

**SORPTION AND LEACHING CHARACTERISTICS OF HEAVY METALS
IN ARTIFICIAL SOIL**

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
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
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ABSTRACT

The objective of this study was to investigate the heavy metal sorption and leaching characteristics of an “artificial soil” formed by blending industrial and municipal by-products and implemented as a beneficial waste reuse and land reclamation strategy. Two primary tasks were undertaken in order to complete this objective: (1) a background study including a review of literature dealing with heavy metal mobility within different artificial soil mixes and biosolids-amended soils, and (2) a laboratory investigation of the general engineering, sorptive, and leaching properties of an artificial soil comprising yard waste, biosolids, cement kiln dust (CKD) and coal ash.

The background literature review shows that previous artificial and biosolids-amended soil mixes have been very effective in immobilizing heavy metals. Use of biosolids-amended soils for agricultural applications results in a substantial increase in crop yield and size. The organic biosolids and mineral fraction of artificial soil mixtures help in immobilizing heavy metals present in the aqueous phase.

Materials for laboratory testing were sampled from a full-scale artificial soil emplacement being implemented as an alternative evapotranspirative (ET) cover system in Hannibal, Missouri (Bobba, 2005; Bobba et al., 2006, Wayllace and Likos, 2006). Materials at the site include an organic-rich O-horizon (yard waste and biosolids) overlying a mineral-rich C-horizon (CKD and coal ash) to simulate a natural residual soil profile. The laboratory investigation consisted of testing for natural (in-situ) moisture

content, pH, carbon content, microstructure (via SEM imaging), batch sorption characteristics, and leaching characteristics determined by flow-through column tests. Moisture content, pH, and carbon content were examined for materials sampled at the field site as a function of depth from the ground surface and as a function of time since soil emplacement. Sorption and leaching testing focused on the metals Cd, Pb, and Zn.

Moisture content profiles in representative “mature” and “young” soil profiles show a consistent trend of increasingly higher moisture contents with depth, indicating a “ponding” condition occurring at the interface of the O and C horizons. The pH of the O-horizon ranged from 6.55 to 7.24 within the mature soil profile and from 7.16 to 7.70 for the young soil profile, suggesting that the horizon becomes more acidic with time. Organic carbon content for the mature and young profiles ranged from 12.4% to 27.5% and 5.5% to 26.2%, respectively. Total carbon contents paralleled the organic carbon profiles, and ranged from 14.0% to 30.8% and 11.6% to 28.6%, respectively. The inorganic carbon profiles with depth are relatively constant. The trends evident in the moisture content, pH, and carbon content profiles support the presence of a cemented Bh layer noted in the field test site at the interface between the O and C Horizon.

Batch sorption tests show the artificial soil mix to be very effective in immobilizing free Cd, Pb, and Zn, even at very large concentrations. Leaching with ammonium nitrate to represent plant available amounts proved to be minimal. Column leaching tests using tap water and a pH-buffered solution confirmed these results, as no detectable amount of Cd, Pb, or Zn leached from prepared soil columns after more than 30 pore volumes of flow. The column leaching tests also show an apparent pH dependence of the leachability of Cd, Pb, and Zn.

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CHAPTER 1

INTRODUCTION

1.1 Background

Alternative landfill covers (AFC) are an increasingly appealing way to achieve the performance criteria outlined in US environmental law. AFCs work in unity with the forces of nature, as compared to conventional landfill covers, which attempt to oppose the forces of nature. Alternative landfill covers provide a suitable soil profile and vegetation to hold and store water until evapotranspiration can remove it. Ideally, native soils are used to produce a soil column that is designed with a specific storage capacity. It is then planted with native plants, capable of producing a root system to aid in evapotranspiration processes. More generally, this type of cover is referred to as an evapotranspirative (ET) cover. Conventional landfill covers, on the other hand, rely on layers of impermeable materials such as compacted clay liners, geomembranes, or asphaltic concrete covers to repel precipitation from reaching the covered waste. The problem with these materials is that they have a potential to fail in the long-term from long-term exposure to the environment. For this reason, AFC's can not only outperform many conventional liners, but they can also be much more cost-effective for construction and provide long-term sustainability.

Artificial soils are engineered by blending various industrial and municipal by-products (e.g., bio-solids, fly ash, blast furnace slag) for their beneficial properties. They have received increasing attention in recent years as a sustainable land reclamation and beneficial reuse strategy (e.g., Reynolds et al., 1999; Cox and Whelan, 2000). An innovative application using an artificial soil as an ET cover system was implemented for

full-scale field evaluation in 2002 at the Continental Cement Company in Hannibal, Missouri (e.g., Bobba, 2005). The soil column, as seen in Figure 1.1, is composed of two layers: an organic-rich topsoil layer (“O” composed of yard compost and biosolids) underlain by a mineral rich layer (“C” composed of fly ash and cement kiln dust, or CKD). Native vegetation is planted on top for evapotranspiration and land reclamation. This design allows for the reuse of locally available wastes to create a renewable resource. The system is intended to be an evapotranspirative barrier that limits percolation into the underlying CKD by storing and subsequently removing water under natural evaporation and transpiration processes. By July 2005, more than 90,000 tons (US) of artificial soil were placed and more than four acres of land have been reclaimed (Table 1).

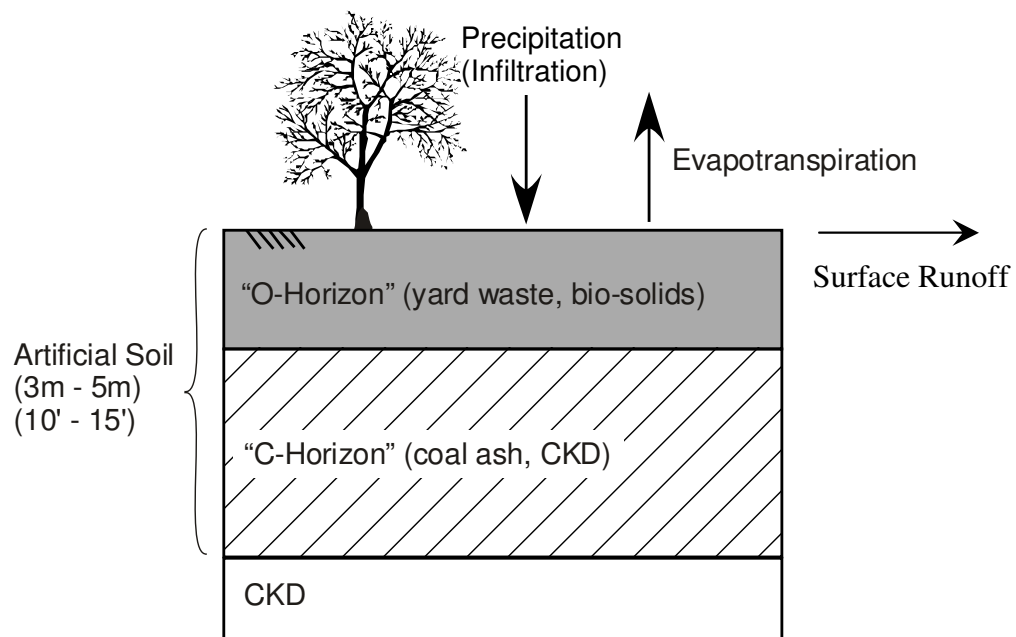


Figure 1.1 Schematic diagram of artificial soil profile (modified from Bobba, 2005)

Table 1.1 Summary of materials placed as artificial soil through July 2005.

Material Placed	Source	Approx. US Tons
Cement Kiln Dust	Continental Cement Company	32,000
Yard Waste	Cities of Quincy, IL, Hannibal, MO Paris, MO, Springfield, IL	28,000
Bio-solids	Metro Sewer District: Hannibal, MO St. Louis, MO	20,000
Power Plant (Coal) Ash	University of Missouri – Columbia	14,000

1.2 Objectives and Scope

The performance of this specific AFC design depends on two criteria. The first criterion is its ability to prevent water infiltration by storing precipitation and removing water via natural processes such as evapotranspiration. The effectiveness of the artificial soil concept as a hydraulic cover system has been investigated by previous research focusing on measuring and modeling the general hydrologic behavior at two full-scale field sites in Hannibal, Missouri. Evidence from both the field monitoring program (Bobba, 2005) and numerical seepage modeling (Wayllace and Likos, 2006) show that the artificial soil acts as an effective cover system, restricting wetting front propagation beyond the interface of the O- and C-horizons, causing water either to evaporate or to flow laterally along that interface.

The second criterion is that the materials used in the construction of the AFC are not an environmental hazard in themselves. Artificial soil is a unique combination and layering of organic and mineral materials with no prior measurements of its long-term physical and chemical stability or metal immobilization characteristics. The products of weathering and their solubilities and fates in the environment remain unknown.

The goal of this research, therefore, is to assess the short- and long-term transport of heavy metals in an artificial soil system formed by blending yard waste, biosolids, cement kiln dust, and coal ash. Specific objectives include:

- 1) Conduct a background literature review to summarize the concerns and factors affecting heavy metal mobility and sorption in porous media and previous investigations of metal mobility within biosolids-amended or artificial soil mixes;
- 2) Quantify the basic properties of artificial soil specimens representative of O-horizon and C-horizon materials, including natural moisture content, pH, micromorphology (via Scanning Electron Microscopy, or SEM), and organic, inorganic, and total carbon;
- 3) Assess the spatial and temporal variability in the above properties at the Hannibal field site by quantifying each property as a function of depth from the soil surface and time since soil placement;
- 4) Assess metal sorption capacity of representative O-horizon and C-horizon materials via a series of batch-sorption tests. Sorption analyses focus on Pb, Cd, and Zn, which have concentrations in the biosolids used in the artificial soil mix typically on the order of 85, 1.29, and 615 ppm, respectively.
- 5) Assess metals transport behavior of representative O-horizon and C-Horizon materials via a series of column leaching tests using tap water and pH-buffered permeant solutions.

1.3 Organization of Thesis

This document presents the results of 9 months of research and laboratory testing. The following chapters represent various aspects of the project. Chapter 2 summarizes and discusses the concerns of heavy metal mobility and various factors that impact metal mobility in soils and residuals. It also summarizes previous studies concerning heavy metal content and/or mobility at other sites utilizing biosolids-amended soils or artificial soil mixes. Chapter 3 summarizes previous research conducted to examine the general engineering and hydrologic properties of artificial soil (Bobba, 2005; Bobba et al., 2006). Chapter 4 presents the laboratory testing program and summarizes results obtained for materials retrieved from the Hannibal test site. Specimens were obtained to represent relatively “young” and relatively “mature” profiles of the O-horizon and C-horizon. Specific tests include profiles of natural moisture content, pH, and soil carbon content. Many of these tests show dynamic relationships with depth and soil layer. Batch adsorption/desorption and column leaching tests were conducted using select specimens to assess metal sorption and mobility using tap water and pH-buffered water as permeant solutions. Chapter 5 discusses the results obtained from the laboratory testing presented in Chapter 4. Finally, Chapter 6 provides a summary of the thesis, conclusions, and several recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1. Introduction

Heavy metal contamination is a common topic in environmental literature today. Recent awareness of the toxic effects and sources of heavy metal contamination/pollution, as well as advances in detection techniques and environmental chemistry, have brought this topic to the forefront of the scientific community. Sub-topics range from behavior of metals in the environment (Bradl, 2004), mobility of heavy metals in the environment (Usman et al. 2004), new or more accurate detection and testing techniques (Yong, 2001 and Koeckritz et al. 2001), to remediation (Marchioretto et al., 2005).

2.2. Concerns and Factors Affecting Heavy Metal Mobility and Sorption

2.2.1 Concerns of Heavy Metal Contamination and Mobility

Heavy metals are widely defined as metallic elements that have a specific gravity of 5.0 or more, and they are “the most toxic inorganic pollutants which occur in soils and can be of natural or anthropogenic origin” (Bradl, 2004). Metallic elements are naturally occurring in all soils in one form or another, and their natural concentration ranges are dependent on the parent material from which the soil formed. Table 2.1 shows the average concentration of metals in natural soils (from McLean and Bledsoe, 1992). Even at low concentrations, some heavy metals can still be very toxic. Naturally occurring concentrations of heavy metals are rarely at toxic levels, however, and most of the concern centers around contamination from anthropogenic sources.

Table 2.1 Content of Various Elements in Soils (Lindsay, 1979) and USEPA Drinking Water Standards (www.epa.gov)

Metal	Selected Average for Soils (mg/kg)	Common Range for Soils (mg/kg)	USEPA Drinking Water Standards (mg/L)
Al	71,000	10,000-300,000	*0.050 to 0.200
Fe	38,000	7,000-550,000	*0.300
Mn	600	20-3000	*0.050
Cu	30	2-100	1.300
Cr	100	1-1000	0.100
Cd	0.06	0.01-0.07	0.005
Zn	50	10-300	*5.000
As	5.0	1.0-5.0	0.010
Se	0.3	0.1-2	-
Ni	40	5-500	-
Ag	0.05	0.01-5	*0.100
Pb	10	2-200	0.015
Hg	0.03	0.01-0.3	0.002

** Secondary Standards – cosmetic and aesthetic effects only, nonenforceable*

High concentrations of heavy metals become a health concern when they are found to be moving from a contaminant source into groundwater sources, crops, and anything else that comes into direct contact with humans or animals. Thus, it is important to properly dispose of and monitor materials that may potentially leach heavy metals into the surrounding environment. It is because of this reason that the use of soil ameliorants such as biosolids and other wastes are debated. Although these resources can provide excellent results with regard to increased crop and plant yield/growth, they are also potential sources of heavy metal contamination that may, under the right conditions, translocate to the crops they help grow or into the groundwater.

2.2.2 Factors Affecting Sorption and Mobility of Heavy Metals

Shuman (1991) describes several “pools” in which metals are found in soils (McLean and Bledsoe, 1992):

- 1) dissolved in the soil solution;

- 2) occupying exchange sites on inorganic soil constituents;
- 3) specifically adsorbed on inorganic soil constituents;
- 4) associated with insoluble soil organic matter;
- 5) precipitated as pure or mixed solids;
- 6) present in the structure of secondary minerals; and/or
- 7) present in the structure of primary minerals.

The last two pools represent native metals in the soil parent materials, while the first five represent those potentially introduced through anthropogenic means. The first two pools usually represent the metals that are mobile in the aqueous phase and are of the greatest concern for possible translocation and contamination. The study of the factors that affect the partitioning and mobility of metal ions in the soil solution allows for a better understanding of how to avoid possible contamination or remediate it.

Sorption, a term representing the general “loss of a metal ion from a aqueous to a contiguous solid phase,” (Bradl, 2004) plays a major role in the mobility of heavy metals. Thus, factors that increase soil sorption also decrease metal mobility, and vice versa. Sorption capacity has been found to be affected by several factors, including: metal speciation and concentration, soil pH, redox potential, clay content and mineralogy, soil organic matter, soil type, Fe and Mn oxides, calcium carbonate content, solid:solution mass ratio, and contact time (Bradl, 2004; McLean and Bledsoe, 1992).

Soil pH is perhaps one of the most important factors in most sorption processes. Soil pH ultimately determines the amount of negatively-charged adsorption sites in many soil constituents, including Fe and Mn oxides, organic matter, carbonates, and the edges of clay minerals (McLean and Bledsoe, 1992; Yong, 2001). Thus, as pH increases (more alkaline), so do the amount of negatively charged sites, which in turn attract the cationic metals. Over a relatively short range of pH from intermediate to alkaline, heavy metal adsorption increases from near zero to near complete adsorption (Bradl, 2004). Soil pH

also strongly controls precipitation of heavy metals, which occurs under alkaline conditions (Yong, 2001). Precipitation also effectively immobilizes heavy metals within a soil profile.

Another of the important factors in immobilization of heavy metals is the organic matter content of the soil. Organic matter generally has a very high cation exchange capacity (CEC) and a high surface area. This large surface area allows for more adsorption sites to retain heavy metals from solution. Organic material also is often negatively charged and pH dependent. Thus, the more organic material in a soil, generally more heavy metal adsorption and immobilization will take place. However, this immobilization may not be permanent due to the nature of the bonding.

2.3. Previous Investigations of Heavy Metal Content and Mobility within Biosolids-Amended or Artificial Soil Mixes

2.3.1 Introduction

There have been several in-depth studies into the heavy metal content and mobility with soil plots amended with biosolids or full-fledged artificial soil mixes of organic and mineral components. However, there are so many variations of soil type, environment, and artificial soil mix components that each study is only generally applicable for that specific artificial soil mixture. Several of these previous studies are summarized below to provide general background.

2.3.2 Effect of Biosolids and Municipal Solid Waste (MSW) on Soil and Plants

Martinez et al. (2003) conducted a study on the effects that biosolids and organic MSW amendments had on soil and vegetation in a semiarid environment. Several

randomly selected, but comparable, plots of land were applied with one of four following treatments of either biosolids or MSW: 0, 40, 80, and 120 Mg ha⁻¹. The mean annual temperature was 16.8°C (62.2°F) and the mean annual precipitation was 350 mm (13.8 in.). Vegetation cover was less than 40% and consisted of herbaceous plants and low-lying shrubs. The soil was described as a loamy sand texture with an average pH of 8.3.

Composite samples were taken from each plot at a depth of 0-15 cm in 1997 (before treatment) and for three years after treatment was initiated. Soil samples were analyzed for organic carbon content, nutrients such as total N, P, and K⁺, as well as for soil heavy metal concentration. Plant samples were also taken for chemical analysis of total N and heavy metal concentration, as well as for biomass production and canopy cover calculations. Table 2.2 shows selected results from this testing regime (Martinez et al. 2003).

Table 2.2 Selected results from biosolids-amended soil (Martinez et al., 2003)

	Treatment	pH	EC	Organic C	Zn	Pb	Cd
	Mg ha ⁻¹	-	dS m ⁻¹	g kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹
1998	0	8.1	0.14	19.5	0.9	2	ND
	40	7.9	0.15	20.9	1	1.9	ND
	80	8.0	0.17	23.8	1.3	2.3	ND
	120	7.9	0.19	21.5	1.4	2	ND
1999	0	8.5	0.22	20.3	0.6	1.9	ND
	40	8.4	0.25	19.8	1.2	2	ND
	80	8.3	0.29	21.5	1.3	2	ND
	120	8.2	0.30	21.5	1.9	2.3	ND
2000	0	8.2	0.17	20.5	0.6	1.4	ND
	40	8.1	0.16	20.9	1.1	1.6	ND
	80	8.1	0.20	20.9	1.3	1.5	ND
	120	8.1	0.20	20.9	1.8	1.7	ND

The results show a relatively stable pH, electrical conductivity (EC) increases in the second year, and unchanged organic carbon contents over the three-year study. For

the metals analysis, cadmium levels were below the detectable limit ($0.1 \text{ mg Cd kg}^{-1}$).

Extractable lead concentrations did not significantly change, and zinc concentrations only changed very slightly. In all three cases, the concentration levels were well below that considered phytotoxic.

In conclusion of this study, the effects of heavy metal contamination of the soil and plant matter due to biosolids application were negligible. Positive affects of the biosolids application were seen in increased soil fertility, biomass production and canopy cover. Applications between 40 and 80 Mg ha^{-1} showed the most improvement with the least risk of environmental contamination, and biosolids seemed to be more effective than MSW.

2.3.3 Heavy Metal Translocation and Leaching Potential of Artificial Soil

Reynolds et al. (2002) conducted a study on the environmental and agricultural effects of the production and use of an artificial soil mix. The mix, called SLASH (Sewage sludge, Lime, and fly-**ash**), combines sewage sludge, class F fly-ash and unslaked lime. It was believed that the quicklime (calcium oxide) in the fly-ash would hydrate exothermically with the moisture in the sewage sludge to raise the temperature and pH to an adequate level to pasteurize the mix. Thus, the pathogens in the sewage sludge would be eliminated, leaving only the desirably high organic content.

Theoretically, heavy metals from the sewage sludge would be bound as insoluble metal hydroxides in the ash, and translocation would be eliminated (Reynolds et al., 2002). In this way, the two components would counter-balance each other and create an advantageous mix from two previously untapped, waste resources.

Testing consisted of leaching tests on the SLASH product to simulate both landfill leaching (acetic acid) and acid rain leaching, heavy metal translocation tests in the soil and plant fiber, and crop yield measurements. Table 2.3 shows results from the acid rain leaching tests and Table 2.4 shows elemental concentrations of the maize grain (Reynolds et al. 2002).

Table 2.3 Results of chemical analysis of acid rain leachate

Element	Leachate Mean (µg/g)	SLASH Product (µg/g)	% leached
As	0.01	< 5	0.2
Cu	132.5	184	72
Cd	0.09	0.081	111
Pb	0.54	3.9	13.8
Mn	121.7	1156	10.5
Se	0.05	4	1.25
Hg	0.005	< 0.2	2.5
B	198.9	203	97.9
Mo	2.4	4.35	55.2
Ni	58.2	52.6	110.6
Zn	16.1	210	7.6
Cr	5.6	804	0.7

Table 2.4 Mean elemental concentration of maize grain (Reynolds et al. 2002)

Treatment	Ni (mg*kg⁻¹)	Cd (mg*kg⁻¹)	B (mg*kg⁻¹)
Control	106.845	9.929	26.605
5% SLASH	102.797	9.361	27.269
10% SLASH	104.45	9.815	29.263
3% Sludge	104.135	9.819	25.613
Limits set by law	400	15.7	80

It is believed that the Ni and Cd leached percentages in Table 2.3 were above 100% due to the fact that these elements are more susceptible to acidic leaching than total digestion (Reynolds et al. 2002). Reynolds et al. also states that the “results indicate that SLASH does not leach in any extreme manner...” This can be attributed to the fly-ash

immobilizing the metals. It does appear, however, that some of the constituent elements leach to moderate percentages regardless of their overall concentrations.

It does not appear from the heavy metals analysis of the maize leaves and grain that metals were translocated to the crops in detectable amounts. The SLASH-treated soils show very similar concentrations to the control soil. Grain yields for the SLASH treatments were 333% better than the control, and plant growth was up to 200% better than the control. These numbers reflect the potential of SLASH as an environmentally-safe soil ameliorant.

2.3.4 Immobilization of Heavy Metals by Artificial Soil

Usman et al. (2004) describe an experimental program centered on investigating the mobility of heavy metals in an artificial soil mix by using batch sorption and desorption testing techniques. Immobilization was estimated to be the difference between the sorption and desorption values. The artificial soil was a mixture of sewage sludge, wood shavings, green compost, and sandy loam, which was open-air composted. The artificial soil had a pH of 7.45, cation exchange capacity of 180 mmol kg⁻¹, organic carbon content of 4.82%, and calcium carbonate (CaCO₃) content of 7.3%. Heavy metal concentrations within the artificial soil are summarized in Table 2.5.

Table 2.5 Heavy Metal Concentrations within the Artificial Soil Mix (Usman et al., 2004)

Cd (mg kg⁻¹)	Cu (mg kg⁻¹)	Ni (mg kg⁻¹)	Pb (mg kg⁻¹)	Zn (mg kg⁻¹)
0.98	44.8	21	42.1	205

Sorption testing consisted of creating solutions of varying concentrations of cadmium, lead, and zinc ions from salts (chlorides) and adding them to artificial soil in a soil:solution ratio of 1:25. The samples were equilibrated and shaken for 24 hours at

room temperature, followed by centrifugation and filtration. The solute was tested before and after to determine the loss of concentration due to sorption. The remaining sediment was extracted with 1 M ammonium nitrate (NH_4NO_3) to estimate plant-available amounts of heavy metals (Usman et al., 2004). Sorption, desorption, and immobilization were plotted on sorption isotherms. Figure 2.1 shows the isotherms for Cd, Zn, and Pb.

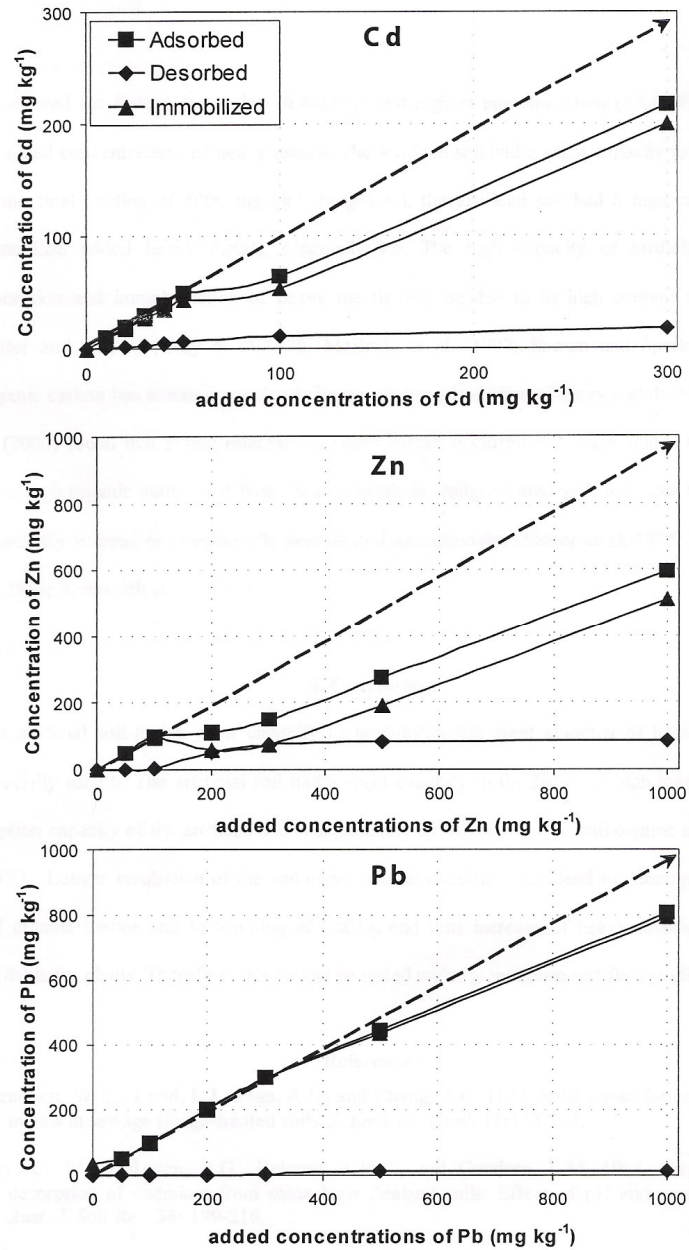


Figure 2.1 Sorption, desorption, and immobilization isotherms of Cd, Zn, and Pb (Usman et al. 2004)

The isotherms in Figure 2.1 show that the artificial soil was very effective at immobilizing all three of the metals to some extent. These isotherms have been plotted as concentration sorbed on the y-axis and initial, or loading, concentration on the x-axis. The sorption curve is very close to the theoretical, 100% sorption curve represented by a dashed line. The desorption curve is very flat and close to zero in all cases. Because of this, the immobilization curve very closely parallels the sorption curve, meaning that most of the sorbed ions remain immobilized despite leaching conditions. The Freundlich equation was used to determine the Freundlich “k” constant (or adsorption coefficient), which describes the partitioning of metal ions between the solid and liquid phase. For this experiment, the sequence of most sorptive to least sorptive was: $\text{Pb} > \text{Cd} > \text{Zn}$. The isotherms also suggest this by the very small amount of Pb desorbed compared to the greater amount of Zn.

The authors’ conclusions were that the artificial soil was “had a great capacity to immobilize the great amounts of heavy metals...” and that this was due to the high organic material content and calcium carbonate content (Usman et al. 2004). Because of this fact, it was suggested that testing for the time-dependent effects of organic decomposition and CaCO_3 leaching, and how these affected metals mobility in the long-term, be completed.

2.4 Summary

These studies of both biosolids-amended soil and artificial soil mixes show negligible heavy metal mobility and environmental repercussions. They also show a great potential for increased plant growth and yield in such uses of biosolids. This

creates an expectation that the artificial soil at the Continental Cement Company in Hannibal, Missouri will show similar characteristics.

CHAPTER 3

HYDROLOGIC PROPERTIES AND BEHAVIOR OF ARTIFICIAL SOIL

3.1 Introduction

The general effectiveness of the artificial soil concept as an AFC has been investigated by previous research focusing on measuring and modeling the general hydrologic behavior at two full-scale field sites in Hannibal Missouri (Bobba, 2005; Wayllace and Likos, 2006). Bobba's research consisted of field investigation complimented by a laboratory investigation and computer modeling. His laboratory investigation is summarized in this chapter, as it provides insight into the relevant properties and behavior of artificial soil.

3.2 Laboratory Investigation

Representative samples of the O horizon, C horizon, and CKD were collected in the field (bulk samples taken from the sides of the newly constructed test pad) and taken to the lab for testing and analysis. Engineering properties determined include: compaction behavior (moisture-density relationships), in-situ bulk and dry density, long term flow behavior, saturated hydraulic conductivity, field moisture capacity, specific gravity, porosity (void ratio), and water retention characteristics. Table 3.1 summarizes the results of this testing.

Table 3.1 Engineering properties of artificial soil from lab investigation (from Bobba, 2005)

Property	Units	O-Horizon	C-Horizon	CKD	Test Method
Field Capacity	m ³ /m ³	0.15	0.17	ND	column test
Specific Gravity	---	1.71	2.12	2.46	ASTM D854
In-situ moisture*	m ³ /m ³	0.21	0.20	0.26	ASTM D4643
In-situ bulk dens	kN/m ³ (pcf)	4.9 (31)	7.1 (45)	7.1 (45)	ASTM D1556
In-situ dry dens	kN/m ³ (pcf)	2.5 (16)	5.0 (32)	4.9 (31)	ASTM D1556
Proctor density	kN/m ³ (pcf)	5.3 (34)	10.8 (69)	ND	ASTM D698
Optimum moist.	%	124	45	ND	ASTM D698
Sat. hyd. cond.	cm/s	7.0-8.3 X 10 ⁻³	8.5-9.3 X 10 ⁻³	ND	ASTM D 2434
at density	kN/m ³ (pcf)	2.6 (16.5)	6.1 (39)	ND	NA
Porosity	---	0.85 – 0.90	0.76 – 0.80	ND	NA

* Measured at time of sensor installation.

Column flow tests were conducted to determine saturated hydraulic conductivity (k_s) and flow behavior of the O and C horizon materials. Samples were prepared in 4-inch (inside) diameter, 24 inch tall clear cylinders. Loosely-placed concrete sand over geotextile was used as a filter to assure that no translocation of material took place. Various setups for the 6 cylinders were used to accurately determine the k_s of the two horizons and three composite samples, as seen in Figure 3.1.

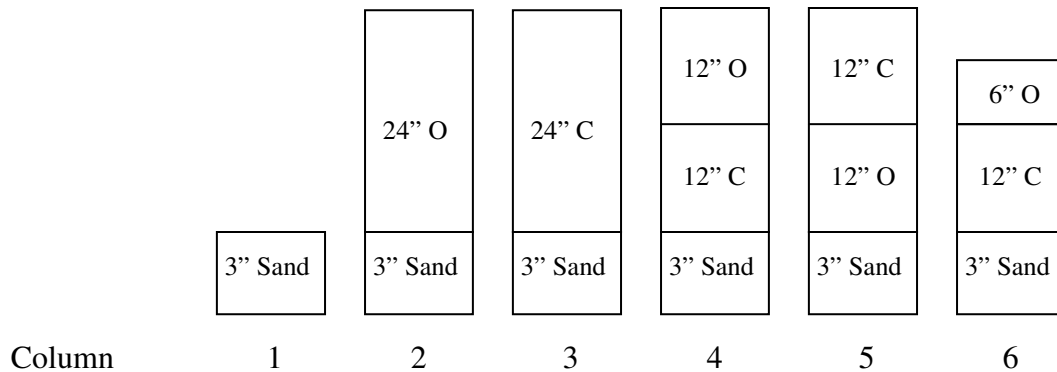


Figure 3.1 Column flow test setup. O = O horizon, C = C horizon (from Bobba, 2005)

Dry densities of 16.5 pcf and 39 pcf were used for placement to replicate in-situ conditions for the O and C-Horizon materials, respectively. The hydraulic gradient (i) was approximately $i = 1.0$ for columns 2 through 6, and $i = 8.0$ for column 1 with the

sand only. A constant head was maintained on the influent. Outflow rates were monitored until a steady-state flow condition was apparent. The results can be seen in Figure 3.2. The saturated hydraulic conductivities for the O horizon and C horizon were then calculated from these flow results using Darcy's Law (results seen in Table 3.1). Figure 3.3 shows the hydraulic conductivities for composite samples of both horizons.

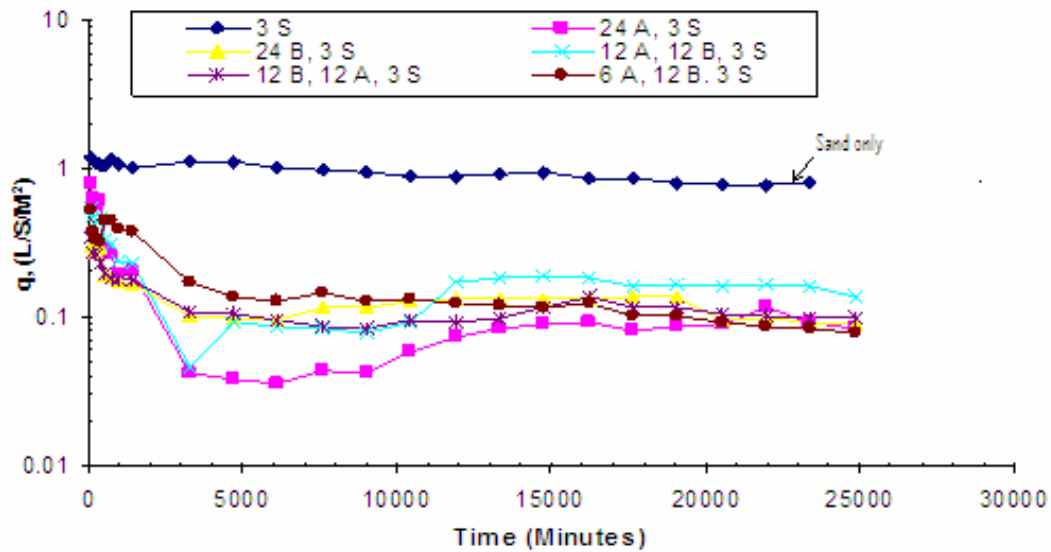


Figure 3.2 Flow rate versus time for the six column flow tests (from Bobba, 2005)

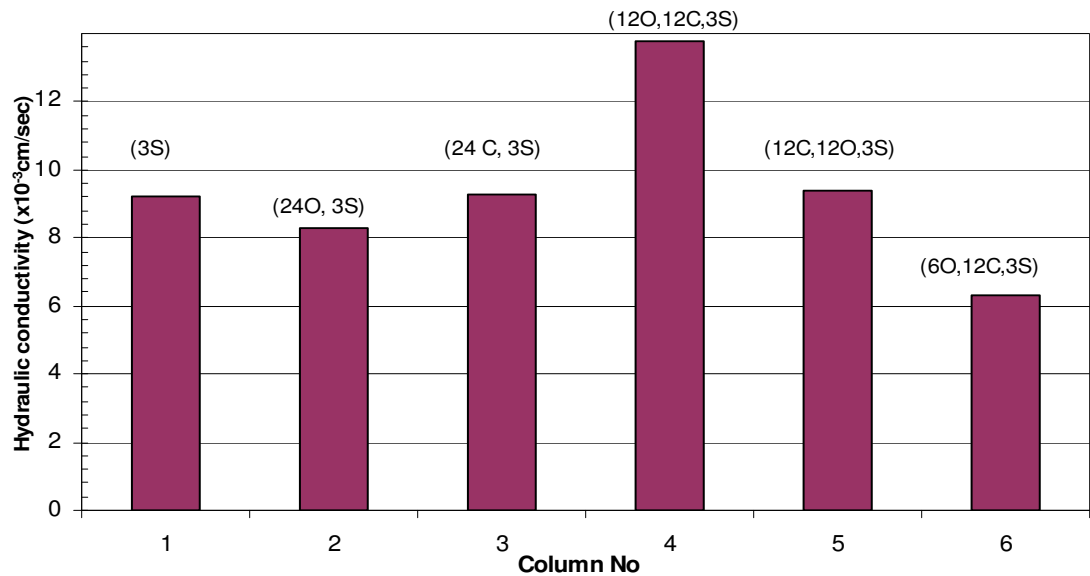


Figure 3.3 Hydraulic conductivities for all six column flow tests, including the composite samples in Columns 4, 5, and 6. (from Bobba, 2005)

Field capacity of the O and C horizons was determined as the final moisture content after allowing the column flow tests to drain under gravity. This property is a measure of the holding capacity of the soil in the field and may be used to estimate initial conditions for numerical modeling. Figure 3.4 shows Bobba's results, which results in volumetric field capacities of 0.15 and 0.17 for the O and C Horizon materials, respectively.

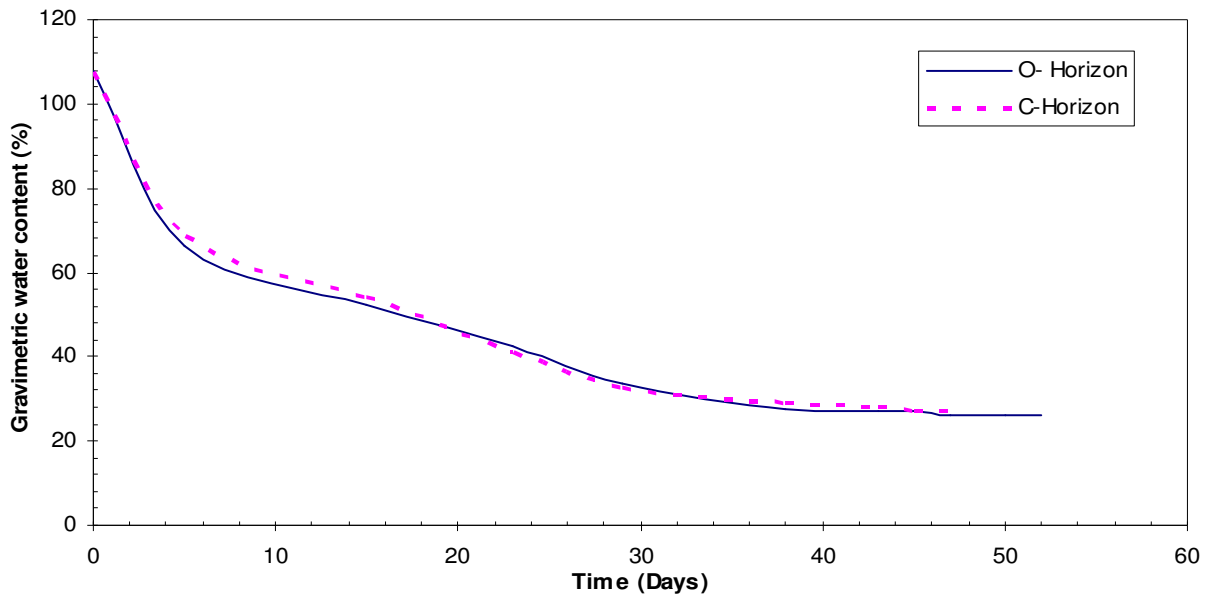


Figure 3.4 Field capacity determination for both O and C horizons (from Bobba, 2005)

Soil-water characteristic curves (SWCC) (moisture retention curves) were determined for the O and C horizons using Tempe extractions cell tests. “Brooks and Corey” and “Van Genuchten” models (Brooks & Corey, 1964, and Van Genuchten, 1980) were used to model the soil-water characteristic curves, and all are shown in Figure 3.5.

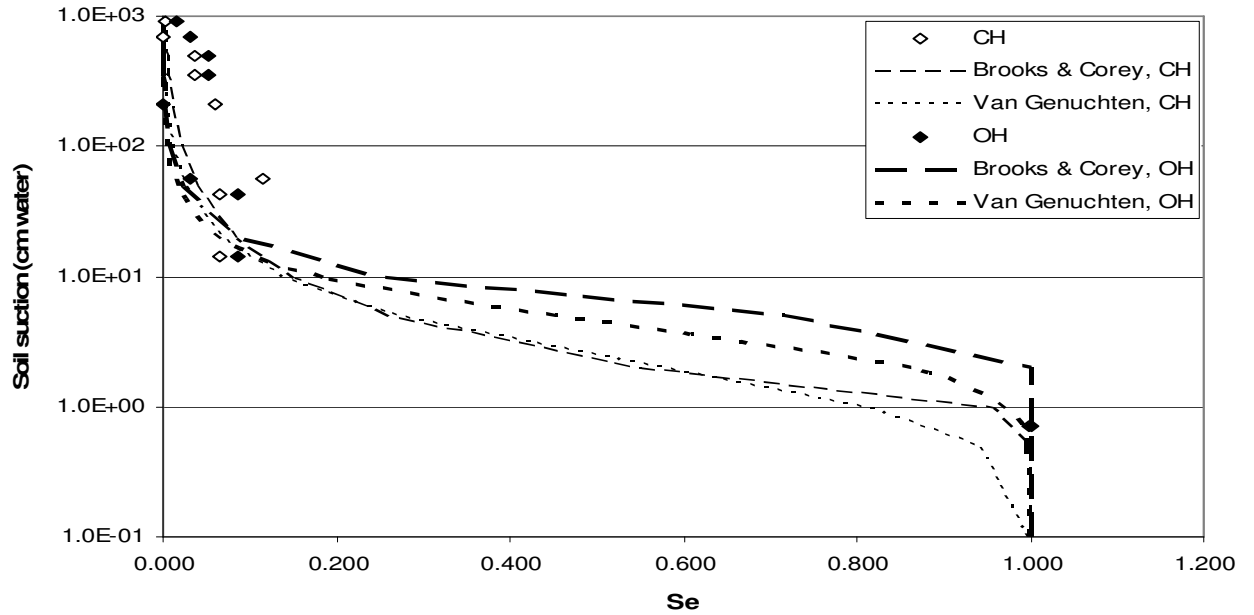


Figure 3.5 Soil-water characteristic curves for O and C horizons (from Bobba, 2005)

3.3 Summary

Bobba's research allows for a background on the specific artificial soil mix used at the Hannibal field site. Table 3.1 summarizes the main engineering properties pertinent to the previous and current study. The hydrologic characteristics of the artificial soil will be especially important in the study of the mobility of heavy metals because contaminants travel through the aqueous phase.

CHAPTER 4

EXPERIMENTAL INVESTIGATION

4.1. Introduction

A laboratory investigation was performed to explore the mobility of heavy metals contained in artificial soil at the Hannibal test site, as well as soil properties that are known to affect ion mobility. Tests for natural moisture content, soil pH, soil carbon content, batch sorption, and column leaching were all completed to help characterize the mobility of heavy metals.

Artificial soil samples used for the lab testing came from two sources. The first batch of samples came from a field trip in late October of 2005 in which samples were taken from two hand-augered boreholes selected to represent “old” (Sample M-O, representing a mature O-horizon sample) and “new” (Sample Y-O, representing a young O-horizon sample) artificial soil profiles. Sample M-O was approximately 6-12 months old prior to sampling, while Sample Y-O was approximately 2 months old. Figure 4.1 shows these two sampling locations with respect to the project site. A sampler was used on the end of the hand auger at irregular intervals, and the soil was sealed in airtight plastic bags to be transported and stored at the University of Missouri-Columbia (UMC) Engineering Building. The samples did not extend past the interface of the O and C horizons due to auger refusal. Thus, this batch was used primarily for comparisons of different properties in the O-Horizon with respect to depth from the surface. The second batch of samples was taken by Ramesh Bobba, a previous graduate research assistant at UMC, from the instrumented test pad on the site approximately one year before testing began. There were samples of both O and C horizon, dug out from the sides of the pad,

without noted depth. These samples were used primarily for comparison of different properties with respect to soil horizon and for comparison with the “old” specimens, and are denoted as M-O (mature O-horizon) and M-C (mature C-horizon) samples. A majority of the soil testing was conducting in the Soil Characterization Lab (SCL) located in Lafferre Hall on the UMC campus.

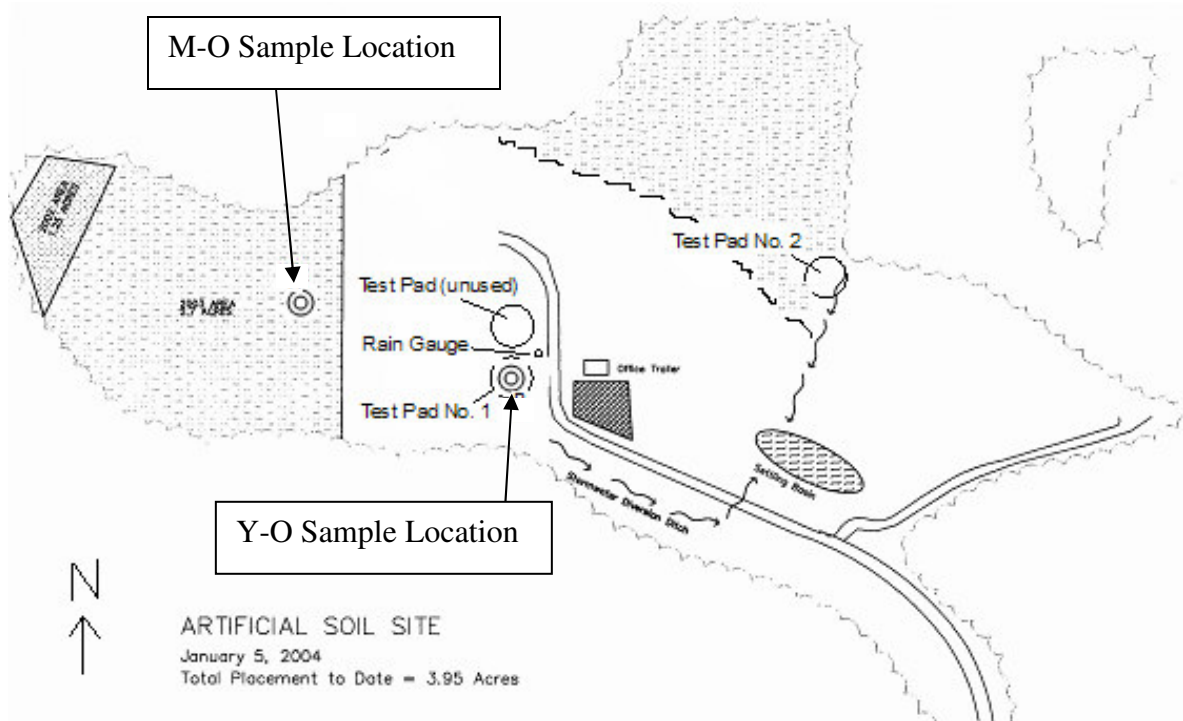


Figure 4.1 Boring Location Plan for Artificial Soil Project at CCC in Hannibal, MO; depicts the M-O soil sample location and the Y-O soil sample location.

4.2. Specimen Imaging

One of the most important properties affecting the mobility of heavy metals is the microstructure of the artificial soil. The microstructure affects the surface area (amount of possible sorption sites) on which inorganic contaminants become immobilized.

Scanning Electron Microscope (SEM) images were obtained of various constituents of the artificial soil. These images allow general qualitative insight into the microstructure

of the artificial soil. Figures 4.2, 4.3, 4.4, and 4.5 show the C horizon at various magnifications. Figures 4.6 and 4.7 show the CKD, and Figures 4.8, 4.9, and 4.10 show wood from the O horizon.

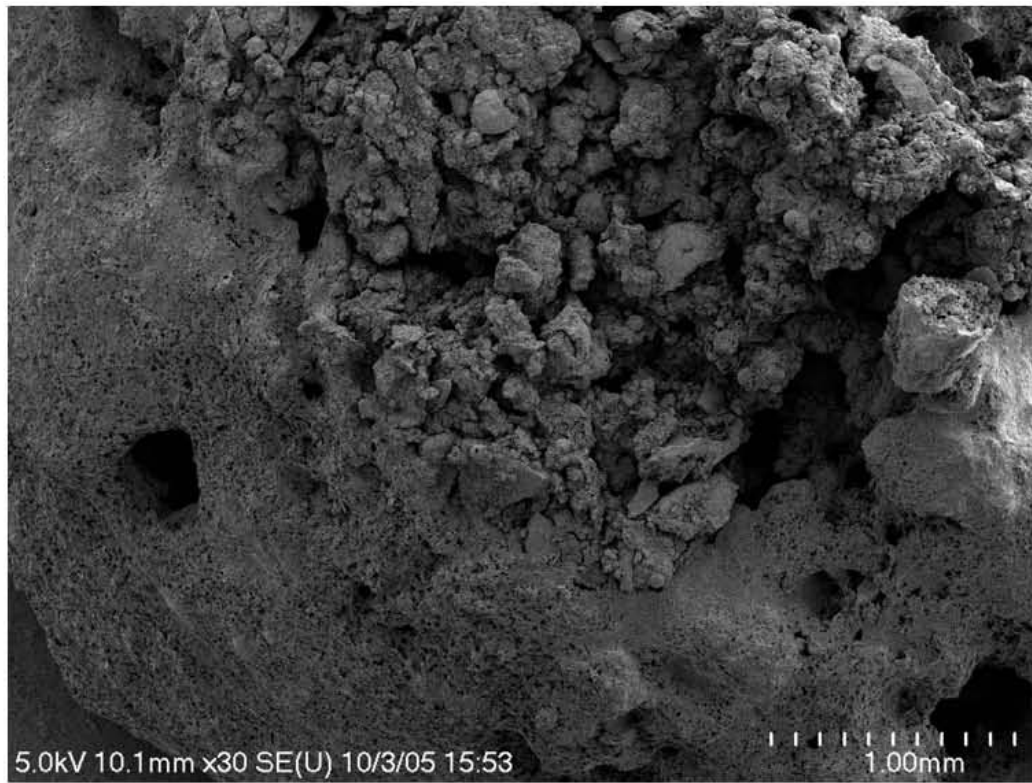


Figure 4.2 SEM image of C horizon material (30x magnification)

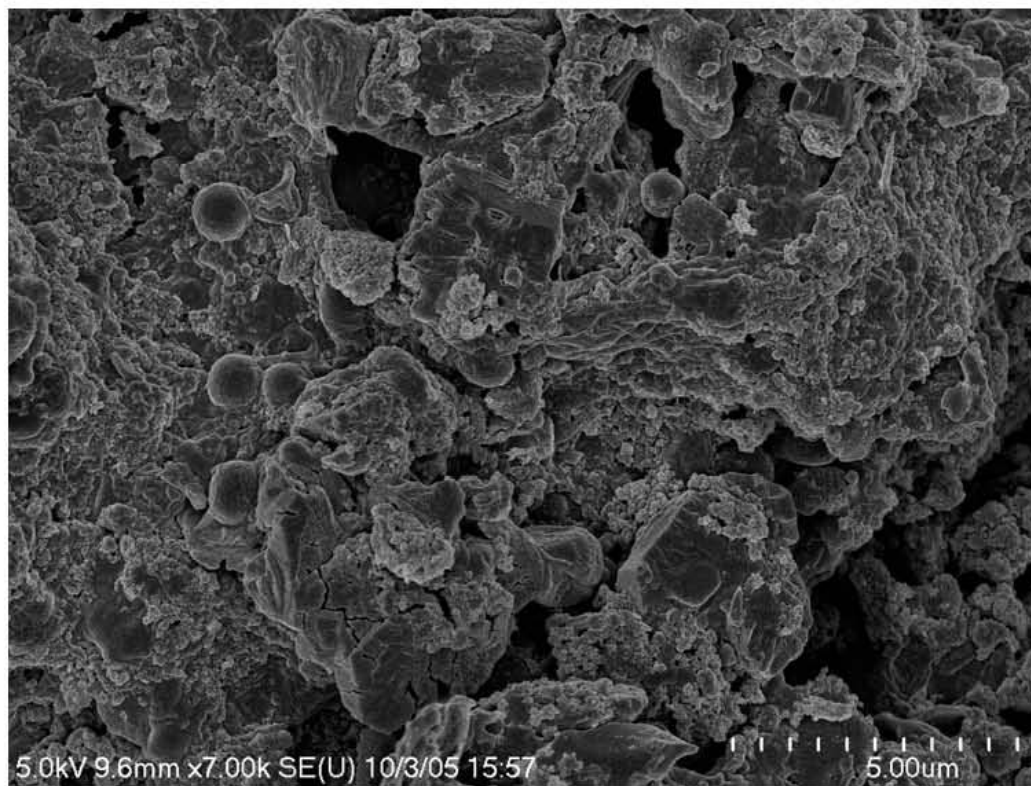


Figure 4.3 SEM image of C-horizon material (7,000x magnification)

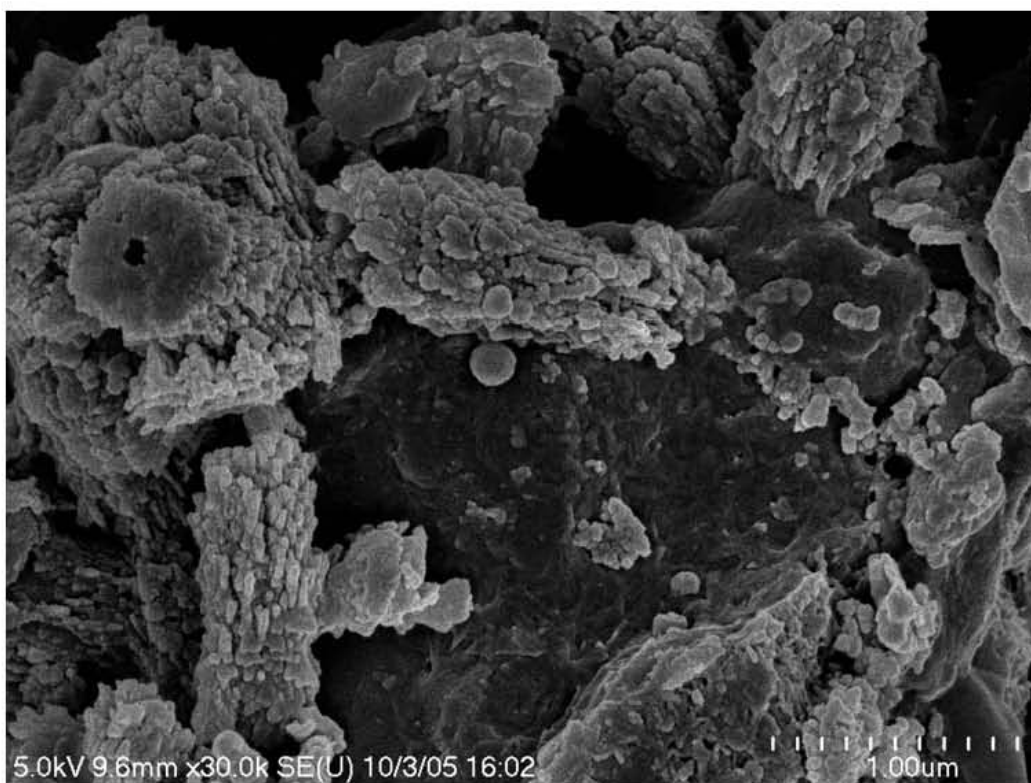


Figure 4.4 SEM image of C horizon material (30,000x magnification)

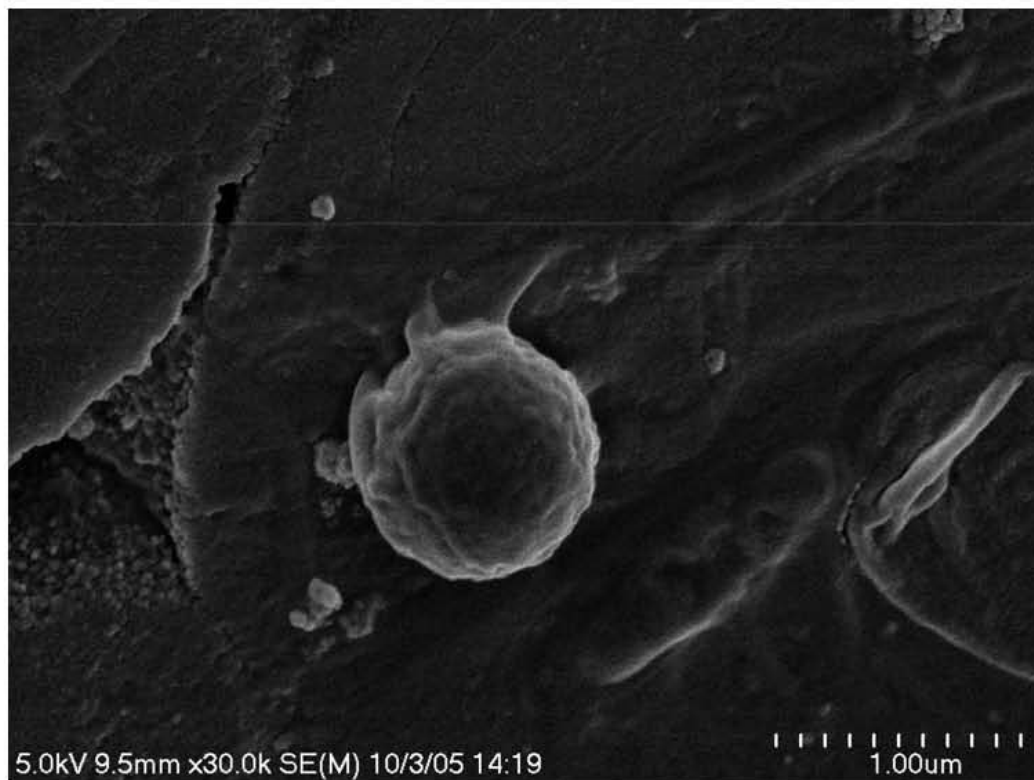


Figure 4.5 SEM image of C horizon material (30,000x magnification)

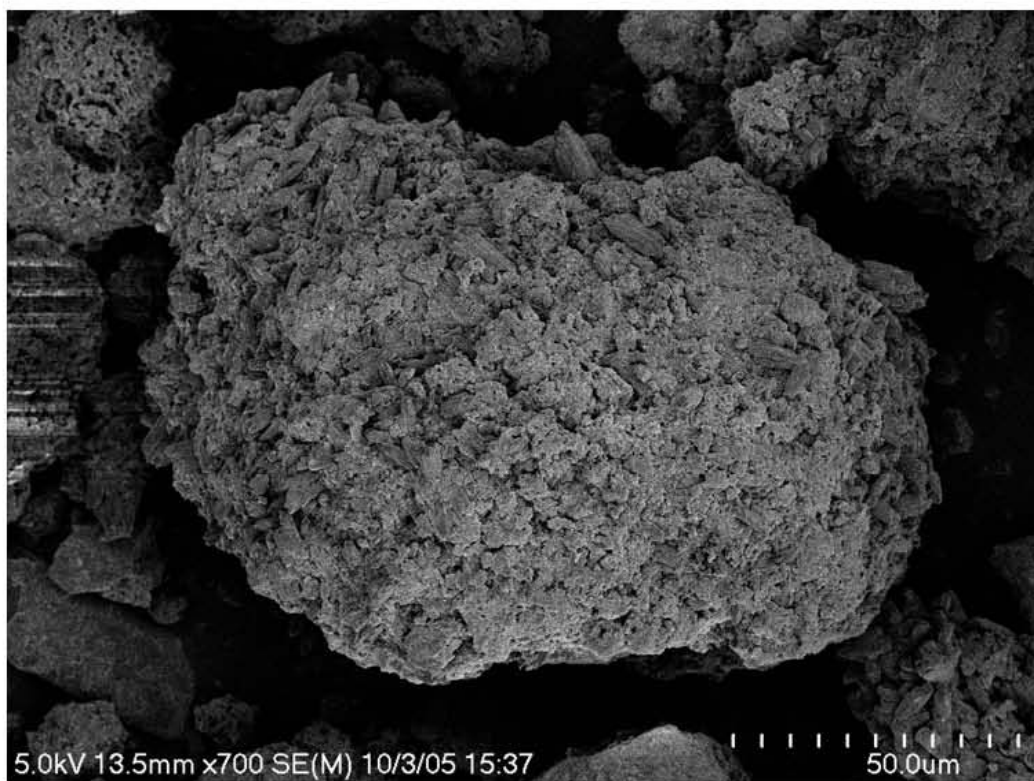


Figure 4.6 SEM image of the CKD (700x magnification)

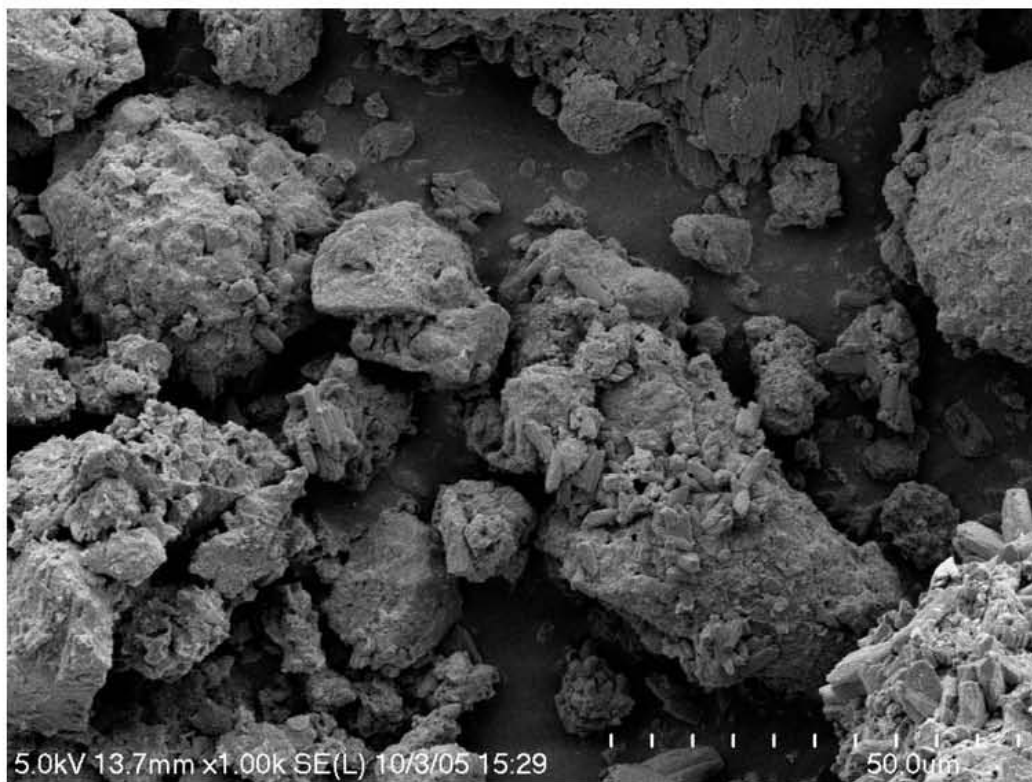


Figure 4.7 SEM image of the CKD (,1000x magnification)



Figure 4.8 SEM image of wood surface (45x magnification)

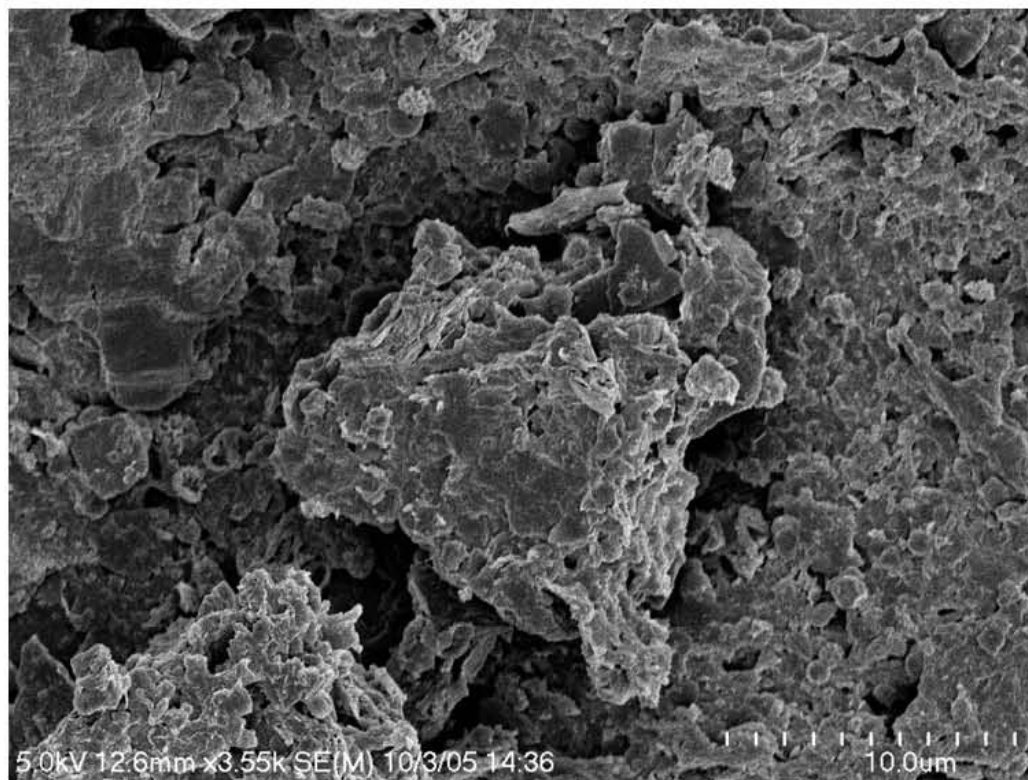


Figure 4.9 SEM image of wood surface (3,550x magnification)

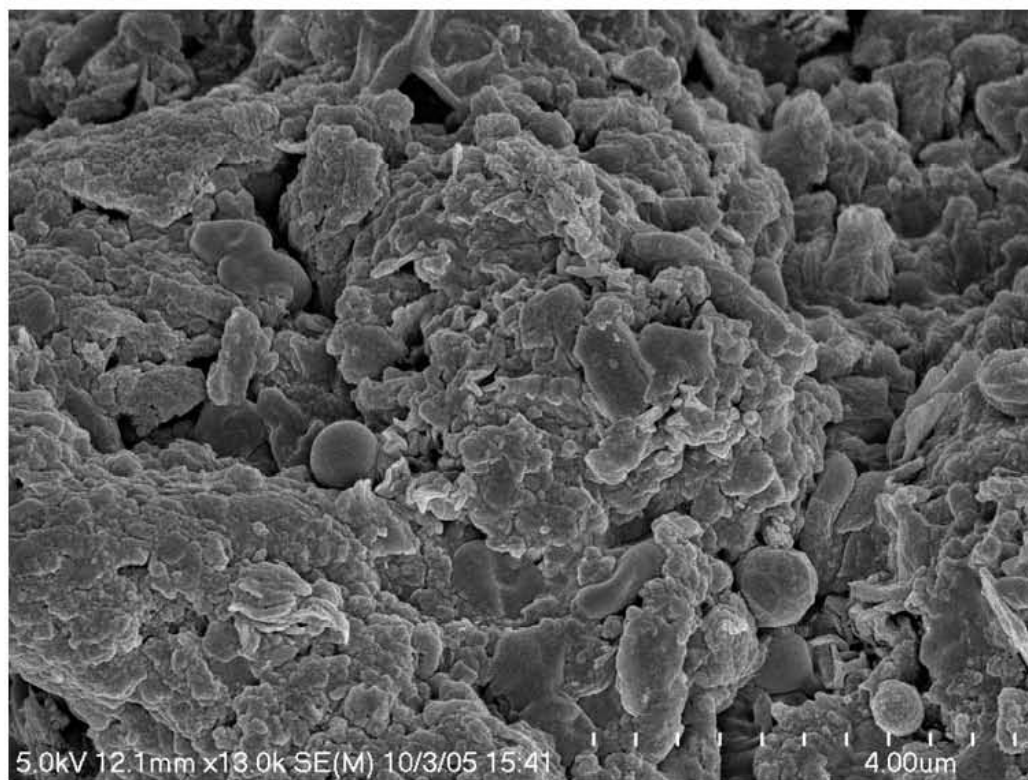


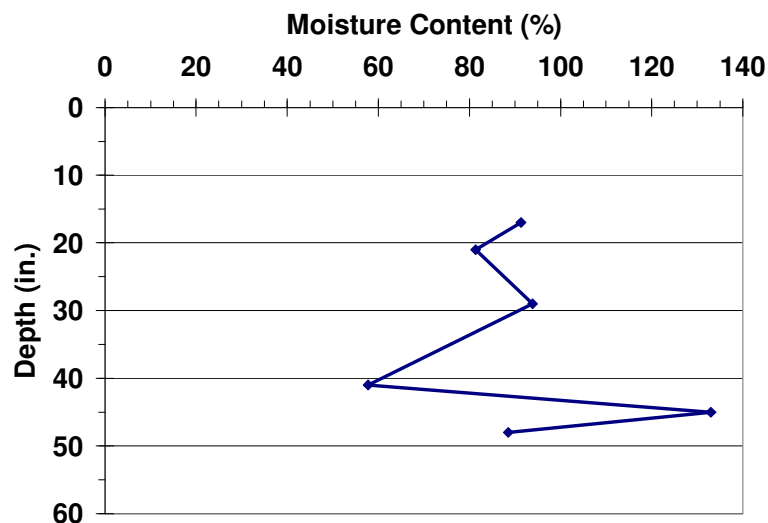
Figure 4.10 SEM image of wood surface (13,000x magnification)

4.3. Natural Moisture Content

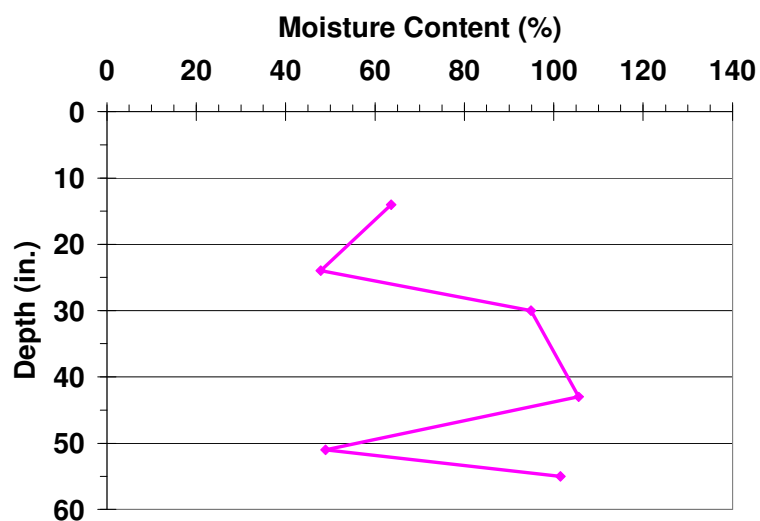
Soil samples from Sample M-O and Y-O were tested for natural gravimetric water content using the procedure outlined in ASTM Standard D 2216. Representative samples from different depths were weighed, dried overnight in an oven at approximately 105°C, and weighed again after 24 hours. Table 4.1 summarizes the results of these tests and Figure 4.11 shows the relationship between natural moisture content and depth for Sample M-O and Sample Y-O.

Table 4.1 Natural Moisture Content with depth

Sample M-O			Sample Y-O		
Sample #	Depth	ω	Sample #	Depth	ω
	(in.)	(%)		(in.)	(%)
O-1	17	91.3	N-1	14	63.6
O-2	21	81.4	N-2	24	47.8
O-3	29	93.9	N-3	30	94.9
O-4	41	57.8	N-4	43	105.6
O-5	45	133.0	N-5	51	49.0
O-6	48	88.5	N-6	55	101.4



(A)



(B)

Figure 4.11 Graph of natural, gravimetric moisture content vs. depth for Sample M-O (A) and Sample Y-O (B).

4.4. Soil pH Tests

Soil pH was determined by using a soil pH electrode calibrated with pH 4, 7, and 10 solutions before testing. Ten grams of each soil sample were mixed with 10 mL of D.I. water (1:1 solution) and shaken on a custom-made shaker-table for 30 minutes, after which the pH was determined. Ten mL of 0.01M calcium chloride (CaCl_2) were then

added to the soil-water mixtures and shaken for another 30 minutes, after which the pH was determined again. Figure 4.12 shows the results for soil pH with varying depth for both Sample M-O and Sample Y-O.

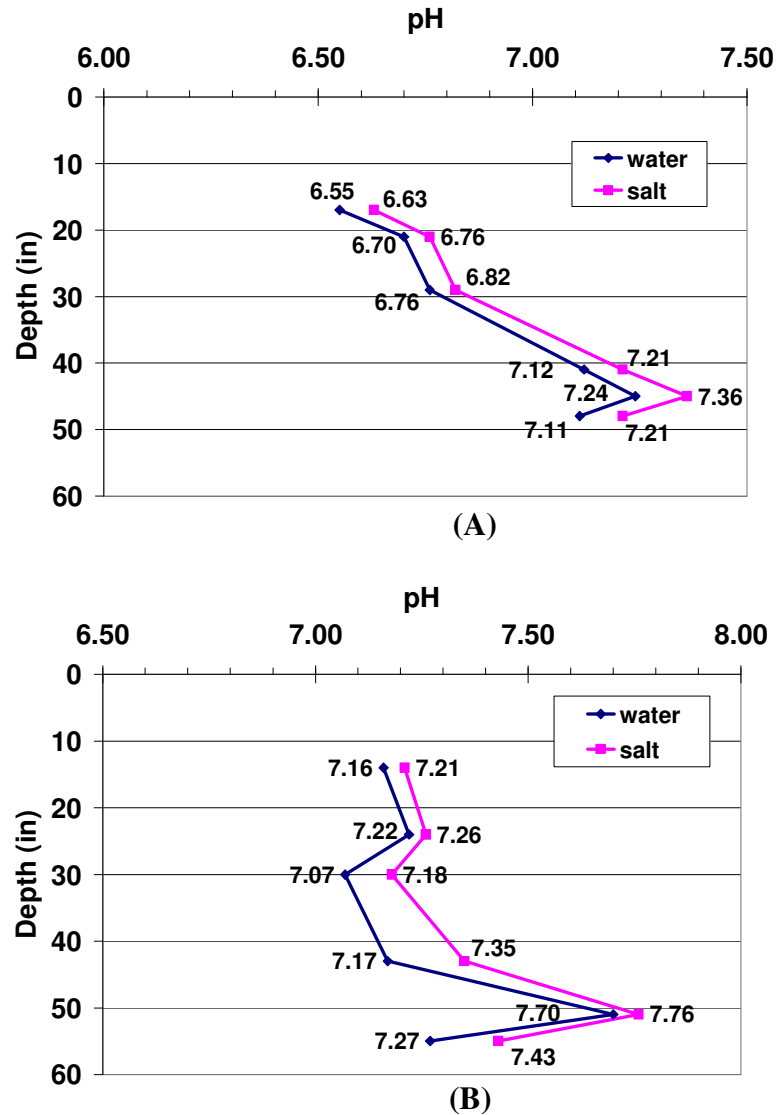


Figure 4.12 Soil pH vs. depth for Sample M-O (A) and Sample Y-O (B) with both D.I. water and CaCl_2 (salt-water)

In order to investigate the change in pH over time within the soil profile, Figure 4.13 compares the results of soil pH vs. depth (using D.I. water) with varying profile age.

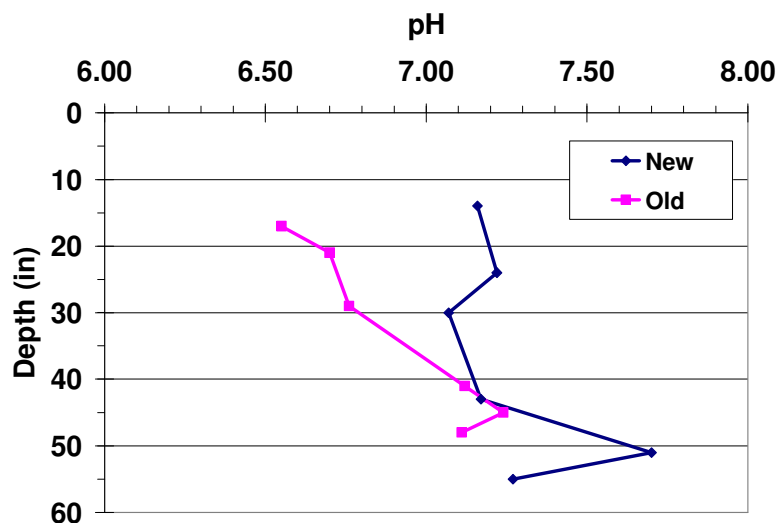


Figure 4.13 Comparison of pH profiles of samples M-O and Y-O.

4.5. Carbon Content

4.5.1 Introduction

Organic and total carbon contents were measured using a LECO combustion furnace set at a specific temperature in order to burn away and measure the carbon. Organic carbon combusts at lower temperature than inorganic, allowing for a distinction between the two with furnaces of varying temperature. The soil samples were first air-dried and then crushed using a mortar and pestle.

4.5.2 Organic Carbon

Organic carbon samples were combusted at approximately 927°C in a LECO C-144 combustion furnace in order to only burn organic carbon in the sample, such as soil organic matter (SOM). Figure 4.14 shows the organic carbon content with depth for both sets of samples. The organic carbon content found using this method may be slightly greater than the actual due to inorganic carbon starting to combust. There was evidence during testing that this was possibly taking place.

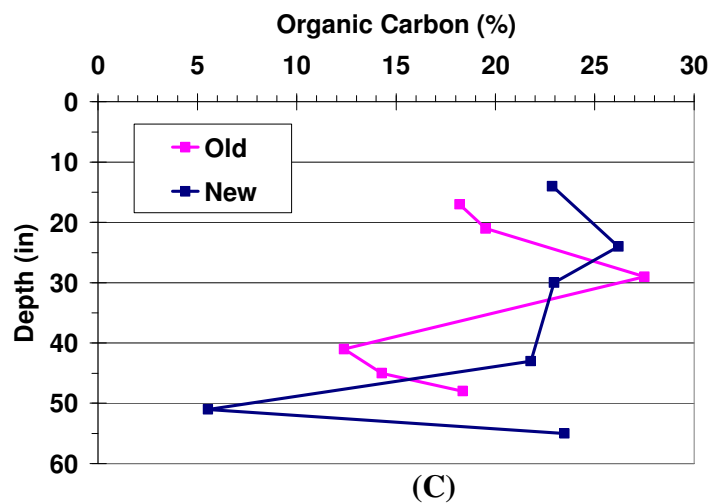
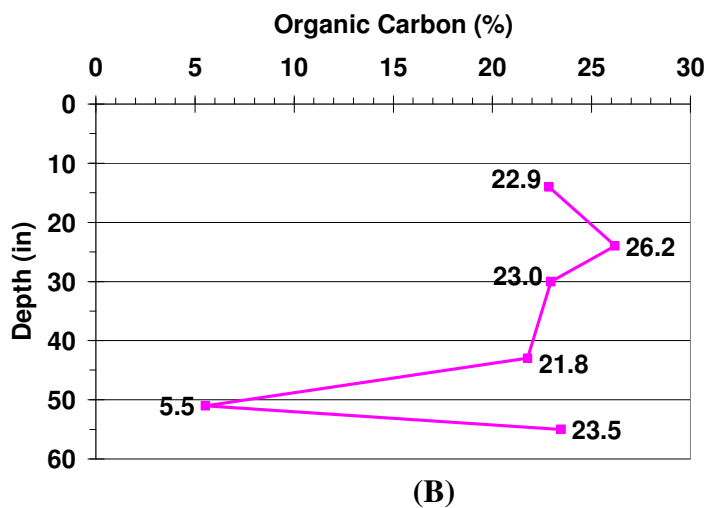
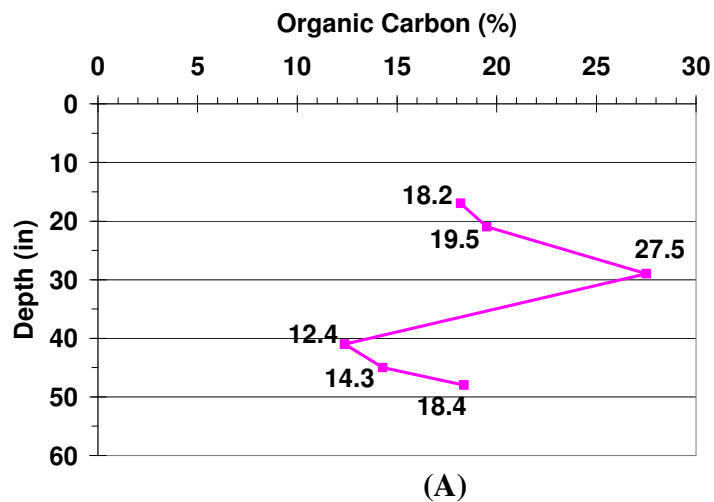


Figure 4.14 Organic carbon vs. depth profiles for Sample M-O (A), Sample Y-O (B), and a comparison of the two samples (C)

4.5.3 Total Carbon

Total carbon samples were burned in a LECO CR12 combustion furnace at a temperature of 2425 °C so as to remove both the organic and inorganic carbon. Figure 4.15 shows the total carbon content with depth for both sets of samples. An interesting phenomenon during testing was the formation of molten spheres in the remaining post-combustion, mineral sample. These spheres appeared to be metallic in nature. If repeated, these spheres should be tested for metals content.

4.5.4 Inorganic Carbon

The SCL in-house method of determining inorganic carbon, such as carbonates, is to find the difference of the total and organic carbon contents. Figure 4.16 shows the total, organic, and inorganic carbon content profiles for both Sample M-O and Sample Y-O. The total carbon content is always equal to or greater than the organic carbon content. The 51 inch depth for Sample Y-O is suspect because the organic carbon content is approximately equal to the inorganic carbon content.

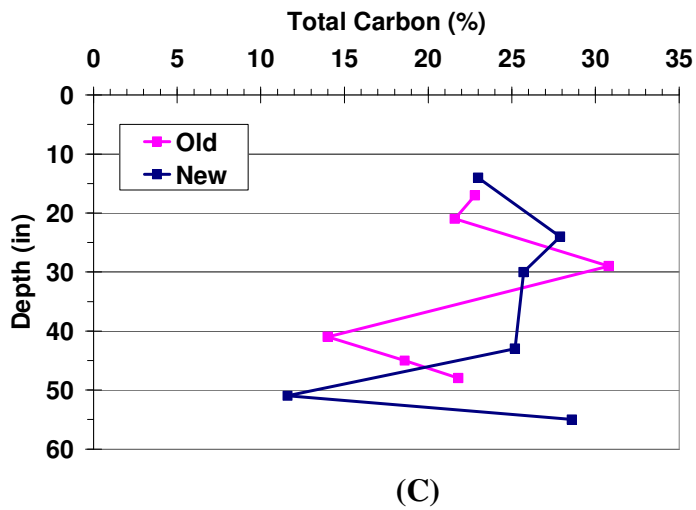
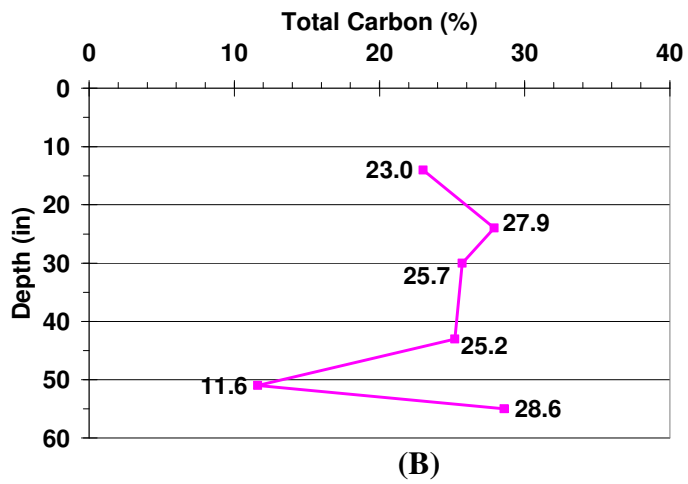
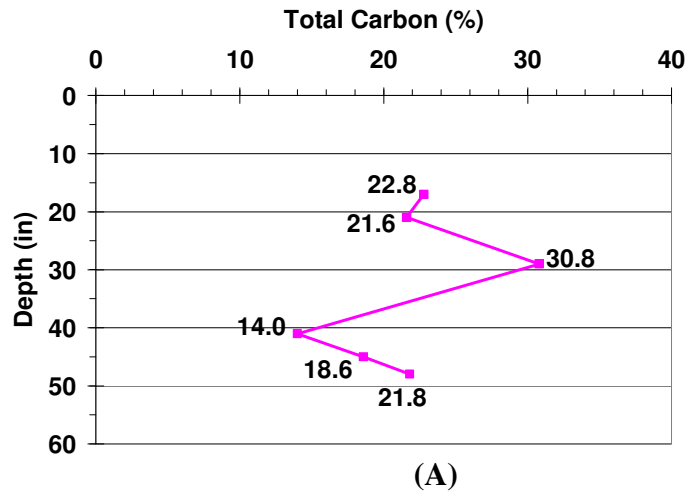


Figure 4.15 Total carbon content vs. depth for Sample M-O (A), Sample Y-O (B), and a comparison of the two total carbon profiles (C).

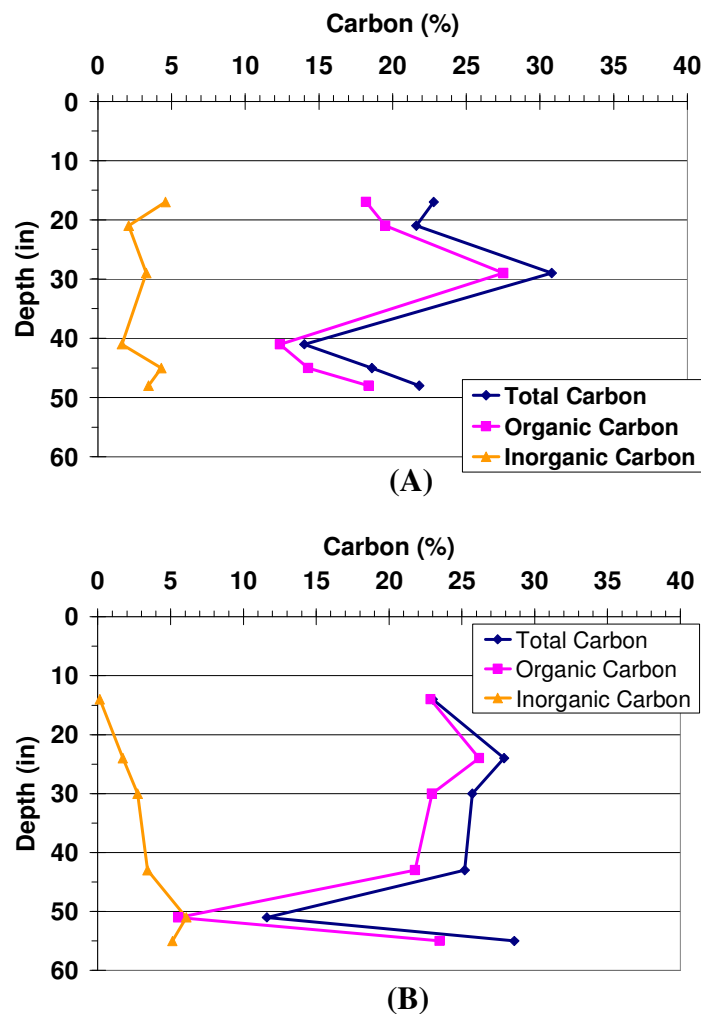


Figure 4.16 Total, organic, and inorganic carbon vs. depth profiles for both Sample M-O (A), and Sample Y-O (B).

4.6. Batch Sorption Tests

4.6.1 Introduction

Batch sorption tests made up the bulk of this investigation. Both adsorption and desorption were tested in soil from Sample M-O, Sample Y-O, and the two mixed samples of “O” horizon material (M-O) and “C” horizon material (M-C). Sample M-O and Y-O were used for the comparison of sorption with varying depth, while samples M-O and M-C were used for comparison of sorption within soil layer.

The soil samples were air-dried for approximately two weeks, then crushed and sieved. The general sorption testing procedure is described by Usman et al., 2004. Solutions of different concentrations of cadmium (Cd), lead (Pb), and zinc (Zn) were created with metal chlorides and added to the soil samples (moisture-corrected) at a soil:solution ratio of 1:25 (3 grams of dry soil to 75 mL of solution). It should be noted that small amounts of nitric acid were used to help dissolve the metal chlorides in the deionized water solutions. Initial aliquots of the solutions were kept for later analysis. The soil solutions were then agitated on a shaker table for 24 hours in order to reach equilibrium, after which they were centrifuged for 30 minutes at 3000 rpm and filtered through Whatman 41 filter paper. The remaining solution was removed from the filtered sediment and tested in a Varian Vista-MPX CCD Simultaneous ICP-OES for Cd, Pb, and Zn concentration. The difference in initial concentration and final concentration, knowing volume of solution and dry mass of soil, allowed for the calculation of the approximate amount of heavy metals adsorbed per gram of soil. A control solution was run with each batch to determine and account for any possible losses. If losses were apparent, the final concentration was corrected accordingly.

Solutions of 1 M ammonium nitrate (NH_4NO_3) were then added to the filtered sediment in order to extract plant-available heavy metals (Usman et al., 2004). Immobilized heavy metals were calculated as the difference between adsorbed and desorbed metals.

4.6.2 Comparative Studies of Depth

Sorption isotherms were created for the samples of varying depths from both Sample M-O and Sample Y-O. Because of the limited amount of each sample, only

cadmium sorption isotherms were developed for Sample M-O, and zinc sorption isotherms for Sample Y-O. Figure 4.17 shows the comparison of cadmium sorption characteristics at various depths in Sample M-O. Distribution coefficients (K_d) were calculated for all four samples. These are graphically represented as the initial, linear portion of the isotherm, and were 24.48, 23.95, 24.43, and 24.51 respectively (increasing depth). They are calculated using the simplified Freundlich equation over a linear range, $K_d = S/C$, where S is the mass of ions sorbed per mass of soil and C is the initial concentration of the ion in the solution. Distribution coefficients represent the partitioning of an ion between solid and liquid phases over a linear range. The range was considered linear from the origin to the first isotherm point (approximately 200 ppm concentration). The distribution coefficients also help to roughly quantify the sorptive capability of each sample.

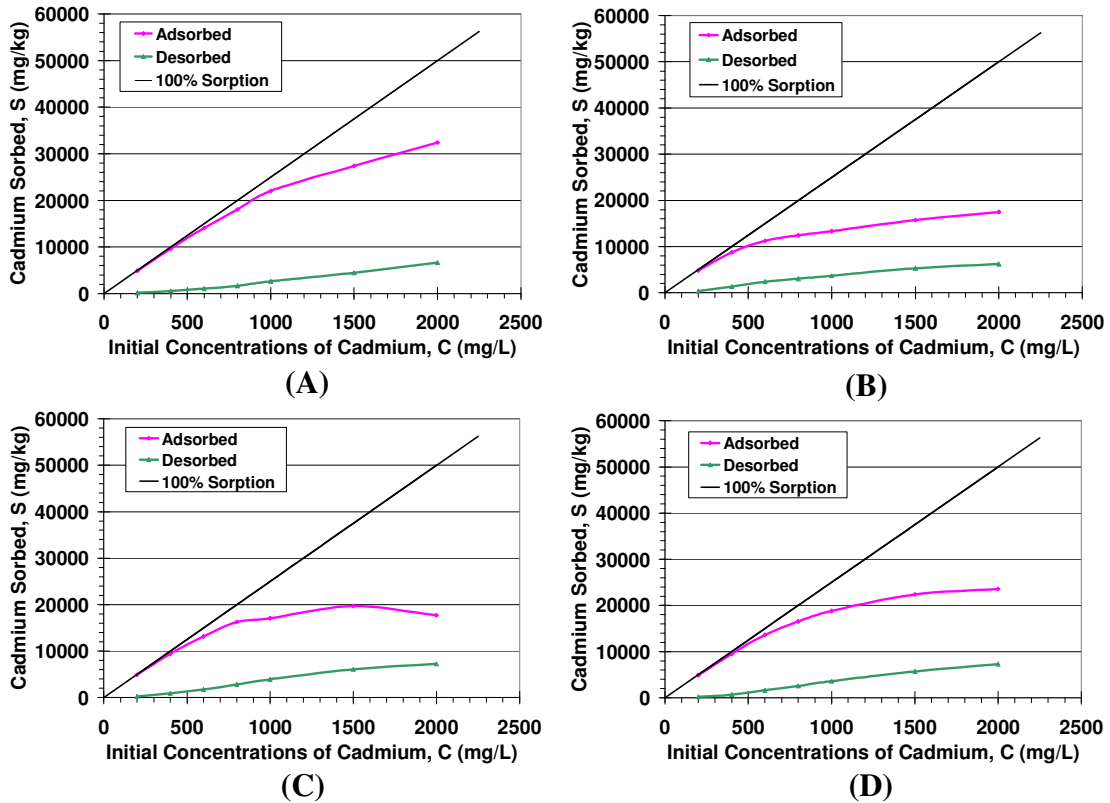


Figure 4.17 Cadmium sorption isotherms for representative “mature” artificial soil profile at depths of 29 in. (A), 41 in. (B), 45 in. (C), and 49 in. (D)

4.6.3 Comparative Studies of Soil Layer

Samples of mixed depth representing the C horizon (mineral) material and O horizon (organic) material were used to compare and contrast sorption characteristics of these two layers. Both sets of samples were “spiked” with solutions of varying concentrations of cadmium, lead, and zinc using the previously outlined procedure. The samples were then extracted using ammonium nitrate, again using the previously outlined procedure. Six adsorption isotherms were created, three for each sample representing the separate metal sorption, desorption, and immobilization. Figure 4.18 shows these resulting isotherms for the O horizon, and Figure 4.19 shows the resulting isotherms for the C horizon.

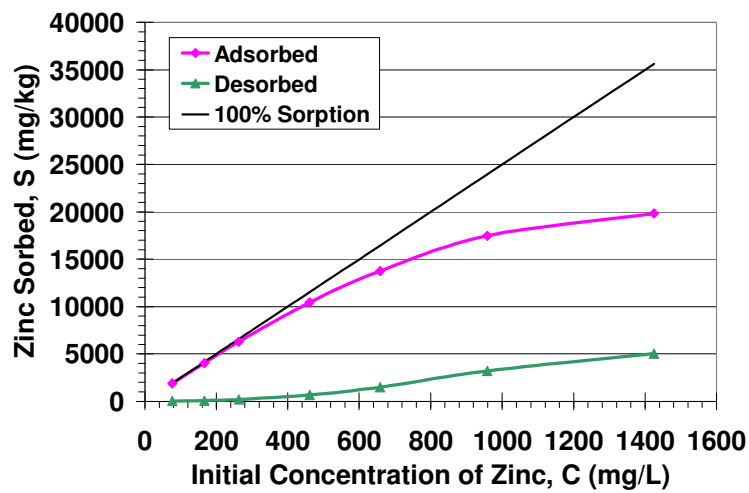
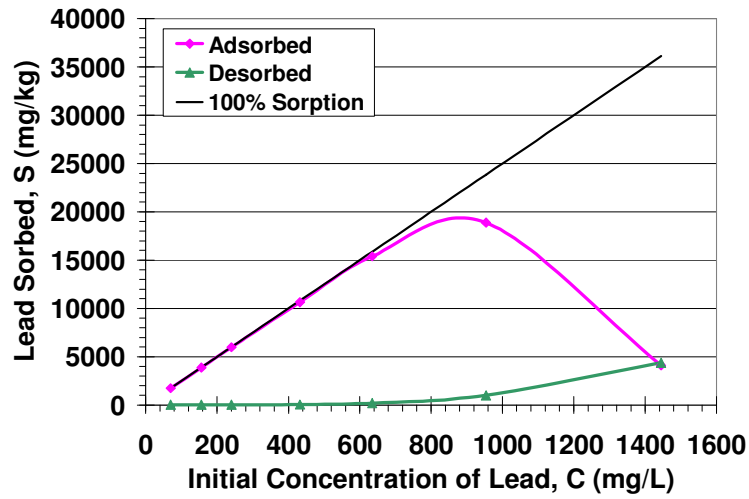
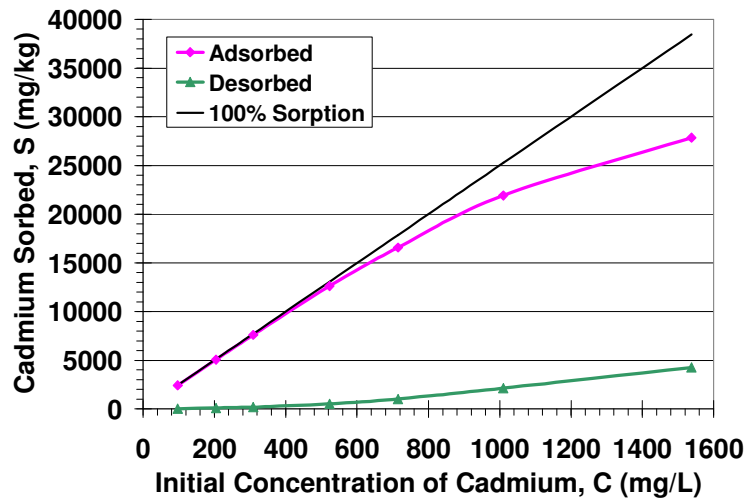


Figure 4.18 Sorption isotherms for O horizon samples with cadmium (A), lead (B), and zinc (C)

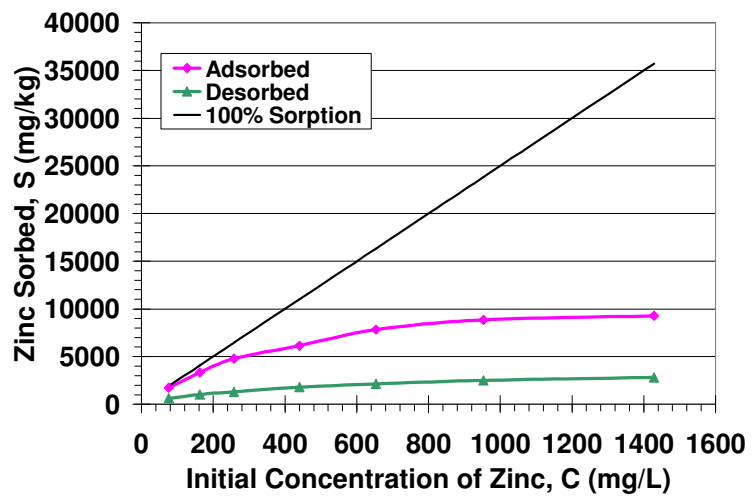
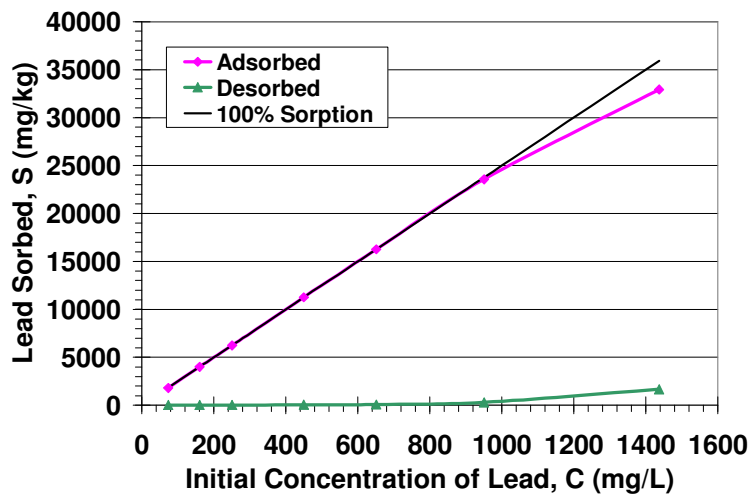
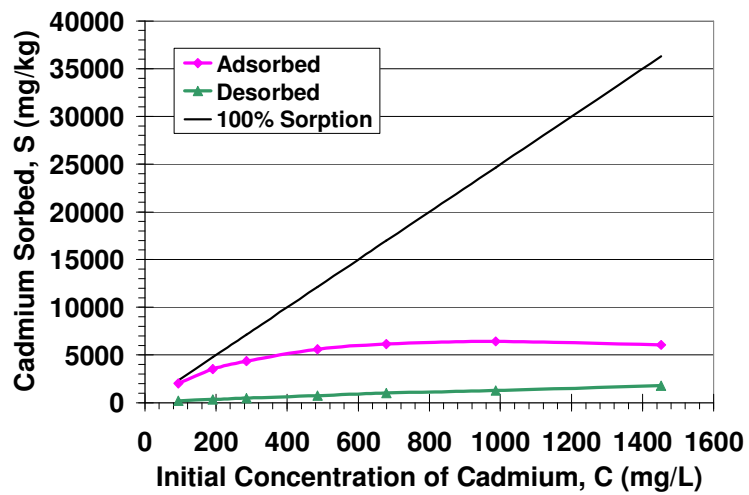


Figure 4.19 Sorption isotherms for C horizon samples with cadmium (A), lead (B), and zinc (C)

Distribution coefficients were also calculated for the isotherms in Figures 4.18 and 4.19. The coefficients for all batch sorption testing are summarized in Tables 4.2 and 4.3. It should be noted that when comparing the M-O and M-C distribution coefficients in Table 4.3, the linear range used to calculate the coefficients was larger (approximately double) for the O horizon material than the C horizon material.

Table 4.2 Distribution coefficient summary for comparative depth study

Depth (in)	Cadmium K_d
29	24.48
41	23.95
45	24.43
49	24.51

Table 4.3 Distribution coefficient summary for comparative horizon study

Metal	Distribution Coefficient, K_d	
	Sample M-O	Sample M-C
Cd	24.55	21.54
Pb	24.95	24.81
Zn	23.76	22.63

4.7 Column Leaching Tests

4.7.1 Introduction

Column leaching tests were used to supplement information about the immobilization of heavy metals within the artificial soil profile. The material in question is exposed to a leachant, and the resulting leachate is analyzed and compared to a standard. The advantage of column leaching tests for this research is that they more

closely represent the natural soil structure (bulk density) of the artificial soil, whereas the batch sorption tests use the soil in suspension with the solution, making available all possible sorption sites and disregarding soil structure.

4.7.2 Standard Leaching Tests

There are several standard leaching tests used to evaluate the leaching potential of a particular material. Table 4.4 (from Bin-Shafique et al, 2003) shows some of the widely used standard leaching tests.

Table 4.4 Outline of several standard leaching procedures (from Bin-Shafique et al, 2003)

Test Procedure	Method	Purpose	Leaching Medium	Liquid-to-Solid Ratio	Particle Size	Time of Extraction
Water Leach Test	ASTM D 3987-85	To provide a rapid means of obtaining an aqueous extract	Deionized water	20:1	Particulate or monolith as received	18 hr
TCLP	EPA SW-846 Method 1311	To compare toxicity data with regulatory level. RCRA requirement.	Acetate buffer *	20:1	< 9.5 mm	18 hr
Extraction Procedure Toxicity (EP Tox)	EPA SW-846 Method 1310	To evaluate leachate concentrations. RCRA requirement.	0.04 M acetic acid (pH = 5.0)	16:1	< 9.5 mm	24 hr
Multiple Extraction Procedure	EPA SW-846 Method 1320	To evaluate waste leaching under acid condition	Same as EP Toxicity, then at pH = 3.0	20:1	< 9.5 mm	24 hr extraction per stage
Synthetic Acid Precipitation Leach Test	EPA SW-846 Method 1312	For waste exposed to acid rain	DI water, pH adjusted to 4.2 to 5	20:1	< 9.5 mm	18 hr

* Either an acetate buffered solution with pH = 5 or acetic acid with pH = 3.0

The water leaching test described in ASTM D 3987-85 is useful to evaluate the leaching potential of a material when exposed to normal precipitation. This method uses decanted water to react with the material in a liquid-to-solid ratio of 20:1. After agitation on a shaker table for 18 hours and settlement for 5 minutes, the liquid phase is removed with decantation, filtered through 0.45 µm paper, and chemically analyzed for inorganic contaminants. This method is not recommended for organic contaminants. The main

disadvantage of ASTM D 3987-85 is that it does not take site specific conditions into consideration.

Another example of a common leaching test is the Multiple Extraction Procedure (MEP) as described in EPA Method 1320. This method is used to simulate leaching caused by frequent acid rain events, and usually describes the highest leachable concentration, or worst condition, of a given contaminant in a natural setting. It utilizes at least eight (8) extractions with a synthetic acid rain solution after an initial extraction with deionized water acidified to pH 5 with acetic acid. After each extraction, the leachate is filtered and subjected to chemical analysis. The MEP test can be used for both inorganic and organic contaminants.

4.7.3 Leaching with Tap Water

Soil samples M-O and M-C were carefully compacted into rigid-wall compaction-type permeameters. The samples were compacted to dry densities intended to replicate the in-situ densities reported by Bobba (2005), and shown in Table 3.1 (16.5 pcf for the O horizon and 39 pcf for the C horizon). Filter paper and porous stones were placed on top and bottom of the sample in order to evenly distribute the percolation. The top valve was connected to a modified bubble tube “reservoir” in order to achieve a constant head on the sample. The bottom valve was connected to a flexible tube that drained into a volumetric flask. After a satisfactory flow of approximately one pore volume per 4 hours was established via the bubble tube, the flask was checked for volume and sampled periodically. The samples’ volume and pH were recorded, followed by testing for Cd, Pb, and Zn via Inductively Coupled Plasma (ICP) spectrometry. The test setup can be seen in Figure 4.20. Plotted results for water leaching can be seen in Figure 4.21.

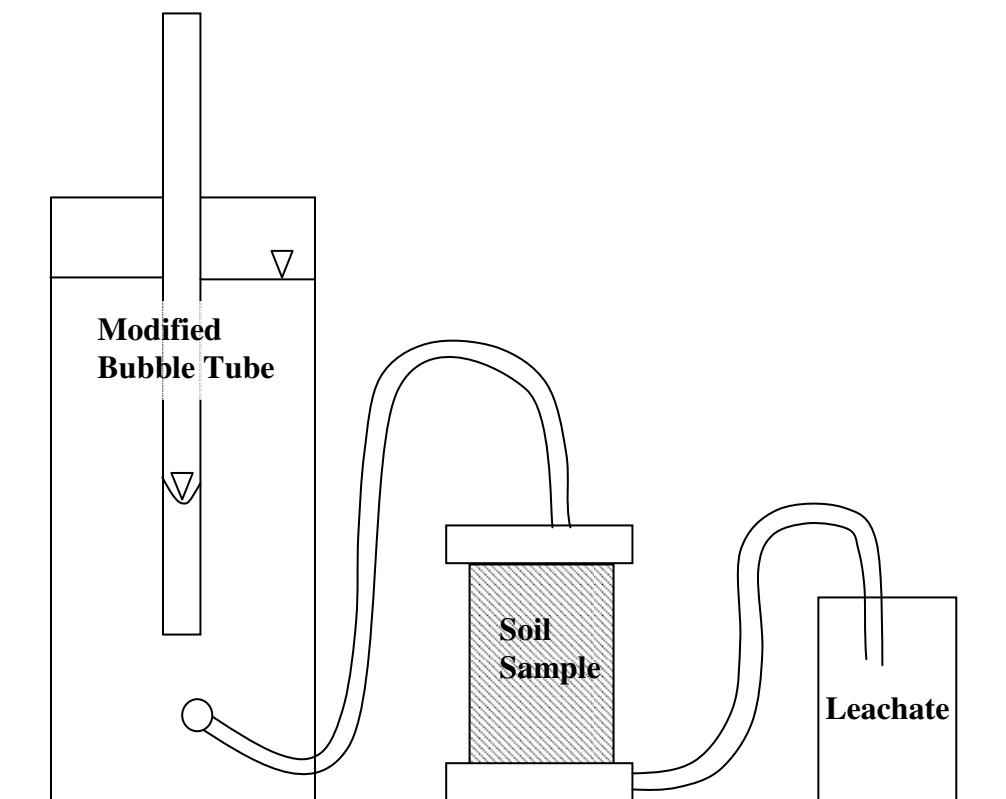


Figure 4.20 Leaching test setup for column leaching tests.

After flushing approximately 33 pore volumes through Sample M-C and 58 pore volumes through Sample M-O, no significant leaching (< 1.0 ppm) was observed with normal tap water in the allotted time. It should be noted that these concentrations are below the detection limits of the ICP analysis, and may not be sufficiently accurate. The detection limits of the ICP used were approximately 0.2 ppm for cadmium and zinc, and 1.5 ppm for lead.

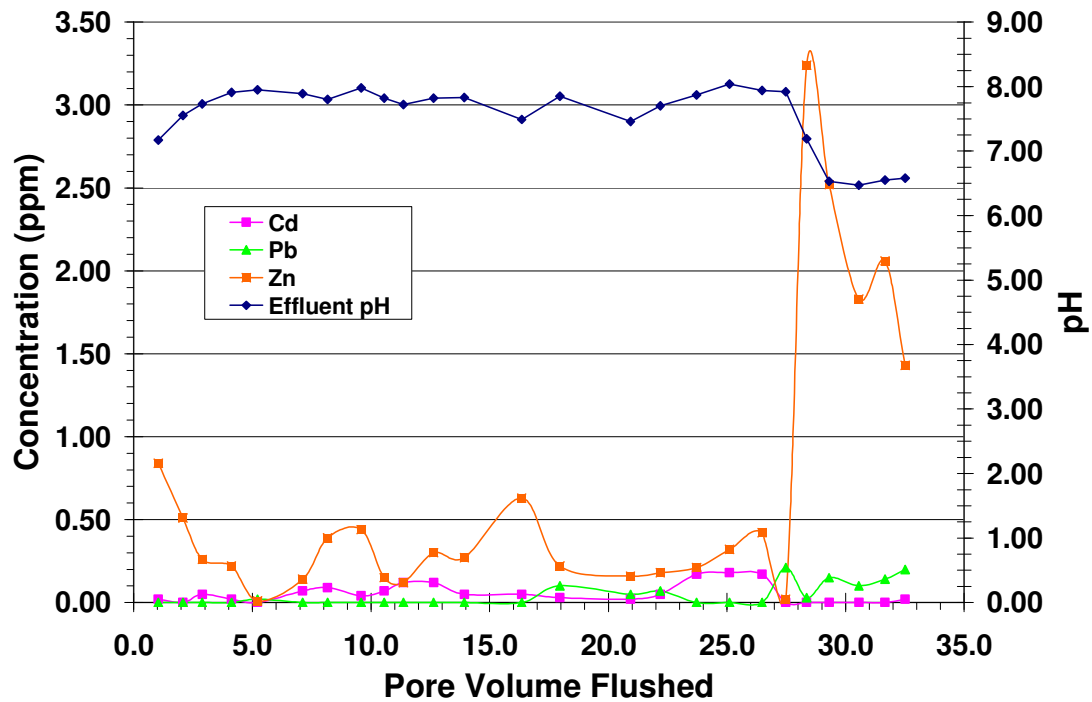


Figure 4.21 Column leaching test results for Sample M-C

4.7.4 Leaching with Varying pH

After flushing the pore volumes with normal tap water, the water was buffered to a lower pH using hydrochloric acid (HCl). The C horizon reservoir (influent) was buffered to a pH of approximately 5.3 at approximately 28 pore volumes and the O horizon reservoir (influent) was adjusted to a pH of approximately 4.6 at approximately 31 pore volumes. Figure 4.22 shows the results of the pH-buffered water leaching tests. Neither sample showed significant leaching with the lower (more acidic) pH in the allotted time. However, it is apparent that the leaching is pH dependent in both soils. In the C horizon, zinc concentrations spiked significantly when the pH dropped below 7.0, or became acidic. In the O horizon, the same behavior is seen in all three metals. This would indicate that the sorption process in the organic horizon are more pH dependent than those of the mineral horizon, except for zinc. This may be due to the fact that the

mineral horizon is more naturally alkaline, and thus better buffered from the critical pH range over which sorption drastically increases or decreases (around pH 6 to 7, normally). This is important to note, since acidic rain would potentially leach the O horizon, which is directly exposed to the atmosphere.

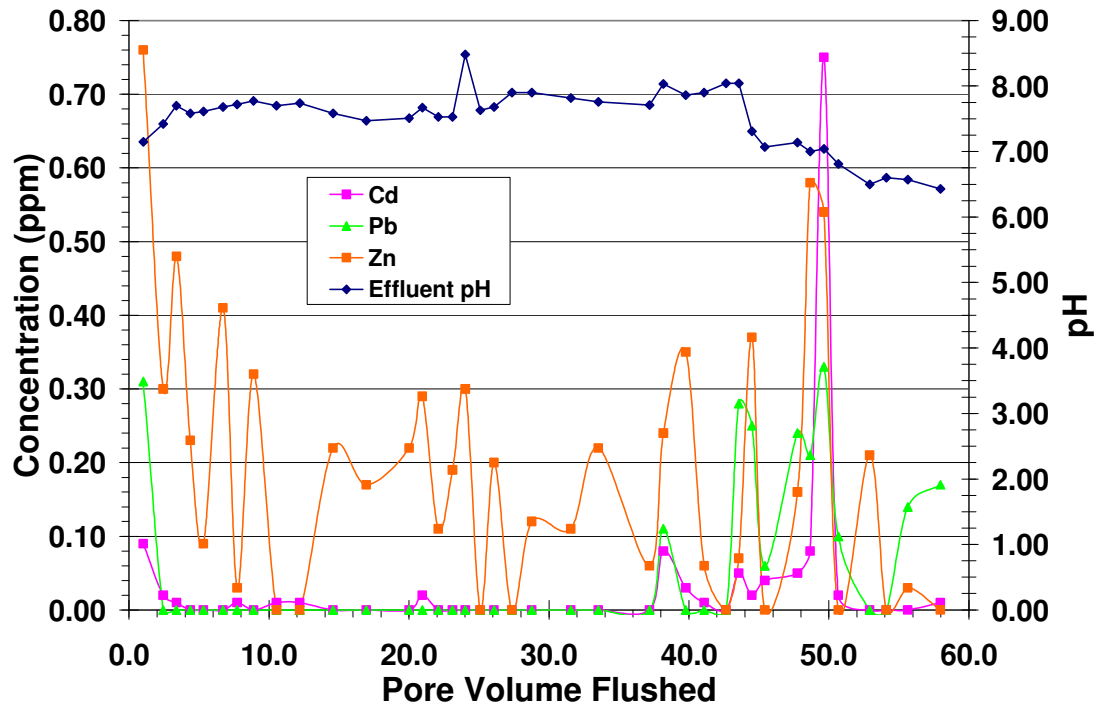


Figure 4.22 Column leaching test results for Sample M-O

4.8 Summary

Four sets of samples were tested: two sample sets with varying depths representing “mature” artificial soil O-horizon (Sample M-O) and “young” artificial soil C-horizon (Sample Y-O), and two sample sets representing the O horizon (Sample M-O) and the C horizon (Sample M-CI) taken from test pad 1. Sample M-O and Sample Y-O were tested for natural moisture content, pH, carbon content, and batch sorption tests using cadmium and zinc (respectively), all comparing changes with depth. The remaining

two sample sets from horizon O and C were used for batch sorption testing and column leaching tests. The results allow for comparison between the soil horizons.

CHAPTER 5

DISCUSSION

5.1 General Soil Properties

5.1.1 SEM Imagery

The SEM images show the large surface area and interesting features (such as the fly-ash sphere) of the artificial soil constituents. These features affect sorption and immobilization.

5.1.2 Natural Moisture Content

The peak natural, gravimetric moisture content was 133% and 105.6% for Sample M-O and Sample Y-O, respectively. Both moisture profiles were similar in that they both showed a zone of low moisture content (57.8% and 49%, respectively) occurring at approximately 41 inches for Sample M-O and 51 inches for Sample Y-O. This “low-moisture” zone was generally preceded by increasingly higher moisture contents with depth, possibly indicating a “ponding” condition at the interface of the O and C horizon.

5.1.3 pH Tests

Soil pH with D.I. water ranged from 6.55 to 7.24 for Sample M-O, and 7.16 to 7.70 for Sample Y-O. This may suggest that the artificial soil becomes more acidic with time. However, the pH difference is only small, and this could also be due to slight differences in mixing/construction or raw constituents, both of which are only relatively controlled. Sample M-O also seems to vary more drastically and linearly with depth than Sample Y-O.

The pH profiles increase (more alkaline) with depth until they reach their peak value at a depth of 45 inches for Sample M-O and 51 inches for Sample Y-O. After this

depth, the pH starts to drop slightly. The depth of the peak value seems to generally correspond with the minimum natural, gravimetric moisture content in both samples. Sample Y-O shows a slight pH drop at 30 inches, but this is assumed to be due to natural, random variation.

5.1.4 Carbon Content

Typical organic carbon contents for near-surface Missouri subsoils generally range from 2% to 5%. Organic carbon content for Sample M-O and Sample Y-O ranged from 12.4% to 27.5% and 5.5% to 26.2%, respectively, which is much higher than typically seen. Total carbon contents paralleled the organic carbon profiles, and ranged from 14.0% to 30.8% and 11.6% to 28.6%, respectively. The carbon profiles with depth seemed to show relatively constant carbon content, with reasonably natural variability, with the exception of a drastic drop to their minimum value at a depth of 41 inches and 51 inches. Once again, these points of interest occur at the depth of minimum natural, gravimetric moisture content and near the maximum pH (most alkaline) values.

Inorganic carbon was found by taking the difference of the total carbon and organic carbon at a certain depth. This method is not without limitations, especially at the high levels of carbon seen in these samples, as some inorganic carbon can possibly start to burn off during the organic carbon test. There was tell-tale evidence of this during the testing.

5.1.5 “Bh” Layer Formation

Bobba (2005) reported the formation of a cemented, greenish-gray “Bh” horizon at the interface of the O and C horizons, as seen in Figure 5.1 (Figure 6.1 from Bobba, 2005). A B horizon represents a primary horizon where organic material has leached

down from the top O or A horizon. The “h” subscript represents illuvial humic material which has accumulated in the B horizon. It was hypothesized that this layer was the result of the precipitation of dissolved constituents in the leachate due to the contact of acidic leachate with the underlying alkaline C horizon. The Bh horizon was estimated to “have a significantly (10 to 100 times) lower hydraulic conductivity than the O- or C- horizons” (Bobba, 2005). This abrupt change in hydraulic conductivity could create a perched water table above the Bh horizon and be responsible for the increases in water content noted with depth and apparent ponding condition.

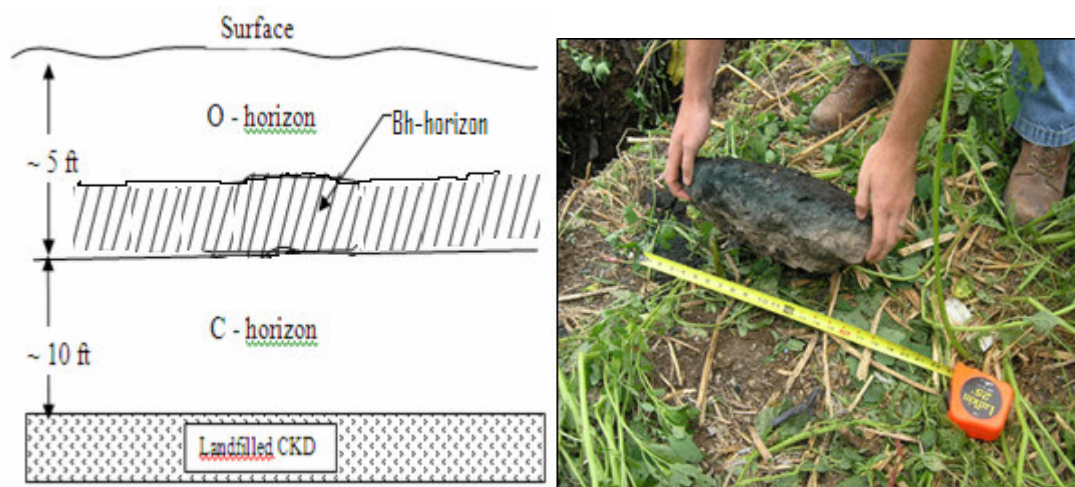


Figure 5.1 Formation of Bh-horizon at the interface of O and C horizons: (a) Schematic diagram (b) photo after 6 months (Figure 6.1 from Bobba, 2005)

The results from the moisture content, pH, and carbon content tests confirm the presence of this cemented layer. Figure 5.2 shows the graphs from these three tests for Sample Y-O, which is representative of the new artificial soil profile. At a depth of 51 inches, or 4.25 feet, the moisture content dropped dramatically to 49%, the pH peaked at 7.76, and the organic carbon content dropped to 5.5%. This indicates the presence of a more alkaline, mineral interface that is acting as a hydraulic barrier (with the high moisture content above indicating ponding, or a perched water table). At 4.25 feet, this

would also be the approximate depth of the previously reported Bh layer. Increased pH could indicate the precipitation of heavy metals, which occurs in more alkaline environments (Yong, 2001). Similar trends can also be seen in the results for Sample M-O. The formation of this Bh layer is important in that it may directly correlate with the ultimate fate of heavy metals in the leachate.

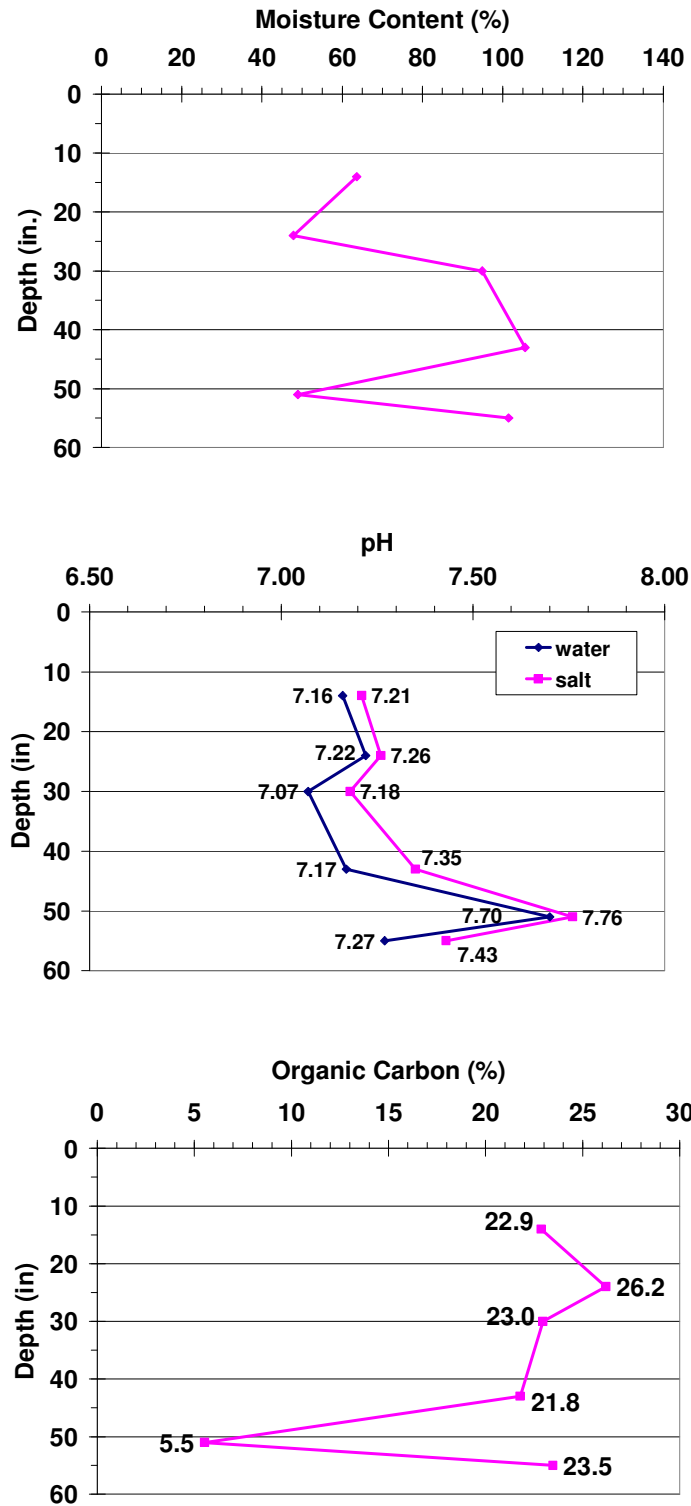


Figure 5.2 Comparison of gravimetric moisture content, pH, and organic carbon content with increasing depth for Sample Y-O

5.2 Batch Sorption Test Results

Two sets of results were gathered in regard to sorption behavior of artificial soil. The first set was a comparative study of the sorption of Cd versus depth in representative samples of old and new artificial soil profiles, respectively. Although a continuous trend cannot be seen in the results, an important correlation can be seen with carbon content tests from the same samples. Cadmium sorption is greatest at a depth 29 inches, where the total carbon content is also greatest at 30.8%. Sorption decreases to the lowest rate at 41 inches, which correlates with the minimum total carbon content of 14%. Sorption then increases with depth at 45 and 49 inches, along with carbon content with values of 18.6% and 21.8%, respectively. This would suggest that the sorption processes seen in artificial soil, at least in the O horizon, are closely linked to the organic materials within the profile, their ultimate locations, and their forms. Desorption remains relatively constant for all depths, suggesting that carbon content is not a factor.

The second set of results shows the sorption behavior of cadmium, lead, and zinc for both O horizon material and C horizon material, and can be seen in Figures 4.9 and 4.10. Table 5.1 shows a summary of the immobilization results for this set. Adsorption was calculated as the difference between the initial and final solute concentrations, divided by the initial concentration. Desorption was calculated as the difference in the extracted concentration divided by the adsorbed concentration. Immobilization percentages in Table 5.1 were calculated as the difference between adsorbed and desorbed concentrations, divided by the initial concentration.

The O horizon most easily adsorbed cadmium, which at its final loading concentration of 1540 mg/kg still showed 72.5% adsorption. Desorption of cadmium

with ammonium nitrate only ranged from 1.4% to 15.3%. Zinc followed at an adsorption of 55.6% at a final loading concentration of 1425 mg/kg, and desorption ranging from 1.1% to 25.5%. Lead, however, showed a very peculiar sorption behavior within the O horizon material. At a loading concentration of 954 mg/kg, the adsorption was 79.2%. The next data point, at a loading concentration of 1445 mg/kg, dropped drastically to an adsorption of only 11.3%. At this final loading point, the adsorption and desorption were approximately equal, meaning that no lead was immobilized in the soil. This might represent breakthrough, where the influent concentration equals the effluent concentration.

The C horizon almost completely adsorbed lead. At the final loading concentration of 1440 mg/kg, 91.6% of the lead was adsorbed and only 5.1% desorbed. A chemical reaction between the lead and the calcium inherent in the artificial soil C horizon constituents (calcium carbonate in the CKD) are most likely creating a strong bond with lead ions. Zinc showed the second-most affinity for the C horizon material, with an adsorption of 26% at the final loading concentration of 1430 mg/kg, and 30.4% later being desorbed. Cadmium showed the least affinity for the C horizon, with only 16.7% being adsorbed at the final loading concentration of 1450 mg/kg and 29.5% being desorbed.

It should be noted that small amounts (< 5 mL) of nitric acid were used in the stock solutions of the zinc and lead chloride solutions to help dissolve the salts, and not used in the cadmium chloride stock solution. In retrospect, even this small amount of acid may have greatly affected the behavior of the zinc and lead sorption. However, this

would only make the results of this study slightly conservative, since a higher pH would only result in more metal ion sorption.

Table 5.1 Immobilization Results Summary for Sample Set 2 (Samples M-O and M-C)

HORIZON	CADMIUM		LEAD		ZINC	
	Initial Concen.	Immobilized	Initial Concen.	Immobilized	Initial Concen.	Immobilized
ORGANIC - O	(mg/kg)	(%)	(mg/kg)	(%)	(mg/kg)	(%)
	98	97.4%	70	97.5%	77	96.8%
	204	97.0%	156	99.2%	166	95.4%
	309	95.8%	240	99.2%	263	92.8%
	523	92.4%	432	97.9%	462	84.6%
	714	87.0%	635	95.7%	658	74.5%
	1010	78.3%	954	75.0%	958	59.5%
	1538	61.4%	1445	-0.8%	1425	41.5%
HORIZON	CADMIUM		LEAD		ZINC	
	Initial Concen.	Immobilized	Initial Concen.	Immobilized	Initial Concen.	Immobilized
MINERAL - C	(mg/kg)	(%)	(mg/kg)	(%)	(mg/kg)	(%)
	94	77.8%	73	97.7%	77	57.2%
	191	66.4%	161	99.2%	162	57.1%
	285	54.2%	250	99.4%	258	53.8%
	485	40.0%	450	99.5%	440	39.8%
	679	30.1%	651	99.4%	654	34.7%
	986	20.9%	950	97.8%	953	26.6%
	1452	11.8%	1437	87.0%	1429	18.1%

5.3 Column Leaching Test Results

The results of the column leaching tests did not show any significant trace elements in the leachate. Any recorded concentrations by the ICP were under the detection limits,. This was true for both the tap water and pH-buffered water, suggesting that the mobility of metals through the artificial soil profile is minimal. The results do show an apparent pH dependence of the leaching mechanisms. However, more detailed testing would be needed for verification. If verified, such a relationship would be

important because average Missouri rainwater pH typically ranges from 4.6 to 5.0 (NADP).

It should also be noted that tap water was used in the reservoirs to feed the column leaching tests. Tap water, especially the well-fed water in Columbia, contains many minerals, such as Ca, Mg, and HCO_3 , that could adversely affect such testing as trace metal analysis and sorption testing. Deionized water should be used for future testing to eliminate errors, especially if using much more precise detection limits than those previously listed.

5.4 Summary

Samples tested for moisture content, pH, and carbon content confirm the presence of a relatively impervious layer near the depth of the previously reported Bh horizon. This Bh layer forms after construction, and is possibly the result of heavy metals and other mineral ions precipitating due to the pH change at the interface of the O and C horizons. This would be evidence that heavy metals are becoming effectively immobilized within the artificial soil profile.

Batch sorption testing showed the effectiveness of artificial soil in sorbing cadmium, lead, and zinc cations from solution and effectively holding them, despite leaching with ammonium nitrate to represent plant-available metals. High adsorption percentages at high loading concentrations, along with relatively low desorption percentages, support this fact. In addition, it would seem that sorption is heavily dependent on the organic matter within the soil profile. This can be seen by the fact that sorption was greater overall in the O horizon. However, the C horizon was particularly effective at the sorption of lead. Column leaching tests seemed to show that the artificial

soil horizons are not noticeable susceptible to leaching of heavy metals, even at lower pH levels.

CHAPTER 6

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

6.1 Summary

This study presents the results of a literature review and laboratory testing program conducted to investigate the mobility of heavy metals within an artificial soil prepared by proportioned mixing of yard waste, biosolids, cement kiln dust (CKD) and coal ash. Soil pH, organic and total carbon content, natural moisture content, batch sorption testing, and column leaching tests were conducted on artificial soil samples representing both O and C horizons, as well as varied depths within the top 50 inches.

6.2 Conclusions

1. Natural moisture content profiles in both the mature and young soil profiles show a consistent trend of increasingly higher moisture contents with depth, possibly indicating a “ponding” condition occurring at the interface of the O and C horizon.

2. The pH of the organic (O) horizon ranged from 6.55 to 7.24 within the mature soil profile and from 7.16 to 7.70 for the young soil profile. This may suggest that the horizon becomes more acidic with time. The soil pH for the mature profile varies more drastically and linearly with depth than in the young profile.

3. The pH profiles in both the mature and young profiles increase with depth and reach peak values at depths from the surface near 45 to 50 inches. After this depth, the pH starts to decrease slightly. The depth of the peak value seems to generally correspond with the minimum natural, gravimetric moisture content in both samples.

4. Organic carbon content for the mature and young profiles ranged from 12.4% to 27.5% and 5.5% to 26.2%, respectively. Total carbon contents paralleled the organic carbon profiles, and ranged from 14.0% to 30.8% and 11.6% to 28.6%, respectively. The carbon profiles with depth are relatively constant.

5. The trends evident in the moisture content, pH, and carbon content profiles support the presence of a cemented Bh layer noted in the field test site at the interface between the O and C Horizon. Natural moisture contents directly above this layer were extremely high, suggesting that water is not moving through the Bh horizon and is instead either ponding above in a perched water table condition or moving laterally. Soil pH shows an increasing trend with depth, as the soil moves from an slightly acidic ($\text{pH} < 7$) organic layer to an alkaline ($\text{pH} > 7$) mineral layer near the depth of the Bh horizon. The carbon contents drop drastically at the impermeable layer, then rebound slightly, confirming that it is inorganic in nature. The conclusion of these tests is that this layer is indeed formed by a pH change at the interface of the O and C horizon, and that inorganic substances leached from the organic layer, possibly heavy metals, are precipitating in the alkaline environment. This would suggest that heavy metals, and other ions, are effectively immobilized at this interface.

6. Batch sorption tests indicate that both the O and C horizons are effective at immobilizing heavy metals, even at high loading concentrations. Adsorption percentages were high, and desorption with ammonium nitrate to represent “plant available” amounts were low. This further confirms that any metals contained in the artificial soil would be

effectively immobilized and not be a source for contamination. However, long term effects of organic decomposition and leaching are still unknown, and this could determine the ultimate fate and mobility of heavy metals within the soil.

7. Trends in Cd sorption capacity with depth appear to correlate with trends in total carbon content with depth, which suggests that the sorption capacity of the O-Horizon is closely linked to the extent of organic materials, their ultimate locations, and their forms.

8. Comparative sorption capacities for Cd, Pb, and Zn show that the O-Horizon most readily adsorbs cadmium, which at its final loading concentration of 1540 mg/L still showed a 72.5% adsorption. Desorption of cadmium with ammonium nitrate ranged from 1.4% to 15.3%. Zinc followed at an adsorption rate of 55.6% at a final loading concentration of 1425 mg/L, and desorption ranging from 1.1% to 25.5%. Lead showed an adsorption of 79.2% at a loading concentration of 954 mg/L. However, at a loading concentration of 1445 mg/L, lead drops to an adsorption of only 11.3%.

9. Comparative sorption capacities for Cd, Pb, and Zn show that the C-Horizon most readily adsorbs lead. At a loading concentration of 1440 mg/L, 91.6% of the lead was adsorbed and only 5.1% desorbed. Zinc showed the second-most affinity, with an adsorption of 26% at the final loading concentration of 1430 mg/L, and 30.4% later being desorbed. Cadmium showed the least affinity for the C horizon, with only 16.7% being adsorbed at the final loading concentration of 1450 mg/L and 29.5% being desorbed.

10. Column leaching tests support the results of the batch sorption tests. Heavy metals present in the artificial soil constituents are not easily leachable with either water or pH-buffered water. Results from column leaching tests using tap water and Ph-buffered water do not show any significant metal concentrations in the leachate after more than 30 pore volumes of flow. Effluent concentrations of Cd, Pb, and Zn were under the ICP detection limits, suggesting that the mobility of metals through the artificial soil profile is minimal. The results show an apparent pH dependence, however, more detailed testing is required for verification.

6.3 Recommendations

1. The bulk of this research involved laboratory testing on specimens assumed representative of field conditions. A field study, piggy-backed onto that of Bobba's (2005) research and Wayllace and Likos' (2006) seepage modeling, would be very beneficial in showing in-situ results of the mobility of heavy metals and would be efficient to implement. With the existing lysimeters in the artificial soil test pads at the Hannibal site, subsurface water samples could be collected and analyzed at different depths of the soil profile. This information would be invaluable in determining whether heavy metals were mobile within the aqueous phase of the profile. Since lysimeters are present in both the older, existing soil and the newer test pad, ageing effects due to decomposition of the organics and acidic leaching of carbonates could also be studied in more depth.

2. It is recommended that several test pits be dug in order to better observe the soil horizons and to collect bulk, representative samples of the O, C, and especially the Bh horizon. Collecting Bh horizon samples in this way would provide visual confirmation of the extent of horizon development (not as easy in auger samples) and would allow a comprehensive metals analysis to be completed. This would provide evidence that the Bh layer either does or does not contain precipitated heavy metals, confirming the findings of this research. For future research, it is recommended that the soil be examined for in-situ metals content. Soil digestions and subsequent analyses were not conducted in this project. However, knowing the type and concentration of existing metals in the soil constituents would greatly assist in future mobility investigations.

3. A potential concern with the use of biosolids in the organic horizon is pathogens. The artificial soil mix cited in the study of Reynolds et al. (2002), for example, consisted of biosolids, unslaked lime, and class F fly ash. It was intended that the moisture in the biosolids would hydrate with the calcium oxide (quicklime) in the fly ash, and that this exothermic reaction would create a sufficient temperature increase and pH increase to pasteurize the mix. Pasteurization would be very desirable when considering the artificial soil as a reclamation project. Such a mix was also shown to still have very desirable growing potential, another benefit for land reclamation. While high temperature (~160° F) were measured at the Hannibal test pads (Bobba, 2005), the temperature regime and corresponding pasteurization effects remain uncertain.

4. It is recommended that more in-depth column leaching tests be completed in the future. Since these represent results comparable to a field study, but with controllable inputs, such testing would be invaluable. The use of deionized water with these

experiments should be stressed as many metal ions form complexes with Cl^- ions, especially cadmium (McLean and Bledsoe, 1992), which are present in tap water. The formation of these complexes reduces or nullifies the free metal ion charge and inhibits adsorption. This fact is a potential source of error in the column tests conducted here, which used tap water.

5. The long term effectiveness of the artificial soil cover in Hannibal, Missouri, is still unknown. If the hypothesis that the Bh layer formation is due to precipitation of heavy metals is true, a long term concern arises. It is the nature of a forming soil to come into balance with its surroundings. A balance will eventually be reached between its “inputs” (such as organic material or erosion deposits) and its “outputs” (such as decomposition of organic material, leaching, and erosion). The environment of Hannibal, Missouri is not ideal to sustain a highly organic soil such as the O horizon of the artificial soil project. It is doubtful that the planting of native perennial plants and grasses alone can replenish the organic matter pool. Thus, it can be expected that decomposition of this horizon will occur over time. The concern is that this decomposition would lead to translocation of heavy metals associated with the organics, increased pH due to decomposition leading to increasing metal mobility, or the ultimate “revealing” of the hard, inorganic Bh layer that would expose heavy metals to weathering conditions and eliminate any land reclamation efforts.

Because the decomposition of the O horizon is not a matter of “if,” but rather “when,” it is recommended that a study be conducted to analyze the rate of such decomposition. Based on the finding of such a research project, it would probably be found necessary to maintain the artificial soil by continually placing organic material

onto the cover to replace that which is decomposing and translocating. This plan of action would help to both characterize, and possibly remediate, and negative long term effects of organic decomposition.

6.4 Closing

This research seems to confirm the effectiveness of the artificial soil at the Hannibal test site in immobilizing heavy metals within the existing soil profile, eliminating environmental concerns for the short-term. Recommendations for future research have been given to further confirm this conclusion and to further investigate the long-term effectiveness and possible alternative design of the soil profile.

It is important to note that this research was performed on a limited number of samples, and does not represent a comprehensive analysis. Because of lateral and vertical variability in both natural and artificially blended soils, a much greater number of samples would be needed to confirm the findings of this project. However, the results seem promising enough to warrant further research into the subject. This research shows the possible environmental benefits of an effective artificial soil design for both landfill covers and land reclamation, and gives support to the efforts of those who are pushing to make AFC's a more commonly used option.

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