Formation of plumbojarosite (PLJ) reduces bioavailability of soil-borne lead (Pb)

Ranju Karna[1], Matt Noerpel[1], Clay Nelson[2], Brittany Elek[3], Karen Herbin-Davis[3], Gary Diamond[4], Karen Bradham[2], Kirk Scheckel[1], David J. Thomas[3]

1. Center for Environmental Solutions & Emergency Response, Cincinnati, OH; 2. Center for Environmental Measurement & Modeling; 3. Center for Computational Toxicology & Exposure, Research Triangle Park, NC, Office of Research and Development, U.S. Environmental Protection Agency; 4. SRC. North Syracuse, NY

David J. Thomas; thomas.david@epa.gov; 919-541-4974

Abstract

Exposure to Pb during early life has long-lasting adverse effects on health. Ingestion of Pb-contaminated soil is a major route for exposure of children to this toxic metal. Soil remediation procedures that alter physiochemical properties of soil-borne Pb can limit exposure by reducing gastrointestinal Pb uptake. A novel approach for remediation of soil Pb uses addition of iron (Fe) sulfate and application of heat to promote formation of PLJ, a poorly soluble Pb-Fe sulfate compound. Here, two Pb-contaminated soils and samples of a low-lead soil spiked with various Pb compounds (i.e., carbonate, chloride, phosphate, or sulfate) were treated to convert native Pb species to PLJ. We used a mouse assay to examine tissue Pb distribution after ingestion of diets amended with untreated or treated soils. Bone and blood Pb levels were determined to evaluate uptake across the gastrointestinal barrier. For both Pb-contaminated soils and all Pb compounds, bone and blood Pb levels were significantly lower ($P<0.001$, student t-test) in mice that consumed diets amended with treated soils than in mice that consumed diets amended with untreated soils. After treatment, estimated relative bioavailability (RBA) of Pb in both soils and for all Pb compounds were reduced by more than 90% compared to RBA estimates for untreated soils or compounds. X-ray absorption spectroscopy was used to determine Pb species in soil-amended diets and in feces excreted by mice consuming these diets. Treatment of Pb-contaminated soils or Pb compounds consistently converted more than 90% of all Pb species in these materials to PLJ. Speciation of Pb in feces from mice fed diets containing soils or Pb compounds treated to promote PLJ formation found no evidence that ingested PLJ underwent chemical transformation during transit of the gastrointestinal tract. This evidence suggests that formation of PLJ could be an effective strategy to reduce the RBA of Pb in soil and minimize this medium's role as a source of exposure to Pb in young children. (This abstract does not represent U.S. Environmental Protection Agency policy.)

Background

Exposure of children to Pb has profound and long-lasting health effects[1]. Extensive release of Pb into the environment has resulted in widespread and persistent contamination of urban soil and dust with this toxic metal[2]. Although Pb levels in some media (e.g., air and food) have declined in recent decades[3,4], soil and dust Pb levels remain elevated. As a consequence, Pb in soil and dust have emerged as significant sources of Pb exposure in one-to-six year-old children[5]. Therefore, reducing exposure of children to Pb through soil or dust ingestion is an important public health goal[6].

Removal of Pb-contaminated soil and its replacement with uncontaminated soil has been a common and effective approach to reduce Pb exposure in children[7,8]. However, soil removal and replacement are expensive and complicated procedures that can be difficult to implement in some settings. If removal and replacement of contaminated soil are not feasible, an alternative approach is to reduce the bioavailability of Pb present in soil and dust. Operationally, bioavailability is defined as the amount of a contaminant absorbed into the body following skin contact, ingestion, or inhalation. In children, age-dependent hand to mouth activity creates a unique and significant pathway for ingestion of Pb in soil and dust[9]. Reducing the bioavailability of Pb in soil or dust ingested by hand to mouth transfer can have the salutary effect of reducing the internal dose of this toxic metal.

The bioavailability of Pb is a function of physical and chemical properties of the matrix in which it is ingested and can vary from 0 to 100%. One approach to reducing the bioavailability of Pb is *in situ* solidification and stabilization to reduce the solubility of Pb in soil[10,11]. Thus, addition of phosphorus as phosphate (P) to Pb-contaminated soil can promote formation of stable and relatively insoluble Pb-P species. Although Pb-P interactions can reduce soil Pb bioavailability[12-14], the limitations of this approach and its applicability to a variety of soil types have not been systematically evaluated. As part of an effort to explore novel options for stabilization of soil Pb, we have evaluated the effect of formation of plumbojarosite, an insoluble iron-sulfate mineral, on the bioavailability of soil Pb. Here, we used adult female mice as the test species in assays to estimate Pb bioavailability in treated and untreated soils[15].

1. Surkan PJ, Zhang A, Trachtenberg F, et al., Neurotoxicology. 2007, 28, 1170-1177
2. Datko-Williams L, Wilkie A, Richmond-Bryant J., Sci. Total Environ. 2014, 468-469, 854-863.
3. Bolger PM, Yess NJ, Gunderson EL, et al., Food. Addit. Contam. 1996, 13, 53-60.
4. Richmond-Bryant J, Meng Q, Davis A, et al., Environ. Health Perspect. 2014, 122, 754-760
5. Zartarian V, Xue J, Tornero-Velez R, et al., Environ. Health Perspect. 2017, 125.
6. Bellinger D.C. Int. J. Environ. Res. Public Health 2011, 8, 2593-2628.
7. Sheldrake S, Stifelman M., Sci. Total Environ. 2003, 303, 105-123.
8. von Lindern I, Spalinger S, Petroysan V, et al., Sci. Total Environ. 2003, 303, 139-170.
9. Xue J, Zartarian V, Moya J, et al., Risk Anal. 2007 27, 411-420.
10. Kumpiene J, Lagerkvist A, Maurice C., Waste Manag. 2008, 28, 215-225.
11. National Research Council. *Innovations in ground water and soil cleanup: From concept to commercialization*. National Academies Press: Washington, D.C, 1997.
12. Scheckel KG, Diamond GL, Burgess MF, et al., J. Toxicol. Environ. Health B Crit. Rev. 2013, 16, 337-380.
13. Hettiarachchi GM, Pierzynski GM, Oehme FW, et al., J Environ Qual. 2003, 32,1335-1345.
14. Bradham KD, Diamond GL, Nelson CM, et al., Environ Sci Technol. 2018, 52:13908-13913.
15. Bradham KD, Green W, Hayes H, et al., J Toxicol Environ Health A. 2016, 79:1179-1826.

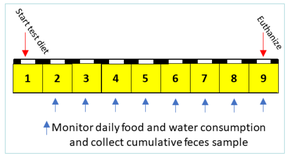
Methods

Test materials – Soil 1 originated in an orchard where lead arsenate had been used as a herbicide. Soil 2 was collected from a former mining site. A soil with low Pb content was spiked with Pb minerals for bioavailability studies. All test soils were sieved to produce a < 250 µm fraction for testing. Pb (lead acetate trihydrate, Sigma-Aldrich, St. Louis, MO) was used as the reference compound in all studies.

Soil treatments – In soils 1 and 2 and in Pb-mineral spiked soils, formation of plumbojarosite, a poorly soluble Pb-Fe sulfate compound, was promoted by addition of iron (Fe) sulfate and application of heat for 8 or 67 hours.

Test Diets – Test materials, (untreated or treated soils, Pb acetate) were incorporated by the vendor (Dyets, Bethlehem, PA) into powdered AIN-93G purified rodent diet. This diet meets the nutritional requirements of rapidly growing immature rodents.

Mouse origin and maintenance – Four week-old female C57BL/6 mice (Charles River) were acclimated for 12 to 14 days in a 12 hour light–12 hour dark photocycle at 20-22°C with free access to rodent diet and tap water before use in the mouse assay.



Mouse assay – In this assay, the bioavailability of Pb in a test material (e.g., soil or mineral) was calculated using data on Pb levels in bone and blood of mice that consumed AIN-93G rodent diet that contained the test material. The diagram shows assay design. Mice were placed in metabolic cages (3 per cage) on the morning of day 1 with free access to amended AIN-93G rodent diet and drinking water. Daily food and water consumption were measured and a cumulative feces sample was collected for each cage. Mice were euthanized by CO_2 anesthesia on day 9. Pooled heparinized blood samples were collected for Pb analysis. Mouse carcasses were defleshed by dermestid beetles; defleshed skeletons were pooled by cage for Pb analysis.

Lead analysis - Pooled skeletons from each cage were homogenized by freeze grinding. Bone samples were digested in ultra-high purity nitric acid in a closed vessel microwave reaction system. Digested samples were diluted to 5 to 10% nitric acid with deionized water. Total Pb in acid-digested bone samples were determined by Inductively-Coupled Plasma-Mass Spectrometry (X-Series II ICP/MS, Thermo Scientific). Pb in blood samples was routinely measured electrochemically by anodic stripping voltammetry (LeadCare Ultra, Magellan Diagnostics, North Billerica, MA). In some cases, blood Pb levels were determined using ICP-high resolution MS. Quality control samples were analyzed with each digestion batch and included reagent blanks, blank spikes, matrix spikes, and a matrix-matched NIST SRM.

Pb speciation analysis – Pb species in samples of diets amended with test materials and cumulative feces samples were determined by X-ray absorption spectroscopy at the DuPont-Northwestern-Dow Collaborative Access Team Sector 5, beam line 5BM-D, at the Advanced Photon Source of the Argonne National Laboratory, Lemont, IL.

Data analysis –Tissue-specific RBAs (bone, blood) were estimated for treated and untreated soils and for treated and untreated soils spiked with Pb minerals. RBA was estimated as the tissue dose ratio (TDR) for the test material TM (e.g. soil or mineral) and reference material (RM, Pb acetate):

$$RBA = TDR_{TM}/TDR_{RM}$$

where the TDR is the ratio of the Pb concentration (mg/kg total skeleton or mg/L blood) to the cumulative Pb dose (mg) for the study.

Confidence limits on each RBA were estimated based on Fieller's Theorem for estimating confidence limits on the ratio of means. A point estimate for the RBA was calculated as the average of tissue-specific RBA values. Confidence intervals on the point estimate were estimated from Monte Carlo simulation of the probability distributions of each tissue-specific RBA.

Results

Figure 1

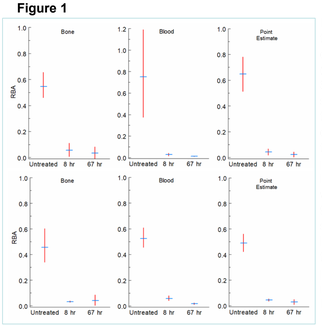


Figure 1 – Effect of treatment on estimates of relative bioavailability (RBA) for Pb in two soils. Soil 1 (upper panel) and soil 2 (lower panel) tested in untreated state or after 8 or 67 hours of treatment to promote plumbojarosite formation. Mean estimates shown with upper and lower 95% confidence intervals shown for RBA estimates based on bone or blood tissue Pb levels. RBA point estimates are means of tissue data RBA estimates.

Figure 2

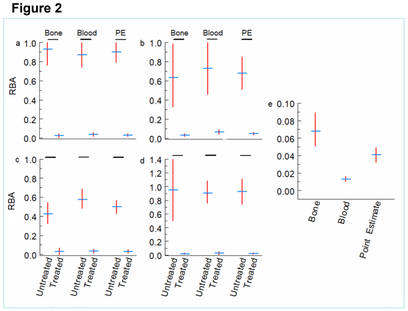


Figure 2 – Effect of treatment on estimates of relative bioavailability (RBA) for Pb in soils spiked with Pb minerals. RBA estimates shown for untreated and treated soils spiked with (a) Pb carbonate, (b) Pb chloride, (c) Pb phosphate, and (d) Pb sulfate. Results shown for soil spiked with authentic plumbojarosite (e). Mean estimates with upper and lower 95% confidence intervals shown for RBA estimates based on bone or blood tissue Pb levels. RBA point estimates are means of tissue data RBA estimates.

Figure 3

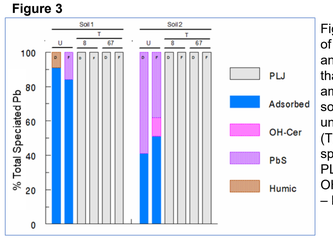


Figure 3 – Contribution of Pb species in diet (D) and feces (F) of mice that consumed diets amended with soil 1 or soil 2. Soils tested in untreated (U) or treated (T) forms. % of each Pb species present shown. PLJ – plumbojarosite; OH-Cer – cerussite; PbS – Pb sulfate

Figure 4

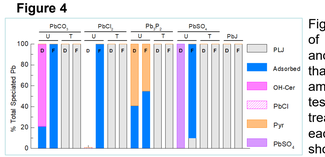


Figure 4 – Contribution of Pb species in diet (D) and feces (F) of mice that consumed mineral-amended diets Minerals tested in untreated (U) or treated (T) forms. % of each Pb species present shown. Legends as in Figure 3; Pyr – pyromorphite.

Conclusions and future directions

1. Treatment of Pb-contaminated soils to promote plumbojarosite formation results in substantial reductions (>90%) in estimates of relative bioavailability of Pb in these soils. The magnitude of reduction in the % relative bioavailability is not strongly affected by the length of time used for soil treatment.
2. For a range of Pb minerals commonly found in contaminated soils, treatment to promote plumbojarosite formation markedly reduces estimated relative bioavailability. For all minerals, estimates of relative bioavailability for treated soils are similar to those obtained for authentic plumbojarosite.
3. Determination of Pb species in diets amended with untreated and treated soils and minerals shows that treatment results in near quantitative conversion of native Pb species to plumbojarosite.
4. Determination of Pb species in feces collected from mice that consumed diets amended with untreated and treated soils and minerals shows that ingested plumbojarosite transits the gastrointestinal tract without alteration.
5. The high efficiency of conversion of soil Pb species to plumbojarosite coupled with evidence of low relative bioavailability for Pb ingested in this form suggests that remediation of soils by plumbojarosite formation *in situ* may be a valuable tool to reduce exposure of children to this toxic metal. Optimization of soil treatment procedures and studies of efficacy of treatment under field conditions are needed to validate this new approach.