

## Research Article

# Lead Speciation and Bioavailability in Apatite-Amended Sediments

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The in situ sequestration of lead (Pb) in sediment with a phosphate amendment was investigated by Pb speciation and bioavailability. Sediment Pb in preamendment samples was identified as galena (PbS) with trace amounts of adsorbed Pb. Sediment exposed to atmospheric conditions underwent conversion to hydrocerussite and anglesite. Sediments mixed with apatite exhibited limited conversion to pyromorphite, the hypothesized end product. Conversion of PbS to pyromorphite is inhibited under reducing conditions, and pyromorphite formation appears limited to reaction with pore water Pb and PbS oxidation products. Porewater Pb values were decreased by 94% or more when sediment was amended with apatite. The acute toxicity of the sediment Pb was evaluated with *Hyalella azteca* and bioaccumulation of Pb with *Lumbriculus variegatus*. The growth of *H. azteca* may be mildly inhibited in contaminated sediment, with apatite-amended sediments exhibiting on average a higher growth weight by approximately 20%. The bioaccumulation of Pb in *L. variegatus* tissue decreased with increased phosphate loading in contaminated sediment. The study indicates limited effectiveness of apatite in sequestering Pb if present as PbS under reducing conditions, but sequestration of porewater Pb and stabilization of near-surface sediment may be a feasible and alternative approach to decreasing potential toxicity of Pb.

## 1. Introduction

Sediments pose a risk to human and ecological receptors in many watersheds throughout the United States and globally due to accumulation of chemicals of anthropogenic origin. The accumulation of chemicals is a result of both the deposition environment and the sorption properties exhibited by sediments. Consequently, each year many millions of cubic meters of sediment are dredged in the nation's waters to improve ecological habit and mitigate risk [1]. Traditional remediation strategies for contaminated sediments call for removal of sediments through dredge operations with containment of dredged material in landfills or capping resulting in both high capital cost and risk of unintentional releases. Due to the cost and risk associated with traditional sediment remediation approaches, the U.S.

Environmental Protection Agency (US EPA) identified in its *Contaminated Sediment Management Strategy* the goal of developing scientifically sound sediment management tools for use in sediment source control and remediation [2]. One approach identified is the in situ stabilization of metals that both reduce metal mobility and bioavailability.

Metal mobility and bioavailability can be decreased in situ through the application of amendments that sequester metals through sorption processes or mineralization. One of the most effective metal sequestration agents is phosphorus which acts as a natural scavenger for cationic metals and is readily available from the mineral apatite [3]. Demonstration of in situ stabilization of cationic metals in soils, in particular lead (Pb), zinc (Zn), and cadmium (Cd), has been verified at a number of sites [4–7]. Laperche et al. [8] have shown direct physical evidence of the formation of pyromorphite, an

extremely insoluble lead phosphate mineral, when synthetic apatite was added to Pb contaminated soils. Other heavy metals (Cd, Zn) have also been studied with considerable success in reducing their bioavailability in soil when amended with apatite [9, 10]. The success of these trials in soil is attributed to the very low solubility of metal phosphate minerals [11]. However, in situ stabilization of metals in sediments has not been widely applied and evaluated with apatite.

To support the US EPA goal of developing scientifically sound tools to remediate sediments, the in situ stabilization of sediment Pb was studied on the shore of Chopawamsic Creek, located on the Marine Corps Base Quantico (MCB Quantico) in Quantico, Virginia. Chopawamsic Creek drains a 12,000-acre watershed entirely within the boundaries of MCB Quantico and has been identified as a valuable nursery area for commercial and sport fish by the Virginia Institute of Marine Science. The source of Pb in Chopawamsic Creek is identified as a former firing range that was remediated by removal Pb shot and Pb contaminated soil. The former firing range contains numerous small streams and drainage points which are released to Chopawamsic Creek that reasonably accounts for the overland transport of Pb.

The objective of this pilot demonstration project was to evaluate the efficacy of using apatite to sequester and stabilize Pb in the Chopawamsic Creek sediments. The objective will be assessed by (i) evaluating Pb speciation in sediments prior to and after addition of apatite, (ii) measuring Pb and phosphate concentrations in sediment pore water, and (iii) performing biological assays to determine the toxicity and bioaccumulation of the sediment Pb after addition of amendments.

## 2. Materials and Methods

**2.1. Field Plot Design and Apatite Amendment.** The pilot demonstration plots were located along the northern shore of Chopawamsic Creek approximately 1.6 km from the confluence with the Potomac River. Sample locations were selected based on historical data as well as exploratory sampling performed prior to plot preparation. Exploratory sampling detected sediment Pb ranging from 490–750 milligrams per kilogram ( $\text{mg kg}^{-1}$ ) (wet weight basis). All exploratory and pilot test sampling was completed during low tide, with minimal standing water.

The study design called for five plots that measure approximately  $1.5 \text{ m} \times 1.5 \text{ m}$  ( $2.25 \text{ m}^2$ ) by 20 cm deep ( $0.45 \text{ m}^3$  plot volume). Plots A and B were uncontaminated reference sediments located upstream from the known area of contamination. Plot A received no treatment while Plot B was treated with 3% phosphorus (as apatite) by mass for the plot volume. Plots C, D, and E were located in the contaminated portion of Chopawamsic Creek. Plot D received no treatment while Plots C and E were treated with 1.5% and 3% phosphorus as apatite by mass for the plot volume, respectively. The apatite used in this demonstration has the trade name Phosfil from PCS Phosphate (a division of Potash Corporation, Aurora, NC). The material has a

phosphate level of approximately 20% (as  $\text{P}_2\text{O}_5$ ) equivalent to 8.7% phosphorus. The 3% phosphorus loading required 290 kg of apatite; the 1.5% phosphorus loading required 145 kg of apatite for the plot volume assuming a sediment density of approximately 1.9 grams per centimeter cubed ( $\text{g/cm}^3$ ). Prior to apatite application, the plots were staked out, the vegetation cut down, and the sediment material was mixed and presampled. Following the initial sampling, apatite was distributed evenly across the plot dimension. A rototiller was then operated across the plot to mix the apatite down to a depth of approximately 20 cm, with mixing accomplished by running the machine in three directions across the full width of each plot.

Preamendment samples were analyzed for sediment composition (i.e., total organic carbon, silt, sand and clay content). Total Pb, pore water Pb, and pore water orthophosphate (ortho-P) were determined via inductively coupled plasma mass spectrometry (ICP-MS; Perkin Elmer). Postamendment samples were collected 90 days after amendment application to allow suitable time for reaction to occur, similar to previous soil-Pb phosphate amendment studies [4]. The postamendment samples were evaluated for the same criteria as preamendment samples and also for biotoxicity and bioaccumulation. Composite samples from each test plot were used to measure the hypothesized effects of reduction in bioavailability using the following endpoints: (1) bioaccumulation in tissue of *Lumbriculus variegatus* (28-day test) and (2) growth and survival of *Hyalella azteca* (28 day test). Approximately 26.5 L of sediment (with porewater) were collected at each test plot for the bioassays. A secondary postamendment sampling consisted of collecting the top 0.5 cm layer of sediment (noted as Plots C, D, and E-Top layer) due to the visual observation of a reddish-orange color of this particular layer that was not consistent with the lower portion of the sediment profile. The Top layer samples may represent the primary contact media for a variety of aquatic organisms and migratory water fowl.

In addition, a composite sample was collected from the firing range source soil to determine if the original soil-Pb speciation was retained in the sediment environment. The sample was sieved to  $<2 \text{ mm}$  to remove coarse soil material and bullet fragments and further processed in the laboratory to  $<250 \mu\text{m}$  fraction for analysis.

**2.2. X-Ray Absorption Spectroscopy (XAS).** Pb  $L_{\text{III}}$ -edge ( $13\,035 \text{ eV}$ ) X-ray absorption spectra were collected at beamlines PNC/XSD 20-BM and MRCAT 10-ID at the Advanced Photon Source at Argonne National Laboratory, Argonne, IL. The electron storage ring was operated in top-up mode at 7 GeV. Spectra were collected in both transmission and fluorescence modes with a 13-element solid-state detector at room temperature. For each sample, a total of three to five scans were collected and averaged. Data were analyzed using the Athena software program [12]. The results for the samples were compared with those from synthesized minerals and mineral specimens acquired from the Smithsonian National Museum of Natural History (USA). All minerals were verified with XRD before use as reference materials for assessment of Pb solid-state speciation.

Sediment Pb speciation was determined by comparison of Pb standards to the field samples by Linear Combination Fitting (LCF). LCF refers to the process of selecting a multiple component fitting function with a least-squares algorithm that minimizes the sum of the squares of residuals. A fit range of  $-20$  to  $100$  eV was utilized for the X-ray absorption near-edge structure (XANES) portion of the XAS spectra which encompassed 240 data points and up to five variables. The best fitting scenarios are determined by the smallest residual error ( $\chi^2$ ) and the sum of all component fractions being close to 1. A minimum of 2 components were necessary to fully describe any particular sample within 1% reproducible error indicating that two Pb species were tested statistically stringent. The reference samples included for LCF were galena (PbS), hydrocerussite ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ), adsorbed Pb (as  $\text{PbNO}_3$  sorbed to ferrihydrite at pH 6), chloropyromorphite ( $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ ), and anglesite ( $\text{PbSO}_4$ ). In general, LCF results are accurate to  $\pm 5\%$ , thus results less than 10% weight contribution should be interpreted with caution even though these components improve the overall error within the fitting process.

**2.3. Bioassay Testing.** Composite sediment samples from each of the five plots were collected 90 days after amendment addition and prepared for bioassay tests according to the procedures and methods outlined by US EPA guidance documents [2, 13]. The procedure measures chronic toxicity through direct sediment exposure to the freshwater amphipod, *H. azteca*, over a 28-day period and bioaccumulation of Pb in the tissue of *L. variegatus*, also during a 28-day period. For the acute toxicity test with *H. azteca*, a composite sediment sample from each plot of sufficient volume was collected, mixed, and split between 12 replicate tanks with 10 organisms per tank. Therefore, 12 mean survival responses and 12 mean growth responses were obtained to evaluate each composite sediment sample for each of the five plots. For the bioaccumulation test using *L. variegatus*, a preliminary four-day toxicity screening test was performed to determine if *L. variegatus* would survive and exhibit normal behavior, for example, burrow into the sediment [13]. Based on the survival and normal behavior of the *L. variegatus* worms in the preliminary test, a 28-day bioaccumulation study was performed as detailed in US EPA guidance documents [2, 13]. Briefly, approximately 5 g (wet-weight) of *L. variegatus* was measured and recorded before being placed into replicates glass tanks, twelve replicates for each of the five sediment test plots. At the end of the 28-day period, *L. variegatus* was allowed to depurate for 24 hours in clean water before being analyzed for Pb tissue concentrations [13]. Ammonia, temperature, pH, dissolved oxygen, hardness, alkalinity, conductivity, and oxygen were measured during the test periods for both the survivability and bioaccumulation tests to account for these potential effects on the organisms in addition to the toxicity of Pb. A laboratory control sediment consisting of quartz sand with test required nutrients was used to observe health affects in the absence of Chopawamsic Creek sediment for both the *H. azteca* and *L. variegatus* bioassay tests. The bioassays results were evaluated with a Dunnett's Test which compared all

test plots to control plots followed by multiple comparisons between test plots.

### 3. Results and Discussion

**3.1. Test Plot Characterization.** Sediment properties for the test plots and amendment design are provided in Table 1. Both uncontaminated (Plots A and B) and contaminated (Plots C, D, and E) plots exhibited a similar proportion of sand, silt, clay, and total organic carbon (TOC) with the plots comprising almost entirely of clay and silt. The TOC for all plots ranged from 13.2% to 20.3% (Table 1). Table 2 provides the preamendment sediment Pb concentration and pore water Pb and ortho-P concentration for each test plot. Plots A and B exhibited sediment Pb concentrations of 122 and 132 milligrams per kilogram-dry weight ( $\text{mg kg}^{-1}\text{-dw}$ ), whereas Plots C, D, and E exhibited sediment Pb concentrations of 2,930, 1,763, and 2,993  $\text{mg kg}^{-1}\text{-dw}$ , respectively. The contaminated plots exceed the standard clean-up value applied for human risk based on the Integrated Exposure Uptake and Biokinetic (IEBEK) Model ( $400 \text{ mg kg}^{-1}\text{-dw}$ ) and exceed both the EPA Ecological Screening Value ( $1,700 \text{ mg kg}^{-1}\text{-dw}$ ) and fresh water sediment benchmarks provided by the Nation Oceanic and Atmospheric Administration (NOAA) Screening Quick Reference Tables (SQuiRTs). Consistent with the sediment Pb concentrations, Pb pore water values were marked between contaminated and uncontaminated plots. Plots A and B exhibited sub-microgram per liter ( $\text{ug L}^{-1}$ ) pore water concentrations, whereas the contaminated plots exhibit levels of 11.3 to 20.7  $\text{ug L}^{-1}$  (Table 2). These concentrations are above US EPA Maximum Contaminant Levels (MCLs) for human consumption and exceed NOAA SQuiRT values. Preamendment pore water ortho-P levels were similar for all plots ranging from 7 to 30  $\text{ug L}^{-1}$  (Table 2).

Ninety days after amendment addition sediment Pb values for Plot C, D, and E were within approximately 20% of their preamendment concentration with Plots C and E, which received apatite, at 1.5% and 3% phosphorus loadings, respectively, both exhibiting an increased in sediment Pb (Table 2). The unamended contaminated plot, Plot D, exhibited a minor reduction in sediment Pb (Table 2). The increase in sediment Pb in Plots C and E may be partly influenced by the sequestration of Pb since the objective of in situ stabilization is to immobilize and sequester the contaminant of concern; therefore, the overall concentration of the contaminant does not diminish as a result of treatment. In fact, overall contaminant concentration in the sediment may increase due to the sequestration of metals as additional mass is transported through the amended sediments and the contaminant selectively partitions to a solid phase (i.e., the apatite). It is also plausible that the change is attributed simply to the inherent variability of working with natural systems in field studies. The alteration of the sediment structure due to rototilling the plots and subsample selection for composites between the preamendment and postamendment collection also provide for a degree of variability due to changes in sediment density.

TABLE 1: Chopawamsic Creek sediment experimental plot contamination identification and amendment rate along with texture and organic carbon characteristics.

Sample	Pb contaminated	Amendment	Sand (%)	Silt (%)	Clay (%)	TOC (%)	pH	Redox potential (mV)
Plot A	No	None	1.8	52.1	46.2	18.7	6.27	-277.6
Plot B	No	3% P apatite	0.3	33.7	66.0	20.4	6.16	-276.7
Plot C	Yes	1.5% P apatite	0.1	41.7	58.3	13.2	6.22	-276.2
Plot D	Yes	None	0.3	34.4	65.3	20.3	6.37	-269.4
Plot E	Yes	3% P apatite	0.1	24.6	75.3	17.9	6.28	-261.2

TABLE 2: Chopawamsic Creek sediment Pb, pore water Pb, and ortho-P concentrations for preamendment and postamendment experimental plots.

Sample	Preamendment			Postamendment		
	Sed Pb <sup>(a)</sup> mg kg <sup>-1</sup>	PW Pb <sup>(b)</sup> µg L <sup>-1</sup>	Ortho-P mg L <sup>-1</sup>	Sed Pb mg kg <sup>-1</sup>	PW Pb µg L <sup>-1</sup>	Ortho-P mg L <sup>-1</sup>
Plot A	122	0.042	0.030	114	0.098	0.002
Plot B	132	0.113	0.020	44	0.042	0.002
Plot C	2930	16.100	0.007	3680	0.903	0.002
Plot D	1763	11.300	0.020	1390	0.501	0.005
Plot E	2993	20.700	0.009	3390	0.513	0.002

<sup>(a)</sup> Sediment Pb concentration determined on a dry weight basis by microwave-assisted acid digestion (EPA Method 3051). <sup>(b)</sup> Porewater Pb concentration determined by ICP-MS.

Postamendment Pb pore water concentrations in Plots A and B were consistent with preamendment values. However, pore water Pb in the contaminated plots, Plots C, D, and E, was significantly lower in the postamendment testing, exhibiting a 94–98% decrease compared to the preamendment concentration. It is noted that Plot D, which was not amended with P, also exhibited a decrease in pore water Pb consistent with the amended plots. The cause of the decrease in pore water Pb in Plot D is unknown and may represent an experimental sampling error or unaccounted for natural variable, but Pb speciation data and the bioassay results indicate differences exist between Pb in amended and unamended plots.

Ortho-P concentrations in sediment pore water were measured for in preamendment and postamendment samples for all plots. In each case, ortho-P concentrations were below the regulatory limit and actually decreased slightly in the postamendment plots receiving the phosphate amendment. This is consistent with the phosphate leaching characteristic of Phosfil, which exhibits a low leaching potential above pH 6 [14].

**3.2. Synchrotron Pb Speciation.** XANES analysis of Plots A and B (noncontaminated plots) was attempted but poor data quality (spectra not shown) due to low Pb concentrations resulted in no useful information for both the preamendment and postamendment samples (Note: these control plots are intended to evaluate the effect of the amendment on benthic arthropods in the absence of harmful Pb levels). Spectra for preamendment samples from Plots C, D, and E are provided in Figure 1. Spectra are shown for both samples maintained in an anoxic environment and for samples allowed to oxidize under atmospheric conditions. Oxidized samples were evaluated to identify potential changes in

Pb speciation during low tide or seasonal dry periods. In addition, Figure 1 provides a spectrum obtained for the Hillside Source which represents the Pb speciation from the firing range soil responsible for contamination of the Chopawamsic Creek sediments. LCF evaluation (fit shown as red circles superimposed over the collected spectra) of the XANES spectra is also provided in Figure 1 with a summary of the results provided in Table 3. Pb minerals identified from the LCF process are also shown for reference.

The source material represented by the Hillside Source sample exhibited Pb species of adsorbed Pb (64%) and hydrocerussite (36%) which are common species found in Pb contaminated soils. In contrast, sediment Pb in preamendment samples occurs almost entirely as PbS. PbS accounts for 94% to 100% of the sediment lead in Plots C, D, and E with minor amounts of adsorbed Pb. Given the geochemical conditions of the sediment, specifically the pH and redox values (Table 1), formation of PbS from the Hillside Source material of adsorbed Pb and hydrocerussite is probable in the low redox sediment environment [15, 16]. Upon exposure to atmosphere conditions, Pb speciation is altered for samples collected from Plots C, D, and E (Figure 1). Oxidation resulted in reduction galena content (39–44%) with appearance of hydrocerussite (46–61%), with minor amounts of adsorbed Pb also observed for Plot E (Table 3). The results for the atmospheric exposed sediments demonstrate that sediment Pb may undergo a reversible conversion to hydrocerussite if removed from a stable reducing environment due to events such as dry periods, redeposition to high ground, or disturbance during dredging operations.

Pb speciation results of the postamendment samples are provided in Figure 2 and summarized in Table 3. In contrast to the preamendment samples which exhibited 94–100%

TABLE 3: Chopawamsic Creek sediment Pb speciation by linear combination fitting (LCF) for preamendment and postamendment experimental plot samples.

Sample	LCF-weighted contributions (%)				Error $\chi^2$ <sup>a</sup>	
	Galena	Hydrocerussite	Adsorbed Pb	Pyromorphite		
Preamendment						
Plot C	98		2		0.003	
Plot D	94		6		0.001	
Plot E	100				0.004	
Plot C-Oxidized	44	56			0.003	
Plot D-Oxidized	39	61			0.011	
Plot E-Oxidized	44	46	10		0.002	
Hillside source		36	64		0.005	
Postamendment						
Plot C	59		27	9	5	0.008
Plot D	63		34		3	0.006
Plot E	59		34	6	1	0.006
Plot C-Top layer	37		26	25	12	0.017
Plot D-Top layer	44	20	20		16	0.009
Plot E-Top layer	23		42	33	2	0.006

<sup>(a)</sup>  $\chi^2 = [(data - fit)^2]/[data^2]$ .

PbS, PbS content is markedly reduced in postamendment sediment from Plots C, D, and E (Table 3) ranging from 59%–63%. After PbS, adsorbed Pb is the most common species of Pb accounting for 27% to 34% of total sediment Pb. All plots also exhibited a small percentage (1–5%) of PbSO<sub>4</sub>, an oxidation product of Pb sulfides, and is a known conversion product of PbS. The anticipated conversion product of sediment Pb due to the introduction of phosphate was pyromorphite; however, pyromorphite only accounts for 9% (Plot C) and 6% (Plot E) of the total sediment Pb [15]. No pyromorphite was observed in the unamended plot (Plot D). The low conversion rate of Pb to pyromorphite is likely driven by the stability of PbS in a low redox, high dissolved organic carbon environment [16, 17]. The pyromorphite that formed in the test plots may be limited by more chemically available Pb, either from aqueous Pb species in the sediment pore water or from oxidized Pb minerals [e.g., PbSO<sub>4</sub> or (Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>)] and adsorbed Pb.

The top layer samples were collected to evaluate potential differences between the top 0.5 cm of sediment, or near-surface portion of the sediment, and the bulk sediment. The near surface sediment is anticipated to represent the portion of sediment more likely to be ingested by benthic arthropods or other marsh dwelling organisms. Plots C and E-Top layer, which received the apatite amendment, exhibited PbS and adsorbed Pb, PbSO<sub>4</sub>, and pyromorphite consistent with the bulk samples. However, pyromorphite formation in the near surface sediment was considerably more abundant (25–33%) compared to the bulk sediment (6–9%) as was the PbS oxidation product PbSO<sub>4</sub> (2–16% in top layer compared to 1–5% in bulk sediment). These results suggest that the oxidation of the sediment and therefore the destabilization of PbS may enhance the conversion of sediment Pb species

to pyromorphite in the presence of apatite. In the absence of apatite (Plot D), no pyromorphite was formed, instead conditions favored the formation of hydrocerussite as an alternative or stable end product for PbS oxidation in the near surface sediment. Also noted in the near surface sediment was a reddish-brown precipitate. The precipitate was identified as an amorphous iron oxyhydroxide by Mössbauer spectroscopy (data not shown) along with pyritic (FeS) materials. The destabilization of PbS by oxidation also results in pyrite-like materials breaking down as well. This iron precipitate observation was more pronounced in the test plots and tended to occur only in areas where the sediment surface was above the water level.

**3.3. Bioassay Results.** Bioassay studies were performed with postamendment sediments to investigate Pb bioaccumulation in the tissue of *L. variegatus*, and growth and survival of *H. azteca*. In the noncontaminated Plots A and B, *H. azteca* exhibited a minor mean differences for growth (0.63–0.71 mg) and survival (91.7–95.8%) in which the apatite amended Plot B had the lower end of both measurements (Table 4). The outcome suggests apatite has minimal or no effect on the health of *H. azteca* based on these measured end points. The contaminated Plots C, D, and E also noted high survival rates ranging from 91.7–95%; however, mean growth was lower for the unamended sediment in Plot D (0.53 mg) in comparison to the apatite amendment sediment in Plots C and E (0.63–0.66 mg) (Table 4). The results suggest that the contaminated sediments in Chopawamsic Creek are not overly detrimental to *H. azteca* at the observed Pb concentrations and the experimental timeframe, but may reduce the organisms' overall health based on the observed growth endpoint. It is noted that the laboratory control

TABLE 4: *Hyaella azteca* survival and growth and *Lumbriculus variegatus* bioaccumulation data for Chopawamsic Creek sediment postamendment experimental plots.

Sample	<i>Hyaella azteca</i> survival and growth						<i>Lumbriculus variegatus</i> bioaccumulation		
	Percent survival			Dry weight (mg)			Wet weight ( $\mu\text{g g}^{-1}$ )		
	Median	Mean	Std Dev	Median	Mean	Std Dev	Median	Mean	Std Dev
Lab Control	90	83.3	18.3	0.34	0.33	0.07	0.071	0.071	0.01
Plot A	100	95.8	9.0	0.71	0.71	0.10	0.226	0.230	0.04
Plot B	100	91.7	11.9	0.66	0.63	0.12	0.266	0.260	0.04
Plot C	100	95.0	6.7	0.61	0.63	0.11	3.00	3.40	0.82
Plot D	100	94.2	7.9	0.50	0.53	0.13	5.16	5.46	1.23
Plot E	95	91.7	10.3	0.69	0.66	0.17	1.69	1.84	0.67

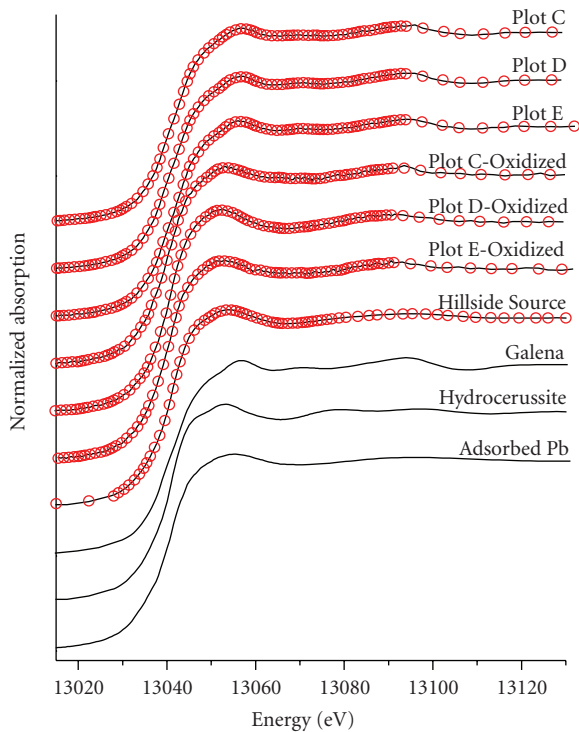


FIGURE 1: XANES spectra and LCF of preamendment Chopawamsic Creek sediment and the firing range source soil (Hillside Source). Plots C–E samples were collected and stored under anaerobic conditions. Plots C–E-Oxidized samples were collected under anaerobic conditions and exposed to atmospheric air for one week prior to analysis. Plot C was amended with 1.5% phosphorus, Plot D was unamended, and Plot E was amended with 3% phosphorus after the collection of these samples. LCF of the spectra are shown as red circles and Pb standards used in the fits are shown for comparison.

exhibited the poorest growth and survival for *H. azteca* (0.33 mg for growth and 83% survival).

The effect of the apatite amendment was more discernable with regard to the bioaccumulation of Pb in *L. variegatus* tissue, specifically in the contaminated test plots. In the contaminated test plots, the mean tissue concentrations were  $3.40 \mu\text{g g}^{-1}$  in Plot C (1.5% phosphorus),  $1.84 \mu\text{g g}^{-1}$

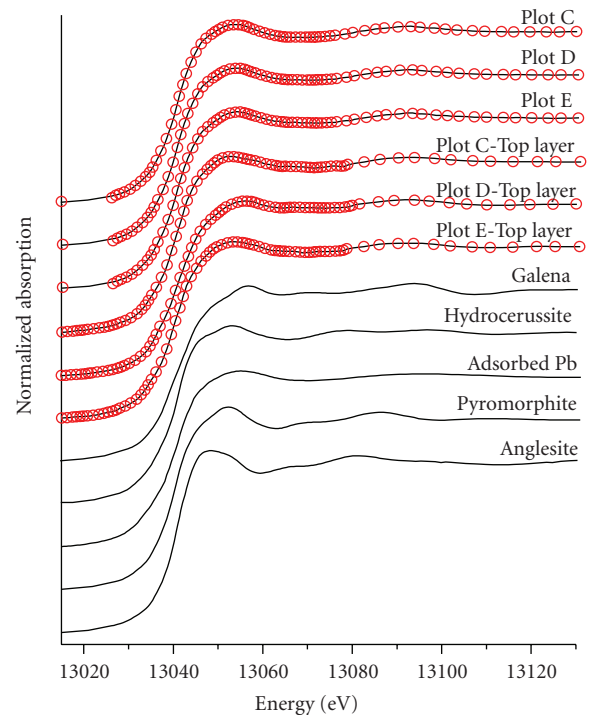


FIGURE 2: XANES spectra and LCF of postamendment Chopawamsic Creek sediment. Plots C–E samples were collected from the top 5–8 cm profile and stored under anaerobic conditions. Plots C–E-Top layer samples were collected from the top 0.5 cm profile and stored under anaerobic conditions. Plot C was amended with 1.5% phosphorus, Plot D was unamended, and Plot E was amended with 3% phosphorus. LCF of the spectra are shown as red circles and Pb standards used in the fits are shown for comparison.

in Plot E (3% phosphorus), and  $5.46 \mu\text{g g}^{-1}$  in Plot D (no phosphorus). The Pb tissue concentrations appear to be influenced by the presence or absence of apatite and possibly the phosphate loading rate. A possible cause of the higher tissue Pb concentration in the unamended sediments may be related to the occurrence of hydrocerussite, which was not observed in either Plot C or Plot E. Hydrocerussite is more soluble (therefore more bioavailable) than PbS based on solubility products [17]. The tissue concentrations do not correlate with the measured postamendment Pb pore water

concentrations indicating that the solid-phase sediment Pb component in this study exhibits a more influential role on the health of the arthropods. In the noncontaminated Plots A and B, mean Pb tissue concentrations of 0.230 and 0.260  $\mu\text{g g}^{-1}$  were observed, respectively, with no apparent influence of the apatite in Plot B at low sediment Pb concentrations.

#### 4. Conclusions

In this study, we examined the impact of apatite amendments on Pb biotoxicity and water quality in Chopawamsic Creek sediments impacted by Pb migration from a nearby shooting range site as well as noncontaminated control sediments. Postamendment samples saw a significant drop in pore water Pb concentrations, a 17- to 40-fold decrease. Synchrotron XAS results identified discernible changes in Pb speciation from galena in the preamendment samples to galena, adsorbed Pb, anglesite, and pyromorphite (only for the apatite amended plots). The sediment Pb species appears to be dependent on the sediment redox condition, with Pb existing as galena under reducing conditions in the bulk sediment and converting to oxidative species when exposed to atmospheric conditions, as observed for near surface sediment or sediment removed from the reducing marsh environment. The formation of pyromorphite is likely limited by the availability of pore water Pb or from more chemically available oxidized Pb species. Conversion of sediment PbS, the most abundant form of Pb in the sediment, to pyromorphite is unlikely due to the stability of PbS under reducing conditions. Biotoxicity testing demonstrated no adverse effects of Chopawamsic Creek sediments to *H. azteca*, but Pb bioaccumulation increased from the noncontaminated plots to the apatite amended plots to finally the highest accumulation in the contaminated, unamended plot indicating a dose response in *L. variegatus*.

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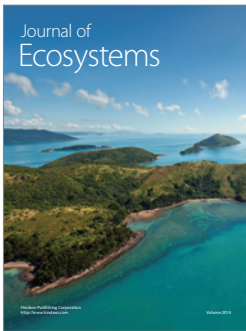
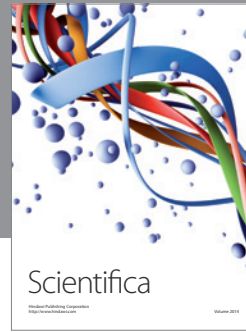
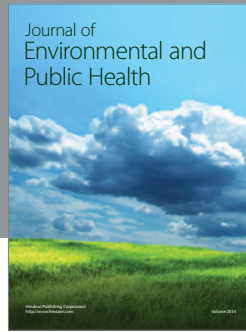
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