Lead in Kansas City soils: Lead source tracking and assessment of wastewater-derived phosphate for fertilization and lead remediation

by

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Abstract

Lead is a toxic, naturally occurring element in soil that is widely elevated in surface soils due to anthropogenic Pb pollution. Various sources have contributed to soil Pb contamination such as leaded gasoline, lead paint, and industrial activities. Knowing the contributors of Pb to soil is crucial for protecting soils from further contamination, choosing mitigation methods, and public health. Isotope tracing is a source-tracing method that strives to utilize natural isotopic variations for the discernment of different sources of the element. For Pb, this method can identify anthropogenic contributions in soil by observing the similarity in ratios between the soil and the unique isotopic signature sources can have. The first objective of this study is to identify the major sources of Pb contamination in Kansas City, MO. Surface soils (0 to 15 cm) were collected from various residential and vacant sites in the area. Three near-pristine subsurface soil cores from the Konza prairie was also collected as a background. Soils were digested using USEPA method 3051, and concentrations were determined using an inductively coupled plasma-optical emissions spectrometry (ICP-OES). Diluted samples were analyzed for isotope ratios in ICP- Triple quadrupole mass spectrometry (ICP-QQQ). Results showed that Pb isotope ratios of Kansas City sites overlapped with leaded paint and gasoline ratios. Konza Prairie Pb isotope ratios were distinct from Kansas City sites.

Phosphorus is a vital nutrient essential for the global agricultural system and maintaining food security for the world's growing population. As the population continues to grow, so does the demand for these fertilizers for increasing crop yields. Phosphorus fertilizers are derived from phosphate rocks which are a non-renewable resource and will soon be scarce due to their growing demand. Wastewater streams from agricultural and urban areas are a renewable resource that contain high concentrations of nutrients such as P and can be extracted from

wastewater in the form of reclaimed nutrient products (RNPs). The objective of the second study is to evaluate the effectiveness of RNP product as an alternative fertilizer and a potential stabilization treatment for Pb in contaminated soils. The RNP for the study was selected based on wet chemical methods and X-ray diffraction (XRD) characterization. The selected RNP had a total P concentration of 12.57% and a citric soluble P content of 35.89% (% of total P). Two P species were identified by XRD; 84.8% octacalcium phosphate (OCP), and 15.2% struvite. Three soils were acquired from a vacant lot different levels of Pb and classified as mild (208 mg/kg), moderate (323 mg/kg), and extreme (2418 mg/kg). Treatments included four P sources, treatments, ammonium polyphosphate (APP), triple superphosphate (TSP), calcium phosphate based RNP, struvite and a control. Phosphorus treatments were applied to soils at equal rates. Completely randomized block design (RCBD) was used with 3 blocks for each plant type (leafy, lettuce and root crop, radish). Lead concentrations were determined with Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS). Other elemental concentrations were determined with ICP-OES, and diluted plant samples Pb isotope ratios were determined with ICP-QQQ. Struvite and RNP treatments showed significant reductions in Pb concentrations for root and leafy crops. Lead concentrations in mild and moderate soils did not exceed FAO/WHO maximum Pb levels for leafy crop. Struvite, RNP and APP showed significant increases compared to the control in P uptake, despite initial excess soil P masking treatment effects. Agronomic levels of P addition had no significant effect on soil Pb bioaccessability. Plant Pb isotope ratios of unamended controls were significantly different than soil Pb isotope ratios, while P treated plants remaining close to the original soil ratios, suggesting selective uptake and/or translocation of soil Pb upon natural attenuation

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Chapter 1 - General Introduction

Urban agriculture has been a growing field of interest as urbanization continues throughout the world, and cities are now focusing on ways to grow their own food to ensure their food security. These new food systems in cities cannot have the same issues that conventional, intensive agriculture has with sustainability and pollution. Soils located in urban areas pose unique challenges to agricultural use due to their unique properties. Urban soils are extremely heterogenous due to anthropogenic additions or mixing of the original undisturbed soils. Their properties are dependent on the topography, original soil properties, and the development history of the area (Yang and and Zhang, 2015). These soils often contain man-made materials and chemical inputs from industrial and residential activity, roads, and atmospheric deposition. Despite their heterogeneity these soils have common characteristics such as higher bulk densities, higher pH, human altered and human transported materials (HAHT), abrupt and discontinuous soil boundaries, and elevated levels of trace elements or contaminants (Riddle et al. 2022). These soils can contain trace metals such as lead (Pb), Cadmium (Cd), Arsenic (As), and other contaminants from anthropogenic activity (Liu et al., 2018).

These contaminants are non-essential and are well known for their toxicity in organisms and ensuring urban soil crops do not become vectors of contamination is important for the development of urban agriculture (Brown et al., 2016; Khan and Frankland, 1983). Lead is the most common contaminant found in these soils due to anthropogenic additions caused by leaded gasoline, lead paint, coal combustion, and industrial activities. Lead has been known to accumulate in plant materials in concentrations considered harmful for human consumption. Different plants and different portions of a plant can accumulate Pb in different amounts, which can limit potential crop types in urban agriculture (Chandrasekhar and Ray, 2019). Despite their

contamination, these soils can undergo remediation to ensure these contaminants pose no threat to human health. However, the various Pb sources in urban areas may complicate remediation plans. Lead sources such as leaded gasoline have been banned for half a century and are no longer contributors to lead pollution but lead paint or industrial emissions could still be active contributors to a contaminated area (Komárek et al., 2008). Knowing the concentration of Pb is not enough, understanding the sources is needed to form remediation plans and for the public health of the city.

For source identification of Pb, isotope tracing techniques can be utilized by looking at the differences in isotopic compositions of soils to collected data on Pb sources. Lead has 4 stable isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb and their isotopic abundances in nature may vary due to their formation from the decay of their parent isotopes and mass fractionation that occurs within the environment (Komárek et al., 2008; Kendall and McDonnell, 1998). These minute changes can be used to identify the source origins and what the main contributors are in the studied soil. Lead isotopic ratios have shown success in identification of Pb contamination of differing contamination sources and has been used to identify blood lead sources in children, aerosol pollutant origins, and can show the changes in economic activity based on sedimentary deposits (Laycock et al., 2022; Zhu et al., 2010; Miller et al., 2014). This information is an important first step for remediation strategies.

Phosphorus is an essential nutrient for organisms and ensuring high crop productivity from the global agricultural system. Phosphorus fertilizers have been crucial for feeding the growing population of the world, but this crucial resource is being depleted. Fertilizer production relies on phosphate rock, which is considered a non-renewable resource. Phosphate rocks are unequally distributed across the Earth with Morrocco and the Western Sahara accounting for

71.5% of global reserves, and as this resource dwindles, fertilizer prices will spike as seen in 2007-2008 when demand far exceeded the supply (Nedelciu et al., 2020). These fertilizers are considered highly inefficient with 80% of P being lost from mine to fork, and only 10% of P is being digested by humans (Cordell et al., 2009). Food systems are a large contributor to P waste due to the excessive use of P fertilizers for maintaining high crop yields with over half of P losses associated with agricultural runoff (Scholz et al., 2013). Phosphorus waste is also prevalent in urban wastewater streams due to human waste and detergents that enter the sewer systems (Ott and Rechberger, 2012).

Excessive P can then drain into rivers and oceans, which can cause the eutrophication of waterways; in fact, most of P is wasted and pours into said waterways. Efforts have been made to recover P in these waste streams through precipitation of phosphate minerals in sludges and leachates (Deng and Dhar, 2023). Current research strives to precipitate specific forms of P, such as calcium phosphorus (Ca-P), for potential use as an alternative P fertilizer. An alternative P fertilizer would be beneficial in an urban agricultural system as this reduces the reliance on non-renewable, traditional P fertilizers, and promotes a circular food system as it reuses the city's P waste, reducing external outputs. This reclaimed P can provide a secondary use as a remediation tool for contaminated soils. Phosphorus can react with Pb^{2+} in soils to form lead phosphates such as pyromorphite (Zheng et al., 2023). Pyromorphites are stable in soils and immobilize bioaccessible Pb. This chemical remediation of soils is preferable to other remediation techniques as it is relatively cheap, less invasive, and simple. Reclaimed P product has the potential to be a sustainable P fertilizer source alternative and it could serve as a remediation tool for contaminated soils, which could greatly benefit the development of urban agriculture in cities. The first study of this thesis, lead isotope tracing, was conducted to determine the isotopic

ratios of sites within Kansas City, MO, with the goal of source identification of the major Pb source contributors of the area. The second study explores the potential use of a reclaimed nutrient product (RNP) derived from a P containing wastewater stream, more specifically wastes from a deep manure pit from swine operation subject to anaerobic digestion, with the goal of testing its efficacy as a fertilizer and a potential remediation tool for Pb contaminated soils.

Chapter 2 - Literature Review

2.1.1 History of human-Pb

Lead (Pb) has been intertwined with humans for roughly 6000 years. Many early records of civilizations using mined Pb-laced ore all the way back in 4,000 BC (Riva et al., 2012). Even in ancient times, people managed to discover the link between Pb exposure and deteriorating health. Early records of Pb exposure leading to Pb poisoning dating back to the 1st century AD where Romans noticed the link between Pb exposure in statues and shipbuilding with sickness (Riva et al., 2012; Lewis, 1985). Despite that, many manufactured goods such as pottery glaze, water pipes, cooking utensils, and even wine sweeteners were still produced with Pb. The usage of Pb may have even been a contributing factor to the fall of the Roman Empire due to the Pb toxicity epidemic that may have caused the ruling class to become more unstable due to Pb neurological damage (Lewis, 1985).

Lead usage since the industrial revolution dwarfed the Roman Empire's usage. Lead was ubiquitous in products in the 19th and 20th centuries with a variety of usages such as in batteries, pipes, paint, anti-knock agents, ceramics, toys, ammunition, and more. This explosion in usage for Pb led to a massive increase in Pb in the environment, and exposure routes (Riva et al., 2012). Higher quantities of Pb prevalence in the environment plus industrial development led to an abundance of Pb in soils and the atmosphere which coincided with widespread Pb poisoning (Riva et al., 2012).

An explosion in Pb usage occurred in the 20th century specifically due to the popularization of lead gasoline and lead paint (Needleman, 1991). Lead was the key component of the anti-knocking agent tetraethyllead (TEL) which was revolutionary for companies because of its use in improving engines at a miniscule expense. This anti-knock agent was inherent to

cars until the 1970s thanks to the invention of the catalytic converter (Seyferth, 2003). Even then lead gasoline was still commonplace until the eventual ban in 1996 after a 25-year phase out plan in the US. Lead paint was commonly used due to its durability throughout the United States up until 1978 when it was officially banned (Jacobs et al., 2002). The legacy of Pb in the environment will remain in the environment as the world was pumped full of lead for nearly a century. Anthropogenic Pb is now one of the most widespread contaminants. As of 2024 there are still 38 million houses still coated in lead paint across the United States that is slowly leaching into the environment (US EPA, 2020). Lead is also a major danger for over 9 million households that still are serviced by Pb pipes (US EPA, 2023).

2.2.1 Soil Lead

Lead naturally occurs in all soils with an average concentration of 15 mg/kg, but can range from 1 to 200 mg/kg (Lindsay, 1979; Zimdahl & Skogerboe, 1977). Lead concentrations are inversely correlated with the depth of the soil due to anthropogenic sources deposition from car emissions, industry, and paint (Dietrich et al., 2021). This deposited surface soil tends to remain relatively immobile due to low solubilities of their compounds. Lead solubility is dependent on various soil properties such as soil pH, organic matter content, Fe-Mn oxides, and clay content (Finžgar et al., 2007; Ettler et al., 2007). Urban soils are well known to have elevated Pb levels that easily exceed normal lithogenic levels due to the history of anthropogenic activity in the area (Hooker and Nathanail, 2006). However, the total Pb concentration by itself does not determine the danger of lead poisoning, as the concentrations and speciation of the Pb can vary wildly in contaminated soils (Manceau et al., 1996; Haque et al., 2021). It is common for people to live in areas with levels exceeding background amounts, but simply having a high concentration in the soil is not the sole determiner of lead poisoning (Lanphear et al., 2002).

With soil, the most important factor in determining the potential harm of Pb exposure to people in contaminated areas is Pb bioavailability (Haque et al., 2021).

2.3.1 Bioavailability

When Pb enters the body, only a portion of Pb will be absorbed into the body and cause lead poisoning. This is dependent on the bioavailable fraction of Pb, which is the fraction of a substance in a soil that can be absorbed by a living (Anderson and Hillwalker, 2008; Hettiarachchi and Pierzynski, 2004). Looking at the bioavailability of Pb is useful, as it can be specifically targeted and immobilized in a soil without costly removal (Ali et al., 2013).

One of the most common chemicals applied to Pb contaminated soils is P. When Pb and P are in soils, P induces Pb to form insoluble Pb phosphate compounds (Azhar et al., 2022). These Pb phosphate compounds will precipitate with Pb and immobilize into a stable mineral like pyromorphite (Karna et al., 2018).

2.4.1 Lead Toxicity

Pb is one of the most common contaminants in the world due to human usage throughout time. Anything with Pb is considered a neurotoxic material which has no safe level of exposure. Lead can cause a variety of different illnesses with a few shown in Table 2-1. Lead has also been associated with behavioral problems, and it has been suggested that Pb emissions lead to an increase in violent crime due to Pb poisoning (Higney et al., 2022). Lead has 2 main pathways of entering the human body: inhalation and ingestion (Patrick, 2006). Inhalation of toxic fumes or dust can lead to the quick absorption of Pb into your bloodstream through the alveoli of the lungs (Wani et al., 2015). While ingestion can be from contaminated materials such as water, food, paint chips, contaminated plants, and soil. The ingestion pathway tends to be more prevalent for children as many kids tend to put random objects in their mouths. This makes Pb incredibly

dangerous for children as Pb can stunt various developmental milestones in them (Peng et al., 2019; Naranjo et al., 2020).

Table 2-1: A non-exhaustive list of health issues lead poisoning can cause.

Systems	Issues associated with Pb
Cardiovascular	Hypertension, increased risk of heart disease and stroke
Neurological	Brain damage, loss of fine motor control, increased aggression, memory loss, depression, poor executive function
Reproductive	Infertility, pre-eclampsia, pregnancy complications

2.5.1 Isotopes

Isotopes are nuclides that consist of the same number of protons but contain different numbers of neutrons. Nuclides are a species of atom that is characterized by the makeup of the nucleus, focusing on the nuclear properties independent of the chemical properties. The isotopic compositions of planetary systems are related to the nuclear processes of stars and planet formation (Kendall and McDonnell, 1998). After initial formation, these isotope ratios change due to radioactive decay, cosmic ray interactions, and mass fractionation. There are two types of isotopes, radioactive and stable isotopes. Radioactive isotopes are nuclides that spontaneously disintegrate to form stable isotope. Stable isotopes are isotopes that have had no recorded decay over time. Stable isotopes forms can either be formed by the decay of radioactive isotopes, or they were originally present during the formation of the solar system (Kendall and McDonnell, 1998). Isotopes that are produced by radioactive decay are known as radiogenic isotopes. Other nuclides are formed through atomic displacement of a proton with a neutron or the addition of

neutrons produced by alpha decay of other neutrons. These two methods of isotope formation are considered lithogenic (Kendall and McDonnell, 1998). Over time, environmental isotopic compositions will change due to these various processes, which can lead to unique abundances of these isotopes.

2.5.2 Mass Fractionation

The chemical bonds of different isotope species tend to differ due to their masses. Heavier isotopes are more stable than lighter isotopes. The variances in mass leads to different energy requirements for chemical reactions, and lighter isotopes require less energy for these reactions due to differences in their zero point energies (Perrin, 2003; Walters, 2019).

2.5.2a Equilibrium Fractionation

Equilibrium fractionation is the partial separation of isotopes in chemical equilibrium. Despite having equal forward and backwards reactions, heavier isotopes will preferentially accumulate in the compound containing a higher oxidation state (Walters, 2019). Chemical equilibrium involving phase changes will have the heavier isotopes preferentially accumulate in the less energetic phase. For example, water vapor will accumulate the lighter isotopes of ^{1}H and ^{16}O while liquid water will contain larger amounts of ^{2}H and ^{18}O (Gourcy et al., 2005). The fractionation effect in equilibrium is reduced as temperature increases due to a decrease in their differences in zero-point energy (Kendall and McDonnell, 1998).

2.5.2b Kinetic Fractionation

Isotopes can separate due to unidirectional chemical processes through kinetic fractionation. Isotope fractionations may be unidirectional if the reaction products become isolated from the reactants. These reaction rates are dependent of the isotope masses and their vibrational energies (Young et al., 2002). Lighter isotopes bonds are broken easier than heavier

isotope bonds, and thus react faster, concentrating the lighter isotopes in the products and enriching the heavier isotopes in the reactants Kinetic fractionations are usually larger than equilibrium fractionations with the same reaction and conditions (Kendall and McDonnell, 1998).Biological processes are known for kinetic fractionation as organisms will preferentially use the lighter isotopic species as less energy is required to break their molecular bonds. Isotopic tracing studies have been used for plant uptake of various elements such as Fe, Cd, Mg, and more (Garnier et al., 2017; Wei et al., 2018; Bolou-Bi et al., 2012; Wiggenhauser et al., 2022).

2.5.3 Isotope Ratios

Isotopes have relative abundances, which is the distribution of different isotopes of the same element in a single sample. Elements have natural baseline abundances in the environment that can be used in detection of elemental cycling in the environment (Komárek et al., 2008). These abundances can be converted into isotopic ratios, which is the comparison of two different ratios' abundances. Different soils may have different ratios due to anthropogenic inputs, local geology, and preferential reactions with lighter isotopes due to mass fractionation (Hansmann and Köppel, 2000). The isotopic ratio from a sample can be compared to the natural ratios of the world. The differences in abundances can be treated as a unique isotopic fingerprint that can then be matched to different geographical regions of the world due to variances in different ratios. Source tracing uses "tracers" which are trackable substances that reveal the source point and pathway of it. A wide variety have been used for environmental pollutant tracking ranging from heavy metals (Pb, Cd, As) to radionuclides (Wang et al., 2022; Augagneur et al., 1997). Isotopes of hydrogen and oxygen ratios have been used to date the sources of water in aquifers (Tweed et al., 2019). Carbon and nitrogen isotope ratios have been used to determine diets of animals. Radioactive isotopes such as carbon-14, uranium-235, and chlorine-36 have been used for dating

the age of materials (Guidon and Delibrias, 1986; van Calsteren and Thomas, 2006; Phillips et al., 1986).

2.5.4 Lead Isotopes

Lead has 4 stable isotopes that occur naturally in the world ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb with relative abundances of 1.4%, 24.1%, 22.1%, and 52.4%, which can be seen in Table 2-2 (Komárek et al., 2008). Isotopes ^{206}Pb, ^{207}Pb, and ^{208}Pb are radiogenic and are products formed from the radioactive decay of ^{238}U, ^{235}U, and ^{232}Th. Lead-204 is the only non-radiogenic isotope (Komárek et al., 2008).

Table 2-2: Lead isotope abundance in nature and their parent isotopes half-lives.

Pb Isotope	Parent Isotope	Parent Half Life (years)	Relative Abundance (%)
^{204}Pb	-	-	1.4
^{206}Pb	^{238}U	4.47E+09	24.1
^{207}Pb	^{235}U	7.04E+08	22.1
^{208}Pb	^{232}Th	1.40E+10	52.4

Lead isotope abundance is dependent on the initial amounts of Pb, U, and Th that created the Earth during its initial formation. ^{206}Pb, ^{207}Pb, and ^{208}Pb are the end products of decay chains of their parent isotopes ^{238}U, ^{235}U, and ^{232}Th respectively (Zhu et al., 2021). Lead-204 is the only Pb isotope that is not formed from radioactive decay, and ^{204}Pb concentrations are fixed and have been unchanging since the initial formation of the Earth. Each parent isotope of Pb has a different decay rate, causing alterations in the relative abundances of the various ratios. 99.3% of the world's uranium is in the form of ^{238}U, and the remaining .7% is ^{235}U (Laeter et al., 2003).

The pool of ^{235}U has almost fully transitioned to ^{207}Pb due to its relatively shorter decay rate. Uranium-237's half-life is an order of magnitude higher than ^{235}U and will thus have a greater contribution to isotope ratio differences as there is more material to decay and produce ^{206}Pb. Thorium-232 has a decay rate of 14 billion years, greater than the age of the Earth. This long half-life means that ^{232}Th decay has contributed minimally to world total ^{208}Pb concentrations. Lead-206 is the greatest contributor to changing isotope ratios (Komárek et al., 2008; Hansmann and Köppel, 2000).

2.6.1 Lead Isotope Source Tracing

Lead isotope ratios are utilized to identify anthropogenic lead deposition as all manufactured products such as Pb gasoline, Pb batteries, and Pb paint can be traced to a regional Pb source as a mine had to extract this Pb (Mihaljevič et al., 2006; Rabinowitz, 1995; Potra and Moyers, 2017). This can trace and identify manufacturers as polluters based on where they sourced their Pb. Even nations can be traced as a polluter based on transboundary deposition of Pb (Peng et al., 2022; Wang et al., 2019). Pollution could then be identified by obtaining natural, geogenic samples in the area versus theoretically contaminated sample. The ratios are commonly expressed as $^{206Pb/207}Pb$ or $^{208Pb/206}Pb$ to display the differences in anthropogenic and natural sources. This is due to ^{206}Pb being the main contributor to isotope changes due to having the largest pool of undecayed parent isotopic material. However, others such as $^{206Pb/204}Pb$ and $^{207Pb/204}Pb$ can be used to have a larger range for differentiation. These ratios can then be used to create Isotope ratio graphs where various samples can be displayed and then compared to other isotope ratio data.

Lead isotope ratios in different pollutants such as lead gasoline, and paint can vary due to differences in ore types (Resongles et al., 2021; Dunlap et al., 2000). Analytically, these data

points are only a portion of the information needed. The ratios would need to be cross referenced with other studies, historical lead usage investigated in the area, geographic background, and potential pathways (Komárek et al., 2008).

2.7 Lead Isotopes of Anthropogenic Sources

2.7.1 Lead gasoline

Leaded gasoline is one of the main sources of global lead pollution despite its phase out. The isotopic composition of the ores used to manufacture the antiknock additives; tetraethyl lead (TEL) and tetramethyl lead (TML) are key to determining the isotopic composition of these additives (Dunlap et al., 2000; Komárek et al., 2008). Natural ore ratios have been collected through various studies to pinpoint where the raw materials came from. The $^{206/204}$Pb and $^{206/207}$Pb range from 16.0-18.5 and 1.19-1.25 respectively (Hansmann and Köppel, 2000). There are a few exceptions to this range, such as the Mississippi Valley ore deposit in the US with $^{206/204}$Pb > 20 and $^{206/207}$Pb = 1.31-1.35. The isotopic composition and deposition of Pb isotopes for gasoline changed over time due to changing ore sources because of Pb ore availability and price (Hovorka et al., 1999). The changing of ore sources leads to mixed deposition, and it is important to identify the origin of where countries imported their ores for accurate source identification.

2.7.2 Lead Paint

Lead paint is commonly found in residential areas, especially in buildings built before 1978 in the U.S. due to the Pb paint ban. Paint can be a continuous and active contamination source of Pb in households and the soil as it chips, peels, and flakes over time. Paint ratios have been used to estimate the original ore sources of 17th century paintings (D'imporzano et al., 2021), and showed lead paint may have overlapping ore sources. Paint has shown higher

intersample variability due to the painting history of the object, location (i.e outdoors or indoors), and the manufacturing process (D'imporzano et al., 2021; Rabinowitz, 1995). Lead paint manufacturing in The Netherlands had ores melted and mixed for homogenization, which was assumed to have given it a homogenous ratio. Variations in isotopic alterations of lead paint has been suggested due to effects post-manufacturing such as pigments mixing with other substances such as oils, varnishes, extenders, and even other pigments (D'imporzano et al., 2021).

2.7.3 Coal

Coal was the predominant source of atmospheric Pb before the creation of leaded gasoline and clean air regulations for thermal plants. The $^{206/207}$Pb isotopic ratios of coals gathered from around the world varied from roughly 1.15-1.24 (Komárek et al., 2008). Coal isotope ratios differ based on the source, with Europe and Asia contained less radiogenic Pb than South America and North America. Differing ratios may occur from the decay of U and Th in these coals since their formation, differing dominant chemical forms in coal influencing chemical behavior and mobility, and potential leaching of Pb isotopes from these coal deposits (Kylander et al., 2008; Harlavan et al., 2021). Emissions from burning coal can undergo long-range transport in the wind currents, and can be seen with Chinese coal isotopes overlapping with Western U.S aerosols (Jaffe et al., 1999; Osterberg et al., 2008).

2.7.4 Metallurgy

Lead emitted from smelting and other metallurgical activities closely reflects the isotopic composition of the processed material (Komárek et al., 2008). Lead isotopes variances are not precise enough to pinpoint unique smelters due to the differing ore sources each smelter uses (Rabinowitz, 2005). Due to the transportation of Pb ores from afar, these ratios from smelters and refineries can be used to discern anthropogenic Pb from the ambient Pb.

2.7.5 Waste Incineration

Fly ash from incinerators reflect the average values of the various waste products (e.g rubber, paper, plastic) that are burned. Isotopic contributions from differing sources is influenced by whether it is a low oxygen or high oxygen environment in the incinerator (Shao et al., 2018).

2.8 Lead Isotopes in Natural Sources

2.8.1 Aerosols

Atmospheric Pb is heterogeneous in nature due to the changing inputs from industry, traffic, winds, rainfall, and other variables. This heterogenous Pb can then be transported over long distances, which makes isotopic interpretation complicated. Lead in Saharan dust has been shown to influence the isotopic composition in European aerosols (Doucet and Carignan, 2001). The atmospheric aerosol ratio of $^{206/207}$Pb has changed quite rapidly due to changing industrial practices, the introduction and banning of leaded gasoline (Tomašević et al., 2013; Zhu et al., 2010).

2.8.2 Peat Deposits

Peat deposits can be used for records on historical Pb pollution and deposition. Isotopic changes in these peat bogs are dependent on their localities (Komárek et al., 2008). Ombrotrophic peat deposits are a useful source of evaluating environmental changes as they receive their nutrients from precipitation, not surface waters, and are optimal for studying atmospheric deposition trends (Novák et al., 2003). These deposits can trace back changes in Pb ratios due to anthropogenic sources from thousands of years ago (Fiałkiewicz-Kozieł et al., 2018).

2.8.3 Sediments

Marine and lake sediments can act as historical archives of Pb pollution as the deposition of sediments can show fluctuations in Pb over time that can be attributed to anthropogenic activity (Komárek et al., 2008). These records can date back centuries and can show the changes in industrial or mining activity in a region (Miller et al., 2014). These changes in isotopic values in the sediment layers can aid in the chronology of differing sources. With layers showing different isotope ratios that can show whether the major contributor was leaded gasoline, mining waste, or other sources. Stream sediments are beneficial in mapping the spread of pollutants based on their deposition downstream. These deposits can be used to trace pollutants upstream to geogenic or anthropogenic sources (Xu et al., 2022).

2.8.4 Soils

Lead contamination mainly concentrates in the surface soil horizons, and the vast majority of Pb in soil comes from anthropogenic sources. However, lead concentrations can arise from natural processes. Isotopic compositions of Pb in uncontaminated soils tend to be more radiogenic with a $^{206/204}$Pb range of 18.5-19.5. This ratio tends is contributed from weathered bedrock and its natural isotopic composition is based on the ^{238}U to ^{206}Pb. This can be discerned from ores as ores tend to be less radiogenic in composition, with a $^{206/204}$Pb range of 16-18.5 (Komárek et al., 2008). This difference in ore versus bedrock is due to the their high Pb/U and Pb/Th ratios in comparison to bedrock and these ore ratios are considered anomalous to general rocks (Hansmann and Köppel, 2000).

2.8.5 Trees

Trees have been used for historical records of changes in atmospheric Pb isotope ratios and are used as biomonitors for current atmospheric pollution for trace metals such as lead

(Hagemeyer, 2000). Tree leaves can show the major source contributors of Pb over time. One study showed that Pb isotope ratios in leaves in Belgrade changed concurrently with the switch from Australian to Chinese Pb ore for leaded gasoline additives (Tomašević et al., 2013). Tree rings can provide soil and atmospheric contributions of Pb but is dependent on the tree species and its suitability for dendroanalysis. Dendroanalyses assume separate tree rings reflect the composition of the environment of that time. Lead has minimal mobility within the xylem of trees, making it suitable for isotopic dendroanalysis (Conkova and Kubiznakova, 2008; Watmough and Hutchinson, 2002). Various species such as beech, oak, pine, and sycamore have been analyzed for their lead isotope ratios and concentrations for source identification.

2.9 Lead Isotope Analyses

2.9.1 Inductively Coupled Plasma Mass Spectrometry

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a spectroscopic method that can be applied to a wide variety of elements. It works by nebulizing a liquid sample and introducing it to argon gas that is in a radio field, which is excited into plasma and ionizes the sample (Komárek et al., 2008). This ionized sample is then introduced to an electric field which selectively sorts samples based on their mass – charge ratio. There are several types of inductively coupled plasma mass spectrometers (ICP-MS) including quadrupole ICP-MS, multicollector ICP-MS, and time of flight ICP-MS. The ability to measure multiple elements at a time also makes it incredibly beneficial for analyzing multiple isotopes at once. Speedy sample preparation comes at the cost of interference vulnerability due to the complex matrices of the samples (Lum & Leung, 2016).

2.9.2 TIMS

Thermal Isotope Method Spectrometry (TIMS) is a useful method in isotope analysis where a sample is heated up and evaporates the sample, which in turn ionizes the sample. The thermally ionized sample is then passed through a magnetic field which sorts different atoms based on their mass – charge ratio (Weis et al., 2006). It is a precise method that can analyze low concentrations with minimal background noise. However, sample preparation can be time-consuming, and it performs poorer with elements with higher ionization potentials.

2.9.3 Common Measurement Issues for Isotope Analysis and Corrections

Mass bias is one of the most common forms of error where different isotopes are measured to varying degrees of accuracy, leading to heavier masses being favored and lighter masses being underestimated (Begley and Sharp, 1997). This can often be corrected through the usage of internal standards such as Tl for a stable $^{203}Tl/^{205}Tl$ ratio, along with an external mass bias correction with a known isotopic composition such as NIST 981 (Baker et al., 2004; Hirata, 1996).

Another common issue is Dead time, which is inherent to every machine. It is where the machine receives a signal analysis and must process it, and while processing cannot take in another signal (Nelms et al., 2001). This leads to underestimations in values as some atoms cannot be read during that time. A dead time correction factor (DTCF) can be mathematically applied to consider any sample it misses during that time (Held and Taylor, 1999; Nelms et al., 2001).

Unlike mass bias and dead time, signal drift is a continuous issue that needs to be addressed throughout machine analysis (Bolea-Fernandez et al., 2021). Signal drift is when the signal intensity of the analyte decreases or increases over time leading to issues with accuracy

and precision. It can be caused by signal interferences between atoms with similar mass to charge ratios, instrumental degradation, sample matrix variability, and even just fluctuations in plasma gas over the analysis (Bolea-Fernandez et al., 2021). This can be amended by the usage of external standards such as NIST 981 or other specific Pb isotope materials depending on the sample being analyzed. This can be run every couple of samples to correct the signal intensity by looking at an expected ratio (Yuan et al., 2016; Hirata, 1996).

2.10 Remediation Techniques

2.10.1 Capping and Encapsulation

This is where the surface of contaminated soil is covered by an impermeable layer. Capping is relatively inexpensive as a simple material such as clay, asphalt, concrete, or anything that is a well performing impermeable material can be placed it (Abd Elnabi et al., 2023). There are no efforts in trying to remove the material or change its mobility. It just halts the spread by not allowing it to interact with rainfall or water (Liu et al., 2018). Although cheap, it is a temporary solution. Overtime it will break down and will need constant maintenance as a crack in the barrier could cause it to spread. The land also is restricted and cannot be redeveloped as that land is now a container for the contaminants (Liu et al., 2018).

Encapsulation is like capping, where an impermeable cap is placed over a contaminated soil's surface. The key difference is that they also add subsurface horizontal walls to avoid horizontal flow of contamination and sometimes may even have a subsurface floor cap to prevent any mobility (Liu et al., 2018). Encapsulation shares similar problems to capping, as constant monitoring and maintenance is needed to prevent an active contamination breach.(Council et al., 1997)Both methods still have their place, usually in short term contamination mitigation. These tend to be used for small scale contaminated sites that need immediate stabilization and

prevention from spreading any further such as radionuclides, fossil fuel waste, asbestos, and other dangerous contaminants (Meuser, 2012).

2.10.2 Soil Flushing

An extraction fluid that promotes the chemical leaching of the contamination is inserted into the soil (Liu et al., 2018). The chemical agents mobilize the pollutants through various means such as chelation, complexation, desorption, and solubilization in order to then remove them from the soil (Aparicio et al., 2022).

2.10.3 Phytoremediation

The addition of plants to a contamination site is used to extract or stabilize various contaminants like heavy metals. This treatment type is appealing as all one needs are ground cover and time (Song et al., 2019). However, not just any plant may be used, as the plants must be able to accumulate large concentrations of metals without suffering from phytotoxic damage (Verbruggen et al., 2009). There are specific plants known as hyperaccumulators which can accumulate metals at concentrations hundreds to thousands of times greater than what most plants could tolerate (Deng et al., 2018). Hyperaccumulators grow uniquely well in metal laden soils due to their unique capabilities to absorb, translocate, detoxify, and sequester metal ions thousands of times greater than normal plants in their tissues (Reeves et al., 2018). Unfortunately, there are many issues with phytoremediation, as the plant types are already limited by climate and most hyperaccumulators tend to only accumulate specific metals, have shallow root systems, and yield low biomass (Liu et al., 2018). Phytoremediation also may take decades just for a mild reduction in contamination, as the effectiveness of it is tied to the available concentration in soils (Li et al., 2012). After multiple years of successive cropping and extraction, there is a linear or logarithmic decrease in both the bioavailable soil fraction and the

phytoextracted amount (Van Nevel et al., 2007). Phytoremediation has too long of a time scale with minimal results but can still be used in tandem with other techniques to improve soil quality and extract heavy metals.

2.10.5 Bioremediation

Bioremediation is considered a minimally invasive and cost-effective method using microbes to remediate the site. It can be a stabilization method for transitioning the contaminant into an immobilized molecule through various biological methods such as valence transformation, external chemical precipitation, or volatilization (Garbisu and Alkorta, 2003; Mokrani et al., 2024). Certain microbes within the rhizosphere can promote heavy metal tolerance in plants and enhance their growth in contaminated soils (Mishra et al., 2017). These microorganisms would be sprayed or injected into the soil along nutrients and amendments to assist in bioremediation and promote microbial activity (Liu et al., 2018).

2.10.6 Electrokinetic Extraction

Heavy metal contaminants are removed from the soil through an electric current run through an installed electrode in the soil (Liu et al., 2018). The current allows cations and anions to migrate to the anode or cathode. Additives are used to help promote mobilization of these metal species which then flow through the electric field and are removed through electroplating, precipitation, and ion exchange resins (Alcántara et al., 2012). The process is highly dependent on the soil physical and chemical properties. As soil pH, hydraulic conductivity, background ions, and organic content can alter the effectiveness either way (Figueroa et al., 2016).

2.10.7 Chemical Immobilization

Also known as chemical solidification or stabilization, chemical immobilization traps contaminants in soil through the introduction of chemical agents that react with the soluble and

exchangeable forms of the contaminant (Liu et al., 2018). Chosen chemicals are used to encourage reactions that form precipitates or sorption moieties with the agent instead of forming soluble mobile compounds. A variety of materials have been tested in their effectiveness to reduce their bioavailability with phosphates and carbonates proving to be the most effective agents for heavy metal stabilization (Basta and McGowen, 2004; Tang et al., 2009). This is due to their wide availability and low costs from their common application as a fertilizer or pH adjuster on farms (Liu et al., 2018).

2.11 Trace Metal Dynamics in Soils

2.11.1 Sorption/Desorption Process

Charged metal solute species can be retained by charged surfaces of soil components that is broadly classified between specific and non-specific retention (Bolan et al., 1999; Sparks, 2003). Specific adsorption is where a chemical bond is formed between the surface and the ions in solution. Non-specific adsorption is where an ion charge balances the charge of a soil particle due to electrostatic attraction. Soil properties and soil solution determine the dynamic equilibrium of the soil solution and soil solid phase (Bolan et al., 2014). Metal concentrations in solution is influenced by organic and inorganic ions along with soil pH. Free metal ion activities tend to lower when the pH >6, which has been attributed due to increasing surface charges on Fe, Al, and Mn oxides. Organic matter may also chelate these free metal ions at greater pH values (Bolan et al., 2014).

2.11.2 Precipitation/Dissolution

Precipitation of free metal ions as metal hydroxides occurs in the presence of ions such as CO_3^{2-} ,SO_4^{2-}, OH^-, and HPO_4^{2-} and when metal concentrations in solution are high (Hong et al., 2007; Harter and Naidu, 1995; Bolan et al., 2014). It is one of the main mechanisms of

immobilization of Pb (Harter and R., 1995; Hong et al., 2007). Phosphorus has been shown to decrease the leaching of various metals such as Cd, Pb, and Zn. Liming soils is one method of retaining these metals in soils and increasing pH has shown to increase retention and precipitation of these metals in soils (Bolan et al., 2014).

2.11.3 Oxidation/Reduction

Metals can be influenced by microbial redox reactions which will influence their mobility and speciation. There are two main categories for these redox reactions, assimilatory and dissimilatory (Brock et al., 1994). Assimilatory reactions are when the metal is involved in the metabolic function of the organism through its use as a terminal electron acceptor. Dissimilatory reactions are where the metal is not directly used metabolically and indirectly initiates a redox reaction.

2.11.4 Methylation/Demethylation

Methylation is when a methyl group is added to a substrate. Organisms can convert heavy metals into methyl forms which can then be removed by volatilization (Frankenberger Jr. and Losi, 1995). It is common in elements such as As, Hg, and Se which can originate from various chemical and biological processes (N. Bolan et al., 2014).

2.12 Phosphorus based in situ remediation

Phosphorus application can reduce the mobility and bioavailability of Pb in soils using both soluble and insoluble phosphate compounds. Their effectiveness in Pb immobilization is determined on their rate of dissolution (Park et al., 2011). There are three major categories of phosphate compounds that are utilized for Pb immobilization: readily soluble phosphates (i.e diammonium phosphate and phosphoric acid), moderately soluble phosphates (i.e mono and dicalcium phosphates), and insoluble phosphates (rock phosphates and bone meal) (Park et al.

2011). Using soluble fertilizers such as DAP, SSP, and TSP lower the soil pH, promoting dissolution of both P and Pb then precipitation of lead phosphates (Bolan et al., 2003). Application of soluble phosphates can be environmentally detrimental due to the potential of releasing excess P that will leach out of the soil or runoff, promoting eutrophication (Conley et al., 2009). Phosphorus application focuses on the concept of bioavailability which is the portion of a substance that an organism can uptake (Hettiarachchi and Pierzynski, 2004). The application of phosphorus encourages the soluble and free-floating ions of Cd^{2+} and Pb^{2+} to form insoluble precipitates that immobilize the contaminants with Cd in the form of Cadmium Phosphate and for Pb in pyromorphite minerals (Shao et al., 2020). Pyromorphites are known for their low solubility products and lo entropy state, which would make P application an ideal remediation technique for Pb immobilization (Karna et al., 2018).

2.13 Phosphorus Cycle and Soil

Globally, the phosphorus cycle has four major processes. First there is the tectonic uplift of P bearing rocks which are exposed to surface weathering. Physical erosion, biological and chemical weathering of P bearing rocks can provide P in the form of dissolved P and particulate P into soils and water bodies. Phosphorus is transported through aboveground or subsurface flow of water to lakes and oceans. Particulate phosphorus will undergo sedimentation in lakes, rivers, and oceans (Filippelli, 2008). Phosphorus that is available for plant uptake mainly comes from weathering of phosphorus rocks where microorganisms and plants can then uptake it. This phosphorus will return to the soil after organisms and plants die and decay. Anthropogenic activity has drastically altered the phosphorus cycle due to the use of phosphorus fertilizers that are derived from phosphate rock (Chen and Graedel, 2016; Huang et al., 2024). Now phosphate fertilizers, plant residues, and animal manures are all applied to increase the amount of

bioavailable P in soil. Phosphorus in soil is mostly found in unavailable forms (Vitousek et al., 2010) as the bioavailable P becomes unavailable due to:

i) Adsorption – phosphorus binds to the surfaces of clay minerals and Fe and Al oxides.
ii) Precipitation – phosphorus reacts with metals to form various phosphates.
iii) Immobilization - microbes convert available phosphorus into insoluble organic forms.

2.14 Phosphorus Pools in Soil

2.14 Organic Phosphorus

Organic phosphorus is phosphorus that is bound to organic molecules. This phosphorus forms complex compounds, which require microbial decomposition of these materials through mineralization. This portion of phosphorus makes up 30-65% of the total phosphorus in the surface layer of the soil.

2.14 Inorganic Phosphorus

Inorganic phosphorus (P_i) is phosphorus which is not bound to organic molecules. Only a small portion of P_i is freely available for plant uptake in the form of soil solution P. Soil solution P species are dependent on pH with PO_4^{3-} at low pH, $H_2PO_4^-$ at pH of 4-6, and HPO_4^2 in alkaline soils. Adsorbed phosphorus is P_i attached to clay surfaces and metal oxides such as Al, Ca, and Fe due to surface charges of these adsorbents. Inorganic phosphorus can also form various insoluble phosphate compounds.

2.15 Phosphorus Fertilizers

Conventional P fertilizers are highly soluble with it being immediately available to plants. They saturate the soil with high P concentrations, but this soluble P is incredibly vulnerable to leaching and fixation (Vaccari, 2009). Phosphorus fertilizers have been used due to their characteristics of high-water solubility, available, total P, and available P which is the water-soluble and citric acid soluble fractions (Chien et al., 2011) Some phosphorus fertilizers can provide nitrogen as ammonium. Conventional fertilizers are useful due to their solubility, which makes the dissolved P readily available for plant uptake. Soil pH initially decreases after phosphorus fertilizer application and will increase the concentration of Fe and Al in solution, promoting the adsorption/precipitation of P. Phosphorus fertilizers are the plants the P they need in their early stages of growth to provide the nutrients needed instantaneously (Nachimuthu et al., 2009). However, phosphate fertilizers are highly inefficient with roughly 15-30% of fertilizer uptake in crops, and the rest is wasted as it is immobilized, leached out of the soil, or gets washed away in runoff (Veneklaas et al., 2012). Conventional phosphate fertilizers have also been under increasing scrutiny due to potential introduction of contaminants such as Cd into the soil due to their phosphate rock source (Roberts, 2014).

Table 2-3: Various conventional phosphorus fertilizers and their phosphorus and nitrogen content. Data from Ohio cooperative Extension Service (LaBarge, 2023).

Fertilizer	N %	Total P* %	Available P* %	Water solubility* %
Ammonium Polyphosphate	10	34	34	100
Concentrated Superphosphate	0	45	45	85
Diammonium Phosphate	18	47	46	90
Monoammonium Phosphate	11	49	48	82
Superphosphate	0	21	20	85

*Data as a percentage of total P_2O_5

2.16 Phosphorus Inefficiencies and Concerns

2.16.1 Finite Resource

The key component of phosphate fertilizers is rock phosphate, with a total amount as of 2019 of roughly 69.5 billion tons (Fafu et al., 2021). Phosphates are a staple fertilizer for modern agriculture and have only grown in their usage with production increasing fivefold from 1961 to 2013 (Chen and Graedel, 2016). There is only a limited amount of phosphate rock in the world, which has led to growing concern over the over-reliance and inefficiency of its use in modern agricultural systems. Global supplies of phosphorus may begin to run out by the end of the 21st century as population reaches a carrying capacity in what the planet can feed sustainably (Huang et al., 2024; Scholz et al., 2013).

2.16.2 Phosphorus Loss

In agriculture, P has been used liberally due to its low motility and scarcity in soils (George et al., 2016). Unfortunately, most of the P tends to be washed out or leached from the soil with more than 80% of inorganic P being lost or unused in the current P fertilizer system at

every level from mining, fertilizer production, crops, and livestock nutrition (Chiu, 2022; Cordell et al., 2009). This massive loss of an essential, finite resource that fuels the world's agricultural sector needs to be addressed by maximizing its efficiency while also minimizing losses. Municipal wastewater contributes to P waste due to human waste, cleaning products, and industrial sources (Di Capua et al., 2022). This excess P is notorious for causing the eutrophication of waterways, killing off aquatic life, and polluting drinking water. These are not just small incidents either, P runoff from agricultural waste has helped to contribute to the creation of seasonal dead zones like in the Gulf of Mexico. This can harm aquatic environments through mass die-offs of aquatic species and making it uninhabitable for certain species (Rabotyagov et al., 2014).

2.17 Phosphorus Reclamation Technologies

2.17.1 Chemical Precipitation

Chemical precipitation of phosphorus relies on the usage of divalent or trivalent metal ions to promote the precipitation of insoluble phosphates from wastewater (de-Bashan and Bashan, 2004). These phosphates can then be removed by settling or filtration. Aluminum, calcium, and iron salts are commonly used for P removal. Chemical precipitation of phosphorus is performed in a multi-stage process in wastewater treatment plants (WWTP) where the precipitated phosphates end up in primary, secondary, and tertiary sludges after treatment (R. Jupp et al., 2021). Although effective at removal, chemical precipitation with coagulants Al and Fe create phosphates are not agronomically useful due to the strong bonds formed with the P, making it less bioavailable to plants (Mehta et al., 2015). Currently, most WWTPs focus on P removal, but not its reuse in phosphate fertilizers.

2.17.2 Biological Processes

The principal objective of an EBPR process is the removal of excessive dissolved P in wastewater effluent with phosphate accumulating organisms (PAOs). These PAOs can grow both aerobically and anaerobically, converting them into various compounds such as storage polymers and orthophosphates (Zheng et al., 2023). Aerobic granular sludge (AGS) technology simplifies the EMBR process and allows for simultaneous removal of excess nutrients such as carbon, nitrogen, and phosphorus along with pollutants (Amorim de Carvalho et al., 2021).

2.17.3 Membrane Separation

This method uses membrane materials as a separation medium. When a driving force (e.g concentration difference, potential difference, or pressure difference) is applied to both sides of the membrane, components will flow based on the gradient and the membrane selectively filters and separates these components (Chen et al., 2022). For wastewater treatment, pressure is commonly used and is based on pore sizes. Microfiltration and ultrafiltration have large pore sizes, which are utilized for removing particulate P in raw wastewater or collect P precipitate in post-treatment (Li et al., 2021). Emerging membrane technologies are focusing on the enrichment of specific nutrients such as N and P for removal and recovery. Forward osmosis separates water using a draw solution which produces an osmotic pressure gradient, promoting the flow of wastewater through, leaving the nutrients behind. Recent studies for forward osmosis have explored the capacity and efficiency of P concentration and retention in wastewater, urine, and sludges (Wu et al., 2017; Mihelcic et al., 2011; Xie et al., 2014). Membrane distillation is another technique which focuses on the separation of volatile ammonia gas from a liquid phase while retaining inorganic nutrients such as phosphorus. Membrane distillation has been shown to be beneficial when integrated with anaerobic membrane bioreactors for wastewater P removal,

with one example showing up to 95% removal of P (Song et al., 2018; Caroline Ricci et al., 2021). Electrodialysis is another method which uses ion-exchange membranes in a direct electrical field to separate ammonium and P from the water (Dong et al., 2020).

2.17.4 Adsorption

This method uses adsorbents that will attract and bind pollutants in wastewater due to adsorbent's surface charge and surface area. It is considered incredibly efficient as a technology due to its low cost, selectivity, and phosphorus removal effectiveness. Adsorption is often combined with other treatment methods for increased effectiveness of P removal. Several adsorbents have been developed for P removal such as bioachar, nanoparticles, and P binding proteins (Zheng et al., 2019; Wu et al., 2017; Brune et al., 1998).

2.18 Wastewater Precipitates

2.18.1 Struvite

There are a variety of different chemical agents that can be used in P precipitation such as lime, alum, and iron (Ren et al., 2022). These agents do not allow for recovery of the critical nutrients such as P and N inside them, instead rendering them immobile as waste that needs to be further treated. Reclaimable nutrient products have been previously recovered through a variety of chemical precipitates such as (($MgNH_4PO_4 \cdot 6H_2O$), K-struvite ($KMgPO_4 \cdot 6H_2O$), hydroxyapatite (HAP, $Ca_5(PO_4)_3OH$), vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$), etc. Precipitation of Struvite ($MgNH4PO_4$ or KNH_4PO_4) precipitation with magnesium (Mg) has been a precipitate of interest due to its unique qualities (Deng and Dhar, 2023). What makes struvite a potential candidate as a suitable candidate as a sustainable fertilizer is its low solubility (Kataki et al., 2016). It becomes readily soluble in acidic conditions which the rhizosphere can trigger (Tumbure and Schmalenberger, 2024). This means that it will gradually dissolve in soils throughout the

growing season and has the added benefit of potentially dissolving as needed when root systems encounter them and trigger rhizosphere acidification (Bowden et al., 1980; Tumbure and Schmalenberger, 2024). Struvite could be precipitated once instead of multiple times like conventional fertilizers and would be a potential way of closing the nutrient loop (Shu et al., 2006). However, its low solubility may not provide adequate growth for certain plants for the first few weeks due to its slow release and may struggle in more alkaline and neutral soils (Hertzberger et al., 2020; Tumbure and Schmalenberger, 2024). Struvite relies heavily on what the wastewater is made of and requires the wastewater with high P and nitrogen (N) amounts, and it would require magnesium (Mg) to achieve a 1:1:1 ratio between the three elements (Monballiu et al., 2019).

2.18.2 Calcium Phosphate Precipitates

Wastewater phosphates may precipitate as calcium phosphate (CaP) species when there the ratio of Calcium to Phosphorus (Ca/P) along with the pH are high enough to form a wide range of precipitate which can be seen in Table 2-4 below:

Table 2-4: Various forms of calcium phosphates and their Ca/P ratios for formation.

Calcium Phosphate Species	Abbreviation	Formula	Ca/P
Amorphous Calcium Phosphate	ACP	$Ca_3(PO_4)_2$	1.50
Dicalcium phosphate anhydrate/Monotite	DCPA	$CaHPO_4$	1.00
Dicalcium phosphate dihydrate/Brushite	DCPD	$CaHPO_4 \cdot 2H_2O$	1.00
Hydroxyapatite	HAP	$Ca_5(PO_4)_3OH$	1.67
Octacalcium Phosphate	OCP	$Ca_4H(PO_4)_3 \cdot 3H_2O$	1.33
Tricalcium Phosphate	TCP	$Ca_3(PO_4)_2$	1.50

All phases have the potential to be used as fertilizers and other use cases, and each has their advantages and drawbacks. The general rankings of their potential use as a fertilizer correspond with the amount of available P they can provide to crops. Their availability is dependent on their solubility order which is DCPD > TCP = ACP > HAP (Deng and Dhar, 2023). DCPD has the greatest solubility and would be able to provide available P in acidic, neutral, or alkaline soils. However, ACP, HAP, and TCP have a greater effectiveness in acidic soils (Daneshgar et al., 2019). In precipitation of calcium phosphates, OCP, DCPD, and brushite are often precipitated in acidic solutions, while HAP is preferentially formed under neutral or basic conditions. Octacalcium phosphate is considered a precursor mineral that undergoes hydrolysis to form an apatite-like phase which a lower Ca/P ratio than stoichiometric HAP (Johnsson and Nancollas, 1992). Struvite is considered to have a higher fertilizer value due to it being a source of both N and P, but CaP has a lower cost, and a wider pH range of formation while still providing excellent P nutrient recovery (Barua et al., 2019; Schott et al., 2022).

2.19 Urban Soil Characteristics

Urban soils provide a unique challenge to agriculture due to their extensive heterogeneity with the soils undergoing constant change due to anthropogenic development (De Kimpe and Morel, 2000). These soils physical characteristics are incredibly disturbed due to the mixing, removal, and addition of materials into the area, where they may contain various anthropogenic materials due to past construction and development. Urbanization also leads to a variety of contaminants in the soil due to industrial activity, construction, waste disposal, and transportation emissions (Cachada et al., 2012; Luo et al., 2012). A common form of contamination heavy metals such as Cadmium (Cd) and lead (Pb) with Pb being the most widespread soil contaminants that is omnipresent in urban areas due to its usage in leaded

gasoline, paint, and a variety of other products (Levin et al., 2021). This is a source of concern for many urban farmers, who worry that their crops will become another exposure pathway for lead and would be harmful to consume (Brown et al., 2016).

2.21 Objectives

The first objective of this thesis research is to identify the sources of Pb in vacant and residential lots in the Kansas City area. The source identification for soil Pb will also provide novel data points of the isotopic fingerprints of Kansas City, which have not been done before in the area. The second objective of this thesis research is to evaluate the effectiveness of reclaimed phosphorus from wastewater as a fertilizer and a potential tool for in situ stabilization of Pb contaminated urban soils. This objective is part of a broader effort to make urban agriculture systems more circular, thereby enhancing their sustainability.

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Chapter 3 - Source identification of Pb in surface soils from urban areas of Kansas City, Missouri, using isotope ratios

Abstract

Lead contamination is common in cities due to its historic use in leaded gasoline, lead paint, and industrial emissions. This study was conducted to identify the sources of Pb contamination in Kansas City, Missouri, by analyzing Pb isotopic compositions found in the area. Surface soil samples (0 to 15 cm) were collected from vacant and residential sites with elevated Pb levels (>200 mg/kg) and were compared with data from previous studies on Pb isotope ratios. To capture lithogenic Pb ratios, a near-pristine soil from the Konza Prairie was sampled with an auger with extensions to a depth of 70+ cm (C horizon, representing natural geogenic Pb). All soils were air dried, sieved to 2 mm, and subjected to acid digestion to recover the total Pb in soils. Concentration data were obtained using inductively coupled plasma optical emissions spectrometry (ICP-OES). Lead isotopic data were determined using an inductively coupled plasma triple quadrupole mass spectrometer (ICP-QQQ). Samples were diluted to below $1x10^6$ counts per second (CPS) to ensure measurement in pulse mode, and a digested NIST 981 was used for mass drift correction. Residential and vacant lot site isotope ranges had distinct separation from Konza Prairie isotopic ranges. These lots overlapped in ratios with lead paint, leaded gasoline, and mining spoil acquired from a mining site in El Paso, Texas. Former industrial activities in the Kansas City area may be a major contributor to Pb contamination in the studied Kansas City, MO, vacant lots.

3.1 Introduction

Lead is a ubiquitous environmental contaminant that has been a consistent hazard for humans since humans, began mining and smelting materials thousands of years ago, with lead poisoning being recognized as early as 2000 BC in Greece (Lewis, 1985; Riva et al., 2012). Despite its toxicity, lead was used for a variety of manufactured goods due to its low workability, low melting point, durability, and low-cost production. Lead was even known to be toxic throughout history, with lead poisoning being recognized as early as 2000 BC in Greece. It was well known during the Industrial Revolution. Lead production and emissions grew as it was used for a wide variety of goods, including batteries, ceramics, and pigments (Lewis, 1985). However, it became inescapable after the introduction of tetraethyl lead (TEL), which was an anti-knock agent for cars. Eventually, leaded gasoline was phased out at the end of the 20th century, but these anthropogenic Pb emissions have now deposited in the soils of the world (Wang et al 2022). Lead concentrations are higher in the topsoil than in the subsurface soil due to anthropogenic Pb contributions. Lead surface soil concentrations show an inverse correlation with distance from roads, showing their anthropogenic effects (Komárek et al., 2008). Elevated lead in soils is a danger to humans, as lead can potentially be inhaled as dust or ingested, as it can cause a variety of adverse and chronic health issues (Wani et al, 2015).

Urban areas are known for elevated levels of trace elements such as Pb due to the addition of human-transported materials or from alteration from anthropogenic activity (Yang & and Zhang, 2015). Urban soil health is a growing concern for human health as the world continues to urbanize. Cities are dynamic environments with shifting land use, and it is important to understand the history of the soils that are being altered and developed on. The prevalence of contaminants has caused some plots of land to remain vacant due to the potential harm of these

contaminants. There is also uncertainty about whether the contaminated site still has an active source of contamination. Lead is found at higher concentrations in urban soils, but it is crucial to identify the sources that contributed to the contamination (Riddle et al., 2022; Brown et al., 2016). Leaded gasoline and paint are the two most common sources of contamination in urban soils in the United States. Leaded gasoline was common due to increased vehicular use in the 20th century, after the United States passed the 1956 Interstate Highway Act, which created transportation corridors for the growing suburban population to commute to cities. Vehicle exhaust was concentrated as suburbanites commuted into the cities (Levin et al., 2021). Lead paint was widely used for its corrosion resistance, with red lead oxides used for ships, bridges, and cars (Jacobs et al., 2002). Lead paint was also commonly used for painting residences, due to its vibrant colors, durability, resistance to mold and mildew, and quick drying time. Millions of residences still contain Pb paint and remain an active source of contamination, as paint chips enter the soil (Rabinowitz and Hall, 2002). Industrial areas in cities also contribute to lead contamination, with emissions from metallurgical activities entering the atmosphere and eventually depositing into the soil. Waste incinerators can be another source, as the burning of a variety of heterogeneous materials in municipal waste can produce Pb emissions (Komárek et al., 2008). Coal ore contains Pb, and the burning releases this Pb into the atmosphere. These forms of atmospheric Pb emissions make it difficult to determine which sources have contaminated an urban area, meaning a contaminated site may have multiple sources. Lead isotopes are used to identify sources of Pb contamination. Lead has four isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb, each with a different relative abundance in nature. Lead-204 is a primordial isotope, meaning it has remained at a constant level on Earth since its formation. The other three are radiogenic isotopes formed by the radioactive decay of Uranium and Thorium isotopes. These parent isotopes of Pb

have different decay rates, which lead to changes in the relative abundance of Pb over time as U and Th decay into these isotopes. These isotopic compositions can provide unique fingerprints to lead in nature, such as ores, bedrock, soil, and atmospheric Pb (Rabinowitz and Hall, 2002). Manufactured Pb materials will share the isotopic compositions of the Pb ores used for their production. Different chemical reactions can also alter isotopic composition through mass fractionation, in which lighter isotopes are favored due to the lower energy needed to break and form their bonds (Young et al., 2002). Lead isotope tracing can help identify Pb contamination sources, map the dispersion of these contaminants, and can be used to aid treatment plans for Pb remediation of these sites.

This study aims to identify sources of Pb contamination in various vacant lots and residential sites of Kansas City, Missouri, using mass spectrometry. There have been some studies on isotopic contamination in the Midwest, but none on Pb source identification in the area. This method can be used for Pb by looking at its four natural isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. Their ratios can then be used as unique fingerprints to identify whether the lead is from paint or gasoline, and they can even be used to trace its original source.

3.2 Materials and Methods

3.2.1 Kansas City Background

Kansas City was founded in the 1830s originally as a trade port between the Kansas and Missouri rivers. Kansas City was known for its thriving cattle industry and was a major connection between eastern and western markets due to the transcontinental railway systems built through it. Industry was found in the district of West Bottoms where meatpacking plants, steelworks, train yards, and stockyards were located. Industry diminished in importance post WWII and the West Bottoms was severely damaged by a flood in 1951, never fully recovering. By the 1960s the city had suffered urban decay, and many residential buildings were demolished for office buildings and parking lots as the city became a place to work instead of habitation. Railroads declined after WWII as cars and planes became the new standard of travel. The city continued to grow in land size from the 40s to the 70s, but the population density decreased as the population shifted from the city core to the suburbs. Kansas City's development over the past two centuries reveals various potential sources of Pb contamination. Cars due to constant commuting from the suburbs into the city when leaded gasoline was around, coal fuel from trains as they transported cattle, lead paint from buildings, and Pb from various industrial activities in the city's West Bottoms district.

3.2.2 Konza Prairie Site Background

The site was a tallgrass field located near the Konza Prairie Biological Station. The field had been used for farming at the beginning of the 20th century, but there were no known buildings or developments upon the site. The area has been undisturbed since the formation of the Konza Prairie.

3.2.3 Samples Collection and Preparation

Samples were collected from various residential and vacant lot sites in the Kansas City, Missouri area. These sites were provided by the Ivanhoe Neighborhood Association and the Community LINC in Kansas City, MO. Sites were first screened for evidence of elevated Pb levels (Pb > 200 mg/kg) using a portable X-ray fluorescence spectrometer (p-XRF, Niton XL3t XRF analyzer). Each chosen sampling location had its GPS coordinates recorded, and the soil was then sampled to a depth 0-15 cm using a soil probe. For the Konza prairie, three samples were collected at 70+ cm depth at three different locations manually, using a soil auger with an extension for a background reference for lithogenic Pb comparison. Soils were air-dried, ground, homogenized, and then sieved to separate the <2 mm fractions with a stainless-steel mesh. This fraction is considered the whole soil. Source data samples of leaded paint, coal, leaded gasoline, and other sources were all acquired from past studies as reference data.

3.2.4 Sample Digestion and Dilution

A portion of the sample was digested using the USEPA method 3051a (U.S. EPA, 2007) for Pb concentration and analyzed using an Agilent 5800 ICP-OES. Briefly, 0.5 grams of the sample were weighed into Teflon tubes along with 10 mL of 70% trace metal grade nitric acid. Each batch had two duplicates, NIST 2711 Montana Soil, and a blank run for quality assurance and control. Filtered samples were then further diluted for inductively coupled plasma optical emission spectrometry (ICP-OES) analysis.

3.2.5 Sample Analysis

Digested samples were first analyzed using an Agilent 5800 ICP-OES for total Pb concentrations. These concentrations were recorded and then used for further dilution for isotope analysis using an Agilent 8900 inductively coupled plasma triple quadrupole mass spectrometer

(ICP-QQQ). Isotopic measurements were performed in pulse mode, which requires the counts per second (CPS) of the instrument to be below 1,000,000. Samples were diluted below that threshold to avoid analysis in analog mode. Pulse mode has improved accuracy and precision when measuring isotope ratios compared to analog mode, and it is best to ensure the signal does not alternate between modes (Wu et al., 2018). All masses listed in Table 3.1 were measured with no reaction gas additions in tandem mass spectrometry mode (MS/MS), which uses the first and last quadrupoles as mass filters for improved accuracy. A NIST 981 solution that underwent USEPA method 3051a (U.S. EPA, 2007) was used as an external standard during analysis. The digested NIST 981 ran every 10 samples to correct for instrument drift.

Table 3-1: Measured elements and assigned quadrupole masses, and integration times. 201Hg and 202Hg monitored for Hg interference with ^{204}Pb.

Element	Q1 -> Q2	Integration Time
^{201}Hg	201 -> 201	0.3
^{202}Hg	202 -> 202	0.3
^{204}Pb	204 -> 204	6.0
^{206}Pb	206 -> 206	3.0
^{207}Pb	207 -> 207	3.0
^{208}Pb	208 -> 208	3.0

Mercury-201 and Mercury-202 were monitored to see if there was any potential Hg interference, as Hg presence can influence the measurement of ^{204}Pb due to associated isobaric

interferences (Woods, 2014.). Each sample underwent 8 replicate analyses in a 6-point peak pattern with 500 sweeps per replicate.

3.2.6 Calculations

Background and Hg counts were corrected in Masshunter software. Mercury counts were found to not be a significant interference. Data from past studies were used for source ranges for KC data comparison included: Wang et al., 2019, Chow et al., 1975; Dunlap et al., 2000; Rabinowitz, 1987; Jaeger et al., 1998; Bollhöfer and Rosman, 2001.

3.3 Results and Discussion

3.3.1 Total concentrations of lead in soils

Natural soils commonly range from 1-200 mg/kg due to lithogenic Pb contributions (Zimdahl & Skogerboe, 1977). The USEPA's current recommended soil screening level for residential soils is 200 mg/kg (US EPA, 2024), and levels above would also suggest anthropogenic Pb concentrations, as it exceeds natural ranges.

Most soils contained elevated levels of Pb as seen in Table 3-2, with only V1 and V5 containing levels below 200 mg/kg, which fall in range of lithogenic soil concentrations. All other soils in sites had considerable elevation, with all exceeding the >200 mg/kg requirement for elevated Pb level classification. These samples were all taken from the top 15 cm of soil, where lithogenic sources are less influential, and anthropogenic deposition is common (Ettler et al., 2005; Teutsch et al., 2001).

3.3.2 Isotope ratios of potential lead sources

Lead isotope ratios for Kansas City (KC) sites showed a wide range compared to other sources, likely due to soil heterogeneity and mixed inputs for contamination. A clear divide is evident in

Figure 3-1 to 3-4, with Kansas City sites displaying lower isotopic ratios compared to data from sources, forming a left-right divide. Konza Prairie samples showed no overlap with KC sites, indicating these soils have had anthropogenic contributions. The Konza Prairie samples aligned closer with leaded gasoline and lead paint. This prairie site is undeveloped, which makes lead paint contamination unlikely, and the only potential sources contributing to this site would be aerosols and leaded gasoline. Past studies have shown that anthropogenic Pb exhibits strong vertical mobility in soil profiles, but they focus upon concentrations on surface soils up to 30 cm (Ettler et al., 2005; Puchelt et al., 1993). This is because metals tend to accumulate in this region, but minor fractions of certain metals, such as Cd and Zn, can migrate through preferential pathways up to 2 m due to earthworm channels (Sterckeman et al., 2002). It is possible that the deep roots of prairie grasses could grant minor fractions of Pb a preferential pathway for downward mobility. However, less than 0.1% of Pb in the mobile Pb pool will migrate downward, out of the first 25 cm, per year (Semlali et al., 2004). This indicates that the weathered bedrock of the prairie soil is contributing to the ratio, and not the leaded gasoline values, because of the minuscule amount that would be transferring down the profile. Lead paint ratios overlapped with KC sites, but many points had no overlap with sources. This would mean Pb paint does not fully explain the Pb isotopic ratio, and another source must be contributing to these sites, which may just be lithogenic background contributions. Kansas City values did share values with the El Paso mining spoil samples; their $^{206/204}$Pb ratio given in Table 3-3, falls within $^{206/204}$Pb ore ranges of 16-18.5 (Komárek et al., 2008). This overlap indicates a potential influence from industrial sources. Their site ratios overlapped with leaded gasoline, El Paso mining samples, aerosols, and leaded paint. Konza Prairie had significantly higher $^{206/207}$Pb ratios than Kansas City sites and showed some commonality with lead gasoline values. Industrial

activities may have influenced these sites, and records indicate past smelting, steel production, and manufacturing within KC during the 20th century (Wood & Burcham, 1964). A combination of industrial aerosols and lead paint may be the main contributors of Pb contamination in the area.

Table 3-2: Total Pb concentrations in samples from residential (R) and vacant (V) samples in KC, MO.

Site	Pb Range (mg/kg)	Average (mg/kg)
V1(10)#	111.2-249.6	167.8
V2 (5) #	64-600	383.4
V3 (4) #	188.12-1165.12	531.1
V4 (20) #	42.81-3116.44	449.97
V5 (17) #	44-549.54	172.42
V6 (15) #	49.73-777.88	246.47
R1 (7) #	99.57-833.63	332.59
R2 (10) #	134.4-1221.6	611.3
R3 (7) #	74.09-887.39	303.95

Number of individual soil samples analyzed per site

Table 3-3: Ranges of various sources and KC sites, split between residential (R) and vacant lots (V). Gas and paint data collected from past studies (Wang et al., 2019; Chow et al., 1975; Dunlap et al., 2000; Rabinowitz, 1987; Jaeger et al., 1998).

Sample Type	206/204 Range	206/207 Range	208/206 Range	208/207 Range
Leaded Gas	18.50-19.05	1.185-1.211	2.048-2.068	2.444-2.470
Lead Paint	16.93-19.12	1.094-1.233	2.032-2.126	2.410-2.508
Coal	18.52-19.72	1.182-1.252	1.964-2.086	2.458-2.490
Residential	17.10-18.42	1.124-1.182	2.041-2.145	2.394-2.436
Vacant	16.88-18.46	1.090-1.189	2.060-2.182	2.358-2.518
Konza Prairie	18.60-18.75	1.201-1.207	2.049-2.056	2.467- 2.470

3.3.3 Isotope ratios of residential and vacant lot soils

Vacant lots displayed significantly lower $^{206/207}$Pb values than residential sites, but still had significant overlap in ranges, as seen in Table 3-3. This is potentially due to differences in site land use, as vacant lots may have formerly been industrial sites or are currently sites of dumping activity and pollutants. Despite the statistical differences between these site types, this does not prove that one site type has or does not have a source of contamination. Concentrations did not influence the isotopic ratios, with those with higher average Pb concentrations overlapping those with lower average concentration data, indicating shared sources with different deposition amounts. This data suggests that sites may have different total source contributions, even though they both still overlap in values. Lead paint is also known for its heterogeneity in the environment due to the painting history of the object, exposure to the outdoors, and differences in manufacturing processes across paint batches (D'imporzano et al., 2021). Studies have sought to determine the unique isotopic patterns in Pb paints, but they were too variable to identify based on brand (Rabinowitz & Hall, 2002). Using Pb isotopes for the identification of

different sites proves to be unfeasible, as can be seen in Figure 3-5. Most of these sites overlap due to their shared sources, but their heterogeneous sources may homogenize their isotopic sources. Leaded gasoline during its recordings had been shown to change in isotopic ratio in the atmosphere over time, providing evidence that it was a contributor, but these atmospheric contributions can homogenize, making it difficult to isolate (Dunlap et al., 2000; Sangster et al., 2000). Isotopic ratios may continue to homogenize due to international trade and use of these ores, as time progresses these signatures will lose their uniqueness when all of these products and emissions spread across the world (Sangster et al., 2000). Lead isotopes can provide meaningful information. Still, it does not directly identify the actual sources as it only shows a ratio to compare with other data points for similarities. However, these limits do not prevent it from being an effective tool in discerning the general sources and narrowing down the source contributors in the soil.

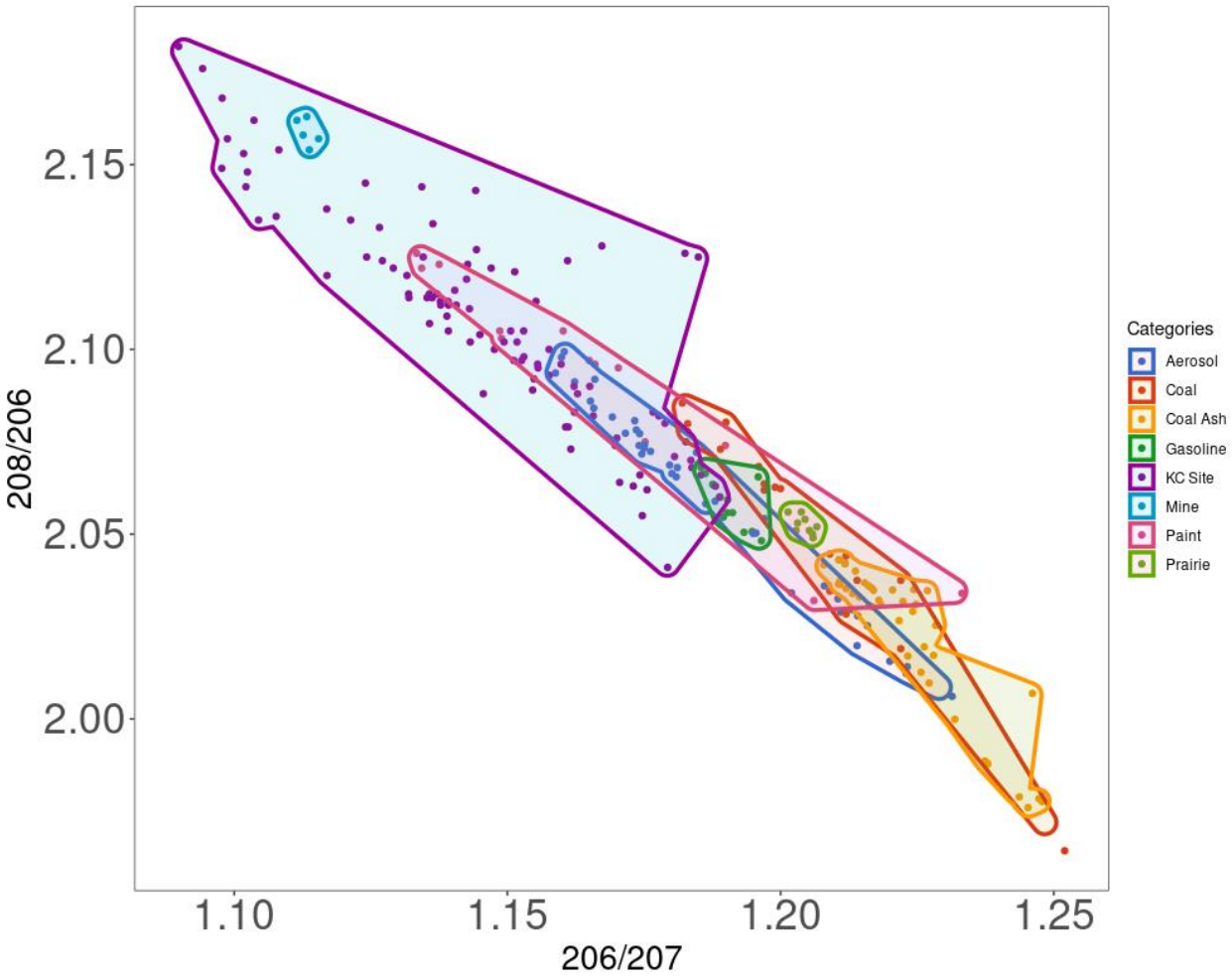

Figure 3-1: $^{206/207}$Pb and $^{208/206}$Pb ratios of KC sites and Konza samples compared to possible Pb sources. Gasoline, paint, aerosol, coal, and coal ash data were collected from past studies (Wang et al., 2019; Chow et al., 1975; Dunlap et al., 2000; Rabinowitz, 1987; Jaeger et al., 1998; Bollhöfer and Rosman, 2001).

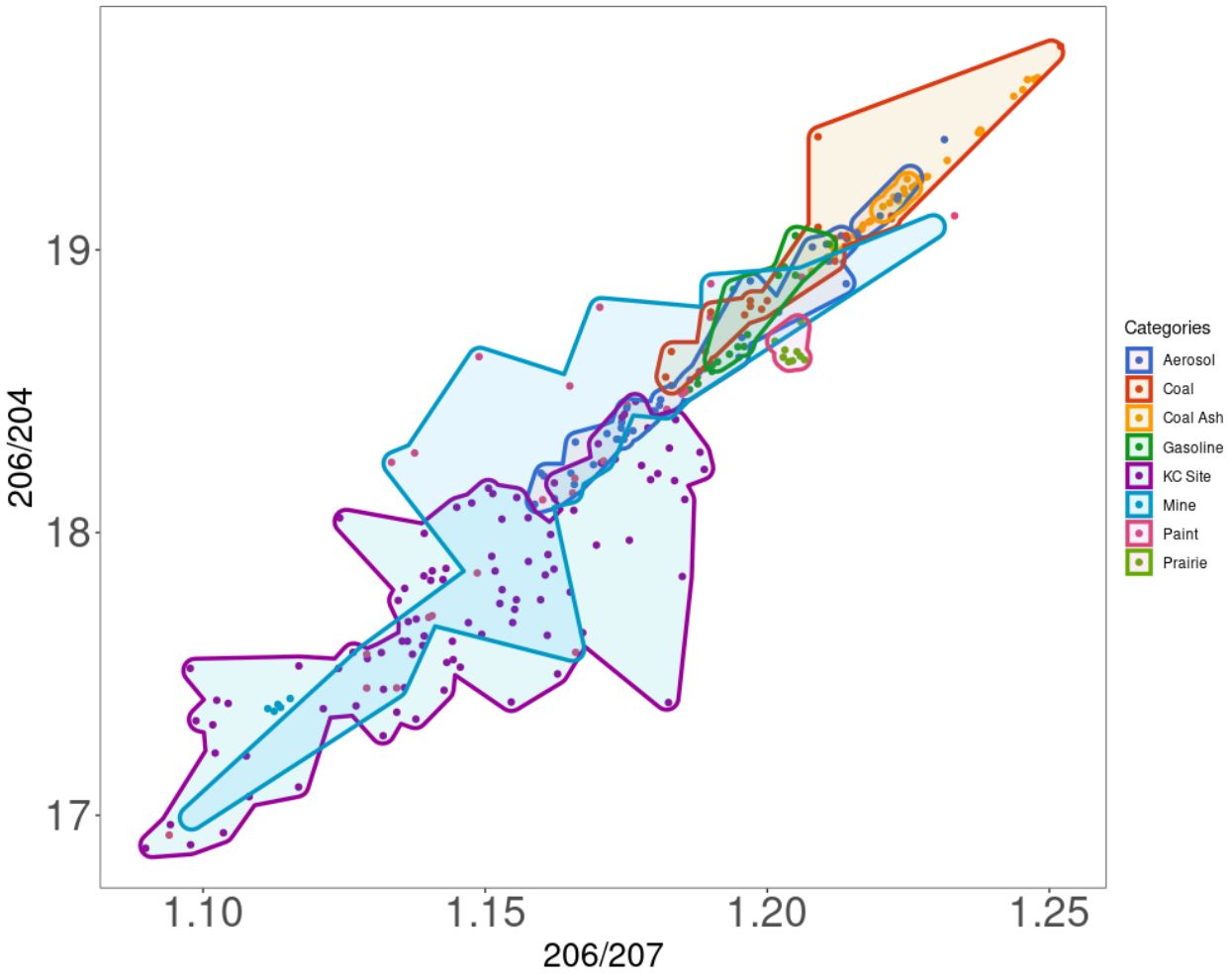

Figure 3-2: $^{206/207}$Pb and $^{206/204}$Pb ratios of KC sites and Konza samples compared to possible Pb sources. Gasoline, paint, aerosol, coal, and coal ash data were collected from past studies (Wang et al., 2019; Chow et al., 1975; Dunlap et al., 2000; Rabinowitz, 1987; Jaeger et al., 1998; Bollhöfer and Rosman, 2001).

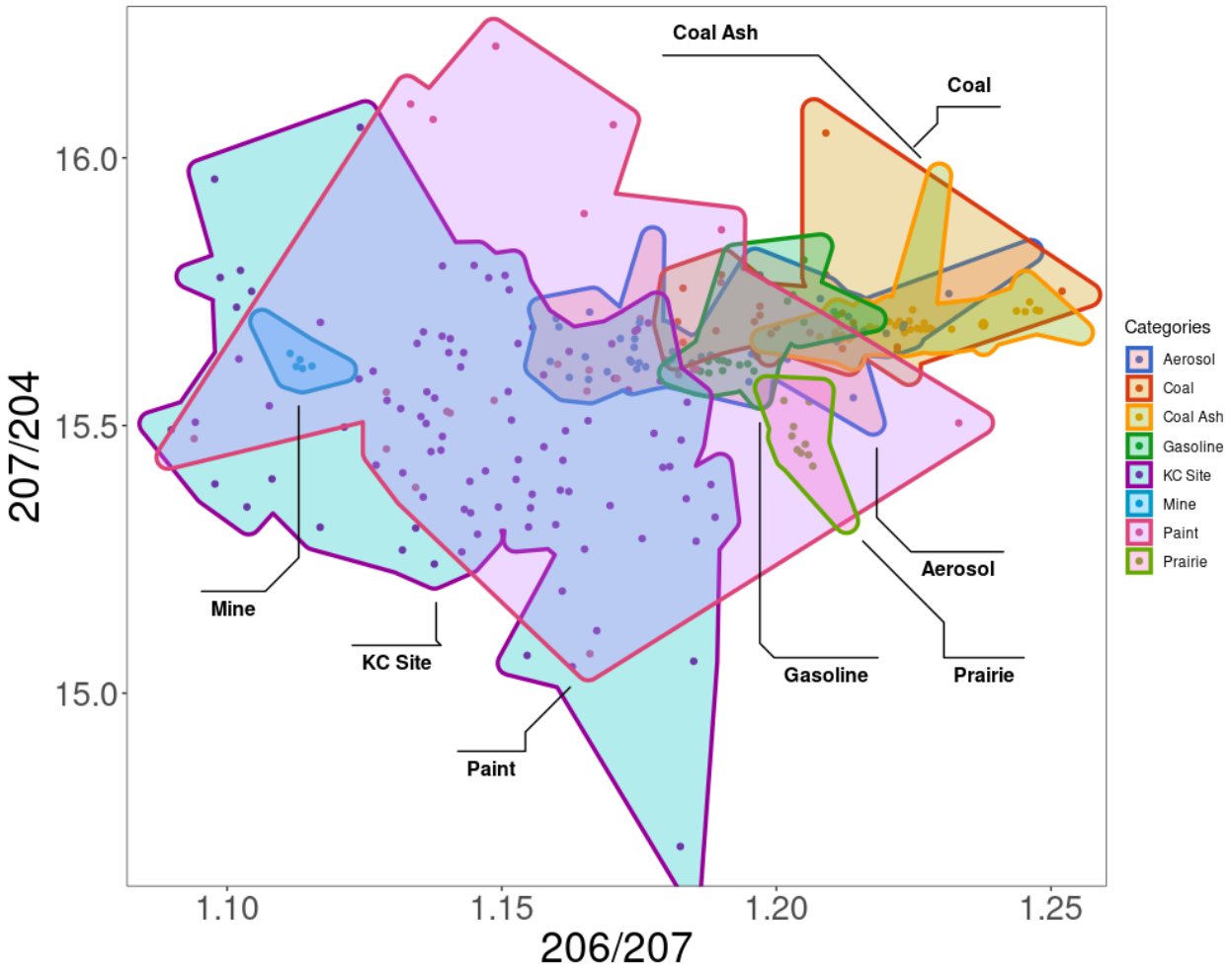

Figure 3-3: $^{206/207}$Pb vs $^{207/204}$Pb Isotopic ratios of Konza Prairie and KC sites compared to possible sources. Gasoline, paint, aerosol, coal, and coal ash data were collected from past studies (Wang et al., 2019; Chow et al., 1975; Dunlap et al., 2000; Rabinowitz, 1987; Jaeger et al., 1998; Bollhöfer and Rosman, 2001).

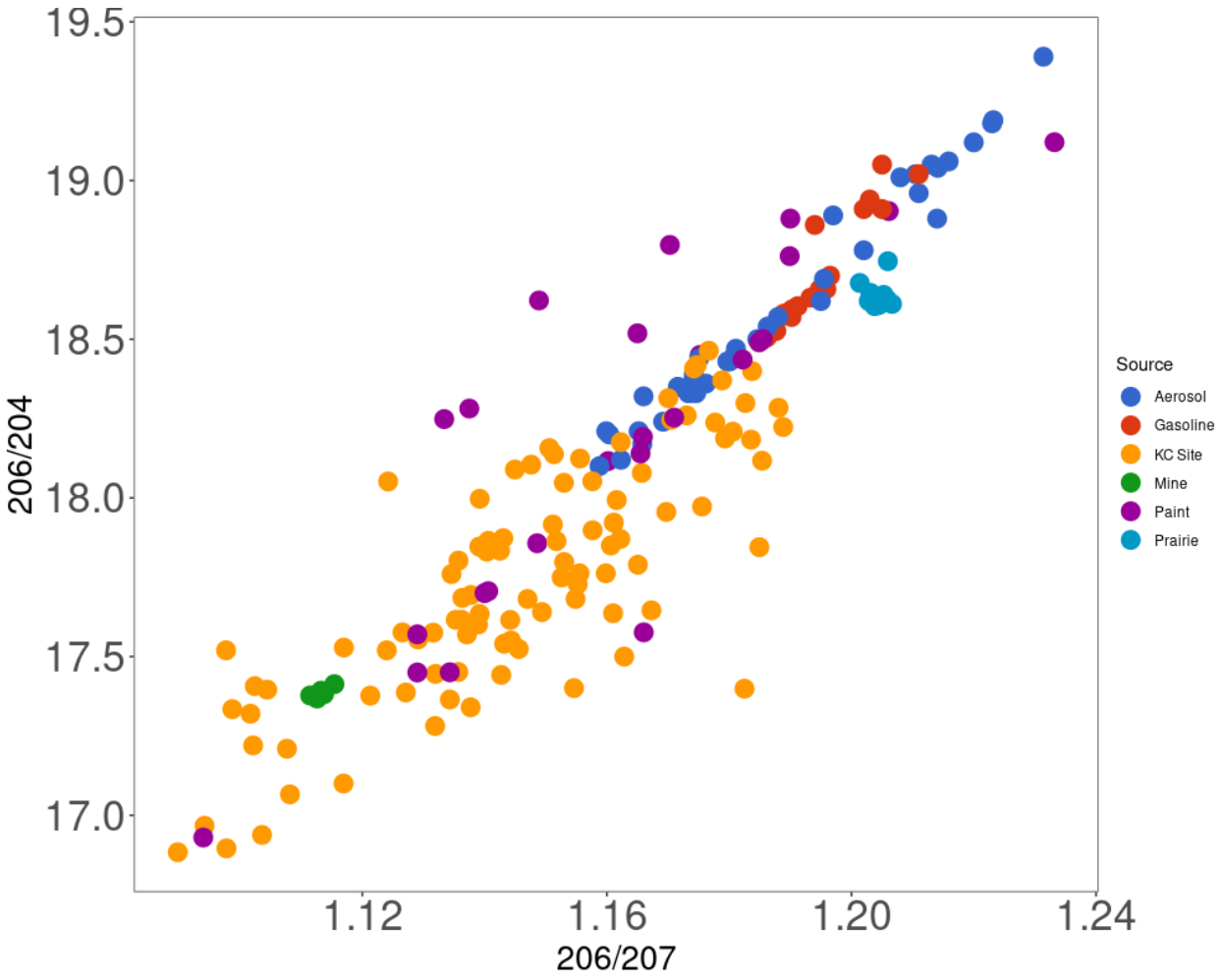

Figure 3-4: Simplified plot of $^{206/207}$Pb vs $^{206/204}$Pb Isotopic ratios of residential and vacant lots compared to overlapping sources. Gasoline, paint, and aerosol data were collected from past studies (Wang et al., 2019; Chow et al., 1975; Dunlap et al., 2000; Rabinowitz, 1987; Jaeger et al., 1998; Bollhöfer and Rosman, 2001).

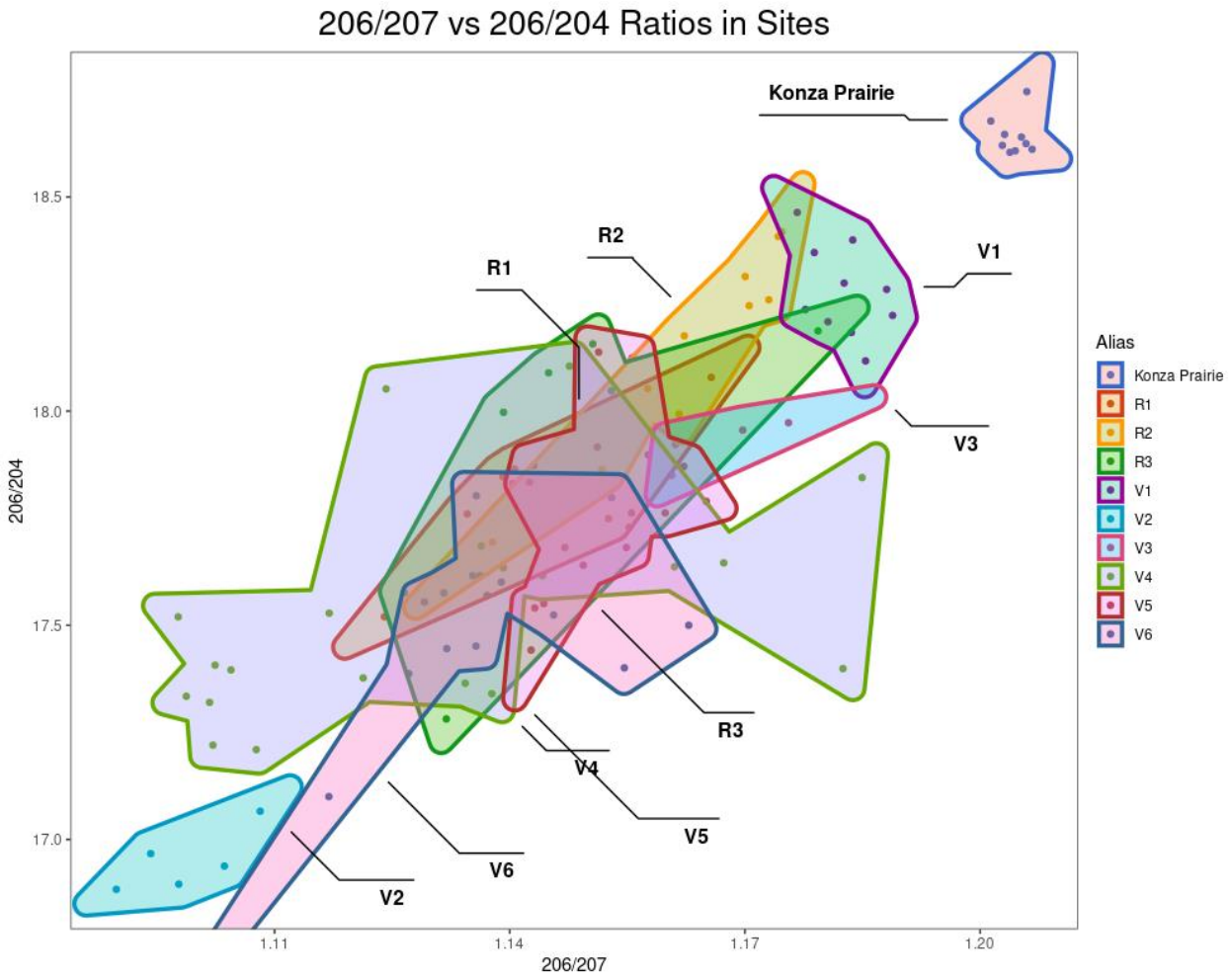

Figure 3-5: $^{206/207}$Pb vs $^{206/204}$Pb isotope ratios of individual sites mapped on cluster plot along with Konza Prairie. V represents vacant lot, R represents residential.

3.4 Conclusions

This study aimed to provide novel data on Pb isotopic ratios in the KC area and to identify the main source contributions of Pb in their soils. It was found that lead paint and mining spoil overlapped the most with residential and vacant lots. Site ratios were lower than those of most comparable sources and fell within $^{206/204}$Pb values of ore samples. This low range suggests that industrial activity is a major contributor, and further samples from industrial portions of KC will need to be taken for confirmation. Lead paint showed a significant overlap in KC site values. Leaded gasoline and aerosol values showed minor overlap, indicating they are minor contributors to Pb in KC sites. Konza samples were distinct from KC site samples and matched values similar to aerosols and gasoline, but these values do not indicate Pb contamination. These values for the Konza sample reflect the lithogenic background of the Konza Prairie. In the future, further samples should be acquired in the KC area for future background comparisons. Residential sites displayed a narrower range than vacant lots, most likely because of the differing land use history of the vacant lots.

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Chapter 4 - Utilizing Reclaimed Wastewater Phosphorus as both a Fertilizer and a Remediation Tool for Urban Agriculture

Abstract

Global phosphorus (P) reserves are depleting and much of this crucial nutrient for life is lost due to runoff, causing damage to waterways. Recovering P from wastewater streams is important to bolster the resiliency of food systems and promote a circular economy. Phosphorus application can also be a potential remediation tool for urban soils, which commonly suffer from lead (Pb) contamination. A reclaimed nutrient products (RNPs) from swine wastewater in the form of precipitated calcium phosphates were tested for its effectiveness as a fertilizer and in situ soil amendment for reducing bioavailability of soil Pb to both plants and humans. Three soils from three different locations at a vacant lot site in Kansas City, MO, were collected, analyzed, and classified as mild (208 mg/kg), moderate (323 mg/kg), and extreme (2418 mg/kg). A greenhouse study was conducted with 5 treatments: ammonium polyphosphate (APP), triple superphosphate, struvite, RNP, and a control on a leafy (lettuce, *Lactuca sativa 'Grand Rapids'*) and a root crop (radish *'Raphanus sativus 'Champion'*). Phosphorus treatments were applied at agronomic rates and were harvested on their respective harvest dates. Plant and soil samples were acid digested and analyzed for Pb and P concentrations using graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma-optical emissions spectrometry (ICP-OES), respectively. Soils underwent the physiologically based extraction test (PBET) for determination of bioaccessible Pb. Lead isotopic compositions in lettuce digestates were determined with inductively coupled mass spectrometry (ICP-MS). The RNP was effective at reducing Pb concentrations in the radish roots, while lettuce and aboveground plant tissues showed low Pb

concentrations overall. However, the agronomic rate of P addition did not significantly reduce bioaccessible Pb in soil to humans, further research with P applications based on soil Pb concentration is needed. Phosphorus concentrations in plants were not significantly affected by the P treatments because Mehlich-3 P in the soils was excessive, masking treatment effects. The RNP may have the potential to mitigate Pb uptake in root crops and meet the P requirement in vegetable crops; however, more research is needed to show if it is an effective P fertilizer.

4.1 Introduction

Phosphorus is an essential nutrient for life on Earth. Their use as P fertilizers has been crucial in increasing crop yields and feeding the ever-growing human population (Cordell et al., 2009). Traditional P fertilizers are harvested from phosphate rocks, and the application of P tends to be incredibly inefficient in agricultural systems with roughly 80% of P being lost during its production and use (Huang et al., 2024). Phospohrus demand continues to increase, with an estimated production peak by 2030, and the estimated time for reserves to be depleted will be in the next 50-100 years (Illakwahhi et al., 2024; Cordell et al., 2009). Fewer people are now farming, as the world continues to urbanize, with urban populations exceeding rural populations in 2008 (Satterthwaite et al., 2010). Cities do not produce their food and rely on other productive lands to feed them, as fewer and fewer people are producing the majority of the world's food (Satterthwaite et al., 2010; Orsini et al., 2013). Their demands lead to the complex food system where they can acquire steak from a ranch in Brazil, and soybeans from a farm in Kansas. The global system distances the consumer from the producers, and there has been a growing movement towards urban agriculture, which shortens the supply chain, reduces the environmental impact of food, and optimally uses land within a city (Deelstra & Girardet, 2000; Gunapala et al., 2025). Now there is a growing interest in P recovery techniques, to make their use as efficient as possible and to make prospective urban farmers use fewer external input to promote a sustainable, closed food system (Ghahremani et al., 2024). The main problem with P usage inefficiency is due to its tendency for quick immobilization, and if the plant roots are not close to the P, then it will most likely be converted into insoluble inorganic P, or organic P by microbes before the plant root interacts with it (Lambers, 2022). Phosphorus also can adsorb to clays or precipitate into insoluble minerals inaccessible to plants (Weihrauch and Opp, 2018).

The available P ions need to be around in solution long enough for the plants to uptake, and pH plays a crucial factor in keeping P in solution (Penn and Camberato, 2019). The consensus is that the optimal range for P availability for plants is at a near neutral pH (Lindsay, 1979). If the soil acidifies, it starts to be fixated with aluminum or iron at more alkaline conditions, it is fixated by calcium (Price, 2006). Large amounts of P so that even if most is lost, enough is still absorbed by the plants. This is done because farmers would rather spend a bit more on P and overapply it than face a potential loss in crop yield and revenue (Kile et al., 2025). The issue is that the plant cannot take up all that P at once, and that leads to most of the P fertilizer being wasted as it transitions into different unavailable forms or is washed out of the system (Schachtman et al., 1998). A large portion of fertilizer P loss occurs as surface runoff, as these available nutrients can be washed out. Precipitation may turn valuable nutrient into runoff, where excessive P is considered a hazardous pollutant as it promotes the eutrophication of waterways (Withers et al., 2015; Sarkar et al., 2025; Di Capua et al., 2022). Phosphorus pollution is not just produced by farming, though. In urban areas P is a common source of pollution in water due to food, detergents, wastewater, and food waste (van Dijk et al., 2016). As urban agriculture grows, it would be beneficial to ensure that the urban food system promotes a circular economy and avoids the same problems as modern agricultural systems. Reclaimed P from wastewater can be a step toward a self-sufficient alternative that supports sustainable agriculture and reduces the environmental impact of agriculture. Reclaiming P from wastewater may provide not just a viable alternative local fertilizer for urban agricultural systems; it may also be a potential remediation tool for heavy metal contamination (e.g., Pb, Cd, Hg) that are found in city soils globally (Wani et al., 2015). Pb is an omnipresent contaminant in any urban soil due to the usage of Pb gasoline, industry, and Pb paint (Levin et al., 2021). Even though Pb usage was

curtailed and eventually banned in the 1970s in the United States, the contamination remains (Wang et al., 2022). Lead is extremely harmful to human health causing a wide range of problems such as brain damage, anemia, infertility, and even death (Wani et al., 2015). Soil Pb into humans through direct ingestion, inhalation of dust (Hettiarachchi and Pierzynski, 2004). When this Pb is transferred, the total Pb consumed is not how much will be in an organism's system. It will be the bioavailable Pb, which is the portion that can be absorbed into living organisms (Hettiarachchi and Pierzynski, 2004). This bioavailable Pb is in the form of Pb^{2+} and can compete with various ions such as Ca^{2+} and Fe^{2+} in various metabolic reactions (Patrick, 2006; Wani et al., 2015)Potential plant uptake of Pb is a major concern as potential farmers already have to put in much work in soils that may be harmful to the plants, and these crops can be another vector for lead to be introduced to the body (Attanayake et al., 2021). Phosphorus application has proven to be a promising remediation technique that is less intensive and cost effective in comparison to other remediation techniques (Shao et al., 2020), which reduces the Pb solubility, thus the toxicity and bioavailability of Pb. With Pb, phosphates produce pyromorphite, a stable mineral that is several magnitudes less soluble than other common soil Pb minerals (Karna et al., 2018).

4.2 Materials and Methods

4.2.1 Soil Selection and Sampling

Multiple locations of different vacant lots were tested using a portable X-ray fluorescence spectrometer (p-XRF, Niton XL3t XRF analyzer). for a satisfactory site. This process was guided by past survey maps of Pb distribution using the p-XRF. A vacant lot site was chosen based on two conditions, which were a) Pb concentrations >200 mg/kg and b) heterogeneous concentrations above 200 mg/kg. After site selection, surface soil samples (0 to 15 cm) were collected in three different locations within the site, classified as low, moderate, and extreme Pb soils.

4.2.2 Initial Soil Characterization

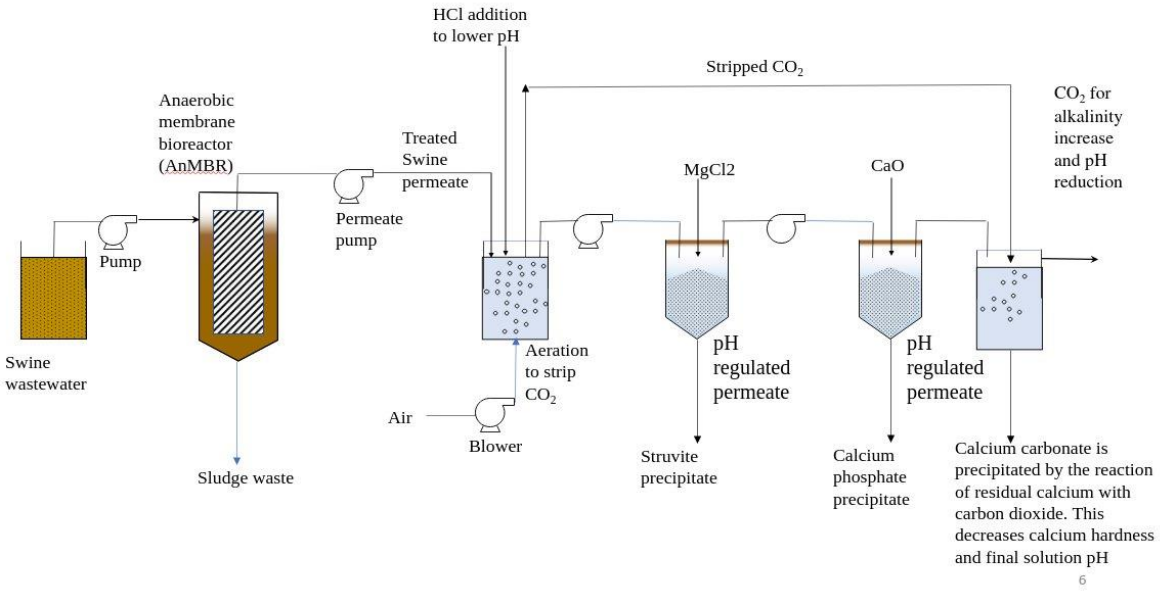
The three soil samples with contrasting soil Pb concentrations were air-dried and sieved to < 2 mm before undergoing analysis. Three replicates of each soil were analyzed for pH in a 1:5 soil:water extract (Watson and Brown, 1998). The cation exchange capacity (CEC) was determined using the displacement method (Soil Survey Staff, 2011). The maximum water-holding capacity was measured using the protocol from Jenkinson and Powlson, 1976. Soil texture was determined using the hydrometer method (Soil Survey Staff, 2011). Total Organic carbon and Nitrogen were determined by the dry combustion method as described by Nelson and Sommers, 1996. The soil micronutrients Cu, Fe, Mn, and Zn were measured using diethylenetriaminepentaacetic acid (DTPA) extraction (Whitney, 1998). Inorganic N in the forms of nitrate and ammonia was measured using KCl extraction (Gelderman and Beegle, 1998). For total Pb concentrations, samples underwent the USEPA digestion method SW846-3051A (U.S 2007). The digestates were then analyzed by Agilent 5800 ICP-OES for their Pb and other selected elemental concentrations. Further subsamples of soils were analyzed for plant available

P using the Mehlich-3 method (Frank et al., 1998) and analyzed in a Beckman DU 800 spectrophotometer following the Murphy and Riley Procedure (Frank et al., 1998).

4.2.3 Nutrient product recovery

Nutrients were recovered from swine wastewater that went through an Anaerobic membrane bioreactor (AnMBR). This permeate was rich in N and P nutrients which went through multiple phases to reclaim P. The calcium phosphates were produced after calcium oxide was added (CaO) to this permeate. All steps can be seen in Figure 4-1 and further information can be found in Mckee-Rist, 2025.

Figure 4-1: Wastewater nutrient recovery used for obtaining calcium phosphates (Source: Mckee-Rist 2025). More information can be found in patent WO2025102022A1.



4.2.4 Product Characterization

Semi-solid nutrient-rich samples were freeze-dried and digested using USEPA method SW846-3051A (U.S. EPA, 2007) in a microwave digestion unit. The digestate was analyzed for nutrient composition and selected potentially toxic trace metal(loid)s using an Agilent 5800 inductively coupled plasma optical emissions spectrometer (ICP-OES). Two

percent (w/v) citric acid analysis was performed using a modified method used by the Association of Official Agricultural Chemists (1945), for freeze-dried products. This test is used to identify the fertilizer value of the product. A portion of the freeze-dried product was directly used as powder for XRD analysis for identification of phosphorus phases in the RNP using a PANalytical Empyrean Multi-Purpose X-Ray Diffractometer using Cu Kα radiation at a wavelength of 1.54 Å and generator settings of 45 kV and 40 mA. Measurements were made using a continuous-scanning technique from 5 to 70 °2θ and a scan speed of 0.024° per second as discussed in Haputhanthri Gamage, 2023. Profex software (Doebelin and Kleeberg, 2015) was used to identify phosphorus species within the RNP. Two products were selected and combined based on these traits, and the combined product underwent additional XRD analysis for phase identification.

4.2.5 Greenhouse Study

All soils were then packed into plastic pots to achieve a bulk density of 1.1 g/cm3. Each pot contained 2 kg of air-dried soil. Radish (*Raphanus sativus 'Champion'*) and lettuce (*Lactuca sativa 'Grand Rapids'*) seeds were left to germinate in a Sungro growing mix for 2-3 weeks before two were placed in each pot.

A total of 90 pots filled with 2 kg of soil (30 each for each soil type) were divided into two for each plant type. Each plant type had 45 pots, each pot receiving 5 treatments (4 P treatments plus the control) with three replications in the three different soils. Pots were arranged in 3 blocks of 30 in order to minimize the effects of any environmental variables such as sunlight and temperature in the greenhouse. Each block consisted of 15 radishes and 15 lettuces structured in 6 rows containing 5 pots. With the 5 being a replicate of each individual treatment. Five treatments were: two conventional fertilizers (liquid APP and TSP), two reclaimed products

(Struvite and reclaimed wastewater product, RNP) and zero P control. Phosphorus treatments were applied to lettuces and radishes at equal rates of 60 kg P/ha (0.023 g of P per pot). The P fertilizers were all thoroughly mixed throughout the soil, except for APP, which was mixed in the top 5 cm. Each soil received the application of equal amounts of potassium and nitrogen in the forms of potassium chloride and ammonium nitrate to ensure all plants had the necessary nutrients, which would prevent potassium and nitrogen from being confounding variables. These were applied and mixed in the top 5 cm of the soil. Afterwards each pot was watered until they reached 55% maximum water holding capacity. Two seedlings were placed with even spacing in each pot. Pots were randomly shuffled in each row every time they were watered. Greenhouse temperature was maintained at an average of about 21°C with a 16-h photoperiod (6:00 a.m. to 10:00 p.m.).

Upon harvesting on their respective recommended harvest days of 28 days for radishes and 45 days for lettuce. The aboveground and root portions were washed sequentially to remove all soil particles. First, in milli-Q water, followed by a 5% sodium lauryl sulfate ($CH_3(CH_2)_{10}$ CH_2 OSO_3Na) bath to remove adhered soil particles, and another thorough rinse in milli-Q water. The plants were then blotted dry using paper towels, placed in paper bags. Plants samples were dried in a forced air oven at 70° C until they reached a constant weight. Their dry mass was then recorded, and then dried samples were ground using a Willey Mini Mill-Arthur Thomas–type grinder (Thomas Scientific), so that they could undergo microwave digestion for further analysis.

Soil samples were extracted from each pot and air-dried for analysis preparation. Briefly, four soil core samples from each pot were taken from 0-15 cm depth and air-dried for post-treatment analysis.

4.2.6 Post-Harvest Soil Analysis

Soil pH of each sample was measured using a 1:5 soil:water solution (Watson and Brown ,1998). Another portion of soil was sieved to <250 μm for the physiologically based extraction test (PBET) to assess gastric-phase bioaccessible Pb (Ruby et al., 1996). Gastric solution for PBET was prepared by mixing 2 L of milliQ water with 1 g of citrate, 1 g of malate, 840 μL of lactic acid, 1 mL of acetic acid, and 2.5 g of pepsin. The mixture pH was adjusted with hydrochloric acid to a starting pH of 2.5 (± 0.01 pH units). The solution was thoroughly mixed and heated to 37 °C. After heating (to 37°C), 100 mL of gastric solution were added to 1 g of soil sample in HDPE bottles. These bottles were placed in a TCLP extractor (end-over end shaker) with a temperature-controlled water bath heated to 37°C. Total extraction time was an hour. At 30 minutes the mixing would be halted to check for pH fluctuations and adjust the pH if it fell out of the 2.4-2.6 range. Three duplicate samples and a blank were used with each batch for quality control. These samples were then filtered with Whatman grade 42 filter paper and then underwent analysis with an Agilent 5800 ICP-OES.

4.2.7 Plant Sample Digestion and Analysis

For lettuce, 0.5 g of sample was weighed into a Teflon tube and mixed with 10 mL of 70% trace metal grade nitric acid. For radishes, 0.1 or 0.25 g of sample was weighed and mixed with 5 mL of 70% trace metal grade nitric acid. These weights were differed due to the lack of dried samples for digestion. Each batch of samples was placed into a MARS Microwave digestion unit, heated to 200° C,

maintained at 200° C for 15 minutes before cooling down. Each batch had duplicate plant tissue samples, one NIST 1515 apple leaf sample, and a blank. Plant Pb concentrations were determined using a Varian graphite tube analyzer (GTA) 120-AAS. Samples were diluted to fit

within the standard range of 0-100 ug/L. All other recorded elements were determined using an Agilent 5800 ICP-OES. Lettuce samples were further diluted and analyzed for Pb isotopic ratios through an Agilent 8900 ICP-QQQ.

4.2.8 Statistical Analysis

All data was analyzed using Rstudio software. Treatment comparisons were done using ANOVA and post-hoc TukeyHSD testing with $\alpha = 0.1$ significance. Outliers were present in Pb concentration analysis, and the voting method was used to remove outliers due to the low sample size

4.3 Results and Discussion

4.3.1 Initial Soil Characterization

All soils were slightly alkaline silt loam soils, with the moderate and extreme soils having twice as much sand as the mild soil (Table 4-1). All soils had excess Mehlich-3 extractable P (>100 mg/kg). Urban soils have displayed P accumulation due to past use of anthropogenic additions such as sewage sludge and industrial waste. One study showed urban soils in Nanjing, China reached total P concentrations of 15000 mg/kg and Olsen extractable P levels as high as 400 mg/kg (Yang and and Zhang, 2015; Zhang et al., 2001). Total soil Pb concentrations in the mild and moderate soils were at levels commonly found in urban gardens and areas (Attanayake et al., 2014; 2015; 2021). Iron, zinc, and manganese were significantly less available in the extreme soil. Copper was found in typical background concentrations in soils, ranging from 5-50 mg/kg (Mengel et al., 2001). Ammonium nitrogen levels were within the typical range of 2-10 mg/kg in all soils and contained low levels of nitrate-N (Horneck et al., 2014). The extreme soil contained twice the total organic carbon as mild and moderate soils, and all contained similar levels of low total nitrogen.

Table 4-1: Initial greenhouse study soil characteristics.

General Properties	Mild	Moderate	Extreme
pH (1:5 Soil:H_2O)	8.07	7.65	7.52
CEC (meq/100 g)	24.68	25.04	29.79
TOC (%)	3.3	3.2	6.4
TN (%)	0.3	0.3	0.4
Texture	Silt loam	Silt loam	Silt loam
Clay	26	24	26
Sand	9	18	20
Silt	65	58	54
Nutrients			
Mehlich-3 P (mg/kg)	169.7	165.3	179.2
NO_3-N (mg/kg)	6.3	7	15.9
NH_4-N (mg/kg)	4.9	6.9	9.8
DTPA Extractable Cu	11.6	31.6	40.6
DTPA Extractable Fe	44.6	35.7	1.1
DTPA Extractable Mn	11.1	10.3	4.6
DTPA Extractable Zn	75.9	96.7	9.8
Metals (mg/kg)			
Total Pb	207.6	323.1	2418.1
Bioaccessible Pb	29	61.3	1464

4.3.2 Product Characterization

The recovered waste product consisted of two different recovered P products derived from agricultural (RNP) and municipal wastewater (~100% struvite from Ostara). The RNP contained 12.57% P and a citric acid P percentage of 35.89%. The speciation of the RNP was 84.8% octacalcium phosphate (OCP) and 15.2% struvite (Figure 4-2).

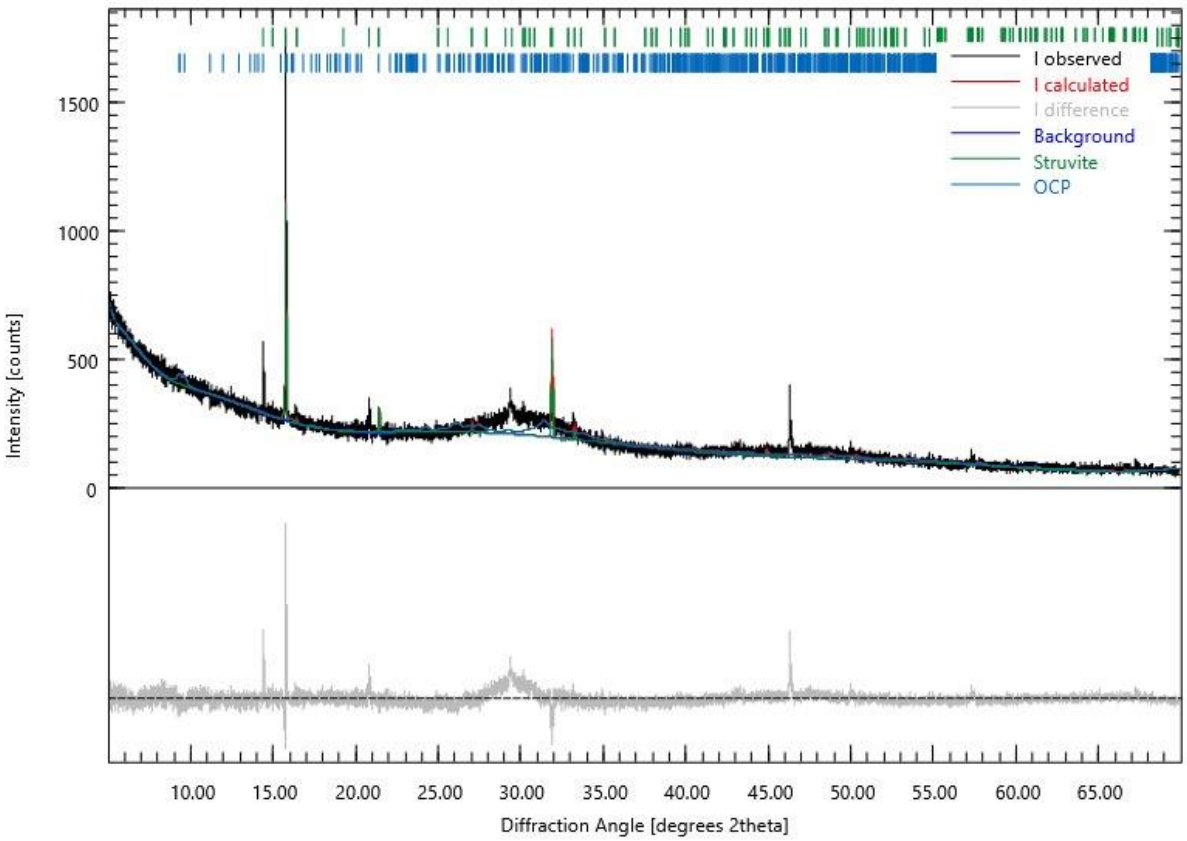


Figure 4-2: XRD characterization of the combined RNP product used for the greenhouse experiment.

4.3.3 Soil pH

Initial soil pH (1:5 soil:water) values were 8.07, 7.65 and 7.52, for mild, moderate and extreme soils, respectively. All soils underwent mild acidification under growing conditions, which is expected due to fertilization (especially N fertilizers) and watering. All soils had

starting pHs > 7.2, which could promote acidity due to H^+ dissociation from $H_2PO_4^-$ (Padhi et al., 2020; Weeks Jr and Hettiarachchi, 2020). Soil treated with APP fertilizer-treated soils had a significantly lower pH than all other treatments, as shown in Figure 4-3.

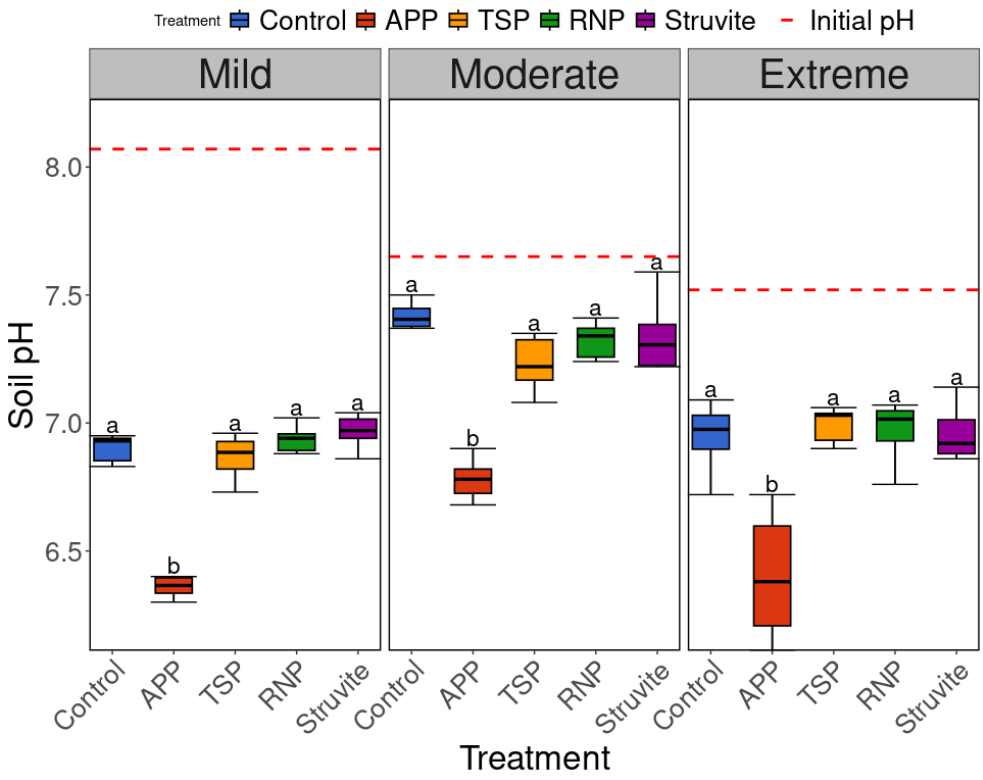


Figure 4-3: Final pH values of all treatments in differing soils. Dashed lines indicate initial soil pH values for mild (8.07), moderate (7.65), and extreme (7.52). Different letters indicate significance difference within the category at 0.1 probability level and similar letters indicate no significant differences within categories.

Polyphosphate is chemically different from TSP, as APP is a combination of orthophosphate and pyrophosphates (McBeath et al., 2008), whereas conventional fertilizers like TSP consist of solely orthophosphate. When APP hydrolyzes, NH_4^+ is released along with H^+ in the soil solution over an extended period, whereas a conventional fertilizer like TSP would quickly dissolve, rapidly decrease the pH and then stabilize after complete dissolution.

Ammonium ions in soil undergo nitrification, which contributes to acidity (Weeks Jr & Hettiarachchi, 2020).

4.3.4 Dry Biomass

In mild soil, for radishes, all treatments increased in dry biomass for the aboveground vegetation, while there was no significant treatment effect for root biomass (Figure 4-4b). Struvite provided a significant increase in aboveground biomass compared with the RNP in both moderate and extreme soil, and it also increased biomass compared with the control in the moderate soil. In the moderate soil, the radish root biomass showed that APP significantly reduced root biomass compared to other treatments. In the extreme soil, there was no significant difference in treatment type, likely due to the high Pb concentration in the soil, which kept P unavailable for plant uptake. Greater biomass was generated in the aboveground vegetation than in the below-ground biomass for radishes (Figure 4-4).

Lettuce biomass showed no treatment effect in mild and moderate soils (Figure 4-5). In the extreme soil, APP and TSP were outperformed by RNP in biomass. Although plants were grown under greenhouse conditions, they were grown in the summer months at higher temperatures, which led to bolting in the plants. This could have inhibited root growth in radishes and leaf growth in lettuce (Kaya, 2023; Pereira et al., 2024). Radishes grown in moderate and extreme soils exhibited chlorosis. The extreme soil had the most severe symptoms and the lowest amount of available Fe. Iron sulfate was added to the extreme soil radishes to correct any potential iron deficiency. However, leaf chlorosis and stunted growth continued. Phosphorus is known to reduce iron availability in soils and may have rendered this application ineffective (Lindsay, 1979). Despite being in a greenhouse, radishes were grown during the summer and the heat may have impacted their growth. These symptoms could also suggest Pb

poisoning as chlorosis, stunted growth, and shriveled leaves have been exhibited in past studies (Gopal & Rizvi, 2008; Khan & Frankland, 1983). However, this study used naturally contaminated urban soils, while corroborating studies added lead salts, or used artificial mediums. Lettuce did not show signs of chlorosis even in extreme soils, even with its longer growth period of 45 days. This suggests that radishes are more sensitive to excess Pb, or other soil conditions (Fe deficiency), as observed in the extreme soil. Although the extreme soil was included in the study for comparison, it is not advisable to grow crops in soils with extremely high soil Pb concentrations.

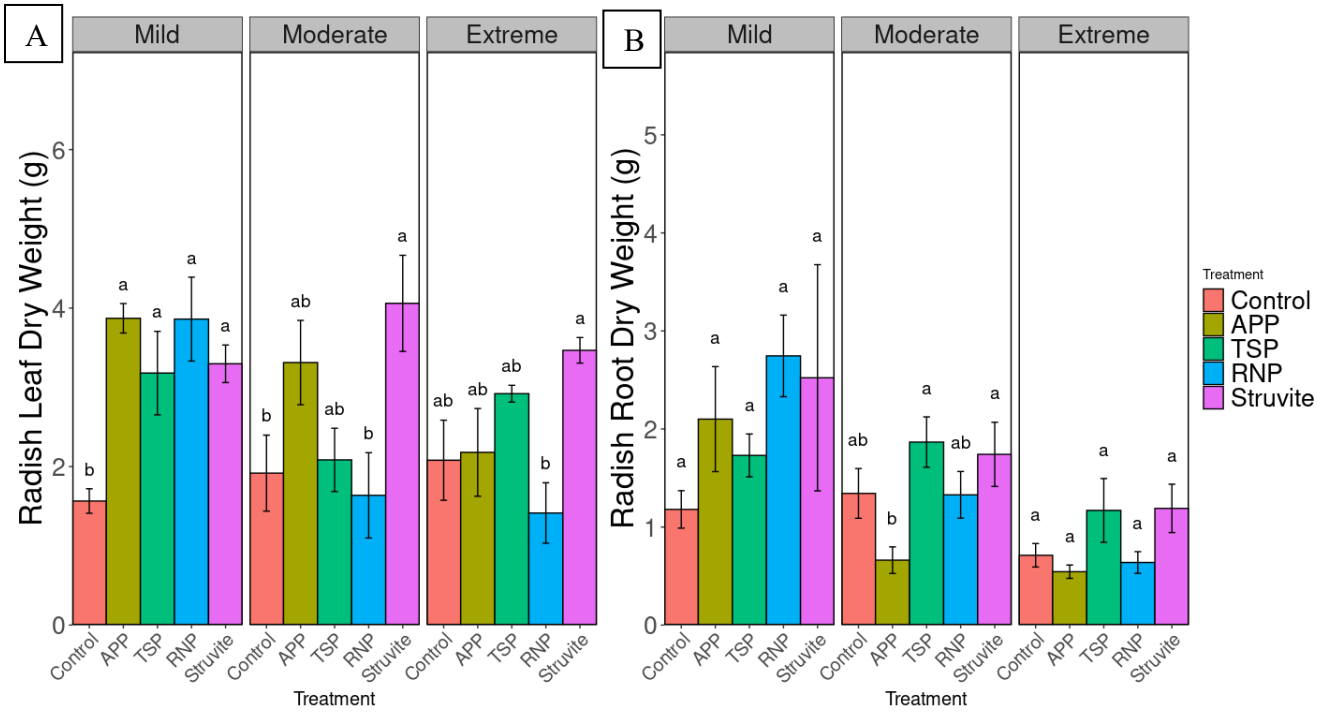


Figure 4-4: Dry radish root biomass (A) and dry radish leaf biomass (B). Different letters indicate significance difference within the category at 0.1 probability level and similar letters indicate no significant differences within categories.

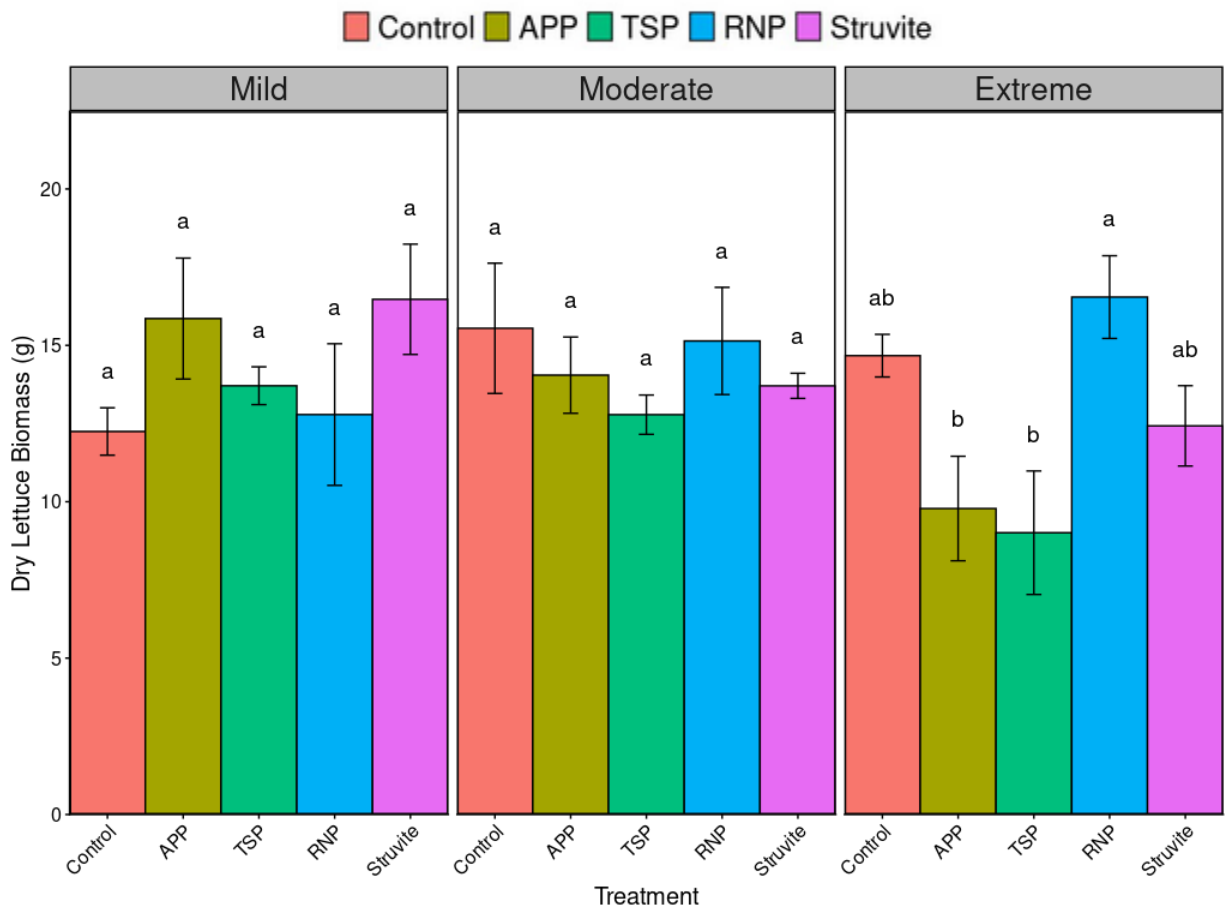


Figure 4-5: Dry lettuce biomass in soils. Different letters indicate significance difference within the category at 0.1 probability level, and similar letters indicate no significant differences within categories.

4.3.5 Lead Concentrations in plant tissues

In radish roots (Figure 4-6b), phosphorus fertilizer treatments showed significant reductions in Pb, with only TSP showing no significant decrease compared to the control in the low soil. In extreme soils, the RNP and struvite were the best performers in Pb reduction. In radish leaves (4-6a) there was less Pb in tissue (6.81 mg/kg dry weight basis), and treatments displayed most effectiveness in low soils, with no treatments reducing Pb in other soils. It is known that leafy portions of plants uptake less Pb, as most lead precipitates and reacts within the

root system and aboveground vegetation is more vulnerable to airborne dust and metals adhering to the surface of leaves (Attanayake et al., 2014).

Lettuce displayed similar results (Figure 4-7) to radish leaf concentrations, with treatments displaying less significance in soils. The APP fertilizer, in mild and moderate treatments displayed increased Pb levels in soils. This can be explained by APP's pH reduction seen in Figure 4-2 as acidification may have increased the availability of Pb^{2+} in solution (Hettiarachchi and Pierzynski, 2004; Lindsay, 1979).

Radishes exhibited damage in the form of chlorosis and shriveled leaves in moderate and extreme soils, likely due to Fe deficiency, whereas lettuce showed no toxicity effects. Radishes are more sensitive to micronutrient deficiencies than lettuce (Abdel, 2016; Adams et al., 1986).

Using FAO/WHO CODEX standards for vegetables, lead concentrations were compared with the maximum Pb levels (MLs for Pb) allowed for international trading. For leafy vegetables, it is 0.3 mg/kg of fresh weight, and for root crops, 0.1 mg/kg of fresh weight (JECFA., 1993, last modified in 2023). In this study, the MLs for Pb concentrations were calculated on the dry weight basis to be 5 mg/kg for leafy crops and 1.5 mg/kg for root crops. Note that these maximum limits do not factor in bioavailability assessments, just total Pb concentrations in vegetables, assuming 100% bioavailability (Attanayake et al., 2021). Lead concentrations in radish roots were below this maximum level (1.5 mg/kg) with struvite, RNP, and TSP treatments. For moderate to extreme soils, all radish roots exceeded these levels and would not be safe for consumption. Radish leaves in mild and moderate soils were all below the leafy maximum level (5 mg/kg), excluding the RNP in the moderate soil. None of the Pb concentrations in radish leaves were below in extreme soils. In mild lettuce samples, all treatments were below the maximum limit of 5 mg/kg, with APP the only one approaching the

maximum. Moderate lettuce samples in the control, TSP, and struvite were below these maximum levels. No lettuce grown in extreme soil was below the maximum limit. Lead concentrations were below this maximum level for radish roots (1.5 mg/kg) with struvite, RNP, and TSP treatments. For moderate to extreme soils, all radish roots exceeded these levels and would not be safe for consumption. Radish leaves in mild and moderate soils were all below the leafy maximum level (5 mg/kg), excluding the RNP in the moderate soil. For lettuce, all treatments were below the maximum limit (5 mg/kg) in mild soils, with APP the only one approaching the maximum. Moderate lettuce samples in the control, TSP, and struvite were below these maximum levels. No lettuce grown in extreme soils were below the maximum limit. None of the Pb concentrations in radish leaves were below in extreme soils. However, it should be noted here that Pb is found to be in the peel of root crops, and further peeling may potentially lower radishes to below FAO/WHO limits (Attanayake et al., 2021). Lettuce displayed greater concentrations in Pb, but the differing harvest times would allow lettuce more time to accumulate Pb in their tissue. When comparing the radish leaves to roots, there was a significant increase in Pb concentration in radish roots, which confirms past findings that root crops accumulate most Pb in their roots (Attanayake et al., 2014; McBride, 2013).

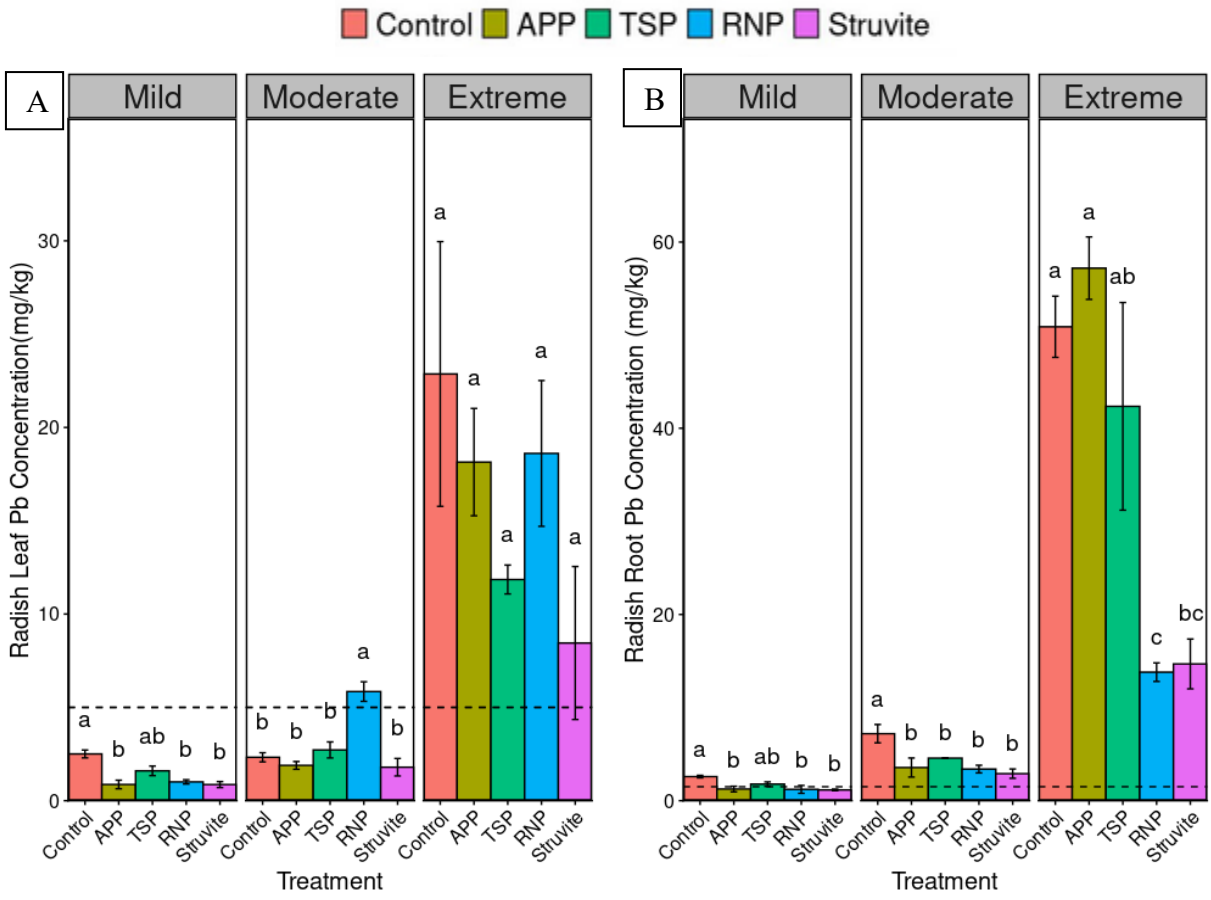


Figure 4-6: Lead concentrations in radish leaves (A) and roots (B). The dashed line represents calculated FAO/WHO maximum Pb level limits, 5 mg/kg for A and 1.5 mg/kg for B. Different letters indicate significance difference within the category at 0.1 probability.

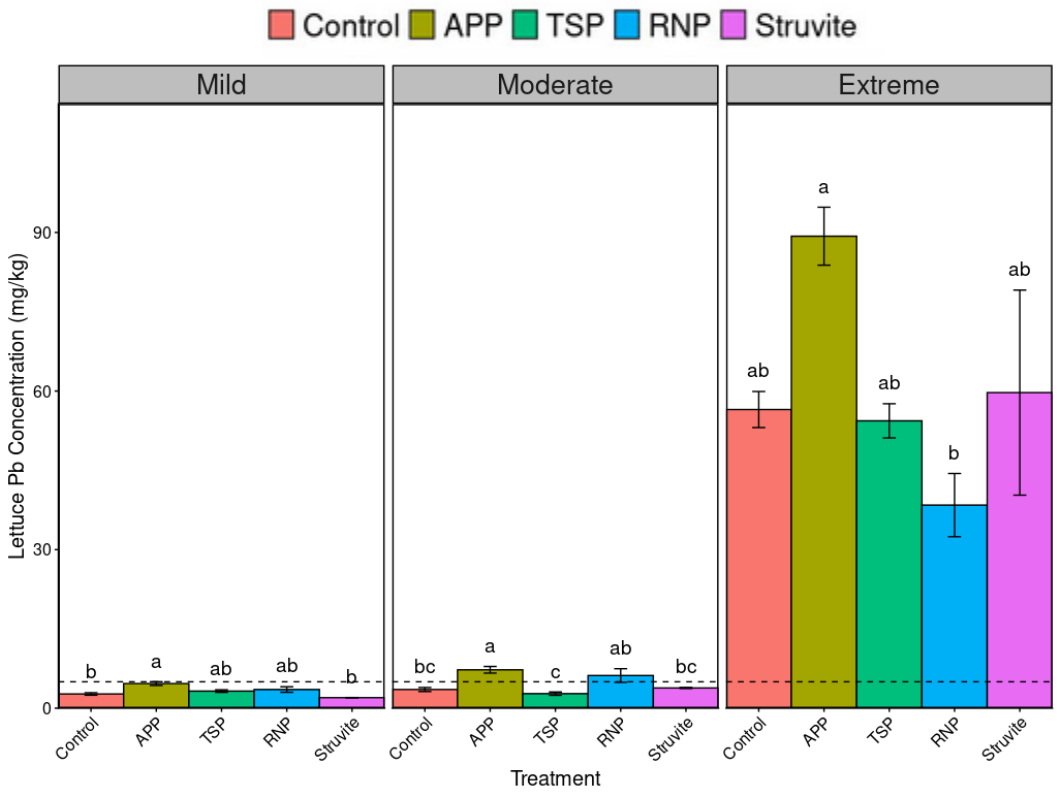


Figure 4-7: Lead concentrations in lettuce. The dashed line represents FAO/WHO calculated maximum limit of 5 mg/kg of Pb. Different letters indicate significance difference within the category at 0.1 probability level and similar letters indicate no significant difference.

4.3.6 Lead uptake by plants

Lettuce plants displayed higher values of Pb uptake in comparison to radishes. This could be due to differences in harvest dates, as the longer a plant grows, the longer its exposure time to contaminants. Bioconcentration factors (BCFs), seen in Figure 4-8, were considerably higher than radish portions, from highest to lowest: Lettuce> Radish Roots > Radish Leaves. Both plant species exhibited significantly smaller bioconcentration factors (<1) which indicate they are Pb excluders (Collin et al., 2022). The harvest dates may have impacted BCFs due to the longer harvest period of lettuce. However, lettuce produced more biomass, which should dilute the Pb

concentrations within the plant (Attanayake et al., 2014; Brown et al., 2016). Instead, it achieved a higher BCF and Pb concentration than either portion of the radish.

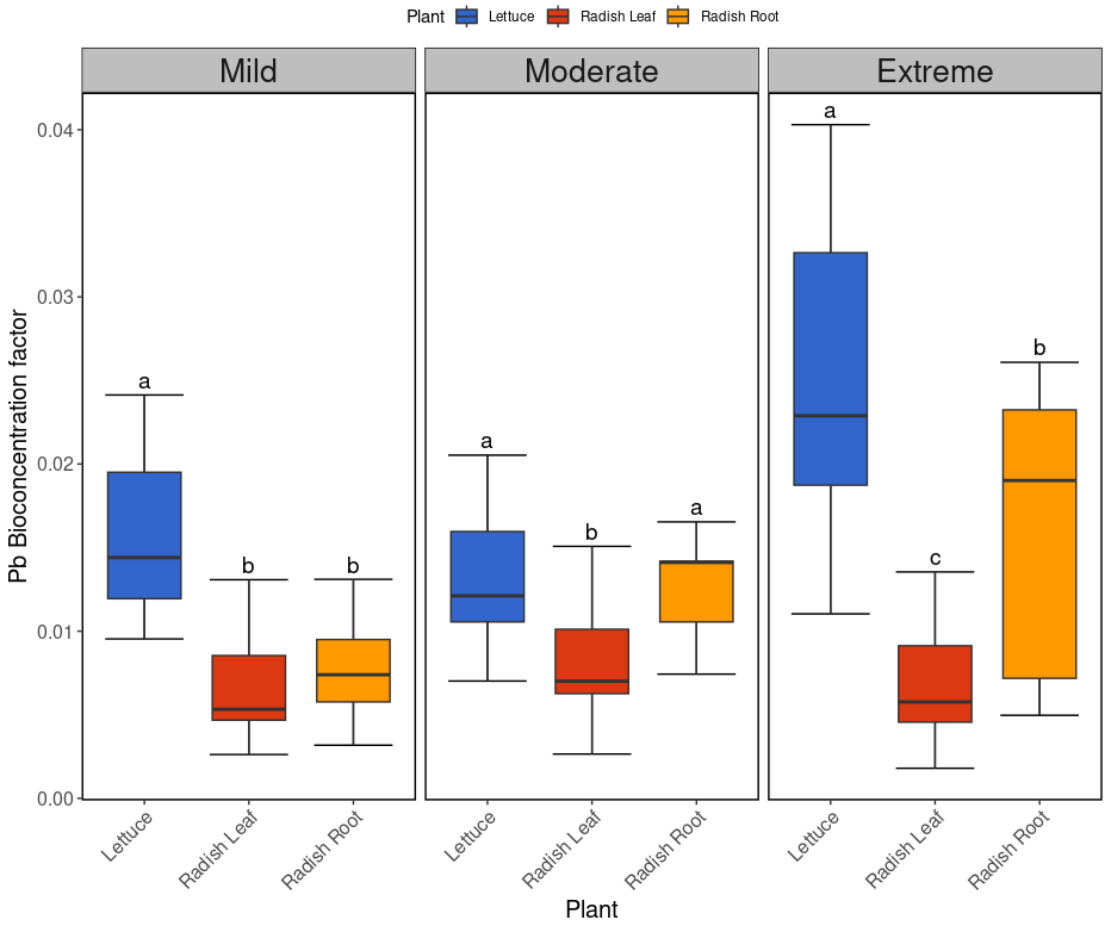


Figure 4-8: Bioconcentration of Pb in aboveground lettuce, radish leaf, and radish roots. Different letters indicate Tukey test significance difference within the category at 0.1 probability level and similar letters indicate no significant differences within categories.

4.3.7 Plant Phosphorus

No treatment effects were found for aboveground radishes (Figure 4-9a) and lettuce vegetation in mild soils (Figure 4-10). For radish roots in mild soils, struvite showed a significant increase in P concentrations in comparison to the control. Phosphorus concentrations were significantly higher in lettuce with APP treatments in comparison to the control and RNP. While radish aboveground vegetation showed a significant increase in P concentration for RNP in comparison to the treatment. Radish roots showed no treatment effect in moderate soils. No treatment effects were seen in the extreme soils for all plants. Initial available P was considered excessive, with all soils containing >100 mg/kg of Mehlich-3 P. This excess P could mask the treatment effectiveness of the different P products.

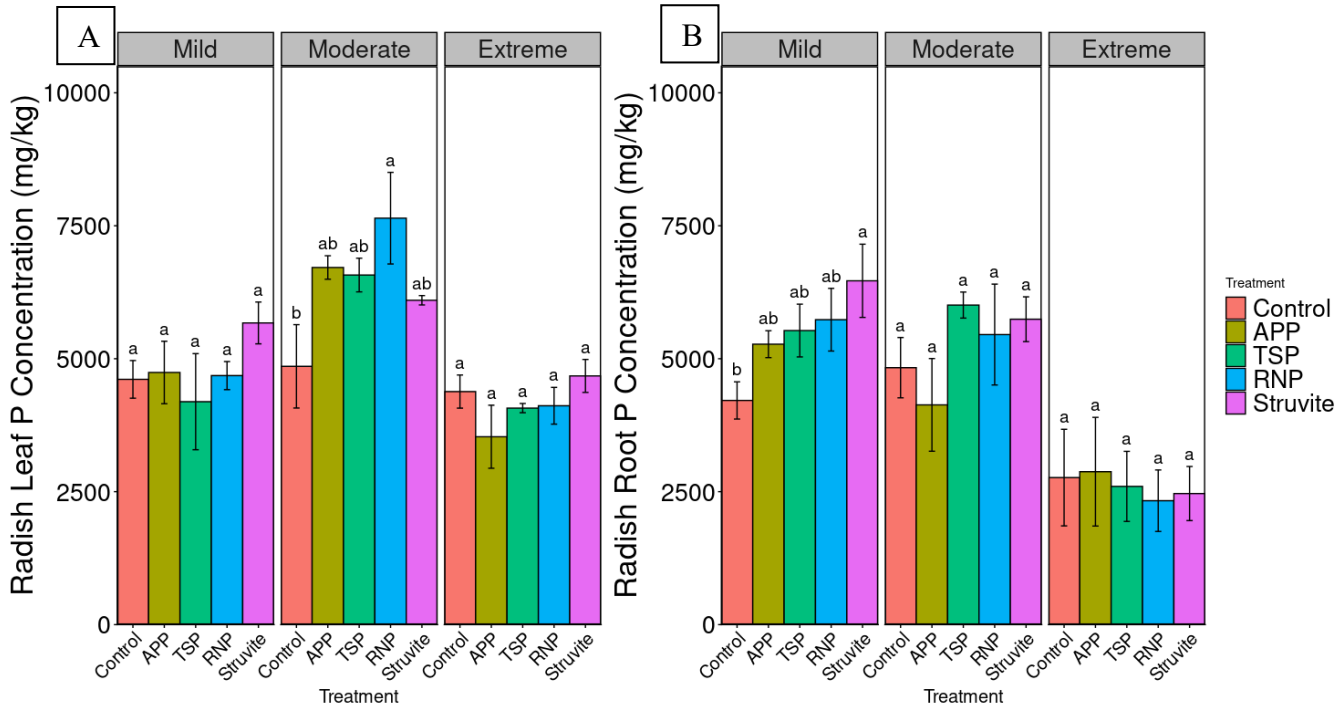


Figure 4-9: Phosphorus concentrations within the Radish Leaf (A) and Radish Root (B). Different letters indicate Tukey test significance difference within the category at 0.1 probability level and similar letters indicate no significant differences within categories.

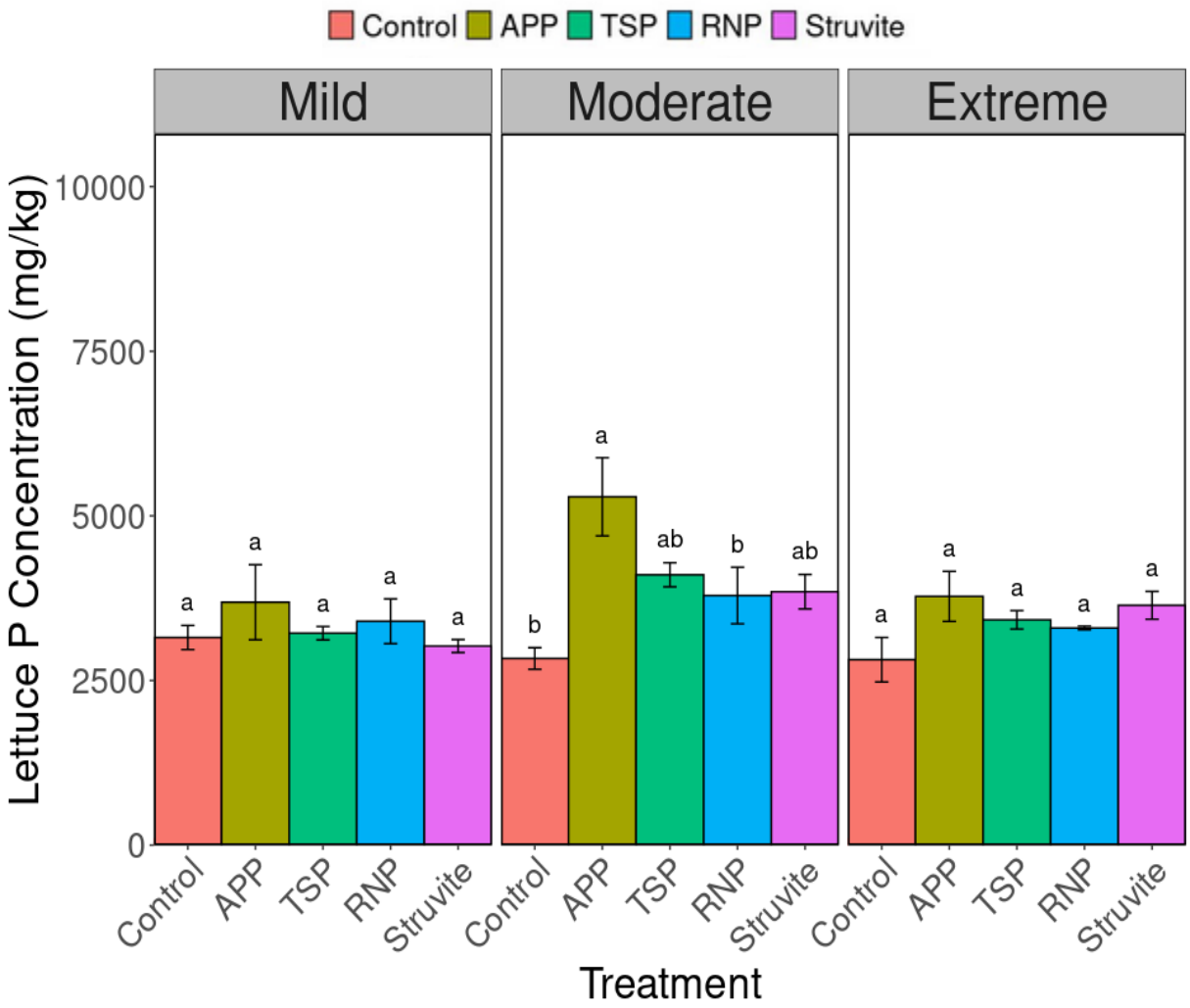


Figure 4-10: Lettuce P concentrations. Different letters indicate Tukey test significance difference within the category at 0.1 probability level and similar letters indicate no significant differences within categories.

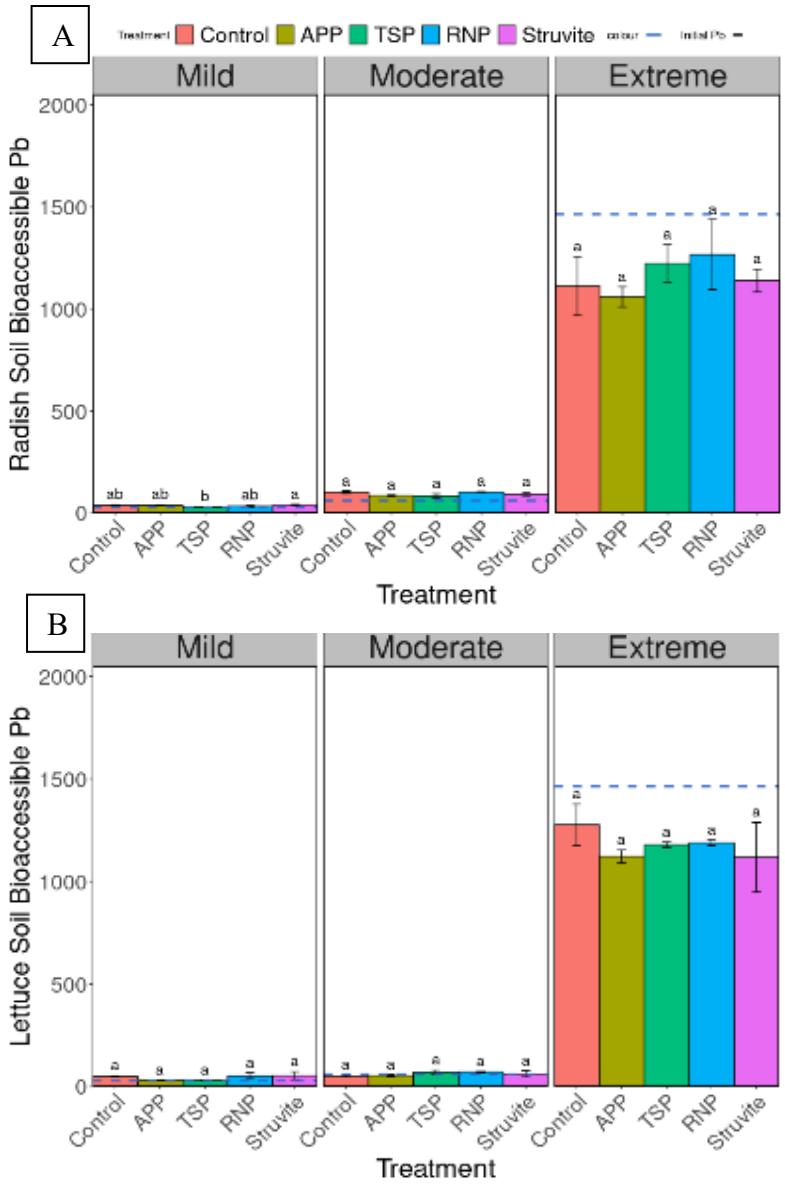


Figure 4-11: Comparison of bioaccessible Pb concentrations in radish (A) and lettuce (B) soils. Dashed lines represent initially measured Pb bioaccessible levels in soil. Initial bioaccessible Pb: mild (29 mg/kg), moderate (61.33 mg/kg), extreme (1464 mg/kg) Different letters indicate Tukey test significance difference within the category at 0.1 probability level and similar letters indicate no significant differences within categories.

4.3.4 Bioaccessible Pb

No treatment effect was found in all plant soils (Figure 4-11). Phosphorus treatments were applied for plant growth, not specifically for remediation effects. For Pb immobilization, P application rates should be calculated based on the amount of P necessary for pyromorphite formation, using the total Pb concentration in soil. Plant root exudates and acidification from soluble P fertilizers (TSP and APP) may have remobilized Pb into solutions, negating potential remediation effects on bioaccessible Pb.

4.3.5 Lettuce Isotope Values

Moderate soils exhibited separate clustering that was significantly higher in ratio values compared to low and extreme treatment lettuce isotope ratios (Figure 4-12). This suggests that concentration does not influence the isotopic ratio, and that the low and high could share a source, or sources. For $^{206/207}$Pb ratios, there was no significant difference between soil pre-treatment (PRE) ratios to different treatments. Phosphorus treatments in the moderate soils shared plant $^{206/207}$Pb ratios with PRE, while the control (CTL) was significantly lower. All phosphorus treatments in the moderate soil were significantly different than the CTL isotopic ratios. In extreme soils, all treatments except struvite showed significant differences with PRE isotopic values. All significant soil treatments in soils had lower $^{206/207}$Pb values. The treatment influence on plant isotopic ratios could be affected by the concentration of Pb metals in soil, as treatment isotopic variations were most significant in the order of extreme > moderate > low soils. The CTL plants in moderate and extreme soils deviated most from the PRE samples. In the extreme soil, APP showed significant deviation from PRE samples as well. The pre-treatment soils may have differed in isotopic composition due to disturbance, and once these soils underwent natural attenuation, their isotopes adjusted as the soil environment reaches a new

equilibrium during development. The plant isotopic ratios of the CTL may be reflective of the available Pb fraction in the soil, not the total Pb, and plants are known to reflect the soil isotopic composition (Marguí et al., 2006).

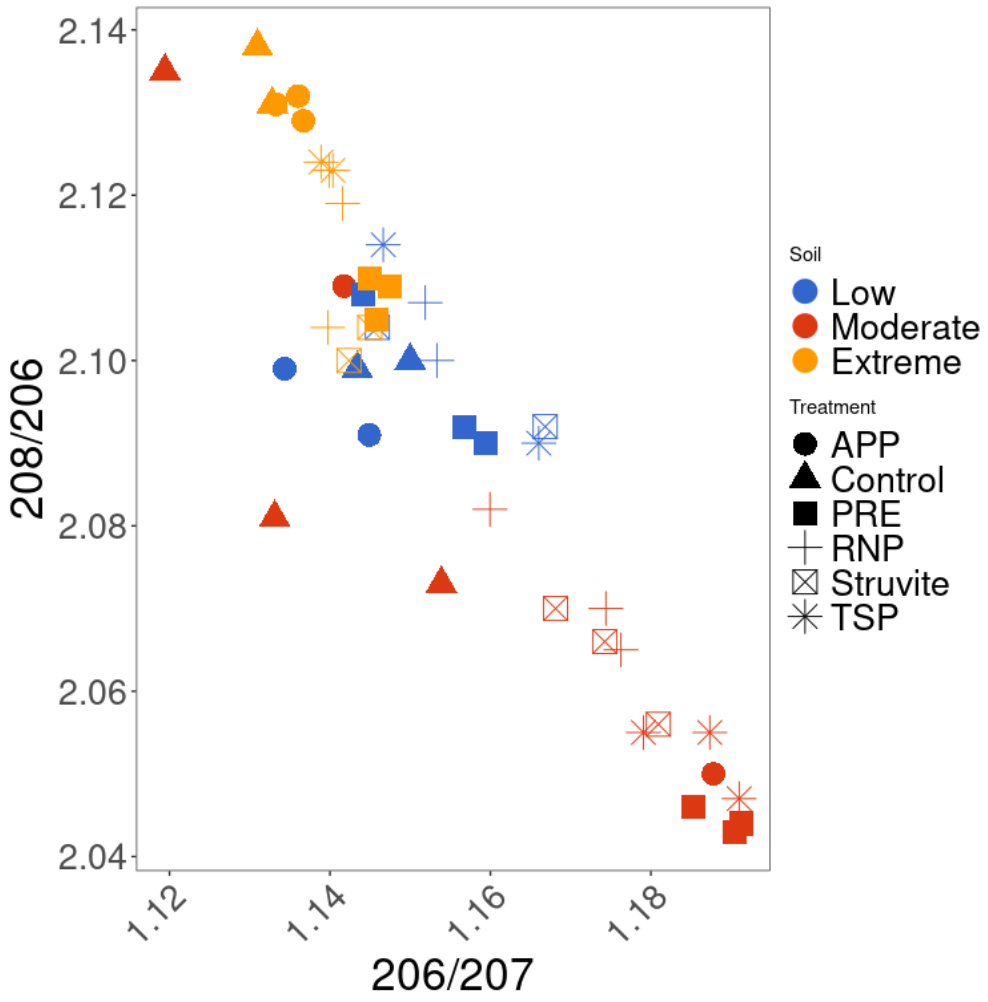


Figure 4-12: $^{206/207}$Pb ratio values versus $^{208/206}$Pb values of harvested lettuce plant matter with different treatments compared to pre-treatment soil (PRE).

4.4 Conclusions

This study investigated the potential agronomic utility of wastewater RNPs as alternative P fertilizer sources and their potential for soil remediation by observing plant biomass, P uptake, Pb concentration in two selected vegetable types: a leafy vegetable and a root crop. An exploratory investigation into Pb isotope ranges between plants and soils. Results indicated that the wastewater-derived nutrient products, RNP and struvite, outperformed traditional P fertilizers in reducing Pb uptake in plants. Ammonium polyphosphate displayed increased Pb uptake in plants due to acidification. Biomass showed treatment effects in mild soils, but initial soil excess P may have masked treatment effect due to increased P uptake. Despite excess P in soils, RNP and struvite showed significant increases in P uptake compared to the control. Leafy portions of radishes accumulated less Pb than their roots and displayed chlorosis and stunted growth in moderate and extreme soils compared to lettuce. For lettuce Pb isotope ratios, plants showed a deviation from the initial Pb soil isotopic ratios, and control plants had the greatest deviation from initial soil Pb isotopic ratios. The control plants potentially display Pb ratios similar to the current ratios of plant available Pb in the soil due to natural attenuation as the soil ages.

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Chapter- 5 Summary and Conclusions

As of the current writing, there have been no studies performed in the KC area for identification of Pb sources in the area. The Chapter 3 study aimed to achieve 2 goals; provide novel data of the isotopic fingerprints of soil from KC urban core and to identify contamination sources based on previous sources. Novel samples were collected from the Konza and KC sites and successfully acquired these isotopic ratios. These Pb isotope ratios showed KC sites overlapped with sources of leaded gasoline, lead paint, and mining spoil. Lead gas and paint did not fully explain the contamination, with KC sites showing $^{206/204}$Pb values resembling those of ores. More samples nearby former industrial areas need to be collected for contributor confirmation. These findings can help aid future studies as a reference for soil Pb isotopic values in the Midwest.

In Chapter 4, the main goals were to assess the effectiveness of the RNP as a fertilizer, and to assess its usage as a P source for remediation of soil Pb contamination. Utilizing RNPs is crucial for improving resiliency and assisting in creating a circular economy in urban food systems. The RNP showed effectiveness in increasing radish leaf biomass with other P treatments. However, in most soils, the treatment effect was concealed due to the excess P already present in soils. Soils with low available P would be beneficial for testing their full effectiveness. The RNP showed promising results as a remediation tool, with significant Pb reductions in radish roots and struvite showing similar reductions. The leafy portions of the radish and lettuce had less treatment response as most Pb uptake would be limited to the roots. The bioaccessible Pb showed no treatment effects as these P applications were applied for fertilizer applications (i.e., agronomic rate) and analyzed bioaccessability to see if P treatments could simultaneously immobilize Pb and fertilize plants. Acidification from APP could

potentially increase uptake of Pb into plants and was the most acidifying fertilizer. The success of the RNP and struvite as a fertilizer should be further explored in soils without excess P to eliminate any masking effects of initial P, however urban areas tend to accumulate higher levels of P. The length of time these wastewater derivates supply P to plants could be explored along with its potential losses in comparison to conventional fertilizers.

Plant isotopic ratios showed unique clustering, with the moderate soil having significantly different ratios than low and extreme soils. This difference indicates that source contributions differ between the soils and reveals the heterogeneity of an urban soil system. Plant ratios drifted from the initial isotopic signature of the disturbed soil, while plants grown in untreated control soil closely resemble the isotope ratios of soils, which could indicate the soil reverting to its undisturbed isotopic ratio through natural attenuation.