Alterations of lead speciation by sulfate from addition of flue gas desulfurization gypsum (FGDG) in two contaminated soils

Nadeesha H. Koralegedara^{a, d}, Souhail R. Al-Abed^{, b}, Sanjeewa K. Rodrigo^a, Ranju R. Karna^c, Kirk G. Scheckel^b, Dionysios D. Dionysiou^d.*

^a Pegasus Technical Services, Inc., 46 E. Hollister St, Cincinnati, OH 45219, United States.

^b U.S. Environmental Protection Agency, National Risk Management Research Laboratory, 26 W. Martin Luther King Dr., Cincinnati, OH 45268, United States.

^c Oak Ridge Institute for Science and Education, Oak Ridge, TN 37831-0117, United States.

^d Environmental Engineering and Science Program, Department of Biomedical, Chemical and Environmental Engineering (DBCEE), 705 Engineering Research Center, University of Cincinnati, Cincinnati, OH 45221-0012, United States.

***Corresponding Author**

Email: al-abed.souhail@epa.gov. Phone: (513) 569-7849. Fax: (513) 569-7879.

Abstract

This is the first study to evaluate the potential application of FGDG as an *in situ* Pb stabilizer in contaminated soils with two different compositions and to explain the underlying mechanisms. A smelter Pb contaminated soil (SM-soil), rich in ferrihydrite bound Pb (FH-Pb), cerussite and litharge with a total Pb content of 65123 mg/kg and an organic matter rich orchard soil (BO-soil), rich in FH-Pb and humic acid bound Pb with a total Pb content of 1532 mg/kg were amended with 5% FGDG (w/w). We subjected the two soils to three leaching tests; toxicity characteristic leaching protocol (TCLP), synthetic precipitation leaching protocol (SPLP), kinetic batch leaching test (KBLT) and in-vitro bioaccessibility assay (IVBA) in order to evaluate the FGDG amendment on Pb stabilization. Solid residues of original and FGDG amended soil were analyzed using X-ray absorption spectroscopy (XAS) to identify changes in Pb speciation after each leaching test. The leachate Pb concentrations of FGDG amended soil were lower compared to those of in non-amended soil. The linear combination fitting analysis of XAS confirmed the formation of anglesite and leadhillite in FGDG amended soil. FGDG reduced the Pb desorption from ferrihydrite (FH), by forming FH-Pb-SO₄ ternary complexes. FGDG decreased the Pb adsorption onto humic acid (HA) possibly due to the release of divalent cations such as Ca and Mg, which can compete with Pb to get adsorbed onto HA. The FGDG can successfully be used to remediate Pb contaminated soil. The efficiency of the treatment highly depends on the soil composition.

Keywords

Flue Gas Desulfurization Gypsum, leaching test, ferrihydrite bound Pb, humic acid bound Pb leadhillite, anglesite.

Abbreviations

FGDG – Flue gas desulfurization gypsum

HA-Pb – Humic acid bound lead

FH-Pb – Ferrihydrite bound lead

KBLT – Kinetic batch leaching test

1. Introduction

Lead (Pb), a highly toxic metal, is known to cause irreversible health effects in humans is naturally found in soil. Anthropogenic activities such as smelting, the use of leaded gasoline and various industrial processes have increased the lead accumulation in soil. A number of studies have been conducted on remediation of lead contaminated soil using different soil amendments such as phosphate sources (phosphoric acid, rock phosphate, super phosphate) (Cao *et al.*, 2008, Ma *et al.*, 1995, Barth *et al.*, 2005), apatite (Xu and Schwartz, 1994, Laperche *et al.*, 1996), lime, phosphogypsum, red gypsum, dolomitic residues (Rodriguez-Jorda *et al.*, 2010, Illera *et al.*, 2004, Garrido *et al.*, 2005), red mud (Luo *et al.*, 2012) compost (Hashimoto *et al.*, 2011) and blast furnace slag (Barth and Sass, 2007). Among these treatments, phosphorous (P) sources are the most effective treatment in stabilizing Pb by forming pyromorphite, which is one of the most stable Pb compounds in soil (Scheckel *et al.*, 2013). However, addition of P sources into soil is expensive (Kumpiene *et al.*, 2008) and can lead to eutrophication impacts in freshwater bodies. Therefore, the need for an inexpensive and effective way to stabilize Pb in contaminated soil still exists.

Flue gas desulfurization gypsum (FGDG) is a waste product generated in large quantities every day in many coal power plants around the world. FGDG mainly consists of CaSO_4 . However, some impurities and toxic metals may be available depending on the coal composition, the conditions of the desulfurization process and the chemistry of the additives used. The modern FGDG, produced by wet scrubbing of flue gas after fly ash removal and forced oxidation has very low content of toxic contaminants (Chaney *et al.*, 2014, Al-Abed *et al.*, 2008). Hence, it is being used in many beneficial applications. While a number of studies have used fly ash to

remediate Pb contaminated soil (Stouraiti *et al.*, 2002, Kumpiene *et al.*, 2007, Falciglia and Vagliasindi, 2013), the use of FGDG in the same purpose was limited. Chen *et al.*, 2015 reported the effect of FGDG on toxic element distribution in sodic soils and found that it minimizes the downward migration of Pb, Cd, As, Cr and Hg in the soil profile. The presence of SO_4^{2-} , Fe, Al and CO_3^{2-} in FGDG can be useful to form insoluble metal sulfates or carbonates and to provide oxide sorbents to adsorb contaminants in soil.

Ferrihydrite (FH) and humic acid (HA) are two main soil components that have greater affinity to adsorb metals in soil. The presence of certain anions (SO_4^{2-} , CO_3^{2-} , PO_4^{3-}) and cations (Ca^{2+} , Mg^{2+} , Al^{3+}) can affect the metal sorption by these soil components (Swedlund *et al.*, 2003, Trivedi *et al.*, 2003, Zhu *et al.*, 2014, Liu and Gonzalez, 2000, Zhou *et al.*, 2005, Pehlivan and Arslan, 2006, Orsetti *et al.*, 2013). As FGDG brings significant amounts of Ca^{2+} and SO_4^{2-} to the soil, it could affect the Pb sorption by FH and HA in soil. However, there is no literature precedence on interactions between FGDG and FH or FGDG and HA in regards to metal sorption, up to date.

The present study evaluates the potential use of FGDG as an *in situ* Pb stabilizer in two contaminated soils. The efficiency of FGDG amendment to stabilize Pb in soils with different composition was evaluated using three different leaching tests and one bioaccessibility test. The main objective of this research was to understand the changes in Pb speciation of contaminated soil with two different compositions after FGDG amendment. The Pb speciation in each soil is determined by X-ray absorption spectroscopy (XAS). These findings will indicate the effectiveness of the Pb stabilization by FGDG in soils with different compositions.

2. Materials and Methods

All the solid materials were characterized for total elemental composition by acid digestion (U.S. EPA Method 3051) followed by Inductively Coupled Plasma-Atomic Emission Spectrometric (ICP-AES) analysis (EPA Method 6010B) with an IRIS Intrepid (Thermo Scientific, MA) instrument. ACS reagent grade chemicals and Milli-Q[®] super quality water were used in all the experiments, which were performed at room temperature (21-23 °C).

2.1 Contaminated soil

Pb contaminated sandy-loam soil, obtained from an abandoned Pb smelter (SM-soil) and an organic matter rich silty-loamy Pb contaminated soil collected from an orchard (BO-soil) were used as the contaminated soil sources. Both soils were collected from EPA superfund sites in United States. Detailed description of the sampling sites is given in the supplementary information.

2.2 Gypsum amendment

Commercially available flue gas desulfurization gypsum (FGDG) from a coal power plant in mid-western USA was used to amend the contaminated soils. This FGDG, which was produced post fly ash removal, had been washed with water to remove soluble anions before collecting from the power plants. Three application rates (5%, 10%, 20%) were used in preliminary experiments and 5% was chosen for further studies as the Pb concentrations of the leachates corresponding to all three application rates were below detection limit (0.228 mg/L). The contaminated soils were mixed with FGDG at 5% dry weight ratio by tumbling overnight in a

closed drum followed by homogenizing using the cone and quarter method (Schumacher *et al.*, 1990).

2.3 Leaching and bioaccessibility tests

All the leaching tests and bioaccessibility tests were performed in triplicates and the average is reported. The final pH of the leachates was measured at the end of each test. All the supernatants were separated by filtering through 0.45 μm polypropylene membrane filters and preserved with conc. HNO_3 acid for metal analysis by ICP-AES. The solid residues of each leaching test were freeze-dried, homogenized and subjected to XAS and X-ray diffraction (XRD) analyses.

2.3.1 Kinetic batch leaching test (KBLT)

The KBLT was performed to understand the leaching behavior of Pb in both FGDG-amended and non-amended soil over 60 days (Windt *et al.*, 2011). Five grams of solid material was mixed with 100 mL of deionized water maintaining a liquid: solid (LS) ratio of 20:1 in 125 mL high-density polyethylene (HDPE) bottles. Samples were mixed by end over rotation at 30 rpm and collected at different time intervals (10 minutes, 1 hr, 3 hrs, 7 hrs, 24 hrs, 48 hrs, 72 hrs, 7 days, 14 days, 30 days and 60 days).

2.3.2 Synthetic Precipitation leaching protocol (SPLP)

The SPLP (EPA-Method 1312) (US. EPA, 1994) was used to understand the Pb leaching behavior of both FGDG-amended and non-amended soil under simulated acid rain conditions. Deionized water of which the pH was adjusted to 4.20 using a mixture of conc. H_2SO_4 and conc. HNO_3 (40:60 weight percent ratio-2:3 mL) was used as the extraction fluid. Five grams of solid material was mixed with 100 mL of the extraction fluid (LS ratio of 20:1) in 125 mL HDPE bottles. Samples were mixed by end over rotation at 30 rpm for 18 hours.

2.3.3. Toxicity characteristic leaching protocol (TCLP)

The TCLP (EPA-Method 1311) (US. EPA, 1992) simulates the leaching conditions inside a municipal solid waste landfill. The acetic acid used in the TCLP extraction fluid enables the extraction of constituents associated with organic matter. As BO-soil is rich in organic matter, TCLP was used to study the Pb leaching behavior of such soils. A mixture of glacial acetic acid and deionized water of pH 2.88 was used as the extraction fluid. Five grams of solid material was mixed with 100 mL of extraction fluid to maintain 20:1 LS ratio. HDPE bottles were used to mix the samples. Samples were tumbled at 30 rpm for 18 hours.

2.3.4 In-vitro bioaccessibility assay (IVBA)

The in-vitro bioaccessibility assay (EPA-Method 1340) (US. EPA, 2013) and a modified pH version of EPA-method 1340 (Minka *et al.*, 2013) were used to estimate bioaccessible Pb (the fraction of an ingested dose that crosses the gastrointestinal epithelium and becomes available for distribution to internal target tissues and organs (US. EPA, 2007) at pH 1.5 and 2.5, respectively using an extraction fluid of 0.4 M glycine adjusted to pH 1.5 and pH 2.5 with conc. HCl at 37 °C. Based on poor correlation of in-vitro/ in-vivo studies on bioaccessible Pb subjected to phosphate-amended, Pb-contaminated soils, EPA-Method 1340 at its prescribed pH (1.5) is not recommended for phosphate-amended soils (US. EPA, 2013); however, much better in-vivo/in-vitro correlations on bioaccessible Pb are observed when the Method 1340 extraction pH is 2.5 (Scheckel *et al.*, 2013). This artifact at pH 1.5 for phosphate-amended soils has not been evaluated for other soil amendments in in-vivo studies, such as FGDG, thus the results are observational. The modification for Method 1340 in this study was adjusting the pH of the extracting solution to 2.5. The modified IVBA (at pH 2.5) was used to simulate the gastric digestion of Pb ingested with diet, which reduces the acidity of the gastric fluid (Beyer et al.,

2016). The LS ratio of 100:1 and 200:1 were used for BO-soil (both FGDG amended, non-amended) and SM-soil (both FGDG amended, non-amended), respectively. Higher LS ratio was used with SM-soil to avoid the potential Pb-salt (PbCl_2) saturation due to its high Pb content (US.EPA, 2013).

2.4 Sample analysis

2.4.1 XAS Analysis

The Pb L-edge (13035 eV) XAS spectra were collected at Materials Research Collaborative Access Team's (MRCAT) beamline 10-ID (Segre *et al.*, 2000) at the Advanced Photon Source (APS), Argonne National Laboratory (ANL), Argonne, IL. The electron storage ring operated at 7 GeV in top-up mode. A liquid nitrogen-cooled double-crystal Si(111) monochromator was used to select incident photon energies, and a platinum coated mirror was used for harmonic rejection. Samples were pressed into pellets, and three scans were collected for each sample (-200 to 800 eV) in fluorescence mode using a four-element silicon drift detector and a Pb-metal reference foil (13035 eV) was collected congruently with each sample scan to correct for energy drifts. Each scan was calibrated by assigning the first derivative inflection point of the absorption edge of the Pb-reference foil. The three scans were averaged, aligned and merged to obtain the final scan for each sample. The background correction was performed using a linear fit to the pre-edge region. The spectral step heights were normalized using a post-edge. The XAFS region was chosen for the analysis and the spectra were converted to k -space and weighted k^1 .

Previously collected Pb standards (prepared according to the procedure described in Juhasz *et al.*, 2014) were analyzed to facilitate linear combination fitting (LCF) of the sample spectra to investigate the likely presence of Pb species in the samples. Principal component analysis (PCA) and target transformation (TT) were conducted using ATHENA software (Ravel and Newville,

2005) to determine which standards to include in the LCF procedure and the maximum combination of standards to allow per fit. PCA indicated that up to four components (standards) were sufficient to explain the majority of the variance in the system on the basis of their SPOIL values (Table S3 and S4). The LCF was then performed using the chosen four standard spectra. Fitting was done over 0.5 to 6.75 Å⁻¹ in k-space. The combination with the lowest χ^2 was chosen as the most plausible Pb species in the given sample.

2.4.2 X-ray diffraction analysis

The samples were analyzed for mineralogy using Philips PW3040/00 X'pert-MPD diffractometer system with a Cu anode ceramic diffraction X-ray tube at 50 kV and 40 mA. The diffraction data were collected in the range of 2 θ (5-90°, step = 0.02°). The XRD profiles were analyzed by X'Pert High Score Plus software using PDF-2 database (ICDD, 2005).

3. Results and Discussion

The FGDG used in this study mainly consisted of gypsum (CaSO₄). In addition, dolomite, calcite, brucite, Mg-calcite, siderite, hematite and Fe, Mg, Al silicates are also present (Figure S1). This FGDG contains Ca, Fe, Mg and S in about 27%, 0.1%, 0.1% and 18% weight, respectively (Table S1). The average particle size of the FGDG was 60 µm and the pH was 8.46 (Table S2). Even though this FGDG contains some toxic elements such as As, Cd, Cr, Se, Ni and Hg, the release of these elements under different environmental conditions was negligible (Koralegedara *et al.*, 2015).

The changes in leaching patterns and Pb speciation after FGDG amendment in contaminated soils are discussed separately for the two Pb contaminated soils.

3.1 Smelter lead contaminated soil (SM-soil)

As determined by ICP-AES analysis, SM-soil has a total Pb content of 65123 mg/kg. According to XAS analysis, the most dominant Pb species in SM-soil is ferrihydrite bound Pb (FH-Pb) (66%). Litharge (PbO) (17%) and cerussite (PbCO₃) (17%) are also found as Pb bearing minerals (Table 1).

3.1.1 SM-soil Leaching data

Two phases of Pb leaching were observed with the SM-soil in the kinetic batch leaching test (KBLT); initial elevated Pb leaching observed during the first two days of the experiment and a continuously increased leaching from 14th day till the 60th day (Figure 1a). The Pb leaching observed in KBLT is most likely due to the dissolution of cerussite and litharge. Interestingly, the Pb release from FGDG amended SM-soil was not detectable throughout the KBLT, except on 7th day and 14th day, where the Pb levels reached 0.36 mg/L and 0.46 mg/L, respectively. However, this increased Pb leaching was less as compared to the non-amended soil on the corresponding time intervals (0.49 mg/L on the 7th day and 0.89 mg/L on the 14th day).

Figure 1. (a) Pb leached from smelter Pb contaminated soil (SM-soil) and flue gas desulfurization gypsum (FGDG) amended SM-soil (SM-soil+FGDG) as a percentage of the total Pb in soil (65123 mg/kg) under kinetic batch leaching test (KBLT), (b) pH variation during the KBLT. Error bars represent the standard deviation of three replicate samples.

Similar to KBLT, Pb leaching from FGDG amended SM-soil was negligible (<0.228 mg/L) under SPLP (Figure 2), while non-amended soil leached about $<0.1\%$ of the total Pb content in SM-soil. Even though an extraction fluid of pH 4.2 was used in SPLP, final pH of the system (SM-soil = pH 8.6, SM-soil+FGDG = pH 7.6) was not acidic due to the high buffering capacity of SM-soil. Hence, significant Pb leaching was not observed even in non-amended soil.

TCLP, which uses acetic acid as the extraction fluid showed the highest Pb leaching from both FGDG amended (717 mg/kg) and non-amended SM-soil (2627 mg/kg) compared to other leaching tests (Figure 2). This could be due to the higher acidity of the TCLP leachates (SM-soil = pH 5, SM-soil+FGDG = pH 4.1) compared to the leachates of KBLT and SPLP. The higher

affinity of acetic acid that present in TCLP extraction fluid to extract Pb in soil could also play a role (Yang *et al.* 2006). The great affinity of Pb to organic ligands in the aqueous phase prevents the Pb adsorption onto soil constituents thereby increasing the Pb leaching. In addition, the higher solubility of $\text{Pb}(\text{CH}_3\text{COO})_2$ may have caused to increase the Pb concentrations of TCLP leachates.

Figure 2. Pb leached from soil contaminated with smelter Pb (SM-soil) with and without flue gas desulfurization gypsum (FGDG) amendment as a percentage of the total Pb in soil (65123 mg/kg) under Synthetic precipitation leaching protocol (SPLP) and Toxicity characteristic leaching protocol (TCLP) (Y-axis is in log scale). Error bars represent the standard deviation of three replicate samples. Pb leaching from FGDG amended soil were below method detection limit (0.228 mg/L)

According to IVBA, 80% and 76% of total Pb in SM-soil is bioaccessible at pH 1.5 and pH 2.5, respectively (Figure 3). After FGDG amendment, IVBA results are reduced to 77% and 65% at pH 1.5 and 2.5, respectively indicating the reduction of bioaccessible Pb content of soil by FGDG.

Figure 3. Pb leached from soil contaminated with smelter Pb (SM-soil) with and without flue gas desulfurization gypsum (FGDG) amendment as a percentage of the total Pb in soil (65123 mg/kg) in in-vitro bioaccessibility assay (IVBA) at pH 1.5 and 2.5. Error bars represent the standard deviation of three replicate samples.

3.1.2 Pb speciation in SM-soil

According to LCF analysis of XAFS data, the most important observation to note is the formation of leadhillite ($\text{PbSO}_4(\text{CO}_3)_2(\text{OH})_2$) in the KBLT residue of FGDG amended SM-soil (Table 1). The Pb leached from the dissolution of Pb bearing minerals and FH may have formed leadhillite in the presence of CO_3^{2-} and SO_4^{2-} in FGDG amended soil while reducing the Pb levels in the leachates. As non-amended soil does not contain high SO_4^{2-} as the FGDG-amended soil, the formation of leadhillite was not prominent in the non-amended SM-soil. Lee, 2007 reported the formation of leadhillite in the process of solidifying Pb contaminant using Portland cement. Stability of leadhillite (solubility in water at 293 K = 1.08×10^{-5} mol L⁻¹) greatly depends on the pH, SO_4^{2-} and CO_3^{2-} content of the system (Abdul-Samad *et al.*, 1982). Leadhillite is more stable at neutral pH. Acidic pH and high SO_4^{2-} converts leadhillite into anglesite (PbSO_4) whereas alkaline pH and high CO_3^{2-} alters it to cerussite (PbCO_3)/hydrocerussite

($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$). The slightly elevated Pb concentrations observed in FGDG amended soil leachates between 7th – 14th day could be attributed to the slow dissolution of FGDG and cerussite, which would only provide inadequate amounts of SO_4^{2-} and CO_3^{2-} to react with all the releasing Pb to form leadhillite. However, after the second week, SO_4^{2-} (from FGDG) and CO_3^{2-} (from FGDG and cerussite) content in the aqueous phase might have reached the required level to entrap all the released Pb in leadhillite dropping Pb levels below 0.228 mg/L.

Table 1: Estimation of Pb species in flue gas desulfurization gypsum amended smelter Pb contaminated soil (SM+FGDG) and non-amended (SM) after different leaching tests as obtained by linear combination fitting of XAFS analysis.

	Estimation of Pb species (%)							Chi squared value	R-factor
	Cerussite	Litharge	Pb-FH	Pyromorphite	Leadhillite	Anglesite	Pb-HAP		
Original SM-soil	18 (1)	17 (2)	66 (3)					0.013	0.05
SM-KBLT-R	11 (3)		81 (3)	7 (1)			2 (4)	0.018	0.05
SM+FGDG-KBLT-R			46 (2)	8 (0.6)	46 (2)			0.009	0.03
SM-SPLP-R	18 (2)	22 (3)	56 (3)	4 (0.9)				0.016	0.06
SM+FGDG-SPLP-R		14 (1)	27 (3)	10 (0.9)	48 (3)			0.01	0.04
SM-TCLP-R	37 (1)		58 (1)	5 (0.8)				0.012	0.02
SM+FGDG-TCLP-R	18 (0.9)		62 (1)			20 (1)		0.008	0.03

Values within the parentheses represent the uncertainty of the value

Similar to KBLT, the formation of leadhillite in FGDG amended SM-soil is the main difference between the FGDG amended and non-amended soil residues of SPLP (Table1). Even though all cerussite, litharge and FH-Pb fractions of FGDG amended SM-soil are less compared to non-amended soil after SPLP, the leachate Pb concentration of non-amended SM-soil was higher than that of FGDG amended SM-soil. This indicates the prevention of Pb leaching from SM-soil by forming leadhillite in the presence of FGDG.

Despite the elevated Pb leaching compared to other tests, the interesting observations made under TCLP condition were the increase of cerussite fraction in non-amended SM-soil (from 18% to 37%) and the formation of anglesite in FGDG amended soil (Table 1, Figure S4). The acidic pH of the TCLP extraction fluid (pH= 2.88) may have increased the dissolution of carbonate minerals present in the soil, which consequently increased the CO_3^{2-} content of the system. The Pb released into the system from FH and the dissolution of litharge may have formed cerussite with the aid of this elevated CO_3^{2-} content in non-amended SM-soil under mild acidic conditions (pH=5). The prevailing acidic conditions (pH = 4.1) and high SO_4^{2-} content of the FGDG amended SM-soil may have formed anglesite instead of leadhillite or cerussite (Table 1). Anglesite ($K_{sp} = 2.53 \times 10^{-8}$) has low solubility in water and is more stable under acidic condition. The formation of anglesite in the presence of FGDG in acidic conditions may have reduced the bioaccessibility of Pb in SM-soil. Both FGDG amended and non-amended SM-soil increased the bioaccessible Pb leaching at pH 1.5 relative to pH 2.5 probably due to the increased solubility of cerussite and litharge at low pH.

3.2 Pb contaminated orchard soil (BO-soil)

The total Pb content of BO-soil (1532 mg/kg) is relatively low compared to SM-soil (65123 mg/kg). Similar to SM-soil, the majority of Pb in BO-soil (80%) is ferrihydrite bound (FH-Pb) and the rest (20%) is bound to humic acid (HA-Pb) (Table 2). Tiberg *et al.*, 2013 and Trivedi *et al.*, 2003 reported different FH-Pb sorption complexes of variable stability depending on system pH. According to Trivedi *et al.*, 2003, at pH > 5, only the bidentate edge-sharing mononuclear configuration is observed. When pH < 5, either a combination of bidentate edge-sharing mononuclear and mono-dentate mononuclear configurations or mono-dentate mononuclear and bidentate corner sharing mononuclear configurations are available. Meng *et al.*, 2012, reported that the Pb bound in mono-dentate mononuclear configuration can be easily desorbed than other two. The Pb bound to HA is more stable compared to the Pb sorbed on to FH (Violante *et al.*, 2010). Carboxylic and phenolic groups are the most common cation binding sites in HA (Gondar *et al.*, 2006).

3.2.1 Leaching data

Unlike in SM-soil, a single phase of Pb leaching was observed with non-amended BO-soil in KBLT (Figure 4a). Non-amended BO-soil showed a continuous increase of Pb leaching up to 14th day whereas FGDG amended BO-soil did not leach Pb above the detection limit. At low pH (pH below the point of zero charge (PZC) of humic acid ~ 3.5) the protonation of carboxylic group increases the Pb desorption from HA. Nevertheless, the pH drop (from 7.2 to 6.3) observed during the first two weeks of the experiment was not sufficient to enhance the Pb desorption from HA (Figure 4b). Therefore, the Pb leaching from non-amended BO-soil should be mainly coupled with desorption from FH. This is probably due to the release of weakly sorbed Pb on FH. From the 14th - 60th day, both the Pb concentration and the pH of the non-amended

BO-soil have decreased gradually. Interestingly, the Pb levels of the leachates of FGDG amended BO-soil were below 0.228 mg/L throughout the experiment (60 days), indicating the potential of the FGDG treatment to reduce Pb leaching in soil under neutral pH condition.

Figure 4. (a) Pb leached from Pb contaminated orchard soil (BO-soil) and flue gas desulfurization gypsum (FGDG) amended BO-soil (BO-soil+FGDG) as a percentage of the total Pb in soil (1532 mg/kg) under kinetic batch leaching test (KBLT), (b) pH variation during the KBLT. Error bars represent the standard deviation of three replicate samples. Pb leaching from FGDG amended soil were below method detection limit (0.228 mg/L)

Similar to KBLT, no Pb leaching was detected (<0.228 mg/L) from BO-soil with FGDG amendment under SPLP leaching conditions (Figure 5). However, FGDG amendment increased the Pb leaching in BO-soil under TCLP conditions (Figure 5).

Figure 5. Pb leached from BO-soil with and without flue gas desulfurization gypsum (FGDG) amendment as a percentage of the total Pb in soil (1532 mg/kg) at different leaching conditions; Synthetic precipitation leaching protocol (SPLP) and Toxicity characteristic leaching protocol (TCLP). Pb leaching from FGDG amended soil were below method detection limit (0.228 mg/L) at SPLP test. Error bars represent the standard deviation of three replicate samples.

Unlike in SM-soil, IVBA showed different results with BO-soil tested at two different pH values (Figure 6). After FGDG amendment, IVBA results of BO-soil are reduced at pH 1.5 (non-amended BO-soil = 97% and FGDG amended BO-soil = 89%), while it slightly increased at pH 2.5 (non-amended BO-soil = 56% and FGDG amended BO-soil = 57%), compared to non-amended soil. HA in BO-soil becomes insoluble below pH 2, hence the availability of Pb at pH 1.5 is mainly dependent on Pb adsorption onto FH. As FGDG amendment increased the Pb sorption onto FH, the bioaccessible Pb concentration is lesser in FGDG amended BO-soil compared to non-amended soil at pH 1.5. However, above pH 2, HA in BO-soil becomes soluble and more Pb can sorb onto HA. As the FGDG reduced the Pb sorption onto HA, the bioaccessible Pb concentration of FGDG amended BO-soil is slightly higher compared to that of non-amended BO-soil at pH 2.5.

Figure 6. Pb leached from BO-soil with and without flue gas desulfurization gypsum (FGDG) amendment as a percentage of the total Pb in soil (1532 mg/kg) in in-vitro bioaccessibility assay (IVBA) at pH 1.5 and 2.5. Error bars represent the standard deviation of three replicate samples.

3.2.2 Pb speciation in BO-soil

According to the XAS analysis of the BO-soil residues of all leaching tests, the major change occurred is the alteration of relative abundancy of HA-Pb fraction and FH-Pb fraction. In KBLT, the non-amended BO-soil itself reduced the initially elevated Pb levels from 14th day-60th day. This reduced Pb leaching could be effected by two ways, either by re-adsorption of released Pb on to FH in a more stable configuration given the stability of different Pb configurations and the pH of the system or the released Pb could have adsorbed onto HA in the system. As observed in LCF analysis, the HA-Pb fraction of BO-soil residue has increased compared to that in BO-soil before leaching (Table 2). This verifies that the adsorption of released Pb onto HA is more favorable than to FH. After the 30th day of the experiment, the pH of the system decreased below 5 accumulating a high positive charge on FH surface (PZC of FH ~ 8). Most likely, the electrostatic repulsion between Pb²⁺ and the positive charge of the FH hinders the re-adsorption.

FGDG reduced the Pb leaching in BO-soil under both KBLT and SPLP conditions. At this juncture, XAS data are useful showing that the change of FH-Pb fraction of FGDG amended

BO-soil in both KBLT and SPLP is lower compared to that of non-amended soil (Table 2). This indicates the stabilization of Pb-O-Fe by forming sulfate complexes on FH surface. Swedlund *et al.*, 2003 described the formation of FeOHMeSO_4 ternary complexes (where, Me = metal) on FH surface using modeling parameters. Ostergren *et al.*, 2000 and Elzinga *et al.*, 2001 reported similar ternary complexes on goethite surfaces, which can stabilize the sorbed Pb. Therefore, the SO_4^{2-} released from FGDG should have formed similar complexes (FeOHPbSO_4) on FH surface preventing the Pb desorption. The FT-IR spectra of FH-Pb- SO_4 ternary complexes identified in laboratory synthesized ferrihydrite-FGDG-Pb system are shown in Figure S5.

Table 2: Estimation of Pb species formed in flue gas desulfurization gypsum amended orchard soil (BO+FGDG) and non-amended (BO) soil after different leaching tests as obtained by linear combination fitting analysis of XAFS data.

	Estimation of Pb species (%)			Chi squared value	R-factor
	Pb-FH	Pb-HA	Pyromorphite		
Original BO-soil	80 (4)	20 (4)		0.013	0.05
BO-KBLT-R	59 (3)	30 (3)	10 (0.8)	0.016	0.03
BO+FGDG-KBLT-R	69 (3)	20 (3)	11 (0.8)	0.013	0.02
BO-SPLP-R	81 (4)	12 (4)	7 (1)	0.026	0.05
BO+FGDG-SPLP-R	85 (3)	9 (3)	6 (0.8)	0.018	0.04
BO-TCLP-R	47 (3)	48 (3)	6 (0.7)	0.012	0.02
BO+FGDG-TCLP-R	60 (4)	28 (4)	11 (1)	0.025	0.04

Values within the parentheses represent the uncertainty of the value

Further, as shown in Table 2, an increase in FH-Pb fraction relative to the original BO-soil was observed in SPLP residue of FGDG amended BO-soil, indicating that the FGDG amendment increased the Pb adsorption onto FH. Swedlund *et al.*, 2003 reported Pb adsorption onto FH is enhanced by the presence of SO_4^{2-} . According to Zhu *et al.*, 2014, SO_4^{2-} forms both inner and outer sphere adsorption complexes on FH. These complexes provide additional surfaces to adsorb Pb. Since FGDG is rich in SO_4^{2-} , similar mechanisms may have increased the Pb adsorption onto FH in FGDG amended BO-soil. The acidic pH of SPLP leaching conditions yields a positive charge on FH surface, and this positive charge build-up should promote SO_4^{2-} adsorption onto FH affecting enhanced Pb adsorption.

The opposite trend of Pb leaching in BO-soil observed in TCLP condition is well explained by LCF data of TCLP residues of both FGDG amended and non-amended BO-soil. As shown in Table 3, the biggest reduction of Pb-FH fraction compared to original BO-soil has occurred in TCLP residues of both FGDG amended and non-amended soil. The formation of ternary complexes with SO_4^{2-} in FGDG, may have been hindered under TCLP conditions due to one, or combination of the following reasons: (1). CH_3COO^- may compete with SO_4^{2-} to get sorbed onto positively charged FH under acidic condition, (2). Ca^{2+} might have formed chelating compounds with acetic acid and SO_4^{2-} could be associated with the coordination sphere (Baruah *et al.*, 2000), or (3). At low pH, SO_4^{2-} may become protonated and form H_2SO_4 . As a result, the stabilization of FH-Pb by FGDG observed under other leaching conditions was not prominent under TCLP.

The biggest increase of HA-Pb fraction was also observed under TCLP condition for both FGDG amended and non-amended BO-soil compared to other leaching conditions (Table 2). Conte and Piccolo, 1999 studied the effect of different solvents on the structural changes of humic substances. They found that the methyl group in acetic acid plays an important role in disrupting

the large molecular size arrangement of HA by altering the residual hydrophobic forces. This leads to the generation of several small molecular size fragments of HA, which contain large number of cation binding sites. As a result, HA-Pb fraction is increased in both amended and non-amended soil. However, FGDG releases a number of cations such as Ca^{2+} , Mg^{2+} , Sr^{2+} , K^{+} and Fe^{3+} , which can compete with Pb for adsorption onto HA causing higher Pb concentration in leachates of FGDG amended soil. Therefore, HA-Pb fraction of FGDG amended BO-soil is smaller compared to that of non-amended BO-soil. Zhou *et al.*, 2005 also reported the inhibition of Ni^{2+} complexation with HA in the presence of Ca^{2+} due to the competition between Ca^{2+} and Ni^{2+} to form complexes with HA. Since, there is very low organic matter content in SM-soil, the Pb released from FH-Pb, cerussite and litharge cannot be stabilized by adsorption onto HA as in BO-soil. Instead, anglesite was formed in FGDG amended SM-soil reducing Pb leaching relative to the non-amended SM-soil. Unlike in SM-soil, the formation of anglesite was not prominent in FGDG amended BO-soil. It is postulate that this could be due to the low Pb concentration of BO-soil compared to that of in SM-soil. Thermodynamically the formation of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ($\Delta H_f^\theta = -1848.6 \text{ kJ/mol}$) is more favorable than the formation of PbSO_4 ($\Delta H_f^\theta = -920 \text{ kJ/mol}$). Therefore, under TCLP condition, only $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ may have formed in FGDG amended BO-soil, due to the low Pb content of the system, whereas both $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ and PbSO_4 have formed in SM-soil, which has significantly high amount of Pb.

4. Conclusions

This study evaluates the potential application of FGDG as an *in situ* Pb stabilizer in contaminated soils and the underlying mechanisms. Previous studies have reported the use of coal combustion by-products to stabilize heavy metals in soils. However, this is the first study to

report the use of FGDG alone to stabilize Pb in contaminated soil and to provide insight to the underlying mechanisms. KBLT, SPLP and TCLP were used to evaluate the Pb leaching from FGDG amended contaminated soil. FGDG effectively reduced the Pb leaching in both SM-soil and BO-soil under most of these leaching conditions. The XAS analysis verified the formation of less water soluble leadhillite and anglesite in FGDG amended soil under neutral and acidic conditions, respectively. The SO_4^{2-} released from FGDG has involved in these mineral formation along with the CO_3^{2-} released from the dissolution of carbonate bearing minerals in soil. The Pb adsorption onto HA is reduced in the presence of FGDG. The efficiency of Pb stabilization by FGDG is dependent on the composition of the soil, the amount of Pb and the Pb speciation. A long-term field study is suggested in order to assess the stability of the altered Pb speciation under the influence of changing environmental conditions over time.

5. Acknowledgment

This research was performed and funded by the U.S. EPA National Risk Management Research Laboratory, Cincinnati, Ohio. This paper has been subjected to the Agency's internal review and quality assurance approval. The views and conclusions presented herein do not reflect the views of the Agency or its policy. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. The authors thank Dr. Raghuraman Venkatapathy for the valuable comments on the manuscript.

6. References

- [1]. Abdul-Samad F.; Thomas J.H.; Williams P.A.; Bideaux R.A.; Symes R.F. Mode of formation of some rare copper(ii) and lead(ii) minerals from aqueous solution with particular reference to deposits at tiger, Arizona. *Transition Metal Chemistry*. **1982**, 7 (1), 32-37.
- [2]. Al-Abed S.R.; Jegadeesan G.; Scheckel K.G.; Tolaymat T. Speciation, characterization, and mobility of As, Se, and Hg in flue gas desulphurization residues. *Environmental Science and Technology*. **2008**, 42, 1693-1698.
- [3]. Barth E.F.; Succop P.A.; Evans M.L. Evaluation of lead availability in amended soils monitored over a long term time period. *Environmental Monitoring and Assessment*. **2005**, 110, 257-270.
- [4]. Barth E.D.; Sass B.; Chattopadhyay S. Evaluation of blast furnace slag as a means of reducing metal availability in a contaminated sediment for beneficial use purposes. *Soil & Sediment Contamination*. **2007**, 16, 281-300.
- [5]. Baruah M.K.; Gogoi P.C.; Kotoky P. Sulphate behavior from dissolution of gypsum in organic acids. *Fuel*. **2000**, 79, 211-216.
- [6]. Beyer W.N.; Basta N.T.; Chaney R.L.; Henry P.F.P.; Mosby D.E.; Rattner B.A.; Scheckel K.G.; Sprague D.; Weber J. Bioaccessibility tests accurately estimate bioavailability of lead to quail. *Environmental Toxicology and Chemistry*, **2016**. (doi: 10.1002/etc.3399)
- [7]. Cao X.; Ma L.Q.; Singh S.P.; Zhou Q. Phosphate –induced lead immobilization from different lead minerals in soils under varying pH conditions. *Environmental Pollution*. **2008**, 152, 184-192.
- [8]. Chaney R.L.; Watts D.B.; Schomberg H.H.; Torbert H.A. Soluble Calcium amendment: Minimizing negative environmental impacts (253-9). Proceeding at ASA, CSSA and SSSA international annual meeting, November 2-5, **2014**. Long Beach, CA.
(<https://sciosoc.confex.com/sciosoc/2014am/webprogram/paper88561.html>)
- [9]. Chen Q.; Wang S.; Li Y.; Zhang N.; Zhao B.; Zhuo Y.; Chen C. Influence of flue gas desulfurization gypsum amendments on heavy metal distribution in reclaimed sodic soil. *Environmental Engineering Science*. **2015**, 32 (6), 470-478.
- [10]. Conte P.; Piccolo A. Conformational arrangement if dissolved humic substances. Influence of solution composition on association of humic molecules. *Environmental Science and Technology*. **1999**, 33, 1682-1690.
- [11]. Elzinga E.J.; Peak D.; Sparks D.L. Spectroscopic studies of Pb (II)-sulfate interactions at the goethite –water interface. *Geochemica et Cosmochimica Acta*. **2001**, 65 (14), 2219-2230.
- [12]. Falciglia P.P.; Vagliasindi F.G.A. Stabilisation/solidification of Pb polluted soils: Influence of contamination level and soil: binder ratio on the properties of cement-Fly ash treated soils. *Chemical, Engineering Transactions*. **2013**, 32, 385-390.

- [13]. Garrido F.; Illera V.; Garcia-Gonzalez M.T. Effect of addition of gypsum-and lime rich industrial by-products on Cd, Cu and Pb availability and leachability in metal –spiked soils. *Applied Geochemistry*. **2005**, 20, 397-408.
- [14]. Gondar D.; Lopez R.; Fiol S.; Antelo J.M.; Arce F. Cadmium, lead, and copper binding to humic acid and fulvic acid extracted from an ombrotrophic peat bog. *Geoderma*. **2006**, 135, 196-203.
- [15]. Hashimoto Y.; Yamaguchi N.; Takaoka M.; Shiota K. EXAFS speciation and phytoavailability of Pb in a contaminated soil amended with compost and gypsum. *Science of the Total Environment*. **2011**, 409, 1001-1007.
- [16]. Illera V.; Garrido S.S.; Garcia-Gonzalez M.T. Immobilization of the heavy metals Cd, Cu and Pb in an acid soil amended with gypsum and lime rich industrial by products. *European Journal of Soil Science*. **2004**, 5, 135-145.
- [17]. International center for diffraction data (ICDD), JCPDS PDF-2 database, Newton Square, PA, USA. **2005**.
- [18]. Juhasz A.L.; Gancarz D.; Herde C.; McClure S.; Scheckel K.G. In situ formation of pyromorphite is not required for the reduction of in vivo Pb relative bioavailability in contaminated soils. *Environmental Science and Technology*. **2014**, 48, 7002-7009.
- [19]. Koralegedara N.H.; Al-Abed S.R.; Arambewela M.K.J.; Dionysiou D.D. Impact of leaching conditions on element leaching from flue gas desulfurization gypsum and FGDG-soil mixture. *Journal of Hazardous Materials*. **2015**. (doi:10.1016/j.jhazmat.2016.01.019)
- [20]. Kumpiene J.; Lagerkvist A.; Maurice C. Stabilization of Pb and Cu contaminated soil using coal fly ash and peat. *Environmental Pollution*. **2007**, 145, 365-373.
- [21]. Kumpiene J.; Lagerkvist A.; Maurice C. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments- a review. *Waste Management*. **2008**, 28, 215-225.
- [22]. Laperche V.; Traina S.J.; Gaddam P.; Logan T.J. Chemical and mineralogical characterizations of Pb in a contaminated soil: reactions with synthetic appetite. *Environmental Science and Technology*. **1996**, 30, 3321-3326.
- [23]. Lee D. Formation of leadhillite and calcium lead silicate hydrate (C-Pb-S-H) in the solidification/stabilization of lead contaminants. *Chemosphere*. **2007**, 66, 1727-1733.
- [24]. Liu A.; Gonzalez R.; Modeling adsorption of copper (ii), cadmium (ii) and lead (ii) on purified humic acid. *Langmuir*. **2000**, 16, 3902-3909.
- [25]. Luo H.; Huang S.; Luo L.; Wu G.; Liu Y. Modified granulation of red mud by weak gelling and its application to stabilization of Pb. *Journal of Hazardous Materials*. **2012**, 227-228, 265-273.
- [26]. Ma Q.Y.; Logan T.J.; Traina S.J. Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. *Environmental Science and Technology*. **1995**, 29, 1118-1126.

- [27]. Meng S.; Liu H.; Yang C.; Wei Y.; Hou D. Sorption/desorption differences among three ferrihydrites prepared by different synthesis methods. *Applied Surface Sciences*. **2012**, 258, 4449-4454.
- [28]. Minka K.K.; Basta N.T.; Scheckel K.G. Using the Mehlich-3 soil test as an inexpensive screening tool to estimate total and bioaccessible lead in urban soils. *Journal of Environmental Quality*. **2013**, 42 (5), 1518-1526.
- [29]. Orsetti S.; Marco-Brown J.L.; Andrade E.M.; Molina F.V. Pb (II) binding to humic substances: an equilibrium and spectroscopic study. *Environmental Science & Technology*. **2013**, 47, 8325-8333.
- [30]. Ostergren J.D.; Brown G.E.; Parks G.A.; Persson P. Inorganic ligand effects on Pb (ii) sorption to Goethite (α -FeOOH), ii. Sulfate. *Journal of Colloid and Interface Science*. **2000**, 225, 483-493.
- [31]. Pehlivan E.; Arslan G. Uptake of metal ions on humic acid. *Energy Sources, Part A-Recovery, Utilization and Environmental Effects*. **2006**, 28 (12), 1099-1112.
- [32]. Ravel B.; Newville M. ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiation*. **2005**, 12 (4), 537-541.
- [33]. Rodriguez-Jorda M.P.; Garrido F.; Garcia-Gonzalez M.T. Potential use of gypsum and lime rich by-product for induced reduction of Pb, Zn and Ni leachability in an acid soil. *Journal of Hazardous Materials*. **2010**, 175, 762-769.
- [34]. Scheckel K.G.; Diamond G.L.; Burgess M.F.; Klotzbach J.M.; Maddaloni M.A.; Miller B.W.; Partridge C.R.; Serda S.M. Amending Soils with Phosphate as Means to Mitigate Soil Lead Hazard: A Critical Review of the State of the Science. *Journal of Environmental Toxicology. Health B*. **2013**, 16, 337-380.
- [357]. Schumacher B.A.; Shines K.C.; Burton J.V.; Papp M.L. Comparison of three methods for soil homogenization. *Soil Science Society of America Journal*, **1990**, 54, 1187-1190.
- [36]. Segre C.U.; Leyarovska N.E.; Chapman L.D.; Lavender W.M.; Plag P.W.; King A.S.; Kropf A.J.; Bunker B.A.; Kemner K.M.; Dutta P.; Duran R.S.; Kaduk J. The MRCAT Insertion Device Beamline at the Advanced Photon Source. In *CP521, Synchrotron Radiation Instrumentation: Eleventh U.S. National Conference*; Pianetta P; et al., Eds.; American Institute of Physics; New York **2000**; 419-422.
- [37]. Stouraiti C.; Xenidis A.; Paspaliaris I. Reduction of Pb, Zn and Cd-availability from tailings and contaminated soils by the application of lignite fly ash. *Water, Air and Soil pollution*. **2002**, 137 (1-4), 247-265.
- [38]. Swedlund P.J.; Webster J.G.; Miskelly G.M. The effect of SO_4 on the ferrihydride adsorption of Co, Pb and Cd: ternary complexes and site heterogeneity. *Applied Geochemistry*. **2003**, 18, 1671-1689.
- [39]. Tiberg C.; Sjostedt C.; Persson I.; Gustafsson J.P. Phosphate effects on copper (ii) and lead (ii) sorption to ferrihydrite. *Geochimica et Cosmochimica Acta*. **2013**, 120, 140-157.

- [40]. Trivedi P.; Dyer J.A.; Sparks D.L. Lead adsorption onto ferrihydrite. 1. A macroscopic and spectroscopic assessment. *Environmental Science and Technology*. **2003**, 37, 908-914.
- [41]. Violante A.; Cozzolino V.; Perelomov L.; Caporale A. G.; Pigna M. Mobility and bioavailability of heavy metals and metalloids in soil environments. *Journal of soil science and plant nutrients*. **2010**, 10 (3), 268-292.
- [42]. Windt L.D.; Chaurand P.; Rose J. Kinetic of steel slag leaching: Batch tests and modeling. *Waste Management*, **2011**, 31(2), 225-235.
- [43]. Xu Y.; Schwartz F.W. Lead immobilization by hydroxyapatite in aqueous solutions. *Journal of Contaminant Hydrology*. **1994**, 15, 187-206.
- [44]. Yang J.Y.; Yang X.E.; He Z.L.; Li T.Q.; Shentu J.L.; Stoffella P.J. Effect of pH, organic acids and inorganic ions on lead desorption from soils. *Environmental Pollution*. **2006**, 146, 9-11.
- [45]. Zhou P.; Yan H.; Gu B. Competitive complexation of metal ions with humic substances. *Chemosphere*. **2005**, 58, 1327-1337.
- [46]. Zhu M.; Northrup P.; Shi C.; Billinge S.J.L.; Sparks D.L.; Waychunas G.A. Structure of sulfate adsorption complexes in ferrihydrite. *Environmental Science and Technology Letters*. **2014**, 1, 97-101.
- [47]. US. EPA. Method 1311: Toxicity Characteristic Leaching Procedure, part of test methods for evaluating solid waste, physical/chemical methods. 1992. (<https://www.epa.gov/hw-sw846/sw-846-test-method-1311-toxicity-characteristic-leaching-procedure>) (Accessed - 9/12/15)
- [48]. US. EPA. Method 1312: Synthetic precipitation leaching procedure, part of test methods for evaluating solid waste, physical/chemical methods. 1994. (<https://www.epa.gov/hw-sw846/sw-846-test-method-1312-synthetic-precipitation-leaching-procedure>) (Accessed – 9/12/15)
- [49]. US. EPA. Method 1340: In vitro bioaccessibility assay for lead in soil. 2013. SW-846 update vi. SW-846 on-line (<http://www3.epa.gov/epawaste/hazard/testmethods/sw846/online/>) (Accessed – 12/15/16)
- [50]. US. EPA. Guidance for evaluating the oral bioavailability of metals in soils for use in human health risk assessment. 2007. (<https://www.epa.gov/superfund/soil-bioavailability-superfund-sites-guidance>) (Accessed – 9/8/16)