JAAS

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/jaas

Impact of Humidity on Speciation and Bioaccessibility of Pb, Zn, Co and Se in House Dust

Pat E. Rasmussen (1,2), Suzanne Beauchemin (3), Lachlan C.W. Maclean (4), Marc Chénier (1), Christine Levesque (1), H. David Gardner (2)

(1) Exposure and Biomonitoring Division, Healthy Environments and Consumer Safety Branch, Health Canada, 50 Colombine Driveway, Tunney's Pasture, AL 0800C, Ottawa, ON Canada K1A 0K9; (2) University of Ottawa, Ottawa, ON, Canada K1N 6N5; (3) Natural Resources Canada, CANMET Mining, Ottawa, ON, CanadaK1A 0G1; (4) SRK Consulting , Saskatoon, SK, Canada S7L 6M6.

Keywords: metals, exposure assessment, synchrotron speciation, in vitro bioaccessibility assay, indoor environmental quality

Abstract

Understanding bioaccessibility, defined as the fraction of an element that is soluble under gastrointestinal conditions, has become an important component of human health risk assessments. This study investigated the impact of humidity on the bioaccessibility of lead (Pb), zinc (Zn), cobalt (Co) and selenium (Se) in house dust. Three dust samples (two vacuum samples and NIST 2584 Indoor Dust) were weathered in an oxygenated humidity chamber for four months. Bioaccessibility was determined in original and weathered samples using a simulated gastric extraction followed by Inductively-Coupled Plasma Optical Emission Spectrometry (ICP-OES) and/or Mass Spectrometry (ICP-MS) as required. Exposure to humid conditions significantly increased bioaccessibility in all samples by 45-93% for Pb and by 21-65% for Zn. In contrast, bioaccessibility of Se was significantly decreased in all three weathered samples (by 75-93%), whereas bioaccessibility of Co displayed a variable response (16% increase; no significant change; 35% decrease respectively). Synchrotron XAS analysis of Pb speciation in the original and weathered dust samples determined that Pb transformed from less bioaccessible inorganic species towards more bioaccessible organic species under humid conditions. These results indicated that chemical transformations in damp microenvironments where house dust accumulates, such as window troughs or the base of carpets, may increase the bioaccessibility of particle-bound elements. Changes in bioaccessibility caused by weathering were shown to be significant in the context of the nationally representative Canadian House Dust Study (n=1025). The national datasets indicated that bioaccessibility is element-dependent (median 59% for Pb; 67% for Zn; 33% for Co; and 13% for Se). Variations in the frequency distributions were attributed to site-specific differences in speciation and the varied bioaccessibility of individual species. The importance of speciation in determining overall bioaccessibility was further demonstrated by measurements of dozens of Pb, Zn and Co compounds that could feasibly occur in house dust. It was concluded that interactions between these elements and the organic matter content of house dust are key to understanding element bioaccessibility and accumulation behaviour in the indoor environment.

Introduction

Characterization of elements in house dust improves the accuracy of residential exposure assessments, with oral ingestion of house dust by children being the pathway of primary concern as this can be a significant source of lead exposure.[1] Research efforts continue to improve physiologically-based extraction tests to assess bioaccessibility of elements following ingestion,[2] and adjustments for oral bioaccessibility are increasingly incorporated into human health risk assessments of contaminated sites in Canada,[3] USA[4, 5] and Europe.[6] Oral bioaccessibility refers to the fraction of a metal that is soluble under gastrointestinal conditions, and is a practical measurement for predicting metal bioavailability, which refers to the fraction that is actually absorbed.[7] Interlaboratory method comparisons using standard reference materials (SRM) for soil demonstrate that element bioaccessibility results vary as a function of the extraction method that is selected[7-9] with pH conditions being the main control.[10]Even when identical extraction protocols are applied to a given SRM, different analytical approaches (e.g. use of matrix-matched calibration standards for ICP-MS determination) can influence bioaccessibility results.[11] Particle size can be an important influence on element concentration and bioaccessibility in house dust,[12-14] but speciation studies have demonstrated that the chemical form (species) of the element may override the effect of particle size.[15] Speciation studies reveal a wide variety of indoor and outdoor sources of elements in house dust,[16] and help to explain spatial variations in element distribution from room to room within a house.[17, 18] The strong influence of speciation on the bioaccessibility of metals in house dust was demonstrated empirically ($R^2 = .85$; $p < .0001$) for Pb-rich samples from the Canadian House Dust Study.[19]

The present study investigates the effect of damp indoor microenvironments on bioaccessibility of four elements in house dust (Pb, Zn, Co and Se) by exposing dust samples to a humid atmosphere for a four month period. The selection of Pb, Zn, Co and Se for this study was based on their contrasting behaviours with respect to enrichment in house dust, and to provide indoor dust concentration and bioaccessibility information to support Health Canada risk assessments of these elements under the Chemicals Management Plan.[20] In a residential study in Ottawa, Canada,[21] total concentrations of Pb and Zn were elevated by a factor of 6:1 in house dust compared to garden soil, with indoor/outdoor median ratios (mg/kg) of 222/34 for Pb and 633/100 for Zn. Indoor/outdoor ratios were even higher when considering bioaccessible concentrations (mg/kg): approximately 25:1 (147/ 5.9) for Pb and 17:1 (410/18) for Zn.[15, 22] In contrast, other elements did not display enrichment in the indoor environment: cobalt (Co) and selenium (Se) were examples of elements with indoor/outdoor ratios that approached unity (8.8/8.1 for Co and 0.8/0.7 for Se; median values in mg/kg).[21]

Domestic humid microenvironments, such as the base of carpets and between window panes, are places in the home where the growth of microorganisms (fungus, mould and bacteria) contributes to airborne allergen levels in homes.[23, 24] The present study represents a first effort to investigate the impact of humidity on metals associated with dust that collects in such damp indoor microenvironments. This study builds on a previous experiment[25] which showed that prolonged exposure of pure Pb compounds to humid conditions caused transformations of less soluble Pb species into more soluble Pb species. Whereas the Pb transformations observed in the previous study[25] occurred in the absence of house dust, this study examines the impact of humidity on the bioaccessibility of Pb and three additional elements (Zn, Co and Se) present in house dust vacuum samples. Transformations of the four study elements are quantified in dust samples after prolonged weathering in a humidity chamber. Bioaccessible concentrations observed for the four elements in the humidity experiment are then placed into the context of the nationally representative Canadian House Dust Study. Synchrotron X-ray Absorption Spectroscopy (XAS) methods are used to identify transformations in Pb species in the weathered dust, and metal bioaccessibilities are determined for a variety of reference compounds relevant to the present and future XAS speciation studies.

Experimental

Dust sample collection and preparation

Protocols for recruitment and dust sampling for the Canadian House Dust Study (CHDS) have been described previously.[19, 26] Briefly, a three-stage stratified sampling design was developed for the purpose of obtaining a random and representative population-based sample of single family homes in large Canadian cities (population >100,000). Samples were collected from a total of 1025 homes across 13 cities during the winter seasons from 2007 to 2010. Settled dust samples reported in the present study were collected from bare floors and carpets following the CHDS protocol in which a composite sample of fresh (active) dust was collected from dry living areas of the home, including bedrooms, family rooms, offices, hallways and finished basements. In all homes, a Pullman-Holt High-Efficiency Particulate Air (HEPA) vacuum sampler (model 102 ASB-12PD) was used, in which dust particles follow a direct pathway from the floor to the vacuum bag, without passing internal mechanical parts, thus avoiding potential contamination of the sample. Vacuum dust samples were air-dried at room temperature (21°C) for a minimum of 24 hrs. Pet and human hair and large particles were manually removed, and the dust samples were then sieved to < 80 µm in a metal-free fumehood. To avoid cross-contamination, the fumehood was vacuumed after processing each sample, and sieves were cleaned using an ultrasonic bath and oven-dried between samples.

Experimental design for humidity chamber experiment

Two dust samples from the CHDS (HM112, CA034), plus a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) for indoor dust (NIST SRM 2584 Indoor Dust), were selected for the humidity chamber experiment (based on having sufficiently elevated elemental concentrations for subsequent XAS speciation). Four replicates of each of the dust materials (HM112, CA034 and NIST SRM 2584) were placed in an oxygenated humidity chamber described previously.[25] Each replicate (approx. 250 mg dust per replicate) was evenly distributed on a labelled Teflon disc to maximize surface contact with air. Distilled water was maintained at a constant volume in a well below the sample rack to keep humidity inside the chamber at 100% RH, evidenced by condensation droplets on the inside of the chamber walls. Water-saturated pure air entered the chamber continuously through an inlet to maintain oxygenated conditions. Apart from this inlet, the chamber was sealed to prevent dust contamination from external sources. The dust materials were exposed to these conditions ("weathered") in the humidity chamber under ambient light for a period of four months. As some samples displayed visible growth of microbial colonies within the first month, HDPE walls were erected around each disc to prevent cross-contamination between samples. After four months the samples were removed and air-dried in a clean laminar flow hood. Concentrations of bioaccessible Pb, Zn, Co and Se were determined in 25 mg subsamples of the four aged replicates and four replicates of the original non-weathered material, as described below, and were compared using 2-tailed t-tests (Excel Analyse-It Standard Edition).

Total and bioaccessible element determination

Bioaccessible element concentrations (Pb_S, Zn_S, Co_S and Se_S) were determined in dust samples, NIST SRM 2584, and XAS reference compounds at Health Canada using a dilute hydrochloric acid extraction modified for house dust from the EN-71 (Part 3) European Toy Safety Protocol as described previously.[15] Validation exercises including participation in interlaboratory and intermethod comparison studies[10, 11] demonstrated that the modified EN-71 method yielded similar results to the "gastric-only" *in vitro* bioaccessibility assay recommended by the US-EPA.[4, 27] The modified EN-71 protocol used a 25 mg sample of dust in 50 mL of 0.07M HCl, and proceeds at 37.5°C for 2 hr in a covered agitating water bath (1 hr with agitation and 1 hr without) to simulate solubility in stomach conditions. After dilution and centrifugation the sample digests were analyzed using a Perkin Elmer Optima 5300V Inductively Coupled Plasma – Optical Emission Spectrometers (ICP-OES) for XAS reference compounds and a Perkin Elmer Sciex Elan DRC II Inductively Coupled Plasma Mass Spectrometer (ICP-MS) for dust samples and NIST 2584. The ICP-OES was operated in radial view using argon gas for the plasma (15 L/min) and nitrogen as the shear gas and the RF cooling gas, with 1400 watts RF power and pump rate 1mL/min. The ICP-OES was equipped with a GemCone high solids nebulizer (0.9L/min), quartz torch and baffled cyclonic spray chamber. The ICP-MS was operated in standard mode and equipped with a Meinhard concentric quartz nebuliser, cyclonic spray chamber, platinum skimmer and sampler cones and an AS93Plus autosampler (PerkinElmer). Germanium, scandium, indium, rhodium and rhenium were used as internal ICP-MS standards. Calibration standards and extracts were prepared with deionized distilled water (18.2 MΩ cm), high purity standard stock solutions (Delta Scientific Laboratory Products Ltd. Mississauga, ON) and ultra-pure concentrated HCl and HNO_3 reagents (Seastar Chemicals Inc., Sydney, BC). Acid concentrations in the ICP-MS calibration standards matched those of the sample digests as detailed previously.[11]

Total elemental concentrations (Pb_T, Zn_T, Co_T and Se_T) were determined in 1 g sieved CHDS samples by Actlabs Inc. (Ancaster, ON) using a 4-acid digestion (HF, $HClO_4$, HNO_3 and HCl) followed by Inductively-Coupled Plasma Optical Emission Spectrometry (ICP-OES) and/or Mass Spectrometry (ICP-MS) as required. Duplicate samples and reference materials (including NIST SRM 2584) were inserted blind after every 10 samples to evaluate quality of the total elemental analyses. Duplicates were reported as averages. Analytical results for the four study elements in NIST 2584 (mean ± sd; n = 10) were as follows: lead 9634 ± 979 mg/kg (certified value 9761 ± 67 mg/kg); zinc 2251 ± 184 mg/kg (reference value 2580 ± 150 mg/kg); cobalt 9.7 ± 1.3 mg/kg (information value = 10 mg/kg); and selenium 2.1 ± 0.4, n=10 (information value = 2 mg/kg). Limits of detection (LOD) for total elemental determinations reported by Actlabs Inc. were: 0.5 for Pb; 0.2 for Zn; 0.1 for Co; and 0.1 mg/kg for Se.

The bioaccessible concentration (e.g., Pb_S) was divided by the total elemental concentration (e.g., Pb_T) to calculate bioaccessibility expressed as a percentage ($Pb_S/Pb_T * 100$). To calculate % bioaccessibility for the synthesized compounds and natural minerals, total concentrations (the denominator) were determined analytically (acid digestion followed by ICP-OES), whereas for the pure reference compounds, the denominator was calculated stoichiometrically. Percentage bioaccessibility results for Pb, Zn and Co in the CHDS samples and in the reference compounds were reported as “relative bioaccessibility” by normalizing to results obtained for their respective water soluble species (Pb acetate108%, Zn acetate 114%, and Co acetate 106%) as recommended by US-EPA guidance.[4, 27]

The reason for using a small dust mass for the bioaccessibility extraction (25 mg) was to obtain the optimum acid volume to sample mass ratio of 2000 mL g^{-1}.[15] The disadvantage of using a small sample mass was the increased variability of analytical results. For example, 25 mg subsamples of NIST 2584 yield 9682 ± 1676 mg/kg for Pb_T (range 8302-12859; n=5) and 2248 ± 486 mg/kg for Zn_T (range 1773-3164; n=5) which reflected higher variability (17% RSD for Pb and 22% RSD for Zn) than obtained for 1 g subsamples (10% RSD for Pb and 8% RSD for Zn as reported above). The increased variability was attributed mainly to the typically heterogeneous distribution of metals and minerals within dust samples (and also to increased weighing uncertainty associated with small sample mass). Limits of detection (LOD) for bioaccessible element determinations in the weathering experiment were: 1.8 for Pb; 1.5 for Zn; 0.1 for Co; and 0.1 mg/kg for Se.

Characterization of speciation using synchrotron XAS

A series of XAS reference standards for Pb (22 compounds), Zn (22 compounds), and Co (21 compounds) were purchased or synthesized to represent a wide range of species that could feasibly occur in house dust from indoor sources or tracked in from outside. Reference standards included metal compounds found in interior and exterior house paints (e.g., carbonate, hydroxyl carbonate, sulphate, chromate, naphthenate); metals adsorbed to common soil compounds (cysteine, humate); metals adsorbed to Fe-, Al- and Mn-oxyhydroxides (goethite, gibbsite, birnessite); elemental metals; alloys; sulfides; metal soaps reported in art paints (stearate, palmitate, azelate); and other potential constituents of drying agents, fillers, extenders and plasticizers (acetate, citrate, oxalate). Synthesis of Pb reference standards for metal soaps and adsorbed species have been described previously.[17] Synthesis methods for Zn-rich phyllosilicates, Zn-Al double layer hydroxide and Zn species adsorbed at pH 6.5 on humate, ferrihydrite, gibbsite, birnessite and kaolinite have been reported in Beauchemin *et al*.[28] Co species adsorbed on ferrihydrite, gibbsite and birnessite were also synthesized at pH 6.5 using the same approach as described for Zn.

Samples of the natural minerals hemimorphite (Zn silicate), smaltite $(Co, Fe, Ni)As_2$, cobaltite (CoAsS) and erythrite ($Co_3(AsO_4)_2.8H_2O$) were obtained from CANMET Mining Minerals Library (Natural Resources Canada, Ottawa, ON); leadhillite ($Pb_4SO_4(CO_3)_2(OH)_2$) was obtained from the Geological Survey of Canada minerals collection (Natural Resources Canada, Ottawa, ON); and smithsonite ($ZnCO_3$) was purchased from Wards research minerals. XRD analysis (Rigaku D/MAX-2500 rotating anode X-ray powder diffractometer) was used to confirm the purity of the natural minerals and purchased or synthesized standards.

Details on XAS sample preparation and XAS modeling for Pb speciation have been described previously.[16,17] Bulk XAS analyses at the Pb L-111 edge were conducted at the beamline X-11A at the National Synchrotron Light Source, Brookhaven National Laboratory (New York). Briefly, the Pb reference compounds were finely ground and diluted in boron nitride to achieve an optimized edge step of one for data collection in transmission mode. Two to four scans were collected and averaged for each Pb reference compound. The household dust samples were directly mounted behind Kapton tape in a 380-µm Teflon holder and analyzed in fluorescence mode using a solid-state germanium, multielement detector. Four to seven scans were collected and averaged for each dust sample. Speciation was achieved by least-squares fitting of the extended X-ray absorption fine structure (EXAFS) spectra using all binary and ternary combinations of the following Pb reference compounds: Pb oxide (PbO, PbO_2), Pb sulfide (PbS), Pb metal, Pb sulfate [mixture of $Pb_2O(SO_4)$ and $(PbSO_4)$], Pb phosphate (pyromorphite), Pb carbonate ($PbCO_3$), Pb hydroxyl carbonate [$(PbCO_3)_2•Pb(OH)_2$], leadhillite, Pb chromate [$Pb(CrO_4)$], Pb acetate, Pb citrate, Pb oxalate, Pb stearate, Pb palmitate, Pb azelate, Pb naphthenate, Pb adsorbed on cysteine, humate, goethite, gibbsite or birnessite. The best combinations obtained by fitting the EXAFS spectra were then tested on the XANES for reliability.

Efforts to collect XAS data for Co in the studied dust samples were made at beamline 20-BM (PNC-CAT) at the Advanced Photon Source, Argonne National Laboratory, Illinois. Interferences caused by high Fe concentrations in the dust samples prevented identification of Co species for the present study.

Results and discussion

Impact of humidity on elements in dust

Table 1 summarizes changes in bioaccessible concentrations (Pb_S, Zn_S, Co_S and Se_S) observed in three samples of house dust that were aged in a humid atmosphere for a four month period. The comparative results in Table 1 were obtained using a simulated gastric acid digestion of four replicates each of original (unweathered) versus weathered dust material. In this section, results are discussed consecutively for each of the four elements, interpreted in the context of population-based national baseline concentrations obtained by applying the same simulated gastric extraction protocol to the 1025 samples collected in the CHDS (Table 2). Elemental concentration data for the CHDS are neither normally nor lognormally distributed [19, 26] therefore the national baseline data are most appropriately described using percentiles (although arithmetic means and geomeans are included in Table 2 for information).

Lead

Weathering in the humid environment significantly increased the bioaccessible Pb (Pb_S) concentrations of all three dust samples (Table 1). In the context of the national CHDS baseline for Pb_S (Table 2), the original Pb_S concentration for sample HM112 (1131 mg/kg) exceeds the 97.5th percentile of the CHDS and that of NIST 2584 (7816 mg/kg) exceeds the maximum CHDS value for Pb_S. Previously, three subpopulations were identified [19] in the CHDS Pb_S data: “background” (< 250 mg/kg); “elevated” (250 – 975 mg/kg); and “anomalous” (> 975 mg/kg). Both HM112 and NIST 2584 fell into the uppermost subpopulation considered anomalously high for urban Canadian homes. After weathering, Pb_S increased by 45% for NIST 2584 and by 75% for HM112, placing them both above the 99% percentile of the national baseline. The original Pb_S concentration determined in sample CA043 (146 mg/kg, Table 1) fell just below the 90th percentile of the CHDS dataset (Table 2) within the category considered typical of urban background concentrations for Canada.[19] However, weathering this sample in a humid environment more than doubled the Pb_S concentration (Table 1), placing it above the 90th percentile (into the “elevated” category) of the CHDS (Table 2).

Zinc

Weathering significantly increased bioaccessible Zn (Zn_S) in all three dust samples (Table 1), indicating that the impact of humidity is similar on Pb and Zn in house dust. Before weathering, the original Zn_S concentrations in samples CA043 and HM112 (Table 1) fell between the 90th and 95th percentiles of the CHDS (1038-1285mg/kg; Table 2) and NIST 2584 exceeded the 98th percentile (>1696 mg/kg). Exposing the samples to a humid environment increased Zn_S by 21 % for NIST 2584, by 65% for CA043, and by 33% for HM112 (Table 1), placing them all above the 98th percentile of the CHDS (Table 2).

Cobalt

Bioaccessible Co (Co_S) displayed a different response to weathering in each of the three samples (Table 1). The effect of humidity on NIST 2584 was to decrease Co_S by 35% (Table 1), from 3.92 mg/kg (which corresponds to the 90th percentile in the CHDS) to 2.55 mg/kg (<75th percentile in the CHDS; Table 2). In contrast, aging sample HM112 caused a 16% increase in Co_S, from 5.31 to 6.18 mg/kg (Table 1), which fall within the 95th to 97.5th interval of the CHDS (Table 2). No significant change was observed in sample CA043 (1.79 – 1.58 mg/kg; Table 1) which contained the lowest Co_S concentrations of the three samples, corresponding to the 25th-50th percentile range of the CHDS (Table 2). The variability of response amongst the three samples suggests variability of chemical forms of Co in dust, resulting in different molecular binding environments, from one sample to another.

Selenium

Initial bioaccessible selenium concentrations (Se_S) in the samples used in the weathering experiment were “elevated” in the context of the national CHDS baseline (Table 2). Prior to weathering, Se_S concentrations in the three dust samples ranged from 0.54 to 0.80 mg/kg (Table 1), which corresponded to the 90th to 97.5th percentile range of the CHDS (Table 2). Prolonged humid conditions led to a significant decrease in Se_S in all three dust samples: by 75% in NIST 2584, by about 90% in sample CA043, and by 80% in sample HM112 (Table 1). In the context of the national baseline (Table 2) the overall impact of exposure to humidity was to decrease Se_S concentrations from “elevated” to levels equal to or below the CHDS median (0.20 mg/kg).

Although the specific processes are unknown, the experimental results show that the impact of humidity on bioaccessibility of Se in dust (which displays a decrease in all samples) contrasts with that of Pb and Zn (both of which display an increase in all samples). Co bioaccessibility displays a variable response to humid conditions, depending on the sample. In the present paper, these results are investigated further for Pb only, by conducting speciation studies on subsamples of the weathered and unweathered dust material.

Impact of humidity on lead speciation

X-ray absorption spectroscopy (XAS) was used to characterize the dominant Pb species present in the original and weathered dust samples containing the highest Pb concentrations (HM112 and NIST 2584), following the methodology detailed in Beauchemin *et al*.[17] and MacLean *et al*.[16] Table 3 summarizes the results of least-squares fitting for Pb speciation in these samples. The fitting results in Table 3 are illustrated for XANES and EXAFS spectra in the Electronic Supplementary Information (Figures S-1 to S-3).

In the original (unweathered) HM112 sample, Pb predominantly occurred in inorganic forms as Pb carbonates (mainly hydrocerussite, a Pb hydroxyl carbonate, with a smaller amount of $PbCO_3$, both of which are used as white pigments in paint), while organic Pb species accounted for about one third of total Pb (Table 3). Modeling of the HM112 sample indicated that the organic Pb species may be Pb citrate and/or Pb humate (or a similar compound) but the precise identity of the organic species could not be resolved. This trend was reversed after exposure to humidity: organic Pb species (Pb humate and Pb oxalate) represented more than 75% of the total Pb in the weathered HM112 sample while hydrocerussite (or Pb hydroxyl carbonate) had decreased to less than 25% (Table 3).

Pb speciation in the original (unweathered) NIST 2584 dust consisted mainly of two common paint pigments: Pb hydroxyl carbonate (72.6%) and Pb chromate (27.5%; Table 3). This analysis is consistent with the recent XANES study by Jiang *et al.*[29] who also found that Pb hydroxyl carbonate is the dominant form of Pb in NIST 2584.Pb chromate was not included in their standards so could not be identified using XANES, but their SEM-EDX analyses confirmed a Cr-Pb (Ti) phase in NIST 2584 that was identified as Pb chromate. XANES at the Cr edge also supports the occurrence of Cr (VI) in this dust.[29]

Table 3 shows that weathering NIST 2584 in a humid environment resulted in a significant increase in organic Pb (54.2%) at the expense of the Pb hydroxyl carbonate (which decreased to 34.1%) and the Pb chromate (which decreased to 11.7%). In the latter fit, the occurrence of Pb naphthenate should be interpreted in a general way as an indication of the presence of an organic Pb species, likely with a structure similar to that of Pb naphthenate.[17] Uncertainties in the XAS fittings are discussed further in the Electronic Supplementary Information (Figure S-4).

Fig. 1 illustrates the evolution of Pb speciation during weathering in both studied dust samples, showing how exposure to humidity results in an increase of the organic Pb pool at the expense of the inorganic Pb pool. In sample HM112, the proportion of Pb in the organic vs inorganic pool increases from a ratio of 35:65 to a ratio of 76:24 (Fig. 1). In NIST 2584, Pb speciation evolves from 100% inorganic to an organic:inorganic ratio of 54:46 (Fig. 1).

The evidence of Pb redistribution to organic matter in dust (Table 3; Fig. 1) supports previous studies which emphasized the importance of elevated organic carbon content in house dust (27.8 wt % organic carbon) compared to garden soil (5.1 wt % organic carbon) in the interpretation of the behaviour of metals in indoor settled dust.[15, 22] Whether metals are tracked indoors from outside, or arise from indoor sources such as paints or consumer products, several lines of evidence indicate that metal enrichment in house dust (elevated indoor/outdoor ratio) is linked to the ability of the organic-rich dust matrix to accumulate metals with an affinity for organic matter, such as Pb and Zn, to higher concentrations than found in outdoor soil.[15, 17, 22]

Bioaccessibility of XAS reference compounds

Fig. 2 summarizes percentage bioaccessibilities for Pb (22 compounds), Zn (22 compounds), and Co (21 compounds) to represent a wide range of species that could feasibly occur in house dust from indoor sources or tracked in from outside. The percentage bioaccessibilities reported for Pb, Zn and Co in Fig. 2 are expressed relative to the water soluble acetate form used in toxicological assays, which enables comparisons with bioavailability results obtained with animal models.

Estimates of bioaccessibility for individual Pb species observed in the XAS dust analysis (Table 3) assists in the interpretation of the increased Pb_S concentrations caused by weathering (Table 1), as follows. Fig. 2 indicates that Pb bioaccessibility of Pb naphthenate, Pb citrate and Pb adsorbed on humate is 74%, 84% and 85%, respectively. On the other hand, Pb oxalate has a much lower bioaccessibility (18%). Thus, the impact of weathering on the overall Pb bioaccessibility depends largely on the type of organic compounds formed. With respect to Pb species observed in HM112 dust (Table 3), an overall increase in bioaccessibility after weathering can be attributed to the increase of organic Pb in the form of Pb humate (85% bioaccessibility; Figure 2) at the expense of Pb carbonate (73%) and Pb hydroxyl carbonate (76%). In the case of the NIST 2584 dust, an increase in Pb bioaccessibility after weathering can be attributed to the formation of a naphthenate-like organic Pb species at the expense of Pb chromate, since the bioaccessibility of Pb chromate is only 8.9% compared to 74% for Pb naphthenate (Fig. 2). The increase in Pb naphthenate at the expense of Pb carbonates should not significantly affect the overall bioaccessibility given the similarities in bioaccessibility of Pb naphthenate (74%), Pb carbonate (73%) and Pb hydroxyl carbonate (76%).

Other Pb species such as Pb metal and Pb sulfate which have been reported in house dust[16, 17, 19] may occur in the original dust samples in minor amounts (undetectable by bulk XAS analysis), and these compounds may also contribute to the bioaccessible Pb pool in the weathered samples. Support for this supposition arises from previous work on pure Pb compounds using the same experimental design[25] which demonstrated that humidity induced the transformation of Pb metal to Pb hydroxyl carbonate and Pb sulfate to leadhillite (Pb sulfate carbonate hydroxide) in the absence of house dust. Both transformations resulted in greater overall Pb bioaccessibility, since the bioaccessibility of Pb metal is only 12% compared to 76% for Pb hydroxyl carbonate (as shown in Fig. 2). Likewise, the bioaccessibility of Pb sulfate is only 14% versus 81% for leadhillite (Fig. 2).

In conclusion, the results from XAS speciation indicate that the aging of the dust samples generally favours the formation of more bioaccessible Pb species.Information on bioaccessibilities of Zn and Co reference compounds is included in Fig. 2 to assist in future XAS studies. The high bioaccessibility of metal-organic phases, such as Zn adsorbed to humate (98%) and Pb adsorbed to humate (85%) demonstrates the importance of including organic metal compounds in future XAS studies for a complete understanding of metal speciation and bioaccessibility in environmental media rich in organic matter such as dust. The set of Co reference compounds in Fig. 2 was prepared with the aim of investigating Co speciation in the present study but this was prevented by interferences caused by the co-occurrence of high Fe concentrations relative to Co concentrations in the studied house dust samples. Discreet Co particles were detected in another house dust sample with higher Co_T identified as an organo-metallic compound (unpublished data). Reference compounds were not obtained for further investigation of Se bioaccessibility and speciation due to the very low concentrations in the study dust samples. Based on this preliminary study, future weathering studies are planned in which house dust will be spiked with reference compounds to achieve concentrations suitable for XAS speciation analysis.

Population-based distributions of Pb, Zn, Co and Se bioaccessibility in house dust

Nationally representative frequency distributions for Pb, Zn, Co and Se bioaccessibility in typical urban house dust are shown in Fig. 3. These histograms were generated by dividing the bioaccessible concentration by the total concentration determined in each of the 1025 CHDS fresh dust samples, expressed as percentages.

The bioaccessibility of an element in dust sampled from a given house depends largely on speciation (apart from the influence of analytical protocol and particle size fraction, which are consistent throughout the present study). The speciation is governed by which indoor and outdoor sources are present, and, as shown in the present study, by subsequent transformations and accumulation processes in the dust matrix. As such, the spread in the frequency distributions for Pb, Zn, Co and Se bioaccessibility in the national baseline dust samples (Fig. 3) suggests that a wide variety of species of each element can be expected to occur in typical residential dust (with a wide range of bioaccessibilities as shown in Fig. 2). Zn species that have been observed in house dust using synchrotron approaches include Zn carbonate, Zn associated with Fe hydroxide phases, Zn sulphide (sphalerite), and Zn oxide.[15, 18] A variety of Pb species have been observed in house dust to date, including Pb carbonate, Pb hydroxyl carbonate, Pb sulphate, Pb chromate, Pb oxide, Pb citrate, Pb metal, Pb adsorbed to Fe- and Al-oxyhydroxides, and Pb adsorbed to humate.[16, 17, 19, 29] Although no information on either Co or Se speciation in house dust could be found in the literature, Stopford *et al.*[30] investigated bioaccessibilities of 12 Co compounds considered potential candidates for residential exposures, using five artificial human tissue fluids and human serum at different extraction times; however, their results cannot be compared directly with Co bioaccessibilities in Fig. 2 due to differences in protocol.

Statistical summaries of media-specific metal bioaccessibility results, such as the CHDS baseline values for house dust in Fig. 3, are used in human health risk assessments for predicting the bioavailable fraction of metals at contaminated sites. Default bioaccessibility values to adjust total elemental concentrations in risk assessments are generally based on the central tendency, but calculation approaches vary.[3, 6] Specific examples are provided in the USEPA guidance document[4] which established 60% as the national default absorption factor for lead in soil, and in the Sudbury Area Risk Assessment[3] which used the upper 95th% confidence limit of the mean of As, Co, Cu, Pb, Ni and Se bioaccessibility measurements in soil and dust samples.

The CHDS baseline data (Table 2; Fig. 3) provide a point of comparison for site specific studies at contaminated sites. USEPA guidance[31] emphasizes that use of default bioaccessibility values should not substitute for site-specific assessments, because speciation (which affects bioaccessibility/bioavailability) can be expected to vary from site to site, or within a given site. The spread in the bioaccessibility frequency distributions in Fig. 3 illustrates and underscores the point that a large percentage of homes are characterized by higher bioaccessibilities than would be predicted by a default value based on the central tendency. Exposures to (and potential hazards from) dust metal concentrations in these homes would be higher than a default assumption. For example in the CHDS, higher Pb bioaccessibilities (>75%) were observed in homes with the most elevated dust Pb concentrations (>250 mg/kg), explained by the higher proportion of bioaccessible Pb compounds used as pigments in older paints (Pb carbonate and Pb hydroxyl carbonate).[19] In the Sudbury study,[3] Se bioaccessibility in house dust collected from homes near mining and smelting operations (mean 43%; upper CI= 67%) was elevated compared to the CHDS values (median 13%; upper CI=15%; Table 4) obtained using a comparable gastric extraction. Conversely, if the measured bioaccessibility of metal in dust at a given site is found to be less than the central tendency, it may be concluded that exposures to (and hazards from) the metal at that site are probably lower than typical default assumptions.

Similarly, default bioaccessibility values established for soil cannot be assumed to apply to house dust, due to the dissimilar chemical and physical characteristics of the two media.[22] In addition to soil minerals and compounds that are tracked into the house from outdoors, the composition of house dust is enriched in organic matter and anthropogenic compounds from indoor sources such as consumer products (including personal hygiene and pharmaceutical products), hobbies, and building materials. In the Sudbury mining and smelting district Se bioaccessibility was nearly three times higher in house dust (mean 43%) compared to soil (mean 15%), whereas in the same study there was little difference between Co bioaccessibility in house dust (28%) and in soil (26%).[3] A study in Ottawa, Canada[15] reported that Zn bioaccessibility was nearly three times higher in indoor dust (median 68%) compared to soil (median 24%). Despite the similarity between the median bioaccessibility value of 59% established for Pb in house dust in the CHDS (Fig. 3) and the USEPA default bioaccessibility value of 60% established for Pb in soil,[4] the co-occurrence of higher Pb bioaccessibility (> 75%) in homes with higher dust Pb concentrations in the CHDS[19] underscores the importance of site-specific measurements of the indoor environment.

Handling outliers >100% in bioaccessibility datasets

An exercise to evaluate the impact of excluding values exceeding 100% bioaccessibility is summarized in Table 4. Bioaccessibility values exceeding 100% were observed for all four elements (not shown in Fig. 3 histograms). These outliers arose from the analytical uncertainty in the numerator and/or denominator in combination with heterogeneous distribution of metals and minerals in the dust matrix. Table 4 shows that removing outliers >100% for Pb bioaccessibility had the effect of lowering the median from 59% (n=1025) to 58% (n=1013). The Pb dataset passed the Shapiro-Wilks test for log normality ($p = .060$) if outliers were excluded, but did not pass ($p<.0001$) if outliers were included (Table 4). Removing outliers from the Zn dataset had no impact on the median (67%) but lowered the mean from 67% to 66% (Table 4). Removing outliers for Co had no impact on either the median or mean (both = 33%; Table 4). It was not possible to calculate a mean for the Se dataset due to the large percentage of bioaccessibility values below the detection limit (approximately 5% bioaccessibility).

In general, simply removing outliers > 100% to calculate the central tendency was not considered appropriate. For the Se dataset, 41 outliers were identified in an initial analysis of all 902 samples exceeding the LOD for Se_T (0.1 mg/kg). Examination of these outliers revealed a large proportion falling between LOD and the limit of quantification (LOQ, 0.3 mg/kg), but simply excluding them biased the median by 3 percentage points (10% compared to 13 %; not shown in Table 4). It was more appropriate to examine the subset of 847 samples in which the denominator (Se_T) exceeded LOQ, as this decreased the number of outliers to 16 and improved uncertainty associated with the median (Table 4).

Deciding on the best approach for handling bioaccessibility results exceeding 100% requires an understanding of the cause. Follow-up replicate analyses of samples yielding >100% can yield valuable information (such as biomodal or polymodal bioaccessibility distribution within a single sample). In practice the ability to investigate samples displaying >100% bioaccessibility can be limited by lack of adequate sample material and/or resources. In datasets where a large percentage of values approach the LOD, it is recommended to apply the more rigorous quality criterion (LOQ) to minimize the occurrence of outliers.

Conclusions

Experimental results show that weathering under prolonged humid conditions significantly increased Pb and Zn bioaccessibility in all studied samples of indoor dust. In contrast, bioaccessibility decreased in all samples for Se and was sample dependent for Co. These results provide new information about transformation processes that occur in dust that collects in damp microenvironments in the home and adds health-based evidence in support of international guidelines for preventing and controlling excess moisture and dampness in residential environments.[32]

Pb speciation, investigated using Synchrotron XAS methods, evolved in response to weathering in both studied dust samples toward an increase of the organic Pb pool at the expense of the inorganic Pb pool. These results point to the significance of metal-organic interactions and organo-metallic species in house dust exposed to damp conditions. Given the greater enrichment of organic matter in house dust (27.8 wt %) compared to garden soils (5.1 wt %),[15] these results help to clarify differences in metal bioaccessibility and accumulation behaviour in indoor dust compared to outdoor soil. Growth of microorganisms was visible on the dust samples after a few weeks of exposure to humidity, and it is likely that microbial activity plays an important role in converting metal compounds, particularly in organic-rich house dust that collects in damp microenvironments.

The ultimate goal of this research is to understand bioaccessibility of accidentally ingested metals in dust to inform risk characterization. Risk assessments often rely on the central tendency (median or mean) as a default bioaccessibility value to adjust total metal concentrations. National baseline data from the Canadian House Dust Study display wide variations in Pb, Zn, Co and Se bioaccessibility, attributed to the wide variation in site-specific speciation and the varied bioaccessibility of individual species. This study demonstrates that metal bioaccessibility in house dust is strongly site specific and that many situations may occur where reliance on default assumptions could result in an underestimate of exposure and potential hazard.

In conclusion, the bioaccessibility of an element in house dust is mainly governed by which species are present. Speciation is determined by the minerals and compounds that are tracked into the house from outdoors, combined with indoor sources such as consumer products (including personal care products and pharmaceuticals), hobbies, paints and renovation materials, and/or by metal interactions with the enriched organic matter content of house dust which can enhance metal bioaccessibility, as described for Pb in the present study.

Acknowledgments

The Canadian House Dust Study was approved by Health Canada's Research Ethics Board. Special thanks go to the study participants, and to Water & Earth Science Associates (WESA) Inc., Carp, ON. The authors are very grateful to T. MacKinnon, Innocent Jayawardene and Luyza Avramescu for valuable assistance, and to Anca-Maria Tugulea and Kaela Lalonde for helpful review comments on an earlier draft. XAS analyses were conducted at the beamline X-11A at the National Synchrotron Light Source, which is supported by the US Department of Energy, Division of Material Sciences and Division of Chemical Sciences, under contract number DE-AC02-98CH10886. Dr. Kumi Pandya's precious help was sincerely appreciated during the set-up at the beamline. The Geological Survey of Canada Mineral Library (Ottawa, Canada) is thanked for the leadhillite donation for bioaccessibility analysis. Funding and support from Health Canada's Chemicals Management Plan, Contaminated Sites Division and the Federal Contaminated Sites Action Plan (FCSAP), HECS Branch and RAP Branch and in-kind contribution from Natural Resources Canada's Green Mining Initiative are gratefully acknowledged.

References

1 D. J. Paustenbach, B. L. Finley and T. F. Long, *Int. J. Toxicol.,* 1997, **16**, 339-362 (DOI:10.1080/109158197227008).

2 O. T. Butler, W. R. L. Cairns, J. M. Cook and C. M. Davidson, *J. Anal. At. Spectrom.,* 2014, **29**, 17-50.

3 SARA Group, *Sudbury Soils Study Vol. 2 Human Health Risk Assessment May 2008* , 2, 2006.

4 USEPA, *Validation Assessment of In Vitro Lead Bioaccessibility Assay for Predicting Relative Bioavailability of Lead in Soils and Soil-like Materials at Superfund Sites* , OSWER 9200.3-51, United States Environmental Protection Agency, 2009.

5 K. D. Bradham, B. D. Laird, P. E. Rasmussen, R. A. Schoof, S. M. Serda, S. D. Siciliano and M. F. Hughes, *Hum. Ecol. Risk Assess.,* 2014, **20**, 272-286.

6 RECORD, *Bioavailability and Bioaccessibility of Pollutants in Contaminated Soils: State of Present Knowledge and Research Avenues*, 10-0671/1A, France, 2012.

7 J. Wragg, M. Cave, N. Basta, E. Brandon, S. Casteel, S. Denys, C. Gron, A. Oomen, K. Reimer, K. Tack and T. Van de Wiele, *Sci. Total Environ.,* 2011, **409**, 4016-4030 (DOI:10.1016/j.scitotenv.2011.05.019).

8 A. G. Oomen, A. Hack, M. Minekus, E. Zeijdner, C. Cornelis, G. Schoeters, W. Verstraete, T. Van De Wiele, J. Wragg, C. J. M. Rompelberg, A. J. A. M. Sips and J. H. Van Wijnen, *Environ. Sci. Technol.,* 2002, **36**, 3326-3334 (DOI:10.1021/es010204v).

9 S. Saikat, B. Barnes and D. Westwood, *J. Environ. Sci. Health Part A Toxic Hazard. Subst. Environ. Eng.,* 2007, **42**, 1213-1221 (DOI:10.1080/10934520701435486).

10 I. Koch, K. J. Reimer, M. I. Bakker, N. T. Basta, M. R. Cave, S. Denys, M. Dodd, B. A. Hale, R. Irwin, Y. W. Lowney, M. M. Moore, V. Paquin, P. E. Rasmussen, T. Repaso-Subang, G. L. Stephenson, S. D. Siciliano, J. Wragg and G. J. Zagury, *J. Environ. Sci. Health Part A Toxic Hazard. Subst. Environ. Eng.,* 2013, **48**, 641-655 (DOI:10.1080/10934529.2013.731817).

11 M. Dodd, P. E. Rasmussen and M. Chénier, *Hum. Ecol. Risk Assess.,* 2013, **19**, 1014-1027 (DOI:10.1080/10807039.2012.719381).

12 Y. Ibanez, B. L. E. Bot and P. Glorennec, *Eur. J. Mineral.,* 2010, **22**, 629-637 (DOI:10.1127/0935-1221/2010/0022-2010).

13 A. Turner, *Environ. Geochem. Health,* 2011, **33**, 331-341 (DOI:10.1007/s10653-011-9386-2).

14 P. I. Beamer, C. A. Elish, D. J. Roe, M. M. Loh and D. W. Layton, *J. Environ. Monit.,* 2012, **14**, 839-844 (DOI:10.1039/c2em10740f).

15 P. E. Rasmussen, S. Beauchemin, M. Nugent, R. Dugandzic, M. Lanouette and M. Chénier, *Hum. Ecol. Risk Assess.,* 2008, **14**, 351-371 (DOI:10.1080/10807030801934960).

16 L. C. W. MacLean, S. Beauchemin and P. E. Rasmussen, *Environ. Sci. Technol.,* 2011, **45**, 5491-5497 (DOI:10.1021/es2001503).

17 S. Beauchemin, L. C. W. MacLean and P. E. Rasmussen, *Environ. Geochem. Health,* 2011, **33**, 343-352 (DOI:10.1007/s10653-011-9380-8).

18 S. R. Walker, H. E. Jamieson and P. E. Rasmussen, *Environ. Sci. Technol.,* 2011, **45**, 8233-8240 (DOI:10.1021/es2008227).

19 P. E. Rasmussen, S. Beauchemin, M. Chénier, C. Levesque, L. C. W. MacLean, L. Marro, H. Jones-Otazo, S. Petrovic, L. T. McDonald and H. D. Gardner, *Environ. Sci. Technol.,* 2011, **45**, 4959-4965 (DOI:10.1021/es104056m).

20 CMP, *Chemicals Management Plan*, Canadian Gazette 145 (41), Government of Canada, Ottawa, Ontario, 2011.

21 P. E. Rasmussen, K. S. Subramanian and B. J. Jessiman, *Sci. Total Environ.,* 2001, **267**, 125-140 (DOI:10.1016/S0048-9697(00)00775-0).

22 P. E. Rasmussen, *Can. J. Anal. Sci. Spectrosc.,* 2004, **49**, 166-174.

23 P. H. Baker, G. H. Galbraith, R. C. McLean, C. Hunter and C. H. Sanders, *Indoor Built Environ.,* 2006, **15**, 357-364 (DOI:10.1177/1420326X06067351).

24 G. Emenius, J. Korsgaard and M. Wickman, *Clin. Exp. Allergy,* 2000, **30**, 418-425 (DOI:10.1046/j.1365-2222.2000.00761.x).

25 L. C. W. MacLean, S. Beauchemin and P. E. Rasmussen, *Environ. Geochem. Health,* 2013, **35**, 153-159 (DOI:10.1007/s10653-012-9467-x).

26 P. E. Rasmussen, C. Levesque, M. Chénier, H. D. Gardner, H. Jones-Otazo and S. Petrovic, *Sci. Total Environ.,* 2013, **443**, 520-529.

27 J. W. Drexler and W. J. Brattin, *Hum. Ecol. Risk Assess.,* 2007, **13**, 383-401 (DOI:10.1080/10807030701226350).

28 S. Beauchemin, P. Rasmussen, L. MacLean and T. MacKinnon, *Impact of humidity on the transformation of zinc in house dust: Summary of XAS speciation*, CANMET-MMSL report 12-038(CR), Natural Resources Canada, Ottawa, Ontario, 2012.

29 M. Jiang, Y. Nakamatsu, K. A. Jensen and S. Utsunomiya, *Atmos. Environ.,* 2014, **82**, 364-374 (DOI:10.1016/j.atmosenv.2013.10.035).

30 W. Stopford, J. Turner, D. Cappellini and T. Brock, *J. Environ. Monit.,* 2003, **5**, 675-680 (DOI:10.1039/b302257a).

31 USEPA, *Guidance for evaluating the bioavailability of metals in soils for use in human health risk assessment*, OSWER 9285.7-80, United States Environmental Protection Agency, 2007.

32 WHO, *WHO guidelines for indoor air qualit: dampness and mould*, ISBN 978 92 890 4168 3, World Health Organization, Copenhagen, Denmark, 2009.

Figure Captions

Fig. 1. Transformation of Pb speciation caused by exposing dust samples (top = HM112; bottom = NIST 2584) to a humid environment for four months. Details in Table 3 and Electronic Supplementary Information.

Fig. 2. Bioaccessibility of Pb, Zn, Co compounds used as XAS Standards expressed as percentages relative to their soluble reference salts (=100% as described in Methods). Mean values for 2-5 replicates per compound.

Fig. 3. Frequency distribution curves showing 25th, 50th (median), and 75th percentile bioaccessibility of Co, Zn, Pb and Se in the Canadian House Dust Study. Percentage bioaccessibility results for Pb, Zn and Co are expressed relative to their soluble reference salts (=100% as described in Methods). See Table 4 for statistical details including 95% confidence limits (n=1025 for Pb, Zn and Co; n=847 for Se).

Electronic Supplementary Information on Pb Speciation using EXAFS and XANES includes Figures S-1 to S-4.

Fig. S1. (A) Pb L-111 edge XANES, (B) k^2-weighted EXAFS and (C) Fourier transformed k^2-weighted EXAFS (uncorrected for phase shift) for the original and 4-month weathered HM112 dust (solid black line = measured; dotted grey line = fitted data #1 from Table 3). Reference compounds of hydrocerussite (Pb hydroxyl carbonate), Pb carbonate and Pb adsorbed on humate are illustrated for comparison.

Fig. S2. (A) Pb L-111 edge XANES, (B) k^2-weighted EXAFS and (C) Fourier transformed k^2-weighted EXAFS (uncorrected for phase shift) for the original and 4-month weathered N2584 dust (solid black line = measured; dotted grey line = fitted data - Table 3). Reference compounds of hydrocerussite (Pb hydroxyl carbonate), Pb naphthenate and Pb chromate are illustrated for comparison.

Fig. S3. Comparison of Pb XANES (A) and EXAFS (B) spectra for house dust HM112 and N2584 before (dark solid line) and after 4-month aging (grey solid line) in an oxygenated, humidity chamber.

Fig. S4. Comparison of Pb XANES (A) and EXAFS (B) spectra for Pbnaphthenate (dark solid line) and Pb adsorbed on humate (grey solid line).

Table 1.BioaccessiblePb, Zn, Co and Se (mg/kg) in the original and 4-month weathered dust samples determined using a simulated gastric extraction and ICP-MS determination (n= 4 for all calculations).

	Original (before aging) mean ± sd	**After aging mean ± sd**	**t-test *p* value**	**Significant change**
BioaccessiblePb (mg/kg)				
NIST 2584 Indoor Dust	7816 ± 282	11304 ± 497	<0.001	+ 45%
CA043 house dust	146 ± 17	353 ± 82	0.013	+142%
HM112 house dust	1131 ± 119	1875 ± 411	0.032	+ 75%
Bioaccessible Zn (mg/kg)				
NIST 2584 Indoor Dust	1822 ± 82	2212 ± 110	0.002	+ 21%
CA043 house dust	1164 ± 71	1917 ± 323	0.016	+ 65%
HM112 house dust	1283 ± 81	1710 ± 336	0.081	+ 33%
Bioaccessible Co (mg/kg)				
NIST 2584 Indoor Dust	3.92 ± 0.21	2.55 ± 0.40	0.003	- 35%
CA043 house dust	1.79 ± 0.07	1.58 ± 0.70	0.590	none
HM112 house dust	5.31 ± 0.40	6.18 ± 0.52	0.039	+16%
Bioaccessible Se (mg/kg)				
NIST 2584 Indoor Dust	0.80 ± 0.09	0.20 ± 0.13	0.001	- 75%
CA043 house dust	0.54 ± 0.16	0.04 ± 0.09[†]	0.003	- 93%
HM112 house dust	0.66 ± 0.11	0.13 ± 0.13	0.001	- 80%

[†] <LOD of 0.1 for Se (instrument reading used in calculations)

Table 2. National baseline concentrations (mg/kg) for total and bioaccessible Pb, Zn, Co and Se in dust collected from 1025 homes in the Canadian House Dust Study. <LOD = below Limit of Detection.

	Lead		**Zinc**		**Cobalt**		**Selenium**	
	Total[†]	Bioaccessible[‡]	Total[†]	Bioaccessible	Total	Bioaccessible	Total	Bioaccessible
No. < LOD	0	0	0	0	0	0	123	421
Geomean	119	74	749	558	6.11	2.04	n/a	n/a
Mean ± sd	210 ± 446	144 ± 322	833 ± 470	634 ± 394	7.4 ± 6.1	2.4 ± 1.6	n/a	n/a
Range (min-max)	14.2-7800	7.9-3916	144-6630	88-4207	0.65-70.2	0.27-23.2	<LOD-11.0	<LOD-9.0
Percentiles								
5	42.2	22	383	276	2.90	0.92	< LOD	< LOD
10	48.5	27	453	326	3.30	1.10	<LOD	< LOD
25	66.3	39	558	406	4.20	1.40	0.50	< LOD
50 (median)	100	63	725	534	5.60	1.99	0.90	0.20
75	173	108	964	740	7.80	2.71	1.40	0.35
90	357	246	1290	1038	13.6	3.98	2.47	0.50
95	760	539	1627	1285	19.1	5.30	3.40	0.70
97.5	1331	921	2037	1557	24.8	6.59	4.40	1.00
98	1554	1238	2124	1696	27.6	7.02	4.75	1.05
99	2027	1642	2601	2307	35.2	9.25	6.90	1.57

[†] Total Pb and Zn previously reported in Rasmussen et al. (2013).[26]

[‡] BioaccessiblePb previously reported in Rasmussen et al. (2011).[19]

Table 3. Best linear combination fitting results for the EXAFS χ(k)•k2 data using all binary and ternary combinations of the 22 Pb reference standards. Fitting results obtained on the XANES spectra use the best combination of standards retained after fitting the χ(k)•k2 data.

		% of total Pb[†] (± standard error)		
Sample	**Pb standards[†]**	**$\chi(k)\bullet k^2$**	**XANES**	
HM112 original		2.2 to 6 Å^{-1}	-40 to 100 eV	E_0 shift (eV)
Replicate #1	Pb carbonate	9.9 (±1.4)		
	Pb citrate	35.3 (±2.9)	57.9 (±2.0)	-0.53
	Hydrocerussite	54.8 (±0.0)	42.1 (±0.0)	0.23
	∑ before norm.[‡]	*97.4*	*98.9*	
	Reduced χ^2	*0.0417*	*0.0025*	
Replicate #2	Pb carbonate	21.0 (±1.2)	17.9 (±1.0)	-0.61
	Pbhumate	25.9 (±2.4)	36.0 (±2.4)	-0.66
	Hydrocerussite	53.1 (±0.0)	46.0 (±0.0)	-0.40
	∑ before norm.	*105.5*	*99.9*	
	Reduced χ^2	*0.0435*	*0.0027*	
HM112 weathered		2.2 to 6 Å^{-1}	-40 to 100 eV	E_0 shift (eV)
	Pb oxalate	12.7 (±1.8)		
	Pbhumate	63.3 (±3.9)	78.1 (±2.5)	-0.33
	Hydrocerussite	24.0 (±0.0)	21.9 (±2.5)	0.91
	∑ before norm.	*85.6*	*99.6*	
	Reduced χ^2	*0.0607*	*0.0036*	
N2584 original		2.2 to 8 Å^{-1}	-40 to 100 eV	E_0 shift (eV)
	Pb chromate	27.5 (±3.0)	30.0 (±2.0)	-0.63
	Hydrocerussite	72.6 (±0.0)	70.0 (±0.0)	-1.29
	∑ before norm.	*87.7*	*102.5*	
	Reduced χ^2	*0.3853*	*0.0086*	
N2584 weathered		2.2 to 9 Å^{-1}	-40 to 100 eV	E_0 shift (eV)
	Pb chromate	11.7 (±2.2)	11.9 (±1.9)	-1.47
	Pbnaphthenate	54.2 (±5.1)	46.7 (±3.4)	-0.71
	Hydrocerussite	34.1 (±0.0)	41.4 (±4.1)	-0.80
	∑ before norm.	*109.2*	*101.8*	
	Reduced χ^2	*0.2536*	*0.0056*	

[†] % of total Pb after normalization to sum = 100%

[‡] ∑ before norm.: Sum of fractions before normalization to sum 100%

Table 4. Central tendency (median and/or mean) and 95% confidence interval (CI) for % bioaccessibility (%bio) of Pb, Zn, Co and Se in the Canadian House Dust Study. Results are provided with and without statistical outliers.[†]

		outliers >100% included[†]	outliers >100% excluded[†]
% bio Pb	median (95% CI)	59 (58-60)	58 (57-59)
	mean ± sd	59 ± 16	59 ± 15
	no. included	1025	1013
	Shapiro-Wilk	p<.0001	p = .06
% bio Zn	median (95% CI)	67 (66-67)	67 (66-68)
	mean ± sd	67 ± 13	66 ± 12
	no. included	1025	1005
	Shapiro-Wilk	p<.0001	p =.001
% bio Co	median (95% CI)	33 (33-34)	33 (32-33)
	mean ± sd	33 ± 12	33 ± 11
	no. included	1025	1023
	Shapiro-Wilk	p<.0001	p<.0001
% bio Se	median (95% CI)	13 (10-15)	12 (9-14)
	no. included	847[‡]	831
	Shapiro-Wilk	p<.0001	p<.0001

[†] outliers defined as >100% bioaccessibility and > Q3 + 1.5 × IQR, where IQR = Q3 − Q1
[‡] includes all CHDS samples exceeding LOQ for total Se (0.3 mg/kg)

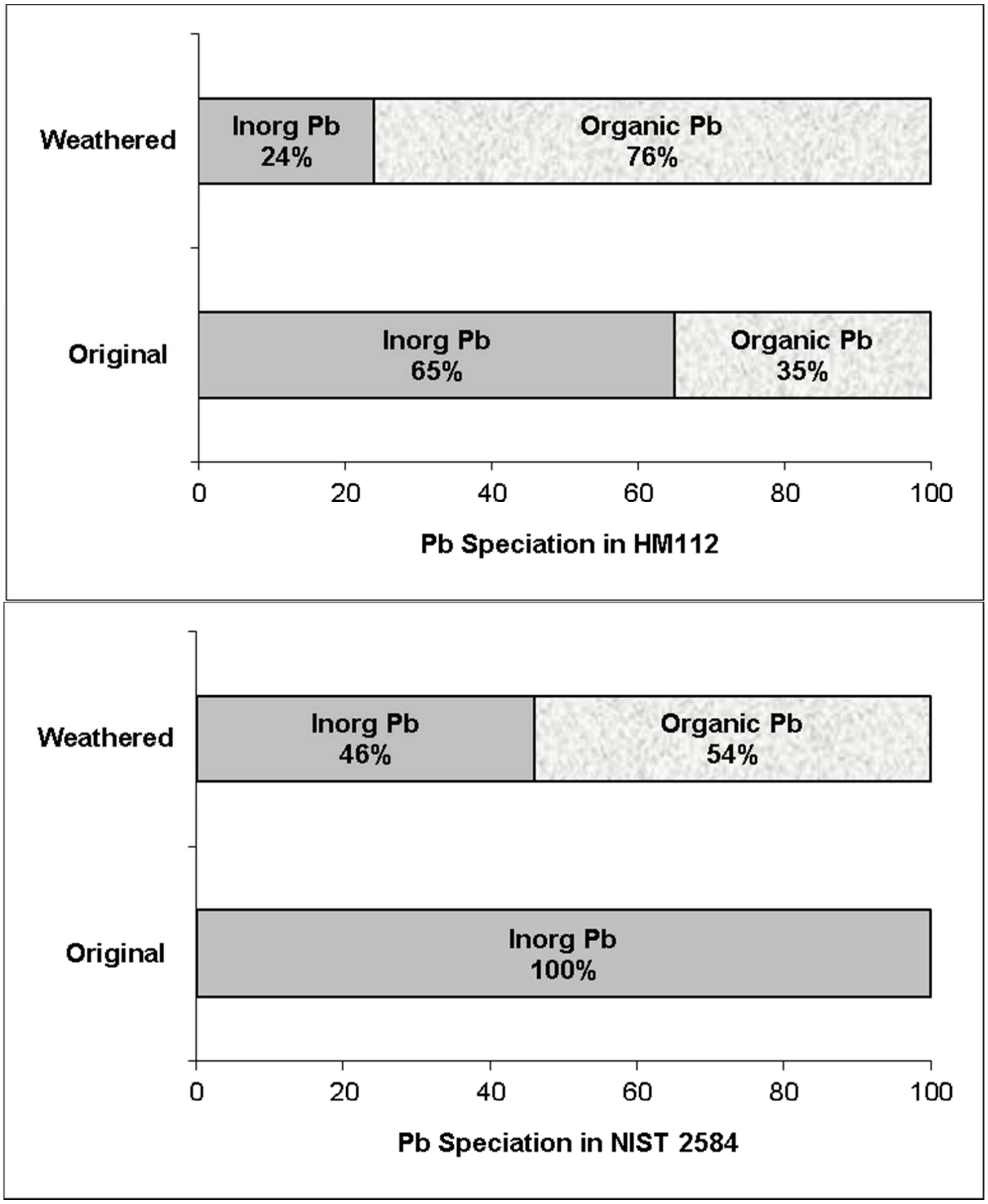
Weathered
Inorg Pb 24%
Organic Pb 76%
Original
Inorg Pb 65%
Organic Pb 35%
0
20
40
60
80
100
Pb Speciation in HM112
Weathered
Inorg Pb 46%
Organic Pb 54%
Original
Inorg Pb 100%
0
20
40
60
80
100
Pb Speciation in NIST 2584

Fig. 1

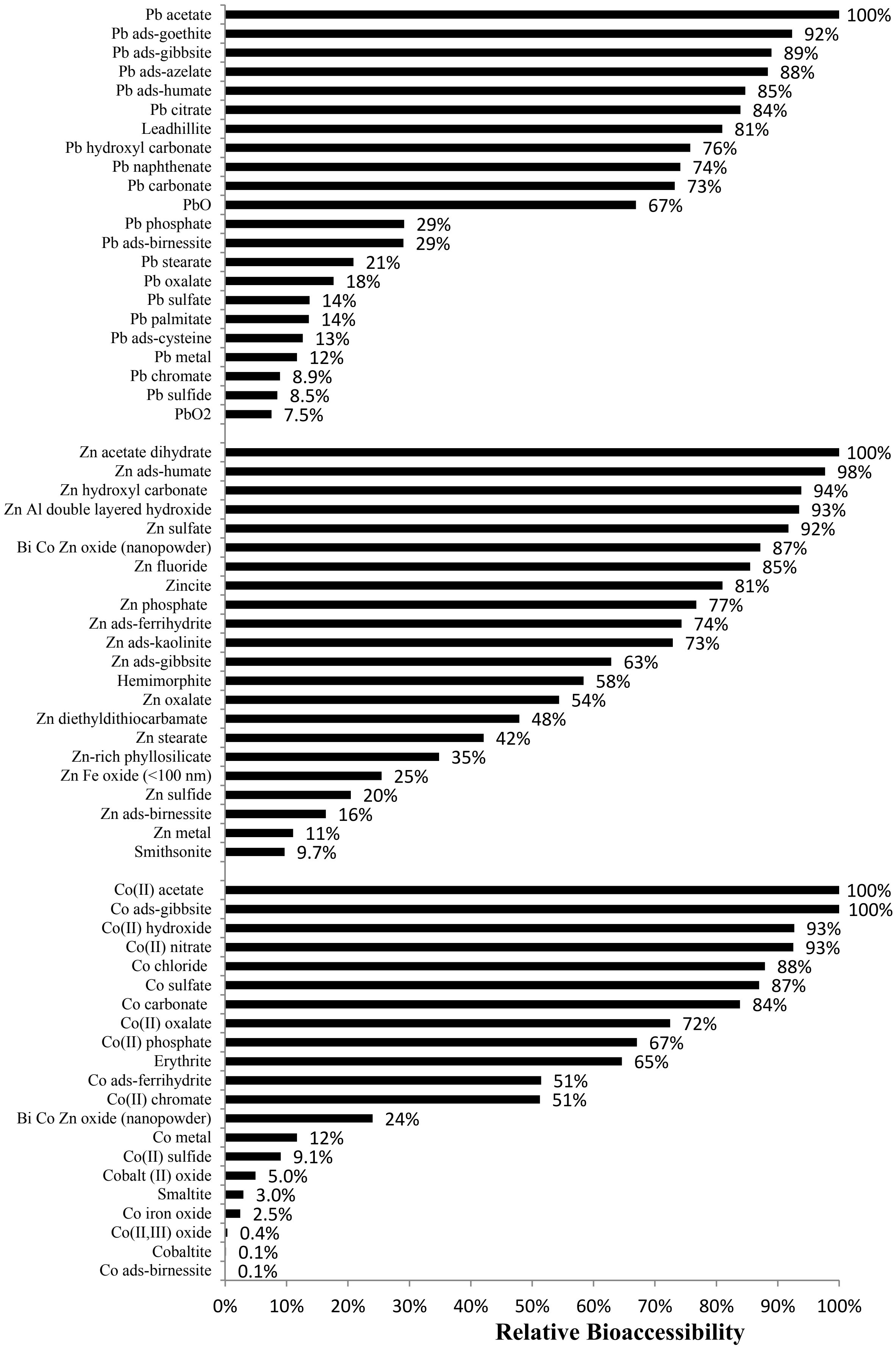
Pb acetate 100%
Pb ads-goethite 92%
Pb ads-gibbsite 89%
Pb ads-azelate 88%
Pb ads-humate 85%
Pb citrate 84%
Leadhillite 81%
Pb hydroxyl carbonate 76%
Pb naphthenate 74%
Pb carbonate 73%
PbO 67%
Pb phosphate 29%
Pb ads-birnessite 29%
Pb stearate 21%
Pb oxalate 18%
Pb sulfate 14%
Pb palmitate 14%
Pb ads-cysteine 13%
Pb metal 12%
Pb chromate 8.9%
Pb sulfide 8.5%
PbO2 7.5%
Zn acetate dihydrate 100%
Zn ads-humate 98%
Zn hydroxyl carbonate 94%
Zn Al double layered hydroxide 93%
Zn sulfate 92%
Bi Co Zn oxide (nanopowder) 87%
Zn fluoride 85%
Zincite 81%
Zn phosphate 77%
Zn ads-ferrihydrite 74%
Zn ads-kaolinite 73%
Zn ads-gibbsite 63%
Hemimorphite 58%
Zn oxalate 54%
Zn diethyldithiocarbamate 48%
Zn stearate 42%
Zn-rich phyllosilicate 35%
Zn Fe oxide (<100 nm) 25%
Zn sulfide 20%
Zn ads-birnessite 16%
Zn metal 11%
Smithsonite 9.7%
Co(II) acetate 100%
Co ads-gibbsite 100%
Co(II) hydroxide 93%
Co(II) nitrate 93%
Co chloride 88%
Co sulfate 87%
Co carbonate 84%
Co(II) oxalate 72%
Co(II) phosphate 67%
Erythrite 65%
Co ads-ferrihydrite 51%
Co(II) chromate 51%
Bi Co Zn oxide (nanopowder) 24%
Co metal 12%
Co(II) sulfide 9.1%
Cobalt (II) oxide 5.0%
Smaltite 3.0%
Co iron oxide 2.5%
Co(II,III) oxide 0.4%
Cobaltite 0.1%
Co ads-birnessite 0.1%
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%
Relative Bioaccessibility

Fig. 2

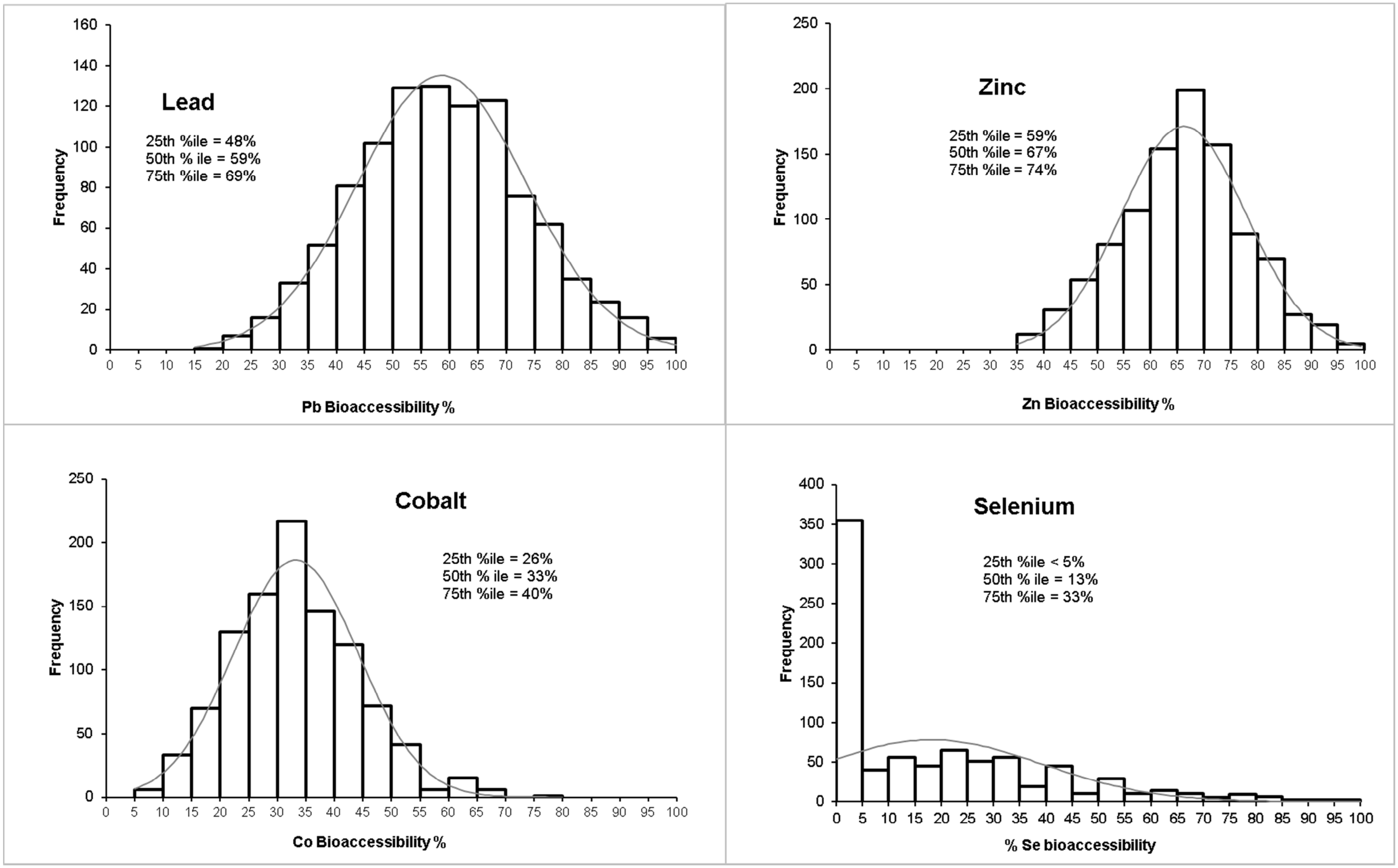
Lead
25th %ile = 48%
50th % ile = 59%
75th %ile = 69%
Frequency
0
20
40
60
80
100
120
140
160
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100
Pb Bioaccessibility %
Zinc
25th %ile = 59%
50th %ile = 67%
75th %ile = 74%
Frequency
0
50
100
150
200
250
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100
Zn Bioaccessibility %
Cobalt
25th %ile = 26%
50th % ile = 33%
75th %ile = 40%
Frequency
0
50
100
150
200
250
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100
Co Bioaccessibility %
Selenium
25th %ile < 5%
50th % ile = 13%
75th %ile = 33%
Frequency
0
50
100
150
200
250
300
350
400
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100
% Se bioaccessibility

Fig. 3

Humidity increases the bioaccessibility of Pb and Zn in dust that collects in damp microenvironments (such as window troughs).
240x320mm (180 x 180 DPI)