EPA Public Access

Author manuscript

Appl Geochem. Author manuscript; available in PMC 2018 September 19.

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Published in final edited form as:

Appl Geochem. 2017 August ; 83: 31–40. doi:10.1016/j.apgeochem.2017.01.025.

Assessing metal mobilization from industrial lead-contaminated soils in an urban site

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Abstract

A series of leaching and partitioning tests (Toxicity Characteristic Leaching Procedure (TCLP), Synthetic Precipitation Leaching Procedure (SPLP), Controlled Acidity Leaching Protocol (CALP), Acid Neutralization Capacity (ANC), and sequential extraction) were applied to three different soils to study the potential mobility of metals into groundwater. Two of these soils were lead (Pb)-contaminated soils (Hotspot 1 and Hotspot 2) collected from an urban site associated with lead smelting and other industrial operations. The third sample (Stockpile) was soil affected by previous contamination in the area, removed from residential properties, stockpiled, and selected to be used as fill material in the studied site. The TCLP and CALP showed that Pb could be released from both hotspots, but were not released in the acidic rainfall extraction fluid of the SPLP. The sequential extraction showed that Pb in the hotspot soils was associated with the carbonate fraction, while As was associated with the Fe and Mn oxides. The stockpile released traces of Pb or As in the TCLP and CALP, but the ANC only released Pb under acidic conditions and the SPLP did not release Pb or As. Overall, the projected repository with Stockpile would not pose imminent danger to groundwater because, under the expected environmental conditions, Pb and As tend to remain in the solid phase.

Keywords

Arsenic; Metals leaching; Sustainability; Repository

1. Introduction

Lead (Pb) smelting operations have been found to pollute air, surrounding soils, and surface waters via air emissions through plant stacks, fugitive emissions, and from outdoor handling and storage of raw materials and wastes containing Pb and other metals common to the pyrometallurgical industry. Lead is a toxic metal that is included in the United States Environmental Protection Agency (U.S. EPA) 'probable carcinogen' list, and its toxicity to human health has been well documented (EPA, 2004, Fell, 1984, Murata et al., 2009, Todd et al., 1996). Lead exposure has been catalogued as a worldwide problem (Tong et al., 2000)

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and contaminated soils have been found nearby lead smelters in numerous locations around the world (Markus and McBratney, 2001). Pb concentrations found in 436 surveyed Superfund sites in the U.S. range from 0.16 to 366,000 mg/kg (Paff and Bosilovich, 1995). Recently, the U.S. EPA added an urban site located in the U.S. Midwest to the Superfund National Priorities List. This site was found to contain Pb-contamination generated by a lead smelter and other industrial lead-related operations. The U.S. EPA also issued a time-critical removal action to address contaminated soils on a number of properties with Pb concentrations 400 mg/kg, and in residences with children having elevated blood lead levels within the impacted area. This removal action removed the top 15 cm of the contaminated soil from the residences and replaced it with clean soil to reduce the risk of lead exposure.

The removed soil was stockpiled within the city limits. Later, the city proposed the utilization of this stockpiled soil as a fill to expand an existing city park. To prevent the potential exposure to the lead-contaminated soil, the city proposed that the park would be capped with 30 cm of clean soil. Nonetheless, it was uncertain if the Pb and other contaminants in the stockpiled soil, or in the site itself, would migrate into groundwater.

Leaching tests such as the Toxicity Characteristic Leaching Procedure (TCLP), the Synthetic Precipitation Leaching Procedure (SPLP), the Constant pH Leaching Test (a.k.a. Controlled Acidity Leaching Protocol (CALP)) and sequential extractions have been used in the past to determine metal mobility from contaminated soils, sediments, and mine waste (Hardison et al., 2004, Macías et al., 2012, Melamed et al., 2003, Pinto et al., 2011, Van Benschoten and Matsumoto, 1997). Results from of leaching tests, taken together, provide an extensive dataset of Pb leaching under municipal solid waste landfill conditions (TCLP), slightly acidic rainfall (SPLP), and long term rainfall release (CALP). The sequential extraction procedure provided details about metal mobilization according to operationally defined fractions of the tested soils. Chen et al. (2009) evaluated metal mobility and bioavailability from soils collected at a lead smelting site in Liaoning Province, China, using single step extractions and a sequential extraction. The study concluded that Pb present in the contaminated soil had the potential to move into the groundwater and become a public hazard.

The objectives of this study were to determine if the stockpiled soil was suitable for the intended fill purpose and to predict the environmental risk of elements migrating from the studied soils into groundwater using leaching tests.

2. Materials and methods

2.1. Description of the site and sampling locations

The studied site is located in the U.S. Midwest. The northern portion of the site was formerly used for several purposes, including white lead manufacture, equipment storage, parking lot, etc. As part of the site evaluation and cleanup by U.S. EPA, soil Pb concentrations were measured at 76 different points using a portable X-ray fluorescence (pXRF) and a map of the site was delineated with areas of Pb isoconcentration (Fig. 1). We used this map to collect soil samples from the two areas with the highest Pb concentrations

(hotspots) to proceed with the environmental risk evaluation from the worst-case scenario perspective. Fifteen kg of sample was collected at the center of each hotspot within a maximum depth of 15 cm.

‘Hotspot 1’ had a pXRF estimated Pb soil concentration of >4000 mg/kg, while ‘Hotspot 2’ had a soil Pb pXRF concentration >7000 mg/kg. These two hotspots were used to evaluate metal leachability from these highly contaminated soils. The ‘Stockpile’ sample corresponded to the surface soil removed from the residential properties during the previous cleaning phase, and proposed as fill material. Twenty aliquots were sampled from selected stockpiles and integrated into one composite sample to be representative of the soil to be used to fill the site.

A soil named “Agvise Soil RMN-LS” (sandy loam) was selected to represent the clean topsoil that could be used to cap the site and was obtained from Agvise Laboratories (Northwood, ND). This soil can be classified as uncontaminated soil based on its low Pb content (4.90 mg/kg) according to ATSDR (2007). Additionally, a native subsoil sample that corresponded to the Horizon C soil layer of the studied site was also collected. The RMN-LS and the Native subsoil were characterized using the SPLP to test Pb and As migration through the proposed repository, but were not used in other leaching tests.

2.2. Soils characterization

The moisture content of the soil samples was acquired by ASTM Method D2216–10. The pH of the soils was measured according to U.S. EPA Method 9045D. The soil surface area was analyzed using the Brunauer, Emmett, and Teller (BET) Method in a Tristar 300 (Micromeritics, Norcross, GA) porosimeter analyzer. Total organic carbon (TOC) and inorganic carbon (IC) were determined by using a TOC-V CHP Analyzer (Shimadzu Scientific Instruments, Columbia, MD) equipped with a solid sample module SSM-5000A. The bulk density of the disturbed soils was measured as described by Bashour and Sayegh (2007). The samples were placed on slides for XRD analyses following the pipette-in-glass technique according to Gibbs (1965). X-ray diffraction (XRD) analyses were conducted in an X’Pert-MPD PW3040/00 Diffractometer (PANalytical, Westborough, MA) with a Copper X-ray source ($K\alpha_1$ 1.5460 Å) generated at 40 mA and 45 kV. The 2θ ranged from 5° to 90° , with a 0.02° step, and a 2 s count time at each step. XRD results were processed using Highscore Plus software (PANalytical, Westborough, MA). Two types of acid digestion were employed: U.S. EPA Method 3052 with HNO_3 and HF aimed for the complete digestion of metals including the silicate matrix of the soils and U.S. EPA Method 3051 with HNO_3 and HCl was used to extract the soil metals without completely digesting the soil matrix. Both methods were necessary since it was desired to evaluate the acidic extraction efficiency in these soils. All these analyses were performed after sample homogenization. Particle size distribution (PSD) was determined by ASTM Method D6913–04 with sieve mesh sizes of 2, 0.422, 0.251, 0.178, and 0.075 mm on dry samples. All analytical work was performed in triplicate except for PSD and XRD.

2.3. Batch leaching tests

We performed the TCLP test, which was designed to simulate contaminants leaching in equilibrium with an extraction solution that mimics landfill leachate at pH 4.93 (U.S. EPA Method 1311) and the SPLP test, which was used to simulate leaching due to precipitation at slightly acidic conditions with a solution at pH 4.20 (U.S. EPA Method 1312). In these tests, 50 mL of extraction fluid was mixed with 2.5 g of unsieved, oven dried soil (60 °C). This mixture was tumbled for 18 h at 30 rpm in triplicates. An Acid Neutralization Capacity Test (ANC) was run following a modification of the method of Tiruta-Barna et al. (2004): 1.0 g of the soil sample (<1 mm) was equilibrated with HNO₃ in increasing concentrations and tumbled at 30 rpm in triplicates for 168 h in 50 mL vials. The SPLP results were loaded into a chemical equilibrium software Visual Minteq 3.0/3.1 (Gustafson, 2013) to study As and Pb speciation.

2.4. Controlled Acidity Leaching Protocol

The CALP is a test developed to provide constant Eh-pH conditions for solids leaching, making the environmental evaluation closer to a real disposal scenario, where the main physicochemical characteristics of the surroundings (pH and Eh) would not be affected by the sample. The constant pH leaching protocol described by Jegadeesan et al. (2008) was followed. Briefly, 100 g of each soil (<0.125 mm) was equilibrated with 2 L of the SPLP extraction fluid (pH = 4.2). Constant pH (4.2 ± 0.2) was maintained using HNO₃ or NaOH as needed in a 2.4 L glass reactor continuously stirred with a magnetic bar at ~300 rpm. The test was carried out for 168 h with sampling events at 0.17, 2, 4, 8, 24, 48, 96 and 168 h. The stirring was stopped for 10 min prior to the sampling events. The 168th hour samples were used to compare the CALP results with the batch leaching tests, while the leaching profile with time was used to evaluate the long-term leaching trends for the metals of interest.

Cappuyns and Swennen (2008) performed constant pH experiments for several soils, sediments, and wastes and found that the cumulative release of an element with time (RL_m) could be described by the equation:

$$RL_m(t) = RC_1(1 - \exp(-r_1t)) + RC_2(1 - \exp(-r_2t)) \quad (1)$$

where: RC_i (mg/kg) is the release capacity of the buffer system i, r_i (h⁻¹) is the rate coefficient, and *t* is the time after starting the experiment. These two identified stages, RC₁ and RC₂, imply the presence of two dominant ‘pools’ that release metals at different rates. These pools were operationally defined and are not related to particular sample components or fractions. It is relevant, nevertheless, that the metal release profiles can be divided into a ‘labile’ pool, constituted by the more soluble components, and a ‘slowly labile’ pool, which demands more acid than the initial content of the extraction fluid to be released. RC₁, r₁, RC₂, and r₂ values were calculated for Pb, zinc (Zn), and arsenic (As) using SigmaPlot 10.0 (Systat Software Inc., San Jose, CA) to process the CALP results. The solid residues from the CALP test were acid digested by U.S. EPA Method 3051 and the elemental composition was used to obtain a mass balance with the concentrations found in the 168-h leachate and the initial concentrations in the studied solids.

2.5. Sequential extraction

A seven-step sequential extraction procedure was performed to study mobilization, origin, and route of transportation of the target trace metals, as described by Jegadeesan et al. (2008). The primary fractions extracted were: water soluble (S1) with deionized (DI) water at 25 °C for 2 h, exchangeable (S2) using 1M MgCl₂ at pH 7 and 25 °C for 2 h, carbonate bound (S3) extracted with 1M CH₃COONa at pH 5 and 25 °C for 6 h, amorphous iron oxides (S4) using 0.04M NH₂OH·HCl in 25% acetic acid at 95 °C for 6 h, crystalline iron oxides (S5) using 0.2 M NH₄OCOCOONH₄·H₂O (Tamm's reagent) at pH 3 and 25 °C for 2 h, organic matter (S6) extracted with 0.7 M NaOCl at pH 8.5 and 90 °C for 6 h, and residual (S7) consisting of a HNO₃ acid digestion according to U.S. EPA Method 3051. For the initial step, 35 mL of DI water was placed in a vial with 1.75 g of dry sample with particle size "as received" (liquid-solid ratio 20:1). The aqueous phases were then centrifuged and decanted. The residue was used in the next step after rinsing with 10 mL of DI water. The leaching concentrations from the first three steps were added to obtain the 'labile fraction', S4 and S5 were added to calculate the 'Fe and Mn Oxides' fraction, and steps S1 to S6 were added to calculate the 'Total mobile fraction'. A linear correlation between the concentrations of different metals in each fraction was calculated using Microsoft Excel.

2.6. Metals analysis

Elemental composition was obtained using an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, IRIS Intrepid, Thermo Electron Corporation, CA) according to U.S. EPA Method 6030. All aqueous samples were centrifuged or filtered (0.45 µm PVDF media) and acidified. The method reporting limits for this analysis are reported in Table SI1 in the Supplementary Information. Aqueous phase digestion, if applicable, was performed using U.S. EPA Method 3015. Table SI2 contains a summary of the quality controls applied to the analytical procedures.

3. Results and discussion

To be concise, we focused our discussion to Pb and As results; however, we presented results of other leached elements for the benefit of the reader.

3.1. Proposed repository structure

To level off the city park with other properties, the Stockpile soil will be used as fill material on top of the Pb-contaminated soil and will be capped by a layer (0.3 m) of clean soil (RMN-LS). The soil samples Hotspot 1 and 2 (because they had the highest Pb concentrations) were used to assess As and Pb migration to the aquifer (7 m depth) and passing through the Native soil (5.95 m thickness, Fig. 2).

3.2. Soils characterization and ANC

As expected, the soils had different physiochemical characteristics. Table 1 shows soils pH, moisture, surface area, TOC and IC, and Table 2 reports their elemental composition. Particle size distribution (by mass) was relatively similar for all studied samples, with 11–14% in the <0.075 mm range, 0–11% in the 0.075–0.178 mm range, 1–7% in the 0.178–0.251 mm range, 4–14% in the 0.251–0.422 mm range, 30–44% in the 0.422–2 mm range,

and 24–39% in the >2 mm range. The texture of all these soils can be classified as ‘sandy’ based on PSD (USDA, 1987).

3.2.1. Hotspot 1—XRD results indicated the presence of quartz, ferric oxide, calcium carbonate, aluminum sulfide, and lead oxide carbonate (Fig. SI1). Pb was found in concentrations of 4970 mg/kg by U.S. EPA Method 3052 (total Pb) and 3900 mg/kg by U.S. EPA Method 3051 (acid extractable Pb). The difference in the Pb concentrations (~22%) determined using the two methods could be due to the Pb content within the structural silicate matrix of the soil.

3.2.2. Hotspot 2—The XRD diffractogram showed that the mineral structure of Hotspot 2 was similar to Hotspot 1: quartz, ferric oxide, calcium carbonate, lead carbonate, and aluminium sulfide. Hotspot 2 had the highest Pb concentrations of the studied soils (45,300 mg/kg total Pb and 38,400 mg/kg acid extractable Pb). The high content of carbonate (4.07% IC) would provide Hotspot 2 a high acid neutralization capacity, and therefore, leaching of metals due to acidic solutions may be limited. However, the XRD results identified lead carbonate oxides in this sample. We therefore expected significant lead leaching under moderate acidic conditions, and this was confirmed by the ANC test (Fig. SI2). Most of the Pb in this sample was acid extractable (Table 2), therefore, it could be potentially mobilized at low pH. Arsenic (with a large portion of the total mass being acid extractable (734 of the 758 mg/kg total) was also found at high levels in Hotspot 2.

3.2.3. Stockpile—The Stockpile XRD mineral composition included: quartz, sodium aluminum silicate, ferric oxide, and braunite. This sample contained total Pb of 274 mg/kg, acid extractable Pb of 208 mg/kg, and low levels of As. The ANC test showed that Pb leached in the hotspots at acidic pH (pH < 5), but stockpile released Pb only at pH 2 or less. Arsenic was very stable at pH > 2 in all soils (Figure SI2c).

3.2.4. Native subsoil—The native subsoil had Pb at 20.6 mg/kg and As at 1.13 mg/kg. The XRD analysis detected quartz, ferric oxide, sodium aluminum silicate, and braunite.

3.3. TCLP, SPLP, and the CALP comparison

The TCLP and SPLP tests were applied to the soils, and their results compared with the 168-h leachate of the CALP test to obtain useful insight regarding the environmental fate of the studied metals under different experimental conditions.

3.3.1. Hotspot 1—Each of these tests provided different metal leaching concentrations for Hotspot 1 (Table 3). The TCLP leachate had a final pH of 5.84 and a Pb concentration of 8.11 mg/L, which is above the Resource Conservation and Recovery Act (RCRA) regulated level of 5 mg/L; therefore, the soil can be classified as ‘hazardous waste’, which means that is to be disposed of in a hazardous waste landfill, and not in a municipal solid waste landfill. No other regulated metal was found above their respective regulatory levels in this sample. The Pb concentration found in the CALP 168-h leachate (126 mg/L) was one order of magnitude higher than the TCLP leachate, and two orders of magnitude higher than the SPLP leachate. The extraction fluid chemistry, contact time, shaking energy, and pH might

have played substantial roles that can explain the differences in metal release concentrations. The TCLP extraction fluid contains acetic acid, which is able to form acetate chelates, which increases Pb dissolution and complexation and, therefore, increasing Pb release (Wadanambi et al., 2008). Also, the presence of organic matter in the soils would favor higher levels of Pb release with the acetates in the TCLP due to complexation reactions (Dermatas et al., 2006).

In addition, the buffered nature of the TCLP solution tends to maintain acidic pH, in contrast to the non-buffered SPLP extraction fluid (Dungan and Dees, 2009) which lets the natural buffering capacity of the soil have stronger influence over the final pH. Dermatas et al. (2006) reported that the 18-h TCLP of firing range soils did not reach equilibrium, and under an extended equilibration time (68 h) obtained higher Pb concentrations in the leachate. After only 4 h the CALP leachate contained 22 mg/L, which is greater than the TCLP or the SPLP leachates. This could be due to lower pH, and to some extent, the influence of the high stirring intensity applied in the CALP (~300 rpm). The mechanical intensity of the stirring promotes fracturing soil peds, which increases the amount of soil surface area affected by the extraction fluid. The sequential extraction showed that ~72% of the Pb in Hotspot 1 (Fig. 4a) was associated with the carbonate fraction, which is important because PbCO_3 tends to precipitate in aquatic systems since its solubility decreases with increasing pH (Marani et al., 1995). The constant pH conditions of the CALP affected metal leaching; for example, Pb, Mn, or Zn could be in soluble form at pH 4.2, but could precipitate at pH 8.43. As shown with pH, the impact that the sample can exert over the extraction fluid in a batch test can significantly alter metal (or other contaminants) leaching amounts. The CALP, with a constant pH, better resembles an actual disposal scenario, where physicochemical conditions are minimally affected by the disposed waste mostly due to the large volume and extent of many disposal sites. For example, landfill leachate could be minimally affected by a certain amount of waste entering the landfill. The CALP test showed that Pb was released from both hotspot samples at increasing concentrations with time up to 168 h (Fig. 3b), suggesting that extraction time of the SPLP and TCLP may be too short to reach contaminant equilibrium with the extraction solutions. Based on these results, Pb migration may be possible from the hotspots, particularly if pH tends to be acidic.

3.3.2. Hotspot 2—Considering the very high levels of Pb found in Hotspot 2, it was expected that it would leach high amounts of Pb. This expectation was proven true only under acidic conditions, probably because Pb would precipitate at neutral pH. Pb release is also influenced by the soil natural pH, organic matter presence, soil cation exchange capacity, particle size, buffering capacity, and soil mineralogy. The effect of these parameters could be more important than concentration to determine Pb leachability from a soil (Dermatas et al., 2006). The TCLP leachate had a Pb concentration of 335 mg/L at a final pH of 5.11, which classifies it as ‘hazardous waste’ according to RCRA. No other metals were found in the leachate in concentrations above the RCRA regulatory levels. For this sample, the SPLP had the lowest Pb leaching levels, as it was for Hotspot 1. The SPLP leachate had a pH of 8.19 and Pb concentration of 3.61 mg/L. The CALP was the test that produced the highest metal leaching concentrations among the compared tests for this sample with a concentration of 2010 mg/L of Pb in its leachate after 168 h and 129 mg/L after 4 h at pH 4.2. Hotspot 2 had the highest As concentration of all studied samples, but As

leaching occurred at minimum levels, and was substantially below the RCRA regulatory levels. Comparing Pb release from Hotspot 2 with Hotspot 1, a greater Pb leachability ratio (leachate concentration/Pb constituent concentration) was found for Hotspot 2 in all these tests. Based on these results, Pb mobilization could occur from Hotspot 2, but As mobilization was negligible.

3.3.3. Stockpile—The Stockpile contained the lowest trace metal concentrations of the three studied soils (Table 2). The XRD results showed that silicates were the main constituents of this soil and it is considered that Pb and silicates do not have high affinity (Emmanuel and Erel, 2002). In spite of that, low Pb leaching occurred in the TCLP (0.05 mg/L), but not in the SPLP (<0.02 mg/L). The Stockpile showed somewhat higher Pb concentrations in the CALP leachate, but was still very low as compared to the hotspots: 0.03 mg/L after 4 h and 0.06 mg/L after 168 h (Fig. 3b). As levels in the CALP leachate remained at the same level (~0.05 mg/L) from the 2nd hour up to the end of the experiment. The Stockpile soil could be classified as ‘non-hazardous’ in accordance with RCRA regulations, and the low concentrations leaching from this soil suggested that it may be suitable to be used as a fill due to low leaching, in spite of its moderate Pb content.

3.3.4. Native and agvise soils—These two soils provided undetectable concentrations for Pb and As in the SPLP leachate and their SPLP final pH was 5.92 for the Agvise and 6.74 for the Native soils. It seems that these two would partially neutralize the SPLP extraction fluid acidity.

3.4. Controlled Acidity Leaching Protocol

The CALP depicted different profiles for the studied metals (Fig. 3), and the metal concentrations released in this test were used to calculate the Eq. (1) parameters (Table SI4). The average weights of the solid residues from the CALP tests, after being dried at 60 °C, were: 93.0 g for Hotspot 1, 83.6 g for Hotspot 2, and 92.4 g for Stockpile. Considering that all tests started with a similar weight of 100 g, the sample with the higher soluble concentration was Hotspot 2 with 16.4%. The other two soils were in the range of 6–8% (see CALP mass balance results, Fig. SI3). Therefore, the metals that were released with the soluble fraction of the studied solids into the leachate can be considered potentially labile, and could migrate into aquifers at acidic pH.

All tested soils depicted a quick release of As in the CALP test. The highest initial As release was obtained from Hotspot 2. Stockpile soil released smaller concentrations of As compared to Hotspot 2, and remained at ~0.05 mg/L until the end of the test. Hotspot 1 started with the lowest concentrations in the initial hours, but had higher levels for the last two time points than any of the other studied samples. This release had large error bars as only one of the three reactors had high As concentrations (~0.40 mg/L), while the other two were in the lower range (~0.06 mg/L). According to the patterns identified by Cappuyns and Swennen (Table SI4), arsenic follows the Type 4 profile, which depicts re-adsorption or precipitation after the initial release. According to Cappuyns and Swennen (2008), arsenic re-adsorption as anions (arsenate and arsenite) onto the soil surfaces is more likely than precipitation. This behavior also explains the poor fitting of As in Eq. (1). In spite of the

significant differences between the calculated and the observed concentrations in the leachates, Hotspot 2 and Stockpile data were highly correlated ($R^2 > 0.9$, Table SI4). This Type 4 profile was not applicable for Hotspot 1, because of the already explained high As release in one of the reactors increased the average release during the experiments. The mass balance showed that acid digestion was able to extract higher concentrations of As from the CALP solid residues (170% for Hotspot 2 and 130% for Hotspot 1) than from the original soils, while in the Stockpile, the As extracted was lower than the concentration found in the original Stockpile soil (57%). This observed high (170%) As recovery from the CALP solid residues could be due to the intensive mechanical stirring applied in the CALP, which may have decreased soil particle size, and increased the release of other compounds into the aqueous phase (e.g., carbonates), allowing a higher concentration of some insoluble elements in the solid residues. Also, As was associated with the Fe and Mn oxides crystalline fraction according to the sequential extraction, which were probably not released in the CALP, allowing the higher concentrations in the solid residues. Considering the low concentrations found in the leachate and the observed re-adsorption or precipitation behavior, it seemed that As mobilization from Hotspot 1 to local groundwater is unlikely.

Hotspot 2 had the highest Pb release among the studied samples in the CALP, with a level of ~2000 mg/L at the 168th h of testing. Pb was released at increasing concentrations throughout the test in all three reactors. It seemed that a labile fraction kept on releasing Pb and probably was not depleted after 168 h. Hotspot 1 also showed Pb release that kept increasing with time, but at a lower level, reaching a maximum of 126 mg/L by the end of the test. Pb also followed the Type 3 release pattern ($RC_2 > RC_1$) in both Hotspots, suggesting slow Pb dissolution/desorption. These two samples fit well with Eq. (1). In spite of the high concentrations found in the Hotspot 1 leachate, the concentrations extracted from the solid residues of the CALP were higher than those extracted from the original soil (125%). This fact could be related to the high stirring intensity used in the CALP. Meanwhile, the concentration extracted from Hotspot 2 solid residues were lower (83%) than those of the original soil. The Pb concentration in the solid residue of the original soil was 131% of the concentration in the Stockpile. Hotspots 1 and 2 may pose an environmental risk due to Pb mobilization because of their high concentrations released in the CALP at pH 4.2. The Stockpile soil leached Pb at low concentrations, and may not pose an environmental concern.

3.5. Sequential extraction

The elements associated with the operationally defined fractions of the sequential extraction process, expressed as percentages of the total amount extracted, along with the obtained concentrations are shown in Fig. 4.

3.5.1. Hotspot 1—The total Pb concentration in Hotspot 1 was 4970 mg/kg, and was mostly associated to the carbonate-bound fraction (72%), while the As concentration was 58.3 mg/kg, and was mostly associated with the crystalline Fe and Mn oxides (74%) (Fig. 4a). Only Ba (2%) was released in measurable amounts in the first step. Hence, no significant portion of contaminants was considered to be readily soluble when in contact with deionized water. The second fraction (S2) was considered ‘exchangeable’, releasing

metals that are retained by weak electrostatic interactions or those that could be released by ion-exchange processes (Gleyzes et al., 2002). The exchangeable fraction released only Ba (24%) and Zn (5%) in appreciable amounts (Fig. 4a). The third fraction used sodium acetate at pH 5 to aim at the metals which could have co-precipitated with carbonates, or some specifically sorbed metals on clay, organic matter and Fe-Mn oxides. The sodium acetate efficiently dissolves carbonates, but only partially dissolves dolomite (Gleyzes et al., 2002). At the same time, at pH 5, it is considered aggressive enough to release specifically sorbed metals that are not affected by the previous steps (Gleyzes et al., 2002). Pb (72%), Mn (26%), Zn (24%), Ba (22%), and As (4%) leached with the S3 fraction. These three steps (S1-S3) represent the 'labile fraction' of the soil, the fraction that could become an environmental risk for groundwater. The fraction bound to amorphous Fe and Mn oxides released by the hydroxylamine (S4) allowed the release of Mn (46%), Zn (31%), As (30%), Pb (17%), and other metals in minor proportions. The fraction bound to crystalline Fe and Mn oxides (S5) was released using ammonium oxalate, and contained As (44%), Fe, Zn, Ba (all ~10%) and other metals in lower percentages. The S5 fraction released with ammonium oxalate aimed at the Fe(III) oxides, which tend to form a complex with oxalate, but the oxalate can also extract Al oxides (Gleyzes et al., 2002). Both S4 and S5 aimed at Fe and Mn oxides, but only 24% of Fe was removed in spite of the high temperature, long contact time, and low pH (a final pH of ~2 was obtained for S5), which are the factors influencing Fe dissolution (Gleyzes et al., 2002). Higher Mn release was observed (51%). Gleyzes et al. (2002) reported that Mn dissolution is faster than Fe dissolution in these steps of the sequential extraction. Al release in these fractions reached 10% of the total Al content. The S6 fraction used NaOCl at pH 8.5, aiming at the dissolution of the organic fraction. Only Ba (18%) and Pb (4%) were released by this reagent. Finally, the residual fraction (S7), released Al (86%), Fe (75%), Zn (30%), Mn (21%), As (19%), and Ba (13%) by acid digestion with concentrated nitric acid. Aluminum and iron were confirmed to be part of the structural matrix of the soil, while portions of As and Zn were strongly bound to this matrix. Considering the behavior of the analyzed metals during the seven steps of the sequential extraction, there was a strong correlation (correlation coefficient 0.99) between Al and Fe leaching, probably because these are both constituents of the soil mineral structure. Another important correlation was found between Ca and Pb (correlation coefficient 0.98), which could be due to similar adsorption patterns in the studied fractions for both metals. Other researchers have found that Pb cations have the ability to displace Ca cations in minerals and surface adsorption sites (Martínez-Villegas et al., 2004). A third correlation was found between As and P (correlation coefficient 0.89), may be because these elements predominantly occur as anions (AsO_4^{3-} and PO_4^{3-}) in the examined matrices. This similarity in behavior has been used to extract specifically-sorbed As from soils and waste using phosphate (Manning and Goldberg, 1996). The major environmental risk in this sample could be Pb mobilization, since an important portion of it was associated with the carbonate fraction, considered labile under acidic conditions. The second environmental risk could be As mobilization under reducing conditions, which could mobilize the Fe and Mn oxide fractions.

3.5.2. Hotspot 2—The amount of Pb found (45,300 mg/kg) was predominantly associated to the carbonate bound fraction (72%), and As (758 mg/kg) was mostly linked

with the crystalline Fe and Mn oxides (74%). The presence of lead concurred with the XRD results, which indicated the presence of lead oxide carbonate. In general, Hotspot 2 depicted a similar leaching behavior during the sequential extraction as Hotspot 1. The S1 fraction released only a small portion of Ba (2%). The exchangeable fraction also contained Ba (10%), while S3 contained a high proportion of Pb (72%), along with Zn (34%), Mn (32%), Ba (26%), and minor amounts of Al and As. Considering the high concentration of Pb released in S3 (29,900 mg/kg), this sample may pose a significant environmental risk. The S4 fraction released Zn (30%), Mn (26%), Pb and Ba (10%), As (9%) and smaller proportions of Al and Fe (~5%). Interestingly, 62% of As was released by S5, indicating a strong association between As and Fe oxides, as reported by Al-Abed et al. (2007). In addition to As, Fe (28%), Zn and Mn (12%), Ba (10%), and other metals in minor amounts were found to be released with the crystalline Fe-Mn oxides. The organic bound fraction released Ba (20%), Pb (7%), and other elements in lower concentrations. The acid digestion of the residual fraction released high amounts of Al (88%) and Fe (67%) and considerable portions of Mn (29%), As (26%), Ba and Zn (21%), and Pb (10%). The residual fraction is unlikely to be mobilized into the environment. The correlations found in Hotspot 1 between Al and Fe (correlation coefficient 0.93) and between Ca and Pb (correlation coefficient 0.93) were also present in this sample. Nevertheless, in this case there was no strong correlation between As and P. The greatest environmental risks associated with this soil are the high amounts of Pb released with carbonates, and As released under reducing conditions.

3.5.3. Stockpile—Stockpile soil contained lower concentrations of As (24.3 mg/kg) associated with the amorphous (20%) and crystalline (24%) Fe, Mn oxides and the residual fractions (42%), and Pb (274 mg/kg) associated with the carbonate bound (25%) and the amorphous Fe-Mn oxide (41%) fractions (Fig. 4c). The soluble fraction released As and Ba (<2%). The exchangeable fraction released Ba (29%), Zn (14%), and minor amounts of the other analyzed elements. S3 released carbonates along with Zn (27%), Pb (25%), Ba (22%), As (9%), and Mn (8%). Ba and Zn were the most labile metals in Stockpile, but the release of Pb in the carbonate bound fraction was substantial. Manganese and lead dominated the elemental release in S4, while As dominated S5 (Fig. 4c). Finally, the residual fraction confirmed the high amounts of Al and Fe (86%) that make up the matrix of the soil with a portion of As (42%), Zn (28%) and Pb (8%) that is not likely to be mobilized. Pb was mobilized from the carbonate bound fraction (25%) and from the Fe and Mn oxides (48%) in the Stockpile. As was mobilized by the carbonate bound fraction (9%) and mostly under reducing conditions (S4 and S5 with 44%). As for Hotspot 1 and 2, correlations for Al-Fe (correlation coefficient 1.00) and As-P (correlation coefficient 0.73) were also observed in the Stockpile. Considering the low labile fraction of the Stockpile, this soil seems to pose a low risk of metal mobilization into the area groundwater.

3.5.4. Mobile fractions—The ‘mobile fraction’ of each soil can be obtained by adding fractions S1 to S6 (Fig. 4). In Hotspot 1, the mobile concentrations of Pb and As were 3150 mg/kg (63%) and 57.0 mg/kg (98%), respectively. Al and Fe mobilized only small proportions during the sequential extraction (4% and 19%, respectively), confirming that these are associated with the lithogenic matrix of the soil. In the case of Hotspot 2, the mobile concentration of Pb was 37,400 mg/kg (equivalent to 83%) and As was 642 mg/kg

(85%). Other metals like Fe, Ba, Mn, and Zn were only partially released. Al was not mobile. Since the total Pb mobile fraction of this sample is significant, it could pose metal mobilization risk into the groundwater. The Stockpile had 203 mg/kg for the total Pb mobile fraction (74%) and 13.6 mg/kg for As (56%), both being highly mobile. Ba, Mn, and Zn were also highly mobile. Only a small portion of Al and Fe were mobilized. These three soils showed As and Pb mobility, suggesting that the groundwater could be at risk of contamination.

3.6. Lead and arsenic migration to the aquifer

According to the leaching tests, metal mobilization from the hotspots in the projected repository could occur if acidic rain reaches the hotspot soils. Nevertheless, this acidic rain will likely be neutralized while percolating through the clean soil and the Stockpile soil (final pH 7.71 in the SPLP). At this pH, As mobilization from the hotspots is improbable. Just 0.134 mg/L of As was mobilized in the SPLP from Hotspot 2 and an undetectable concentration from Hotspot 1. This small As amount will probably be retained in the Native soil because 97% of it would precipitate as As_2O_5 according to a Visual Minteq simulation. This small As migration is also supported by the As amounts that were mobilized in the first three steps of the sequential extraction, because most of the As is associated with the Fe-Mn oxides. Lead, in the other hand, would somewhat mobilize from the hotspots even at alkaline pH (0.205 mg/L in the Hotspot 1 SPLP at pH 8.43 and 3.61 mg/L at pH 8.19 in the Hotspot 2 SPLP), these small concentrations would be also retained in the Native soil because 99.8% of it would precipitate as $\text{Pb}(\text{OH})_2$ according to the Visual Minteq simulation. The sequential extraction of the hotspots determined that a significant portion of the Pb was carbonate bound and would require acidic environment to migrate, which is unlikely to happen in the projected repository. In spite of the possible As and Pb migration from the hotspots, there are some factors that would reduce the actual amounts reaching the aquifer: adsorption onto the Native soil, organic matter, precipitate retention in the soil matrix. This attenuation will reduce the amounts of contaminants able to percolate the native soil even if some fractures or channels allow small amounts of contaminants to pass through. Finally, the actual amounts of contaminants that reach the aqueous phase would be diluted at the aquifer. Hence, it can be concluded that As and Pb is unlikely to harm the environment if the repository used the Stockpile soil on top of the hotspot soils as projected.

4. Conclusions

The comprehensive leaching tests applied in this study (TCLP, SPLP, CALP, ANC, and sequential extraction) found that contaminated soils Hotspot 1 and 2 released Pb at significant concentrations at acidic pH, and both can be classified as 'hazardous' according to RCRA regulations. Hotspot 2 was the only sample leaching As, but at $\text{pH} < 2$. Among the applied leaching tests, the CALP provided the highest leachable contaminant concentrations, and could be considered a plausible conservative evaluation for metal mobilization under a long term, worst-case scenario than the batch tests because the sample does not change the extraction fluid pH and its high stirring, which are two of the main factors affecting leaching.

The contaminated soil selected as fill material (i.e., Stockpile soil) did not show metal mobility in levels that represent an environmental hazard, and its use could be an environmentally feasible option. In the case of constructing the proposed repository, the As and Pb migration to groundwater would be mostly contained by the Native soil and the underneath aquifer would receive concentrations too small to consider them environmentally harmful. This study applied leaching tests to recommend the use of an industrially Pb-contaminated soil as a fill material; even though the characteristics of the studied soils were specific, the utilized methodology to evaluate the environmental risk of this action can be applied elsewhere.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

This research was funded by the Engineering Technical Support Center and performed at the National Risk Management Research Laboratory of the U.S. EPA, Cincinnati, Ohio. Additional funding was provided by the U.S. EPA Office of Research and Development, Office of Science Policy through its Superfund and Technology Liaison (STL) Program. The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency. Mention of trade names and commercial products does not constitute endorsement or recommendation for use. The authors thank Mr. Christopher Holder, Mr. Anthony Morris for laboratory assistance.

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Fig. 1.

Map of the studied site. The XRF Pb levels shown were used to determine the sampling points for this study (Hotspot 1 and Hotspot 2). The historical locations of industrial structures are shown in the map with basemap lines.

Fig. 2. Multilayered soil profile of the proposed repository. From top to bottom, layers and thicknesses are: A. RMN-LS (0.3 m), B. Stockpile (0.6 m), C. Hotspot 2 (0.15 m), D. Native (5.95 m), and E. Aquifer.

Fig. 3. Constant Acidity Leaching Procedure results comparing studied soil samples (a: Arsenic, b: Lead).

a. Hotspot 1

b. Hotspot 2

c. Stockpile

Fig. 4.

Sequential Extraction and test results comparing studied soil samples, including all target metals (a: Hotspot 1, b: Hotspot 2, c: Stockpile). All units are reported in mg/kg.

Table 1.

The pH, moisture, surface area, total organic carbon, inorganic carbon content, and bulk density. of the studied soils.

Sample	pH	Moisture (%)	Surface area (m ² /g)	TOC (%)	IC (%)	Bulk density (kg/L)
Hotspot 1	7.99	0.15	13.2	2.85	1.66	1.03
Hotspot 2	8.14	0.06	2.23	5.25	4.07	1.58
Stockpile	7.34	0.23	13.3	3.28	0.64	0.78
Agvise	8.72	0.07	–	0.90	0.38	1.20
Native	7.71	0.12	–	0.27	0.03	1.27

Table 2.

Elemental composition of the studied soils (mg/kg).

Sample	Digestion method	Al	As	Ba	Fe	Mn	Pb	Zn
Hotspot 1	3051	9160	46.1	199	19000	450	3890	212
Hotspot 1	3052	53400	58.3	569	35100	490	4960	289
Hotspot 2	3051	4880	734	132	38300	488	38400	411
Hotspot 2	3052	33400	758	470	36800	523	45300	414
Stockpile	3051	15400	28.7	269	24600	676	208	210
Stockpile	3052	56600	24.3	672	29100	725	274	272
Agvise	3051	4280	3.15	83.6	6480	596	4.90	31.4
Native	3051	1430	1.13	8.54	974	15.5	20.6	53.1

Table 3.

Metal release in the performed leaching tests from the studied soils (mg/L).

Sample	Test	Final pH	Al	As	Ba	Fe	Mn	Pb	Zn
Hotspot 1	TCLP	5.84	<0.095	<0.035	2.19	<0.105	2.52	8.11	1.04
	SPLP	8.43	0.404	<0.035	0.869	0.226	0.017	0.205	0.057
	CALP	4.19	3.53	0.170	3.11	<0.105	12.1	126	5.59
Hotspot 2	TCLP	5.11	<0.095	0.078	0.840	0.270	3.53	335	2.14
	SPLP	8.19	0.441	0.134	0.637	0.141	0.016	3.61	0.089
	CALP	4.20	5.02	0.148	1.44	0.136	7.38	2010	6.33
Stockpile	TCLP	5.21	<0.095	0.052	2.23	<0.105	0.935	0.054	1.18
	SPLP	7.71	1.14	<0.035	0.776	0.432	0.023	<0.017	0.117
	CALP	4.09	<0.095	0.048	3.83	<0.105	7.87	0.062	3.09
Agvise	SPLP	5.92	1.15	<0.035	0.284	1.44	0.172	<0.017	0.169
Native	SPLP	6.74	<0.095	<0.035	0.236	0.042	0.014	<0.017	0.043