Phytoremediation of Heavy Metals and PAHs at Slag Fill Site:

Three-Year Field-Scale Investigation

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Abstract: Big Marsh is a 121-hectares site, representative of many other sites in the Calumet region (near Chicago, IL, USA), which has been significantly altered by the steel industry and decades of legal and illegal dumping and industrial filling. The slag-containing soil at the site has been found to be contaminated with polycyclic aromatic hydrocarbons (PAHs) and heavy metals. Due to the large size of the area to be remedied, and variable distribution of the contaminants throughout the shallow depth at slightly above the risk-based levels, phytoremediation is considered as a green and sustainable remedial option. The objective of this work was to investigate the use of phytoremediation in a 3-year field–scale study, specifically determine plant survival and the fate of PAHs and heavy metals in soil and plant roots and stems. Replicate test plots were prepared by laying a thin layer of compost at the ground surface and then tilling and homogenizing the slag-soil fill to a depth of approximately 0.3 m. Nine native and restoration plant species were selected and planted at the site, and their survival and growth were monitored and fate of contaminants in soil and plants were also monitored for three growing seasons. Sequential extraction procedure was performed to determine the fractionation of the heavy metals in soils before and after planting. The results showed a decrease in PAHs concentrations in the soil, probably due to enhanced biodegradation within rhizosphere. No significant decrease in heavy metal concentrations in soil was found, but they were found to be immobilized. Contaminant concentrations were found below detection limits in the plant roots and shoots samples, demonstrating insignificant uptake by the plants. Overall, selected native grasses in combination with compost amendment to the soil proved to be able to survive under the harsh site slag fill conditions, helping to degrade or immobilize the contaminants and lowing the risk of the contaminants to public and the environment.

Keywords: Mixed contamination; soils; compost amendment; rhizosphere; degradation; immobilization

1. Introduction

Big Marsh is one of the largest sites within the Calumet region, representative of many other sites in this region which have been significantly altered by the steel industry and decades of legal and illegal dumping. The site has been massively altered from original conditions by industrial filling, and these fill materials as well as the groundwater and surface water have been found to be contaminated with polycyclic aromatic hydrocarbons and heavy metals above or near the legal limits (CDM 2010, Terracon 2011, IEPA 2014). Such sites with mixed contamination pose technical challenges due to different physico–chemical properties of the multiple contaminants, making application of remediation technologies difficult and expensive. In this context, phytoremediation has potential to be a benign, cost effective alternative for the treatment of contaminated sites with mixed contamination (Cameselle et al. 2013). Phytoremediation can cause the contaminant removal, stabilization or degradation in soils due to different mechanisms such as rhizofiltration, phytodegradation, phytoaccumulation (or phytoextraction), phytostabilization, and rhizodegradation (also called phytostimulation) (Sharma and Reddy 2004).

A previous study showed that the mixed contamination in the soil can have a significant effect on the plant growth (Chirakkara and Reddy, 2014). The ability of the plants to survive in high impacted areas and the low bioavailability of the contaminants in the soil are some of the limiting factors that influence phytoremediation efficiency. Phytoremediation can be enhanced by selecting plants with increased capability for contaminant uptake or by amending the soil to increase plant growth and the microbial communities that could assist in the biodegradation of organic contaminants. The addition of organic matter to the soil can improve the soil and increase the plant biomass in phytoremediation (Masciandaro et al., 2013). The addition of compost to the soil can improve plant growth as well as increase soil microbial activity (Ghanem et al., 2013). Compost is expected to immobilize the metal

contaminants in the soil, as well as buffer the elevated pH in slag, thus plant germination and growth are expected to improve in composted soil (Alvarenga et al., 2014).

The aim of our study was to investigate the potential for using phytoremediation of PAHs and heavy metals in near surface soils and fill materials at the Big Marsh site. Three different areas of the site were identified and investigated: a slag disposal area, a wet meadow area, and an upland area (Amaya-Santos, 2016). This paper presents the study results for the slag disposal area. Specifically, the study was conducted over three growing seasons to evaluate plant survival and growth and the fate of contaminants in the soil and plants.

2. Research Methodology

2.1. Initial Soil Characterization

A delineation survey was conducted to determine the extent and boundary of the slag disposal area at Big Marsh. The initial baseline sampling was conducted on the site in order to identify the existing heavy metal and organic contaminants present in the soil and to inform the subsequent plot set-up. Five composite samples were taken along transects representing roughly equivalent conditions at the Slag Disposal Area. Sampling locations were recorded using a GPS. Collected soil samples were characterized for their physico-chemical properties and contaminant concentrations (using the methods detailed in Section 2.6). Some of the contaminant concentrations were found to slightly exceed the allowable risk-based levels, hence remediation deemed necessary (Amaya-Santos, 2016).

2.2. Test Section Preparation

Based on the initial baseline soil sampling, two plots- an experimental plot and an adjacent plot, each of size 16m x 16m, were demarcated in the slag disposal area. Figure 1 shows the experimental and adjacent plots layout. The soil in both plots was prepared by adding a thin layer of compost on the surface and then tilling and homogenizing the soil to an approximate depth of 0.3 m (the maximum depth that was feasible with the use of conventional equipment).

The experimental plot consisted of two different types of subplots for herbaceous (GP, or Grasses and Plugs) and woody plants (TS, or Trees and Shrubs) (Figure 1a). A total number of 5 subplots, each 3m x 4m in size, were selected as GP plots. Each subplot was divided further into 6 groups of size 1.3m x 1.3m, and each group was divided into 16 cells of size 0.3m x 0.3m (Figure 1b). Another 5 subplots of size 3m x 3m each, were selected as TS plots, and each subplot was divided into 4 groups, each 1.5m x 1.5m (Figure 1c).

The adjacent plot (16m x 16m) was delineated next to the experimental plot with the purpose of monitoring plant survival and grow characteristics of the grass species.

One composite soil sample from each group location at each subplot of the experimental plot was collected for baseline soil characterization and contaminant concentration analysis.

2.3. Plant Selection and Planting

The plants were selected from a list of native plants of interest for site restoration purposes, with additional consideration for their fitness to adapt to site-specific soil characteristics and for literature-demonstrated potential phytoremedial properties. A total of nine plant species were chosen, including five species of grass and plugs and four species of trees and shrubs (Table 1).

These plant species were planted in each block as individual species and as a mix to assess any plant synergistic effects. Each species was planted with 16 specimens in each of five individual subgroups, and three plants of each species were planted in the mixed subgroup. A total of 96 grass samples were planted within the experimental plot, and 20 grass samples were planted in the adjacent plot.

Within the plot intended for planting trees and shrubs (TS plots), a subdivision into groups for the different species was also performed. In this case, no subgroup was intended for planting mixed species. At each subgroup, only one particular woody species was planted, and a total of 20 woody species (trees and shrubs) were planted within the experimental plot. No woody samples were planted in the adjacent plot. Table 1 shows the experimental and adjacent plots along with the total number of plant samples planted.

2.4. Watering and Monitoring

Once soil preparation and planting was completed, the test plots were watered twice a week throughout the first summer months (June to August) and monitored weekly for survival, leaves, pests and infection, and height of the woody plants during the first growing season. At the adjacent plot, only survival monitoring was performed. Table 2 shows the rating system used to assess plant monitoring.

During the second growing season, the test plots were monitored bi-weekly during the summer. No additional water or pest control was performed in order to allow the plants to grow under normal conditions and assess the suitability of the native plants to cope with the natural site conditions and compete against the invasive species.

2.5. Termination Sampling

6

At the end of the second growing season, a first set of soil and plants sampling was performed. Six soil samples from each of five GP plots where plants survived were collected, resulting in a total of 30 soil samples. All soil samples were kept on ice and transported to laboratory. Vegetative biomass from surviving plants was also taken from each GP plot, divided into above ground (leaves and shoots) and belowground (roots) biomass.

At the end of the third growing season, a terminal sampling was performed. A total of 30 soil samples were collected from all GP subplots where plants survived. Vegetative samples consisting of roots, leaves and shoots were also collected from each surviving species.

Additionally, two grab samples from invasive vegetation (Sweet Clover) were also taken.

Target contaminants (BaP, As, Cr, Pb and Mn) were analyzed in all soil and vegetative tissues samples. Also, complete analysis of metals and PAHs was performed on selected soil and vegetative samples. Soil samples were also tested for physico-chemical properties.

2.6. Analytical Methods

The soil characterization included measurements of the pH, electrical conductivity (EC), organic carbon (OC), oxidation–reduction potential (ORP), water holding capacity (WHC), grain size distribution (GSD), and nutrient content.

The soil pH and ORP were determined according to the ASTM D4972 – 01 Standard Test Method for pH of Soils (ASTM 2007). The values were measured in the laboratory using an Orion Model 720-A pH/ISE meter. Water content values were measured according

to ASTM D 2216 Standard Test method for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass (ASTM 2005). Organic carbon was determined using ASTM D 2974 Standard Test Method for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils (ASTM 2000). The electrical conductivity of the soil was measured in a 1:5 soil: water suspension, using a Fischer Scientific model TRACEABLE^{TM} conductivity meter. Grain size distribution was determined according to ASTM D 422-63 Standard Test Method for Particle Analysis of Soils (ASTM 2002). To analyze exchangeable nitrogen, 1 g soil was shaken with 10 mL of 2M KCl solution for 1 h (Xu et al., 2013). The filtered extractant was analyzed using Spectronic Genesys Spectrophotometer, following the procedure given by Sattayatewa et al. (2011). To determine the exchangeable fractions of potassium and phosphorus, 1 g soil was shaken with 1M ammonium acetate for 1 h. The solution was filtered, and the extractant was analyzed for phosphorus with Spectronic Genesys Spectrophotometer, as per the procedure given by Sattayatewa et al. (2011). The water holding capacity (WHC) of the soil was determined following the ASTM D2980 – 04 Standard Test Method for Volume Mass, Moisture – Holding Capacity and Porosity of Saturated Peat Materials (ASTM 2010).

Soil and vegetative samples were sent to STAT Analysis Corporation (Chicago, IL, USA) for sample acid digestion and analysis of total metal concentrations (EPA method SW6020) with Inductively Coupled Plasma Mass Spectrometry (ICP/MS). Polycyclic Aromatic Hydrocarbons (EPA method SW8270C) were also tested by Gas Chromatography Mass Spectrometry (GC/MS).

Sequential extraction analyses of soil and plant samples were performed using the procedure summarized in Table 3 in order to determine the speciation of the contaminants in the soils both before and after the phytoremediation technique is implemented. This procedure was originally developed by Tessier et al. (1979) and has been extensively used for

the speciation of trace metals in natural soils and sediments into five fractions: (1) Exchangeable, (2) Bound to carbonates, (3) Bound to Fe-Mn oxides, (4) Bound to Organic Matter, and (5) Residual (which consists of the prior four fractions summed – up and subtracted from the total concentration). However, the residual fraction of the soil in this work was obtained by acid digestion, following the EPA 3050 method. Samples from sequential extraction were sent to STAT Analysis Corporation (Chicago, IL, USA) for analysis of total metal concentrations (EPA method SW6020) with Inductively Coupled Plasma Mass Spectrometry (ICP/MS).

Very limited statistical analyses were performed due to limited sets of data. Where possible, mean and standard deviation were calculated using Microsoft Office Excel 2013. To check whether a significant difference exists between the result sets, the t-test was performed with Microsoft Office Excel 2013. The alpha value was taken as 0.05 for the t-test.

3. Results and Discussion

3.1. Initial Soil Characterization

The results for the initial soil characterization are shown in Table 4. The average pH value of the surface soil at the beginning of this study was 7.48. The slag dumped throughout the region is mainly iron slag generally characterized by a high alkalinity. The results for pH found in the surface, were lower than expected, possibly due to that soil was sampled mainly from the surface, where there was a thin top soil layer that covered the high pH slag layer underneath. The oxidation–reduction potential (ORP) is an index of the exchange activity of electrons among elements in solution. The results show a negative potential, which indicates reducing conditions in the initial soil. The organic matter content found initially in the soil

9

was also very low, evidencing the need to amend the soil to increase the survival probabilities of the plants. Grain size distribution shows that the soil has a high fraction of coarse grained particles, mainly due to the predominance of debris and fill material in the experimental area.

Table 5 shows the concentration (mg of contaminant per kg of dry soil) for different polynuclear aromatic hydrocarbon (PAHs) compounds and metals that were found initially in the soil at the experimental area. Benzo(a)pyrene, with the highest concentration in the initial soil (0.43 mg/Kg –dry soil) is the target contaminant representative of the presence of PAHs in the experimental area, due to its known carcinogenic and mutagenic potential. Numerous heavy metal species were found in the initial soil. Some of them such as chromium (300 mg/kg – dry soil) and lead (400 mg/Kg- dry soil) were found in concentrations above the maximum allowable risk–based levels (Amaya-Santos, 2016).

3.2. Soil Characterization after Compost Amendment and Tilling

As expected, tilling and homogenization affected the soil physical properties. The soil pH after the amendment and tilling increased to 9 as compared with the values obtained for the initial soil sampling (Table 4). The mixing of the alkaline slag layer underneath the top soil during homogenization could have induced this increase, masking the possible effect of the addition of compost on the soil pH. However, the organic matter incorporation had a direct immediate impact on organic carbon content which increased from 4% to 8%, as well as the magnitude of the reduction potential also increased. The exchangeable nitrate concentration increased up to 46% after the addition of compost amendment. The water holding capacity increased in the soil after adding compost, resulting in more water available for the plants. The grain size distribution showed a decrease of coarse fraction and an increase of fines after tilling, reflecting constituents in the compost.

The total PAHs concentrations of the soil after adding compost are shown in Table 5. No significant differences in the concentration values were found before and after the soil preparation. However, concentrations of metals such as As and Pb increased in soil after tilling. The reason why the presence of heavy metals in the soil is greater after tilling, could be the same as that for the pH increase. When tilling the surface soil, the underlying slag layer that is rich in metals, is mixed with the top soil cover, thus increasing these values in the mixed soil.

The results of the percentages of the different fractions of metals in the soil before and after tilling are shown in Table 6, and the results for heavy metals such as As, Cr, Pb and Mn, the selected target contaminants in the present study, are plotted in Figure 2. As it can be observed, the exchangeable fraction of metals in the soil is very low (Table 6), and it remains constant after tilling and compost addition. Overall, the amended soil showed an increase in the organic bound fraction of the metals, which was likely due to the effect of compost addition. The residual fraction of As and Cr decreased slightly while that of Pb and Mn increased after adding compost (Figure 2).

3.3. Plant Monitoring

Figure 3(a) shows the surviving percentages of the plants based on monitoring results for the first and second growing seasons. During the first growing season, the native grass species had stronger growth and survivorship rates than the woody species. Such is the case of Switchgrass (SWG), Purple Prairie Clover (PPC) and Little Bluestem (LBS), which performed the best across the test plot area with 100% of survival at the end of the first growing season. The survival rates found in the adjacent plots were similar to those at the experimental plots. The increasingly growth of invasive species in the study area made it very

difficult to record the growth monitoring of the study plants in detail during the second growth year. Trees and shrubs showed poor performance compared to grass species at the end of the second season. The plants survival and leaf quality assessment (Figure 3b) and the height (cm) of the trees and shrubs (Figure 3c), were monitored only during the first growing season, with the aim of carrying out a detailed monitoring of the development and growth of plants and their adaptation to the ground. Due to the presence of invasive species and the poor survival rates of trees species, height values were not recorded during the second season.

No monitoring was performed during the third growing season. However, field observations made when the terminal sampling took place revealed lower survival rates than in the prior two seasons in the test area. At the end of the experiment, only 4 out of the 9 species initially planted survived in the contaminated site, all of them being grass species. The soil pH and high contaminant concentration could be the main reason of the poor performance of the woody species. A special investigation during the experimental period took place on site, in order to measure the changes of soil pH with depth. These results showed that the soil at a depth 22 cm below the surface within the experimental plot area had an average pH of 9.9 (results not shown). According to the USDA plants database, all of the woody species used in our study had an optimum pH range from slightly acid to neutral (USDA) and the prevailing pH at the site are not optimal for survival and growth conditions for all the species. Additionally, the trees and shrubs used in this experiment were also visibly affected by the presence of invasive species and pests in the field.

Trees have been suggested as a low cost, sustainable and ecologically sound solution to remediation of heavy metal–contaminated land (Dickinson, 2000) and benefits can arise mainly from stabilization of the soil. However, before these benefits can be realized, the trees must become established on a site, and this establishment can be inhibited by high concentrations of heavy metals (Pulford et al., 2003). Other factors may limit trees growth,

such as macronutrients deficiencies (Pulford 1991) and physical conditions. The harsh conditions at the experimental area, the presence of invasive species, and the proximity of the slag layer underneath the composted top soil, combined with the high concentration of contaminants could have been the main causes of the poor survival of trees within the experimental area.

Previous results obtained from a lab-scale study pointed that phytotoxicity could be the cause of the poor performance of the plants in contaminated areas and it showed low growth characteristics as well as the survival rates by the combined contaminated conditions (Chirakkara and Reddy, 2015). Therefore, the addition of compost may have decreased the bioavailable contaminants, leading to low phytotoxicity and better performance of grasses and plugs. The experimental area is an upland, barren slag field that was expected to hinder growth and survivorship of plants due to the lack of topsoil and existence of high pH. However, the presence of native grasses was noticeable in all the subplots at the end of the experiment. The effect of the slag layer did not seem to cause an important impact on grasses. On the other hand, compost did not countered the negative effects of the slag layer to the woody species, possibly due to that the soil amendment was not applied to a sufficient soil depth required for the development and establishment of the relatively depper root system of these trees.

Contrary to what occurs with native species, the presence of invasive species Sweet Clover was predominant in the experimental area, and it seemed to thrive towards the end of third growing season. The ability of this species to fix atmospheric nitrogen is attributed to rhizobium symbiosis, which could be the key to resist metal toxicity (Chaudri et al, 2000). Other studies showed that legumes are the dominant portion of wild species that survive in long–term metal contaminated environments (Del Rio et al. 2002).

3.4. Fate of PAHs

The overall results for PAHs concentrations throughout the experiment can be found in Table 5. No significant differences ($p > 0.05$) were found in the PAHs concentrations of the unplanted initial soil and after compost amendment and tilling. On the contrary, the results in the soil at the end of the third season, in presence of plants, show an overall decrease in the PAHs concentrations. Results show that concentration of BaP in the planted soil decreased at the end of the third growing season ($p < 0.05$). Table 7 shows in detail the results for contaminant concentrations in the soil for the surviving species at different plot locations at the end of the second and third seasons. As compared with the values obtained in the soil samples before planting (Table 5), the concentration of PAHs decreases in all the surviving species plots, reaching in some cases undetectable levels. The Benzo(a)pyrene concentrations in the soil decreased 28% in the Switchgrass plot, 38% in the Little Bluestem plot, 45% in the Purple Prairie Clover plot and 47% in the Yellow Coneflower plot. Similar tendency is observed for the rest of the PAHs analyzed (Tables 5 and 7).

Table 8 shows the results for the PAHs contaminant concentration in the vegetative aerial tissue (stems and leaves). As it can be seen, at the end of the second growing season, no significant presence of PAHs was found either in leaves or stems, since all concentrations were below detection limits. At the end of the third season, only Benzo(a)pyrene concentration was analyzed, and the results show that the concentration of this organic contaminant was below detection limits for all the surviving species. Similar response was observed in the invasive species Sweet Clover, where PAHs content in leaves and stems was insignificant (results not shown). The PAH concentrations in the roots of the surviving species are shown in Table 9. As it can be observed, the majority of PAH concentrations were

found below detection limits or in a very low concentration. Overall, these results show that the initial concentration of PAHs is dissipated in the soil at the end of the experiments.

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds with multiple aromatic rings, with low volatility and their persistence in the environment. In soils, these compounds can be dissipated by either one or a combination of mechanisms such as microbial degradation and volatilization (Gabet, 2004; Park et al., 1990; Saison, 2001). Although the dissipation of low molecular weight and volatile PAHs can be achieved by natural dissipation through soil indigenous microbes (Huang et al., 2004, Zhang et al., 2012), the compost has been shown to enhance PAH degradation in a number of studies by improving soil texture for oxygen transfer, and providing energy to the microbial population (Haritash and Kaushik, 2009). The presence of plants can also be the cause of the dissipation of PAHs in the soil, since they can break down or degrade the contaminants by metabolic processes (Kang 2014, Balasubramaniyam 2015, Wang et al., 2012). However, there are no congruent evidences that there are synergistic effects between plants and compost in terms of PAHs dissipation. While there are studies that confirm that the organic contaminants are degraded in the presence of plants and in amended soils (Vouillamoz and Milke., 2001; Chirakkara and Reddy., 2015), but there are also studies in which degradation of PAHs did not show such synergistic effect (Ghanem et al., 2013, Wang et al., 2012). Although the results of this study show that there is a degradation of the PAHs initially present in the soil, the specific degradation mechanisms are unclear. In general, the dissipation of the organic contaminants can occur either by one or a combination of the following mechanisms: (1) *rhizodegradation*- degradation in the roots of the plants as a result of microorganism activity and root enzymes and exhudates (Myresiotis et al., 2012, Huesemann et al., 2009, Schnoor et al., 1995), and (2) *phytodegradation*- direct uptake of contaminants and metabolization in the plant tissues (Al-Baldawi et al., 2015).

Regardless of the degradation mechanism, numerous factors can also contribute to the degradation rate of the PAHs, such as the number of rings (Park et al., 1990, Huang et al., 2004). In the present study, the soil samples at Yellow Coneflower plot show a higher concentration of PAHs of 5 and 6 rings such as Benzo(b)fluoranthene (Table 7), and in some cases, such as Benzo(g,h,i)perylene and Benzo(k)fluoranthene, the dissipation is insignificant. A high pH media such as the soil of this study, can also affect PAHs dissipation. The results obtained by Moretto et al. (2005) showed that PAHs degradation decreases due to high pH and when organic matter is added.

The results of the present work are consistent with numerous studies that have evidenced the degradation of PAHs in presence of Switchgrass (Pradhan et al. 1998, Murphy et al. 2011, Meggo et al, 2013), and Little Bluestem (Pradhan et al, 1998). However, little information is known about the effect of Yellow Coneflower and Purple Prairie Clover on the degradation of those organic compounds.

Despite some studies observed that the addition of organic matter to the soil improves the degradation of organic contaminants, the effect of the plants in absence of soil amendment in the degradation of PAHs has not been the scope of the present study. Therefore, the invidual versus synergistic effect of compost amendment and the surviving species in PAHs degradation cannot be ascertained. However, results of the present study confirm that the presence of compost seems to enhance the plant growth under hard surviving conditions and reduce the phytotoxicity by the contamination. Therefore, compost or other organic amendment provides a promising approach for enhancing phytoremediation of mixed contaminated soils (Chirakkara and Reddy, 2015).

3.5. Fate of Heavy Metals

The overall results of heavy metal concentrations in soil are shown in Table 5. As compared to the unplanted soil after compost addition and tilling, no significant differences can be found at the end of the third growing season, except for As that showed slight increase ($p < 0.05$). The results for the total metals concentration in soil at the plots of the surviving species are presented in Table 7. These results show that the metals in the soil tend to remain unchanged in the soil after compost addition (Table 5) and throughout the experiment. Similar tendency for heavy metals present in the soil such as Cr, Pb and Mn is observed for all surviving species plots, which suggests that the presence of plants in the experimental plots did not affect the concentration of heavy metals in the soil. Arsenic, on the other hand, has a different behavior, and its concentration tends to increase when compared to the unplanted soil (Table 5). However, it does not show significant differences between the different plot locations ($p > 0.05$).

The total metals concentrations in stems and leaves of the surviving species can be found in Table 8. At the end of the third growing season, only the results for the target contaminants (As, Cr, Pb and Mn) are shown. As it can be observed, the concentrations of heavy metals in the plants were below detection limits in all cases, except for Mn that was detected in the aerial vegetative tissue at the end of the third growing season, although there are no significant differences in the average values at the end of the second and third growing seasons ($p > 0.05$).

The total metal concentrations in roots was also measured and results can be found in Table 9. The concentration of heavy metals such as Cd and As was not detectable in roots throughout the experiment. However, it did not occur the same way for Cr, Pb, Mn and Zn, which were detected in the roots of the surviving plants. Although the concentration of Cr and Mn did not show significant difference in the roots of the surviving species throughout the experiment ($p > 0.05$), their average values in SWG roots when they were collected at the

17

end of the second growing season showed high variability (SD ±108 and ±8223, respectively). The concentration of Pb only showed differences in SWG roots, were slightly decreased at the end of the experiment (p<0.05).

The metal fractionation results based on the sequential extraction procedure in the soil at the plots of the different surviving species at the end of the experiment are shown in Table 10, and the results for the target heavy metals are plotted in Figure 3. As it can be observed, at the end of the third growing season, the exchangeable fraction of the metals present in soil remains very low, without significant changes in the soil for the different species. Generally, no changes are observed in the distribution of the fractions in which metals present in the soil during the entire project duration. As explained above, the percentage of metal retained in the organic fraction increased after the addition of compost amendment during soil preparation. However, no significant changes were observed in the distribution of metals from then onwards.

Among the target contaminants studied in the present work (Figure 3), As is the metal (metalloid) that presents certain percentage retained in the exchangeable fraction. However, the concentration of this metal in the vegetative tissue of the surviving species was undetectable (Tables 8 and 9). The low mobility of As could be due to the fact that a major percentage was retained in the residual fraction. Although Pb also presents a high percentage retained in the residual fraction, concentrations of this metal in the roots of the surviving species were detected. The distribution of Pb in other fractions more assimilable by the plant, such as Fe–Mn oxides bound, could be a determinant factor to its uptake. Cr and Mn, however, present a higher percentage of retention in the Fe–Mn oxides bound fraction, with Mn almost completely retained in this fraction. The presence of these metals in the plant suggest the existence of specific mechanism to uptake Mn and Fe oxides by the plant, which make other metals retained in this fraction available for the plant as well.

18

The results obtained in the present study show a low mobility of heavy metals in the soil during the entire project duration, possibly due to its retention in the solid phase. Welp et al. (1999) showed that the partitioning of metals between the solid and liquid phase is mainly controlled by pH, becoming stronger with high values of pH. In general, sorption increases when increasing pH, which means that the more soil is acidic, the more metal can be found in solution and thus more metal can be mobilized. The adsorption mechanisms tend to be higher when the values of pH are also high (Sherene, 2010). However, the mobilization in alkaline soils can also be subjected to kinetic limitations (Villén–Guzmán et al. 2015). With the addition of organic amendments, such as compost, and in presence of plants, heavy metals are expected to form soluble complexes with organic ligands (McLean and Bledsoe, 1992; Karami et al., 2011). Nevertheless, at the conclusion of this study, no significant variation in the metal concentration values (P>0.05) were found in the soil. These results are consistent with those obtained by Alvarenga et al (2009), in which pseudo total concentration of soil metals did not change significantly when organic residues were applied, pointing that besides pH, the addition of organic amendments with a high proportion of humified organic matter is an important factor to control metal bioavailability.

Although the of As in soil is detected at the end of the experiment, no presence of this metalloid was found either in the plant nor roots, suggesting that the As was not chemically mobilized, and therefore was not available. The chemical speciation of As is a major concern when remediation techniques are applied. Studies suggest that the presence of soil amendment with high content of organic matter, such as compost, reduces the content of As(III) (Maňáková et al.,2014) or promotes the oxidation of As(III) to As(V) (Hartley et al., 2009). The latter study, suggests that the microbial mediated activity, favored by the presence of compost, plays an important role in changing the speciation of this compound. Similarly, the toxicity and mobility of Cr in soil depends on its oxidation state. Thus, Rendina et al.

(2011) reported that the addition of compost to the contaminated soil increased Cr(III) concentration, less toxic, compared to the unamended soil that presented higher concentration of Cr(VI). The results obtained by Banks et al. (2006) suggested that the organic matter played a significant role in mobility of Chromium in soil due to the reduction of the mobile Cr(VI) to the relatively immobile Cr(III). In the present study, oxidation state of metals was not studied, but the low concentration of Cr and As in the vegetative tissue, suggest that the solubility of these compounds is very low, making them not available for plant uptake.

According to Shahid et al. (2012) and Hashimoto et al. (2009), organic ligands are capable of modifying Pb speciation by forming organo–metallic complexes and hydroxyl complexes that can increase solubility, bioavailability and toxicity of this metal. Although this could explain the presence of Pb in roots, the concentration of this metal decreases in the plant at the end of the experiment, with negligible detection in the leaves and stems (Table 10), indicating that there is no effect on the mobilization of this metal, inside the plants.

Juárez-Santillán et al (2010) showed that alkaline and reducing substrate conditions favor the presence of Mn^{2+}, which is the most soluble form of Mn, as well as the most assimilable form by plants. This could explain the higher concentration of Mn found in the present study in stems and leaves (Table 8) and in roots (Table 9), as compared to the rest of heavy metals. However, the results for the fractionation of Mn in the present study, are not consistent with those obtained by Juárez-Santillán (2010), where the residual soil fraction was the highest, followed by Mn–Fe oxides. In the present work, the highest retention of Mn was found in the fraction bounded to Mn–Fe oxides followed by the residual fraction.

The ability of Switchgrass and Little Bluestem to uptake or immobilize heavy metals in soil has been found in the literature. Results obtained by Levy et al. (1999) showed that metal concentration in alkaline soils amended with organic matter were found under detection limits in Switchgrass shoots, consistently to those results obtained in the present study.

Gudichuttu (2014) showed that the Pb concentrations in Switchgrass and Little Bluestem shoots are lower at high compost treated soil, as compared to the unamended soils. The same tendency is shown in the results obtained by Chen et al (2012), where metal concentrations in the plant were directly proportional to the increase of heavy metal in the solution. However, the conditions of the latter study are slightly different, while hydroponic cultures with contaminated solutions instead of soils are used. No evidences in the use of Yellow Coneflower or Purple Prairie Clover have been found in the literature.

Although unfortunately the plant growth in unamended contaminated soil was not studied in the present work, literature suggests that the presence of compost is key in the immobilization of the contaminants. As far as it has been surveyed in the present study, the addition of compost amendment was the main contributor to plants survivorship and reduced the toxicity caused by the presence of heavy metals. However, the results in the present work show that the contribution of compost amendment towards the stabilization of heavy metals in the soil is not conclusive.

3.6. Fate of Contaminants in Root Soil

In order to evaluate the differences in the bulk soil versus in the root zone soil (rhizosphere), soil from the surviving species roots were collected and analyzed. The rhizosphere encompasses the millimeters of soil surrounding a plant root where complex biological and ecological processes occur. Table 11 compares the bulk soil characterization results to those obtained from the root zone soil characterization, at each surviving species subplots. As it can be observed, the pH values in the root zone soil is slightly lower for LBS and YCF, compared to the pH in the bulk soil in the same plots. As it was expected, higher values of organic content are found in the root zone soil, likely due to the presence of humic acids, roots

exudates and living organisms in the root system. On the other hand, the moisture content of the soil at the root zone was very low as compared to the bulk soil, but not representative of field conditions due to this soil was collected from the roots once the samples were oven dried in the lab.

The results of the root zone soil sequential extraction are shown in Table 12, and the comparison of the fractionation percentages in the soil inside and outside the root zone can be found in Figure 4. As it can be observed, the distribution of As in the root zone soil does not present significant changes in the studied plant species, with the exception of YCF, that exhibits a mobilization of the residual fraction towards the organic and residual phases. In the case of Cr, there are observable certain changes in the distribution of this metal. For SWG, the fraction retained in the organic phase increases to the detriment of the fractions retained in the Fe and Mn oxides and in the organic–bound fraction. Moreover, in LBS the fraction of Cr retained in the residual fraction is also higher in the root zone soil, where also increases the fraction bounded to the organic matter. This tendency is also observed for YCF. The distribution of Pb in the root soil is very similar to that in the bulk soil, with the difference of a higher retention in the residual fraction observed in the three species analyzed. Mn, on the other hand, is the metal that presents major changes. While it remains predominantly retained in the Fe–Mn oxides bound fraction, the percentage decreases slightly in the root zone soil, increasing the percentage retained in the residual fraction. However, an increase of retention in the carbonates–bound fraction is also observed, which could explain a higher mobility of this element.

Rhizodegradation is plant-assisted biodegradation or bioremediation in the rhizosphere (the soil around the roots of a plant). The root exudates of plants can improve the living environment of indigenous microorganisms indirectly by reducing the toxicity of soil contaminants, improving the spatial heterogeneity of the rhizosphere environment, and

promoting the growth of rhizosphere microorganisms, thereby resulting in the enhancement of biological activity of microorganism, and ultimately improving the degradation ability of the rhizosphere microorganism to PAHs (Chaudhry et al., 2005 and Parrish et al., 2005).

4. Practical Implications

The harsh conditions of the slag disposal area at Big Marsh site were exacerbated due to tilling. The mixing of underlying slag with the surface soil could have jeopardized the success of the plants. It would be advisable, accordingly with the results obtained from this study, to homogenize and mix the top soil layer, without mixing with the underlying slag as much as possible.

In phytoremediation, plants are ideally chosen such that they can cover a significantly large root surface area and are capable of adapting to the conditions of the soil. From an economic viewpoint, plants that require less maintenance such as fertilizing or frequent trimming are preferable. As such, feasibility studies have focused on the *Graminaeae* family or commonly known as grass since these species have very fibrous root systems which extend over a large surface area and penetrate deeper into the soil. The use of deep rooted prairie grasses to stimulate the degradation and detoxification of toxic and recalcitrant organic chemicals at low soil concentrations represents a potential low-cost, effective, and low-maintenance remedial option. Due to the low survival rate of trees and shrubs, they are not recommended to be used for remediation in the study area. However, due to the beneficial effects of their use in phytoremediation, it would be appropriate to establish the necessary conditions for their development by planting and growing herbaceous plants in the first instance. Herbs, due to their high rate of renewal and their proven efficiency in reducing soil

toxicity, may help prepare the ground for the subsequent implementation of woody species, thus enhancing the effect of this sustainable technique.

The phytoremediation of contaminated soils with the mixed contaminants (organic and inorganic contaminants) can be enhanced by several strategies. The addition of compost amendment to the slag disposal area enhanced the survival rates by providing nutrients and organic matter, promotes the stabilization of the heavy metals in the soil and expedites the biodegradation of organic contaminants by reducing the stress of the plants. Although the technique developed showed highly effectiveness in removing organic contaminants from the soil, proving that phytoremediation is highly suitable for this purpose, it would be highly recommendable the study of the presence of byproducts and or metabolites derived from PAHs degradation, in order to study the final fate of these compounds and assess the effectiveness of this technique in reducing the toxicity produced by these organic contaminants.

The toxic inorganic contaminants, such as Cr or Pb, although they were not removed from the soil, also neither were uptaken by plants, which represents a decreased risk of exposure for living organisms. The results from sequential extraction of metals showed that the exchangeable fraction of the metals studied had the lowest concentration. However, since the total concentrations of heavy metals remain above the established limits, it is highly recommended to track the remediated area, as it is a dynamic system and it is important to check the bioavailability of inorganic contaminants would not change over the time.

Big Marsh is representative of many other unrestored wetland sites in the region which have been significantly altered by the steel industry. Many other sites in the Calumet area and the Grand Calumet Area of Concern have similar conditions to Big Marsh, and this project results are immensely valuable in evaluating the potential for using native plants to remediate other wetland sites.

24

This study identified several native plant species suitable for re-vegetation and restoration of heavily impacted, urban/industrial sites with historic soil contamination. The results suggest that native plant species may promote organic contaminant degradation and soil neutralization once established in slag-impacted zone.

5. Conclusions

The present study demonstrates that the compost amendment significantly improves the long-term growth and survival of plants at highly impacted slag areas with very thin topsoil. Although results showed that compost amendment of soil together with the presence of plants promotes the biodegradation of organic pollutants (PAHs), the individual effects of the compost amendment or the surviving species in PAHs degradation could not be ascertained. On the other hand, the presence of plants did not affect the mobility of heavy metals in soil, which were neither assimilated by the plants, with exemption of Mn. Results show that native grass species have higher phytoremedial potential than woody species that show higher vulnerability to soil contamination, invasive species, and pests. Overall, compost amendment provides a promising approach for enhancing phytoremediation of mixed contaminated soils using native species such as Switchgrass and Little Bluestem, which are shown to survive under the harsh site slag conditions and reduce the organic contaminants while not affecting heavy metals mobility, thus leading to reduced risk to public and the environment.

Acknowledgement

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Table 1. Species selected for restoration of slag disposal area

| Type | Scientific Name | Common Name | Sample ID | Number of samples | |
				Experimental Plot	Adjacent Plot
Grasses and Plugs	*Andropogon scoparius*	Little Bluestem	LBS	95	50
	Bouteloua curtipendula	Side Oats Grama	SOG	95	50
	Dalea purpurea	Purple Prairie Clover	PPC	95	50
	Panicum virgatum	Switch Grass	SWG	95	50
	Ratibida pinnata	Yellow Coneflower	YCF	95	50
Trees	*Celtis occidentalis*	Hackberry	HBY	20	0
	Quercus velutina	Black Oak	BOK	20	0
Shrubs	*Cornus racemose*	Gray Dogwood	GDW	20	0
	Circis canadensis	Eastern Redbud	ERB	20	0

Table 2. Monitoring rating system

Parameter	Measurement
Height (H)	Height in cm[1]
Survival (S)	Scale 1-4 (1 =dead; 2 =dying; 3 =no change in growth; 4 =evidence of new growth)
Leaves (L)	Scale 1-4 (1 = >50% leaves are dead; 2 = >25% leaves are dead, discoloration and/or wilting is present; 3 = <25% of leaves are discolored and/or wilting with no dead or dying leaves present; 4 = No discoloration, wilting or dead/dying leaves.)

1For woody species only.

Table 3. Sequential extraction procedure for speciation of heavy metals

Fraction	Designation	Extraction Procedure (per 1g dry soil sample)
1	Exchangeable	An amount of 8 mL of 1 M sodium acetate solution (pH = 8.2) was added and mixed continuously for 1h.
2	Carbonates – bound	To the residue from above, 8 mL of 1M sodium acetate (pH adjusted to 5 with acetic acid) was added and mixed continuously for 5h.
3	Fe – Mn oxides – bound	To the residue from above, 20 mL of 0.04 M hydroxylamine hydrochloride ($NH_2OH.HCL$) was added in 25% (v/v) acetic acid, and heat to 96ºC with occasional stirring for 6h.
4	Organic – bound	To the residue from above, 3 mL of 0.02M nitric acid (HNO_3) and 5mL of 30% Hydrogen Peroxide (H_2O_2) (pH adjusted to 2.0 with HNO_3) was added and mixed continuously for 3h. Cool the mixture and add 5mL of 3.2 M ammonium acetate (NH_4OAc) in 20% (v/v) HNO_3. Finally, dilute to 20 mL and mixed continuously for 30 min.
5	Residual	Acid digestion EPA 3050 method.

Table 4. Soil characterization before, after tilling and at the end of the third growing season.

Soil Parameter	Initial Values	After Tilling Values	Season 3
pH	7.48	9.26	8.16
Oxidation-reduction Potential, ORP (mV)	-44.36	-156.79	-91.76
Organic Content, OC (%)	4.2	8.02	7.68
Electrical Conductivity, EC (mS/cm)	0.18	0.01	0.06
Moisture Content, MC (%)	16.47	17.62	11.82
Water Holding Capacity, WHC (%)	27.08	37.06	30.91
Exchangeable Phosphate (mg/L)	0.08	0.067	0.06
Exchangeable Nitrate (mg/L)	1.51	2.16	2.39
% Gravel	51.8	56.4	29.5
% Sand	26.8	31.5	32.9
% Fines	21.4	12.1	37.6

Table 5. Contaminant Concentrations in Soil

Contaminant	Concentration (mg/Kg – dry soil)			
	Initial Soil	After Tilling	Season 2	Season 3
PAHs				
Acenaphthene	<DL (0.03)	<DL (0.03)	<DL (0.03)	<DL (0.03)
Acenaphthylene	0.03	<DL (0.03)	<DL (0.03)	<DL (0.03)
Anthracene	0.05	0.05	0.05	0.06
Benz(a)anthracene	0.2	0.29	0.13	0.12
Benzo(a)pyrene	0.43	0.41	0.48	0.25
Benzo(b)fluoranthene	0.36	0.36	0.23	0.31
Benzo(g,h,i)perylene	0.35	0.27	0.18	0.2
Benzo(k)fluoranthene	0.16	0.31	0.17	0.21
Chrysene	0.29	0.36	0.19	0.2
Dibenz(a,h)anthracene	<DL (0.03)	0.12	0.07	<DL (0.03)
Fluoranthene	0.26	0.45	0.2	0.17
Fluorene	<DL (0.03)	<DL (0.03)	<DL (0.03)	<DL (0.03)
Indeno(1,2,3-cd)pyrene	0.21	0.24	0.15	0.18
Naphthalene	0.08	<DL (0.03)	<DL (0.03)	<DL (0.03)
Phenanthrene	0.18	0.14	0.06	0.09
Pyrene	0.26	0.36	0.17	0.14
Metals				
Aluminum	5200	7925	6325	6675
Antimony	3.7	4	5	4.3
Arsenic	6.8	9.6	10	12.1
Barium	95	138	140.0	124
Beryllium	0.7	0.9	1	1
Cadmium	4.4	14	13.5	13.6
Calcium	130000	150000	155000	123750
Chromium	300	275	241	248
Cobalt	9.2	8.6	7.6	8.4
Copper	85	79.5	79	94
Iron	360000	257500	180000	192500
Lead	745	938	966	1011
Magnesium	23000	20000	21250	20500
Manganese	19000	20750	17195	18308
Mercury	0.03	0.03	0.05	0.04
Nickel	64	128	51	54.4
Potassium	320.0	2175	1333	1538
Selenium	0.9	1.1	1.4	1.8
Silver	0.9	2.5	2.1	2.1
Sodium	200	625	533	485
Thallium	0.9	1	1.3	1.7
Vanadium	150	173	210	181
Zinc	3900	6075	7675	7275

DL= Detection Limit.

Table 6. Percent fractionation of metals in the soil before planting.

Metal	Initial soil					Soil after tilling				
	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5
Antimony	8	8	41	17	26	6	11	28	20	35
Arsenic	2	2	7	3	87	2	5	12	9	72
Barium	1	20	57	4	19	1	10	57	13	19
Beryllium	9	9	43	18	22	7	14	36	26	18
Cadmium	3	5	19	5	68	1	6	19	5	69
Chromium	0	0	51	3	46	0	1	52	7	40
Cobalt	2	2	18	5	73	4	7	26	13	50
Copper	1	1	3	17	78	1	3	6	28	62
Lead	0	1	38	2	59	0	1	31	4	65
Manganese	0	1	69	5	24	0	4	59	7	30
Nickel	0	2	29	3	65	1	2	47	9	42
Selenium	9	10	42	18	21	6	11	28	20	35
Thallium	9	9	43	18	22	7	14	36	26	18
Vanadium	0	0	66	2	31	0	1	64	7	29
Zinc	0	0	15	0	84	0	2	13	1	84

F1. Exchangeable fraction; F2. Carbonates – bound fraction; F3. Fe – Mn oxides bound fraction; F4. Organic – bound; F5. Residual.

Table 7. Soil contaminant concentrations at different plot locations.

Contaminant	Concentration (mg/kg – dry soil)							
	Season 2				Season 3			
	SWG	LBS	PPC	YCF	SWG	LBS	PPC	YCF
PAHs								
Acenaphthene	<DL (0.04)	<DL (0.04)	<DL (0.05)	<DL (0.04)	<DL (0.03)	<DL (0.04)		<DL (0.04)
Acenaphthylene	<DL (0.04)	<DL (0.04)	<DL (0.05)	<DL (0.04)	<DL (0.03)	<DL (0.04)		<DL (0.04)
Anthracene	<DL (0.04)	<DL (0.04)	<DL (0.05)	<DL (0.04)	<DL (0.03)	<DL (0.04)		0.06
Benz(a)anthracene	0.08	0.13	0.16	0.15	0.11	0.11		0.13
Benzo(a)pyrene	0.18	0.28	0.20	0.28	0.3	0.25	0.23	0.22
Benzo(b)fluoranthene	0.16	0.27	0.26	0.24	0.27	0.13		0.34
Benzo(g,h,i)perylene	0.12	0.20	0.17	0.22	0.16	0.14		0.29
Benzo(k)fluoranthene	0.1	0.17	0.19	0.22	0.1	0.1		0.32
Chrysene	0.11	0.19	0.22	0.22	0.14	0.17		0.25
Dibenz(a,h)anthracene	0.05	0.08	0.08	0.09	<DL (0.03)	0.08		<DL (0.04)
Fluoranthene	0.11	0.20	0.26	0.24	0.13	0.15		0.21
Fluorene	<DL (0.04)	<DL (0.04)	<DL (0.05)	<DL (0.04)	<DL (0.03)	<DL (0.04)		<DL (0.04)
Indeno(1,2,3-cd)pyrene	0.10	0.17	0.15	0.18	0.12	0.12		0.23
Naphthalene	<DL (0.04)	<DL (0.04)	<DL (0.05)	<DL (0.04)	<DL (0.03)	<DL (0.04)		<DL (0.04)
Phenanthrene	0.04	0.06	0.09	0.08	0.06	0.07		0.12
Pyrene	0.10	0.17	0.22	0.2	0.11	0.11		0.17
Metals								
Aluminum	5900	6700	5900	6800	7850	6200	6600	6050
Antimony	<DL (5)	<DL (5)	<DL (5)	<DL (5)	<DL (5)	<DL (5)	<DL (5)	<DL (5)
Arsenic	10	10	10	9	12	12	12	12
Barium	120	150	160	130	135	110	130	120
Beryllium	0.9	1	1	1.1	1.2	1	1.1	0.9
Cadmium	14	10	18	12	11	12	19	12.5
Calcium	140000	170000	140000	170000	130000	110000	140000	115000
Chromium	256	298	302	284	237	240	260	253
Cobalt	7.4	7.1	8.4	7.3	8	8	8.8	9.2
Copper	87	63	94	73	82	87	110	99
Iron	200000	140000	210000	170000	200000	200000	170000	200000
Lead	1213	1006	1066	1018	995	1070	1006	973
Magnesium	18000	23000	23000	21000	18000	16500	32000	15500
Manganese	19400	20000	21400	21400	18000	18333	18400	18500
Mercury	0.03	0.05	0.06	0.06	0.04	0.04	0.05	0.04
Nickel	64	40	48	50	53	48	49	68
Potassium	930	1400	1400	1600	1400	1700	1300	1750
Selenium	<DL (2)	<DL (2)	<DL (2)	<DL (2)	<DL (2)	<DL (2)	<DL (2)	<DL (2)
Silver	2.1	1.7	2.8	1.9	1.65	1.95	3.1	1.75
Sodium	540	440	680	470	460	410	660	410
Thallium	<DL (2)	<DL (2)	<DL (2)	<DL (2)	<DL (2)	<DL (2)	<DL (2)	<DL (2)
Vanadium	170	240	220	210	190	155	190	190
Zinc	8800	6100	8800	7000	6800	7950	7300	7050

SWG= Switch Grass; LBS= Little Bluestem; YCF = Yellow Cone Flower; PPC = Purple Prairie Clover; DL = Detection Limit.

Table 8. Contaminant concentration per surviving species in stems and leaves.

Contaminant	Concentration (mg/Kg)							
	Season 2				Season 3			
PAHs	SWG	LBS	YCF	PPC	SWG	LBS	YCF	PPC
Acenaphthene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)				
Acenaphthylene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)				
Anthracene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)				
Benz(a)anthracene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)				
Benzo(a)pyrene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)
Benzo(b)fluoranthene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)				
Benzo(g,h,i)perylene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)				
Benzo(k)fluoranthene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)				
Chrysene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)				
Dibenz(a,h)anthracene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)				
Fluoranthene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)				
Fluorene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)				
Indeno(1,2,3-cd)pyrene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)				
Naphthalene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)				
Phenanthrene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)				
Pyrene	<DL(0.3)	<DL(0.3)	<DL(0.3)	<DL(0.3)				
Metals								
Aluminum	54	48	56	<DL(38)				
Antimony	<DL(4)	<DL(4)	<DL(4)	<DL(4)				
Arsenic	<DL(3)	<DL(3)	<DL(3)	<DL(3)	<DL(13)	<DL(15)	<DL(10)	<DL(19)
Barium	4	7.4	5.2	5.5				
Beryllium	<DL(1)	<DL(1)	<DL(1)	<DL(1)				
Cadmium	<DL(1)	<DL(1)	<DL(1)	<DL(1)				
Calcium	8200	5100	26000	16000				
Chromium	<DL(3)	<DL(3)	<DL(3)	<DL(3)	<DL(13)	<DL(15)	<DL(10)	<DL(19)
Cobalt	<DL(2)	<DL(2)	<DL(2)	<DL(2)				
Copper	<DL(5)	<DL(5)	12	6.3				
Iron	330	570	850	570				
Lead	6.37	3.85	12	4.22	<DL(6)	<DL(8)	<DL(6)	<DL(9)
Magnesium	1300	1600	4800	1400				
Manganese	100	87	153	70	63	117	99	72
Mercury	<DL(0.02)	<DL(0.02)	<DL(0.02)	<DL(0.02)				
Nickel	<DL(2)	<DL(2)	<DL(2)	<DL(2)				
Potassium	5200	9300	38000	14000				
Selenium	<DL(2)	<DL(2)	<DL(2)	<DL(2)				
Silver	<DL(2)	<DL(2)	<DL(2)	<DL(2)				
Sodium	<DL(110)	<DL(110)	<DL(110)	<DL(110)				
Thallium	<DL(2)	<DL(2)	<DL(2)	<DL(2)				
Vanadium	<DL(2)	<DL(2)	<DL(2)	<DL(2)				
Zinc	24	75	97	72				

SWG= Switch Grass; LBS= Little Bluestem; YCF = Yellow Cone Flower; PPC = Purple Prairie Clover; DL = Detection Limit.

Table 9. Contaminant concentration in roots of surviving plant species.

| Contaminant | Concentration (mg/Kg) | | | | | | | |
| | Season 2 | | | | Season 3 | | | |
PAHs	SWG	LBS	PPC	YCF	SWG	LBS	PPC	YCF
Acenaphthene	<DL(0.05)		<DL(0.04)	<DL (0.01)	<DL(0.03)	<DL(0.03)		<DL(0.03)
Acenaphthylene	<DL(0.05)		<DL(0.04)	<DL (0.01)	<DL(0.03)	<DL(0.03)		<DL(0.03)
Anthracene	<DL(0.05)		<DL(0.04)	<DL (0.01)	<DL(0.03)	<DL(0.03)		<DL(0.03)
Benz(a)anthracene	<DL(0.05)		<DL(0.04)	0.08	<DL(0.03)	<DL(0.03)		<DL(0.03)
Benzo(a)pyrene	0.05	<DL(0.04)	<DL(0.04)	<DL (0.05)	<DL(0.03)	<DL(0.03)	<DL(0.03)	<DL(0.03)
Benzo(b)fluoranthene	<DL(0.05)		<DL(0.04)	0.18	<DL(0.03)	<DL(0.03)		<DL(0.03)
Benzo(g,h,i)perylene	<DL(0.05)		<DL(0.04)	0.14	<DL(0.03)	<DL(0.03)		<DL(0.03)
Benzo(k)fluoranthene	<DL(0.05)		<DL(0.04)	0.1	<DL(0.03)	<DL(0.03)		<DL(0.03)
Chrysene	<DL(0.05)		<DL(0.04)	0.1	<DL(0.03)	<DL(0.03)		<DL(0.03)
Dibenz(a,h)anthracene	<DL(0.05)		<DL(0.04)	<DL (0.01)	<DL(0.03)	<DL(0.03)		<DL(0.03)
Fluoranthene	<DL(0.05)		<DL(0.04)	<DL (0.01)	0.05	<DL(0.03)		<DL(0.03)
Fluorene	<DL(0.05)		<DL(0.04)	<DL (0.01)	0.07	<DL(0.03)		<DL(0.03)
Indeno(1,2,3-cd)pyrene	<DL(0.05)		<DL(0.04)	0.11	<DL(0.03)	<DL(0.03)		<DL(0.03)
Naphthalene	<DL(0.05)		<DL(0.04)	<DL (0.01)	<DL(0.03)	<DL(0.03)		<DL(0.03)
Phenanthrene	<DL(0.05)		0.51	<DL (0.01)	0.05	0.04		0.04
Pyrene	<DL(0.05)		<DL(0.04)	<DL (0.01)	<DL(0.03)	<DL(0.03)		<DL(0.03)
Metals								
Aluminum	1600		240	600	200	290		330
Antimony	14		17	15	<DL(5)	<DL(5)		<DL(5)
Arsenic	<DL(3)	<DL(3)	<DL(3)	<DL(3)	<DL(3)	<DL(3)	<DL(3)	<DL(3)
Barium	52		11	17	4.95	7.4		12
Beryllium	<DL(2)		<DL(2)	<DL(2)	<DL(1)	<DL(1)		<DL(1)
Cadmium	<DL(2)		<DL(2)	<DL(2)	<DL(1)	<DL(1)		<DL(1)
Calcium	100000		16000	23000	6400	9400		18000
Chromium	76	13	6	9	4.1	7.83	<DL(3)	12
Cobalt	<DL(3)		<DL(3)	<DL(3)	<DL(3)	<DL(3)		<DL(3)
Copper	11		10	34	23	19		22
Iron	44000		6400	8000	6200	7100		7300
Lead	52	110	39	78	24	53	6	88
Magnesium	8100		2500	2600	2450	860		3000
Manganese	5523	697	238	468	221	285	69	650
Mercury	<DL(0.02)		<DL(0.02)	<DL(0.02)	<DL(0.02)	<DL(0.02)		<DL(0.02)
Nickel	<DL(3)		<DL(3)	<DL(3)	<DL(3)	<DL(3)		<DL(3)
Potassium	4800		14000	19000	5250	890		9800
Selenium	<DL(3)		3.1	<DL(3)	<DL(3)	<DL(3)		<DL(3)
Silver	<DL(3)		3.1	<DL(3)	<DL(3)	<DL(3)		<DL(3)
Sodium	<DL(180)		240	<DL(190)	<DL(170)	<DL(130)		<DL(110)
Thallium	<DL(3)		3.1	<DL(3)	<DL(3)	<DL(3)		<DL(3)
Vanadium	<DL(160)		13	19	4	8		21
Zinc	430		430	470	275	400		390

SWG= Switch Grass; LBS= Little Bluestem; YCF = Yellow Cone Flower; PPC = Purple Prairie Clover; DL = Detection Limit.

Table 10. Soil Sequential Extraction of different plots at Season 3.

Metal	SWG					LBS					YCF				
	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5
Aluminum	0	0	32	12	56	0	0	31	9	59	0	0	28	8	63
Antimony	6	13	16	24	40	6	11	28	18	37	7	14	36	24	18
Arsenic	2	5	12	9	72	3	6	14	9	68	3	7	17	11	62
Barium	1	9	54	17	19	1	10	59	15	15	2	18	51	11	18
Beryllium	9	17	21	32	21	7	14	36	24	18	7	14	36	24	18
Cadmium	1	5	19	4	72	2	7	26	6	60	2	10	16	8	64
Calcium	3	32	54	6	5	2	29	59	5	5	5	54	33	4	5
Chromium	0	0	52	10	37	0	0	58	12	29	0	1	44	6	48
Cobalt	4	7	21	14	55	4	8	30	14	44	4	8	21	14	53
Copper	1	1	43	23	32	2	3	7	37	52	1	2	5	46	47
Iron	0	0	62	6	31	0	0	73	4	23	0	0	16	2	82
Lead	0	0	27	5	67	0	1	41	3	55	0	1	29	6	64
Magnesium	2	10	54	12	22	2	7	67	11	13	4	14	45	13	24
Manganese	0	3	63	7	28	0	3	76	8	14	0	8	58	3	31
Nickel	1	1	33	21	43	1	1	42	20	36	1	2	40	14	43
Potassium	30	11	13	2	44	26	18	13	2	41	44	18	7	2	30
Selenium	7	14	35	26	18	7	14	36	24	18	7	14	36	24	18
Silver	6	12	15	22	45	6	11	28	19	36	7	14	35	23	20
Sodium	53	42	4	0	0	43	52	5	0	0	50	47	2	0	0
Thallium	9	17	21	32	21	7	14	36	24	18	9	18	22	29	22
Vanadium	0	0	59	12	28	0	0	67	10	23	0	1	53	14	31
Zinc	0	1	10	1	87	0	2	21	2	75	0	3	12	1	85

F1. Exchangeable fraction; F2. Carbonates – bound fraction; F3. Fe – Mn oxides bound fraction; F4. Organic – bound; F5. Residual.

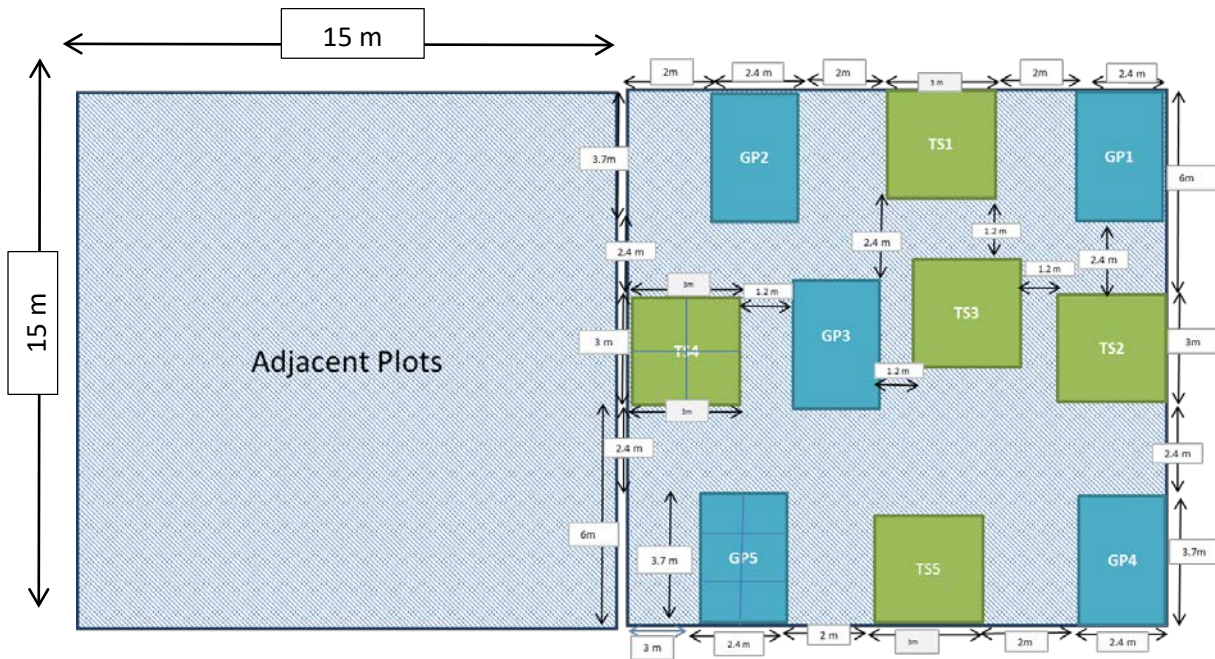Table 11. Comparison of bulk soil vs. root soil characterization results

Parameter	Bulk Soil			Root Zone Soil		
	SWG	LBS	YCF	SWG	LBS	YCF
pH	8.25	8.05	8.18	8.08	7.87	7.78
Moisture Content, MC (%)	10.88	13.37	11.22	6.07	5.96	9.01
Organic Content, OC (%)	8.34	7.52	8.66	31.58	38.42	49.79
Electrical Conductivity, EC (mS/cm)	0.047	0.06	0.06	0.05	0.05	0.04
Oxidation-reduction Potential, ORP (mV)	-97.08	-85.65	-85.65	-69.46	-55.85	-50.87
Exchangeable Nitrate (mg/L)	1.45	3.2	2.5	3.2	4	
Exchangeable Phosphate (mg/L)	0.05	0.06	0.07	0.5	0.2	

Table 12. Root Soil Sequential Extraction.

Metal	R-SWG					R-LBS					R-YCF				
	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5
Antimony	6	11	28	21	34	20	9	23	18	29	13	9	51	17	11
Arsenic	2	5	12	9	71	3	6	14	11	66	4	7	19	14	56
Barium	2	10	61	10	18	3	15	38	12	31	2	15	44	15	24
Beryllium	7	14	35	27	17	7	14	35	27	17	7	14	35	27	17
Cadmium	2	5	25	6	62	1	5	17	5	71	2	7	26	8	57
Chromium	0	0	46	8	46	0	1	11	25	63	0	1	15	38	46
Cobalt	3	7	27	13	50	4	7	20	14	55	3	7	34	17	39
Copper	1	2	9	40	48	1	1	7	64	26	1	1	7	72	19
Lead	0	0	34	5	60	0	1	21	3	75	0	1	30	4	65
Manganese	0	4	63	4	28	0	7	40	7	46	0	9	55	9	26
Nickel	1	1	43	11	44	1	1	18	24	56	1	1	27	37	34
Selenium	7	14	35	27	17	7	14	35	27	17	7	14	35	27	17
Thallium	7	14	35	27	17	7	14	35	27	17	7	14	35	27	17
Vanadium	0	1	60	14	24	0	1	31	40	28	0	1	31	45	22
Zinc	0	1	20	1	77	0	1	12	3	84	0	2	19	6	73

F1. Exchangeable fraction; F2. Carbonates – bound fraction; F3. Fe – Mn oxides bound fraction; F4. Organic – bound; F5. Residual.

a. Overview of Plot Layout

b. Grass and plugs (GS) subplots planting layout

Note: PPC- Purple Prairie Clover; SWG- Switch Grass; YCF- Yellow Coneflower; SOG-Side Oats Grama; LBS- Little Bluestem; MIX-All GS Species in one plot
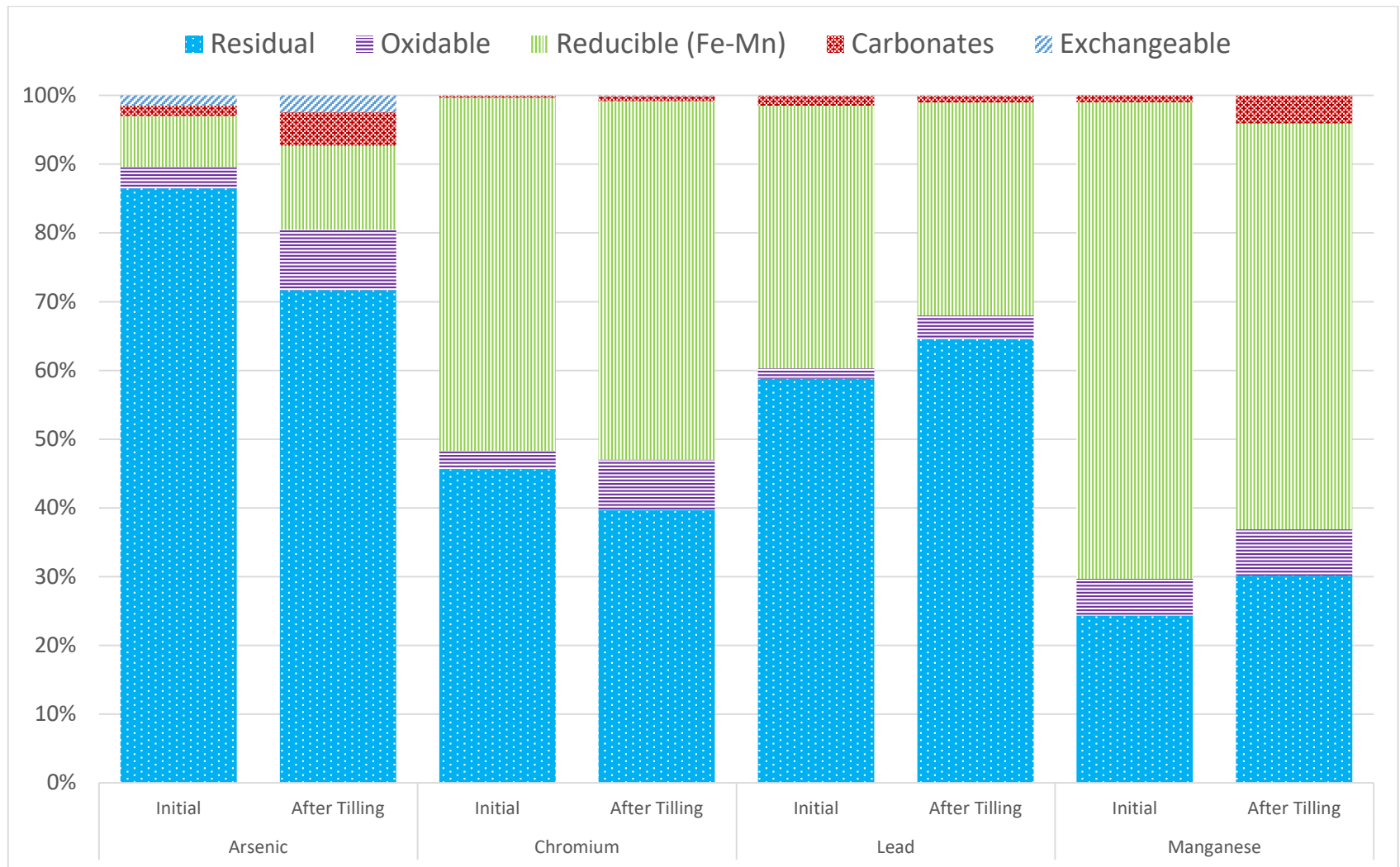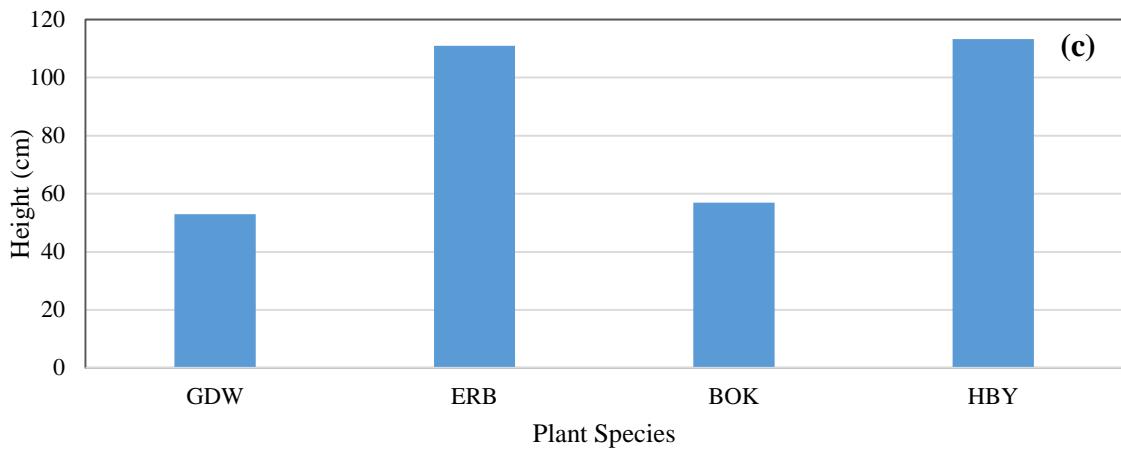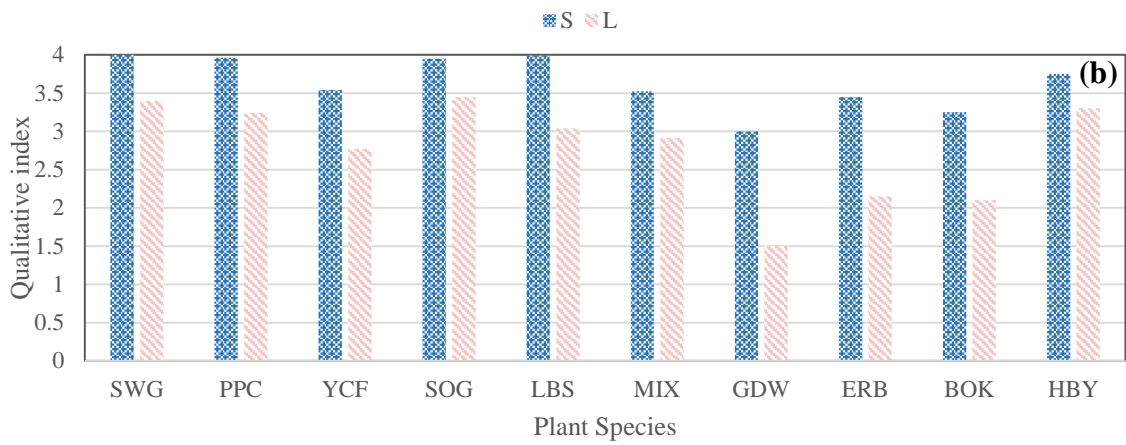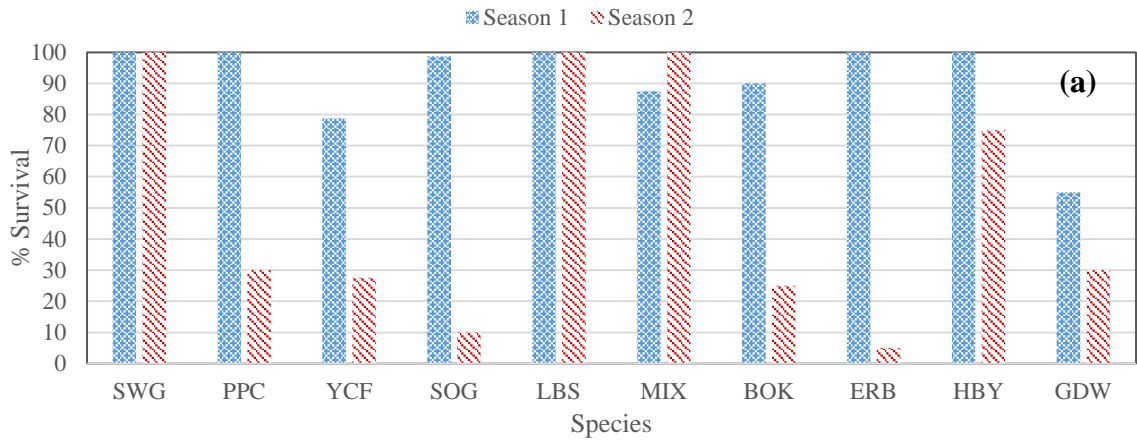

c. Trees and shrubs (TS) subplots planting layout.

Note: HBY- Hackberry; BOK- Black Oak; GDW- Gray Dogwood; ERB-Eastern Redbud

**Figure 1. Plots and subplots delineation layout.**

Figure 2. Comparison of metal distribution in soil before and after tilling.

Figure 3. Monitoring rating results (a) Plant survival in the experimental plots at the end of the first and second growing season. (b) Plant survival (S) and leaf quality (L) in grasses and trees at the end of the first growing season. (c) Height of the trees (cm) at the end of the first season.
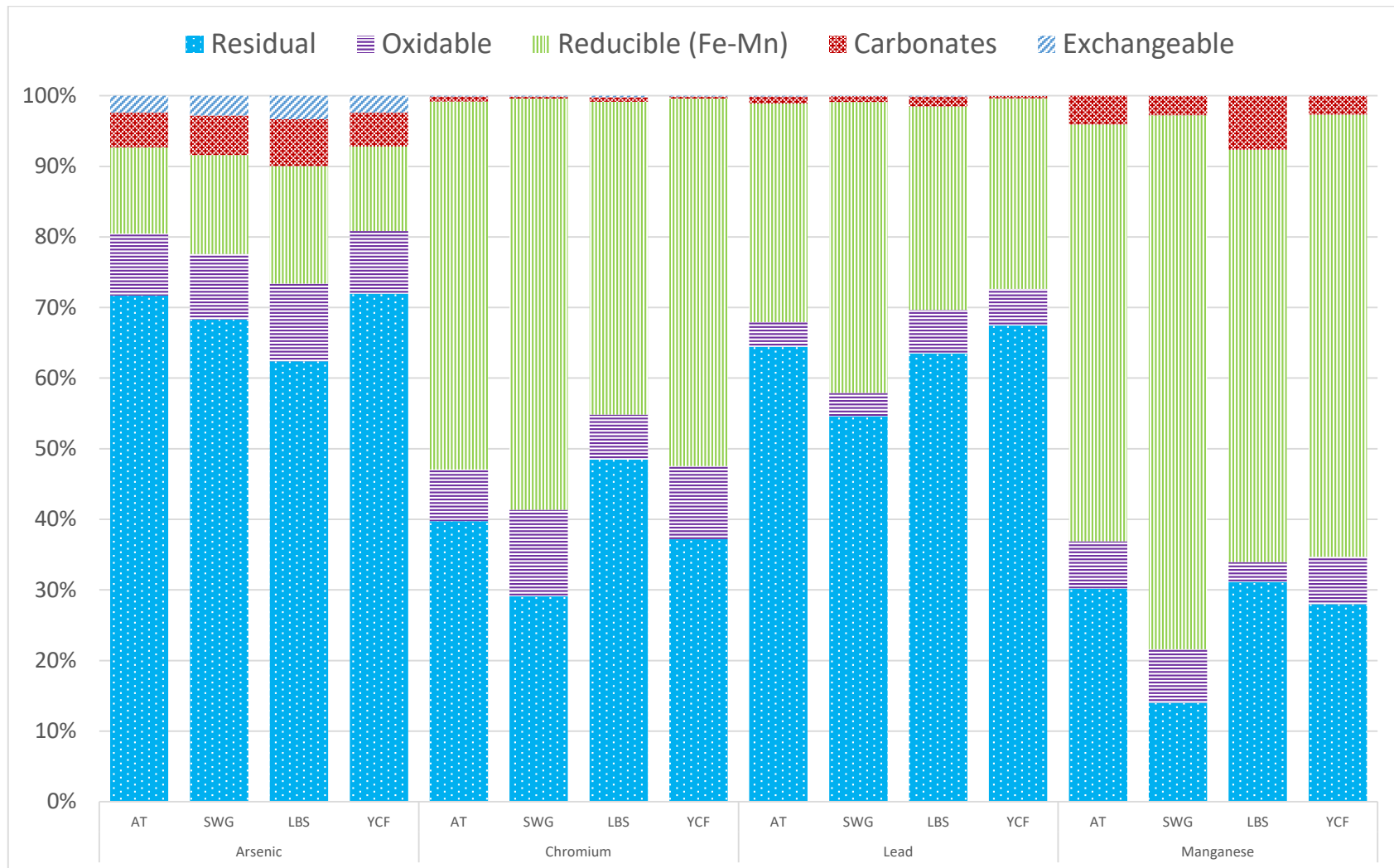
Figure 4. Metal distribution comparison between soil after tilling (AT) and soils at surviving plant plots at the end of the third season, Switchgrass (SWG), Little Bluestem (LBS) and Yellow Cone Flower (YCF).
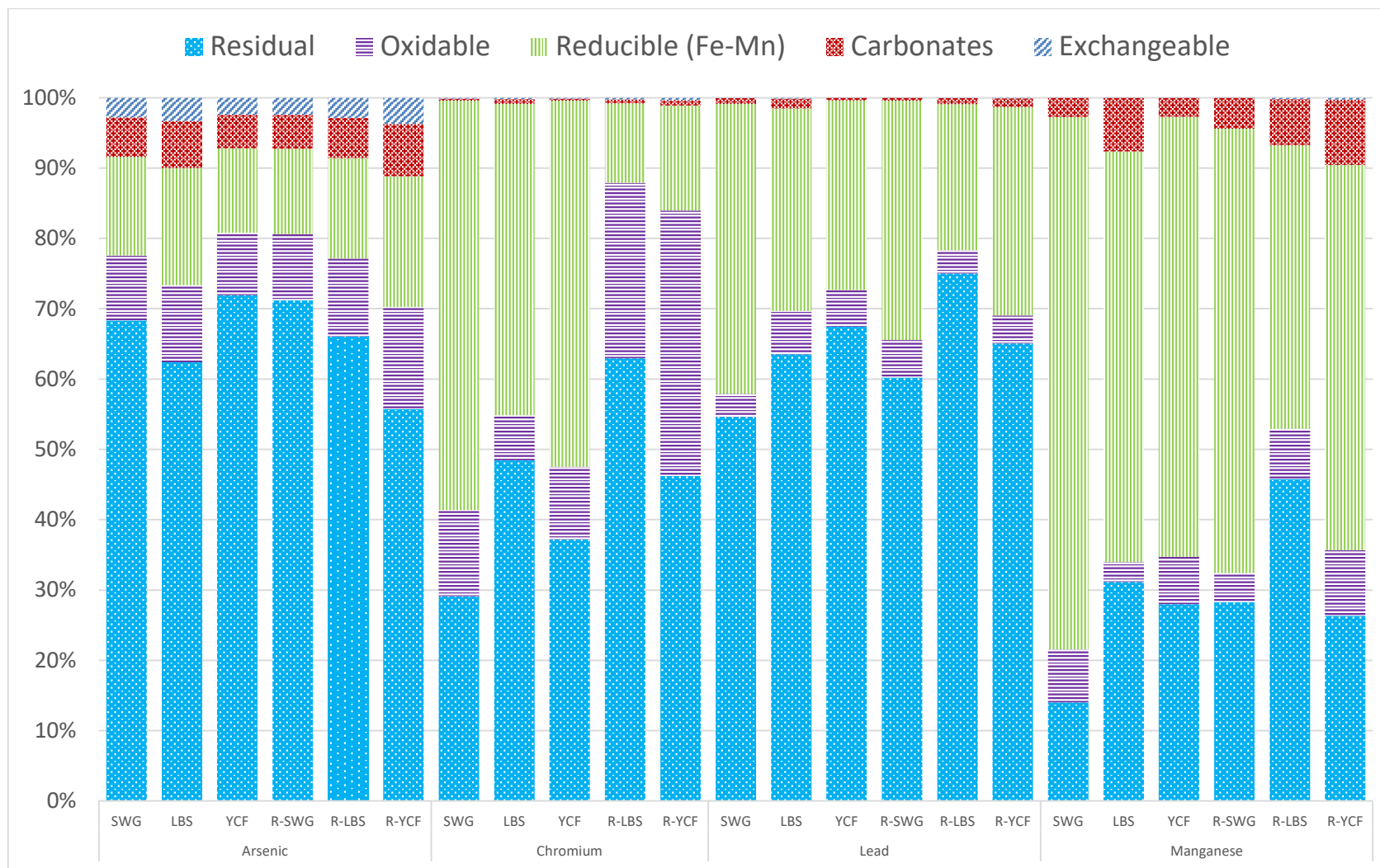
Figure 5. Metal distribution comparison between soils of surviving plant plots, Switchgrass (SWG), Little Bluestem (LBS) and Yellow Cone Flower (YCF) and root soil (R-SWG, R-LBS, R-YCF) at the end of the third season.