URBAN BROWNFIELDS TO GARDENS:
MINIMIZING HUMAN EXPOSURE TO LEAD AND ARSENIC

by

PHILLIP PETERSON DEFOE

B.S., State University of New York-Plattsburgh, 2003
M.S., Tuskegee University, 2008

AN ABSTRACT OF A DISSERTATION

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DOCTOR OF PHILOSOPHY

Department of Agronomy
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ABSTRACT

Urban gardens have been a popular re-use option in the transformation of brownfields—located in older industrialized cities and near peri-urban developments. They provide accessible, available, and affordable supplies of fresh fruits and vegetables, effectively reducing the enigma of "food deserts" across U.S. cities. However, direct (soil ingestion, inhalation) and indirect (soil-plant-human) human exposure concerns about real or perceived trace element contamination in urban soils persist due to previous use.

Elevated lead (Pb) and/or arsenic (As) concentrations were found at two (Tacoma and Seattle, WA) urban gardens. The Tacoma site was contaminated with Pb (51 to 312 mg kg^{-1}) and As (39 to 146 mg kg^{-1}), whereas soil Pb at the Seattle site ranged from 506 to 2,022 mg kg^{-1}, and As concentrations were < 20 mg kg^{-1}. Experimental design at both sites was a randomized complete block with a split-plot arrangement (main plots: biosolids/compost vs. non-amended control; sub-plot: plant type). Tacoma site treatment included a Class A biosolids mix (TAGRO) with dolomite. The Seattle site was amended with Cedar-Grove Compost (CGC) plus dolomite. Efficacy of biosolids/compost amendment in reducing Pb and As concentrations was evaluated using root, leafy, and fruit vegetables. Soil Pb and As bioaccessibility were also evaluated. Food chain transfer of Pb and As in vegetables due to surface contamination of produce samples were evaluated on the basis of cleaning procedures. A laboratory incubation study and a controlled greenhouse experiment were conducted on soils collected from the Tacoma site. Effectiveness of addition of laboratory synthesized ferrihydrite (Fh: iron oxyhydroxide) and TAGRO mix, each alone or in combination were screened and tested on the Pb and As co-contaminated Tacoma soil. Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy studies of Pb and As

were conducted on incubation study samples to understand treatment-induced Pb- and As-speciation changes.

Dilution of soil Pb (10 to 23%) and As (12 to 25%) were observed for biosolids amendment at the Tacoma site, while CGC amendment resulted in 20 to 50% dilution in soil Pb at the Seattle site. Biosolids and CGC amendments reduced Pb concentrations in the vegetables by 50% to 71%. At both sites, Pb concentrations of root vegetables exceeded the MLs established by the Food and Agriculture Organization (FAO) and the World Health Organization (WHO). Arsenic concentrations in vegetables were below an estimated ML and were reduced by 46% to 80% when grown on biosolids amended soils. Laboratory cleaning further reduced Pb and As food-chain transfer in vegetables grown in contaminated urban soils. Laboratory incubation and greenhouse studies showed dissolution of Pb in TAGRO plus Fh, and Pb concentrations in Fh amendments were significantly lower than the other amendments. Bioaccessible Pb and As were low. Significant reductions in bioaccessible As were observed when soils were amended with both TAGRO and Fh. X-ray absorption spectroscopy results indicated that chloropyromorphite-like (stable Pb phosphates) phases were the most dominant Pb species. Arsenic existed mainly as As^{5+}, scorodite ($FeAsO_4 \cdot 2H_2O$)-like species in all the treatments ranging from about 60% (control) to about 70% (TAGRO plus ferrihydrite). Amendments utilizing both biosolids and Fh significantly reduce human exposure risks present in urban soils contaminated with Pb and As.

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Approved by:

Major Professor
Ganga M. Hettiarachchi

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DEDICATION

To my parents:

Victoria Regina Defoe

Peter Defoe

To my brother and only sibling:

Theodore Defoe

To my wife:

Patrell Carey-Defoe

CHAPTER 1 - GENERAL INTRODUCTION

Urban gardens have been a promising re-use option in vacant, and abandoned land found across many cities in the United States (U.S.). The establishment of gardens is primarily due to sustainability concerns. The rapid pace of urbanization and the development of industrialized agriculture has altered the system whereby Americans obtained or produced their food (Broadway, 2009). Historically, settlements depended on nearby productive arable land for their food supply (Broadway, 2009). The revitalization of this practice over the past decades have provided increased food security for low income families and city residents (Lovell, 2010). Urban residents can either grow their own food or gain easier access to affordable supplies of vegetables or fresh produce from nearby farmers markets—reducing the food deserts in these cities. Consequently, the energy consumption of food is reduced since the food travels from a nearby field to the kitchen table. In addition to providing fresh produce, gardens improve public health through increased physical activity and promote integration and social cohesion among urban neighbors (Glover et al., 2005; Lovell, 2010; Teig et al., 2009).

However, public health concerns about the perceived risks of gardening on urban soils continue to hinder the revitalization process. These vacant and/or abandoned lots are often referred to as “brownfields” to distinguish them from never-before-developed sites (Leigh and Coffin, 2000) and are complicated by the presence or potential presence of hazardous substances, pollutants, or contaminants. Common urban soil contaminants include lead (Pb), arsenic (As), cadmium (Cd), zinc (Zn), and polycyclic aromatic hydrocarbons (PAHs) (Alloway, 2004; Chaney et al., 1984; Roussel et al., 2010; Spittler, 1979). Of these contaminants, Pb and As are the most dominant in urban environments, in some cases both occurring at above normal soil concentrations. Mean Pb and As concentrations are 22 and 7 mg kg^{-1}, respectively, in

uncontaminated surface soils of the U.S. (Smith et al., 2013). Higher soil concentrations of Pb and As are due to mining, leaded paint and gasoline, industrial stack emissions from smelting (e.g. sulfide ores) operations, lead-arsenate pesticides, and wood/timber preservation (Alloway, 1995; Bhattacharya et al., 2007; Duker et al., 2005; Nriagu, 1990; Smith et al., 1998). Chronic Pb exposure at low levels (< 10 μg/dL) in young children have resulted in central nervous system (CNS) and kidney damage, decreased intelligence, muscle, and bone growth (Canfield et al., 2003; Koller et al., 2004; Lanphear et al., 2002). Arsenic is a known carcinogen, and chronic oral exposure results in skin pigmentation, CNS and kidney damage (Ahsan et al., 2006; Centeno et al., 2002).

Lead is most extensively studied due to its ubiquitous nature in urban soil environments and its continuing effects on children's health (Binns et al., 2004; Clark et al., 2008; Mielke and Reagan, 1998; Mielke et al., 2010). Though less extensively studied, As is sometimes present as a co-contaminant with Pb. Soils in the residential community of Pueblo, CO were contaminated with both As and Pb. Soil As concentrations were as high as 67 mg kg^{-1}, while Pb concentrations exceeded 300 mg kg^{-1} (Diawara et al., 2006). Defoe et al. (chapter 3) also reported elevated soil Pb and As concentrations for soils at an urban garden site in Tacoma, WA. Soil Pb concentration ranged from 88 to 312 mg kg^{-1}, while As ranged from 37 to 146 mg kg^{-1} (chapter 3).

The primary route of Pb exposure arises through ingestion or inhalation of contaminated soil dust (Dudka and Miller, 1999; Hettiarachchi and Pierzynski, 2004; U.S. EPA, 2012), while the primary exposure route for As has been due to the consumption of contaminated soil or water containing inorganic As (Smith et al., 2000; Thornton, 1996). Previous risk assessment studies have focused on the ingestion of contaminated soil Pb (Kelley et al., 2002; Ruby et al., 1999). A secondary exposure pathway for both Pb and As is the soil-plant-human pathway (Clark et al.,

2006; Finster et al., 2004). Lettuce grown on a former Pb-Zn smelter site with soil pH of 6.5 and clay content of 12% containing 1626 mg kg^{-1} Pb had Pb concentration of 0.693 mg kg^{-1} (fresh weight) and exceeded the Australian Food Standards maximum level of Pb (0.1 mg kg^{-1} fresh weight) (Kachenko and Singh, 2006). Arsenic concentrations in lettuce grown on soils collected from Dewey-Humboldt, AZ home gardens, containing total soil As concentrations ranging from 2.35 to 533 mg kg^{-1}, were as high as 23 mg kg^{-1} (dry weight basis) (Ramirez-Andreotta et al., 2013).

In 2012, the Centers for Disease Control and Prevention recommended lowering the definition of elevated blood lead in children from10 µg dL^{-1} to 5 µg dL^{-1}. There are approximately half a million U.S. children ages 1 to 5 with blood Pb levels above 5 µg dL^{-1} (CDC, 2012). This recent development necessitates looking at minimizing all possible pathways. Children are most adversely affected and a vulnerable population subgroup (Hough et al., 2004) because of their very high (~50%) intestinal absorption rates of ingested Pb compared to adults (5 to 10%) (Maddaloni et al., 1998).

The absence of regulations governing “safe” urban soil levels where crops may be grown, in addition to differences of opinion on exposure criteria to humans is a cause for concern. Further, there is a lack of sound scientific data upon which a coherent remediation strategy can be formulated. Minimizing the exposure risks of Pb and As in contaminated urban gardens should utilize remediation efforts that focus on reducing the bioaccessibility/bioavailability of these contaminants. With reference to Pb and As, bioaccessibility is defined as the fraction/percentage of the metal(loid) that interacts at an organism’s contact surface and is potentially available for adsorption or absorption (McGeer, 2004). Bioavailability of metal(loid)s is defined as the extent to which bioaccessible metals adsorb onto or absorb into and across the

biological membrane of an organism (McGeer, 2004). It is often expressed as a fraction of the total amount of metal(loid) that the organism is proximately exposed to during a given time and under defined conditions (McGeer, 2004).

Due to ethical concerns and similar digestive systems with humans, immature swine usually serve as surrogates in bioavailability studies. The animal feeding studies are laborious and extremely costly. Consequently, *in vitro* techniques have been developed to determine the bioaccessibility of metal(loid)s from contaminated soils. Estimated Pb bioavailability in mine waste materials and mine-impacted soils, using the physiological based extraction test (PBET) that mimic gastrointestinal dissolution developed by Ruby et al. (1996), has shown a strong correlation with animal studies, including adult humans (Maddaloni et al., 1998). Additionally sequential extraction procedures have been used to determine As bioaccessibility (Keon et al., 2001; Wenzel et al., 2001).

Lead phosphates, particularly pyromorphites are one of the most stable forms of Pb in soils under a wide range of environmental conditions (Lindsay, 1979; Nriagu, 1974). X-ray diffraction (XRD) identification of pyromorphite-like minerals were observed in an *in situ* stabilization study of Pb-contaminated mine soils amended with P sources (phosphate rock (PR), triple super phosphate (TSP), phosphoric acid (PA)) (Hettiarachchi et al., 2001). Cao et al. (2002) reported the formation of chloropyromorphite by XRD when soils from a former battery recycling salvage yard were amended with PA and PR used alone or in combination. X-ray fluorescence microbe analysis and XAFS results were used to identify the lead speciation in mine waste soils amended with various P sources (Ryan et al., 2004). Observed reductions in soil lead bioavailability of some treatments could be explained by the corresponding increased pyromorphite formation observed for the treatments (Ryan et al., 2004).

Biosolids compost have been used previously as an i*n situ* amendment to successfully reduced Pb bioaccessibility in urban soils contaminated with Pb (Brown et al., 2003; Farfel et al., 2005). Farfel et al. (2005) reported on the use of composted biosolids in a one year Pb stabilization study. Biosolids (Orgro®) were applied at a rate of 110 to 180 dry t/ha and incorporated to the yards by rototilling. Bioaccessible Pb concentrations in the urban yard soils were reduced by 64% (Farfel et al., 2005). Additionally, Brown et al. (2003) reported 43% reductions in Pb bioaccessibility in an urban soil (2000 mg Pb kg^{-1}) amended with a high iron compost applied at a rate of 100 g kg^{-1}. The reductions in Pb bioaccessibility after amending Pb-contaminated soils with biosolids may be an indication of the formation of stable lead phosphates (Brown et al., 2003, 2005).

For Arsenic, iron oxides have been primarily identified as the major sinks of arsenic in soils (Dixit and Hering, 2003; Kumpiene et al., 2008; Raven et al., 1998; Smith et al., 2002). In a study of the adsorption behavior of arsenite and arsenate on ferrihydrite, Raven et al. (1998) reported that at relatively high As concentrations, arsenite reacted faster than arsenate with the ferrihydrite. The retention capacity of As on these iron oxides is affected by changes in pH, redox and the presence of competing ions.

Remediating Pb and As co-contaminated brownfields is challenging. The addition of P has been an effective *in situ* treatment that can be used to reduce Pb bioaccessibility of Pb contaminated soils. However, P amendments have been found to limit the degree of As sorption in soils—enhancing its mobility and bioaccessibility (Manning and Goldberg, 1996; Smith et al., 2002). For this reason, it is particularly important to take into consideration factors that can result in the simultaneous immobilization of both Pb and As in urban brownfields where the co-contaminants have been identified to cause potential risk to humans.

Objectives

1. The objectives of the first study, Safety of gardening on lead- and arsenic-contaminated brownfields (Chapter 3), were to i) evaluate the effectiveness of two organic soil amendments on reducing plant availability and bioaccessibility of lead and arsenic, and ii) evaluate the effect of cleaning procedures in reducing Pb and As concentrations in the edible portion of vegetables.
2. The objectives of the second study, Evaluation of *in situ* soil amendments on speciation and bioaccessibility of lead and arsenic in an urban soil: An incubation study (Chapter 4), were to i) evaluate the effectiveness of the addition of biosolids (TAGRO) and ferrihydrite (Fh) alone or in combination on reducing lead and arsenic bioaccessibility from a contaminated urban soil, and ii) determine chemical alterations of lead and arsenic in TAGRO and ferrihydrite treated contaminated soils using X-ray Absorption Spectroscopy (XAS) studies.
3. The objectives of the third study, *In situ* soil amendments reduce transfer of lead and arsenic in an urban soil to vegetables and humans: A greenhouse study (Chapter 5), were to i) evaluate the effectiveness of TAGRO and ferrihydrite on plant growth, and the concentration of Pb and As in the edible portions of the vegetables, and ii) investigate the effect of plant growth on the bioaccessibility of Pb and As in the TAGRO and ferrihydrite treated contaminated soil.

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CHAPTER 2 - LITERATURE REVIEW

BROWNFIELDS

Definition

Brownfields means real property, the expansion, redevelopment, or reuse of which may be complicated by the presence or potential presence of a hazardous substance, pollutant, or contaminant (USEPA, 2014).

Location and rise of brownfields

Brownfields are located predominantly in former industrial districts, and within the perimeter of urban areas throughout most cities in the United States (US). It is estimated that there are over 450,000 brownfields in the US (US Conference of Mayors, 2010; USEPA, 2014). The number of brownfields have increased steadily in and around city centers partly due to economic, environmental, and regulatory factors. Some of the underlying factors have been deindustrialization and peri-urban developments (De Sousa, 2006; Greenberg et al., 1998; Litt, 2002). For example, in a survey conducted by the US conference of Mayors, 67 cities identified approximately 11,824 brownfield sites in 1993, representing approximately 15,228 acres, while 75 cities estimated that in 2010 the number of brownfield sites totaled 29,624, representing approximately 45,437 acres (US Conference of Mayors, 2010).

The individual size of brownfields may vary according to the type of activity or industrial operation that previously existed. For example, brownfields can be the location of previous gas stations, laundry facilities, factory units or industrial complexes. Consequently, brownfields size may range from 1 to over 13 acres (Council for Urban Economic Development, 1999).

Deindustrialization and peri-urban developments

The deindustrialization (plant closings, community abandonment and the dismantling of basic industry) of the US began to appear in print in the early 1980's (Cowie and Heathcott, 2003). Big steel lost market share to American mini-mills located in non-traditional areas such as Roanoke, Virginia, or Florida (Glaeser et al., 1991). The regional concentration of steel (in Pennsylvania) and auto (in Michigan) meant that factory closures would inevitably leave many abandoned structures in these cities (Glaeser et al., 1991). Consequently, manufacturing facilities which were primarily located in the Midwest cities sat idle or underutilized for decades despite their enviable locations, with developers held at bay by fears of liability for any residual contamination (USEPA, 2009a).

The relocation of other industries to other cities or regions in the country have also lead to sites that were once used for chemical operations. For example the 10-acre Lewiston's Bates Mill textile complex located in Maine, was cleaned up for polychlorinated biphenyls (PCBs) and volatile organic compounds (VOCs) (USEPA, 2008). From 1868 to 1950, the Oshkosh Gas Light Co. in Wisconsin converted coal into gas, through coal gasification in this industrial area (USEPA, 2010). The gas was used to replace other, less efficient fuels. Over its years of operation, the plant produced coal tar, a by-product of the coal gasification process, which infiltrated the property's soil and ground water. After a natural gas pipeline was built in 1950 to transport gas into the city, the facility was rendered obsolete (USEPA, 2010).

Peri-urban development often gives rise to brownfields and the distribution of contaminants that are associated with these businesses. Table 2.1 shows some common land use contaminants that are linked to peri-urban developments.

Reuse options for Brownfields

There are several re-use options for brownfield sites. The type of re use option chosen is often site specific and will depend on the feasibility of carrying out the project as well as the economic viability. They often include green spaces (parks), urban gardens, reinvestment in apartment complexes (Deason et al., 2001; De Sousa, 2006; Geller, 2003; USEPA, 2014). Brownfields redevelopment stimulates the re-utilization of the city's built environment, remediate contaminants, and transforms socially and economically neglected neighborhoods (Deason et al., 2001). Parks and open spaces helps improve the state of the biophysical environment, public health and enhances urban life quality (De Sousa, 2004; Geller, 2003). Additionally, the community benefits from the aesthetic improvements (blight elimination), habitat restoration, and increased economic activity that often occurs with brownfield development (De Sousa, 2004).

Construction of an 84-unit housing property was built on a former commercial and light industrial area (2.57-acre) of Salt Lake City, UT (USEPA, 2007). A 4,000-gallon underground storage tank (UST) was removed, the soils (contained elevated levels of petroleum) excavated and the ground water was remediated (USEPA, 2007). A former 7-acre manufacturing gas plant located in Oshkosh, WI was developed into a public performance venue and greenspace (USEPA, 2010). The site comprises of large Amphitheater (with capacity for 7,000), and hosts large summer concerts including the annual waterfest, which draws over 60,000 visitors (USEPA, 2010).

Table 2.1. Common contaminants found in peri-urban developments (Adapted from Boulding and Ginn, 2004).

Land use[†]	Common contaminants
Car wash, parking lots, road maintenance depot, vehicle services	Metals, polycyclic aromatic hydrocarbons (PAHs), petroleum products
Dry cleaning	solvents
Existing commercial or industrial building structures	Asbestos, lead paint, Polychlorinated Biphenyls,
Junkyards	Metals, petroleum products, solvents, sulfate
Underground and above ground storage tanks	Pesticides/herbicides, petroleum products, solvents

[†]Adapted from Boulding and Ginn, 2004.

Economic benefits to brownfield revitalization

The USEPA (2014) reported that revitalization of brownfield sites brings an average of $17.79 per EPA dollar expended, and leveraged 90, 363 jobs nationwide (USEPA, 2014). Additionally, residential properties surrounding brownfield sites have increased in value by 5.1% to 12.8% upon completion of site cleanup (USEPA, 2014). Cleaning up and reinvesting in these properties protects the environment, reduces blight, and takes development pressures off greenspaces and working lands.

Brownfields to urban gardens

Across the country, communities are adopting the use of urban agriculture and community gardens for neighborhood revitalization (USEPA, 2012). Former auto-manufacturing sites, industrial complexes, small individual lots in commercial and residential areas, are being considered as potential sites for growing food (USEPA, 2012). Some of these sites may be capped with concrete before gardening in uncontaminated soil, while raised beds may be used in other cases.

A former residential property located on Allen Street, Somerville, MA that lay idle since the 1950s was revitalized into a sprawling urban garden (USEPA, 2009b). The garden was completed in late 2007, and provides a place to grow flowers, vegetables, and enjoy the neighborhood in the fifteen constructed garden plots (USEPA, 2009b). An abandoned steel galvanizing plant in Northeast Philadelphia was converted into a one-acre farm with a nursery, and a farmers market by Greensgrow farms (Broadway, 2009). The soil was capped with concrete. The city of Seattle consists of about 85 to 90 community gardens that are coordinated by the P-Patch organization (Seattle Department of Neighborhood, 2014). Some of these gardens are located on previously contaminated sites. For example, the Leo St. garden located in the Rainier valley district, Seattle, WA previously contained a water tower. Soil lead (Pb)

concentrations at that site ranged from 500 to 2300 mg kg^{-1} (Defoe et al., Chapter 3). The surrounding soils were highly contaminated with Pb due to repeated sand blasting and repainting of the water tower with leaded paint.

Gardening on urban brownfields

The benefits of community gardening vary from simply supplementing food crops for urban households to improving community cohesion. Low income residents gardening on vacant lots, improve food access to their families while saving on the exorbitant costs of vegetables (Lovell, 2010, Teig et al., 2009). In US cities, there is a lack of affordable, nutritional foods that residents can access and is often termed as “food deserts”. Minority residents and people of low economic status suffer the most (Powell et al., 2007). Low-income neighborhoods have fewer chain supermarkets with only 75% of that available in middle-income neighborhoods (Powell et al., 2007).

Larger sized food stores such as supermarkets are likely to stock healthful foods (Horowitz et al., 2004) and offer foods at a lower cost than smaller stores (Chung and Myers, 1999). Moreover, Cheadle et al. (1991) reported that reduced shelf-space allocation in community grocery stores to “healthier” products was associated with lower consumption of such foods among the local residents. When low-income households reside in close proximity to a supermarket, higher fruit and vegetable intake, and better diet quality is observed (Bodor et al., 2008).

Due to the food constraints, urban residents embrace the opportunity to produce their own food on vacant or abandoned city lots. In some instances, community garden associations will lease or rent land to produce food for sale in nearby farmers markets. For example, the neighborhood garden association in Philadelphia helped community members gain title to vacant

land and provided technical assistance in vegetable gardens (Hanna and Oh, 2000). Community gardens located in Philadelphia located on former brownfield sites are now community assets for the neighborhood (Hallberg et al., 2009). Gardening provides greater autonomy on the types of vegetables grown and consumed. Foods grown on these brownfield sites are shared with neighbors (Kaufman and Bailkey, 2000) and the excess sold to farmers markets (Broadway, 2009).

URBAN SOILS

Urban soil definition

Urban soils are defined as any unconsolidated mineral or organic material at the Earth's surface that has the potential to support plant growth (Hollis, 1991) having a nonagricultural, man-made surface layer more than 50-cm thick, that has been produced by mixing, filling, or contamination of land surfaces in urban and suburban areas (Craul, 1992). In urban settings, human activities impacts soils both spatially and temporally (Efland and Pouyat, 1997; Alberti, 2005) as evidenced in the continuum of intermixed "natural" soil bodies with human soil bodies in metropolitan districts (Efland and Pouyat, 1997).

Urban soil characteristics

Urban soils are often areas of high compaction with abrupt physical and chemical barriers to rooting depth (De Kimpe and Morel, 2000). High compaction reduces water infiltration rates and results in drier soils in urban soils compared to undisturbed landscapes (Gregory et al., 2006; Pitt et al., 2008). Urban soils are generally nutrient deficient and often have higher bulker densities compared to rural soils (Jim, 1998; Lorenz and Lal, 2009). Soil temperatures in urban

soils are usually higher than soils under similar management in more rural areas (Savva et al. 2010).

LEAD

Description and Occurrence

Lead (Pb) is a soft gray metal with an atomic number of 82 and is positioned in group 4 of the periodic table. Lead has four naturally occurring stable isotopes 204, 206, 207 and 208. The isotopic composition of Pb varies because of the radioactive decay of ^{238}U to ^{206}Pb, ^{235}U to ^{207}Pb, and ^{232}Th to ^{208}Pb; ^{204}Pb is not radiogenic (Doe, 1970; Russell and Farquhar, 1960). The partitioning of Pb isotopes is affected by mass separation divided by atomic weight and changes in oxidation state (Doe, 1970). Source of radioactive decay has also affected atomic weight. Doe (1970) reported on widely differing Pb isotopic compositions (Table 2.2). If variations in $^{206}Pb|^{204}Pb$ and $^{208}Pb|^{204}Pb$ do not occur together or the absence of ^{208}Pb, may lead to lower the average abundance of Pb (Doe, 1970). For this reason, the averaged-abundance atomic weight of Pb is not always 207.2 g/mol as is thought.

Table 2.2. Calculated atomic weights of common leads showing different isotopic compositions.

Sample origin[†]	Isotope percentage (%)				Atomic Weight (amu)
	^{204}Pb	^{206}Pb	^{207}Pb	^{208}Pb	
Bathurst, New Brunswick	1.37	24.95	21.53	52.14	207.27
San Antonio Mine, Mexico	1.343	25.28	21.21	52.16	207.27
Joplin, Missouri	1.245	27.29	20.01	51.45	207.25
Ace Mine, Saskatchewan	1.044	41.87	19.45	37.64	206.93

[†]Modified from Doe, 1970. Lead isotopes in Geology.

Properties and general uses

The metal has many unique physical and chemical properties that has been exploited for various applications by humans. Lead has a high density (11.35 g cm^{-3}), low melting point and low ductility. Due to its high density, the metal has been used in fishing nets weights, scuba diving belts, and anchors. Lead's high density favors the use of the metal as a sound absorber and in radiation shields during x-rays. The metal's low melting point makes casting and the production of small arms ammunition and shotgun pellets possible. The metal is very malleable and was used in the construction metal pipes, Pb construction sheeting, and detail casting materials.

The chemical properties of Pb are widely known especially as an anti-corrosive metal. In the United States (US), the metal was commonly used in the production of lead-acid batteries for automobiles. Lead-acid batteries consist of metallic Pb and lead dioxide (PbO_2) as the electrodes with sulfuric acid as the electrolyte. In Pb storage batteries, PbO_2 and lead sulfate produces a charge and discharge during the reversible reaction.

Lead-based paints

One of the common uses of Pb was as a paint pigment. The two most common paint pigments are lead (II) carbonate, "white lead" and lead chromate ($PbCrO_4$), "chrome yellow" (Minca and Basta, 2013; Royal Society of Chemistry, 2007). These pigments were added to paints to maintain a fresh appearance, durability, and resist moisture that would ultimately lead to corrosion. For this reason, these paints were used to coat construction structures such as bridges, metal pipes, and in households.

Although the use of Pb-based paints in US households were banned in 1978 (U.S Consumer Product Safety Commission, U.S. CPSC 1977), adults and children living in houses

built prior to 1978 still face exposure risks. In 2000, the number of US houses containing indoor lead-based paint was estimated to be about 38 million (Jacobs et al., 2002). Their study revealed that an estimated 63% of these houses had significant lead-based paint hazards (deteriorated paint, dust lead, or bare soil lead), and of these households, 5% housed low-income (<US$30,000 per annum) families with children under the age of six years old (Jacobs et al., 2002). Generally, low-Income minorities disproportionately reside in housing units containing lead-based paint hazards (CDC, 2004; Jacobs et al., 2002).

Lead in gasoline

Following the discovery of Pb as a gasoline additive in 1921, the use of the metal increased astronomically (Nickerson, 1954). Tetraethyl lead or TEL [$(CH_3CH_2)_4Pb$] was used as an inexpensive gasoline additive to increase the gasoline octane number in internal combustion (IC) engines (Nriagu, 1990). Premature combustion of gasoline in IC engines results in knocking or pinging sound. Increasing the octane number, increases the "anti-knock" property of the gasoline; resulting in better fuel economy and higher IC engine power output.

In 1980, leaded gasoline contained about 0.30 gm/liter of Pb (Thomas et al., 1999). About 75 percent of gasoline lead was emitted from exhaust pipes in the form of a fine lead dust along traffic ways and into the atmosphere (Mielke, 1999). The wide extent of environmental and health damage caused by the leaded gasoline exacerbated the commencement of its phasing out in US motor vehicles in 1986 (Mielke, 1999).

Lead alloys

Other uses of the metal have been in the alloying process. The most common metals with which Pb is alloyed are Antimony (Sb), Calcium (Ca), and Tin. (Sn). Type metal (Pb-Sb-Sn) are used in mechanical and stereo plate (highly detailed) castings. Calcium-lead alloys are used to

produce battery grids and in some casting applications. Solder (Pb-Sn) is used extensively in electrical, electronics and plumbing applications to join metal “work-pieces.”

Lead toxicity and Human Health

Lead toxicity and poisoning may result from both acute and prolonged Pb build in the human body tissues over several months or years. Lead-based paint and lead contaminated dusts are the major sources of human Pb exposure. Exposure pathways include accidental ingestion of soil or inhalation of contaminated dusts while working or playing in environments with high incidence of Pb contamination. Its toxicity is based on the ability to form strong bonds with sulfhydryl groups on proteins; effectively distorting enzymes and protein structure (Needleman, 2004). Although lead poisoning in adults has been diagnosed in the kidneys or found to adversely affect both the male and female reproductive system, the central nervous system (CNS) is the target organ and the most affected (Needleman, 2004).

Lead competes with calcium for binding sites on cerebellar phosphokinase C at very low concentrations (Markovac and Goldstein, 1988). The hindrance of calcium entry into the cells affects neuron signals and enhances spontaneous neurotransmitter release (Bressler and Goldstein, 1991). Other deleterious effects of Pb on the CNS include interferences with the synthesis of myelin, collagen, and slower brain development (Davis and Svendsgaard, 1987; Krigman, 1978; Needleman and Gastonis, 1990).

Children are more adversely affected than adults because their intestines absorbs Pb more readily than adults and their developing CNS is more vulnerable than that of adults (Maddaloni et al., 1998; Needleman, 2004). In adults, 80 to 90% of ingested Pb is excreted, while the remainder is stored in the bone as a result of calcium and Pb interchange (Lessler, 1988). Approximately 80 to 95% of the total body Pb lead is stored in the bone skeleton, compared to

about 73% in children (Papanikolaou et al., 2005). Comparatively, absorption rates in infants and young children could be as high as 50% (Maddaloni et al., 1998; Markowitz, 2000; Ziegler et al., 1978). Lead absorption rates in children's gut increases with low dietary intakes of iron, calcium, phosphorus, or zinc (Markowitz, 2000; Rabinowitz et al., 1980).

Lead blood concentrations

Blood lead concentrations (BLCs) has been a long-standing indicator of Pb toxicity and exposure indicator in children. Once in the blood stream, Pb has a half-life of 35 days (Roberts et al., 2001). In contrast, the residence time of Pb in bone can be as high as 20 to 30 years (Papanikolaou et al., 2005; Rabinowitz et al., 1976). Consequently, BLCs is more an indication of recent exposure (Markowitz, 2000; Rabinowitz et al., 1976).

Adjustments in "safe" BLCs, in children have been done based on its effects on cognitive parameters such as intelligence quotient (Bellinger and Dietrich, 1994, Bellinger et al., 1992). The Centers for Disease Control and Prevention (formerly called the Centers for Disease Control, CDC) reduced the acceptable BLC from 25 μg dL^{-1} to 10 μg dL^{-1} (sub-clinical lead concentration, Pirkle et al., 1998) in 1991 (CDC, 1991), and a new guidelines for the treatment of lead levels ≥15 μg dL^{-1} were recommended (Papanikolaou et al., 2005). However, cognitive deficiencies have been documented for children who have BLCs lower than the 10 μg dL^{-1} safe limit.

By comparison, the Centers for Disease Control and Prevention (CDC) currently considers 5 μg dL^{-1} the threshold for "elevated" blood lead, while pointing out that "no safe blood lead level in children has been identified" (CDC, 2012). Koller et al. (2004) also suggested that there be no safety margin of existing Pb exposures after they reported BLC in a cohort of children whose lifetime peak blood levels were consistently < 10 μg dL^{-1}.

Lanphear et al. (2000) assessed the relationship between blood Pb concentration and test performances on arithmetic skills, reading skills, nonverbal reasoning and short term memory among 4853 children ages six to 16 years old. Data test scores were collected from the cohort of students that participated in the Third National Health and Nutrition Examination Survey (NHANES III), conducted from 1988 to 1994. Their study identified an inverse relationship BLCs and arithmetic and reading scores for children with BLCs lower than 5.0 μg dL^{-1}. For instance, for every 1 μg dL^{-1} increase in BLC, there was a 0.7-point decrement in mean arithmetic scores, an approximately 1-point decrement in mean reading scores, and a 0.5-point decrement in mean scores on a measure of short-term memory (Lanphear et al., 2000).

Lead concentration in soils

The low solubility of the metal allows for longer residence times in soils compared to other soil pollutants (Davies, 1995). Elevated soil Pb concentrations are predominantly due to historical use of leaded-paint (Attanayake et al., 2014; Jacobs et al., 2002), gasoline additives (Chaney et al., 1984; Mielke, 1999), batteries, ammunition, alloys in addition to mining and smelting activities (Brown et al., 2003, 2012; Hettiarachchi et al., 2000).

Mean background soil Pb concentration of uncontaminated surface soils in the United States is about 22 mg kg^{-1} (Smith et al., 2013). In soils, Pb is mostly present in an ionic form adsorbed onto clays, hydroxides and or organic matter or lead oxides and sulfides (Rabinowitz 1993).

Lead in soil environments

Lead has an electronic configuration of: $[Xe]6s^2 4f^{14} 5d^{10} 6p^2$ (Miessler and Tarr, 2003). Although, Pb has three oxidation states: Pb^0, Pb^{2+}, and Pb^{4+}, the divalent cation (Pb^{2+}) is the most

common in soil environments (Davies, 1995; Essington, 2004). The Pb^{4+} cation is rarely seen in soils since soils are always more reduced than pe + pH of 20.61 (Lindsay, 1979).

The stability of lead (II) compounds can be explained by the relative ease with which the electrons in lead's 6s and 6p orbital are involved in the bonding process. The combined first and second ionization energies for Pb are 2, 165 KJ mol^{-1} (Emsley, 1991). The third and fourth ionization energies of Pb are 3,081 and 4,083 KJ mol^{-1}, respectively (Emsley, 1991). In order to form lead (II) ion, it is easier for lead to lose the two electrons in the 6p orbitals, leaving the more stable 6s electrons unmoved—due to the theory of relativistic contraction (Miessler and Tarr, 2003; Thayer, 2005).

The two electrons in the 6s orbital are often referred to as the "inert pair" (Miessler and Tarr, 2003; Sidgwick, 1933). Here, the 6s electrons are closer to the nucleus and much more difficult to remove as is evident by the very high 3rd and 4th ionization energies. The relativistic contraction is very high for Pb because of its very high density.

Solubility and Stability of Pb minerals in soils

Table 2.3 shows the equilibrium stability reactions of these minerals. The dissociation constant in equation 1, is an indication why the element is rarely found as a pure metal in nature. Instead, the metal is usually associated with ores of sulfur—galena (PbS), anglesite ($PbSO_4$); oxygen—lead (II) oxide (PbO); and carbonate—cerussite ($PbCO_3$) (Nedwed and Clifford, 1998).

Table 2.3. Equilibrium reactions of some lead minerals in soils.

No.	Equilibrium reaction	Log K°
1	$Pb^{2+} + 2e^- \Longleftrightarrow Pb\ (c)$	-4.33
2	$PbO\ (litharge) + 2H^+ \Longleftrightarrow Pb^{2+} + 2H_2O$	12.72
3	$PbCO_3\ (cerussite) + 2H^+ \Longleftrightarrow Pb^{2+} + CO_2(g) + H_2O$	4.65
4	$PbSO_4\ (anglesite) + 2H^+ \Longleftrightarrow Pb^{2+} + SO_4^{2-}$	-7.79
5	$PbS\ (galena) \Longleftrightarrow Pb^{2+} + H_2O$	-27.51
6	$Pb_5(PO_4)_3OH\ (c)\ (hydroxypyromorphite) + 7H^+ \Longleftrightarrow 5Pb^{2+} + 3H_2PO_4^-$	-4.14
7	$Pb_5(PO_4)_3Br\ (c)\ (bromopyromorphite) + 6H^+ \Longleftrightarrow 5Pb^{2+} + 3H_2PO_4^- + Br^-$	-19.49
8	$Pb_5(PO_4)_3Cl\ (c)\ (chloropyromorphite) + 6H^+ \Longleftrightarrow 5Pb^{2+} + 3H_2PO_4^- + Cl^-$	-25.05
9	$Pb_5(PO_4)_3F\ (c)\ (fluoropyromorphite) + 6H^+ \Longleftrightarrow 5Pb^{2+} + 3H_2PO_4^- + Fl^-$	-12.98

Adapted from Lindsay, 1979

The solubility and stability of Pb and its associated minerals in soil environments are affected by changes in pH, adsorption with organic complexes, clay minerals, Fe-Mn- and Al-hydrous oxides (Jørgensen and Willems, 1987; Lindsay, 1979). Cao et al. (2008) investigated phosphate-induced lead immobilization from different Pb minerals in soils under varying pHs. A Pb-contaminated soil, and three soils spiked with litharge (PbO), cerrusite ($PbCO_3$), or anglesite ($PbSO_4$) were equilibrated with KCl and $Ca(H_2PO_4)_2 \cdot H_2O$ at pH ranging from 3 to 7. At pH range of 3 to 5, Pb solubility followed PbO-soil > $PbCO_3$ > $PbSO_4$, while at pH 7, it was $PbSO_4$ > PbO > $PbCO_3$ (Cao et al., 2008). While precipitation of Pb minerals are important in controlling Pb solubility in highly contaminated soils, adsorption of Pb is important in controlling Pb solubility in mildly-contaminated urban soils.

Lead adsorption

The adsorption behavior of Pb on soils and soil constituents (clays, oxides, oxyhydroxides, and organic matter) have been thoroughly investigated (Bradl, 2004; McKenzie, 1980; Strawn and Sparks, 2000). Lead adsorption has been known to increase with increasing pH and organic matter content of soils (Appel and Ma, 2002; Martinez and Motto, 2000; Sauve et al., 2000). Soil pH also affects metal hydrolysis, ion-pair formation organic matter solubility, as well as surface charge of iron and aluminum oxides organic matter, and clay edges (Appel and Ma, 2002).

In a study of adsorption mechanisms of lead on a montmorillonitic smectite from Wyoming, Strawn and Sparks (2000) revealed that the divalent cation adsorbed on the clay surface via inner or outer sphere complexation, depending on ionic strength and pH. They deduced that at low pH (moderately acidic, ~4) and low ionic strength, the sorption mechanism was inner sphere, while at higher pH (slightly alkaline, ~8), and high ionic strength, outer sphere complexation was the adsorption mechanism. They also investigated the effects of soil organic matter (SOM) on

sorption and desorption behavior by treating the soil with sodium hypochlorite to remove the SOM fraction. Using a soil with about six times as much SOM, they concluded sorbed lead for the higher SOM soil was 102 mmol kg^{-1} compared to 27 mmol kg^{-1} (Strawn and Sparks, 2000). Additionally, phosphates, chloride, and carbonate influence lead reactions in soils either by precipitation of minerals of limited solubility or by reducing the adsorption through complex formation (Rickard and Nriagu, 1978). Lead may precipitate in soils if soluble concentrations exceed about 4 mg L^{-1} at pH 4 and about 0.2 mg L^{-1} at pH 8 (Rickard and Nriagu, 1978). The solubility limits of Pb decreases to 0.3 mg L^{-1} at pH 4 and 0.001 mg L^{-1} at pH 8 in the presences of phosphate and chloride (Rickard and Nriagu, 1978). Bargar et al. (1998) studied Pb(II) sorption on goethite and γ-alumina in aqueous 0.1 *M* NaCl solutions as a function of pH. They reported that, in the presence of chloride solutions, Pb may precipitate as solid PbOHCl. At pH 7, the presence of Cl^- has little effect on the Pb(II)/goethite and Pb(II)/γ-alumina adsorbate spectra (Bargar et al., 1998). At pH ≤ 6, the XAFS spectra indicated the presence of Pb(II)-chloro ternary complexes on goethite (Bargar et al., 1998).

REMEDIATION OF SOIL LEAD

Lead Remediation Approaches in urban soils

Unlike organic contaminants, the breaking down/destruction of trace elements such as Pb is not possible. Thus, long standing remediation approaches in soils have focused on replacing excavated contaminated soil with “clean” soil, or simply capping the contaminated area (Hettiarachchi et al., 2000). More recently, the high cost of this traditional approach in conjunction with low allocation of resources to remediate contaminated sites have led researchers to seek alternative measures (Kumpiene et al., 2008). Soil chemical stabilization has

been seen as an alternative technique that is cost-effective and less disruptive to the environment (Kumpiene et al., 2008). Chemical stabilization involves the addition of materials/chemicals capable of adsorbing, or complexing the trace metal, effectively rendering it immobile.

Chemical stabilization of soil Pb using inorganic phosphate sources

Chemical stabilization of soil Pb takes into account factors that ultimately control the solubility of the metal. Lead phosphates have been found to be the most stable environmental Pb form controlling Pb solubility under a wide variety of conditions (Nriagu, 1974, Ruby et al., 1994). Lead precipitates as phosphates, hydroxides and carbonates in alkaline environments, hence Pb solubility decreases at high pH. Phosphate rock (Basta et al., 2001; Brown et al., 2005; Cao et al., 2004; Ma et al., 1993), phosphoric acid/hydroxyapatite (Cao et al., 2009; Hettiarachchi et al., 2001; Yang et al., 2001), and biosolids (Basta et al., 2001; Brown et al., 2003, 2005, 2012) are common amendments used stabilize soil Pb.

Ma and Rao (1999) investigated the feasibility of using Florida PR to immobilize Pb from 13 Pb-contaminated (lead arsenate, mining and smelting) soils from a wide cross section of the US. They reacted 4 g of each soil with 0, 0.5, or 1 g of PR in 40-mL polycarbonate centrifuge tubes containing 25 mL of deionized water and shook the suspensions from 2 to 96 hr. Soil Pb concentrations ranged from 198 to 40,100 mg kg^{-1}, while pH ranged from 5.53 to 8.59 (Ma and Rao, 1999). Lead immobilization greatly increased with increasing PR addition. For example, at 0.5 g of PR, Pb immobilization ranged from 22 to 94% but increased to 33 to 100% with 1 g of PR addition (Ma and Rao, 1999).

The application of different phosphorus sources has also been examined. Cao et al. (2002) conducted a field study on $4m^2$ plots of a Pb-contaminated site to evaluate the efficacy of P-induced Pb immobilization. In this study a field demonstration was conducted at a Pb-

contaminated site (former battery recycling and salvage yard site with discharge of waste oil) to assess the effectiveness of P-induced Pb immobilization. Phosphoric acid (PA), calcium phosphate ($CaH_2PO_4)_2$), and PR were applied at 4.0 molar ratio of P to Pb in three treatments: 100% of P from PA; 50% P from PA + 50% P from $Ca(H_2PO_4)_2$; and 50% P from PA + 5% PR (Cao et al., 2002).

Chloropyromorphite ($Pb_5(PO_4)_3Cl$) formation was noted in all treatments and soil pH decrease was evident particularly when phosphate source was solely PA. Transformations from non-residual soil Pb fractions to residual fractions were successful; Pb increases ranging between 19 to 48% (100% of P from PA), 22 to 50% (50% P from PA + 50% P from $Ca(H_2PO_4)_2$), and 11 to 55% (50% P from PA + 5% PR), respectively (Cao et al., 2002). Ionic exchange reactions involving phosphate amendments and soil Pb leads to the production of pyromorphite-like materials which have very low solubility and bioaccessibility (Hettiarachchi et al., 2001; Scheckel and Ryan, 2003). Yang et al. (2001) also observed successful Pb immobilization when a smelter site soil was amended with PA. The addition of 10,000 mg of P kg^{-1} (PA) was found to reduce Pb immobilization by about 60% (Yang et al., 2001). Comparatively, PA addition is usually favored over PR since it results in lower pH (Melamed et al., 2003). Lower soil pH facilitates greater Pb dissolution and the rapid formation of pyromorphite-like species with soluble P (Melamed et al., 2003; Yang and Mosby, 2006).

In situ soil Pb stabilization using biosolids composts

In the past decade, composted biosolids have been an alternative supply of P due to its low cost and its effectiveness in reducing Pb bioaccessibility in low pH soils (Basta and Sloan, 1999; Brown et al., 2003, 2005, 2012; Haering et al., 2000). Biosolids amendments have been successfully implemented on former smelter sites (Brown et al., 2003; Stuczynski et al., 2007),

and urban gardens (Farfel et al., 2005; Attanayake et al., 2014; Defoe 2014, Thesis Chapter 4). Brown et al. (2003) reported that the addition of high iron biosolids 10% (w/w) reduced in vitro Pb bioaccessibility in a contaminated (2000 mg Pb kg^{-1}) urban soil by 43%. In addition to the high P concentrations, many biosolids have high Fe concentrations.

ARSENIC

Description of arsenic

Arsenic is the 33rd element in the periodic table with an atomic weight of 74.92. It ranks as the twentieth most abundant element in the earth's crust (Bissen and Frimmel, 2003). Classified as a metalloid (has both metallic and non-metallic properties), the most stable form of the element (gray arsenic) has a density of 5.73 g/cc. It has an electronic configuration of $[Ar]4s^2 3d^{10} 4p^3$ and exists in four valence states: -3, 0, +3, and +5 (Oremland and Stolz, 2003).

Uses of arsenic

In the US, the majority of the arsenic mined, was primarily used in the production of insecticides (Mandall and Suzuki, 2002). Arsenic has also been used in wood preservation (Bissen and Frimmel, 2003; Hingston et al., 2001).

Arsenical Insecticides

In the early 20th century, calcium arsenate [$Ca_3(AsO_4)_2$] was found as a viable chemical method for controlling the disastrous effect that the boll weevil had on cotton plantations in the south. Although less extensively used, lead arsenate ($PbHAsO_4$) was another arsenical used to fight the codling moth on apple orchards from 1905 to 1947 before the introduction of DDT (dichloro-diphenyl-trichloroethane) and organophosphorus insecticides in the 1950's (Metcalf

1973). Arsenical's popularity among farmers and the agricultural industry was mainly due to effectiveness as an insecticide, persistence in the field, ease of use and their low costs (Schooley et al., 2009). Lead arsenate was also used to preserve tobacco leaves.

Arsenic in Chromated Copper Arsenate

Chromated copper arsenate (CCA) was used to preserve fence-posts, wooden patios, utility posts, and playground equipment such as swings and benches (Brooks, 2010). Chromated copper arsenate is an effective fungicide and insecticide used in wood preservation due to ease of waterborne formulations, wood penetration (Hingston et al., 2001). In 2003, the USEPA decided that wood materials pressure treated with CCA should be phased out for use in residential settings such as gazebos and child play areas (USEPA, 2011).

Secondary uses of Arsenic

The metalloid has been found to be useful in smaller quantities. For example in the glass industry, As is used as a glass decolorizer and a bubble dispersant (Farmer and Johnson, 1990; Ishiguro, 1992) helping to refine the overall quality of the glass material. Arsenic trioxide was previously used as an opacifier in the ceramic industry for the production of glazes and enamels (Gittings, 1947). The element's semi-metallic properties enable its use in the electronics industry. Currently, there has been an increase in the number of semiconductors that are present in light emitting diodes (LEDs) and solar cells. Some of the semiconductors used in these LEDs are made with gallium arsenide (GaAs) (Blakemore, 1982; Jenkins et al., 1994; Mukherjee et al., 2007).

Arsenic toxicity and human health

The lethal dose of inorganic arsenic is 100 to 200 mg of arsenic trioxide for an adult individual, although people have survived larger doses (Hindmarsh and McCurdy, 1986; Mathieu et al., 1981). Regulatory limits are often based on total soil As concentrations rather than the bioavailable fractions (Smith et al., 1998). The toxicity of As is inherently linked to its inorganic forms present in soil solution. Arsenite (As^{3+}) is considered as more toxic than arsenate (As^{5+}) (Liu et al., 2005; Raven et al., 1998). The health implications of As are linked to the ability of both inorganic species to hinder energy-linked functions of the mitochondria by altering the activity of enzymes. For example, once in the cell, As^{5+} competes with phosphate and interferes with the synthesis of adenosine triphosphate (ATP) (Hughes, 2002). Arsenite (As^{3+}) has a high affinity for sulfhydryl groups (Buschmann et al., 2006; Ramirez et al., 1997). Consequently, it is able to denature proteins and affect enzyme activity in the human body.

Chronic As poisoning has been related to the drinking of contaminated As water or ingesting As contaminated soil. Symptoms of chronic As exposure are skin lesions (Das et al., 1996) usually characterized by hyperpigmentation or hyperkeratosis, hypopigmentation (Cebrian et al., 1983). Other deleterious health effects include gastrointestinal tract, respiratory tract, liver, cardiovascular system, hematopoietic system, and nervous system complications (Mandal and Suzuki, 2002). Epidemiological reports have listed arsenic as a human carcinogen (Centeno et al., 2002; Lee-Feldstein, 1986; Smith et al., 1992).

Arsenic concentration in soils

Mean soil As concentration of uncontaminated soil in the US is ~6 mg kg^{-1} (Nriagu, 1994; Smith et al., 2013). Elevated soil As concentrations are mainly due to anthropogenic sources such as smelting of copper ores, the use of chromated copper arsenate (CCA) as a wood

preservative and the use of lead arsenate pesticides (Bissen and Frimmel, 2003; Welch et al., 2000). For example, the Washington State Department of Ecology (1994) reported uniform (1 to 10 mg kg^{-1}) As distribution in Washington state soils. High (> 50 mg kg^{-1}) As concentrations detected in the Tacoma vicinity or the Yakima basin have been attributed to the presence of a copper smelter (near Tacoma) and extensive use of arsenic-based pesticides (Yakima agricultural basin).

A primary area of organoarsenical herbicide use in the United States includes the cotton-belt states of Alabama, Arkansas, Louisiana, Mississippi, and Texas (Bednar et al., 2002). Bednar et al. (2002) reported on point sources of arsenic from soil and water samples collected at Mississippi and Arkansas. They reported that although agricultural point sources might be responsible for increased arsenic concentrations in local irrigation wells, As concentrations did not exceed 10 μg L^{-1} in any of the wells sampled.

Arsenic in soil environments

The dominant inorganic forms of arsenic in soil environments are As^{3+} and As^{5+} (Bhattacharya et al., 2007; Masscheleyn et al., 1991; Walsh and Keeney, 1975; Welch et al., 2000). They do exist in solution as oxyanions—As^{3+} as arsenite and As^{5+} as arsenate (Sadiq, 1997).

Their respective compounds are highly soluble in water (Vaughan, 1993) and are affected by changes in pH (Manning and Goldberg, 1997; Pierce and Moore, 1982; Sadiq, 1997; Smedley and Kinniburgh, 2002) and redox conditions (Cherry et al., 1979; Masscheleyn et al., 1991). The pentavalent oxyanion dominates in oxic conditions and is mobilized at high pH, while the trivalent inorganic species is predominant under reducing environments (Sadiq, 1997; Smedley and Kinniburgh, 2002).

In oxic environments, it is assumed that the total As exists as As^{5+} and are in forms of $H_3AsO_4^0$, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} (Sadiq 1997). Since most soil solutions are within the pH range of 4 to 10, the activities of $H_3AsO_4^0$ and AsO_4^{3-} within that range can be both ignored. Below this range, $H_3AsO_4^0$ is dominant while AsO_4^{3-} dominance increases beyond pH 10. O' Neill (1990) listed the thermodynamically probability of As^{5+} in soil solutions (shown below; Eq. 1 to 3). From the dissociation constants, the most dominant As^{5+} species in typical oxic soil solution environments at pH range of 4 to 8 are $H_2AsO_4^-$, and $HAsO_4^{2-}$ (1991; Sadiq, 1997; Smith et al., 1998; Li et al., 2007).

In suboxic and anoxic environments, As^{3+} species are more dominant and exists in addition to As^{5+} species. These species include $HAsO_2^0$, $H_3AsO_3^0$, AsO_2^-, $H_2AsO_3^-$, $HAsO_4^{2-}$ and AsO_3^{3-} (Sadiq, 1997). Reactions 4, 5, and 6 lists the probability of arsenous acid (As^{3+}) (O' Neill (1990). The most thermodynamically stable species is $H_3AsO_3^0$ (Li et al., 2007; Smith et al., 2002).

$H_3AsO_4 + H_2O \Longleftrightarrow H_2AsO_4^- + H_3O^+$	pK_a 2.20	Eq. 1
$H_2AsO_4^- + H_2O \Longleftrightarrow HAsO_4^{2-} + H_3O^+$	pK_a 6.97	Eq. 2
$HAsO_4^{2-} + H_2O \Longleftrightarrow AsO_4^{3-} + H_3O^+$	pK_a 11.53	Eq. 3
$H_3AsO_3 + H_2O \Longleftrightarrow H_2AsO_3^- + H_3O^+$	pK_a 9.22	Eq. 4
$H_2AsO_3^- + H_2O \Longleftrightarrow AsO_3^{2-} + H_3O^+$	pK_a 12.13	Eq. 5
$AsO_3^{2-} + H_2O \Longleftrightarrow AsO_3^{3-} + H_3O^+$	pK_a 13.4	Eq. 6

Arsenic Sorption

Sorption of As in soil solutions are based on pH, redox conditions, clay percentage or composition of soil minerals, and the presence/absence of competing ions (Manning and Goldberg, 1997; Smith et al., 2002). Manning and Goldberg (1997) investigated As^{3+} adsorption

on kaolinite, illite, montmorillonite, and amorphous aluminum hydroxide (am-$Al(OH)_3$) as a function of pH and ionic strength and compared their findings with As^{5+} adsorption. Effects of solution pH on the homogeneous oxidation of As^{3+} to As^{5+} was evaluated by programming a titrator to maintain 60-mL volumes of 0.4 μM As^{3+} in 0.005 *M* NaCl at pH 4, 6, 8, 9, and 10 for a total of 72 hours using 0.01 *M* NaOH or HCl titrant (Manning and Goldberg, 1997). Recovery of adsorbed As from As^{3+}-treated clay mineral solids showed that oxidation of As^{3+} to As^{5+} was enhanced by heterogeneous oxidation on kaolinite and illite surfaces. Manganese minerals (cryptomelane:α-MnO_2; birnessite:δ-MnO_2), iron oxides (goethite, hematite, and magnetite) (Deschamps et al., 2003; Oscarson et al., 1983), and aluminum oxides have also been reported to play a role in adsorption of As^{3+} to As^{5+} in soil solutions. Iron oxides have been reported to have a higher affinity for As than manganese oxides. Manning et al. (2002) also reported on arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite. Surface coverages achieved for As(III)- and As(V)-treated syntheticMnO$_2$ were 266 and 50.7 mmol kg^{-1} As (8.79 and 1.67 μmol m^{-2} As), respectively (Manning et al., 2002). The As(III)-treated MnO_2 sample analyzed by EXAFS had a comparable surface coverage to the 100 mg L^{-1} MnO_2 batch reaction (7.91 μmol m^{-2} As) (Manning et al., 2002).

Effect of competing ions

Arsenic sorption is also affected by the presence of competing anions such as phosphate (PO_4^{3-}), and molybdate (MoO_4^{2-}), and cations such as calcium (Livesey and Huang, 1981; Roy et al., 1986; Smith et al., 2002). Smith et al. (2002) investigated the effect of PO_4^{3-}, Na^+, and Ca^{2+} on the sorption of As^{5+} and As^{3+} by an Oxisol, a Vertisol, and two Alfisols. They concluded that with phosphorus (P) additions (0.16 mmol L^{-1}), there was a significant decrease in As^{5+} sorption by soils containing low Fe oxides (<100 mmol kg^{-1}), indicating competitive adsorption

between P and As^{5+} for sorption sites. The also observed that the competitive adsorption between P and As^{5+} for sorption sites was negligible for soils with high Fe content (>800 mmol kg^{-1}). Smith et al. (2002) suggested that increase sorption of As^{5+} on the soils in the presence of Ca^{2+} was due to changes in the surface charge characteristics of the soils.

Roy et al. (1986) evaluated the adsorption behavior of anionic mixtures (binary-solute combinations of arsenate, molybdate, and phosphate) by a Cecil clay, an Ultisol and a Catlin silt loam using a multicomponent Freundlich-type adsorption equation. They reported that phosphate and molybdate both suppressed As sorption in the Cecil clay; with phosphate being more effective than molybdate. Livesey and Huang (1981) evaluated the effect of chloride, nitrate, and sulfate on As sorption in four soils of Saskatchewan, Canada. They reported that chloride, nitrate and sulfate (at concentrations usually present in saline soils) had little effect on the adsorption of As.

REMEDIATION OF SOIL ARSENIC

Arsenic Remediation

There are several technologies that have can be used for reducing As contamination in soils (Hartley and Lepp, 2008; Mulligan et al., 2001; Wang and Mulligan, 2006). These technologies include solidification/stabilization using inorganic binders, *in situ* extraction, and *in situ* chemical immobilization (Kumpiene et al., 2008; Mulligan et al., 2001). *In situ* extraction is very expensive and arduous, and finding a relatively clean soil source can be burdensome. The use of binding agent such as cement would not be feasible if one intends to garden directly in the soil. For this reason, i*n situ* chemical immobilization of As in urban soils is more suited.

In situ chemical immobilization

In situ chemical immobilization of As involves the use of several inorganic amendments such as clays, amorphous Al and Mn oxides, and amorphous iron oxides (Manning and Goldberg, 1997; Wang et al., 2006).

Garcia-Sanchez et al. (2002) reported on the use of synthetic Fe oxyhydroxides, Al hydroxides and natural clay minerals to attenuate two mine waste soils containing arsenopyrite. The reported very high As(V) adsorption capacity on both synthetic Al hydroxide (122 mg/g at pH: 5) and Fe oxyhydroxide (76 mg/g at pH 5) (Garcia-Sanchez et al., 2002). The water-extractable fraction decreased by 55-79% for one soil and by nearly 100% for another when synthetic $Al(OH)_3$ and FeOOH were used together (Garcia-Sanchez et al., 2002).

Moore et al. (2000) used $FeSO_4$, and $FeSO_4$ + lime to remediate soils that contaminated with As-containing wood-preserving solution. The contaminated soil resulted in the groundwater plumes that contained up to 25 mg L^{-1} As, with As (V) being the predominant species. They reported that Fe:As molar ratio of 2 reduced As soluble concentrations below 50 mg L^{-1} (Moore et al., 2000). Additionally, Yang et al. (2007) reported on the use of $FeSO_4$, $FeSO_4$ + $KMnO_4$, $FeSO_4$ + $KMnO_4$ + lime in reducing As concentrations on two sandy loam soils that were previously contaminated by herbicide applications. Using the toxicity characteristic leaching procedure tests, they reported decreases in As leachability for all treatments, with the $FeSO_4$ being the most effective treatment.

Mench et al. (2006) amended soils obtained adjacent to a derelict As smelter with iron grit (1%), beringite (5%), or iron grit (1%) + beringite (5%) in a six year study. The treatments were formulated as percent by soil weight. Arsenic bioaccessibility in untreated soils, iron grit + beringite amended soils and iron grit amended soil was 12%, 7.4%, and 3% respectively (Mench et al., 2006).

Other natural As sorbents such as red mud (byproduct of the industrial process that refines bauxite into aluminum oxide) or iron rich oxide materials such as goethite, magnetite and hematite are used for As remediation. Lombi et al. (2004) used two red muds, a red gypsum and two water treatment sludges (WTS) to attenuate As in a soil collected from an agricultural grassland soil located near a former copper and As mine. Soil As was very high (2% w/w) and the amendments contained high concentrations (17 to 33% w/w) of iron oxides and had a neutral to alkaline pH. Using the physiologically based extraction test (PBET) developed by Ruby et al. (1999), they reported that bioaccessibility of As was low (<5%) and decreased only in the WTS-A treatment (Lombi et al., 2004). The WTS and red gypsum treatments decreased concentrations of As in soil pore water and extractable As (Lombi et al., 2004).

Remediating soils contaminated with multi contaminants

Elevated concentrations of multi contaminants at contaminated sites presents complex and challenging remediation approaches. Effects of pH, redox conditions, and the presence or absence of competing cations/anions for sorption sites have to be taken into consideration. Cao et al. (2004) evaluated the effect of phosphate rock (PR) additions on retention mechanisms of Pb, Cu, and Zn in both a pH-control and pH-free sorption systems. In the Pb–Cu–Zn ternary system, reported sorption capacity reductions of Pb, Cu, and Zn were 15.2%, 48.3%, and 75.6% respectively (Cao et al., 2004). Metal sorption was affected by changes in pH conditions. Desorption of Cu and Zn was more sensitive to decreases in pH conditions, while Pb desorption was enhanced only at extremely high pH (2.93) (Cao et al., 2004). Other products such as lime and fly ash have been used to remediate Pb. Iron oxides and iron salts (e.g. iron sulfate) have also been used to attenuate cationic and anionic soil contaminants with some success. The

acidification caused by these amendments have been countered by limited amounts of lime addition, thus reducing the leaching potential of anionic contaminants (Warren et al., 2003).

Bioavailability assessment of Lead and Arsenic

Until recently, the environmental risks posed by toxic elements in soils, have been based upon their total elemental concentrations. Advances in the literature have shown that bioaccessibility tests are a more accurate predictor of environmental risk than total elemental concentrations. The latter assumes 100% bioavailability, resulting in overestimation of risks resulting from human exposure to these contaminants (Bruce et al., 2007). Soil bioavailability characterizes the amount of a chemical/compound absorbed into the circulatory system of an organism following removal from the soil under physiological conditions. The total fraction released from the soil matrix and available for absorption in the gastrointestinal tract is referred to as the bioaccessible fraction.

Ethical concerns prohibits the use of humans as test subjects. Rats, juvenile swine, and in some cases monkeys have been used to estimate the relative bioavailability of both Pb and As (Schoof et al., 1995; Casteel et al., 1997; Roberts et al., 2002; Hettiarachchi et al., 2003; Juhasz et al., 2007). Juhasz et al. (2007) conducted an in vivo study on large (20 to 25 kg) female white swine to examine As bioavailability using soils from railway corridors, cattle tick dip sites, mine sites and gossans (areas containing naturally elevated concentrations of As) in Australia. Slurries (10-25 g of soil in 150 ml of As free water) of As contaminated soil were fed to fasting swine. Arsenic bioavailability ranged from 6.9 ± 5.0% (mine soils) to 74.7 ± 11.2% railway corridors). A comparative in vitro study following a simplified physiological based extraction test, conducted alongside the in vivo study revealed a strong correlation (r^2=0.92) between both methods.

Despite the advantages of the swine model, such studies are very expensive, time consuming, require elaborate set-up procedures, and strict ethical guidelines must be adhered to. Consequently, relative successes of in vitro methods developed over the past decade have been utilized as a guidance for determining the relative bioavailability of contaminants found in urban soils. Ruby et al. (1996) developed an in vitro method to evaluate Pb solubility from different mine wastes in the gastrointestinal (GI) tract. Lead concentrations from the soil materials (mine composite, tailings, former Pb and zinc (Zn) smelters) ranged from 1388 to 10, 230 mg/kg, while As concentrations ranged from 170 to 3900 mg kg^{-1}. Soil materials were subjected to gastric solutions at a soil to solution ratio of 1:160 (assume soil density of 1.6 g/cm^3) at varying acidic pH (1.3, 2.5, and 4). They deduced that Pb solubility in the stomach, hence its bioaccessibility increased with decreasing pH, and strong correlation was observed when compared with Pb bioavailability data. Unlike Pb, As dissolution was not influenced by changes in solution pH and predictive bioavailability estimates derived from the study appeared to be somewhat conservative. There have not been *in vitro* tests developed specifically for urban soils.

Bioaccessibility tests have not solely been restricted to soils with prior history mining and smelting. A physiologically based *in vitro* method developed by Oomen et al. (2002) was used to evaluate Pb bioaccessibility on soils contaminated with pottery flakes with varying Pb concentrations (50 to 2400 mg kg^{-1}). The bioaccessibility of pottery flake lead was considerably less (0.3 ± 0.2%) than lead in soil without pottery flakes (42 to 66% at the same site, and 28 to 73% at other sites in the same town) (Oomen et al., 2002). Their results clearly showed that the amount of bioaccessible Pb was not related to the total concentrations, indicating that the bioaccessibility of the metal was due to its partitioning in the soil medium. Soil partitioning in addition to a physiologically based extraction test (PBET) evaluated Pb, As, and Chromium (Cr)

in horizons A, and B of a Melton Valley series soil incubated for a period of 400 d (Fendorf et al., 2004). They observed with the exception of Pb, the bioaccessibility of As, and Cr decreased with aging and postulated the occurrence might be due to changes in contaminant binding mechanisms. In horizon B (0.73% carbon vs. 4.0% carbon in A), there was a pronounced decrease in the percent bioaccessibility until about day 90 before leveling off (Fendorf et al., 2004). These binding mechanisms include inner-sphere and outer sphere complexation. For example, both cations and anions will typically adsorb rapidly to soil surfaces forming outer-sphere (electrostatic or physical) complexes (Fendorf et al., 2004). Zhang and Sparks (1989) reported the development of inner-sphere (chemical) complex formed after initial physical adsorption.

Use of X-Ray Absorption Spectroscopy in Pb and As contaminated soils

X-ray absorption spectroscopy (XAS) studies have been employed in order to gain further understanding of the mechanisms of sorption in soils (Kelly et al., 2008; Scheidegger and Sparks, 1996). X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) are two primary techniques utilized. X-ray absorption Fine Structure (XAFS) is a key spectroscopy technique that gives a pictorial view of interatomic distances between the sorbed ions, and the central atom that are present in the complex. An understanding of the information gained by XAFS, helps one deduce the coordination number of central atoms that are present in the complex and particularly the oxidation state of the bound metal ion. Oxidation state is an important criterion in the determination of transport, bioavailability, and fate of some trace elements such as As in soil environments.

The EXAFS spectra are obtained by measuring the X-ray absorption or fluorescence of a given sample as a function of the wavelength (Manceau at al., 1996). The spectral scan is

performed in the vicinity of an X-ray absorption edge of a chosen target element and is an element-specific, bulk-sensitive, and nondestructive method (Manceau et al., 1996). However, direct determination of the chemical form of trace metals is a difficult task (Manceau et al., 1996). This structural technique has the necessary elemental specificity, short-range order sensitivity, and unrivalled detection limit, presently equal to ~ 100 mg kg^{-1} (Manceau et al., 2000). Consequently, conducting EXAFS studies for soils with lower concentration of elements can be challenging (Manceau et al., 2000; Scheckel et al., 2005).

Niazi et al. (2011) examined arsenic (As) speciation and phytoavailability of As-contaminated cattle dip sites in northern New South Wales and three railway corridors in South Australia. They were able to identify arsenate (As^{5+}) on the surface of crystalline iron oxides and on a mineral phase of 10 of 18 cattle dip sites.

Scheckel and Ryan (2004) reported on XAFS studies conducted on a residential soil adjacent to a lead smelter that was amended with various P sources. Pyromorphite concentration ranged from 0% in control soil to 45% for 1% phosphoric acid amendment, following 32 months of residence time (Scheckel and Ryan, 2004). Their studies also revealed that Pb existed mainly (53%) as Pb-sulfur species. Additionally, supplemental addition of an iron amendment as an iron-rich byproduct with triple superphosphate enhanced pyromorphite formation relative to independent TSP amendment of like concentrations (41 versus 29%) (Scheckel and Ryan, 2004).

X-ray absorption near-edge structure (XANES) has been used to identify small shifts in the energy position of the As *K*-absorption edge to determine its oxidation states (Fendorf and Sparks, 1996). Detecting Pb and As bearing minerals and their phases provides greater credence to toxicity recommendations. An understanding of the speciation of these elements is critical in relating the effectiveness of the treatments in these urban soils to their bioavailability potential.

Due to inherent problems associated with Pb and As XAS, wet chemical analysis and plant uptake data are often important in helping explain mechanisms and trends.

LEAD AND ARSENIC CONCENTRATIONS IN PLANTS

Lead concentration in plants

Finster et al. (2004) reported on Pb transfer from soil through the root to the leaves of root, leafy and fruiting vegetables grown on urban residential soils in Chicago, IL. Lead concentration of swiss chard grown on 902 mg Pb/kg soil were as high as 22 mg kg^{-1} (dry weight basis) (Finster et al., 2004). Plants were washed with tap water and a mild detergent to get rid of adhered soil particles (Finster et al., 2004).

In order to assess the intake of lead by consumers of home grown vegetables in urban areas, Moir and Thornton (1989) replicated experimental plots of uniform size in 94 gardens located in 9 towns and cities in England. Lead concentrations in the vegetables ranged from <0.25 μg g^{-1} to 16.7 μg g^{-1} (dry weight) (Moir and Thornton, 1989). Soil Pb concentrations in the gardens ranged from 27 to 1,676 μg g^{-1}).

Nabulo et al. (2011) reported on the concentrations of Pb in soils and five contrasting tropical leafy vegetables grown in a replicated field trial at five contaminated urban agriculture sites in Kampala City, Uganda. Soil Pb concentrations at the sites ranged from 51 to 653 mg kg^{-1}. They reported Pb concentration in the plant tissues ranging from 0.243 to 144 mg kg^{-1} (dry weight basis) (Nabulo et al., 2011). The highest Pb concentration was observed in *S. aethiopicum* (Ethiopian eggplant) grown at the Kololo site (Nabulo et al., 2011). The Pb concentrations in the vegetables cleaned with deionized water were 73% lower than the edibles that were not washed (Nabulo et al., 2011).

Arsenic concentration in plants

Food chain transfer of As has been attributed to growing crops on As contaminated soils (Alam et al., 2003; McBride, 2013) or irrigating crops with contaminated As ground water (Das et al., 2004; Duxbury et al., 2003). Alam et al. (2003) sampled and screened various vegetables grown in Samta village in the Jessore district of Bangladesh for As, and other trace metals. Mean As concentrations (dry weight basis) in snake gourd, taro, and green papaya were 0.489, 0.440, and 0.389 $\mu g\ g^{-1}$, respectively. They also reported low bioconcentration factors (BCF) (dry weight basis) for the vegetables studied. For example, BCF-As for snake gourd and green papaya were 0.038 and 0.030, respectively.

McBride (2013) reported As concentrations in lettuce, carrots, green beans, and tomatoes that were grown in orchard soils historically contaminated by Pb arsenate pesticides. The plants were grown under greenhouse conditions and soil As concentrations ranged from 6 $mg\ kg^{-1}$ (uncontaminated soil) to 211 $mg\ kg^{-1}$ (McBride, 2013). Arsenic concentrations in lettuce, unpeeled carrots, and green beans exceeded the international health standard of 0.1 $mg\ kg^{-1}$ (fresh weight) at the highest soil As concentration (211 $mg\ kg^{-1}$) (McBride, 2013). Additionally, the crop type strongly affected As accumulation and followed the order lettuce >> carrot ≥ bean >> tomato (McBride, 2013). Peeling reduced the As concentrations in carrot's roots (McBride, 2013).

Muñoz et al. (2002) analyzed total and inorganic arsenic concentrations in the edible part of 16 agricultural products (roots, stems, leaves, inflorescences, and fruits) grown in northern Chile. The total arsenic concentrations ranged from 0.008-0.604 $\mu g\ g^{-1}$ (wet weight basis). The concentrations of total and inorganic arsenic found in edible roots and leaves were higher than those found in fruit (Muñoz et al., 2002).

Das et al. (2004) conducted a study on 100 samples of crops and vegetables grown in three regions of Bangladesh. They concluded that concentrations of arsenic in vegetables like Kachu sak (*Colocasia antiquorum*), potato (*Solanum tuberosum*), and Kalmi sak (*Ipomea reptans*) exceeded the old WHO/FAO food safety limit of 1.0 mg kg^{-1} (Das et al., 2004).

Assessing safe concentrations of Pb and As in crops

Crop contaminants impair the quality of food and have the potential to cause adverse risks to human health. In a response to the exponential increases in global food trade, the World Health Organization (WHO) and the Food and Agricultural Organization (FAO) established the CODEX Alimentarius Committee (CAC) in 1963. The committee's primary purpose was to address international food standards, guidelines, and codes of practice as they contribute to the safety, quality, and fairness of this international food trade. Standard guidelines provide safety assurances to both food producers and consumers. Maximum levels (MLs) have been used as a guide for assessing safety limits for contaminant concentrations in vegetables and crops.

Reported MLs are based on the analysis of the edible plant part and are expressed on a fresh weight basis assuming 100% bioavailability. However, there are not universal established MLs for all crop contaminants (e.g. arsenic). Lead MLs in root and fruiting vegetables were set at 0.1 mg kg^{-1}, while leafy vegetables are 0.3 mg kg^{-1} (FAO/WHO-CODEX 1995; 2010 amendment). However, due to international trade obligations, Australia has established a standard of 0.1 mg kg^{-1} for As (fresh weight basis) in food edibles. The MLs were established because it serves an effective risk management function and for those foods which provide a significant contribution to the total dietary exposure (Australian Federal Register of Legislative Instruments, 2011). Consequently, since plant As concentrations is often reported on dry weight basis, the ML of 0.1 mg kg^{-1} (fresh weight basis) should first be converted on a dry weight basis

before any comparison can be made. Additionally, crops grown in different climatic conditions may have varying moisture content and can affect absolute MLs.

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CHAPTER 3 - SAFETY OF GARDENING ON LEAD- AND ARSENIC-CONTAMINATED BROWNFIELDS

Phillip P. Defoe[1], Ganga M. Hettiarachchi[1,*], Christopher Benedict[2], Sabine Martin[1]

[1]Department of Agronomy, Throckmorton Plant Sciences Center, Kansas State University, Manhattan, KS 66506, USA

[2]Whatcom County Extension, Washington State University, Bellingham, WA 98225, USA

ABSTRACT

Elevated levels of lead (Pb) and arsenic (As) are not uncommon for urban soils. Test plots were established at urban gardens in Tacoma and Seattle, WA. The Tacoma site was contaminated with Pb (51 to 312 mg kg^{-1}) and As (39 to 146 mg kg^{-1}), whereas the Seattle site had high Pb soil concentrations ranging from 506 to 2,022 mg kg^{-1}, and As concentrations of < 20 mg kg^{-1}. Efficacy of biosolids mix and compost amendment in reducing Pb and As concentrations in three vegetables (carrots, lettuce, and tomatoes) and bioaccessibility of soil Pb and As were evaluated. Food-chain transfer of Pb and As were evaluated by measuring plant Pb and As concentrations following kitchen-style washing, a laboratory cleaning procedure, or peeling. The experimental design was a randomized complete block with a split-plot arrangement. Tacoma site treatments included a Class A biosolids mix (TAGRO) with dolomite, and soil at the Seattle site was amended with Cedar-Grove Compost (CGC) plus dolomite. TAGRO amendment diluted soil Pb by 10 to 23% and As by 12 to 25% at the Tacoma site, and CGC plus dolomite resulted in 20 to 50% dilution in soil Pb at the Seattle site. Both amendments reduced Pb concentrations in vegetables by 50% to 71%, and As reductions ranged from 46% to 80%. At the Tacoma site, Pb concentrations in carrots exceeded the MLs established by the Food and Agriculture Organization (FAO) and the World Health Organization (WHO) in 2010. Plant As concentrations were below the MLs for all vegetables. Carrots and kitchen-cleaned lettuce and tomatoes at the Seattle site exceeded Pb MLs. Laboratory cleaning further reduced Pb and As food-chain transfer in vegetables grown in contaminated urban soils.

INTRODUCTION

The number of community gardens on vacant/underutilized residential and commercial properties in United States (US) cities has increased steadily over the past decade. In 2008, the

American Community Gardening Organization (ACGA) estimated that there were 18,000 community gardens throughout the US and Canada. One reason for establishing community gardens is the desire for improved access to affordable, fresh fruits and vegetables, especially in urban food deserts (Alaimo et al., 2008; Armstrong, 2000; Dunnett and Qasim, 2000; Lovell, 2010). Other benefits include reducing the supply of vacant, unproductive urban land; improving the public image of troubled neighborhoods; and increased self-sufficiency among urban residents who grow food for themselves and others (Kaufman and Bailkey, 2000).

Despite growing interest in urban gardens, concern about the presence of real or perceived trace elements persists. Trace element contamination problems in urban soils are well documented (Chaney et al., 1984; Kachenko and Singh, 2006; Moir and Thornton, 1989). Lead (Pb) is one of the most ubiquitous and extensively studied trace elements in urban environments (Chaney et al., 1984; Mielke et al., 1984; Schwarz et al., 2012). Anthropogenic sources of Pb include leaded paint and gasoline, soldering/ammunition products, Pb-based pesticides, aerosols or dusts from former smelters or mine sites, and abandoned car batteries (Alloway, 1995; Hindmarsh et al., 1986; Tiller, 1989).

In soil environments, Pb exists primarily as the complexed, sorbed, or precipitated divalent metal cation (Pb^{2+}), and the major exposure pathway is through inadvertent ingestion or inhalation of contaminated soil dust (Chaney and Ryan, 1994; Hettiarachchi and Pierzynski, 2002; Mielke, 1999). Chronic exposure to elevated Pb levels results in stunted growth and neurological, central nervous system (CNS), and kidney damage (Chisolm et al., 1975; Lanphear et al., 2005; Needleman, 2004). Children are more adversely affected because of their very high (~50%) intestinal absorption rates of ingested Pb compared to adults (5 to 10%) (Maddaloni et al., 1998; Ziegler et al., 1978).

Until recently, the environmental risks posed by Pb in urban soils have been based on total elemental concentrations assuming 100% bioaccessibility. The total fraction released from the soil matrix and available for absorption is referred to as the bioaccessible fraction. Bioaccessibility tests are a more accurate predictor of environmental risk than total elemental concentrations.

Community garden owners and operators often resort to using raised beds, rectangular wooden boxes (usually constructed over plastic liners) filled with “clean” or uncontaminated soil, to avoid liability from the exposure risks of soil contaminants. This approach is very expensive, and finding a readily available source of uncontaminated soil can be burdensome. Phosphate addition has been proposed as a cheaper, less destructive *in situ* Pb stabilization approach. Transformation of soil Pb into less mobile and bioavailable forms such as pyromorphites is well documented (Hettiarachchi et al., 2001; Ma et al., 1995; Melamed et al., 2003; Ryan et al., 2001; Zhang and Ryan, 1999).

Phosphate sources demonstrating high Pb immobilization include phosphate rock (PR), phosphoric acid (PA), and biosolids compost (Basta and McGowen, 2004; Basta et al., 2001; Cao et al., 2009; Hettiarachchi and Pierzynski, 2002). Hettiarachchi et al. (2001) examined Pb bioavailability in three contaminated soils obtained from repositories and two mine spoils from the Tri-State Mining Region (Kansas, Missouri, and Oklahoma) using PR and PA (applied at 2,500 mg P kg^{-1} soil). The contaminated soils and mine spoils were affected by Pb/zinc smelter activities. Phosphate rock reduced bioaccessible Pb by 20% (Hettiarachchi et al., 2001). Yang et al. (2001) observed similar results when using PA (10,000 mg P kg^{-1} soil) to immobilize Pb in a smelter-contaminated urban soil (4,360 mg Pb kg^{-1}); lead bioaccessibility was reduced by 60%. Amendment with PA was favored over PR because of its ability to lower the soil pH and

facilitate the dissolution of soil Pb. In low-pH soils, bioaccessible Pb has been reduced when amended with biosolids (Basta and Sloan, 1999; Brown et al., 2003; Haering et al., 2000).

Urban soils can commonly be contaminated by more than one contaminant at levels that need to be addressed. Although As occurs naturally in areas across the US, it is a common Pb co-contaminant in urban soils due to past usage of Pb-arsenate pesticides and mining/smelting activities. The most dominant inorganic forms of the metalloid (As) in soil environments are arsenate (As^{5+} in oxyanionic form, AsO_4^{-3}) and arsenite (As^{3+} in oxyanionic form, $H_3AsO_3^0$) (Bhattacharya et al., 2007; Masscheleyn et al., 1991). Arsenate occurs in oxic conditions and is mobilized at high pH, whereas arsenite (As^{3+}) is predominant under reducing environments (Sadiq, 1997; Smedley and Kinniburgh, 2002). Generally, As^{3+} has a weaker adsorption affinity to soil mineral surfaces than As^{5+} and is more mobile (Korte and Fernando, 1991; Manning and Goldberg, 1997; Raven et al., 1998). The major exposure pathway for the metalloid in contaminated soils is through ingestion. The Agency for Toxic Substances and Disease Registry (ATSDR) ranks As and Pb as the most hazardous substances in the US (ATSDR, 2011). Damage to the CNS, kidneys, and wart formation are some of the symptoms of long-term oral As exposure (Ahsan et al., 2006; Centeno et al., 2002).

Remediating soils contaminated with both Pb and As can be challenging. Arsenate and phosphate are chemical analogues with similar sorption patterns (Tu et al., 2004), so As mobility can be enhanced by P treatments. In addition to the presence of competing anions, As solubility is influenced by pH changes and redox conditions. Martinez and Motto (2000) observed an inverse relationship between cation solubility and soil pH during an incubation study involving six acid mineral soils, and a calcareous soil. Although Pb solubility decreases with increasing pH, As solubility increases at alkaline soil pH. Consequently, a narrow range may exist where

one can achieve maximum cationic reduction in soils without having a significant negative impact on its anionic co-contaminants.

Several urban gardens in the Seattle and Tacoma metropolitan area have reported trace element contamination. Surface soils sampled at various locations at a community garden in Tacoma, WA, had Pb and As concentrations ranging from 122 to 217 and 88 to 118 mg kg^{-1} of soil, respectively. In Seattle, WA, soil Pb concentrations at a site intended for community gardening were from 506 to 2,022 mg kg^{-1}. Contamination of the Tacoma site has been attributed to dust deposition from a copper smelter that operated in Ruston, WA, for over 100 years. An interactive map from the Washington Department of Ecology estimates that properties within a 1-mile radius to the north and southwest of Ruston smelter site have elevated levels of As above 100 mg kg^{-1}. Properties within a 1-mile radius to the southeast of the smelter site had soil As concentrations from 40 to 100 mg kg^{-1} (Washington State Department of Ecology, 2013). High Pb concentrations at the Seattle site have been attributed to deposition of lead-based paint caused by frequent sand-blasting of a water tower present at a corner of the site until early 1980s.

Evaluation of the Tacoma and Seattle test sites provided a prime opportunity to assess the suitability of gardening safely on these soils. Consumption of crops grown in these soils may present the opportunity for indirect soil-plant-human transfer whereby trace elements can enter the human system and cause potential harm. The lack of proper cleaning procedures, especially for root and low-growing plants (to which soil particles usually adhere) can be a cause of concern. The lack of science-based maximum concentration limits for common contaminants in vegetables and other crops has resulted in alarmist concerns, indecision, and reliance on hearsay.

To address these concerns, we conducted *in situ* field-based studies on plots alongside the urban gardens at both locations. The soil-plant-human indirect pathway was evaluated using

three common vegetable crops with three very different growth and contaminant uptake patterns (a root crop, a leafy vegetable, and a fruiting crop) planted over two growing seasons. Here, the effectiveness of two different organic amendments to reduce Pb and As uptake in the crops was assessed. A locally produced biosolid (TAGRO) product plus dolomite were evaluated at the Tacoma site, and Cedar-Grove Compost (recycled yard and food waste) plus dolomite (CGC plus dolomite) was evaluated at the Seattle site.

The effectiveness of cleaning procedures in reducing Pb and As concentrations in the edible portion of vegetables was also evaluated. The three cleaning protocols used were kitchen-style washing, thorough laboratory cleaning, and peeling (carrots only). Bioaccessibilities of soil Pb and As were measured in the test soils at the end of the growing season to evaluate soil-human direct exposure pathway.

MATERIALS AND METHODS

Study Sites

Located in Pierce County, WA, the Tacoma urban garden is within three miles south of a former 67-acre copper (Cu) smelter that was designated as part of the Commencement Bay Superfund Site in 1983 (Fig. 3.1). The Superfund area encompasses northwestern Tacoma and the entire town of Ruston, WA. The Commencement Bay Superfund Site is located at the southern end of Puget Sound (an inlet to the Pacific Ocean, part of the Salish Sea that consists of waterways and basins).

The test site (site A) was located on property owned by a local church on the west side of the city of Tacoma, WA (47°16′ N, 122°31′ W). Prior to plot establishment, the site was under continuous shrub/heavy vegetative cover. The site is mapped as the Alderwood soil series (glacial till soil), and the soil is classified as a loamy sand (loamy-skeletal, isotic, mesic Aquic

Dystroxerepts), with the A horizon having about 2% cobbles. The Tacoma garden (~ 1000 m^2) was subdivided into small plots where gardeners cultivated vegetables in raised beds. Gardeners were not allowed to grow anything directly in the soil due to litigation concerns. Surface soils (0 to 15 cm) sampled prior to plot establishment in May 2010 indicated a moderately acidic pH (5.6) environment, electrical conductivity (EC) of 0.1 dS/m, and total organic carbon (TOC) of 1.7% (see Table 3.1 for selected soil properties). Within this garden, test plots (6.4 m x 6.4 m) were installed *in situ*.

The second test site (site B) was in the Rainier Valley district of Seattle, WA, at the intersection of 51st Ave. South and South Leo St. (47°30′ N, 122°16′ W), approximately 32 miles northeast of site A (Fig. 3.1). The site was on a long-term lease by the Seattle Department of Neighborhoods from a local resident for the community garden. The garden (~1,400 m^2) is located on an abandoned lot previously occupied by a water tower. Water towers constructed in the 1960s and their support bases of metal pylons were coated with lead-based paints repeatedly for many years. The tower was sand-blasted and painted annually, so paint chips and their associated lead residues were deposited in the immediate vicinity of the tower and made their way into the soil surface.

The Seattle site is classified as a sandy loam and mapped as the Alderwood soil series. Soil pH is moderately acidic (5.6), electrical conductivity (EC) is 0.3 dS/m, and TOC is 2.7% (see Table 3.1 for selected soil properties).

Site Screening

Direct field screening for trace element concentrations was done using a Niton XL3t portable x-ray fluorescence (XRF) analyzer (Billerica, MA) on a grid format. The analyzer was placed on a cleared soil surface and held for a period of 120 seconds. Surface (0 to 15 cm) soil

samples were collected at random garden/property locations using a plastic hand trowel. Urban debris (broken glass, metal, wood, asphalt, and plastics) and plant materials were removed prior to soils being placed in air-tight Ziploc bags. Soil sampling points were geo-referenced with a Garmin eTrex 10 (Garmin, US) GPS receiver to account for spatial distribution. Following total digestion (EPA 3051A), soil digestates were analyzed for total metals by ICP-OES to confirm XRF results.

Soil samples were taken before and after amending the soil and immediately following harvest. All soil samples were air-dried and sieved (<2.0 mm) to obtain a working sample for conducting pH, electrical conductivity, total Pb and As, available N, and extractable P and K. Within a test plot, soils were chosen from four to five locations and composited to obtain a representative sample.

Test Plot Preparation

The sites were cleared with a brush cutter and later tilled to a depth of 15 to 18 cm using a 13-horsepower rototiller. Site A was a square transect (6.4 m x 6.4 m) comprising four randomized complete blocks (Fig 3.2a). A block (3.05 m^2) was divided equally (1.52 m x 3.05 m) into two main plots (a non-amended control and a treated plot). The blocks at site B were arranged in a straight line with 0.6 m distance between them due to positions of the remnant cut-out pylons (Fig. 3.2b). The experimental design at site B was also a randomized complete block.

The outer edge of the blocks and the plot dividers were marked with plastic lawn garden edging pieces (20 cm high). Garden edging pieces were aligned such that ~ 12 cm was aboveground. A corridor (0.3 m) between blocks helped to facilitate gardening activities such as weeding, fertilizer application, and harvesting.

The amended plot at the Tacoma site consisted of TAGRO biosolids plus dolomite. TAGRO (50% biosolids, 25% sand, and 25% sawdust) was obtained from the TAGRO facility located in Tacoma, WA. At the Seattle site, CGC plus dolomite was used as the amendment. Annual application rate of TAGRO and CGC per block was 28 kg/m^2. The amendment was applied evenly across the plot and incorporated into the soil to a depth of 15 cm using a garden fork. Dolomite was added to increase the soil pH to near neutral (6.8 to 7.4). Subsamples of both amendments were sent to an agricultural testing lab for general characterization. Additional samples were digested via microwave digestion (EPA 3051A) and analyzed for trace metals by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

Soil pH (soil:deionized water; 1:5) was measured using a Thermo Scientific Orion 9157BNMD glass electrode (Beverly, MA). Soil texture was determined using the hydrometer method (Bouyoucos, 1962). Total organic C and N were measured by dry combustion on a LECO CN-2000 Elemental Analyzer (LECO Corporation, St. Joseph, MI) following pretreatment with phosphoric acid to remove excess carbonates. Extractable P was determined using the Mehlich-3 P test (Mehlich, 1984), extractable K by the ammonium acetate extraction method, available nitrogen (N) by KCl (2.0 *M*) extraction (Keeney and Nelson, 1982), and cation exchange capacity (CEC) by the summation method (Chapman, 1965).

Planting Material, Spacing, and Harvesting

A root vegetable (carrot), a leafy vegetable (lettuce), and a fruit vegetable (tomato) were selected for the study at both test sites. Carrots (*Daucus carota* var. *Red Cored Chantenay*), were seeded directly in two rows (30 cm apart) in the center of the plots (0.9 m x 1.5 m). Lettuce (*Lactuca sativa* var. *North Star*) seedlings obtained from Sterino Farms (Puyallup, WA) were planted 30 cm between and within rows, and tomato (*Solanum lycopersicum* var. *Early Girl*)

seedlings were planted 46 cm apart. At the Tacoma site, overhead irrigation was used, while at the Seattle site soaker hoses were utilized. At both sites, a daily timer was set to maintain consistent soil moisture during the dry summer months.

Lettuce and carrots were harvested at 8 and 14 weeks, respectively, and tomato fruits were harvested upon turning red (14 weeks old on average). The harvesting knife and hand shovel were cleaned with Liquinox (Alconox Inc., White Plains, NY) solution between subplots. Liquinox is a biodegradable, phosphate-free laboratory detergent. Produce was placed in labeled Ziploc bags, packaged with icepacks in cooler bags, and shipped overnight to the Kansas State University Agronomy Soil Chemistry Laboratory. Once received, the produce was weighed, photographed, and separated into two equal portions in preparation for cleaning procedures.

Kitchen cleaning was mimicked by washing thoroughly with tap water. A laboratory cleaning procedure included washing with a solution of 5 g kg^{-1} sodium lauryl sulfate (SLS) ($CH_3(CH_2)10CH_2OSO_3Na$) followed by thorough rinsing with deionized water to remove any adhering soil particles. Sodium lauryl sulfate is a preferred anionic surfactant because of its low toxicity, excellent dispersive properties, and stability at low pH (Tricca, 1994). A third cleaning procedure (peeling) was used for carrots; here, the epidermis of some of the kitchen-cleaned carrots was removed. All plant samples were dried in a model 6921 Fisher Scientific Isotemp oven (Marietta, OH) at 65 °C for 5 days or until a constant weight was obtained. Each plant sample was subsequently ground in a stainless steel model 3383-L10 Wiley mill (Swedesboro, NJ) to pass a 60-mesh screen. The powdered plant material was then stored in labeled polyethylene vials until future analysis.

Soil Sample Preparation and Laboratory Analyses

Soil pH, TOC, and extractable P were analyzed as described above. About 10 g of soil was ground using a porcelain mortar and pestle. From this homogenized sample, 1.0 g was carefully weighed out into a 75 mL Teflon tube. A 20-mL aliquot of trace metal-grade concentrated nitric acid (70%) was added to each tube. The soil samples were digested on a CEM Microwave Accelerated Reaction System, model MARS (Matthews, NC) according to USEPA method SW846-3051A (USEPA, 2007). Following digestion, the samples were filtered with Whatman No.42 filter papers into polyethylene vials. Digests were analyzed for total Pb and As on an ICP-OES (Varian Inc., Australia) or graphite furnace atomic absorption spectrometer (240Z GFAAS, GTA 120; Varian Inc., Australia). For quality assurance and quality control (QA/QC), a reagent blank and a standard reference material (2711a-Montana soil) were digested with each set of soil samples. All samples were digested in duplicate. A few treatment samples were spiked with known amounts of Pb to calculate recoveries.

Plant Sample Preparation and Laboratory Analyses

Plant samples were handled in an ESCO Class II type A2 biological safety cabinet (ESCO Technologies, Hatboro, PA) equipped with Ultra Low Particulate Air (ULPA) filters to avoid contamination by lab air. The previously ground plant material was mixed thoroughly, prior to weighing out 0.5 g on a model SA120 Scientech precision balance (Scientech, Boulder, CO), and placed into 55 mL Teflon tubes (CEM, Mathews, NC). A 10-mL aliquot of trace metal-grade concentrated nitric acid (70%) was carefully added, and the contents allowed to sit for 15 minutes in the fume hood to allow venting. Teflon tubes were tightened with a torque wrench to 5 ft.*lbs., placed on the carousel, and digested on the CEM MARS unit (Matthews, NC). The tubes were ramped up to 200 °C and held for 15 minutes (1600 W @ 100%, 15-minute ramp

time, 15-minute cooling time). Following digestion, the tubes were removed from the unit and left to cool in the fume hood for an hour or until the contents were at room temperature. Teflon tubes were uncapped slowly, and the solution was filtered through Whatman No. 42 filter papers into screwed plastic scintillation vials under the fume hood. Samples were then stored at 4 °C until chemical analysis.

All plant samples were prepared in triplicate. National Institute of Standards and Technology (NIST) standard reference materials (tomatoes: 1573a; apple leaves: 1515) were digested and analyzed alongside the plant materials. Plant samples were analyzed on an AA240Z graphite furnace atomic absorption spectrometer (Varian Inc., Australia) with Zeeman background correction.

Bioaccessible Pb and As Measurement

A physiologically based extraction test (PBET) as described by Ruby et al. (1996) was modified following Medlin (1997) to evaluate soil ingestion risks at the garden test sites. Composite soil samples from each of the treated subplots were used for the PBET procedure. Gastric solution was prepared and acidified to pH 2.5 with trace metal-grade HCl. An aliquot (100 mL) of the prepared solution was added to 1-g soil sample (sieved to <250 µm) in a 250-mL high-density polyethylene bottle (HDPE) and secured tightly. The mixture was placed on a model 4730 Queue Orbital Shaker (Parkersburg, WV) for an hour at 37 °C. Following extraction, the pH of the supernatant was re-evaluated to observe any deviation by more than 0.05 log units and adjusted accordingly with trace metal-grade HCl. A 20-mL aliquot of the supernatant was then filtered through 0.45-µm syringe filters into scintillation vials and analyzed within three days. To ensure the repeatability and consistency of the PBET method, a NIST soil standard

(SRM 2711a; a moderately contaminated soil from Montana) and blanks were routinely included in PBET analysis.

Data Analysis

Statistical analyses were performed using SAS for Windows version 9.2 (SAS Institute Inc., 2009). The data were analyzed using PROC ANOVA. Tukey's Honestly Significant Difference (HSD) test was used for means separation ($\alpha = 0.05$).

RESULTS AND DISCUSSION

The physicochemical properties of the selected urban garden site test plots are presented in Table 3.1. The soil at the Seattle tower site test plots can be classified as a sandy loam (66% sand), whereas Tacoma site test plots are loamy sand (78% sand). The Tacoma site also had a significant amount of large gravel, some ranging from 10 to 16 cm in diameter. Soil pH at both test plots was moderately acidic (5.6, Table 3.1). Like most urban soils, the nutrient content at both sites was poor and almost inadequate to be used as a growing medium for community gardens. The available nitrogen at both test sites was low (Table 3.1). At the Tacoma site, available nitrogen was ~ 25 mg kg^{-1} and ~ 10 mg kg^{-1} at the Seattle site. The cation exchange capacities (CEC) at both sites were similar (9 to 13 meq/100g) and moderate for these soils, although the clay content at the Tacoma site was half (6%) that of Seattle site (12%) (Table 3.1). Prior to the establishment of test plots, the soils were under continuous grass (Seattle) and heavy brush/shrub (Tacoma) cover for more than three years. Percentage TOC at the Seattle site is about 54% higher than the Tacoma site, which may be due to the higher clay content found at the undisturbed Seattle site.

Selected properties of the amendments used at each site are presented in Table 3.2. Both amendments have similar moisture content and pH (slightly alkaline). Percentage organic carbon

in Cedar-Grove composts is higher (~ 3 times) than TAGRO mix biosolids. Total Fe (%) in Cedar-Grove composts was high (1.11%), which is not entirely unusual for leaf-based compost. Green waste compost used by Hartley et al. (2009) to remediate three brownfields soils had 1.6% Fe. TAGRO mix biosolid has a slightly higher percentage P (0.34 vs. 0.29) than the compost, which has about five times the amount of soluble salts (Table 3.2). Lead and As concentrations (9.55 and 3.21 mg kg^{-1}, respectively) in the TAGRO mix biosolid were comparable to those found in biosolid composts used by Cao and Ma (2004). Higher Pb and As concentrations (40 and 15 mg kg^{-1}, respectively) were observed for CGC, while significantly lower Pb (18 mg kg^{-1}) and As (4.24 mg kg^{-1}) concentrations have been reported for some other green waste/leaf composts (Hartley et al., 2009; Sauvé et al., 2000).

Lead in Tacoma soils

Soil Pb concentrations at the Tacoma test plots were heterogeneous and ranged from 88 mg kg^{-1} to 312 mg kg^{-1} in 2010 (Fig. 3.3). In 2011, soil Pb concentration decreased slightly (51 mg kg^{-1} to 269 mg kg^{-1}) (Figs. 3.5 & 3.6)], most likely due to the dilution effect of previous TAGRO additions. The total Pb concentration of TAGRO is ~ 10 mg kg^{-1} (Table 3.2). When TAGRO is added to the soil, the overall soil Pb concentration is lowered, hence the dilution effect. The level of soil Pb contamination at this site is not uncommon compared to urban soils where gardening activities have been practiced (Minca and Basta, 2013; Nabulo et al., 2010; Spittler and Feder, 1979). Attanayake et al. (2014) evaluated soil-plant transfer in vegetables grown on a highly compacted urban garden in Kansas City, MO, with 21% clay content and soil Pb concentrations ranging from 60 to 300 mg kg^{-1}.

Treatment plots amended with TAGRO plus dolomite had significantly (α =0.05) lower soil Pb concentrations than non-amended plots for both growing seasons. Soil Pb concentrations

after treatment application were reduced by 10 to 23% (data not presented). Compost amendments have been known to have a dilution effect on soil Pb concentrations. Farfel et al. (2005) reported a 12 to 20% decrease in mean soil Pb concentrations of urban yards (800 to 2,003 mg kg^{-1}) when they were amended with Orgro biosolids compost (110 to 180 dry t/ha). More recently, Attanayake et al. (2014) reported decreases (29 to 52%) in soil Pb concentration in an urban garden soil amended with leaf compost.

Assessing safe Pb concentrations in Tacoma vegetables

Lead levels in the edible portions of the three crops grown at the site are presented in Figs. 3.3, 3.4, and 3.5. Plant Pb concentration was consistently highest in the root vegetable (*D. carota* var. *Red Cored Chantenay)*, followed by lettuce and tomato. In 2010, Pb concentrations in peeled carrots grown in non-amended plots were 19.4 mg kg^{-1}, and those grown in TAGRO plus dolomite amended plots were 8.9 mg kg^{-1} (Fig. 3.3). Lead accumulation in carrots (root) was about 16 to 18 times higher than the lettuce (leaves) and tomatoes (fruits) analyzed. Lead accumulation has been found to be high in roots due to their ability to bind Pb in the xylem, consequently limiting its translocation to other plant parts (Finster et al., 2004; MacFarlane and Burchett, 2000). Despite varying uptake values among vegetable types, Pb concentrations were significantly (α=0.05) lower in plots amended with TAGRO + dolomite (Figs. 3.3 to 3.5). The Pb concentration values of lettuce and tomatoes showed a greater response to the applied treatment. Plant Pb concentrations in these vegetables were about 25 to 80% lower when grown on the TAGRO plus dolomite-amended plots vs. those grown on non-amended plots (Figs. 3.3 to 3.5). In addition to the dilution effect, transformation of soil Pb induced by amendment addition may have resulted in less soluble Pb available for absorption into the plant and translocation of absorbed Pb from roots to aboveground plant parts. Compounds and treatments with high

phosphorus (P) content have been found to bind soil Pb and make them less mobile in soil as well as in roots (Basta and McGowen, 2004; Hettiarachchi and Pierzynski, 2002; Laperche et al., 1997; Yang et al., 2001).

The World Health Organization (WHO) and the Food and Agricultural Organization (FAO) established the CODEX Alimentarius Committee to develop maximum levels (MLs) of contaminant concentrations in vegetables and crops. Maximum levels were deduced on the analysis of the edible plant part; expressed on a fresh weight basis. The MLs for Pb in root or tuber vegetables, and fruiting vegetables were set at 0.1 mg kg^{-1} (FAO/WHO-CODEX 1995; 2010 amendment). Brassica and leafy vegetables MLs for Pb are 0.3 mg kg^{-1} (FAO/WHO-CODEX 1995; 2010 amendment). The values were derived on the assumption that 100% of Pb present in produce is bioavailable, so these safe limits are overly protective. We evaluated plant Pb in the vegetables on a dry weight basis. For comparison purposes, CODEX MLs were converted to a dry weight basis using moisture content of the sampled materials.

The water content of carrots have been found to range from 88 to 93% (Patras et al., 2011; Sipahioglu and Barringer, 2003; Tsukakoshi et al., 2009). Moisture content of lettuce is 94 to 95% (Agüero et al., 2008; Patras et al., 2011), and tomatoes have 92 to 95% moisture (Martínez-Valverde et al., 2002; Patras et al., 2011). Calculated Pb MLs (dry weight basis) took into account the range of moisture content for the vegetables. Carrot, lettuce, and tomato MLs on a dry weight basis ranged from 0.8 to 1.4 mg kg^{-1}, 5 to 6 mg kg^{-1}, and 1.3 to 2.0 mg kg^{-1}, respectively.

Irrespective of treatment and planting period, plant Pb concentration in carrots exceeded (~ 4 to 6 times) the calculated MLs (Fig. 3.3). Effective accumulation of Pb in carrots presents the potential for associated Pb health risks if these crops are consumed. For this reason,

gardeners should refrain from growing root vegetables directly in soils with mildly elevated Pb levels (> 200 mg kg^{-1} in sand-rich soils with low pH), even when amended with biosolids or compost materials. Our results revealed that Pb concentrations in both lettuce and tomato were below their respective calculated MLs (5 to 6 mg kg^{-1}, lettuce; 1.3 to 2 mg kg^{-1}, tomato) (Figs. 3.4 and 3.5). Consumption of lettuce and tomato grown at our Tacoma site does not present a health risk.

Effect of cleaning on Tacoma vegetables

Generally, the lab cleaning procedure was more effective in reducing Pb concentrations in the vegetables (Figs. 3.3 and 3.4). For tomatoes (Fig. 3.5), only the laboratory cleaning method was done (insufficient mature fruits collected during harvest, fruit loss due to shipping). The surfactant (SLS/sodium dodecyl sulfate) acts as a wetting agent, breaking the electrostatic attractions between adhered soil particles and the edible portions of the vegetables.

Mixed results were observed for carrots during both field trials (Fig. 3.3). Lead concentrations in peeled carrots were highest in 2010 in both control and TAGRO plus dolomite plots. In 2011, lead concentrations in peeled carrots and those cleaned with SLS showed no statistical difference (Fig. 3.3 control plots). Measured Pb concentrations were about 25% lower when cleaned with SLS compared with those washed by the kitchen-cleaning method. A possible reason could be the rough surface area (presence of nooks/crevices) of carrots contributing to incomplete removal of adhered soil particles irrespective of the cleaning solution used. A similar study conducted by Attanayake et al. (2014) showed no statistical difference in cleaning procedures for Pb concentrations in carrots (peeled, kitchen-cleaned, use of SLS) when plants were grown on a compacted urban garden site with high clay content (21%). Our Tacoma garden site was a predominantly glacial till soil with significantly less clay (6% clay content).

Unlike for carrots, Pb concentrations in lettuce cleaned with the surfactant were significantly lower than kitchen-cleaned lettuce (2010; α=0.05; Fig. 3.4). In 2010, Pb concentrations decreased 25% when lettuce harvested from non-amended plots was cleaned with SLS solution (5 g kg^{-1}). A greater reduction (50 to 55%) was observed for plants grown on TAGRO plus dolomite plots (Fig. 3.4; 2010). Minimal reductions (10 to 15%) were observed in 2011 (Fig. 3.4). For leafy vegetables, greater reductions in plant Pb concentrations may be obtained when SLS is used as a cleaning agent.

The effectiveness of the surfactant may vary based on the strength of the electrostatic attractions as affected by soil pH and soil texture. Compared to a pH of 7.1 at the Kansas City, MO, site, our soil pH was moderately acidic (5.6). Increased dissolution of soil solids has been shown to occur when SLS is used at higher pH (Jinno et al., 2000). Clay's higher surface area allows for stronger attraction to the outer surface of the vegetable. The absence of the wetting agent in the kitchen cleaning procedure may leave some clay particles on the edible portion of the vegetable. Greater reductions in plant Pb concentration can be expected when plants grown on clay soils are cleaned with a surfactant, but the difference in Pb concentrations on produce cleaned by the various methods is not always significantly different. Finster et al. (2004), for example, found no significant difference (water-only washed/kitchen cleaning vs. detergent-washed) in Pb concentrations of leafy edibles grown on a wide range (27 to 4580 mg kg^{-1}) of Pb-contaminated gardens in Chicago, IL.

Arsenic in Tacoma soils

The Washington State Department of Ecology and the United States Geological Survey have determined that the natural background level of arsenic in the state is 7 mg kg^{-1} (Washington State Department of Ecology, 1994). Arsenic concentrations found in soils at the

Tacoma test site ranged from 37 to 146 mg kg^{-1} (Figs. 3.7 and 3.8). Soil As concentrations at the garden site exceed Washington State's 20 mg kg^{-1} cleanup limit for unrestricted land use areas. (Washington Administrative Code, 2007).

Assessing safe As concentrations in Tacoma vegetables

In general, As concentrations in all three vegetables were low (< 840 µg kg^{-1}) (Figs. 3.6, 3.7, and 3.8). A previous study reported mean As concentrations in lettuce (dry weight basis) that were as high as 6,770 µg kg^{-1} when the plants were grown on a former smelter site with soil As concentrations from 489 to 1,184 mg kg^{-1} (Warren et al., 2003). Soil pH of the former smelter site was 7.3, and clay content was 21.7% (Warren et al., 2003).

Arsenic concentrations in tomatoes were the lowest (<130 µg kg^{-1}) amongst the vegetables grown, whereas As in lettuce ranged between 134 µg kg^{-1} in TAGRO plus dolomite amended plots to 830 µg kg^{-1} in control plots (Fig. 3.7). Arsenic concentration in carrots ranged from 111 to 314 µg kg^{-1}, and there was no significance in treatment (Fig. 3.6). Lettuce grown on TAGRO plus dolomite-amended plots had As concentrations about four times lower than those grown on non-amended plots (Fig. 3.7). The TAGRO plus dolomite amendment reduced As concentrations in lettuce and tomato fruits (46 to 80%), whereas little or near zero (<10%) reductions were obtained for carrots. Cao and Ma (2004) reported a reduction of 79 to 86% in plant As concentrations of carrots and lettuce (grown in greenhouse pots) when amended with biosolids. In their study, soil As concentrations were from 27 to 43 mg kg^{-1}, and soil pH was moderately acidic (obtained near CCA-treated fences, pH 6.1) to mildly acidic (obtained near utility poles, pH 6.7).

Unlike for Pb, there are no established maximum levels for As in vegetables. We used a conservative maximum level of 1,800 µg kg^{-1}. The Integrated Risk Information System (USEPA,

1993) lists inorganic As reference dose level of 0.0003 mg kg^{-1} day^{-1}. Safe arsenic dose/day (0.09 mg kg^{-1} fresh weight) for a 60-kg human was determined assuming they have a 200 g daily (fresh weight basis) consumption of the vegetable. Using the moisture content of vegetables previously listed (carrots: 88 to 93%; lettuce: 94 to 95%; and tomatoes: 92 to 95%), estimated As MLs (dry weight basis) were calculated (carrots: 750 to 1,286 µg kg^{-1}; lettuce: 1,500 to 1,800 µg kg^{-1}, and tomato: 1,125 to 1,800 µg kg^{-1}).

Lead in Seattle soils

The Pb concentration at the Seattle site was high, from 695 to 1,854 mg kg^{-1}, prior to amendment (Table 3.7). Total soil Pb concentrations were measured before and after incorporating the CGC plus dolomite treatment. A 20 to 50% dilution effect was observed following compost addition (Table 3.7). High variability within blocks at the site could be attributed to the wide range in dilution observed. For example, Pb concentrations in the amended plots (prior to amendment) were from 695 to 1,661 mg kg^{-1} in 2011 and 699 to 1,854 mg kg^{-1} in 2012 (Table 3.7). Research has demonstrated that the addition of biosolids and other organic amendments to contaminated soils had a dilution effect on total soil elemental concentrations, often leading to reduced bioaccessibility of the metals/metalloids (Attanayake et al., 2014; Brown et al., 2003; Brown et al., 2012; Farfel et al., 2005).

The application of CGC resulted in significant reductions in the uptake of Pb among all of the vegetables. The results were in agreement with other studies that evaluated the efficacy of compost addition as a viable *in situ* remediation strategy. Lettuce grown in a contaminated urban soil where the Pb concentration was 3,250 mg kg^{-1} had uptake values as high as 37.6 mg kg^{-1} dry weight (Bassuk, 1986). The addition of “muck” and decomposed organic manure (25% by volume) resulted in a reductions of Pb uptake of lettuce by 73% and 63% respectively.

Assessing safe Pb concentrations in Seattle vegetables

Lead concentrations in vegetables grown at the Seattle site are presented in Figs. 3.9 to 3.11. Because soil Pb concentrations were high, Pb concentrations in all the vegetables grown at the site were also high. A clear trend was observed in the uptake pattern of Pb in the edible portions analyzed. Plant Pb concentrations for the vegetables in decreasing order were carrots > lettuce > tomatoes. Lead concentrations exceeded FAO/WHO-CODEX limits, and the calculated MLs. Tomato fruits analyzed had Pb concentrations about 15 to 20 times lower than carrots, which indicated that translocation of Pb to fruits is minimal irrespective of soil contaminant level or treatment application. Our results are consistent with the observations of most researchers who have documented higher Pb accumulations in root vegetables or other plant roots (Chaney et al., 1984; Cobb et al., 2000; Finster et al., 2004; Samsøe-Petersen et al., 2002). A similar order of Pb concentrations in vegetables was observed at our Tacoma site where total Pb concentrations in soils were less than 300 mg kg^{-1}.

Plant Pb concentrations of carrots grown at the Seattle site were about 2 to 3 times greater than those grown at the Tacoma site (Figs. 3.3 and 3.9). Greater differences (3 to 5 times higher) were observed for lettuce grown at both sites (Figs. 3.4 and 3.10). For tomatoes, Pb concentrations were relatively similar despite differences in soil Pb (51 to 312 mg kg^{-1} at Tacoma vs. 506 to 2,022 mg kg^{-1} at Seattle). Our results are in agreement with Finster et al. (2004), who reported significant correlations between root and soil Pb.

Effect of cleaning on Seattle vegetables

In general, the lab cleaning procedure was more effective than kitchen-style washing in reducing the Pb concentrations in lettuce and tomatoes grown at the Seattle site (Figs. 3.9 to

3.11). Lettuce grown on CGC plus dolomite amendments and cleaned by the kitchen-cleaning procedure had 55% less Pb than those grown in non-amended soils (1,132 to 1,579 mg kg^{-1}).

Mixed results were observed for carrots cleaned by the three procedures for the two growing seasons. In 2011, Pb concentrations of peeled carrots were significantly (p=0.05) higher than the other cleaning procedures, irrespective of treatment (Fig. 3.9). Lead accumulates in the inner meristematic cells of carrots (Codling et al., 2007). Because the cortex layer is reduced during peeling, higher Pb concentration is observed in peeled carrots. In 2012, peeled carrots had lower Pb concentrations than either kitchen-cleaned or lab-cleaned carrots. The lower Pb concentrations in peeled carrots during 2012 may be a result of a greater quantity of produce used for analysis.

Bioconcentration Factor

Bioconcentration factor (BCF) is an important parameter used to evaluate food-chain transfer of crop contaminants (Alam et al., 2003; Samsøe-Petersen et al., 2002). The BCF was calculated as the ratio of dry weight basis concentrations of the contaminant in the vegetable and in the soil in which plants were grown. Both Pb and As bioconcentration factors were calculated using the plant concentrations of the lab-cleaned vegetables. The BCF-Pb was low for all of the crops (Table 3.3). Carrots BCF-Pb were the highest in both the amended and non-amended plots (2010, 2011). In the control plots, carrots BCF-Pb was 0.141 and about two orders of magnitude higher than tomatoes, although soil Pb concentrations were similar (~ 172 mg kg^{-1}). This indicates that soil metal concentration is not solely responsible in the determination of plant Pb uptake. Generally, BCF-Pb in all of the vegetables was lower when grown on the amended plots (Table 3.3). TAGRO plus Dolomite amendments helped reduce BCF-Pb by a factor of six in lettuce plots. A similar pattern was observed for As.

Samsøe-Petersen et al. (2002) evaluated the uptake of seven trace elements and five polyaromatic hydrocarbons (PAHs) in fruits and vegetables grown on soils with varying levels of trace element contamination. From a heavily contaminated soil (soil Pb of 1,000 mg kg^{-1}), they observed Pb-BCFs in lettuce and peeled carrots as 0.001 and 0.05, respectively. Our study revealed a BCF-Pb in lettuce grown on non-amended soils of 0.02. Physicochemical parameters such as soil type, soil pH, and soil metal concentrations may account for the differences in BCF-Pb observed for both studies. Organic matter has been reported to bind certain trace metals in the soil medium, particularly Pb, thus limiting uptake into the plant system (Alloway, 2013; Dudka and Miller, 1999; Hooda et al., 1997; Samsøe-Petersen et al., 2002). Lead solubility increases with decreasing pH (Jørgensen and Willems, 1987; Martinez and Motto, 2000). Thus, Pb mobility was affected by the moderately acidic pH (5.6) found at the Tacoma site.

The BCF-As were very low for all of the vegetables (Table 3.4). The BCF-As for carrots in TAGRO plus dolomite-amended plots were slightly higher (2010) or equivalent (2011) to non-amended plots. In contrast, BCF-As in lettuce and tomatoes were lower for TAGRO plus dolomite plots. In 2010, the BCF-As for lettuce and tomatoes grown in TAGRO plus dolomite treatments were lower than those grown on non-amended plots by a factor of 1.8 and 1.7, respectively. In 2011, BCF-As for lettuce grown in TAGRO plus dolomite treatments were lower than those grown on non-amended plots by a factor of 4.5 and 1.5, respectively. By comparison, with the exception of tomato plots, BCF-As in 2011 for both non-amended and TAGRO plus dolomite treatments were higher than in 2010 (Table 3.4). The increased biomass obtained when composts are utilized may have a dilution effect on plant As concentrations, especially in leafy vegetables.

Bioaccessible Pb and As

Bioaccessible Pb results for the Tacoma and Seattle sites are presented in Figs. 3.12 and 3.13 as a percentage of total Pb concentrations in each subplot soil. In 2010, PBET-Pb for control plots were ~ 15%, whereas TAGRO plus dolomite-amended plots were 8.5 to 11% (Fig. 3.12). In 2011, with the exception of carrot plots (21%), bioaccessible Pb in the other plots was less than 11% for non-amended plots. Compared with non-amended plots, bioaccessible Pb in amended plots was lower by 6 to 7%. Repeated applications of biosolids amendment could result in successive decreases in bioaccessible Pb. Farfel et al. (2005) evaluated Pb bioaccessibility in urban yards in Maryland with soil Pb concentrations > 800 mg kg^{-1}. Farfel et al. (2005) reported high (55 to 50%) Pb bioaccessibility for soils amended with biosolids compost when bioaccessibility was measured using glycine-buffered HCl at pH 2.2. They reported high (55 to 70%) Pb bioaccessibility for soils amended with biosolids compost. Differences in soil Pb concentrations between the two study sites (Maryland vs. Tacoma) and other chemical parameters may account for the difference (>55% vs. <15%) in percentage Pb bioaccessible values reported.

Lead bioaccessibility at the Seattle test site was generally less than 30%. On average, Pb bioaccessibility for non-amended plots was about 20 to 25% at the Seattle site compared with 15 to 20% at the Tacoma site. Differences in sources of soil contamination may lead to variations in Pb bioaccessibilities at both sites. Common forms of lead in paint include lead oxides (Pb_3O_4), lead (II) carbonate ($PbCO_3$), and lead chromate ($PbCrO_4$) (Minca and Basta, 2013; Royal Society of Chemistry, 2007). Lead oxides and carbonates are the most soluble lead species in soil environments (Cao et al., 2003; Lindsay, 1979). When weathering of lead-based paint occurs in

soils, small particles of lead are released and are most likely highly bioavailable (Minca and Basta, 2013). This was evident in the high Pb bioaccessibilities obtained for the Seattle site.

The CGC plus dolomite amendment at the Seattle site was effective in reducing bioaccessible Pb. Lead bioaccessibility in CGC plus dolomite-amended plots was lower by 13 to 15% compared with non-amended plots in both growing seasons (carrot and lettuce plots only) (Fig. 3.13). There was a 4% decrease in 2011, and ~ 13% in 2011 for tomato plots (Fig. 3.13). Low (<30%) Pb bioaccessibility results reported at both sites is an indication that in urban gardens, exposure risks by accidental ingestion of soils may be minimal.

Bioaccessible As at the Tacoma site was low (< 12%). Bioaccessible As at the site was generally enhanced with TAGRO plus dolomite amendment. Percentage PBET-As in control plots were 8.1, compared with 12.0 in amended plots (data not presented). The enhancement may be attributed to the high P content of the TAGRO mix or the incorporation of dolomite in the treatment. Phosphorus has been reported to compete with and replace sorbed As, thus limiting the degree of sorption of As in soils (Manning and Goldberg 1996; Smith et al., 2002). Speciation results (XANES) from an incubation study on the same soil indicated a predominance of As^{3+} (44%) when amended with TAGRO at 10% (w/w) (Defoe et al., 2014, manuscript in preparation). We did not observe the desired increase in soil pH following the addition of dolomite (data not presented). On average, soil pH in TAGRO plus dolomite-amended plots at the end of the 2010 and 2011 growing seasons was ~ 5.5 and 5.9, respectively. The TAGRO may be causing an acidifying effect.

Gardening Implications

Based on our findings, the lettuce and tomatoes grown at the Tacoma site were safe to eat, and exposure risks based on the soil-plant-human pathway were negligible. Some

researchers have recommended complete abstinence from consumption of vegetables grown in soils with Pb concentrations exceeding 400 mg kg^{-1}. Finster et al. (2004) recommended that soils with Pb levels from 400 to 1000 mg kg^{-1} should not be used for gardening. A few studies have suggested certain soil Pb concentration limits that they have deemed unsafe for cultivating certain crops. We opt for a more comprehensive approach in solving the problem on a site-specific basis, since potential urban gardens may vary according to contamination source and complexity, soil physical/chemical characteristics, and the availability of remediation resources. In general, the application of organic amendments and or biosolids (properly tested to ensure that high levels of trace metals/contaminants are not present) on urban soils while maintaining a healthy soil pH is encouraged.

CONCLUSION

Results from this study indicated clear differences in contaminant uptake by the various edible portions of the vegetables analyzed. Lead concentration was high in carrots (9 to 79 mg kg^{-1}) and exceeded the FAO-WHO ML of 0.8 to 1.4 mg kg^{-1} at both test sites. Tomato Pb concentrations were very low (< 2.0 mg kg^{-1}), irrespective of soil Pb level or soil amendments. Low As concentration in all vegetables is an indication that food-chain transfer of As would not be a problem for urban gardeners. The addition of the amendment (TAGRO plus dolomite or CGC plus dolomite) significantly reduced Pb and As uptake in all of the vegetables studied. Leafy vegetables grown on sandy soils where Pb concentrations are greater than 1,000 mg kg^{-1} exceed MLs (5 to 6 mg kg^{-1}), even when amended with CGC plus dolomite. In general, the food-chain transfer of Pb and/or As can be further reduced through the proper cleaning of vegetables. Further studies evaluating a variety of root crops and leafy vegetables grown at different sites

with similar or different contaminant compositions and soil physicochemical parameters such as soil pH and clay content are required to provide greater scientific clarity to urban gardeners.

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Table 3.1. Selected soil physicochemical properties of the urban garden test sites.

Soil property	Test site

	Tacoma	Seattle
pH	5.6	5.6
Sand (%)	78	66
Silt (%)	16	22
Clay (%)	6	12
TOC %	1.7	2.7
TON %	0.13	0.20
Mehlich-3 P (mg/kg)	35.9	30.7
Ext. K (mg/kg)	63.5	88
NH_4-N (mg/kg)	7.0	9.5
NO_3-N (mg/kg)	18.5	0.8
Electrical conductivity(dS/cm)	0.1	0.3
CEC (meq/100g)	12.5	9.4

Table 3.2. Selected physicochemical properties of the amendments used in the study.

Property	TAGRO	Cedar-Grove compost
pH	7.6	7.3
% moisture	53.8	62.4
Iron, %	0.53	1.11
OC, %	10.4	31.8
Organic N, %	0.56	1.48
NH_4^+-N, %	0.13	0.02
NO_3^--N, %	0.04	0.001
P, %	0.34	0.29
K, %	0.1	1.0
Calcium, % Ca	0.4	1.6
Magnesium, % Mg	0.2	0.4
Pb (mg kg^{-1})	9.55	40.9
As (mg kg^{-1})	3.21	15.1
Soluble salts, dS/m	1.53	9.88

Table 3.3. Bioconcentration factor (BCF) of Lead (Pb) in crops grown under non-amended control and TAGRO + dolomite amended plots at an urban garden site in Tacoma, WA, in 2010 and 2011.

	2010		2011	
Crop type†	Non-amended	TAGRO + dolomite	Non-amended	TAGRO + dolomite
	----------mg kg^{-1} DW: mg kg^{-1} DW----------			
Carrot	0.141	0.104	0.130	0.131
Lettuce	0.020	0.003	0.011	0.003
Tomatoes	0.005	0.004	0.012	0.007

†Lab-cleaned samples

Table 3.4. Bioconcentration factor (BCF) of As in crops grown under non-amended control and TAGRO + dolomite-amended plots at an urban garden site in Tacoma, WA, in 2010 and 2011.

	2010		2011	
Crop Type[†]	Non-amended	TAGRO + dolomite	Non-amended	TAGRO + dolomite
	----------mg kg^{-1} DW: mg kg^{-1} DW----------			
Carrot	0.0018	0.0023	0.0040	0.0040
Lettuce	0.0018	0.0010	0.0118	0.0026
Tomatoes	0.0012	0.0007	0.0003	0.0002

[†]Lab cleaned samples

Table 3.5. Soil Pb concentration at the Seattle garden in 2011 and 2012 prior to planting.

	2011			2012		
		CGD†			CGD	
Blocks	Control	Before	After	Control	Before	After
	----------mg kg^{-1}----------					
1	1352 ± 43	1661 ± 34	998 ± 14	1217 ± 45	1854 ± 54	1359 ± 21
2	1333 ± 38	1414 ± 11	1367 ± 30	1395 ± 38	1544 ± 40	915 ± 43
3	1481 ± 27	1289 ± 10	1101 ± 33	1213 ± 19	1298 ± 39	756 ± 24
4	1066 ± 41	695 ± 38	544 ± 11	956 ± 19	699 ± 21	455 ± 19

†CGD = Cedar-Grove (compost) + Dolomite

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Figure 3.1. Location of urban garden test sites in Tacoma-Seattle metropolitan area.

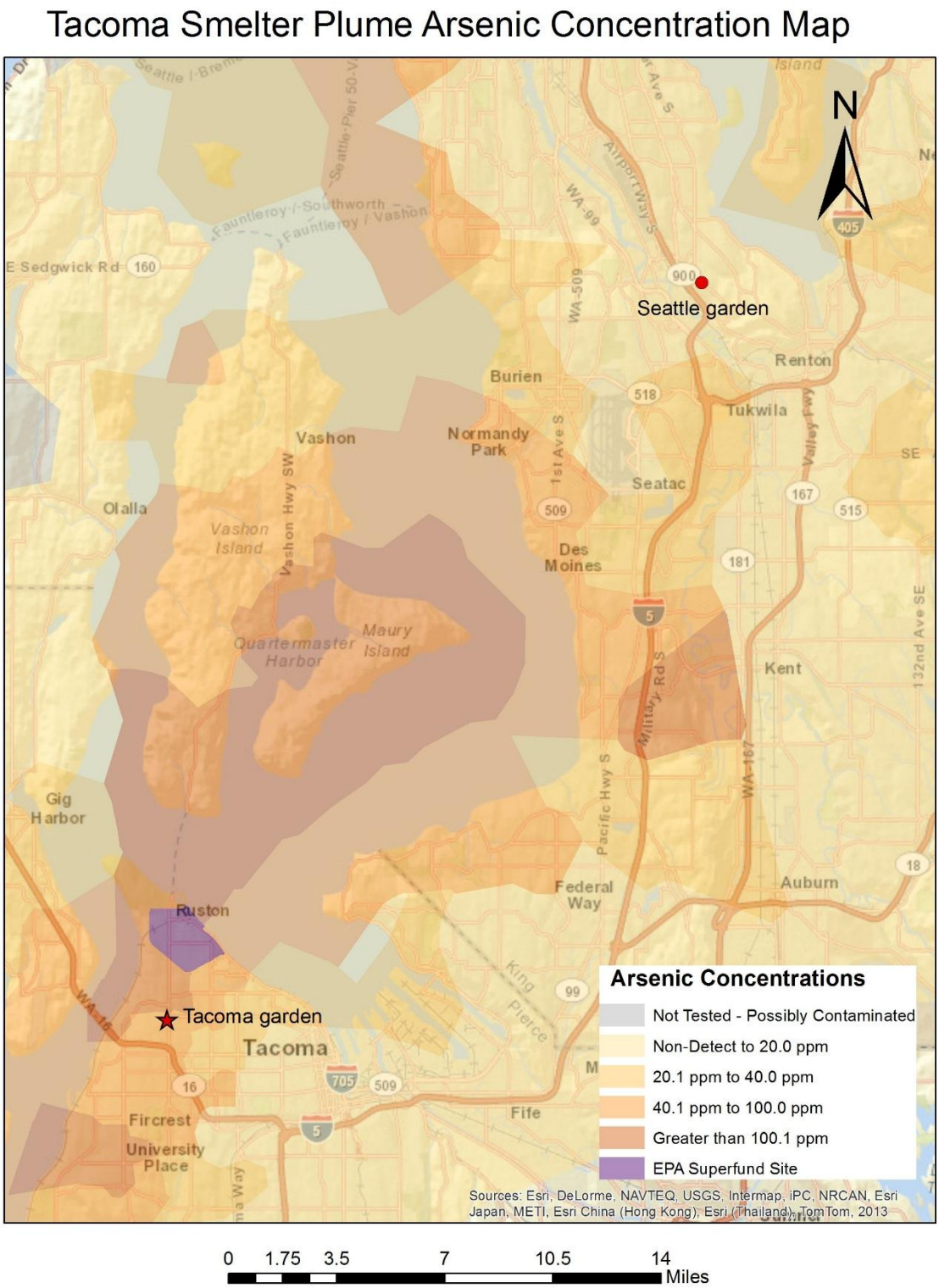


Figure 3.2. Plot diagrams of the Tacoma (A) and Seattle (B) test sites.

A

TAGRO plus dolomite amended plot

Non-amended plot

B

Non-amended plot

CGC plus dolomite

Figure 3.3. Pb concentration in carrots harvested at the Tacoma garden in 2010 and 2011 following three cleaning procedures. Vertical bars represent the mean of four replicates. Different letters within a category indicate significance difference (α=0.05).

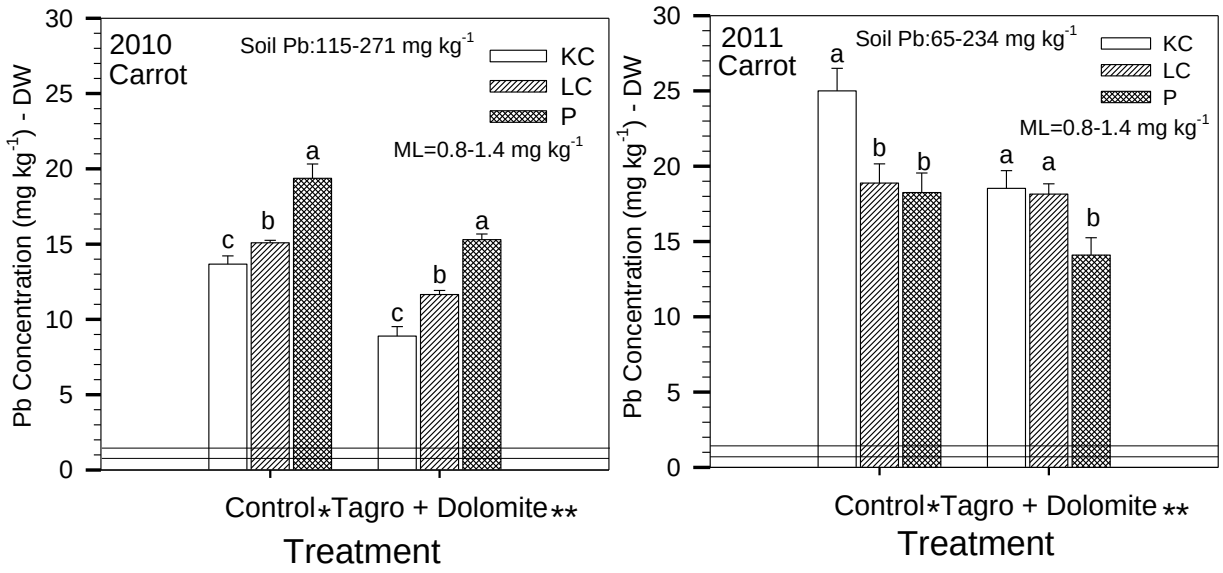


Figure 3.4. Pb concentration in lettuce harvested at the Tacoma garden in 2010 and 2011 following two cleaning procedures. Vertical bars represent the mean of four replicates. Different letters within a category indicate significance difference (α=0.05).

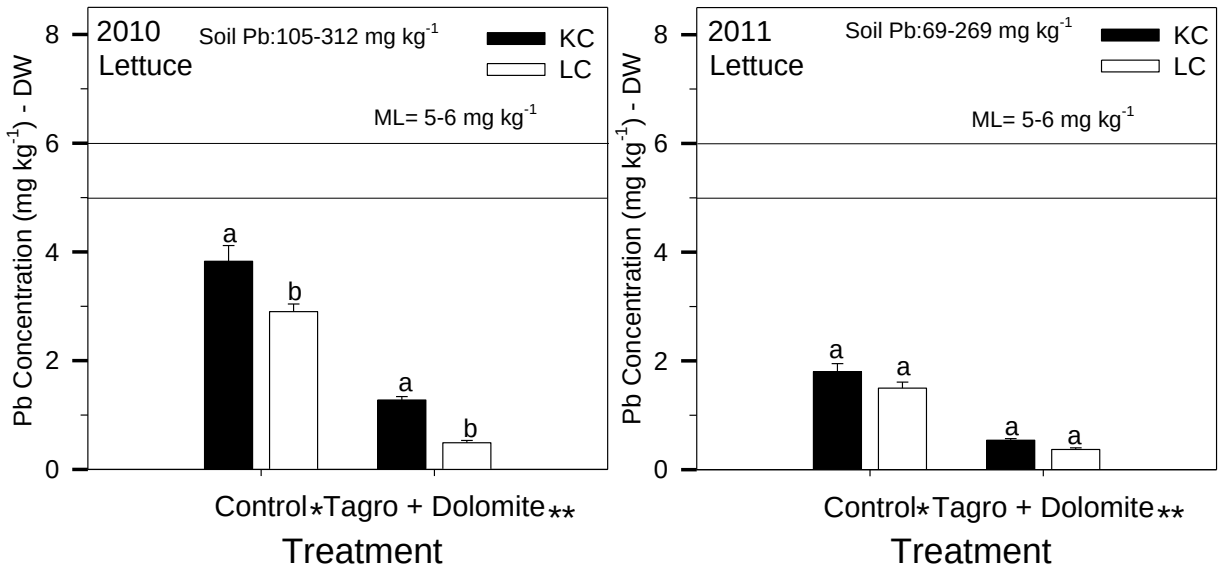


Figure 3.5. Pb concentration in tomatoes harvested at the Tacoma garden in 2010 and 2011 following the lab cleaning procedure. Vertical bars represent the mean of four replicates. Different letters within a category indicate significance difference (α=0.05).

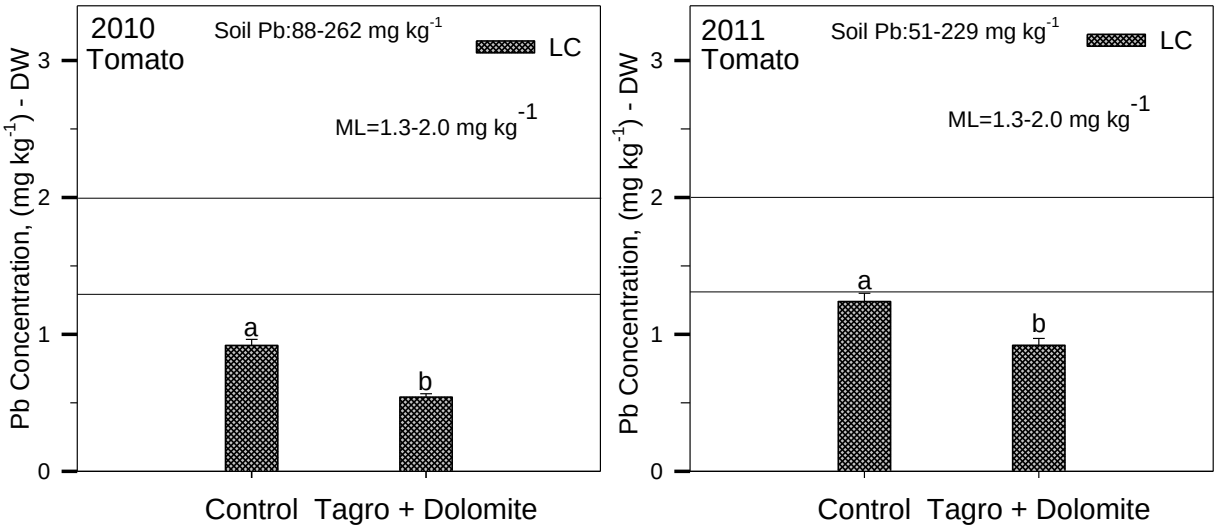


Figure 3.6. As concentration in carrots harvested at the Tacoma garden in 2010 and 2011 following three cleaning procedures. Vertical bars represent the mean of four replicates. Different letters within a category indicate significance difference (α=0.05).

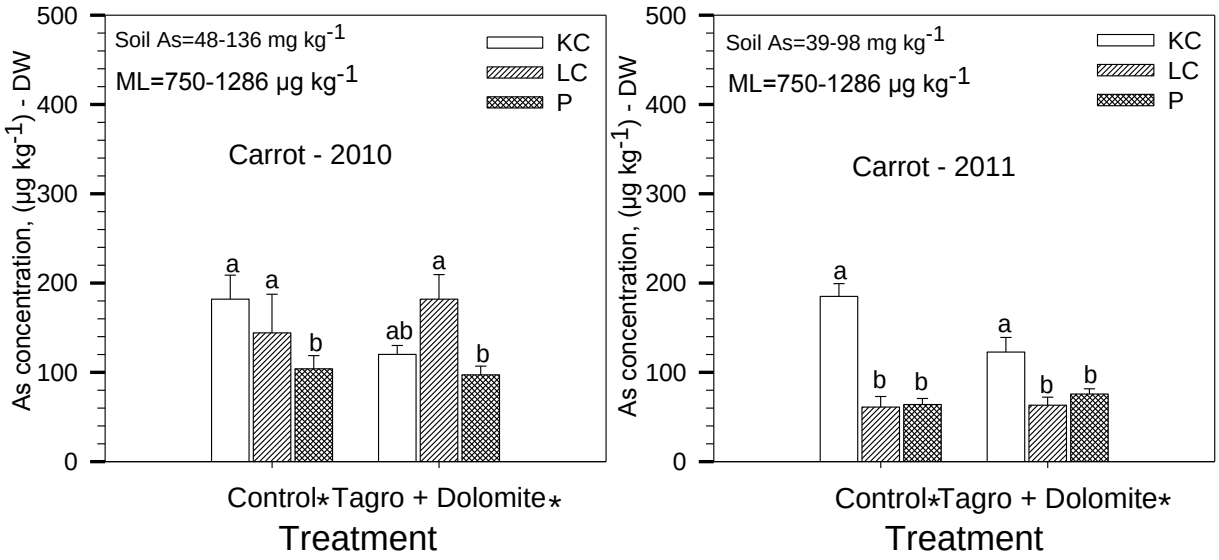


Figure 3.7. As concentration in lettuce harvested at the Tacoma garden in 2010 and 2011 following two cleaning procedures. Vertical bars represent the mean of four replicates. Different letters within a category indicate significance difference (α=0.05).

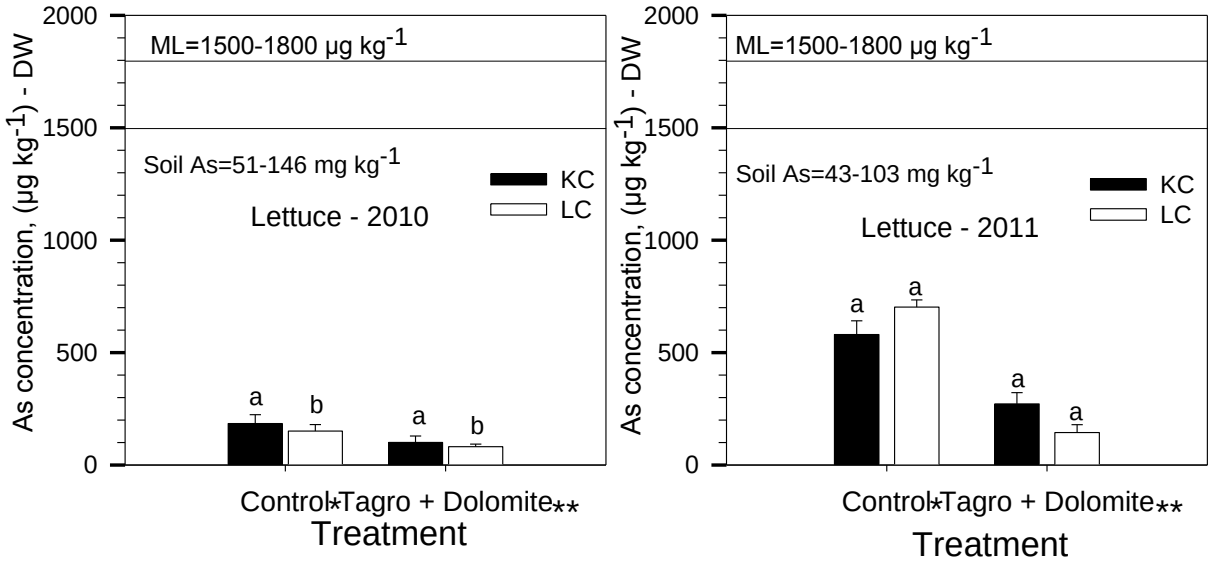


Figure 3.8. As concentration in tomatoes harvested at the Tacoma garden in 2010 and 2011 following the lab cleaning procedure. Vertical bars represent the mean of four replicates. Different letters within a category indicate significance difference (α=0.05).

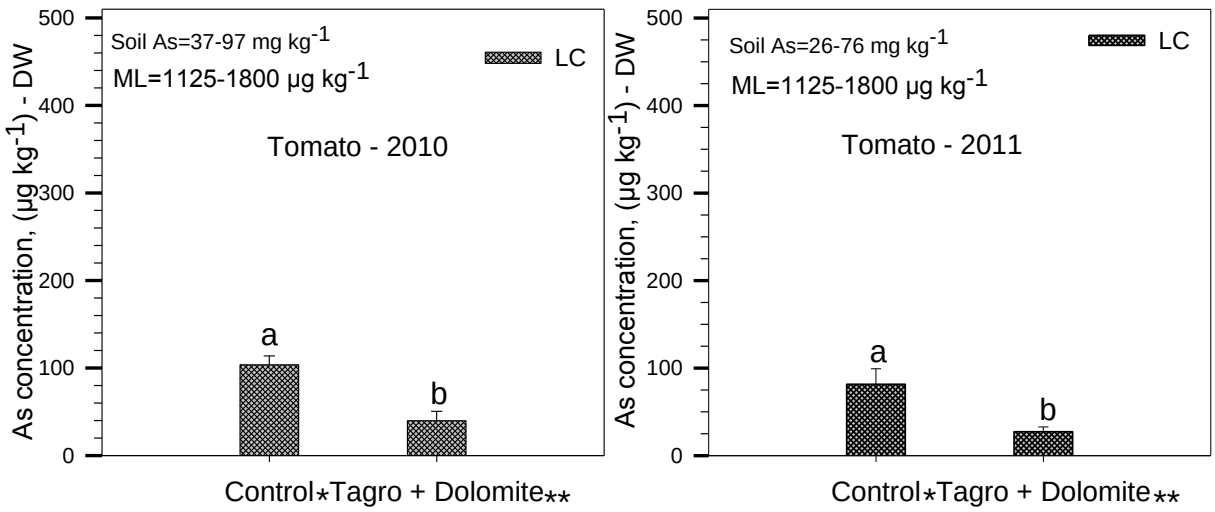


Figure 3.9. Pb concentration in carrots harvested at the Seattle garden in 2011 and 2012 following three cleaning procedures. Vertical bars represent the mean of four replicates. Different letters within a category indicate significance difference (α=0.05).

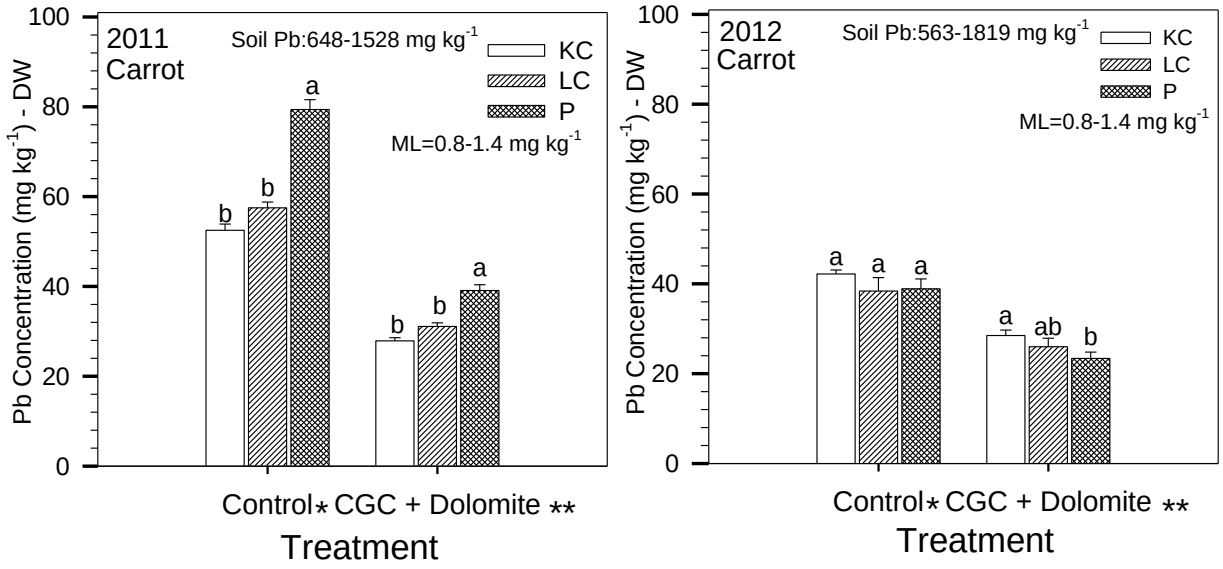


Figure 3.10. Pb concentration in lettuce harvested at the Seattle garden in 2011 and 2012 following two cleaning procedures. Vertical bars represent the mean of four replicates. Different letters within a category indicate significance difference (α=0.05).

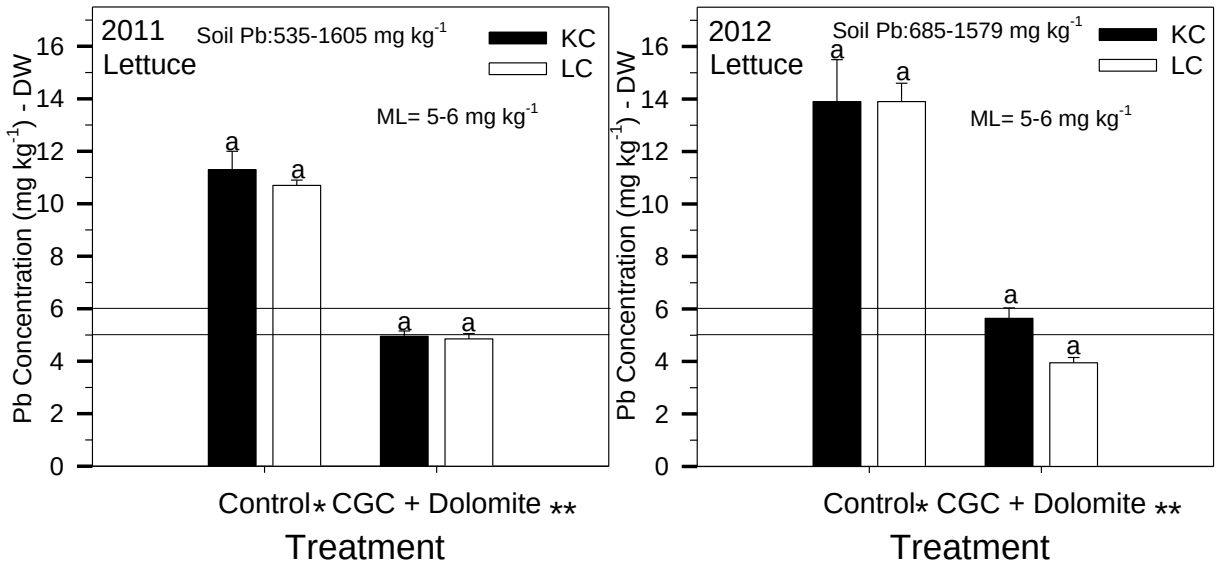


Figure 3.11. Pb concentration in tomatoes harvested at the Seattle garden in 2011 and 2012 following two cleaning procedures. Vertical bars represent the mean of four replicates. Different letters within a category indicate significance difference (α=0.05).

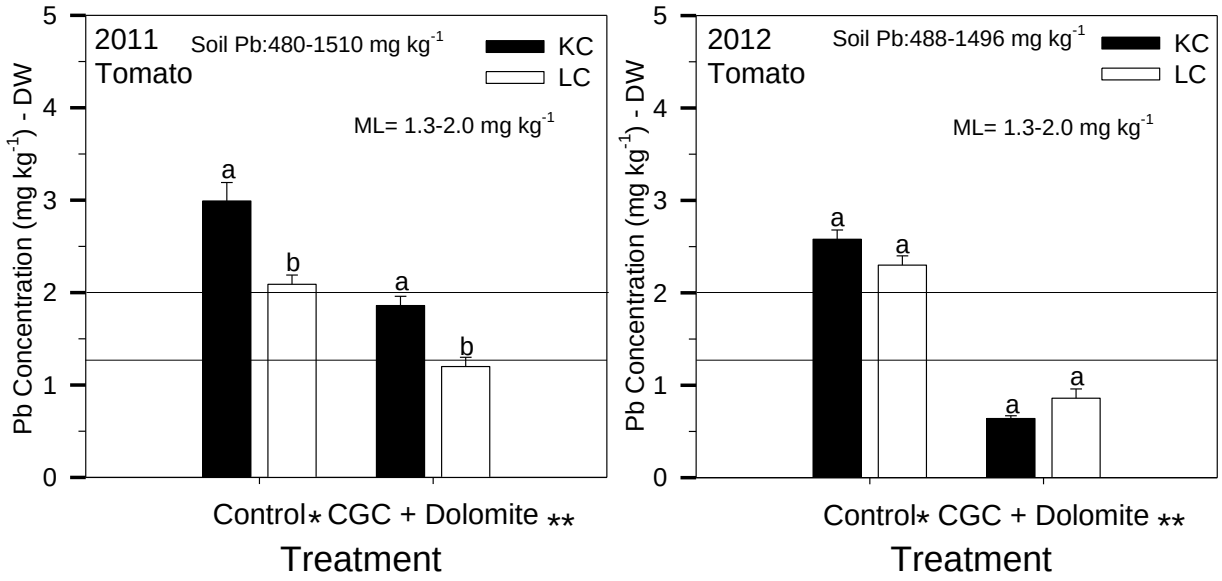


Figure 3.12. Percentage bioaccessible Pb at Tacoma vegetable plots in 2010 (A) and 2011 (B). Different letters within a category indicate significance difference (α=0.05).

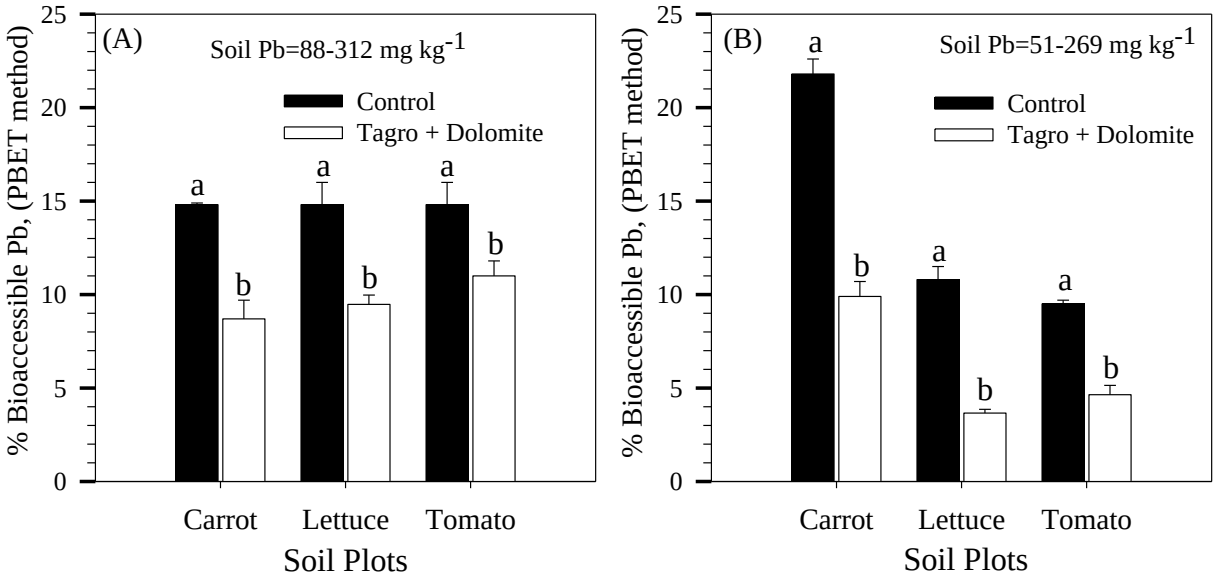
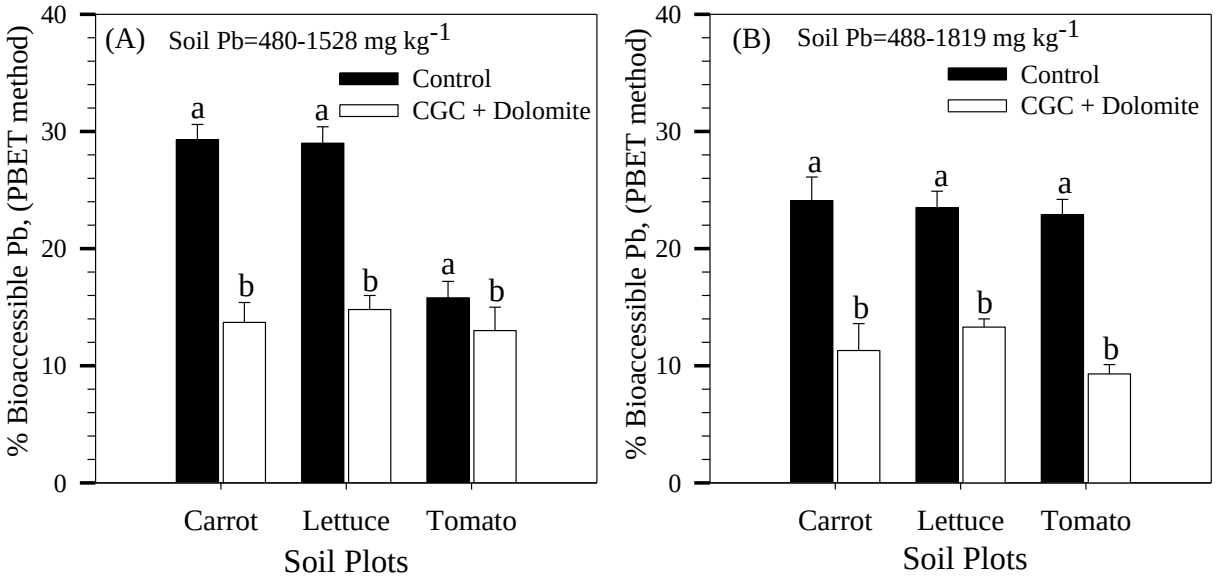


Figure 3.13. Percentage bioaccessible Pb at Seattle vegetable plots in 2011 (A), and 2012 (B). Different letters within a category, indicate significance difference (α=0.05).



CHAPTER 4 - EVALUATION OF IN SITU SOIL AMENDMENTS ON SPECIATION AND BIOACCESSIBILITY OF LEAD AND ARSENIC IN AN URBAN SOIL: AN INCUBATION STUDY

Phillip P. Defoe[1], Ganga M. Hettiarachchi[1,*], Christopher Benedict[2], Gary M. Pierzynski[1] and Michel D. Ransom[1]

[1]Department of Agronomy, Throckmorton Plant Sciences Center, Kansas State University, Manhattan, KS 66506, USA

[2]Whatcom County Extension, Washington State University, Bellingham, WA 98225, USA

ABSTRACT

Phosphorus (P) and iron oxyhydroxides containing materials have been used to bind trace elements such as lead (Pb) and arsenic (As) in contaminated soils effectively. Most of these studies have been conducted on soils either contaminated with Pb or As only. The efficacy of a biosolids amendment (TAGRO) and ferrihydrite (Fh) on reducing bioaccessibility of Pb and As in a contaminated urban soil from Tacoma, WA was evaluated using a six month laboratory incubation study. Soil Pb and As concentrations in soils were 142 and 105 mg kg^{-1}, respectively. Six treatments used were: a non-amended control, ferrihydrite (Fh) 1%, TAGRO 10%, TAGRO 20%, TAGRO 10% + Fh1%, and TAGRO 20% + Fh1%. Changes in bioaccessible Pb and As over time were measured using a modified physiological based extraction test (PBET) and a two-step extraction procedure, respectively. Chemical changes of Pb and As were studied using x-ray absorption spectroscopy (XAS). In general, soil pH of all treated soils decreased slightly. The pH of the TAGRO plus Fh amendments was consistently lower than that of the other treatments throughout the duration of the study. Percent bioaccessible Pb in TAGRO plus Fh, and Fh amendments were significantly (α=0.05) lower than the other amendments. The additions of TAGRO plus Fh and Fh alone treatments were the most effective in controlling the bioaccessibility of soil Pb and the reductions ranged from 34 to 60% compared to the control.

Bioaccessible As ranged between 2 and 8 mg kg^{-1} (5.8 to 14.1%) of soil. The addition of Fh or TAGRO plus Fh reduced As bioaccessibility more than the addition of TAGRO alone or the control. The TAGRO alone treatments (TAGRO 10% and TAGRO 20%) performed similarly to the amended control while a significant reduction was observed when TAGRO is combined with Fh. X-ray absorption spectroscopy results indicated that chloropyromorphite-like Pb phosphates were the most dominant and scorodite-like As(V) was the predominant As species. Percentage of scorodite-like As species increased with TAGRO plus Fh amended soils.

This study suggests, in urban soils contaminated with both Pb and As, amendments consisting of organic matter and ferrihydrite like sources are effective in reducing human exposure risks.

INTRODUCTION

Urban soils are a reconditioned medium partly due to anthropogenic activities. Two of the most ubiquitous urban soil contaminants with potential for human health exposure risks are lead (Pb) and arsenic (As) (Nriagu, 1989; Thornton, 1991). Anthropogenic sources of Pb (leaded paint and gasoline, soldering/ammunition products, Pb-based pesticides, aerosols/dusts from smelters/mine sites, and abandoned car batteries), and As (mining and smelting of non-ferrous ores, combustion of coal, the use of chromated copper arsenate (CCA), and application of arsenate based pesticides on croplands) are well documented (Alloway, 1995; Bissen and Frimmel, 2003; Hindmarsh et al., 1986; Nriagu, 1979; Senesil et al., 1999; Tiller, 1989). The Agency for Toxic Substances and Disease Registry (ATSDR) lists As and Pb as the top two most hazardous substances on the National Priority List (NPL) in the United States (ATSDR, 2011). Ranking of these hazardous substances are based upon three main criterion: i) frequency of occurrence at NPL sites, ii) toxicity levels, and iii) potential for human exposure (ATSDR, 2011).

Exposure to these contaminants while working in urban gardens have been a growing concern to city residents, and health officials. For Pb, the deleterious effects of chronic exposure at low levels (< 10 μg/dL) particularly in young children is real and well documented (Canfield et al., 2003; Jusko et al., 2008; Lanphear et al., 2000). Damage to the central nervous system (CNS), kidneys, decreased intelligence, muscle, and bone growth are the main symptoms (Baghurst et al., 1992; Canfield et al., 2003; Koller et al., 2004; Lanphear et al., 2002;

Needleman et al., 1990). Long-term oral As exposure results in darkening of the skin, wart formation, CNS and kidney damage (Ahsan et al., 2006; Centeno et al., 2002). The International Agency for Research on Cancer (IARC) classifies As and its inorganic compounds as a Class I human carcinogen for incidences of skin cancer (IARC, 2012). The accidental ingestion of soil or inhalation of contaminated soil Pb dust has been identified as the major pathway of environmental risk to humans (Chaney and Ryan, 1994; Hettiarachchi and Pierzynski, 2004). Primary exposure route for As has been due to the consumption of contaminated soil or water containing inorganic As (Smith et al., 2000; Thornton 1996).

Inorganic Pb exists primarily as the divalent cation (Pb^{2+}) in soil solution, while arsenic exists as oxyanions, As^{3+} as arsenite and As^{5+} as arsenate (Bhattacharya et al., 2007; Masscheleyn et al., 1991; Walsh and Keeney, 1975; Welch et al., 2000). Arsenate dominates in oxic conditions and is mobilized at high pH, while arsenite is predominant under reducing environments (Sadiq, 1997; Smedley and Kinniburgh, 2002). The most dominant As^{5+} species in typical oxic soil solution environments with pH ranging from 7 to 8 are $H_2AsO_4^-$, and $HAsO_4^{2-}$ (Sadiq, 1997; Xu et al., 1991). In suboxic and anoxic environments, As^{3+} become more dominant while As^{5+} become a minor species. The most dominant of As^{5+} and As^{3+} species particularly in soil solutions having low redox conditions (pe + pH < 6) are $HAsO_2^0$ and $H_3AsO_3^0$ (Sadiq, 1997). Generally, As^{5+} has a stronger adsorption affinity to soil surfaces than As^{3+} and is often considered as less mobile and potentially less bioavailable (Korte and Fernando, 1991; Manning and Goldberg, 1997; Raven et al., 1998).

Limiting the dissolution of the metal(loid)s to a less toxic form by the use of chemical sorbents have been widely used. Through chemical stabilization, the element's leaching potential, bioaccessibility, and the extent of human exposure is reduced. Phosphorus (P) based

products have been effective *in situ* amendments added to Pb-contaminated soils. X-ray Absorption Spectroscopy (XAS) studies conducted on soils amended with P, revealed chloropyromorphite-like species as the most stable Pb species (Ryan et al., 2001). Recent studies have evaluated the efficacy of biosolids as a suitable amendment to decrease soil Pb bioaccessibility (Brown et al., 2003, 2005). For As contaminated soils, amendments bearing iron oxyhydroxides have been shown to be the primary sinks (Cances et al., 2005). Common sources of iron oxides used in remediating soils are lepidocrocite, hematite, and goethite (Bowell, 1994). Their high sorption capacity coupled with the ability to form inner-sphere surface complexes with As, allows for their extensive use in As remediation studies (Smith et al., 2002; Warren and Alloway, 2003).

However, the retention or release of As from these surfaces may not always be permanent and is often influenced by changes in soil pH environment, the occurrence of redox reactions, and the presence of competing anions such as phosphates (Williams et al., 2003). Goethite, magnetite and an amorphous iron oxide (HFO) at varying solution compositions were used in a study by Dixit and Hering (2003) to observe the combined effects of As^{5+} and As^{3+} sorption on these minerals and the implications of As mobility. When goethite and magnetite solutions were supplied at a rate of 0.5 g L^{-1}, maximum sorption densities for both As forms were observed from pH 5 to 8. Adsorption of As^{3+} on iron oxides is low at low pH (<4), increasing to a maximum at around pH of 8, while As^{5+} desorption has been found to increase appreciably with increasing pH (Dixit and Hering, 2003; Pierce and Moore, 1982; Raven et al., 1998). On the other hand, low pH conditions favor the dissolution of metal cations such as copper (Cu), zinc (Zn) and Pb (Hartley et al., 2004; Warren and Alloway, 2003). Reducing soil conditions favors the reduction of As^{5+} to As^{3+}. Consequently, high reducing conditions are environmentally

unfavorable since As^{3+} is more prone to leaching due to its high solubility. The oxidation of added Fe^{2+} may also result in the reduction of As^{5+} to As^{3+} (Roberts et al., 2004).

Phosphorus amendments added to reduce the Pb availability in soils, have been found to limit the degree of As sorption in soils (Li et al., 2014; Manning and Goldberg, 1996; Smith et al., 2002). Arsenate and phosphate (PO_4^{3-}) are considered as chemical analogues, because the respective pentavalent oxyanions ($H_2AsO_4^-$/$HAsO_4^{2-}$ and PO_4^{3-}) are similar in structure, chemical reactivity, and sorption patterns (Antelo et al., 2005; Guan et al., 2008). So, remediating urban soils co-contaminated with Pb and As presents a huge challenge. The challenge has been primarily due to P-based treatment combinations or soil amendments yielding positive reductions for Pb, may increase the mobility and availability of As. To our knowledge, there is a paucity of information on investigations that attempt the simultaneous attenuation of Pb and As in co-contaminated soils. Xenidis et al. (2010) conducted a one-month pot study on a contaminated soil obtained from a former mining and metallurgic site. Monocalcium phosphate was added to the contaminated soil at phosphate to Pb molar ratios in the range of 0 to 2.5, whereas ferrous sulfate ($FeSO_4$) was added to have Fe to As molar ratios between 0 and 20. They reported that amendments consisting of combined mixtures of phosphates and $FeSO_4$ were most effective in immobilizing Pb and As (Xenidis et al., 2010). However, soil pH decreased from 7.8 to 5.6 (Xenidis et al., 2010). Cui et al. (2010) also observed a 0.6 drop in pH when $FeSO_4$ was added to a Pb and As contaminated soil and it is well-know that Fe oxidation produces an equivalent amount of protons and thereby, reduces pH (Thompson et al., 2006).

Understanding the biogeochemical processes in soil that reduce Pb and As to less bioavailable forms requires direct speciation studies using techniques such as x-ray based advanced spectroscopic techniques. Synchrotron based x-ray spectroscopic techniques allow

elucidation of underlying mechanistic biogeochemical processes responsible for contaminant stabilization**.** X-ray absorption spectroscopy studies have been used to speciate trace element in soils (Cances et al., 2005; Manning, 2005). Once chemical alteration is confirmed, the next challenge is assessing the reduction in exposure and human health risk associated with stabilized soil Pb and As.

Appropriate animal model studies or *in vitro* gastrointestinal (GI) methods that correlate well with animal model studies are needed to evaluate changes in Pb bioavailability. In this study, a modified physiological based extraction test (PBET) was used to assess changes in bioaccessible Pb over time, while the first two steps of a sequential extraction procedure (Wenzel et al., 2001) were used to assess bioaccessible As. Sequential extraction procedures have been used to examine the distribution of As among different soil phases (Lombi et al., 2000; Wenzel et al., 2001).

The purpose of this study was to conduct an incubation experiment on an urban garden soil contaminated with both Pb and As to evaluate the effectiveness of *in situ* treatments on reducing soil Pb and As bioavailability. Additionally, chemical alterations of Pb and As in the *in situ* treatments were determined using XAS. Solid-state speciation techniques provide support to bioaccessibility/bioavailability tests and operationally defined sequential extraction procedures that are often used to provide toxicity recommendations.

MATERIALS AND METHODS

Soil collection and processing

The soil used in this study was collected from an unused area adjacent to an urban garden (Fig. 4.1) located in Pierce County, Tacoma, WA (47°16′ N, 122°31′ W). The soil was excavated

to a depth of 15 cm (6″) with a garden spade over a 3m x 3m area. Urban artifacts and visible plant debris were removed from the soil before being placed into 5 gallon plastic buckets that were lined with 13-gallon polyethylene bags. The contents of the bucket were secured and shipped immediately to the Kansas State University soil chemistry laboratory for further processing. Upon arrival, the soil material was spread out evenly and left to air-dry in the greenhouse for about 5 days at 25 °C before being sieved with a number 10 stainless steel sieve (2-mm opening). After sieving, the soil was thoroughly mixed (by hand) so as to achieve as much homogenization as possible.

Experimental set-up

An initial 1 month pilot study was conducted using two iron-oxide sources [goethite (Gt) and ferrihydrite (Fh)], and a class A biosolids mix, referred to as TAGRO obtained from Tacoma, WA (described in treatment section) with the objective of screening some selected treatments for their efficacy. Following the pilot study, a six-month long incubation study was conducted. In this study, only TAGRO and ferrihydrite were used to formulate amendment combinations as the pilot study showed ferrihydrite was more promising in reducing the bioaccessibility of Pb and As compared to the goethite. The experimental design was a completely randomized design with 6 treatments and three replications. Two hundred grams of soil were added with each treatment on a w/w basis. Since the soil's pH was low, all treatments were adjusted with calcium oxide (CaO) powder to a targeted near neutral pH (6.8 to 7.5) at the commencement of the study. Amount of CaO needed for each treatment was pre-determined during the pilot study. The treatments were placed in 250 mL high density polyethylene containers, moistened with deionized water to 60% maximum water holding capacity (MWHC) of soil, and mixed thoroughly with glass rods before covering with clear plastic wrap and

securing with a plastic rubber band. Individual batches of treatments were prepared and incubated for 33, 93 and 183 days in a precision low temperature incubator at 25 °C.

The containers were examined weekly and treatments below the 60% MWHC level adjusted accordingly with deionized water. All treatments were thoroughly, but carefully mixed with a glass rod before returning to the incubator. Thorough mixing helped maintain good aeration during the incubation period. At the end of each time period, the corresponding batch of treatments were removed from the incubator and analyzed for pH, PBET-Pb, bioaccessible-As, total Pb and As. The containers were then sealed and kept frozen at -20 °C until XAS spectroscopy was conducted.

Iron-oxide preparation

Goethite (α-FeOOH) and Fh ($Fe_5HO_8 \cdot 4H_2O$; 2-line) were prepared in the laboratory as described by Schwertmann and Cornell (2008). Goethite was prepared by mixing 180 mL of 5 *M* KOH with 100 mL of 1 *M* $Fe(NO_3) \cdot 9H_2O$. The suspension was diluted to 2 L and aged for 60 h at 70 °C in a water bath. Ferrihydrite was prepared by neutralizing a 0.2 *M* ferric nitrate solution with 1 *M* KOH to a pH between 7 and 8 (Schwertmann and Cornell, 2008). The suspensions were centrifuged at 3000 rpm for 10 minutes (5810R Eppendorf, Hamburg, Germany), residues washed free of excess salts with ultrapure water (Milli-Q, Millipore, 18 MΩ·cm) and freeze dried (Labconco freeze dryer, Kansas City, MO). The iron-oxides were characterized/verified with an X-ray diffractometer (Philips X-Ray diffractometer, Mahwah, NJ) with a theta compensating slit and curved crystal graphite monochromator. Measurements were taken using Cu Kα radiation at a wavelength of 1.54 Å and were step scanned at a speed of 2° 2 θ per minute (Baker et al., 2014). The potential was 35 kV, and the amperage was 20 mA.

Treatments

A total of six treatments were prepared for each of the time periods (30, 90, and 180 d) in triplicates for the incubation study (total of 6*3*3 = 54). Treatment compositions/amendments are as follows:

(1) non-amended control: 200 g soil and 0.3 g of Calcium oxide (CaO);

(2) Fh (1%): 198 g soil, 2 g of Fh, and 0.3 g of CaO;

(3) TAGRO (10%): 180 g of soil, 20 g of TAGRO, and 0.3 g of CaO;

(4) TAGRO (20%): 160 g of soil, 40 g of TAGRO, and 0.3 g of CaO;

(5) TAGRO (10%) + Fh (1%) mixture; 178 g of soil, 20 g of TAGRO, 2 g of Fh, and 0.3 g of CaO;

(6) TAGRO (20%) + Fh (1%) mixture: 158 g of soil, 40 g of TAGRO, 2 g of Fh, and 0.3 g of CaO.

TAGRO is a class A biosolids product of the Central Wastewater Treatment Plant in Tacoma, WA. The biosolid is produced using a two-step dual digestion, aerobic process. The waste water is first pasteurized in autothermal thermophilic aerobic digesters at temperatures that exceed 55 °C (Eschborn and Thompson, 2007). In the second step, thorough anaerobic digestion is facilitated by the pre-conditioning achieved in the aerobic step. The pasteurized, pre-conditioned biosolids are digested in a series of three anaerobic phases descending in temperature from thermophilic to high mesophilic to low mesophilic (Eschborn and Thompson, 2007). The thermophilically digested class A biosolids ‘‘cake’’ is mixed with sawdust and sand at a volume of 2:1:1 (Krucker et al., 2010). Selected properties of TAGRO are presented in Table 4.2. The TAGRO biosolid is readily available for free pick up at the processing facility or home delivery at a small cost.

Chemical analyses

Prior to commencement of the study, the soil was characterized for several physico-chemical parameters (Table 4.1). Soil pH (soil:deionized water; 1:5) was measured using a Thermo Scientific Orion glass electrode (Beverly, MA). Soil texture was determined by the hydrometer method (Bouyoucos, 1962) and total organic C and N by dry combustion method using a LECO CNS-2000 analyzer (St. Joseph, MI). Plant available phosphorus (P) was determined using the Mehlich-3 P test (Mehlich, 1984), extractable K by 1 *M* ammonium acetate (Helmke and Sparks, 1996), available nitrogen (N) by 2 *M* KCl extraction (Keeney and Nelson, 1982), and cation exchange capacity (CEC) was determined by summation method (Chapman, 1965).

Soil samples (triplicate) chosen from the homogenized soil were digested by microwave (MARS®, Matthews, NC) according to method SW 846 Method 3051A. Filtered (Whatman 42) samples were analyzed for total Pb and As by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Varian Inc., Australia). Reagent blanks and a standard reference soil (NIST 2711a-Montana II) were digested and analyzed along with soil samples to evaluate digestion and analytical procedures. For accuracy and precision, internal standards were used where appropriate (recoveries within 100 ± 10%).

Determination of bioaccessible Pb

Bioaccessible Pb was evaluated by conducting a modified physiologically based extraction test (PBET) as described by Ruby et al. (1996) and modified according to Medlin (1997). The prepared gastric solution (1.25 g pepsin, 0.50 g citrate, 0.50 g malate, 420 µL lactic acid, and 500 µL acetic acid in 1 L deionized water) was acidified to pH 2.5 with 12 *M* HCl (trace metal grade) and heated to 37 °C on a hot plate prior to soil addition. A 100-mL aliquot of

the gastric solution was added to a 1-g soil sample (sieved to <250 µm) in a 250 mL wide mouth high density polyethylene (HDPE) bottle. The mixture was then shaken for one hour at 150 rpm on a Queue orbital shaker (Parkersburg, WV) maintained at 37 °C. Following extraction, the pH of the samples were evaluated and adjusted with varying volumes of trace metal grade concentrated HCl for samples with deviations greater than 0.05 log units. Approximately a 20 mL aliquot of the supernatant was then filtered through 0.45 µm syringe filters into plastic scintillation vials and analyzed within three days. The NIST soil standard SRM 2711a, a moderately contaminated soil from Montana, and blanks were routinely included in PBET analysis.

Determination of bioaccessible As

Sequential extraction is an analytical process that chemically removes elements out of soil or sediment samples using a series of selected extracting solutions to mimic the release of elements into solution under different environmental conditions. The idea behind all sequential extractions is that the most mobile fractions are removed first and followed by removing fractions in order of decreasing mobility (Tessier et al., 1979). The first two steps of a sequential extraction procedure (SEP) developed by Wenzel et al. (2001) were used to evaluate bioaccessible As in the soils. The extraction was carried out in 50 mL centrifuge tubes, and the supernatants filtered through 0.45-µm nylon membrane syringe filters (Environmental Express, Charleston, SC)), and then the filtrate was acidified with 2 drops of 2% trace metal grade nitric acid. Since the most risk of arsenic is based on the forms that are biologically available for absorption, we focused on targeting the first two operationally defined phases of As in the soil.

The first step targeted the non-specifically bound As fraction, while the second step evaluated the specifically-bound or mobilizable fraction of As in the soil. Details of the extraction procedures are summarized below:

Step 1: A 25-mL aliquot of 0.05 *M* $(NH_4)_2SO_4$ was added to a 1-g amended soil sample placed in a 50 mL centrifuge tube and sealed carefully. This procedure was repeated for the remaining treatments. The tubes were placed on an end-to-end shaker for 4hrs (~250 rpm). The mixture was centrifuged at 3000 rpm for 10 minutes, and the supernatant collected with 0.2 µm nylon syringe filters. Supernatants were acidified with two drops of 2% nitric acid (trace metal grade) and stored at 4 °C prior to analysis. All extractions were performed in duplicates.

Step 2: Twenty five (25) mL aliquots of 0.05 *M* $NH_4H_2PO_4$ were added to each of the residual treatments in step 1, and the tubes sealed. The tubes were placed on an end-to-end shaker for 16hrs (~250 rpm) and centrifugation and filtration procedures were followed as in step 1.

Total As was determined as described before. Percent bioaccessible As was calculated as a percentage of the measured total concentration of As in soil. Treatment efficiency was evaluated on their relative ability to decrease the proportion of bioavailable As, as compared to the control.

Bioaccessible As (%) = [(∑ extracted As step 1 + extracted As step 2, mg kg^{-1}) / (total As, mg kg^{-1})] x 100

Chemical analysis of Pb and As

Extractable As (steps 1 and 2) and PBET-Pb were both analyzed on a graphite furnace atomic absorption spectrometer (GF-AAS, Varian Inc., Australia) with a Zeeman background correction. For PBET-Pb, a modifier (1000 µg/ml $NH_4H_2PO_4$) was used. Modifiers help improve the detection limits of the elements of interest and reduce signal interferences (Havezov et al.,

1995; Ortner et al., 2002). For As, a 500 µg/ml palladium (Pd) modifier was prepared from 0.2% Pd in 5% nitric acid stock solution. Palladium modifiers have been found to be very effective in the formation of different analyte species (e.g. As^{3+}, As^{5+}, Se^{4+}, Se^{6+}) (Russeva et al., 1993). For quality assurance and quality control (QA/QC), a reagent blank, and a standard reference material (2711a-Montana soil) were extracted with each set of soil samples.

Sample preparation for bulk XAFS analysis

For Pb, composite samples (air-dried) were prepared by mixing equal amounts of soil from each replicate per treatment per time-period. Soil samples were ground to a fine powder with an agate mortar and pestle to ensure maximum homogenization. The samples were packed in Plexiglas slits (1900 µm x 600 µm x 150 µm: L x W x D), sealed with Kapton tape, and labeled prior to being mounted on the sample stage.

For As, composite samples (prepared from frozen samples in an anaerobic glove-box) were placed in 20 mL polyethylene vials and transported in a 2.5 L Oxoid anaerobic jar (Thermo Fisher Scientific, Waltham, MA). The jar was kept in a freezer bag with ice-packs during transportation to the Advanced Photon Source and then stored in a freezer prior to sample preparation. Sample preparation was done in a disposable glove-box to limit air exposure. Plexiglas and Kapton tape were used as before for Pb analysis to prevent moisture loss and x-ray absorption.

Bulk XAFS data collection and analysis

Bulk Pb- and As-XAFS of the soil samples were collected at beamline 5 BM-D (DuPont-Northwestern-Dow Collaborative Access Team, DND-CAT) at the Advanced Photon Source at Argonne National Laboratory, Argonne, IL. This beamline has an energy range of 3.6 to 75 keV.

The Si (111) double crystal monochromator consists of a Ge solid-state 13-element detector (Canberra Inc.). The monochromator was detuned 65% to minimize the harmonic contamination in the incident beam. The X-ray energy was calibrated using a Pb metal foil or As filter (As^{3+}). The XAFS spectra of standard Pb and As compounds relevant to soils were collected in transmission mode, while soil samples were collected in fluorescence mode. Standard Pb compounds include lead chloride ($PbCl_2$), lead nitrate ($PbNO_3$), galena (PbS), anglesite ($PbSO_4$), cerussite ($PbCO_3$), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), leadhillite ($Pb_4(SO_4)$ $(CO_3)_2(OH)_2$), plumboferrite ($Pb_2Mn_{0.2}Mg_{0.1}Fe_{10.6}O_{18.4}$), plumbogummite ($PbAl_3(PO_4)_2(OH)_5{\cdot}H_2O$), and chloropyromorphite ($Pb_5(PO_4)3Cl$). Standard As compounds include arsenic trioxide (As_2O_3), arsenic pentoxide (As_2O_5), scorodite ($FeAsO_4{\cdot}2H_2O$), arsenic (+5) sorbed onto Fh (As^{5+}-Fh), and arsenic (+3) sorbed onto Fh (As^{3+}-Fh).

Lead XAFS measurements were collected at ambient temperature while for As, the sample holder was continuously sprayed with liquid N_2 at -127 to -129 °C using a cryogenic crystal cooler (X-stream™). Lead XAFS (Pb L_{III} edge) was collected from 12835 to 13584 eV, while As XAFS (K-edge) was collected from 11665 to 12415 eV. A minimum of 16 to 18 spectral scans were collected for Pb, and 9 for As.

Data quality from the extended X-ray absorption fine structure region was poor. Consequently, the XANES region was used for data analysis. For Pb, the region of 13,020 to 13,075 eV was isolated for linear combination fitting (LCF). Replicate scans were aligned using a reference spectrum (Pb foil). Aligned spectra were averaged and averaged spectra were background corrected and normalized in Athena. Linear combination fitting (LCF) was used to obtain combination fits using all of the Pb standards mentioned above. Although a small region was used for the fitting, the results can be used to describe and compare treatment differences. A

similar approach was used for As-XAS analysis. For As, the region of 11,840 to 11,900 eV was isolated for LCF analysis. The LCF was done using the As standards mentioned above. Data processing and (LCF) was done using IFEFFIT software package (Ravel and Newville, 2005). The LCF procedure utilizes several standard spectra and a system of algorithms to generate a "goodness of fit" when samples are integrated. Through trial and error, undesirable standard components (< 5%) were eliminated from the combination pool and the remaining standards refitted. Combinations with lowest reduced χ^2 were selected as the best fit because they included the most likely set of elemental species (Hettiarachchi et al., 2006).

Statistical Analysis

Wet-chemical data were analyzed using PROC MIXED in SAS for Windows version 9.2 (SAS Institute Inc., 2009). Treatment differences were characterized using Tukey's Honestly Significant Difference (HSD) test for means separation ($\alpha = 0.05$). Changes in bioaccessible Pb and As were evaluated as a function of time and treatment.

RESULTS AND DISCUSSION

Soil characterization

The soil was characterized as a loamy sand with the surface horizon having about 2% small gravels. Soils in Pierce County, WA form part of the Alderwood series (Natsuhara, personal communication). The concentration of soil Pb was 142 mg kg^{-1}, while As was 105 mg kg^{-1} (Table 4.1). Although soil Pb concentration can be considered as only mildly elevated, soil As concentration is about 5 times the regulatory state limit of 20 mg kg^{-1}. Total organic carbon (TOC) percentage was approximately 2%, with moderately acidic pH (Table 4.1).

Effects of treatments on soil pH

The pH of all amendments was adjusted to 6.8 to 7.5 prior to commencement of the incubation study. Results of pH measurements for each treatment during the study are presented in Fig. 4.2. With the exception of the control and the ferrihydrite treatment, pH of the remaining treatments decreased after one-month of incubation. Measured pH in the control treatment increased to 7.6 following 93-d incubation, then decreased to about 7.1 and came back up to 7.5 at the end of the study. The ferrihydrite treatment increased slightly after 33-d, then decreased to ~ 7.4 at 93-d till the end of the study. The TAGRO only treatments (10% and 20%) consistently had the lowest pH throughout the incubation period, indicating that the TAGRO may be having an acidifying effect on the treatments.

Previous studies have reported decreases in soil pH subsequent to TAGRO and composted biosolids application to urban or mine reclaimed soils (Defoe et al., Chapter 3, McIvor et al., 2012, Stehouwer et al., 2006). Soil pH in urban garden plots amended with TAGRO ranged between 5.35 to 5.75, while pH of non-amended control plots was 6.43 (McIvor et al., 2012). Similar results were observed in a field study where soil pH of TAGRO plus dolomitic lime amended plots decreased by about 0.5 to 1.0 pH log units during the growing period (3 to 4 months, Defoe et al., Chapter 3). Biosolids processing in particular the presence or absence of alkaline materials have been reported to influence whether increases or decreases in soil pH occur following land application (Sullivan et al., 2007). Biosolids consisting of calcium oxides and hydroxides or exchangeable calcium and magnesium often resulted in increased soil pH (Sullivan et al., 2007). Excess protons in the soil solution react with the hydroxide producing carbon dioxide and water. In contrast, the presence of soluble salts and organic nitrogen and sulfur may result in temporary increases in soil acidity (Stehouwer et al., 2006; Sullivan et al., 2007). Mineralization of organic N to NH_4^+ followed by nitrification to NO_3^- produces protons and results in a drop in pH. It is

also possible that the soluble salts in the TAGRO could displace protons bound to clay or organic matter, and bring them into the soil solution.

The lowering of soil pH may negatively affect As solubility. Pierce and Moore (1982) reported maximum adsorption of As^{3+} on hydrous oxides at pH 7, while As^{5+} is preferentially sorbed between pH 4 and 7. The increased dissolution of As^{3+} due to decreasing soil pH is considered unfavorable, since As^{3+} is considered to be about 25 to 60 times more toxic than As^{5+} (Korte and Fernando, 1991). On the contrary, pyromorphite formation in soil requires the dissolution of Pb and P amendments (Hettiarachchi and Pierzynski, 2004; Kumpiene et al., 2006). Additionally, pyromorphite formation is enhanced with acidification (Miretzky and Fernandez-Cirelli, 2008; Yang et al., 2001). In order to negate the effects of acidification due to ferrihydrite and TAGRO additions, adjustment of soil pH with CaO to a range between 6.8 and 7.5 was targeted in this study.

Residence time and treatment effects on Pb bioaccessibility

The PBET procedure was used to evaluate Pb bioaccessibility and ascertain the impact of treatment additions on reducing soil ingestion exposure risks of humans. Bioaccessible Pb concentrations were low and ranged from 4.07 to 23.1 mg kg^{-1} (3.1 to 11.3% of total Pb in soil) (Figs. 4.3 and 4.4). Similar results were observed for urban soils amended with biosolids (Brown et al., 2003; Farfel et al., 2005). Due to similar trends observed between PBET-Pb and percent bioaccessibility, our discussion will focus on percent Pb bioaccessibility (Fig. 4.4). Percent bioaccessibility values are “normalized” for differences in total Pb concentrations that may be found in soils. Consequently, the dilution effect caused by large additions of TAGRO is negated.

Our results indicated that percent bioaccessible Pb was affected by treatment and aging. We observed slight fluctuations in percent bioaccessibility for the non-amended control over the incubation period. This fluctuation may be due to constant changes in the system to

counterbalance the perturbation (CaO and maintaining soil at 60% MWHC). Additionally, this suggests that a small percent of Pb in this soil may be weakly bound, therefore, exchangeable depending on soil pH. Slight fluctuations were also observed in the soils amended with TAGRO alone. Compared to the non-amended control, increased percent bioaccessible Pb was observed for soils treated with TAGRO alone. It may be possible that effect of enhanced dissolved organic C (DOC) has a dominating effect on Pb solubility. The TAGRO biosolids had about 179 g kg^{-1} organic matter (104 g kg^{-1} OC). Increased additions of high organic matter would favor the formation of soluble organo-Pb complexes (Sauvé et al., 1998). The pH in the TAGRO only amendments ranged between 6.5 and 7 at the end of the study. Although a slight acidification was noticed with increasing incubation time, we do not believe that soil pH alone was responsible for the enhancement in percent bioaccessible Pb although acidic conditions favors Pb solubility (Hettiarachchi et al., 2001). In contrast, percent bioaccessible Pb decreased with incubation time for ferrihydrite and TAGRO plus ferrihydrite treatments (Fig. 4.4). On average, in ferrihydrite and TAGRO plus ferrihydrite amended soils relative reductions in percent bioaccessible Pb ranged between 34 and 60% compared to the non-amended control (Fig. 4.4). Iron oxides have a high capacity to adsorb Pb and concomitantly maintain a low free Pb^{2+} activity in solution (Sauvé et al., 2000). It may be possible that the ferrihydrite is mainly responsible for adsorbing the Pb in solution, thus reducing its bioaccessibility. It is plausible that the TAGRO plus ferrihydrite combinations would be most effective since the mixture contains both high amounts of P and iron oxyhydroxide; compounds that have been reported to reduce Pb bioaccessibility significantly. Brown et al. (2005) reported 37% reduction in Pb bioaccessibility upon an addition of high iron compost to a Pb contaminated soil.

Aging and treatment effect on As bioaccessibility

Results of As bioaccessibility obtained by combining the extracted As by first two sequential extraction steps are presented in Fig. 4.5, and percent bioaccessibility of As in the treatments presented in Fig. 4.6. Mean As concentrations in the treatments were low, and ranged from 2.3 to 8.3 mg kg^{-1} (Fig. 4.5). This is equivalent to 5.8 to 14.1% bioaccessibility (Fig. 4.6). Although they did not follow the same approach, Brown et al. (2012) reported slightly higher (22%) As bioaccessibility for a rural smelter contaminated soil with total soil As concentrations of 71 mg kg^{-1}. Since extraction procedures and materials are different, it is not possible to compare results directly.

Arsenic bioaccessibility was significantly affected by treatment. With the exception of TAGRO amendments, percent bioaccessible As decreased with aging. The lowest percent bioaccessible As was observed in the ferrihydrite and TAGRO plus ferrihydrite amended soils (Fig. 4.6). Compared to the control, the relative percent bioaccessible As of ferrihydrite and TAGRO plus ferrihydrite amendments were about 50% lower (Fig 4.6). Although minimal decreases in percent bioaccessible As was observed for the ferrihydrite amendment in comparison with TAGRO plus ferrihydrite amendment, percent bioaccessible Pb values were similar (Fig. 4.6).

In contrast, TAGRO only amendments enhanced percent bioaccessible As compared to the control. Mehlich-3 extractable P in the TAGRO biosolids was 34 mg kg^{-1}. Previous studies have indicated that increased P additions have resulted in increased As bioaccessibility (Cui et al., 2010; Melamed et al., 1995; Peryea, 1998; Smith et al., 2002). The presence of phosphates particularly at higher concentrations in the soil solution compared to As, can outcompete arsenate for sorption sites on iron oxide materials (Manning and Goldberg, 1996). In addition to

phosphate concentration, soil pH may also be controlling the As sorption. At the end of our study, the lowest pH was recorded for the soil amended with TAGRO at 20% (w/w). Maximum adsorption of As^{3+} on hydrous oxides occur at pH 7, whereas maximum adsorption of As^{5+} on hydrous oxides occur at pH 4 to 7 (Pierce and Moore, 1982). Our results differ from Tu and Ma (2003) who reported slightly higher soluble arsenate concentrations with higher phosphate applications compared to low phosphate levels.

Further, changes in percent bioaccessible As with time may be explained by the As bonding mechanisms to Fe oxyhydroxides. Weaker outer-sphere electrostatic complexes formed by adsorption of anions and cations on soil materials may be transformed to much stronger inner-sphere complexes with time (Bradl, 2004).

Effect of treatment on Pb speciation

X-ray absorption fine structure (XAFS) spectroscopy studies were conducted on four treatments at the end of the incubation study. The treatments chosen were the non-amended control, ferrihydrite, TAGRO 10%, and TAGRO 10% plus ferrihydrite. Bulk Pb X-ray absorption near edge spectroscopy (XANES) results indicated that the dominant form of Pb appeared to be chloropyromorphite-like species (Fig. 4.7). The formation of pyromorphite in garden soils have been previously reported in soils with Pb concentration ranging from 2,400 to 22,800 mg kg^{-1} (Cotter-Howells and Thornton, 1991) and are known to be most stable form of Pb phosphates in soils (Lindsay, 1979; Ryan et al., 2001). It should be noted here that we did not have any Pb sorbed onto phosphates as a standard, therefore, this data need to be evaluated for possible sorbed Pb to known phosphate minerals such as apatite. As Roberts et al. (2002) pointed out, the accuracy of LCF depends on the data quality and how well the reference spectra fit the experimental samples. In this case, the best fit compositions may not give the true composition

(Baker et al., 2014). The inclusion of a few more standards spectra should help further refining/confirming our present results. In addition to pyromorphite-like Pb mineral, plumboferrite-like Pb mineral was also observed as a minor Pb species. Both these minerals have low solubility, therefore, the results obtained here, support the low Pb bioaccessible results obtained from the PBET-Pb analyses. The source of contamination was due to aerial deposition from a former copper smelter site. Air deposition from smelter emissions contain galena from Pb ore, which over time can oxidize to anglesite, and lead (II) oxide in minute concentrations (Clevenger et al., 1991). It is possible that soluble minerals such as anglesite have been transformed to more stable Pb phosphate-like minerals over time.

Amendments of TAGRO and Fh added solely or in combination have shown a redistribution in Pb species resulting in an apparent decrease in the abundance of chloropyromorphite-like Pb species (Fig. 4.7). Acidic conditions and high P/Pb availabilities favors pyromorphite formation (Hettiarachchi et al., 2001; Scheckel and Ryan, 2004).

Effect of treatment on As speciation

Bulk As XANES analyses were also conducted on the same selected treatments used for the bulk Pb XANES analysis. Speciation results are shown in Fig. 4.8. X-ray absorption near edge structure (XANES) analysis indicates that As^{5+} is the dominant oxidation state in non-amended control and the treated soils. Impellitteri (2004) also reported a high dominance of As^{5+} in soils from a former Pb smelter characterized by XAS. Linear combination fitting of the XANES data revealed As^{5+} precipitated as scorodite ($FeAsO_4 \cdot 2H_2O$)-like species. For all the soils examined, contribution from scorodite-like species was ranged from about 60% (control) to about 70% (TAGRO plus ferrihydrite). This suggests that most of the As^{5+} in our soils are probably bound to Fe or may co-precipitate with Fe. Moreover, our results also indicated the

absence As^{3+} in all of the soils. Our spectroscopy data is in agreement with the chemical extraction results. Low bioaccessible As was obtained for the soils irrespective of amendment. Notwithstanding the low bioaccessibility results, it appears that our treatments enhanced slightly the presence of scorodite-like species with the TAGRO plus ferrihydrite amendment having the highest proportion (~70%).

Increased of P upon TAGRO alone-amendment did not affect the As speciation results. It has been reported that excess P enhances As solubility (Dixit and Hering, 2003). The presence of a high percentage of scorodite-like species in the non-amended control soil might be attributed to its amorphous Fe concentration. Amorphous iron concentration of the bulk soil was 3733 mg kg^{-1}. The study was conducted for six months under controlled conditions. It may be possible if carried out under field conditions and for a longer period of time, the speciation results may differ. The transformation of metastable amorphous ferrihydrite to more stable and crystalline oxides such as goethite is possible in the field environment and could lead to the re-mobilization of As that was previously precipitated. Consequently, it is critical that soil pH be constantly monitored and maintained (above pH 8) to limit the transformation of ferrihydrite to more crystalline iron oxides.

CONCLUSION

Bioaccessible Pb and As in the urban soil was low and was further reduced when amended. Additionally, percent bioaccessible Pb and As in the treatments decreased with increasing incubation time, indicating changing mechanisms of Pb and As sorption with time (i.e., initial outer-sphere to inner-sphere). The most effective treatment in reducing both bioaccessible Pb and As was TAGRO plus ferrihydrite amendment. Lead and As speciation in

the non-amended control soil and treated soils were not significantly altered. We did not observe the presence of any XANES detectable As^{3+} species in the treated soils. Instead, it appears that scorodite-like As species (Fe arsenate- like) are the most dominant in all samples. Due to slight decreases observed in treatment pH throughout the study, it may be necessary to monitor and adjust soil pH if these amendments are used in the field setting. From a risk assessment perspective, it is necessary to consider P based amendments when remediating soils contaminated with both Pb and As. Solely P-based amendments may enhance As mobility and bioaccessibility and P amendment alone may not be suitable as *in situ* soil amendment.

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Table 4.1. Selected properties of incubation soil.

Property	Value
pH, (water)	5.61
Sand, (mg kg^{-1})	780
Silt (mg kg^{-1})	160
Clay, (mg kg^{-1})	60
Organic C, (g kg^{-1})	20.1
Mehlich-3 extractable P, (mg kg^{-1})	35.9
Extractable K, (mg kg^{-1})	63.5
Available N (NH_4-N + NO_3^--N), (mg kg^{-1})	25.5
Total Pb (mg kg^{-1})	142.0
Total As (mg kg^{-1})	105.0

Table 4.2. Selected properties of TAGRO biosolids.

Property	Value
pH, (1:5; soil:deionized water)	7.6
Moisture, %	21.0
Soluble salts, dS/m	1.53
Iron, (mg kg^{-1})	5,300
Organic C, (g kg^{-1})	104
Mehlich-3 extractable P, (mg kg^{-1})	34
Extractable K, (mg kg^{-1})	10
Available N (NH_4-N + NO_3^--N), (mg kg^{-1})	1.7
Total Pb, (mg kg^{-1})	9.55
Total As, (mg kg^{-1})	3.21

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Figure 4.1. Location of soil used for the incubation study. Surface soil (0 to 15 cm) was collected at location in the inset highlighted with the yellow circular disk.

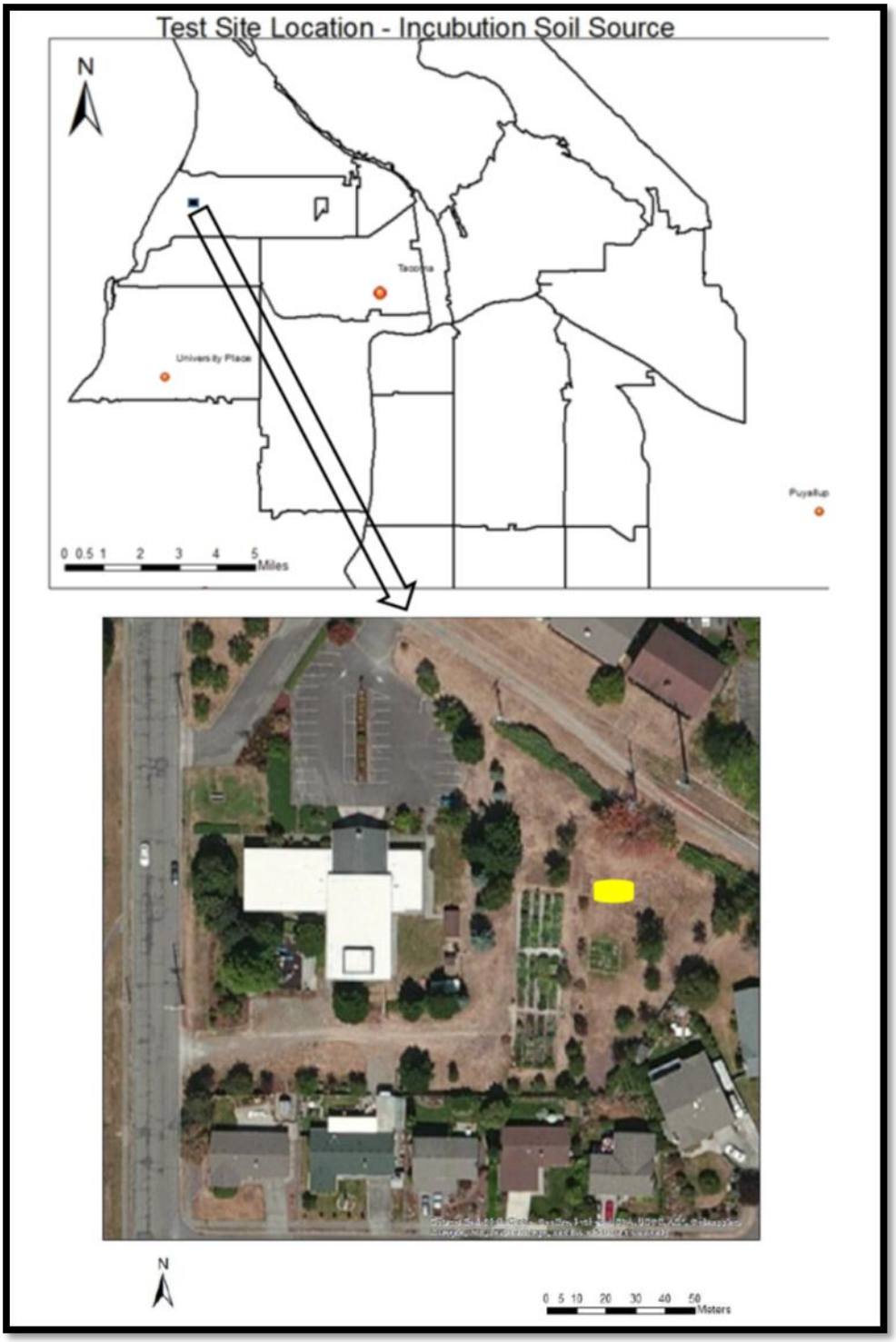


Figure 4.2. Soil pH of treatments during incubation study.

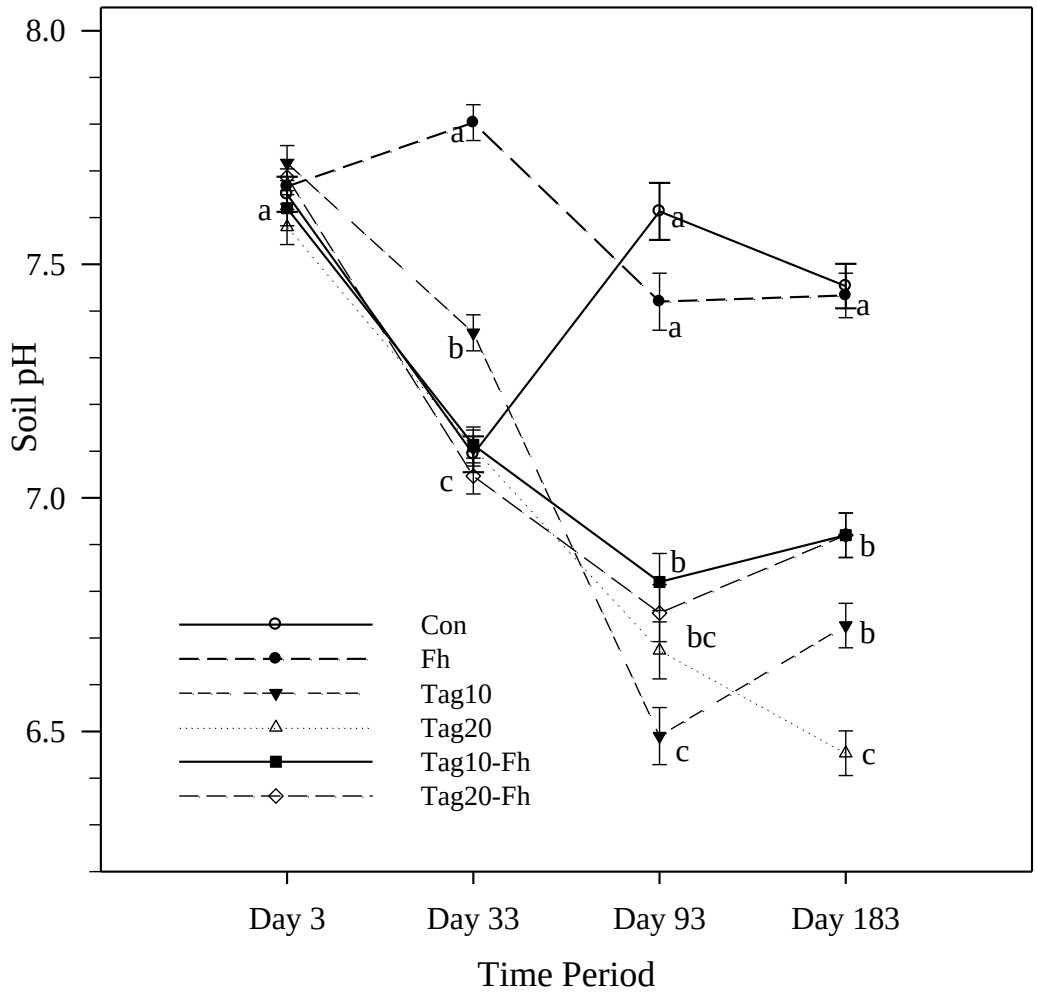


Figure 4.3. Bioaccessible Pb (PBET method) concentrations of treatments during the incubation study. Different letters within a time period indicate significance difference (α=0.05).

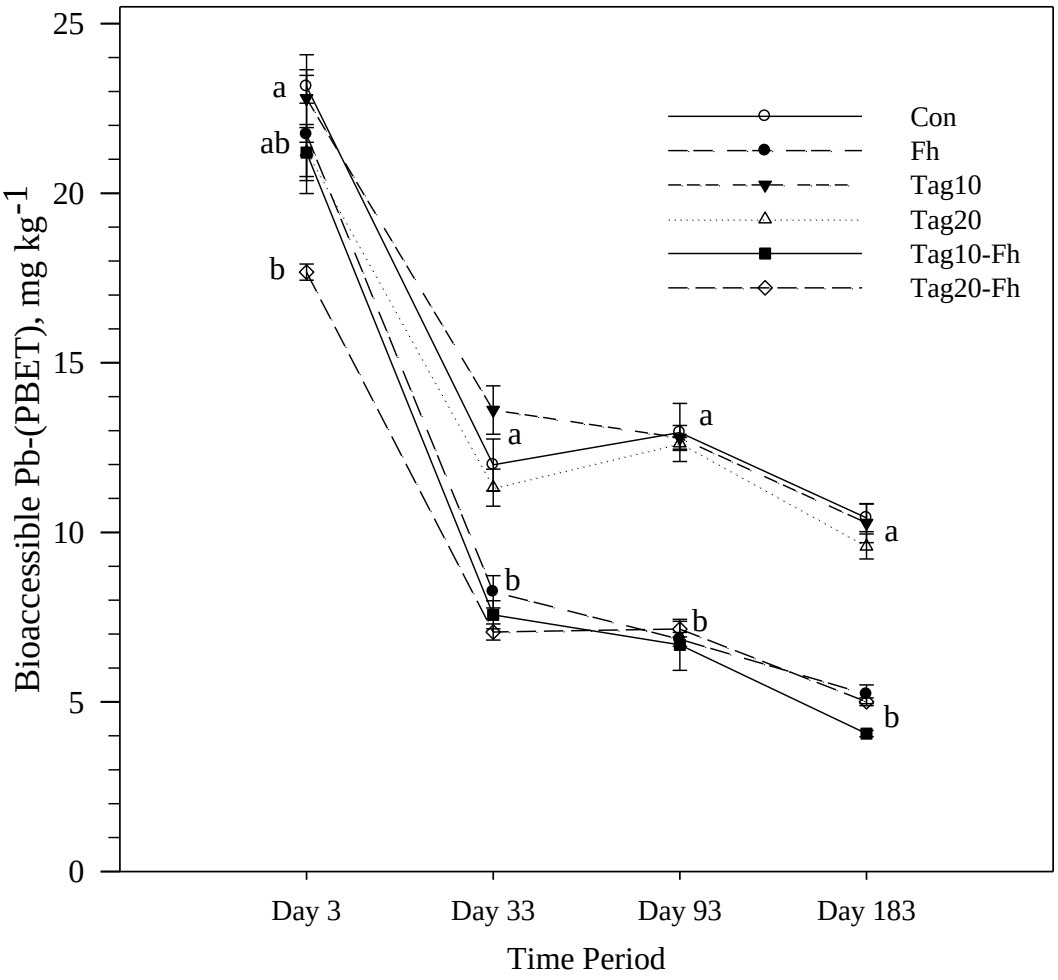


Figure 4.4. Percent bioaccessible Pb at day 33, 93 and 183 of the incubation study. Values above bars represent the exact calculated percentages. Different letters within a time period indicate significance difference (α=0.05).

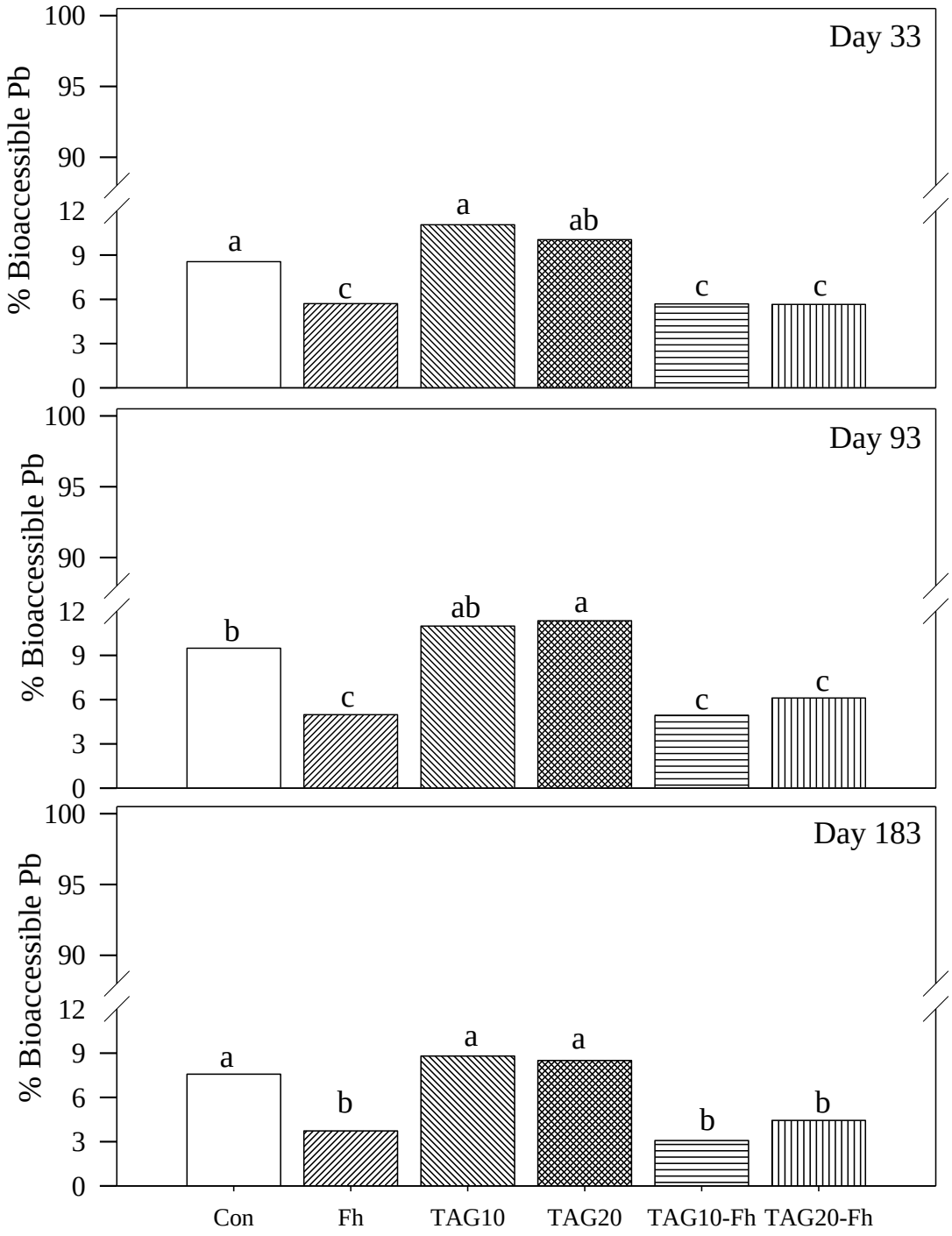


Figure 4.5. Bioaccessible As concentrations of treatments during the incubation study. Different letters within a time period indicate significance difference (α=0.05).

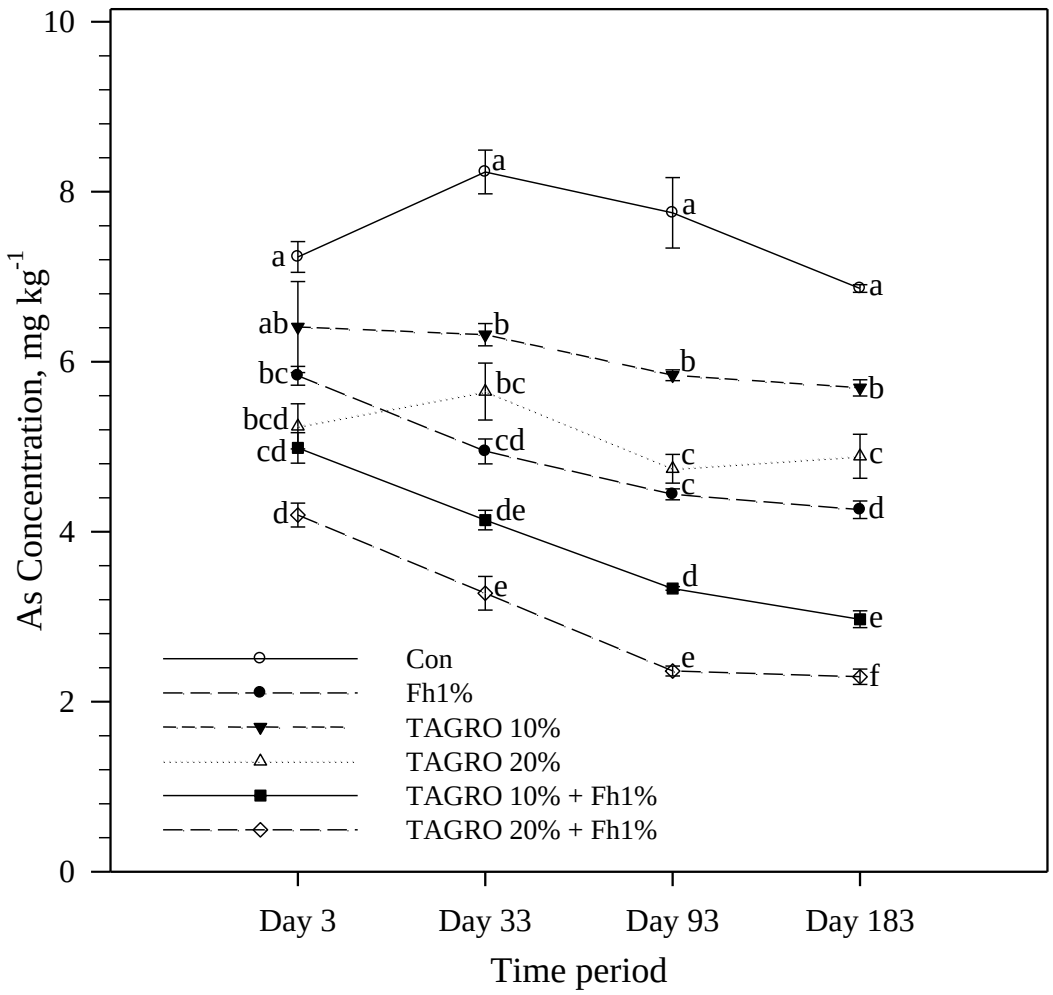


Figure 4.6. Percent bioaccessible As at day 33, 93 and 183 of the incubation study. Values above bars represent the exact calculated percentages. Different letters within a time period indicate significance difference (α=0.05).

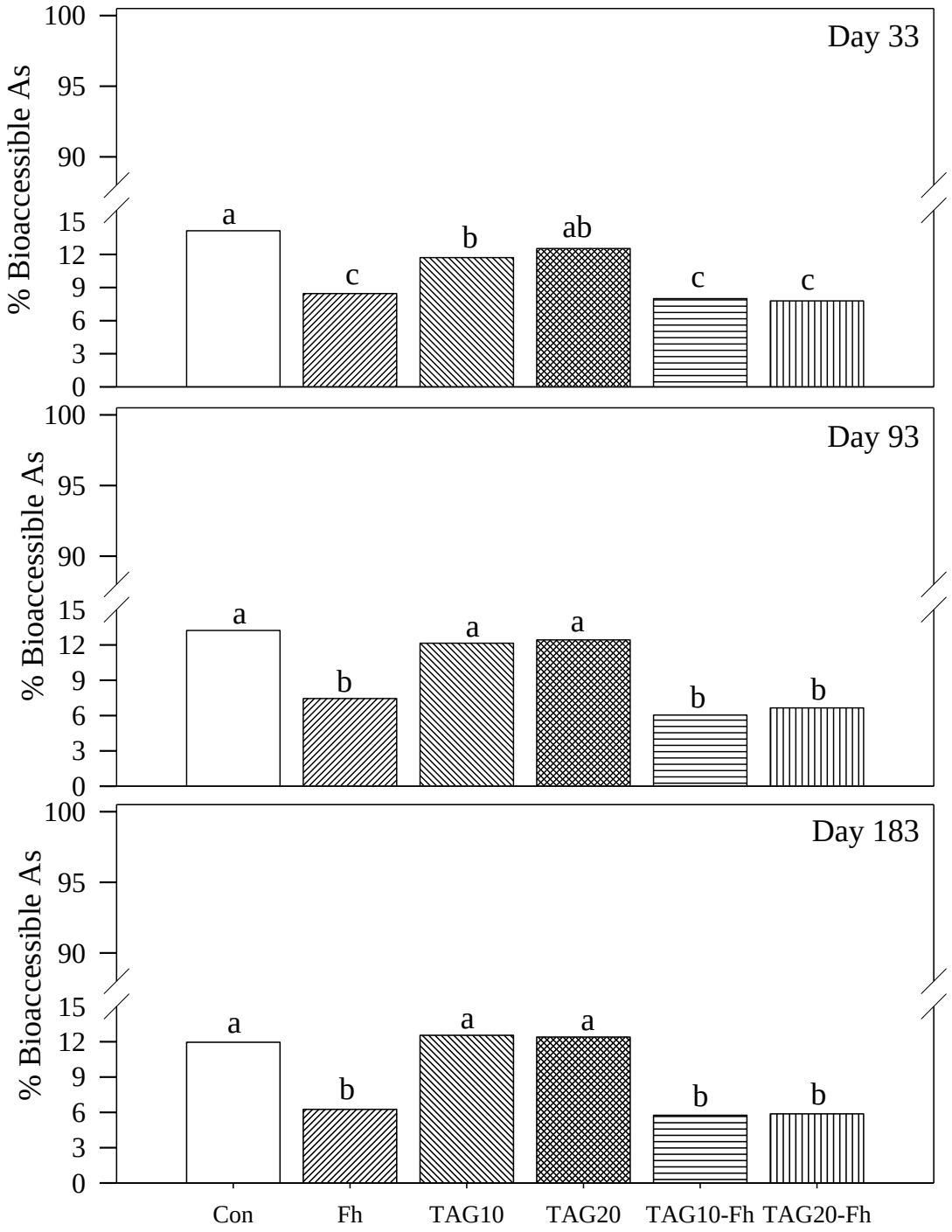


Figure 4.7. Normalized X-ray absorption near edge structure (XANES) Pb absorbance spectra of selected treatments at day 183. The dotted line overlying the XANES spectra of the treatments is the result of a linear least squares fit using Pb standard spectra as components.

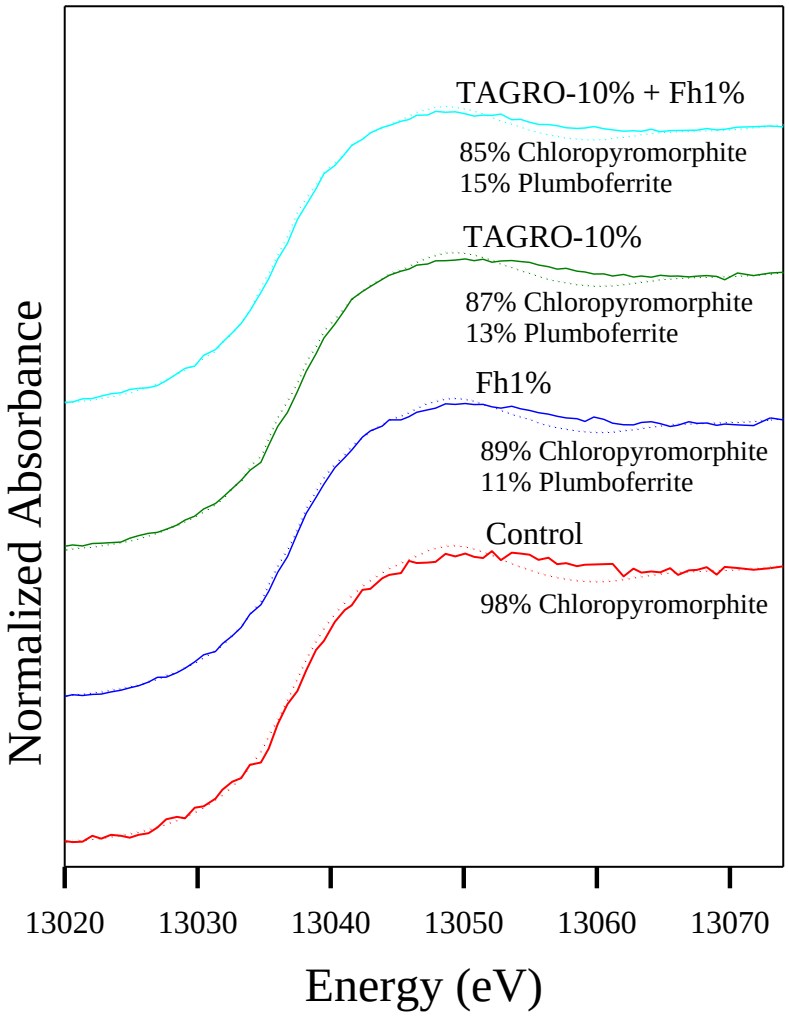
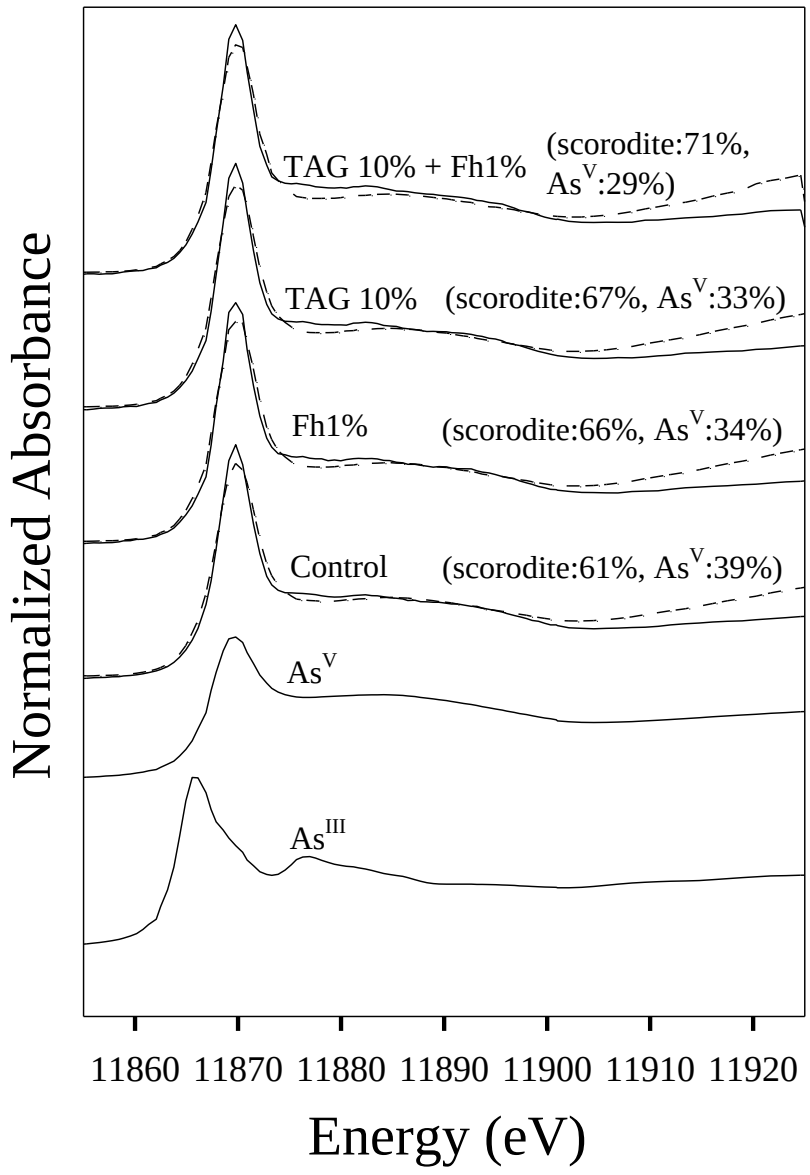


Figure 4.8. Normalized X-ray absorption near edge structure (XANES) As absorbance spectra of selected treatments at day 183. The dotted line overlying the XANES spectra of the treatments is the result of a linear least squares fit using As standard spectra as components.



CHAPTER 5 - IN SITU SOIL AMENDMENTS REDUCE TRANSFER OF LEAD AND ARSENIC IN AN URBAN SOIL TO VEGETABLES AND HUMANS: A GREENHOUSE STUDY

Phillip P. Defoe[1], Ganga M. Hettiarachchi[1,*], Larry E. Erickson[2], DeAnn R. Presley[1], Michel D. Ransom[1], and Gary M. Pierzynski[1]

[1]Department of Agronomy, Throckmorton Plant Sciences Center, Kansas State University, Manhattan, KS 66506, USA

[2]Department of Chemical Engineering, Durland Hall, Kansas State University, Manhattan, KS 66506, USA

ABSTRACT

In situ stabilization of urban soils co-contaminated with Pb and As can be attained by the addition of biosolids and ferrihydrite (Fh) (Chapter 4). Research studies evaluating the influence of these amendments on plant growth and possibility for these contaminants to transfer from soil-plant-human are needed. Further the effect of plant growth on the bioavailability of these contaminants are not clearly understood. Carrots, beets and lettuce were grown on a mildly contaminated soil containing 104.5 mg kg^{-1} of Pb and 46.9 mg kg^{-1} of As until maturity in a controlled greenhouse experiment. Study treatments included a non-amended control, Fh 1%, biosolids mix TAGRO 10%, and the combination of TAGRO 10% and Fh 1%; each treatment replicated three times for each vegetable. All treatments were adjusted to pH 6.8 to 7.5 with calcium oxide. Following harvest, bioaccessible Pb was measured using a physiologically based extraction test (PBET) while bioaccessible As was determined by using first-two steps of a sequential extraction procedure. Results indicated significant treatment by crop-type interactions for soil pH, PBET-Pb, Pb concentrations, and As concentrations in vegetables. Bioaccessible Pb in soils was low, and ranged between 3.9 and 6.1% in the amended and the non-amended control soils indicating that further reductions can be achieved through *in situ* treatments of Fh or the combination of TAGRO and Fh. Percent bioaccessible As in the non-amended control was 15.2%. Application of Fh amendment reduced percent bioaccessible As to 13.9% whereas bioaccessible As in TAGRO and TAGRO plus Fh amended soils were 17.2% and 15.6%, respectively. Plant lead concentrations were in the order: lettuce<beet<carrot. Beet and carrot Pb concentrations exceeded the FAO/WHO established maximum levels (MLs) for root vegetables. Arsenic concentrations in vegetables were low, an indication that food chain transfer of As would not be a concern if consumed. It is possible to reduce Pb and As bioavailability simultaneously while effectively growing crops on TAGRO plus Fh amended urban soils.

INTRODUCTION

The deleterious effects of continuous lead (Pb) and arsenic (As) exposure on humans is well documented (Centeno et al., 2002; Koller et al., 2004; Needleman, 2004). Chronic exposure to elevated Pb levels results in stunted growth, central nervous system (CNS), and kidney damage, and low intelligence quotient (IQ) scores (Canfield et al., 2003; Lanphear et al., 2005; Needleman, 2004). Arsenic is a known carcinogen known to cause lung, bladder, kidney and liver cancer (Centeno et al., 2002; Roy and Saha, 2002; Smith et al., 2009). Additionally, continuous oral As exposure results in hyperkeratosis, skin pigmentation, and CNS damage (Centeno et al., 2002; Mandal and Suzuki, 2002). Children are the most sensitive group due to sensitivity of their developing vital organs and their frequent hand to mouth activities (Markowitz, 2000; Koller et al., 2004; Mielke and Reagan, 1998).

The primary and direct exposure pathway to soil contaminants is through the ingestion or inhalation of contaminated dust (Hettiarachchi and Pierzynski, 2002; Mielke, 1999). Until recently, numerous studies have focused on this primary method of exposure especially in soils contaminated by mine impacted activities. Populations in urban areas and city centers place humans in close proximity to previously contaminated land that was not previously zoned for residential purposes. The source of these contaminants are linked to past anthropogenic use—leaded paint and gasoline, pesticides (Folkes et al., 2001; Mielke, 1999; Mielke et al., 2010; Nriagu, 1990) mining, smelting of sulfide ores, and timber preservation (Bhattacharya et al., 2007; Hingston et al., 2001; Khan et al., 2006). Urban soil contamination persists due to the non-biodegradable nature of these contaminants and in most cases increased enrichment occurs with time following further deposition.

Additionally, a secondary and indirect exposure pathway of these contaminants is through soil-plant-human transfer. Ingestion of vegetables grown in soils contaminated with

trace elements may pose possible risks to human health (Cobb et al., 2000; Warren et al., 2003). Finster et al. (2004) reported on Pb transfer from soil through the root to the stem and leaves of root, leafy and fruiting vegetables grown on urban residential soils. There was a significant correlation between Pb in root crops and soil lead concentrations (Finster et al., 2004). Plants were washed with tap water and a mild detergent to get rid of adhered soil particles (Finster et al., 2004). The problem is not restricted to root crops. Lead concentration of swiss chard grown on 902 mg Pb/kg soil were as high as 22 mg kg^{-1} (dry weight basis) (Finster et al., 2004). Additionally, lettuce grown on a former Pb-Zn smelter site with soil pH of 6.49, 12% clay content and 1626 mg kg^{-1} soil Pb concentrations, had Pb concentration of 0.693 mg kg^{-1} (fresh weight) and exceeded the Australian Food Standards maximum level of Pb (0.1 mg kg^{-1} fresh weight) (Kachenko and Singh, 2006). In a greenhouse study, Cao and Ma (2004) assessed As concentrations for carrots and lettuce grown in contaminated soils collected near fences and poles that were previously treated with chromated copper arsenate (CCA). Arsenic concentrations of the soil collected near the pole and fence were 43 and 27 mg kg^{-1}, respectively, while soil pH was 6.11 and 6.69 (Cao and Ma, 2004). Arsenic in carrots and lettuce grown in the untreated soils were as high as 43 and 32 mg kg^{-1}, respectively.

The transfer potential of contaminants from the soil to plants are often evaluated based on bioconcentration factor (ratio of contaminant concentration in plant to that present in the soil). Evidently, this factor is influenced by plant species, soil type, the concentration and type of contaminant present, and other environmental factors (Greger, 1999; Smical et al., 2008).

The constant perturbation of these soils and/or prolonged consumption of crops grown directly in this environment exposes humans to both exposure pathways. The severity of the risk is influenced by the chemical composition and physical characteristics of the soils, and the type

of vegetables cultivated (Cobb et al., 2000; Cui et al., 2004). It has been a customary practice to use the total soil concentration of urban contaminants in the determination of soil environmental quality standards (Wang et al., 2006). However, predicting soil-to-plant transfer based on total soil contaminant concentrations is questioned because metal speciation and bioavailability in soils vary due to physicochemical properties (Wang et al., 2006). The term "bioavailability" means the portion or fraction of an element or substance that is available for absorption into and across the biological membrane of an organism during a given period and under defined conditions (McGeer, 2004). Although the terms bioavailability and bioaccessibility are used interchangeable, they are different. Bioaccessibility refers to the portion or fraction of the contaminant that is released from the soil into the gastrointestinal (GI) tract and is potentially available for absorption or adsorption (if bioactive upon contact) by the organism (McGeer, 2004). Reducing the bioaccessible fraction of the contaminant would in effect limit human exposure risk and ensure adequate environmental protection. Lead and As bioaccessibility are inherently linked to their speciation (i.e., chemical forms) in soils (Scheckel and Ryan, 2004). Speciation is affected by soil pH, organic matter content (Scheckel and Ryan, 2004; Suavé et al., 2000) and the presence and abundance of phosphorus, manganese oxides and iron oxides/oxyhydroxides (Cances et al., 2005; Hettiarachchi et al., 2000; Kumpiene et al., 2008).

In situ remediation of contaminants in soils using soil amendments focuses mainly on reducing their human health and environmental risk by biogeochemical reactions that convert soil contaminants to forms with low bioavailability. Challenges of using in situ remediation techniques in urban soils are intensified by unique soil characteristics, poor soil quality, and presence of co-contaminants. Consequently, soil amendments capable of stabilizing all the contaminants, and effectively reducing their mobility in the soil environment would be preferred.

In Pb and As co-contaminated soils, it is imperative that simultaneous immobilization of both contaminants can be achieved. *In situ* remediation of soils containing elevated levels of Pb and As have not been adequately studied. There is a paucity of studies examining the bioaccessibility of Pb and As in urban soils.

In a previous incubation study (Chapter 4), biosolids (TAGRO) and ferrihydrite alone or in combination were used to amend a mildly elevated Pb and As co-contaminated soil. These treatments reduced the bioaccessibility of Pb and As by about 30 to 40% compared to the non-amended control soil. Before these amendments can be used in field studies, it is necessary to investigate the interactions of soil amendments and plants. Because BCF varies according to plant species (Cobb et al., 2000; Cui et al., 2004), we conducted a greenhouse study to grow carrots, beets and lettuce. We evaluated the effectiveness of TAGRO and ferrihydrite on plant growth, and the concentration of Pb and As in the edible portions of the vegetables. We also investigated the effect of plant growth on the bioaccessibility of Pb and As in the TAGRO and ferrihydrite treated contaminated soil at the end of the greenhouse study by measuring bioaccessibility of Pb and As. A modified *in vitro* GI method, hereafter referred to as the PBET method, was used to evaluate Pb bioaccessibility. The modified PBET method has shown good correlation with animal model studies (Bruce et al., 2007; Hettiarachchi and Pierzynski, 2004; Scheckel et al., 2009) conducted with mine- impacted soils and mine waste materials. Arsenic bioaccessibility was assessed using the first two steps of a sequential extraction procedure developed by Wenzel et al. (2001) for soil As.

MATERIALS AND METHODS

Soil and treatments

Surface soils (0 to 15 cm) were obtained from an unused area of an urban garden property in Tacoma, WA (47°16′ N, 122°31′ W). Gardeners cultivate a wide variety of leafy, root, and fruit vegetables in raised beds to minimize exposure risks of contaminants. A homogenous batch of this contaminated soil was previously screened to remove urban debris and used for an incubation study assessing the bioaccessibility of Pb and As (Chapter 4). The experimental site soil was a loamy sand with 780 g kg^{-1} sand; 160 g kg^{-1} silt; 60 g kg^{-1} clay; 5.6 pH in 1:5 soil:water; 3.2 g kg^{-1} organic carbon; 26 mg kg^{-1} available nitrogen.

The four treatments evaluated were: control soil; ferrihydrite (Fh) 1%, TAGRO 10%, and TAGRO 10% plus Fh 1%. Treatment were applied on a w/w basis to total weight of 2 kg per each pot. The TAGRO treatments were applied on a moist weight basis. The soil was weighed and the amendments were added and thoroughly mixed by hand to ensure even distribution throughout the soil. Deionized water was added to bring the soil samples to 20% gravimetric water content (Hettiarachchi and Pierzynski, 2002). All treatments were adjusted to a near neutral pH (6.8 to 7.5) with predetermined amounts of CaO, mixed thoroughly for a second time and left to equilibrate for three days. Treatments were then placed in a 3.8-L nursery pots (top and bottom pot diameters were 15 and 13 cm, respectively). The nursery pots were lined with a cellophane bag with only a few small holes to avoid free drainage.

Ferrihydrite (Fh, $Fe_5HO_8 \cdot 4H_2O$) was prepared in the laboratory as described by Schwertmann and Cornell (2008) in bulk amounts. Ferrihydrite was prepared by neutralizing a 0.2 *M* ferric nitrate solution with 1 *M* KOH to a pH between 7 and 8 (Schwertmann and Cornell, 2008). Following pH adjustment, the mixtures were centrifuged at 3000 rpm for 10 minutes on

an Eppendorf centrifuge (Hamburg, Germany) and the residues washed free of excess salts with deionized water. The supernatants were decanted and samples were freeze-dried (Benchtop Labconco freeze dryer, Kansas City, MO). Each batch of ferrihydrite was characterized on an X-Ray diffractometer (APD-3520 Philips, Mahwah, NJ) and then all were thoroughly mixed to obtain one homogenous sample.

TAGRO (50% biosolids, 25% sand, and 25% sawdust) material was obtained from the TAGRO facility in Tacoma, WA. The material is classified as a class A biosolid and is widely used in Tacoma gardens. The TAGRO was stored in 5 gallon plastic containers at 4 °C until it was time for amending the soil.

Greenhouse experiment

The greenhouse study was conducted under controlled environmental conditions at the Department of Agronomy, Kansas State University, Manhattan, KS. The study was conducted using three vegetables and four treatments, each replicated three times in a completely randomized design. Two root vegetables and a leafy vegetable were chosen for the study. Carrots (*Daucus carota* c.v. Red Cored Chantenay), beets (*Beta vulgaris* c.v. Detroit dark red), and lettuce (*Lactuca sativa* c.v. North Star) were first seeded directly to a depth of 1-cm in horticultural grade Metromix growing medium placed in plastic germination trays (contained cell packs). Metromix (MVM/MM-200; Hummert International, Topeka, KS) contained 50-60% horticulture grade vermiculite, Canadian sphagnum peat moss, horticultural grade perlite, and dolomitic limestone. After emergence, homogenous seedlings of each vegetable type were carefully selected for transplanting—one seedling per treatment pot.

To ensure good growth, seedlings were transplanted approximately two weeks following the seeding. Pots were watered ad lib daily (50 - 80 mL per pot). A 16 h daylight and 8 h dark

photoperiod regime was maintained with overhead sodium lights (150 Wm^{-2}). Temperature during the study was within the range of 17 to 23.5 °C. The positions of treatment pots in the greenhouse were rotated weekly to ensure that all pots received equal amounts of light.

Harvesting and sample preparation

Plants were grown until maturity and then harvested. Lettuce was harvested at 9 weeks following transplanting, while carrots and beets were harvested after 13 weeks. At harvest, the roots and leaves were separated. Lettuce roots were cut at the base of the head, approximately 1-cm above the soil surface. Additionally, the lower 2-3 leaves with direct contact to the soil were discarded prior to being placed in labeled Ziploc bags. Any visible soil and root hairs were removed around carrot and beet roots. Wet weights of all samples were recorded on a top loading balance (model B042007, Denver Instrument Company, Arvada, CO).

Lettuce, carrot and beet roots were cleaned using a laboratory cleaning procedure (Attanayake et al., 2014). The vegetables were first washed thoroughly with tap water. They were then washed with a 5 g kg^{-1} sodium lauryl sulfate (SLS) ($CH_3(CH_2)10CH_2OSO_3Na$) solution, and rinsed meticulously with deionized water, removing any adhering soil particles. This anionic surfactant (SLS) has excellent dispersive properties and is low in toxicity (Tricca, 1994). All plant materials were blotted with brown napkins, and left to air-dry for about 30 minutes. Lettuce leaves were thinly chopped with a knife and carrot and beet roots were cut into thin pieces (~ 2 to 4 cm^3). Carrot and beet root pieces were placed in their respective labeled weighing dishes, while the chopped lettuce samples were placed in perforated sealed brown paper bags. Plant samples were dried in a Fisher Scientific Isotemp oven (Marietta, OH) at 65 °C for 5 days or until uniform weight. Dried plant samples were then ground in a stainless steel Wiley mill (Swedesboro, NJ) and the powdered plant material stored in polyethylene vials until

digested. Plant samples were handled in a biological safety cabinet (ESCO Technologies, Hatboro, PA) equipped with Ultra Low Particulate Air (ULPA) filters to avoid contamination by lab air.

Chemical analysis

Ground samples of 0.5 g plant material were digested with 10 mL of trace metal grade nitric acid in Teflon tubes via microwave (CEM, Mathews, NC). The digestion unit was ramped up to 200 °C and held for 15 minutes (1600 W @ 100%, 15-minute ramp time, 15-minute cooling time). Plant digests were filtered with Whatman 42 filter papers into screwed plastic scintillation vials under the fume hood. Samples were then stored at 4 °C until analyzed for Pb and As on graphite furnace atomic absorption spectrometer (GF-AAS, Varian Inc., Australia).

Standard soil reference materials (1573a Tomato leaves, 1515 Apple leaves) from the National Institute of Science and Technology (NIST, Gaithersburg, MD) were digested and analyzed alongside the plant materials as part of the quality assurance–quality control (QA/QC) protocol (accuracies within 100 ± 20%). For QA/QC, reagent blanks, internal standards and spiked-digestions were used where appropriate.

The nursery pots were emptied individually onto clean piece of paper, air-dried and were thoroughly mixed. A subsample (~ 150 g) was sieved through a 2-mm sieve to remove root and other vegetative material prior to analysis for pH, total, and bioaccessible Pb and As. Soil pH was determined in 1:5 soil:deionized water using an Orion glass electrode (model 9157BNMD, Beverly, MA). A physiological-based extraction procedure as modified by Ruby et al. (1996) and described in Chapter 4 was used to determine the bioaccessible Pb. Bioaccessible As was determined using the first two steps of a sequential extraction procedure as described by Defoe et al. (Chapter 4). Total soil Pb and As concentrations of the treatments were determined as

described by Defoe et al. (Chapter 3, 4). Filtered (Whatman 42) soil digests were analyzed on GF-AAS (Varian Inc., Australia). Statistical analyses were performed using SAS for Windows version 9.2 (SAS Institute Inc., Cary, NC). Data were analyzed using Proc mixed and Tukey's Honestly Significant Difference (HSD) test used for means separation (α= 0.05).

RESULTS AND DISCUSSION

Soil pH

The soil used for the study was characterized as loamy sand (780 g kg^{-1} of sand), and is mapped as the Alderwood series (moderately deep, moderately well drained soils formed in glacial till). Sandy soils have very little capacity to buffer pH (Melamed et al., 2003; Vitosh et al., 2000). Despite the additions of calcium oxide to raise and maintain pH between 6.8 to 7.5, pH in soils collected at the end of the greenhouse study ranged from 5.74 to 6.41 (Fig. 5.1). The pH in the amended soils were lower compared to the control soil (Fig. 5.1). There was a treatment by crop type interaction (Table 5.1). Generally, pH of amended soils where lettuce was grown were slightly higher (5.8 to 6.41) compared to the two root crops (5.74 to 6.19, Fig. 5.1). Carrot pots amended with ferrihydrite had the lowest soil pH (Fig. 5.1). Compared to the control, soil pH in carrot pots amended with TAGRO alone showed no significant (α=0.05) difference. Soil pH in lettuce pots amended with TAGRO only or TAGRO in combination with ferrihydrite had the lowest pH (5.95 and 5.87, respectively) and were about 0.5 log units lower than the control, indicating that acidulating effect of ferrihydrite was greater.

Similar results were observed in a six-month long incubation study conducted by Defoe et al. (Chapter 3) using this same soil and similar treatments when the soil was adjusted with CaO to obtain a pH of 6.8 to 7.5. McIvor et al. (2012) also reported decreases in soil pH following TAGRO and GroCo biosolids based amendments applied to urban gardens in Tacoma.

GroCo amendments are produced from class B biosolids and are blended with wood chips (1:3). Soil pH of plots amended with biosolids at a rate of 200 Mg ha^{-1} (dry weight) ranged between 5.35 to 5.75, while that of non-amended control plots was 6.43 (McIvor et al., 2012). The differential responses of soil pH with respect to crop type and treatment may be explained by two reasons. Firstly, the root vegetables displayed similar treatment effects on pH, because roots crops were harvested about 4 weeks later than the lettuce harvesting. Similar treatments used in our previous soil incubation study (i.e., no plants) also showed a further reduction in soil with increasing incubation time (Chapter 4). The second possible reason might be the effect of root exudates. Changes in rhizosphere pH have been attributed to the ability of plant roots to counterbalance a net excess of cations or anions entering the roots by releasing either H^+ or OH^- /HCO^{-3} (Hinsinger et al., 2003). Root exudates comprise of compounds such as amino acids, organic acids, sugars, and other secondary metabolites (Walker et al., 2003). The composition of root exudates and organic acids have been reported to vary considerably between plant species (Neumann and Römheld, 1999) and among genotypes of a given species (Pellet et al., 1995). Similar soil pH response was observed for the two root vegetables irrespective of applied treatment may be due to their comparable root exudate compositions.

Influence of treatments on plant growth

Without exception, plant growth among all of the vegetables studied was sensitive to applied amendments (Table 5.2, Appendix C). Carrots, beets and lettuce grown in ferrihydrite amended pots showed very poor growth compared to non-amended control and other amended pots. Yield data (fresh weight basis) of the edible portion of the vegetables clearly indicated growth suppression in ferrihydrite amended pots (Table 5.2). We believe that the poor growth observed may be a consequence of iron toxicity instead of soil pH. Mean soil pH in the

ferrihydrite treatments for the vegetables ranged from 5.74 to 6.14. Although soil pH influences nutrient solubility and their availability for plant uptake, in this case, the soil pH may not have been significant or critical to control nutrient uptake. Alternatively, Fe toxicity seems a much more logical reason. It is likely that the proton-or biologically-induced reductive dissolution of ferrihydrite may have increased Fe^{2+} in the soil solution. Moreover, iron oxides have been reported to affect vegetation growth (Hartley and Lepp, 2008; Mench et al., 1999).

Alternatively, the increased biomass observed in TAGRO and TAGRO plus ferrihydrite amendments (except carrot in TAGRO plus ferrihydrite treated pots) was not surprising. Biosolids composts in particular, TAGRO mix, has been proven to improve total carbon and nitrogen, extractable phosphorus and increase water infiltration (McIvor et al., 2012; Brown et al., 2011). Our field studies (Chapter 3) conducted at the site where the soils for this study were collected, showed significant (about 4 times) increases in yield when crops were grown on TAGRO amended field plots compared to non-amended control plots. With the exception of beet where an increase in biomass was observed, the addition of ferrihydrite to TAGRO in carrots and lettuce pots observed lower biomass (Table 5.2).

Influence of treatments on plant Pb concentrations

Plant Pb concentrations of the vegetables are presented in Fig. 5.2. Due to poor growth in the ferrihydrite amended pots, there was insufficient carrot samples for the plant Pb determination. In the case of lettuce grown in ferrihydrite amended soil, harvest of all replicates (all 3 pots) were composited to obtain a representative sample for digestion.

Generally, plant Pb concentrations were low and ranged from 0.24 to 10.05 mg kg^{-1} (dry weight basis; Fig. 5.2). Plant lead concentrations increased in the order: lettuce<beet<carrot (Fig. 5.2). Similar trends were reported for lettuce and carrot grown on plots amended with biosolids

or Cedar-Grove compost (Chapter 3). High accumulation of lead in roots has been attributed to their ability to bind Pb in the xylem (MacFarlane and Burchett, 2000) ultimately limiting its translocation to other plant parts (Finster et al., 2004). The incorporation of TAGRO and ferrihydrite amendments applied alone or in combination further reduced Pb concentrations in the vegetables. The TAGRO biosolids contain high P (Chapter 3). High P amendments bind soil Pb consequently making them less mobile in the soil (Basta and McGowen, 2004; Hettiarachchi et al., 2002; Laperche et al., 1997), thus less available to be taken up by plant roots.

Food chain transfer of crop contaminants are usually evaluated on bioconcentration factor (BCF) (Alam et al., 2003; Samsøe-Petersen et al., 2002). The ratio of dry weight basis concentrations of the contaminant in the vegetables and in the medium where they were grown represents the BCF. Among all of the treatments, carrots accumulate Pb by a factor of 3.5 to 5 over beets (Table 5.3). For both root crops, the TAGRO plus ferrihydrite amendment being the most effective in reducing Pb soil-plant transfer. Comparatively, the BCF-Pb for lettuce are about 2 orders or magnitude lower. The lack of accumulation of Pb in lettuce leaves (or low BCF) can also be attributed to high biomass obtained (Appendix C), when grown in soils treated with amendments containing high organic matter and essential plant nutrients. Moreover, the addition of TAGRO effectively reduced the soil Pb concentration via dilution.

Concentrations of Pb in lettuce were below the MLs established by the Food and Agriculture Organization (FAO) and the World Health Organization (WHO) in 2010 (FAO/WHO-CODEX 1995; 2010 amendment) (Fig. 5.2). Unlike lettuce, carrot and beet Pb concentrations far exceeded the MLs established by the FAO/WHO in 2010 (Fig. 5.2). The estimated MLs by FAO/WHO (expressed on fresh weight basis) were calculated assuming 100% bioavailability in the edible portion of the crops, therefore, may be overly protective. For ease of

comparison, established FAO/WHO Pb MLs (0.1 mg kg^{-1} for root crops; 0.3 mg kg^{-1} for leafy vegetables) were converted to dry weight basis using reported moisture content of the vegetables. Moisture content used for carrots and beets range from 88 to 93% (Patras et al., 2011; Sipahioglu and Barringer, 2003), while lettuce was 94 to 95% (Patras et al., 2011). Consequently, calculated Pb MLs (dry weight basis) for carrots and beet ranged from 0.8 to 1.4 mg kg^{-1}, while lettuce values were 5 to 6 mg kg^{-1} (Fig. 5.2). If we assume that about 20 to 30% of Pb in the vegetables is bioavailable, carrots would still exceed the MLs, while it may be safe to consume beets grown in amended soils.

Influence of treatments on plant As concentrations

Plant As concentrations are given in Fig. 5.3. Without exception, plant As concentrations in the vegetables were very low, ranging between 170 and 600 µg kg^{-1} (Fig. 5.3). Arsenic concentrations in the vegetables increased in the order: beet<carrot<lettuce. Arsenic concentrations in beet roots were least sensitive to soil amendments. For carrots, slightly higher concentrations were observed for TAGRO and TAGRO plus ferrihydrite treatments (Fig. 5.3). Increasing P applications have been reported to cause an increase in As concentrations (Creger and Peryea, 1994). Creger and Peryea (1994) reported that the application of monoammonium phosphate added to a Burch loam soil containing lead arsenate residues, increased As concentration of apricot liners (young plants usually propagated from stock). This effect was not biased by biomass dilution because shoot and root biomasses were constant (Creger and Peryea, 1994). In contrast, As concentrations in the lettuce grown in TAGRO amended pots, were about 40 to 60% lower than the lettuce grown in the non-amended control, ferrihydrite or TAGRO plus ferrihydrite amended pots. Similar reductions in lettuce As concentrations were observed in field studies where TAGRO biosolids were used as an amendment (Chapter 3). Our results indicate

that the effect of phosphate, if there is any, can be negated due to the beneficial effect of TAGRO (enhanced biomass production). For the lettuce, with the TAGRO amendment there was 17% reduction in total As concentration in soil (data not presented) and had the lowest plant As concentration (Fig. 5.3). In the TAGRO plus ferrihydrite amended pots, total soil As concentration was reduced by ~ 26% and plant As concentrations were 50% lower than lettuce grown in TAGRO only amendments (Fig. 5.3). Comparatively, a 26% increase in biomass was observed when lettuce was grown in TAGRO amendments alone vs. TAGRO plus ferrihydrite amended soil (Table 5.2). Consequently, although the TAGRO only amendment did not achieve the lowest soil As dilution, it was effective in having the lowest BCF-As and the highest plant biomass.

An accurate assessment of soil-plant transfer of As is achieved with analysis of BCF as it would not be affected by the dilution effect due to large addition of some soil treatments (Table 5.4). The BCF-As of carrots and beet roots (Table 5.4) indicated that different plant species may respond differently when grown in similar amendments.

Influence of plant growth on soil Pb bioaccessibility

Values of bioaccessible Pb in the soils were low irrespective of treatment application and ranged between 4.0 and 8.0 mg kg^{-1} (Fig. 5.4). Percent bioaccessible Pb was below 6.2% irrespective of treatment or the crop-type that grew in the soil (Fig. 5.5). Generally, both ferrihydrite alone and TAGRO plus ferrihydrite amendments significantly reduced bioaccessible Pb in all soils, irrespective of the vegetable type that were grown-in. It seems that some plants may be affecting percent bioaccessible Pb. For example, though not statistically significant, increased bioaccessible Pb was observed in TAGRO amendment compared to the control soils where carrots and lettuce were grown. In contrast, clear treatment differences were observed in

soils where beet was grown (Fig. 5.7). Moreover, the highest percent bioaccessible Pb was observed in the control, and the most significant reductions (~50%) were observed for the ferrihydrite and TAGRO plus ferrihydrite amendments. Compared to the control soil, the higher concentration of organic C in the biosolids amended soils may be responsible for forming stable complexes with soil Pb, effectively reducing its bioavailability (Brown et al., 2003). These results are not surprising since previous studies have reported low Pb bioaccessibility in urban soils (Ge et al., 2000). Although the soil Pb concentration was mildly elevated (105 mg kg^{-1}), amorphous iron (Fe) concentration was 3.73 g kg^{-1}. Amorphous Fe has been known to be a sink of Pb in contaminated soils (Ruby et al., 1994; Zia et al., 2011).

Influence of plant growth on soil As bioaccessibility

Arsenic bioaccessibility was evaluated using the first two steps of a sequential extraction procedure as described by Wenzel et al. (2001). Generally, As bioaccessibility was low, and was not influenced by plant growth (Fig. 5.6). Earlier experiments had demonstrated low As bioaccessibility in control soils with further reductions upon application of amendments (Chapter 4). For similar amendments, As bioaccessibility ranged from approximately 3 to 7 mg kg^{-1} in the previous incubation study while mean As bioaccessibility in this study ranged between 5.5 and 6.5 mg kg^{-1}. Low bioaccessible As may be explained by As speciation in these soils, particularly due to its anthropogenic origin (Wang et al., 2007). Arsenic contamination in this soil was due to aerial deposition from a nearby Cu smelter. Speciation analyses have identified As^{5+} as the main As species in soils that were contaminated from aerial deposition from Cu smelters (Sánchez-Rodas et al., 2007). However, in our study, a predominance of As^{5+}, scorodite ($FeAsO_4 \cdot 2H_2O$)-like species was observed in all soils (both non-treated control and treated soils). Arsenic present in this form is generally considered to be less mobile and bioaccessible in soil environments.

Percent As bioaccessibility ranges from 13.9% to 17.2% (Fig. 5.7). The highest percent bioaccessibility was observed for the TAGRO amendment. Similar results were found in previous experiments (Chapter 4). We hypothesize that the dilution effect of TAGRO amendment overrode the negative effect from increased P concentration. It is evident that trace element bioaccessible values without consideration of the percent bioaccessible fraction within that specific treatment can be misleading (Fig. 5.6). For this reason, it may be more important to assess percent bioaccessibility to ascertain the effect of treatment. Percent bioaccessibility normalizes the effect of dilution, allowing for treatment effect comparisons.

CONCLUSION

Lead and Arsenic bioaccessibility was assessed in the edible portions of two root vegetables and a leafy vegetable grown in a controlled greenhouse study. Lead concentrations in carrots and beet roots were significantly higher than lettuce (carrots>beets>lettuce) and exceeded the established FAO/WHO MLs. The TAGRO plus ferrihydrite amendment was most effective in reducing Pb concentration in the vegetables. Generally, As concentrations in the vegetables were very low, indicating that the food chain transfer of As would not be a significant pathway of As exposure from urban soils to humans. The BCF-As for the vegetables grown on non-amended or amended soil ranged from 0.005 to 0.012. Vegetables grown in ferrihydrite only amendments showed poor growth, while having satisfactory reductions in bioaccessible Pb and As. The amendments used in this experiment should be harnessed using the field validation studies to ascertain a better understanding of human exposure risks. Since the bioavailability of the contaminants are affected by physical, biological and chemical properties and processes, field studies should be conducted evaluating the ability of these amendments to be effective in a variety of urban soils.

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Table 5.1. Summary ANOVA table

	pH	Bioaccessible Pb	Bioaccessible As	Plant-Pb concentration	Plant-As concentration
Treatment	<0.0001	<0.0001	<0.0001	0.0009	0.0527
Crop type	<0.0001	0.0845	0.0727	<0.0001	<0.0001
Treatment x Crop type	0.0210	0.011	0.3518	0.0131	<0.0001

Proc mixed, LS means/Tukey, (α=0.05)

Table 5.2. Harvest weights (fresh wt.) of edible portion of vegetables grown in various treatments.

Treatment	Crop type		
	Carrot†	Beet	Lettuce
	---------- g ----------		
Control	38.7 ± 5.6	18.7 ± 1.9	45.0 ± 13
Fh1%	9.4 ± 3.8	2.17 ± 1.1	0.2 ± 0.1
TAGRO 10%	101.3 ± 19.2	76.0 ± 3.5	166.0 ± 8.1
TAGRO 10% + Fh1%	26.0 ± 1.2	96.3 ± 22.8	123.3 ± 19.8

†Values are means of three triplicates

Table 5.3. Bioconcentration factor (BCF) of Lead (Pb) in vegetable crops grown in various amendments. The BCF was calculated as the ratio of dry weight basis Pb concentrations (mg kg^{-1}) of the contaminant in the vegetable and in the soil (mg kg^{-1}) in which plants were grown.

Treatment	Crop-type		
	Carrot	Beet	Lettuce
	----------mg kg^{-1} DW: mg kg^{-1} DW----------		
Control	0.096	0.032	0.018
Fh1%	n.a†	0.033	0.005
TAGRO 10%	0.103	0.020	0.003
TAGRO 10% + Fh1%	0.070	0.020	0.008

†insufficient sample collected for analysis

Table 5.4. Bioconcentration factor (BCF) of Arsenic (As) in vegetable crops grown in various amendments. The BCF was calculated as the ratio of dry weight basis As concentrations (mg kg^{-1}) of the contaminant in the vegetable and in the soil (mg kg^{-1}) in which plants were grown.

Treatment	Crop-type		
	Carrot	Beet	Lettuce
	----------mg kg^{-1} DW: mg kg^{-1} DW----------		
Control	0.006	0.007	0.012
Fh1%	n.a[†]	0.006	0.012
TAGRO-10%	0.011	0.007	0.005
TAGRO-10% + Fh1%	0.010	0.005	0.012

[†]insufficient sample collected for analysis

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Figure 5.1. Soil pH of various amendments where lettuce, carrot and beet roots were grown. Vertical bars represents the means of three replicates. Different letters within a crop type indicate significant difference (α=0.05).

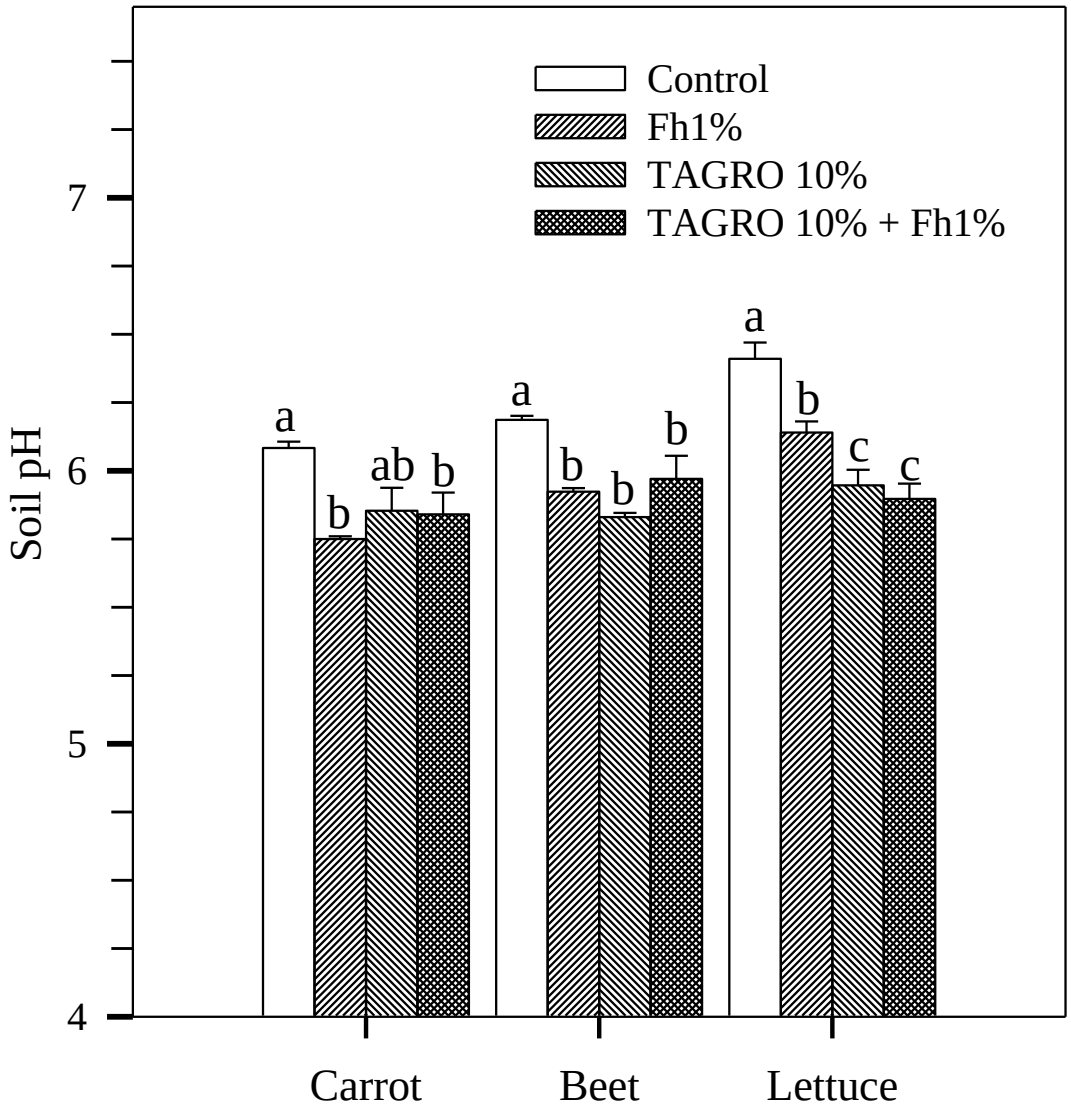


Figure 5.2. Plant lead (Pb) concentrations in lettuce, carrot and beet roots. Vertical bars represents the means of three replicates. Different letters within a crop type indicate significant difference (α=0.05). Asterisk (*) denotes concentration of composited replicates (insufficient sample size for individual replicate analysis).

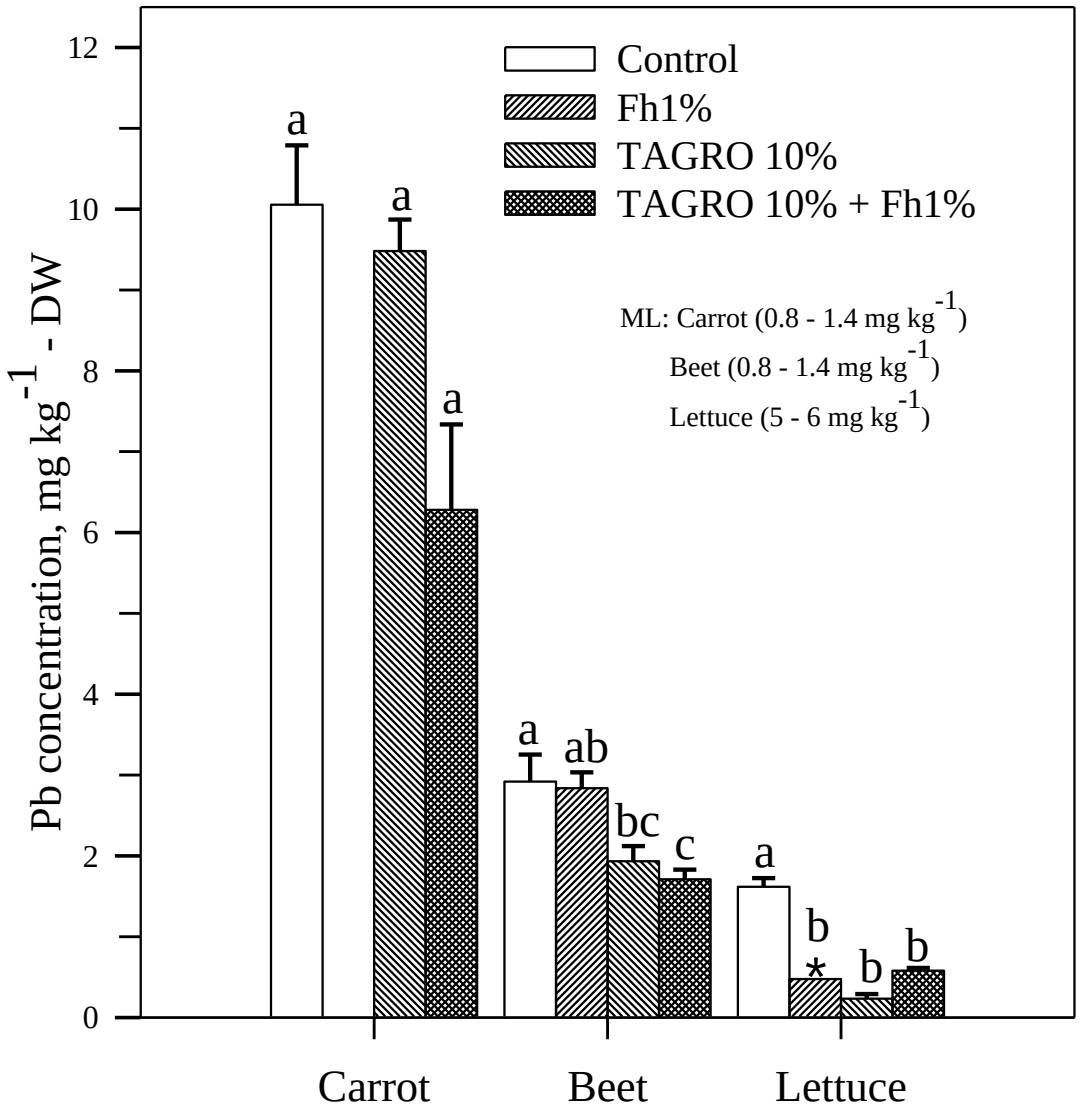


Figure 5.3. Plant arsenic (As) concentrations in lettuce, carrot and beet roots. Vertical bars represents the means of three replicates. Different letters within a crop type indicate significant difference (α=0.05). Asterisk (*) denotes concentration of composited replicates (insufficient sample size for individual replicate analysis).

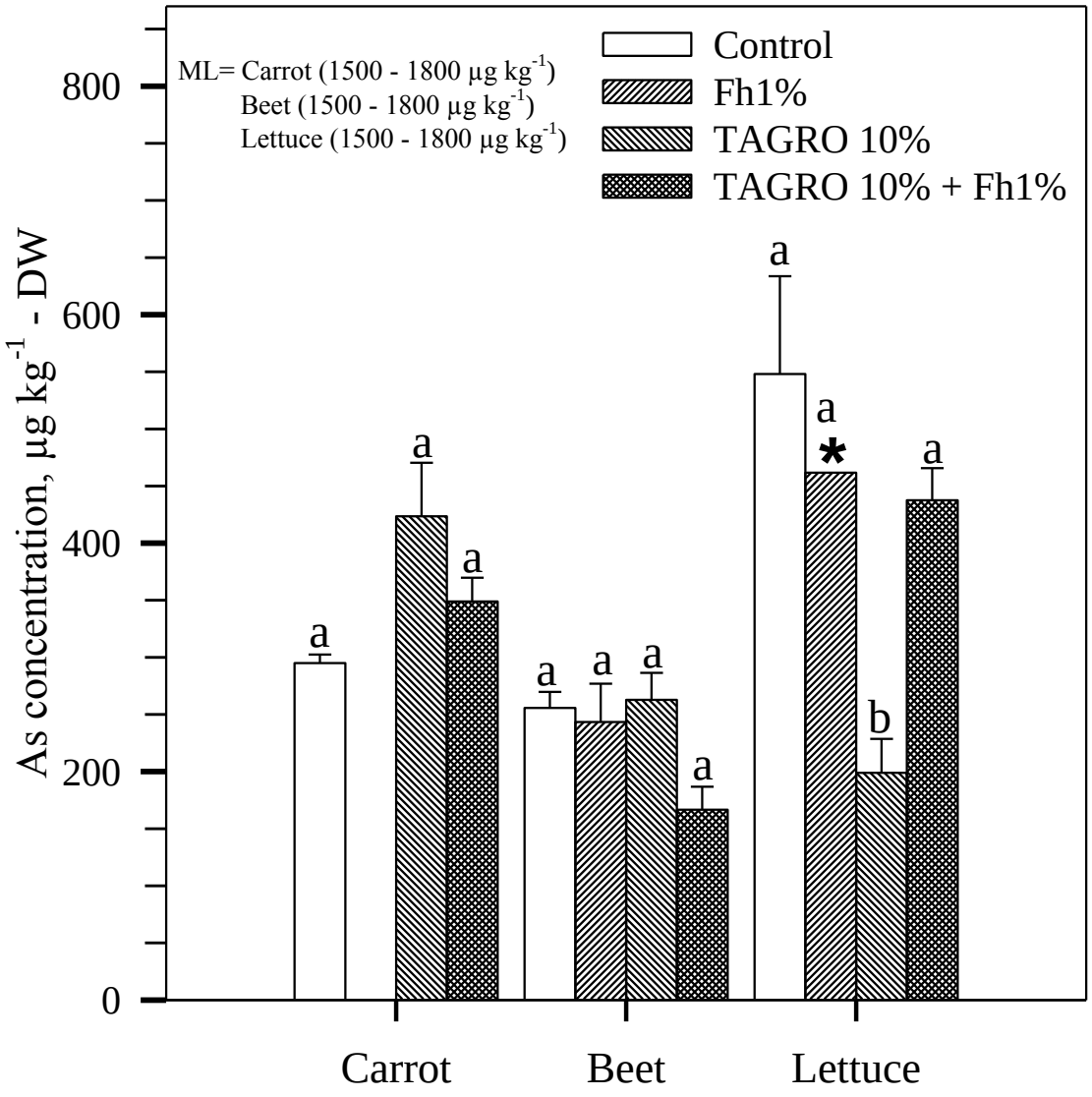


Figure 5.4. Bioaccessible Pb by PBET for the contaminated soil amended with biosolids and ferrihydrite. Vertical bars represents the means of three replicates. Different letters within a crop type indicate significant difference (α=0.05).

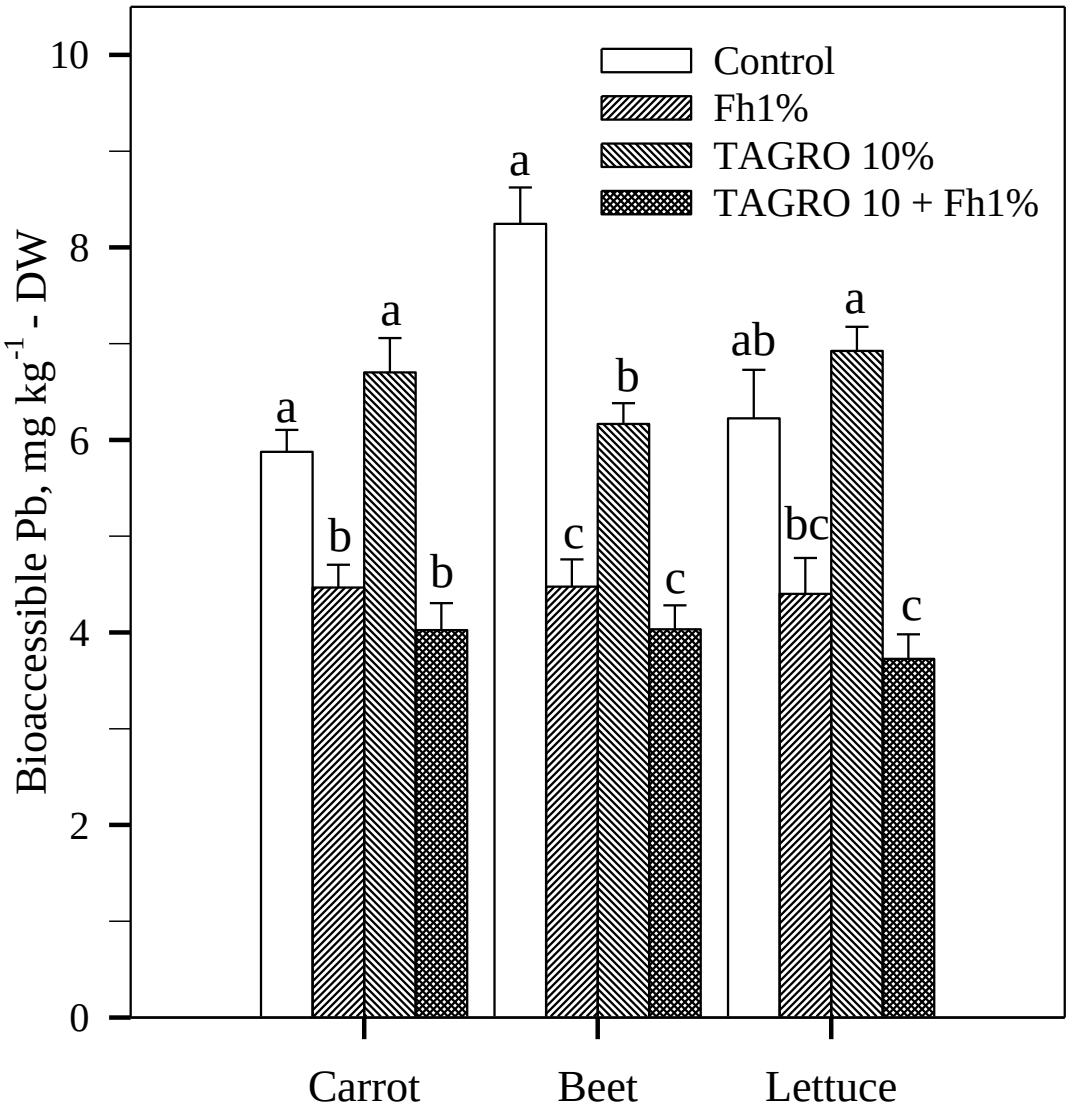


Figure 5.5. Bioaccessible Pb by PBET for the contaminated soil amended with biosolids and ferrihydrite. Vertical bars represents the means of three replicates. Different letters within a crop type indicate significant difference (α=0.05).

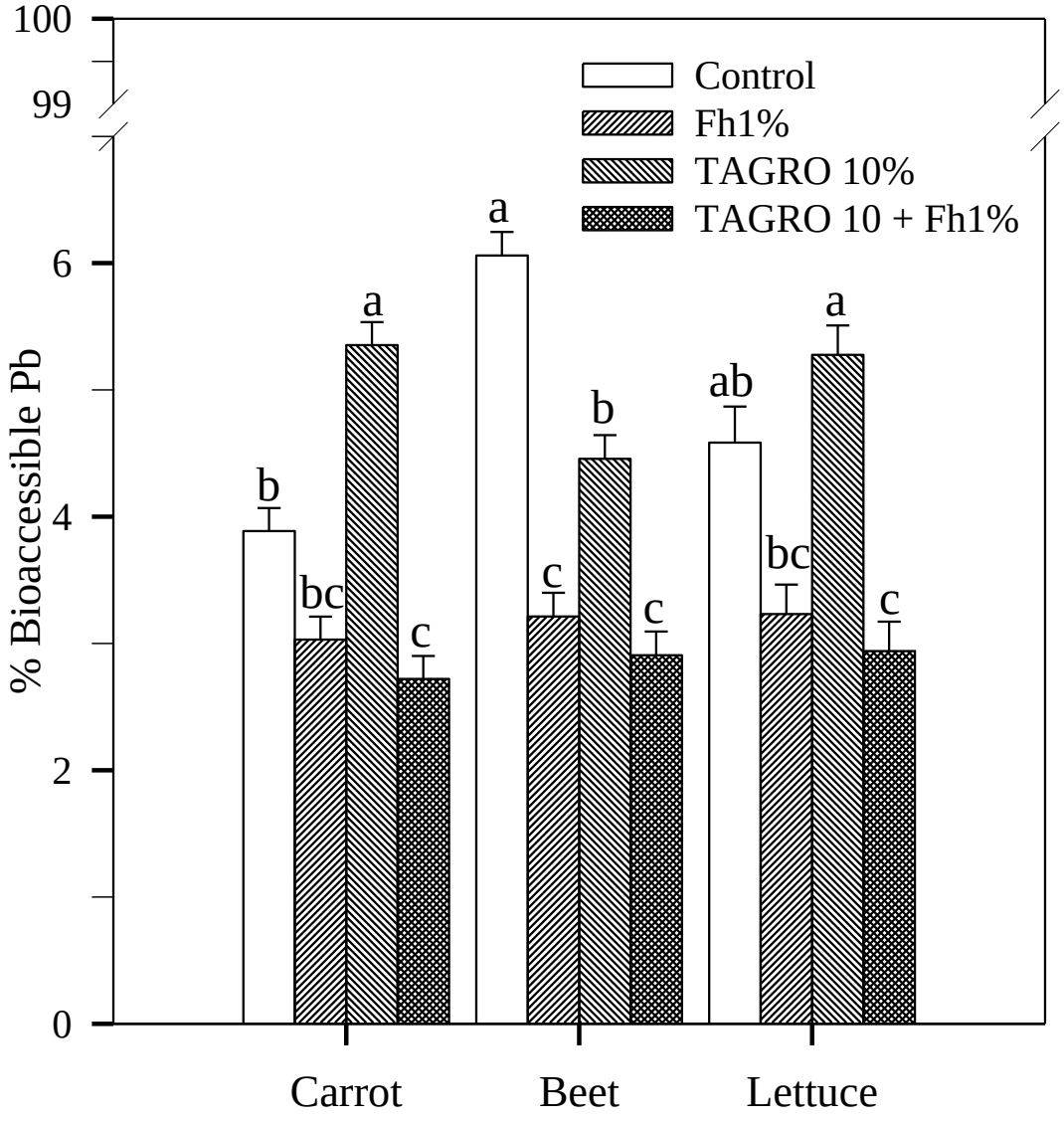


Figure 5.6. Bioaccessible Pb by PBET for the contaminated soil amended with biosolids and ferrihydrite. Vertical bars represents the means of three replicates. Different letters within a crop type indicate significant difference (α=0.05).

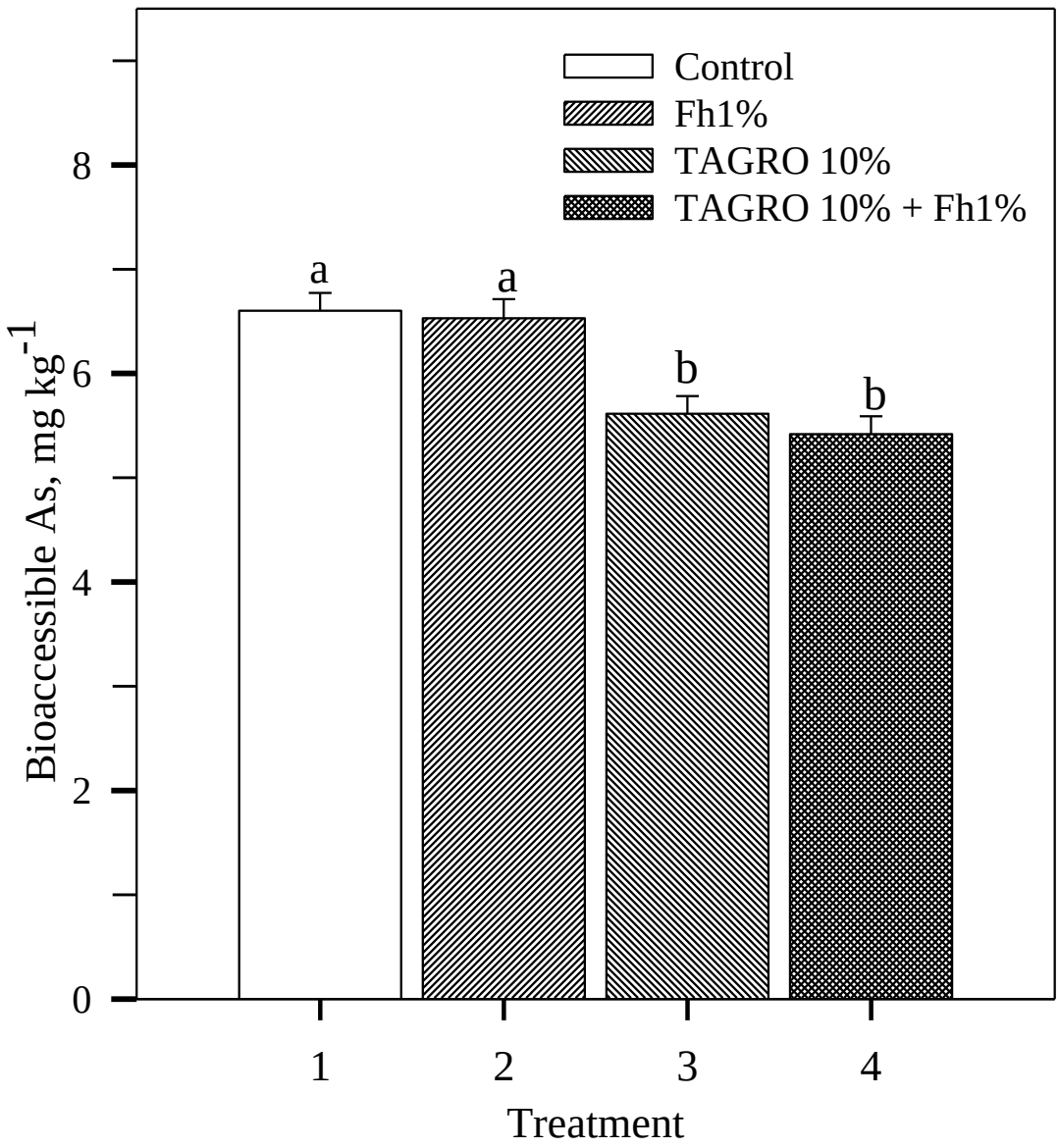
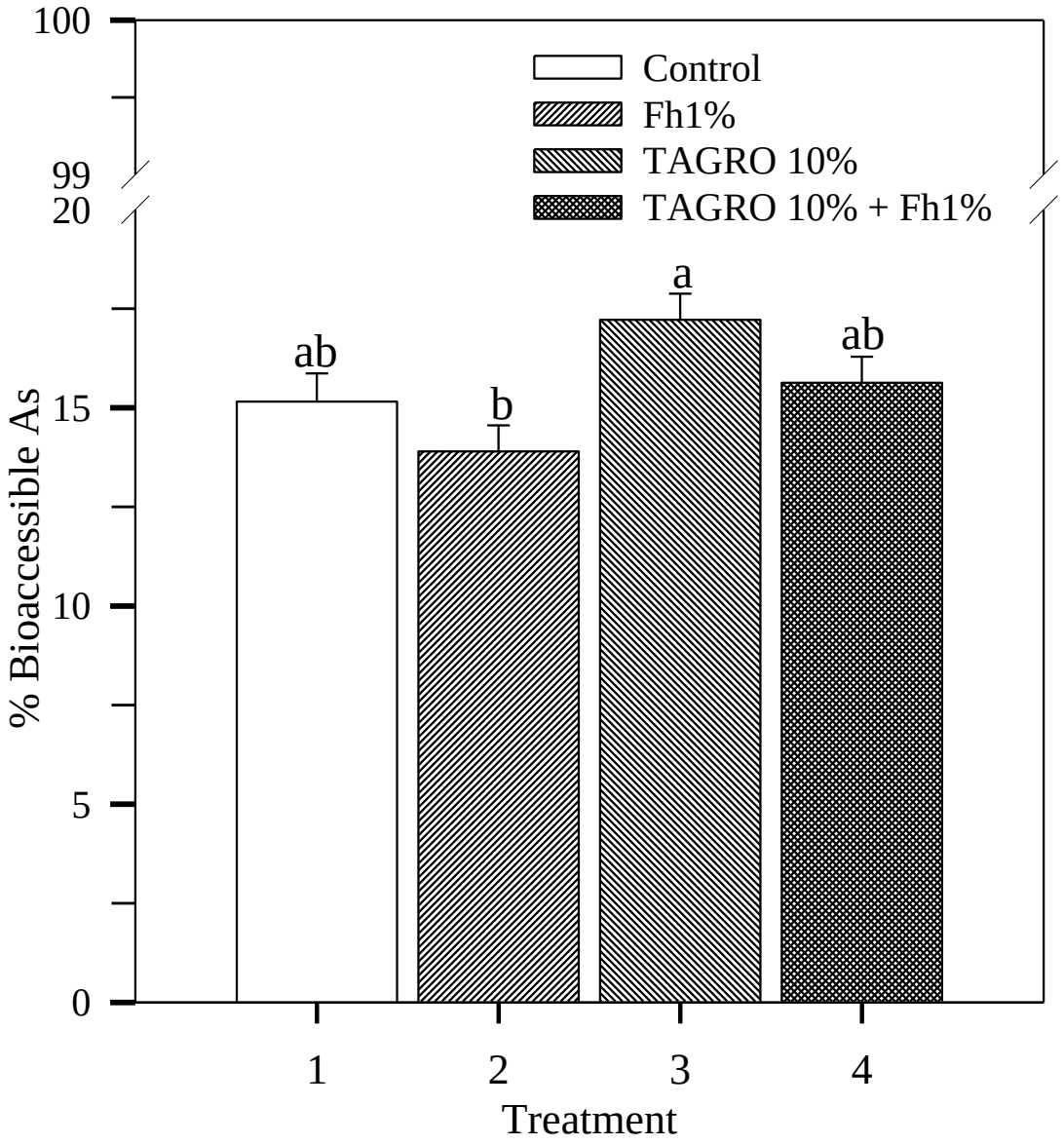


Figure 5.7. Percent bioaccessible As for the contaminated soil amended with biosolids and ferrihydrite. Vertical bars represents the means of three replicates. Different letters within a crop type indicate significant difference (α=0.05).



CHAPTER 6 - GENERAL CONCLUSIONS AND STUDY IMPLICATIONS

A series of field, laboratory and greenhouse studies were conducted on Pb and As contaminated soils to understand the potential transfer of these contaminants to urban gardeners, and other humans through direct exposure or food chain transfer. Effectiveness of *in situ* soil treatments utilizing organic amendments and an iron source solely or in combination was also tested using in vitro bioaccessibility test and x-ray absorption spectroscopy for understanding underlying mechanisms of reducing Pb and As bioavailability, thereby minimizing their exposure risk to humans.

Field studies

1. The application of TAGRO biosolids and Cedar-Grove compost amendments was effective in reducing the total soil Pb and As concentration through dilution.
2. At the Tacoma site, co-contaminated with Pb and As, total Pb and As concentrations were 10 to 25% lower in TAGRO and dolomite amendment soils compared to the non-amended control.
3. At the Seattle site, contaminated with Pb, soil Pb concentrations were diluted by 20 to 50% when soils were amended with Cedar-Grove composts. Both test sites (Tacoma and Seattle) had inherently low bioaccessible Pb and As concentrations, indicating that direct exposure through accidental ingestion of contaminated garden soils would be low. However, best management practices focusing on reducing direct exposure to contaminated soils should be a priority as it would be the main exposure pathway of the contaminants in garden soils to humans.

4. Growing root crops directly in some soils (examples, sandy soils with low pH) where total Pb concentrations were greater than 300 mg kg^{-1} can result in Pb concentrations in root crops that exceed the WHO/FAO MLs of 1.5 mg kg^{-1} (dry weight).
5. Leafy and fruiting vegetables in soils contaminated with Pb at levels equal to the HUD/USEPA's residential soil limits (i.e., 400 mg kg^{-1}) will not result in concentrations greater than the MLs established by the FAO/WHO in 2010 for those vegetables.
6. Arsenic concentrations in vegetables were low even without amendment, and below the calculated MLs based on the EPAs daily inorganic As exposure limits. Consequently, As exposure risks based on the soil-plant-human pathway under urban gardening situation would be low.
7. Food-chain transfer of Pb and/or As can be reduced with the use of a surfactant/detergent to remove the surface contamination of produce with contaminated dust/soil particles.
8. At both sites, crop yields in the compost amended soils were significantly higher than non-amended control soils. This high biomass production in the compost amended soils is an indication that contaminants transferred from the soils to plants is again diluted by high biomass production.

Incubation and greenhouse studies

1. Additions of ferrihydrite alone and TAGRO and ferrihydrite in combination were both significantly effective in minimizing human exposure risks in Pb and As co-contaminated soils.
2. Percent bioaccessibility values help to separate dilution effect from the chemical effect of *in situ* soil treatments. Generally, percent bioaccessible Pb and As in amended soils with ferrihydrite alone or TAGRO and ferrihydrite in combination decreased with incubation

time, indicating that these reductions were not only due to dilution of total Pb or As in soils.

3. Repeated applications of TAGRO and iron in combination may be successful in further reductions of Pb and As bioaccessibilities where they are of great concern.
4. Plant growth was severely affected when grown in ferrihydrite treated soils. Due to the plant growth limitation of the ferrihydrite amendment, the TAGRO and ferrihydrite in combination can be considered to be the most effective treatment out of the treatments tested in this study.
5. The greenhouse study revealed that crop type may affect Pb and As bioaccessibility in treated soils.

Study Implications

According to recent statistics, growing food in urban areas is still on the rise. Therefore, we believe that it is important to study the effect of key natural geochemical and biological processes induced by plant growth on the permanence of sequestered Pb and As in treated urban soils.

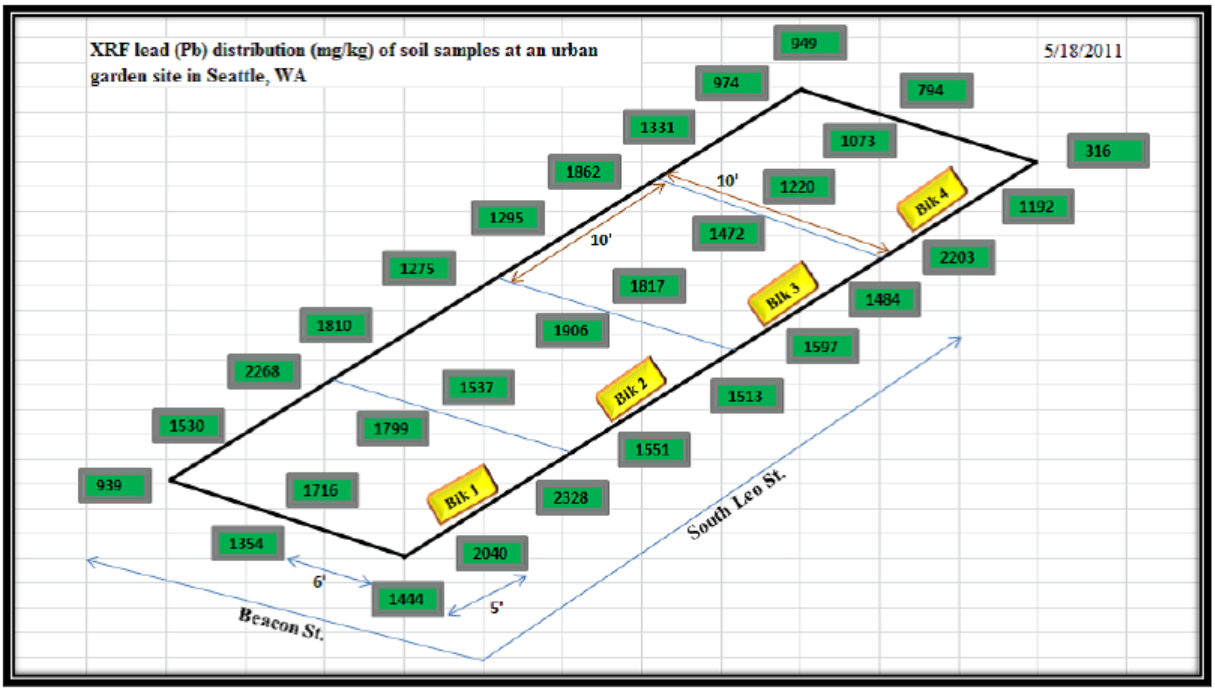
Research evaluating a variety of root, leaf, and fruit vegetables, as well as other soil amendments is required to build a database for safe gardening practices on urban soils in the U.S.

1. Further studies are also required to evaluate the efficacy of the TAGRO plus ferrihydrite amendment on reducing both Pb and As bioavailability under field conditions.
2. The application of organic amendments where available and/or application of iron-rich materials such as iron-rich class-A biosolids may be useful in urban gardens contaminated with Pb and As.

3. It should be noted that the soils studied were loamy sand with moderately acidic pH. Contaminant concentrations, soil texture and chemical characteristics may differ from site to site. Therefore, treatment effectiveness may vary.
4. Effective communication between scientific community and gardeners, community leaders, government agencies and extension personnel would be essential to face challenges in urban gardening.

APPENDIX A

1) An XRF grid study showing the distribution of soil Pb at the Seattle test plots in 2011.



2) Electrical conductivity in soils from subplots grown under various treatments at the Tacoma urban garden site, Tacoma, WA in 2011.

Plant sub-plot	Control	TAGRO + dolomite[†]
	----------dS/m----------	
Carrot	0.35 ± 0.02	2.60 ± 0.1
Lettuce	0.34 ± 0.02	2.22 ± 0.25
Tomato	0.32 ± 0.02	2.68 ± 0.1

[†]TAGRO is a class A biosolids

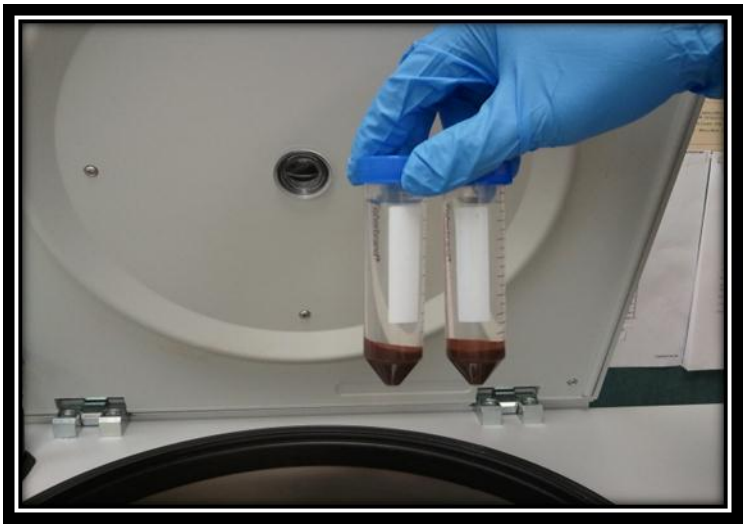
3) Picture illustrating tomatoes being dried in the Fisher Scientific Isotemp oven (Marietta, OH) at 65 °C.

4) Harvested carrots from Block 1, non-amended control (CST-S1-CON-Cp) and TAGRO plus dolomite (CST-S1-LT-Cp) plots.

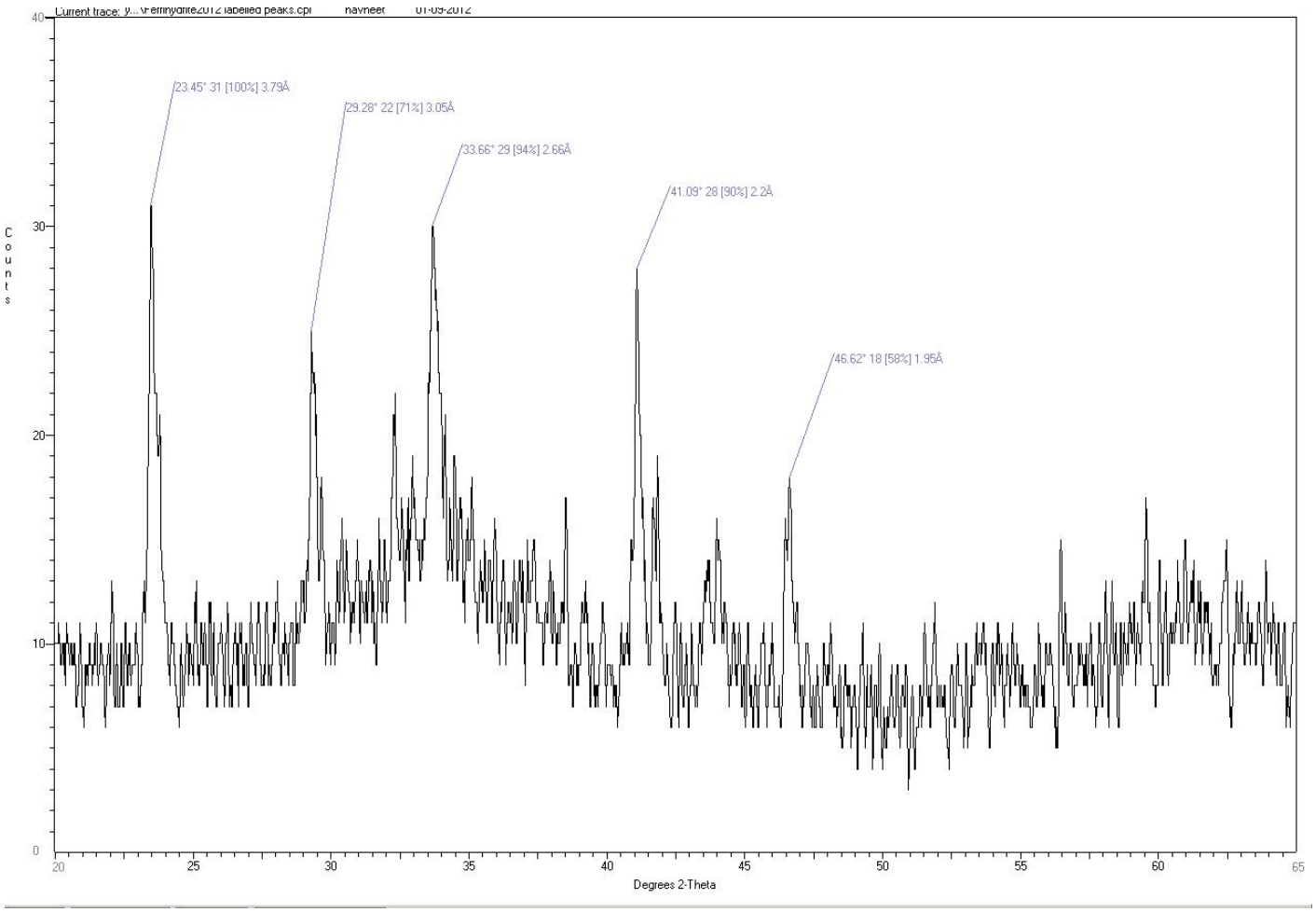
APPENDIX B

1) Incubation study samples incubated at controlled temperature incubator maintained at 25°C for six months.

2) Ferrihydrite preparation centrifugation step.



3) X-ray diffraction pattern of 2-line ferrihydrite.



APPENDIX C

1) Pictures of carrots, beet, and lettuce at the end of the greenhouse study prior to harvest. For each crop type, the treatments from left to right (L-R) are: Fh1%, non-amended control, TAGRO 10%, and TAGRO 10% plus Fh1%.