ANALYSIS OF THE EPA-MANDATED SOIL AMENDMENTS AT TAR CREEK SUPERFUND SITE

By:

MADISON PEPPERS

Bachelor of Science, 2016
Oklahoma State University
Stillwater, Oklahoma

Submitted to the Graduate Faculty of the
College of Science and Engineering
Texas Christian University
In partial fulfillment of the requirements
For the degree of

Master in Science

May 2018

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Thesis approved:

Major Professor

For The College of Science and Engineering

# ACKNOWLEDGEMENTS

I would like to thank the Quapaw Tribe of Oklahoma and the Environmental Protection Agency for allowing me to conduct research at Tar Creek and providing me with data throughout the duration of my study. Additionally, I would like to thank fellow teaching assistants for their support: Brynn Huzzen, Katie Smith, Kristen Debone, Katelyn Leham, and Sharra Blair-Kucera.

I am extremely appreciative for my advisor, Becky Johnson, who has helped me with the analysis and collection of data along with support during the thesis process. Additionally, Tory Bennett has been a great support throughout my two years at Texas Christian University. Lastly, I would like to thank Dr. Slattery and Dr. Holbrook for their helpful feedback on my research and writing for my thesis.

Ultimately, my family and friends, especially my mom and husband, have been the backbone to my success the past two years and I could not have done it without them.

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Introduction

Mining is the process of extracting useful minerals from the Earth, with 1,950 active mines globally as of 2015 (Mero et al, 2017; Statista, 2016). While many minerals are acquired via surface mining, metals are typically derived from underground or subsurface mining (DOE, 2013). As of 2015, there were 92 active underground metal mines in the United States alone (CDC, 2017). In particular, the metals lead and zinc are almost exclusively mined underground (DOE, 2013).

During the lead and zinc mining process the ore is removed by drilling and blasting and is taken through a shaft and brought to the surface (DOE, 2013). The lead and zinc content of the mined ore is 4% and 3% to 10%, respectively (Richards, 2018; Goodwin & Pinikvar, 2018). Once the ore is removed, the rock is finely crushed and ground or milled, removing as much waste rock or rock that is not economically viable as possible (U.S. DOT, 2016). Beneficiation of the fine particles occurs through a method called floatation that consists of slurry reagents and/or chemicals (conditioners and regulators) that modify the pH and help metals float to the surface while waste sinks to the bottom (DOE, 2013; Goodwin and Ponikvar, 2018). The metal-containing fine particles are then dried and sent to the smelter containing 50 to 60 percent of the desired metal (DOE, 2013).

During the concentration of ore approximately 95% ends up being waste rock and tailings (Falagan et al., 2017). Tailings are the undesirable or uneconomical by-products of floatation (DOE, 2013). In the United States alone, 1.8 billion tons of waste is produced annually from mineral processing, accounting for nearly half of all of the solid waste generated each year (U.S. DOT, 2016). The majority of metal mining waste is disposed of onsite as it can potentially be used for road or other construction (EPA, 2018; U.S DOT, 2016). However, the waste rock and tailings can include base metals, sulfides, chemicals, or other elements associated with the ore, host rock, and the concentration process (DOE, 2013). Because the stockpiled waste is in direct contact with the soil and vegetation and these stockpiles typically have no barrier against rainfall, they can potentially contaminate soil, vegetation, storm water and groundwater.

Among mining wastes, tailings are considered to be the greatest threat to aquatic systems and soil ecological stability due to their high heavy metal content in contrast to naturally occurring concentrations and fine particle size (Azhari et al., 2017). Heavy metals present in tailings can reach nearby environments as particles or can dissolve into slightly acidic precipitation and can accumulate in soil and sediments (Azhari et al., 2017). Soil heavy metal contamination is of the utmost concern because of its toxicity to microorganisms, plants, and animals in addition to the potential to reach the human food chain via plant uptake of contaminants from impacted soils (Azhari et al., 2017).

While negative impacts from metal mining are seen throughout the world, this thesis will focus on the local example of the former Tri-State Mining District (TSMD) of Missouri, Kansas, and Oklahoma where large scale mining for lead and zinc took place from 1914 until the mid-1950s (EPA, 2018a). The subsurface mining produced approximately 16 tons of chat (metal-contaminated tailings from lead and zinc milling) for every ton of ore produced (Quapaw Tribe, 2015), accumulating roughly 500 million tons of chat in the tri-state area (ODEQ, 2015). While the mining has ceased, chat still remains in stockpiles on the surface throughout the region (EPA, 2018a). A portion of this region has come to be known as the Tar Creek site, for its location along Tar Creek, as seen in Figure 1.The Tar Creek site currently has approximately 83 chat stockpiles that reach heights of up to 200 feet high, with an estimated volume of 8.4 million tons (EPA, 2018a).

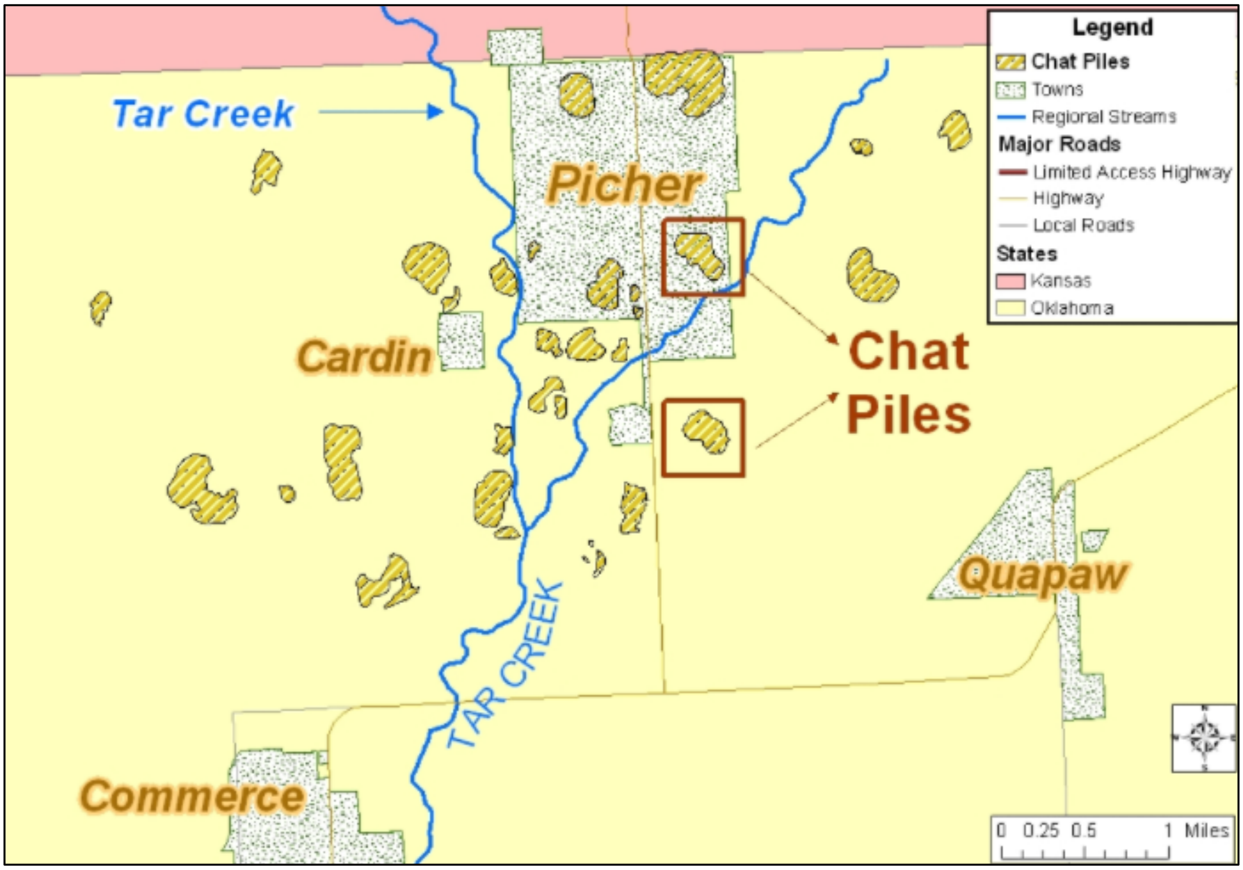

Figure 1: Tar Creek site in proximately to Tar Creek (Tar Creek Superfund Site, 2018)

These stockpiles have adversely impacted the soils in the region through direct contact with the chat, windblown metal contaminated particles, and contaminated storm water runoff. High concentrations of heavy metals, specifically lead (Pb), zinc (Zn), and cadmium (Cd), are still present within the soil and water systems (Beattie et al., 2017). The metal contamination present at the Tar Creek site can negatively influence the environment, surrounding ecosystems, and human health (EPA, 2018a).

Background

Production of lead and zinc ore at the Tar Creek site was conducted using underground mining methods and Room-and-Pillar techniques (EPA, 2018a). Room-and-Pillar technique leaves pillars of rock behind, typically in uniform size, to support the roof of the mine (Harraz, 2014). Then, to remove the ore, large rooms, with ceiling as high as 100 feet were connected by horizontal tunnels known as drifts (EPA, 2018a). Mining conducted at the Tar Creek site primarily occurred within a 50 to 150 foot thick ore-bearing zone within the Mississippian Boone Formation; however, the maximum depth of the mine reached approximately 385 feet below ground surface (EPA, 2018a). The low to middle Mississippian Boone Formation consists primarily of limestone, dolomite, and chert, with lesser quantities of sandstone and shale (USEPA, 2008). The two principal minerals that contain the lead and zinc ore are galena and sphalerite with the primary mineralization being zinc sulfide (ZnS) and lead sulfide (PbS) (USEPA, 2008; King, 2018).

Because of the threat to human health and the environment that the Tar Creek site poses, it was added to Superfund Program in 1983 (EPA, 2018a). Superfund or the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) program aims to protect human health and the environment by funding and managing the cleanup of the nation's worst hazardous waste sites in the event that the Potentially Responsible Parties (PRP) could not be found (EPA, 2016). PRPs could not be found and/or held responsible for cleanup of the Tar Creek site because mining operation ceased in the 1950s.

Tar Creek qualified as one of the nation's worst hazardous sites because of the adverse effects caused by the metal contamination present. Metals in the chat have contaminated soils, and dust from the chat blows throughout the region. Exposure routes could include ingestion via uptake of metals by plants and/or livestock that grazed on plants grown in the contaminated soil and inhalation of windblown dust. However, inhalation poses the greatest threat to human health as inhaled contaminants are more readily absorbed in the body (Robbins et al., 1989). Lead can cause damage to the liver, kidneys, heart, reproductive, and immune systems and zinc can cause pancreas damage (Robbins et al., 1989). Cadmium has shown to be a human carcinogen, in addition, to causing emphysema, lung disease, and kidney damage (USEPA, 2006).

Tar Creek Superfund Site (TCSS) is in the extreme northeastern corner of Oklahoma in Ottawa County (36. 98591483, -94.82934508), encompassing the towns of North Miami, Picher, Cardin, Quapaw, and Commerce, and ranges across 40 square miles or 25,600 acres (Quapaw Tribe, 2015; ODEQ, 2015). Because parts of the TCSS are within the Quapaw Tribe of Oklahoma's land the EPA has partnered with them to facilitate cleanup. Soils within the site of Tar Creek are typically clay or silt loams with a background concentration of 20 ppm for Pb and 74 ppm for Zn (USDA, 2018; Shacklette and Boerngen, 1984). Background concentrations of Cd have not been established for TCSS; however, typical natural concentrations of Cd in soil range from 0.1 to 0.5 ppm (ICdA, 2018).

Since the establishment of the TCSS, EPA has established 5 operable units (OU) and teams of remediation staff to address contamination outlined below (EPA, 2018a):

- <u>OU1 (1984): Surface Water/Groundwater</u> – Plugging abandoned wells to reduce the potential for contaminants in the shallow Boone Aquifer.

- OU2 (1995) : Residential Areas – EPA excavated contaminated soil at public areas and residences in Miami, Afton, Commerce, Fairland, Narcissa, North Miami, Peoria, Quapaw, and Wyandotte.
- OU3 (2000): Eagle-Picher Office Complex, Abandoned Mining Chemicals Removal Action – 120 containers of chemicals were removed from the office and laboratory complex that was run by one of the former mining companies.
- OU4 (2008-Current): Chat Piles, other Mine and Mill Waste, and Smelter Waste – Risk and pathways addressed by the cleanup activities include health risk from people ingesting, touching or inhaling contaminates in soil. This is the current remediation plan with the EPA continuing to work closely with the Quapaw Tribe and the Oklahoma Department of Environmental Quality (ODEQ) on the implementation of Tar Creeks' remedy.
- OU5 (Future date TBD): Surface Water and Sediments – Human health risk assessment of potential risks related to surface water and sediment exposure

Soil Amendments

Metal contamination in soil occurs throughout the world not only from hard rock mining that is seen at TCSS but also with coal mining, refining and smelting, and construction sites. While contaminants range from site to site, the most common practice has been to dig up the impacted soil and place it in a specially constructed and lined landfill, typically on or near the contaminated site. Soils are removed to differing depths, based on the sampling and analysis of the metals levels that are acceptable to leave in place. This method removes millions of tons of topsoil per year from productivity (either agricultural or ecosystem) and potentially leaves behind a worse problem as landfills deteriorate, leak, and potentially re-contaminate areas that have been previously remediated.

As an alternative, EPA has developed a process whereby soil amendments are applied to contaminated soil to bind the metals and prevent uptake by plants after chat piles are removed. These amendments preserve topsoil, keep the land in productivity, and hopefully limit the potential for humans and livestock to ingest metals via the food chain. Soil amendments are based on the properties of the soils on site and typically consist of a mix of organic matter, soil acidity/pH adjustments, and mineral amendments or conditioners that can take many forms as seen in Table 1 (USEPA, 2007).

Table 1: Types of Soil Amendments (Quapaw Tribe, 2015)

Amendment Component	Forms
Organic Soil Amendments	Biosolids, Manures, Composts, Digestates, Papermill Sludges, Yard and Wood Waste, Ethanol Production Byproducts
Soil Acidity/pH Soil Amendments	Lime, Wood Ash, Coal Combustion Products (CCPs), Sugar Beet Lime, Cement Kiln Dust, Red Mud, Lime-stabilized Biosolids
Mineral Soil Amendments and Conditioners	Foundry Lime, Steel Slag, Dredged Materials, Gypsum, Water Treatment Residuals (WTR), Coal Combustion Products (CCP)

Topsoil at and near TCSS ranges from inches to several feet of the soil profile (USDA, 2018). Removing the topsoil in this area for remediation renders the land non-productive as it takes a minimum of 100 years to new form an inch of topsoil (NRCS, 2018). EPA is exploring amendment application for this region so that impacted topsoil does not need to be removed. The land can be used for open space, either as range land for cattle and/or for limited recreation use (USEPA, 2007). The EPA chose appropriate soil amendments to address contaminants at Tar Creek (Pb, Zn, and Cd). Various studies that determined routes of exposure and potential solutions, as seen in Table 2, assisted in determining the Remedial Goals that are outlined in Table 3. These remedial goals establish metals levels that are considered safe to be left in soils, posing no threat to human health or the environment.

Table 2: Description of the use of Soil Amendments for metals of Pb, Zn, and Cd (Quapaw Tribe, 2015)

Contaminate	Exposure	Interactions	Solutions
Cadmium to Zinc Ratio	Food Chain	Higher ratio=greater bioavailability (risk) of Cd	Add Zn to reduce the Cd:Zn ratio
Lead (Pb)	Soil ingestion	Low phosphorus (P)= more toxic	With no As present, raise pH to 6.0 or greater (i.e. Tar Creek)
Zinc (Zn)	Phytotoxicity	Low pH = more toxic; low P = more toxic	Raise pH (7.0-8.0), OM, and sorbents, i.e. iron and manganese oxides

Table 3: Remedial Goals for Contaminants of Concern (Quapaw Tribe, 2015)

Contaminates of Concern	Clean Up Standard	Basis for Cleanup Level
Lead	500 mg/kg	Human Health Risk Assessment
Cadmium	10 mg/kg	Ecological Risk Assessment
Zinc	1100 mg/kg	Ecological Risk Assessment

The aim of the soil amendments is that the metals will be chemically precipitated and/or sequestered by complexion and sorption mechanisms (USEPA, 2007). Additionally, metal availability to plants is minimized, metal leaching into groundwater can be reduced, and metal availability below the treated area can be reduced (USEPA, 2007). The soil amendment currently implemented at Tar Creek consists of agricultural lime, chicken litter, and mushroom compost with pHs of 8.3, 8.16, and 5.75, respectively (Sprenger, 2016). This amendment was tilled into the soil at approximately 12 inches at a rate of 20 tons/acre of mushroom compost, 5 tons/acre of chicken litter, and 10 tons/acre of agriculture lime (Sprenger, 2016). Agricultural lime is an acidity/pH soil amendments that aims to increase the pH, decreasing the bioavailability of the metals, especially that of Pb (USEPA, 2007). Chicken litter is an organic soil amendment and serves at a nutrient and organic matter source for the soil (USEPA, 2007). Mushroom compost also falls under the organic soil amendments and adds nutrients and organic matter to the soil (USEPA, 2007). The organic soil amendments not only serve a purpose of decreasing the bioavailability of the metals, but also stabilize the soil from runoff and erosion by providing an environment that is suitable for plant growth (Sprenger, 2016).

While applying soil amendments can be a more time-intensive process than removing the contaminated soil and taking it to the landfill, this particular process has been chosen to preserve topsoil, with the ultimate goal to turn the land back into productive range land and/or limited recreational use (Sprenger, 2014). After soil amendments are applied, the Quapaw Tribe was required to do short term sampling to analyze the agriculture parameters (pH, Organic Matter (OM), Phosphorus (P), Potassium (K), and Nitrogen (N)) quarterly for a year (Sprenger, 2016). This is due to the complexation and sorption mechanisms within the contaminated soil and plant growth necessary to stabilize the landscape and prevent erosion, reducing surface water runoff and sediment loading to receiving streams, as seen in Figure 2 *(*USEPA, 2007*).*

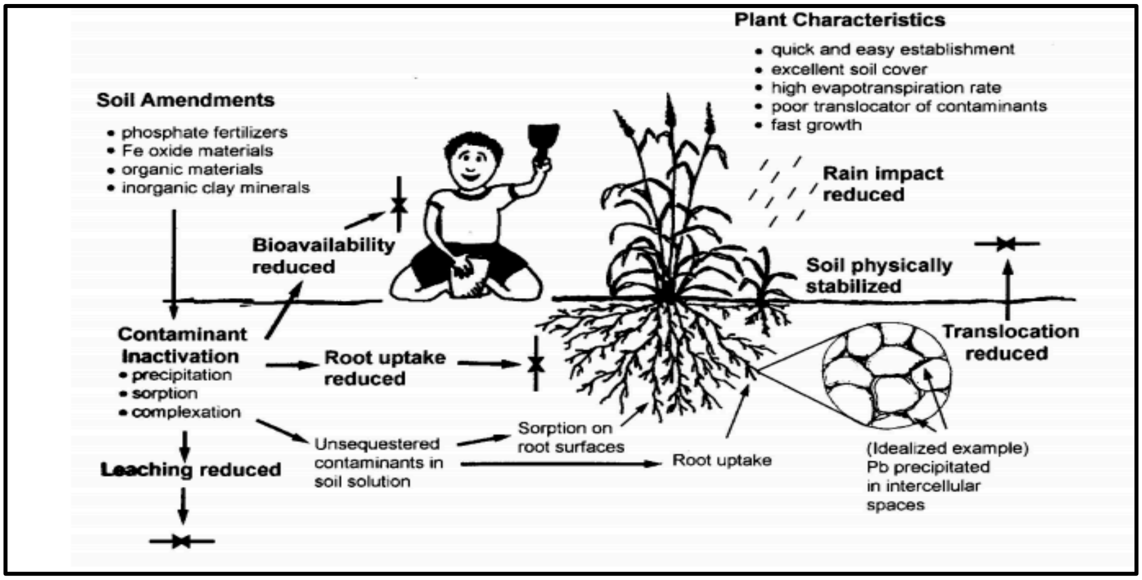

Figure 2: The Role of Soil Amendments to Plants in Metal-Contaminated Soils (USEPA, 2007)

Within the TCSS, this study will focus on the site of CP009 (36.944950, -94.876795), as seen in Figure 3. This specific site was chosen because it is one of the first sites to implement soil amendments to address contamination instead of digging and hauling contaminated soil to the repository. Levels of Pb, Zn, and Cd in soil were taken in March of 2016 by the Quapaw Tribe to establish a benchmark for CP009. The levels identified in the preliminarily testing determined what soils are over the remedial goals in one or more of the metals, as seen in Figure 4. The grids that tested over the remedial levels were grids 08, 11, 12, 16, 17, 18, 21, and 23. For the purposes of this study, grids 11 and 18, along with two control grids, West and Field, were chosen to analyze quarterly.

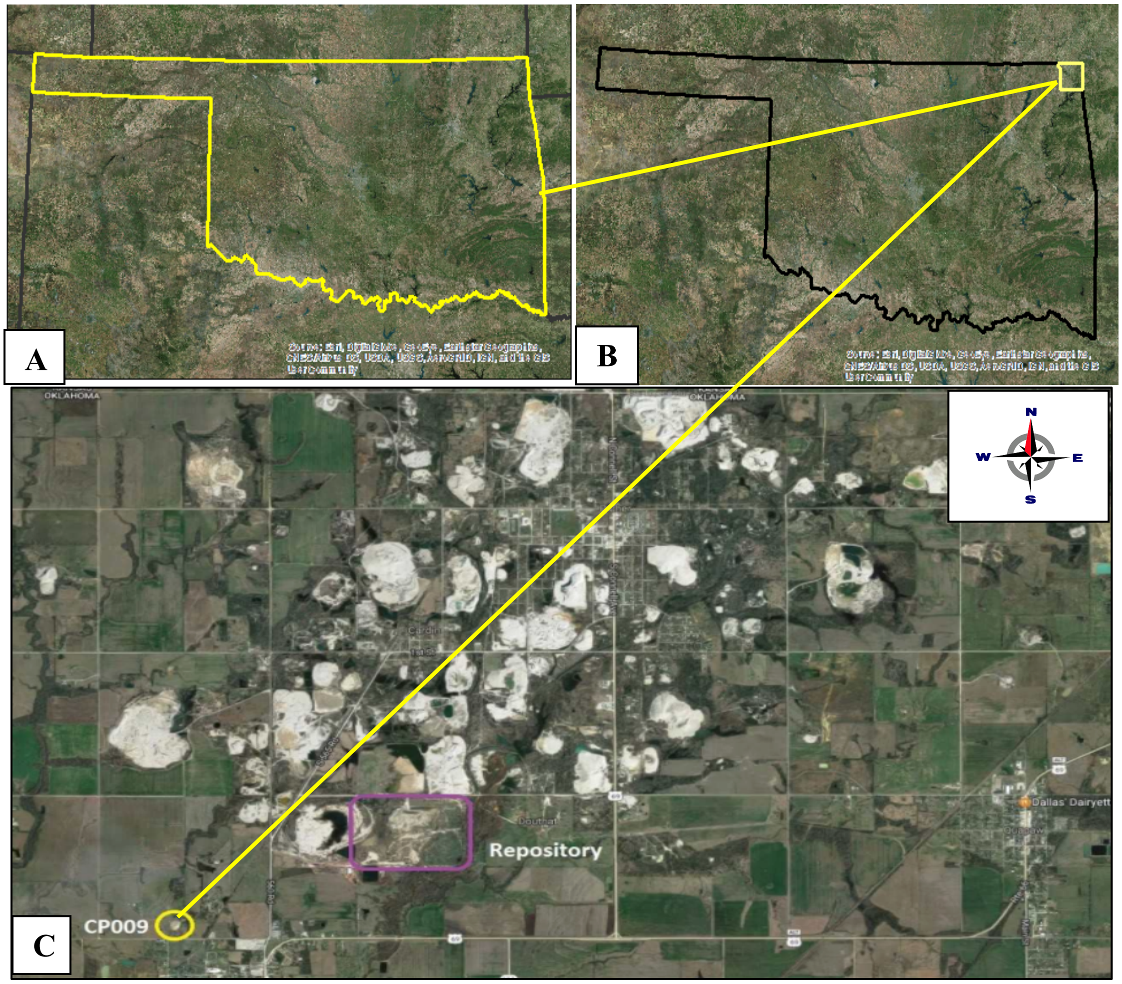

Figure 3: A) Oklahoma state map, B) Oklahoma state map with Ottawa County (location of Tar Creek) highlighted, and C) Site CP009 with the TCSS

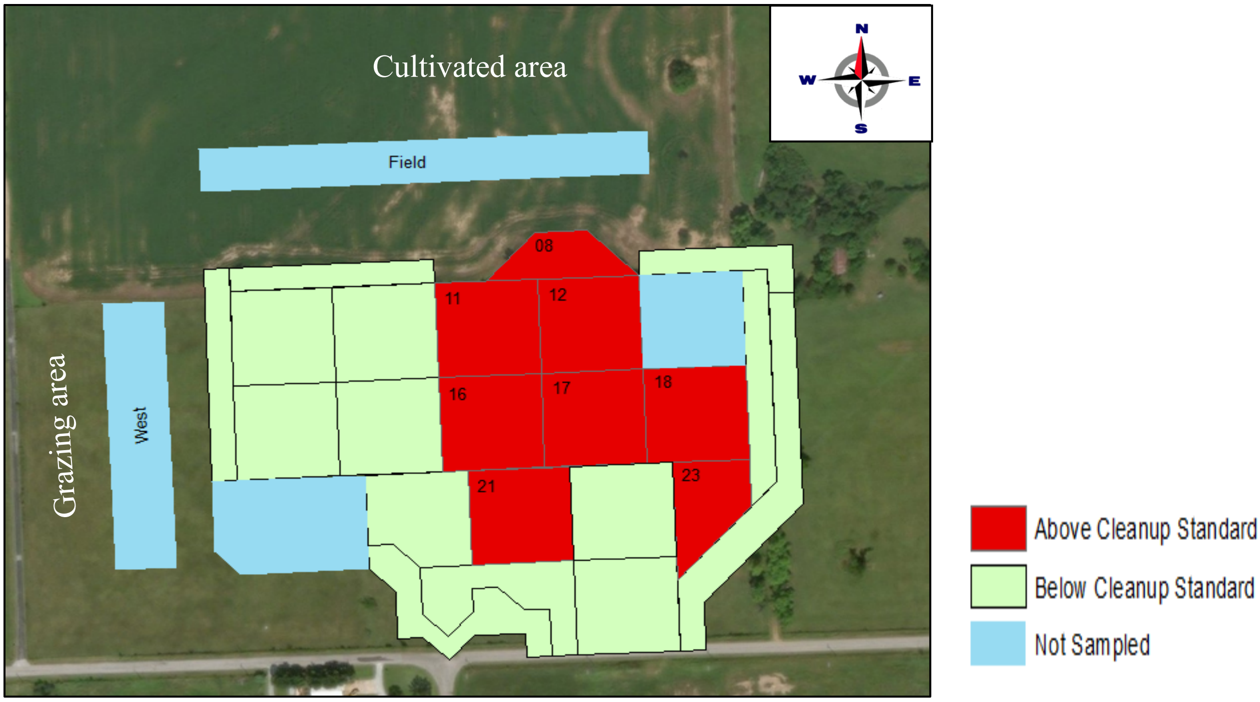

Figure 4: Results for confirmation sampling for CP009 of Pb, Zn, and Cd conducted by the Quapaw Tribe in March 2016. 1 acre grids were established at CP009 for sampling purposes, the grids highlighted in red (08, 11, 12, 16, 17, 18, 21, and 23) were above the remedial goals in one or more area, the green grids were below the remedial goals for all the metals, and the blue grids were not sampled during the confirmation sampling.

The Quapaw Tribe measured the agriculture parameters in the grids that were over the remedial goals at CP009 to determine if the land will be viable for grazing land in the future. However, these parameters do not indicate if the soil amendment is reducing/stabilizing the metal contamination present.

The overall objective of this thesis is to determine whether the current EPA-mandated amendments are effectively reducing the amount of heavy metal contamination in the soil, specifically the metals of Pb, Zn, and Cd. The assumption is that the soil amendment applied will reduce the contamination present within the soil system.

To determine effectiveness, two grids that were above the remedial goals during benchmarking, Grids 11 and 18, were chosen in addition to two control grids, Field and

West, that were assumed not impacted by the presence of the chat. Grids 11 and 18 were chosen because all three metals, Pb, Zn, and Cd, exceeded the remedial goals. The Field control grid is located in a cultivated field north of CP009, and the West control grid is located west of the CP009 in a grazing area. Neither of these areas had chat deposits directly on them but were immediately adjacent to the chat pile. Likewise, neither of these grids received amendments and are reflective of the typical land uses in the area

Methods and materials

The Quapaw Tribe sampled grids that exceeded the remedial goals of 500 ppm for Pb, 1100 ppm for Zn, and 10 ppm for Cd, during confirmation sampling in March 2016, refer to Figure 4, on a quarterly basis for agriculture parameters (OM, P, K, N, and pH) in December 2016, March, June, and September 2017. This study was conducted concurrently and analyzed soil texture, vegetation by Daubenmire, forage clips, agriculture parameters (OM, P, K, N, and pH) and total metals in soil for grids 11, 18, West, and Field during March, June, September, and December 2017. Grids 11 and 18 were not sampled during March 2017 because consultants for the tribe decided to not analyze the March samples for metals after field work was complete. The methods for each of these types of sampling are described below.

Soil Texture

To determine soil texture, soil was taken from each grid, 11, 18, West, and Field, and air dried. The dried soil for each grid was then weighed to approximately 60 grams (g). The 60 g of soil was put in a series of sieves (5, 10, 35, 80, and 100) and shaken in a rotap for approximately 10 minutes. The soil retained in the pan contained the silt and clay present in each soil. To determine the portion of clay and silt left in the soil, a hydrometer test was conducted. To conduct the hydrometer test, the clay and silt were mixed with 100 mL of dispersing solution (50 grams of Sodium Hexametaphosphate in 1 liter of water) and 50 mL of distilled water. The mixture was then poured into a 1000 mL graduated cylinder and filled to the 1000 mL mark with distilled water, as seen in Figure 5. The mixture was thoroughly homogenized, and then the hydrometer was inserted noting the reading at 40 seconds, 2, 5, 8, 15, 30, 60 minutes, and after 24 hours. The percentages of sand, silt, and clay were then plotted on the soil texture triangle. Potential sources for error is soil texture analysis include chat being tilled into the soil profile in addition to frequent earth moving taking place at the site.

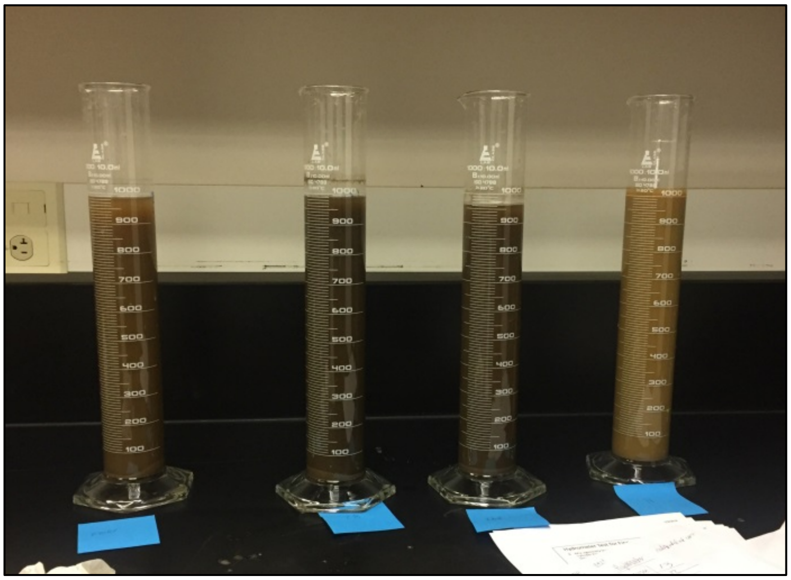

Figure 5: Hydrometer test for soil texture for grids 11, 18, West, and Field

Vegetation Survey by Daubenmire

A Daubenmire frame was randomly placed in proximity to the GPS coordinates listed in Table 4 for grids 11, 18, West, and Field, also seen as Figure 6. The Daubenmire frame was constructed with PVC pipe and approximately 20 x 50 centimeters (Coulloudon et al., 1999). The Daubenmire is used to estimate the percent cover, frequency, and composition of vegetation present (Coulloudon et al., 1999). Noting these characteristics helped to identify how vegetation changed over time in the field. Additionally, the use of the Daubenmire frame helped to identify if there was a relationship between the levels of metals within the soil and the vegetation present.

Forage Sampling

For the cultivated field control grid (Field), grab samples from young leaves of winter wheat and soybeans were taken and sent to Oklahoma State University Soil, Water, and Forage Analytical Lab (SWAFL) for analysis. SWAFL used the *Soil, Plant, and Water Reference Methods for the Western Region* to analyze uptake of metals in plant tissue (Gavlaket al., 2003). These samples were collected during the March 2017 sampling event for the winter wheat and the September 2017 sampling event for the soybeans. The samples were cut with sheers at the root within an area approximately 20 x 50 centimeters, then put in a gallon plastic bag and sent to the SWAFL lab. The percentage of Pb, Zn, and Cd identified in the crop was then compared to total metals present in the soils to determine uptake of metals by the crop.

Soil Sampling for Agriculture Parameters

To determine the agriculture parameters, one composite sample from each grid from 0-6 inches was taken. Each soil sample was composited from five grab sub-samples collected with a stainless-steel hand auger. For grids 11 and 18 the five sub-samples were collected at the four corners and the center of the grid, using an X pattern, as seen in Figure 6. Since the control grids of West and Field could not follow the X pattern due to field constraints, they were taken in a long and narrow straight line, as seen in Figure 6; GPS coordinates for each sub-sample location are documented in Table 4. The five sub-samples collected were placed together in a plastic bag and were thoroughly homogenized to form the composite sample (Quapaw Tribe, 2015). The stainless-steel hand auger was cleaned in a 5-gallon bucket with distilled water and detergent after sampling was completed for each grid. These soil samples, along with the Quapaw soil samples being tested for agriculture parameters, were taken to

Oklahoma State University SWAFL that uses the *Soil, Plant and Water Reference Methods for the Western Region* for analysis (Gavlak et al., 2003). OM is analyzed by determining the total carbon present in the soil, but that also includes fungi, bacteria, plant roots and inorganic sources such as calcium carbonate ($CaCO_3$). The total carbon is therefore multiplied by an industry standard conversion factor of 58% (used by most researches/laboratories) to result in the total organic carbon present in the soil (Schumacher, 2002). Lastly, the results is multiplied by 1.7 (another industry standard conversion) to get percent of organic matter in the soil (Schumacher, 2002). The agriculture parameters are monitored to ensure the nutrients needed for plant growth are present, as one of the potential future uses for CP009 is grazing land.

Soil Sampling for Metals Analysis

To determine the content of Pb, Zn, and Cd, the soil was acquired the same way and at the same time as for the agriculture parameters analysis. Per the recommendation of the EPA publication "*Use of Soil Amendment for Remediation, Revitalization, and Reuse*" the composite soil samples being tested for metals were taken to a commercial lab, Meridian Analytical lab that uses EPA method 6010B for metals analysis (USEPA, 2007). Potential sources of error for metals analysis include; accidently introducing chat into soil samples when going from grid to grid and the site not being a natural landscape (i.e. one sample might have a large amount of the host rock within it).

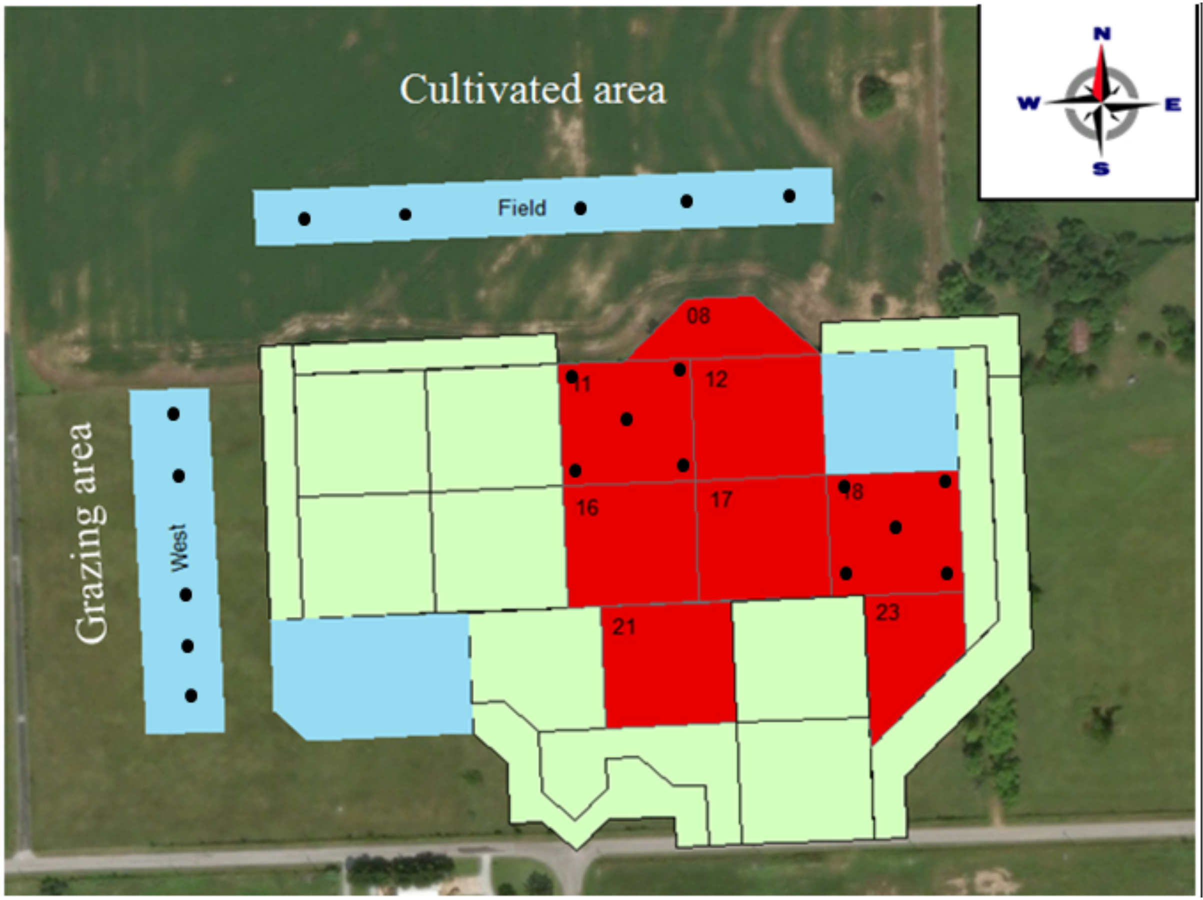

Figure 6: Estimates of sub-sampling points for agriculture parameters and metals

Table 4: GPS locations of sub-samples for grids 11, 18, West, and Field.

Grid	GPS coordinates	
CP009-11A	36.94546284 N	-94.87712453 W
CP009-11B	36.94565879 N	-94.87735616 W
CP009-11C	36.94528995 N	-94.87737492 W
CP009-11D	36.94529842 N	-94.87692207 W
CP009-11E	36.94564032 N	-94.8768870 W
CP009-18A	36.94495762 N	-94.87578282 W
CP009-18B	36.94515309 N	-94.87578282 W
CP009-18C	36.94478574 N	-94.87598257 W
CP009-18D	36.94479983 N	-94.87598257 W
CP009-18E	36.94516080 N	-94.87553038 W
WEST-A	36.94535410 N	-94.87889182 W
WEST-B	36.94515922 N	-94.87885056 W
WEST-C	36.94495490 N	-94.87881077 W
WEST-D	36.94447593 N	-94.87878196 W
WEST-E	36.94447593 N	-94.87889266 W
FIELD-A	36.94616908 N	-94.87559361 W
FIELD-B	36.94616645 N	-94.87580659 W
FIELD-C	36.94619563 N	-94.87593784 W
FIELD-E	36.94620594 N	-94.87605085 W
FIELD-F	36.94623295 N	-94.87631797 W

Comparison of Lab Methods 6010B and 3050B

The labs selected for this study conform to the parameters being analyzed and follow the recommendations set out by the Quality Assurance Project Plan developed by the Quapaw Tribe (Quapaw Tribe, 2015). The Oklahoma State University SWAFL uses method 3050B and Meridian Analytical lab uses method 6010B for metals analysis; however, these methods are very similar. Duplicate sampling and analysis by both methods determined that the results are comparable (USEPA, 1984). The duplicate sampling run in September had a general average of 30% or less difference between the two methods, refers to Appendix B.

However, there were a few outliers, in the West grid Zn and Cd was 405 ppm and 15.2 ppm higher, respectively with method 6010B, for grid 18 Pb and Cd were 206 ppm and 2.75 ppm lower, respectively with method 6010B, and in the grid Field, Cd was 1.7 ppm lower with method 6010B. These outliers can be accounted for by the sampling method that entails combining five sub-samples to make one composite sample. Because there can be a significant difference in metals levels among the grid, soils could have different levels of metals during duplicate sampling. Similarities between methods 6010B and 3050B include, the use of inductively coupled plasma mass spectrometry (ICP-AES), analysis run at ambient temperature, and the digestion completed with concentrated nitric acid (EPA 1996a; EPA1996b). The major differences between the two methods is that method 6010B uses a microwave and 3050B uses a digestion block for the extraction process, 6010B includes some additional QA/QC measures once analysis is complete, and 3050B uses H_2O_2 instead of HCL for a reagent (EPA 1996a; EPA1996b).

The difference with using the microwave verses the digestion block can be accounted for because the microwave method is more expensive but takes less time, whereas the digestion block is less expensive and takes more time. However, the results are comparable, as the use of a digestion block versus a microwave has virtually no effect on the resulting extraction and analysis.

Results

The results from the soil texture testing, Daubenmire vegetation surveys, forage clips, agricultural parameters, and metals sampling are presented below to help determine effectiveness of the EPA-mandated amendments implemented at CP009 in reducing/stabilizing the levels of Pb, Zn, and Cd present in the soil. Each parameter of this study was conducted in grids 11 and 18 along with the control grids, West and Field, with the exception of the forage clips only being obtained from the Field grid.

Soil Texture

The soil texture analysis revealed that the soils in grid 11 were sandy clay, with 40% clay, 14% silt, and 46% sand. Grid 18 was a clay loam with 31% clay, 27% silt, and 42% sand. Field and West were sandy clay loam with 24%, 17% silt, and 53% sand and 29% clay, 19% silt, and 52% sand, respectively. These soil textures, especially clays, tend to increase the sorption of metals because of high surface area (Ouli & Kavannagh, 1999).

Daubenmire

Daubenmire results for grids 11 and 18 were collected by the Quapaw Tribe during their quarterly sampling to establish how vegetation was impacted by the application of the amendment. For this study, the Daubenmire results taken after the amendment was applied (March 2017) where compared to the last quarterly sampling period that the Quapaw Tribe conducted (August 2017). The results, as seen in Table 5, indicate an increase in litter and forbes and a decrease of bare ground for grid 11 and 18. While there was a slight decrease in grasses for grids 11 and 18, 9% and 20% respectively, the overall vegetation increased from 77% to 93% for grid 11 and 90% to 97% for grid 18.

Grids 11 and 18 were then compared to the two control grids, West and Field, as the grids establish a baseline of typical vegetative cover without the application of the amendments. The West control grid had essentially the same vegetative cover for both sampling periods; whereas, the Field had slightly more cover (7%) in September. The Field grid could have had an increase in vegetation during September because litter from the previous crop was still present in the field. While neither the West nor Field control grid received soil amendments, the West grid is more indicative of typical vegetation at CP009 as it is not a cultivated area. Therefore, since the West grid did not have an increase in vegetative cover; whereas, the grids that received the soil amendments did, it can be inferred that the application of the amendment increased the vegetation present at CP009, as seen in Figure 7.

Table 5: Daubenmire results in percentage of vegetation for grids 11 and 18.

Grid11	**Mar-17**	**Aug-17**
Grass	43%	39%
Forbes	6%	12%
Litter	28%	42%
Bare ground	23%	8%
Rock	0%	0%
Overall Vegetation	**77%**	**93%**

Grid 18	**Mar-17**	**Aug-17**
Grass	45%	36%
Forbes	0%	15%
Litter	45%	46%
Bare ground	3%	3%
Rock	6%	0%
Overall Vegetation	**90%**	**97%**

West	**Mar-17**	**Sept-17**
Grass	24%	28%
Forbes	1%	0%
Litter	64%	63%
Bare ground	11%	8%
Rock	0%	0%
Overall Vegetation	**89%**	**91%**

Field	**Mar-17**	**Sept-17**
Grass	80%	79%
Forbes	3%	5%
Litter	2%	8%
Bare ground	15%	2%
Rock	0%	0%
Overall Vegetation	**85%**	**92%**

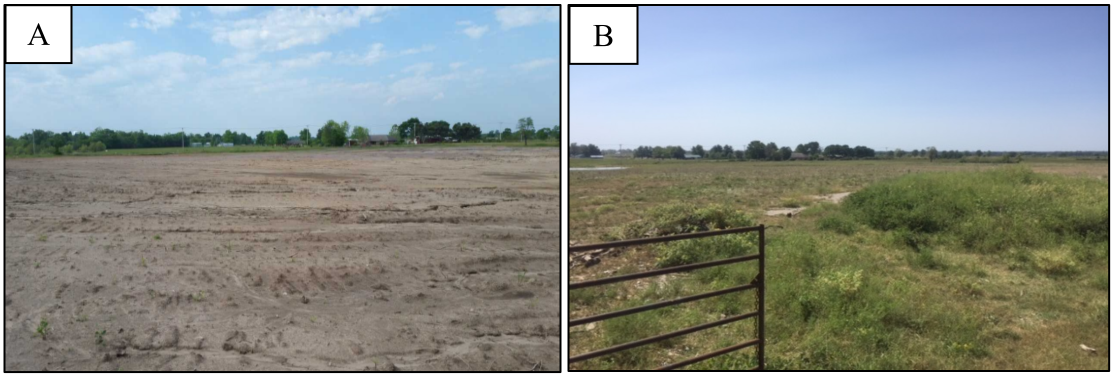

Figure 7: A) CP009 post chat removal B) Vegetation establishment at CP009 during September 2017 sampling period.

Forage

While crop production is not a designated future use for CP009, the amount of Pb, Zn, and Cd present in the crops adjacent to CP009 were evaluated. To determine the amount of Pb, Zn, and Cd that were taken up by plants, the crops grown in the Field grid were sampled (note that two crops winter wheat and soybeans are grown in the Field grid) and compared to the concentrations in soil, as seen in Table 6. Percent uptake was calculated to determine if the plants exceeded concentrations that would adversely impact plant growth. According to the EPA publication, *Heavy-Metal Accumulation in Soil and Vegetation from Smelter Emissions,* if plants exceed 10 ppm of Pb, 400 ppm for Zn, or 1.35 ppm of Cd, it is possible that the vegetation will have growth reduction (Ratsch, 1974). The results indicate that Pb was absorbed at the lowest percentage 8-9%, while Zn was absorbed at 39-92% and Cd was absorbed at 55-81%, depending on the crop. Only one forage sample exceeded the levels set out by the EPA publication; Cd in the soybeans (September 2017). However, the Daubenmire tests revealed no evident sign of decreased plant growth in the field, as seen in Figure 8.

Table 6: Concentrations in soil and wheat and soybeans crops within field grid.

Metal (threshold)	Soil Conc. (Mar 2017)	Conc. in Wheat (ppm)	Percent uptake	Soil Conc. (Sept 2017)	Conc. In Soybean (ppm)	Percent uptake
Pb (10 ppm)	80.6	7.1	9%	81.4	6.6	8%
Zn (400 ppm)	127.8	103.3	39%	189.8	174.6	92%
Cd (1.35 ppm)	1.8	0.7	81%	2.9	**1.6**	55%

Figure 8: Soybeans within Field grid during September 2017 sampling period.

Because CP009 has a designated potential future use of grazing, the plant uptake levels were compared to studies of metals poisoning in cattle. For lead, poisoning could occur in animals if the concentrations of Pb in the bloodstream are over 0.35 ppm, 10 ppm for the liver or kidney (Blakley, 2018). Additionally, many countries have deemed blood lead concentrations greater than 0.05 ppm to be a notifiable disease in food-producing animals (Blakley, 2018). For zinc, animals can suffer from zinc toxicity if their diets contain levels of zinc greater than 2,000 ppm (Cahill-Morasco, 2018). For cadmium, one study found that levels of Cd in muscles, liver, and kidney of cattle for human consumption should not exceed 0.05, 0.5, and 1.0 ppm, respectively (Lane and Canty, 2018). While it is difficult to convert levels of plant uptake to bloodstream or tissue concentrations, the percent uptake of metals by the two crops should be noted and further studied. The concentrations of Pb, Zn and Cd that can cause problems for animals and/or food supplies vary by plant, amount consumed, species, and a host of other variables.

Agriculture Parameters

The agriculture parameters (OM, P, K, N, and pH) were analyzed on a quarterly basis, as seen in Table 7. The addition of the amendment increased OM, P, K, N, and pH in both grids 11 and 18, with the percent change noted in Table 7. In grid 11, N was highest in September; however, the rest of the agriculture parameters (P, K, OM, and pH) were highest in June. In grid 18, N was highest in December, K was highest in June, and P, OM, and pH were highest in September. .

Organic Matter: OM in grids 11 and 18 is highest in June and September. This could be because on average, June and September are the hotter months in the TCSS, therefore fostering the most microbial activity (U.S. Climate Data, 2018; FAO, 2005).

Potassium and pH: Potassium and pH levels increase after the amendment is applied and stay relatively constant throughout the sampling period.

Phosphorus: Levels of P are highest during the hottest months of the year at the TCSS, June and September. This infers that P is highest in June and September because these months have the highest pH, therefore limiting the fixation of P under acidic conditions to other nutrients present in the soil (Crouse, 2017).

Nitrogen: Typically, N leaches from soil easily, as seen in grid 18 (Crouse, 2017); however, grid 11 shows N concentration in the soil staying relatively consistent throughout the duration of testing.

The control grids, West and Field, stayed consistent throughout the sampling period, with the exception of the increase in P and K and the decrease of N in the Field grid during June. The increase in the agriculture parameters is essential to the amendment process, because the increase of nutrients leads to an increase in complexation and sorption of metals to the soil (USEPA, 2007). Additionally, the increase of the nutrients fosters plant growth that will stabilize the landscape and prevent erosion (USEPA, 2007).

Table 7: Quarterly average post amendment and percent change for agriculture parameters (N, P, K, OM, and pH) for grids 11, 18, West, and Field.

Grid 11	Nitrogen (lbs/A)	Phosphorus (lbs/A)	Potassium (lbs/A)	OM%	pH
May-16 PreAmed	2	8	199	1.5	5.2
Dec-16	10	20	268	1.38	5.8
Mar-17	14	6	316	1.17	5.4
Jun-17	11	170	457	3.04	6.5
Sep-17	24	26	336	1.42	5.8
Dec-17	12	15	414	1.4	6.3
Avg PostAmed	14.2	55.5	358.2	1.6	5.9
% Change	610	594	80	12	13

Grid 18	Nitrogen (lbs/A)	Phosphorus (lbs/A)	Potassium (lbs/A)	OM%	pH
May-16 PreAmed	2	19	154	1.7	5.3
Dec-16	17	47	470	2.14	6.1
Mar-17	1	31	458	1.95	6.5
Jun-17	7	295	706	3.26	7
Sep-17	2	316	476	4.11	7.1
Dec-17	0	133	411	2.72	7
Avg PostAmed	5.4	177.3	504	2.8	6.7
% Change	170	807	227	67	26

West	Nitrogen (lbs/A)	Phosphorus (lbs/A)	Potassium (lbs/A)	OM%	pH
Mar-17	1	11	133	2.78	5.7
Jun-17	2	21	162	5.3	5.2
Sep-17	0	10	93	2.7	6
Dec-17	1	26	194	2.7	6
Average	1.3	17	140.5	3.33	5.6

Field	Nitrogen (lbs/A)	Phosphorus (lbs/A)	Potassium (lbs/A)	OM%	pH
Mar-17	11	255	356	2.14	5.7
Jun-17	1	501	671	2.1	5.2
Sep-17	12	222	391	2	5.8
Dec-17	15	76	345	1.6	6
Average	9.75	255.33	440.75	2.13	6

Metals

The results from the confirmation sampling performed by the Quapaw Tribe in March 2016 were compared against quarterly sampling of grids 11 and 18 along with two control grids, West and Field. Grids 11 and 18 were sampled during June, September, and December 2017; whereas, West and Field were sampled during March, June, September, and December 2017. The quarterly sampling results from grids 11, 18, West and Field and the average post amendment levels for grids 11 and 18 can be found in Table 8.

For grids 11 and 18 the average post amendment value was calculated to identify if the overall levels of Pb, Zn, and Cd had decreased/stabilized over the sampling period. The average post amendment levels for Pb and Cd decreased from the pre-amendment or Benchmark sampling. In grid 11, Pb decreased by 45% and Cd decreased by 55%; whereas, in grid 18 Pb decreased by 77% and Cd decreased by 33%. However, Zn increased in both grids 11 and 18, 108% and 39%, respectively.

The average post amendment concentrations indicate if the amendment decreased or increased the metals concentrations from the pre-amendment levels for grids 11 and 18; however, the metals had significant variance throughout the quarterly analysis, as seen in Table 8. From quarter to quarter, the percent change was calculated, in addition to the percent change from pre-amendment to average post amendment concentration. For grid 11, the largest percent difference from quarter to quarter for Pb (20 fold) and Cd (1000 fold) was between the June to September sampling period; whereas, for Zn the largest quarterly difference (2 fold) was between the March to June sampling period. For grid 18, the largest percent difference from quarter to quarter for Pb (4 fold) was between the June to September sampling period and Zn (4 fold) and Cd (2 fold) was between the September to December sampling period. Since the control grids, West and Field, did not have a pre-amendment level, the percent change was calculated from the initial sampling in March 2017 to the last sampling period, December 2017. This study did not establish clear patterns of metals behavior or concentrations through quarterly sampling. The large variances from quarter to quarter, as seen in Table 8, are also provided in maps of CP009 (figures 9-11) to help visualize the changes seen throughout the study.

Table 8: Quarterly sampling results and percent change of Pb, Zn, and Cd from quarter to quarter for grids 11, 18, West, and Field.

LEAD Results (in ppm) (Percent Change by Quarter)						
Remedial Goal < 500 ppm						
Grid	**Mar-16 PreAmendment**	**17-Mar**	**17-Jun**	**17-Sep**	**17-Dec**	**Average of quarterly results (compared to Pre-Amend)**
CP009-11 (% Change)	561	-	31.60 (-94%)	644 (1938%)	248 (-61%)	308 (45% reduction)
CP009-18 (% Change)	1110	-	46.70 (-96%)	194 (315%)	510 (193%)	250 (77% reduction)
West (% Change)	-	403	83.30 (-79%)	107 (28%)	98.90 (-8%)	173 (75% reduction)
Field (% Change)	-	110.20	67.70 (-16%)	55.50 (-18%)	49.20 (-11%)	70.65 (39% reduction)
ZINC Results (in ppm) (Percent Change by Quarter)						
Remedial Goal < 1100 ppm						
Grid	**Mar-16 PreAmendment**	**17-Mar**	**17-Jun**	**17-Sep**	**17-Dec**	**Average of quarterly results (compared to Pre-Amend)**
CP009-11 (% Change)	1910	-	3350 (75%)	4640 (39%)	3910 (-16%)	3966 (108% increase)
CP009-18 (% Change)	1300	-	2470 (90%)	551 (-78%)	2400 (336%)	1807 (39% increase)
West (% Change)	-	480	132 (-73%)	544 (312%)	159 (-71%)	329 (67% reduction)
Field (% Change)	-	168	100 (-22%)	132 (32%)	86.3 (-35%)	122 (32% reduction)
CADMIUM Results (in ppm) (Percent Change by Quarter)						
Remedial Goal < 10 ppm						
Grid	**Mar-16 PreAmendment**	**17-Mar**	**17-Jun**	**17-Sep**	**17-Dec**	**Average of quarterly results (compared to Pre-Amend)**
CP009-11 (% Change)	10.60	-	0.01 (-100%)	10.20 (101900%)	4.24 (-58%)	4.80 (55% reduction)
CP009-18 (% Change)	13.10	-	15.50 (-18%)	3.15 (-80%)	7.84 (149%)	8.83 (33% reduction)
West (% Change)	-	5.30	1.39 (-74%)	17.40 (1152%)	1.39 (-92%)	6.37 (74% reduction)
Field (% Change)	-	3	1.28 (-29%)	1.22 (-5%)	0.01 (-99%)	1.40 (99% reduction)

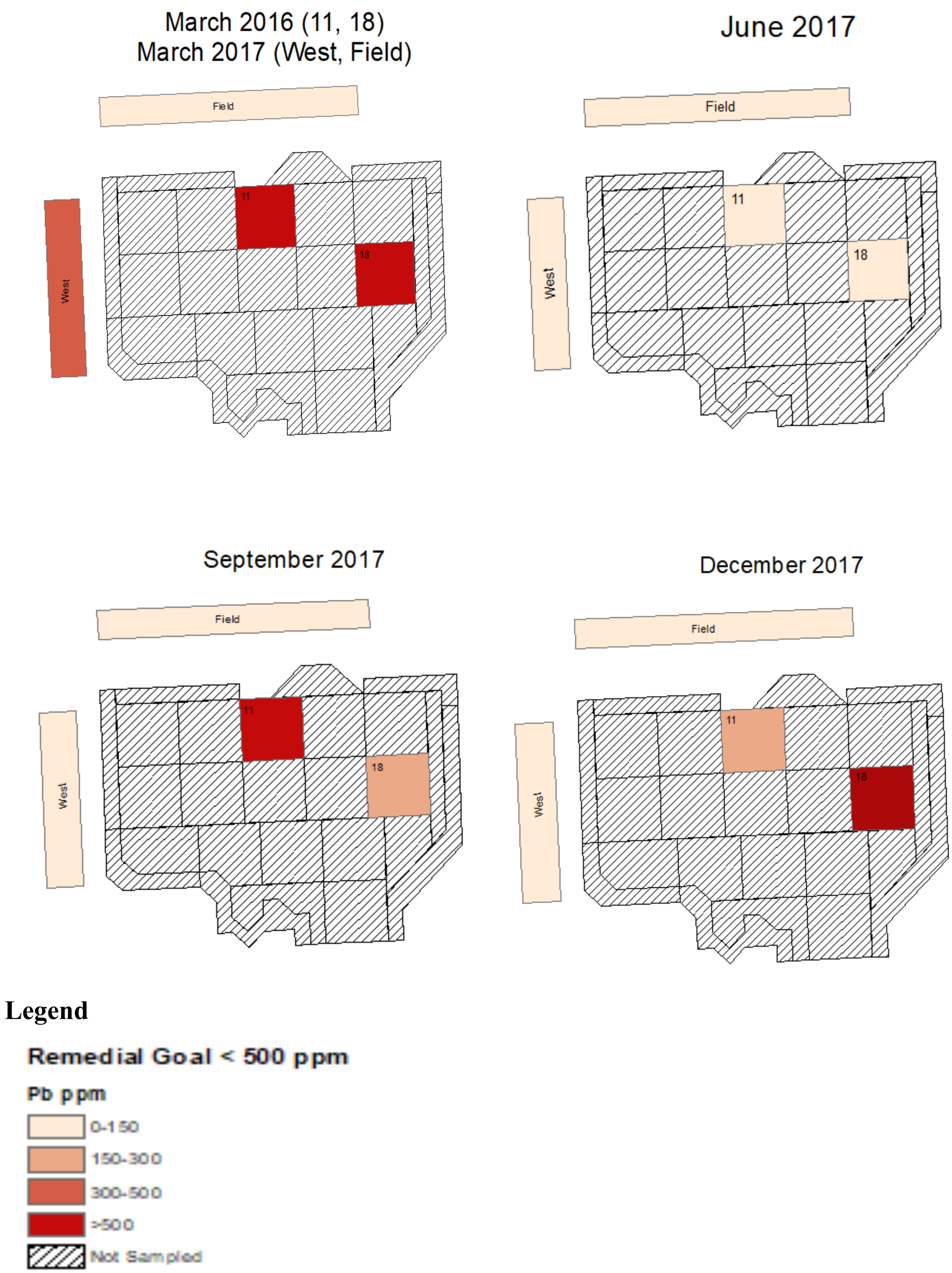

Figure 9: Pb levels for grids 11, 18, West, and Field for each sampling quarter

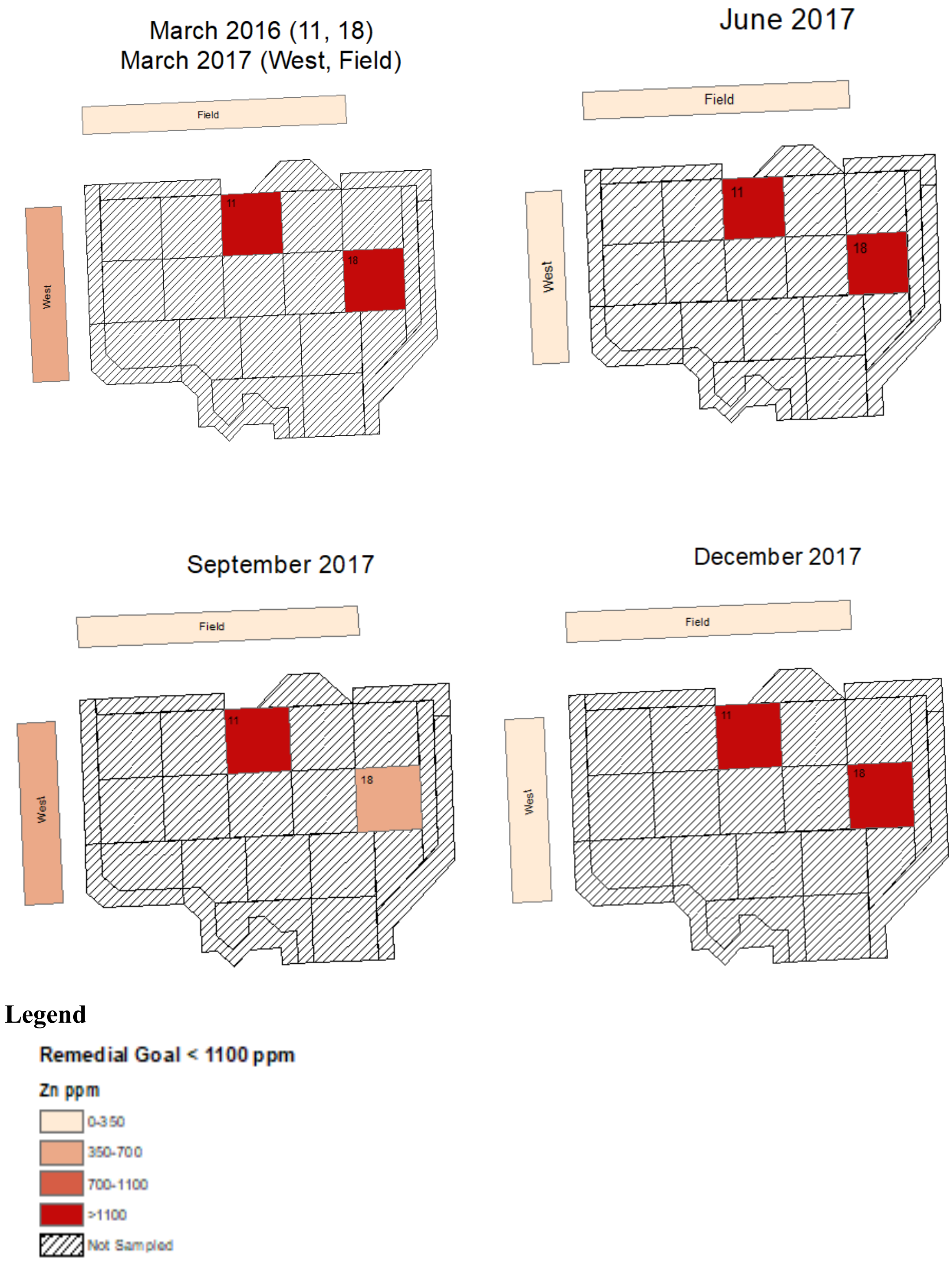

Figure 10: Zn levels for grids 11, 18, West, and Field for each sampling quarter

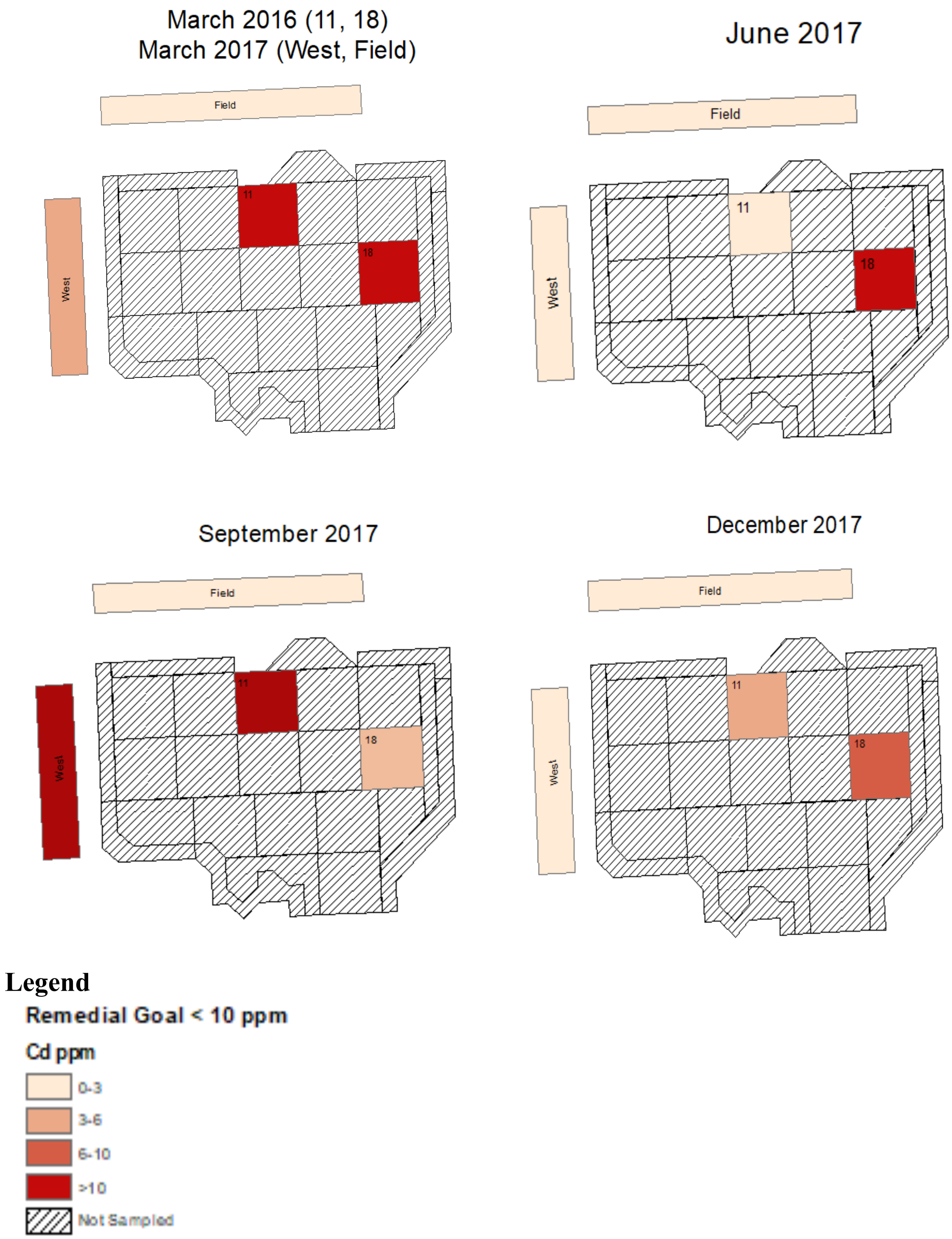

Figure 11: Cd levels for grids 11, 18, west, and field for each sampling quarter

Agriculture Parameters and Metals Correlations

The data for each agriculture parameter (OM, P, K, N, and pH) along with Pb, Zn, and Cd concentrations were projected on a scatterplot to determine if correlations were present, as seen in Figures 12-16. Note that there were not enough sample points collected for these correlations to be statistically significant. The correlations were run to simply establish whether potential trends exist in the data. Correlations between the agriculture parameters and the metals could give insight to the quarterly metals variability seen at CP009. Typically, an increase in nutrients increases the sorption of metals to soils, therefore, an inverse relationship between nutrients and the concentrations of the metals is anticipated (USEPA, 2007).

Organic Matter: The most notable correlation was the inverse relationship between the metals, Pb, Zn, and Cd and OM, as seen in figure 12. This strong relationship is seen during the June sampling period, as the increase in OM is accompanied by a decrease Pb, Zn, and Cd with the exception of Zn and Cd on grid 18. Significant portions of metals will be bound by OM, so as the OM increases the sorption of metals to the soil will increase (Quenea et al, 2009).

Potassium and pH: There is no evident consistent trend when K or pH is compared to Pb, Zn, and Cd, with the exception of the inverse relationship with K and Pb as seen in figure 13-14.

Phosphorus: Phosphorus exhibits an inverse relationship with the metals, with the exception of Cd on grid 18, as seen in figure 15. The inverse relationship with P and Pb, Zn, and Cd may be the result of P increasing the sorption of metals in the soil (Bolan et al, 2003).

Nitrogen: Nitrogen has a positive relationship to Pb, Zn, and Cd, as the increase in nitrogen causes an increase in the metals concentrations, with the exception of Pb for Grid 18, as seen in figure 16.

The control grids, Field and West, stay relatively consistent throughout the quarterly sampling, as seen in figures 12-16, with Field being controlled by cultivation and West being controlled by cattle grazing within the area

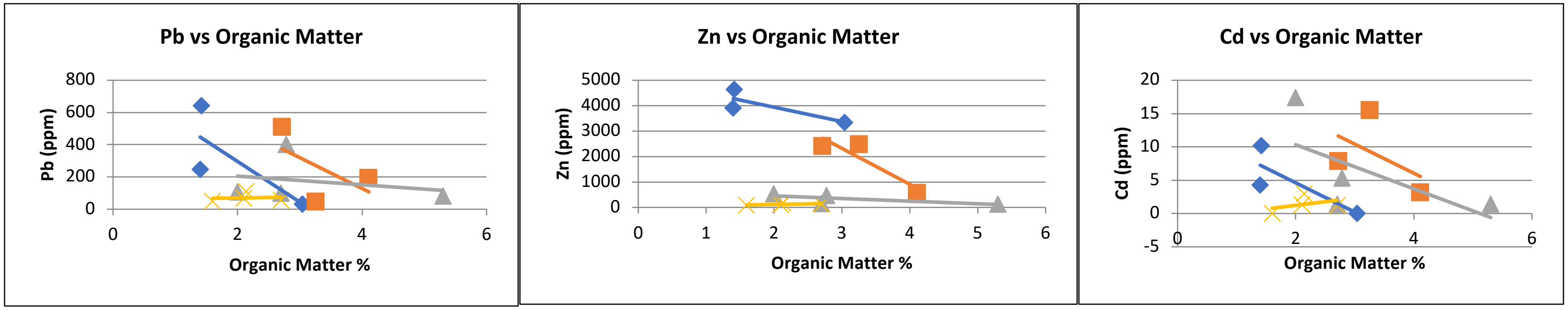

Figure 12: Comparison of Pb, Zn, and Cd to Organic matter

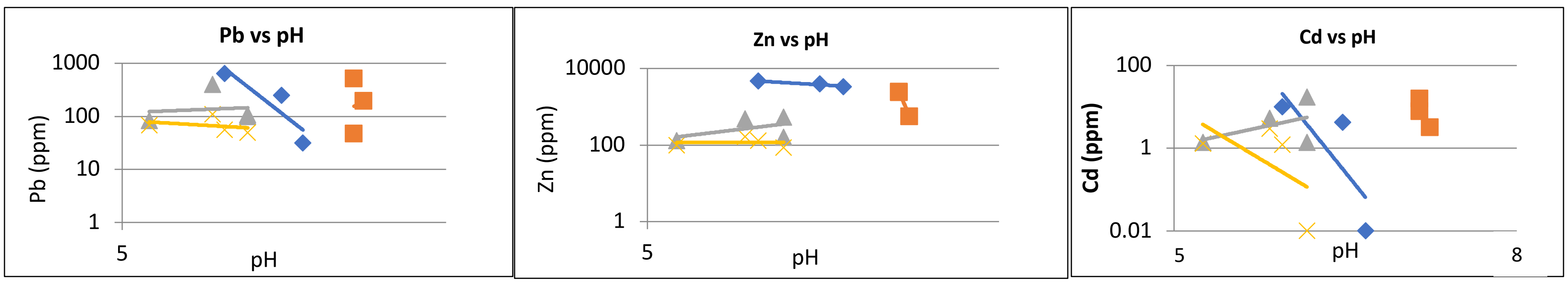

Figure 13: Comparison of Pb, Zn, and Cd to pH (scale is in logarithm)

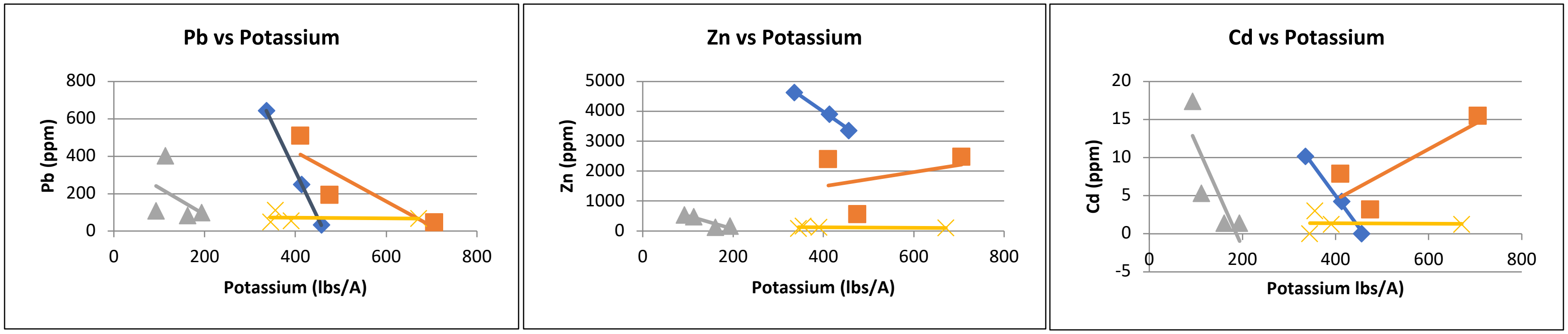

Figure 14: Comparison of Pb, Zn, and Cd to Potassium

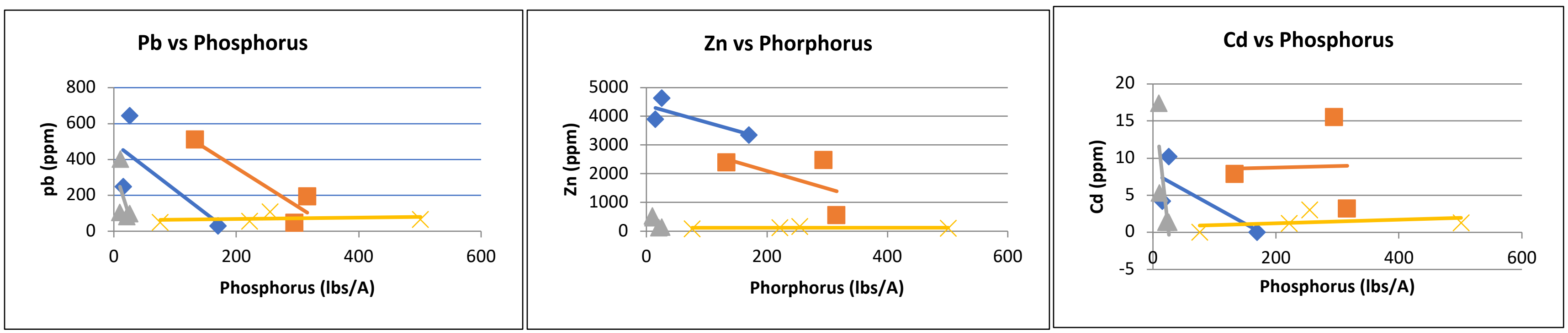

Figure 15: Comparison of Pb, Zn, and Cd to Phosphorus

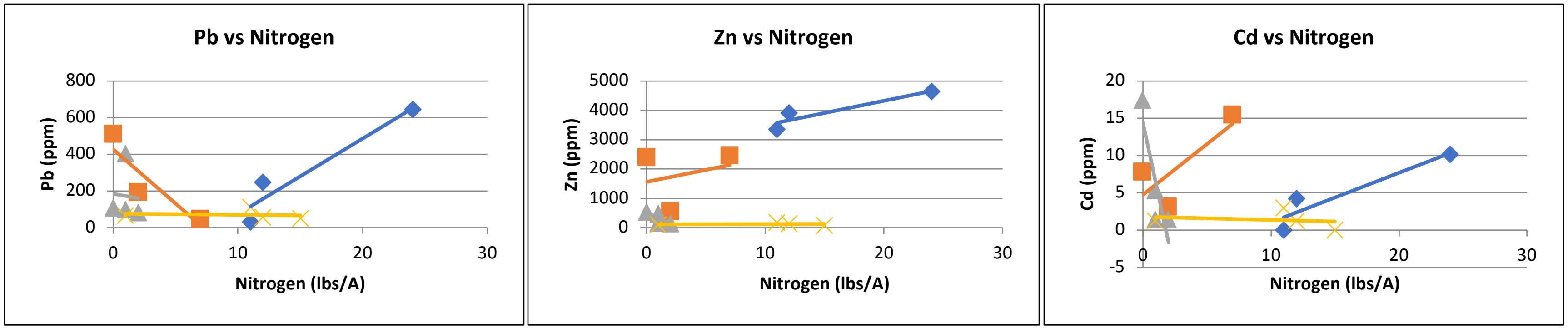

Figure 16: Comparison of Pb, Zn, and Cd to Nitrogen

Legend

Grid 11 — Linear (Grid 11)

Grid 18 — Linear (Grid 18)

West — Linear (West)

Fie ld — Linear (Field)

Discussion and Conclusions

This thesis was a pilot study for this specific kind of amendment being applied on a site without topsoil removal and the first time metals analysis has been done on a quarterly basis within the TCSS. While there is literature noting the impacts of different kinds of soil amendments on metals concentrations, this is the first time a combination of chicken litter, ag lime, and mushroom compost have been used to sorb metals.

To fully characterize the impact from the application of the amendment, various parameters such as soil texture, vegetation surveys, forage sampling, agriculture parameters, and metals concentrations were analyzed during this study. Soil textures throughout TCSS are silt loam and clay loam (USDA, 2018), which generally align with the soil textures found at CP009; sandy clay (grid 11), clay loam (grid 18), and sandy clay loam (West and Field). These soil textures have a high surface area, especially that of clay, which form a matrix and reduce bioavailability of metals to vegetation (Ouli & Kavannagh, 1999). When Daubenmire results were analyzed, the results indicated that vegetation present within grids 11 and 18 at CP009 exhibited positive growth patterns despite the high metal concentration in the soil. The increase in vegetation could be due to the immobilization of metals and/or the increase in nutrients from the soil amendments. Positive growth patterns for vegetation in metal contaminated soil were also seen in a study that applied a soil amendment of manure that increased radish growth (Walker et al., 2003).

The forage clips taken within the Field grid indicate that the metals were taken up at high rates from both crops, with Pb absorbed at the lowest rate 8-9%, Zn from 39-92% and Cd from 55-81%. These results can serve as indicators of bioavailability, especially for that of Pb and Cd as they are not essential elements for plants (Pugh et al., 2002). While forage within the Field grid did not display phytotoxic levels of Pb, Zn, or Cd, if vegetation within CP009 absorbed similar percentages, phytotoxic conditions could occur. Potential phytotoxic levels of Zn and Pb have occurred in other Pb/Zn mining areas, in vegetation such as bog blueberry (*Vaccinium uliginosum*) and willow (*Salix*) (Pugh et al., 2002).

Throughout the sampling period there were notable variances in quarterly concentrations of Pb, Zn, and Cd. The concentrations of Pb and Cd are typically under the benchmark of 500 ppm for Pb and 10 ppm for Cd; whereas, the concentrations of Zn are consistently over the benchmark level of 1100 ppm. During the quarterly analysis, Cd had the most variance, followed by Pb and Zn. Since the variance did not follow a pattern within the sampling period, similar to the study by Brown (2004), the mean concentrations were determined in an effort to eliminate temporal variability. When the means were calculated, Pb and Cd in grid 11 and 18 decreased, while Zn increased from the pre-amendment levels. Another study that used sewage sludge as organic matter also found an increase in Zn after the application of the amendment, specifically the leachability of Zn (Herwijnen et al., 2007).

To help determine the reactions of metals in the field, the correlations between agricultural parameters and the metal concentrations were established. Note these correlations are not statistically significant and are purely to establish trends throughout the study. The most notable correlation found during this study period was the inverse relationship between organic matter and metal concentrations. This correlation could exist because OM is a contributing factor to cation exchange capacity (CEC) within the soil and the organic fraction has a significant influence on metal binding (Brown and Lemon, 2018; Rieuwerts et al, 2015). Walker (2003) found that when amendments of compost and manure were applied, CEC increased by 38 and 21% respectively. Additional studies found that the solubilization of Pb, Zn, and Cd have occurred because of complexes with organic matter (Rieuwerts et al., 2015).

While there was not a consistent correlation between the metals and the pH, this could be due to the pH not increasing enough to have an impact on metals concentrations. This relationship was found in another study where a compost soil amendment had little effect on the pH due to a high buffer capacity of the soil (Herwijnen et al, 2007). However, it should be noted that pH and metals had a high correlation coefficient; therefore, if more data was acquired to make the correlations statistically significant, an inverse relationship could be established.

Other patterns noted, were the inverse relationship with P and the metals. This relationship could be the results of P increasing the sorption of metals in the soil (Bolan et al., 2003). Additionally, a similar inverse pattern was established between K and Pb, however not with Zn or Cd. One atypical pattern established by the correlations was the positive relationship between nitrogen and the concentrations of the metals, as typically an increase in nutrients would increase the sorption mechanism in the soil (USEPA, 2007).

Overall, this study found that the means of Pb, Zn, and Cd along with the correlations for the agricultural parameters indicate that the amendment was successful in reducing/stabilizing levels of Pb and Cd, however not Zn.

Areas of Future Study

Patterns established during this study can help facilitate future research on the soil amendments being applied at TCSS. Since there is evidence of the relationship between organic matter and concentrations of metals, future research could focus on the rate that organic matter breaks down and when it needs to be reapplied by continuing to test quarterly until OM is stabilized. This is essential because as OM decomposes the metals that were previously adsorbed might be rereleased and become available to plants and animals (Herwijnen et al, 2007). Since organic matter fosters aerobic activity, research focusing on how microorganisms influence cation exchange capacity within soil particles, as their activity could potentially account for variation seen in the quarterly sampling at CP009 is recommended.

Additionally, since one potential use for CP009 is grazing land, the uptake of Pb, Zn, and Cd by cattle should be monitored. These studies could indicate how cattle will be influenced if they are ingesting contaminated vegetation on a regular basis. Monitoring is especially important as lead poisoning in animals can cause ataxia, blindness, salivation, twitching of eyelids, muscle tremors, and convulsions (Blakley, 2018). Similarly, zinc toxicity can cause anorexia, vomiting, diarrhea, and lethargy; in particular, large animals often show a decrease in weight gain and milk production (Cahill-Morasco, 2018), and cadmium toxicity can damage kidneys and bones (Lane and Canty, 2018).

Lastly, there was a significant amount of variability within the quarterly analysis, therefore, it would be beneficial to sample twice a year, for a minimum of 5 years. This sampling method will help to establish better trends in metal concentrations over time and help eliminate some temporal and spatial variability. Overall, future research is essential, not only at Tar Creek but worldwide, as soil amendments can help to reduce/stabilize metals and preserve vital topsoil.

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APPENDIX A

Agriculture parameters for all grids over the remedial level taken by the Quapaw Tribe

P (lbs/A)	May-16	Dec-16	Mar-17	Jun-17	Sep-17	Dec-17
CP009-08	25	49	62	37	29	-
CP009-11	8	20	6	170	26	15
CP009-12	56	53	67	43	52	-
CP009-16	644	14	171	204	61	-
CP009-17	553	123	39	56	832	-
CP009-18	19	47	31	295	316	133
CP009-21	5	21	10	12	48	
CP009-23	-	27	13	25	56	-

N (lbs/A)	May-16	Dec-16	Mar-17	Jun-17	Sep-17	Dec-17
CP009-08	11	11	2	6	3	-
CP009-11	2	10	14	11	24	12
CP009-12	2	23	3	14	2	-
CP009-16	1	17	10	50	11	-
CP009-17	1	17	3	9	18	-
CP009-18	2	17	1	7	2	0
CP009-21	3	22	1	6	5	-
CP009-23	-	20	1	3	2	-

K (lbs/A)	May-16	Dec-17	Mar-17	Jun-17	Sep-17	Dec-17
CP009-08	241	303	221	220	239	-
CP009-11	199	268	316	457	336	414
CP009-12	155	340	575	473	441	-
CP009-16	212	243	532	547	520	-
CP009-17	122	339	391	557	660	-
CP009-18	154	470	458	706	476	411
CP009-21	162	427	326	433	399	-
CP009-23	-	177	169	428	348	-

pH	May-16	Dec-17	Mar-17	Jun-17	Sep-17	Dec-17
CP009-08	7	7.2	7.5	7.5	7.5	-
CP009-11	5.2	5.8	5.4	6.5	5.8	6.3
CP009-12	5.9	6.5	6.6	5.9	6.8	-
CP009-16	5.2	5.7	5.2	5.9	5.9	-
CP009-17	5.1	5.3	5.5	5.3	6.1	-
CP009-18	5.3	6.1	6.5	7	7.1	7
CP009-21	5.9	6.3	6.1	5.8	6.8	-
CP009-23	-	5.2	5	5.6	5.8	-

OM %	May-16	Dec-16	Mar-17	Jun-17	Sep-17	Dec-17
CP009-08	2.12	3.52	2.42	2.88	2.62	-
CP009-11	1.5	1.38	1.17	3.04	1.42	1.4
CP009-12	1.88	2.19	2.25	2.13	2.22	-
CP009-16	1.19	1.32	1.75	1.89	1.59	-
CP009-17	1.3	2.09	1.69	1.97	4.03	-
CP009-18	1.7	2.14	1.95	3.26	4.11	2.72
CP009-21	1.65	2.03	1.51	1.2	2.38	-
CP009-23	-	2.24	2.06	2.69	3.31	-

APPENDIX B

Calculated percent change between methods 3050B and 6010B for grids West, Field, 11 and 18

	3050B	**6010B**	**% Change**
West (Pb)	96.9	107	10
West (Zn)	139.4	544	290
West (Cd)	2.2	17.4	691
Field (Pb)	81.4	55.5	-32
Field (Zn)	189.8	132	-30
Field (Cd)	2.9	1.2	-58
Grid 11 (Pb)	503	644	28
Grid 11 (Zn)	4986	4640	7
Grid 11 (Cd)	11.7	10.2	13
Grid 18 (Pb)	400	194	52
Grid 18 (Zn)	591	551	7
Grid 18 (Cd)	5.9	3.15	47

VITA

Madison Michele Peppers is from Borger Texas and is the daughter of Mark and Cathy McKinney. She graduated from Borger High School in Borger, TX in 2012. She then went to Oklahoma State University and received a Bachelor of Science in Environmental Science in 2016. While at Oklahoma State she worked with the Quapaw Tribe of Oklahoma and the Environmental Protection Agency to address soil and water contamination within the Superfund Site of Tar Creek

Furthering her education and her research at Tar Creek, she attended Texas Christian University (TCU). At TCU, her research focused on the effectiveness of applying soil amendments to contaminated soil as a remedial effort within the Tar Creek Superfund Site. While working on her Masters she held a Teaching Assistantship from 2017-18 and is currently a candidate for a Masters in Science in Environmental Science. After graduation, she plans to join Targus Environmental Group to become an environmental consultant.

ABSTRACT

ANALYSIS OF THE EPA-MANDATED SOIL AMENDMENTS AT TAR CREEK SUPERFUND SITE

By Madison Peppers, M.S. 2018
School of Geology Energy and the Environment
Texas Christian University

Thesis Advisor: Becky Johnson, Professor of Professional Practice

Committee Members: Dr. John Holbrook, Professor of Geology

Dr. Michael Slattery, Professor of SGEE

Tar Creek Superfund Site had extensive lead and zinc mining that caused contamination throughout the soil and water systems. Remediation is currently ongoing and includes application of soil amendments to reduce concentrations of lead (Pb), zinc (Zn), and cadmium (Cd). As part of this study, we tested whether this mandated amendment was effective by conducting quarterly sampling for a year after amendments were applied. Samples were submitted for laboratory analysis to determine total levels of Pb, Zn, and Cd, in addition to organic matter (OM), pH, phosphorus, potassium, and nitrogen. Results show an overall decrease in the amount of Pb and Cd within the soil system, but an increase in Zn. Additionally, an inverse relationship between metals and OM and metals and select nutrients was identified. Future research could focus on how each component of the soil amendment combined with weather and precipitation impacts the success of such remediation methods.