Risk and Stability of Phosphate-Immobilized Lead in Contaminated Urban Soil and Mining Sites in the Jasper County Superfund Site

---

A Thesis presented to the Faculty of the Graduate School
University of Missouri- Columbia

In partial Fulfillment
Of the Requirements for the Degree
Master of Science

By
XI TANG

Dr. John Yang and Dr. Keith Goyne, Thesis Supervisors
MAY 2007

The undersigned, appointed by the Dean of the Graduate School, have examined the thesis entitled

Risk and Stability of Phosphate-Immobilized Lead in Contaminated Urban Soil and Mining Sites in the Jasper County Superfund Site

Presented by Xi Tang

A candidate for the degree of Masters of Science

And hereby certify that in their opinion it is worthy of acceptance

_____

Dr. John Yang. Soil, Environmental, and Atmospheric Sciences

_____

Dr. Keith Goyne. Soil, Environmental, and Atmospheric Sciences

_____

Dr. Baolin Deng. Civil and Environmental Engineering

ACKNOWLEGEDMENTS

Firstly, I would like to thank Dr. John Yang, my major advisor, for accepting me as a graduate student and including me in this important project. Your invaluable guidance made me learn a lot since being part of this research. I also want to express sincere appreciation to Dr. Keith Goyne, my second advisor, for your patient guidance and helpful advice. Thanks are going to Dr. Baolin Deng, who spent the time to serve as a member of my committee.

Thanks to Lincoln University for letting me use their well-equipped lab. Dr. Abua Ikem spent long time to help me operating the ICP instrument. Jimmie Garth provided me technical assistance in the lab. Dr. Hwei-Yiing Johnson technically helped me with the microbial toxicity analysis and gave me support and encouragement as well. Dr. Zhengyu Wang collected the data for March 2004. I would like to say thank you to the above people. Thanks also go to my officemates, Sara Merchan Paniagua and Si Hyun Wu for encouraging me and sharing the academic experiences with me. Special thanks are given to my friends in Columbia, Pingping Jiang, Catherine Ann Bohnert, and Xiao Wang, for the understanding and support that they gave throughout this project. Thanks to my parents for believing in me and supporting me for so long. Last but not least, this research was funded by the U.S. Environmental Protection Agency (EPA), National Center of Environmental Science (NCER), Science to Achieve Results (STAR) Program.

TABLE OF CONTENTS

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Figures **Page**

ABBREVIATIONS

PBET	Physiology-based extraction test
ICP-OES	Inductively coupled plasma- optical emission spectroscopy
OM	Organic matter
PA	Phosphoric acid
SA	Surface application
RT	Rototilling
PI	Pressure injection
CEC	Cation exchangeable capacity
TSP	Triple-super-phosphate
FESEM	Field emission scanning electron microscopy
EDS	Energy-dispersive x-ray spectrometer
BSE	Backscattered electron
CV	Critical value
LSD	Least significant difference

Risk and Stability of Phosphate-Immobilized Lead in Contaminated Urban Soil and Mining Sites in the Jasper County Superfund Site

Xi Tang

Dr. John Yang, Thesis Advisor

Dr. Keith W. Goyne, Thesis Co-advisor

ABSTRACT

In situ application of soluble phosphates and organic matter is considered to be a cost-effective remediation technique for immobilizing lead (Pb) and other heavy metals and reducing health and ecological risks associated with contaminated soils. However, a long-term assessment of risk reduction induced by metal immobilization is needed to verify efficacy and gain regulatory and public acceptance of phosphate-based and organic matter-based remedial technologies. The study sites included a smelter-contaminated urban site, a mill-waste contaminated site, and a mining-waste contaminated site within the Jasper County Superfund Site, Southwestern Missouri. Field plots at the urban site were treated with phosphoric acid at a rate of 10 g kg^{-1} using surface application (SA), rototilling (RT), and pressure injection (PI); plots at the mill-waste site were treated with phosphoric acid at rates of 7.5 and 10 g kg^{-1} and incorporated using rototilling; plots at the mining-waste site were treated with different types of organic amendments, including biosolids and agricultural byproducts.

The parameters chosen to assess long-term risk reduction were: (1) metal bioavailability to organisms; (2) metal availability to plants (i.e., phytoavailability); (3) toxicity of treated soils to microorganisms; (4) phosphate and metal stability; and (5)

solid phase P and Pb speciation assessed using microscopic, spectroscopic, and chemical fractionation techniques.

Results demonstrated that most of the phosphoric acid and OM treatments significantly reduced bioavailability, phytoavailability, and leachability of metals (Pb and Cd) in the contaminated soil. Analysis of P and Pb fractionation confirmed these reductions as well. In addition, most of treatments did not significantly impact toxicity in the soil to microorganisms. Thus, the in situ remediation of metal contaminated soil using phosphoric acid and OM is considered to be a practical remediation strategy with long-term benefits.

CHAPTER 1

INTRODUCTION

Significance of Study

Studies investigating the impacts of heavy metals on the environment have become increasingly more prevalent during the past three decades. Lead (Pb), a member of Group 14 (formerly Group IVB) of the Periodic Table of the elements, is nonessential and harmful element for plants or animals (Alloway, 1995). In soils contaminated with Pb, strategies that immobilize and transform Pb to very low or relatively insoluble species may reduce the leaching of Pb through soil, minimize dissolution within the human gastrointestinal tract, and mitigate harmful effects of Pb on human health and the environment (Yang et al., 2006).

In situ phosphate treatment, which transforms soil Pb into pyromorphite [$Pb_5(PO_4)_3$ (OH, Cl, F…)] via land application of phosphoric acid (H_3PO_4), has been proven to effectively reduce soil Pb bioavailability as determined using *in vivo* swine tests (Casteel et al., 1997) and *in vitro* extraction test (Yang et al., 2001; EPA, 2004). Previous research has also determined that *in situ* phosphate treatment significantly reduces the mobility of cadmium (Cd) and Pb in the soil (EPA, 2004). However, the long-term impact metal immobilization using phosphate treatment has not been thoroughly assessed (Fransworth et al., 2003). Thus, we do not understand the long-term impact of phosphate addition on soil biological and chemical properties.

This study was initiated to assess the long-term effects of phosphate and organic matter amendments and the sustainability of Pb immobilization in polluted soils using physio-chemical and biological analyses. Laboratory investigations integrated with field

plot trials focused on evaluating soil properties at three differing field sites established in urban and mining areas within Jasper Co, Missouri. Results from this study will prove useful for evaluating the efficacy and ecological safety of phosphate-based Pb remedial technology and further our understanding of metal immobilization strategies. Ultimately, this work may have a positive impact human health and the environment by encouraging others to implement similar *in situ* techniques to treat heavy metal contaminated soils in other locales (Yang et al., 2002).

Objectives

The overall goal of this study was to assess the long-term impact on chemical and biological soil properties at heavy metal contaminated sites treated with phosphate and organic matter amendments. More specifically the objectives of this study were to:

1. Assess reductions in the long-term bioavailability or risk to human health and ecosystems of heavy metal contaminated soils treated with phosphate and organic matter additives by investigating *in vitro* bioavailability, phytoavailability, and microbial toxicity.
2. Evaluate the long-term leachibility/stability of immobilized metals and phosphate in phosphate-treated and organic matter amended soils by subjecting samples to differing chemical and biological conditions via the leachability test.
3. Identify solid or chemical metal species responsible for the risk reduction in phosphate and organic amended soil through sequential extraction fractionation procedures and electron-beam microscopy.

CHAPTER 2

LITERATURE REVIEW

Heavy Metal Contamination

Heavy metals, commonly defined as metals having a specific density > 5 g cm^{-3}, have been used in many areas for thousands of years. For instance, Pb has been used for 5000 years as a building material and pigment, Cd pigments were in use during the mid 1800's (Jarup, 2003), and mercury (Hg) was utilized as a raw material for medicine in ancient China. However, the Industrial Revolution resulted in the global spread of heavy metals through mining, smelting and military activities (Hoilett, 2006).

As world economies have grown, the consumption of heavy metals has greatly increased over the past two decades. For example, the production of copper (Cu) has increased 64% from 8.3 million tons (Mt) to 13.6 Mt from 1999 to 2002, and the production of zinc (Zn) and nickel (Ni) increased by 9.2% and 14%, respectively (Landner and Reuther, 2004). Similarly, the consumption of Pb increased over 30% from the years of 1975 to 2000 (Kabata-Pendias and Pendias, 1992). Increases in the consumption of heavy metals has, however, caused environmental contamination in the United States (Warren and Delavault, 1960; Cannon and Bowles, 1962; Yang et al., 2002), England (Davies and Holmes, 1972), New Zealand (Ward and Brooks, 1974), Egypt (Belal and Saleh, 1978), Hong Kong (Ho, 1990), China (Yang et al., 1997), Mexico, Poland, and many other countries (Hoilett, 2006).

Heavy metals enter the air by burning of coal and other fossil fuels,smelting activities, and wind erosion, thereby, adversely impacting air quality. Some heavy metals, such as selenium (Se), Pb, Cd, and tin (Sn), have been found in the atmosphere at concentrations

1000 times greater than normal air concentrations (Kabata-Pendias and Pendias, 1992). Recently, greater attention has been paid to fly ash, one of main heavy metal air pollution sources, in the countries of India (Kanungo et al., 2000), the United States (Fleming et al., 1996), and the Philippines and Thailand (Brigden et al., 2002). Due to atmospheric processes, heavy metals released from source areas may pollute water and soil resources great distances away from the point of release (Kabata-Pendias and Pendias, 1992).

Water resources have also been polluted by heavy metal discharge into the environment. Streams entering the San Diego Bay and San Francisco Bay were reportedly polluted by silver (Ag), Cd, Cu, and Pb (Flegal and Sanudo-Wilhelmy, 1993). In Colorado, the Arkansas River is polluted with Cd, Cu, and Zn discharged from historic mining operations (Kiffney and Clements, 1993). Although heavy metals generally exist as less soluble forms and stay at the bottom of water bodies, they are still considered dangerous to the safety of the food chain. Fish in contaminated waters have been found to contain metals in their bodies in Norway and Russia (Amundsen et al., 1997), Hungary (Farkas et al., 2000), Australia (Broek et al., 2002), and other areas of the world as well.

Due to increasing human activities since the industrial revolution, soil has become the sink for heavy metals that were released from various of sources, such as mining, smelting, and the combustion of fossil fuels, etc. (Han et al., 2001). Recently, vast amounts of wastewater, sewage sludge, animal waste, and even city garbage compost have been produced yearly that could introduce heavy metals to soil (Han et al., 2001). Research has shown that the metals of greatest concern in sewage sludge are Cd, Zn, Pb, Ni, Cu, and Cr and in animal waste, Cu, Zn, Mn, As, and Se are of concern (Han et al., 2001). For the reasons above, soil heavy metal contamination has been documented

worldwide, including Australia (Sultan, 2007), India (Krishna and Goril, 2007), Italy (Bretzel and Calderisi, 2006), Korea (Lee et al., 2006), and China (Yang et al., 2006), etc. The most concerned heavy metals in these areas were As, Cu, Zn, Pb, Cd, and Cr.

Lead Contamination of Soils

Soil is a natural reservoir for heavy metals and soil can act as the vehicle to transform heavy metals in the ecosystem (Ma, 1996). Heavy metal contamination is considered particularly serious because metals do not degrade in the soil (Schulthess and Huang, 1990), thus heavy metals are contaminants that can persist in toxic forms for hundreds to thousands of years. Although there are numerous heavy metals that can and are found as contaminants in soil, the remainder of this section will focus on Pb since it is central to the research conducted.

Lead is one of the most abundant heavy metal elements in the earth's crust, and the Pb content of the crust is ~15 mg kg^{-1} (Adriano, 2001; Alloway, 1995). Among the over 200 Pb-bearing minerals, the three most common and economically important forms are galena (PbS), cerussite ($PbCO_3$), and anglesite ($PbSO_4$; Adriano, 2001). In uncontaminated soils, Pb concentrations are usually less than 1 mg kg^{-1}. However, mean concentrations of 12, 18, and 27 mg Pb kg^{-1} have been reported in Canada, the United States, and China, respectively (Adriano, 2001; Chen et al., 1991). In contrast, Pb concentrations in ore deposits may exceed 10% (Adriano, 2001).

Soil acts as a sink for anthropogenic Pb that comes from mining, smelting, manures, sewage sludge, and vehicle exhaust emissions (Alloway, 1995). Lead tends to accumulate at the soil surface in contaminated areas and concentrations decrease with depth (Adriano, 2001; Alloway, 1995). However, Pb can move from contaminated soils through various

processes (i.e., leaching, water erosion, and wind erosion) resulting in elevated Pb concentrations in lands surrounding contaminated sites (Xintaras, 1992). Even though the leaching of Pb is very slow under most natural conditions, this process can occur when the Pb concentration in soil approaches or exceeds soil sorption capacity or in instances when soil solution pH is decreased (Xintaras, 1992).

As noted previously, Pb released via vehicle emissions has contributed to soil contamination. Lead in vehicle emissions can be attributed to the addition of Pb alkyls to gasoline as a means to avoid uneven combustion in the engine cylinders of vehicles, and this practice rapidly became a standard in early 1920's (Alloway, 1995). Subsequently, unusually high concentrations of Pb have been found in soils near roads (Warren and Delavault, 1960), and this problem has been noted the United States (Cannon and Bowles, 1962), England (Davies and Holmes, 1972), New Zealand (Ward and Brooks, 1974), Egypt (Belal and Saleh, 1978), and Hong Kong (Ho, 1990).

Vehicle exhaust is but one source that has resulted in soil contamination of Pb. Fleming and Parle (1977) reported a concentration of 540 mg Pb kg^{-1} in urban soils of Dublin, Ireland. They suggest that vehicle fumes, coal, plastics and rubber factories, insecticides, car batteries, and old paint could be all have been Pb sources. Furthermore, mining, milling, and smelting of Pb can result in accumulations of soil Pb if appropriate environmental controls are not implemented. For example, a comprehensive investigation of Pb-contaminated soils in Wales documented soil Pb concentrations ranging from 90 to 2900 mg Pb kg^{-1} in the alluvial soils in the Ystwyth valley where Pb industries were located compared to 24-56 mg Pb kg^{-1} in a neighboring valley (Alloway and Davis, 1971).

Agricultural activities may also contaminate soil with heavy metals. Since the supplies of farmyard manure, often considered a desirable soil amendment material and good provider of plant nutrients, have decreased in some regions of the world, farmers have tried to find alternative materials. In Holland, household wastes with Pb content were land applied (Lustenhouwer and Hin, 1993), and 12 million wet tons of sewage sludge is land applied annually in United Kingdom (Davis, 1987). However, household wastes and sewage sludge can cause soil heavy metal contamination due to high metal contents.

Impacts of Lead and Other Heavy Metals on Human Health

Lead is ranked as the number one priority hazardous substance by the Agency for Toxic Substances and Disease Registry (ATSDR) and the EPA (Hoilett, 2006). It is also the most common heavy metal contaminant in Superfund sites (47% of sites), followed by arsenic (As; 41%), chromium (Cr; 37%), Cd (32%), nickel (Ni; 29%), and zinc (Zn; 29%) (Gobran et al, 2001). Heavy metals enter the human gastrointestinal system through hand-to-mouth activity, indicating that heavy metal bioavailability is mainly caused by direct exposure contaminated soils (Basta, 2001). Research has shown that exposure to Pb can cause body pain, kidney damage, and behavioral disturbances, and children are at higher risk due to their behaviors (e.g., significant hand-to-mouth activity; Jarup, 2003). Other heavy metals may cause kidney and skeletal damages, cancer, lung damage, heart disease, vascular disease, and depression (Jarup, 2003). Therefore, the remediation of heavy metal contaminated soils is necessary to protect human and environmental safety (Hoilett, 2006), and the need to treat contaminated soils has increased the market for remediation of metal contaminated sites (Gobran et al, 2001).

Remediation Methods

Remediation of heavy metal contaminated soil does not have a long history. The USEPA prefers methods that can permanently and significantly reduce the toxicity or mobility of hazardous substances (Adriano, 2001). Numerous Superfund sites are contaminated with heavy metals and ~16% of signed Record of Decisions (RODs) list heavy metals as the sole contaminants and 49% of RODs are for sites co-contaminated with heavy metals (EPA, 1997).

At present, there are three major categories of methods for remediation of heavy metal contaminated sites: (1) physical methods, which protect humans and the environment from metals by removing or restricting access to the contaminants; (2) chemical methods, which enhance or reduce the mobility of the contaminants through altering their speciation; and (3) biological methods, which use biochemical processes to extract or to immobilize metals (Adriano, 2001).

Physical methods of remediation include vitrification, encapsulation, soil washing, artificial ground freezing, and electrokinetics. Vitrification is a solidification technique that utilizes heat to a melt and hardens contaminated soil into a glass-like material. The technique works well for organic contaminants but waste gases may be emitted during the process (Adriano, 2001). Encapsulation involves covering a contaminated site with an impermeable material to minimize exposure and contaminant mobility (Adriano, 2001). Soil washing uses acid or chelating solutions to extract contaminants from the soil, sometimes followed by sedimentation, centrifugation, and filtration (Adriano, 2001). With artificial ground freezing, the ice between soil particles reduces the soil permeability and it may concentrate the contaminants in the soil (Adriano, 2001).

Electrokinetic methodologies involve the use of electrodes to migrate contaminant ions for removal (Adriano, 2001). This *in situ* method was proved efficient for removing Pb, Cr, Cd, and uranium (U) at initial soil concentrations of 200 mg kg^{-1} (EPA, 1989).

The chemical methods use chemical treatment to remove or decrease the availability of metals to living things and groundwater, and they include neutralization, solidification, and *in situ* stabilization. Neutralization is the method that neutralizes soil acidity or alkalinity to reduce the activity of metals resulting in high pH soils. This method has been used in waste sites where batteries have leaked and at a dredge material disposal site in Delaware (Palazzo and Reynolds, 1991). Solidification is the most widely used chemical method that employs *ex situ* mixing of soil with binder materials to immobilize metals and water by chemical interactions (Adriano, 2001). I*n situ* stabilization treatments utilize application of inexpensive materials, such as lime and hydroxyapatite, to immobilize metal ions by formatting low solubility materials in the soil (Adriano, 2001).

Biological methods make use of plants and microorganisms to remedy metal contaminated soil. Phytoremediation employs plant species to clean up contaminated soil. This technology can be further separated into: (1) phytostabilization or the use of metal-tolerant plants to stabilize metals in soil; (2) phytoimmobilization or the use of plants to reduce metal mobility in soil; (3) phytoextraction or the use of plants to extract metals and organic constituents from soil; and (4) phytovolatilization or the use of plants and enzymes to transform contaminants in the soil ecosystem to reduce contamination (Adriano, 2001).

In situ Immobilization of Lead

Compared with other remediation methods, *in situ* immobilization is relatively

inexpensive, easy to operate, and impacts natural ecosystems less than excavation, extraction, and disposal methods (Iskandar, 2001). In 1990, the U.S. EPA in cooperated with The Ohio State University to find a suitable and wide-range use *in situ* method to transform labile forms of Pb into stable forms by using inexpensive, readily available, and nontoxic reagents (Iskandar, 2001). Based on an examination of existing chemical and geochemical knowledge of Pb, lead phosphates were considered as the most stable form of Pb in the surface soil environment, and they can act as a sink for Pb in the environment (Zhang et al., 1998; Iskandar, 2001; Yang et al., 2001; Yang and Mosby, 2006).

Previous studies have show that Pb can be precipitated from aqueous solution and immobilized as solid pyromophite (hydroxypyromorphite, fluoropyromophite, or chloropyromorphite) in 30 min under pH 3 to 7 conditions (Ma et al., 1993). It was reported later that phosphates could also be sorbed by other metals (Al, Fe, Cu, Cd, Ni, and Zn), but not as efficiently as lead (Ma et al., 1994). Further research suggested that optimizing phosphate and chloride reactivity, pH, water content, and mixing rate could increase the rate of transformation from galena to pyromorphite (Ruby et al., 1994). Since the formation of pyromorphite needs sufficient soluble P and Pb, Yang et al. (2001) applied phosphoric acid (H_3PO_4) instead of phosphates to Pb contaminated soil. The results showed that H_3PO_4 treatment efficiently reduced the bioaccessibility and solubility of soil Pb, and formation of a chloropyromorphite-like compound was observed by microprobe analysis (Yang et al., 2001).

It should be noted that phosphate remediation methods might introduce excess quantities of P in the soils. However, Iskandar (2001) argues that the excess P can

decrease the uptake of pyromorphite-P by plants, and the association of growing plants and applying phosphates may be a prudent idea because: (1) vegetation cover can prevent soil erosion and transport the contamination offsite; (2) low Pb-tolerant plant species can be planted on bare, contaminated sites after treatment; and (3) plants can be grown not only for remediation purposes but for agricultural purposes as well.

Recent research has also show that using biosolids to remedy heavy metal contaminated soil can be another cost-effective method to reduce metal bioavailability (Brown and Chaney, 1997; Brown et al., 1999; Brown et al., 2003). Biosolids (sewage sludge) are rich of nitrogen (N), P, organic matter (OM), and often have high concentrations of Fe and Mn (Chaudri et al., 2001; Brown et al., 2003). In addition to municipal biosolids, composts, manures, and peat have been used to immobilize Pb, Cd, and Zn in contaminated soils (Basta et al., 2001; Brown et al., 1996).

Although the mechanisms responsible for observed reductions of available Pb in biosolids-amended soils are not clear, sorption reactions (i.e., adsorption and precipitation) are generally considered responsible for reductions (Brown et al., 2003). High OM and P in biosolids may lead to the formation of Pb-phosphate or Pb-OM complexes and limit metal solubility (Li et al., 2000). Elevated contents of Fe and Mn in some biosolids may also induce formation of Fe and Mn oxides that sorb Pb and make the toxic metal less bioavailable (Ma and Rao, 1997).

Iskandar (2001) suggests that selection of a remediation method(s) for cleaning up a Pb-contaminated site should be based on site conditions, the degree of contamination, intended redevelopment of the site, and financial considerations. The remediation of Pb-contaminated soil by using phosphates or H_3PO_4 with revegetation can be an efficient,

cost-effective, alternative method for agricultural, residential soils, and industrial sites (Zhang et al., 1998; Iskandar, 2001; Yang et al., 2001; Yang and Mosby, 2006). Therefore, it warrants further consideration and study to verify the long-term viability and environmental safety of the *in situ* immobilization treatments.

CHAPTER 3

STUDY SITES DESCRIPTION AND SAMPLING

Site Descriptions and Soil Treatments

The three sites chosen for study are located at the Oronogo- Duenweg Mining Belt Superfund Site in Jasper Co., Missouri, and this site is on the Superfund National Priorities List (NPL). Beginning in 1850's, Pb and Zn mining, milling, and smelting operations were established in this portion of Southwestern Missouri. These facilities include the Eagle-Picher Smelter located in the northwestern corner of Joplin, MO and this facility was operational until the 1970's (EPA, 2004). Subsequently, these operations contaminated Jasper Co. with high levels of heavy metals and resulted in formation of 1460 ha of unvegetated and partially-vegetated mine waste lands (MDNR, 2002). The huge amount of mining, milling, and smelting wastes were causing significant risk to the environment and threatening people's health in these areas (Hoilett, 2006). A large-scaled health study by Missouri Health Department in 1991 showed that about 14% of children less than 7 years of age had blood Pb levels higher than 100 $\mu g\ L^{-1}$ (EPA, 2002; Missouri Health Department, 1994).

In order to remedy contaminated soils in this area, the USEPA collaborated with the Missouri Department of Natural Resources (MDNR), U.S. Department of Agriculture-Agricultural Research Service (USDA-ARS), and the University of Missouri to initiate two studies (Iskandar, 2001; Hoilett, 2006). The first study was designed to elucidate the efficacy of applying phosphoric acid to reduce Pb toxicity and bioavailability at the contaminated sites. In the second study, organic amendments were land applied to contaminated surface soils to promote re-vegetation and mitigate heavy metal

contamination (Hoilett, 2006). These studies resulted in the development of three separate study areas that were used for this study. Greater details of the study sites are provided on following pages.

Urban Site

The urban site is a 0.27 ha vacant lot in northwest Joplin and the surrounding area is used for residences, commerce, and industry (Appendix 1). Soil at this site was contaminated with Pb from a smelter previously located 0.16 km northeast of the experimental site. Lead concentrations at this site range from 400 to 6000 mg kg^{-1} (Yang et al., 2002).

Experimental treatments at this site consist of 2 x 4 m plots arranged in a completely randomized block design with quadruplicate replication. A plastic garden divider was installed to reduce cross-contamination between treatment plots. Phosphoric acid was applied to the plots in 1998 as follows: (1) 10 g P kg^{-1} application rate to soil surface and incorporation via rototilling (RT); (2) 10 g P kg^{-1} application rate to soil surface (SA) with nor incorporation; (3) 10 g P kg^{-1} application rate via subsurface pressure injection (PI); and (4) no treatment (i.e., control plots). In order to provide a sufficient Cl source for the formation of chloropyromorphite, 500 mg Cl kg^{-1} soil as KCl was applied in the soil. All calculations were based on a 15 cm surface soil depth.

For RT-treated plots, topsoil was rototilled before the application of the materials. Then half of the phosphoric acid and KCl was applied followed by another time of rototilling. The remaining half of phosphoric acid and KCl were applied, subsequently, and application was completed following a third rototilling event. The procedures of surface application (SA) were similar with RT, but soil was scratched with a garden

aerator on the surface instead of rototilling. For the pressure injection (PI) method, KCl was initially applied; and then phosphoric acid was equally injected by a pressure injector into 15 cm deep topsoil at a 15 cm interval in the horizontal direction. Two lysimeters were separately installed 30 cm below soil surface in Plot 14 (RT) and Plot 13 (Control) to collect soil water. Tall fescue was planted after the treatments in the urban site.

Mill-Waste Site

The mill-waste site is located in a historic mill tailings impoundment, 3.6 km northeast of Joplin, MO in Jasper Co. The site is covered by an organic-rich soil horizon (5-15 cm thick) overlying mine tailings that consist of silts and fine sands derived from wet flotation processes. Lead concentrations in the soil range from 1800 to 5000 mg kg^{-1}. Ca (4790~ 20,286 mg kg^{-1}), Zn (6780~ 24,510 mg kg^{-1}), and Fe (16,770~ 40,830 mg kg^{-1}) are also detected at significant concentrations.

Present at this site are three separate H_3PO_4 treatments initiated in October 2000 and replicated in quadruplicate (Fig. 3.1). Treatments at this site consist of the following: (1) Treatment A, 10 g P + 500 mg KCl kg^{-1} soil; (2) Treatment B, 7.5 g P + 500 mg KCl kg^{-1} soil; and (3) Treatment C, control (no treatment). Fertilizer grade H_3PO_4 (85% P_2O_5) was applied to a depth of 15 cm. About 37.8 L of H_3PO_4 was applied to each 1% H_3PO_4 plot (Treatment A) and 28.4 L of H_3PO_4 was applied to each 0.75% H_3PO_4 plot (Treatment B). Plots were rototilled before and after the application of reagents. Two lysimeters were separately installed 30 cm below soil surface in Treatment A (1% PA) and Treatment C (Control) to collect soil water. Tall fescue was planted 15 days following treatment.

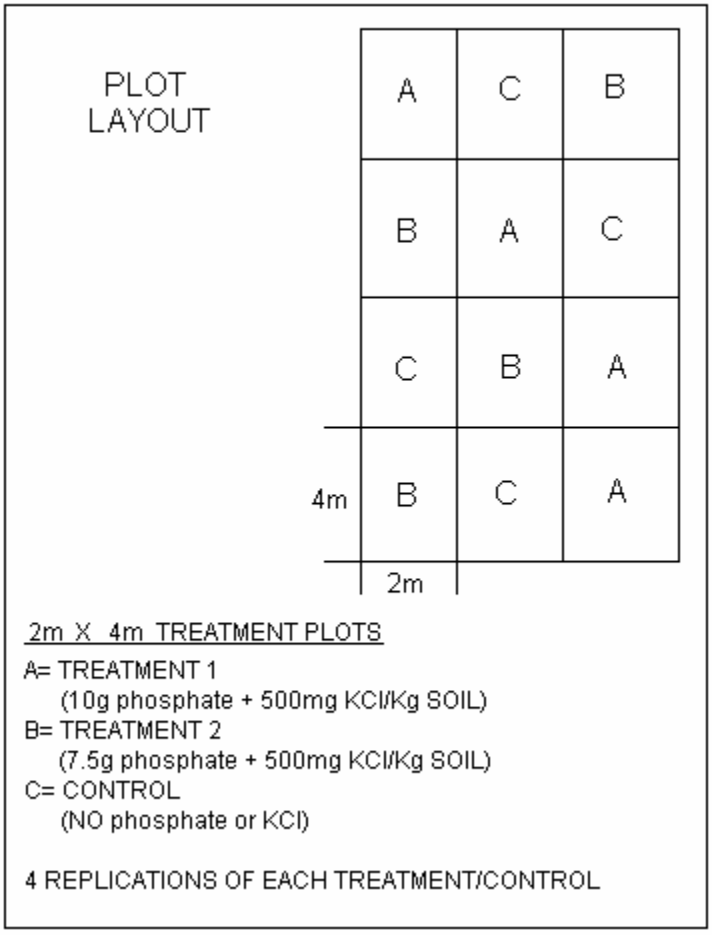


Figure 3.1. Schematic diagram of mill-waste test plots.

Mining Waste Site

The mining waste study site is located within the historical Tri-State Lead Mining district approximately 1.6 km north of Webb City, Missouri, on the floodplain and uplands surrounding Center Creek. The project site was split into two locations, 4 ha at what has come to be known as the Upland Site and 18.2 ha within the floodplain of Center Creek. The materials in this site are mainly the mixtures of the mine waste from the processes of dry gravity separation and wet flotation separation. The mixtures contain chat and tailing, which are fine gravel waste with diameters ranging from sand to 0.64 cm

and finer waste in the size between silt and fine sand. The finer waste, tailing, has higher heavy metal concentrations than the chat in this site.

Both sites can be characterized as completely barren or mostly barren with islands of vegetation occurring in areas along small waterways and depressions where surface water runoff accumulates. Heavy metal concentrations at the Center Creek Site range from 230-3800 mg Pb kg^{-1}, 840-11,000 mg Zn kg^{-1}, and 17-285 mg Cd kg^{-1}, with mean values of 1004, 3492, and 68 mg kg^{-1} for Pb, Zn, and Cd, respectively.

Two organic matter (OM) amendments, including SMC (spent mushroom compost) and MDM (Mizzou Doo mix), were firstly applied to the Upland at dry weight rates of 75 and 150 tons per acre, respectively. Six OM amendments were applied later on the Center Creek site at the rates ranged from 50 to 100 dry tons per acre by October 1998 (Fig. 3.2). The agricultural by-products applied are as follows: (1) Mizzou Doo® (MD), a locally manufactured propriety blend of animal waste, post consumer paper, sawdust and other patented ingredients, with a 0.08% P content; (2) spent mushroom compost (SMC), with a 0.36% P content; (3) composted biosolids (CSS), municipal sewage sludge composted with sawdust, with a 1.93% P content; (4) composted chicken litter (CL), chicken litter composted with sawdust and peanut skins, with a 1.73% P content; (5) turkey litter (TL), with a 1-2% P content; and (6) Mizzou Doo® Landscape Mix (MDM), consisting of one part Mizzou Doo® and two parts topsoil. Information of the mining waste site is obtained from MDNR document (Mosby et al., 2002).

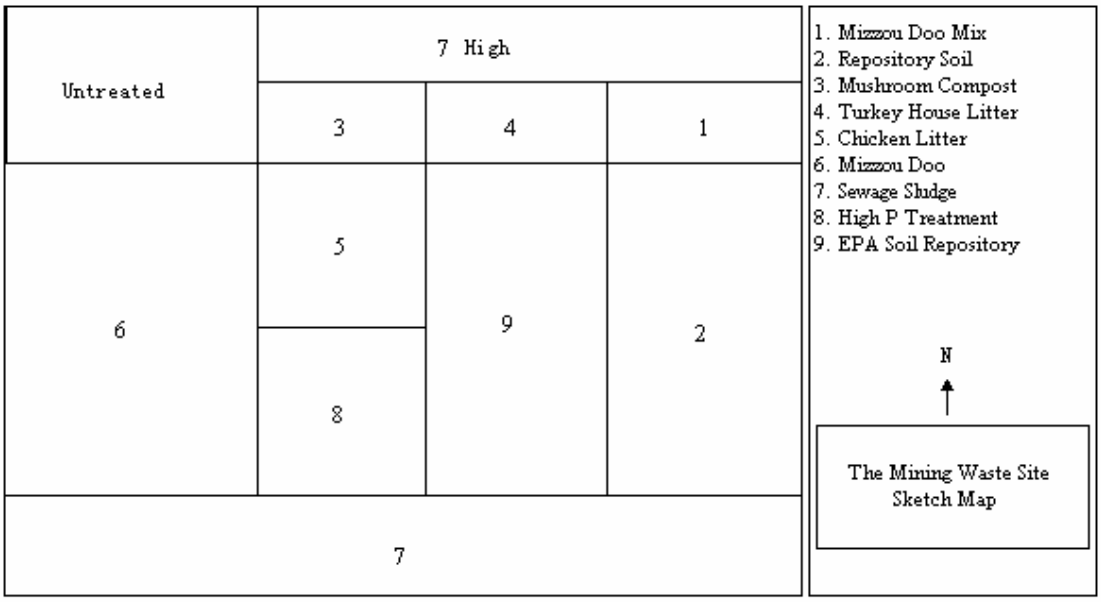


Figure 3.2. Schematic design of organic matter amendments at the Center Creek Site.

Besides the six OM amendments above, triple super phosphate (TSP) and EPA Repository soils were considered as forms of treatment. There were four areas in the Center Creek Site, in which over 5000 mg kg^{-1} concentrations of Pb and Zn were found, treated by TSP prior to the OM amendments. Totally, 3 acres of mine waste were treated with 2700 lbs TSP $acre^{-1}$ and 1.5 acres of contaminated soil from the soil repository treated with 5400 lbs TSP $acre^{-1}$. Piezometers ($7/8^{th}$ in. diameter, 3 ft length pieces of PVC covered with microwell screens) were installed using a post-hole digger and backfilled with the excavated chat to monitor shallow groundwater.

Sampling and Preparation

Soil samples (surface and subsurface), plant tissue samples, and water samples (surface/groundwater) were collected every 3 to 5 months from March 2004 to February 2006. In all the study sites, three topsoil samples (0-5 cm) and 1 subsurface sample (30 cm) were collected from each plot, air-dried and passed through a 0.25 mm sieve. In the

mining waste site, three random collections of the soil sample were mixed for every sample. After collection, plant samples (tall fescue) were oven-dried at 70^{o}C for at least 24 h and ground. Surface water samples were collected directly from ponds near treatment areas and groundwater samples were collected from piezometers at the Center Creek site and from lysimeters at mill-waste and urban sites. All the water samples were filtered through Whatman 0.45 μm filter paper prior to analysis.

LITERATURE CITED IN CHAPTER 1- 3

Adriano, D.C. 2001. Trace elements in terrestrial environments biogeochemistry, bioavailability, and risks of metals, 2nd edition. Springer-Verlag, New York.

Alloway, B.J., and B.E. Davies. 1971. Trance element content of soils affected by base metal mining in Wales. Geoderma 5:197-208.

Amundsen, P.A., F.J. Staldvik, A.A. Lukin, N.A. Kashulin, O.A. Popova, and Y.S. Reshetnikov. 1997. Heavy metal contamination in freshwater fish from the border region between Norway and Russia. Sci. Total Environ. 201(3):211-224.

Basta, N.T., R. Gradwhol, K.L. Snethen, and J.L. Schroder. 2001. Chemical immobilization of lead, zinc and cadmium in smelter-contaminated soils using biosolids and rock phosphate. J. Environ. Qual. 30:1222-1230.

Belal, M., and Saleh, H. 1978. Uptake of lead near roads in Egypt. Atmos. Environ. 12:1561-1562.

Bradl, H. 2005. (ed.) Heavy metals in the environment: origin, interaction and remediation. Elsevier Academic Press, Amsterdam, The Netherlands.

Bretzel, F., and M. Calderisi. 2006. Metal Contamination in urban soils of Coastal Tuscany (Italy). Environmental Monitoring and Assessment. 118:319-335.

Brigden, K., and D. Santillo. 2002. Heavy metal and metalloid content of fly ash collected from the Sual, Mauban and Masinloc coal-fired power plants in the Philippines, 2002. Greenpeace Research Laboratories Technical Note 07/2002. Exeter, UK.

Brigden, K., D. Santillo, and R. Stringer. 2002. Hazardous emissions from Thai coal-fired power plants: toxic and potentially toxic elements in fly ashes collected from the Mae Moh and Thai Petrochemical Industry coal-fired power plants in Thailand, 2002. Greenpeace Research Laboratories Technical Note 08/2002. Exter, UK.

Broek, J.V.D., K. Gledhill, and D. Morgan. 2002. Heavy Metal Concentrations in the Mosquito Fish, Gambusia holbrooki, in the Manly Lagoon Catchment. UTS Freshwater Ecology Report 2002, Department of Environmental Sciences, University of Technology, Sydney.

Brown, S.L., and R.L. Chaney. 1997. A rapid in-vitro procedure to a mimicked in-situ remediation study of metal-contaminated soils characterize the effectiveness of a variety of in-situ lead remediation with emphasis on Cd and Pb. J. Environ. Qual. 23:58–63.

Brown, S.L., R. Chaney, and B. Berti. 1999. Field test of amendments to reduce the in situ availability of soil lead. p. 506–507. *In* Abstracts of the 5th Int. Conf. on Biogeochemistry of Trace Elements, Vienna, Austria. 11–15 July. 1999. Int. Soc. for Trace Element Res., Vienna.

Brown, S., R.L. Chaney, J.G. Hallfrisch, and Q. Xue. 2003. Effects of biosolids

processing on lead bioavailability in an urban soil. J. Environ. Qual. 32: 100-108.

Cannon, H.L., and J.M. Bowles. 1962. Contamination of vegetation by tetraethyl lead. Science. 137:765-766.

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.

Chaudri, A.M., C.M.G. Allain, S.H. Badawy, M.L. Adams, S.P. McGrath, and B.J. Chambers. 2001. Cadmium content of wheat grain from a long-term field experiment with sewage sludge. J. Environ. Qual. 30:1575-1580.

Chen, J., F. Wei, Y. Wu, and D.C. Adriano. 1991. Background concentrations of elements in soils of China. Water, Air, Soil Pollut. 57-58:699-712.

Davies, B.E. 1995. Lead. p. 207-223. *In* B.J. Alloway (ed.) Heavy metals in soils. Blackie Academic & Professional, London.

Davies, B.E. and P.L. Holmes. 1972. Lead contamination of roadside soil and grass in Birmingham, England, in relation to naturally occurring levels. Journal of Agricultural Science (Cambridge) 79:479-484.

Davies, R.D. 1987. Sensitive measurement of fluctuation in the cosmic microwave background. Water Sci. Technol. 19:1-8.

EPA (Environmental Protection Agency). 1989a. Technology Demonstration Summary, Technology Evaluation Report, Site Program Demonstration Test, HAZCON Solidification. Douglassville, PA.

EPA (Environmental Protection Agency). 1997. Recent development for in-situ treatment of metal contaminated soils. Sci. Technol. 26:337-368.

EPA (Environmental Protection Agency). 2002. Five-year review report: first five-year review report for the Oronogo-Duenweg Mining Belt Site, Jasper County, Missouri.

EPA (Environmental Protection Agency). 2004. Mine waste technology program phosphate stabilization of heavy metals contaminated mine waste yard soils, Joplin, Missouri NPL site. EPA/600/R-04/090.

Farkas, A., J. Salanki, and I. Varanka. 2000. Heavy metal concentrations in fish of lake Balaton. Lakes & Reservoirs: Research & Management 5(4):271-279.

Flegal, A.R., and S.A. Sanudo-Wilhelmy. 1993. Comparable levels of trace metal contamination in two semi-enclosed embayments: San Diego Bay and Sooth San Francisco Bay. Environ. Sci. Technol. 27:1934-1936.

Fleming, G.A., P.J. Parle, and I.J. Agric. 1977. Heavy metals in soils, herbage and vegetables from an industrialized area west of Dublin city. Res. 16:35-48.

Fleming, L.N., N.A. Harrison, and I.I. Hilary. 1996. Leachant pH effects on the leachability of metal from fly ash. J. Soil Contam. 5:53-59.

Fransworth, C., D. Giammar, and L.Y. Xie. 2003. Dissolution of lead phosphates. Washington University. St. Louis.

Gobran, G.R., W.W. Wenzel, and E. Lombi. 2001. Trace elements in the rhizosphere. CRC Press-Lewis Publishers, Boca Raton, FL.

Han, F.X., W.L. Kingery, and H.M. Selim. 2001. Accumulation, redistribution, transport and bioavailability of heavy metals in waste-amended soils. p. 145-173. *In* I.K. Iskandar (ed.) Trance elements in soil. CRC Press, Boca Raton, FL.

Ho, Y.B. 1990. The effect of Pb reduction in petrol on the Pb content of kerbside dust in Hong Kong. Sci. Total Environ. 93:411-418.

Hoilett, N. 2006. Microbial properties as affected by in situ phosphate treatment in lead contaminated soils. Graduate thesis of University of Missouri-Columbia, MO.

Laperche, V. 2001. Immobilization of lead by in situ formation of lead phosphates in soils. p. 61-76. *In* I.K. Iskandar (ed.) Environmental restoration of metals-contaminated soils. Lewis Publishers, Boca Raton, FL.

Jarup, L. 2003. Hazards of heavy metal contamination. British Medical Bulletin 68: 167-182.

Kabata-Pendias, A., and H. Pendias. 1992. Trace elements in soils and plants (2nd edition). CRC Press, Boca Raton, FL.

Kanungo, S.B., and R. Mohapatra. 2000. Leaching behavior of various trace metals in aqueous medium from two fly ash samples. J. Environ. Qual. 29:188-196.

Kiffneg, P.M., and W.H. Clements. 1993. Bioaccumulation of heavy metals by beuthic invertebrates at the Arcansas River, Colorado. Environ. Tox. & Chem. 12(8): 1507-1517.

Krishna, A.K., and P.K. Govil. 2007. Soil contamination due to heavy metals from an industrial area of Surat, Gujarat, Western India. Environmental Monitoring and Assessment. 124:263-275.

Laperche, V. 2001. Immobilization of lead by in situ formation of lead phosphates in soils. p. 61-76. *In* I.K. Iskandar (ed.) Environmental restoration of metals-contaminated soils. Lewis Publishers, Boca Raton, FL.

Lander, L., and R. Reuther. 2004. Metals in society and in the environment. Kluwer Academic Publishers, Dordrecht, The Netherlands.

Lee, S.W., B.T. Lee, J.Y. Kim, K.K. Kim, and J.S. Lee. 2006. Human risk assessment for

heavy metals and as contamination in the abandoned metal mine areas, Korea. Environmental Monitoring and Assessment. 119:233-244.

Li, Y.M., R.L. Chaney, G. Siebielec, and B. Kerschner. 2000. Response of four turf grass cultivars to limestone and biosolids-compost amendment of a zinc and cadmium contaminated soil at Palmerton, Pennsylvania. J. Environ. Qual. 29:1440–1447.

Lustenhouwer, J. and J. Hin. 1993. Biosignificant content of heavy metals in compost. Sci.Total Environ. 128:269-278.

Ma, Q.Y., S.J. Traina, T.J. Logan, and J.A. Ryan. 1993. In-situ lead immobilization by apatite. Environ. Sci. Technol. 27:1803-1810.

Ma, L.Q., T.J. Logan, S.J. Traina, and J.A. Ryan. 1994. Effects of aqueous Al, Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by Hydroxyapatite. Environ. Sci. Technol. 28:1219-1228.

Ma, L.Q. 1996. Factors influencing the effectiveness and stability of aqueous lead immobilization by hydroxyapatite. J. Environ. Qual. 25:1420-1429.

Ma, L.Q., and G.N. Rao. 1997. Effects of phosphate rock on sequential chemical extraction of lead in contaminated soils. J. Environ. Qual. 26:788-794.

MDNR. 2002. Preassessment screen and determination, Jasper County Superfund Site, Jasper County, Missouri. Missouri department of natural resources, U.S. department of interior.

Missouri Health Department. 1994. Area- Wide Human Health Risk Assessment for Jasper County Superfund Site, Jasper County, Missouri. Prepared for USEPA Region VII, Kansas City, KS.

Mosby, D.E., S. Miller, C. Bishop, and J. Mehuys. 2002. Former and abandoned lead and

zinc mines demonstration project. Missouri department of nature resources final report. Lincoln University, Jefferson City, MO.

Palazzo, A.J., and C.M. Reynolds. 1991. Long-term changes in soil and plant metal concentrations in an acidic dredge disposal site receiving sewage sludge. Water, Air, Soil Pollut. 57-58:839-848.

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. Tchnol. 28:646-654.

Schulthess, C.P., and C.P. Huang. 1990. Adsorption of heavy metals by silicon and aluminum oxide surfaces on clay minerals. Soil Sci. Soc. Am. J. 54:679-688.

Sultsn, K. 2007. Distribution of metals and arsenic in soils of central Victoria (Creswick-Ballarat), Australia. Environ. Contam. Toxicol. 52(3):339-346.

Warren, H.V., and R.E. Delavault. 1960. Observations on the biogeochemistry of lead in Canada. Trans. Roy. Soc. Can. 54:1-20.

Ward, N.I., and R.R. Brooks. 1974. Effect of lead from motor-vehicle exhausts on trees along a major thoroughfare in Palmerston North, New Zealand. Environ. Pollut. 6:149-158.

Xintaras, C. 1992. Analysis paper: Impact of lead-contaminated soils on public health. Agency for Toxic Substances and Disease Registry, Atlanta, Georgia 30333.

Yang, J., R.W. Blanchar, and S.W.Casteel. 1997. Reduction of bioavailable lead by phosphoric acid. Agron. Abstr. 193.

Yang, J.J., D.E. Mosby, S.W. Casteel, and R.W. Blanchar. 2001a. Microscale pH variability for assessing efficacy of phosphoric acid treatment in lead-contaminated soil. Soil Science. 166(6):374-381.

Yang, J.J., D.E. Mosby, S.W. Casteel and R.W. Blanchar. 2001b. Lead immobilization using phosphoric acid in smelter-contaminated urban soil. Environ. Sci. Technol. 35:3553-3559.

Yang, J., D.E. 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. Arch. Environ. Contam. Toxicol. 43:399-405.

Yang, J., and D. Mosby. 2006. Field assessment of treatment efficacy by three methods of phosphoric acid application in lead-contaminated urban soil. Sci. Total Environ. 366(1):136-142.

Yang, Y.G., C.Q. Liu, W.Pan, G.P. Zhang, and W.H. Zhu. 2006. Heavy metal accumulation from zinc smelters in carbonate rock region in HeZhang County, GuiZhou Province, China. 174:321-339.

Zhang, P.C., J.A. Ryan, and J.Yang. 1998. In vitro soil Pb solubility in the presence of hydroxyapatite. Environ. Sci. Technol. 32:2763-2768.

CHAPTER 4

LONG-TERM METAL BIOAVAILABILITY & RISK REDUCTION ASSOCIATED WITH IN-SITU SOIL TREATMENT

ABSTRACT

In-situ soil treatment using phosphate and organic matter is being evaluated as cost-effective remedial technology for immobilizing heavy metals in contaminated soil and for reducing health and ecological risks. However, long-term assessment of metal bioavailability and risk reduction of immobilized metals in soil amended with these treatments is necessary to verify efficacy and gain regulatory and public acceptance of these remedial technologies. In this study three sites, including a smelter-contaminated urban site, a mill waste contaminated site, and a mining waste contaminated site found within the Jasper County Superfund Site, Southwestern Missouri, were investigated to evaluate amendment effects on metal bioavailability and risk reduction. Field plots at the urban site were treated with phosphoric acid at a rate of 10 g kg^{-1} using surface application (SA), rototilling (RT), and pressure injection (PI); plots at the mill waste site were treated with phosphoric acid at rates of 7.5 and 10 g P kg^{-1} using rototilling and incorporation; plots at the mining waste site were treated with different types of organic amendments, including biosolids and agricultural by-products. Soil and plant samples were collected 8 yr (6 yr for mill-waste site) after treatment from experimental plots and analyzed for *in vitro* metal bioavailability, metal phytoavailability, and microbial toxicity. In the urban site, SA reduced *in vitro* bioavailable Pb by 86.8% and RT reduced phytoavailable Pb by 75.2%. In mill-waste site, the application at the rate of 10 g P kg^{-1} soil reduced *in vitro* bioavailable Pb by 88.9%; however, the reduction percentage of this

treatment was 22.3% for Pb phytoavailability. Treatments applied in the mining waste site all reduced in vitro bioavailability of Pb by more than 90%; the best three treatments for both *in vitro* and phytoavailable Pb reduction were SMC, CSS, and P. Most treatments in the three study sites did not significantly impact the soil toxicity to microbes. The results verify that phosphate and organic matter treatments were effective for reducing human and ecological risk several years after initial treatment. Immobilization induced by phosphate and organic matter treatments reduced heavy metal threats to humans, plants, and microorganisms.

INTRODUCTION

By definition, the bioavailability of metals in soil is a measure of the physicochemical access that the metal has to the biological processes of an organism (EPA, 2004). The greatest risk of metals to humans is mainly derived from the fraction of metals that enter the human body through the gastrointestinal (GI) tract (Adriano, 2001). Bioavailability or bioaccessibility of metals in soil is associated with metal dissolution rates in GI tract as well (Zhang et al., 1998; Ruby et al., 1992). Lead is one of the most harmful metals to human health, especially to children under 6 yr of age (Adriano, 2001; Yang et al., 2001; Zhang et al., 1998). Adults can absorb 10% to 15% of total Pb that is ingested from GI tract; however, pregnant women and children can absorb as much as 50% of total ingested Pb (Adriano, 2001). Research indicates that children living in urban areas and smelter communities have obviously different blood Pb levels when the soil Pb concentrations were considerable (Clark et al., 1991). In Jasper County, Missouri, 14% of children under the age of 7 yr were found to have blood Pb levels higher than 100 μg

L^{-1} (City of Joplin Health Department, 1995). Once entering the body from the GI tract or respiratory tract, Pb is primarily distributed in blood and accumulated in soft tissues (e.g., liver, brain, and kidney), and mineralizing tissues (bones and teeth) (ATSDR, 1992, 1993).

It is widely believed that Pb phosphates, including pyromorphites [$Pb_5(PO_4)_3$ (OH, Cl, F…)], are a very stable environmental form of Pb in surface soils and less soluble under equilibrium conditions than oxides, hydroxides, carbonates, and sulfates (Ruby et al., 1994; Zhang et al., 1998; Yang et al., 2001, 2002). Several studies have shown that the application of various sources of P to Pb contaminated soil, such as phosphate rocks (Ma et al., 1995), synthetic hydroxapatite (Xu and Schwartz, 1994; Zhang et al., 1998), and phosphoric acid (Yang et al., 1997, 2001, 2002), results in formation of pyromorphites. Subsequently, concentrations of soluble Pb and bioavailable soil Pb are reduced (Casteel et al., 1997). Several factors were also reported that can influence the bioavailability of metals in the soil, such as, pH, OM, redox potential, and Fe and Mn oxides (Adriano, 2001; Zhang et al., 1998; Yang et al., 2001).

It has been reported that total Pb in soils is usually not a good indicator of Pb bioavailability. Thus, Pb extraction and *in vivo* techniques have been developed to measure bioavailable Pb (Adriano, 2001). The *in vivo* Pb bioavailability test developed by Dr. Stan Casteel at the University of Missouri-Columbia, Veterinary Medical Diagnostic Laboratory was developed through dosing swine with contaminated soil followed by tissue analyses to determine Pb concentrations (Casteel, 1995; Ruby et al., 1996; Schroder et al., 2003). Another bioavailable Pb test, the *in vitro* physiologically based extraction test (PBET), has been used to mimic GI tract conditions and

bioavailability data produced by this test correlatewell with *in vivo* measurement of Pb bioavailability in animal models (Ruby et al., 1996). The fraction of dissolved Pb produced by the *in vitro* procedure is considered as the bioaccessible fraction that can be absorbed by organisms (Ruby et al., 1996). For this project, the less expensive *in vitro* PBET, as described by Ruby et al. (1992) and Yang et al. (2001), was used to measure Pb bioavailability in treated and untreated metal contaminated soils.

Based on the definition of metal bioavailability, the phytoavailability of metals in soil is also a measure of the physicochemical access that the metal has to the biological processes of plants. Phytoavailable metals absorbed by plants can enter the food chain through direct consumption of a plant or via metal absorption by grazing animals that can then threaten human health (Bolan et al., 2003). In 1994, accumulation of Cd in the kidneys and liver of grazing animals in New Zealand and Australia made this food supply unsuitable for human consumption (Roberts et al., 1994). Another episode of Cd bioaccumulation in potato, wheat, and rice crops was reported to seriously impact the local and international agricultural product markets of New Zealand and Australia in year 2000 (McLaughlin et al., 2000).

Higher plants uptake metals dissolved in soil solution via absorption through plant roots (Barber, 1984; Ge et al., 2001). However, metals in soil solution exist as differing aqueous chemical species including free ions, inorganic ion pairs, and organic complexes (Ge et al., 2001). With respect to plant uptake, several studies support the hypothesis that free metal activities represent the most phytoavailable form of heavy metals in soil (Pavan et al., 1982; Sauve et al., 1996, 1998; McGrath, 2001).

The overall phytoavailability of metals in soil is, however, determined not only by

the aqueous metal species, but by metal interactions with soil particles (i.e., sorption reactions), mineral dissolution and precipitation reactions, and soil characteristics (e.g., pH, clay content, OM content, and soil water content; Naidu et al., 2003). Additionally, the growth of plants can modify soil characteristics by means of root exudation and impact contaminant uptake (Gobran et al., 2001). Previous research indicates that plant uptake of Pb is associated with higher soil Pb levels, especially in sandy soils (Baumhardt and Welch, 1972; Rolfe, 1973; Naidu et al., 2003). It has also been determined that the distribution of Pb is mostly in plant roots and only limited amounts of Pb can be translocated to other parts of the plant (Motto et al., 1970; Wallace and Rommy, 1977).

In this thesis, soil toxicity refers to the degree of soil toxicity to soil microorganisms. Chemicals may interact with each other in the soil that the use of bioassay to measure long-term soil toxicity was considered as a convincing and direct way to estimate the soil toxicity (Kungolos et al., 2004). Biomonitoring provides a direct measurement of the environmentally relevant toxicity of contaminated soils, which can be used to assess potential impacts that phosphate-immobilized chemical remediation method might induce (Kungolos et al., 2004). The *V. fischeri* bioluminescence inhibition assay (Microtox™ test) that was used in this project, is a widely used standardized alternative test, which requires little substance and it is not as time-consuming relative to other methods (Kaiser and Palabrica, 1991; Bonnet et al., 2007).

In summary, the risks of *in situ* soil treatment using phosphoric acid to immobilize heavy metals depends on the treatments toxicological effects on humans, plants, and microbial communities. The long-term assessment of risk reduction using phosphate immobilization is needed to verify treatment efficacy, and to gain regulatory and public

acceptance of this remediation technique. Therefore, the objectives of this research were to: (1) measure the *in vitro* bioavailability of heavy metals in contaminated soils amended with phosphate and organic matter using chemical extraction procedures; (2) assess plant uptake of metals from phosphate-treated and organic amended soils using plant tissue analyses; (3) examine the alteration of soil toxicity induced by phosphate treatment as measured using a bacteria-based toxicological analysis.

MATERIALS AND METHODS

Site Descriptions and Soil Treatments

Site location, landscape, history, description of heavy metal contamination, and methods of remediation are described in Chapter 3. Soil and plant sampling and preparation of samples are also described in Chapter 3.

Analysis Procedures

***In vitro* Bioavailability Test:** The *in vitro* bioavailability test is a modified physiology-based extraction test (PBET) that uses chemical extraction procedures to extract bioavailable heavy metals from soil to simulate metal dissolution in the GI tract. Analyses were performed as described in Yang et al. (2001). In brief, the PBET was performed by adding 0.4 g of soil sample to a 100 ml Nalgene bottle containing 40 ml of 0.011 M HCl. Samples were then rotated at 30 rpm at 37 ^{o}C for 60 min on a platform shaker. Solutions were removed using a 10 ml plastic syringe and immediately filtered through Whatman 0.45 µm filter paper. Prior to analysis of Pb concentration via inductively coupled plasma – optical emission spectroscopy (ICP-OES), filtrates were diluted with deionized water.

Phytoavailability Test: Concentrations of Pb and Cd in plants collected from the experiment area are important indexes to judge risk and stability of the treatment. To determine concentrations of these metals in plants, plant samples from each plot were oven-dried (70 °C) for at least 24 h and ground. Plant samples (0.5 g) were weighted and microwave-digested in 15 ml of concentrated HNO_3 and 2 ml H_2O_2 for 20 min. Supernatant solutions were filtered through 0.45 μm Whatman filter paper and diluted to a volume of 25 ml with deionized water. Metal concentrations in solution were then determined using an ICP-OES.

ICP Analysis: For ICP-OES analyses, samples were diluted 10 times in deionized water (18 MΩ cm, Millipore Milli-Q). Varian's ICP-OES Expert software, which provided automatic analysis and nine decades of linear calibration range, controlled the procedures fully and detected the standard solution every 15 samples for quality control. The standard reference material for the analysis, SRM 1640 Trace Elements in Natural Water, was purchased from the National Institute of Standards and Technology.

The Microtox™ Test: The Microtox™ test is a bacteria-based assay that tests potential toxicity of contaminants to microorganisms and it can be used for determining contaminant toxicity in a variety of soil or water environments. This assay was conducted using the marine bacteria *Vibro fischeri*, a strain of *Photobacterium phosphoreum*, which is self-luminescent and responds to toxic environments by decreasing luminescence. Luminescence emitted by *Vibro fischeri* was measured photometrically as cells responded to contaminants after 15 min of contact, and the toxicity of contaminants to the bacteria was determined by comparison of luminescence produced in control samples (i.e., no contaminants). To perform this test, 2.5 g of soil was reacted in 20 ml of

deionized water (1:8 w/v solid to solution ratio) for 18 h. After reaction, 2.5 ml of extract was used to test for toxicity using the microorganism *Vibro fischeri* and the Microtox™ Model 500 Analyzer. Analyses were conducted within three days after end of the reaction period.

Statistical Analysis

Data were analyzed using standard of analysis of variance (ANOVA) for treatment, time and the interaction of treatment and time for a randomized block design using the general two-way ANOVA analysis procedure in Statistix 8.1. Critical values (CV) and least significant differences (LSD) were calculated to separate means of each treatment or time at the 5% probability level.

RESULTS AND DISCUSSION

Urban Site - *In vitro* Bioavailability

Statistical analysis revealed that *in vitro* bioavailable Pb in the contaminated soil was significantly ($P<0.01$) reduced by all the three H_3PO_4 application methods used at the urban site (Figure 4.1). However, *in vitro* bioavailable Pb was not significantly affected by season or treatment by season interaction ($P>0.05$). The order of reduction percentages for *in vitro* Pb at the urban site was SA (86.8%) > RT (81.8%) > PI (71.3%). This indicates that the SA treatment induces the highest mean reduction of bioavailable Pb in the two-year sampling period relative to other treatments. It was later confirmed (see Figure 6.2 in Chapter 6) that the sum of bioavailable Pb fractions in each soil, as determined using the modified method of Chang and Jackson (1957), followed the order: Control (16%)> PI (15%) > SA (1%) = RT (1%).

Hettiarachchi et al (2001) reported a significant reduction of *in vitro* Pb after the

treatment of 2500 mg kg^{-1} phosphoric acid in contaminated soil in Joplin area. The reduction of bioavailable Pb in the soil was similar with the result (66%) of the field amendment for the same soil with 1% phosphoric acid by Brown et al (2004). This result is also in agreement with Yang and Mosby (2006) where it was observed that the SA application has the greatest (higher than 80%) efficiency for reducing *in vitro* soil Pb in the urban surface soil and PI has the lowest efficiency rate among the three H_3PO_4 treatments. The reducing of *in vitro* Pb suggested that PA treatments had transformed part of soil Pb to less bioavailable forms. For the PI treatment, the redistribution rate of injected P was greatly dependent on diffusion process and controlled by PA gradients around the injected zone (Yang and Mosby, 2006). The reduction percentage of PI was relatively low, because the rate of diffusion was normally slow and could decrease with time (Yang and Mosby, 2006). Furthermore, in this study a higher reduction in *in vitro* Pb (71.3%) was observed than the reduction percentage (51%) observed by Yang and Mosby (2006). Differences between the two studies may be due to greater spread and better mixing of P within the soil matrix with time. Precipitation, leaching, soil enzyme activities, and root exudates may have also contributed to P reaching, thus, helping to transform labile Pb to more stable forms.

When the data were analyzed to compare the mean bioavailable Pb in soils across the sample dates (Figure 4.2), significant differences were observed. For example, in October 2004, soil had the highest mean bioavailable Pb and the lowest values of bioavailable Pb were found in March 2004 and September 2005. The reduction of *in vitro* bioavailable Pb by three treatment methods, relative to the control, was significant in every sampling date, even 8 yr after application.

Figure 4.3 shows that all three application methods can reduce *in vitro* bioavailable Cd, but only the SA and PI methods significantly ($P<0.01$) reduce *in vitro* Cd. This result demonstrated that soil Cd was partially transformed into lower bioavailable forms. The Cd reduction percentage of 38.5% for the SA was the highest rate in the urban site. These results are in agreement with other studies demonstrating that P application to metal contaminated soils can reduce the bioavailability of metals other than Pb, although the technique is less effective (Ma et al.1994; EPA, 2004). Season and treatment by season interactions also influence the *in vitro* bioavailable Cd concentrations in soil significantly ($P<0.01$). Significant differences of bioavailable Cd were observed among five sample dates as well (Figure 4.4). From October 2004 to February 2006, both the lowest concentrations of *in vitro* bioavailable Pb and Cd were observed in June 2005.

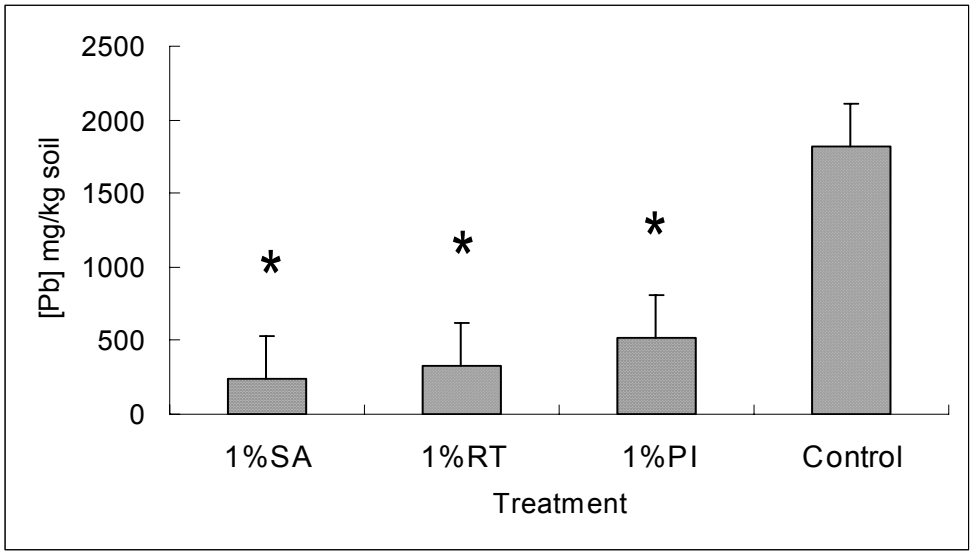


Figure 4.1. Mean *in vitro* bioavailable Pb (mg kg^{-1} soil) from six sample dates for soils collected at the urban site. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

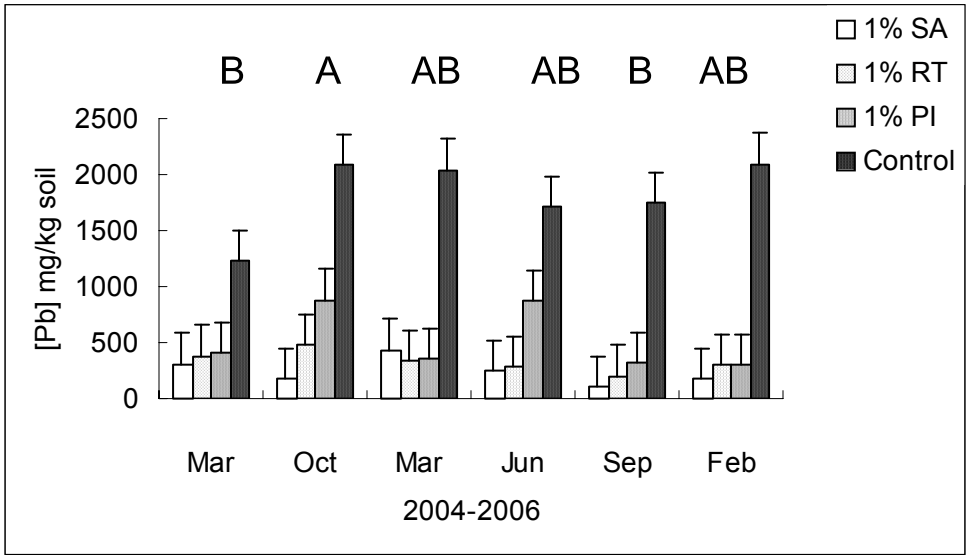


Figure 4.2. *In vitro* bioavailable Pb (mg kg^{-1} soil) in soils collected from the four treatment methods at the urban site on differing dates. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate the critical value (CV) (α=0.05).

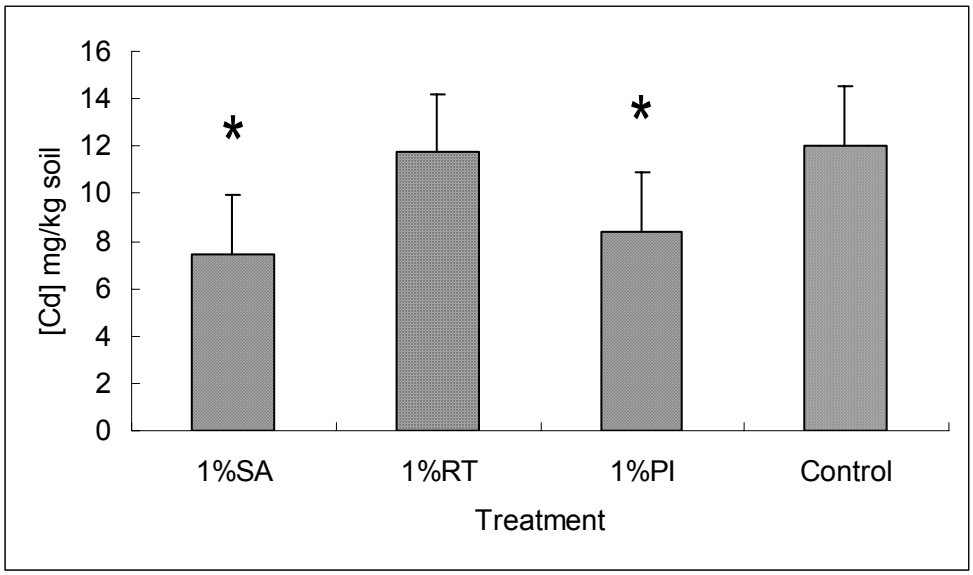


Figure 4.3. Mean *in vitro* bioavailable Cd (mg kg^{-1} soil) from five sample dates for soils collected at the urban site. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

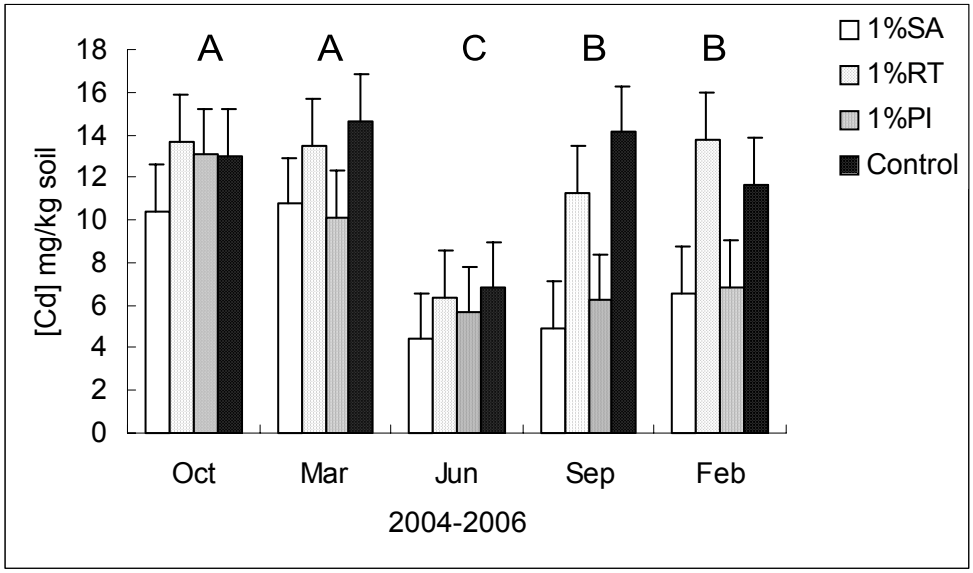


Figure 4.4. *In vitro* bioavailable Cd (mg kg^{-1} soil) in soils collected from the four treatment methods at the urban site on differing dates. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate the critical value (CV) (α=0.05).

Urban Site – Phytoavailability

Figure 4.5 shows that all three treatments significantly reduced phytoavailable Pb ($P<0.01$); however, the RT treatment resulted in the lowest concentration of Pb in plant tissue. Plant uptake of Pb was found strongly correlated with the concentration of free ions of Pb in the soil (Ge et al., 2002). The reduction of phytoavailable Pb indicates the reduction of free Pb ions in the soil, as well as the transformation of less phytoavailable Pb was induced by the PA application. This finding coincides with the result from Brown et al (2004), where it was reported that plant uptake of Pb was reduced by the 1% PA application in the field of Joplin area. Season and treatment by season interaction did not significantly affect Pb phytoavailability ($P>0.05$). The order of reduction percentages of phytoavailable Pb at the urban site was RT (75.2%) > SA (66.3%) > PI (58.5%). The rhizosphere for plant roots is mainly distributed in the surface soil horizon, where the plants absorb nutrients and heavy metals. Yang and Mosby (2006) reported that the order for the concentration of bioavailable Pb from the depth of 5 cm to 20 cm was PI > SA > RT, and this order is completely the same with that observed in this study. Significant differences of mean phytoavailable Pb was discovered only between June 2005 and the other sample dates (Figure 4.6). The highest mean concentration of phytoavailable Pb in plant tissues was found in June 2005, and this corresponds with the greatest amount of precipitation and plant growth during the year. Except for September 2005, all treatment applications significantly reduced phytoavailable Pb in the soil.

Similar to the phytoavailable Pb results, phytoavailable Cd can be reduced significantly ($P<0.01$) by all the three application methods (Figure 4.7). This finding suggests that PA application can also reduce the amount of phytoavailable Cd by

transforming labile Cd into less phytoavailable Cd in the contaminated soil. No significant difference ($P>0.05$) of Cd availability was observed by season and the treatment-season interaction, the highest mean concentration of phytoavailable Cd in plant tissues was found in June 2005 (Figure 4.7). The highest phytoavailable Cd reduction percentage was induced by the RT treatment (74.3%). However, the PI treatment did not always significantly reduce phytoavailable Cd in the contaminated soil on different sampling dates.

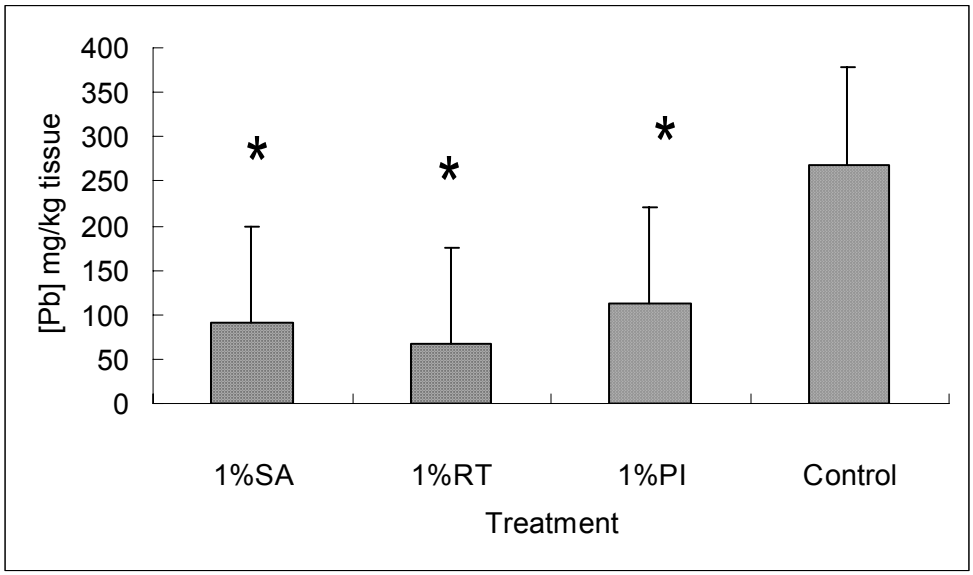


Figure 4.5. Mean phytoavailable Pb (mg kg^{-1} tissue) from four sample dates for plant samples collected at the urban site. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

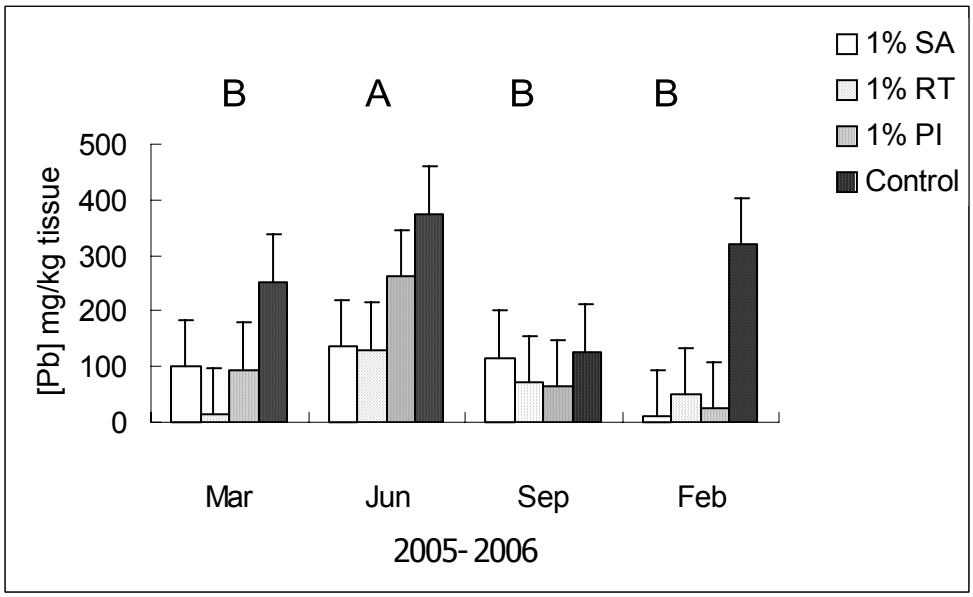


Figure 4.6. Phytoavailable Pb (mg kg^{-1} tissue) in tissue samples collected from the four treatment methods at the urban site on differing dates. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate critical value (CV) (α=0.05).

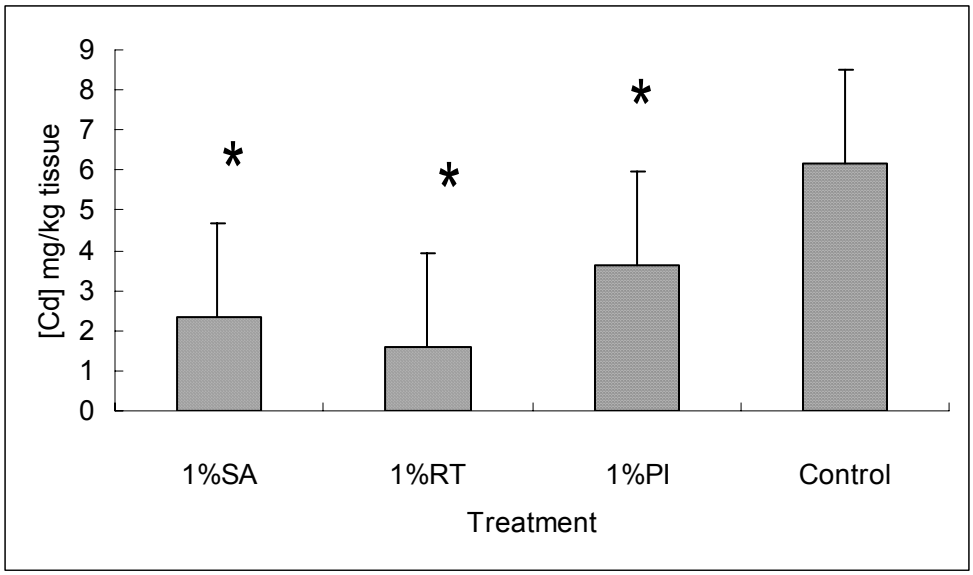


Figure 4.7. Mean phytoavailable Cd (mg kg^{-1} tissue) from four sample dates for plant samples collected at the urban site. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

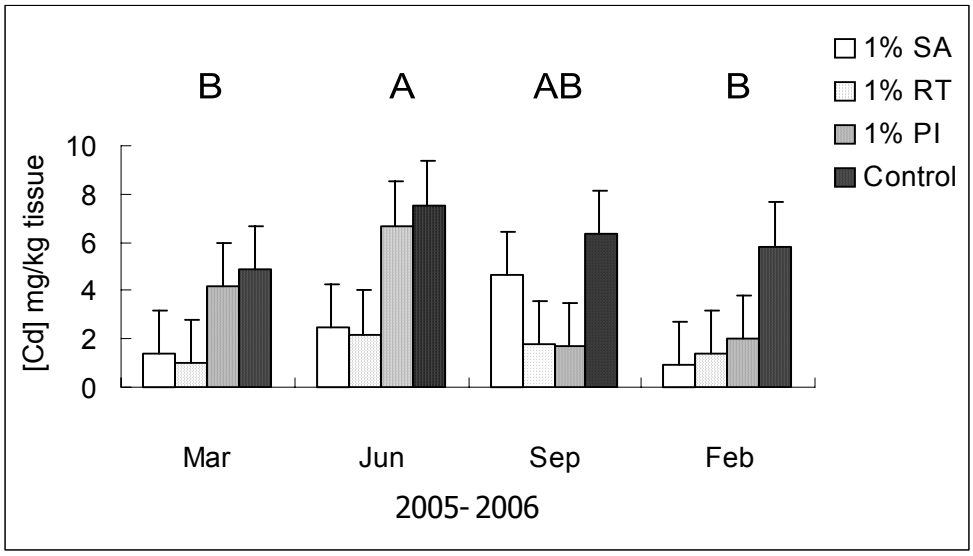


Figure 4.8. Phytoavailable Cd (mg kg^{-1} tissue) in tissue samples collected from the four treatment methods at the urban site on differing dates. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate critical value (CV) (α=0.05).

Urban Site - Relationship Between *in vitro* Bioavailable Pb and Phytoavailable Pb

Figure 4.9 shows the relationship between mean concentrations of *in vitro* bioavailable Pb and mean phytoavailable Pb for four sampling dates at the urban site. From the figure, a significant correlation can be observed between bioavailable tests (r^2=0.82, P<0.01). The high degree of correlation indicates that the amount of of *in vitro* bioavailable Pb is highly related with that of phytoavailable Pb in the urban soil. Correlation between these two parameters was not as strong when treatments were evaluated independently as evidenced by low r^2 values for SA (r^2=0.226) and RT (r^2=0.4096) data sets; however, the r^2 value for PI treated soils substantially higher (r^2=0.9371).

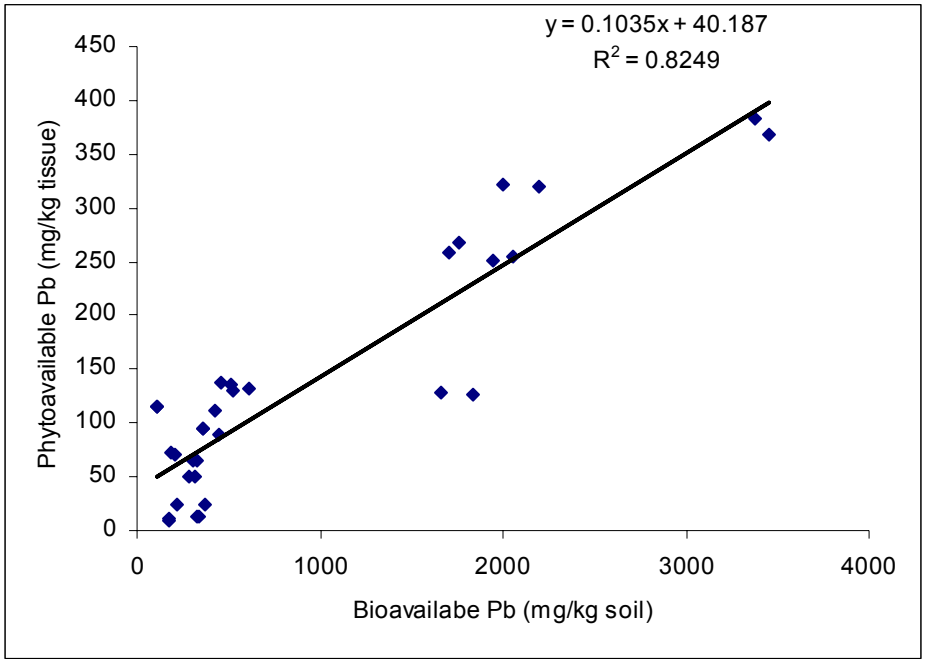


Figure 4.9 Correlation between *in vitro* Pb and phytoavailable Pb for the urban site.

Urban Site - Microbial Toxicity (Microtox™ test)

Microbial toxicities of treated and untreated soil at the urban site were significantly affected by treatment ($P<0.01$), but not by the season and treatment-season interaction ($P>0.05$). As shown in Figure 4.10, though SA application slightly increased soil microtoxicity, the RT and PI applications reduced the microtoxicity of contaminated soil significantly. This result indicates that the application of phosphoric acid did not negatively impact soil toxicity and in two of the three treatments soil toxicity was significantly reduced. The RT method had the lowest percent effect among three treatment methods. Research of Kao et al (2005) reported that the increasing of soil metal concentration could increase the microbial toxicity of the soil. However, the linear relationship between toxicity and metal bioavailability is positive but weak ($y= 0.0043x + 55.86$; $R^2= 0.071$). One possible explanation for this occurrence is that the Microtox test works not only for heavy metals, but also for pure chemicals, complexed compounds, and samples of prokaryotic organisms (Bonnet et al., 2007). The remediation of metal-contaminated soil might alter these factors and, subsequently, influence results from the Microtox™ test.

Based on the statistic analysis of microbial toxicities of four treatment methods in different sample dates (Figure 4.11), there is no significant difference among first three sample dates, but an increase in toxicity was observed in September 2005 and February 2006. No single treatment consistently reduced toxicity significantly over the four sampling dates, and no treatment reduced microbial toxicity significantly in February 2006 (Figure 4.11).

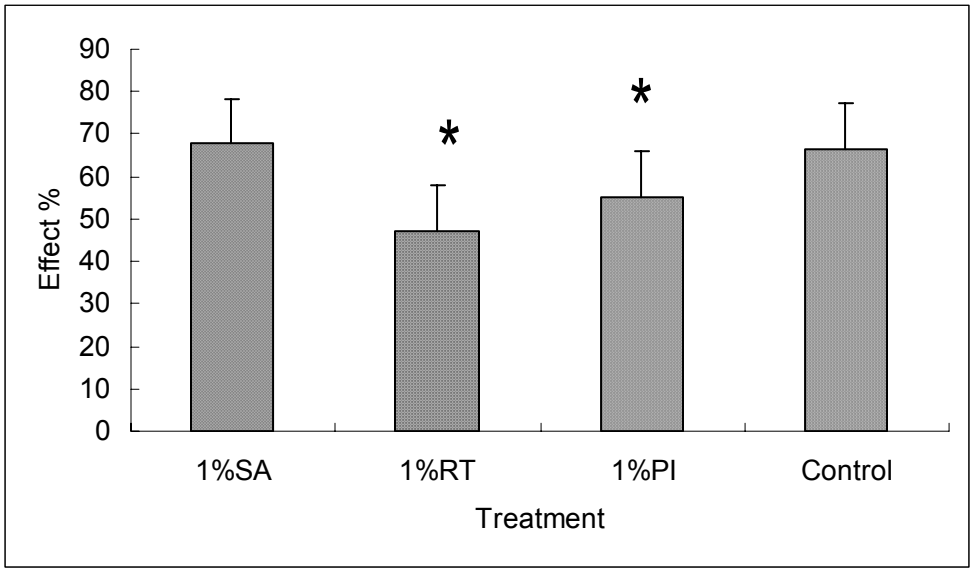


Figure 4.10. Mean microbial toxicities determined for soils collected on four sample dates at the urban site. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

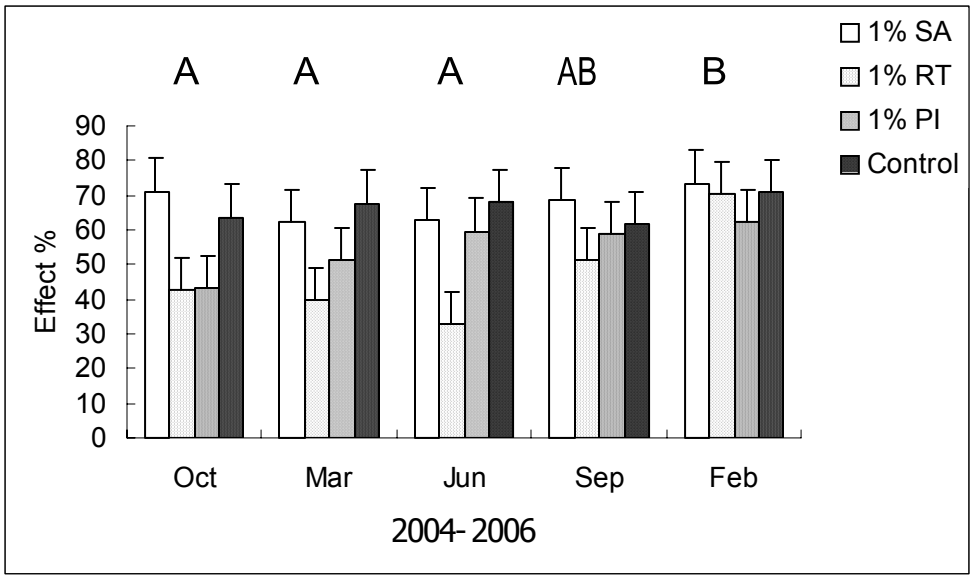


Figure 4.11. Microbial toxicities for soils collected from the four treatment methods at the urban site on differing dates. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate critical value (CV) (α=0.05).

Mill-Waste Site - *In vitro* Bioavailability Results

According to the statistic analyses (Figure 4.12), 1% PA and 0.75% PA application rates reduced *in vitro* bioavailable Pb in the soil significantly ($P<0.05$). However, season and treatment by season interaction did not have significant efforts to the reduction ($P>0.05$). The application rate of 1% PA had a higher reduction percentage of *in vitro* bioavailable Pb (88.9%) than 0.75% PA (73.1%) based on six sampling dates. This confirms previous hypotheses that increasing the rate of P application increases the reduction of *in vitro* bioavailable Pb (Yang et al., 2001; Hettiarachchi et al., 2001). The result also indicates that the treatments are long-term effective. Significant differences are also observed for mean bioavailable Pb in soils sampled on different dates (Figure 4.13). Soil collected in March 2004 had the highest mean bioavailable Pb, whereas, the lowest value was found in February 2006. Additionally, it was also noted that *in vitro* bioavailable Pb in the treated soils were not always significantly reduced in every season.

Results for *in vitro* bioavailable Cd are similar to that of Pb (Figures 4.14 and 4.15). Significant effects were seen by treatment ($P<0.05$), but not by the season and treatment-season interaction ($P>0.05$). The two treatment methods reduced *in vitro* Cd significantly, and 0.75% PA had the highest Cd reduction percentage (37.4%; Figure 4.14). Significant differences were observed among the mean Cd bioavailability values on different sampling dates (Figure 4.15), and the data follow a seasonal trend similar to bioavailable Cd at the urban site (Figure 4.4). The highest values were observed for the October 2004 and March 2005 sampling dates, the lowest value of bioavailable Cd was found for the June 2005 sampling date. Both treatments reduced soil bioavailable Cd in every sample date, but the effect was not always statistically significant.

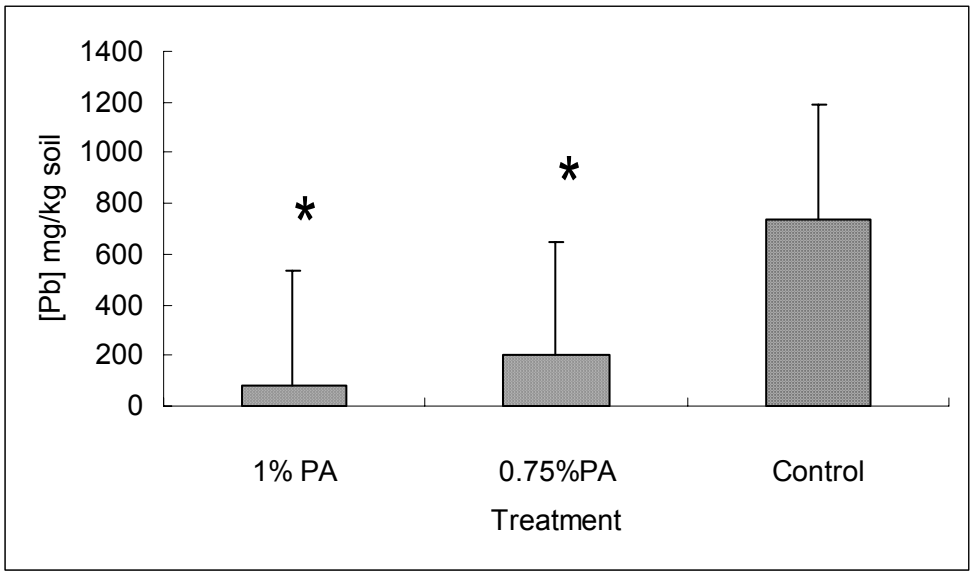


Figure 4.12. Mean *in vitro* bioavailable Pb (mg kg^{-1} soil) from six sample dates for soils collected at the mill-waste site. 1% PA: 10 g P kg^{-1} soil; 0.75% PA: 7.5 g P kg^{-1} soil; Control: no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

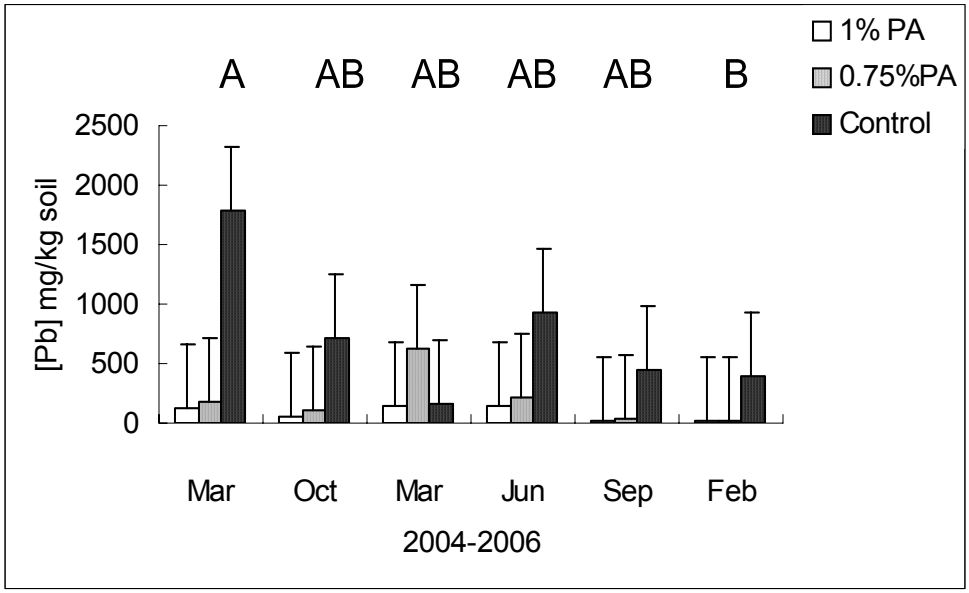


Figure 4.13 *In vitro* bioavailable Pb(mg kg^{-1} soil) for three treatment methods at the mill-waste site for each sample date. 1% PA: 10 g P kg^{-1} soil; 0.75% PA: 7.5 g P kg^{-1} soil; Control: no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate the critical value (CV) (α=0.05).

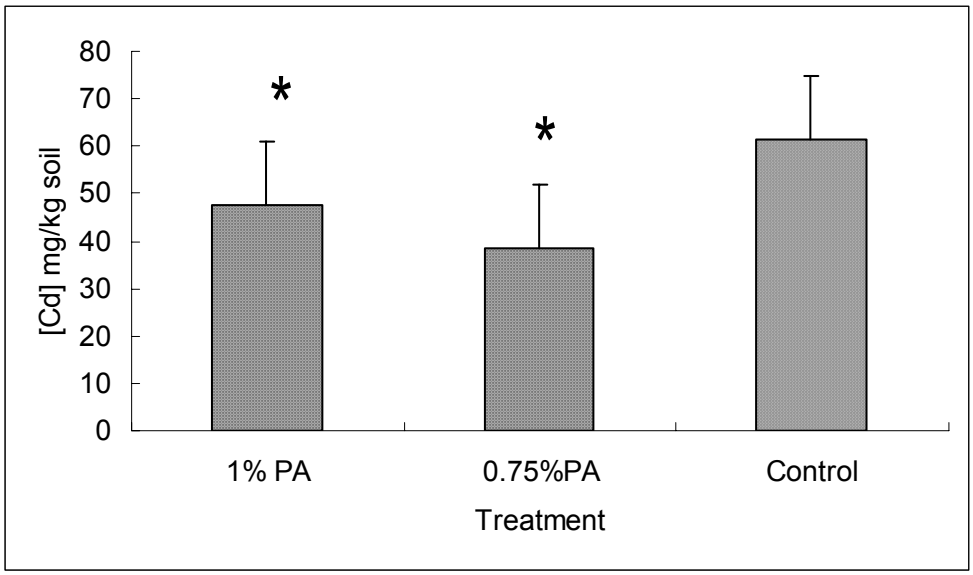


Figure 4.14 Mean *in vitro* bioavailable Cd (mg kg^{-1} soil) from six sample dates for soils collected at the mill-waste site. 1% PA: 10 g P kg^{-1} soil; 0.75% PA: 7.5 g P kg^{-1} soil; Control: no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

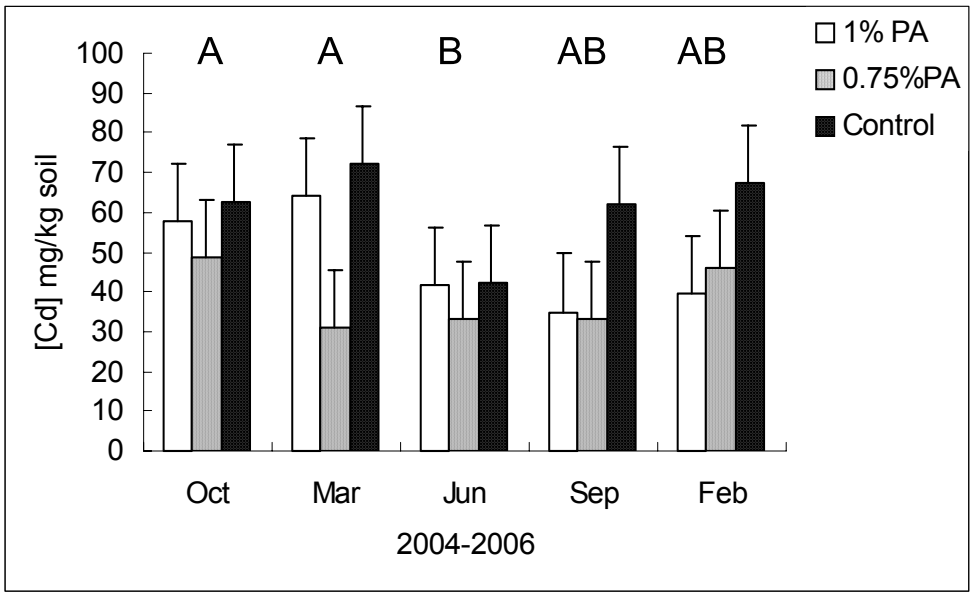


Figure 4.15 *In vitro* bioavailable Cd (mg kg^{-1} soil) for three treatment methods in the mill-waste site for each sample date. 1% PA: 10 g P kg^{-1} soil; 0.75% PA: 7.5 g P kg^{-1} soil; Control: no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate the critical value (CV) (α=0.05).

Mill-Waste Site - Phytoavailability

Statistic analysis indicates phytoavailable Pb at the mill-waste site was not impacted by treatment, sampling date, and treatment by date interactions ($P>0.05$). The 1% PA treatment did reduce the phytoavailability of Pb by 22.3%, but the reduction was not significant (Figure 4.16). In June 2005, plants had the highest concentration of Pb in their tissues and in September 2005 tissue Pb concentrations were lowest (Figure 4.17). This trend is very similar to phytoavailability data collected for the urban site plant samples. Based on annual precipitation in the Joplin area (see figure in Appendix 2) and seasonal trends in phosphatase enzyme activity at the mill-waste site (Hoilett, 2006), June 2005 was wet month and microbial activity in the soil was high. These factors may have accelerated plant absorption of nutrients and Pb, thus increasing Pb in plant tissue. The mean phytoavailable Pb in September 2005 was significantly lower than the other sample dates that may relate to very low soil organic matter in that month based on data from (Hoilett, 2006). Figure 4.17 also shows that there was no significant reduction in phytoavailable Pb in plots treated with 1% PA treatment on the different sampling dates.

With respect to phytoavailable Cd, analysis of the data revealed that treatment, season, and treatment by season interactions did not significantly influence the concentration of phytoavailable Cd at the mill-waste site ($P>0.05$). No reduction in phytoavailable Cd was observed; however, a slight increase of Cd concentration in plant tissues was observed in the 1% PA treated plots (Figure 4.18). This result suggests that 1% PA application was not effective for reducing phytoavailable Cd in the mill-waste soil. Figure 4.19 shows that there was no significant difference among the various sampling dates, and the 1% PA method did not always reduce the phytoavailable Cd.

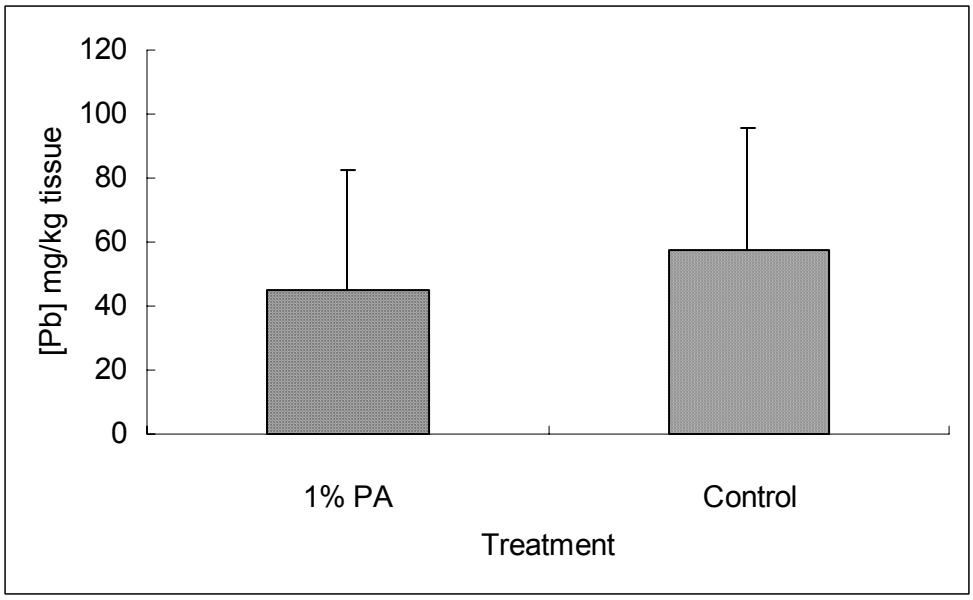


Figure 4.16 Mean phytoavailable Pb (mg kg^{-1} tissue) from four sample dates for Mill-waste Site. 1% PA: 10 g P kg^{-1} soil;; Control: no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

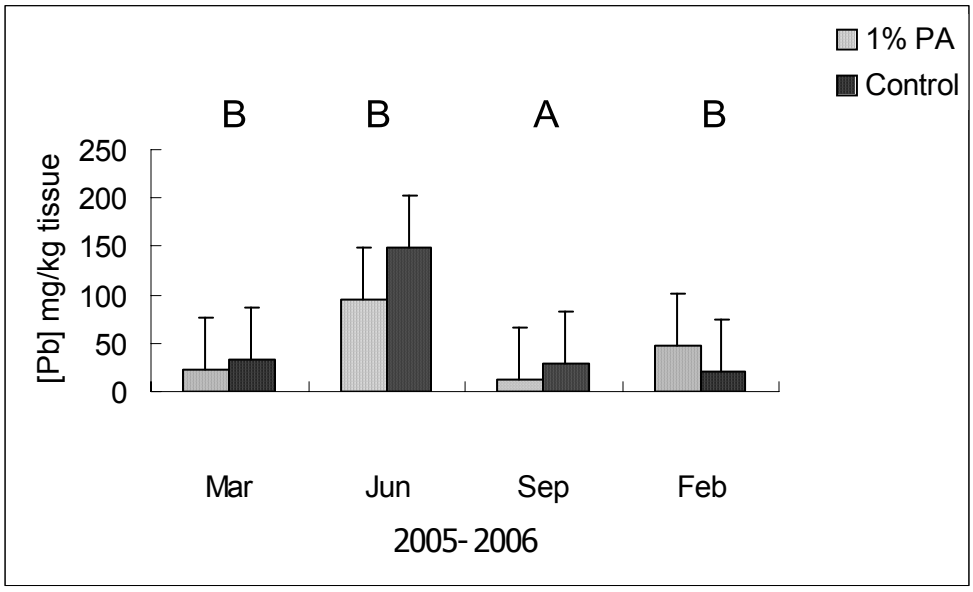


Figure 4.17 Phytoavailable Pb (mg kg^{-1} tissue) for three treatment methods in the mill-waste site for each sample date. 1% PA: 10 g P kg^{-1} soil;; Control: no treatment.. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate critical value (CV) (α=0.05).

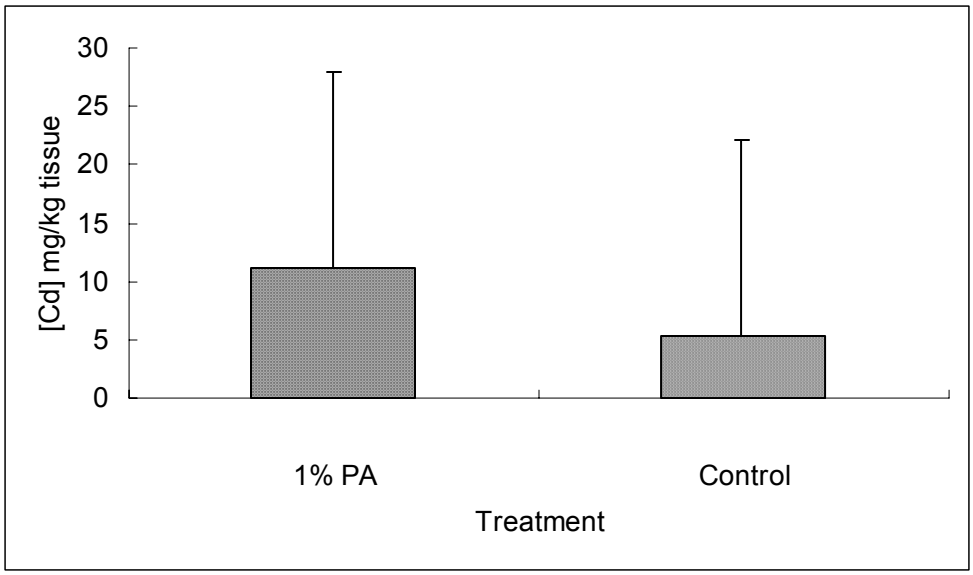


Figure 4.18 Mean phytoavailable Cd (mg kg^{-1} tissue) from four sample dates for Mill-waste Site. 1% PA: 10 g P kg^{-1} soil;; Control: no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

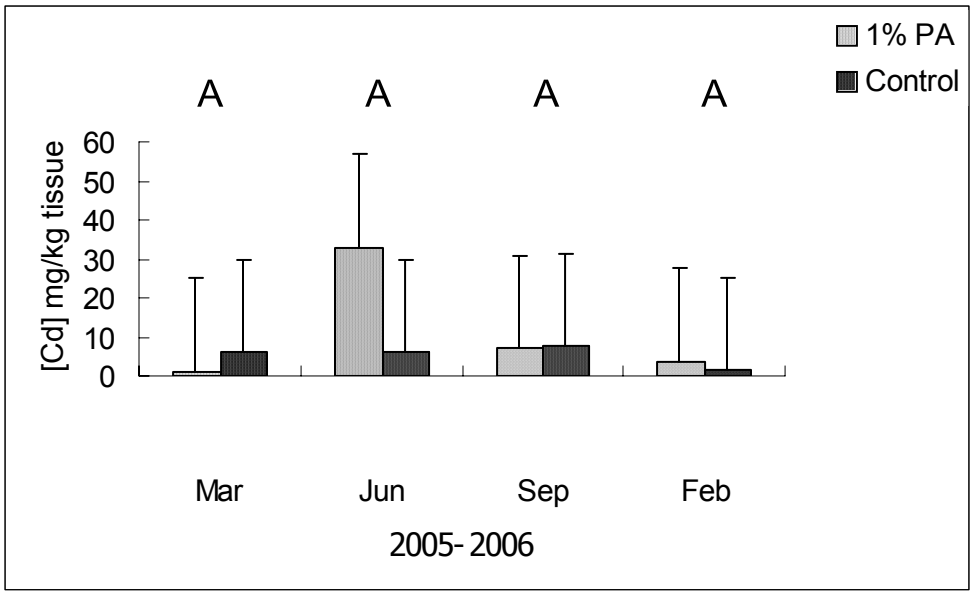


Figure 4.19 Phytoavailable Cd (mg kg^{-1} tissue) for three treatment methods in the Mill-waste Site for each sample date. 1% PA: 10 g P kg^{-1} soil;; Control: no treatment.. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate critical value (CV) (α=0.05).

Mill-Waste Site - Relationship Between *in vitro* Bioavailable and Phytoavailable Pb

Figure 4.20 represented the correlation between mean concentrations of *in vitro* bioavailable Pb and mean phytoavailable Pb for four sampling dates in the soil of the mill-waste site. From the figure, a strong correlationship (R^2=0.61) is observed between the measurement, regardless of different sampling dates. This indicates that the amount of *in vitro* bioavailable Pb was highly related with that of phytoavailable Pb in the mill-waste soil.

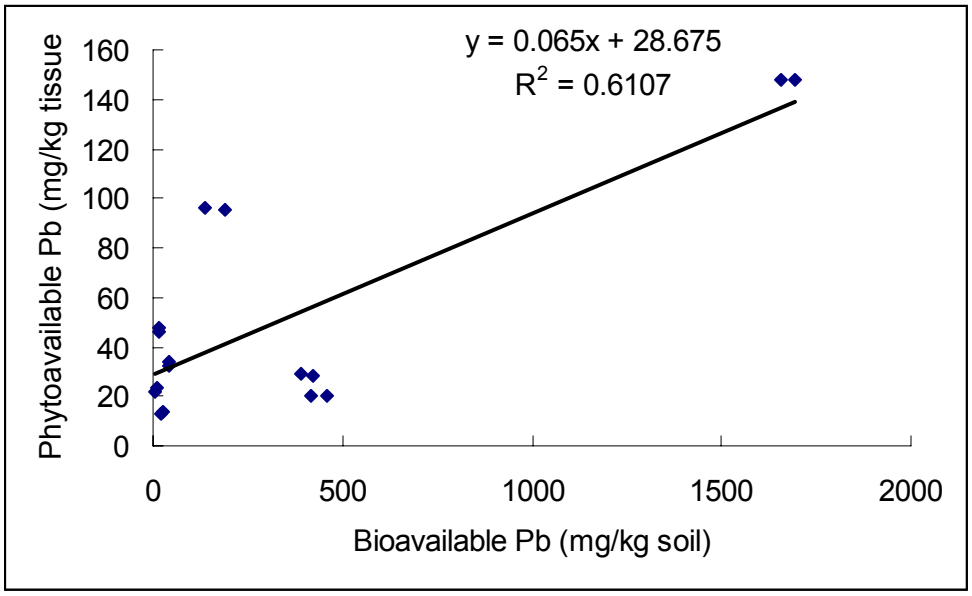


Figure 4.20 Correlation between *in vitro* Pb and phytoavailable Pb for the mill-waste site.

Mill-Waste Site - Microbial toxicity (Microtox™ test)

The statistic analysis of microbial toxicity of three treatment methods at the mill-waste site indicates that treatment did not significantly influence toxicity of the soil to microorganisms ($P>0.05$), but season and treatment by season interactions did affect the toxicity significantly ($P<0.05$). Data analysis also indicates that the 1% PA treatment slightly increased microbial toxicity of soil, and the 0.75% PA treatment significantly increased toxicity (Figure 4.21). This finding is in agreement with Hoilett (2006), where it was observed that phosphate-treated soil had lower microbial activity than the control. Hoilett (2006) also observed that 0.75% PA had a lower mean pH (5.35) than the 1% PA (pH 5.50) and control (pH 5.85) treatments. Lower pH may be the main reason for the higher toxicity of these treatments to microbes. No significant correlation was found between results of toxicity test and concentrations of bioavailable metals (data not shown).

Figure 4.22 shows that soils collected in March and June 2005 had significantly higher mean microbial toxicities than soils collected on the other three dates. Soils collected from seasons exhibiting lower microbial toxicity seasons (i.e., October 2004, September 2005, and February 2006), microbial toxicity of the treated soils was observed to be significantly higher than the control (untreated) soil. This trend is similar to the trend observed for phytoavailability of metals at the mill-waste.

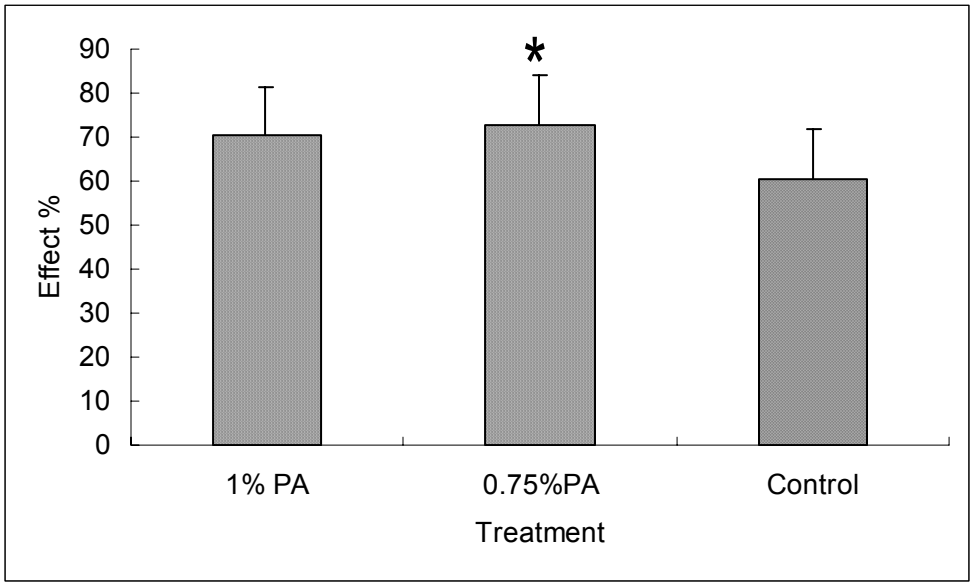


Figure 4.21 Mean microbial toxicities determined for soils collected on four sample dates at the Mill-waste Site. 1% PA: 10 g P kg^{-1} soil; 0.75% PA: 7.5 g P kg^{-1} soil; Control: no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

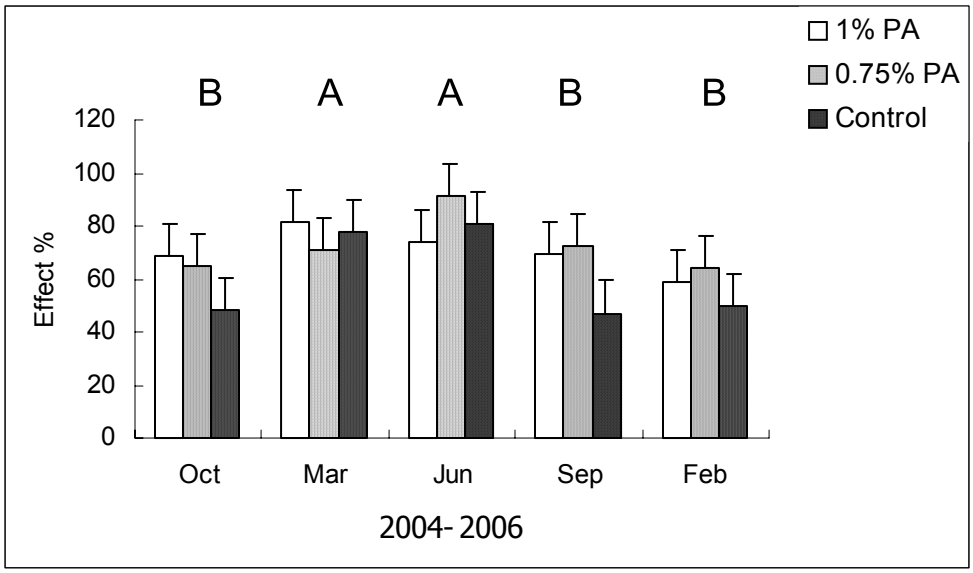


Figure 4.22 Microbial toxicities for soils collected from the three treatment methods at the Mill-waste Site on differing dates. 1% PA: 10 g P kg^{-1} soil; 0.75% PA: 7.5 g P kg^{-1} soil; Control: no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate critical value (CV) (α=0.05).

Mining Waste Site - *In vitro* Bioavailability

In vitro bioavailable soil Pb at the mining waste site was significantly affected by treatment ($P<0.01$), but not by the season and treatment by season interaction ($P>0.05$). All treatment methods were found to significantly reduce bioavailable Pb concentrations in the contaminated soil (Figure 4.23). This result suggests that the OM treatments can transform bioavailable Pb into less bioavailable Pb forms. The hierarchy for the reduction percentages of bioavailable Pb among treatments based on t-tests is CSS (99.2%) > SMC (99.1) > P (98.5%) > TL (98.3%) > MD (98.1%) > EPA (97.8%) > CL (97.4%) > RS (96.5%) > MDM (95.7%) > CSSH (94.8%). It indicates that composted OM had higher reduction efforts than uncomposted OM, which can be explained by the stability of their longer chains (Brady and Weil, 2002). Figure 4.24 shows no significant difference among six sample dates, and all of the treatments reduced bioavailable

Statistic analysis for *in vitro* bioavailable soil Cd concentrations in the mining waste site revealed that treatment significantly affected bioavailable Cd in the soils tested ($P<0.01$), but season and treatment by season interaction did not significantly affect measured concentrations ($P>0.05$). Only three treatments reduced bioavailable Cd (CSS, MD, and TL), but no treatment significantly reduced bioavailable Cd in soils collected from the mining waste site (Figure 4.25). The hierarchy for the concentration of bioavailable Cd among treatments was MDM > CSSH > RS > EPA > CL > P > UN > SMC > TL > MD > CSS. MDM increased soil bioavailable Cd significantly, while MD reduced bioavailable Cd. The only difference between MDM and MD was that some topsoil (2 parts of topsoil and 1 part of MD) was mixed with MD prior to application to create MDM. The different content of MDM may cause changes in soil pH or OM content that increased bioavailable Cd in the soil. Alternatively, the additive topsoil introduced Cd into the site, thus, increasing bioavailable Cd significantly. Among the five sampling dates (Figure 4.26), a significant difference was observed between the highest mean concentration of bioavailable Cd (February 2006) and the lowest mean concentration (June 2005).

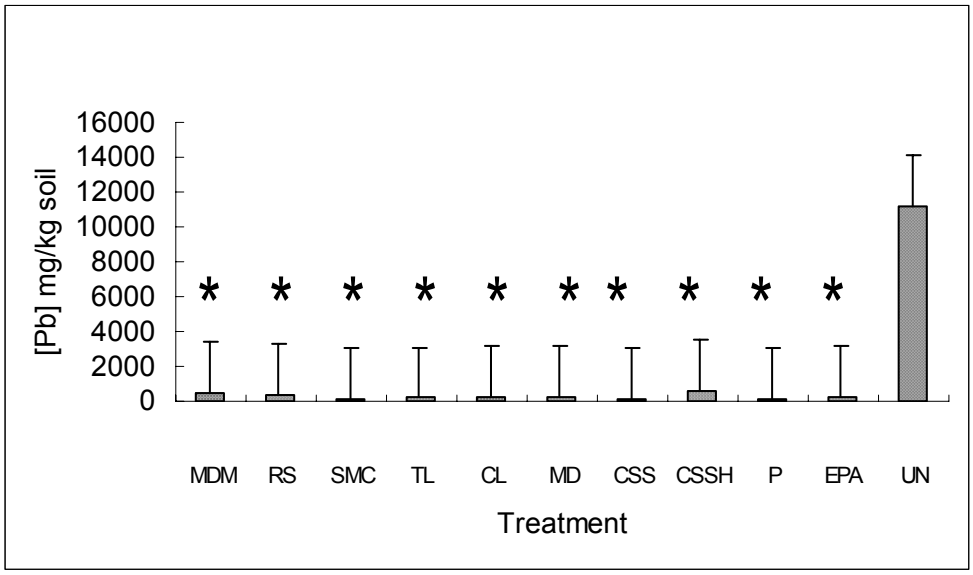


Figure 4.23 Mean *in vitro* bioavailable Pb (mg kg^{-1} soil) from six sample dates for soils collected at the mining waste site. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

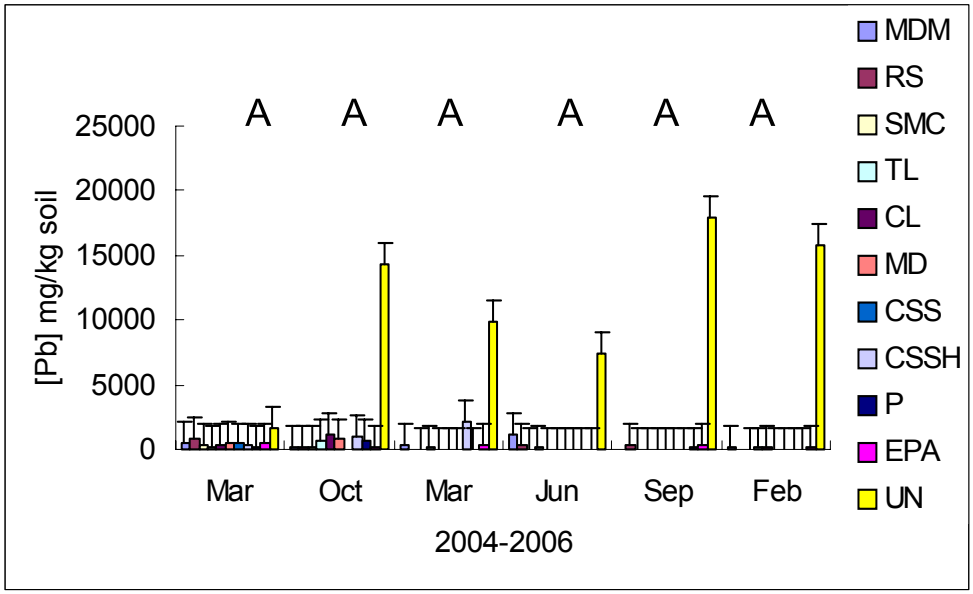


Figure 4.24 *In vitro* bioavailable Pb(mg kg^{-1} soil) for eleven treatment methods at the mining waste site for each sample date. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate the critical value (CV) (α=0.05).

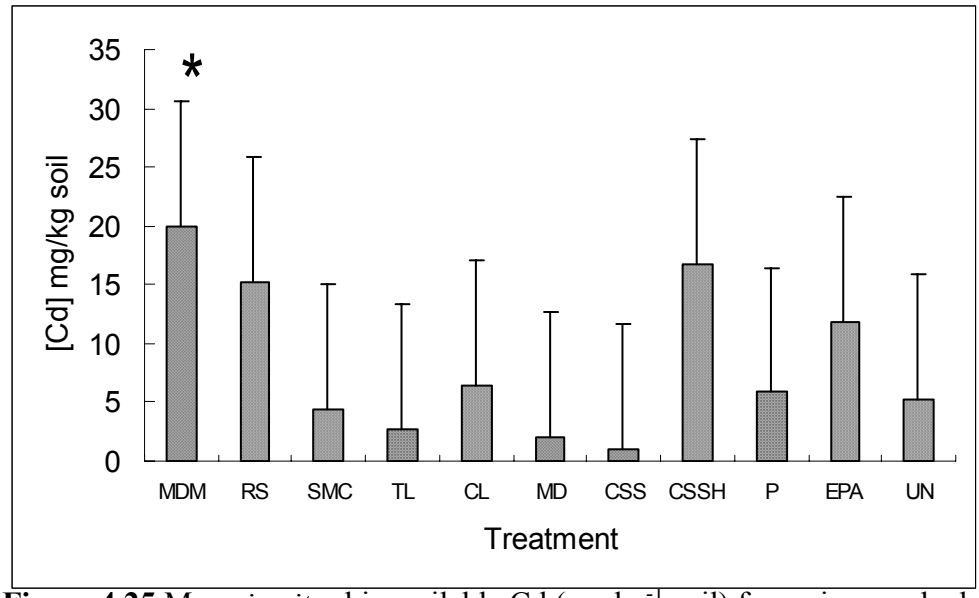


Figure 4.25 Mean *in vitro* bioavailable Cd (mg kg^{-1} soil) from six sample dates for soils collected at the mining waste site. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

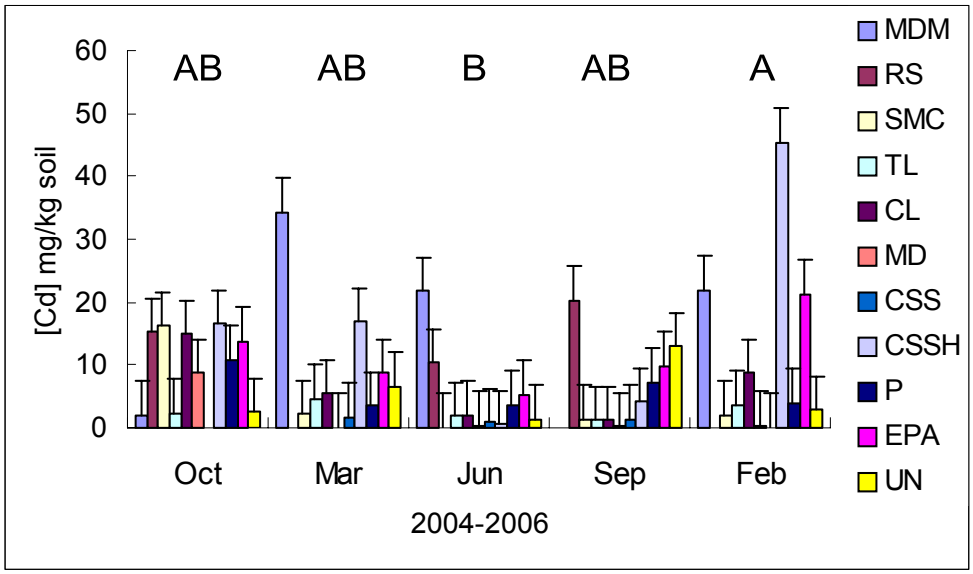


Figure 4.26 *In vitro* bioavailable Cd (mg kg^{-1} soil) for eleven treatment methods at the mining waste site for each sample date. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate the critical value (CV) (α=0.05).

Mining Waste Site - Phytoavailability

Statistic analysis of the Pb phytoavailability data revealed that treatment, season, and treatment by season interaction did not significantly affect Pb phytoavailability within the mining waste plots ($P>0.05$). Although no plants are growing on untreated soils at the site, phytoavailabile Pb of the treated soils can still be used as an index to judge effects induced by the various treatments. The hierarchy for concentrations of phytoavailable Pb among treatments (Figure 4.27) based on t-tests was RS > CSSH > EPA > CSS > TL > CL > P > MDM > SMC > MD. It should be noted that the SMC, CSS, and P treatment methods rank in the top five treatments for reducing of both *in vitro* bioavailable and phytoavailable Pb in the soil. When data were analyzed across the four sample dates, no significant differences in time were observed (Figure 4.28).

Based on the statistic analysis for phytoavailable Cd, treatment had no significant effect ($P>0.05$). However, season and treatment by season interaction affected phytoavailable Cd significantly ($P<0.05$). The hierarchy for the concentration of phytoavailable Cd among treatments (Figure 4.29) based on t-tests was CSSH > MDM > TL > P > CL > EPA > RS > CSS > SMC > MD. The three best treatment methods for reducing *in vitro* bioavailable and phytoavailable Cd were SMC, MD, and CSS. Among the four sampling dates, the concentration of phytoavailable Cd was significantly higher in September 2005, relative to the other sampling dates (Figure 4.30).

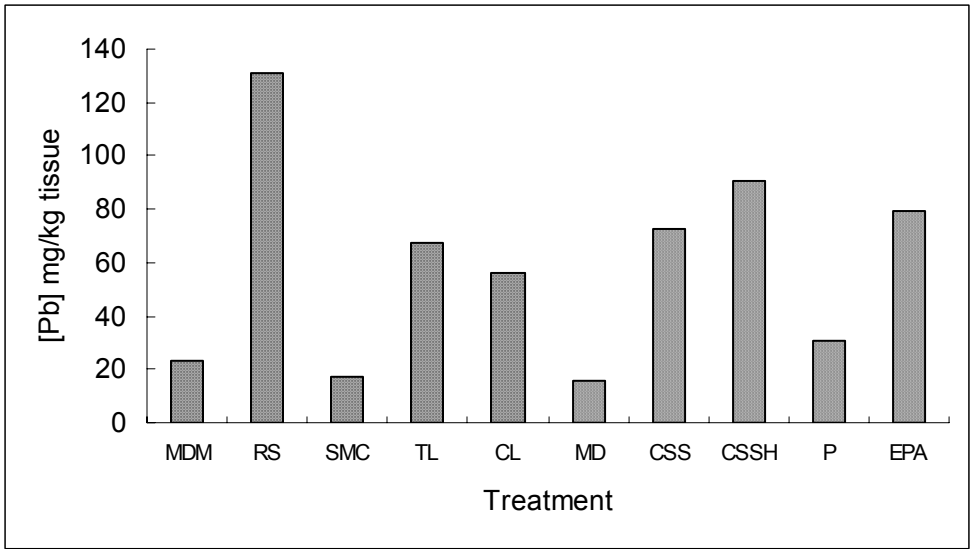


Figure 4.27 Mean phytoavailable Pb (mg kg^{-1} tissue) from four sample dates for the mining waste site. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository.

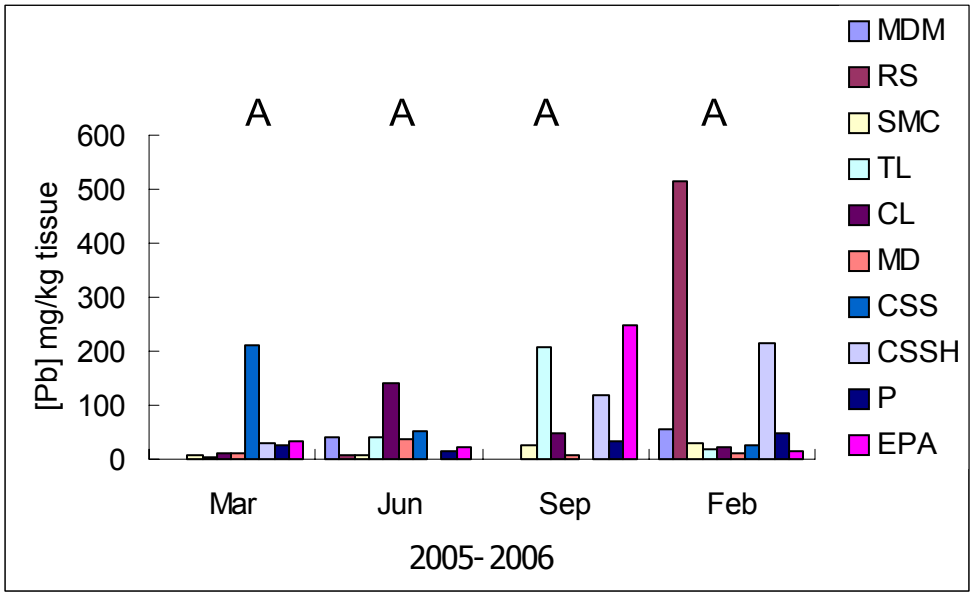


Figure 4.28 Phytoavailable Pb (mg kg^{-1} tissue) for three treatment methods at the mining waste site for each sample date. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. (α=0.05).

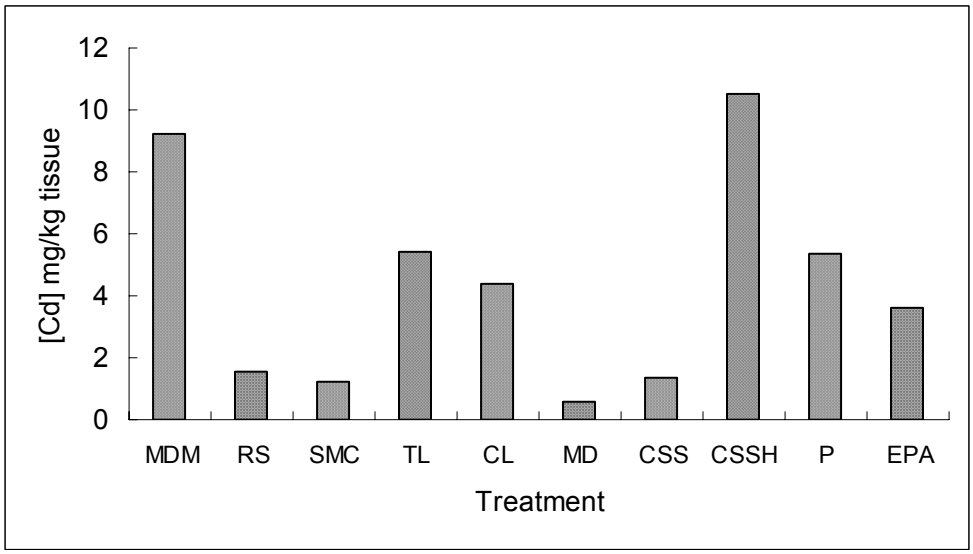


Figure 4.29 Mean phytoavailable Cd (mg kg^{-1} tissue) from four sample dates for the mining waste site. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository.

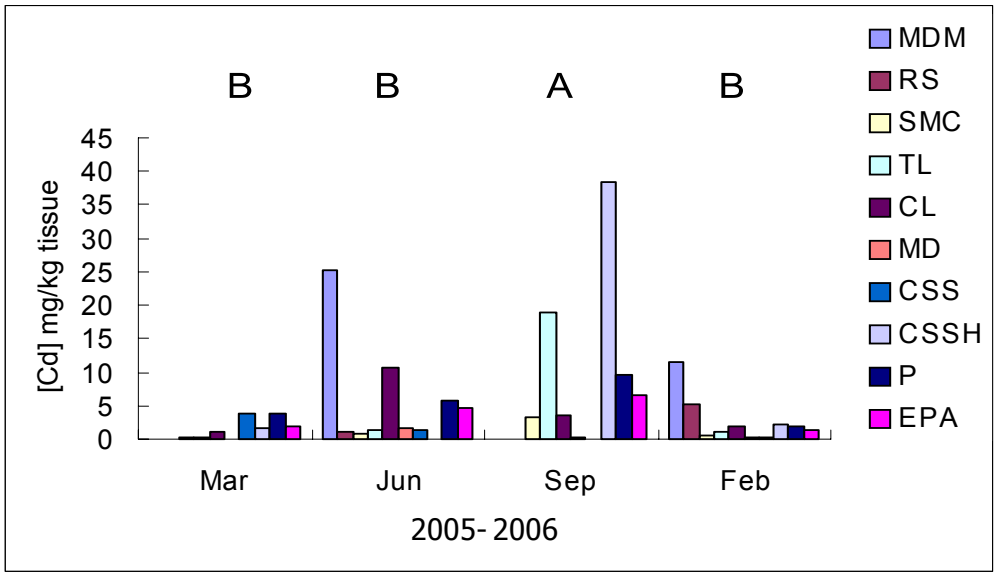


Figure 4.30 Phytoavailable Cd (mg kg^{-1} tissue) for three treatment methods at the mining waste site for each sample date. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. (α=0.05).

Mining Waste Site - Relationship Between *in vitro* Bioavailable Pb and Phytoavailable Pb

Figure 4.31 represented the correlation between mean concentrations of *in vitro* bioavailable Pb and mean phytoavailable Pb for four sampling dates in the soil of the mining waste site. The treatments included in this figure were SMC, TL, CL, MD, CSS, P, and EPA. From the figure, we observe that there is no clear relationship ($r^2 = 0.0055$) between *in vitro* bioavailable Pb and pytoavailable Pb at this site.

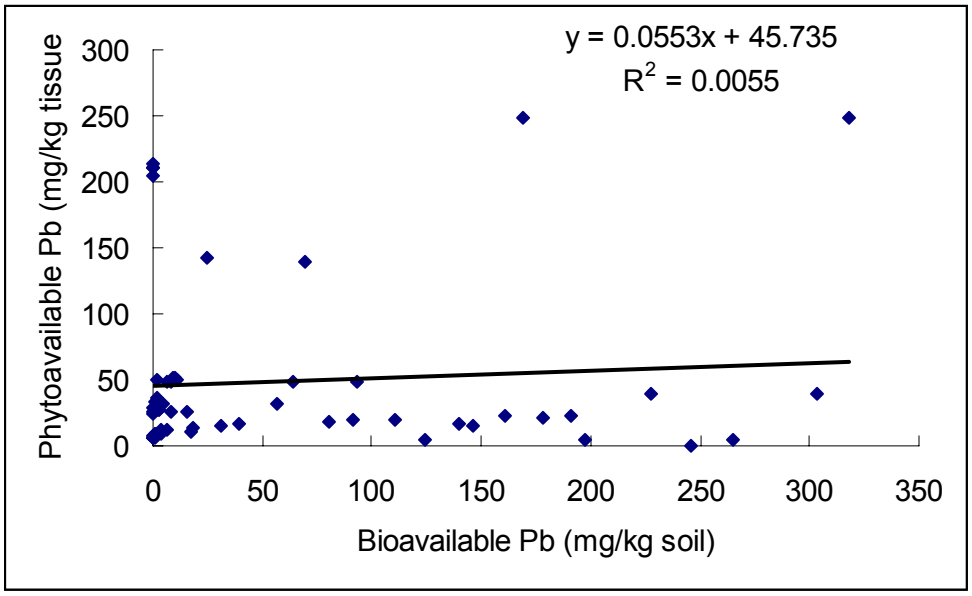


Figure 4.31 Correlation between *in vitro* Pb and phytoavailable Pb for the mining waste site.

Mining Waste Site - Microbial toxicity (Microtox™ test)

The statistic analysis of microbial toxicity data collected for the eight treatment methods at the mining waste site indicates that treatment, season, and treatment by season interactions affected microbial toxicity significantly ($P<0.05$). Based on Figure 4.32, all treatments increased microbial toxicity of the soil except EPA treatment, but the increase was significant only for the CSSH treatment. The toxicity of each treatment plot was not correlated with the concentration of bioavailable metals measured at this site (data not shown). The hierarchy for the microbial toxicities among treatments was CSSH > MDM > P > CL > SMC > TL > UN > EPA. The order of soil microbial toxicity does not completely comply with the order of Pb concentration in the soil, because the bacteria are sensitive to not only heavy metals but also some other factors, such as, chemicals and soil pH, etc.

Statistic analysis of mean microbial toxicities of determined for the eight treatment methods on four different sample dates indicate that all sampling dates were significantly different from each other (Figure 4.33). The P treatment always increased microbial toxicity of the mining soil, slightly, for each date sampled.

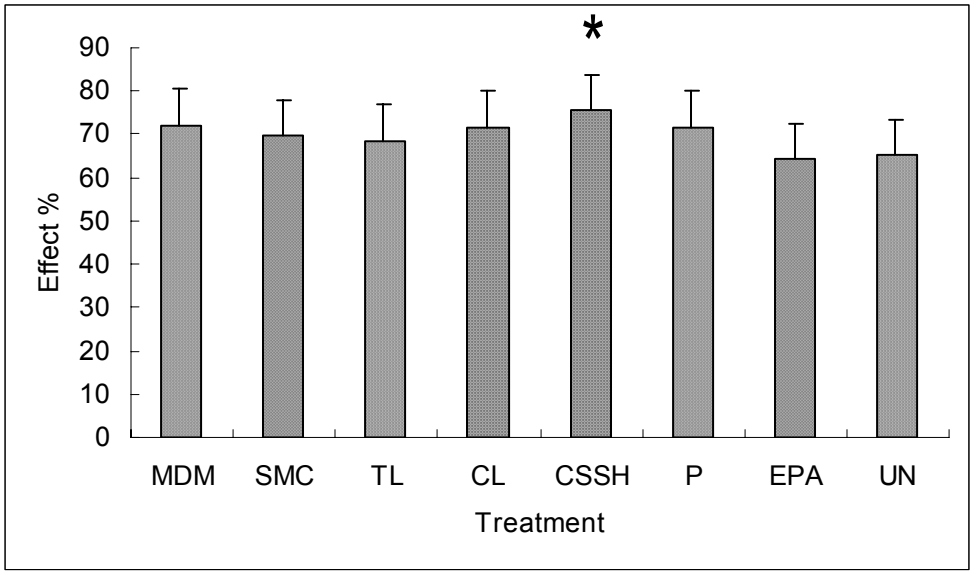


Figure 4.32 Mean microbial toxicities determined for soils collected on four sample dates at the mining waste site. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

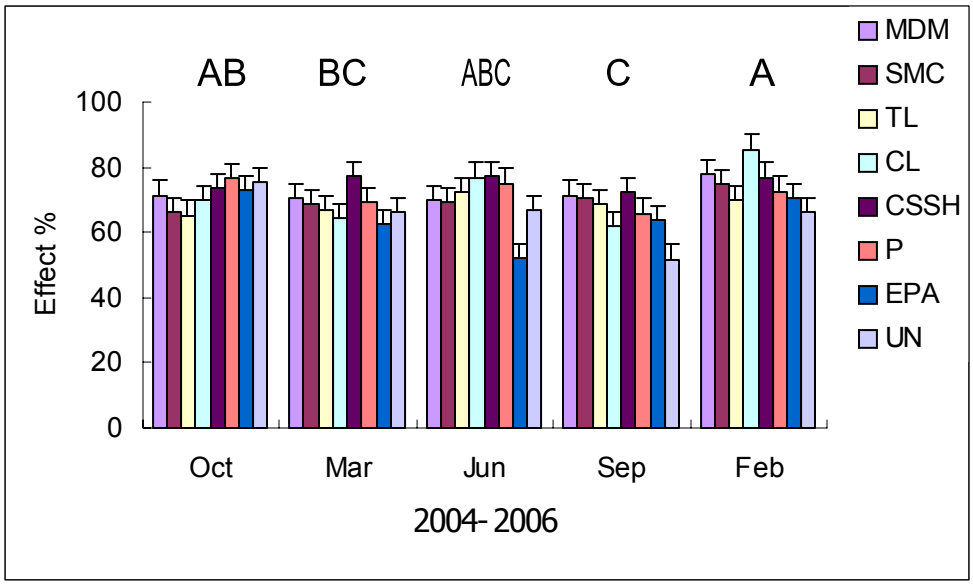


Figure 4.33 Microbial toxicities for soils collected from the eleven treatment methods at the mining waste site for each sample date. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate the critical value (CV) (α=0.05).

CONCLUSIONS

Examination of *in vitro* bioavailablity and phytoavailability of Pb and Cd, and soil toxicity to microorganism at three sites amended with phosphoric acid and organic matter indicates that these amendments are viable *in situ* remediation technologies. Application of phosphoric acid to urban site plots reduced *in vitro* bioavailable and phytoavailable Pb and Cd, and the treatments did not impact soil toxicity to microorganisms. At the mill-waste site, application of phosphoric acid at rates of 0.75 and 1% was shown to reduce *in vitro* bioavailable metals significantly. However, the reduction of phytoavailable Pb was not significant; and the treatment did not reduce phytoavailable Cd in the mill-waste site. Both 0.75% and 1% PA treatments increased soil microbial toxicity, but increases at the 1% PA were not significant. Results for the mining waste site suggest that all treatments can significantly reduce *in vitro* bioavailable Pb; however, only SMC, TL, MD, and CSS reduced *in vitro* bioavailable Cd. The SMC and CSS treatments appear to be the best treatment options located at this site as they were found to reduce *in vitro* bioavailable and phytoavailable metals (e.g. Pb and Cd). Except for CSSH, treatments did not impact soil toxicity to microbes significantly.

LITERATURE CITED

Adriano, D.C. 2001. Trace elements in terrestrial environments biogeochemistry, bioavailability, and risks of metals, 2nd edition. Springer-Verlag, New York.

ATSDER (Agency for Toxic Substances and Disease Registry). 1992. Lead Toxicity. U.S. Dept Health and Human Services, Atlanta, GA.

ATSDER (Agency for Toxic Substances and Disease Registry). 1993. Toxicological Profile of Lead. U.S. Dept Health and Human Services, Atlanta, GA.

Barber, S.A. 1984. Soil nutrient bioavailability: a mechanistic approach. John Wiley, New York.

Baumhardt, G.R., and L.F. Welch. 1972. Lead uptake and corn growth with soil applied lead. J. Environ. Qual. 1:92-94.

Bolan, N.S., and V.P. Duraisamy. 2003. Role of inorganic and organic soil amendments on immobilization and phytoavailability of heavy metals: a review involving specific case studies. Aust. J. Soil Res. 41:533-555.

Bonnet, J.-L., F. Bonnemoy, M. Dusser, and J. Bohatier. 2007. Assessment of the potential toxicity of herbicides and their degradation products to nontarget celld using two microorganisms, the bacteria vibrio fischeri and the ciliate tetrahymena pyriformis. Environ. Toxicol. 22(1):78-91.

Brady, N., and R. Weil. 2002. The nature and property of soils. Prentice Hall, Upper Saddle River, NJ.

Brown, S., R. Chaney, J. Hallfrisch, J.A. Ryan, and W. R. Berti. 2004. In situ soil treatments to reduce the phyto- and bioavailability of lead, zinc, and cadmium. J. Environ. Qual. 33:522-531.

Casteel, S.W. 1995. Project manual for systemic availability of lead to young swine from subchronic administration of lead-contaminated soil. Veterinary medical diagnostic laboratory, University of Missouri-Columbia, Columbia, MO.

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.

Chang, S.C., and M.L. Jackson. 1957. Fractionation of soil phosphorus. Soil Sci.

84:133-144.

City of Joplin Health Department. 1995. Report to Jasper County EPA Superfund citizen's task force: 1995. City of Joplin Health Department, Joplin, MO.

Clark, S., R. Bornschein, P. Succop, S. Roda, and B. Peace. 1991. Urban lead exposures of children in Cincinnati, OH. Chem. Speciation Bioavailability. 3:163-167.

Ge, Y., P. Murry, S. Sauve, and W. Hendershot. 2001. Low metal bioavailability in a contaminated urban site. Environ. Toxicol. Chem. 21(5):954-961.

Hettiarachchi, G.M., and G.M. Pierzynski. 2002. In situ stabilization of soil lead using phosphorus and manganese oxide: influence of plant growth. J. Environ. Qual. 31:564-572.

Kao, P-H., C.C. Huang, and Z.Y. Haeu. 2005. Response of microbial activities to heavy metals in a neutral loamy soil treated with biosolid. Chemosphere 64:63-70.

Kaiser, K.L.E., V.S. Palabrica. 1991. Photobacterium phosphoreum toxicity data index. Water Pollut. Res. J. Can. 26:361-364.

Kungolos, A., S. Hadjispyrou, M. Petala, V. Tsiridis, P. Samaras, and G.P. Sakellaropoulos. 2004.Toxic Properties of metals and organotin compounds and their interactions on daphnia magna and vibrio fischeri. Water, Air, Soil Pollut. 4:101-110.

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. 27:1118-1126.

McGrath, S. 2001. Bioavailability of metals to soil microbes. p. 69-86. *In* H. Allen (ed.) Bioavailability of metals in terrestrial ecosystems: importance of partitioning for bioavailability to invertebrates, microbes and plants. SETAS, Pensacola, FL.

McLaughlin, M.J., R.E. Hamon, R.G. McLaren, T.W. Speir, and S.L. Rogers. 2000. A

bioavailability-based rational for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. Aust. J. Soil Res. 38:1037-1086.

Motto, H.S., R.H. Daines, D.M. Chilko, and C.K. Motto. 1970. Lead in soils and plants: its relationship to traffic volume and proximity to highways. Environ. Sci. Technol. 4:231-237.

Naidu, R., D. Oliver, and S. McConnell. 2003. Heavy metal phytotoxicity in soils. p. 235-241. *In* A. Langley et al. (ed.) Proceedings of the fifth national workshop on the assessment of site contamination, Adelaide, Australia. May. 2002. SA. Austraila.

Paven, M.A., F.T. Bingham, and P.F. Pratt. 1982. Toxicity of aluminum to coffee in ultisols and oxisols amended with $CaCO_3$, $MgCO_3$, and $CaSO_4 \cdot 2H_2O$. Soil. Sci. Sco. Am. J. 46:1201-1207.

Robert, A.H.C., R.D. Lomghurst, and M.W. Brown. 1994. Cadmium status of soild, plant and grazing animals in New Zealand. New Zealand Journal of Agricultural Research 37:99-107.

Rolfe, G.L. 1973. Lead uptake by selected tree seedlings. J. Environ. Qual. 2:153-157.

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. Tchnol. 28:646-654.

Ruby, M.V., A. Davis, R. Schoof, S. Eberle, and C.M. Sellstone. 1996. Estimation of lead and arsenic bioavailability using a physiologically based extraction test. Environ. Sci. Technol. 30:422-430.

Sauve, S., N. Cook, W.H. Hendershot, and M.B. McBride. 1996. Linking plant tissue concentrations and soil copper pools in urban contaminated soils. Environ. Pollut. 94:153-157.

Schroder, J.L., N.T. Basta, J.T. Si, S.W. Casteel, T. Evans, and M. Payton. 2003. In vitro gastrointestinal method to estimate relative bioavailable cadmium in contaminated soil. Environ. Sci. Technol. 37:1365-1370.

Wallace, A., and E.M. Romney. 1977. Trace Elements in the terrestrial environment. *In* H. Drucker et al. (ed.) Biological implications of metals in the environment. CONF-750929. NTIS, Springfield, VA.

Xu, Y., and F.W. Schwartz. 1994. Lead immobilization by hydroxyapatite in aqueous solutions. J. Contam. Hydrol. 15:187-206.

Yang, J., R.W. Blanchar, and S.W.Casteel. 1997. Reduction of bioavailable lead by phosphoric acid. Agron. Abstr. 193.

Yang, J.J., D.E. Mosby, S.W. Casteel, and R.W. Blanchar. 2001a. Microscale pH variability for assessing efficacy of phosphoric acid treatment in lead-contaminated soil. Soil Science. 166(6):374-381.

Yang, J.J., D.E. Mosby, S.W. Casteel and R.W. Blanchar. 2001b. Lead immobilization using phosphoric acid in smelter-contaminated urban soil. Environ. Sci. Technol. 35:3553-3559.

Yang, J., D.E. 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. Arch. Environ. Contam. Toxicol. 43:399-405.

Zhang, P.C., J.A. Ryan, and J.Yang. 1998. In vitro soil Pb solubility in the presence of hydroxyapatite. Environ. Sci. Technol. 32:2763-2768.

CHAPTER 5

LEACHABILITY OF HEAVY METALS AND PHOSPHATE IN PHOSPHATE- AND ORGANIC-AMENDED SOILS

ABSTRACT

In-situ soil treatment using phosphate and organic matter is being evaluated as cost-effective remedial technology for immobilizing heavy metals in contaminated soil and for reducing health and ecological risks. However, long-term assessment of metal and phosphorus stability or leachability and water quality in soil amended with these treatments is necessary to verify efficacy and gain regulatory and public acceptance of these remedial technologies. In this study three sites, including a smelter-contaminated urban site, a mill waste contaminated site, and a mining waste contaminated site found within the Jasper County Superfund Site, Southwestern Missouri, were investigated to evaluate amendment effects on metal and phosphorus leachibility and water quality. Field plots at the urban site was treated with phosphoric acid at a rate of 10 g P kg^{-1} using surface application, with and without incorporation, and subsurface injection; plots at the mill waste site were treated with phosphoric acid at rates of 7.5 and 10 g P kg^{-1} using surface application and incorporation; plots at the mining waste site were treated with different types of organic amendments. Soil and water samples were collected 8 yr (6 yr for mill-waste site) after treatment from experimental plots and analyzed for P, Pb and Cd leachability and concentrations of these ions in water samples. The phosphoric acid applications in urban and mill-waste sites all significantly increased P leachability in the soil. However, the Pb and Cd leachability were reduced by 98.7% and 58.9% at most with the RT treatment in the urban soil; and the maximum leachable Pb and Cd reduction

in the mill-waste site was 86.4% and 57.2%, respectively. In the mining waste site, only TL, CL, and MD significantly increased P leachability. All treatments nearly 100% reduced Pb leachability in this site; and the leachable Cd reduction percentage ranged from 16.9% (EPA) to 94.9% (CSS). The results show that all P and organic applications enhanced leaching of P; however, most of the applications reduced soil Pb and Cd leaching significantly.

INTRODUCTION

Heavy metals in soil can present ecological and human health risks when leached into surface or ground waters from metal contaminated areas (Robinson et al., 2006; Yang et al., 2002; Zhang et al., 2004). This is of concern because even slight heavy metal concentration increases in water resources can be hazardous to ecological systems (Borg and Johansson, 1989). The leachability (i.e., potential for leaching or metal migration) of heavy metals in soil depends on physical and chemical associations and metal solubility (Bubb and Lester, 1991; Zhang et al., 2004). Based findings from metal sequential extractions studies, water soluble and exchangeable forms are the most mobile and labile metal fractions within soil environments. Thus, these fractions exhibit higher leaching potentials than other less soluble metal fractions (Brummer, 1986; Li and Shuman, 1996).

Soil pH is considered an important chemical parameter governing Pb solubility and leachability in soils (Adriano, 2001; Alvarez et al., 2001; Yang et al., 2002). For example, changes in soil exchangeable Pb fractions as a function of pH were observed in contaminated soils from Upper Silesia, Poland. When soil pH was less than pH 5.6, more exchangeable Pb was present than when soil pH >5.6 (Chlopecka et al., 1996). Lead

exists primarily as Pb^{2+} species in soil when pH ranges from 4 to 7; the $PbOH^{+}$ species predominates when pH is raised to pH 8; and $Pb(OH)_2$ is the predominant species when pH > 8, regardless of the existence of other metal complexing ligands (Harter, 1983). Furthermore, soil clay content has been shown to influence the leachability of Pb due to the influence of clay content on Pb sorption processes (Adriano, 2001). Soils with higher clay content tend to have higher CEC (cation exchangeable capacity), which reduces Pb leachability by providing a higher sorption capacity for Pb and other metal cations (Adriano, 2001).

The transformation of soil Pb to pyromorphite [$Pb_5(PO_4)_3$ (OH, Cl, F…)], a stable and insoluble Pb phosphate mineral in the surface soil environment, via addition of soluble P to soil has been found to reduce soil Pb bioavailability and leachability (Ruby et al., 1994; Zhang et al., 1998; Yang et al., 2001, 2002). Previous studies have demonstrated that phosphate amendments can stabilize and reduce leachable heavy metals (e.g., Pb, Zn, Cd, and Cu) in industrial wastes (Crannell et al., 2000; Eighmy et al., 1997).

Recently, a greater number of studies have focused on reducing metal bioavailability and leachability in contaminated soils using organic matter (OM) amendments. Addition of OM to metal contaminated soils induces the formation of OM-metal complexes via ion exchange mechanisms; thereby reducing metal mobility in OM amended soil (Adriano, 2001; Brown et al., 2003). The high sorption capacity of OM for Pb has been confirmed in several studies (Harter, 1979; Scialdone et al., 1980; Zimdahl and Foster, 1976). However, the ability of OM to immobilize Pb and other metals depends on a variety of factors, including pH, redox, competing ions, and the nature of the OM (Adriano, 2001).

The immobilization of soil Pb, either through application of P and OM amendments, can intorduce large quantities of OM into soil. Although addition of P can mitigate metal mobility and bioavailability, P loss from amended sites could potentially threaten surface and ground water quality (Yang et al., 2002). Phosphorus lost from sites via runoff or leaching can cause surface water eutrophication (Bachmann et al., 2006; Nixon, 1995). For example, long-term land application of swine manure was reported to result in P leaching and accumulation in shallow groundwater underlying the application site, and migration of P via subsurface water flow could cause P enrichment of surface waters in the nearby vicinity (Novak et al., 2000). Yang et al (2002) found that the application of phosphoric acid in Pb contaminated soil enhanced P leaching; however, P leaching decreased sharply with increasing depth from surface, and the fraction of P leached reduced bioaccessible Pb in subsoils at this site. However, long-term effects of P leaching on P concentrations in groundwaters underlying P- and OM-treated soils are not well documented.

The objective of this study was tomeasure the leachability of P and soil metals (i.e., Pb and Cd) in metal contaminated soils amended with phosphate and organic matter using a water extraction procedure.

MATERIALS AND METHODS

Site Descriptions and Soil Treatments

Site location, landscape, history, description of heavy metal contamination, and methods of remediation are described in Chapter 3. Soil and water sampling and preparation of samples are also described in Chapter 3.

Analysis Procedures

Leachability Test: Since plant root growth and soil acidity may affect the metal stability in the amended soils, evaluating the long-term chemical and biological stability of the immobilized metals under normal surface soil conditions is crucial for evaluating the success of these *in situ* treatment technologies and their ability to protect human health and the environment. To test the stability of phosphate-immobilized heavy metals, 1 g of air-dried soil was added to a 100 ml Nalgene bottle and suspended in 100 ml of deionized water adjusted to pH 4 using 1M HNO_3. Suspensions were rotated at 200 rpm on a platform shaker at 25^{o}C. Suspension pH was determined after 2 h of reaction and readjusted to pH 4 as necessary followed by an additional 2 h reaction time. After reaction, an aliquot of solution was removed using a 10 ml plastic syringe and immediately filtered through Whatman 0.45 μm nominal pore size filter paper. Filtrates were acidified (pH < 2) by adding one drop of concentrated HNO_3 and stored for analysis of P, Pb, and other metals by ICP-OES.

Measurement of Elemental Concentrations in Solution: Elemental concentrations in solution were measured using a Varian ICP-OES. Varian's ICP-OES Expert software, which provided automatic analysis and nine decades of linear calibration range, controlled the procedures fully and detected the standard solution every 15 samples for the quality control. The standard reference material for the analysis, SRM 1640 Trace Elements in Natural Water, was purchased from the National Institute of Standards and Technology.

Statistical Analysis

Data were analyzed using standard of analysis of variance (ANOVA) for treatment,

time and the interaction of treatment and time for a randomized block design using the general two-way ANOVA analysis procedure in Statistix 8.1. Critical values (CV) and least significant differences (LSD) were calculated to separate means of each treatment or time at the 5% probability level.

RESULTS AND DISCUSSION

Urban Site - Leachability

Statistic analysis of leachable P in the urban soil indicated that treatments significantly affected extractable P concentrations ($P<0.01$), but season and treatment by season interaction did not significantly affect extractable P concentrations ($P>0.05$). This is supported by Figure 6.1 that all the treatments increased Al-Fe (non-occluded) forms of P, which are relatively soluble in the treated soil. Figure 5.1 showed that all treatments significantly increased leachable P in the soil, which is in agreement with other studies using P to immobilize Pb (McGowen et al., 2001; Yang and Mosby, 2006; Yoon et al., 2007; Zhang et al., 1998). The 1% RT treatment had the greatest impact on leachable P and the 1% PI treatment had lowest amount of leachable P. This finding is in agreement with previous results obtained from this study site indicating that all three treatments increased soil extractable P and extractable P is lowest for the PI treated soil (Yang and Mosby, 2006).

Average values of leachable P reported by Yang and Mosby (2006) were 7788 and 5386 mg P kg^{-1} for the SA and RT treatments, respectively. In this study, leachable P concentrations were determined to be 2123 and 1687 mg P kg^{-1} for the RT and SA treatments. Differences in potentially leachable P between the two studies are,

presumably, due to differences in the extractants used to measure leachable P. Yang and Mosby (2006) used 0.011 M HCl (~ pH 2) as an extractant and in this study deionized water adjusted to pH 4 with HNO_3 was employed as an extract. Thus, it seems plausible that the more acidic extractant would enhance proton attack of P-containing minerals resulting in higher values of leachable P. Differences in the data sets may also be attributed to lost of soil P content due to long-term leaching and runoff activities.

Irrespective of the cause for differences between results of the two studies, the data indicate that the PI treatment results in higher probability for soil P leaching than the other applications several years after application. Additionally, when the data were analyzed across the sampling dates, no significant differences of leachability on different sampling dates were observed (Figure 5.2). Phosphorus treatments increased leachable P in the soil in all the sampling dates, and there is no apparent increase or decrease in P leachability with time.

Analysis of Pb leachability from the urban site soils indicates that this measurement was significantly affected by treatment ($P<0.01$), but not by season and treatment by season interaction ($P>0.05$). All treatments reduced leachable Pb in the contaminated soil significantly (Figure 5.3), and the 1% RT treatment exhibits the lowest leachable Pb concentration among the samples analyzed. The order for reduction percentages of leachable Pb is RT (98.7%) > SA (90.9%) > PI (89.9%). The reduction percentages in this study are higher than those ranged from 73% to 79% in Yoon et al (2007) where phosphate rock (PR) and PA were mixed with Pb contaminated soil at a lower rateof application. McGowen et al (2001) found that the application of 2300 mg P kg^{-1} diammonium phosphate (DAP) significantly reduced Pb leachability. This result is in

agreement with data presented in Figure 4.5 demonstrating a similar trend in phytoavailable Pb reduction in the three treatments present at this experimental site, but the same trend is not present in the Pb bioavailability data (Figure 4.1). Previous studies have noted similar occurrences. Podlesakov et al (2001) observed that potential mobility or leachability of heavy metals could not be systematically correlated with metal bioavailability, but could be well correlated with phytoavailability.

Significant differences in leachability were observed among five sampling dates with the highest leachable Pb concentration appearing in March 2005 and the lowest concentrations appear in October 2004 and February 2006 (Figure 5.4). Phosphorus treatments reduced leachable Pb on every sampling date; however, decreases in leachable Pb observed for the three treatments in February 2006 were not significant.

Based on statistic analysis of Cd leachability data obtained for the urban soil, treatment, season, and treatment by season interaction affected the concentration of leachable Cd significantly ($P<0.05$). Similar to the Pb leachability data, all treatment methods reduced Cd leachability significantly (Figure 5.5) and the 1% RT treatment resulted in the lowest extractable Cd concentration. Previous research has indicated that other phosphates such as DAP, apatite, and synthetic hydroxyapatite minerals treatment could also reduce the Cd leachability in the soil (Chen et al., 1997; Ma et al., 1994; McGowen et al., 2001). The order of reduction percentages for leachable Cd was RT (58.9%) > PI (58.5%) > SA (52.4%). This result is in partial agreement with phytoavailable Cd reduction observed in Figure 4.7, which indicates that the RT treatment yields the greatest reduction in phytoavailable Cd.

Figure 5.6 shows that significant differences exist between leachable Cd data

collected on the five sampling dates, and the three P treatments reduced leachable Cd for all sampling dates. Similar to the leachable Pb results, the highest concentration of leachable Cd was observed in March 2005 samples and the lowest was observed for those samples collected in October 2004.

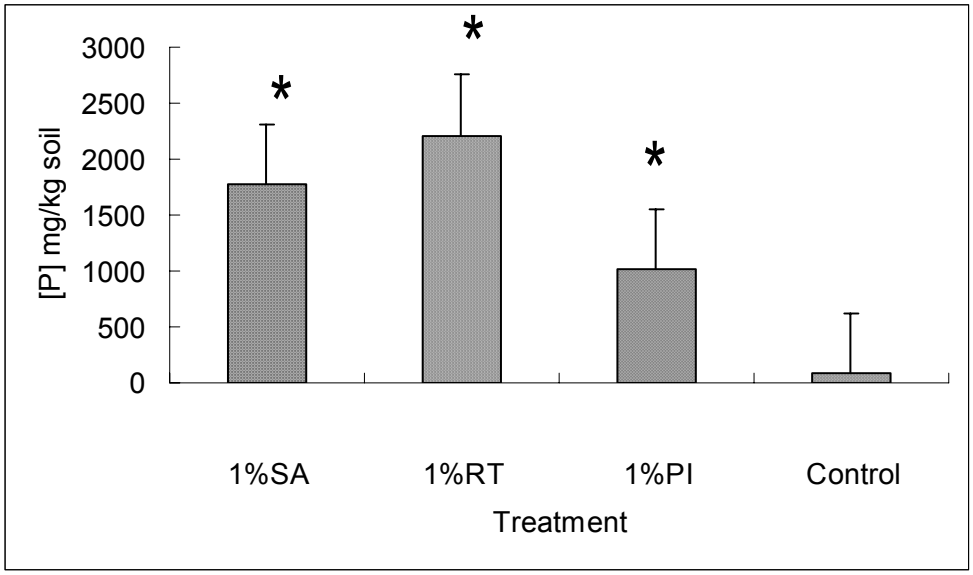


Figure 5.1. Mean leachable P (mg kg^{-1} soil) for soils collected at the urban site on five separate sampling dates. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

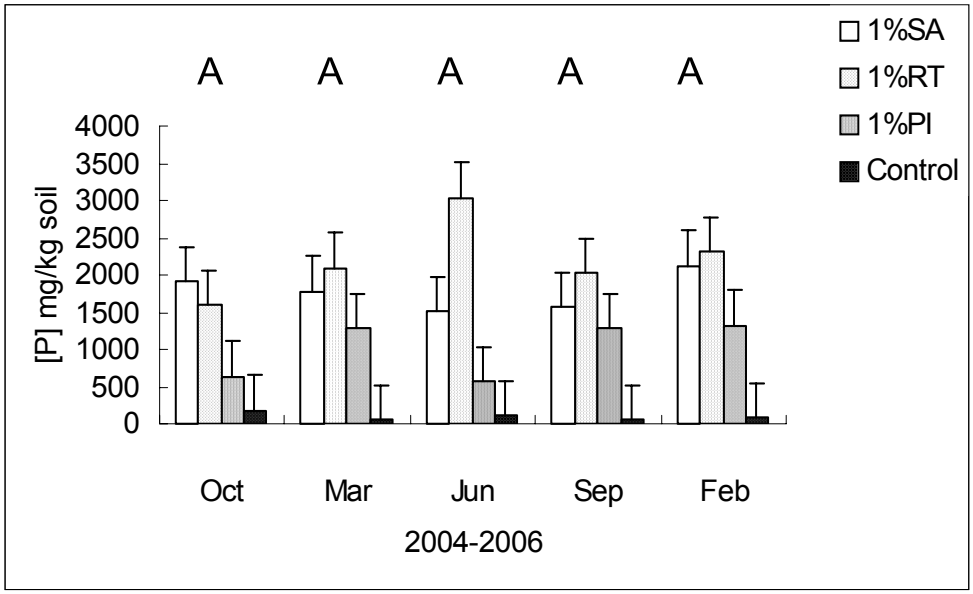


Figure 5.2. Leachable P (mg kg^{-1} soil) in soils collected from the four treatment methods at the urban site on differing dates. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate critical value (CV) (α=0.05).

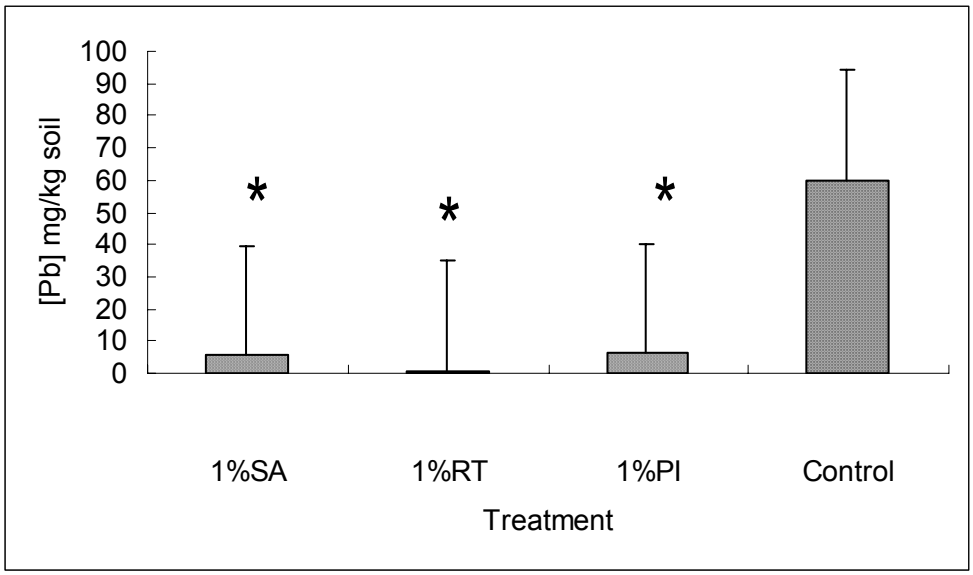


Figure 5.3 Mean leachable Pb (mg kg^{-1} soil) for soils collected at the urban site on five separate sampling dates. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

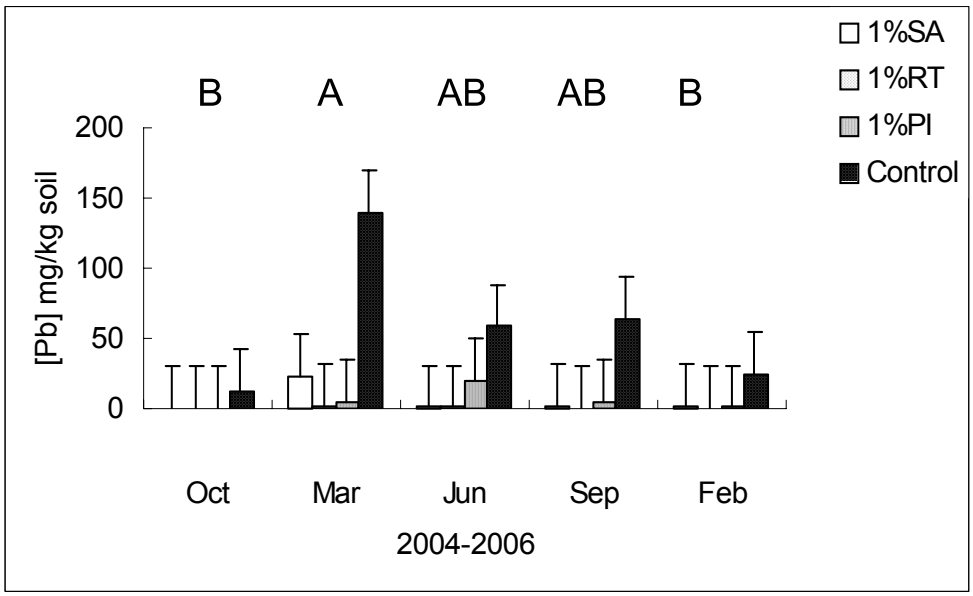


Figure 5.4 Leachable Pb (mg kg^{-1} soil) in soils collected from the four treatment methods at the urban site on differing dates. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate critical value (CV) (α=0.05).

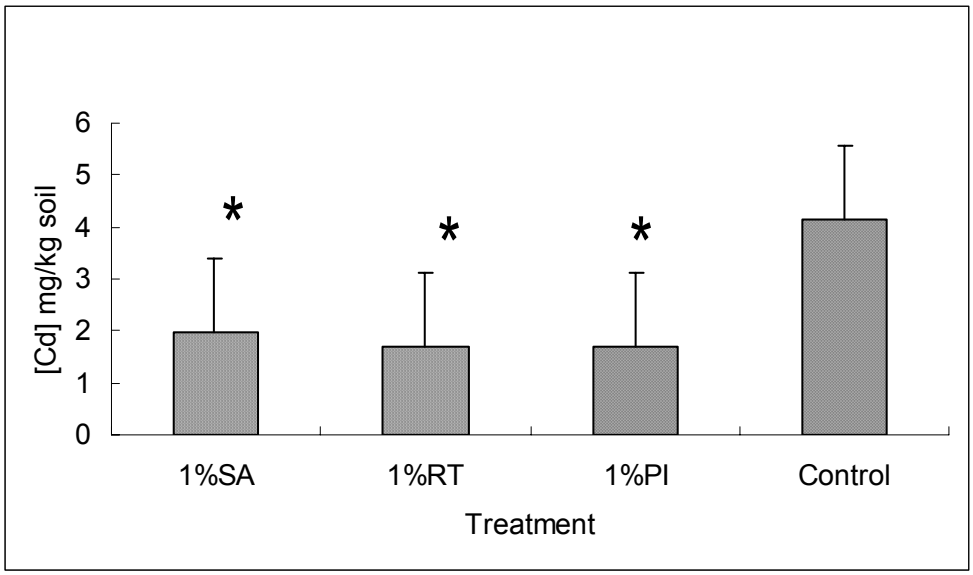


Figure 5.5 Mean leachable Cd (mg kg^{-1} soil) for soils collected at the urban site on five separate sampling dates. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

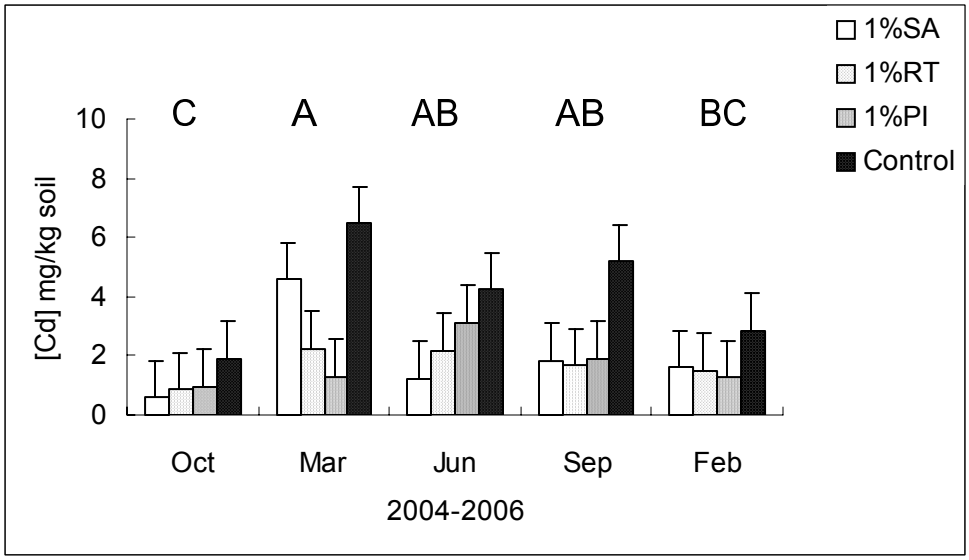


Figure 5.6 Leachable Cd (mg kg-1 soil) in soils collected from the four treatment methods at the urban site on differing dates. SA, surface application; RT, roto-tilling; PI, pressure injection; Control, no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate critical value (CV) (α=0.05).

Mill-Waste Site - Leachability

The statistic analysis of P leachability data collected for soils from the mill-waste site indicate that treatment influenced the concentration of leachable P significantly ($P<0.01$), but season and treatment by season interaction did not influence leachable P significantly ($P>0.05$). The 1% PA and 0.75% PA treatments significantly increased P leachability from soil and the 1% PA treatment had the extractable P concentration (Figure 5.7). This finding is proved by Figure 6.8 that the PA treatment increased non-occluded (Al-Fe) P, which is more labile than occluded and Ca bound P in the soil. Comparison of this data to Figure 4.12 shows that the 1% PA treatment results in a greater reduction of bioavailable Pb but the treatment also has a higher P leaching potential.

The statistic analysis among the five sampling dates shows that there were significant differences in P leachability on the different sampling dates (Figure 5.8). In March and June 2005, soil P leachability was the highest and values were lowest in October 2004. However, the P treatments significantly increased soil P leachability for every date sampled.

Analysis of Pb leachability data for the mill-waste site demonstrates that treatment, season, and treatment by season interaction did not affect Pb leachability significantly ($P>0.05$). Figure 5.9 indicates that the 1% PA and 0.75% PA treatments can reduce leachable Pb by 82.5% and 86.4%, respectively, but these reductions are not significantly different from the control plots. This finding is similar to Pb phytoavailability data presented in Figure 4.16.

When data were analyzed across the sampling dates, the results show that the March 2005 had the highest leachable Pb level and September 2005 and February 2006 had the

lowest values (Figure 5.10). This trend is similar to that found for the urban site (Figure 5.4); Pb leachability was highest in March 2005 and lower than the control plots for all sampling dates.

Three factors (treatment, season, and treatment by season interaction) were found to significantly affect leachable Cd at the mill-waste site based on statistic analysis of the data ($P<0.01$). Both P treatments significantly reduced Cd leachability in the soil (Figure 5.11). Similar to the Cd bioavailability data at the mill-waste site (Figure 4.14), the 0.75% PA treatment resulted in the lowest level of leachable Cd. The reduction percentages for leachable Cd were 49.6% and 57.2% for the 1% PA and 0.75% PA treatments, respectively. However, this finding does not appear to be correlated with Cd phytoavailability results shown in Figure 4.18.

Statistic analysis also shows significant differences among five sampling dates, where October 2004 had the lowest leachable Cd concentration and March and June 2005 had the highest concentrations among the samples analyzed (Figure 5.12). This trend is similar to the trend observed for leachable Pb at this same site.

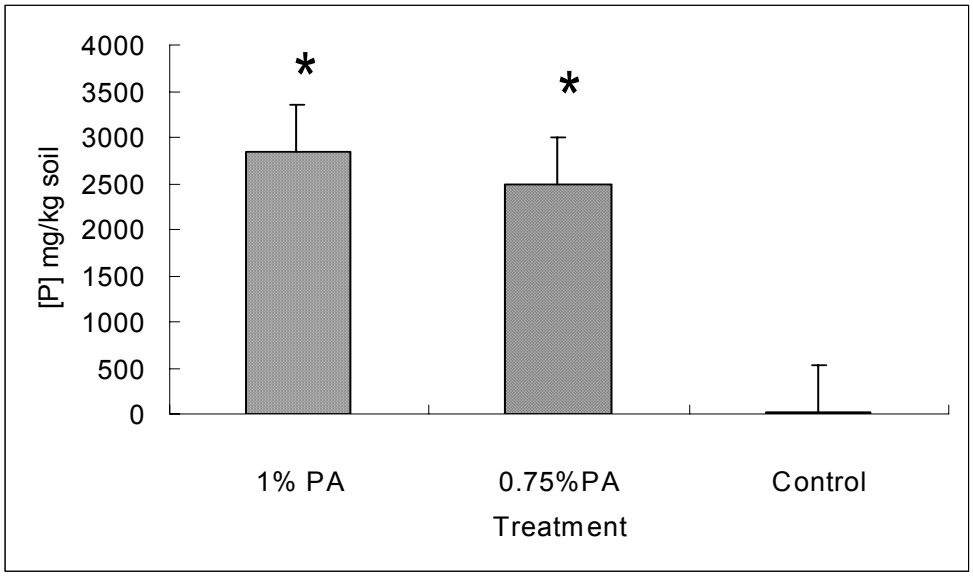


Figure 5.7 Mean leachable P (mg kg^{-1} soil) for soils collected at the mill-waste site. 1% PA: 10 g P kg^{-1} soil; 0.75% PA: 7.5 g P kg^{-1} soil; Control: no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

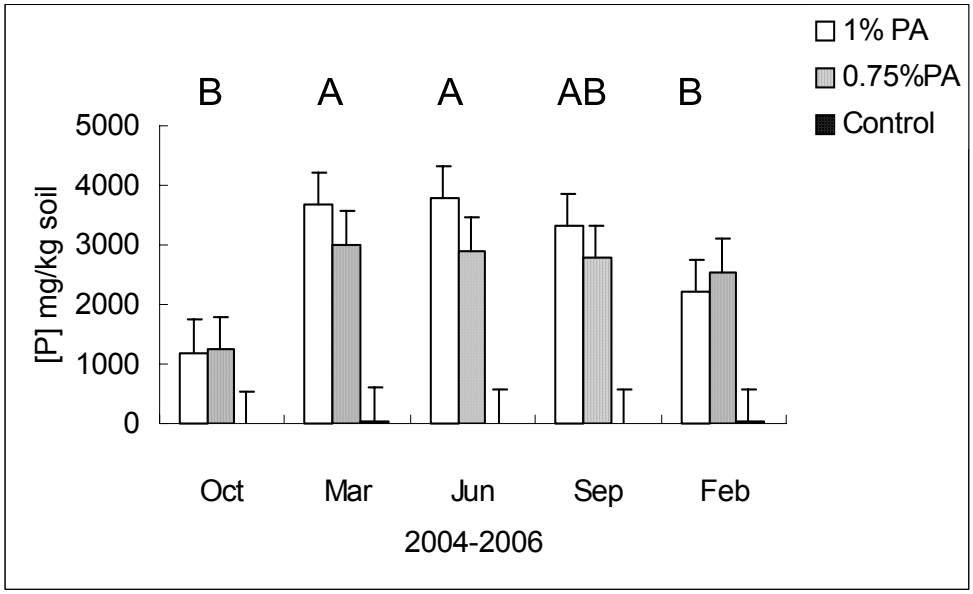


Figure 5.8 Leachable P (mg kg^{-1} soil) in soils collected from the three treatment methods at the mill-waste site on differing dates. 1% PA: 10 g P kg^{-1} soil; 0.75% PA: 7.5 g P kg^{-1} soil; Control: no treatment.. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate the critical value (CV) (α=0.05).

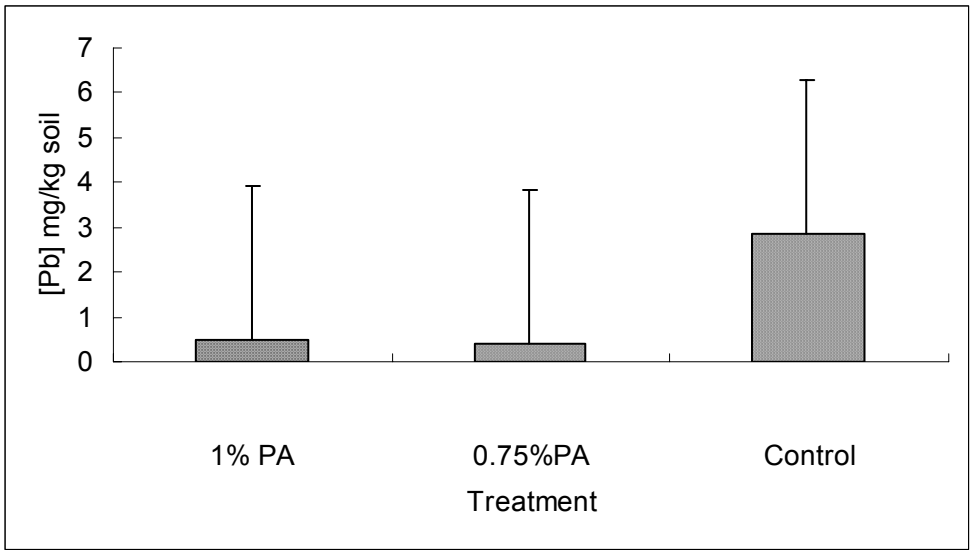


Figure 5.9 Mean leachable Pb (mg kg^{-1} soil) for soils collected at the mill-waste site. 1% PA: 10 g P kg^{-1} soil; 0.75% PA: 7.5 g P kg^{-1} soil; Control: no treatment.. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

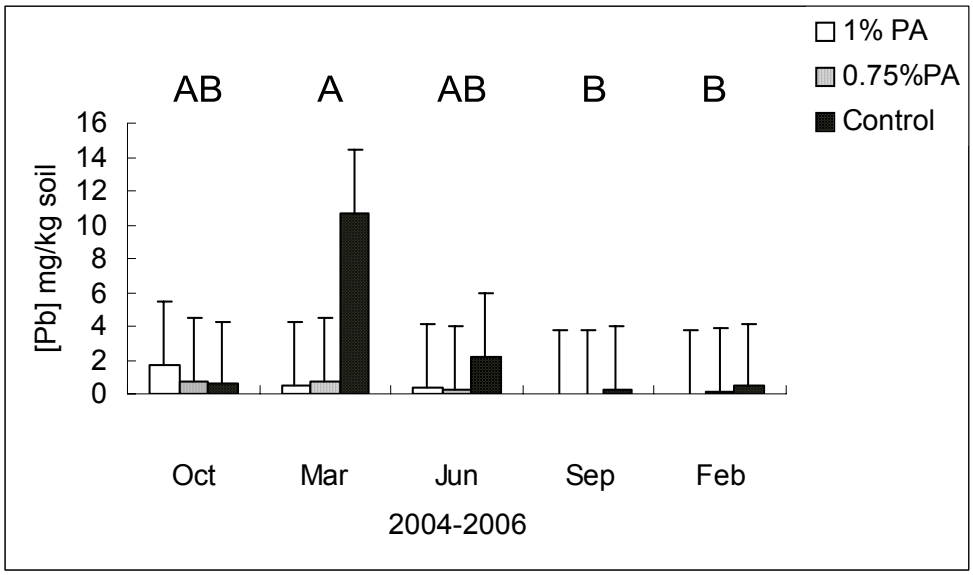


Figure 5.10 Leachable Pb (mg kg^{-1} soil) in soils collected from the three treatment methods at the mill-waste site on differing dates. 1% PA: 10 g P kg^{-1} soil; 0.75% PA: 7.5 g P kg^{-1} soil; Control: no treatment.. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate the critical value (CV) (α=0.05).

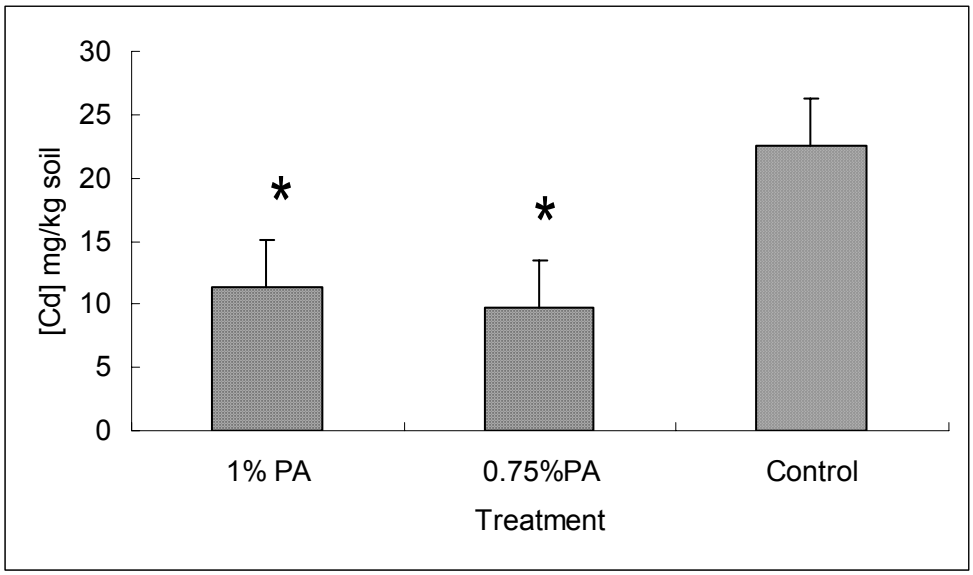


Figure 5.11 Mean leachable Cd (mg kg^{-1} soil) for soils collected at the mill-waste site. 1% PA: 10 g P kg^{-1} soil; 0.75% PA: 7.5 g P kg^{-1} soil; Control: no treatment.. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

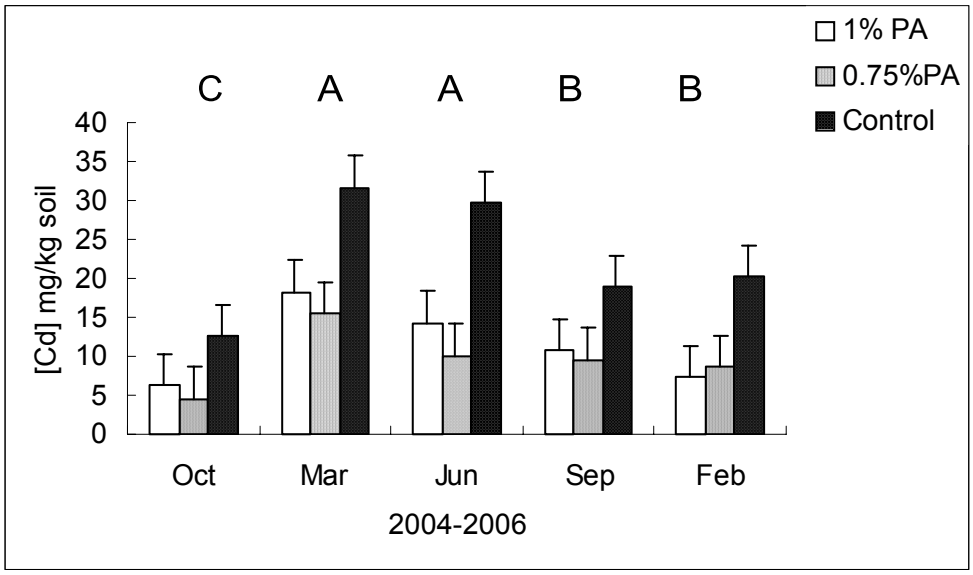


Figure 5.12 Leachable Cd (mg kg^{-1} soil) in soils collected from the three treatment methods at the mill-waste site on differing dates. 1% PA: 10 g P kg^{-1} soil; 0.75% PA: 7.5 g P kg^{-1} soil; Control: no treatment.. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate the critical value (CV) (α=0.05).

Mining-Waste Site - Leachability

Leachable soil P at the mining-waste site was significantly affected by treatment ($P<0.01$), but not by the season and treatment by season interaction ($P>0.05$). All treatment methods were found to increase leachable P concentrations in the contaminated soil, but only three methods (TL, CL, and MD) significantly increased P leachability (Figure 5.13). This finding suggests that composted OM with longer chain may have higher stability than uncomposted OM in the soil (Brady and Weil, 2002). The result of P fractionation test (Figure 6.14) in agreement to this finding that all the OM appications increased more labile Al-Fe P fraction in the soil. Based on the treatment descriptions of this mining waste site, contaminated soils were treated with triple-super-phosphate (TSP) fertilizer prior to application of organic amendments at rates based on contamination levels of 1000 mg Pb kg^{-1} and 4000 mg Zn kg^{-1}. TSP could be considered high leachable in the sandy soil that Elliot et al (2002) found that only TSP application significantly increased P leachability after the treatment in the soil comparing to other 8 biosolids and chicken manure applications.

Organic P contents of three OM treatments having significantly higher P leaching potential are: TL, 15,000 mg P kg^{-1}; CL, 17,300 mg P kg^{-1}; and MD, 800 mg P kg^{-1}. One possible reason explaining why MD, a low P content additive, had the highest P leaching potential was the prior treatment by TSP. It was possible that the MD plot was treated with higher rate of TSP prior to application of MD. Low P leachability in MDM (258.03 mg P kg^{-1} soil) plot would seem to support this explanation. The hierarchy for the concentration of leachable P among treatments based on t-test was MD > CL > TL > CSS > SMC > RS > EPA > MDM > P > CSSH > UN.

Figure 5.14 shows some significant differences among five sample dates; samples collected in October 2004 had the lowest P leachability. The SMC, TL, CL, and MD treatments significantly increased P leachability for four out of the five dates sampled.

Statistic analysis of the leachable Pb data for the mining-waste site revealed that treatment significantly affected the concentration of leachable Pb in the soil ($P<0.01$), but the season and treatment by season interaction did not significantly affect Pb leachability ($P>0.05$). As shown in Figure 5.15, all treatments significantly reduced Pb leachability by almost 100% at the mining-waste site. The hierarchy for leachable Pb concentrations among treatments is UN > RS > CSSH > CL > EPA > TL > P > SMC > MD > CSS > MDM. Among the five sample dates (Figure 5.16), significant differences can be observed. The highest concentration of leachable Pb occurs in February 2006 and the lowest concentration occurs in September 2005. Lead leachability was reduced by all the treatments for all dates sampled.

Similar to the leachability of P and Pb from samples at this site, statistic analysis shows that treatment significantly affected Cd leachability ($P<0.01$); however, season and treatment by season interaction did not significantly affect Cd leachability ($P>0.05$). Although not statistically significant, most of the treatments (seven of the ten) did reduce Cd leachability at the mining-waste site (Figure 5.17). Reduction percentages ranged from 16.9% (EPA) to 94.9% (CSS). As for the case of bioavailable Cd at this site, MDM was the only treatment that significantly increased soil Cd leachability. This may be caused by the higher Cd concentration in topsoil, which was added to MD; or the lower application rate of OM in MDM (Antoniadis and Alloway, 2002). Furthermore, the hierarchical order of Cd leachability was also similar to Cd bioavailability: MDM

>CSSH > RS > UN > EPA > CL > P > SMC > TL > MD > CSS. Figure 5.18 shows that there is no significant difference between Cd leachability values among five sampling dates.

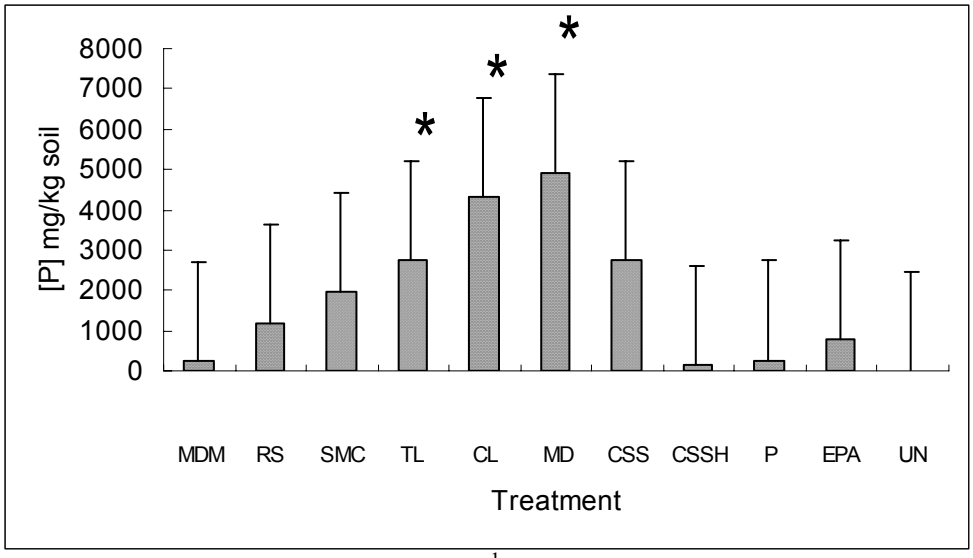


Figure 5.13 Mean leachable P (mg kg^{-1} soil) for soils collected at the mining waste site. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

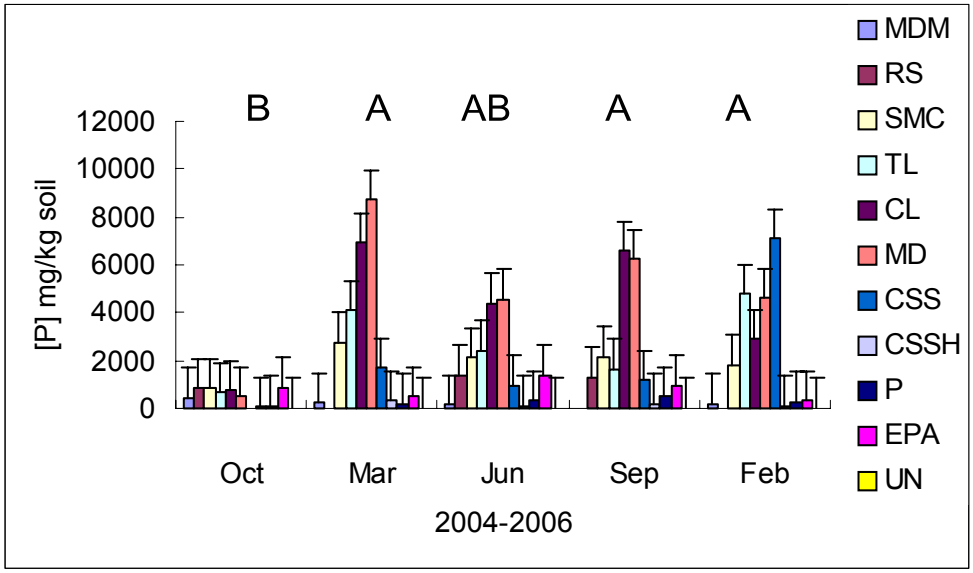


Figure 5.14 Leachable P (mg kg^{-1} soil) in soils collected from the eleven treatment methods at the mining waste site for each sample date. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate the critical value (CV) (α=0.05).

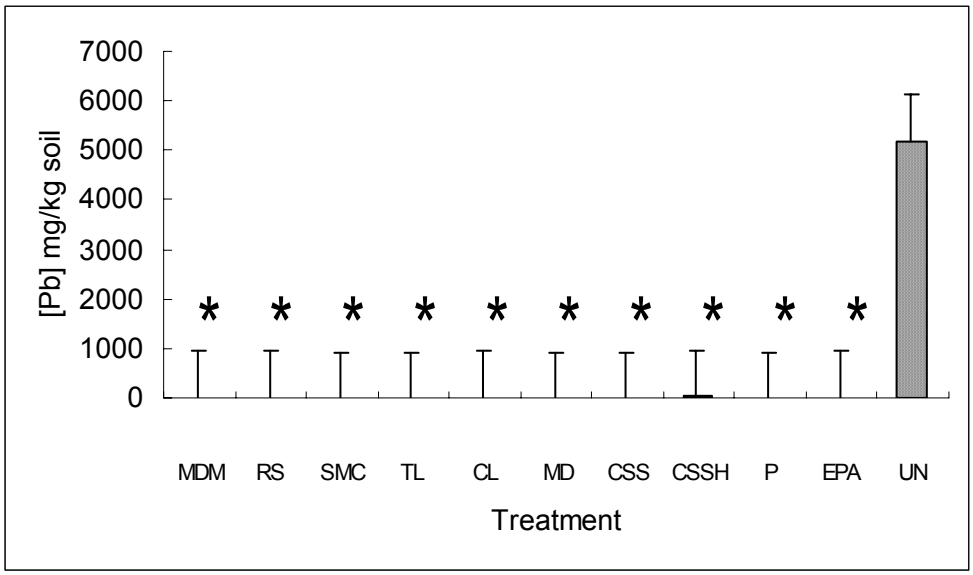


Figure 5.15 Mean leachable Pb (mg kg^{-1} soil) for soils collected at the mining waste site. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

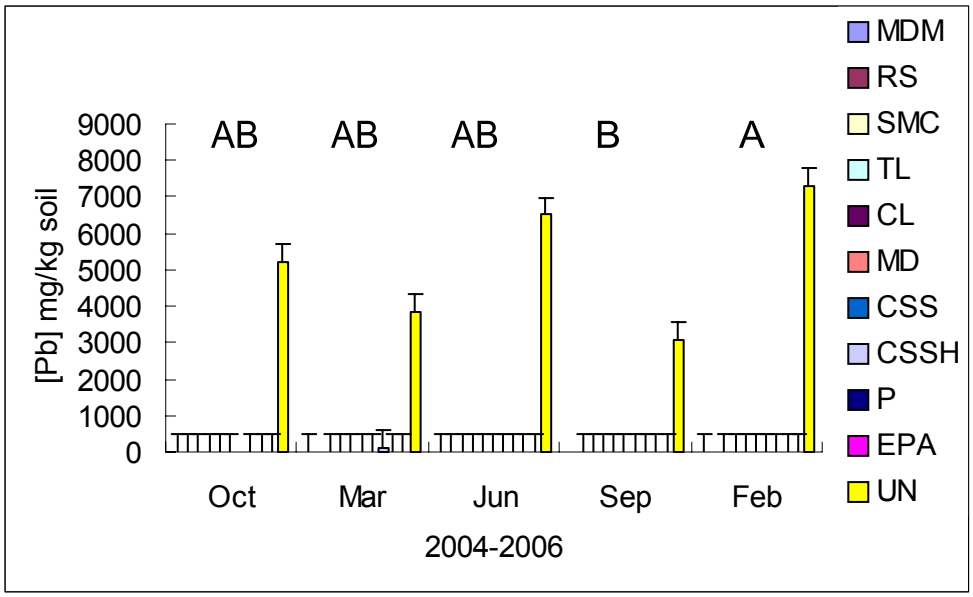


Figure 5.16 Leachable Pb (mg kg^{-1} soil) in soils collected from the eleven treatment methods at the mining waste site for each sample date. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate the critical value (CV) (α=0.05).

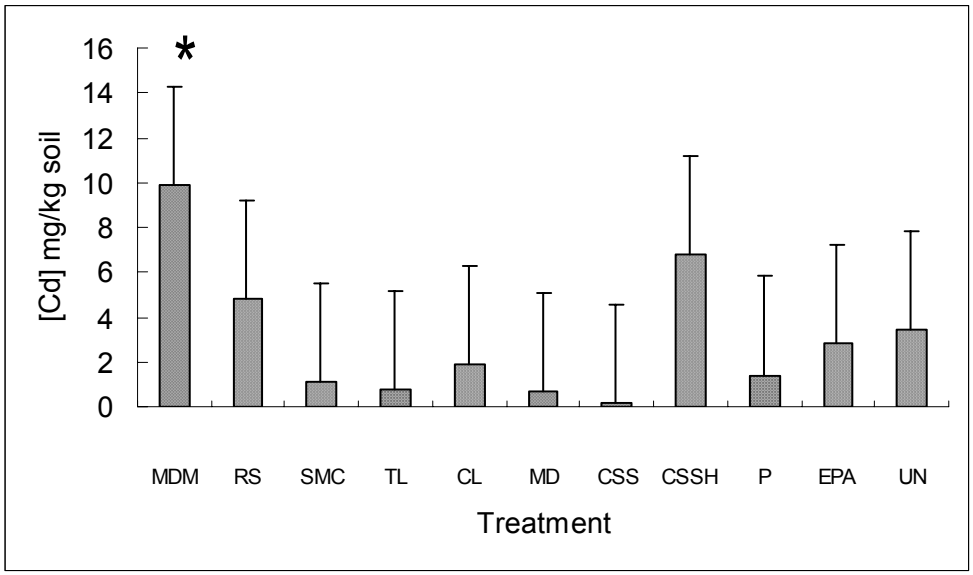


Figure 5.17 Mean leachable Cd (mg kg^{-1} soil) for soils collected at the mining waste site. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment. Asterisks indicate significant differences and vertical bars indicate the critical value (CV) (α=0.05).

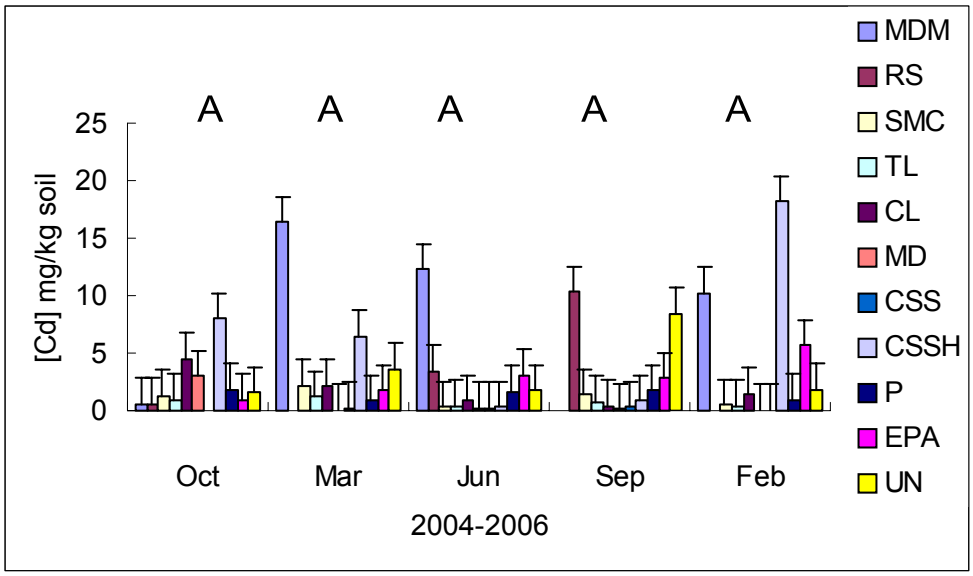


Figure 5.18 Leachable Cd (mg kg^{-1} soil) in soils collected from the eleven treatment methods at the mining waste site for each sample date. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment. Letters show differences among the sample dates; same letter indicates no significant difference. Vertical bars indicate the critical value (CV) (α=0.05).

CONCLUSIONS

In the urban site, all three treatments (e.g. SA, RT, PI) increased P leachability and reduced the leachability of Pb and Cd significantly, in which RT was the most effective treatment. The reductions of leachable Pb and Cd corresponded with reductions of phytoavailable Pb and Cd (Chapter 4).

At the mill-waste site, both 1% PA and 0.75% PA treatments significantly raised lechable P in the soil and significantly reduced the leachability of Pb and Cd. The 0.75% PA was the most effective treatment. Only Pb leachability result was positively correlated with Pb phytoavailability result (Chapter 4). The seasonal trends of Pb and Cd leachability were similar to that in the urban soil site.

Phosphorus leachability was raised by all the treatments in mining waste, but only three treatments (MD, CL, and TL) were significant. All treatments reduced Pb leachability by nearly 100%. Seven out of ten treated plots were found reducing Cd leachability that the reduction percentages ranged from 16.9% (EPA) to 94.9% (CSS). The most three effective treatments for reducing metal leachability were CSS, MD, and SMC. So far, the treatments of SMC and MD were tested most effective in terms of *in vitro* bioavailability, phytoavailability, microbial toxicity, and leachability.

LITERATURE CITED

Adriano, D.C. 2001. Trace elements in terrestrial environments biogeochemistry, bioavailability, and risks of metals, 2nd edition. Springer-Verlag, New York.

Alvarez, J.M., J. Novillo, A. Obrador, and L.M. Lopez-Valdivia. 2001. Mobility and leachability of zinc in two soils treated with six organic zinc complexes. J. Agric. Food Chem. 49:3833-3840.

Antoniadis, V., and B.J. Alloway. 2002. Leaching of cadmium, nickel, and zinc down the profile of sewage sludge-treated soil. Commun. Soil Sci. Plant Anal. 33(1&2):273-286.

Bachmann, R.W., J.E. Cloern, and R.E. Heckey et al. (ed.) 2006. Eutrophication of freshwater and marine ecosystems. Limnol. Oceanogr. 51(1):351–800.

Borg, H., and K. Johansson. 1989. Metal fluxes to Swedish forest lakes. Water, Air, Soil Pollut. 47:427-440.

Brady, N., and R. Weil. 2002. The nature and property of soils. Prentice Hall, Upper Saddle River, NJ.

Brown, S., R.L. Chaney, J.G. Hallfrisch, and Q. Xue. 2003. Heavy metals in the environment: effect of biosolids processing on lead bioavailability in an urban soil. J. Environ. Qual. 32:100-108.

Brummer, G.W. 1986. Heavy metal species: mobility and availability in soils. p. 169-192. *In* M. Bernhard (ed.) The importance of chemical “speciation” in environmental process. Springer-Verlag, Berlin, Germany.

Bubb, J.M., and J.N. Lester. 1991. Impact of heavy metals on low land rivers and implications for the man and the environment. Sci. Total Environ. 100:207-58.

Chen, X., J.V. Wright, J.L. Conca, and L.M. Peurrung. 1997. Evaluation of heavy metal remediation using mineral apatite. Water Air Soil Pollut. 98:57-78.

Chlopecka, A., and D.C. Adriano. 1996. Mimicked in-situ stabilization of metals in a cropped soil: bioavailability and chemical form of zinc. Environ. Sci. Technol. 30:3294-3303.

Crannell, B.S., T.T. Eighmy, J.E. Krzanowski, J.D.Jr. Eusden, E.L. Shaw, and C.A. Francis. 2000. Heavy metal stabilization in municipal solid waste combustion bottom ash using soluble phosphate. Waste Management 20:135-148.

Eighmy T.T., B.S. Crannell, J.E. Krzanowski, F.K. Cartledge, E.F. Emery, and D. Oblas et al. 1997. Heavy metal stabilization in municipal solid waste combustion dry scrubber residue using soluble phosphate. Environ. Sci. Technol. 31:3330-3338.

Elliott, H.A., G.A. O'Connor, and S. Brinton. 2002. Phosphorus leaching from biosolids-amended sandy soils. J. Environ. Qual. 31:681-689.

Harter, R.D. 1979. Adsorption of copper and lead by Ap and B2 horizons of several northeastern United States soils. Soil Sci. Soc. Am. J. 43:679-683.

Harter, R.D. 1983. Effect of soil pH on adsorption of lead, copper, zinc, and nickel. Soil Sci. Soc. Am. J. 47:47-51.

Li, Z., and L.M. Shuman. 1996. Extractability of zinc, cadmium, and nickel in soil amended with EDTA. Soil Sci. 161:226-232.

Ma, L.Q., T.J. Logan, S.J. Traina, and J.A. Ryan. 1994. Effects of aqueous Al, Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by Hydroxyapatite. Environ. Sci. Technol. 28:1219-1228.

McGowen, S.L., N.T. Basta, and G.D. Brown. 2001. Use of diammonium phosphate to reduce heavy metal solubility and transport in smelter-contaminated soil. J. Environ. Qual. 30:493-500.

Nixon, S.W. 1995. Coastal marine eutrophication: a definition, social causes, and future concerns. Ophelia 41:199–219.

Novark, J.M., W.W. Watts, P.G. Hunt, and K.C. Stone. 2000. Phosphorus movement through a coastal plain soil after a decent of intensive swine manure application. J. Environ. Qual. 29:1310-1315.

Robinson, B., N. Bolan, and S. Mahimairaja. 2006. Solubility, Mobility, and Bioaccumulation of Trace Elements: Abiotic Processes in the Rhizosphere. p. 97-110. *In* M.N.V. Prasad et al. (ed.) Trace elements in the environment: biotechnology, and bioremediation. Technology & Industrial Arts. CRC Press, Boca Raton, FL.

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. Tchnol. 28:646-654.

Scialdone, R., D. Scognamiglio, and A.U. Ramunni. 1980. The short and medium term effects of organic amendments on lead availability. Water, Air, Soil Pollut. 13:267-274.

Yang, J.J., D.E. Mosby, S.W. Casteel and R.W. Blanchar. 2001. Lead immobilization using phosphoric acid in smelter-contaminated urban soil. Environ. Sci. Technol. 35:3553-3559.

Yang, J., D.E. 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. Arch. Environ. Contam. Toxicol. 43:399-405.

Yoon, J.K., X. Cao, and Q. Ma. 2007. Application methods affect phosphorus-induced

lead immobilization from a contaminated soil. J. Environ. Qual. 36:373-378.

Zhang, P.C., J.A. Ryan, and J.Yang. 1998. In vitro soil Pb solubility in the presence of hydroxyapatite. Environ. Sci. Technol. 32:2763-2768.

Zhang, M.K., Z.L. He, P.J. Stoffella, D.V. Calvert, X.E. Yang, Y.P. Xia, and S.B. Wilson. 2004. Solubility of phosphorus and heavy metals in potting media amended with yard waste-biosolids compost. J. Environ. Qual. 33:373-379.

Zimdahl, R.L., and I.M. Foster. 1976. The influence of applied phosphorus, manure, or lime on uptake of lead form soil. J. Environ. Qual. 5:31-34.

CHAPTER 6

ALTERATION OF METAL SPECIATION INDUCED BY PHOSPHATE TREATMENTS

ABSTRACT

Assessments of metals and P bioavailability and leachability indicated that *in situ* soil treatments using phosphate-based amendments were cost- effective remedial technologies for immobilizing soil metals and reducing health and ecological risks. Lead and P speciation was a good indicator that evaluates chemical behavior in soil . Three soils from smelter-contaminated urban site, a mill waste site, and a mining waste site in the Jasper County Superfund Site, Southwestern Missouri were treated with phosphoric acid or P-enriched OM using three application methods and two rates. Soils were collected 6-8 yr after treatment and analyzed for chemical or solid P species using sequential extraction procedures and microscopic methods. Based on data for five sample dates, all treatments increased non-occluded (labile) P fractions in the soil, which was the primary reason for the increasing of soil P leachability in P-treated soil. Most phosphoric acid applications in the urban site and mill-waste site increased soil residual Pb fraction by over 90%. In the mining waste site, residual soil Pb fraction was found higher than 90% in TL, MD, and CSS treated plots. Microprobe analysis using the SEM-EDS confirmed that pyromorphites or lead phosphates formed after the treatments. The results demonstrated that the phosphoric acid and OM treatments in the Pb contaminated soil could effectively transfer soil Pb from labile forms into stable forms or from nonresidual to residual, thus prevented humans and the environment from Pb pollution.

INTRODUCTION

Lead contamination in environment is a threat to humans and environment because of its toxicity and mobility (Ma and Rao, 1997a; Yang et al., 2002; Yang and Mosby, 2006). Total Pb in soil may give extent or degree of the contamination, but doesn't provide information of their chemical behaviors such as toxicological effect and mobility (Adriano, 2001; Amore et al., 2005; Ma and Rao, 1997a, 1997b; Ramos et al., 1994; Tsadilas, 2001). Determination of Pb speciation, which is defined as "the chemical species or form that determine the mobility and bioavailability of soil metal to other environmental compartments, such as water, plants, and biota", is needed to understand Pb behavior in the soil, bioavailability to organisms, and mobility in the environment (Ramos et al., 1994).

Soil metals can be fractionated into several chemical forms using the sequential extraction techniques. Those forms include water soluble, exchangeable, carbonate, organic, Fe-Mn oxides, and residual fractions, in which the solubility is from the most soluble to relatively insoluble (Ma and Rao, 1997a, 1997b; Ramos et al., 1994; Tsadilas et al., 1995). Water soluble and exchangeable metals were found highly leachable or bioavailable (Xian, 1989; Zhang et al., 2003); exchangeable and carbonate metals were phytoavailable (Pierzynski and Schwab, 1993; Samaras and Tsadilas, 1997).

Metal chemical forms can be changed dramatically by changing soil chemical properties such as metal concentration, OM content, pH or E_h, etc. (Tsadilas, 2001). Transformation of the chemical forms can cause metal redistribution in environment, which may affect metal mobility and bioavailability (Amore et al., 2005; Gambrell, 1994; Tsadilas, 2001).

In mine-contaminated soils, Pb was found mostly associated with the Fe-Mn oxides and secondly with carbonates in alkaline soils in the Donana National Park, Spain (Ramos et al., 1994). Lead in contaminated acidic soils of southwestern Poland was found associated with Fe-Mn oxides, organic, and carbonates (Chlopecka et al., 1996). Lead immobilization or risk reduction by phosphate treatments can be assessed by a fractionation scheme that evaluates the Pb transformation from labile to insoluble forms (Ma and Rao, 1997b).

Based on Roberts et al. (2005), metal speciation contains the chemical species in soil solution, gaseous phase, and in the soil solid phases. Due to rapid kinetic formation of pyromorphite, the extraction method cannot prove that pyromorphite is not formed during the extraction procedure (Scheckel et al., 2003). In this study, additional to the sequential extraction procedures, solid-phase speciation of Pb was also determined by the SEM-EDS microprobe (Scanning electron microscopy - energy dispersive spectroscopy) to verify the formation of pyromorphites.

Immobilization of soil Pb by applications of P and OM would add large amount of P to soil, which may become a potential threat to surface and ground water quality (Yang et al., 2002). The understanding of soil P forms by identifying and quantifying P compound could help protect water system from P pollutions (e.g. eutrophication) (Sui et al., 1999).

According to the soil P sequential extraction procedures, soil P can be differentiated into nonoccluded Fe-Al bound P, carbonate sorbed P, occluded oxides bound P, and Ca-bound P. Ca-P was reported dominant in sand and silt soil (Syers et al., 1969). Hartikainen reported that the potential P availability decreased in the order of soluble P>Fe-Al P>Ca-P. This fractionation schemes for inorganic P would fit this project

because the phosphate amendments used for the soil treatments were phosphoric acid, and more inorganic P in the biosolids (Gerritse and Vriesema, 1984). This method would gave a more meaningful separation of soil inorganic P, especially in calcareous soils (Olsen and Sommers, 1982).

The objectives in this research were (1) to quantitatively determine the chemical speciations of Pb and P in phosphate or biosolid treated soils; and (2) to identify and determine elemental composition of solid-phase Pb species in soil.

MATERIALS AND METHODS

Site Descriptions and Soil Treatments

The locations, landscape, history, situations of heavy metal contaminations, and the methods of remediation were described in Chapter Three. The sampling and preparation of samples were also described in Chapter Three.

Analytical Procedures

Phosphorus fractionation Test: Phosphate speciation was performed by the selective chemical extraction procedures described by Olsen and Sommers (1982), including Fe- Al bound P (non-occluded), Fe oxides occluded P, and Ca-P (Table 6.1)

Lead sequential extraction Test: Identifying Pb species and determining chemical phases responsible for metal and phosphate mobility or leachability are critical for ensuring the success of phosphate treatments and better understanding the mechanisms of Pb immobilization processes. Sequential extraction procedures described by Ma and Rao (1997) and Ramos et al. (1994) were slightly modified and used to differentiate Pb fractions in the soil. The selective, sequential fraction procedures are shown in Table 6.2.

Table 6.1. Reagents and procedures used phosphate speciation

TARGET PHASE	EXTRACTANT	PROCEDURE
Non-occluded Al-and Fe-bound P	0.1 N NaOH-1 M NaCl	Add 10 ml to 0.2 g of soil. Shake on a rotary shaker at room temperature for 17 hours; centrifuge tubes for 15 min at 2400 rpm.
P sorbed by carbonates during NaOH extraction	1 M NaCl	Wash the residue twice with 8 ml by stirring and centrifuging.
	0.3 M citrate solution + 1 M $NaHCO_3$ solution	Add 8 ml of citrate and 1 ml of $NaHCO_3$ solution and heat in water bath to 85 °C for 15 min, centrifuge. Combine the two solutions.
P occluded within Fe oxides and hydrous oxides	0.3 M citrate solution + 1 M $NaHCO_3$ solution	Add 8 ml of citrate and 1 ml of $NaHCO_3$ solution and heat in water bath to 85 °C.
	$Na_2S_2O_4 \cdot 2H_2O$	Add 0.2g with rapid stirring. Continue heating the suspension at 85 °C for 15 min, centrifuge.
	Saturated NaCl solution	Add 5 ml; wash and centrifuge. Combine the two solutions.
Ca-bound P	1 N HCl	Add 10 ml; shake 1h, centrifuge.

Table 6.2. Reagents and procedures used for removing specified target phases in the sequential extraction procedure

EXTRACANT	TARGET PHASE	PROCEDURE
Deionized water	Water soluble	Add 15 ml to 1 g of soil; shake for 2 h Milli-Q Wash
1 M $MgCl_2$ (pH 7.0)	Exchangeable	Add 8 ml; shake for 1 h Milli-Q Wash
1 M NaOAc (pH 5.0)	Carbonate	Add 8 ml; shake for 5 h Milli-Q Wash
0.04 M $NH_2OH \cdot HCl$ (in 25% (v/v) HOAc)	Fe-Mn Oxides	Add 8 ml; place in 96^oC with occasional agitation for 6h Milli-Q Wash
0.02 M HNO_3 + 30% H_2O_2	Organic	Add 3 ml of HNO_3 + 5 ml of H_2O_2 place in 85 °C water bath for 3h with intermittentagitation.
3.2 M NH_4OAc (in 20% (v/v) HNO_3)		After cooling, 5 ml NH_4OAc is added and the sample diluted to 20 ml and agitated continuously for 30 min Milli-Q Wash
1 N HNO_3 & conc. HNO_3	Residual	Add 15 ml conc. HNO_3 and 2 ml of H_2O_2; microwave-digested

Measurement of Elemental Concentrations in Solution: For the inductively coupled plasma (ICP) analysis, samples were diluted 10 times by deionized water (18 MΩ cm, Millipore Milli-Q) and P and Pb concentrations were determined by Varian's ICP-OES (optical emission spectroscopy), which provided automatic analysis and nine decades of linear calibration range. A NIST standard solution, SRM 1640 Trace Elements in Natural Water, was run every 15 samples for the quality control.

Solid-phase microprobe analyses: Solid-phase speciation, combined with chemical speciation, would provide a better understanding of immobilization mechanisms and chemical transformation induced by phosphate treatments. Soil samples were mounted on 25-mm-diameter Al stubs using double-sided sticky carbon tape and then coated with ~20 nm of carbon. SEM imaging and microprobe analyses were performed by the Hitachi S-4700 field emission scanning electron microscopy (FESEM) and the Thermo Electron System Six energy-dispersive x-ray spectrometer (EDS), with a silicon-lithium (SiLi) thin-window detector. Soil Pb particles were first identified by the backscattered electron (BSE) imaging with a Robinson YAGBSE detector, and then EDS was used to determine chemical composition of the Pb particles at 15 keV and a 30° take-off angle. Data was collected for 90 seconds. A chloropyromorphite standard was included in the analyses for quality control and assurance.

Statistical Analysis

Data analysis was performed by the standard of variance analysis (ANOVA) for treatment, time and the interaction of treatment x time with a randomized block design, using the general two-way ANOVA analysis procedure in Statistix 8.1. Critical values (CV) and least significant differences (LSD) were calculated to separate means of each

treatment or time at the 5% probability level.

RESULTS AND DISCUSSION

Urban Site - Chemical fractionation of P and Pb

Results of sequential extraction of P in the urban soil indicated that three phosphoric acid application methods all increased non-occluded P fractions, including Al-P, Fe-P, and carbonate sorbed P during the NaOH extraction procedure (Figure 6.1). Hu et al. (2001) observed that the solubility of inorganic P fractions was Fe-P> Al-P> occluded P> Ca-P and that occluded P and Ca-P were not phytoavailable. Zhang et al (2004) and Akhtar et al (2002) also reported that Al-P and Fe-P were more soluble and bioavailable than occluded P and Ca-P. This supports data in Figure 5.1 that P leaching potential was increased in all the treated plots. The untreated soil had the highest occluded P fraction 34%, while the 1% PI treatment had 16%, the 1% RT treatment 16%, and the 1% SA treatment 12%. Based on Adhami et al (2005), occluded P is the P associated with crystalline Fe oxides such as goethite, which is lower soluble than non-occluded P. All the PA treatments in the urban site reduced the occluded P fractions, which also could result in the decreasing of P stability, thus enhanced leachability in the treated soil. For the Ca-P, which is generally considered as apatite (Williams et al., 1967), the treatments of 1% RT and 1% PI had increased the fraction from 20% to 22% and 25%, but 1% SA treatment reduced to 8%. The treatments all increased the total amount of P and the more soluble fractions of P in the soil as well. This would explain the reason why the P leachability was increased by the phosphoric acid treatment.

Figure 6.2 showed that residual fraction of Pb in the urban soil was greatly increased

to 91% by 1% SA treatment and 95% by 1% RT treatment. However, the fraction was slightly reduced to 20% by 1% PI treatment, as compared with 23% of the untreated (control) soil. The 1% SA treatment reduced the non-residual (the sum of organic, Fe-Mn, carbonate, exchangeable, and water soluble) Pb fractions by 9%, in which 5% were organic form and 3% Fe-Mn form. The 1% RT treatment reduced non-residual Pb by 5%, in which 3% were organic form and 1% Fe-Mn form. In the 1% PI treatment, residual and Fe-Mn forms of Pb fractions decreased while the organic Pb fraction increased, and the water soluble and exchangeable fractions of Pb was reduced by the treatment as well. Xian (1989) and Zhang et al. (2003) found out that water soluble and exchangeable Pb were more leachable or bioavailable; exchangeable and carbonate fractions of Pb were responsible for Pb phytoavailability (Pierzynski and Schwab, 1993; Samaras and Tsadilas, 1997). This result greatly supported the results of Pb phytoavailablity and leachability in Figure 4.5 and Figure 5.3, where it was observed that phytoavailable and leachable Pb was significantly reduced by all the treatments in the contaminated soil. Also, the results provided a good stand for the *in vitro* availability results in Figure 4.1. It was obvious that the reduction of water soluble and exchangeable soil Pb fractions could be responsible for the reductions of the phytoavailability of Pb in the urban soil.

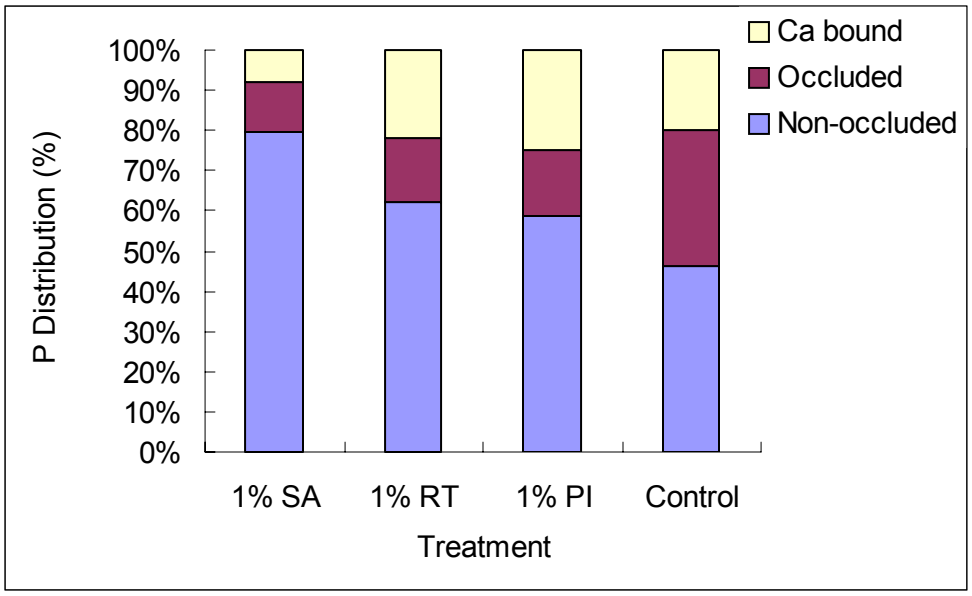


Figure 6.1 Phosphorus distributions in different fractions of four treatment methods from five sample dates for Urban Site. SA: surface application; RT: roto-tilling; PI: pressure injection; Control: no treatment.

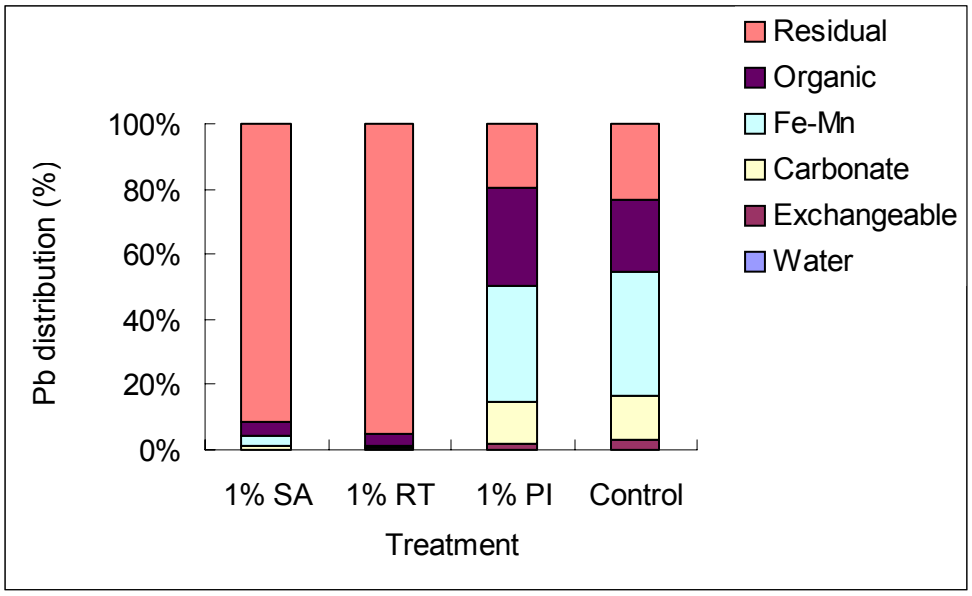


Figure 6.2 Lead distributions in different fractions of four treatment methods from five sample dates for Urban Site. SA: surface application; RT: roto-tilling; PI: pressure injection; Control: no treatment.

Urban Site - Solid Speciation of Pb

The solid phase Pb speciation by the microprobe analysis was performed to verify the formation of Pb-phosphates or pyromorphites in the P-treated soils. Figure 6.4 showed a similar spectrum with P, Pb, and Cl peaks to Figure 6.3, which meant 1% RT treatment of soil could result in the formation of chloropyromorphite or chloropyromorphite-like compound. Three out of ten Pb particles analyzed were the solids containing Pb, P and Cl in the 1% RT treatment soil (Table 6.3). In Scheckel et al. (2004), 1% PA treatment was reported resulting in 45% pyromorphite concentration of the total Pb concentration in the urban site soil, and this finding is in agreement restults observed in this study. Some other field studies that used similar phosphate amendments showed significantly more pyromorphite (70%-82%) formed as determined via selective sequential extractions. However, selective extraction techniques may over-estimate the amount of pyromorphite formed due to quick pyromorphite formation during the extraction procedures (Scheckel et al., 2003). The transformation of soil labile Pb to pyromorphite resulted in the reduction of *in vitro* bioavailable, phytoavailable, and leachable Pb in the contaminated soil (Chapter 4).

The FESEM photographs indicated that the chloropyromorphite-like compounds were *ca*. 40 μm in diameter and distributed heterogeneously in the soil (Figure 6.5). Figure 6.6 showed the EDS spectrum of untreated urban soil containing no P or Cl, indicating that Pb might exist as unstable forms of $PbCO_3$, PbO, etc. in the soil. Figure 6.7 was the FESEM photograph for untreated soil Pb particles that was highlighted and in the diameter of *ca.* 50 μm.

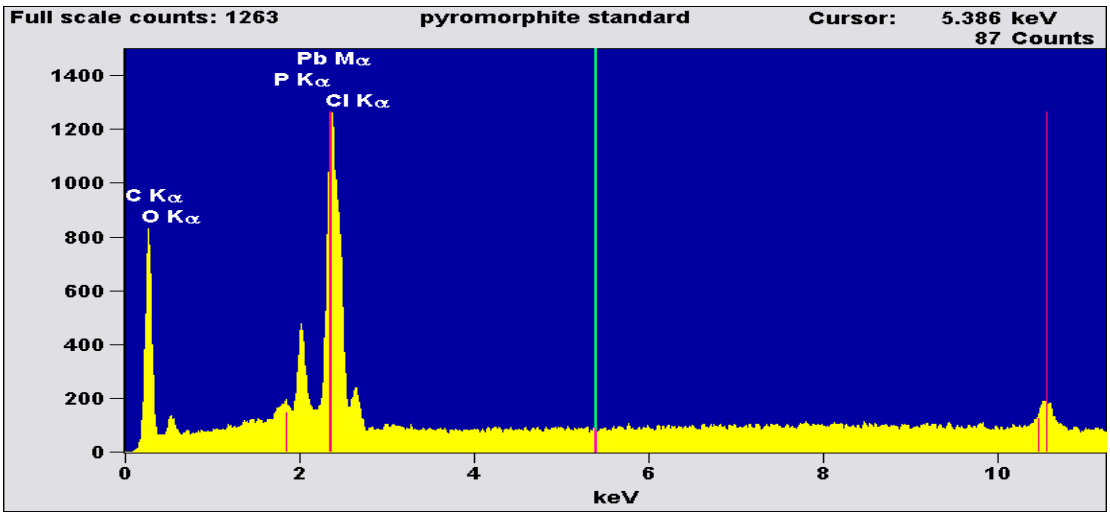


Figure 6.3 EDS patterns for chloropyromorphite standard in the soil sample.

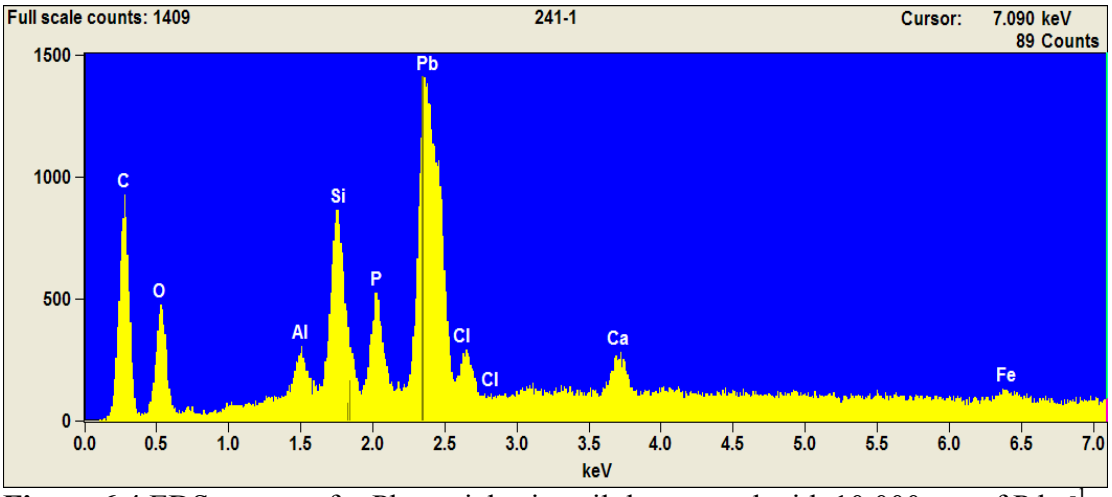


Figure 6.4 EDS patterns for Pb particles in soil that treated with 10,000 mg of P kg^{-1} and roto-tilled (RT) at the urban site.

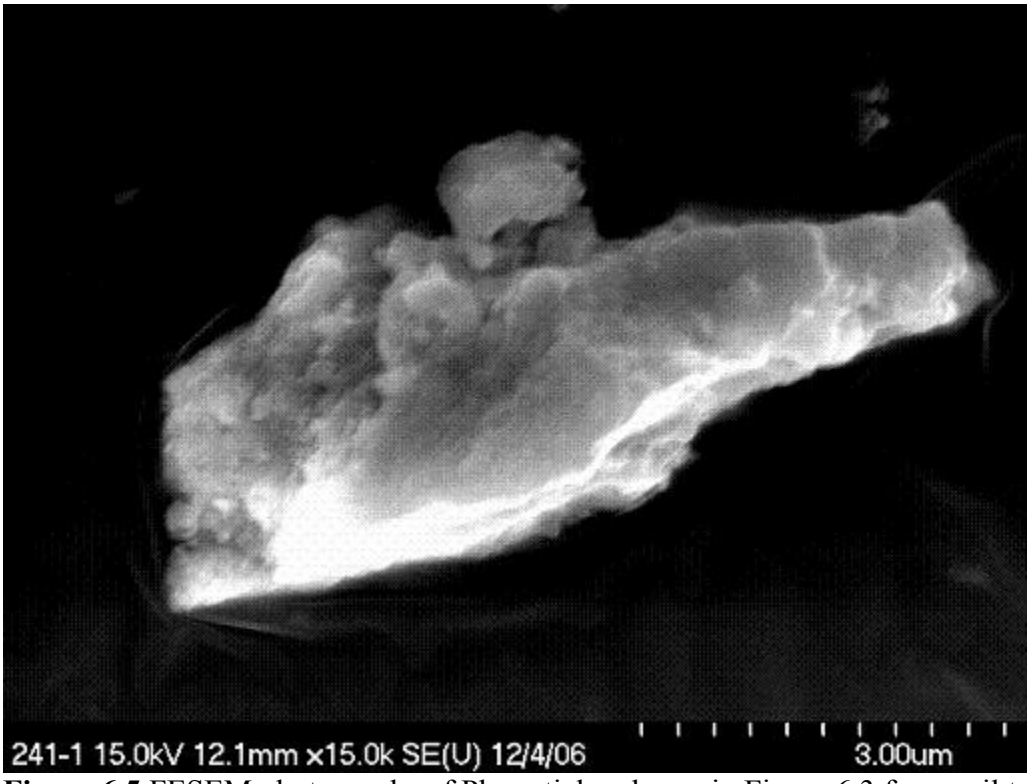


Figure 6.5 FESEM photographs of Pb particles shown in Figure 6.3 from soil treated with 10,000 mg of P kg^{-1} and roto-tilled.

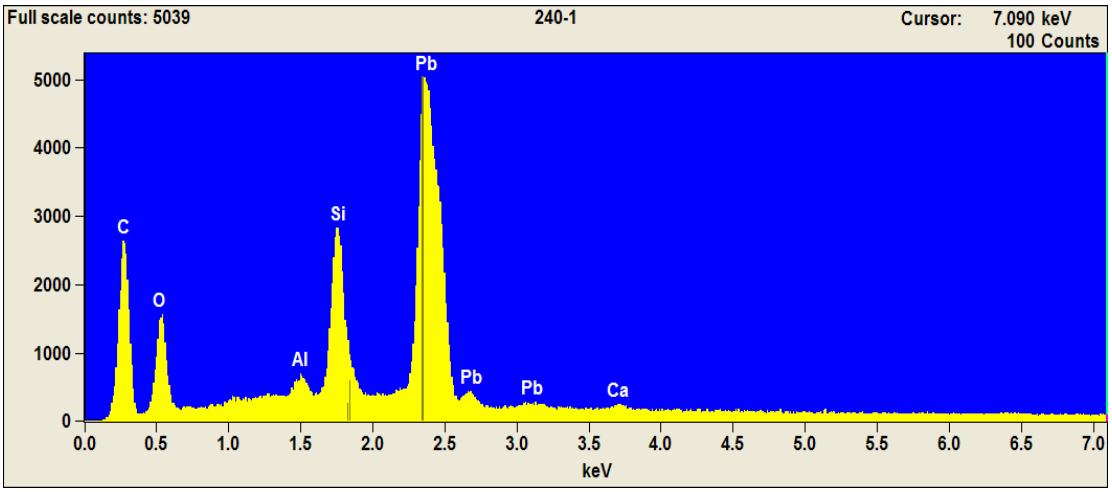


Figure 6.6 EDS patterns for Pb particles in untreated (Control) soil in the urban site.

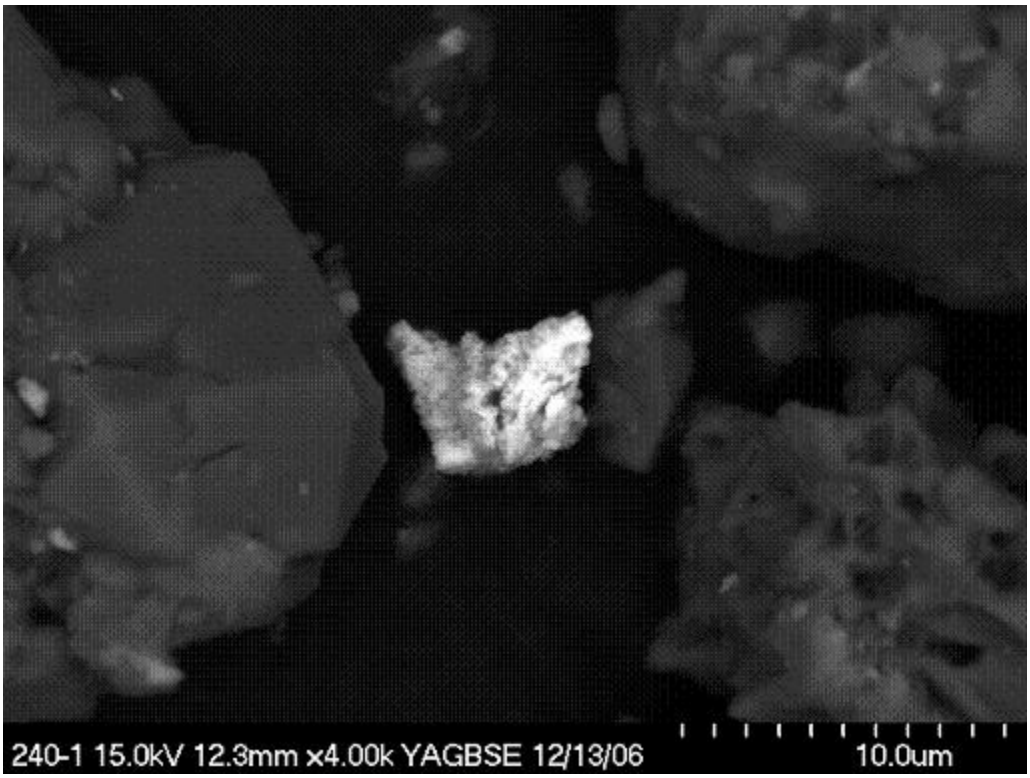


Figure 6.7 FESEM photographs of Pb particles shown in Figure 6.5 from untreated (Control) soil.

Mill-Waste Site - Chemical fractionation of P and Pb

The application of 1% phosphoric acid to the soil increased the total amount of P in the soil; also the percentage of non-occluded P fraction, including Al-P and Fe-P, was increased by 40% in the mill-waste soil (Figure 6.8). This result can be considered as the primary reason for the significant increase of soil P leaching in the mill-waste after the treatment (Figure 5.7). Moreover, the application of P could also increase soil organic P, which could promote soil P leachability as well (King, 1997). Increased non-occluded P fraction was mainly responsible for increasing Al-Fe bound P fraction, which is the most labile form of soil inorganic P (Hu et al., 2001). Data analysis indicates that the decreases of occluded P and Ca bound P(the most stable form of soil inorganic P), were found to be reduced by 16% after the treatment; P occluded by Fe oxide, the second stable form, was found reduced from 42% to 19%. Additionally, the promotion of total P concentration in the soil by PA application is also responsible for the increasing of P leachability.

As a result of the treatments, almost 100% soil Pb had been changed into residual Pb (Figure 6.9), thus reducing organical-bound Pb by 11%, Fe-Mn associte Pb by 44%, and carbonate forms by 8%. The decrease of soluble and bioavailable Pb in contaminated soil confirmed the decrease of *in vitro* bioavailability (Figure 4.12), phytoavailability (Figure 4.16), and leachability of Pb (Figure 5.9). The increasing of residual Pb in the soil could reduce the risk of Pb to humans and the environment.

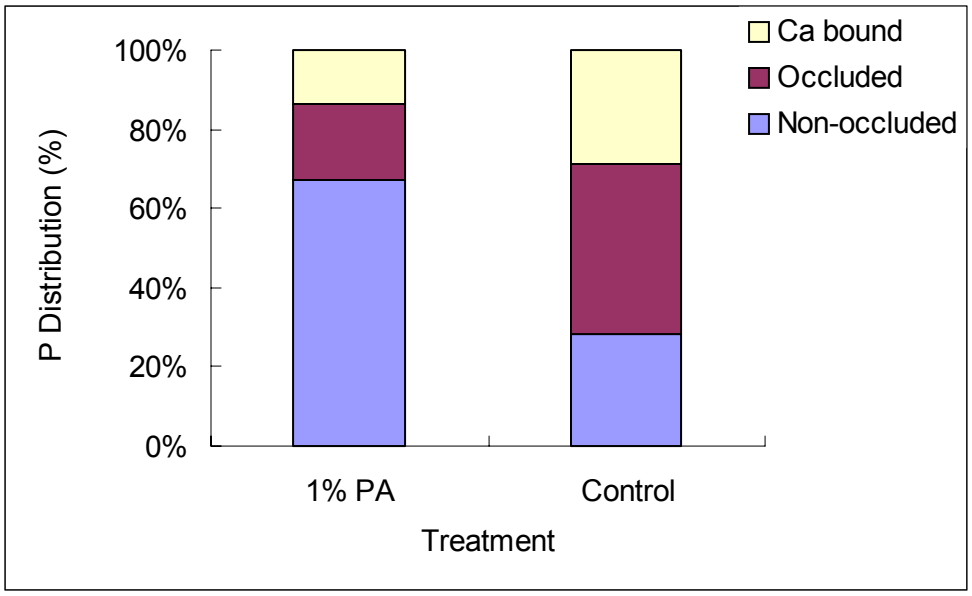


Figure 6.8 Phosphorus distributions in different fractions of two treatment methods from five sample dates for mill-waste site. 1% PA: 10 g P kg^{-1} soil; Control: no treatment.

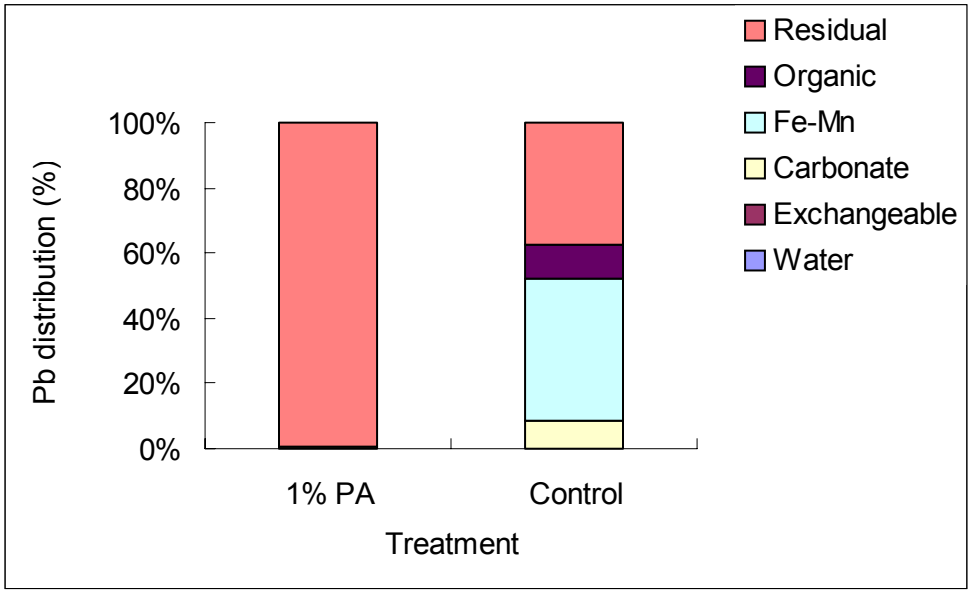


Figure 6.9 Lead distributions in different fractions of two treatment methods from five sample dates for mill-waste site. 1% PA: 10 g P kg^{-1} soil; Control: no treatment.

Mill-Waste Site - Solid Speciation of Pb

Figure 6.10 showed a similar EDS spectrum pattern with P, Pb, and Cl peaks to chloropyromorphite standard sample (Figure 6.3), indicating that chloropyromorphite or chloropyromorphite-like compounds were observed after 1% PA soil treatment at the mill-waste. About 30% of the soil Pb particles contained P and Cl (Table 6.3). This finding also agrees with the finding of Scheckel et al (2004), where 45% pyromorphite formation was observed after 1% PA application. The FESEM photographs indicated that the chloropyromorphite-like compounds were distributed heterogeneously in the mill-waste soil (Figure 6.11). It is agreed with Scheckel et al (2004) that it is very difficult to distinguish the hexagonal crystals of pyromorphite from the arrays of hexagonal minerals. Yang et al (2001) also found the "chloropyromorphite-like" mineral heterogeneously distributed in the sample and not in hexagonal crystal structure.

Figure 6.12 was the EDS spectrum for untreated mill-waste that showed P and Cl were not associated with Pb. About 80% of the Pb particles had no association with P and Cl (Table 6.3). Figure 6.13 was the FESEM photograph for the only Pb particles in untreated mill-waste.

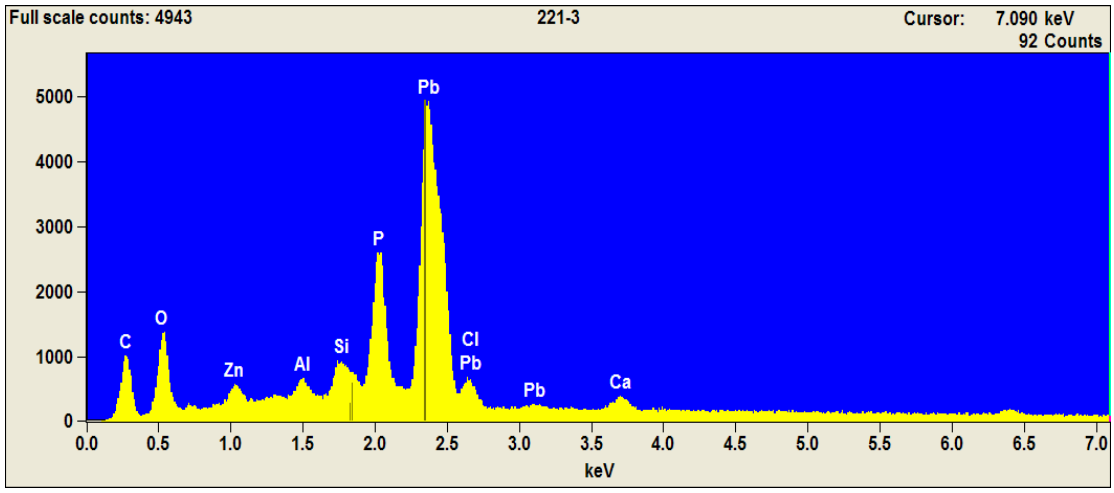


Figure 6.10 EDS patterns for Pb particles in soil that treated with 10,000 mg of P kg^{-1} in the Mill-waste Site.

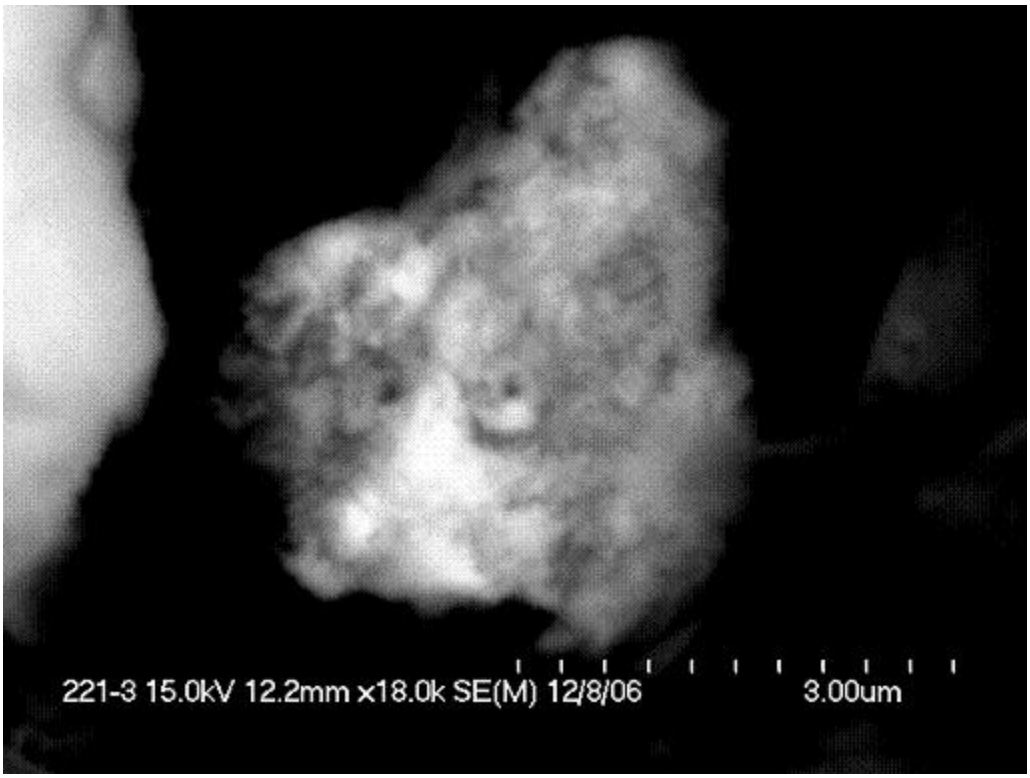


Figure 6.11 FESEM photographs of Pb particles shown in Figure 6.9 from soil treated with 10,000 mg of P kg^{-1} in the Mill-waste Site.

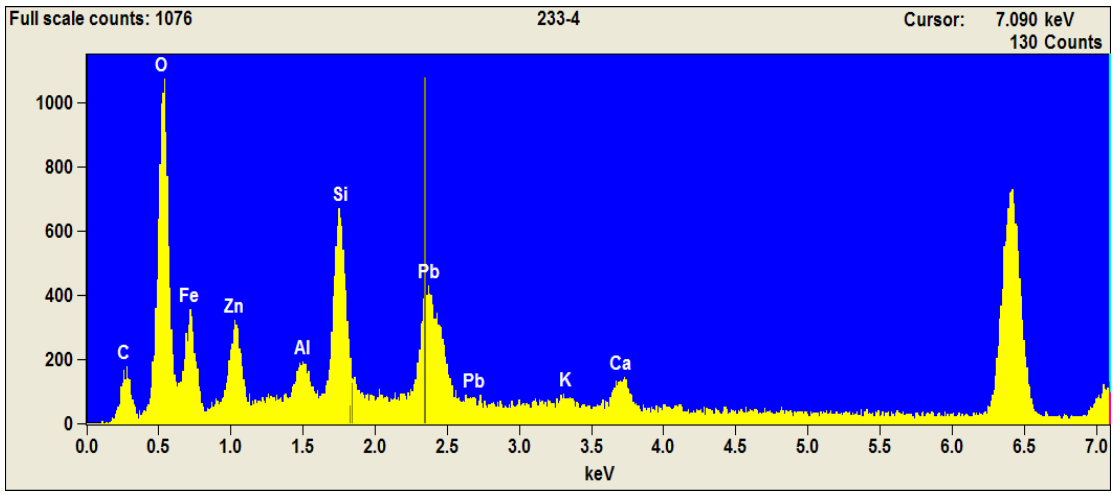


Figure 6.12 EDS patterns for Pb particles in untreated (Control) soil in the Mill-waste Site.

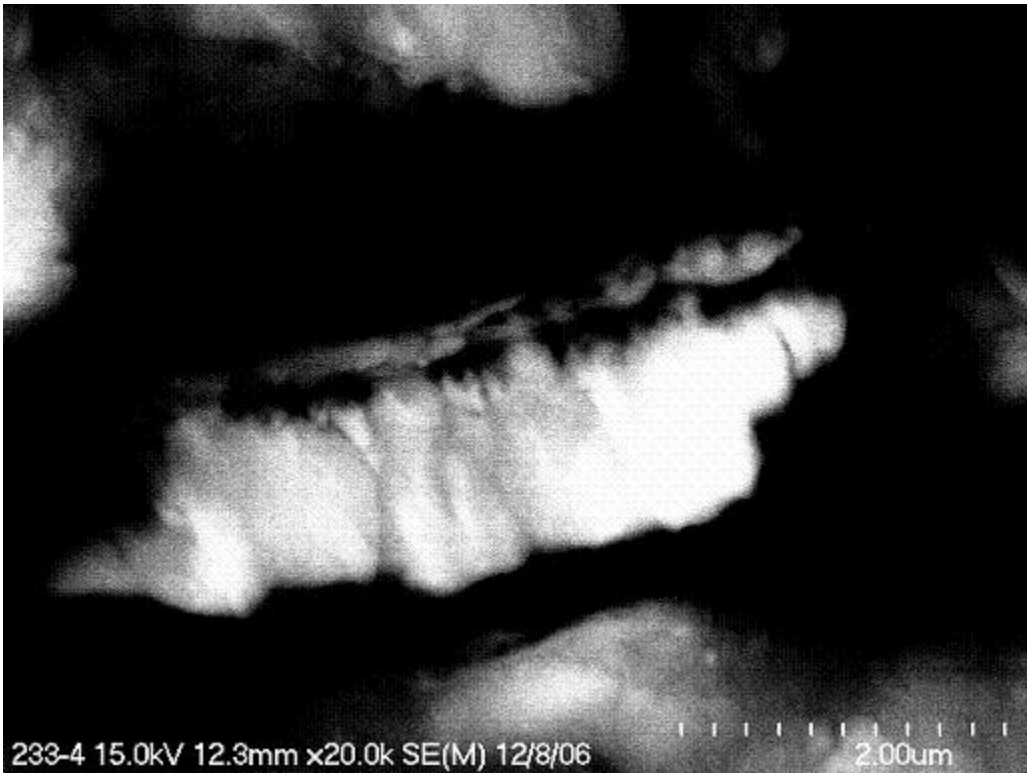


Figure 6.13 FESEM photographs of Pb particles shown in Figure 6.11 from untreated (Control) soil.

Mining Waste Site - Chemical fractionation of P and Pb

Figure 6.14 indicated that all the biosolid applications had higher percentage of soil non-occluded (Al-Fe) P than that of the untreated soil. This result is agreed with Akhtar et al (2002) and Maguire et al (2000) that non-occluded P increased greatly after sludge application. Non-occluded P in the OM-amended soil was reported that could be affected by soil type, OM application, sampling time, and temperature (Akhtar et al., 2002). Chang et al. (1983) reported that predominant Ca-P fraction in the calcareous soil was changed into Al-Fe P after 5 yr of biosolids application. The increasing of non-occluded P in the soil can promote soil P leachability. The hierarchy of non-occluded P in mining waste was MDM (67%)>CSSH (65%)>EPA (60%)>P (59%)=RS (59%)>CSS (43%)>SMC (32%)>CL (17%)=MD (17%)>TL (16%)>UN (10%). Compare to the untreated soil, the occluded P fraction that is less plant-available than Al-Fe P, was largely decreased in all the treated soil. Akhtar et al (2002) suggested that the decrease of occluded P might because soil solubilized Fe and Al oxides and released P occluded within it once soil became temporarily anaerobic by the OM application.

However, most treatments also had higher percentage of Ca bound P fraction, which is the most stable form in sandy soil (Maguire et al., 2000). The hierarchy of Ca bound P fraction was TL (62%)>MD (53%) >CL (52%)>SMC (50%)>CSS (29%)>P (24%)>EPA (23%)>RS (21%)> UN (16%)> MDM (12%). Compare these results with P leachability result in Figure 5.13, which the hierarchy of P leachability was MD>CL>TL>CSS >SMC>RS> EPA>MDM>P>CSSH >UN, that first three treatments significantly increased soil P leachability. It was observed that the 7 treatments that had highest leachable P followed the order of total amount of P in the soil; however, the 7 treatments

that had lowest leachable P were the treatments that had lowest non-occluded P; SMC, RS, and EPA were in common. Olsen and Sommers (1982) suggested that the application of fractionation methods to soils that were heavily fertilized was uncertain because of the persistence of the intermediate reaction products and their dissolution and exchange behavior. The P content of treatments MD, CL, TL, and CSS, which were over 15,000 mg kg^{-1} soil, could be too high to be analyzed by fractionation method.

From Figure 6.15, all biosolid treatment had increased the percentage of residual Pb fraction in mining waste, except MDM treatment. The hierarchy of residual Pb percentage was CSS (96%)>TL (91%)=MD (91%)>CL (85%)>RS (79%) >SMC (75%)>P (43%)>EPA (42%)>CSSH (38%)>UN (37%)>MDM (33%). This result partly followed the results of chapter 4 and chapter 5. The lowest residual fraction of Pb in MDM plot may explain why the highest *in vitro* bioavailable Pb occurred in MDM among all the treatments in the mining waste. However, the zero percent of water soluble Pb in MDM was the reason for low Pb phytoavailability and leachability in MDM.

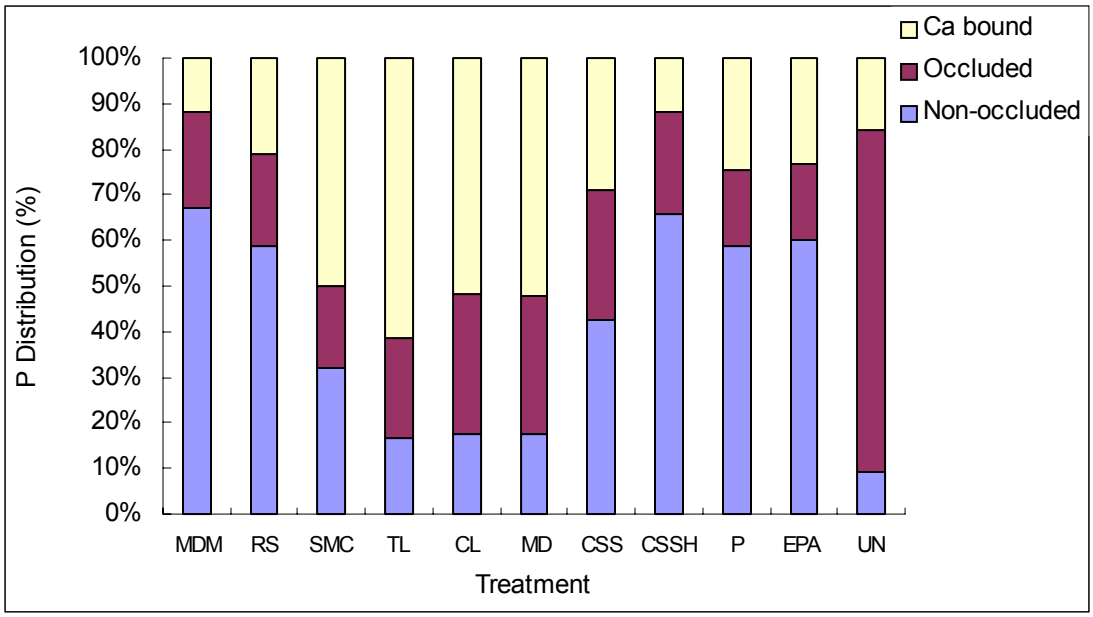


Figure 6.14 Phosphorus distributions in different fractions of eleven treatment methods from five sample dates for Mining Waste Site. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment.

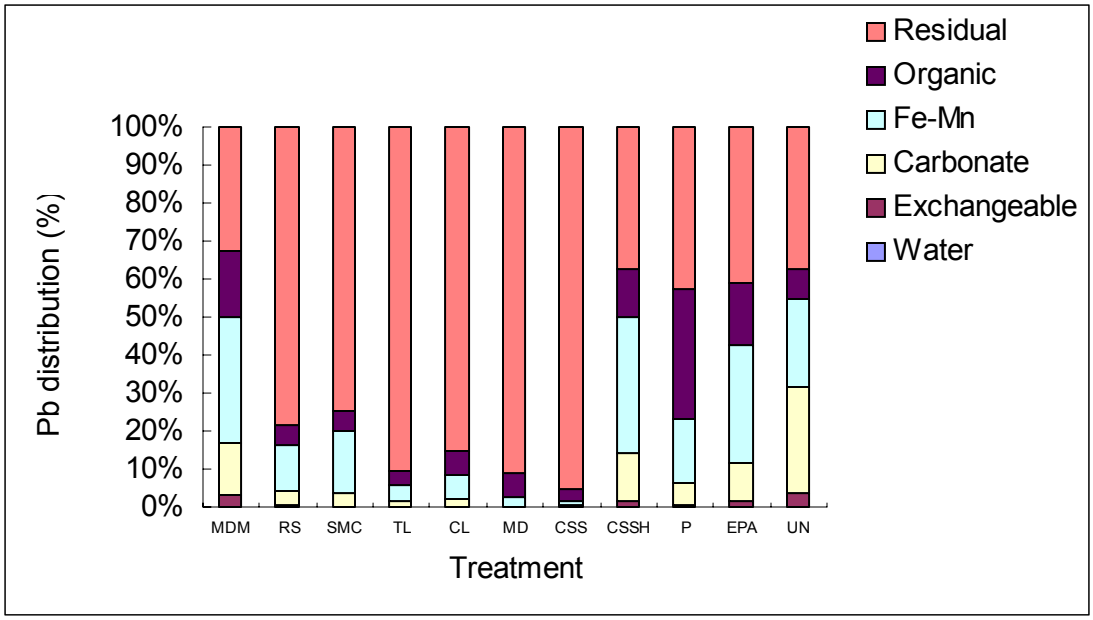


Figure 6.15 Lead distributions in different fractions of eleven treatment methods from five sample dates for Mill-waste Site. MDM: Mizzou Doo Mix; RS: repository soil; SMC: spent mushroom compost; TL: turkey house litter; CL: chicken litter; MD: Mizzou Doo; CSS: composed sewage sludge; CSSH: composed sewage sludge higher terrain; P: high phosphorus application; EPA: EPA soil repository; UN: no treatment.

Solid Speciation of Pb

Although chloropyromorphite or chloropyromorphite-like compounds were found in the soil (20% of the Pb particles), the most common Pb compound in SMC and MD treatment plots was other Pb-phosphate (7 in 10 times). This finding is in agree with Scheckel et al (2004) that pyromorphite formation was not enhanced by the OM applications. Lang and Kaupenjohann (2003) explained the reasons for the insignificant formation of pyromorphite in the high OM amended soil were: (1) pyromorphite formation might be decreased by Pb-OM complexation; (2) pyromorphite crystal could be coated by organic coats that inhibited further pyromorphite formation; and (3) the organic coatings on pyromorphite crystal might remove it from measured profile by enhancing the colloidal transport of pyromorphite. Both Figure 6.16 and Figure 6.18 showed similar spectrums containing P and Pb peaks that verified the formation of Pb phosphates. FESEM photographs (Figure 6.17 and Figure 6.19) showed the Pb-phosphate particles in the diameter of about 40 μm. Most of chioropyromorphite was found heterogeneously distributed. However, the Pb phosphate particle, which was treated with MD was in the classic pyromorphite "five-sided columnar structure", though the spectrum did not show the peak of Cl, hydroxypyromorphite [$Pb_5(PO_4)_3OH$] might be formed with the MD treatment. The formation of crystalline or poorly-crystalline chloropyromorphite and other relatively stable Pb phosphates might explain the decrease of Pb solubility and bioavailability in the treated soil.

Figure 6.20 was the most common spectrum for untreated mining waste that showed Pb only particle particles in the soil (90% probability). Figure 6.21 was the FESEM photograph for soil Pb particles 40 μm-sized in the untreated mining waste.

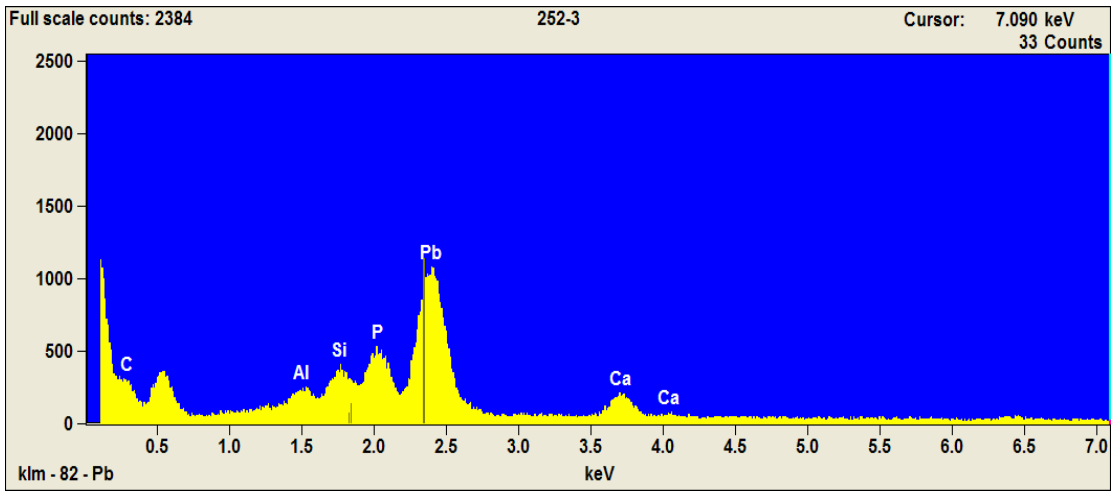


Figure 6.16 EDS patterns for Pb particles in soil that treated with spent mushroom compost (SMC) in the Mining Waste Site.

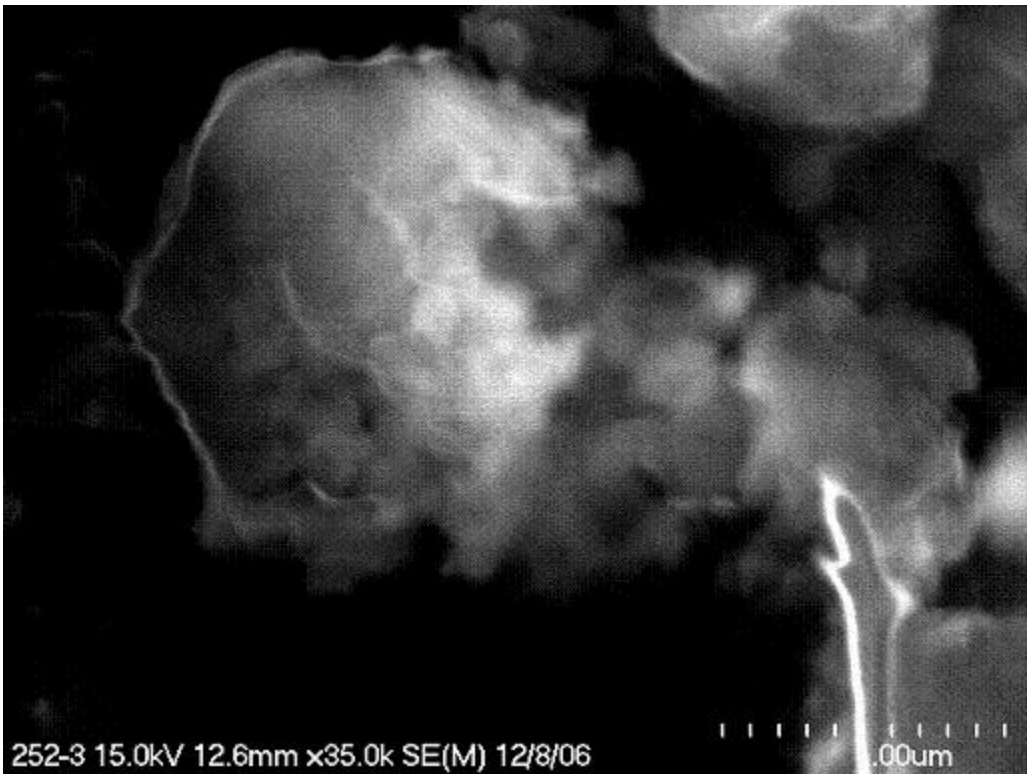


Figure 6.17 FESEM photographs of Pb particles shown in Figure 6.15 from soil treated with spent mushroom compost (SMC) in the Mining Waste Site.

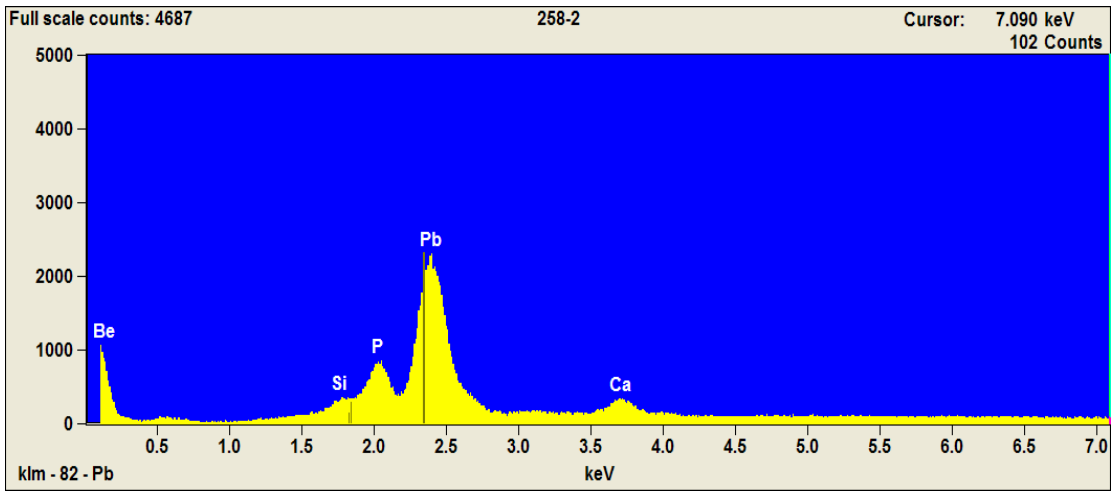


Figure 6.18 EDS patterns for Pb particles in soil that treated with Mizzou Doo (MD) in the Mining Waste Site.

Figure 6.19 FESEM photographs of Pb particles shown in Figure 6.17 from soil treated with Mizzou Doo (MD) in the Mining Waste Site.

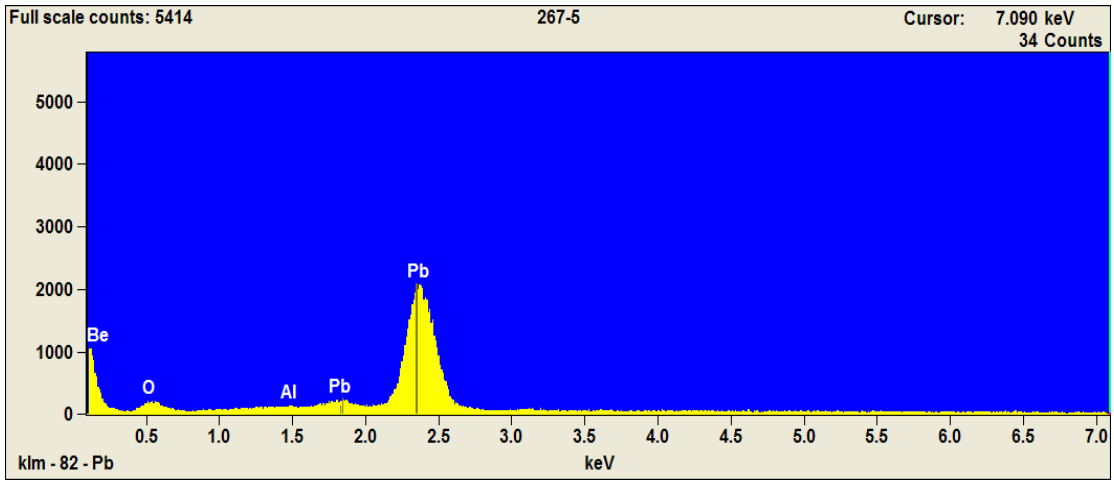


Figure 6.20 EDS patterns for Pb particles in untreated (UN) soil in the Mining Waste Site.

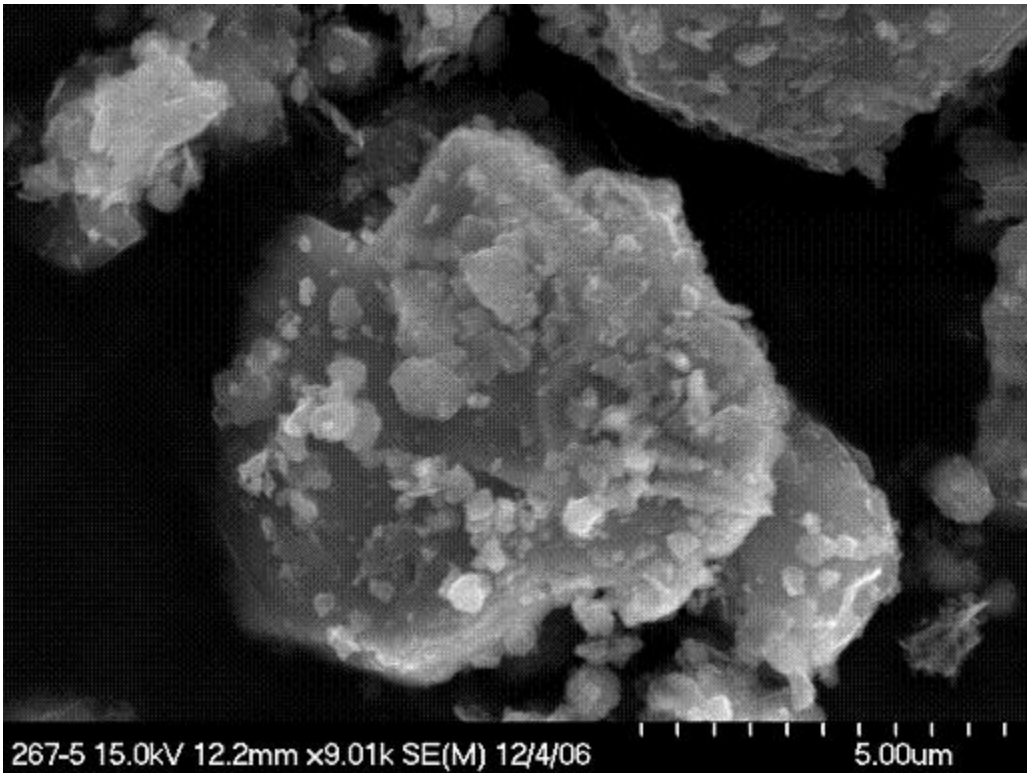


Figure 6.21 FESEM photographs of Pb particles shown in Figure 6.18 from untreated (UN) soil in the Mining Waste Site.

Sites	Sample ID	Pb	Pb, P	Pb, P, Cl
Mill-waste	1% PA (221)	10%	60%	30%
	Control (233)	80%	20%	0%
Urban	Control (240)	70%	30%	0%
	1% RT (241)	10%	60%	30%
Mining Waste	SMC (252)	10%	70%	20%
	MD (258)	10%	70%	20%
	Untreated (267)	90%	10%	0%

Table 6.3 The chance of three types of lead particles were observed while collecting.

CONCLUSIONS

In the urban soil, the application of phosphoric acid by three methods all increased non-occluded P fractions in the soil, including Al-P and Fe-P. The increased non-occluded P fractions led to the increase of P leaching potential in the soil. The RT and PI treatments increased Ca-P fraction, which was the most stable form in soil inorganic P content. From chapter4 and chapter5, all three treatments reduced Pb bioavailability to organisms and Pb leachability in the soil significantly. This could be explained by the reduction of carbonate, exchangeable, and water soluble fractions of Pb in the soil. The solid phase microprobe analysis also showed that most of soil Pb was transformed into stable Pb phosphates and pyromorphites as a result of the treatments. Results indicated that the phytoavailability of Pb could be directly influenced by the fractions of water soluble and exchangeable Pb in the soil.

In the mill-waste, the increase of non-occluded P fraction by the application of phosphoric acid was also found, which significantly increased the potential of soil P leaching P in the treated soil. The reduction of carbonate, exchangeable, and water soluble fractions of Pb could account for reduced *in vitro* Pb bioavailability, phytoavailability, and leachability in the soil. This could also be proved by the spectrum and image of solid phase microprobe analysis that most of soil Pb was transformed into stable Pb phosphates and pyromorphites 6 years after the initial treatment. The increase of soil residual Pb could reduce the risk of Pb to humans and ecosystem in mill-waste.

The increase of P leachability by all the treatments in the mining waste was caused by the increasing of non-occluded fractions of soil P that was introduced by the P-enriched biosolid applications. The result indicated that the fractionation method was

uncertain to heavily fertilized soils, such as MD, CL, TL, and CSS. Similar to the other sites, the reductions of *in vitro* bioavailability, phytoavailability, and leachability of Pb resulted from reduced exchangeable and water soluble forms of Pb in the soil. Solid phase microprobe analysis showed that most of soil Pb was transformed into stable Pb phosphates and pyromorphites 8 years after the initial treatment.

LITERATURE CITED

Adhami, E., M. Maftoun, A. Ronaghi, N. Karimian, J. Yasrebi, and M.T. Assad. 2006. Inorganic phosphorus feactionation of highly calcareous soils of Iran. Communications in Soil Science and Plant Analysis. 37:1877-1888.

Adriano, D.C. 2001. Trace elements in terrestrial environments biogeochemistry, bioavailability, and risks of metals, 2nd edition. Springer-Verlag, New York.

Akhtar, M., D.L. McCallister, and K,M, Eskridge. 2002. Availability and fractionation of phosphorus in sewage sludge-amended soils. Commun. Soil Sci. Plant Anal. 33(13&14):2057-2068.

Amore, J.J., S.R. Al-Abed, K.G. Scheckel, and J.A. Ryan. 2005. Methods for speciation of metals in soils: a review. J. Environ. Qual. 34:1707-1745.

Chang, A.C., A.L. Page, F.H. Sutherland, and E. Grgurevic. 1983. Fractionation of phosphorus in sludge-affected soils. J. Environ. Qual. 12:286-290.

Chang, S.C., and M.L. Jackson. 1957. Fractionation of soil phosphorus. Soil Sci. 84:133-144.

Chlopecka, A., and D.C. Adriano. 1996. Mimicked in-situ stabilization of metals in a cropped soil: bioavailability and chemical form of zinc. Environ. Sci. Technol.

30:3294-3303.

Gambrell, R.P. 1994. Trace and toxic metals in wetland. J. Environ. Qual. 23:883-891.

Gerritse, C.P., and R. Vriesema. 1984. Phosphate distribution in animal waste slurries. J. Agric. Sci. 102:159-161.

Hu, H.Q., C.Y. Tan, C.F. Cai, J.Z. He, and X.Y. Li. 2001. Availability and residual effects of phosphate rocks and inorganic P fractionation in a red soil of Centeral China. Nutrient Cycling in Agroecosystems. 59:251-258.

King, N.T. 1997. Phosphorus distribution and availability in a Missouri Ozark watershed. Graduate thesis of University of Missouri-Columbia, MO.

Lang, F., and M. Kaupenjohann. 2003. Effect of dissolved organic matter on the precipitation and mobility of the lead compound chloropyromorphite in solution. Eur. J. Soil Sci. 54:139-147.

Ma, L.Q., and G.N. Rao. 1997a. Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils. J. Environ. Qual. 26:259-264.

Ma, L.Q., and G.N. Rao. 1997b. Effects of phosphate rock on sequential chemical extraction of lead in comtaminated soils. J. Environ. Qual. 26:788-794.

Maguire, R.O., J.T. Sims, and F.J. Coale. 2000. Phosphorus fractionation in biosolids-amended soils: relationship to soluble and desorbable phosphorus. Soil Sci. Soc. Am. J. 64:2018-2024.

Olsen, S.R., and L.E. Sommers. 1982. Phosphorus. p. 403-427. In A.L. Page et al. (ed.) Chemical and microbiological properties. (2nd edition) ASA-SSSA, Madison, WI.

Pierzynski, G.M., and A.P. Schwab. 1993. Bioavailability of zinc, cadmium, and lead in a metal contaminated alluvial soil. J. Environ. Qual. 22:247-254.

Ramos, L., L.M. Hernandez, and M.J. Gonzales. 1994. Sequential fractionation of copper, lead, cadmium, and zinc in soils from or near Donana National Park. J. Environ. Qual. 23:50-57.

Roberts, D., M. Nachtegaal, and D. Sparks. 2005. Speciation of metals in soils. p. 619-637. In Al-Amoodi, L., W.A. Dick, M.A. Tabatabai, and D.L. Sparks (ed.) Chemical processed in soils. SSSA, Madison, WI.

Samaras, V., and C.D. Tsadilas. 1997. Distribution and availability of six heavy metals in a soil treated with sewage sludge. Proc. Int. Conf. Biogeochemistry of Trace Elements, Berkeley, CA.

Scheckel, K.G., C.A. Impellitteri, J.A. Ryan, and T. McEvoy. 2003. Assessment of a sequential extraction procedure for perturbed lead contaminated samples with and without phosphorus amendments. Environ. Sci. Technol. 37:1892-1898.

Scheckel, K.G., and J.A. Ryan. 2004. Spectroscopic speciation and quantification of lead in phosphate-amended soils. J. Environ. Qual. 33:1288-1295.

Sui, Y.B., M.L. Thompson, and C. Shang. 1999. Fractionation of phosphorus in a mollisol amended with biosolids. Soil Sci. Soc. Am. J. 63:1174-1180.

Syers, J.K., R. Shah, and T.W. Walker. 1969. The fractionation of phosphorus in two alluvial soils and particle-size separates. Soil Sci. 108:283-289.

Tsadilas, C.D., T. Matsi, N. Barbayiannis, and D. Dimoyiannis. 1995. Influence of sewage sludge application on soil properties and on the availability of heavy metals fractions. Commum. Soil Sci. Plant Anul. 26(15-16):2603-2619.

Tsadilas, C.D. 2001. Soil pH effect on the distribution of heavy metals among soil fractions. p. 107-119. In I.K. Iskandar (ed.) Environmental restoration of

metals-contaminated soils. CRC Press, Boca Raton, FL.

Williams, J.D.H., J.K. Syers, and T.W. Walker. 1967. Fractionation of soil inorganic phosphate by a modification of Chang and Jackson's procedure. Soil Science Society of America Proceedings. 31:736-739.

Xian, X. 1989. Effect of chemical forms of cadmium, zinc, and lead in polluted soils on their uptake by cabbage plants. Plant Soil 113:257-264.

Yang, J.J., D.E. Mosby, S.W. Casteel and R.W. Blanchar. 2001. Lead immobilization using phosphoric acid in smelter-contaminated urban soil. Environ. Sci. Technol. 35:3553-3559.

Yang, J., D.E. 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. Arch. Environ. Contam. Toxicol. 43:399-405.

Yang, J., and D. Mosby. 2006. Field assessment of treatment efficacy by three methods of phosphoric acid application in lead-contaminated urban soil. Sci. Total Environ. 366:136-142.

Zhang, M.K., Z.L. HE, P.J. Stoffells, D.V. Calvert, X.E. Yang, and Y.C. Li. 2003. Phosphorus and heavy metal attachment and release in sandy soil aggregate fractions. Soil Sci. Soc. Am. J. 67:1158-1167.

Zhang, M.K., Z.L. HE, P.J. Stoffells, D.V. Calvert, X.E. Yang, Y. P. Xia, and S. B. Wilson. 2004. Solubility of Phosphorus and Heavy Metals in Potting Media Amended with Yard Waste–Biosolids Compost. J. Environ. Qual. 33:373–379

CHAPTER 7

SUMMARY

The results of the studies described in this thesis indicated that the integrated risk assessments were effective (1) to assess long-term reductions of bioavailability or risk of soil metals to human health and ecosystems by the *in situ* soil treatments using phosphate-based amendments in metal contaminated soils; (2) to evaluate the leachibility/stability of immobilized metals and phosphate in phosphate-or OM-treated soils and surface or ground water quality; and (3) to identify solid or chemical metal species formed upon soil phosphate treatment, which accounted for metal immobilization by the treatments.

Results in Chapter 4 showed that *in vitro* bioavailabilities of Pb and Cd were reduced significantly by the application of phosphoric acid in the urban soil and mill-waste soil. The reductions of phytoavailable Pb and Cd in the urban site were significant, however, the phytoavailable metal reduction in the mill-waste was not effective as that in urban soil. Except for the 0.75% PA treatment in the mill-waste, all treatments did not have negative impacts on soil microbial toxicity in the two sites. In the mining waste, all OM treatments would significantly reduce *in vitro* bioavailability of Pb, while only SMC, TL, MD, and CSS reduced *in vitro* bioavailable Cd. Except for CSSH, treatments did not significantly impact soil microbial toxicity. Additionally, SMC and CSS were found most effective for reducing both *in vitro* bioavailable and phytoavailable metals.

In Chapter 5, all treatments, including inorganic P and OM applications, were found increasing P leachability in the soil. The leachability of Pb in all treated soil was greatly

reduced in three study sites; the leachable Cd was reduced by all phosphoric acid treatments and some biosolid treatments. SMC and MD were observed the best in terms of *in vitro* availability, phytoavailability, microbial toxicity, and leachability tests. The water quality test confirmed the immobilization of Pb in the surface soil, and the increase of soil P leachability by the treatments.

The results of soil P fractionation in chapter 6 indicated that all application of P increased the non-occluded fractions of P in the soil, which was responsible for enhanced soil P leachability in all the treated sites. The sequential extraction of soil Pb indicated that the transformation of soil Pb from carbonate adsorbed, exchangeable, and water soluble fractions to residule fraction would accounted for the reductions of the Pb *in vitro* availability, phytoavailability, and leachability in all the sites (chapter 4, chapter 5). Solid phase speciation by the microprobe analyses confirmed the formation of pyromorphates or lead phosphates in the treated soils.

This study also observed that (1) *in vitro* bioavailable Pb were positively correlated with phytoavailable Pb in all three study sites; (2) the reductions of leachable Pb were positively correlated with the reductions of phytoavailable Pb in most phosphoric acid treated soils; and (3) the phytoavailability of Pb appeared to be correlated with the fractions of water soluble and exchangeable Pb in the soil.

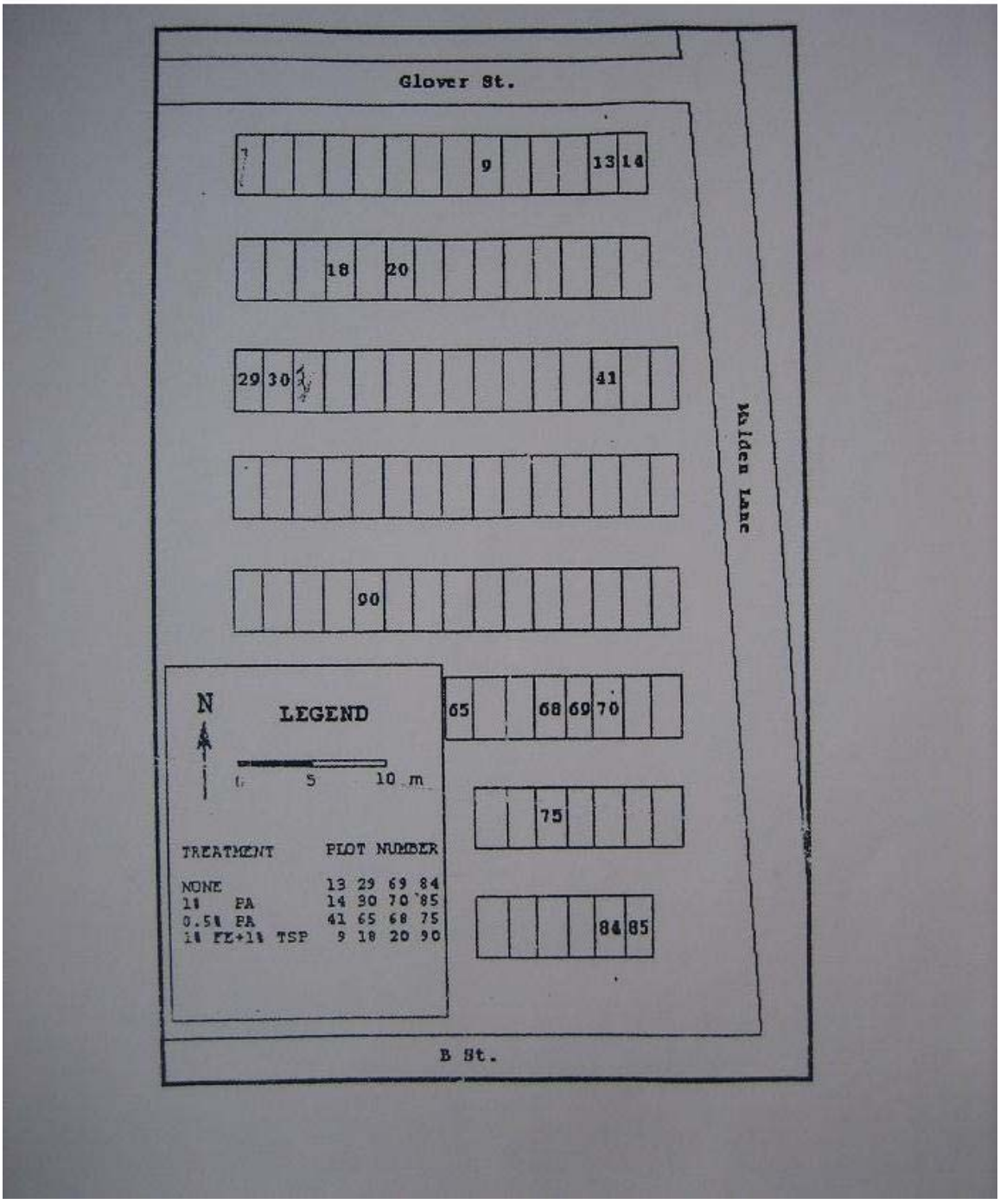
Treatment effects in most measurements were significant, but not the season and the interaction of treatment x season. This would indicate that the treatments would be a primary factor influence the risk reductions.

In summary, this study demonstrated that the phosphoric acid and OM application in urban soil and mine wastes effectively reduced metal (e.g. Pb, Cd) bioavailability and

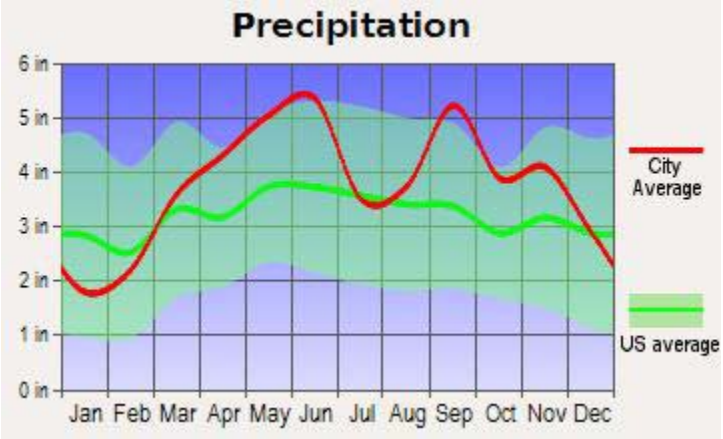
leachability through transforming labile forms of metal to stable forms. The treatments did not significantly impact microbial toxicity in the soil and water, and may help to improve water quality. The *in situ* immobilization would be a long-term, cost- effective, and ecological-safe remedial technology that safeguards human health and ecological system from metal contamination.

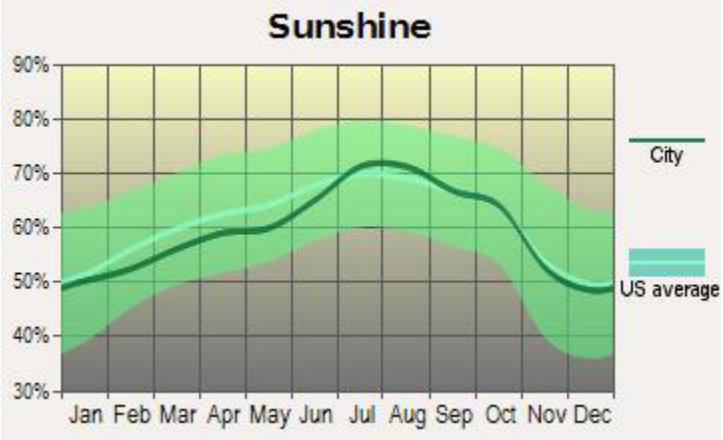
APPENDICES

Appendix 1: Diagram of plot layout for urban soil



Appendix 2: Annually precipitation and sunshine trends of the Joplin area





From //www.City-data.com.

Appendix 3: Raw data for microbial toxicity of each sampling date

Microtoxicity	Joplin	10-2004			
Mill-waste		Urban		Mining Waste	
Sample ID	Effect %	Sample ID	Effect %	Sample ID	Effect %
A (1% TR)	68.48	1% SA (1)	71.16	Mizzou Doo Mix (T2)	71.29
B (0.75%TR)	64.68	Control (13)	63.70	SMC (T4)	65.97
C TOP (Control)	48.19	1% RT (14)	42.80	Turkey Litter (T5)	65.23
		1% PI (31)	43.16	Chicken Litter (T6)	69.73
				Sewage Sludge (8H)	73.67
				Phosphorus (T9)	76.60
				EPA Soil (T10)	72.81
				UNTREATED	75.20
03-2005					
Mill-waste		Urban		Mining Waste	
Sample ID	Effect %	Sample ID	Effect %	Sample ID	Effect %
A (1% TR)	81.20	1% SA (1)	62.36	Mizzou Doo Mix (T2)	70.25
B (0.75%TR)	70.73	Control (13)	67.78	SMC (T4)	68.49
C TOP (Control)	77.46	1% RT (14)	39.64	Turkey Litter (T5)	66.58
		1% PI (31)	51.35	Chicken Litter (T6)	64.24
				Sewage Sludge (8H)	77.35
				Phosphorus (T9)	69.03
				EPA Soil (T10)	62.37
				UNTREATED	66.18
06-2005					
Mill-waste		Urban		Mining Waste	
Sample ID	Effect %	Sample ID	Effect %	Sample ID	Effect %
A (1% TR)	73.78	1% SA (1)	62.95	Mizzou Doo Mix (T2)	69.83
B (0.75%TR)	91.20	Control (13)	68.10	SMC (T4)	69.07
C TOP (Control)	80.53	1% RT (14)	32.64	Turkey Litter (T5)	72.11
		1% PI (31)	59.67	Chicken Litter (T6)	76.76
				Sewage Sludge (8H)	77.11
				Phosphorus (T9)	74.97
				EPA Soil (T10)	51.86
				UNTREATED	66.74
09-2005					
Mill-waste		Urban		Mining Waste	
Sample ID	Effect %	Sample ID	Effect %	Sample ID	Effect %
A (1% TR)	69.23	1% SA (1)	68.63	Mizzou Doo Mix (T2)	71.28
B (0.75%TR)	72.31	Control (13)	61.45	SMC (T4)	70.44
C TOP (Control)	47.09	1% RT (14)	51.10	Turkey Litter (T5)	68.63
		1% PI (31)	58.73	Chicken Litter (T6)	61.99
				Sewage Sludge (8H)	72.15
				Phosphorus (T9)	65.76
				EPA Soil (T10)	63.73
				UNTREATED	51.83
02-2006					
Mill-waste		Urban		Mining Waste	
Sample ID	Effect %	Sample ID	Effect %	Sample ID	Effect %
A (1% TR)	58.65	1% SA (1)	73.46	Mizzou Doo Mix (T2)	77.66
B (0.75%TR)	63.96	Control (13)	70.87	SMC (T4)	74.61
C TOP (Control)	49.53	1% RT (14)	70.34	Turkey Litter (T5)	69.83
		1% PI (31)	62.44	Chicken Litter (T6)	85.46
				Sewage Sludge (8H)	76.91
				Phosphorus (T9)	72.47
				EPA Soil (T10)	70.25
				UNTREATED	66.13

Appendix 4: Raw data and calculations for water quality in March 2004

	P (mg/L)	AVG	STD	Pb (mg/L)	AVG	STD
Mill-waste	0.095	0.085	0.015	0.095	0.085	0.015
	0.074			0.074		
Urban	0.067	0.059	0.012	0.046	0.041	0.007
	0.050			0.036		
Mining waste						
Mizzou Doo Mix (T2)	0.108	0.097	0.016	0.284	0.244	0.057
	0.085			0.204		
Repository Soil (T3)*	0.846	0.798	0.068	0.147	0.132	0.022
	0.750			0.116		
Mizzou Doo (T7)	0.248	0.234	0.020	0.226	0.192	0.048
	0.220			0.158		
Mizzou Doo (T7)*	0.915	0.819	0.064	0.155	0.116	0.023
	0.812			0.112		
	0.849			0.115		
	0.754			0.091		
	0.840			0.125		
	0.745			0.098		
Sewage Sludge (T8)	0.128	0.121	0.010	0.265	0.237	0.040
	0.114			0.209		
Sewage Sludge (T8)*	0.968	0.864	0.147	0.128	0.115	0.019
	0.760			0.101		
Phosphorus (T9)*	7.285	6.725	0.792	0.044	0.039	0.007
	6.165			0.034		
EPA Soil (T10)	0.467	0.441	0.037	0.085	0.076	0.013
	0.415			0.067		
Constructive Pond	0.110	0.104	0.008	0.104	0.088	0.023
	0.098			0.072		

Appendix 5: Raw data of EC50 for water quality in March 2004

	EC50 (%)	STD
Mill-waste	24.26	1.57
Urban	54.98	12.72
Mizzou Doo Mix (T2)	8.06	1.16
Repository Soil (T3)*	10.83	2.06
Mizzou Doo (T7)	22.99	2.52
Mizzou Doo (T7)*	35.36	10.91
Sewage Sludge (T8)	5.2	0.37
Sewage Sludge (T8)*	12.51	2.61
Phosphorus (T9)*	74.88	4.46
EPA Soil (T10)	17.38	1.98
Constructive Pond	68.61	4.13

Appendix 6: Raw data and calculations for phytoavailability of each sampling date

Phytoavailability 08-2003		P(mg/kg)	AVG	STD	Cd(mg/kg)	AVG	STD	Cr(mg/kg)	AVG	STD	Pb(mg/kg)	AVG	STD	Zn(mg/kg)	AVG	STD
Urban	1% PA (14)	11926.10	12449.15	739.70	27.05	28.78	2.44	93.71	102.23	12.06	4199.92	4246.42	65.77	3618.38	3895.86	392.42
		12972.20			30.50			110.76			4292.93			4173.34		
	0.5% PA (41)	4530.75	4537.45	9.49	4.67	4.66	0.01	14.44	14.32	0.16	103.24	100.03	4.53	361.28	367.61	8.94
		4544.16			4.65			14.21			96.83			373.93		
Mining Waste	4 pic.72	13153.60	13050.85	145.31	0.28	0.31	0.05	17.92	18.08	0.23	4.89	4.93	0.05	111.81	104.58	10.23
		12948.10			0.35			18.24			4.96			97.35		
	4 pic.73	14649.25	14500.85	209.87	17.46	16.54	1.31	40.75	40.25	0.71	280.49	261.89	26.31	3177.10	3025.34	214.61
		14352.45			15.61			39.75			243.28			2873.59		
	8 pic.65	2021.94	2052.30	42.94	0.38	0.40	0.04	36.82	39.03	3.12	15.08	14.72	0.51	93.17	96.30	4.43
		2082.67			0.43			41.23			14.36			99.43		
03-2004	Jue-young leaf	1478.43	1542.47	90.57	2.37	2.28	0.13	55.25	54.85	0.56	37.76	39.99	3.16	324.08	286.21	53.55
		1606.52			2.18			54.45			42.23			248.35		
	Jue-old leaf	746.72	753.12	9.05	3.82	4.30	0.68	53.23	52.76	0.67	83.81	85.00	1.69	535.94	571.38	50.11
		759.52			4.78			52.28			86.20			606.81		
	Jue-root	1181.66	1150.79	43.66	22.30	21.33	1.37	132.60	124.31	11.72	282.60	275.32	10.30	937.00	864.33	102.77
		1119.92			20.36			116.03			268.04			791.67		
	Flower-root	6282.15	6282.15		19.18	19.18		8.22	8.22		115.95	115.95		1048.53	1048.53	
	Flower-flower	4740.32	4740.32		21.99	21.99		29.48	29.48		5.60	5.60		128.09	128.09	
	Flower-shoot	4451.35	4385.08	93.72	12.04	11.92	0.17	31.20	29.88	1.86	5.64	5.97	0.47	210.35	204.39	8.43
		4318.81			11.80			28.57			6.31			198.42		
	Flower-ball	2911.23	2873.22	53.75	11.90	11.56	0.49	16.32	15.89	0.62	27.98	25.90	2.94	610.57	580.27	42.85
		2835.22			11.22			15.45			23.82			549.97		
10-2004		**P(mg/kg)**	**AVG**	**STD**	**Cd(mg/kg)**	**AVG**	**STD**	**Cr(mg/kg)**	**AVG**	**STD**	**Pb(mg/kg)**	**AVG**	**STD**	**Zn(mg/kg)**	**AVG**	**STD**
Mill-waste	A	5725.60	5705.42	28.53	26.55	25.96	0.83	17.73	17.34	0.54	58.69	59.21	0.72	1535.67	1520.69	21.18
		5685.25			25.37			16.96			59.72			1505.72		
	B like pic.I	9667.55	9667.97	0.60	27.65	28.38	1.02	70.03	64.48	7.85	714.50	745.70	44.12	4540.91	4679.13	195.48
		9668.40			29.10			58.93			776.89			4817.36		
	C like pic.A	2493.11	2548.41	78.21	42.51	43.48	1.37	4.19	4.24	0.08	13.05	13.86	1.14	794.26	821.07	37.93

		2603.72			44.44			4.30			14.67			847.89		
Urban	1	3425.90	3434.95	12.80	5.88	5.79	0.12	12.68	12.64	0.06	405.61	406.45	1.18	816.58	821.17	6.49
		3444.00			5.71			12.60			407.29			825.75		
	31	3706.07	3591.28	162.34	7.50	7.94	0.62	53.32	51.66	2.36	697.64	805.22	152.15	1007.26	1017.69	14.75
		3476.49			8.38			49.99			912.81			1028.12		
Mining Waste	2 pic.68	6631.70	6636.92	7.39	2.95	3.43	0.67	7.14	7.20	0.09	40.00	38.49	2.14	425.57	481.18	78.65
		6642.15			3.90			7.26			36.98			536.80		
	5 pic.71	3615.30	3544.93	99.51	0.92	0.94	0.02	22.65	22.37	0.39	55.29	50.44	6.86	475.16	466.27	12.58
		3474.57			0.96			22.10			45.59			457.37		
	6 pic.62	5810.65	5810.65		15.27	15.27		29.83	29.83		5.60	5.60		956.93	956.93	
	P9	4269.76	4302.93	46.90	4.84	4.81	0.05	14.37	14.53	0.24	124.73	0.13		2127.68	2138.00	14.59
		4336.09			4.77			14.70						2148.31		
03-2005		**P(mg/kg)**	**AVG**	**STD**	**Cd(mg/kg)**	**AVG**	**STD**	**Cr(mg/kg)**	**AVG**	**STD**	**Pb(mg/kg)**	**AVG**	**STD**	**Zn(mg/kg)**	**AVG**	**STD**
Mill-waste	1% PA	507.94	512.43	6.34	1.15	1.17	0.02	11.62	11.73	0.16	23.32	22.73	0.83	281.81	281.22	0.84
		516.91			1.18			11.84			22.15			280.63		
	Control	423.89	423.00	1.26	6.12	6.16	0.05	7.96	8.00	0.05	32.66	33.27	0.86	515.55	510.16	7.62
		422.10			6.19			8.03			33.88			504.77		
Urban	1% PA (1)	5709.85	5729.60	27.93	1.53	1.38	0.20	26.44	25.62	1.16	111.43	100.12	16.00	345.34	319.66	36.32
		5749.35			1.24			24.79			88.80			293.97		
	Control (13)	1659.28	1648.02	15.92	4.93	4.87	0.08	20.66	20.33	0.46	254.30	252.68	2.30	444.43	440.06	6.19
		1636.77			4.82			20.01			251.05			435.68		
	1% PA (14)	3404.53	3365.39	55.35	0.96	0.99	0.05	1.73	1.65	0.11	13.78	13.84	0.09	134.17	132.86	1.85
		3326.25			1.03			1.58			13.90			131.55		
	1% PI (31)	1173.14	1176.34	4.53	4.11	4.17	0.08	29.04	29.25	0.30	94.04	94.64	0.85	303.05	305.64	3.66
		1179.54			4.23			29.47			95.24			308.23		
Mining Waste	SMC (T4)	980.01	961.34	26.40	0.20	0.20	0.00	1.43	1.36	0.09	8.46	8.03	0.61	152.13	148.63	4.94
		942.68			0.20			1.30			7.60			145.14		
(T5)	Turkey Litter	714.74	704.72	14.17	0.20	0.18	0.03	1.15	1.04	0.16	4.76	4.40	0.51	240.33	237.28	4.32
		694.70			0.16			0.93			4.05			234.23		
(T6)	Chicken Litter	594.14	591.90	3.16	1.08	1.07	0.02	1.20	1.17	0.05	12.63	12.69	0.08	285.39	284.06	1.87

		589.67			1.05			1.13			12.75			282.74		
(T7)	Mizzou Doo	736.53	726.29	14.49	0.17	0.08	0.12	4.10	4.13	0.04	9.50	9.51	0.00	51.83	51.37	0.64
		716.05			0.00			4.16			9.51			50.92		
(T8)	Sewage Sludge	2777.46	2786.23	12.40	3.78	3.77	0.01	96.23	96.06	0.23	213.18	212.02	1.64	1062.70	1057.14	7.87
		2795.00			3.76			95.89			210.86			1051.57		
	T8 high	933.40	932.10	1.84	1.68	1.60	0.11	2.89	2.74	0.20	31.26	31.04	0.31	130.39	130.23	0.23
		930.80			1.52			2.60			30.83			130.07		
(T9)	Phosphorus	811.37	810.96	0.58	3.81	3.82	0.01	11.02	10.84	0.26	25.08	25.13	0.07	477.33	474.03	4.67
		810.55			3.83			10.66			25.18			470.73		
(T10)	EPA Repository	3566.79	3568.24	2.05	3.65	3.71	0.09	14.90	14.93	0.04	93.55	92.91	0.91	295.67	296.04	0.53
		3569.69			3.77			14.96			92.27			296.42		
	T10	814.86	807.88	9.86	0.21	0.20	0.02	0.00	0.00	0.00	4.23	4.70	0.66	141.76	141.03	1.04
		800.91			0.19			0.00			5.16			140.30		
	T10	1643.65	1660.03	23.16	1.69	1.68	0.02	0.00	0.00	0.00	1.06	0.66	0.58	75.76	75.71	0.08
		1676.40			1.67			0.00			0.25			75.65		
06-2005		**P(mg/kg)**	**AVG**	**STD**	**Cd(mg/kg)**	**AVG**	**STD**	**Cr(mg/kg)**	**AVG**	**STD**	**Pb(mg/kg)**	**AVG**	**STD**	**Zn(mg/kg)**	**AVG**	**STD**
Mill-waste	1% PA	2556.98	2566.89	14.01	32.88	32.91	0.05	34.53	34.63	0.14	95.74	95.99	0.36	459.27	461.63	3.34
		2576.80			32.95			34.73			96.25			464.00		
	Control	2663.62	2653.41	14.44	6.04	6.03	0.01	16.01	15.74	0.39	148.03	148.11	0.11	964.52	953.48	15.61
		2643.20			6.03			15.46			148.19			942.44		
Urban	1% PA (1)	3424.22	3421.01	4.54	2.46	2.48	0.04	14.84	14.65	0.26	137.93	136.60	1.88	268.76	268.66	0.14
		3417.80			2.51			14.47			135.28			268.56		
	Control (13)	2445.11	2405.46	56.07	7.58	7.54	0.06	99.98	98.65	1.88	382.71	375.24	10.57	814.47	799.72	20.85
		2365.81			7.50			97.32			367.77			784.98		
	1% PA (14)	3982.28	3932.39	70.56	2.27	2.19	0.12	18.07	17.76	0.43	132.13	131.02	1.57	343.41	338.34	7.17
		3882.50			2.10			17.46			129.91			333.27		
	1% PI (31)	2411.78	2460.52	68.92	6.52	6.69	0.24	18.01	18.56	0.79	257.63	262.79	7.29	411.01	419.53	12.05
		2509.25			6.86			19.12			267.94			428.05		
Mining Waste	Mizzou Doo Mix	2093.53	2120.67	38.37	24.96	25.37	0.57	6.88	7.03	0.21	37.18	38.95	2.49	1471.19	1493.58	31.66
	(T2)	2147.80			25.77			7.18			40.71			1515.97		

(T3)	Repository Soil	2868.90	2872.22	4.69	1.22	1.22	0.01	9.06	9.07	0.02	7.93	8.28	0.50	391.87	393.35	2.09
		2875.53			1.23			9.08			8.64			394.83		
(T4)	SMC	2362.77	2328.47	48.51	0.79	0.76	0.04	4.09	4.06	0.04	6.12	6.36	0.34	187.80	187.41	0.56
		2294.17			0.74			4.03			6.60			187.01		
(T5)	Turkey Litter	2250.05	2246.16	5.50	1.51	1.46	0.06	6.35	6.24	0.15	38.79	39.41	0.88	1147.77	1135.26	17.70
		2242.27			1.42			6.13			40.04			1122.74		
(T6)	Chicken Litter	3438.56	3406.63	45.16	10.90	10.83	0.10	13.81	13.85	0.06	141.77	140.88	1.26	1296.68	1283.18	19.09
		3374.70			10.76			13.89			139.99			1269.68		
(T7)	Mizzou Doo	1636.67	1608.91	39.26	1.62	1.58	0.05	7.43	7.34	0.12	36.76	35.28	2.09	321.55	317.98	5.05
		1581.15			1.54			7.25			33.80			314.40		
(T8)	Sewage Sludge	3755.22	3766.27	15.62	1.41	1.40	0.01	16.78	17.04	0.38	51.81	51.54	0.37	328.65	330.10	2.04
		3777.31			1.39			17.31			51.28			331.54		
(T9)	Phosphorus	3233.16	3239.22	8.57	5.81	5.89	0.12	5.21	5.00	0.29	17.14	16.25	1.26	856.38	853.18	4.52
		3245.28			5.98			4.80			15.36			849.99		
(T10)	EPA Repository	3687.12	3653.48	47.58	4.71	4.67	0.06	6.64	6.63	0.01	22.54	21.15	1.96	320.40	317.70	3.83
		3619.83			4.62			6.63			19.76			314.99		
09-2005		**P(mg/kg)**	**AVG**	**STD**	**Cd(mg/kg)**	**AVG**	**STD**	**Cr(mg/kg)**	**AVG**	**STD**	**Pb(mg/kg)**	**AVG**	**STD**	**Zn(mg/kg)**	**AVG**	**STD**
Mill-waste	1% PA	1175.52	1168.20	10.35	7.06	6.98	0.11	10.96	10.72	0.34	13.73	13.36	0.52	269.10	267.39	2.42
		1160.88			6.90			10.47			12.99			265.68		
	Control	2046.88	2052.88	8.49	7.49	7.48	0.01	8.30	8.67	0.52	28.15	28.72	0.81	479.40	479.25	0.21
		2058.88			7.48			9.04			29.30			479.10		
Urban	1% PA (1)	3720.12	3747.21	38.31	4.62	4.63	0.01	9.88	9.78	0.14	115.72	115.64	0.12	431.81	433.76	2.75
		3774.30			4.64			9.69			115.55			435.71		
	Control (13)	2393.36	2407.01	19.30	6.28	6.36	0.11	4.23	4.27	0.06	125.63	127.19	2.20	374.81	377.21	3.39
		2420.66			6.44			4.31			128.75			379.61		
	1% PA (14)	5055.82	5016.47	55.65	1.87	1.77	0.14	7.31	7.18	0.19	72.70	72.11	0.84	208.76	210.08	1.88
		4977.12			1.66			7.05			71.51			211.41		
	1% PI (31)	3706.25	3721.64	21.77	1.64	1.68	0.05	8.94	8.89	0.07	64.73	64.67	0.08	183.77	184.65	1.25
		3737.03			1.72			8.84			64.62			185.54		

Mining Waste	SMC (T4)	3441.02	3398.61	59.98	3.39	3.39	0.00	3.76	3.76	0.00	26.37	25.22	1.64	390.37	385.75	6.54
		3356.20			3.39			3.76			24.06			381.13		
(T5)	Turkey Litter	2144.45	2117.14	38.62	19.18	19.01	0.25	4.22	4.13	0.13	211.25	208.19	4.32	763.97	751.20	18.06
		2089.83			18.83			4.03			205.13			738.43		
(T6)	Chicken Litter	4160.23	4142.35	25.30	3.67	3.63	0.06	4.54	4.51	0.05	49.88	49.23	0.92	1104.96	1111.73	9.58
		4124.46			3.59			4.47			48.58			1118.50		
(T7)	Mizzou Doo	2261.65	2283.53	30.95	0.33	0.36	0.05	1.40	1.45	0.07	6.10	6.46	0.50	202.85	204.89	2.89
		2305.42			0.39			1.50			6.81			206.94		
	T8 high	3143.76	3143.12	0.91	38.44	38.32	0.18	8.17	8.12	0.08	119.65	119.52	0.19	1493.54	1491.53	2.85
		3142.47			38.19			8.06			119.38			1489.52		
(T9)	Phosphorus	4119.75	4163.85	62.38	9.61	9.68	0.10	7.52	7.58	0.09	31.58	32.05	0.67	820.27	825.32	7.13
		4207.96			9.75			7.64			32.53			830.36		
(T10)	EPA Repository	1950.60	1954.36	5.32	6.61	6.62	0.01	79.64	79.70	0.09	247.87	248.21	0.49	850.57	846.97	5.09
		1958.12			6.63			79.77			248.56			843.38		
02-2006		**P(mg/kg)**	**AVG**	**STD**	**Cd(mg/kg)**	**AVG**	**STD**	**Cr(mg/kg)**	**AVG**	**STD**	**Pb(mg/kg)**	**AVG**	**STD**	**Zn(mg/kg)**	**AVG**	**STD**
Mill-waste	1% PA	842.61	839.45	4.47	3.62	3.72	0.14	18.73	18.68	0.07	46.35	47.18	1.18	424.44	425.11	0.95
		836.29			3.81			18.63			48.02			425.78		
	Control	982.57	983.82	1.77	1.61	1.58	0.04	10.07	9.91	0.23	20.39	20.46	0.09	222.65	220.99	2.36
		985.07			1.55			9.75			20.53			219.32		
Urban	1% PA (1)	3130.56	3101.00	41.80	0.91	0.90	0.01	4.36	4.17	0.26	9.76	10.00	0.34	133.59	132.03	2.21
		3071.45			0.90			3.99			10.25			130.47		
	Control (13)	1512.62	1514.01	1.96	5.84	5.85	0.02	9.24	9.22	0.03	319.33	320.19	1.21	436.69	436.44	0.35
		1515.40			5.87			9.21			321.05			436.19		
	1% PA (14)	3809.75	3825.39	22.12	1.44	1.38	0.09	13.78	13.83	0.06	49.74	49.93	0.27	171.00	171.16	0.23
		3841.03			1.32			13.87			50.12			171.33		
	1% PI (31)	2586.84	2598.31	16.22	2.00	2.01	0.01	4.25	4.42	0.25	24.32	23.84	0.67	149.21	149.95	1.04
		2609.78			2.02			4.60			23.37			150.69		
Mining Waste	Mizzou Doo Mix	1371.33	1387.49	22.85	11.37	11.51	0.19	1.26	1.45	0.27	53.65	53.89	0.34	502.38	508.05	8.02
	(T2)	1403.64			11.64			1.64			54.13			513.72		

(T3)	Repository Soil	2891.22	2897.36	8.69	5.11	5.09	0.04	38.21	38.25	0.05	514.35	514.62	0.38	723.13	722.09	1.48
		2903.51			5.06			38.29			514.88			721.04		
(T4)	SMC	1701.17	1707.73	9.27	0.44	0.44	0.01	1.45	1.64	0.26	27.41	28.07	0.94	208.08	209.39	1.84
		1714.28			0.43			1.83			28.73			210.69		
(T5)	Turkey Litter	1016.94	1004.76	17.22	1.02	1.05	0.04	0.40	0.41	0.01	19.68	18.80	1.25	977.84	970.91	9.79
		992.58			1.08			0.41			17.91			963.99		
(T6)	Chicken Litter	1095.47	1093.42	2.90	2.03	2.02	0.01	0.79	0.87	0.12	22.94	21.85	1.55	407.39	406.27	1.57
		1091.37			2.01			0.95			20.75			405.16		
(T7)	Mizzou Doo	973.82	976.71	4.08	0.18	0.18	0.01	2.31	2.28	0.04	10.03	12.00	2.78	76.91	78.36	2.05
		979.60			0.18			2.25			13.96			79.80		
(T8)	Sewage Sludge	1183.39	1172.74	15.06	0.29	0.33	0.05	5.92	5.75	0.24	27.49	27.71	0.31	209.69	208.74	1.35
		1162.09			0.36			5.59			27.93			207.78		
	T8 high	1467.54	1451.03	23.35	2.27	2.25	0.03	4.49	4.28	0.29	214.60	212.97	2.31	620.02	613.53	9.17
		1434.52			2.23			4.08			211.33			607.05		
(T9)	Phosphorus	921.75	920.78	1.38	1.94	1.94	0.00	18.67	18.63	0.06	48.73	48.55	0.25	263.60	264.54	1.34
		919.80			1.94			18.58			48.37			265.49		
(T10)	EPA Repository	1247.67	1232.50	21.45	1.47	1.42	0.07	0.68	0.56	0.17	16.74	15.81	1.31	268.40	264.98	4.84
		1217.34			1.37			0.45			14.88			261.55		

Appendix 7: Raw data and calculations for *in vitro* bioavailability of each sampling date

Soil Sample	Invitro	Joplin 03-2004		
Mining Waste	AVG_P (mg/kg soil)	STD	AVG_Pb (mg/kg soil)	STD
Mizzou Doo Mix (T2)	295.82	48.01	512.01	53.50
Repository Soil (T3)	616.48	42.23	796.16	49.37
SMC (T4)	1044.01	54.60	397.25	24.03
Turkey Litter (T5)	1912.24	341.62	189.49	28.46
Chicken Litter (T6)	1822.15	257.26	287.84	37.01
Mizzou Doo (T7)	421.22	35.08	508.92	19.11
Sewage Sludge (T8)	400.99	74.16	426.42	18.39
Sewage Sludge (8H)	799.30	81.76	330.45	57.69
Phosphorus (T9)	6018.42	696.19	144.80	21.61
EPA Soil (T10)	705.10	76.41	426.02	21.29
UNTREATED	115.65	9.67	1707.91	154.12
Mill-waste	AVG_P (mg/kg soil)	STD	AVG_Pb (mg/kg soil)	STD
A (1% TR)	3650.12	455.45	131.42	26.73
B (0.75% TR)	2315.99	325.82	186.45	18.36
C (Control)	134.51	10.38	1787.98	191.06
Urban	AVG_P (mg/kg soil)	STD	AVG_Pb (mg/kg soil)	STD
1% SA (1)	3639.88	309.10	305.51	35.19
Control (13)	127.78	14.64	1225.14	122.90
1% RT (14)	3603.99	776.75	383.08	30.58
1% PI (31)	4100.96	326.39	402.83	24.37
Joplin 08-2004				
Mining Waste	AVG_P (mg/kg soil)	STD	AVG_Pb (mg/kg soil)	STD
Mizzou Doo Mix (T2)	284.68	36.09	644.31	106.16
Repository Soil (T3)	141.13	20.25	869.23	304.21
SMC (T4)	140.22	6.17	852.33	200.03
Turkey Litter (T5)	1075.20	124.29	523.63	126.98
Chicken Litter (T6)	1847.49	334.69	251.11	50.80
Mizzou Doo (T7)	1824.78	144.32	422.16	79.88
Sewage Sludge (T8)	380.02	5.64	607.57	56.86
Sewage Sludge (8H)	116.14	22.95	959.94	117.09
Phosphorus (T9)	380.32	72.08	506.91	45.61
EPA Soil (T10)	832.86	114.23	450.56	84.02
UNTREATED	290.14	131.15	467.39	124.33
Mill-waste	AVG_P (mg/kg soil)	STD	AVG_Pb (mg/kg soil)	STD
A (1% TR)	5188.07	834.56	171.26	35.65
B (0.75% TR)	606.11	59.41	467.88	53.98
C (Control)	3330.12	109.34	164.72	25.99
Urban	AVG_P (mg/kg soil)	STD	AVG_Pb (mg/kg soil)	STD
1% SA (1)	2164.43	360.64	273.97	83.38
Control (13)	478.46	48.16	356.26	29.08
1% RT (14)	114.99	20.45	1953.14	382.44
1% PI (31)	75.18	8.29	1074.35	71.26

In-vitro	Joplin 10-2004	P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
Mining Waste	Mizzou Doo Mix (T2)	857.49	821.64	31.12	2.20	2.11	0.08	0.22	0.26	0.06	146.93	131.77	24.22	251.88	242.04	9.12

		801.66			2.08			0.33			103.83			240.36		
		805.77			2.05			0.23			144.55			233.88		
	Repository Soil (T3)	3931.94	3975.56	58.56	15.13	15.22	0.13	0.50	0.52	0.02	168.90	152.92	14.02	2028.34	2011.33	23.51
		3952.63			15.17			0.54			142.71			2021.16		
		4042.11			15.37			0.52			147.15			1984.50		
	SMC (T4)	2470.16	2513.16	59.66	15.81	16.22	0.47	0.42	0.43	0.04	198.27	198.08	10.88	1425.38	1435.17	58.02
		2581.27			16.74			0.40			187.10			1497.46		
		2488.06			16.13			0.47			208.86			1382.66		
	Turkey Litter (T5)	1730.15	1691.13	46.28	2.38	2.30	0.07	0.74	0.85	0.10	672.55	631.11	37.39	4686.87	4555.62	121.15
		1703.25			2.28			0.94			620.88			4531.92		
In-vitro		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
		1640.00			2.24			0.87			599.91			4448.08		
	Chicken Litter (T6)	1391.80	1351.53	35.47	15.23	14.95	0.24	0.33	0.38	0.05	1243.10	1169.56	64.08	4222.08	4193.48	25.18
		1324.89			14.80			0.40			1125.77			4174.61		
		1337.91			14.81			0.42			1139.80			4183.76		
	Mizzou Doo (T7)	1559.11	1516.96	44.55	8.87	8.77	0.20	0.38	0.45	0.11	754.84	741.41	14.31	7560.16	7435.34	275.90
		1521.43			8.90			0.57			726.36			7626.78		
		1470.34			8.54			0.40			743.03			7119.09		
	Sewage Sludge (8H)	128.08	135.27	6.26	16.69	16.58	0.19	0.29	0.32	0.11	1039.32	1054.75	15.47	1752.48	1754.41	11.57
	TOP	138.23			16.68			0.22			1054.68			1766.82		
		139.49			16.36			0.44			1070.26			1743.93		
	Sewage Sludge (8H)	76.00	79.71	7.19	11.55	10.44	1.12	0.26	0.15	0.14	894.88	868.20	58.91	1743.95	1595.19	155.33
	SUB	88.00			10.46			0.00			909.05			1607.58		
		75.14			9.30			0.20			800.66			1434.03		
	Phosphorus (T9)	341.00	336.02	5.07	10.78	10.92	0.21	0.31	0.41	0.13	681.86	662.98	17.11	3467.60	3443.09	81.12
		336.21			11.16			0.38			648.51			3509.13		
		330.86			10.83			0.55			658.57			3352.54		
	EPA Soil (T10)	2613.62	2692.37	69.09	13.73	13.78	0.09	0.51	0.45	0.06	209.00	209.03	1.02	2096.53	2123.79	24.00
		2720.65			13.89			0.44			210.06			2133.14		
		2742.83			13.72			0.40			208.03			2141.71		
	UNTREATED	50.67	45.13	5.93	2.64	2.46	0.27	0.56	0.53	0.18	13407.50	14369.90	1394.0	796.80	780.33	77.93
		45.85			2.59			0.70			15968.50			848.71		
		38.86			2.15			0.34			13733.70			695.48		
Mill-waste	A TOP (1% TR)	5441.21	5428.06	123.54	58.18	57.76	1.18	0.56	0.47	0.09	52.59	54.68	2.96	12299.70	12090.53	274.65
		5298.47			56.43			0.39			58.07			11779.50		
		5544.50			58.68			0.44			53.37			12192.40		
	A SUB (1% TR)	521.37	531.90	16.93	27.62	28.44	1.22	0.29	0.24	0.05	1425.91	1490.40	68.03	5533.70	5728.11	233.07
In-vitro		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD

		522.90			27.86			0.25			1561.49			5664.15		
		551.43			29.84			0.19			1483.81			5986.48		
	B TOP (0.75%TR)	7317.16	7069.79	215.25	49.81	48.59	1.07	0.36	0.42	0.06	105.93	115.10	9.62	14486.80	14133.63	357.94
		6967.05			47.80			0.48			114.27			13771.10		
		6925.15			48.15			0.40			125.10			14143.00		
	B SUB (0.75% TR)	433.55	425.18	7.59	20.20	20.26	0.11	0.23	0.20	0.03	995.31	1014.16	20.18	3998.35	3977.94	18.20
		423.26			20.20			0.19			1011.72			3972.09		
		418.74			20.39			0.17			1035.44			3963.39		
	C TOP (Control)	19.44	18.21	1.64	62.83	62.36	2.42	0.57	0.64	0.07	757.89	722.75	77.08	7079.91	7061.43	297.21
		16.35			59.74			0.65			634.36			6755.41		
		18.85			64.51			0.70			776.00			7348.97		
	C SUB (Control)	10.38	9.35	1.08	73.30	73.78	1.86	0.87	0.79	0.08	949.53	907.96	88.56	9234.95	9107.41	556.59
		8.23			75.84			0.71			968.09			9589.17		
		9.45			72.22			0.78			806.27			8498.12		
Urban	1% SA (1)	5064.41	4810.70	250.86	10.80	10.43	0.32	0.97	0.92	0.14	192.07	174.18	28.34	1530.88	1455.78	65.05
		4562.79			10.25			0.76			141.51			1419.63		
		4804.90			10.24			1.02			188.96			1416.83		
	Control (13)	541.72	405.31	129.96	12.88	13.02	0.14	0.42	0.32	0.09	2091.92	2081.98	116.17	1748.27	1697.73	43.91
		391.27			13.15			0.25			1961.16			1675.96		
		282.94			13.04			0.30			2192.86			1668.95		
	1% RT (14)	3826.73	3985.17	142.88	13.26	13.69	0.37	0.34	0.36	0.04	420.54	480.88	52.77	1857.42	1864.52	9.65
		4024.54			13.87			0.41			518.40			1860.63		
		4104.24			13.94			0.33			503.71			1875.51		
	1% PI (31)	1637.48	1508.23	125.17	13.45	13.07	0.36	0.49	0.48	0.06	980.24	880.99	89.18	1587.02	1507.87	71.33
		1387.59			12.74			0.42			807.60			1448.57		
		1499.63			13.01			0.54			855.13			1488.02		
In-vitro	Joplin 03-2005	P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
Mill-waste	A1 TOP (1% TR)	2883.54	2847.47	38.76	15.70	15.66	0.25	3.60	3.57	0.07	400.06	397.99	5.73	2829.86	2827.73	22.10
		2852.38			15.88			3.63			402.39			2848.68		
		2806.48			15.40			3.49			391.51			2804.64		
	A1 SUB (1% TR)	497.43	498.79	1.84	24.42	24.33	0.19	2.53	2.57	0.04	676.14	676.76	4.06	4566.36	4563.70	25.32
		498.06			24.46			2.61			681.09			4587.58		
		500.88			24.11			2.56			673.05			4537.16		
	A2 TOP (1% TR)	443.20	445.98	3.94	5.04	5.08	0.05	0.21	0.18	0.05	11.26	10.84	0.59	908.91	916.29	10.43
		448.77			5.11			0.15			10.43			923.66		

	A2 SUB (1% TR)	0.69	0.53	0.47	4.67	4.67	0.05	0.20	0.17	0.03	142.97	141.67	6.77	849.15	841.40	15.35
		0.89			4.62			0.14			134.34			823.73		
		0.00			4.73			0.17			147.70			851.34		
	A3 TOP (1% TR)	286.62	306.10	27.33	2.99	3.01	0.03	0.09	0.09	0.03	5.93	6.48	0.48	605.67	604.71	10.18
		294.35			3.00			0.12			6.67			594.09		
		337.34			3.04			0.06			6.82			614.38		
	A3 SUB (1% TR)	24.20	26.94	2.51	3.44	3.74	0.26	0.16	0.19	0.04	56.02	62.98	6.03	843.29	937.34	83.35
		27.47			3.89			0.17			66.46			966.66		
		29.13			3.90			0.24			66.47			1002.07		
	B1 TOP (0.75%TR)	2470.78	2414.69	49.46	20.43	19.72	0.61	2.55	2.45	0.09	704.37	686.16	15.91	3214.82	3141.14	64.54
		2377.34			19.40			2.44			679.13			3114.00		
		2395.94			19.33			2.37			674.98			3094.60		
	B1 SUB (0.75% TR)	410.77	415.32	3.97	18.17	18.39	0.19	2.80	2.82	0.02	653.23	659.71	6.01	3535.74	3562.56	24.39
		418.08			18.55			2.84			665.11			3583.40		
		417.10			18.45			2.82			660.79			3568.54		
	B2 TOP (0.75%TR)	4493.94	4499.55	70.65	16.34	16.29	0.34	4.93	4.93	0.05	679.95	678.48	12.09	2425.22	2440.15	38.27
		4431.88			15.93			4.88			665.72			2411.60		
		4572.84			16.59			4.97			689.77			2483.64		
In-vitro		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
	B2 SUB (0.75% TR)	1461.69	1442.68	26.89	14.52	14.39	0.18	1.54	1.53	0.02	696.50	698.44	2.74	3665.64	3629.31	51.38
		1423.67			14.26			1.52			700.38			3592.98		
	B3 TOP (0.75%TR)	2766.88	2738.41	34.71	10.36	10.25	0.11	2.91	2.89	0.03	488.28	484.07	6.53	2343.22	2309.23	35.64
		2748.60			10.27			2.90			487.38			2312.34		
		2699.74			10.14			2.85			476.55			2272.14		
	B3 SUB (0.75% TR)	1163.59	1148.71	13.00	7.21	7.15	0.05	1.14	1.14	0.00	532.29	528.29	3.65	1774.34	1761.40	11.39
		1142.99			7.11			1.14			525.13			1752.90		
		1139.56			7.12			1.14			527.44			1756.96		
	C1 TOP (Control)	1.17	0.39	0.67	5.70	5.86	0.20	0.16	0.13	0.03	43.12	44.82	1.52	669.64	684.72	16.51
		0.00			5.79			0.12			45.27			682.16		
		0.00			6.09			0.10			46.06			702.36		
	C1 SUB (Control)	0.00	0.00	0.00	4.93	4.82	0.30	0.20	0.18	0.01	94.99	92.65	5.46	873.71	844.23	60.11
		0.00			4.48			0.17			86.41			775.06		
		0.00			5.04			0.18			96.55			883.91		

	C2 TOP (Control)	66.86	65.83	1.36	14.47	14.27	0.18	1.05	1.06	0.02	373.11	372.80	2.27	2273.98	2250.93	27.20
		66.34			14.21			1.08			374.91			2257.88		
		64.30			14.13			1.05			370.39			2220.92		
	C2 SUB (Control)	138.38	137.23	2.93	20.87	20.98	0.13	2.77	2.76	0.03	656.58	660.58	5.20	4186.70	4223.91	37.29
		133.89			20.96			2.72			658.70			4223.76		
		139.41			21.12			2.77			666.45			4261.28		
	C3 TOP (Control)	0.44	1.04	0.63	3.40	3.57	0.15	0.12	0.04	0.07	37.42	40.11	2.64	714.33	753.45	34.22
		1.70			3.65			0.00			42.69			768.16		
		0.98			3.67			0.00			40.23			777.85		
	C3 SUB (Control)	0.44	0.35	0.32	4.04	4.10	0.05	0.00	0.00	0.00	77.95	80.30	2.50	1000.88	999.22	8.98
		0.00			4.12			0.00			82.93			1007.24		
		0.62			4.13			0.00			80.03			989.53		
In-vitro		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
Urban	1% PA (1)	1489.26	1486.21	13.19	5.56	5.39	0.30	0.65	0.93	0.34	427.63	434.56	9.47	822.67	784.31	41.26
		1497.60			5.56			1.31			445.35			789.59		
		1471.76			5.04			0.83			430.70			740.65		
	Control (13)	4.58	3.50	3.10	7.48	7.33	0.39	0.79	0.76	0.05	2050.50	2036.15	82.09	875.76	850.92	35.85
		5.91			6.88			0.70			1947.83			809.83		
		0.00			7.63			0.79			2110.12			867.18		
	1% PA (14)	2426.20	2361.30	58.20	6.73	6.74	0.08	0.52	0.75	0.21	332.37	331.99	1.71	940.40	923.66	16.25
		2343.94			6.67			0.82			333.48			907.94		
		2313.76			6.83			0.92			330.12			922.65		
	1% PI (31)	1370.26	1422.86	51.02	5.14	5.08	0.14	0.73	0.91	0.20	365.84	356.29	9.40	606.62	575.22	33.26
		1426.19			5.17			0.88			355.97			578.68		
		1472.14			4.91			1.12			347.05			540.37		
In-vitro		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
Mining Waste	Mizzou Doo Mix (T2)	133.24	143.70	14.79	17.23	17.13	0.15	0.00	0.09	0.13	315.41	315.30	0.15	2269.60	2241.22	40.14
		154.16			17.02			0.18			315.19			2212.84		
	bottom	9.33	6.95	3.36	5.73	5.64	0.14	0.04	0.02	0.03	1888.62	1864.49	34.12	2876.60	2862.44	20.03
		4.58			5.54			0.00			1840.36			2848.28		
	SMC (T4)	939.63	970.36	43.47	2.54	2.56	0.03	0.00	0.00	0.00	9.58	11.09	2.13	1901.20	1933.19	45.24
		1001.10			2.58			0.00			12.60			1965.18		
	top	853.91	843.83	14.25	0.74	0.49	0.36	0.00	0.00	0.00	0.00	0.92	1.30	150.00	135.62	20.33

		833.76			0.23			0.00			1.84			121.25		
	top	780.17	792.75	17.79	0.25	0.23	0.03	0.72	0.57	0.20	0.00	0.00	0.00	141.68	141.51	0.24
		805.32			0.21			0.43			0.00			141.33		
	bottom	133.30	132.33	1.37	6.59	6.65	0.09	0.30	0.15	0.21	405.09	423.78	26.44	7628.36	7656.86	40.31
		131.37			6.71			0.00			442.48			7685.36		
	Turkey Litter (T5)	3044.08	3195.25	213.79	2.56	2.72	0.22	1.41	0.98	0.61	181.86	197.59	22.25	3474.82	3586.42	157.83
		3346.42			2.87			0.55			213.32			3698.02		
In-vitro		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
	top	3927.42	3660.24	377.85	3.49	3.21	0.38	1.46	1.48	0.03	116.72	124.40	10.86	2566.54	2419.09	208.53
		3393.06			2.94			1.50			132.07			2271.64		
	top	5385.36	5488.73	146.19	1.07	1.06	0.02	0.55	0.78	0.33	6.54	6.79	0.35	974.40	971.80	3.67
		5592.10			1.04			1.02			7.04			969.21		
	bottom	223.39	220.28	4.40	2.93	2.86	0.09	0.73	0.37	0.52	440.50	450.26	13.80	3824.28	3790.92	47.18
		217.16			2.80			0.00			460.01			3757.56		
	Chicken Litter (T6)	2032.48	2019.33	18.60	8.15	8.24	0.13	1.50	1.19	0.44	153.02	150.10	4.13	998.40	991.84	9.29
		2006.18			8.33			0.88			147.18			985.27		
	top	3246.92	3284.97	53.81	0.00	0.00	0.00	0.00	0.00	0.00	6.75	6.04	1.01	79.39	69.72	13.68
		3323.02			0.00			0.00			5.32			60.05		
	top	4683.10	4826.22	202.40	0.00	0.00	0.00	0.00	0.27	0.37	4.14	3.51	0.90	42.25	45.11	4.05
		4969.34			0.00			0.53			2.87			47.98		
	bottom	201.14	178.21	32.43	4.19	4.10	0.13	0.41	0.21	0.29	564.92	568.74	5.39	1644.90	1612.07	46.42
		155.27			4.01			0.00			572.55			1579.25		
	Mizzou Doo (T7)	3732.06	3637.33	133.97	0.15	0.07	0.10	0.20	0.10	0.14	0.00	3.27	4.62	44.77	45.41	0.91
		3542.60			0.00			0.00			6.53			46.06		
	top	5061.60	4953.55	152.81	0.00	0.00	0.00	0.00	0.36	0.51	0.00	0.00	0.00	79.13	62.05	24.16
		4845.50			0.00			0.72			0.00			44.97		
	top	4739.46	4773.23	47.76	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.71	2.41	32.34	25.97	9.01
		4807.00			0.00			0.00			3.41			19.60		
	bottom	96.33	80.56	22.29	0.22	0.29	0.10	0.57	0.52	0.07	443.23	420.82	31.69	247.11	225.14	31.06
		64.80			0.36			0.46			398.41			203.18		
	Sewage Sludge (T8)	2193.18	2228.89	50.50	1.08	0.99	0.12	0.94	0.77	0.25	0.00	0.00	0.00	484.28	466.17	25.62
		2264.60			0.91			0.59			0.00			448.05		
	top	2925.52	2817.81	152.32	0.76	0.64	0.16	0.00	0.41	0.58	0.00	0.00	0.00	573.37	553.62	27.93
		2710.10			0.53			0.82			0.00			533.87		

	top	1638.58	1832.29	273.94	0.83	0.97	0.20	0.64	0.96	0.45	2.65	1.32	1.87	355.08	367.01	16.86
In-vitro		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
		2026.00			1.11			1.27			0.00			378.93		
	bottom	410.23	434.12	33.79	0.29	0.30	0.02	0.93	0.47	0.66	340.90	343.07	3.07	985.93	988.48	3.60
		458.02			0.31			0.00			345.24			991.02		
	Phosphorus (T9)	167.93	168.29	0.51	2.17	2.24	0.10	0.90	0.45	0.63	25.01	26.64	2.30	535.66	546.66	15.56
		168.66			2.32			0.00			28.26			557.66		
	top	112.10	108.75	4.74	1.71	1.65	0.09	0.53	0.26	0.37	17.46	15.63	2.60	425.30	395.46	42.21
		105.39			1.59			0.00			13.79			365.61		
	top	6.45	3.23	4.56	1.50	1.41	0.14	0.40	0.20	0.28	7.70	8.43	1.04	338.54	326.19	17.47
		0.00			1.31			0.00			9.17			313.84		
	bottom	49.69	99.37		2.36	4.72		0.00	0.00		387.31	774.62		354.33	708.66	
		0.00			0.00			0.00			0.00			0.00		
	EPA Soil (T10)	11.22	24.93	19.38	0.97	1.12	0.21	0.67	0.33	0.47	173.19	264.89	129.69	341.46	417.28	107.22
		38.64			1.27			0.00			356.60			493.10		
	top	102.94	151.76	69.03	4.74	5.04	0.42	0.40	0.20	0.29	324.29	343.42	27.05	717.65	688.72	40.91
		200.57			5.33			0.00			362.55			659.79		
	top	542.70	593.85	72.34	6.94	6.96	0.03	0.09	0.31	0.30	232.75	246.05	18.81	1199.61	1185.41	20.09
		645.01			6.98			0.52			259.35			1171.20		
	Sewage Sludge (8H)	66.31	101.48	49.74	8.12	8.40	0.40	0.36	0.18	0.26	2190.58	2077.20	160.34	1111.53	1125.13	19.24
		136.65			8.69			0.00			1963.83			1138.74		
	Untreated Soil	0.00	3.76	5.32	3.20	3.32	0.18	0.52	0.53	0.02	9968.66	9871.13	137.93	1002.37	976.82	36.13
		7.52			3.45			0.54			9773.60			951.28		
In-vitro	Joplin 06-2005	P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
Mill-waste	A1 TOP (1% TR)	7246.95	7141.90	148.56	66.61	65.32	1.84	2.10	2.10	0.00	188.93	190.24	1.85	13663.60	13485.85	251.38
		7036.85			64.02			2.10			191.54			13308.10		
	A1 SUB (1% TR)	2131.19	2116.50	20.78	107.49	106.82	0.95	2.99	2.74	0.36	1288.52	1277.23	15.97	17891.10	17669.40	313.53
		2101.80			106.15			2.49			1265.93			17447.70		
	A2 TOP (1% TR)	10311.21	10529.51	308.72	115.79	117.46	2.36	2.15	2.27	0.17	486.81	479.40	10.47	17439.30	17643.15	288.29
		10747.81			119.13			2.39			472.00			17847.00		
	A2 SUB (1% TR)	461.93	449.44	17.67	100.94	103.14	3.12	3.26	3.16	0.14	3005.23	3059.99	77.44	16495.50	16653.35	223.23
		436.94			105.35			3.07			3114.74			16811.20		
	A3 TOP (1% TR)	10485.21	10653.81	238.44	65.09	66.30	1.71	2.62	2.66	0.06	130.27	136.47	8.77	11647.70	11766.90	168.57
		10822.41			67.51			2.70			142.68			11886.10		

	A3 SUB (1% TR)	858.98	847.61	16.07	80.93	81.40	0.68	2.98	3.05	0.10	1391.40	1439.31	67.75	18359.00	18534.10	247.63
		836.25			81.88			3.12			1487.21			18709.20		
	B1 TOP (0.75%TR)	6335.06	6190.32	204.69	91.08	89.52	2.22	1.79	1.74	0.07	822.62	790.70	45.15	14109.10	13889.35	310.77
		6045.58			87.95			1.69			758.77			13669.60		
	B1 SUB (0.75% TR)	316.57	312.93	5.15	70.50	68.36	3.03	3.54	3.11	0.62	2366.04	2263.06	145.64	13323.30	12751.95	808.01
		309.29			66.21			2.67			2160.08			12180.60		
	B2 TOP (0.75%TR)	7615.63	7659.48	62.01	62.01	62.74	1.03	1.64	1.70	0.08	78.96	79.66	0.98	10275.80	10339.35	89.87
		7703.32			63.47			1.75			80.35			10402.90		
	B2 SUB (0.75% TR)	1485.02	1475.78	13.07	77.97	78.34	0.52	2.68	2.68	0.01	2193.13	2256.65	89.83	17551.20	17706.10	219.06
		1466.54			78.71			2.67			2320.17			17861.00		
	B3 TOP (0.75%TR)	6477.34	6401.97	106.59	46.46	45.95	0.72	2.13	1.99	0.20	374.07	369.67	6.21	11876.80	11794.40	116.53
		6326.60			45.44			1.84			365.28			11712.00		
	B3 SUB (0.75% TR)	1815.09	1824.09	12.72	31.39	31.56	0.25	1.33	1.29	0.05	1355.11	1363.08	11.26	8781.47	8720.00	86.93
		1833.08			31.74			1.26			1371.04			8658.53		
	C1 TOP (Control)	87.61	92.43	6.82	108.03	105.07	4.18	1.92	1.62	0.42	1818.93	1692.25	179.15	13106.10	12511.35	841.10
		97.26			102.12			1.32			1565.57			11916.60		
	C1 SUB (Control)	49.33	50.42	1.54	104.84	105.62	1.10	3.31	3.32	0.01	1883.89	1929.29	64.20	17005.40	17118.40	159.81
		51.51			106.40			3.32			1974.68			17231.40		
	C2 TOP (Control)	61.83	56.59	7.41	67.60	68.71	1.57	2.28	2.39	0.15	1610.75	1657.60	66.26	11962.70	12121.45	224.51
In-vitro		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
		51.35			69.82			2.49			1704.45			12280.20		
	C2 SUB (Control)	70.32	71.27	1.35	80.62	81.84	1.72	3.41	3.45	0.06	1679.84	1734.18	76.84	17299.20	17539.95	340.47
		72.22			83.05			3.49			1788.51			17780.70		
	C3 TOP (Control)	129.16	134.58	7.67	80.10	80.51	0.57	3.78	3.80	0.02	2162.93	2183.43	28.98	20018.40	20106.50	124.59
		140.00			80.92			3.81			2203.92			20194.60		
	C3 SUB (Control)	136.82	129.76	9.99	69.02	69.91	1.26	3.09	3.25	0.23	2680.21	2743.52	89.53	14150.10	14233.65	118.16
		122.69			70.80			3.41			2806.82			14317.20		
Urban	1%SA (1)	4363.76	4290.66	103.39	9.18	8.85	0.47	2.11	2.24	0.19	462.99	488.59	36.20	1189.51	1140.77	68.93
		4217.55			8.51			2.38			514.19			1092.03		
	Control (13)	228.62	226.89	2.43	13.61	13.63	0.02	0.98	1.05	0.09	3372.48	3412.83	57.06	1694.14	1671.01	32.72
		225.17			13.64			1.11			3453.18			1647.87		
	1% PA (14)	7095.77	7172.83	108.97	12.62	12.78	0.24	1.59	1.40	0.27	610.85	567.46	61.36	1693.35	1679.11	20.14
		7249.88			12.95			1.21			524.06			1664.87		
	1% PI (31)	963.00	964.07	1.51	11.22	11.29	0.10	0.97	0.92	0.07	1704.30	1733.76	41.66	1485.15	1492.58	10.50
		965.13			11.37			0.86			1763.22			1500.00		
Mining Waste	Mizzou Doo Mix	342.18	340.29	2.67	41.05	43.48	3.43	1.88	1.71	0.24	2443.22	2393.73	70.00	5659.24	5769.09	155.35
	T2	338.40			45.91			1.54			2344.23			5878.94		

	Repository Soil	1773.75	1781.65	11.17	24.42	24.36	0.09	1.16	1.16	0.00	753.89	767.77	19.63	2130.31	2101.78	40.35
	T3	1789.55			24.29			1.15			781.65			2073.24		
	top	6817.44	6459.91	505.62	14.91	14.61	0.42	1.79	1.76	0.04	521.81	529.50	10.88	2057.16	2008.36	69.02
		6102.38			14.31			1.73			537.20			1959.55		
	top	5365.49	5437.94	102.45	23.19	23.12	0.11	1.54	1.39	0.21	530.99	540.75	13.79	2432.21	2418.59	19.27
		5510.38			23.04			1.24			550.50			2404.96		
	bottom	418.59	390.05	40.37	46.81	46.71	0.14	0.40	0.43	0.04	792.72	801.48	12.39	2088.34	2063.56	35.05
		361.50			46.62			0.46			810.24			2038.77		
	SMC (T4)	1615.90	1569.07	66.23	0.09	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	83.95	75.62	11.79
		1522.23			0.09			0.00			0.00			67.28		
	top	1126.55	1150.94	34.49	0.21	0.21	0.01	0.00	0.00	0.00	0.00	0.00	0.00	120.93	108.26	17.91
In-vitro		P (mg/kg soil)	AVG	STD	Cd (mg/kgsoil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb (mg/kgsoil)	AVG	STD	Zn (mg/kgsoil)	AVG	STD
		1175.32			0.20			0.00			0.00			95.60		
	top	1199.41	1207.98	12.12	0.13	0.11	0.03	0.00	0.00	0.00	0.00	0.00	0.00	64.74	53.65	15.68
		1216.55			0.09			0.00			0.00			42.57		
	bottom	357.33	326.78	43.20	6.93	6.71	0.31	2.58	2.08	0.71	1344.69	1229.34	163.13	7946.97	7905.02	59.33
		296.24			6.49			1.58			1113.99			7863.07		
	Turkey Litter (T5)	12361.00	10574.82	2526.05	4.29	3.62	0.95	6.91	4.90	2.85	193.41	120.92	102.52	4934.43	4492.92	624.39
		8788.63			2.95			2.88			48.43			4051.41		
	top	11066.90	9761.29	1846.41	4.37	3.80	0.80	7.29	5.13	3.06	348.83	227.21	171.99	5625.47	5294.15	468.56
		8455.68			3.24			2.97			105.60			4962.83		
	top	9594.27	8323.06	1797.76	4.21	3.69	0.74	4.94	3.58	1.92	445.11	303.76	199.90	5830.19	5386.05	628.12
		7051.85			3.17			2.22			162.42			4941.90		
	bottom	634.72	654.01	27.28	3.87	3.95	0.12	1.45	1.47	0.03	1145.23	1189.35	62.40	5737.14	5960.62	316.05
		673.29			4.04			1.50			1233.47			6184.10		
	Chicken Litter (T6)	6327.89	6491.93	231.99	9.48	9.72	0.34	0.37	0.32	0.08	20.33	25.01	6.61	1772.80	1783.79	15.54
		6655.97			9.96			0.26			29.69			1794.77		
	top	6985.07	6928.75	79.66	0.43	0.37	0.08	0.20	0.25	0.07	1.65	2.13	0.68	151.04	147.43	5.11
		6872.42			0.31			0.30			2.62			143.82		
	top	3035.36	3222.27	264.33	2.08	2.09	0.01	0.88	0.58	0.42	74.81	69.04	8.17	803.24	799.55	5.23
		3409.18			2.10			0.28			63.26			795.85		
	bottom	255.46	255.13	0.46	32.38	32.41	0.04	0.66	0.60	0.08	2093.02	2094.30	1.81	3193.57	3211.50	25.35
		254.81			32.44			0.55			2095.58			3229.42		
	Mizzou Doo (T7)	5145.60	4909.73	333.57	2.68	2.56	0.17	0.98	0.87	0.16	31.08	25.11	8.44	521.20	471.92	69.69
		4673.86			2.44			0.76			19.14			422.64		
	top	6592.76	6582.64	14.32	0.25	0.26	0.02	0.46	0.42	0.06	1.81	2.13	0.47	125.21	124.65	0.80
		6572.51			0.27			0.38			2.46			124.08		
	top	5558.20	5394.15	232.01	0.06	0.08	0.03	0.79	0.50	0.40	2.19	1.09	1.55	179.95	141.61	54.21

		5230.09			0.10			0.22			0.00			103.28		
	bottom	113.01	113.78	1.09	3.06	3.21	0.22	1.99	2.32	0.46	325.52	357.21	44.81	954.92	944.59	14.61
		114.55			3.37			2.64			388.89			934.26		
In-vitro		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
	Sewage Sludge (T8)	3222.21	3176.83	64.18	1.64	1.60	0.06	1.12	1.12	0.00	9.98	8.94	1.47	600.52	569.77	43.49
		3131.45			1.56			1.13			7.90			539.02		
	top	3295.09	3335.48	57.12	1.54	1.55	0.02	1.59	1.52	0.10	6.79	6.75	0.05	630.20	611.68	26.19
		3375.87			1.57			1.45			6.71			593.16		
	top	3749.55	3473.82	389.95	2.06	1.96	0.15	1.37	1.34	0.04	7.92	10.01	2.95	834.15	763.58	99.81
		3198.08			1.86			1.31			12.10			693.01		
	bottom	247.51	253.09	7.89	0.92	0.95	0.03	3.86	3.96	0.14	111.30	118.84	10.66	328.94	301.59	38.67
		258.67			0.97			4.05			126.38			274.24		
	Phosphorus (T9)	426.21	436.56	14.64	17.00	17.05	0.08	0.87	0.78	0.12	40.97	39.30	2.36	3535.02	3539.31	6.06
		446.92			17.11			0.70			37.64			3543.59		
	top	340.81	341.55	1.05	2.49	2.49	0.00	0.89	0.85	0.05	8.03	8.57	0.77	613.02	631.75	26.49
		342.29			2.49			0.81			9.11			650.49		
	top	509.87	525.82	22.55	2.33	2.38	0.07	1.11	1.04	0.09	32.39	31.20	1.68	532.19	504.56	39.07
		541.76			2.43			0.98			30.01			476.93		
	bottom	116.68	107.75	12.62	6.49	6.54	0.07	1.28	1.60	0.45	633.82	645.90	17.09	874.22	909.30	49.61
		98.83			6.59			1.92			657.99			944.38		
	EPA Soil (T10)	1241.91	1215.14	37.86	11.00	10.97	0.04	0.35	0.40	0.08	160.03	160.58	0.78	1143.12	1116.20	38.08
		1188.37			10.95			0.45			161.13			1089.27		
	top	3310.56	3303.12	10.52	10.20	10.16	0.05	0.65	0.54	0.16	106.03	110.84	6.80	1789.97	1763.12	37.97
		3295.68			10.13			0.42			115.65			1736.27		
	Sewage Sludge (8H)	163.42	164.46	1.48	1.77	1.78	0.00	0.21	0.10	0.15	13.64	13.68	0.06	206.56	177.66	40.86
		165.51			1.78			0.00			13.72			148.77		
	top	565.86	528.53	52.79	1.16	1.15	0.02	0.29	0.19	0.15	13.85	15.91	2.92	369.93	337.50	45.86
		491.20			1.13			0.09			17.98			305.08		
	top	261.14	250.90	14.47	0.56	0.61	0.08	0.00	0.06	0.08	20.80	20.46	0.48	180.41	149.49	43.74
		240.67			0.67			0.11			20.12			118.56		
	bottom	491.74	482.16	13.55	7.44	7.32	0.17	1.87	1.74	0.18	2509.79	2403.21	150.73	3766.96	3629.36	194.60
		472.57			7.20			1.61			2296.63			3491.75		
	Untreated Soil	19.60	18.51	1.53	2.81	2.70	0.15	2.84	2.81	0.05	15467.00	14769.30	986.70	1081.82	1047.12	49.07
		17.43			2.60			2.77			14071.60			1012.42		
In-vitro	Joplin 09-2005	P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
Mill-waste	A1 TOP (1% TR)	4694.82	4646.39	68.50	33.44	33.51	0.10	0.29	0.25	0.06	52.15	27.30	35.14	7646.38	7608.75	53.22
		4597.95			33.58			0.21			2.45			7571.11		

	A1 SUB (1% TR)	2564.16	2597.73	47.48	70.52	71.01	0.69	0.70	0.68	0.03	210.99	216.34	7.56	11996.30	12118.35	172.60
		2631.30			71.50			0.66			221.68			12240.40		
	A2 TOP (1% TR)	4538.37	4600.30	87.58	45.20	45.81	0.85	0.45	0.46	0.01	23.67	23.74	0.11	8628.75	8673.83	63.75
		4662.23			46.41			0.47			23.82			8718.91		
	A2 SUB (1% TR)	511.34	506.97	6.18	90.36	88.13	3.15	1.18	1.16	0.03	604.97	617.22	17.33	14280.75	13881.20	565.05
		502.60			85.90			1.13			629.47			13481.65		
	A3 TOP (1% TR)	4219.44	4182.17	52.71	26.17	25.75	0.59	0.45	0.23	0.32	3.65	4.43	1.10	5232.96	5144.65	124.88
		4144.90			25.33			0.00			5.21			5056.35		
	A3 SUB (1% TR)	150.12	154.17	5.73	57.04	54.99	2.90	1.01	1.08	0.10	645.64	648.60	4.18	11357.95	10990.00	520.36
		158.22			52.93			1.16			651.55			10622.05		
	B1 TOP (0.5%TR)	4409.87	4539.07	182.72	39.14	39.37	0.32	0.56	0.51	0.06	107.91	87.01	29.55	7518.32	7588.66	99.48
		4668.27			39.60			0.47			66.12			7659.01		
	B1 SUB (0.75% TR)	517.68	516.83	1.20	69.67	70.65	1.39	1.41	1.44	0.04	617.22	645.84	40.48	9554.57	9637.13	116.76
		515.98			71.63			1.47			674.46			9719.69		
	B2 TOP (0.75%TR)	3401.35	3315.55	121.35	38.59	37.83	1.08	0.54	0.55	0.01	19.96	19.05	1.28	7378.38	7124.07	359.64
		3229.74			37.07			0.56			18.14			6869.77		
	B2 SUB (0.75% TR)	1219.74	1216.95	3.95	68.65	68.12	0.75	1.08	1.11	0.04	718.40	752.95	48.86	13020.35	12779.10	341.18
		1214.16			67.59			1.13			787.50			12537.85		
	B3 TOP (0.75%TR)	4473.43	4322.44	213.53	22.56	22.20	0.51	0.39	0.38	0.00	7.85	15.82	11.27	6310.84	6236.16	105.61
		4171.45			21.84			0.38			23.79			6161.49		
	B3 SUB (0.75% TR)	1249.66	1201.91	67.53	42.69	40.80	2.67	0.79	0.69	0.14	583.68	579.94	5.29	13307.45	12752.65	784.61
		1154.16			38.91			0.59			576.20			12197.85		
	C1 TOP (Control)	9.79	9.73	0.09	63.49	63.70	0.30	0.58	0.55	0.04	493.48	512.36	26.70	7173.21	7027.12	206.60
		9.66			63.92			0.52			531.24			6881.04		
	C1 SUB (Control)	7.43	5.15	3.23	72.11	72.12	0.02	0.84	0.80	0.06	746.77	754.74	11.26	9515.76	9549.25	47.36
In-vitro		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
		2.86			72.14			0.76			762.71			9582.74		
	C2 TOP (Control)	48.99	48.64	0.48	47.79	50.50	3.83	0.82	0.75	0.10	395.97	420.12	34.16	7796.98	8078.00	397.42
		48.30			53.21			0.68			444.28			8359.02		
	C2 SUB (Control)	1.40	0.70	0.99	51.98	52.47	0.69	0.08	0.12	0.06	584.86	546.72	53.95	8216.82	8215.48	1.89
		0.00			52.95			0.16			508.57			8214.15		
	C3 TOP (Control)	149.88	148.98	1.28	64.51	71.41	9.76	0.88	0.88	0.00	374.58	389.20	20.68	9193.24	10093.64	1273.36
		148.07			78.32			0.87			403.82			10994.05		
	C3 SUB (Control)	9.09	8.16	1.31	87.61	76.11	16.26	1.69	1.54	0.21	1099.30	1028.79	99.72	15480.75	13870.10	2277.80
		7.23			64.60			1.39			958.27			12259.45		
Urban	1% SA (1)	1748.54	1890.41	200.63	4.44	4.91	0.66	0.29	0.29	0.00	104.23	107.12	4.09	640.30	673.10	46.39
		2032.28			5.38			0.29			110.02			705.90		

	Control (13)	74.97	73.62	1.91	14.72	14.11	0.86	0.54	0.36	0.26	1833.42	1745.21	124.75	1583.60	1470.74	159.61
		72.27			13.51			0.18			1656.99			1357.88		
	1% PA (14)	3322.01	3303.15	26.68	11.42	11.27	0.22	0.51	0.40	0.16	191.01	198.08	10.01	1640.49	1588.67	73.28
		3284.28			11.11			0.28			205.16			1536.85		
	1% PI (31)	1615.92	1684.92	97.59	6.14	6.21	0.10	0.32	0.42	0.15	305.59	317.57	16.94	741.44	733.24	11.58
		1753.93			6.28			0.53			329.54			725.05		
Mining Waste	Repository Soil T3	1816.90	1746.74	99.21	38.93	38.22	1.01	0.31	0.24	0.09	300.28	292.67	10.76	3290.42	3209.08	115.03
		1676.59			37.51			0.18			285.06			3127.74		
	top	1830.62	1824.87	8.12	11.26	11.12	0.20	0.42	0.33	0.13	274.25	268.52	8.11	1600.09	1553.90	65.32
		1819.13			10.98			0.24			262.79			1507.72		
	top	1378.86	1462.70	118.57	10.91	11.29	0.55	0.32	0.39	0.09	307.89	329.02	29.88	1538.47	1587.38	69.17
		1546.55			11.68			0.45			350.15			1636.29		
	SMC (T4)	1194.81	1280.85	121.69	1.16	1.20	0.06	0.00	0.00	0.00	0.00	0.00	0.00	331.79	346.74	21.14
		1366.90			1.24			0.00			0.00			361.69		
	top	1243.64	1268.48	35.14	2.21	2.29	0.11	0.00	0.00	0.00	0.00	0.20	0.29	455.53	511.93	79.76
		1293.33			2.37			0.00			0.41			568.34		
	top	1926.99	1925.42	2.21	0.62	0.67	0.07	0.00	0.00	0.00	0.00	0.00	0.00	213.66	215.25	2.25
		1923.86			0.72			0.00			0.00			216.85		
In-vitro		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
	Turkey Litter (T5)	1641.01	1628.89	17.14	0.79	0.77	0.03	0.00	0.00	0.00	0.00	0.00	0.00	299.09	286.46	17.87
		1616.77			0.75			0.00			0.00			273.83		
	top	1606.99	1621.57	20.63	0.75	0.82	0.10	0.00	0.00	0.00	0.00	0.00	0.00	255.36	263.75	11.86
		1636.16			0.89			0.00			0.00			272.14		
	top	1366.35	1393.35	38.19	2.06	2.12	0.09	0.00	0.00	0.00	0.00	0.00	0.00	433.60	568.09	190.20
		1420.36			2.19			0.00			0.00			702.59		
	Chicken Litter (T6)	7535.22	7390.06	205.28	1.32	1.25	0.11	0.76	0.63	0.18	1.56	1.27	0.40	844.76	771.01	104.31
		7244.91			1.17			0.50			0.99			697.25		
	top	8716.40	8494.31	314.08	1.51	1.46	0.07	0.44	0.36	0.12	9.22	10.54	1.86	468.28	433.21	49.58
		8272.22			1.41			0.27			11.85			398.15		
	top	8098.04	7233.13	1223.17	1.04	0.92	0.17	0.49	0.57	0.11	6.80	6.57	0.33	394.00	332.04	87.63
		6368.22			0.80			0.66			6.34			270.07		
	Mizzou Doo (T7)	5665.28	5629.49	50.61	0.21	0.23	0.03	0.38	0.31	0.09	0.00	0.00	0.00	50.15	49.42	1.03
		5593.70			0.25			0.25			0.00			48.69		
	top	4616.91	5077.63	651.56	0.24	0.24	0.01	0.65	0.56	0.13	5.85	4.09	2.49	214.35	180.01	48.56
		5538.36			0.23			0.47			2.33			145.67		
	top	8123.71	8223.61	141.28	0.11	0.11	0.01	0.69	0.54	0.21	1.27	0.97	0.41	179.73	135.57	62.46
		8323.51			0.10			0.39			0.68			91.40		
	Sewage Sludge (T8)	1968.62	2074.05	149.10	1.89	1.98	0.13	1.21	1.15	0.09	16.13	15.53	0.85	831.59	844.27	17.93

		2179.48			2.07			1.08			14.93			856.95		
	top	3149.50	3393.21	344.67	1.23	1.26	0.05	1.33	1.28	0.06	8.96	7.87	1.53	652.92	646.55	9.01
		3636.93			1.30			1.24			6.79			640.18		
	top	2849.44	2945.84	136.34	0.84	0.83	0.03	0.41	0.36	0.07	0.00	1.77	2.50	664.47	653.25	15.87
		3042.25			0.81			0.31			3.53			642.03		
	Sewage Sludge (8H)	225.37	228.24	4.06	10.69	10.92	0.33	0.32	0.16	0.23	53.84	54.19	0.50	999.02	1000.89	2.65
		231.11			11.16			0.00			54.55			1002.77		
	top	447.72	456.41	12.29	0.88	0.87	0.02	0.00	0.00	0.00	25.71	27.76	2.89	242.85	216.58	37.15
		465.10			0.85			0.00			29.80			190.31		
	top	336.78	312.61	34.18	0.71	0.68	0.04	0.00	0.00	0.00	8.54	8.20	0.49	206.35	169.78	51.72
In-vitro		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
		288.45			0.65			0.00			7.86			133.20		
	bottom	163.86	164.74	1.24	6.07	6.02	0.07	0.00	0.12	0.17	1244.07	1261.32	24.40	2484.22	2425.65	82.82
		165.62			5.97			0.24			1278.57			2367.09		
	Phosphorus (T9)	411.77	401.84	14.05	12.08	11.71	0.52	0.00	0.00	0.00	186.36	191.14	6.76	1257.25	1191.30	93.27
		391.91			11.35			0.00			195.93			1125.35		
	top	222.70	208.58	19.98	5.34	4.94	0.57	0.15	0.07	0.10	60.18	56.83	4.74	863.13	780.37	117.04
		194.45			4.54			0.00			53.48			697.61		
	top	2104.75	2107.97	4.55	4.84	4.93	0.13	0.00	0.00	0.00	0.00	4.18	5.91	739.06	717.75	30.14
		2111.19			5.02			0.00			8.35			696.44		
	EPA Soil (T10)	2077.30	2060.45	23.84	10.86	10.88	0.02	0.00	0.00	0.00	496.48	493.07	4.82	1564.24	1526.88	52.84
		2043.59			10.89			0.00			489.66			1489.52		
	top	1191.19	1156.08	49.66	6.95	6.77	0.26	0.07	0.04	0.05	169.78	169.07	1.01	967.59	924.07	61.54
		1120.96			6.58			0.00			168.35			880.55		
	top	1104.35	1091.07	18.79	11.88	11.92	0.06	0.00	0.08	0.12	317.90	317.82	0.12	1780.20	1793.61	18.96
		1077.78			11.96			0.16			317.74			1807.02		
	Untreated Soil	2.71	7.14	6.26	13.67	13.01	0.93	1.63	1.45	0.25	19394.08	17901.73	2110.50	3133.71	2868.91	374.48
		11.57			12.35			1.28			16409.38			2604.11		
In-vitro	Joplin 02-2006	P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
Mill-waste	A1 TOP (1% TR)	3672.26	3896.30	316.84	34.64	36.61	2.79	0.23	0.11	0.16	4.02	2.87	1.62	8607.39	8943.20	474.91
		4120.34			38.58			0.00			1.73			9279.01		
	A1 SUB (1% TR)	6.74	6.08	0.93	56.70	56.68	0.02	0.19	0.09	0.13	0.00	1.98	2.80	3577.02	3707.92	185.12
		5.42			56.67			0.00			3.96			3838.82		
	A2 TOP (1% TR)	5043.78	4834.78	295.57	56.90	55.16	2.47	0.81	0.63	0.26	16.33	17.63	1.84	10505.80	10130.03	531.42
		4625.78			53.41			0.45			18.93			9754.26		
	A2 SUB (1% TR)	2033.86	2024.46	13.30	96.63	96.75	0.16	1.71	1.70	0.01	1045.27	1016.10	41.25	17763.70	17738.20	36.06
		2015.05			96.86			1.69			986.93			17712.70		

	A3 TOP (1% TR)	4498.30	4383.90	161.79	27.94	27.21	1.04	0.57	0.43	0.20	15.23	18.09	4.05	8348.78	8110.41	337.11
		4269.50			26.47			0.29			20.96			7872.04		
	A3 SUB (1% TR)	519.51	516.86	3.75	15.56	16.13	0.81	0.00	0.00	0.00	982.36	1048.52	93.57	2425.78	2445.36	27.69
		514.21			16.70			0.00			1114.69			2464.94		
	B1 TOP (0.75%TR)	4877.46	4854.17	32.94	48.20	48.10	0.15	0.19	0.24	0.06	41.43	42.35	1.30	9101.04	9121.53	28.98
		4830.88			47.99			0.28			43.27			9142.03		
	B1 SUB (0.75% TR)	179.75	192.39	17.88	59.66	56.74	4.13	2.02	1.74	0.41	807.23	868.96	87.29	10242.53	9691.85	778.77
		205.03			53.83			1.45			930.69			9141.18		
	B2 TOP (0.75%TR)	6799.37	7069.78	382.42	47.54	50.99	4.88	0.37	0.49	0.18	11.86	28.78	23.94	10561.20	11120.10	790.40
		7340.19			54.44			0.61			45.71			11679.00		
	B2 SUB (0.75%TR)	3165.79	3207.22	58.58	55.30	56.18	1.23	1.07	1.09	0.03	681.40	694.77	18.91	14613.10	14775.80	230.09
		3248.64			57.05			1.11			708.14			14938.50		
	B3 TOP (0.75%TR)	3023.45	2957.42	93.38	40.51	39.24	1.79	0.25	0.24	0.02	6.65	4.16	3.52	8041.51	7750.58	411.44
		2891.39			37.98			0.22			1.67			7459.65		
	B3 SUB (0.75% TR)	4.80	5.16	0.52	77.58	77.95	0.52	1.85	1.70	0.21	1209.63	1231.56	31.01	10305.93	10426.68	170.77
		5.53			78.32			1.56			1253.48			10547.43		
	C1 TOP (Control)	37.27	38.24	1.36	63.16	63.00	0.22	0.46	0.45	0.00	290.19	314.40	34.24	6649.64	6574.67	106.02
		39.20			62.84			0.45			338.62			6499.70		
	C1 SUB (Control)	14.22	8.82	7.63	85.26	89.99	6.68	2.23	2.25	0.03	1093.27	1174.89	115.43	12098.80	12914.95	1154.2
		3.42			94.71			2.27			1256.51			13731.10		
	C2 TOP (Control)	51.28	49.62	2.34	68.54	71.82	4.64	0.68	0.54	0.20	400.27	418.40	25.64	8559.84	8920.21	509.64
		47.96			75.10			0.40			436.53			9280.58		
	C2 SUB (Control)	2.15	1.96	0.27	60.91	59.27	2.32	0.00	0.11	0.16	616.68	647.41	43.45	9777.95	9594.48	259.46
		1.77			57.63			0.22			678.13			9411.02		
	C3 TOP (Control)	97.95	97.63	0.45	66.80	66.82	0.03	0.82	0.80	0.02	437.09	457.20	28.44	10988.83	11031.58	60.46
		97.31			66.84			0.79			477.31			11074.33		
	C3 SUB (Control)	94.98	97.57	3.67	67.99	67.53	0.66	0.37	0.57	0.29	524.20	534.60	14.71	10942.23	10747.98	274.71
		100.16			67.06			0.78			545.00			10553.73		
Urban	1% PA (1)	3852.11	3865.95	19.57	6.59	6.54	0.08	0.33	0.43	0.15	169.70	173.56	5.46	937.64	897.77	56.39
In-vitro		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
		3879.79			6.48			0.53			177.42			857.90		
	Control (13)	120.16	114.33	8.23	11.77	11.65	0.17	0.45	0.28	0.24	2192.49	2094.72	138.27	1384.42	1327.96	79.85
		108.51			11.53			0.11			1996.94			1271.50		
	1% PA (14)	4703.94	4801.68	138.23	13.69	13.79	0.15	0.74	0.57	0.25	282.81	299.85	24.10	1820.89	1815.77	7.24
		4899.42			13.90			0.39			316.89			1810.65		
	1% PI (31)	2805.26	2535.86	381.00	7.73	6.87	1.23	0.37	0.31	0.08	218.10	297.32	112.02	865.17	749.72	163.28
		2266.45			6.00			0.25			376.53			634.26		
Mining	Mizzou Doo Mix T2	261.52	255.67	8.27	22.29	21.93	0.51	0.00	0.02	0.03	224.41	229.36	7.00	3316.78	3228.25	125.21

Waste																
		249.82			21.57			0.04			234.31			3139.71		
	bottom	331.97	355.95	33.91	33.63	34.18	0.78	0.60	0.60	0.01	1226.09	1405.51	253.73	3706.03	3764.18	82.24
		379.92			34.74			0.61			1584.92			3822.33		
	SMC (T4)	3069.02	3079.59	14.94	2.19	2.09	0.14	0.00	0.00	0.00	2.43	1.22	1.72	657.47	621.60	50.72
		3090.15			1.99			0.00			0.00			585.74		
	bottom	567.87	560.88	9.89	25.44	25.73	0.41	0.66	0.39	0.39	1727.95	1754.95	38.18	9820.43	9885.54	92.07
		553.88			26.02			0.11			1781.95			9950.64		
	Turkey Litter (T5)	13888.20	13228.20	933.38	3.90	3.61	0.41	2.53	2.40	0.18	90.98	85.63	7.57	4849.03	4566.35	399.77
		12568.20			3.32			2.27			80.28			4283.67		
	bottom	3134.96	3075.40	84.24	11.28	11.24	0.06	0.45	0.36	0.13	1636.01	1644.31	11.74	15240.40	15140.70	141.00
		3015.83			11.19			0.26			1652.61			15041.00		
	Chicken Litter (T6)	5632.48	5574.47	82.04	8.87	8.76	0.15	1.37	1.43	0.09	191.14	184.71	9.09	1422.68	1395.69	38.17
		5516.46			8.66			1.49			178.29			1368.70		
	bottom	328.39	314.43	19.74	13.08	13.09	0.02	0.70	0.73	0.05	1427.92	1443.18	21.58	2253.94	2222.54	44.41
		300.47			13.11			0.77			1458.44			2191.13		
	Mizzou Doo (T7)	8188.53	9171.22	1389.73	0.38	0.43	0.07	0.55	0.88	0.47	17.24	17.82	0.81	283.77	289.11	7.56
		10153.90			0.48			1.21			18.39			294.46		
	bottom	910.94	887.21	33.56	0.68	0.71	0.04	1.05	0.95	0.15	130.87	128.91	2.77	207.86	183.43	34.55
		863.48			0.74			0.84			126.96			159.00		
	Sewage Sludge (T8)	13521.80	13521.90	0.14	0.18	0.16	0.03	0.74	0.65	0.13	2.91	2.55	0.51	273.63	237.27	51.41
		13522.00			0.14			0.56			2.18			200.92		
	bottom	578.18	563.05	21.39	1.35	1.33	0.03	1.23	1.09	0.21	1271.12	1218.70	74.14	4863.91	4780.92	117.37
		547.92			1.31			0.94			1166.27			4697.92		
	Sewage Sludge (8H)	164.38	164.80	0.60	45.45	45.40	0.07	0.00	0.00	0.00	14.31	13.26	1.48	5180.02	5129.59	71.32
		165.23			45.35			0.00			12.21			5079.16		
	bottom	34.84	30.58	6.02	11.42	11.19	0.32	0.31	0.22	0.13	5327.09	5222.18	148.37	4504.34	4427.25	109.02
		26.33			10.97			0.13			5117.26			4350.16		
	Phosphorus (T9)	610.77	640.20	41.63	3.71	3.93	0.30	0.18	0.18	0.01	92.85	78.55	20.23	982.83	987.69	6.86
		669.64			4.14			0.19			64.25			992.54		
	bottom	282.10	293.01	15.43	4.66	5.11	0.65	0.39	0.33	0.08	393.98	424.70	43.44	731.28	784.24	74.91
		303.93			5.57			0.27			455.42			837.21		
	EPA Soil (T10)	385.26	383.34	2.72	21.27	21.26	0.01	0.24	0.19	0.08	139.70	142.90	4.52	3429.78	3450.19	28.86
		381.41			21.25			0.13			146.09			3470.60		
	Untreated Soil	11.91	11.60	0.44	2.89	2.81	0.11	0.79	0.84	0.07	15846.70	15738.20	153.44	1150.69	1117.27	47.27
		11.29			2.73			0.89			15629.70			1083.84		

Appendix 8: Raw data and calculations for leachability of each sampling date

Soil Sample	Leachability	Joplin 03-2004		
Mining Waste	AVG_P (mg/kg soil)	STD	AVG_Pb (mg/kg soil)	STD
Mizzou Doo Mix (T2)	217.53	37.50	460.01	33.40
Repository Soil (T3)	487.13	34.94	687.06	68.38
SMC (T4)	838.52	35.93	328.12	24.15
Turkey Litter (T5)	1503.99	173.56	149.40	24.35
Chicken Litter (T6)	1467.43	235.59	230.94	18.73
Mizzou Doo (T7)	333.69	19.77	425.79	26.96
Sewage Sludge (T8)	317.78	52.23	354.63	22.38
Sewage Sludge (8H)	591.48	17.33	246.66	17.87
Phosphorus (T9)	4920.80	514.74	108.85	23.17
EPA Soil (T10)	537.62	65.84	347.63	17.45
UNTREATED	102.03	22.24	1517.29	85.07
Mill-waste	AVG_P (mg/kg soil)	STD	AVG_Pb (mg/kg soil)	STD
A (1% TR)	2910.85	264.51	93.94	27.19
B (0.5% TR)	1758.85	196.64	150.09	23.85
C (Control)	106.48	15.06	1603.68	239.62
Urban	AVG_P (mg/kg soil)	STD	AVG_Pb (mg/kg soil)	STD
1% SA (1)	2991.36	544.92	218.19	63.97
Control (13)	97.22	9.02	1053.97	66.56
1% RT (14)	2996.35	649.36	345.15	21.84
1% PI (31)	3339.22	139.98	336.49	24.61
Joplin 08-2004				
Mining Waste	AVG_P (mg/kg soil)	STD	AVG_Pb (mg/kg soil)	STD
Mizzou Doo Mix (T2)	222.50	30.23	518.51	77.17
Repository Soil (T3)	103.46	3.18	668.96	178.55
SMC (T4)	99.48	40.97	635.38	142.13
Turkey Litter (T5)	727.85	148.63	353.13	60.44
Chicken Litter (T6)	1347.74	237.04	185.93	11.09
Mizzou Doo (T7)	1239.97	204.49	293.27	29.45
Sewage Sludge (T8)	320.97	35.15	470.28	18.95
Sewage Sludge (8H)	97.55	5.54	778.56	93.31
Phosphorus (T9)	263.08	26.74	407.26	21.28
EPA Soil (T10)	608.32	94.96	331.15	66.05
UNTREATED	197.32	38.03	378.26	68.03
Mill-waste	AVG_P (mg/kg soil)	STD	AVG_Pb (mg/kg soil)	STD
A (1% TR)	3673.46	302.69	119.08	47.84
B (0.5% TR)	462.33	44.44	357.01	49.05

C (Control)	2452.30	125.16	154.80	34.51
Urban	AVG_P (mg/kg soil)	STD	AVG_Pb (mg/kg soil)	STD
1% SA (1)	1477.14	66.19	225.44	41.67
Control (13)	362.51	96.52	267.68	52.49
1% RT (14)	113.82	35.76	1539.69	208.43
1% PI (31)	73.80	16.60	781.78	72.19

Leachibility	Joplin 10-2004	P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
Mining Waste	Mizzou Doo Mix (T2)	458.48	436.75	21.58	0.65	0.59	0.06	0.00	0.00	0.00	1.47	0.57	0.78	73.98	85.21	13.97
		415.31			0.54			0.00			0.00			80.80		
		436.46			0.57			0.00			0.26			100.85		
	Repository Soil (T3)	818.93	818.93		0.56	0.56		0.00	0.00		0.00	0.00		157.99	157.99	
	SMC (T4)	763.90	815.88	73.51	1.08	1.30	0.31	0.00	0.06	0.09	1.66	0.83	1.17	125.01	160.61	50.34
		867.86			1.52			0.13			0.00			196.21		
	Turkey Litter (T5)	571.89	678.00	96.11	0.79	0.90	0.09	0.00	0.02	0.04	0.90	0.71	0.64	2065.71	2301.87	211.93
		702.88			0.95			0.00			1.23			2364.41		
		759.23			0.95			0.07			0.00			2475.50		
	Chicken Litter (T6)	839.60	730.54	125.26	5.94	4.49	1.66	0.00	0.06	0.11	8.20	3.63	4.18	1882.42	1479.32	455.45
		758.29			4.84			0.19			2.69			1570.28		
Leachibility		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
		593.73			2.68			0.00			0.00			985.26		
	Mizzou Doo (T7)	567.52	488.82	101.35	3.47	3.03	0.56	0.35	0.14	0.19	5.26	2.21	2.68	3795.97	3292.80	572.43
		524.46			3.23			0.07			1.11			3412.43		
		374.46			2.40			0.00			0.26			2670.01		
	Sewage Sludge (8H)	64.01	67.41	9.23	6.09	7.96	1.65	0.00	0.00	0.00	5.17	5.51	1.25	638.98	826.78	162.72
	TOP	77.86			9.23			0.00			6.90			925.73		
		60.36			8.57			0.00			4.47			915.65		
	Sewage Sludge (8H)	66.47	62.70	10.21	2.20	2.14	0.40	0.00	0.00	0.00	3.99	1.44	2.21	619.69	590.40	103.10
	SUB	70.49			2.51			0.00			0.00			675.68		
		51.14			1.72			0.00			0.32			475.82		
	Phosphorus (T9)	109.84	87.05	32.89	2.38	1.84	0.59	0.00	0.00	0.00	0.00	0.00	0.00	901.89	698.13	233.28
		101.96			1.91			0.00			0.00			748.85		
		49.34			1.22			0.00			0.00			443.67		
	EPA Soil (T10)	823.97	858.11	94.07	0.82	0.93	0.21	0.12	0.04	0.07	0.72	0.88	0.97	201.14	245.82	81.02

		785.89			0.81			0.00			1.92			196.98		
		964.48			1.17			0.00			0.00			339.35		
	UNTREATED	1.43	1.16	0.26	1.48	1.53	0.19	0.00	0.07	0.11	4036.89	5214.28	2668.92	370.56	411.53	72.06
		0.90			1.75			0.20			8269.45			494.73		
		1.15			1.37			0.00			3336.52			369.31		
Mill-waste	A TOP (1% TR)	2032.61	2258.70	197.66	5.07	6.31	1.07	0.00	0.06	0.11	0.00	0.22	0.38	2280.28	2859.15	501.63
		2398.82			6.90			0.00			0.67			3130.80		
		2344.67			6.95			0.19			0.00			3166.38		
	A SUB (1% TR)	141.04	127.28	33.41	10.55	10.53	1.48	0.00	0.01	0.01	4.63	3.14	1.29	1822.24	1857.62	263.15
		151.62			12.01			0.00			2.49			2136.67		
		89.18			9.04			0.02			2.31			1613.94		
	B TOP (0.5%TR)	2244.09	2321.64	68.50	4.22	4.52	0.28	0.00	0.00	0.00	0.00	0.00	0.00	2787.40	2979.00	175.78
		2346.95			4.55			0.00			0.00			3016.77		
Leachibility		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kg soil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
		2373.88			4.77			0.00			0.00			3132.82		
	B SUB (0.5% TR)	196.23	179.37	31.21	9.32	8.88	0.46	0.00	0.00	0.00	2.68	1.45	1.07	1658.44	1607.04	63.65
		198.54			8.91			0.00			0.66			1626.84		
		143.36			8.41			0.00			1.03			1535.84		
	C TOP (Control)	1.67	1.08	0.94	13.92	12.53	1.77	0.00	0.00	0.00	0.00	0.61	0.56	1476.05	1278.68	247.56
		0.00			13.13			0.00			0.73			1359.08		
		1.58			10.54			0.00			1.10			1000.92		
	C SUB (Control)	0.00	0.00	0.00	35.41	33.46	2.76	0.00	0.02	0.03	1.05	0.52	0.74	2492.52	2285.41	292.90
		0.00			31.50			0.04			0.00			2078.29		
Urban	1% PA (1)	2507.95	1909.16	522.05	1.00	0.60	0.35	0.00	0.00	0.00	0.78	0.32	0.41	266.32	166.06	89.44
		1549.53			0.35			0.00			0.17			94.50		
		1670.00			0.43			0.00			0.00			137.35		
	Control (13)	174.23	175.42	2.63	1.88	1.91	0.03	0.00	0.00	0.00	17.53	11.83	6.67	327.79	338.15	10.13
		178.43			1.94			0.00			13.45			338.63		
		173.61			1.92			0.00			4.50			348.04		
	1% PA (14)	1872.18	1602.50	235.90	1.25	0.88	0.33	0.00	0.00	0.00	0.00	0.00	0.00	357.34	256.64	88.23
		1434.40			0.76			0.00			0.00			192.87		
		1500.94			0.63			0.00			0.00			219.72		
	1% PI (31)	580.87	636.44	99.47	0.87	0.97	0.36	0.00	0.00	0.00	0.00	0.35	0.60	155.47	195.82	60.55
		751.28			1.36			0.00			1.04			265.45		
		577.18			0.66			0.00			0.00			166.55		
	0.5% PA (41)	884.16	911.40	46.90	0.66	0.82	0.22	0.00	0.00	0.00	0.00	0.00	0.00	205.85	261.30	54.74
		965.56			1.07			0.00			0.00			315.31		

		884.48			0.72			0.00			0.00			262.74		
Leachibility	Joplin 03-2005	P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kgsoil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
Mill-waste	A1 TOP (1% TR)	3153.06	3145.70	10.40	21.95	21.86	0.13	0.17	0.17	0.01	1.09	1.08	0.02	4308.10	4282.57	36.10
		3138.35			21.77			0.16			1.07			4257.05		
	A2 TOP (1% TR)	4020.77	4024.34	5.05	20.05	20.07	0.02	0.15	0.13	0.03	0.34	0.33	0.02	4326.30	4332.06	8.15
		4027.91			20.08			0.12			0.32			4337.82		
	A3 TOP (1% TR)	3853.31	3848.73	6.47	12.71	12.79	0.10	0.12	0.13	0.01	0.00	0.00	0.00	3290.56	3293.74	4.50
		3844.16			12.86			0.14			0.00			3296.93		
	B1 TOP (0.5%TR)	3029.78	3030.87	1.54	26.83	26.72	0.16	0.17	0.16	0.01	1.90	1.86	0.06	4257.27	4315.22	81.95
		3031.96			26.61			0.15			1.82			4373.17		
	B2 TOP (0.5%TR)	3013.34	3012.81	0.74	10.34	10.31	0.04	0.12	0.12	0.00	0.00	0.00	0.00	3255.35	3241.72	19.28
		3012.29			10.28			0.12			0.00			3228.09		
	B3 TOP (0.5%TR)	2995.08	3003.41	11.79	9.66	9.61	0.06	0.12	0.13	0.02	0.45	0.34	0.16	3150.26	3131.41	26.65
		3011.75			9.57			0.14			0.23			3112.57		
	C1 TOP (Control)	90.89	91.06	0.24	33.56	33.77	0.30	0.05	0.05	0.00	1.51	1.55	0.06	3103.27	3111.79	12.05
		91.23			33.99			0.05			1.59			3120.31		
	C2 TOP (Control)	13.43	13.33	0.14	32.60	32.58	0.03	0.09	0.09	0.00	22.50	22.42	0.11	3750.25	3736.09	20.03
		13.23			32.56			0.09			22.35			3721.93		
	C3 TOP (Control)	36.66	36.22	0.63	28.72	28.68	0.05	0.06	0.06	0.00	8.19	8.15	0.05	4223.35	4259.77	51.51
		35.78			28.65			0.07			8.12			4296.20		
Urban	1% PA (1)	1770.05	1781.47	16.16	4.57	4.57	0.01	0.10	0.12	0.03	22.84	22.88	0.06	837.48	833.93	5.01
		1792.90			4.56			0.14			22.92			830.39		
	Control (13)	52.06	51.77	0.42	6.50	6.48	0.03	0.09	0.07	0.02	139.56	139.02	0.77	700.63	701.35	1.02
		51.47			6.45			0.06			138.47			702.07		
	1% PA (14)	2103.85	2096.33	10.63	2.26	2.26	0.01	0.08	0.09	0.00	2.03	2.05	0.03	484.60	482.73	2.64
		2088.82			2.26			0.09			2.07			480.86		
	1% PI (31)	1278.87	1275.19	5.20	1.29	1.30	0.02	0.06	0.08	0.02	4.25	4.30	0.07	224.87	225.06	0.27
		1271.52			1.31			0.09			4.36			225.26		
Leachibility		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kgsoil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
Mining Waste	Mizzou Doo Mix T2	234.72	235.10	0.54	16.31	16.35	0.06	0.11	0.11	0.00	19.49	19.43	0.09	2079.48	2080.32	1.19
		235.49			16.39			0.10			19.36			2081.16		
	SMC (T4)	1796.64	1794.94	2.40	4.12	4.13	0.01	0.13	0.12	0.02	8.41	8.46	0.06	3067.63	3072.33	6.65
		1793.25			4.13			0.10			8.50			3077.03		
	top	3283.53	3325.33	59.11	1.16	1.16	0.01	0.42	0.41	0.03	1.91	1.90	0.02	765.07	758.61	9.14
		3367.13			1.15			0.39			1.88			752.14		
	top	3221.69	3214.06	10.78	1.16	1.16	0.01	0.33	0.34	0.01	2.04	2.14	0.14	743.93	743.28	0.91
		3206.44			1.15			0.34			2.24			742.64		
	Turkey Litter (T5) top	2636.15	2633.32	4.00	1.38	1.38	0.01	0.26	0.26	0.01	7.76	7.75	0.00	2618.95	2618.83	0.17

		2630.49			1.37			0.27			7.75			2618.71		
	top	3192.59	3194.73	3.03	1.60	1.60	0.00	0.34	0.35	0.01	10.01	10.02	0.01	1818.49	1802.42	22.73
		3196.87			1.60			0.36			10.02			1786.35		
	top	6476.93	6499.11	31.37	0.59	0.59	0.00	0.77	0.77	0.00	1.61	1.57	0.05	831.94	837.48	7.84
		6521.29			0.59			0.77			1.54			843.03		
	Chicken Litter (T6)	2745.54	2735.27	14.52	6.19	6.21	0.03	0.14	0.13	0.01	12.65	12.64	0.01	908.43	908.08	0.49
		2725.00			6.23			0.12			12.64			907.73		
	top	7989.75	7927.27	88.36	0.18	0.18	0.00	0.48	0.49	0.01	3.04	3.13	0.13	169.45	168.28	1.65
		7864.79			0.18			0.50			3.22			167.12		
	top	10026.05	10077.05	72.12	0.08	0.07	0.01	0.30	0.30	0.01	1.48	1.42	0.08	95.86	95.80	0.08
		10128.05			0.06			0.31			1.36			95.74		
	Mizzou Doo (T7)	7555.73	7543.03	17.96	0.11	0.11	0.00	0.48	0.47	0.01	1.94	1.93	0.01	127.57	127.65	0.11
		7530.33			0.10			0.46			1.93			127.73		
	top	9298.95	9186.21	159.43	0.06	0.06	0.00	0.29	0.30	0.01	0.98	0.95	0.04	83.10	82.87	0.33
		9073.48			0.07			0.30			0.92			82.63		
	top	9451.38	9454.82	4.86	0.04	0.04	0.00	0.31	0.30	0.02	0.43	0.43	0.00	64.12	64.39	0.39
		9458.26			0.04			0.28			0.44			64.67		
	Sewage Sludge (T8)	1515.59	1512.29	4.67	0.19	0.20	0.01	0.24	0.25	0.01	0.65	0.59	0.07	181.49	179.86	2.30
		1508.99			0.20			0.26			0.54			178.23		
	top	1910.13	1902.24	11.15	0.15	0.15	0.00	0.23	0.22	0.01	0.55	0.53	0.03	208.26	207.73	0.75
		1894.36			0.14			0.22			0.51			207.20		
	top	1683.00	1680.29	3.83	0.29	0.28	0.00	0.19	0.19	0.00	0.35	0.34	0.01	216.87	218.38	2.14
		1677.59			0.28			0.19			0.33			219.90		
	Phosphorus (T9)	275.63	274.88	1.06	1.14	1.14	0.01	0.10	0.10	0.00	1.45	1.51	0.08	410.87	409.52	1.92
		274.13			1.15			0.09			1.56			408.16		
	top	219.55	219.85	0.43	0.86	0.85	0.01	0.08	0.07	0.01	1.07	1.08	0.01	287.92	286.99	1.31
		220.16			0.84			0.06			1.08			286.07		
	top	64.09	63.88	0.29	0.60	0.60	0.00	0.05	0.06	0.01	0.49	0.49	0.00	208.41	208.35	0.08
		63.68			0.61			0.06			0.49			208.29		
	EPA Soil (T10)	155.13	156.66	2.16	0.72	0.73	0.01	0.06	0.06	0.00	3.81	3.79	0.04	331.58	332.01	0.60
		158.18			0.73			0.06			3.76			332.43		
	top	409.10	409.89	1.13	2.05	2.05	0.01	0.08	0.07	0.01	3.89	3.95	0.09	343.72	345.26	2.17
		410.69			2.06			0.06			4.02			346.79		
	top	837.64	848.45	15.29	2.38	2.38	0.01	0.12	0.11	0.00	1.15	1.22	0.09	590.78	591.20	0.60
		859.26			2.39			0.11			1.28			591.62		
	Sewage Sludge (8H)	312.89	311.69	1.70	6.47	6.45	0.02	0.02	0.03	0.02	133.76	133.60	0.22	882.24	882.50	0.37
		310.48			6.44			0.04			133.44			882.76		
	Untreated Soil	0.00	0.00	0.00	3.61	3.61	0.01	0.00	0.00	0.00	3832.40	3838.08	8.03	625.31	618.91	9.06

		0.00			3.62			0.00			3843.76			612.50		
	Joplin 06-2005															
Mill-waste	A1 TOP (1% TR)	2787.51	2793.57	8.57	9.51	9.51	0.01	0.08	0.08	0.00	0.21	0.17	0.06	2952.25	2937.45	20.93
		2799.63			9.50			0.07			0.13			2922.65		
	A2 TOP (1% TR)	4205.55	4178.70	37.96	23.29	23.15	0.19	0.12	0.11	0.01	0.48	0.50	0.03	4133.18	4126.93	8.84
		4151.86			23.02			0.10			0.52			4120.68		
Leachibility		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kgsoil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
	A3 TOP (1% TR)	4359.19	4365.84	9.40	10.28	10.27	0.01	0.11	0.12	0.01	0.37	0.36	0.02	2824.72	2829.43	6.67
		4372.49			10.27			0.13			0.35			2834.15		
	B1 TOP (0.5%TR)	2941.41	2936.89	6.39	16.65	16.64	0.01	0.09	0.09	0.00	0.34	0.33	0.01	3421.47	3411.94	13.48
		2932.38			16.63			0.09			0.32			3402.41		
	B2 TOP (0.5%TR)	2982.17	2971.26	15.43	6.52	6.50	0.03	0.10	0.09	0.01	0.54	0.58	0.05	2309.27	2321.61	17.46
		2960.35			6.48			0.09			0.61			2333.96		
	B3 TOP (0.5%TR)	2783.30	2790.74	10.52	7.22	7.20	0.02	0.09	0.08	0.01	0.00	0.00	0.00	3116.45	3120.75	6.08
		2798.18			7.18			0.07			0.00			3125.05		
	C1 TOP (Control)	4.35	4.50	0.22	29.78	29.97	0.27	0.00	0.02	0.02	0.39	0.36	0.05	2744.61	2731.55	18.47
		4.66			30.16			0.03			0.32			2718.49		
	C2 TOP (Control)	0.91	0.99	0.10	29.67	29.75	0.11	0.06	0.05	0.02	5.98	5.98	0.00	3608.38	3606.58	2.54
		1.06			29.83			0.03			5.98			3604.79		
	C3 TOP (Control)	3.72	3.58	0.20	29.37	29.27	0.14	0.04	0.05	0.01	0.37	0.33	0.05	4848.80	4839.22	13.54
		3.44			29.17			0.05			0.30			4829.65		
Urban	1% PA (1)	1526.67	1512.64	19.84	1.23	1.23	0.00	0.09	0.09	0.00	0.91	0.91	0.01	281.81	282.50	0.98
		1498.61			1.22			0.09			0.90			283.19		
	Control (13)	102.22	101.74	0.69	4.26	4.26	0.01	0.12	0.13	0.01	58.67	58.57	0.15	532.88	535.02	3.02
		101.25			4.25			0.14			58.46			537.15		
	1% PA (14)	3070.66	3038.09	46.06	2.19	2.19	0.01	0.10	0.09	0.00	0.84	0.83	0.02	511.07	506.02	7.14
		3005.52			2.19			0.09			0.82			500.98		
	1% PI (31)	558.06	558.20	0.20	3.11	3.12	0.01	0.07	0.07	0.00	20.11	20.09	0.02	449.91	452.09	3.07
		558.34			3.12			0.07			20.08			454.26		
Mining Waste	Mizzou Doo Mix (T2)	165.26	165.57	0.44	12.24	12.25	0.01	0.02	0.01	0.01	10.89	10.90	0.02	1860.26	1854.31	8.41
		165.88			12.26			0.00			10.92			1848.36		
	Repository Soil (T3)	532.92	530.34	3.65	4.20	4.19	0.01	0.05	0.05	0.00	0.00	0.00	0.00	578.18	581.00	3.99
		527.76			4.18			0.05			0.00			583.83		
Leachibility		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kgsoil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
	top	1895.10	1894.96	0.21	2.20	2.20	0.01	0.06	0.06	0.00	0.11	0.06	0.08	532.20	531.31	1.27
		1894.81			2.19			0.06			0.00			530.41		
	top	1696.42	1698.76	3.30	3.97	3.97	0.01	0.04	0.04	0.00	0.00	0.00	0.00	716.64	712.51	5.85
		1701.09			3.97			0.04			0.00			708.37		

	SMC (T4)	2719.59	2733.35	19.46	0.30	0.31	0.01	0.24	0.24	0.01	0.00	0.00	0.00	159.26	161.07	2.56
		2747.11			0.31			0.23			0.00			162.88		
	top	1808.72	1815.51	9.60	0.41	0.41	0.00	0.20	0.19	0.01	0.00	0.00	0.00	188.71	189.38	0.95
		1822.30			0.41			0.18			0.00			190.05		
	top	1825.10	1821.64	4.89	0.21	0.21	0.00	0.17	0.18	0.00	0.00	0.00	0.00	103.29	103.37	0.12
		1818.18			0.21			0.18			0.00			103.45		
	Turkey Litter (T5)	2715.50	2702.88	17.85	0.37	0.38	0.01	0.33	0.33	0.01	0.08	0.14	0.09	1034.18	1033.25	1.32
		2690.26			0.38			0.34			0.21			1032.31		
	top	2528.72	2536.13	10.47	0.38	0.38	0.00	0.25	0.24	0.01	0.03	0.08	0.06	1080.29	1078.50	2.53
		2543.53			0.38			0.24			0.13			1076.71		
	top	2013.33	2005.34	11.30	0.43	0.42	0.01	0.22	0.21	0.01	0.53	0.62	0.12	1215.37	1212.26	4.40
		1997.35			0.42			0.20			0.71			1209.15		
	Chicken Litter (T6)	4724.03	4677.34	66.04	1.89	1.88	0.01	0.16	0.16	0.00	1.38	1.44	0.08	601.57	595.53	8.55
		4630.64			1.87			0.16			1.49			589.48		
	top	6468.14	6469.37	1.74	0.14	0.14	0.00	0.28	0.27	0.00	0.73	0.73	0.01	101.55	100.62	1.31
		6470.60			0.14			0.27			0.74			99.69		
	top	2073.27	2068.90	6.19	0.59	0.59	0.00	0.09	0.11	0.03	2.22	2.21	0.03	312.57	315.50	4.14
		2064.52			0.59			0.13			2.19			318.42		
	Mizzou Doo (T7)	2892.49	2903.97	16.24	0.40	0.40	0.00	0.15	0.15	0.01	0.62	0.64	0.03	103.52	103.15	0.53
		2915.45			0.39			0.15			0.66			102.77		
	top	5894.10	5946.49	74.09	0.08	0.08	0.00	0.29	0.29	0.00	0.66	0.68	0.03	70.12	70.09	0.05
		5998.88			0.08			0.29			0.70			70.06		
Leachibility		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kgsoil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
	top	4828.59	4819.52	12.83	0.06	0.06	0.00	0.23	0.23	0.01	0.12	0.06	0.08	66.71	66.64	0.09
		4810.44			0.06			0.24			0.00			66.58		
	Sewage Sludge (T8)	973.25	976.05	3.95	0.19	0.20	0.00	0.17	0.17	0.00	0.00	0.00	0.00	130.23	129.95	0.40
		978.84			0.20			0.18			0.00			129.67		
	top	1023.99	1015.88	11.47	0.17	0.17	0.01	0.20	0.18	0.02	0.00	0.00	0.00	132.89	132.42	0.66
		1007.77			0.17			0.17			0.00			131.95		
	top	908.94	912.46	4.99	0.21	0.21	0.00	0.20	0.19	0.01	0.00	0.00	0.00	165.02	165.18	0.24
		915.99			0.21			0.19			0.00			165.35		
	Phosphorus (T9)	244.99	242.92	2.93	3.65	3.62	0.04	0.11	0.11	0.01	0.34	0.29	0.08	1123.52	1112.89	15.04
		240.85			3.59			0.10			0.23			1102.25		
	top	332.99	330.56	3.44	0.66	0.66	0.00	0.17	0.17	0.00	0.46	0.43	0.04	255.63	256.29	0.93
		328.13			0.66			0.17			0.41			256.94		
	top	332.62	329.70	4.13	0.59	0.59	0.00	0.16	0.17	0.00	1.38	1.35	0.03	196.70	195.79	1.29
		326.79			0.59			0.17			1.33			194.87		
	EPA Soil (T10)	701.08	698.74	3.30	2.69	2.68	0.01	0.10	0.11	0.01	2.68	2.62	0.09	437.04	436.33	1.00

		696.41			2.67			0.12			2.55			435.63		
	top	2077.80	2072.72	7.19	3.52	3.55	0.04	0.11	0.12	0.01	0.56	0.45	0.15	918.57	918.28	0.41
		2067.63			3.58			0.12			0.35			917.99		
	Sewage Sludge (8H)	123.50	121.37	3.00	0.78	0.76	0.02	0.13	0.11	0.03	0.03	0.03	0.00	98.90	97.60	1.84
		119.25			0.74			0.09			0.03			96.30		
	top	117.65	117.60	0.07	0.13	0.13	0.00	0.07	0.06	0.02	0.00	0.01	0.01	58.81	58.66	0.22
		117.56			0.14			0.05			0.02			58.51		
	top	144.11	143.96	0.21	0.17	0.16	0.01	0.09	0.08	0.02	0.00	0.00	0.00	60.14	60.49	0.50
		143.81			0.16			0.07			0.00			60.84		
	Untreated Soil	0.45	0.41	0.06	1.78	1.78	0.00	0.09	0.09	0.00	6546.52	6504.85	58.94	536.28	538.23	2.76
		0.36			1.77			0.09			6463.17			540.18		
Leachibility	Joplin 09-2005	P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kgsoil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
Mill-waste	A1 TOP (1% TR)	2932.00	2928.26	5.30	8.55	8.61	0.08	0.10	0.10	0.00	0.03	0.01	0.02	2689.34	2655.79	47.45
		2924.51			8.67			0.10			0.00			2622.24		
	A2 TOP (1% TR)	3024.24	3000.00	34.28	12.21	12.11	0.14	0.11	0.10	0.01	0.00	0.00	0.00	3404.50	3399.82	6.62
		2975.76			12.01			0.10			0.00			3395.14		
	A3 TOP (1% TR)	3969.59	4002.68	46.80	11.51	11.56	0.07	0.15	0.15	0.00	0.00	0.00	0.00	3664.53	3692.09	38.98
		4035.77			11.62			0.15			0.00			3719.65		
	B1 TOP (0.5%TR)	3022.72	3022.25	0.67	12.12	12.08	0.06	0.08	0.08	0.01	0.00	0.00	0.00	2997.12	2990.83	8.90
		3021.77			12.04			0.09			0.00			2984.53		
	B2 TOP (0.5%TR)	1978.02	1989.52	16.26	7.69	7.70	0.01	0.08	0.07	0.01	0.19	0.11	0.12	2316.75	2312.14	6.53
		2001.02			7.71			0.06			0.02			2307.52		
	B3 TOP (0.5%TR)	3306.11	3328.19	31.23	8.65	8.77	0.17	0.11	0.11	0.00	0.00	0.00	0.00	2394.67	2416.39	30.72
		3350.27			8.89			0.11			0.00			2438.11		
	C1 TOP (Control)	2.07	1.96	0.16	21.65	21.54	0.17	0.05	0.05	0.00	0.03	0.01	0.02	2208.82	2188.01	29.43
		1.85			21.42			0.05			0.00			2167.20		
	C2 TOP (Control)	9.95	9.87	0.12	14.79	14.77	0.03	0.11	0.09	0.03	0.63	0.65	0.04	2113.53	2118.35	6.82
		9.78			14.75			0.07			0.68			2123.17		
	C3 TOP (Control)	38.96	39.10	0.21	20.25	20.15	0.14	0.00	0.00	0.00	0.12	0.14	0.03	2473.43	2473.75	0.45
		39.25			20.05			0.00			0.16			2474.06		
Urban	1% PA (1)	1554.21	1566.80	17.80	1.83	1.84	0.03	0.11	0.11	0.01	1.60	1.63	0.04	391.93	389.14	3.95
		1579.39			1.86			0.10			1.66			386.34		
	Control (13)	57.40	57.41	0.01	5.19	5.18	0.00	0.08	0.09	0.01	64.21	64.17	0.07	637.44	632.11	7.54
		57.42			5.18			0.10			64.12			626.78		
	1% PA (14)	2030.61	2029.54	1.52	1.65	1.66	0.01	0.10	0.11	0.01	0.23	0.40	0.23	442.79	440.62	3.07
		2028.46			1.66			0.11			0.56			438.44		
	1% PI (31)	1254.76	1274.68	28.16	1.90	1.91	0.01	0.15	0.14	0.01	4.80	4.73	0.10	300.86	308.10	10.24
		1294.59			1.92			0.13			4.66			315.34		

Mining Waste	Repository Soil (T3)	1309.29	1297.53	16.64	21.56	21.39	0.25	0.09	0.09	0.00	11.07	10.94	0.18	1998.93	1983.18	22.27
		1285.76			21.21			0.09			10.82			1967.43		
	top	1488.34	1499.64	15.98	5.65	5.65	0.01	0.09	0.10	0.01	8.76	8.82	0.09	980.39	983.76	4.76
		1510.94			5.66			0.11			8.88			987.12		
	top	1154.70	1152.20	3.54	3.93	3.92	0.01	0.08	0.07	0.01	2.89	2.80	0.12	798.12	795.37	3.90
		1149.69			3.91			0.06			2.72			792.61		
	SMC (T4)	2255.59	2243.16	17.58	1.53	1.54	0.00	0.24	0.22	0.03	1.30	1.33	0.05	900.16	895.61	6.43
		2230.73			1.54			0.21			1.37			891.06		
	top	1637.43	1624.86	17.78	2.00	1.99	0.01	0.11	0.12	0.02	1.66	1.57	0.12	1032.37	1033.67	1.84
		1612.29			1.97			0.13			1.48			1034.97		
	top	2689.98	2687.17	3.97	0.60	0.60	0.00	0.25	0.25	0.00	0.12	0.19	0.10	277.81	280.74	4.15
		2684.36			0.60			0.24			0.26			283.67		
	Turkey Litter (T5)	1658.77	1650.04	12.35	0.48	0.47	0.00	0.12	0.13	0.01	0.10	0.11	0.03	252.50	249.71	3.94
		1641.30			0.47			0.14			0.13			246.93		
	top	1854.59	1848.22	9.02	0.60	0.60	0.00	0.17	0.15	0.02	0.39	0.38	0.01	277.42	277.25	0.24
		1841.84			0.60			0.14			0.38			277.08		
	top	1415.89	1419.66	5.33	1.22	1.22	0.00	0.10	0.09	0.00	0.43	0.44	0.01	662.23	660.61	2.28
		1423.43			1.21			0.09			0.44			659.00		
	Chicken Litter (T6)	6944.49	6912.43	45.35	0.46	0.47	0.00	0.31	0.31	0.00	1.00	0.96	0.06	425.05	423.57	2.10
		6880.36			0.47			0.31			0.92			422.08		
	top	6314.77	6301.92	18.17	0.31	0.32	0.00	0.22	0.22	0.00	3.42	3.41	0.00	137.99	138.63	0.91
		6289.07			0.32			0.22			3.41			139.28		
	top	6522.78	6510.81	16.94	0.29	0.29	0.00	0.27	0.26	0.01	3.62	3.64	0.03	144.05	143.62	0.61
		6498.83			0.28			0.25			3.66			143.19		
	Mizzou Doo (T7)	7800.16	7674.91	177.14	0.20	0.20	0.00	0.30	0.30	0.01	1.16	1.15	0.01	92.04	92.37	0.46
		7549.65			0.19			0.31			1.14			92.70		
Leachibility		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kgsoil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
	top	5131.19	5096.08	49.65	0.07	0.07	0.00	0.22	0.22	0.00	0.43	0.44	0.01	58.71	58.78	0.09
		5060.97			0.07			0.22			0.44			58.84		
	top	6019.05	5972.02	66.52	0.03	0.04	0.01	0.21	0.21	0.00	0.15	0.24	0.13	45.72	45.66	0.08
		5924.98			0.04			0.21			0.33			45.60		
	Sewage Sludge (T8)	1181.80	1184.14	3.30	0.55	0.55	0.01	0.32	0.31	0.01	0.86	0.79	0.10	388.40	388.76	0.51
		1186.47			0.56			0.30			0.72			389.12		
	top	905.19	897.12	11.41	0.09	0.10	0.01	0.18	0.18	0.01	0.00	0.00	0.00	105.52	105.74	0.32
		889.05			0.10			0.19			0.00			105.97		
	top	1465.28	1466.93	2.33	0.15	0.15	0.00	0.15	0.14	0.02	0.08	0.04	0.05	233.04	231.56	2.09
		1468.57			0.15			0.13			0.00			230.09		

	Sewage Sludge (8H)	127.28	126.97	0.44	2.16	2.15	0.01	0.05	0.04	0.02	0.11	0.16	0.07	251.59	249.31	3.23
		126.66			2.15			0.03			0.21			247.03		
	top	231.63	230.96	0.96	0.24	0.24	0.00	0.05	0.05	0.01	0.06	0.17	0.15	86.88	87.80	1.30
		230.28			0.24			0.06			0.27			88.72		
	top	191.68	191.28	0.56	0.20	0.20	0.00	0.07	0.07	0.01	0.00	0.00	0.00	74.15	73.73	0.59
		190.88			0.20			0.08			0.00			73.31		
	Phosphorus (T9)	253.53	253.29	0.35	2.56	2.56	0.01	0.09	0.09	0.00	2.12	2.17	0.06	350.01	351.65	2.32
		253.04			2.55			0.09			2.21			353.28		
	top	249.94	250.39	0.64	1.40	1.40	0.01	0.14	0.14	0.00	6.43	6.50	0.09	332.18	334.98	3.97
		250.84			1.41			0.14			6.56			337.79		
	top	915.25	920.61	7.58	1.31	1.32	0.01	0.05	0.05	0.01	0.00	0.00	0.00	286.73	285.51	1.72
		925.97			1.32			0.06			0.00			284.29		
	EPA Soil (T10)	1317.80	1331.36	19.18	3.60	3.62	0.02	0.08	0.08	0.01	7.15	7.18	0.05	704.00	691.50	17.67
		1344.92			3.64			0.09			7.22			679.00		
	top	804.96	804.45	0.73	1.77	1.77	0.00	0.10	0.09	0.01	2.27	2.23	0.06	372.67	374.32	2.32
		803.93			1.77			0.08			2.19			375.96		
Leachibility		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kgsoil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
	top	724.91	716.71	11.60	3.03	3.03	0.00	0.07	0.08	0.01	1.22	1.26	0.06	653.23	656.51	4.64
		708.51			3.03			0.09			1.30			659.78		
	Untreated Soil	0.75	0.50	0.35	8.49	8.45	0.06	0.00	0.00	0.00	3075.62	3072.96	3.77	994.94	1005.03	14.27
		0.25			8.41			0.00			3070.29			1015.12		
Mill-waste	A1 TOP (1% TR)	1647.31	1663.25	22.54	5.37	5.35	0.02	0.07	0.08	0.00	0.00	0.00	0.00	2135.81	2126.52	13.13
		1679.19			5.34			0.08			0.00			2117.24		
	A2 TOP (1% TR)	2404.91	2406.89	2.79	10.30	10.33	0.04	0.10	0.11	0.00	0.00	0.00	0.00	3133.86	3136.84	4.21
		2408.86			10.37			0.11			0.00			3139.82		
	A3 TOP (1% TR)	2565.76	2564.87	1.26	6.06	6.08	0.03	0.10	0.09	0.02	0.00	0.00	0.00	2773.97	2766.53	10.51
		2563.98			6.10			0.07			0.00			2759.10		
	B1 TOP (0.5%TR)	2407.10	2446.33	55.48	9.63	9.68	0.08	0.09	0.10	0.01	0.00	0.00	0.00	2755.24	2775.47	28.61
		2485.56			9.74			0.10			0.00			2795.70		
	B2 TOP (0.5%TR)	3405.96	3435.22	41.37	9.75	9.80	0.07	0.10	0.10	0.00	0.00	0.00	0.00	3168.72	3184.80	22.74
		3464.47			9.85			0.11			0.00			3200.88		
	B3 TOP (0.5%TR)	1761.48	1754.59	9.74	6.49	6.45	0.05	0.09	0.09	0.00	0.42	0.40	0.03	2432.11	2422.08	14.18
		1747.70			6.42			0.09			0.38			2412.06		
	C1 TOP (Control)	10.19	10.47	0.40	21.36	21.10	0.38	0.07	0.05	0.03	0.29	0.27	0.04	2215.95	2199.96	22.61
		10.75			20.83			0.03			0.24			2183.97		
	C2 TOP (Control)	19.41	19.29	0.17	19.23	19.16	0.09	0.05	0.05	0.00	0.71	0.65	0.09	2450.72	2443.04	10.86
		19.17			19.10			0.04			0.58			2435.36		
	C3 TOP (Control)	38.40	38.12	0.40	20.23	20.18	0.07	0.07	0.06	0.02	0.42	0.36	0.09	3034.84	3045.71	15.37

		37.83			20.13			0.05			0.30			3056.58		
Urban	1% PA (1)	2116.07	2123.23	10.12	1.61	1.61	0.00	0.14	0.13	0.02	1.45	1.47	0.03	349.28	351.64	3.34
		2130.38			1.61			0.12			1.49			353.99		
	Control (13)	73.45	73.44	0.01	2.85	2.85	0.00	0.09	0.09	0.00	24.54	24.49	0.06	358.13	356.99	1.61
		73.43			2.85			0.09			24.45			355.86		
Leachibility		P(mg/kg soil)	AVG	STD	Cd(mg/kg soil)	AVG	STD	Cr(mg/kg soil)	AVG	STD	Pb(mg/kgsoil)	AVG	STD	Zn(mg/kg soil)	AVG	STD
	1% PA (14)	2310.58	2305.89	6.64	1.50	1.50	0.00	0.12	0.12	0.00	0.53	0.47	0.09	438.22	438.79	0.82
		2301.19			1.50			0.12			0.41			439.37		
	1% PI (31)	1318.72	1322.23	4.96	1.29	1.28	0.01	0.07	0.07	0.00	0.76	0.79	0.04	202.87	203.00	0.18
		1325.74			1.27			0.07			0.82			203.13		
Mining Waste	Mizzou Doo Mix (T2)	194.69	194.62	0.10	10.20	10.22	0.04	0.07	0.09	0.02	3.32	3.39	0.09	1639.49	1640.38	1.27
		194.55			10.25			0.10			3.45			1641.28		
	SMC (T4)	1842.60	1839.42	4.50	0.50	0.50	0.00	0.17	0.17	0.00	0.00	0.00	0.00	264.37	262.53	2.60
		1836.24			0.50			0.16			0.00			260.69		
	Turkey Litter (T5)	4770.92	4781.18	14.50	0.45	0.44	0.01	0.43	0.44	0.02	0.96	0.94	0.03	1098.82	1096.71	2.98
		4791.43			0.44			0.45			0.92			1094.60		
	Chicken Litter (T6)	2860.66	2871.66	15.55	1.50	1.50	0.01	0.14	0.15	0.01	2.90	2.92	0.03	388.32	384.35	5.62
		2882.65			1.51			0.15			2.94			380.38		
	Mizzou Doo (T7)	4616.87	4596.85	28.31	0.02	0.03	0.01	0.22	0.20	0.03	0.37	0.46	0.14	48.65	49.10	0.63
		4576.83			0.03			0.18			0.56			49.54		
	Sewage Sludge (T8)	7106.07	7079.56	37.50	0.02	0.03	0.01	0.23	0.23	0.00	0.07	0.05	0.04	52.07	52.01	0.09
		7053.04			0.04			0.22			0.02			51.94		
	Sewage Sludge (8H)	99.16	98.89	0.38	18.22	18.15	0.09	0.00	0.00	0.00	0.00	0.00	0.00	2418.88	2400.49	26.01
		98.63			18.09			0.00			0.00			2382.10		
	Phosphorus (T9)	290.08	290.16	0.11	0.90	0.90	0.01	0.07	0.08	0.01	1.58	1.57	0.01	351.41	353.00	2.26
		290.24			0.89			0.09			1.56			354.60		
	EPA Soil (T10)	328.39	326.33	2.91	5.72	5.71	0.02	0.08	0.08	0.00	1.01	1.00	0.02	1106.67	1110.50	5.42
		324.27			5.70			0.08			0.99			1114.34		
	Untreated Soil	0.88	0.65	0.33	1.81	1.81	0.00	0.12	0.13	0.01	7312.92	7300.19	18.00	658.55	659.18	0.89
		0.41			1.81			0.14			7287.46			659.80		

Appendix 9: Raw data and calculations for phosphorus sequential extraction of each sampling date

Soil Sample	Al-Fe			Carbonate			Oxide			Ca bound		
Mill-waste 03-2005	P (mg/kg)	AVG	STD	P (mg/kg)	AVG	STD	P (mg/kg)	AVG	STD	P (mg/kg)	AVG	STD
A (1% TR)	5209.56	4886.58	456.77	3501.85	4210.72	1002.50	3011.60	2468.97	767.40	2143.21	1333.36	1145.29
	4563.59			4919.60			1926.34			523.52		
C (control)	235.43	217.86	24.85	509.93	508.39	2.18	1222.33	1114.68	152.24	752.44	719.99	45.89
	200.29			506.85			1007.03			687.54		
Urban												
1% SA (1)	2784.26	2618.92	233.83	1629.84	1921.04	411.83	1966.08	1251.96	1009.92	717.12	532.48	261.12
	2453.57			2212.25			537.84			347.85		
Control (13)	94.66	90.18	6.33	123.97	127.52	5.02	199.13	156.10	60.86	107.81	106.60	1.72
	85.71			131.07			113.06			105.38		
1% RT (14)	936.71	976.17	55.81	3999.50	3661.87	477.47	1286.27	1105.77	255.27	2795.71	1811.48	1391.90
	1015.63			3324.25			925.27			827.26		
1% PI (31)	485.17	469.81	21.72	2398.62	2226.68	243.16	821.49	715.11	150.44	1373.38	1463.20	127.03
	454.46			2054.75			608.74			1553.03		
Mining Waste												
Mizzou Doo Mix (T2)	377.84	377.84		250.97	250.97		154.16	154.16		107.97	107.97	
SMC (T4)	124.88	136.03	15.76	2902.25	3064.11	228.91	1531.43	1534.23	3.97	5061.18	4876.02	261.86
	147.17			3225.97			1537.04			4690.86		
Turkey Litter (T5)	889.80	798.14	129.63	1244.55	1583.32	479.09	3099.16	4123.94	1449.26	6129.04	12279.74	8698.41
	706.47			1922.09			5148.72			18430.45		
Chicken Litter (T6)	203.80	224.33	29.03	3134.05	3170.20	51.12	6134.72	7324.58	1682.71	9920.37	9989.76	98.13
	244.86			3206.35			8514.43			10059.15		
Mizzou Doo (T7)	240.67	247.63	9.85	2526.17	2661.86	191.89	7925.16	8190.58	375.36	15273.70	14673.20	849.24
	254.60			2797.55			8456.00			14072.70		
Sewage Sludge (T8)	2877.61	3067.00	267.84	5447.42	4900.45	773.54	4520.33	4513.22	10.05	1765.30	1471.76	415.13
	3256.39			4353.47			4506.12			1178.22		
Phosphorus (T9)	395.51	383.47	17.02	266.41	203.17	89.43	66.88	48.87	25.47	68.38	54.51	19.62
	371.43			139.93			30.86			40.63		
EPA Repository (T10)	482.01	399.92	116.10	431.66	479.28	67.34	353.73	302.57	72.34	290.70	337.47	66.15
	317.83			526.90			251.42			384.25		
Sewage Sludge (8H)	289.99	289.99		288.34	288.34		98.58	98.58		76.21	76.21	
untreated	136.38	136.38		2.93	2.93		783.88	783.88		203.45	203.45	
Mill-waste 06-2005	P (mg/kg)	AVG	STD	P (mg/kg)	AVG	STD	P (mg/kg)	AVG	STD	P (mg/kg)	AVG	STD

A (1% TR)	8940.65	8875.12	92.68	2683.07	2721.77	54.73	3425.35	3174.25	355.10	2643.31	1992.24	920.76
	8809.58			2760.47			2923.15			1341.16		
C (control)	104.98	105.39	0.58	80.36	77.85	3.54	529.59	406.65	173.86	376.53	350.97	36.15
	105.80			75.34			283.72			325.41		
Urban												
1% SA (1)	4217.04	4217.04		3313.55	3313.55		865.45	865.45		640.65	640.65	
Control (13)	121.48	121.48		197.35	197.35		284.25	284.25		163.74	163.74	
1% RT (14)	1494.23	1494.23		3901.97	3901.97		1995.91	1995.91		4109.68	4109.68	
1% PI (31)	274.01	274.01		776.38	776.38		337.23	337.23		372.20	372.20	
Mining Waste												
Mizzou Doo Mix (T2)	470.83	467.61	4.57	218.63	229.13	14.86	331.76	331.42	0.48	159.98	160.68	0.98
	464.38			239.64			331.08			161.38		
Repository Soil (T3)	775.10	776.56	2.06	1202.79	1226.34	33.32	1020.65	1022.96	3.27	951.37	951.90	0.75
	778.02			1249.90			1025.28			952.43		
SMC (T4)	115.50	117.07	2.21	3279.83	3297.02	24.31	1844.57	1843.42	1.62	7684.65	7701.21	23.42
	118.63			3314.21			1842.28			7717.77		
Turkey Litter (T5)	645.71	645.67	0.05	1767.28	1772.63	7.56	3106.52	3115.30	12.41	9656.80	9640.14	23.56
	645.64			1777.97			3124.07			9623.48		
Chicken Litter (T6)	238.34	239.22	1.24	2678.56	2676.77	2.53	4485.06	4481.16	5.50	5414.16	5410.85	4.68
	240.10			2674.98			4477.27			5407.54		
Mizzou Doo (T7)	195.78	197.03	1.77	2434.00	2443.86	13.94	2906.75	2908.92	3.07	5199.24	5213.74	20.50
	198.28			2453.72			2911.09			5228.23		
Sewage Sludge (T8)	3180.16	3179.25	1.29	5386.93	5291.31	135.23	3265.60	3275.39	13.85	1420.05	1417.51	3.59
	3178.33			5195.68			3285.19			1414.97		
Phosphorus (T9)	266.60	268.45	2.62	628.59	630.65	2.91	450.81	449.60	1.70	525.38	523.25	3.01
	270.30			632.71			448.40			521.12		
EPA Repository (T10)	596.14	597.11	1.37	1147.04	1146.15	1.25	328.06	326.60	2.07	483.62	487.99	6.18
	598.08			1145.27			325.14			492.36		
Sewage Sludge (8H)	138.29	136.81	2.11	226.48	222.85	5.12	31.31	34.11	3.97	31.92	30.84	1.54
	135.32			219.23			36.92			29.75		
untreated	124.98	126.36	1.95	4.65	9.42	6.74	894.11	889.95	5.88	126.40	125.65	1.06
	127.74			14.19			885.79			124.91		
Mill-waste 09-2005	P (mg/kg)	AVG	STD	P (mg/kg)	AVG	STD	P (mg/kg)	AVG	STD	P (mg/kg)	AVG	STD
A (1% TR)	8169.40	8149.48	28.18	2725.11	2732.36	10.25	3734.70	3725.21	13.41	3288.96	3291.55	3.66
	8129.55			2739.61			3715.73			3294.14		
C (control)	92.53	92.58	0.08	140.02	140.74	1.02	303.79	299.32	6.33	106.33	107.13	1.12
	92.64			141.46			294.84			107.92		

Urban												
1% SA (1)	3156.01	3152.71	4.67	2245.30	2257.02	16.58	650.93	654.54	5.10	431.02	430.98	0.06
	3149.40			2268.75			658.15			430.94		
Control (13)	101.65	101.14	0.73	159.16	161.47	3.27	191.27	188.44	4.00	107.97	105.69	3.22
	100.62			163.78			185.61			103.41		
1% RT (14)	2946.34	2954.68	11.79	3629.51	3661.69	45.52	1471.50	1470.69	1.15	1212.89	1209.68	4.55
	2963.02			3693.88			1469.88			1206.46		
1% PI (31)	433.87	430.74	4.42	2119.33	2117.61	2.43	581.26	577.97	4.66	559.91	558.16	2.48
	427.62			2115.89			574.68			556.41		
Mining Waste												
Repository Soil (T3)	1673.78	1665.55	11.64	1550.46	1547.69	3.92	767.18	770.08	4.10	935.91	937.52	2.27
	1657.32			1544.92			772.97			939.13		
SMC (T4)	144.44	146.45	2.84	2228.83	2210.04	26.58	1390.52	1384.36	8.72	5027.50	5023.31	5.93
	148.46			2191.24			1378.19			5019.12		
Turkey Litter (T5)	147.24	146.78	0.65	2714.18	2698.46	22.24	1628.02	1640.95	18.28	4214.42	4196.49	25.36
	146.32			2682.73			1653.88			4178.55		
Chicken Litter (T6)	271.59	274.22	3.72	2306.38	2313.35	9.86	5648.72	5656.44	10.91	12392.10	12391.50	0.85
	276.85			2320.32			5664.15			12390.90		
Mizzou Doo (T7)	197.42	196.04	1.95	3608.81	3648.76	56.50	6574.21	6567.15	9.98	12140.90	12108.20	46.24
	194.67			3688.71			6560.09			12075.50		
Sewage Sludge (T8)	1545.66	1541.01	6.58	3453.66	3457.86	5.94	1883.41	1887.06	5.17	907.90	906.98	1.30
	1536.36			3462.06			1890.72			906.06		
Sewage Sludge (8H)	108.31	107.36	1.34	424.29	423.29	1.41	496.80	492.47	6.12	182.87	182.25	0.88
	106.41			422.30			488.15			181.63		
Phosphorus (T9)	187.99	189.72	2.45	878.12	877.18	1.34	280.27	275.89	6.19	391.15	389.86	1.83
	191.45			876.23			271.52			388.56		
EPA Repository (T10)	452.25	449.39	4.05	1992.42	1985.81	9.35	590.21	583.86	8.98	1217.91	1215.71	3.11
	446.53			1979.20			577.51			1213.51		
untreated	54.58	54.88	0.42	14.39	10.19	5.94	915.27	920.67	7.63	248.25	246.75	2.12
	55.18			5.99			926.06			245.25		
Mill-waste 02-2006	P (mg/kg)	AVG	STD	P (mg/kg)	AVG	STD	P (mg/kg)	AVG	STD	P (mg/kg)	AVG	STD
A (1% TR)	8417.90	8376.52	58.53	4287.88	4279.52	11.83	3403.32	3423.81	28.99	2273.56	2269.97	5.08
	8335.13			4271.16			3444.31			2266.38		
C (control)	245.76	249.99	5.99	227.83	227.66	0.24	632.02	631.99	0.04	483.37	484.79	2.01
	254.23			227.49			631.96			486.21		
Urban												
1% SA (1)	4619.05	4611.97	10.01	2532.03	2517.84	20.06	1040.76	1052.77	16.99	905.12	906.34	1.72
	4604.89			2503.66			1064.79			907.56		

Control (13)	121.04	121.46	0.59	179.32	173.78	7.83	178.47	179.87	1.98	96.18	97.23	1.50
	121.87			168.25			181.27			98.29		
1% RT (14)	3897.14	3879.52	24.93	3923.46	3908.21	21.57	1686.18	1692.34	8.71	1444.64	1445.99	1.90
	3861.89			3892.96			1698.50			1447.33		
1% PI (31)	367.19	368.82	2.31	2654.13	2651.73	3.39	974.93	975.27	0.48	1571.86	1582.63	15.22
	370.46			2649.33			975.61			1593.39		
Mining Waste												
Mizzou Doo Mix (T2)	293.99	297.20	4.53	215.01	219.30	6.07	90.12	90.86	1.04	46.86	50.41	5.02
	300.40			223.59			91.60			53.96		
SMC (T4)	403.43	406.84	4.83	4571.51	4567.23	6.05	3113.60	3099.40	20.09	4146.48	4131.80	20.77
	410.25			4562.96			3085.20			4117.11		
Turkey Litter (T5)	1146.37	1150.95	6.47	1931.77	1928.69	4.34	5513.23	5501.06	17.22	13521.10	13559.05	53.67
	1155.52			1925.62			5488.88			13597.00		
Chicken Litter (T6)	217.13	218.36	1.73	2366.52	2357.85	12.27	2250.99	2242.99	11.32	5650.75	5625.25	36.07
	219.58			2349.17			2234.99			5599.74		
Mizzou Doo (T7)	180.97	179.24	2.44	3426.66	3418.11	12.09	4579.54	4555.71	33.71	6543.01	6591.04	67.92
	177.51			3409.56			4531.87			6639.07		
Sewage Sludge (T8)	225.44	221.41	5.70	3750.98	3740.78	14.42	7265.74	7248.42	24.49	13575.30	13557.85	24.68
	217.38			3730.58			7231.10			13540.40		
Sewage Sludge (8H)	284.94	286.01	1.51	448.32	448.19	0.19	164.27	159.44	6.84	112.66	115.46	3.97
	287.08			448.05			154.60			118.27		
Phosphorus (T9)	365.63	362.81	3.99	618.77	616.08	3.80	226.64	228.85	3.13	502.01	499.04	4.20
	359.98			613.40			231.06			496.07		
EPA Repository (T10)	355.73	356.17	0.63	540.87	544.39	4.98	470.81	473.26	3.47	257.49	259.37	2.65
	356.62			547.92			475.72			261.24		
untreated	77.08	78.57	2.11	0.29	5.79	7.77	847.95	844.42	4.99	156.96	158.61	2.33
	80.06			11.29			840.89			160.25		

Appendix 10: Raw data and calculations for lead sequential extraction of each sampling date

Soil Sample	Water			Exchangeable			Carbonate			Fe-Mn			Organic			Residue		
Mill-waste 03-2005	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD
A (1% TR)	1.18	1.29	0.16	0.00	0.00	0.00	12.21	12.38	0.25	6.40	6.54	0.19	19.95	19.72	0.33	3410.95	3406.33	6.53
	1.41			0.00			12.55			6.67			19.49			3401.72		
B (0.75% TR)	0.00	0.00	0.00	0.80	0.86	0.08	51.33	51.69	0.51	65.64	65.46	0.25	133.64	133.63	0.01	3871.16	3849.34	30.86
	0.00			0.91			52.05			65.29			133.63			3827.52		
C (control)	0.00	0.00	0.00	4.10	3.89	0.30	190.72	190.64	0.12	953.53	960.14	9.35	348.83	350.57	2.47	1531.43	1527.20	5.99
	0.00			3.68			190.55			966.75			352.32			1522.97		
Urban	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD
1% SA (1)	0.05	0.25	0.29	2.54	2.46	0.11	40.12	40.09	0.04	147.85	148.38	0.75	168.92	167.95	1.38	2022.00	2048.12	36.94
	0.46			2.38			40.07			148.91			166.98			2074.24		
Control (13)	0.02	0.45	0.61	211.34	211.07	0.38	866.08	846.27	28.02	2132.40	2134.75	3.33	1343.12	1342.59	0.75	1100.84	1104.65	5.38
	0.88			210.80			826.46			2137.10			1342.06			1108.45		
1% RT (14)	0.00	0.00	0.00	0.00	0.00	0.00	40.39	40.43	0.06	58.23	58.45	0.31	183.43	182.20	1.73	4557.15	4484.35	102.96
	0.00			0.00			40.47			58.67			180.98			4411.55		
1% PI (31)	0.00	0.00	0.00	28.80	27.90	1.27	220.46	213.48	9.86	604.32	601.68	3.74	312.17	311.13	1.47	508.41	506.93	2.08
	0.00			27.00			206.51			599.03			310.10			505.46		
Mining Waste	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD
SMC (T4)	0.00	0.00	0.00	2.28	2.31	0.03	103.86	99.85	5.67	315.81	316.52	1.01	90.37	90.85	0.68	778.16	775.24	4.12
	0.00			2.33			95.83			317.24			91.33			772.33		
Turkey Litter (T5)	0.00	0.00	0.00	3.41	3.65	0.33	51.61	51.19	0.59	91.13	87.80	4.71	93.37	93.98	0.85	1490.41	1485.28	7.25
	0.00			3.88			50.78			84.47			94.58			1480.15		
Chicken Litter (T6)	0.00	0.00	0.00	0.86	0.90	0.05	50.82	50.69	0.19	148.39	148.82	0.61	130.04	130.18	0.21	1560.87	1572.52	16.48
	0.00			0.93			50.55			149.25			130.33			1584.18		
Mizzou Doo (T7)	0.00	0.00	0.00	0.00	0.00	0.00	0.42	0.37	0.08	6.58	6.61	0.04	25.50	25.74	0.33	298.52	298.30	0.32
	0.00			0.00			0.31			6.64			25.97			298.07		
Sewage Sludge (T8)	0.00	0.00	0.00	0.00	0.09	0.12	0.33	0.66	0.47	2.92	3.08	0.22	9.02	8.54	0.68	375.54	374.73	1.15
	0.00			0.17			0.99			3.24			8.05			373.92		
Phosphorus (T9)	0.00	0.00	0.00	3.63	3.51	0.17	38.68	38.51	0.25	59.54	60.25	1.01	295.30	294.94	0.51	135.10	134.01	1.54
	0.00			3.39			38.33			60.96			294.58			132.92		
EPA Repository (T10)	0.00	0.00	0.00	226.57	222.41	5.89	1438.66	1437.2	2.01	3923.13	3936.83	19.37	2181.94	2169.86	17.08	3646.12	3649.23	4.40
	0.00			218.25			1435.82			3950.52			2157.79			3652.34		
Sewage Sludge	0.00	0.00	0.00	29.68	29.70	0.03	203.55	203.07	0.68	437.14	440.07	4.15	193.35	194.28	1.32	355.05	354.07	1.39

(8H)																		
	0.00			29.72			202.59			443.00			195.21			353.08		
untreated	2.36	1.86	0.71	1047.08	1039.14	11.23	10556.29	10529	39.36	8333.88	8337.56	5.19	2886.72	2873.67	18.46	14068.32	14049.39	26.76
	1.36			1031.20			10500.62			8341.23			2860.62			14030.47		
Mill-waste 06-2005	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD
A (1% TR)	0.59	0.30	0.42	0.56	0.28	0.39	11.95	11.66	0.41	6.85	6.76	0.13	15.58	15.67	0.13	3614.10	3599.55	20.57
	0.00			0.00			11.37			6.67			15.77			3585.01		
B (0.75% TR)	0.85	0.65	0.29	0.69	0.61	0.12	33.26	32.96	0.43	35.09	34.92	0.24	92.79	92.84	0.08	3886.13	3898.53	17.54
	0.44			0.52			32.66			34.75			92.90			3910.93		
C (control)	0.00	0.00	0.00	4.63	4.29	0.48	339.74	341.58	2.60	1806.25	1805.27	1.39	242.94	243.86	1.30	1274.31	1275.30	1.40
	0.00			3.96			343.42			1804.28			244.78			1276.29		
Urban	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD
1% SA (1)	0.00	0.00	0.00	0.51	0.25	0.36	15.70	15.70	0.00	35.48	35.57	0.12	75.07	74.75	0.44	2204.12	2214.18	14.23
	0.00			0.00			15.70			35.65			74.44			2224.24		
Control (13)	0.12	0.11	0.01	167.18	161.28	8.34	687.04	685.95	1.53	1986.01	1988.49	3.51	1109.55	1109.21	0.48	1733.87	1732.28	2.25
	0.11			155.39			684.87			1990.97			1108.86			1730.69		
1% RT (14)	0.00	0.00	0.00	0.29	0.14	0.20	22.92	22.84	0.11	31.21	31.04	0.25	103.56	103.01	0.77	4666.76	4662.94	5.40
	0.00			0.00			22.76			30.86			102.47			4659.12		
1% PI (31)	0.00	0.00	0.00	49.45	49.76	0.44	407.39	407.33	0.08	1089.93	1090.19	0.36	472.11	470.88	1.74	574.52	568.18	8.97
	0.00			50.07			407.27			1090.45			469.65			561.83		
Mining Waste	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD
Mizzou Doo Mix (T2)	0.00	0.00	0.00	123.57	122.98	0.83	544.59	543.23	1.92	1261.83	1260.40	2.02	614.96	613.73	1.75	1134.87	1130.14	6.69
	0.00			122.39			541.88			1258.97			612.49			1125.41		
Repository Soil (T3)	0.00	0.00	0.00	5.32	5.47	0.21	98.99	98.11	1.25	332.20	331.65	0.78	129.60	129.38	0.30	1333.63	1338.52	6.92
	0.00			5.61			97.22			331.09			129.17			1343.42		
SMC (T4)	0.00	0.00	0.00	0.09	0.04	0.06	1.25	1.05	0.28	19.77	19.48	0.40	5.39	5.51	0.18	272.91	272.33	0.82
	0.00			0.00			0.85			19.20			5.64			271.75		
Turkey Litter (T5)	0.00	0.00	0.00	0.27	0.32	0.06	3.06	2.79	0.39	6.11	5.11	1.41	14.88	14.73	0.20	756.55	758.26	2.42
	0.00			0.36			2.51			4.12			14.59			759.97		
Chicken Litter (T6)	0.00	0.00	0.00	0.31	0.16	0.22	4.76	4.53	0.33	18.39	14.80	5.08	60.09	60.19	0.14	887.07	883.23	5.42
	0.00			0.00			4.30			11.20			60.29			879.40		
Mizzou Doo (T7)	0.00	0.48	0.68	0.49	0.25	0.35	6.12	5.23	1.26	25.08	24.70	0.54	45.09	45.18	0.12	704.40	703.29	1.56
	0.96			0.00			4.34			24.32			45.27			702.19		
Sewage Sludge (T8)	0.06	0.03	0.04	0.55	0.34	0.29	1.11	1.13	0.02	3.81	3.30	0.73	10.00	10.26	0.37	481.81	479.85	2.77

	0.00			0.14			1.15			2.79			10.53			477.89		
Phosphorus (T9)	0.00	0.23	0.33	0.93	0.89	0.05	30.22	29.95	0.39	193.59	192.35	1.75	291.23	290.95	0.39	460.68	460.08	0.85
	0.46			0.85			29.67			191.12			290.68			459.48		
EPA Repository (T10)	0.00	0.00	0.00	5.36	5.30	0.08	46.21	46.15	0.08	219.95	220.74	1.11	121.78	121.44	0.48	668.40	667.57	1.17
	0.00			5.24			46.10			221.53			121.10			666.75		
Sewage Sludge (8H)	0.00	0.00	0.00	0.00	0.00	0.00	3.97	3.96	0.01	21.85	21.80	0.06	14.43	14.58	0.21	15.64	15.83	0.27
	0.00			0.00			3.95			21.76			14.73			16.03		
untreated	9.23	9.48	0.35	2704.54	2685.18	27.39	11146.58	11164.3	25.09	7094.57	7096.76	3.09	3182.12	3182.49	0.53	15342.32	15309.94	45.79
	9.73			2665.81			11182.06			7098.94			3182.87			15277.57		
Mill-waste 09-2005	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD
A (1% TR)	1.97	1.51	0.65	0.00	0.00	0.00	7.30	7.28	0.03	5.99	5.99	0.00	11.94	11.36	0.83	3480.64	3476.73	5.53
	1.05			0.00			7.26			5.99			10.77			3472.82		
B (0.75% TR)	0.00	0.00	0.00	0.36	0.23	0.19	20.90	17.44	4.90	57.92	57.87	0.07	95.61	96.39	1.11	3430.89	3443.96	18.49
	0.00			0.10			13.97			57.83			97.18			3457.03		
C (control)	0.00	0.00	0.00	3.67	3.82	0.22	318.54	315.78	3.90	1716.14	1713.71	3.44	448.51	447.00	2.14	1034.44	1033.05	1.97
	0.00			3.98			313.03			1711.28			445.49			1031.66		
Urban																		
1% SA (1)	0.00	0.00	0.00	0.77	0.52	0.35	14.51	13.06	2.05	47.69	47.35	0.48	75.56	75.65	0.13	1338.50	1340.22	2.43
	0.00			0.28			11.61			47.01			75.75			1341.94		
Control (13)	0.54	0.27	0.38	167.29	166.94	0.49	720.52	712.05	11.98	2180.22	2185.90	8.03	1302.14	1296.34	8.21	1182.13	1176.04	8.61
	0.00			166.60			703.58			2191.58			1290.54			1169.95		
1% RT (14)	0.00	0.04	0.06	0.44	0.22	0.31	27.55	26.30	1.76	72.39	72.51	0.16	208.93	208.88	0.07	5360.47	5426.14	92.88
	0.09			0.00			25.06			72.62			208.83			5491.82		
1% PI (31)	0.30	0.38	0.12	57.75	57.23	0.73	452.39	450.05	3.30	1220.36	1222.03	2.36	3558.62	2062.50	2115.83	673.04	673.47	0.62
	0.47			56.71			447.72			1223.70			566.38			673.91		
Mining Waste	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD
Repository Soil (T3)	2.02	1.84	0.26	4.58	4.26	0.45	63.83	63.58	0.35	208.06	207.34	1.03	93.51	94.26	1.06	2044.34	2046.36	2.86
	1.66			3.94			63.33			206.61			95.00			2048.38		
SMC (T4)	0.29	0.19	0.15	0.28	0.37	0.12	15.90	15.55	0.49	127.76	127.17	0.83	30.61	30.87	0.37	582.20	578.17	5.71
	0.08			0.46			15.21			126.58			31.14			574.13		
Turkey Litter (T5)	0.00	0.00	0.00	0.00	0.00	0.00	8.86	8.55	0.43	72.77	72.77	0.01	38.77	39.09	0.45	504.24	507.59	4.73
	0.00			0.00			8.25			72.76			39.41			510.94		
Chicken Litter (T6)	0.00	0.00	0.00	0.00	0.00	0.00	0.64	0.84	0.28	6.82	6.61	0.30	11.85	12.05	0.29	520.21	520.82	0.87

	0.00			0.00			1.04			6.39			12.25			521.44			
Mizzou Doo (T7)	0.00	0.00	0.00	0.00	0.00	0.00	0.94	0.68	0.36	5.52	5.41	0.16	14.48	14.25	0.33	307.73	308.68	1.34
	0.00			0.00			0.43			5.30			14.02			309.62		
Sewage Sludge (T8)	0.00	0.00	0.00	0.00	0.08	0.12	4.58	4.37	0.30	13.56	13.48	0.12	34.27	34.58	0.45	666.72	669.29	3.63
	0.00			0.17			4.16			13.39			34.90			671.86		
Sewage Sludge (8H)	0.12	0.06	0.09	1.10	1.06	0.05	51.77	50.16	2.28	195.31	195.14	0.25	38.95	38.56	0.55	239.44	237.52	2.73
	0.00			1.03			48.55			194.96			38.17			235.59		
Phosphorus (T9)	0.00	0.00	0.00	9.89	10.00	0.16	163.85	164.00	0.21	503.85	498.56	7.49	797.02	793.74	4.65	1235.96	1229.25	9.49
	0.00			10.12			164.15			493.27			790.45			1222.54		
EPA Repository (T10)	0.00	0.00	0.00	11.21	11.07	0.20	161.19	160.54	0.91	522.11	525.55	4.87	208.72	208.40	0.44	1740.02	1740.93	1.29
	0.00			10.92			159.90			529.00			208.09			1741.85		
untreated	0.13	0.06	0.09	594.84	591.11	5.28	11726.43	11696	42.56	15453.37	15543.27	127.13	2126.06	2112.84	18.69	12987.62	12982.24	7.60
	0.00			587.38			11666.24			15633.16			2099.62			12976.87		
Mill-waste 02-2006	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD
A (1% TR)	1.92	1.99	0.11	0.22	0.26	0.06	7.66	7.65	0.02	2.61	2.38	0.33	7.08	7.01	0.10	3168.65	3165.98	3.78
	2.07			0.30			7.63			2.14			6.93			3163.31		
B (0.75% TR)	0.00	0.00	0.00	0.56	0.48	0.11	21.89	21.76	0.19	33.73	33.90	0.24	61.88	62.33	0.63	3637.83	3636.13	2.39
	0.00			0.41			21.62			34.07			62.78			3634.44		
C (control)	0.00	0.00	0.00	3.52	3.41	0.16	251.92	252.27	0.50	1372.13	1368.25	5.49	376.22	374.46	2.50	1175.02	1171.39	5.14
	0.00			3.29			252.63			1364.37			372.69			1167.75		
Urban	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD
1% SA (1)	0.04	0.02	0.03	0.25	0.29	0.06	10.41	10.27	0.20	25.14	25.33	0.26	59.70	59.80	0.14	1780.08	1764.51	22.02
	0.00			0.33			10.13			25.51			59.91			1748.94		
Control (13)	0.00	0.19	0.27	139.22	142.78	5.03	657.82	660.27	3.47	1910.12	1899.28	15.33	1064.99	1061.45	5.00	1022.46	1017.51	7.00
	0.38			146.34			662.73			1888.44			1057.92			1012.56		
1% RT (14)	0.05	0.15	0.13	0.55	0.57	0.03	17.05	17.16	0.16	30.98	30.81	0.25	164.07	163.56	0.73	4462.59	4467.22	6.56
	0.24			0.59			17.28			30.64			163.05			4471.86		
1% PI (31)	0.00	0.18	0.25	55.47	55.07	0.56	355.38	354.24	1.61	1022.57	1025.83	4.62	521.55	522.86	1.85	433.60	433.38	0.31
	0.35			54.68			353.11			1029.10			524.17			433.16		
Mining Waste	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD	Pb (mg/kg)	AVG	STD
Mizzou Doo Mix (T2)	0.00	0.00	0.00	5.32	5.24	0.12	61.22	61.31	0.12	176.50	177.03	0.75	138.39	138.40	0.01	287.96	286.06	2.70
	0.00			5.16			61.40			177.56			138.40			284.15		

SMC (T4)	0.00	0.00	0.00	0.00	0.06	0.09	7.58	7.53	0.07	56.22	56.16	0.08	51.62	51.45	0.25	820.12	819.68	0.62
	0.00			0.12			7.48			56.11			51.27			819.24		
Turkey Litter (T5)	0.00	0.00	0.00	0.91	0.90	0.02	2.54	2.57	0.04	11.17	10.04	1.60	16.93	16.79	0.19	1231.34	1234.30	4.20
	0.00			0.89			2.59			8.91			16.65			1237.27		
Chicken Litter (T6)	0.00	0.00	0.00	0.00	0.14	0.20	35.44	35.45	0.01	159.43	158.77	0.94	102.52	101.65	1.23	1295.32	1315.76	28.91
	0.00			0.29			35.46			158.10			100.78			1336.21		
Mizzou Doo (T7)	0.00	0.00	0.00	0.00	0.05	0.07	0.88	1.02	0.19	13.13	13.12	0.02	27.66	27.26	0.56	394.78	393.24	2.19
	0.00			0.10			1.15			13.10			26.86			391.69		
Sewage Sludge (T8)	0.00	0.00	0.00	0.24	0.12	0.17	0.00	0.00	0.00	2.08	1.99	0.13	2.58	2.54	0.06	234.96	235.55	0.84
	0.00			0.00			0.00			1.90			2.49			236.14		
Sewage Sludge (8H)	0.00	0.00	0.00	0.70	0.74	0.05	23.39	23.75	0.51	112.72	111.99	1.04	24.32	24.01	0.45	207.27	206.76	0.72
	0.00			0.78			24.11			111.25			23.69			206.25		
Phosphorus (T9)	0.00	0.00	0.00	7.31	7.38	0.10	62.36	63.08	1.03	130.95	128.83	3.00	400.01	396.74	4.63	395.16	398.67	4.95
	0.00			7.45			63.81			126.71			393.47			402.17		
EPA Repository (T10)	0.00	0.00	0.00	1.40	1.59	0.27	56.09	56.03	0.08	398.49	397.00	2.12	193.53	192.45	1.54	653.64	657.25	5.11
	0.00			1.78			55.97			395.50			191.36			660.87		
untreated	11.42	9.76	2.35	1902.19	1891.78	14.72	11691.98	11660	44.86	6497.72	6494.94	3.94	4694.76	4688.14	9.36	18425.52	18414.29	15.87
	8.10			1881.38			11628.54			6492.16			4681.52			18403.07		

Appendix 11: Figures of water quality in March 2004

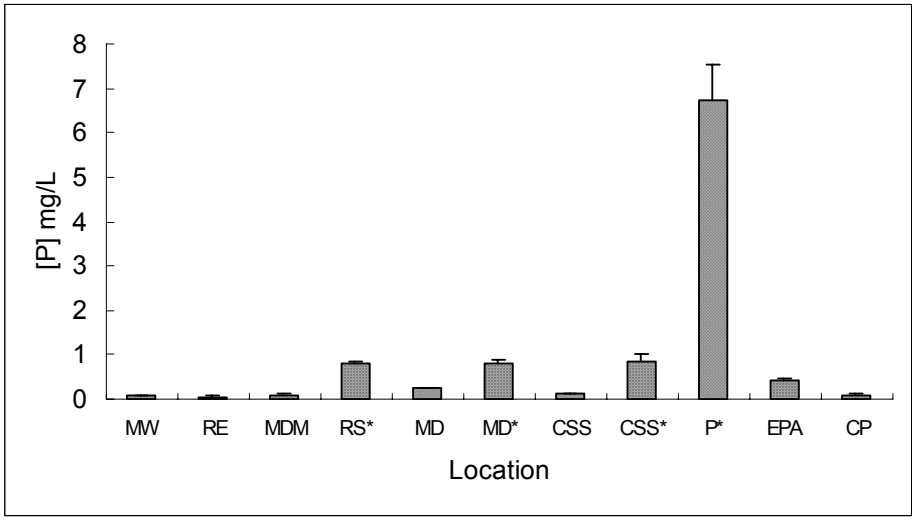


Figure 1. Phosphorus concentrations (mg L^{-1}) in water samples collected from the three study areas in March 2004. MW, mill-waste site; RE, urban site; MDM, Mizzou Doo Mix; RS, repository soil; MD, Mizzou Doo; CSS, composed sewage sludge; P, high phosphorus application; EPA, EPA soil repository; CP, constructed pond. Asterisks indicate groundwater samples. Vertical bars show standard deviation.

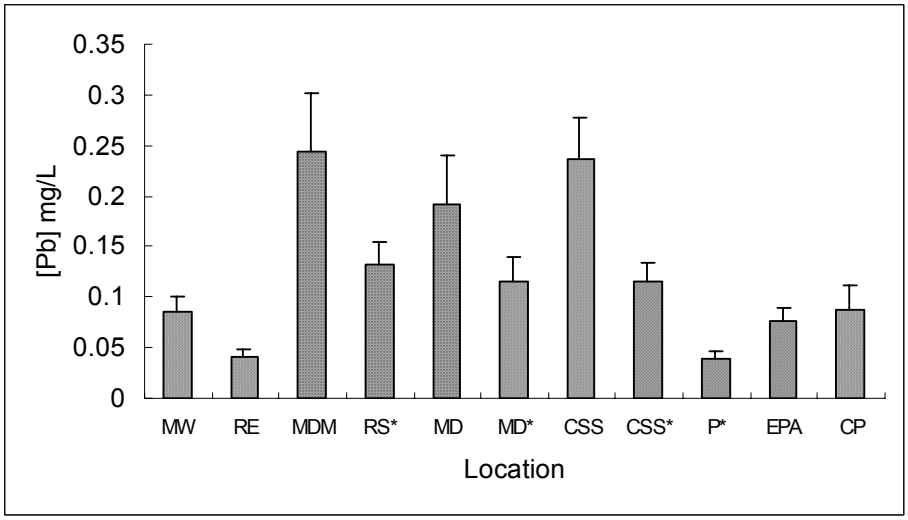


Figure 2. Lead concentrations (mg L^{-1}) in water samples collected from the three study areas in March 2004. MW, mill-waste site; RE, urban site; MDM, Mizzou Doo Mix; RS, repository soil; MD, Mizzou Doo; CSS, composed sewage sludge; P, high phosphorus application; EPA, EPA soil repository; CP, constructed pond. Asterisks indicate groundwater samples. Vertical bars show standard deviation.

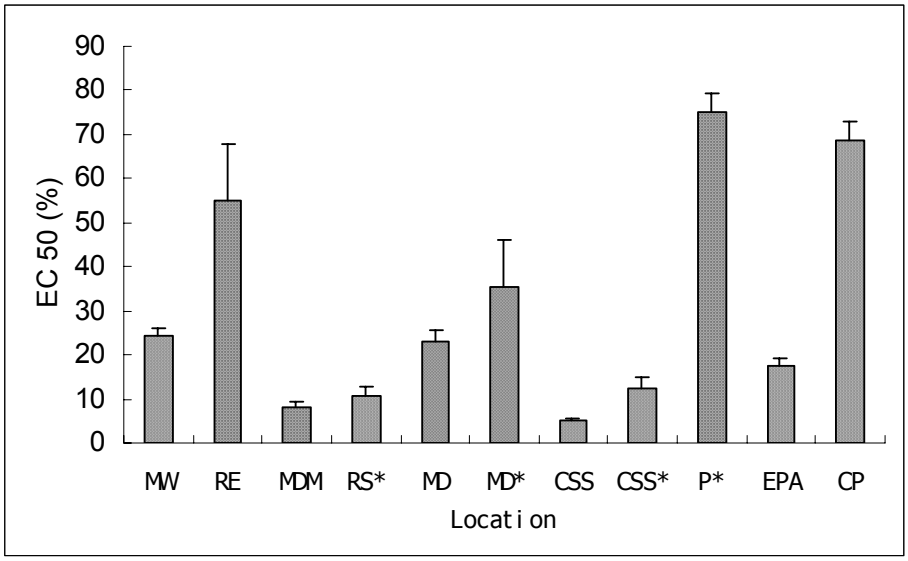


Figure 3. EC50 values in water samples collected from the three study areas in March 2004. MW, mill-waste site; RE, urban site; MDM, Mizzou Doo Mix; RS, repository soil; MD, Mizzou Doo; CSS, composed sewage sludge; P, high phosphorus application; EPA, EPA soil repository; CP, constructed pond. Asterisks indicate groundwater samples. Vertical bars show standard deviation.