

Environmental Implications of Phosphate-Based Amendments in Heavy Metal Contaminated Alluvial Soils of the Big River, southeast Missouri, USA.

Prepared by:

John Weber, U.S. Department of the Interior, Fish & Wildlife Service

Dr. Keith W. Goyne, University of Missouri

Dr. Todd Luxton, U.S. Environmental Protection Agency

Dr. Allen Thompson, Biological Engineering

Dr. John Yang, Lincoln University

Southeast Missouri Lead Mining District

Natural Resource Damage Assessment and Restoration

TABLE OF CONTENTS

1.0 Summary	2
2.0 Introduction	3
<i>2.1 Lead and the Environment</i>	3
<i>2.2 The Big River Drainage of Missouri</i>	3
<i>2.3 Mining and the Big River</i>	5
<i>2.4. Floodplain Soil Contamination</i>	8
<i>2.5 In Situ Phosphate Treatment</i>	8
<i>2.6 Demonstration of Pyromorphite Formation</i>	9
<i>2.7 Environmental Concerns</i>	9
3.0 Objectives and Hypotheses	11
4.0 Materials and Methods	12
<i>4.1 Site Description and Soil Sampling</i>	12
<i>4.2 Sample Characterization and Experimental Protocols</i>	12
<i>4.3 Statistical Analysis</i>	13
<i>4.4 Expected Benefits</i>	14
Timeline	14
References	15

1.0 Research Proposal Summary

Release of heavy metals, primarily lead (Pb), from mining, milling, and smelting have contaminated river sediments and floodplain soils in the Big River watershed of southeast Missouri. Recent environmental research has focused on the immobilization of soluble Pb compounds through the *in situ* application of phosphate-based amendments that induce formation of highly stable, insoluble pyromorphite [$\text{Pb}_5(\text{PO}_4)_3\text{OH,Cl,F}$] compounds. Past studies have focused on pyromorphite formation, the demonstration of long-term reductions in bioavailability, and comparisons of P treatment of Pb contaminated soils with other remedial technologies. However, water quality threats associated P remediation technology continues to be a concern, particularly in riparian areas. To address this issue, the proposed research will investigate the effects of P fertilizer application rates on Pb and P loss via surface water runoff at different time intervals following P application to soil. The research will also include an inquiry into the formation of pyromorphites through the use of X-ray absorption fine structure spectroscopy (XAFS). Big River floodplain soils will be collected and treated with commercially available phosphate fertilizer at four application rates. Control and treated soils will be analyzed for heavy metals, phosphate, other nutrients, and a suite of standard environmental soil assays. Soils will be allowed to react for variable lengths of time after P application and prior to simulated rainfall events in the laboratory. Effluents from treated soils will be collected during simulated rainfall events and analyzed to quantify total and dissolved P and Pb loss. Treated and control soils will also be analyzed using XAFS to determine which treatment level induced pyromorphite formation to the greatest extent. Results from the experiment will be compared to determine the most environmentally beneficial and least harmful treatment levels for application in alluvial settings. Study findings will assist in the decision making process of the Missouri Natural Resource Damage Assessment and Restoration (NRDAR) trustees and other environmental restoration managers throughout the nation regarding environmentally sound stabilization of metals in contaminated soils.

2.0 Introduction

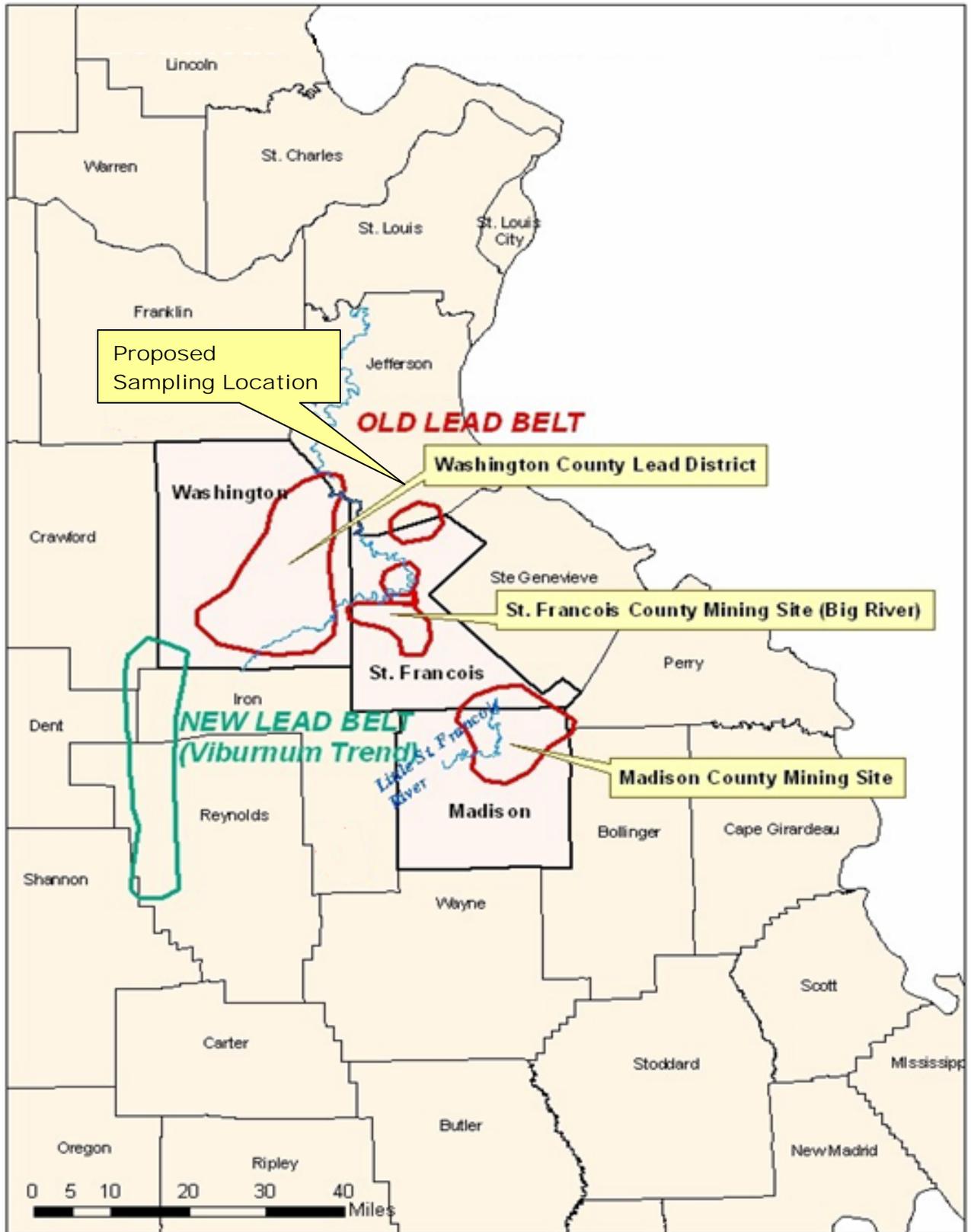
2.1 Lead and the Environment Health. Lead is a bluish-gray element that has been widely mined and used by humans across the world for approximately 7,000 years (Eisler, 1988). Subsequently, anthropogenic contributions of heavy metals into the environment have been occurring around the globe for thousands of years, and Pb poisoning has been recognized for more than 2,500 years (Eisler, 1988). Since the advent of industrial technology in the late 19th century, the scale and scope of releases of heavy metals to the environment has increased drastically (Cotter-Howells and Thornton, 1991).

Soils contaminated with heavy metals are a threat to human and ecosystem health (Cotter-Howells and Thornton, 1991; U.S. EPA, 1998). Lead is neither essential nor beneficial to living organisms and all measured effects are adverse, “including those on survival, growth, reproduction, development, behavior, learning, and metabolism” (Eisler, 1988). The primary exposure pathway contributing to elevated blood Pb levels in humans and wildlife is the incidental ingesting of soil particles containing Pb (Davis *et al.*, 1993). Accordingly, concentrations of Pb in soils can be directly linked to elevated blood Pb levels in humans (Lewin *et al.*, 1999). The element presents pronounced risks to wildlife when present in bioavailable forms in the environment, especially migratory waterfowl that ingest shot; birds of prey that consume other animals containing Pb shot; wildlife near smelters, mining facilities, refineries, and Pb battery recycling plants, and wildlife that forage near heavily traveled roads (Beyer *et al.*, 2005; Casteel *et al.*, 1997). Aquatic organisms downstream or adjacent to mining areas are also threatened by environmental sources of Pb as are organisms in areas where Pb arsenate pesticides are applied (Eisler, 1988). Thus, there is great need to develop and test Pb cost-effective, remediation strategies that reduce Pb bioavailability in the environment.

2.2 Mining in the Old Lead Belt of Missouri . One of the world’s foremost Pb producing regions is the Old Lead Belt Mining District of Southeast Missouri. The Old Lead Belt occurs on the eastern edge of the Ozark Uplift in Missouri and includes portions of St. Francois, Ste. Genevieve, Madison, Washington, and Jefferson Counties (Fig. 1). Lead was first discovered in the area in the early 1700’s. Until the 1860’s, mining in the Old Pb Belt was restricted to shallow workings and pits. The early, primitive mining resulted in small quantities of comparatively highly contaminated mine wastes. The introduction of the diamond-bit core drill in 1869 led to the discovery of numerous Pb-rich ore deposits under what became the towns of Bonne Terre, Desloge, Flat River, Leadwood, and Elvins. As many as fifteen companies were engaged in mining these deposits in the late 1800’s and early 1900’s (McHenry, 2006).

Mining activities in the Old Lead Belt of St. Francois County decreased through the 1950’s and 1960’s as ore bodies were depleted and higher grade ores were discovered in the Viburnum Trend of Crawford, Iron, and Reynolds Counties. The Federal Mine and Mill were the last mining facilities to close in St. Francois County in 1972 (USEPA, 1993). State and federal agencies tasked with protection and regulation of the environment began to investigate and remediate historic mining impacts in southeast Missouri beginning in the late 1970’s. The Environmental Protection Agency (USEPA) listed the Big River Mine Tailings (BRMT) Superfund Site on the National Priorities List in 1992.

Figure 1. The Southeast Missouri Lead Mining District



2.3 The Big River Drainage of Missouri and Big River Mine Tailings Superfund Site.

The principal drainage system for St. Francois County is the north flowing Big River and its tributaries (Fig. 2). Due to local geology, tributaries to the abovementioned drainage frequently gain or lose flow through bedrock and streams can be intermittent or perennial (Fluor Daniel, 1995). Topography of the area is characterized by rolling hills dissected by narrow floodplains, creeks, and river valleys. Hills and ridges are generally steep sided with flat tops consisting of thin mantles of clayey soils. The major physical features of the area are the St. Francois Mountains in the south, the dissected topography of the Salem Plateau in the northern portion, and the Farmington Plain in the eastern section (USEPA, 1993). According to USDA's Washington County soil survey (Skaer and Cook, 2003), the most fertile soils in the Old Lead Belt are the sand and silty alluvial soils of the Big River floodplain. The major soil series mapped in the Big River Floodplain and associated properties are shown in Table 1.

Currently, there exist over 2,800 acres of chat¹, tailings², vegetated chat and transition zone soils contaminated primarily with Pb in and around the six major waste impoundments of the BRMT site. The number of impacted acres is based on a review of topographical maps and aerial photography. Soils contaminated by runoff from tailings, chat, and vegetated chat represent a transition area around the piles of contaminated mine and mill wastes. The transition zone soils vary in width from 50 to 2,800 feet from the piles (USEPA, 2006).

¹ Chat is the waste product of early gravity based milling processes and consists of grain sized particles typically 0.06 to 2.4 mm in diameter (EPA, 2006).

² Tailings are the waste product of a chemical floatation process that produces particles 0.004 to 0.06 mm in diameter (USEPA, 2006).

Figure 2. The Big River Watershed of Missouri

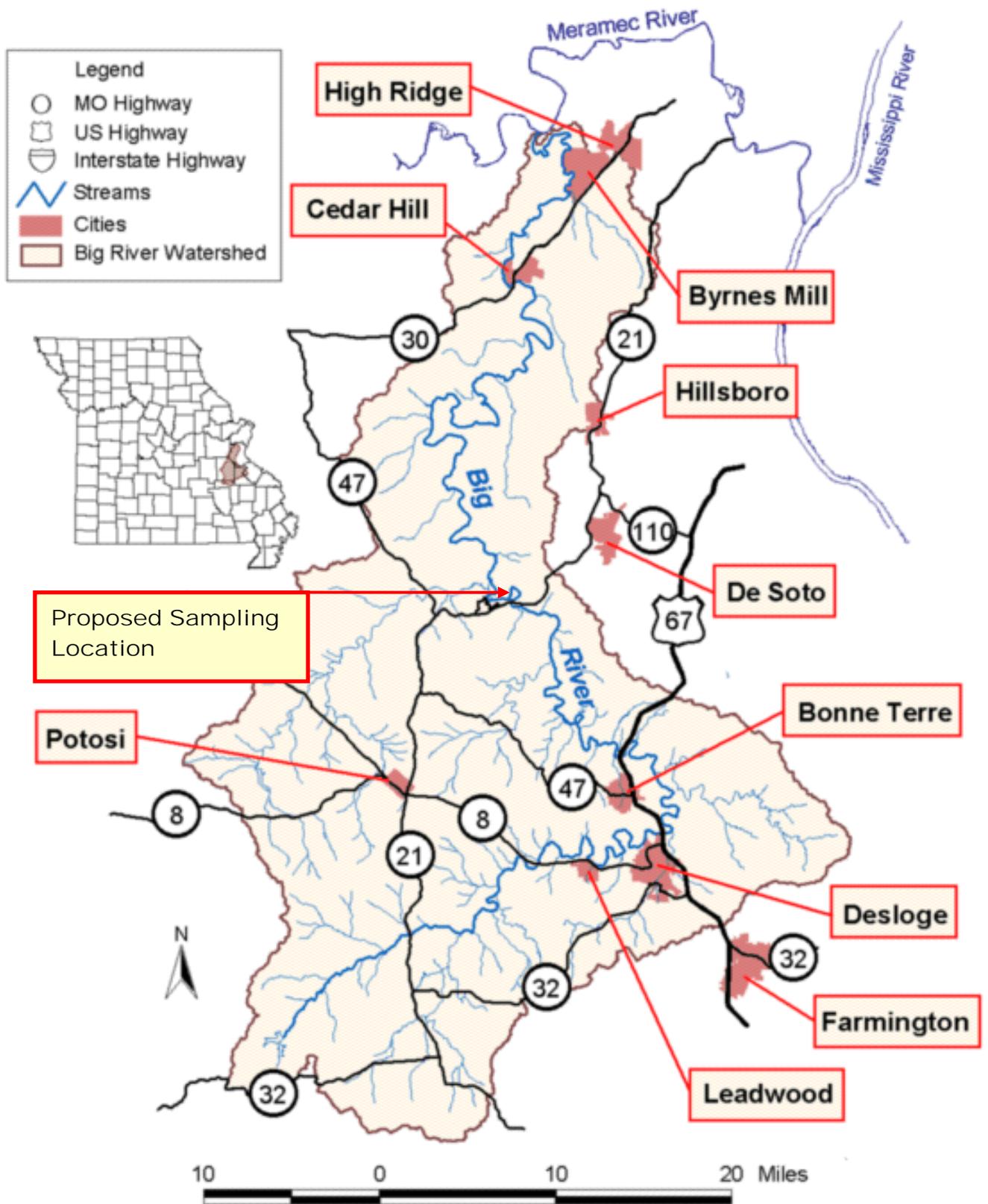


Table 1. Prominent soil series found along the Big River of Missouri (USDA-NRCS, 2010)[†].

Soil Series	Depth Class	Drainage Class	Permeability	Landform	Parent Material	Slope Range	USDA Taxonomic Classification
Freeburg	very deep	somewhat poorly drained	moderately slow	floodplain/ terraces	silty alluvium	0 - 9%	Fine-silty, mixed, superactive, mesic Aquic Hapludalfs
Gabriel	very deep	poorly drained	moderately slow	floodplain	silty alluvium	0 - 3%	Fine-silty, mixed, superactive, mesic Typic Agriaquolls
Haymond	very deep	well drained	moderate	floodplain	silty alluvium	0 - 3%	Coarse-silty, mixed, superactive, mesic Dystric Fluventic Eutrdepts
Horsecreek	very deep	well drained	moderate	stream terrace	silty alluvium	0 - 3%	Fine-silty, mixed, active, mesic Mollic Hapludalfs
Kaintuck	very deep	well drained	moderately rapid	floodplain	loamy alluvium	0 - 3%	Coarse-loamy, siliceous, superactive, nonacid, mesic Typic Udifluvents
Sturkie	very deep	well drained	moderate	floodplain/ natural levee	silty alluvium	0 - 3%	Fine-silty, mixed, superactive, mesic Cumulic Hapludolls

[†] Data obtained from USDA-NRCS, Official Series Descriptions (available at <http://www2.ftw.nrcs.usda.gov/osd>)

2.4 Floodplain Soil Contamination. Due to the construction of the mines and mills in riparian or near riparian areas and the constant discharge of waste products from uncontrolled mine and mill waste piles, releases from mine waste areas have been ongoing since mining activities began in the 18th century. The largest releases were initiated with the advent of industrial scale milling in the late 19th century. As described earlier, the first mills relied upon crushing and gravity to separate Pb from its host rock, whereas the milling process after 1930 employed crushing and various chemical floatation techniques, resulting in massive quantities of tailings or “slime” (McHenry, 2006). The single largest documented release of mining waste occurred in 1977 at the Desloge tailings pile. During a severe storm, an estimated 50,000 to 75,000 cubic yards of tailings were released directly into the Big River (USEPA, 2006). Tailings and chat from this release and others can be observed in the Big River for most of its 93 mile course below the Leadwood Site to the confluence with the Meramec River in Jefferson County. Elevated levels of metals have been found in aquatic and riparian plants and animals in the contaminated portion of the Big River (Buchanon *et al.*, 1979; Schmitt and Finger, 1982; Niethammer *et al.*, 1985; Schmitt *et al.*, 1987; Roberts and Bruenderman, 2000, Roberts *et al.*, 2010).

Presently, almost all chat piles and tailings impoundments created during the mining period have been removed or stabilized. However, it is known that chat and tailings materials released to the river in the past are now presently in transit within the channel system or stored in alluvial deposits (Pavlowsky, 2010). As a result of the transport of heavy metals during flood events over the last century, floodplain sediment deposits are contaminated ($>400 \text{ mg kg}^{-1} \text{ Pb}$) from Leadwood downstream 171 km to the mouth of the Big River. Floodplain sediment Pb concentrations are $>12,000 \text{ mg kg}^{-1}$ near the mining area and decrease in a downstream direction to *ca.* $500 \text{ mg kg}^{-1} \text{ Pb}$ near confluence with the Meramec River. Estimated volume of soil in contaminated floodplain deposits is $86,792,829 \text{ m}^3$ representing 95.9% of the total volume of stored sediment (Pavlowsky, 2010). Contaminated floodplain soils pose a significant threat of recontamination to the in-channel sediments of the Big River and subsequently to the aquatic and aquatic-dependent inhabitants of the river. Contaminated floodplain soils also pose a direct threat to ground feeding and nesting migratory birds.

2.5 In Situ Phosphate Treatment. The toxicity of Pb to organisms is a function of its bioavailability, or the degree to which Pb can be absorbed into the tissues of an organism following ingestion (Casteel *et al.*, 1997). Furthermore, the bioavailability of Pb is determined by chemical speciation and mineralogical associations (Ruby *et al.*, 1992; Davis *et al.*, 1993). Soil Pb poses an ecological threat when it is highly soluble or leachable, factors linked to its chemical form and mineralogical association. Consequently, numerous researchers have succeeded in the alteration of soil Pb chemistry through the addition of phosphate compounds to convert soil Pb species to less soluble minerals called pyromorphites [$\text{Pb}_5(\text{PO}_4)_3(\text{OH}, \text{Cl}, \text{F})$] (Ma *et al.*, 1993, 1995; Xu and Schwartz, 1994; Ruby *et al.*, 1994; Laperche *et al.*, 1996; Zhang *et al.*, 1998). Pyromorphites are the most thermodynamically stable and insoluble Pb minerals over a large pH range (Nriagu, 1974). The above mentioned studies employed a variety of phosphate sources including phosphate fertilizers, phosphoric acid, phosphate rock, and synthetic hydroxyapatite. Recently, Tang *et al.* (2009) demonstrated that P-based treatment of Pb contaminated soil maintains effectiveness at reducing Pb bioaccessibility and leachability up to 10 years after P application.

In order to induce pyromorphite formation, large concentrations of soluble P must be introduced to interact with soluble Pb. Soluble P in soil is easily fixed by a wide variety of soil components, especially aluminum and iron oxides, humic substances, and a variety of clays (Guppy *et al.* 2005; He *et al.*, 2006). Consequently, a large stoichiometric ratio of P:Pb must be applied to contaminated soils to achieve pyromorphite formation (Yang *et al.*, 2002). Yang *et al.* (2001) determined that the bioavailability of Pb decreases as a linear function of increasing soluble P concentrations up to 10,000 mg kg⁻¹ P.

2.6 Demonstration of Pyromorphite Formation. An important goal of remedial research involving *in situ* Pb immobilization is to demonstrate the formation of pyromorphite. Numerous studies have employed selective sequential extraction procedures and demonstrated substantial transformation of soil Pb to pyromorphite (Ryan *et al.*, 2001; Cao *et al.*, 2003). Unfortunately, subsequent research indicates that the abovementioned studies cannot rule out the formation of pyromorphites during extraction of Pb contaminated soils treated with P (Scheckel *et al.*, 2003). Other technologies that have been attempted in the quest to speciate phosphate amended soils include energy dispersive X-ray (EDX) spectroscopy and scanning electron microscopy (SEM) (Davis *et al.*, 1993; Yang *et al.*, 2001; Cao *et al.*, 2003). However, there are visual limitations to the use of both EDX and SEM that make them less practical, especially the similarity of hexagonal pyromorphite crystals to a number of other crystalline soil constituents. Scheckel *et al.* (2004) also demonstrated that X-ray diffraction, selective sequential extraction, and the physiologically-based extraction test were incapable of accurately quantifying the formation of pyromorphites in phosphate amended soils due to the formation of the compounds during the extraction or the immobilization phases of the aforementioned extraction tests. Accordingly, the researchers employed X-ray absorption fine structure (XAFS) spectroscopy to accurately quantify Pb₅(PO₄)₃(OH, Cl, F) formation.

The most significant recent developments in the speciation of metals in heterogeneous soil environments have been achieved using XAFS. XAFS refers to the manner in which x-rays are absorbed near and at the core level binding energies of that atom (Newville, 2004). According to Newville (2004), XAFS is, “the modulation of an atom’s x-ray absorption probability due to the chemical and physical state of the atom”. XAFS is particularly sensitive to the oxidation state, coordination number, and the species of atoms directly surrounding the selected element. Consequently, XAFS is a powerful tool for a large range of scientific disciplines including environmental science, chemistry, and biology (Newville, 2004). Several researchers have utilized XAFS in combination with advanced statistical models to identify the different species of metals in soil environments and have made strides towards the quantification of the species present as well (Isaure *et al.*, 2002; Roberts *et al.*, 2002; Scheinost *et al.*, 2002; Scheckel and Ryan, 2004). Scheckel and Ryan (2003) employed XAFS to speciate Pb compounds in P-amended soils, thereby avoiding the earlier described pitfalls of other methods utilized for the estimation of pyromorphite formation.

2.7 Environmental Concerns Associated with Phosphorous-Based Remediation. The addition of large quantities of P to soils is of environmental concern, as P is the limiting micronutrient associated with eutrophication (Theis and McCabe, 1978; Sharpley and Halvorson, 1994; Sims, 1993; Dermatas *et al.*, 2008). Consequently, the EPA has been working for the past several decades to establish P water quality criteria for surface waters across the United States.

These nutrient criteria range between 8 and 128 $\mu\text{g L}^{-1}$ P depending on the EPA region (USEPA, 2001).

Potential issues with P leaching have only been lightly discussed or mentioned by studies investigating the feasibility of P treatment (Basta and McGowen, 2004; Cao *et al.*, 2002; Dermatas *et al.*, 2008; Yang and Tang, 2007). Using diammonium phosphate and apatite to treat smelter contaminated soils, Basta and McGowen (2004) determined that up to 10% of the P leached from their column studies, despite the relatively low dosage of P applied compared to other treatability studies in the literature. Basta and McGowen (2004) also demonstrated initial leaching of P from treated soils to be $>2000 \text{ mg L}^{-1}$, an extraordinarily large mass per unit volume. Cao *et al.* (2002) applied phosphate at a 4.0 molar ratio of P to Pb with treatments using a varying ratio of H_3PO_4 to phosphate rock. Their work demonstrated that phosphate amendments effectively transformed soil Pb to chloropyromorphite [$\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$], which they identified in the surface soil, subsurface soil, and plant rhizosphere soil. A 50%/50% mixture of H_3PO_4 and phosphate rock was found to yield the best overall results for *in situ* Pb immobilization, with less soil pH change and reduced P leaching. Nevertheless, the same study documented releases of up to 20% of the total P added to treated soils (Cao *et al.*, 2002). Dermatas *et al.* (2008) treated Pb contaminated firing range soils with various P-based treatments while subsequently extracting and analyzing P. The study showed significant P ($>300 \text{ mg L}^{-1}$) leaching under all of their experimental conditions, in both alkaline and acidic soils.

Yang *et al.* (2002) investigated the transport of P following treatment of Pb contaminated soils with H_3PO_4 in a column leaching study. The leachate passing through the columns was found to contain 0.06 mg L^{-1} Pb and 335 mg L^{-1} P in treated soils and 0.19 mg L^{-1} Pb and 0.29 mg L^{-1} P in untreated columns. The researchers noted that P leaching due to surface H_3PO_4 application would most likely increase P transport to groundwater and potentially cause surface and groundwater contamination. Yang *et al.* (2002) concluded that the P issue may not be as burdensome as leaching data suggest due to the relative low mobility of P in soil. The researchers referred to P adsorption to various soil constituents such as Al, Fe, and various clays as noted in the variable solubility of P experiments conducted by Maguire *et al.* (2000). Yang *et al.* (2002) also hypothesized that soil profiles with a deeper horizon ($>1 \text{ m}$) would have much greater sorptivity, thereby reducing P leaching to a minimum.

3.0 Objectives and Hypotheses

The overall objectives of this study are to (1) quantify the impact of phosphate-based remediation of Pb contaminated soil on P and Pb loss via soil surface runoff and (2) quantify the formation of insoluble pyromorphite in soil due to P treatment using XAFS. The ultimate goal of the research will be to determine the level of phosphate treatment that maximizes pyromorphite formation and minimizes P pollution of surface water. The objective will be accomplished by treating Big River floodplain soils with three levels of phosphate amendment and simulating rainfall events at select intervals following treatment to investigate changes in surface water P and Pb transport with time. The specific objectives and hypotheses of this research are as follows:

- ***Objective #1.*** Conduct laboratory investigations to determine the effect of different P treatment levels on surface water P and Pb transport.
- ***Hypothesis #1.*** Floodplain soils with higher levels of applied P will release commensurately higher levels of P to surface water, and overall Pb release will be unaffected by treatment.
- ***Objective #2.*** Conduct laboratory experiments to determine the influence of time post-application of P on surface water transport of P and Pb.
- ***Hypothesis #2.*** Greater losses of P will be observed in soils with shorter intervals in between P application and simulated rainfall compared to soil subjected to longer periods between P application and simulated rainfall.
- ***Objective #3.*** Conduct laboratory experiments to determine which P treatments result in the greatest degree of pyromorphite formation.
- ***Hypothesis #3.*** Soils treated with the highest levels of phosphate will form the greatest percentage of pyromorphite.

4.0 Materials and Methods

4.1 Site Description and Soil Sampling. A description of the study area is provided previously in the introduction. Soil for the experiment will be collected in alluvium of the Big River floodplain at Washington State Park or at nearby private property. The Haymond and Kaintuck series are available at Washington State Park and will be targeted for collection. Samples will be collected from shallow, hand-dug pits in the top 15 cm of soil. Enough soil will be collected to create 32 replicates of 15 liters each. All soil samples will be collected from within a 1000 m² area to minimize differences in spatial variability between samples. Soil samples will then be bulked together and mixed to create a single soil sample stockpile. Bulk density of soils will be measured by collecting soils within the sample area using an Uhland core sampler (3 inches by 3 inches).

After thorough air drying and mixing, the bulk soil stockpile will be sieved to < 2 mm for all experimental trials. Sieving will be accomplished by forcing air dried soil over frames mounted with 2 mm hardware cloth. Four replicates for each treatment level and reaction length period will be created by placing 15 liters of soil in 32 commercially available polyethylene buckets

4.2 Sample Characterization and Experimental Protocols. After air-drying and mixing, a portion of each of the soil samples will be sieved to <2 mm and analyzed for total elemental concentration using X-ray fluorescence (XRF). Target soil Pb concentrations will be 800 to 2000 mg/kg. Approximately 250 ml of dried and sieved sample will be placed into a sealable plastic bag and analyzed for 90 seconds using a Thermo Niton XL3t 600 XRF (Thermo Scientific, Billerica, MA). Ten composite samples consisting of 50 cm³ each will be pulled from the bulk stock pile for analysis. Each sample will be analyzed in triplicate and an arithmetic mean of the total metal values in mg kg⁻¹ reported by the instrument will be calculated.

Ten composite samples consisting of 50 cm³ each will be pulled from the bulk stock pile and sent to the University of Missouri Soil Characterization Lab (Columbia, MO) for routine analyses including pH_{water}, pH_{salt} (0.01M CaCl₂), particle size distribution, extractable Al, titratable acidity, cation exchange capacity (CEC) both buffered and unbuffered, percent organic carbon, and percent total N. The Soil Characterization lab will also perform total nutrients analysis (Morgan extractable P, K, Ca, Mg, Fe, Mn, Zn, Al, and NO₃⁻). Total elemental analysis [HNO₃ digestion Al, As, B, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Ti, V, Zn – Microwave digestion (EPA 3051-6010)] will be performed by the Missouri Department of Natural Resources' State Environmental Laboratory, Jefferson City, MO.

Following XRF analysis, soils will be treated with P as Ca(H₂PO₄)₂ (aq) [i.e., Triple Super Phosphate (TSP)]. The TSP will be administered at four different experimental levels based on Pb:P molar ratios (0, 1:2, 1:4, and 1:8). Actual dosing of P to soils will be based on experimentally derived Pb concentrations in the bulk soil stockpile. The TSP at the three levels will be thoroughly mixed into each sample treatment container. Sample containers will be constructed to allow free drainage. All samples will then be moistened with deionized water until at approximate field capacity. Samples will then be allowed to react for two weeks in a secured outdoor setting at ambient temperatures. Following the first reaction period all soils will be treated with predetermined amounts of hydrated lime (Ca(OH)₂) to adjust pH into the range of

pH 6.5-7.0. Next, four replicates of each of the four P treatment levels will be packed into test beds that are 100 cm by 30 cm by 15 cm deep. Five cm of sand will be packed in the base of the test beds prior to the addition of 10 cm of soil. Soils will be compacted to a level determined by previous bulk density sampling using a mechanical packing device. Soils at each of the four treatment levels will then be exposed to simulated rainfall at the University of Missouri's College of Engineering rainfall simulator using the rainfall simulator described by Regmi and Thompson (2000). The simulator will be adjusted to provide 32 +/- 7 mm/hr flow rate for 60 minutes. The test bed slope will be adjusted to a slope of 2% to simulate the gradual slope of a floodplain environment. Surface runoff will be collected at the downslope end of the test bed from a V-trough in a single collection bottle. Ports in the bottom of the test bed will also facilitate the collection of soil leachate.

Rainfall intensity will be kept constant for all exposure tests. Effluents from the test will be captured and analyzed for total metals (EPA 6010B ICP/MS), dissolved metals (EPA 6010B ICP/MS), total P (EPA 365.4), and dissolved orthophosphate (EPA 365.1). All water chemistry analysis will be performed at the Missouri Department of Natural Resources State Environmental Laboratory, Jefferson City, MO. Following the initial treatment period, remaining soil volumes not utilized in the rainfall simulation will be allowed to air-dry.

Soils not exposed to the first round of rainfall simulation will be allowed to react with the added P for an additional 12 month time period. During this period soils will be exposed to natural precipitation and temperature conditions to encourage further soil reactions and simulate conditions that may be experienced in the field. Effluents from natural precipitation will be collected and analyzed for total metals and total P using the above described methodology. At the end of the 12 month time periods, four more replicates of each treatment level will be exposed to simulated rainfall with effluents collected for analysis in the same manner as described above.

Oven dried samples from the initial and one year reaction periods will then be dry sieved to >250 μm and subjected to x-ray absorption fine-structure spectroscopy (XAFS) at the Advanced Photon Source at the Argonne National Laboratory in Argonne, IL to speciate and quantify the major Pb species in the soil. The goal of the XAFS portion of the experiment will be to determine the degree of formation of pyromorphites in the experimental trials. Lead (13055 eV) L_{III} -XAFS data will be collected. Variables obtained from the fits will include the energy phase shift (ΔE_0), coordination numbers (N), bond distances (R), and Debye-Waller factors (σ^2). XAFS analysis and interpretation of spectra will be performed in conjunction with the U.S. Environmental Protection Agency's Office of Research and Development in Cincinnati, OH.

4.3 Statistical Analysis. Data will be analyzed for phosphate loss and pyromorphite formation using a factorial design. Factor A represents TSP application rates and factor B will be time after application of TSP (2 weeks and 12 months). Four replicates will be performed.

4.4 Expected Benefits. The results of this research will assist in the decision making process of the Missouri Natural Resource Damage Assessment and Restoration (NRDAR) trustees and other environmental managers throughout the nation regarding the environmentally sound restoration of Pb contaminated soils. Results will guide the implementation of large scale restoration projects across the state of Missouri in two separate historic mining districts. The research has the potential to guide the expenditure of tens of millions of restoration dollars.

Timeline:

Project:	2011					2012					2013				
Rainfall Simulation Preparation	■	■													
Soil Sample Collection		■	■												
Soil Treatment and Characterization			■	■	■										
Rainfall Simulation and Analysis			■	■	■										
XAFS Analysis				■	■	■	■	■							
Statistical Analysis						■	■	■							
Thesis and Manuscript Preparation						■	■	■	■	■	■	■	■		

References:

- Basta, N.T., and S.L. McGowen. 2004. Evaluation of chemical immobilization treatments for reducing heavy metal transport in a smelter-contaminated soil. *Environ. Pollut.* 127:73–82.
- Beyer, W. N., J. Dalgarn, S. Dudding, J.B. French, R. Mateo, J. Miesner, L. Sileo, and J. Spann. 2005. Zinc and lead poisoning in wild birds in the Tri-State Mining District (Oklahoma, Kansas, and Missouri). *Arch. Environ. Contam. Toxicol.* 48:108-117.
- Buchanan, A.C. 1979. Mussels (Naiades) of the Meramec River Basin, Missouri. Final report prepared for U. S. Army Corps of Engineers, St. Louis District.
- Cao, X., Ma, L.Q., Singh, S.P., Chen, M., Harris, W.G. and Kizza, P., 2001. Field demonstration of metal immobilization in contaminated soils using phosphate amendments, Florida Institute of Phosphate Research, Gainesville, FL.
- Cao, X., L.Q. Ma, M. Chen, S.P. Singh, and W.G. Harris. 2002. Impacts of phosphate amendments on lead biogeochemistry at a contaminated site. *Environ. Sci. Technol.* 36:5296–5304.
- Cao, R.X., L.Q. Ma, M. Chen, S.P. Singh, and W.G. Harris. 2003. Phosphate-induced metal immobilization in a contaminated site. *Environ. Pollut.* 122:19–28.
- Casteel, S.W., R.W. Blanchar, and J. Yang. 1997. Effect of phosphate treatment on the bioavailability of lead from the Jasper County site—Joplin, Missouri. Missouri Department of Natural Resources, Jefferson City, MO.
- Cotter-Howells J, I., Thomtom. 1991. Source and pathways of environmental lead to children in a Derbyshire mining village. *Environ Geochem Health* 13(2):127–135
- Davis, A., J.W. Drexler, M.V. Ruby, and A. Nicholson. 1993. Micromineralogy of mine wastes in relation to lead bioavailability, Butte, Montana. *Environ. Sci. Technol.* 27:1415–1425.
- Dermatas, D.; Chrysochoou, M.; Grubb, D. G.; Xu, X. 2008. Phosphate treatment of firing range soils: lead fixation or phosphorus release. *J. Environ. Qual.* 37:47–56.
- Eisler, R. 1988. Lead hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Fish Wildl. Serv. Biol. Rep. 85(1.14).
- Fluor Daniel, 1995. Draft Initial Remedial Investigation Big River Mine Tailings Sites, Old Lead Belt, St. Francois County, Missouri. Prepared for the Doe Run Company. April 1995.
- Guppy, C. N., N. W. Menzies, F. P. C. Blamey and P. W. Moody. 2005. Do decomposing organic matter residues reduce phosphorus sorption in highly weathered soils? *Soil Sci. Am. J.* 69:1405-1411.

- He, Z., T. Ohno, B. J. Cade-Menun, M. S. Erich and C. W. Honeycutt. 2006. Spectral and chemical characterization of phosphates associated with humic substances. *Soil Sci. Soc. Am. J.* 70:1741-1751.
- Isaure, M.-P., A. Laboudigue, A. Manceau, G. Sarret, C. Tiffreau, P. Trocellier, G. Lambelle, J.-L. Hazemann, and D. Chateigner. 2002. Quantitative Zn speciation in a contaminated dredged sediment by μ -PIXE, μ -SXRF, EXAFS spectroscopy and principal component analysis. *Geochim. Cosmochim. Acta* 66:1549–1567.
- Laperche, V., S.J. Traina, P. Gaddam, and T.J. Logan. 1996. *In situ* immobilization of lead in contaminated soils by synthetic hydroxyapatite: chemical and mineralogical characterizations. *Environ. Sci. Technol.* 30:3321–3326.
- Lewin, M.D., Sarasua, S., Jones, P.A., 1999. A multivariate linear regression model for predicting children's blood lead levels based on soil lead levels: a study at four superfund sites. *Environmental Research Section A* 81, 52e61
- Ma, Q.Y., S.J. Traina, and T.J. Logan TJ. 1993. *In situ* lead immobilization by apatite. *Environ. Sci. Technol.* 27:1803–1810.
- Ma, Q.Y., T.J. Logan, and S.J Traina. 1995. Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. *Environ. Sci. Technol.* 29:1118–1126.
- Maguire, R.O., J.T. Sims, and F.J. Coale. 2000. Phosphorus solubility in biosolids-amended farm soils in the mid-Atlantic region of the USA. *J Environ Quali* 29:1225–1233
- McHenry, R. E. 2006. Chat dumps of the Missouri lead belt, St. Francois County, Missouri, with an illustrated history of the lead companies that built them. Marceline. 400 pages.
- Newville, M. 2004. Fundamentals of XAFS. Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL.
- Niethammer, K. R., R. D. Atkinson, T. S. Baskett and F. B. Samson. 1985. Metals in riparian wildlife of the lead mining district of southeastern Missouri. *Arch. Environ. Contam. Toxicol.* 14: 213-223.
- Nriagu, J.O. 1974. Lead orthophosphates-IV: Formation and stability in the environment. *Geochim. Cosmochim. Acta* 38:887–898.
- Pavlovsky, R. 2010. Distribution, geochemistry, and storage of mining sediment in channel and floodplain deposits of the Big River system in St. Francois, Washington, and Jefferson Counties, Missouri. The Ozarks Environmental and Water Resources Institute, Missouri State University, Springfield, MO.

- Regmi, T.P. and A.L. Thompson. 2000. Rainfall simulator design for laboratory studies. *Applied Engineering in Agriculture J. of ASAE*, Vol 16(6):641-647.
- Roberts, A.D. and S. Bruenderman. 2000. A reassessment of the status of freshwater mussels in the Meramec River Basin, Missouri. Report prepared for the U.S. Fish and Wildlife Service, Whipple Federal Building, 1 Federal Drive, Fort Snelling, Minnesota 55111-4056. 141 pp.
- Roberts, A.D., D. Mosby, J. Weber, J. Besser, J. Hundley, S. McMurray, S. Faiman. An assessment of freshwater mussel (*Bivalvia*: Margaritiferidae and Unionidae) populations and heavy metal sediment contamination in the Big River, Missouri. Final Report for the U.S. Fish and Wildlife Service, Natural Resource Damage Assessment. 110 p.
- Roberts, D.R., A.C. Scheinost, and D.L. Sparks. 2002. Zn speciation in a smelter contaminated soil profile using bulk and micro-spectroscopic techniques. *Environ. Sci. Technol.* 36:1742–1750
- Ruby, M.V., A. Davis, J.H. Kempton, J. Drexler, and P.D. Bergstrom. 1992. Lead bioavailability: dissolution kinetics under simulated gastric conditions. *Environ. Sci. Technol.* 26:1242–1248.
- Ruby, M.V., A. Davis, and A. Nicholson. 1994. *In situ* formation of lead phosphates in soils as a method to immobilize lead. *Environ. Sci. Technol.* 28:646–654
- Ryan, J.A., P.C. Zhang, D. Hesterberg, J. Chou, and D.E. Sayers. 2001. Formation of chloropyromorphite in a lead-contaminated soil amended with hydroxyapatite. *Environ. Sci. Technol.* 35:3798–3803
- Scheckel, K.G., and J.A. Ryan. 2003. In vitro formation of pyromorphite via reaction of Pb sources with soft-drink phosphoric acid. *Sci. Total Environ.* 302:253–265.
- Scheckel, K.G., and J.A. Ryan. 2004. Spectroscopic Speciation and Quantification of Lead in Phosphate-Amended Soils. *J. Environ. Qual.* 33:1288-1295
- Scheinost, A.C., R. Kretzschmar, and S. Pfister. 2002. Combining selective sequential extractions, X-ray absorption spectroscopy, and principal component analysis for quantitative zinc speciation in soil. *Environ. Sci. Technol.* 36:5021–5028
- Schmidt, C.J., and S.J. Finger. 1982. The dynamics of metals from past and present mining activities in the Big and Black River watersheds, southeastern Missouri. Final report to the U.S. Army Corps of Engineers, St. Louis District, project No. DACW43-80-A-0109.
- Schmitt, C.J., S.E. Finger, T.W. May, and M.S. Kaiser. 1987. Bioavailability of lead and cadmium from mine tailings to the pocketbook mussel (*Lampsilis ventricosa*), in Neves, R.J., ed., *Proceedings of the Workshop on Die-offs of Freshwater Mussels in the United States*: Rock Island, Illinois, U.S. Fish and Wildlife Service and Upper Mississippi River Conservation Committee, p. 115–142.

- Sharpley A.N. and A.D. Halvorson 1994. The management of soil phosphorus availability and its impact on surface water quality. In: Lal R, Stewart BA (eds) Soil processes and water quality. Lewis, Boca Raton, FL, pp 7–90.
- Sims J.T. 1993. Environmental soil testing for phosphorus. *J Prod Agric* 6:501–507.
- Skaer, D.A. and M.A. Cook. 2003. Soil Survey of Washington County, Missouri. USDA-NRCS. U.S. Gov. Print. Office, Washington, DC.
- Tang, X. J. Yang, K.W. Goyne, and B. Deng. 2009. Long-term risk reduction of lead-contaminated urban soil by phosphate treatment. *Env. Eng. Sci.* 26(12): 1747-1754.
- Theis, T.L., and P.J. McCabe. 1978. Phosphorus dynamics in hypereutrophic lake sediments. *Water Res.* 12:677-685.
- U.S. EPA. 1993. Engineering Evaluation/Cost Analysis for the Big River Mine Tailings Site, Desloge, Missouri. U.S. Environmental Protection Agency, Region 7, Kansas City, KS.
- U.S. EPA. 1998. Jasper County site area wide baseline ecological risk assessment, Jasper County, Missouri. US EPA Region VII, Kansas City, KS
- U.S. EPA. 2001. Nutrient criteria development; Notice of ecoregional nutrient criteria. Federal Register, Vol. 66, No. 6. USEPA, Washington, DC.
- U.S. EPA. 2006. Ecological risk assessment Big River mine tailings site St. Francois County, Missouri July 2006. U.S. Environmental Protection Agency, Environmental Services Division, USEPA Region 7 and Black and Veatch Special Projects Corporation.
- Xu, Y., and F.W. Schwartz. 1994. Lead immobilization by hydroxyapatite in aqueous solutions. *J. Contam. Hydrol.* 15:187–206.
- Yang, J., D. Mosby, S.W. Casteel, and R.W. Blanchar. 2001. Lead immobilization using phosphoric acid in a smelter-contaminated soil. *Environ. Sci. Technol.* 35:3553–3559.
- Yang, J., D. Mosby, S.W. Casteel, and R.W. Blanchar. 2002. *In vitro* lead bioaccessibility and phosphate leaching as affected by surface application of phosphoric acid in lead-contaminated soil. *Environ. Contam. Toxicol.* 43, 399–405.
- Zhang, P.C., J.A. Ryan, and J. Yang. 1998. *In vitro* soil solubility in the presence of hydroxyapatite. *Environ. Sci. Technol.* 32:2763–276