IVBA Pb and As predicts fairly homogeneous mineralogy in different soil size fractions in all test four soils.

The relationship of As and Pb %IVBA in the <250 μm sieved size fraction vs sieved <250 μm to >150 μm , <150 μm to >75 μm , <75 μm to >38 μm , and <38 μm ; and <250 μm ground, and <150 μm sieved and ground are shown in Figure 2. Figure 2A illustrates the As %IVBA in the size fraction groups (<250 μm to >150 μm , <150 μm to >75 μm , <75 μm to >38 μm , and <38 μm) relative to As %IVBA in the <250 μm sieved size fraction are nearly identical regardless of particle size in HSJ 583 ($p=0.80$, As and $p=0.69$, Pb), IKJ 583 ($p=0.36$, As and $p=0.31$, Pb), BO ($p=0.25$, As and $p=0.15$, Pb), SoFc-1 ($p=0.36$, As and $p=0.43$, Pb). The same 1:1 agreement with the size fraction groups for Pb %IVBA is observed in Figure 2C. On the issue of <250 μm versus <150 μm for sieved and ground samples, Figures 2B and 2D demonstrate a close correlation when the <250 μm sieved size fraction is compared to the <250 μm ground, <150 μm sieved, and <150 μm ground size fractions. In fact, regression curves for the <250 μm sieved versus <150 μm sieved have slopes of 0.97 (As, $R^2 = 0.998$) and 1.00 (Pb, $R^2 = 0.999$), indicating little to no difference in As and Pb %IVBA at these two particle sizes in HSJ 583 ($p=0.21$, As and $p=0.30$, Pb), IKJ 583 ($p=0.84$, As and $p=0.60$, Pb), BO ($p=0.56$, As and $p=0.78$, Pb), SoFc-1 ($p=0.70$, As and $p=0.22$, Pb) and further supporting that past research efforts (i.e., IVIVC) utilizing the <250 μm sieved size fraction will not be impacted with a move to the <150 μm sieved size fraction for bioavailability testing.

Lead Speciation

Lead XAS data of the test soils are presented in Table 1, which includes percentage of Pb-reference compounds used for the best LCF with the lowest χ^2 . The major species across all four test soils regardless of contamination source were sorbed Pb to Fe hydr(oxides), plumbojarosite ($Pb_{0.5}Fe_3(SO_4)_2(OH)_6$), anglesite ($PbSO_4$), magnetoplumbite ($Pb(Fe^{3+}, Mn^{3+})_{12}O_{19}$), litharge (PbO), hydroxypyromorphite ($Pb_5(PO_4)_3OH$), and Pb complexed with humic acid.

Evaluating Pb-species based on soil types, plumbojarosite was found as the dominant Pb-mineral in the mining impacted soils ranging from 82 to 93% (IKJ 583), and from 44 to 74% (HSJ 583) across all soil size fractions including bulk and ground soils of <150 μm and <250 μm size. Lead jarosite is a member of the jarosite family $AFe_3(SO_4)_2(OH)_6$, and alunite supergroup of minerals. Plumbojarosite occurs in Pb-bearing soils (O'zacar et al., 2000), areas of sulfide minerals oxidation, and some hydrometallurgical processes (Dutrizac and

Jambor, 2000; Hochella et al., 2005). The A site present in jarosite is commonly occupied by alkali metal ions such as K^+ or Na^+ , however many other substitutions have been reported that makes jarosite structure flexible towards ion size and charge accommodation (Hendricks, 1937). Generally, plumbojarosite is not rimmed by any other Pb bearing phases, and is considered the stable phase after galena oxidizes (Davies et al., 1993). The presence of plumbojarosite in IKJ 583 and HSJ 583 explains the lower % IVBA Pb results as this mineral has very low solubility ((Log Ksp) ranging from -24.3 to -26.2 as a function of temperature in the range $5-45\text{ }^{\circ}\text{C}$) (Forray et al., 2009), which is close to the Log Ksp of galena (-27.51), and chloropyromorphite (-25.05) (Lindsay, 1979). The other minor Pb-minerals detected in IKJ 583 includes lead phosphate, Pb sorbed to ferrihydrite, and magnetoplumbite ($Pb(Fe^{3+}, Mn^{3+})_{12}O_{19}$). Pb bound to Fe (hydr)oxides is very common in a wide variety of environments in the presence of high Fe (Davis et al., 1993). Similarly, formation of Pb ferromanganese oxides, magnetoplumbite, in IKJ 583 is supported by the presence of high total Fe (12 to 15%) and Mn (398 to 587 mg kg^{-1}), and is considered less soluble than sorbed complexes. Pb-XAS data analysis on BO soils, which is contaminated with lead-arsenate ($PbHAsO_4$) pesticide indicated Pb species mostly as sorbed phases to Fe (hydr)oxides as the dominant species, and Pb complexed with humic acids as the minor component, which is expected in soil with high organic matter and high iron oxides. Pb sorbed to ferrihydrite contributes significantly to the bioaccessible Pb pool, possibly due to dissolution and re-precipitation during IVBA extraction procedure (Beak et al., 2006; Beak et al., 2008; Smith et al., 2011). This explains the reason behind detecting higher %IVBA Pb, ranging from 68.12 to 75.31% in BO soils (Table S3). Similarly, Pb was principally found as anglesite (Log Ksp -7.79) in SOFc-1, which has been reported by several studies in mining impacted soil, and is considered a highly bioavailable form of Pb that is soluble in stomach acid (Hayes et al., 2012). Besides, anglesite, hydroxypyromorphite (Log Ksp of -4.14) was found as the second dominant Pb-mineral, which has also been reported by Ruby et al. (1994) in mining impacted soil, and lead oxides (litharge, Log Ksp 12.9) as the minor Pb-minerals in SOFc-1 that are readily soluble and therefore supports the %IVBA result of 65.12 to 81.62% in SOFc-1 (Table S3).

Arsenic speciation

Arsenic XAS measurements of the test soils are presented in Table 2, which includes percentage of As reference compounds used for best LCF with the lowest χ^2 values. The overall As-speciation included As(V) sorbed to goethite ($\alpha\text{-FeO(OH)-As(V)}$), As(V) sorbed to haematite ($\alpha\text{-Fe}_2\text{O}_3\text{-As(V)}$), arsenopyrite ($FeAsS$), As co-precipitated with pyrite, As sorbed to birnessite ($MnO_2\text{-As(V)}$), Pb-As-pesticide ($PbHAsO_4$), As(V) incorporated in jarosite, and scorodite ($FeAsO_4 \cdot 2H_2O$). Most of the identified As species are As(V) associated with Fe-compounds in all test soils. The arsenate ((As(V)) minerals are more predominant under oxidizing conditions found in weathered environments. Likewise, abundance of As(V) in the test soils may have resulted from weathering of deposited As in oxidized environments (Gimenez et al., 2007), and its higher association with Fe is explained by abundant Fe (Bowell et al., 2014), coprecipitation of As and Fe (sulfides), and the affinity of As oxyanions for the surfaces of Fe oxides (Schwertmann et al., 1991). Since As speciation showed higher association of As to Fe in the test soils, the role of pH in determining As-Fe associated mineral solubility cannot be neglected (Essington, 1988).

When looking at an individual soil, As in IKJ 583 is primarily associated with the weathering products of arsenic sulfide, such as jarosite (52 to 70%), scorodite (hydrous ferrous arsenate) (31 to 38%) and As(V) ions sorbed on goethite (14 to 18%) in all size fractions including bulk and ground soils of <150 μm and <250 μm size. Incorporation of As in jarosite derived from the weathering of As-rich pyrite is well documented (Alpers et al., 1989; Bigham et al., 1996 and Savage et al., 2000a). Arsenic incorporation could influence the solubility of jarosite, potentially stabilizing the structure over a wider range of conditions compared to just pure jarosite (Baron and Palmer, 2002), however this may depend on the mode of incorporation of As in or sorbed on jarosite in both natural and controlled environments (Kendall et al., 2013). By contrast, scorodite is one of the least soluble arsenate phase found at mining sites (Langmuir et al., 2006). Mine tailings dominated by scorodite were reported to have very low bioaccessibility (0.13%) due to its lower solubility (Log K_{sp} of -25.8) (Langmuir et al., 2006 and Meunier et al., 2010). In addition to this, As(V) specifically sorbed onto goethite through an inner-sphere complex via a ligand exchange mechanism (Fendorf et al., 1997 and Waychunas et al., 1993) has been reported to have an intermediate bioaccessibility (Meunier et al., 2010). Despite the presence of As incorporated into jarosite and As(V) sorbed to goethite, presence of scorodite in IKJ 583 mainly supports the result of 6 to 10% bioaccessible As in IKJ 583.

Similarly, As XAS results of HSJ 583 showed somewhat overlapping mineralogy since As incorporated into jarosite (67 to 85%) was the principally found mineral, and As(V) sorbed to goethite (11 to 33%) was less predominant. Iron oxides are final weathering products of iron-sulfide bearing ores in the environment; whereas scorodite and jarosite are considered primary weathering products (Bladh, 1982). The absence of scorodite in HSJ 583 relative to IKJ 583 may indicate that HSJ 583 has undergone more extensive weathering resulting in more As sorbed to iron oxides and possible destabilization of the jarosite structure. In addition to the mode of incorporation of As into jarosite mineral, desorption of arsenate from goethite in the extracting solution with pH 1.5 could be attributable to the increased bioaccessibility of As (64 to 66%) in HSJ 583. Of note is the vast difference in As concentration between HSJ 583 (245 mg kg^{-1}) and IKJ 583 (3958 mg kg^{-1}) as well as Fe concentration, 78,058 vs. 138,400 mg kg^{-1} , respectively, that demonstrates a dilution effect of dispersion for these paired-site samples which may influence the percent IVBA values determined for HSJ 583 and IKJ 583.

Arsenic-speciation in BO soils included As(V) ions sorbed to birnessite (65 to 69%) and Pb-As-pesticide (31 to 36%). BO soil is heavily contaminated with historical use of lead arsenate pesticide (PbHAsO_4) that has been reported to be relatively insoluble and persistent. Presence of As(V) sorbed to birnessite is common as As(V) ions present under oxidized conditions are often sorbed to Fe and Mn hydr(oxides), organic matter, and clays in soils. Presence of higher Mn (1600 mg kg^{-1}) in BO soils supports the formation of As(V) sorbed to birnessite, which has bioaccessibility of 16 to 28 % as reported by Beak et al. (2006). High organic carbon (~7.2%) in BO soils may also have resulted in increased arsenic bioaccessibility in BO soils (29 to 30%). Arsenic(V) sorbed to haematite was found as a dominant mineral ranging from 76 to 95% in SOFc-1. In general, the soil with mining as a source of contamination has lower organic matter, and due to this, ferrihydrite may have converted into haematite resulting in the formation of As sorbed to haematite (Hiemstra,

2013; Michel et al., 2010) in SOFc-1. Among oxides of Fe/Al/Mn, Fe-oxide minerals such as hydrous ferric oxide (HFO), goethite, and hematite are considered to be the most important sinks for As under oxidized conditions (Smedley and Kinniburgh, 2002; Stollenwerk, 2003), however the extent of adsorption depends upon the initial concentration, pH, and competing ions present in solution (Pierce and Moore, 1982). Presence of As(V) sorbed to haematite (76 to 95%) with an intermediate bioaccessibility, and arsenopyrite as the second dominant As species (16 to 33%) with lower bioaccessibility (<1%) may have reduced overall As IVBA in SOFc-1 (15 to 21%) due to slow dissolution kinetics and is likely to lower As bioavailability (Roberts et al., 2007). The above detail mineralogical discussion for the tested soils showing limited variation of Pb and As speciation among size fractions of a particular soil provides more confidence in the bioaccessible Pb and As results; however, the overall message from this study indicates little difference in the % IVBA Pb and As results regardless of the soil size fractions with no influence of pulverization as well.

Conclusion

This study sought to examine the relationship between particle size, dermal adherence and contaminant enrichment regarding the technical basis for updating the recommended particle size fractions sieved at contaminated sites for soil-metal bioavailability testing (USEPA, 2016). The use of <150 µm fraction for bioavailability research has strong support to represent a reasonable upper-bound estimate of the soil and dust fraction that is most likely to stick to hands or objects placed in childrens' mouths and be subsequently ingested (Ruby and Lowney 2012). A significant concern of moving from <250 µm size fraction to <150 µm is that the concentration and bioavailability of Pb in the <250 µm particle size fraction was used to calibrate the Integrated Exposure Uptake Biokinetic Model for Pb in Children (IEUBK model; USEPA, 1994, 2000), and in the development of the *in-vivo* and *in-vitro* bioavailability assays for Pb and As in soil (Bradham et al., 2011, 2013, 2015; Casteel et al., 1997; Diamond et al., 2016; Maddaloni et al., 1998; Ruby et al., 1996; Smith et al., 2011; USEPA, 2007b, 2009).

Despite increasing total Pb and As concentration as well as correlated increasing IVBA extractable Pb and As as particle size fraction decreases, this study clearly demonstrates negligible changes in Pb and As percent bioaccessibility when comparing the <250 µm size fraction to the <150 µm size fraction; as well as various other size fractions and the influence of pulverizing. These results indicate that adaption of the <150 µm size fraction for future bioavailability testing can still utilize existing IVIVC and add to their robustness. An advantage of utilizing the <150 µm size fraction is the enrichment factor that will make detection limits for analytical, *in-vivo* and *in-vitro* measurements easier to overcome; however, a looming disadvantage is the amount of extra soil that will need to be collected to have a suitable sample volume for testing; in some cases, more than twice as much as would be needed for a similar volume of <250 µm fraction.

The primary limitation of this study is that only four soils were examined, of which all have previously undergone *in-vivo* (As), *in-vitro*, and speciation analysis for the <250 µm size fraction. The <150 µm size fraction of the soils studied will be examined *in-vivo* for Pb and

As bioavailability to determine if the move from <250 μm to <150 μm size fraction affects *in-vivo* measurements when compared to previous <250 μm fraction feeding studies. Data from more soils would add further confidence to generalize the results. Further, for these four soils, contaminant speciation did not vary dramatically among the various size fractions. This phenomenon may not hold true for all soils, in which changes in %IVBA for various particle size fractions may change substantially if speciation differs. However, it is not anticipated there would be dramatically different Pb and As species when considering <250 μm vs <150 μm size fractions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Core Ideas

- Findings from this study identify critical knowledge gaps regarding the <250 μm vs. <150 μm particle size being used for *in-vitro* bioaccessibility (IVBA) analysis (EPA Method 1340 or EPA SOP 9200.2-86). The results bring more confidence for wider implementation of the <150 μm size fraction and lessen concern of accuracy of the method for past validation with <250 μm soil size fraction.
- Although, we observed increased in total and IVBA extractable lead and arsenic with decreased soil particle size; changes in %IVBA of Pb and As remained consistent in all the tested soils.
- Advantages of utilizing the <150 size fraction include more accurate risk assessment, and an enrichment factor that will make detection limits for analytical, *in-vivo* and *in-vitro* measurements easier to overcome; however, the disadvantage is the requirement for much higher volumes/masses of soils, which has a huge impact on site assessment sampling practices and costs.
- This study shows the value of using synchrotron based metal speciation to support bioavailability studies and provide geochemical characterization to understand the long-term fate of contaminants.

Figure 1. Particle size distribution in BO soil, HSJ 583, IKJ 583, and USGS Bioavailability Reference Material (SOFc-1).

Figure 2.

The relationship of As and Pb %IVBA in the <250 µm sieved size fraction vs sieved <250 µm to >150 µm, <150 µm to >75 µm, <75 µm to >38 µm, and <38 µm; and <250 µm ground, and <150 µm sieved and ground. **Figure 2A** illustrates the As %IVBA in the size fraction groups (<250 µm to >150 µm, <150 µm to >75 µm, <75 µm to >38 µm, and <38 µm) relative to As %IVBA in the <250 µm sieved size fraction are nearly identical regardless of particle size. The same 1:1 agreement with the size fraction groups for Pb %IVBA is observed in **Figure 2C**. On the issue of <250 µm versus <150 µm for sieved and ground samples, **Figures 2B and 2D** demonstrate a close correlation when the <250 µm sieved size fraction is compared to the <250 µm ground, <150 µm sieved, and <150 µm ground size fractions.

Table 1

Bulk Pb-XAS LCF results for HSI 583, IKJ 583, BO, and SOFe-1 showing % components of lead minerals.

Samples	Pb_Humic Acids	Pb_FH	Magnetoplumbite	Anglesite	Plumbogerrite	Pb-phosphate	Plumbojarosite	Litharge	Hydroxypyromorphite	R-factor
HSI <250 - >150 S	-	-	-	-	-	14	86	-	-	0.107
HSI <150 - >75 S	-	-	-	-	-	3	97	-	-	0.067
HSI <75 - >38 S	-	-	-	-	-	-	96	-	4	0.074
HSI <38 S	-	-	7	-	-	-	93	-	-	0.068
HSI <250 S	-	-	-	-	-	9	91	-	-	0.294
HSI <250 P	-	-	-	-	-	18	82	-	-	0.074
HSI <150 S	-	-	-	-	-	10	90	-	-	0.107
HSI <150 P	-	-	-	-	-	-	92	-	8	0.070
IKJ <250 - >150 S	-	-	36	-	-	-	52	5	7	0.003
IKJ <150 - >75 S	-	-	44	-	-	12	44	-	-	0.008
IKJ <75 - >38 S	-	-	21	-	-	34	37	8	-	0.003
IKJ <38 S	-	-	36	-	-	12	48	4	-	0.003
IKJ <250 S	-	23	-	-	-	-	75	5	-	0.002
IKJ <250 P	-	21	20	-	-	-	59	-	-	0.003
IKJ <150 S	-	22	-	4	-	-	74	-	-	0.003
IKJ <150 P	-	8	22	-	-	12	58	-	-	0.003
BO <250 - >150 S	9	91	-	-	-	-	-	-	-	0.085
BO <150 - >75 S	9	91	-	-	-	-	-	-	-	0.147
BO <75 - >38 S	9	91	-	-	-	-	-	-	-	0.285
BO <38 S	-	100	-	-	-	-	-	-	-	0.102
BO <250 S	-	99	-	-	-	-	-	-	-	0.133
BO <250 P	-	100	-	-	-	-	-	-	-	0.287
BO <150 S	9	91	-	-	-	-	-	-	-	0.133
BO <150 P	7	93	-	-	-	-	-	-	-	0.049
SOFe-1 <250 - >150 S	-	10	-	51	-	-	-	12	27	0.024
SOFe-1 <150 - >75 S	-	-	-	40	11	-	-	16	32	0.022
SOFe-1 <75 - >38 S	-	32	-	46	2	-	-	-	20	0.017

Samples	Pb_Humic Acids	Pb_FH	Magnetoplumbite	Anglesite	Plumboferrite	Pb-phosphate	Plumbojarosite	Litharge	Hydroxypyromorphite	R-factor
SOFc-1 <38 S	-	11	-	56	-	-	-	11	23	0.011
SOFc-1 <250 S	-	10	-	53	-	-	-	10	27	0.025
SOFc-1 <250 P	-	18	-	52	-	-	-	8	23	0.020
SOFc-1 <150 S	-	27	-	49	-	-	-	4	20	0.020
SOFc-1 <150 P	-	32	-	47	-	-	-	-	21	0.025

The letter 'S' indicates sieved, 'P' indicates ground in sample labels. The phase identified as less than 10% may not be significant due to error associated with smaller estimations.

Table 2

Bulk As-XAS LCF results for HSI 583, IKJ 583, BO, and SoFC-1 showing % components of arsenic minerals.

Samples	As(V)_Haematite	Arsenopyrite	As_coppt. With Pyrite	As(V)_GOE	As(V)_BIR	Pb-As-Pesticide	As(V)_Jarosite	Scorodite	R-factor
HSI <250 - >150 S	-	-	-	22	-	-	78	-	0.035
HSI <150 >75 S	-	-	-	33	-	-	67	-	0.021
HSI <75 - G38 S	-	-	-	11	-	-	89	-	0.034
HSI <38 S	7	-	-	22	-	-	71	-	0.036
HSI <250 S	-	-	-	25	-	-	75	-	0.029
HSI <250 P	-	-	-	15	-	-	85	-	0.035
HSI <150 S	5	-	-	19	-	-	80	-	0.031
HSI <150 P	-	-	-	24	-	-	76	-	0.038
IKJ <250 - G150 S	-	-	-	-	-	-	70	30	0.03
IKJ <150 - G75 S	-	-	-	-	-	-	65	35	0.029
IKJ <75 - G38 S	-	-	-	-	-	-	62	38	0.028
IKJ <38 S	-	-	-	18	-	-	49	33	0.086
IKJ <250 S	-	-	-	-	-	-	65	35	0.028
IKJ <250 P	-	-	-	-	-	-	69	31	0.031
IKJ <150 S	-	-	-	14	-	-	52	34	0.019
IKJ <150 P	-	-	-	-	-	-	67	33	0.029
BO <250 - >150 S	-	-	-	-	67	33	-	-	0.055
BO <150 - >75 S	-	-	-	-	67	33	-	-	0.063
BO <75 - >38 S	-	-	-	-	67	33	-	-	0.058
BO <38 S	-	-	-	-	69	31	-	-	0.044
BO <250 S	-	-	-	-	65	36	-	-	0.062
BO <250 P	-	-	-	-	67	33	-	-	0.055
BO <150 S	-	-	-	-	66	34	-	-	0.064
BO <150 P	-	-	-	-	67	33	-	-	0.057
SoFe-1 <250 - >150 S	84	16	-	-	-	-	-	-	0.134
SoFe-1 <150 - >75 S	77	23	-	-	-	-	-	-	0.125
SoFe-1 <75 - >38 S	78	22	-	-	-	-	-	-	0.126

Samples	As(V)_Haematite	Arsenopyrite	As_coppt. With Pyrite	As(V)_GOE	As(V)_BIR	Pb-As-Pesticide	As(V)_Jarosite	Scorodite	R-factor
SOFc-1 <38 S	92	-	8	-	-	-	-	-	0.128
SOFc-1 <250 S	95	-	5	-	-	-	-	-	0.125
SOFc-1 <250 P	77	23	-	-	-	-	-	-	0.13
SOFc-1 <150 S	76	24	-	-	-	-	-	-	0.04
SOFc-1 <150 P	82	33	-	-	-	-	-	-	0.13

BIR- Birnessite, GOE- Goethite in minerals naming. The letter 'S' indicates sieved, 'P' indicates ground in sample labels. The phase identified as less than 10% may not be significant due to error associated with smaller estimations.