Soil Amendments to Decrease Lead and Arsenic Bioaccessibility in Delray, Detroit, MI

by

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Abstract

The Delray neighborhood of Southwest Detroit has a long history of environmental pollution. A section of the neighborhood, located adjacent to a brownfield site, was previously identified for elevated concentrations of soil lead (Pb) and arsenic (As) by researchers at the University of Michigan-Dearborn (Peterman, 2013). In this study, soil samples were collected from three decision units using the Incremental Sampling Methodology (ISM). Samples were treated at 5 and 10% by weight with three different amendments: triple superphosphate (TSP), phosphate rock (PR), and zeolite (ZE). After an incubation period of 48 days, the samples were then processed, underwent bioaccessibility (BA) digestion, and analyzed by ICP-MS for Pb and As. Statistical analysis using a paired t-test showed a very significant decrease in soil Pb BA for both addition rates of PR, and a significant decrease with TSP and ZE. The impact of the amendments on soil As BA was inconclusive. Based on this study, PR shows potential as an efficient and affordable means to remediate the soil Pb contamination in Delray. This finding may also be applicable for other postindustrial cities with similar soil type and contamination profiles.

Chapter I - Introduction

Soil contamination is a longstanding problem in Southwest Detroit, Michigan. This is due in large part to the high concentration of industrial activities in that region, and the associated environmental contamination that has been accumulating in the soil since the late nineteenth century. Many abandoned properties are now brownfield sites, which are defined by the EPA as land on which redevelopment or reuse is complicated due to known or suspected contamination (EPA, 2006). Lead (Pb) and arsenic (As) pollution are especially problematic because they are persistent in the environment. In the Southwest Detroit neighborhood of Delray (Figure 1), a residential area nearly surrounded by industrial facilities, continually increasing levels of Pb and As in the soil have posed an exposure problem for its residents. Of particular concern is exposure for children, who inadvertently ingest contaminants in the soil through hand-to-mouth contact while playing outside (Yang & Cattle, 2015). The neighborhood, currently adjacent to a wastewater treatment facility, an interstate highway, and a number of other industrial facilities, was the subject of a recent soil Pb study completed by the University of Michigan-Dearborn, which drew a connection between soil Pb data and elevated blood Pb levels in children (Peterman, 2013).

Lead occurs naturally in the soil. According to a background soil survey completed by the Michigan Department of Environmental Quality (MDEQ) in 2015, the naturally occurring level of Pb for topsoil in the Huron-Erie Glacial Lobe, which is where Detroit is located, is 11.6 ppm (MDEQ, 2015). The risk-based screening level, or RBSL, in Michigan is currently 400 ppm for direct contact criteria (MDEQ, 2013). However, a proposed state rule for the cleanup criteria requirements will reduce the RBSL to 190 ppm in 2019 (MDEQ, 2017). The area of study in Delray had a mean concentration of 243.1 ppm – a level which is toxic per the proposed rule. The data indicated a hotspot of Pb contamination along Melville Street, which is adjacent to a suspected brownfield site and is the focus of this study (delineated in red in Figure 1). Here, the Pb contamination greatly exceeded the current RBSL in some samples, threatening the health of local residents.

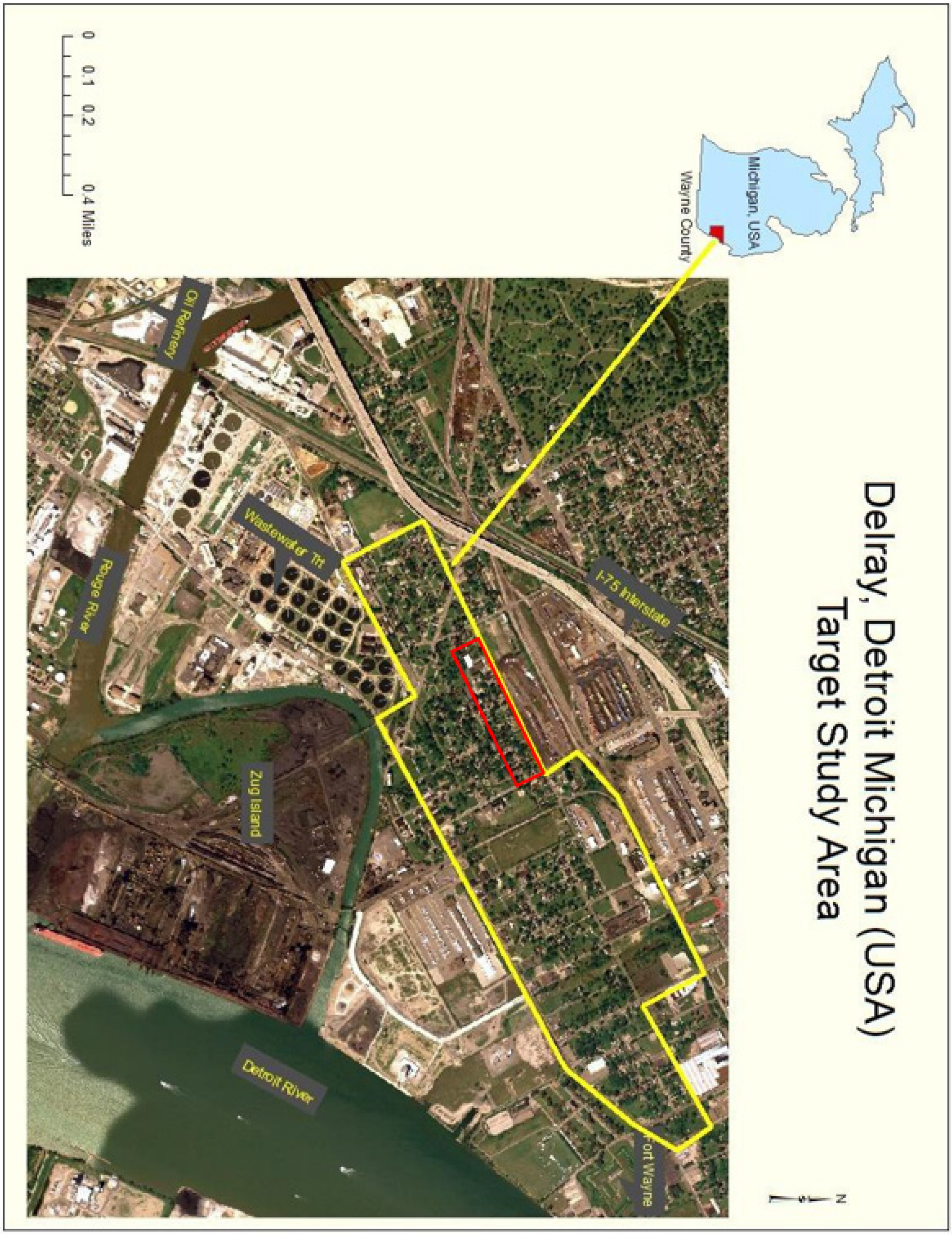

Figure 1. Delray, Detroit Michigan (USA) Map.

According to the Centers for Disease Control and Prevention (CDC), there is no safe level of Pb exposure for children – even low levels have a negative impact on mental development, and the damage is irreversible (CDC, 2012). Inorganic Pb is also classified as a Group 2A probable carcinogen to humans (IARC, 2018). However, the established reference level for elevated blood Pb is 5 ug/dL, which was decreased from 10 ug/dL in 2012 (CDC, 2012). This reference value is the same for adults, who also experience health effects including renal, cardiovascular, reproductive, and cognitive issues with blood lead levels (BLLs) exceeding 5 ug/dL (CDC, 2017). The National Institute for Occupational Safety and Health (NIOSH) program called ABLES (Adult Blood Lead Epidemiology and Surveillance) is a federally funded program to monitor and reduce adult BLLs in the US; the twenty-eight participating states have programs to report BLLs to ABLES in order to monitor trends and address elevated BLLs where they occur (CDC, 2017).

Similarly, soil As contamination is also a long-term problem in Southwest Detroit. Also naturally occurring in soil, the background level of As in topsoil in the Huron-Erie Glacial Lobe is 5.7 ppm (MDEQ, 2015), and the direct contact RBSL for As is 7.6 ppm in the state of Michigan (MDEQ, 2013). Researchers at the University of Michigan-Dearborn collected and analyzed over 350 soil samples from throughout the Delray neighborhood in order to ascertain levels of both Pb and As (Peterman, 2013). The study found an average As soil contamination level of over 12 ppm. On Melville Street and South Street, which were the locations of the highest soil Pb concentration, the average soil As level was 13 ppm.

Exposure to As contaminated soil occurs via the same mechanism as Pb – typically hand to mouth contact of children playing outdoors. To further exacerbate exposure, human gut biota can also increase the BA of As (Yin et al., 2015). Exposure to arsenic, a Group 1 carcinogen, can cause long term health effects such as multiple types of cancer, including kidney, bladder, skin, liver, and lung cancer (IARC, 2018, ATSDR, 2015).

1.1 History of Delray

The Delray neighborhood has changed greatly throughout Detroit's history. Originally named Belgrade, the village was the home of eastern European immigrants, many of whom became employed by the industries which took root there, such as glue and chemical companies. The village was stimulated and thriving during the peak of Detroit industry in the first half of the twentieth century. Most residents worked in the surrounding industries and there was no lack of local businesses supporting the residents there. Its location on the Detroit River also made it a prime center for transportation. However, with the decline of the auto industry and the changes caused by World War II, many factories closed and the Delray population was declining dramatically by the 1950s. When interstate I-75 was built in the 1970s, the neighborhood suffered even further decline since it was then physically separated from the city of Detroit. Delray is bordered by Zug Island, which houses several steel mills and a major wastewater treatment plant, and the Ambassador bridge to Canada, which is a major route for trucks. To further complicate the issues in Delray, a new bridge to Canada is in the planning stages, and the bridge will run right through the eastern edge of Delray. The bridge will require many residents to move, and those that are not bought out or participating in the Bridging Neighborhoods Program, which includes a Home Swap program to different Detroit neighborhoods, will be forced to live with the presence of the bridge. While Delray is pushing for a community benefits package to help mitigate the negative impact brought by the bridge, the community has long been neglected and the low socioeconomic status and racial minorities, as well as its small population, estimated at about 2000 residents, put their voice at even more of a disadvantage.

1.2 Sources of Lead and Arsenic in Delray

Lead pollution arises from a number of sources, both historical and current, in Southwest Detroit. One of the major local sources is from historic lead smelter sites. In the mid-twentieth century, it is thought that lead smelters were in operation in ten different locations throughout the city (Figure 2). These facilities likely contributed Pb to the soils and, with the effects of seasonal wind patterns, the contamination became airborne and moved throughout the atmosphere to settle in nearby locations, including Delray (Laidlaw *et al*., 2005).

The locations of these smelter sites correspond to elevated BLLs in children under the age of six, according to a 2009 study by the Michigan Department of Community Health (Figure 3). The area indicated by the oval in Figure 3 shows the location of the present study, and Figure 4 shows the areas of elevated soil Pb concentration identified in previous work by the University of Michigan-Dearborn (Peterman, 2013). Another historical source of Pb nationwide was the use of leaded gasoline until it was banned in the United States in the 1980s. Air pollution from the combustion of leaded gas in automobiles contributed to soil contamination in Delray, which is located right next to an interstate highway—a major commercial route and international border crossing to Canada. Delray's proximity to the highway made it the recipient of atmospheric Pb, which eventually settled into the soil and persisted for many years there (Peterman, 2013). Another ongoing source is lead-based paint, which was popular for painting both the interior and exterior of homes and other buildings in the early twentieth century. In Delray, most of the homes are of older construction; over time, the homes have been worn down and the paint eroded from their surfaces, wearing off and ultimately settling as dust in the soil. This has caused elevated soil Pb concentrations, particularly at the dripline of the homes where the eroded paint typically falls. In recent years, a number of older homes have been demolished; when demolition work is not done properly, the process can generate leaded dust which then settles into the nearby soil; the airborne fugitive dust contains lead which can also work its way into homes, settling on floors and windows (Shihadeh, 2013). Finally, emissions from industrial facilities, both past (brownfield sites) and present, have contributed to and are continuing to contribute Pb to the soil.

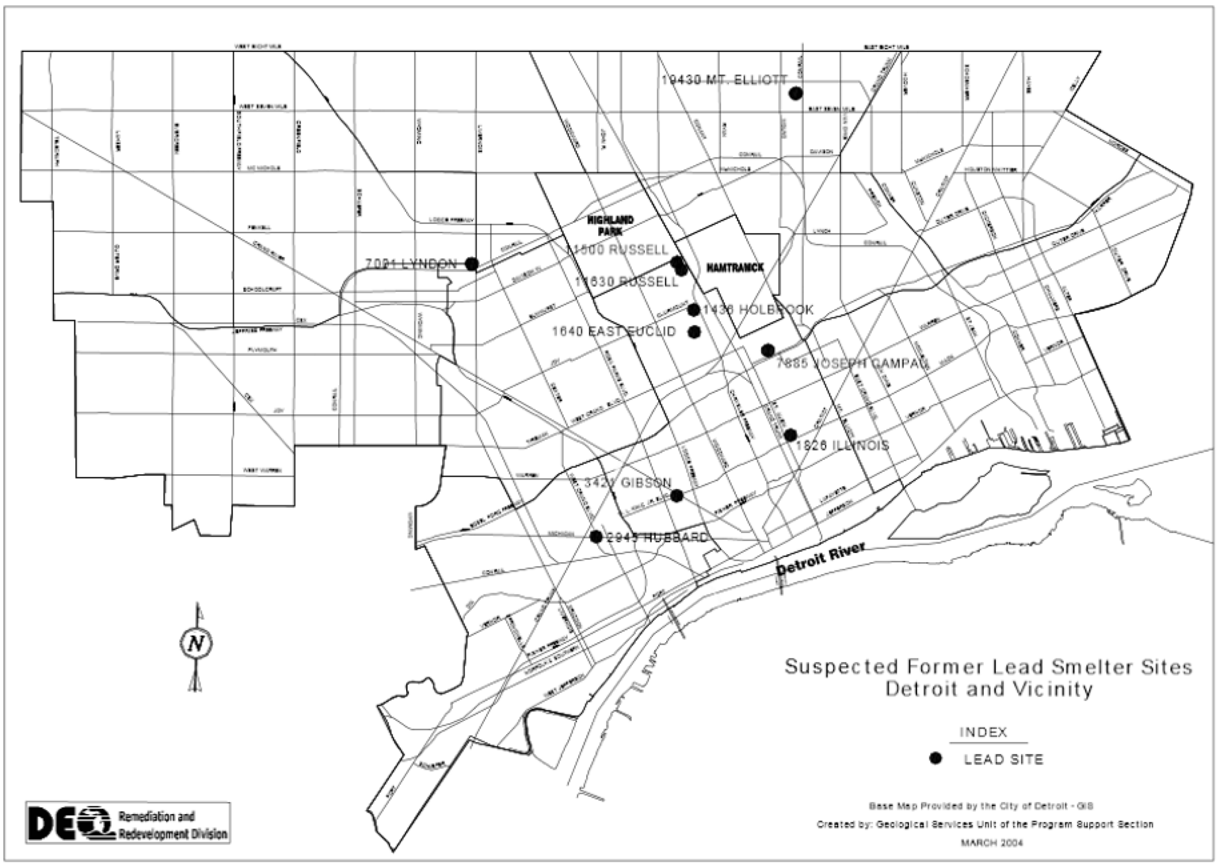

Figure 2. Suspected Former Lead Smelter Sites – Detroit and Vicinity (MDEQ, 2004).

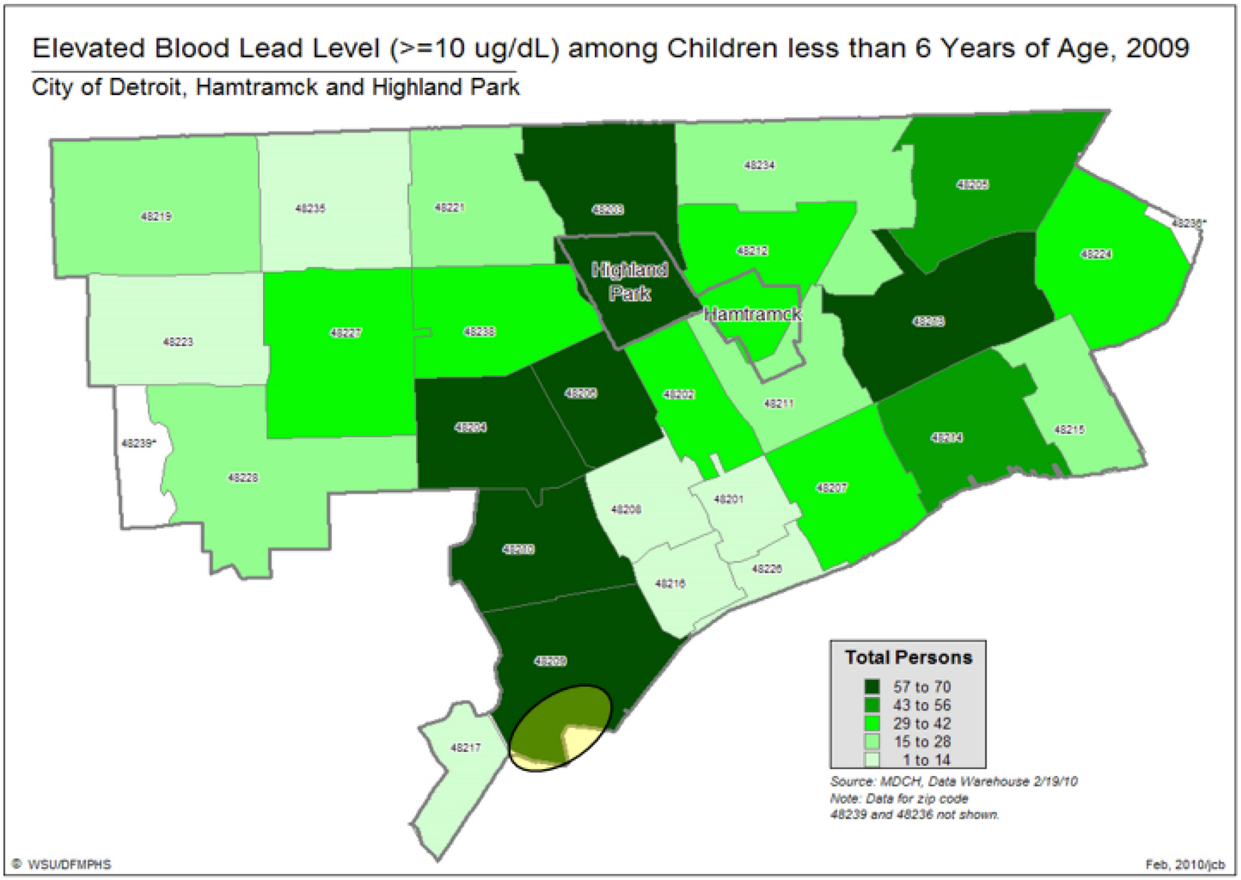

Figure 3. Total number of Pb-poisoned children in the city of Detroit by zip code for 2009. Data supplied by Michigan Department of Community Health. Dark green zip codes have highest number of children. The ellipse represents the approximate area covered in this study.

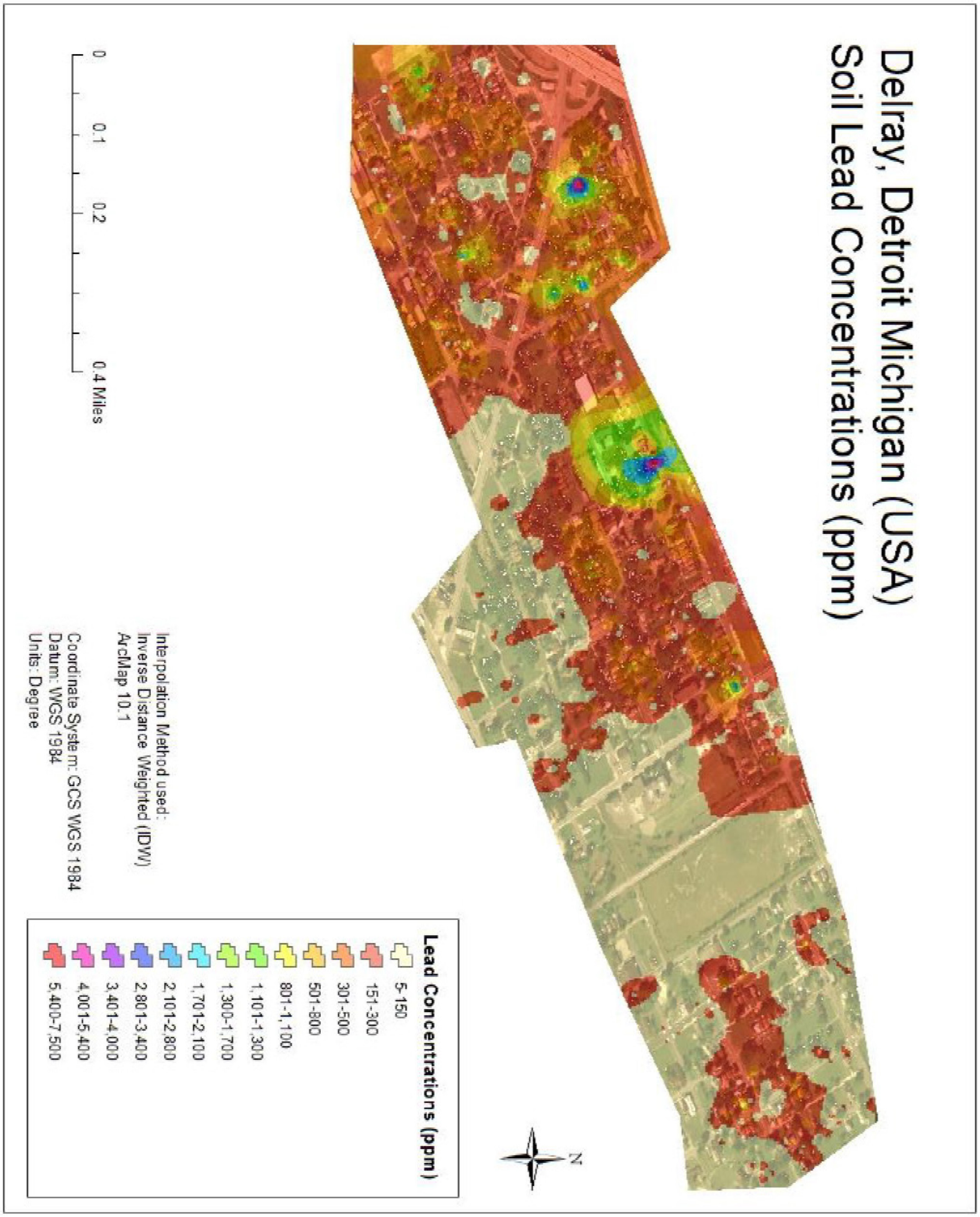

Figure 4. Delray, Detroit Michigan (USA) Soil Lead Concentrations (ppm) (Peterman, 2013).

Arsenic pollution arises from burning of fossil fuels, such as coal, as well as from some industries that have been present in Detroit, such as metal smelting and coal-fired steel manufacturing (Peterman, 2013). Heavy use of coal combustion as fuel for industry in Detroit is a suspected cause of the high soil As levels in Delray, which has concentrations ten times higher compared to other parts of southeast Michigan (Kaufman, *et al*., 2011).

1.3 Soil Amendments to Decrease Pb Bioaccessibility

Since an area of elevated soil Pb has been established by research in Delray, the purpose of this study is to identify a practical solution to reduce Pb levels to below the RBSL. A wide variety of remediation methods have been effective in lowering soil Pb to safe levels, including soil washing, asphalt or soil capping, and offsite solidification/stabilization (Maenpaa *et al.*, 2000). Most of these methods are prohibitively expensive when attempting to remediate a large residential area and therefore not likely feasible for application in Delray without dedicated agency funding. There is an increasing body of research, however, studying the use of soil amendments for remediating environmental pollutants, including Pb and As (Li, *et al*., 2017). A number of amendments, including organic and inorganic materials, have been studied for their ability to immobilize or counteract heavy metals in soil, including Pb. Some of the organic options have been compost, biosolids, manure, and sawdust, while inorganic options include phosphate compounds, fly ash, and lime, among others (Scheckel *et al*, 2016). The mechanisms for this process involve the amendments binding to the Pb and thereby reducing its bioaccessibility (BA), which is the ability of a contaminant to be absorbed into the bloodstream through digestion. Historically, the effect of human exposure to soil Pb was studied through bioavailability, which uses *in vivo* methods to evaluate the impact. However, this method, which involves exposing live animals (typically swine) to Pb via ingestion followed by analysis of their blood Pb levels, is both time consuming and expensive. In 1996, Ruby, *et al*. developed a physiologically based extraction test (PBET) to determine bioavailability of both Pb and As (Ruby, *et al.*, 1996). Since then, a number of other studies have shown that using *in vitro* studies to measure BA has been an accurate indicator of bioavailability, and at a much lower cost than *in vivo* studies (Li, *et al.*, 2015, Drexler & Brattin, 2007).

Soil texture and characteristics play an important role in Pb BA. Lead is most bioaccessible when it is water soluble and exchangeable, but BA decreases for Pb that is bound to iron, manganese and other compounds in the organic soil fraction that have a high molecular weight (Howard et al., 2013). Therefore, BA Pb is usually lower in soils with a higher percentage of organic matter (Saminathan, *et al.*, 2010). Soil Pb BA also increases in highly acidic soils (Saminathan, *et al.*, 2010). Furthermore, soils with high silt and clay content are more likely to bind with heavy metals, such as Pb, due to higher cation exchange capacity, or CEC, as compared to sandy soils. The soil characteristics in the Delray area typically are silty loam or siltey clayey loam, with pH >5 and organic content >5%; these factors make it susceptible to retaining Pb (Peterman, 2013). However, if the soil Pb is further bound to an amendment, its BA to humans can potentially be reduced.

Phosphate amendments have received the most attention and success in decreasing BA Pb in soil. Among the many varieties available, triple superphosphate, phosphate rock, and $NaH_2(PO_4)^3$ have been especially effective at reducing Pb BA (Bosso, *et al.,* 2008). In a number of studies, phosphate rock and triple superphosphate show consistently promising results (Somnez and Pierzyski, 2005, and Hettiarachchi, et al., 2000, Bosso et al., 2008, Weber *et al*., 2015). Zeolites, which are also naturally occurring mineral compounds, are another amendment which has been successful in immobilizing Pb, specifically by controlling the soil properties, such as pH and soil organic matter (Li *et al*., 2009). The mechanism by which zeolite interacts with metals was studied by Edwards, et al. (1999) yet there is some variation in chemical makeup between various sources of the naturally occurring material. While phosphate amendments have been shown to be more effective than zeolites in immobilizing Pb (Li *et al.*, 2016), these three materials are the selected amendments for this study. Some studies have shown that the application of phosphate amendments can cause an increase in As mobility and, to a lesser extent, bioavailability, in soil contaminated with both Pb and As (Kilgour et al., 2008). This study focuses on the use of amendments that have been shown to decrease soil Pb BA, and also evaluates what, if any, impact the amendments have on soil As BA.

Because the phosphate amendment approach essentially adds fertilizer to the soil, there is concern that runoff or leaching of the amendment material into the ecosystem may cause eutrophication. Limited research has been dedicated to this topic, but one study by Weber, *et. al* (2015) investigated the effect of addition rate, rainfall, and vegetation cover post-application. The study found that the ratio of amendment to contaminant should be as low as possible, within a range of significant reduction of soluble contaminant concentration. For this reason, it is advisable to include multiple addition rates of each amendment for study purposes, and then select the lowest rate that will adequately reduce contaminant concentration without causing other adverse environmental impacts.

Naturally, amendment runoff is highest right after application. For this reason, timing is important for planning the amendment application; if the amendment is added right before a heavy rainfall, it increases the amount of phosphorus that will runoff and affect water quality. Similarly, amendment application should be done when the water table is low to prevent excessive leaching of phosphorus into the groundwater. Another method to minimize the potential of eutrophication in nearby water systems is to cover the amended soil with vegetation immediately after application. This will prevent nutrients from running off and instead bind them to the localized area of contamination.

Chapter II - Materials and Methods

2.1 Sample Collection

The Incremental Sampling Methodology (ISM) was used for the collection of soil samples in the Delray neighborhood. This method, developed by the Interstate Technology & Regulatory Council (ITRC), ensures more reliable and consistent results than isolated or composite sampling methods (ITRC, 2012). The concept involves collecting a series of small samples across a decision unit, or volume of soil that will be used to make a decision (Figure 5). In May of 2017, the research team met with community leaders and NGO representatives at the Delray Neighborhood House to discuss the project plans and ensure that all parties were aligned in the approach to communicate with the local community. In May and June, samples were collected from over twenty-five lots in the neighborhood. Prior to sampling, permission slips were signed by the residents of the homes. Samples were obtained using turf probes which collected the top inch of soil from the ground. Increments from each home were composited into a bag. Where soil appeared to be new topsoil, samples were not taken as these areas were not representative of the long term environmental contamination.

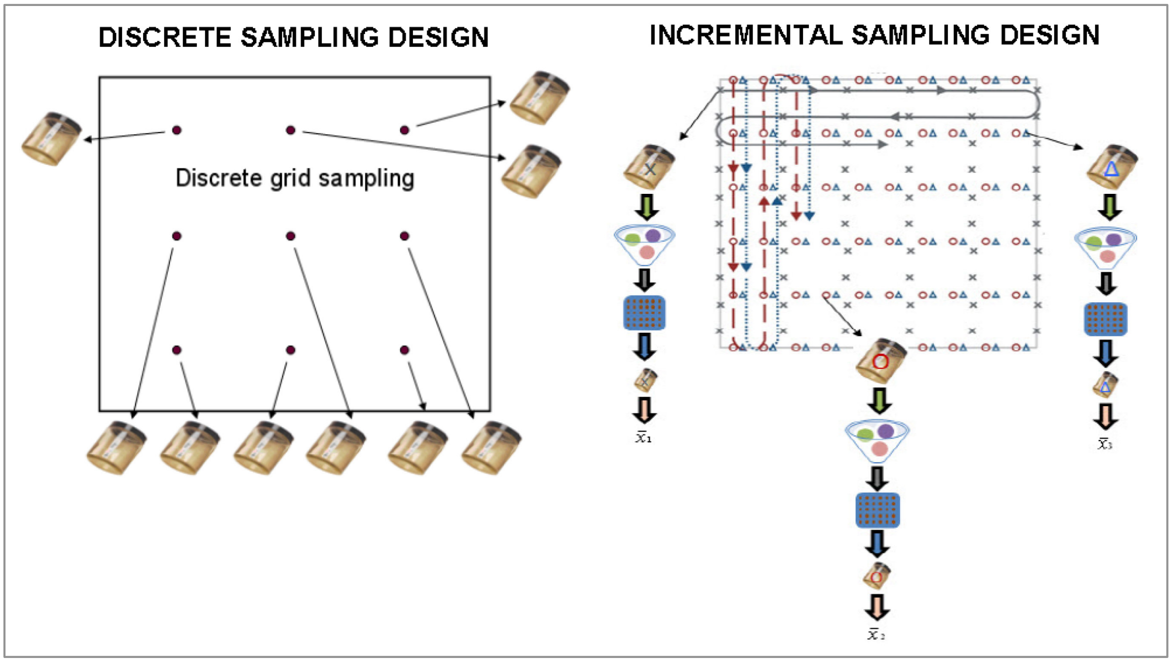

Figure 5. Discrete vs. incremental sampling design (ITRC, 2012).

2.2 Sample Processing

Once returned to the lab, the soil samples were divided into three decision units (DUs) based on location within the neighborhood; DU 1 was located in the area of Melville and South, where the Pb hotspot was concentrated. DUs 2 and 3 were located northeast and southwest of DU 1, respectively, where soil Pb levels were previously shown to be elevated, but not as high as DU 1 (Figure 6). The soil samples were combined into the decision units, organic matter, rocks, and foreign objects were removed from the soil, clumps were manually broken up, and samples were mixed thoroughly.

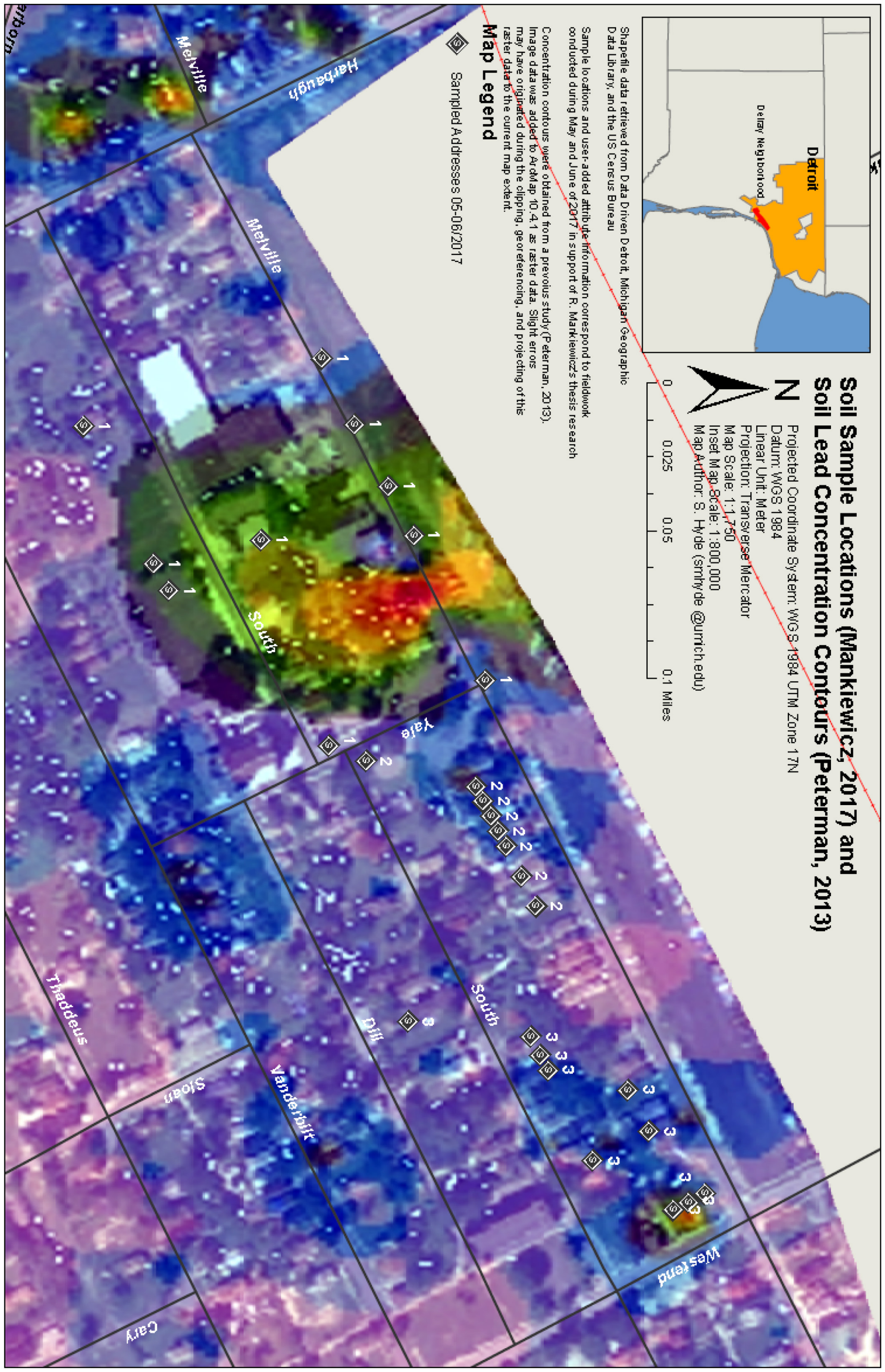

Figure 6. Soil sample locations (Mankiewicz, 2017) and Soil Lead Concentration Contours (Peterman, 2013). Map prepared by S. Hyde (2017).

Next, each DU was divided into seven subsamples using the cone and quarter method (ITRC, 2012) and placed into aluminum mini loaf pans. Triple superphosphate (0-45-0), was purchased in small pellet form from Bonide Products in Oriskany, NY. The product is derived from natural rock phosphate (P_2O_5). Soft rock phosphate (0-5-0) was acquired in powder form from Nitron Industries in Fayetteville, AR. Zeolites were 14-40 mesh clinoptilolite zeolites sourced from Ida-Ore, which mines in the Sheaville deposit in Idaho. The three amendments were added to the samples at levels of 5% and 10% by weight and mixed thoroughly. Each DU also had a control sample. Grass seed was planted in the samples after the amendments were added in order to simulate vegetative cover in the field. The samples were placed in an environmental chamber which was set to 14 hours of light and 10 hours of darkness daily (Figure 7). The samples were kept moist and left to incubate for seven weeks (48 days) to allow time for the amendments to interact with the Pb and As in simulated field conditions.

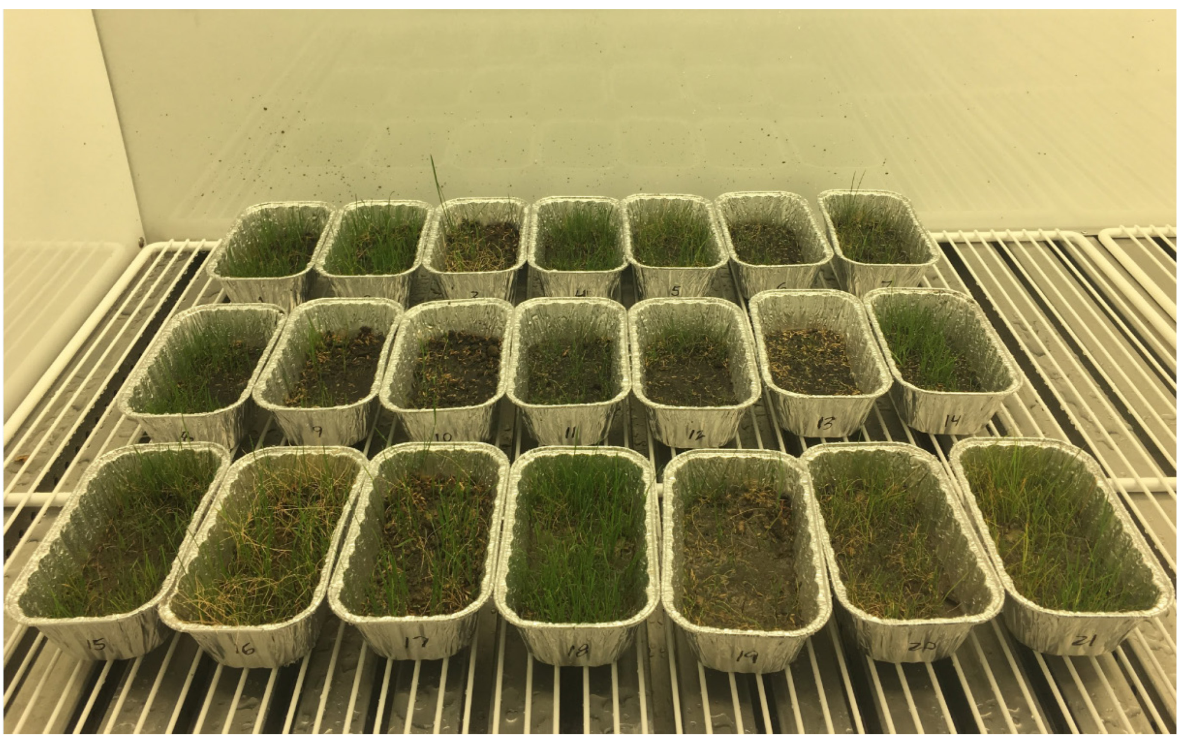

Figure 7. Sample incubation in environmental chamber (Photo by R. Mankiewicz, 2017).

After removal from the environmental chamber, the samples were dried for 24 hours at 40°C. Organic matter was removed and the samples were ground using a mortar and pestle, then sieved to <250um.

2.3 Soil Characterization

The samples were characterized by soil type according to the following Unified Soil Classification System (Table 1).

Table 1. United Soil Classification System (USCS) criteria

Letter	Definition	Letter	Definition
G	Gravel	**P**	Poorly graded
S	Sand	**W**	Well graded
M	Silt	**H**	High plasticity
C	Clay	**L**	Low plasticity
O	Organic		

Each DU was also analyzed for pH using a portable Hanna pH meter and 1:2 w/v suspension of soil in DI water. Total organic carbon (TOC) was analyzed using a modified loss on ignition method (Shirlaw, 1967). After oven drying, samples were placed in a desiccator to cool until analysis. Approximately 5.00 grams of each sample were weighed up into porcelain crucibles, which were then heated over Bunsen burner until reaching a red/orange color (approximately one hour). After cooling, samples were reweighed to determine the total loss.

2.4 Total Pb and As Analysis

Control samples underwent total digestion using EPA Method 3050b (EPA, 1996). One gram of soil and 10 mL 1:1 HNO3 were combined in a glass beaker which was then covered with a watch glass and mixed on a stirring hot plate at 95°C +/- 5°C for 15 minutes. An additional 5 mL of concentrated HNO3 was added and the mixture allowed to reflux for one hour, with HNO3 added as necessary to maintain cover over the bottom of the beaker. The sample was removed from heat and allowed to cool. 3 mL of H_2O_2 (30%) and 2 mL DI water were added to the mixture and heated again to 95°C +/- 5°C. 1 mL addition of H_2O_2 were made, waiting between additions for effervescence to subside, with a total of 10 mL of H_2O_2 added. After cooling, particulates were allowed to settle, and the supernatant was removed via disposable syringe and filtered through a 0.2 um nylon filter attachment. The sample was diluted to 10% in 1% HNO_3 and stored at <4°C prior to analysis by ICP-MS for total Pb and As.

2.5 Bioaccessibility Analysis

All soil samples were then digested for BA testing using EPA's standard method 9200 (EPA, 2008). A 0.4M glycine solution was prepared, and adjusted to pH 1.5 +/- 0.05 using concentrated HCl. For each sample, 1.00 +/- 0.05 gram of soil was obtained using the two dimensional Japanese slabcake method, an incremental sampling method (ITRC, 2012), and placed in a 250-mL glass beaker. 100 +/- 0.5 mL of the glycine solution was added to the beaker, and the solution was heated on a stirring hot plate to 37°C +/- 2°C (body temperature). The solution was mixed at ~300 rpm for one hour at temperature, maintaining pH at 1.5 +/- 0.5. HCl was used to adjust pH during the extraction as necessary. After removing from heat, the particulates were allowed to settle overnight. The supernatant was removed via disposable syringe with a 0.2 um nylon filter attachment and diluted to 10% in 1% HNO_3. Samples were stored at <4°C until analysis by ICP-MS.

Chapter III - Results and Discussion

3.1 Soil Characterization

All three DUs were classified as CL (Clay, low plasticity) in accordance with the USCS criteria. Because the finer fraction of soil is most likely to bind with metals such as Pb, this soil type is especially susceptible to retaining Pb. As summarized in Table 2, pH values were neutral to slightly alkaline, and TOC ranged from 6-8%, which is likely due to the fact that the samples were taken from only the top inch of soil and fine organic debris may account for these levels.

Table 2. Soil characterization data for DUs 1, 2, and 3.

DU	USCS Type	pH	TOC (%)
1	CL	7.3	8.0
2	CL	7.27	7.0
3	CL	7.49	6.0

3.2 Total vs. Bioaccessible Pb and As

Total Pb and As were analyzed in order to define what proportion of the total concentration of contaminants were accessible for human absorption (Table 3). The average results showed that over 97%, 85%, and 99% of total Pb was bioaccessible for DUs 1, 2, and 3, respectively. Although the digestion method (EPA 3050b) was modified significantly from the previous work by University of Michigan-Dearborn, the data reflected the established average Pb concentration of 243.1 ppm for the Delray neighborhood (Peterman, 2013). Furthermore, the total Pb values for each DU did not reflect the hotspot of elevated Pb concentration from the previous project, but this may be attributed to the use of the incremental (ISM) as opposed to discrete sampling method. For As, the total concentration did not indicate a relationship to the bioaccessible concentration. There is little historical data for comparison of the As concentration levels, but the present results include values that approach or exceed the RBSL of 7.6 ppm.

Table 3. Total vs BA Pb and As for DUs 1, 2, and 3.

	Total Pb	**BA Pb**	**Total As**	**BA As**
	All units expressed in ppm			
DU 1	234.1	228.1	5.7	7.3
DU 2	335.7	288.1	6.7	12.7
DU 3	277.8	275.3	8.0	6.8

3.3 Effect of Amendments on Pb and As Bioaccessibility

In general, the addition of each of the three soil amendments, TSP, PR, and ZE caused a decrease in BA Pb for each of the decision units (Figure 8). A statistical paired t-test was applied using a 95% confidence level to determine if there was a significant decrease in BA Pb for each of the amendments at the two addition rates. PR had a statistically significant impact on BA Pb at 5% ($p=0.0074$) and 10% ($p=0.0017$). The mean decrease between the control and amended sample for PR was -76 ppm at 5% and -97 ppm at 10%. TSP did not have a significant effect on BA Pb at 5% ($p=0.8859$), but was significant at 10% ($p=0.0362$). Similarly, ZE's impact on BA Pb was not significant at 5% ($p=0.0555$), but was significant at 10% ($p=0.0127$), with an average decrease of 69.4 ppm.

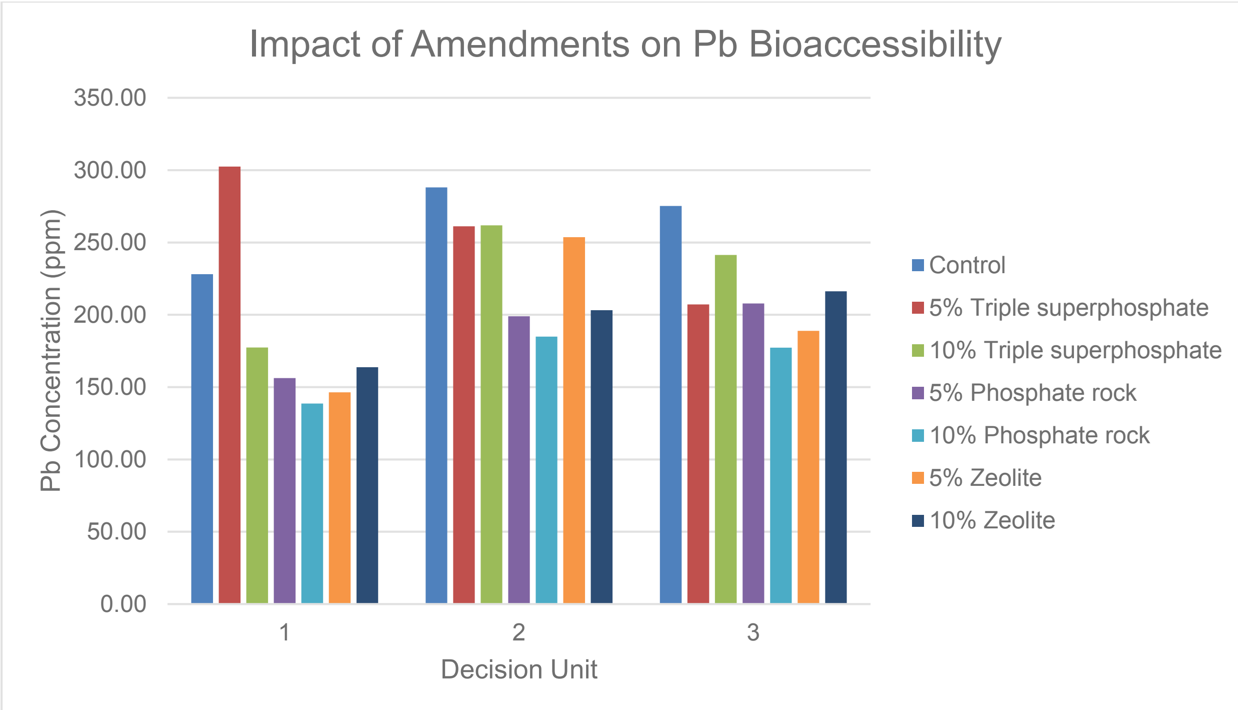

Figure 8. Effect of amendments on Pb bioaccessibility.

The effects of the amendments on As BA did not show a consistent trend (Figure 9); there was no significant impact of the amendments on the As BA based on the paired t-test at a 95% confidence level ($p>0.1$ for all samples), yet the application of amendments appeared to increase solubility in some samples while decreasing it in others. However, there was evidence of interference for the BA method for As; the method blank sample had an As concentration of 2.50 ppm. This may have been caused by contamination of the equipment or chemical supplies, or other interference during the ICP-MS analysis.

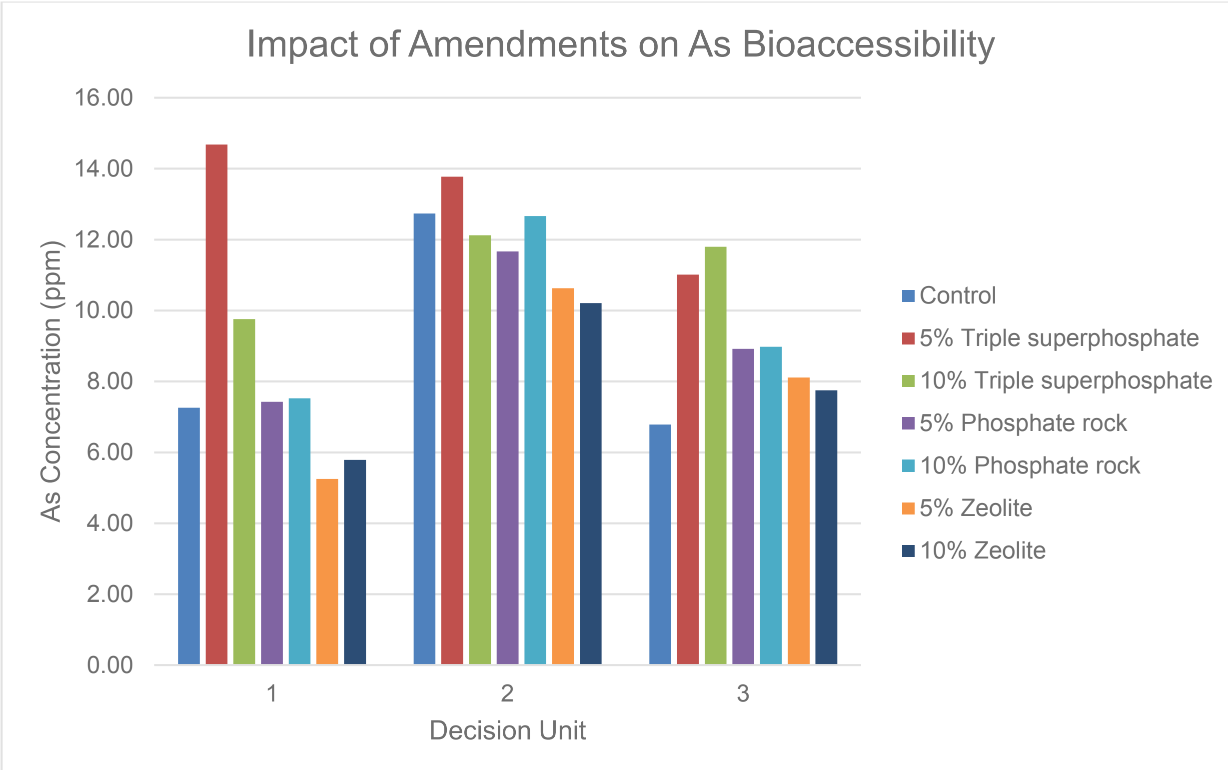

Figure 9. Effect of soil amendments on As bioaccessibility.

Table 4. Summary of soil amendment impact on BA Pb and As.

		CTRL	5% TSP	10% TSP	5% PR	10% PR	5% ZE	10% ZE
DU 1	Pb	228.1	302.5	177.4	156.2	138.7	146.4	163.7
DU 2	Concentration	288.1	261.1	261.8	199.0	184.9	253.7	203.2
DU 3	(ppm)	275.3	207.2	241.4	207.8	177.3	188.9	216.3
DU 1	As	7.3	14.7	9.8	7.4	7.5	5.3	5.8
DU 2	Concentration	12.7	13.8	12.1	11.7	12.7	10.6	10.2
DU 3	(ppm)	6.8	11.0	11.8	8.9	9.0	8.1	7.8

One outlier was observed in DU 1 at the 5% TSP addition rate. In these samples, Pb and As appeared to become more soluble in the soil. However, at the 10% TSP addition rate, bioaccessible Pb significantly decreased, indicating that TSP amendment does not increase Pb solubility in soil. A number of method or human errors could have affected the data for the outlier. During sample processing, the soils were thoroughly mixed prior to allocation into composites.

Through this process, soil clumps were broken up and pebbles and organic matter removed, but because the soil was not dried and milled, there was the potential for variability in Pb and As concentration in the composites. While this method was appropriate because it more closely reflects the application of amendments in the field, it could have allowed for higher concentration in the outlying soil sample.

Another potential source of error was the use of hotplates for both the total digestion and BA methods. As written, the procedures specified the use of enclosed apparatuses (microwave or extraction device in a heated water bath) during the digestion process; the use of the stirring hotplate caused more potential deviations in temperature control and a different mode of agitation, as well as loss of vapors.

One observation noted during review of the data was that the level of Pb concentration was not as high as expected based on previous studies. While the average Pb concentration of 282.5 ppm was higher than the previous neighborhood average of 243.1 ppm, this study focused on the apparent hotspots of Pb contamination along Melville Street so higher concentrations were expected. However, this may also be related to the ISM approach used for this study; the nature of ISM dilutes localized hotspots to obtain a representative average for each DU. This could be a potential downside of ISM if large DUs are used and elevated contamination in a particular home or garden, for example, is not identified.

Given the limitations in this study, there are a few areas where future research is recommended. The sample size in this project was limited due to the labor intensive nature of the ISM protocol and some difficulty in obtaining resident permission to sample the areas of interest, so it is recommended to include a larger number of samples in future studies in order to obtain more reliable statistical data.

One factor that may have caused a difference in effectiveness among soil amendments was particle size. Whereas the particle size of PR, the most successful amendment, was that of a powder, TSP was purchased in a small pellet size, and ZE was the consistency of kitty litter. Although the same w/w amount of each amendment was utilized, the PR was more interspersed throughout the soil and therefore had a greater opportunity to bind with the contaminants. For future studies, one consideration could be to acquire TSP or ZE in a finer particle size or to mill it into a finer consistency. A caveat, however, is that the finer particle size would be more difficult to apply in the field due to wind interference.

Another area of potential interest is the impact of the amendments on the surrounding environment. Because the most successful amendment, phosphate rock, has a small particle size, field application will have to be tested to see if the material will be controllable despite wind. Furthermore, the amendment's impact to the environment and watershed may be higher if the amendment is light and soluble, and therefore may easily run off during rain events.

A final area for additional research is the effect of soil amendments on soil As BA. While the impact of various amendments on soil Pb BA has been studied in depth in recent years, there is less information regarding how the same amendments may impact As BA or which other amendments may be effective in reducing soil As BA. Specifically, because some studies showed an increase in soil As solubility in conjunction with phosphate amendments, the specific soil type and chemical interactions with phosphates should be thoroughly tested prior to application. Since many soils contaminated by Pb are also contaminated by As as a result of industrial pollution, this is an important area of study going forward and should be considered in future work in the Delray neighborhood.

Chapter IV - Conclusion

Overall, the amendments showed promising results for decreasing soil Pb BA in the Delray neighborhood. PR, likely due in part to its small particle size, caused a significant decrease in Pb BA at addition rates of both 5 and 10%. TSP and ZE were less successful, but did cause a significant decrease in Pb BA at 10%. The amendments did not have a conclusive impact on As BA. Because there appeared to be a slight increase in As solubility with the addition of the amendments in some samples, this could be an area of future study to ensure that efforts to reduce soil Pb BA do not simultaneously exacerbate problems with soil As BA.

Based on the results of this study, PR is the most efficient and effective amendment for reducing Pb BA and should be tested further for effectiveness in the local soil and through application in the field. With confirmation from further studies, PR could be an inexpensive, feasible solution to remediate the longstanding problem of soil contamination in Delray and improve the health and quality of life for its current and future residents. This approach could also be relevant in other areas of Detroit and in other postindustrial cities that have similar soil contamination profiles.

Appendix A – Total Pb and As Data (ICP-MS)

Decision Unit	Sample	Total As (ppm)	Total Pb (ppm)
DU 1	1	5.96	247.87
	1a	5.40	220.27
DU 2	8	7.93	314.43
	8a	8.14	357.05
DU 3	15	3.39	282.22
	15a	3.43	273.36
	Blank 1	0.12	0.10

Appendix B – Bioaccessible Pb and As Data (ICP-MS)

Decision Unit	Sample	BA As (ppm)	BA Pb (ppm)
DU 1	Ctrl	6.76	196.36
	Ctrl	7.59	248.85
	Ctrl	7.43	239.04
	5% TSP	14.68	302.46
	10% TSP	9.76	177.36
	5% PR	7.42	156.25
	10% PR	7.53	138.70
	5% ZE	5.25	146.44
	10% ZE	5.79	163.75
DU 2	Ctrl	11.57	251.59
	Ctrl	11.25	278.63
	Ctrl	15.38	333.95
	5% TSP	13.78	261.14
	10% TSP	12.13	261.80
	5% PR	11.67	199.02
	10% PR	12.67	184.95
	5% ZE	10.63	253.70
	10% ZE	10.21	203.20
DU 3	Ctrl	5.43	198.68
	Ctrl	7.39	330.30
	Ctrl	7.55	296.78
	5% TSP	11.01	207.16
	10% TSP	11.80	241.37
	5% PR	8.92	207.81
	10% PR	8.98	177.27
	5% ZE	8.11	188.94
	10% ZE	7.75	216.27
	Method Blank	2.50	-0.33

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