

## **Workshop Report**

### **Assessing the Bioavailability and Risk from Metal Contaminated Soils and Dusts**

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**Running Head:** Bioavailability and Bioaccessibility of Metal Contaminated Soils

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## **ABSTRACT**

Exposure to contaminated soil and dust is an important pathway in human health risk assessment. Physical and chemical characteristics and biological factors determine the bioaccessibility/bioavailability of soil and dust contaminants. Within a single sample, contamination may arise from multiple sources of toxic elements that may exist as different species that impact bioavailability. In turn, the bioaccessibility/bioavailability of soil and dust contaminants directly impacts human health risk. Research efforts focusing on development and application of *in vitro* and *in vivo* methods to measure the bioaccessibility/bioavailability of metal contaminated soils have advanced in recent years. The objective of this workshop was to focus on developments in assessing the bioaccessibility/bioavailability of arsenic-contaminated soils, metals' contamination in urban Canadian residences and potential children's exposures to toxic elements in house dust, an urban community-based study (*i.e.*, West Oakland Residential Lead Assessment), bioavailability studies of soil cadmium, chromium, nickel, and mercury and human exposures to contaminated Brownfield soils. These presentations covered issues related to human health and bioavailability along with the most recent studies on community participation in assessing metals' contamination, studies of exposures to residential contamination, and *in vitro* and *in vivo* methods development for assessing the bioaccessibility/bioavailability of metals in soils and dusts.

**Key Words:** bioavailability, bioaccessibility, metals, exposure, soil, dust.

## INTRODUCTION

Human exposure to soils and dusts is an everyday occurrence. Industrial activities such as mining, smelting, manufacture and use of pesticides, and other human activities influence the chemical makeup of soil and dust. In indoor environments, the heterogeneous mixture known as dust can consist of biological components such as skin and hair, building components such as particles of paint and caulking, and particles of exterior soil that are tracked in from outdoor environments that may be contaminated with chemicals. Thus, ingestion of dust and soil has the potential for overexposures to toxic elements depending on the presence and amount of chemical contamination in each component.

When conducting a risk assessment of hazardous waste sites, the potential for human exposures through ingestion, inhalation, and dermal contact must be considered. With respect to the ingestion pathway, two terms that are important for assessing the extent of absorption of an ingested chemical are bioavailability and bioaccessibility. For ingestion, the U.S. Environmental Protection Agency (USEPA) defines bioavailability as “the fraction of an ingested dose that crosses the gastrointestinal epithelium and becomes available for distribution to internal target tissues and organs” (USEPA 2007a). There are many factors that may affect the bioavailability of soil and dust-bound chemicals: chemical and physical factors related to the soil and dust as well as biological and physiological variables of the exposed individual. Some examples of the factors for soil and dust include pH, particle size, presence of other chemicals, and how long the anthropogenic pollutants have been in contact with the soil (Scheckel *et al.* 2009). Current exposure estimates from ingestion of soils and dusts often do not consider differences between the bioavailability of contaminants in water and soil or dust. Assuming equivalent bioavailabilities in the two matrices can overestimate risk associated with soil and dust ingestion and can significantly affect estimated risk and cleanup goals (Bradham *et al.* 2011).

With the movement of toxicology testing to *in vitro* systems, methods have been developed to determine the bioaccessibility of chemicals. The USEPA defines bioaccessibility as “a measure of the physiological solubility of the metal at the portal of entry into the body” (USEPA 2007b). These types of methods can be done more rapidly, at a lower expense, and more soils and dusts can be processed than *in vivo* bioavailability studies. One major issue with these types of test is whether or not they correlate with *in vivo* exposures.

The objective of this workshop was to focus on recent developments in assessing the bioavailability and bioaccessibility of metal-contaminated soils and dusts as well as efforts to remediate Pb-contaminated urban soil. The following text summarizes the presentation of each speaker.

**RELATIVE BIOAVAILABILITY, BIOACCESSIBILITY, AND SPECIATION OF ARSENIC IN CONTAMINATED SOILS (K.D. Bradham, K.G. Scheckel, C.M. Nelson, P.E. Seales, G.E. Lee, M.F. Hughes, S.M. Serda, and D.J. Thomas)**

The metalloid arsenic (As) is a natural environmental contaminant, detected in the air, water, and soil. Arsenic is ranked the number one substance on the National Priority List of hazardous substances in the United States (ATSDR 2011). Chronic exposure to As can result in toxicities in multiple organ systems (*e.g.*, skin, nervous system) and cancers (NRC 1999). Determination of soil As bioavailability is necessary for reducing uncertainties in risk assessments of As and accurately establishing remediation levels at contaminated sites. However, current assessments that estimate As exposure from ingestion of contaminated soils may disregard discrepancies between the bioavailability of As in water and soil (Ehlers and Luthy 2003). Using default assumptions for bioavailability in As in soil may overestimate risk associated with soil ingestion (Bradham and Wentsel 2010).

*In vivo* animal studies of contaminated soils have been developed to assess the potential bioavailability of As. Such models include rodent, swine, and monkey (Casteel *et al.* 2006; Ng *et al.* 1998; Roberts *et al.* 2007). For our studies, we developed a mouse model to assess the bioavailability of soil-bound As (Bradham *et al.* 2011). The advantages of using a mouse model include low cost of purchase and ease of husbandry, more mice can be used than larger animals, which will increase sample size and hence decrease experimental variability, and the potential for widespread use of a mouse-based assay in many laboratories. While there are differences between the physiology and anatomy between mice and humans, they have some similarities in the disposition of As. These include elimination of absorbed As primarily in urine and a similar pattern of excreted arsenicals (Vahter 1999).

In addition to the *in vivo* assay, As bioaccessibility was determined using an *in vitro* assay (Bradham *et al.* 2011). For our study, this involved extracting soil-bound As in simulated gastric

fluid. We also characterized the physicochemical properties of the soils and used X-ray absorption spectroscopy (XAS) to identify major As species in the soil samples.

Two standard reference materials and nine soils collected from sites affected by mining and smelter activities were evaluated as part of this study. Total As concentrations in the soils ranged from 173 to 6899 ppm. Soil pH values ranged from 2.1 to 7.3. Although pentavalent inorganic As was present in all soil samples, four soils had levels of the more toxic trivalent inorganic As that ranged from 10 to 80% of the total As based on the XAS results. Iron, Mn, and Al were also measured, with Fe levels being the most prominent.

Soil was combined with mouse feed for a total of 1% (wt/wt) soil:diet mixture. An arsenate amended diet (ca. 6 ppm As) was also included to determine the bioavailability of freely soluble As. Female mice 4–6 weeks of age were housed in metabolism cages and provided the amended diets and tap water that contained  $< 11 \mu\text{g/L}$  As *ad libitum* for 9 days. Food consumption was measured daily to determine total As exposure. Urine and feces were collected and weighed daily. Total As in urine and feces was measured by Instrumental Neutron Activation Analysis. Absolute bioavailability (ABA) of As from ingestion of a soil- or arsenate-amended diet was calculated as the ratio of cumulative excretion of As in urine and cumulative dietary intake of As. Percent relative bioavailability (RBA) of soil As was determined by dividing the soil As ABA by the ABA of the sodium arsenate diet multiplied by 100.

Cumulative As consumption ranged from about 100 to 5000  $\mu\text{g}$ . ABA ranged from 7 to 60%, with the highest for the sodium arsenate amended diet. The highest soil ABA was approximately 30%. RBA of soil bound As ranged from 10 to 55%. One soil sample and a NIST standard reference material were run multiple times to assess variability and reproducibility, and showed nearly identical results, indicating the performance of the assay was stable.

The percent *in vitro* bioaccessibility (IVBA) is the measure of extractable metal divided by the total contaminant metal in soil multiplied by 100. For the As contaminated soils, %IVBA ranged from 7% to 65%. The %IVBA correlated very well with %RBA (Pearson correlation = 0.96,  $n = 11$ ). For this study, these two methods were very complementary. Soil characteristics were assessed to examine the influence of selected soil properties on As RBA and IVBA. The sums of the concentrations of extractable soil Fe and Al were the highest predictors of these values. This result suggested that sorption of As to Fe and Al oxides reduced As bioavailability and bioaccessibility.

Overall, the *in vivo* assay was adaptable for use with soils having a wide range of As concentrations and physicochemical properties. The bioavailability and bioaccessibility estimates were highly correlated, and the data on physicochemical properties ((Log [Fe + Al]), mol/kg) of the soils were correlated with both bioavailability and bioaccessibility estimates. The range of RBA estimates in the *in vivo* assay suggests use of 100% default value As RBA in risk assessments may overestimate risk. This study demonstrates development of a complementary set of accurate, low cost bioavailability tools including As *in vivo* mouse bioavailability, *in vitro* bioaccessibility and physicochemical experiments for use in reducing uncertainty in risk assessments of As-contaminated soils.

## **METAL CONTAMINATION IN URBAN RESIDENCES IN CANADA AND POTENTIAL CHILDREN'S EXPOSURES TO TOXIC ELEMENTS IN HOUSE DUST (P.E. Rasmussen, S. Beauchemin, and L. MacLean)**

Results from the recently completed Canadian House Dust Study (CHDS) provide a nationally representative sample of typical dust metal concentrations and loadings in urban Canadian homes (Rasmussen *et al.* 2011; McDonald *et al.* 2011). The CHDS employed a combination of synchrotron and simulated gastric acid extraction techniques to demonstrate that Pb bioaccessibility of dust can be predicted from its solid phase speciation ( $R^2 = 0.85$ ;  $n = 12$ ;  $p < 0.0001$ ). Sampling for the CHDS was conducted during the winter seasons from 2007 to 2010, with vacuum and wipe samples collected from 1,025 detached homes randomly selected from 13 cities across Canada. The distribution pattern in Canadian cities was similar to that previously reported for USA cities, with elevated concentrations ( $>250$  ppm bioaccessible Pb) predominately occurring in older homes located in city centres. Results showed that fresh or “active” dust collected in 924 homes (90% of the homes sampled) contained less than 250 ppm bioaccessible Pb, which was considered the “urban background” subpopulation (Rasmussen *et al.* 2011).

Total Pb concentrations in the recent CHDS (median 100 ppm for total Pb;  $n = 1025$ ; mean construction date = 1965) are lower than results of older surveys conducted in 1987–1991 in Los Angeles and Sacramento, California (Sutton *et al.* 1995) and in 1993 in Ottawa, Canada (Rasmussen *et al.* 2001). Median dust Pb concentrations in Los Angeles and Sacramento homes were 136 ppm ( $n = 275$ ) and 178 ppm ( $n = 188$ ), respectively, corresponding to mean

construction dates of 1946 and 1938, respectively (Sutton *et al.* 1995). The Ottawa study reported a higher median dust Pb concentration (222 ppm,  $n = 48$ ) than the California studies, despite the more recent mean construction date of 1951 (Rasmussen *et al.* 2001). Both older studies (Sutton *et al.* 1995; Rasmussen *et al.* 2001) reported quantitative Pb recoveries (within  $\pm 10\%$ ) using NIST-certified reference materials, which affords confidence in comparing results obtained in different decades and locations. Indoor sources were shown to strongly influence the Ottawa homes, which were characterized by five-fold higher Pb concentrations in indoor dust compared to corresponding garden soil and street dust (Rasmussen *et al.* 2001).

The beneficial effect of home renovation and remediation activities over the past 15–20 years has lowered Pb levels in many older homes, and this has started to blur the relationship between house age and dust Pb content. The CHDS revealed only a moderate correlation between house age and dust Pb content ( $r = 0.58$ ;  $n = 1025$ ;  $p < 0.01$ ). Almost one-third of homes with “urban background” dust Pb levels ( $<250$  ppm bioaccessible Pb) were built before 1960 (33% or 301 out of 924). It is expected that the house age-dust Pb content relationship will continue to weaken as old homes continue to be renovated.

Another factor that blurs the house-age to dust Pb relationship is the presence of elevated dust Pb in younger homes ( $< 10$  yr old). An unexpected finding of the CHDS was that some of the highest dust Pb concentrations in the whole study were observed in younger homes. More than 10% of the subset of 101 homes containing elevated dust Pb ( $>250$  ppm) were built after 1980 (Rasmussen *et al.* 2011). MacLean *et al.* (2011) investigated the speciation of Pb in house dust samples of younger homes (*e.g.*, a 1982 home with  $Pb_{Total} = 1,489$  ppm; a 1999 home with  $Pb_{Total} = 7,719$  ppm; and a 2000 home with  $Pb_{Total} = 3,171$  ppm), and found differences in Pb speciation compared to older homes. Dust samples from younger homes revealed multiple Pb species, including Pb citrate, Pb humate, Pb adsorbed onto Fe oxide, Pb metal, PbO, Pb hydroxyl carbonate, and Pb carbonate, in contrast to dust samples from older homes that were dominated by Pb carbonates. These compounds provide evidence of a variety of Pb sources including tracked-in metals and minerals from exterior sources, and consumer products (*e.g.*, Pb-solder) used in the indoor environment. The authors noted the potential importance of organic Pb compounds that have been used in consumer products such as PVC flooring and vinyl wallpaper.

The CHDS results showed that common Pb paint pigments dominate the speciation of house dust collected in older homes and contribute to both elevated Pb contents and elevated Pb

bioaccessibility (Rasmussen *et al.* 2011). Detailed studies investigated spatial variations within older homes, by comparing samples of indoor dust collected in different rooms and corresponding garden soil collected from the same home (Beauchemin *et al.* 2011; Walker *et al.* 2011). In one case study, Extended X-ray Absorption Fine Structure (EXAFS) and X-Ray Absorption Near Edge Structure (XANES) were used for molecular scale investigations (Beauchemin *et al.* 2011) of paint chips collected during a renovation, pre-renovation house dust and a series of standards (see Figure 1). The case study showed that Pb speciation of old paint layers was identical to that of the pre-renovation dust: both contained  $\text{PbO} \cdot 2\text{PbSO}_4$ ,  $\text{PbCO}_3$  and  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ . These compounds are used as white paint pigments. Dust particles also contained rutile ( $\text{TiO}_2$  paint pigment), calcite and anhydrite (drywall minerals). This study proved definitively that Pb in old paint layers significantly contributed to the Pb signature of the settled indoor dust, even before renovations were undertaken, which underscores the message that steps must be taken to reduce or eliminate exposures to dust at all times, and especially during renovations.

In another case study of an old Ottawa home, characterization of dust particles using synchrotron microprobe techniques (micro-XRD, micro-XRF) showed that Pb in the living room dust was associated with Mn and Fe hydroxide and phosphate minerals, similar to particles identified in the garden soil (Walker *et al.* 2011). The living room dust (main floor) contained 240 ppm Pb, and garden soil contained 650 ppm Pb. In contrast, Pb concentrations of 14,000 ppm were found in floor dust from an upstairs bedroom. Microprobe investigations revealed evidence of bedroom renovation activity in the form of particles containing Pb-based and non-Pb paint pigments as well as gypsum, bassanite ( $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ), and portland cement (calcium hydroxide  $\text{Ca}(\text{OH})_2$ ). This study shows that the practice of renovating different rooms at different times causes Pb concentrations and speciation to vary from one room to the other (in this case by orders of magnitude) depending on the order of renovation.

The lower median Pb concentration in the CHDS (100 ppm total Pb), compared to older house dust studies, may be attributable to the influence of renovations combined with reductions in the use of Pb in paint, fuel, and consumer products, all of which contribute to dust Pb content. It is notable that the CHDS revealed the presence of elevated concentrations of Pb in house dust of some younger homes (< 10 yr old), arising from a variety of sources including consumer products, hobbies and tracking in contaminated soil and dust from outdoors.



**USEPA WEST OAKLAND RESIDENTIAL LEAD ASSESSMENT STUDY (S.M. Serda, S.A. Calanog, K.D. Bradham, K.G. Scheckel, and B.W. Miller)**

Serious health problems, especially in infants and children with respect to cognitive development, can result from exposure to Pb (Sanders *et al.* 2009). Although Pb is a natural element of soil, it can be found at high levels in the soils of hazardous waste sites, smelters, near roadways from past use of leaded gasoline, and dwellings with crumbling exterior Pb-based paint (ATSDR 2007).

The South Prescott area in Oakland, California, is a neighborhood community that is adjacent to the AMCO National Priorities List (NPL) site. In the United States, hazardous waste sites that are qualified for clean-up under the Superfund program are placed on the NPL. AMCO was a former chemical distribution facility that operated until 1989. For the next 10 years, this facility was operated as a scrap metals yard. The soil of this site was analyzed by the USEPA and found to contain chlorinated solvents, petroleum hydrocarbons, and metals (USEPA 2011). Soils at residential properties adjacent to the former AMCO property were analyzed for Pb and concentrations up to 2700 ppm were found (USEPA 2010). Of the 54 properties sampled, the mean total Pb in soil was 843 ppm. USEPA proposed a standard dig-and-haul method to remove contaminated soil on these properties and replace with clean fill. However, after meetings with the South Prescott community, a less intrusive, greener solution was proposed in partnership with the City of Oakland, Alameda County, and local organizations. The overall objective of the project was to minimize the Pb risk to the community, especially the high-risk age group (children 0–6 years of age) from the effects of soil-bound Pb, minimize environmental impacts to the community, and to support the community by using local resources. The proposed method was to treat and then cover the contaminated soil. The soil was treated with naturally derived phosphate in fishbones. The phosphate, in the form of apatite, sequesters divalent Pb in soil to form pyromorphite (Admassu and Breese 1999; Miretzky and Fernandez-Cirelli 2008). This bound form of Pb is less bioavailable, because it has very low solubility in the gastrointestinal tract (Miretzky and Fernandez-Cirelli 2008). The fishbone-treated soil is then covered with clean soil and appropriate plantings. Preliminary results show formation of pyromorphite in the treated soils as demonstrated with x-ray absorption spectroscopy (XAS). Pyromorphite crystals were

observed and confirmed the ratio of lead:phosphate as pyromorphite. Additional research is currently underway to evaluate the bioavailability of the treated soils over time.

This project is a positive example of community engagement in USEPA's efforts to remediate a Pb-contaminated site. Local labor resources are being trained at a job training center funded by an USEPA Brownfield grant to provide unemployed workers basic knowledge and skills that can allow them to pursue environmental clean-up jobs. A sustainable phosphate source (a waste stream from the fish industry) is being used and this project will reduce landfill disposal. To minimize the environmental impact of this project on the local community, solar power, electric vehicles for local transportation, reclaimed water, and reused landscape materials are being used whenever possible.

## **BEYOND LEAD AND ARSENIC: HOW ARE OTHER METALS BEING ADDRESSED?**

**(R.A. Schoof)**

During the past 25 years, substantial progress has been made in developing methods for assessing the relative bioavailability (RBA) of metals in soil and in applying the results to yield more accurate estimates of potential exposures; however, the bulk of this effort has addressed Pb and As. While other metals have been studied, such assessments are not yet routine. Factors to consider in designing such studies and current international status of method development and regulatory policies are reviewed below, followed by illustrative summaries of recent developments for Cd, Ni, Cr, and Hg.

Factors to consider in bioavailability study design include soil metal speciation, variation of toxicity with metal form, toxicokinetics, soil characteristics, and the expected nature of contact with soil.

- The presence of metal forms with low water solubility has been linked to reduced bioavailability, as have various interactions of metal forms with soil constituents (Kelley *et al.* 2002; NRC 2003; Scheckel *et al.* 2009; ENVIRON 2011). Characterizing the metal forms and interactions with soil constituents is useful in determining how broadly applicable bioavailability study results may be.
- Metals such as Hg and Cr for which toxicity varies for different forms (*e.g.*, oxidation states) present particular challenges to assure that forms with comparable toxicity are being assessed (Kelley *et al.* 2002; ENVIRON 2011).

- Toxicokinetic factors including degree of absorption of the soluble metal form, disposition, and long or short half-life are most important for *in vivo* method design, as illustrated by methods used for Pb, that typically include measurements of concentrations in blood, liver, and kidney after repeated dose studies (USEPA 2007b), compared with studies of As based on urine excretion or blood concentrations after either single dose or multiple dose studies (Bradham *et al.* 2011; Casteel *et al.* 2003; Freeman *et al.* 1995; Roberts *et al.* 2007).
- The nature of the soil contact by the exposed person (*e.g.*, hand-to-mouth contact) is also relevant because it governs the particle size fraction that may be ingested and should inform how soil samples are collected (ENVIRON 2011).

A wide variety of *in vitro* methods have been developed, generally mimicking one or more phases of the digestion process (Kelley *et al.* 2002; NRC 2003; ENVIRON 2011). Generally, the goal for these studies is to match results of *in vivo* methods that have proven reliable, and many of the same study design considerations are applicable.

Research to support bioavailability method development for metals in soil has been active internationally. Relative bioavailability adjustments are being applied in health risk assessments under many regulatory frameworks (ENVIRON 2011), including Australia and New Zealand (Ng *et al.* 2010), Canada (Health Canada 2009), Denmark (UK Environment Agency 2007), The Netherlands (Brand *et al.* 2009), the United Kingdom (UK Environment Agency 2011), and the United States (USEPA 2007a). To date, research and methods development efforts, as well as regulatory practice, have focused on evaluation of As and Pb. Extension of these findings to other metals has been a subject of some debate, and in regulatory settings RBAs for other metals have been applied only sporadically at a limited number of contaminated sites. *In vitro* method development, in particular, is being driven by Canadian, European and Australian research teams.

Cadmium, Ni, Cr, and Hg are the most frequently studied metals besides Pb and As, and illustrate a wide range of characteristics that affect *in vivo* bioavailability study design. Repeated dose studies of soil Cd (poorly absorbed and long half-life) have been conducted using rats, mice, and swine with measurement of concentrations in kidney and other tissues from animals dosed with soil vs. those dosed with reference metal compounds (Schoof and Freeman 1995; Juhasz *et al.* 2010). Similar methods have proven useful for Hg when inorganic forms are present (Sin *et al.* 1983; Schoof and Nielsen 1997). Both Ni and Cr are primarily excreted in the urine,

making urinary excretion measurements a viable approach to estimating RBA; however, the soil contribution to urine concentrations will be difficult to detect because background exposures from diet typically greatly exceed the contribution from soil to total exposures.

*In vitro* approaches to estimating RBA may also need to be varied based on both metal characteristics and interactions with soil and dust. Many *in vitro* methods include an initial low pH “gastric” phase, with an option for a second higher pH “intestinal” phase. Available studies suggest that a single gastric phase approach may be used for both Cr and Ni (ENVIRON 2011); although for high Ni concentrations care must be taken to ensure there is sufficient gastric fluid volume so the saturation point is not exceeded (Richardson *et al.* 2006). For Cd and Hg, a two phase approach with RBA based on the intestinal phase is recommended (ENVIRON 2011).

The rapid development of soil metal bioavailability methods raises issues of regulatory acceptance that are likely to have different answers around the world. One critical issue is whether or not method validation for *in vitro* methods against *in vivo* study data is needed on a metal-specific basis. A second issue relates to the weight of evidence required to change default assumptions for site risk assessments. At what point is an RBA less than 100% allowable without site-specific data? Continued research with international sharing of data and discussion will allow evolution of perspectives on these issues.

#### **CONTAMINANT MIXTURES AND MIXED EXPOSURE PATHWAYS: USING *IN VITRO* DIGESTORS TO TEASE OUT HUMAN EXPOSURE TO BROWNFIELD SOILS AND IDENTIFY ENGINEERING SOLUTIONS THAT REDUCE RISK (S.D. Siciliano, K. James, B. Laird, and D. Peak)**

The Lower Base Region of the City of Iqaluit was the focus of several years of research into the fundamental determinants of how polycyclic aromatic hydrocarbons (PAHs) and metals are transferred from contaminated Brownfield soil to humans living in an Arctic residential community. During the course of this work, it became apparent that the City of Iqaluit, in the northern Canadian territory of Nunavut, had layered clean fill material over historically-contaminated soil through normal municipal activities. As a result, the pathways of exposure from the contaminated soils to human residents were interrupted and health risk to residents of the Lower Base Region was mitigated. While investigating these case studies, three key findings

have become apparent related to how metals and PAHs present in soil become bioaccessible to human receptors.

### **Contaminant Bioaccessibility and Particle Size**

The typical particle size of soil that is adhered to human hands is much smaller, *ca.* 45  $\mu\text{m}$  (Siciliano *et al.* 2009; Yamamoto *et al.* 2006), than the 2.5 mm, 4.0 mm or 250  $\mu\text{m}$  size fraction typically used during soil sampling for human exposure assessments at contaminated sites (Bright *et al.* 2006). In addition, contaminant concentrations expressed per unit mass in these small size fractions tend to be much higher than in the larger size fractions of soil. This commonly observed phenomenon, referred to as contaminant enrichment, arises because adsorptive capacity increases with surface area to mass ratio as particles become smaller (Siciliano *et al.* 2009; Krauss and Wilcke 2002; Siciliano *et al.* 2010). Nineteen soils were collected from the Lower Base Region of Iqaluit for particle size determination (as measured by a Horiba model LA-950 laser scattering particle size distribution analyzer) and contaminant bioaccessibility quantification.

Also, as demonstrated by Richardson *et al.* (2006), average particle size at times correlated with metal bioaccessibility under simulated gastric and duodenal conditions (Table 1) (Laird *et al.* 2011). In addition to enrichment and bioaccessibility, it also appears that the identity of dominant PAHs can differ between particle sizes and that the adsorptive strength of the contaminant-soil interaction can change as well (Krauss and Wilcke 2002; Siciliano *et al.* 2010). Although these observations have been reproduced elsewhere (Juhasz *et al.* 2011), it is not yet clear what should be the default target size fraction for soil contaminant characterizations within human health assessments. For example, in certain circumstances using a small size fraction can under-estimate exposure if large, highly contaminated particles are present (Meunier *et al.* 2011). However, it does suggest that standard soil ingestion rates demonstrated using tracer techniques likely need to be revisited because the approach is highly sensitive to what size fraction of soil was ingested (Doyle *et al.* 2010). Thus the re-analysis by Calabrese *et al.* (1996) is likely also necessary for the small particle sizes (e.g., 45  $\mu\text{m}$ ) seen to preferentially adhere to the skin of human hands.

### **Bioaccessibility and Metal Cation Lability**

Differences in the bioaccessibility between soil contaminants are not random and are tightly linked to the fundamental chemical properties of the contaminant of potential concern (Laird *et al.* 2011). For example, we demonstrated that metals' bioaccessibility from soils in Iqaluit was closely correlated to the water exchange rate constant of metal cations (Laird *et al.* 2011). This water exchange rate constant is a measure of how quickly a water molecule within the hydration shell of metal cations is replaced by another from the bulk solvent of aqueous solutions. Therefore, metal lability may explain why variables (*e.g.*, contaminant concentration, nutritional status, etc.) commonly affect bioaccessibility for some metals but not others (Laird *et al.* 2010; Laird *et al.* 2009a,b; Laird *et al.* 2007). This relationship between bioaccessibility and lability was also apparent for several other contaminated sites under simulated gastric but not small intestinal conditions (Laird *et al.* 2011). Additional work exploring the interactions between soil factors, metal lability, and bioaccessibility may facilitate the extrapolation of optimal gastrointestinal model parameters (*e.g.*, pH, liquid:soil ratio, fluid composition, etc.) from one contaminant to another. In contrast to metal contaminants and lability, PAH bioaccessibility is instead linked to the chemical activity of PAHs in soil (James *et al.* 2011). PAH transfer from soil can be thought to occur over a bridge of chyme fluid. In other words, PAHs must desorb from soil into chyme and only thereafter partition into the intestinal epithelium. Thus, in soils where PAH fugacity capacity is very high, *i.e.*, PAHs want to 'flee' the soil, one would expect to see significant transfer to the receptor. Like metal lability, this concept of activity may allow the extrapolation of bioaccessibility for the range of PAH mixtures found in soil (James *et al.* 2011; Siciliano *et al.* 2010).

During the course of the case study, we also explored how nutritional status by comparing *in vitro* bioaccessibility under simulated fasted and fed conditions (Laird *et al.* 2009b). Additionally, the role of microbial activity was quantified by comparing contaminant bioaccessibility in the presence and absence of a simulated colon microbial community cultured under anaerobic conditions (Laird *et al.* 2009b). While we were able to demonstrate that they can significantly affect site-specific *in vitro* bioaccessibility estimates (Laird *et al.* 2007, 2009b), we have not unraveled whether these *in vitro* effects are relevant to human exposures. Understanding these issues may help tremendously in our exposure assessments for sensitive sub-populations within the general human population. In conclusion, the exposure characterizations completed in the Lower Base Region demonstrated that municipal development

and infrastructure (*i.e.*, road paving) effectively mitigated risks posed by the contaminated soils. Additionally, the Iqaluit case study provided the information necessary to build a knowledge base of the fundamental chemical properties that may enable the extrapolation of bioaccessibility results and/or procedures between contaminants of potential concern. Furthermore, the study also demonstrated the need to re-visit the common size fraction used in most human health assessments. Future work will explore how we can use this information to extrapolate between sites and explore how metals and PAHs interact in the human gastrointestinal tract to modulate exposure.

## **WORKSHOP'S SUMMARY AND RECOMMENDATIONS**

Advances in methods used for assessing the bioavailability of metals contaminated soils and dusts were presented during this workshop. Additionally, research on the correlation and verification of *in vivo* and *in vitro* methods for As-contaminated soils was described. Remediation techniques used on Pb contaminated soils at the West Oakland Residential Yard study were described along with preliminary results showing the formation of pyromorphite after using fish bones as the remediation technique. While work has been conducted for Pb and As and a limited number of other soil contaminants, there remains questions about extrapolating *in vitro* data to *in vivo* exposures and extrapolating across species. The usefulness of chemical property predictors has been demonstrated and testing of additional soils and dusts to further elucidate these predictors would be useful. Evaluation of soil and dust particle size are also currently under development as the influence of the particle size on bioavailability is being measured. The importance of Pb sources of tracked in metals, Pb paint, and other consumer products that are still being used in the indoor environment was presented. Additional research to assess the value of remediating outdoor environments relative to indoor environments is needed to assess changes over time.

## **DISCLAIMER**

This manuscript has been reviewed in accordance with the policy of the National Exposure Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the view and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement

or recommendation for use. The workshop's report was edited by HERA's editorial staff for compliance with the journal's formatting and style requirements.

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## Figure Legend

**Figure 1.** Bioaccessibility of Pb compounds relative to Pb acetate (100%) that could feasibly occur in house dust from indoor sources or tracked in from outside (modified from Table S1 in Rasmussen *et al.* 2011).

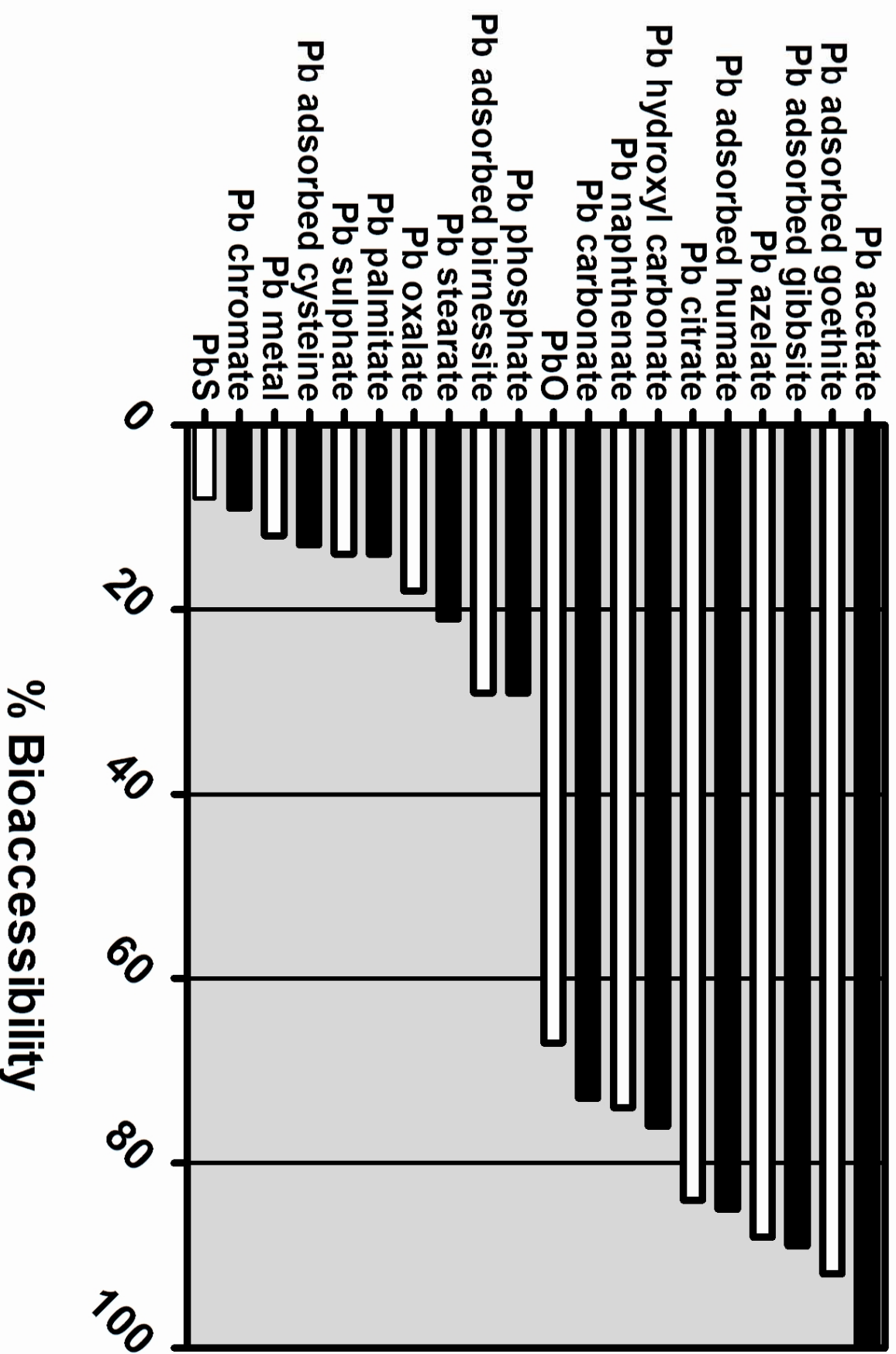


Table 1. Spearman correlation coefficients (\*p<0.05; \*\*p<0.01) demonstrating the correlation between average soil particle size and the percent bioaccessibility of soil metal constituents under simulated gastric (pH = 1.5; Residence Time = 2 hrs; LS Ratio = 40) and simulated duodenal conditions (pH=6.5, Residence Time = 2 hrs; LS Ratio = 60). Modified from Table S2 in Laird *et al.* (2011).

Metal	Simulated Gastric Conditions	Simulated Duodenal Conditions
Be	0.20	-0.40
Al	-0.38	0.26
Ti	0.14	0.01
V	0.06	0.22
Cr	0.27	0.53 <sup>*</sup>
Mn	-0.26	0.30
Fe	-0.09	0.18
Co	-0.18	-0.15
Ni	0.20	0.79 <sup>*</sup>
Cu	0.17	0.04
As	-0.07	-0.20
Sr	-0.03	-0.04
Mo	0.66	0.03
Cd	0.12	0.66 <sup>**</sup>
Sb	-0.31	-0.26
Ba	0.08	0.04
Tl	0.18	-0.78 <sup>**</sup>
Pb	-0.07	0.30
U	0.15	0.10