DEVELOPMENT OF TERNARY RELATIONSHIPS AMONG SOIL CHARACTERISTICS, CAAs AMOUNT, AND GROUNDWATER QUALITY: COLUMN PERCOLATION

by

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A thesis submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In

CIVIL ENGINEERING

(Environmental and Water Resources Engineering)

UNIVERSITY OF PUERTO RICO

MAYAGÜEZ CAMPUS

2012

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ABSTRACT

Coal ash aggregates (CAAs) from a coal power plant was evaluated for use as a backfilling substitute in open pit restoration. The restoration was successfully simulated under laboratory conditions by using three dissimilar soils with factorial design combinations of CAA volumetric amount.

The applicability of CAAs in different soil types was assessed. Better understanding of CAAs applicability in different soil types was provided by this study. In addition was established how dissimilar interactions between CAAs and soils can affect groundwater quality. A statistical 3^3 factorial design was used to evaluate interactive effects of top soil types, top soil to CAA ratio, and sub soil types on water quality parameters such as turbidity, conductivity, pH and hardness. Studies of toxicity and heavy metal concentrations were also made to ensure a safe application of CAAs to soil and groundwater environments.

Best results in terms of water quality were obtained from the combination of top soils with less amount of CAAs and clayey sub soils. A toxicity test showed the absence of acute toxicity, and heavy metal concentrations were below the Maximum Contaminant Levels established by the U.S. Environmental Protection Agency.

RESUMEN

Agregados de cenizas de carbón (CAA) de una planta de generación de electricidad a base de carbón fueron evaluados para el uso como sustituto de relleno en la restauración de canteras. La restauración fue simulada con éxito en condiciones de laboratorio mediante el uso de diferentes tipos de suelo en combinación con CAA y la cantidad volumétrica en un diseño factorial.

La aplicabilidad de las CAAs en diferentes tipos de suelo fue evaluada. Una mejor comprensión de la aplicabilidad CAAs en diferentes tipos de suelo es provista por este estudio y en adición se establece como las diferentes interacciones entre las CAAs y los suelos pueden afectar por consiguiente la calidad del agua subterránea. Un diseño factorial estadístico 3^3 fue utilizado para evaluar los efectos interactivos de los tipos de suelos superiores, la razón de suelo superior a CAA y los tipos de subsuelo, sobre los parámetros de calidad del agua, tales como: la turbidez, la conductividad, el pH y la dureza. Los estudios de toxicidad y de concentraciones de metales pesados también fueron realizados para garantizar el uso adecuado de las CAAs para los suelos y para las aguas subterráneas.

Los mejores resultados en términos de la calidad del agua se obtuvieron de la combinación de los suelos superficiales con la menor cantidad de CAAs y subsuelo arcilloso. Las pruebas de toxicidad mostraron ausencia de toxicidad aguda; además concentración de metales pesados se encontraron por debajo de los niveles de contaminación máximos establecidos por la Agencia de Protección Ambiental de los EE.UU.

Dedicated to

God and my lovely family

ACKNOWLEDGEMENTS

First I must mention that this project was possible with the faith and strength that God gave me. Because during moments of weakness only he gave me the energy to continue working. I thank my family for giving me the support I needed and because they always believed on me. I must also thank my advisor Dr. Sangchul Hwang for his guidance and teaching me to grow as a graduate student. I must mention a very special person that help and advise me unconditionally, Isomar Latorre. Thank you for all your advice and your friendship.

I am also very grateful to all my colleagues in the Laboratory of Environmental Engineering that always cooperated. But especially to my undergraduate student Carolina Guerrero for her disposition and commitment. I would also like to thank AES Puerto Rico for funding this project and making this study possible.

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1. INTRODUCTION

Environmental contamination, waste generation and management, and increasing demand of natural resources are only a few of the environmental issues around the world. The general consensus is that there is a need to find better ways to recycle and reuse industrial byproducts to reduce burdens related to solid waste management and to save and make effective utilization of natural resources for future generations. The motivation for this study was to bridge the gap between such needs and potential engineering efforts to meet them.

Quarries are commonly created in different areas, such as Puerto Rico (PR), where sand or gravel aggregates are removed for utilization in concrete mixing, construction of roads and homes and other civil infrastructures. They are later restored through costly backfilling. Coal ash aggregates (CAAs), a byproduct of AES-PR coal power plant, was effectively used as a backfilling amendment material for open pit quarries (Latorre, 2010). This study established that there were no potential environmental risks associated with soil and groundwater quality. Since increasingly more CAAs are generated therefore more disposal sites such as in open pits are needed. However, more studies are required to study CAAs interactions with soils. This was further justified to perform studies of interactions of CAAs with soils in various combinations.

Coal combustion power plants generated wastes such as fly and bottom ashes that are environmental hazard if not disposed of correctly. It is projected that electricity generation by coal combustion will keep increasing unless other practical alternatives are found for electricity generation. The AES Puerto Rico coal plant located in Guayama, Puerto Rico is the only company in Puerto Rico that generates electricity from coal burning. AES Puerto Rico company transforms the waste into coal ash aggregates (CAAs), an agglomerate of fly and bottom ashes (also known as AGREMAX). This is an innovative alternative that can be used as backfilling amendment in open pits that were produced due to extraction of natural soil and aggregates. Open pits are often abandoned due to high cost of backfilling. Industrial byproducts CAAs can be utilized as a low cost, alternative backfilling material for open pit restoration.

The increased demand for electricity and the need to lower its cost of production it is projected that coal usage will increase even more. The AES Puerto Rico coal burning power plant produces 454 megawatts of electricity representing 15 percent of the electricity consumed in Puerto Rico (AES, 2010). The power plant generates approximately 500 tons of coal fly and bottom ashes per day. Fly and bottom ashes are mixed to produce CAAs which have multiple utilization potential in construction industry and environmental restoration (Hwang and Hernández, 2010).

This study focused on utilization of CAAs as backfilling substitute in conjunction with the different types of top- and sub- soils. Understanding the dissimilar interaction of applied CAAs and different soil types and resulting groundwater quality is vital for successful implementation of CAAs for restoration of open pits located in different geological formations (i.e., soil types). The results of this study showed the burdens of industrial waste contribute to the overall effort of management, specifically coal ashes while at the same time should lead to reduction restoration costs of open pits.

2. SCOPE, OBJECTIVES AND RESEARCH APPROACH

2.1. **Scope**

The main goal of the study was to test feasibility of CAA application as backfilling substitute to open pit restoration, achieving sustainable solid waste management and environmental conservation at the same time. Different soils (highly organic, medium organic, inorganic sand, clayey, high calcium, and sandy soils) were tested with factorial combinations in conjunction with CAA volumetric amount. Resulting water quality including toxicity was monitored.

2.2. **Objectives**

In order to achieve the aforementioned goal, the following specific objectives of this study were made:

- To conduct a factorial experimental design with the factors of soil types and CAA volume to evaluate their main and interactive effects on water quality parameters;
- To conduct and monitor water quality parameters such as: pH, turbidity, conductivity, hardness, heavy metals, and toxicity in resulting groundwater; and
- To develop a ternary relationship among CAAs amount, soil characteristics, and groundwater quality.

2.3. **Research approach**

In order to accomplish the research objectives an experimental study was performed. The investigation includes analysis, and characterization of coal ash aggregate, soils and chemical analysis of infiltrating water passing through columns packed with various combinations of CAAs and soils. A 3^3 factorial design approach was used to clearly establish the combination. Columns were simulated to represent the conditions of open pit restoration. Comprehensive water quality tests were made to determine pH, turbidity, specific conductivity, hardness, heavy metals and toxicity.

3. LITERATURE REVIEW

A review of previous work related to this study provided the motivation for undertaking this study. Research about land restoration, coal combustion products, coal ash aggregates, factorial design analysis, toxicity detection using Microtox and leaching of heavy metals is discussed in this section. The topics discussed here is prove that previous investigations had been successful at using coal ash aggregates in different applications.

3.1. Open Pit Restorations

Many quarries in Puerto Rico are used for the extraction of marble, volcanic gravel, lime and sand. The quarries are located around the island, but are expensive to restore and for this reason many, if not all, of them are left as open pits, putting people in physical danger. Restoration is expensive because, it requires professional supervision to do it in a safe manner and prior studies of the area such as soil structure, vegetation, ecology, water table depth are needed (Phillips, J., 2012 and Tang et al., 2011). In addition, the high cost of soils required for amendment is the major reason why these quarries are abandoned.

Abandoned quarries cause major problems to land because the original ecosystem has been removed leading to significant changes in the topography; also the ecology and biodiversity of the area is strongly affected (Milgrom, T., 2008). Moreover quarries create a negative impact to natural landscape of the area. Also when quarries are not supervised they become favorable areas for people to use as illegal dumpsters (Milgrom, T., 2008). It is necessary to restore the conservation of natural resources by reducing the environmental impact (Wang et al., 2011).

Restoration of disturbed land provides alternative usage for these areas. Depending on the location of the quarry (urban or rural) the restored land can be used for different applications such as: agricultural land, recreational opportunities as public parks, cemetery, residential or commercial areas or just simply a natural recovery of the land (Tang et al., 2011 and Milgrom, T., 2008). For example, in urban areas land space is very limited and restored spaces can be use for green spaces. On the other hand in rural areas restored quarries can be used for agricultural opportunities.

3.2. **Coal Combustion Products**

Coal combustion products (CCPs) are inorganic residues that remain after pulverized coal is burned at coal-fueled power plants, which supply more than half of U.S. electricity (USGS, 2012). Fly ash, bottom ash, boiler slag and flue gas desulfurization materials are byproducts of coal combustion. The Coal Combustion Products Partnership (C^2P^2) recognizes that the recycle and use of CCPs have a number of environmental benefits, including reduction of land disposal, utilization of virgin resources, and reduction of greenhouse gas emission (ACAA, 2010). CCPs are also used in cement and concrete, structural fill, road bases and more.

Each year in the U.S., coal-fueled power plants generate more than 125 million tons of CCPs that can be used in construction and in a wide variety of other commercial or “beneficial” uses (ACAA, 2010). In the European Union approximately 52 million tons of CCPs were produced in 2009 (ECOBA, 2009). In 1999, the use of 30 million tons of CCPs in contructions and other areas had saved $120 million in disposal costs and approximately 350 acres of landfill space and generated $150 millions in sales (USGS, 2012).

3.2.1. Fly Ash

Fly ash is a byproduct from combustion of pulverized coal in power plants which are collected from exhaust gases by, for example, electrostatic precipitations (Pando and Hwang 2006). It is a very fine material similar to a powder and has a spherical shape. The color of fly ash particles can vary from a light tan to gray depending on calcium and carbon contents. Fly ash is a pozzolan; it is a siliceous material that in the presence of water react with calcium hydroxide at ordinary temperatures to produce cementitious compounds (US EPA, 2010). The main chemical compositions of fly ash, bottom ash and CAAs that are generated from the AES are shown in Table 1.

Table 1. Chemical compositions of fly ash, bottom ash and CAAs produced from AES (Pando and Hwang, 2006)

% (wt)	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3
Fly ash	39.4	12.6	4.4	27	12.6
Bottom ash	30.8	12.2	4	36	12.8
CAAs	35	12	4	30	15

Fly ash can be used in numerous applications such as raw material in concrete products, a substitute in the production of cement, fill material for asphalt and in structural applications. This material is also used as a component in road bases and pavement, and it is an ingredient for soil modification and stabilization. In the European Union, the utilization of fly ash in construction industry was around 48% in 2009 (ECOBA, 2009). Studies reveal that fly ash can effectively remove phosphate and heavy metal (Yalvac and Yildiz, 2006). Fly ash is also effective for adsorption of heavy metals from municipal solid waste leachate (Mohan and Gandhimathi, 2009). Several studies show that fly ash is a good alternative to be used for improving soil quality and enhancing its fertility (Chandra and Singh, 2010).

3.2.2. Bottom Ash

Bottom ashes are formed from pulverized coal furnaces. Their large particles are not able to pass through a flue gas thus bottom ashes settle at the bottom of the furnace. Bottom ash has typically grey to black color, and has a porous surface structure (Pando and Hwang, 2006). Like fly ash, the characteristics of bottom ash depend on the combustion method and coal properties used at each power plant. Bottom ash is composed principally of silica, alumina, and iron with smaller percentages of calcium, magnesium, sulfates and other compounds (Table 1).

Bottom ash particles are coarse grains varying from fine sand to fine gravel sizes. It can be used as a replacement for construction aggregates (e.g., gravels and sands), however, it is less durable than other commonly used construction aggregates because of its porous characteristics. On the other hand, its porous characteristics has the advantage of making the material lighter than conventional aggregates and therefore, is useful for lightweight concrete applications (US EPA, 2010).

3.2.3. Coal Ash Aggregates

Coal ash aggregates (CAAs) are a solidified mixture of fly ash and bottom ash particles at a ratio 2:1 (w/w), which were collected from the coal-burning power plant at AES Puerto Rico. AES plant burn coal in a circulating fluidized bed. Selective non-catalytic reaction, circulating dry scrubber with limestone and electrostatic precipitator are used for reductions of nitrogen oxide, sulfur dioxide, and particulate matter, respectively in flue gas emissions (Pando and Hwang, 2006).

The main chemical components of CAAs are silica, alumina, ferric oxide, lime and sulfur (Table 1). These mixtures of chemical components are characteristic of the strength that CAAs gains with time due to cementitious reactions. Coal ash aggregates have a similar gradation to natural gravel, with particle sizes ranging from gravel to fine sand with very low percentages of silt and clay-sized particles (Pando and Hwang, 2006).

Remediation experiments were done before to prove that coal ash aggregates with proper use can be implemented for different purposes. Hwang and Hernández (2010) mentioned that CAAs could be used as sorption media for remediation of TNT containing water. Also preliminary studies by Hernández et al. (2009) showed that presence of CAAs below top soil doesn’t have a negative impact on germination and growth on beans and pumpkins plants. Moreover, with amendment below top soils produced better germination and growth. Escobar et al. (2009) assessed the applicability of CAA as an alternative daily cover material to replace expensive soil excavation and transportation used in landfills. Experimental results showed that CAAs can be benefitiallly applied as alternative daily cover of landfills because reduced leachate toxicity and enhanced biological decomposition was obtained.

3.3. **Factorial Design Analysis**

Factorial designs are used to study the effects of two or more factors on the response variables. By a factorial design each complete trial or replication of the experiment with all possible combinations of the levels of the factors are investigated (Montgomery, 2001). As it is necessary to study the joint effect of several factors on a response, a factorial design provides useful information for understanding an experiment. This type of design has a structural and analytical capability that researchers on academic fields or industries use to assess the quality of their products based on design factors and levels during the manufacturing process (Cheng et al., 2012).

Fractional factorial eliminates some factor-levels from the design, for this reason it is used to save time, materials and cost. A full factorial design needs more time because it requires more experiments and calculations (Cheng et al., 2012). For example, 2^3 full factorial design was used to study the influence of three variables (phosphate concentration, initial pH of solution, and fly ash dosage) on the removal efficiency of phosphate and equilibrium pH of the solution (Yalvac and Yildiz, 2006).

Main and interaction effects on factorial design are studied to have a better understanding of what occurs in an experiment or process. Cheng et al. (2012) used the 3^3 full-factorial design (three factors at three-levels), to investigate the main and interaction effects of design parameters on the performance of a fuel cell. The design was useful to find the significance of factors which produces more power from the fuel cell and in an efficient way.

In addition to factorial plots of main and interaction effect, normal probability plots, surface plot, contour plot and p-value were useful to provide information of significant levels. Bingol et al. (2010) used in a 2^3 full factorial design all the plots mentioned before and p-values to optimize conditions for a maximum adsorption of dye onto septolite. The three factors studied were temperature, pH and ionic strength. The initial pH was demonstrated the greatest influence of dye adsorbed; and interaction between pH and ionic strength had more influence than others interactions.

3.4. **Toxicity Detection with Microtox**

Microtox is an in vitro test system designed by Strategic Diagnostic Inc. It uses natural luminescent bacteria (*Vibrio fischeri*) for the detection of toxicity by monitoring changes in light emissions. *V. fischeri* are nonpathogenic, marine, luminescent bacteria which are sensitive to a wide range of toxicants (SDIX, 2011). When *V. fischeri* are exposed with a toxic substance that causes an interruption in the respiratory process, thus light emission is reduced.

The bioluminescence reaction that occurs in bacteria is related to electron transport in cellular respiration, a decrease of bioluminescence corresponds to a decrease in cellular respiration. When bacteria is in the presence of contaminants cellular respiration is affected which alters the rate of synthesis of proteins and lipids; and thus it affects the level of luminescence emission (García, M.L., 2004).

Microtox have the advantage of measuring acute toxicity in a short period of time, and can be made for water samples (including those turbid and colored), sediments and soil samples. Microtox is recommended by EPA because results have shown more sensitivity and correlation in comparison with results from fishes. Test with fishes were used before to measure toxicity, but they required long exposure time and large sample volume.

Toxicity is expressed in terms of effective concentration (EC_{50}) which is defined as the concentration of a toxicant that produces a 50% reduction in light output over a prescribed incubation time in comparison to the initial light output (Scienceslives, 2010). Boluda et al. (2002) found no significant differences in the effective concentration values ($EC_{10,20,50}$) despite different incubation time. According to Bennett and Cubbage (1992), there was a correlation between EC_{50} and the apparent toxicity level of toxicant (Table 2).

Table 2. Correlation between EC_{50} and the apparent toxicity level of toxicant

(Bennett and Cubbage, 1992)

Microtox EC_{50}	**Apparent Toxicity Level**
0-19	Extremely Toxic
20-39	Very Toxic
40-59	Toxic
60-79	Moderately Toxic
80-99	Slightly Toxic
>100	Nontoxic

Microtox can be used in different types of applications including monitoring of water quality from treatment and remediation processes and identification of toxicity (SDIX, 2011). For example, Flokstra et al. (2008) used Microtox for their study on phytoremediation and subsequent detoxification of TNT and RDX by poplar tissue cultures. Boluda et al. (2001) monitored toxicity of water collected from irrigation channels in Spain.

3.5. **Leaching of Heavy metal**

Heavy metal pollution of groundwater represents a risk to plants, animals, and humans. Is important to monitor heavy metal traces in soils because that is one of the main sources of ground water contamination. Soils are vital for food production, for this reason it is critical to avoid unnecessary soil contamination. Main sources of heavy metals on soils comes from natural pedo-geochemical background, but also from anthropogenic contamination (Doelsch et al., 2006). Accumulation of heavy metals in agricultural soils is a public concern on places where urban and industrial development is increasing. Elevated concentrations of heavy metal can be uptake by crops and can affect food quality and safety (Wong, S.C et al., 2002). Mobility of heavy metals on soils depend on biogeochemical processes that are affected by soil pH, ionic strength, clay and organic matter content in the soil (Chen, G.C. et al., 2006). Latorre et al. (2009) studied the feasibility of open pits restoration with coal ash aggregates and monitored lead and cadmium concentration in percolated water samples and as a positive result no concentration of Pb and Cd were found.

4. MATERIALS AND METHODOLOGY

4.1. Materials

Different materials were required to perform lab-scale experiments which represent open pit restoration. This section includes a brief description of the CAAs and soils used in this investigation. Also a description of the instrumentation used to analyze the water quality parameters, and to characterize soil and CAAs is included.

4.1.1. Coal Ash Aggregates

Coal ash aggregate is a solidified mixture of fly ash, bottom ash and water. CAAs were collected from a coal burning power plant from the AES facility located in Guayama, Puerto Rico. Prior to use, they were crushed with a mechanical crusher, oven dried at 105°C for 8 hours, and sieved to collect particles ranging in size from 2.53 - 9.53 mm. The main CAAs chemical components are (in w/w): 51% mixture of silica, alumina, and ferric oxides, 30% lime, and 15% sulfur trioxide (Table 1). Figure 1 shows the final structure of CAAs after drying.

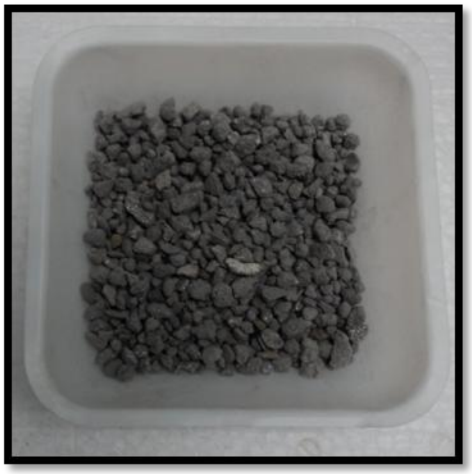


Figure 1. Coal Ash Aggregates Photo

Kochyl and Little (2004) reported physical and mechanical properties of CAAs such as moisture content, specific gravity, strength, permeability and swell index. Chemical composition of fly ash, bottom ash and CAAs of AES are included on Table 3. As shown in Table 3 main chemical components of CAA by weight are SiO_2, Al_2O_3, and Fe_2O_3 which consists the 51% of the content, while lime takes up 30% and SO_3 15%.

Table 3. CAAs chemical compositions by AES Puerto Rico (Source: Pando and Hwang, 2006)

Components	Fly Ash (% by Weight)	Bottom Ash (% by Weight)	CAA (% by Weight)
Silica, SiO_2	39.41	30.83	34.8
Alumina, Al_2O_3	12.59	12.2	12
Ferric Oxide, Fe_2O_3	4.35	3.95	4.19
$SiO_2 + Al_2O_3 + Fe_2O_3$	56.35	46.98	51
Titania, TiO_2	0.51	0.57	0.51
Lime, CaO	27.02	36.02	29.7
Magnesia, MgO	1.27	1.58	1.11
Potassium Oxide, K_2O	1.17	0.66	0.76
Sodium Oxide, Na_2O	0.44	0.55	1.52
Sulfur Trioxide, SO_3	12.57	12.82	14.7
Phosphorous Pentoxide, P_2O_5	0.28	0.37	0.32
Strontium Oxide, SrO	0.14	0.15	0.23
Barium Oxide, BaO	0.23	0.27	0.24
Manganese Oxide, Mn_3O_4	0.02	0.03	0.03
Alkalis as Na_2O (dry coal basis)	1.12	0.95	1.76
Base/Acid Ratio	0.65	0.98	0.79

4.1.2. Soils

Three different topsoils and subsoils were collected from different locations. Topsoils were obtained at a depth ranging from 0 to 20 cm. The three top soils used in this study were sandy soils, according with the amount of organic matter (Table 5) the names of highly organic and medium organic soil were used. Highly organic soil was used for the soil that has 5.69 of organic matter percent, which has more quantity of organic matter in comparison with the medium organic soil (4.89%). The third top soil is inorganic sand which has 0.47% of organic matter. On the other hand the three sub soils considered were clay, sand and limestone (material with high calcium content) which were collected from depths ranging from 20 to 60 cm. It is important to point out that limestone is commonly found in the northern areas of P.R. Prior to use, soils were sieved to collect particle sizes less than 2 mm which are suitable for lab-scale experiments. Finally they were oven-dried for 24 hours at 105°C. Clean sand was mixed with topsoil and subsoil to facilitate the hydraulics of infiltrating water through the soil columns. The clean sand was mixed at a ratio of 60:40 (% by weight) of soil to sand.

A hydrometer analysis for the three top soils was performed by Hernández I. (2009) to establish their grain size distribution based on the USDA classification. Table 4 shows the results obtained in this analysis. Moreover, soil characterization tests were performed on these soils to determine total nitrogen, total phosphorous lead among others as shown in Table 5. For the inorganic sand Molina et al. (2003) obtained physical characteristics and chemical composition as presence in Tables 6 and 7, respectively.

Table 4. Soil classification for sandy soil, highly, and medium organic soils (Source: Hernández , 2009)

	Highly Organic Soil	Medium Organic Soil	Sandy Soil
Sand (%)	75.13 ± 2	67.56 ± 0	74.47 ± 0
Clay (%)	11.62 ± 2	16.19 ± 0	16.19 ± 0
Silt (%)	13.25 ± 0	16.24 ± 0	9.34 ± 0
Soil Texture	Loamy Sand	Sandy Loam	Loamy Sand

Table 5. Soil characterization sandy soil, highly, and medium organic soils (Source: Hernández , 2009)

	Highly Organic Soil	Medium Organic Soil	Sandy Soil
Total Nitrogen as N (mg/g)	0.202 ± 0.009	0.000 ± 0.000	0.000 ± 0.000
Total Phosphorus as P (mg/g)	0.044 ± 0.002	0.002 ± 0.001	0.002 ± 0.001
Lead (mg/g)	0.00 ± 0.000	0.00 ± 0.000	0.00 ± 0.000
Soil Organic Matter (%)	5.69 ± 0	4.89 ± 1	1.92 ± 0
pH	6.50 ± 0	7.43 ± 0	7.94 ± 0

Table 6. Physical characteristics of inorganic sand (Source: Molina et al., 2003)

Property	Inorganic Sand
Clay and Silt Composition	7.40%
USCS Classification	SP
Specific Gravity ($g.cm^{-3}$)	2.83
Specific Surface Area (m^2/g)	16.87
Mineralogy	Quartz/calcite

Table 7. Chemical composition of inorganic sand (Source: Molina et al., 2003)

Property	Inorganic Sand
Ca (ppm)	275
Mg (ppm)	36.4
Na (ppm)	36.4
Cl^- (ppm)	59
Fraction Organic Carbon (%)	0.07
Soil Organic Matter (%)	0.47
Total iron (mg/kg)	6125.7
Total Nitrogen (mg/kg)	<713.00
pH	8.83
Cationic Exchange (mg/100g)	2.1

The clay used for this investigation was obtained from Isabela, PR, and it is composed primarily by quartz and the kaolinite mineral (Molina et al., 2006). This clay is classified based on the USCS as low plasticity clay and its physical and chemical properties are shown in Tables 8 and 9, respectively.

Table 8. Physical characteristics of clayey soil collected from, PR. (Source: Molina et al., 2006)

Properties	Clayey Soil
USCS Classification	CL
Liquid Limit (%)	46.6
Plastic Limit (%)	25.4
Plastic Index (%)	21.2
Specific Gravity ($g.cm^{-3}$)	2.62
Specific Surface Area (m^2/g)	44.4
Mineralogy	Quartz/kaolinite

*Clay, as defined by United Soil Classification System (USCS)

Table 9. Chemical composition of clayey soil collected from Isabela, PR (Source: Molina et al., 2003)

Property	Clayey Sand
Ca (ppm)	307.9
Mg (ppm)	42.3
Na (ppm)	42.3
HCO_3	1
CO_3	<1.00
Cl^- (ppm)	77
Fraction Organic Carbon (%)	0.67
Soil Organic Matter (%)	1.52
Total iron (mg/kg)	7938.8
Total Nitrogen (mg/kg)	914
pH	5.1
Cationic Exchange (mg/100g)	25.7

4.1.3. Analysis

The instruments used to assess water quality parameters and characterizations of soils are listed in Table 10 and Table 11, respectively.

Table 10. Instruments used to measure water quality parameters

Water quality parameter	Instrument
pH	ORION 720A model
Turbidity	HACH 2100P Turbidimeter
Specific conductivity	OAKTON CON 6 Acorn Series
Hardness	HACH Man Ver 2 Buret Titration Method 8226
Heavy metals	Agilent 7500 Series ICP-MS
Toxicity	Microtox Omni Model 500 Analyzer

Table 11. Instruments used for soil and CAAs characterization

Soil and CAAs Characterization	Instrument
Heavy metals	Agilent 7500 Series ICP-MS
Soil texture	Hydrometer tests
Soil organic matter	Loss of ignition

4.2. **Methodology**

4.2.1. Reactors Design

The reactor design is an essential part for the simulation of CAA as a backfilling substitute for open pit restoration. Reactors were constructed using Flex-Columns (Kimble-Kontes) for ternary, binary, and singular systems. The columns had an internal diameter of 2.8 cm and three different lengths of 10, 20 and 30 cm. Deionized water was used to simulate water infiltration and was pumped to the systems at a rate of 480 mL/week. This pumping rate was chosen considering the minimum aqueous sample amount needed for the water quality analysis.

The ternary system had three factors: topsoil, CAAs, and subsoil. Figure. 2 shows a representation of the ternary model system used in this study, where “S” represents the sampling port from which infiltrating water was withdrawn for analysis. An important factor defined in the design was the volumetric application ratio of CAAs to the top soil. Three levels were applied 2:1, 1:2 and 1:1. Therefore, an experiment was formulated with a 3^3 factorial design in duplicates. Accordingly, a total of 27 combinations were tested in a ternary model (Tables 12 - 14). Tables 12 thorough 14 show the experimental combinations used in this study for ternary model using respectively clayey, sand and limestone, as sub soil.

Figure 2. Ternary model

Table 12. Experimental combinations for Ternary model of top soil, CAA and clayey as subsoil

Ternary System		
Top soil/CAA Ratio		
2:1	1:2	1:1
Highly organic soil I CAA I Clayey soil	Highly organic soil I CAA I Clayey soil	Highly organic soil I CAA I Clayey soil
Medium organic soil I CAA I Clayey soil	Medium organic soil I CAA I Clayey soil	Medium organic soil I CAA I Clayey soil
Inorganic sand I CAA I Clayey soil	Inorganic sand I CAA I Clayey soil	Inorganic sand I CAA I Clayey soil

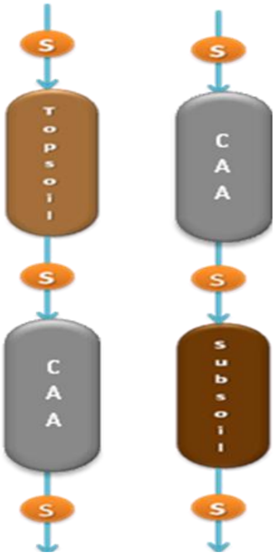
Table 13. Experimental combinations for ternary model of top soil, CAA and sandy soil as subsoil

Ternary System		
Top soil/CAA Ratio		
2:1	1:2	1:1
Highly organic soil I CAA I Sandy soil	Highly organic soil I CAA I Sandy soil	Highly organic soil I CAA I Sandy soil
Medium organic soil I CAA I Sandy soil	Medium organic soil I CAA I Sandy soil	Medium organic soil I CAA I Sandy soil
Inorganic sand I CAA I Sandy soil	Inorganic sand I CAA I Sandy soil	Inorganic sand I CAA I Sandy soil

Table 14. Experimental combinations for ternary model of top soil, CAA and high calcium soil as subsoil

Ternary System		
Top soil/CAA Ratio		
2:1	1:2	1:1
Highly organic soil I CAA I High calcium soil	Highly organic soil I CAA I High calcium soil	Highly organic soil I CAA I High calcium soil
Medium organic soil I CAA I High calcium soil	Medium organic soil I CAA I High calcium soil	Medium organic soil I CAA I High calcium soil
Inorganic sand I CAA I High calcium soil	Inorganic sand I CAA I High calcium soil	Inorganic sand I CAA I High calcium soil

Also a binary system was tested with a combination of the Top soil/CAA and the CAA/Subsoil (Figure 3). For Top soil/CAA a total of 9 combinations in duplicate were performed (Table 15) and 6 different combinations in duplicate were used for CAA/Subsoil (Table 16). For a clear understanding of independent influence of each factor in water quality parameters, a singular model was studied (Figure 4). A total of 11 reactors including top soil, CAA, and subsoil were analyzed in duplicates (Table 17).



(A) (B)

Figure 3. Binary model

Table 15. Experimental Combinations for Binary System of Top Soil/CAA

Binary System		
Top Soil/CAA Ratio		
2:1	1:2	1:1
Highly organic soil I CAA	Highly organic soil I CAA	Highly organic soil I CAA
Medium organic soil I CAA	Medium organic soil I CAA	Medium organic soil I CAA
Inorganic sand I CAA	Inorganic sand I CAA	Inorganic sand I CAA

Table 16. Experimental Combinations for Binary System of CAA/Subsoil

Binary System	
CAA/Subsoil Ratio	
2:3	1:3
CAA I Clayey soil	CAA I Clayey soil
CAA I Sandy soil	CAA I Sandy soil
CAA I High calcium soil	CAA I High calcium soil

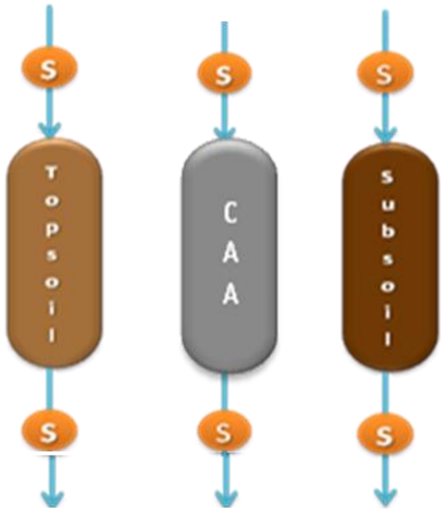


Figure 4. Singular model

Table 17. Singular system for soil and CAA

Singular System		
Reactor Length (cm)		
10	20	30
CAA	CAA	n.m.
Highly organic soil	Highly organic soil	Clayey soil
Medium organic soil	Medium organic soil	Sandy soil
Inorganic sand	Inorganic sand	High calcium soil

n.m.= not measured

Columns were packed using the same method for each one, a small fraction of soils (4 g) was added to columns and little bumps were made to accommodate soil. This procedure was repeated until column was completely filled. Table 18 includes the packing density calculated for each type of column.

Table 18. Packing density for different types of columns

Column Material		Length of Columns (cm)	Packing Density (g/cm^3)
Top Soils	**Highly Organic Soil**	10	1.36
		20	1.26
	Medium Organic Soil	10	1.28
		20	1.26
	Inorganic Sand	10	1.25
		20	1.32
Amendment	**CAA**	10	0.60
		20	0.60
Sub Soil	**Clayey Soil**	30	1.24
	Sandy Soil	30	1.30
	High Calcium Soil	30	1.30

4.2.2. Sampling Procedure

Each combination was run with duration of 3 weeks; water was pumped to each setting from Monday to Friday for 2 hours each day. Sampling was made on two alternative days (e.g., Tuesdays and Thursdays) in each week with a total of 6 sampling days.

In order to analyze water samples the following procedure was used:

- Samples were taken from each sampling port after one hour of water infiltration.
- Samples65or were filtered using a 0.45 µm membrane filter prior to each analysis.
- After filtration, samples were analyzed for the water quality parameters of turbidity, conductivity, pH, and hardness.
- Heavy metal analysis and toxicity analysis were conducted for the final samples obtained during the third week (Day 6).

4.2.3. Toxicity Analysis

Toxicity analysis was made using the Microtox OMNI 500 equipment from AZUR Environmental Company. Microtox provides capability to conduct two different types of test, acute toxicity and genotoxicity. The test that was suitable for this investigation was the Microtox Acute Toxicity Test, which required specific acute reagent.

The following materials are required to perform the toxicity test:

- Microtox Acute Reagent Vials
- Reconstitution Solution
- Microtox Diluent
- Osmotic Adjusting Solution (OAS)
- Disposable Cuvettes

The key element of the Microtox acute toxicity test reagent is a freeze-dried marine bacterium *Vibrio fischeri*. Every vial of reagent contains one hundred million test microorganisms that have luminescent properties. The shelf life of this reagent is about one year, when stored at (-)20 to (-)25 °C. A reconstitution solution is mixed with the reagent to rehydrate the freeze-dried bacteria providing a suspension of ready to use microorganisms. Reagent needs to be used within one to three hours after reconstitution because sensitivity of reagent can be significant after this time. Time and dates were recorded to ensure the proper use of the reagent.

Reconstitution Solution is nontoxic ultra pure water and is used to reconstitute marine bacterium at reagent vial. Microtox diluent consists of a nontoxic 2% Sodium Chloride (NaCl) solution used to dilute the water sample and the reagent. This special diluent is required to protect bacteria from osmotic changes. Moreover, the osmotic adjusting solution is a nontoxic 22% NaCl and is used to adjust osmotic pressure of samples near 2% NaCl. Finally nontoxic disposable cuvettes wore used to contain the water samples, the controls and the reagent during testing. Every material was bought directly from the SDIX company to prevent contamination in the laboratory, because production of uncontaminated solutions is very difficult. Any contamination of the material may affect testing and lead to erroneous results. A calibration was made following the 3-Basic Test Protocol using a phenol standard to ensure the performance of the system. The 81.9% Basis Test procedure is summarized herein, but more details of the test is included in the Appendix A.

- Samples were collected, identified and stored in a refrigerator. The time of analysis after collection of samples should be as soon as possible to avoid toxicity changes.
- Measurements of pH were obtained. It was important to keep this value ranging between 6.0 and 8.0 since the *Vibrio fisheri* bacterium present in the reagent is sensitive to values of ph out of this range. Those samples with pH values out of this range where adjusted with HCL or NaOH.

- After the 81.9% Basic test protocol was performed, cuvettes were placed inside incubator wells.
- Reconstitution solution was added to reagent well, and diluent to indicated cuvettes on test.
- Sample, osmotic adjusting solution were added and mixed; serial dilutions of 1:2 were made and mix after each transfer of samples.
- Reagent was reconstituted at reagent well and record time.
- Read blanks, add reagent to samples and read samples at the times indicated on the test.

4.2.4. Schematic View

The following schematic view shows a better projection and understanding of the system designed for experimentation. The system consisted of a water tank, pump, flex tubing, columns, and ports. The water tank contained deionized water (DI water) which was used to simulate the infiltration of water through columns. Water was pumped at a specific flow rate to carry water through columns.

Water collections for samples were taken at different ports located strategically to obtain water from specific points (S- sampling port). Depending on the different systems, the numbers of samples to be collected and the port used were different. The three different systems as mentioned before were: singular system (control columns), binary systems (Top soil/CAA Columns, CAA /Sub soil Columns), and ternary system (Top soil/CAA/Sub Soil). The control column system had one port at the water tank and the other after each column (Figure 5). The following abbreviations were used in Figures 5 to 8: CAA (Coal Ash Aggregates), TS (Top Soil), and SS (Sub Soil).

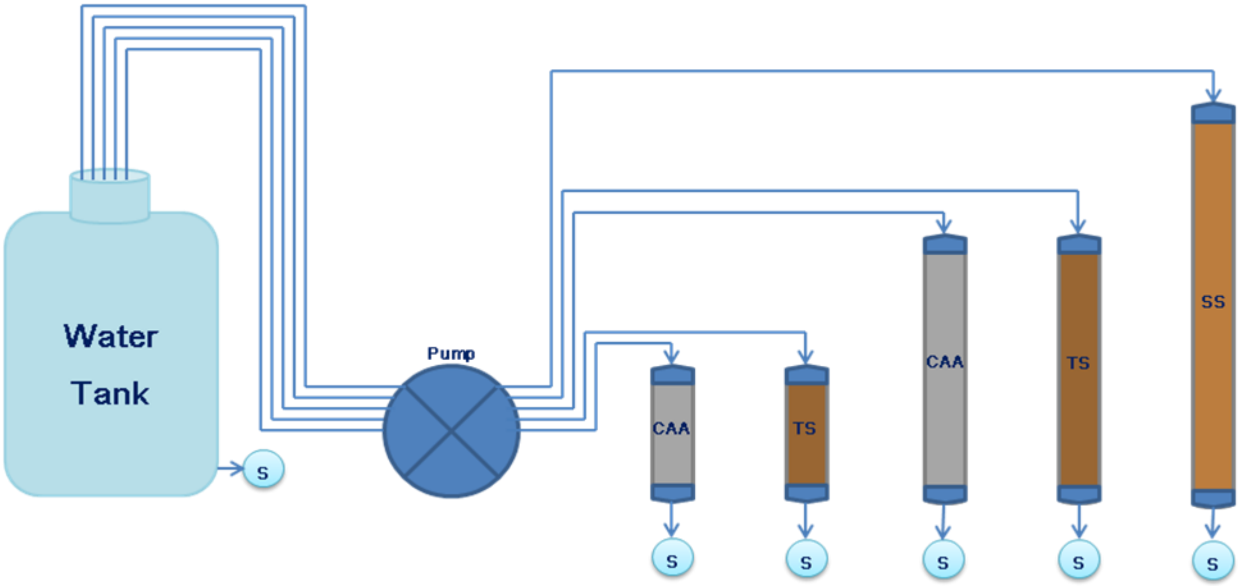


Figure 5. Schematic view of control columns

Binary systems had top soil and CAA columns or CAA and sub soil columns. After each column, sampling ports were placed. In other words, each binary combination had two sampling ports (Figures 6 and 7). For ternary systems, each combination had top soil, CAA and subsoil which required three sampling ports per combination (Figure 8). Figure 9 shows a picture of the setting used in this study for the ternary and binary column systems.

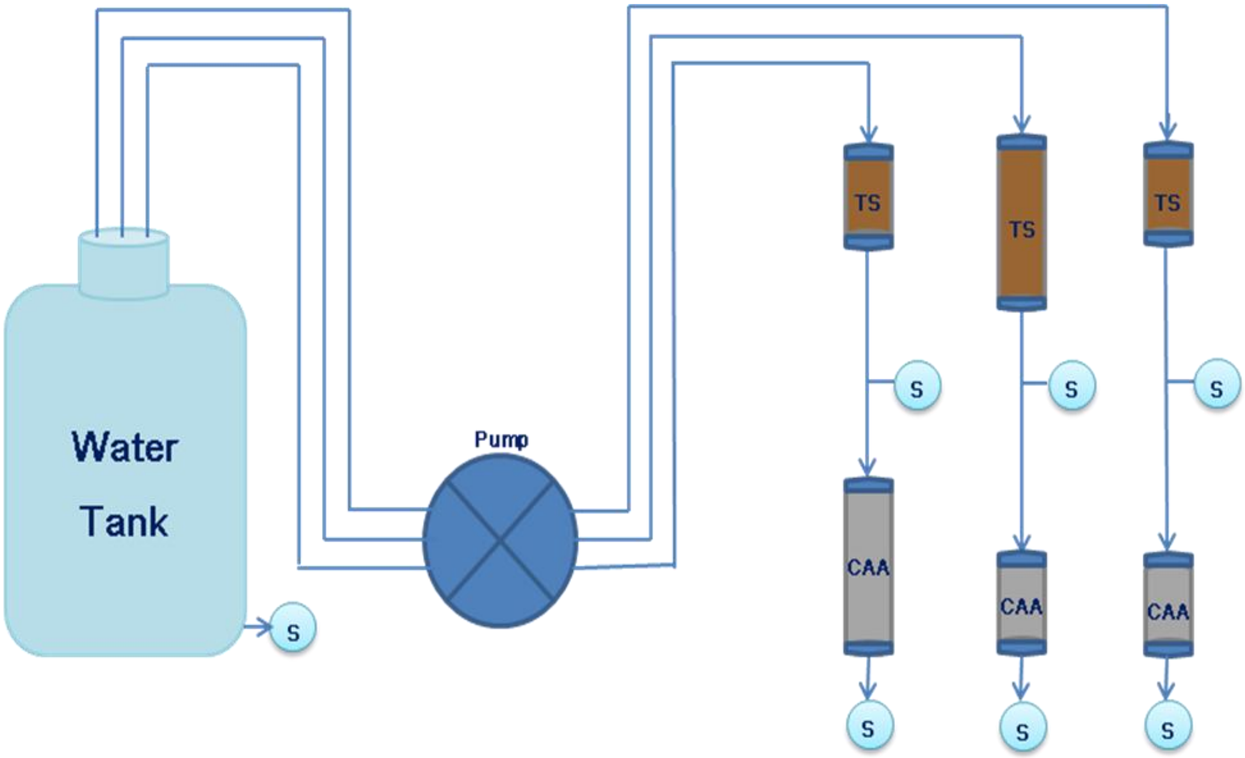


Figure 6. Schematic view of binary system Top Soil/CAA columns

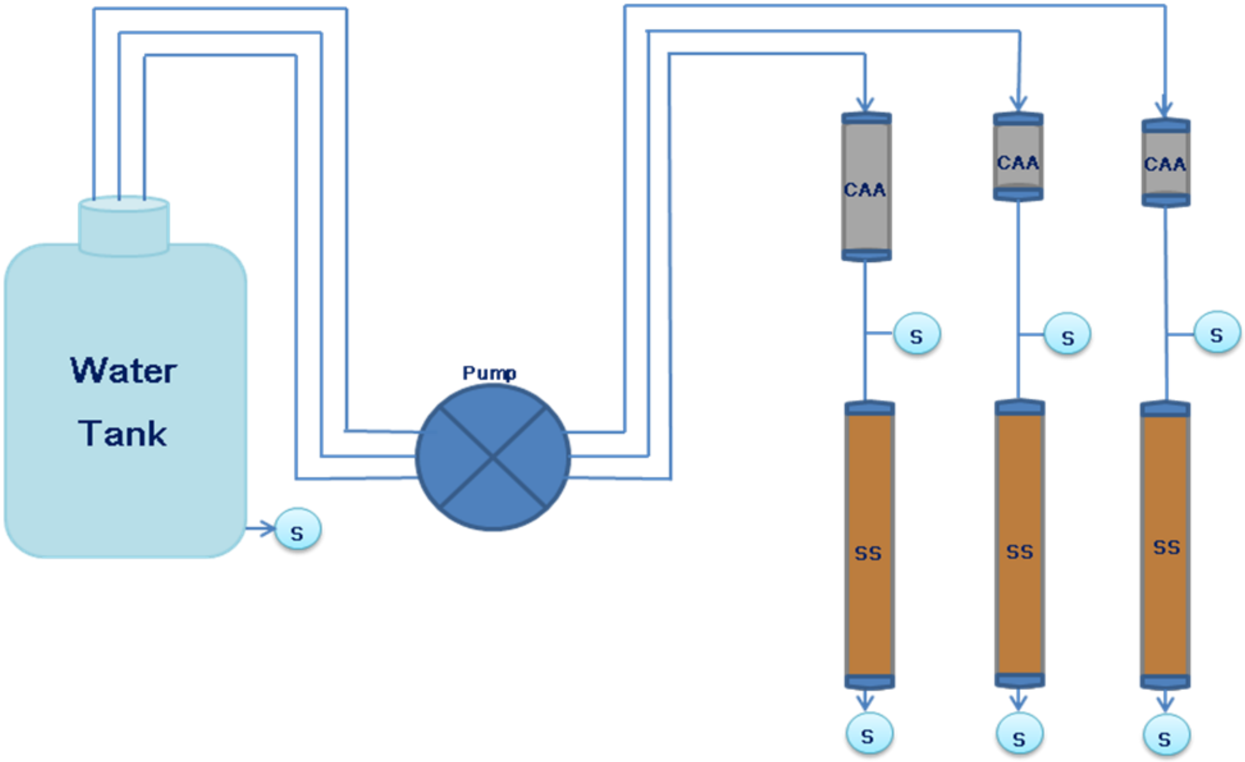


Figure 7. Schematic view of binary system CAA/Sub soil columns

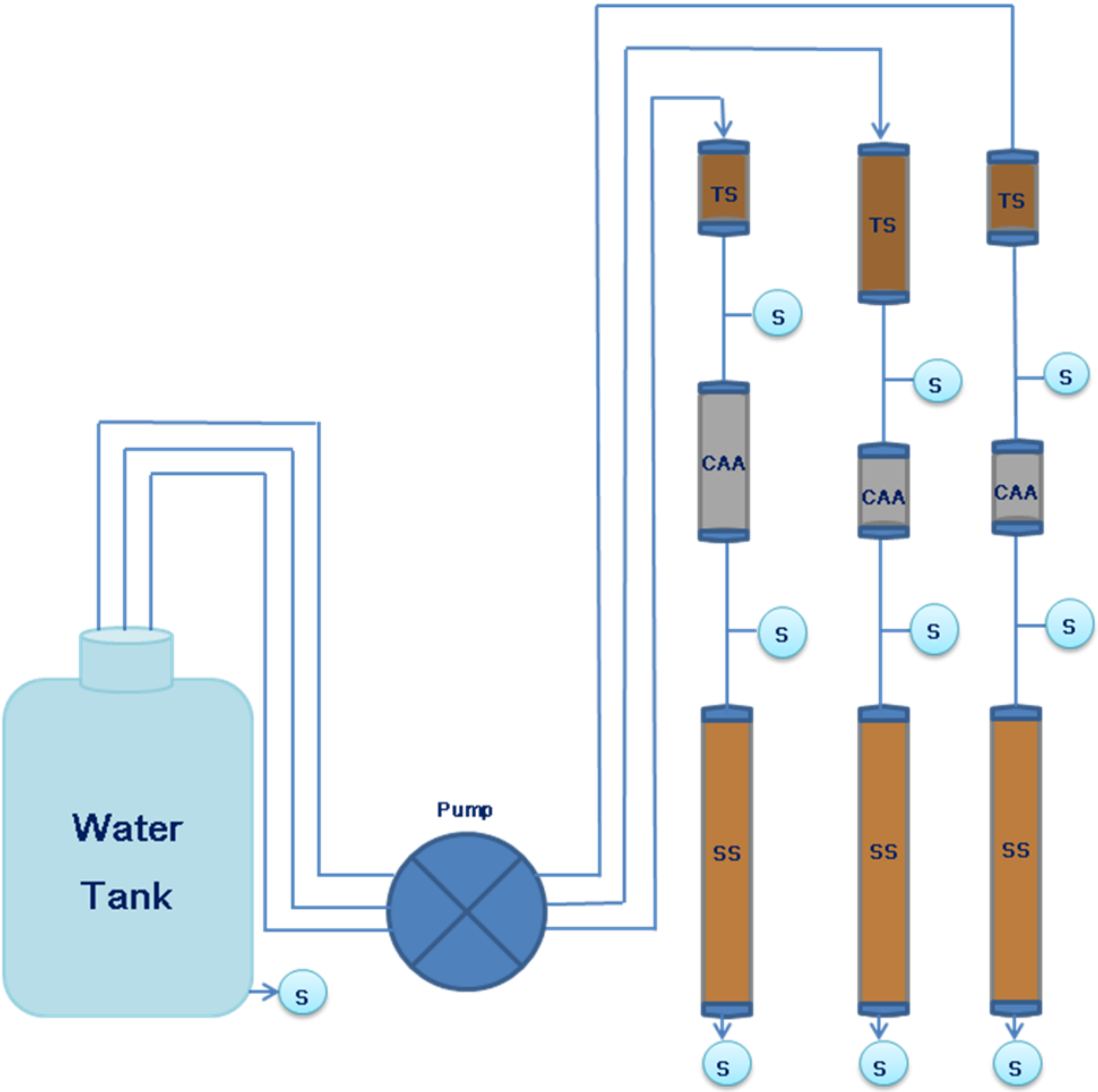


Figure 8. Schematic view of ternary system (Top Soil/CAA/Sub Soil)

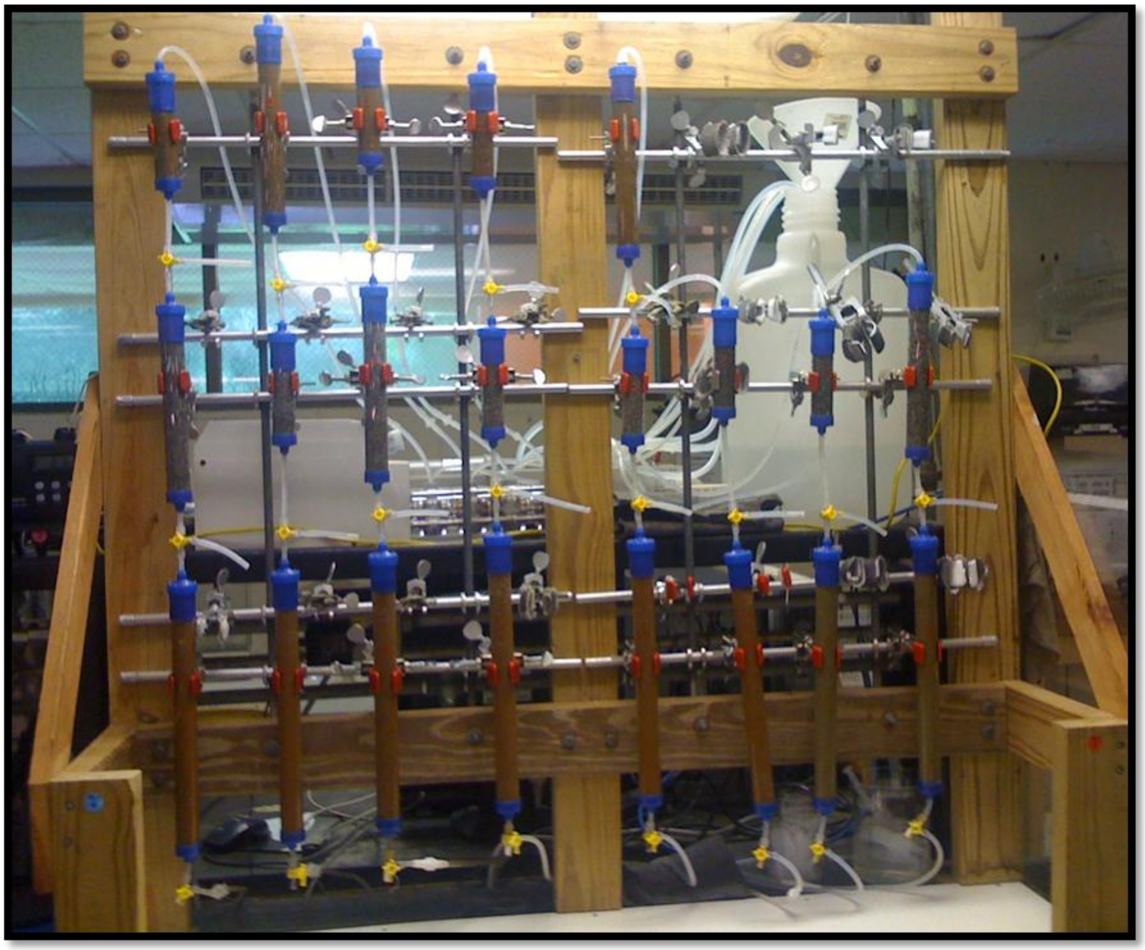


Figure 9. Assembly of columns in the laboratory

5. RESULTS AND DISCUSSION

5.1. Controls

Control columns were used to measure the individual characteristics of percolated water quality from each type of soil and CAAs. The water quality parameters analyzed for each control were turbidity, conductivity, pH and hardness. Each top soil (Highly organic soil, Medium organic soil and Inorganic soil) and CAA were analyzed in columns of 10 and 20 cm in length, while sub soils (Clayey soil, High calcium soil, and Sandy soil) were analyzed in columns of 30 cm in length. Abbreviations presented in Table 19 were used for identification of soils and CAAs. It is important to mention that the numbers included in each abbreviation (10, 20 or 30) represents the column length in centimeters.

Table 19. Abbreviations for soils and coal ash aggregates

Abbreviation	Complete Name
HOS	Highly Organic Soil
MOS	Medium Organic Soil
IS	Inorganic Sand
Cl	Clayey Soil
HCS	High Calcium Soil
SS	Sandy Soil
CAA	Coal Ash Aggregates

5.1.1. Turbidity

Turbidity is a water quality indicator and measures water cloudiness. It is important to maintain low turbidity levels to avoid microorganisms which cause diseases. Microorganisms such as viruses, parasites and some bacteria can cause nausea, diarrhea, and other symptoms (USEPA, 2012).

Turbidity in the percolated water from top soils, sub soils, and CAAs showed low values. The highest values were obtained from medium organic soils and inorganic sand as top soils (Figure 10), and high calcium soil and sandy soil as sub soils (Figure 11).

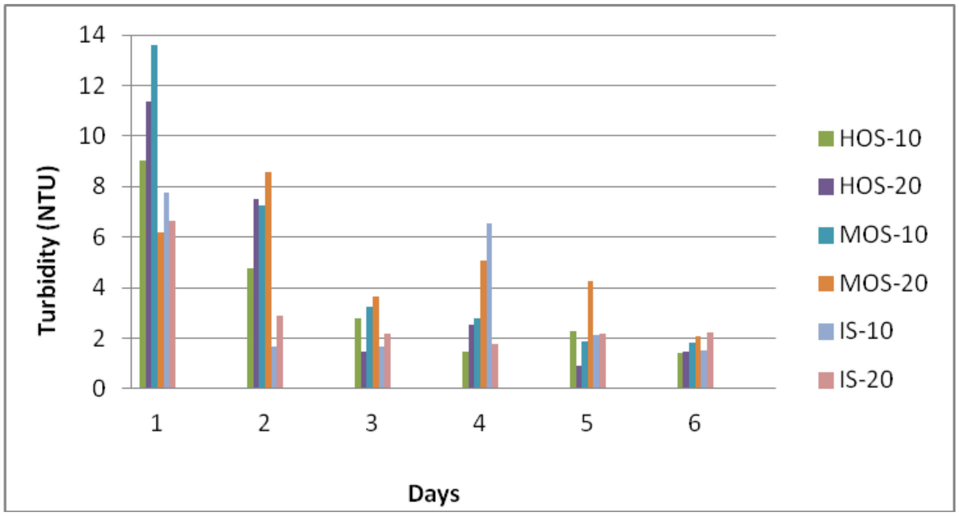


Figure 10. Turbidity of top soil control columns

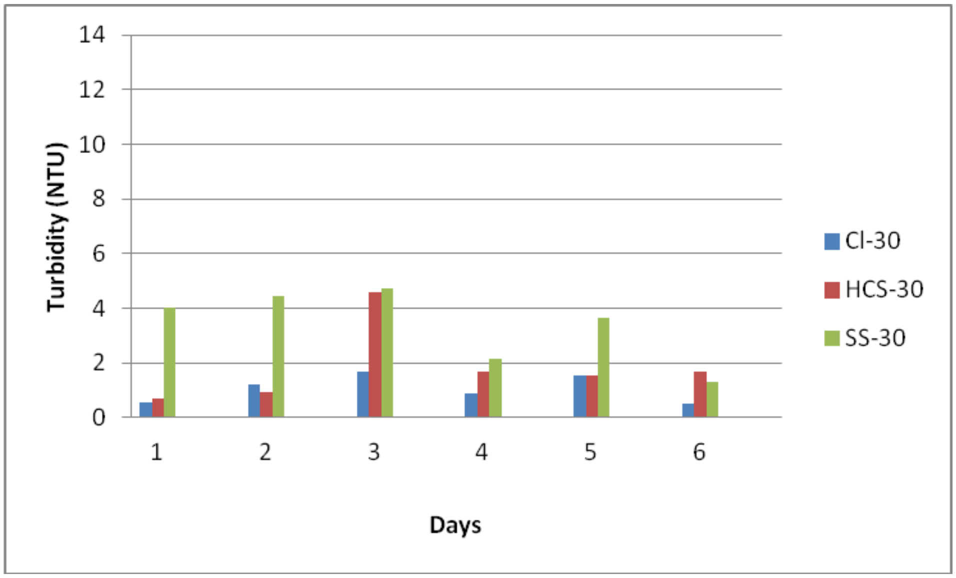


Figure 11. Turbidity of sub soil control columns

As shown in Figure 12, the percolated water from CAAs control columns showed lower turbidity than that from the soil control columns presented in Figures 10 and 11, with turbidity being at 1 NTU or lower. In general, it is concluded that CAAs application to soils would not deteriorate water quality in terms of turbidity.

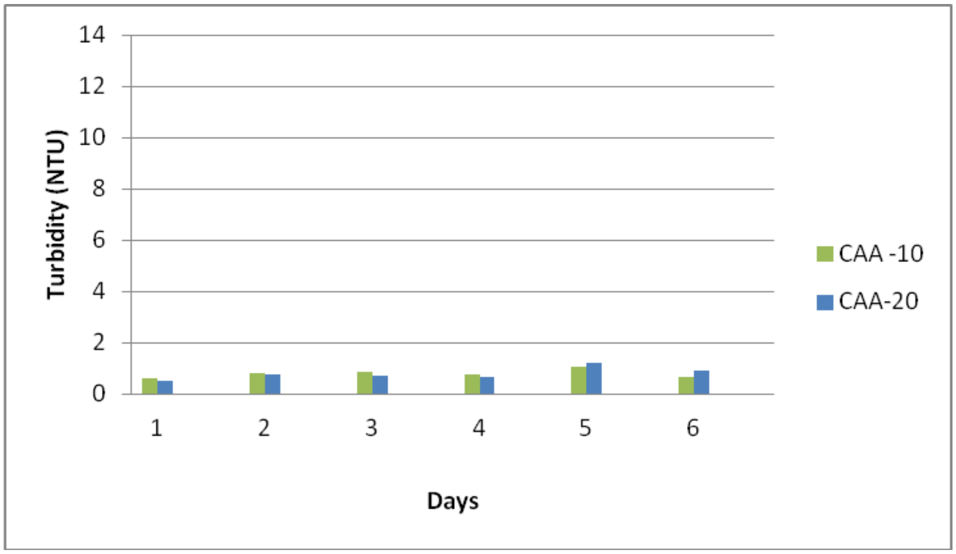


Figure 12. Turbidity of CAA controls columns

5.1.2. Conductivity

Conductivity is a parameter that depends on the type of geologic formation where it is measured. Because of higher presence of materials that ionize in water (dissolve into ionic components), higher conductivity is obtained (USEPA, 2012). Table 20 presents the classification for different ranges of conductivity from EPA. Conductivity in the percolated water from CAAs columns resulted in much higher values in comparison to that from soil columns.

As shown in Figures 13 and 14, conductivity in the percolated water from top soils and sub soils were below 50 µS/cm for the last 5 days of sampling, which are similar to the lower end of conductivity range for rivers (Table 20). A noticeable difference was observed for high calcium soil used as subsoil, which showed higher values in comparison with clayey and sandy soils. During the last day of measurents, conductivity from high calcium soil was higher than 150 µS/cm, which is in the conductivity range for inland fresh waters (Table 20).

Table 20. Classification for conductivity from EPA, 2012

Conductivity	
Classification	**Range (µS/cm)**
Distilled water	0.5 to 3.0
Rivers	50 to 15,000
Inland fresh waters	150 to 500
Not suitable for certain species	> 500
Industrial waters	> 10,000

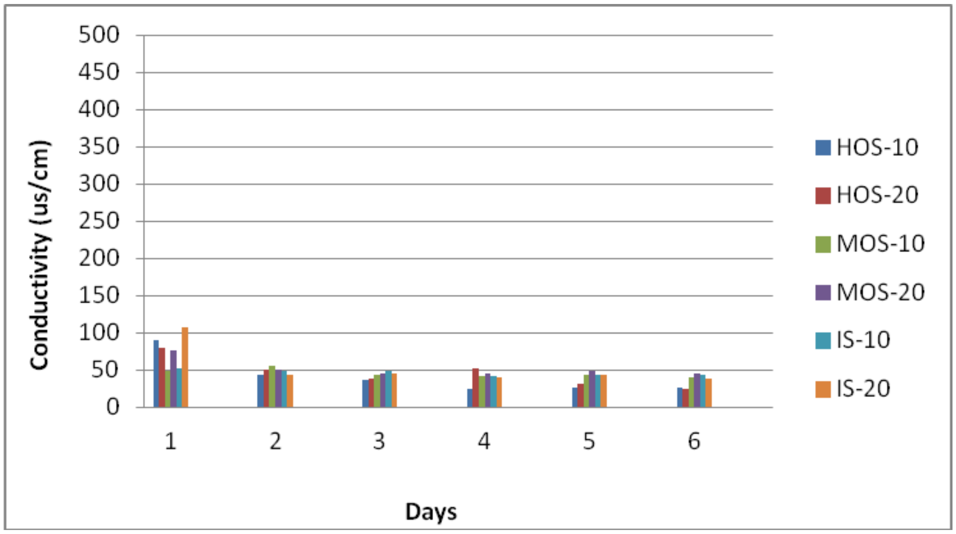


Figure 13. Conductivity of top soil control columns

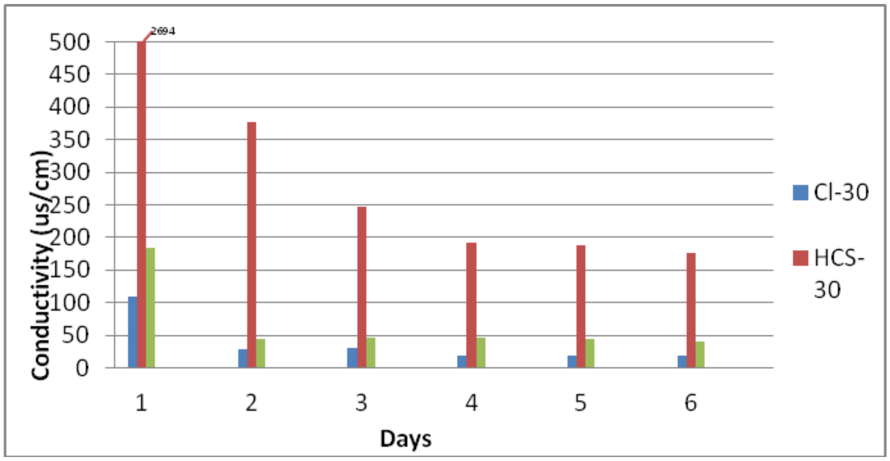


Figure 14. Conductivity of sub soil controls columns

On the other hand, the samples from CAAs columns showed higher conductivities during the first two days of sampling, but however for the last four days of sampling the conductivity in the water was reduced to value ranging from 160 to 260 μS/cm (see Figure 15). Conductivity from CAA columns had higher values than soil columns and, as a result, it is expected that CAA amendment will increase conductivity after subsoil section in ternary columns. However, conductivity values measured from CAA columns are not as high as those values typically found in rivers and inland fresh waters.

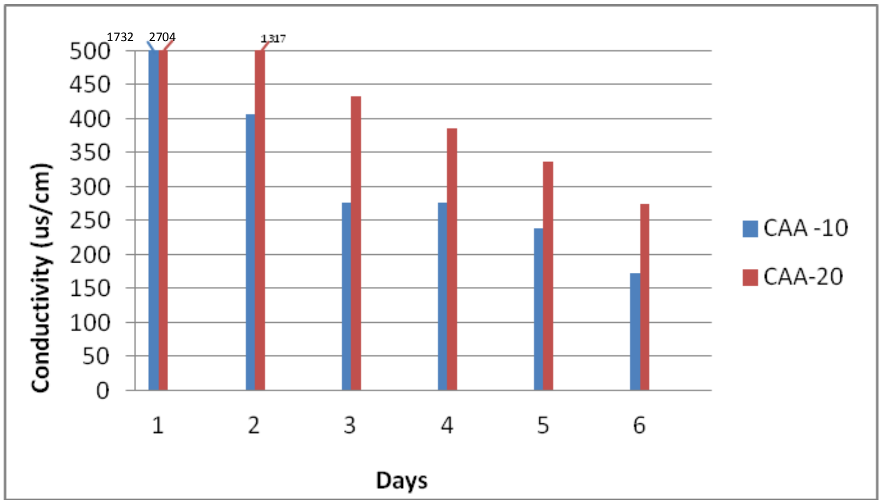


Figure 15. Conductivity of CAA controls columns

5.1.3. pH results

Values of pH were monitored in all the specimens prepared for this investigation to verify that the water percolated from CAAs will not affect natural biochemical processes in water. According to the drinking water standard, pH value should be in the range of 6.5 to 8.5 (USEPA, 2012).

Figures 16, 17 and 18 show pH values measured for top soil, sub soil and CAA control columns, respectively. Top and sub soils showed basic pH values which were below 9. For top soils, the medium organic soil showed the highest pH values in comparison with highly organic soil and inorganic sand (Figure 16). Medium organic soil had pH values as high as 9.4 while the highest pH values measured for highly organic soil and inorganic soil were 8.5 and 8.2, respectively.

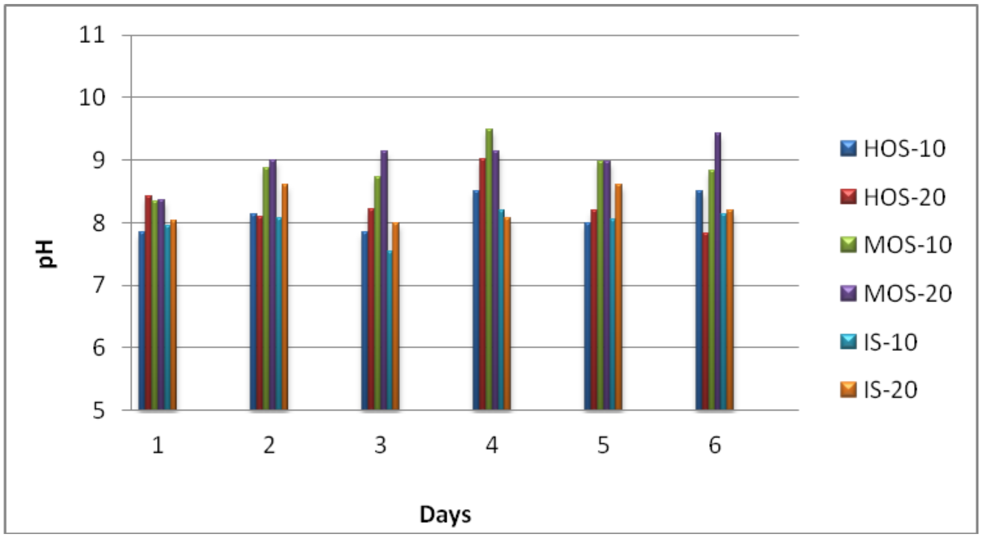


Figure 16. pH of Top Soil controls

Moreover for sub soils the highest pH values were obtained from high calcium and sandy soil columns showing pH values at last day of sampling of 9.3 and 8.9, respectively (Figure 17). Clayey soil resulted in a more neutral pH value of 7.4. Therefore, it is believed that clayey soil is the most favorable type of soil that can be used as a sub soil with CAAs amendment. In this way, the increment in pH due to CAA application will be buffered with a decreased in pH that will be produced from the clayey sub soil, thus maintaining a pH value within the recommended range of 6.5 – 8.5.

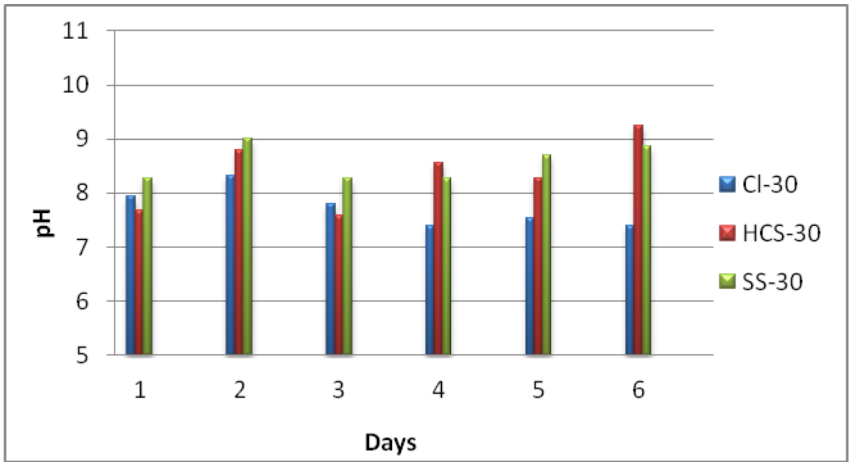


Figure 17. pH of sub soil control columns

As expected, the pH values from CAA columns were noticeably higher in comparison with soil columns, showing values ranging from 9.5 and 10.5. Also, larger columns of CAA (20 cm) showed the highest pH values of up to 10.5 while the small columns (10 cm) had values up to 9.5 at the last day of sampling. This performance was observed during all sampling days (Figure 18).

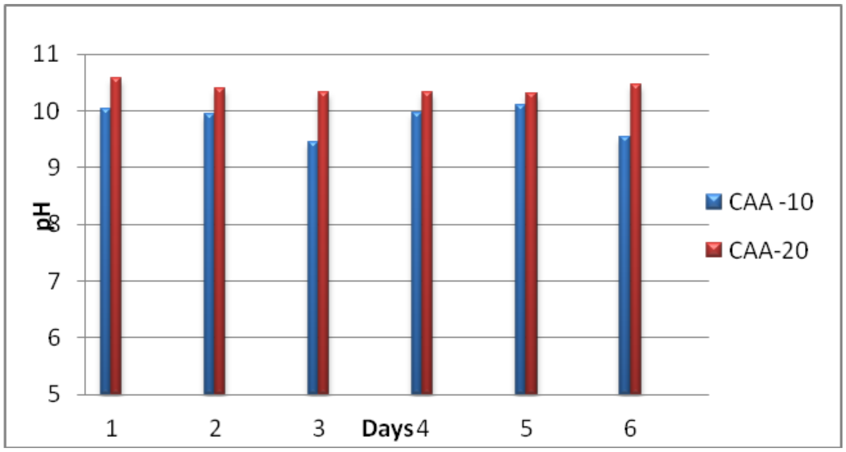


Figure 18. pH of CAA controls columns

5.1.4. Hardness

Hardness is an indicator of the presence of calcium and magnesium ions and metals in water. Table 21 shows a general guideline for water classification based on hardness levels water according to the USEPA, 2012, calcium and magnesium ions are the minerals responsible for making water hard; they dissolve in water as it moves through soils. For this reason water hardness will vary depending on the type of soil.

Table 21. Hardness classification for water from US EPA, 2012

Hardness	
Classification	**Range (mg/L)**
Soft	0-17.1
Slightly hard	17.1-60
Moderately hard	60-120
Hard	120-180
Very hard	180 or greater

Measurements of water hardness for the different controls used in this investigation are presented in Figures 19 to 21. In general, top soils produced lower hardness than sub soils and CAA controls. All controls showed higher values during the first days of sampling, however, at later days values of hardness decreased. Top soils at the last day of sampling showed values ranging from of 7 to 14 mg/L as $CaCO_3$ (Figure 19). Based on the values shown in Table 21 this water classifies as soft. It is interesting to note that columns with sandy soil generated slightly hard water (17.1 - 60 mg/L), but only during the first day of sampling, for the rest of the sampling days the water classified as soft.

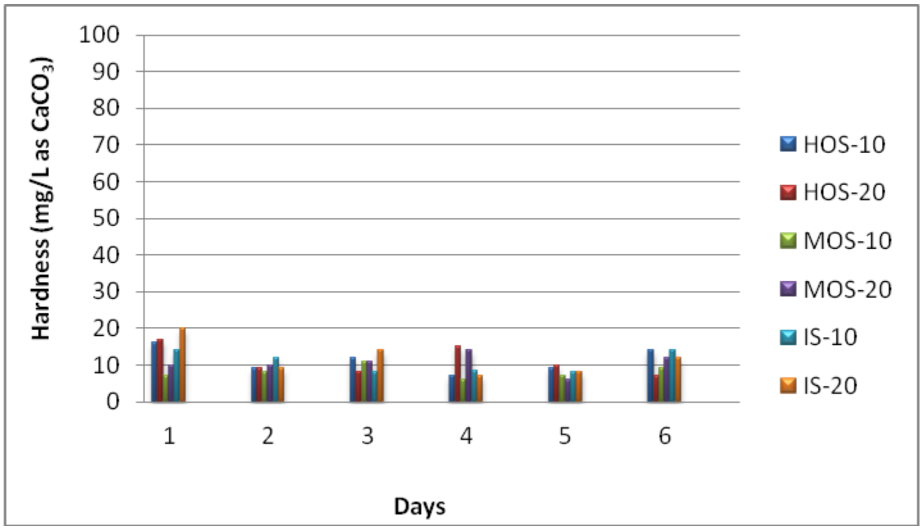


Figure 19. Hardness of top soil controls

For sub soils, the high calcium soil showed the highest hardness values (Figure 21). For this type of soil, the water was classified as hard for the first day of sampling (134 mg/L as $CaCO_3$), however, after the second day the classification decreased to slightly hard value. Hardness values from water samples obtained from clayey soil and sandy soil columns were classified as soft.

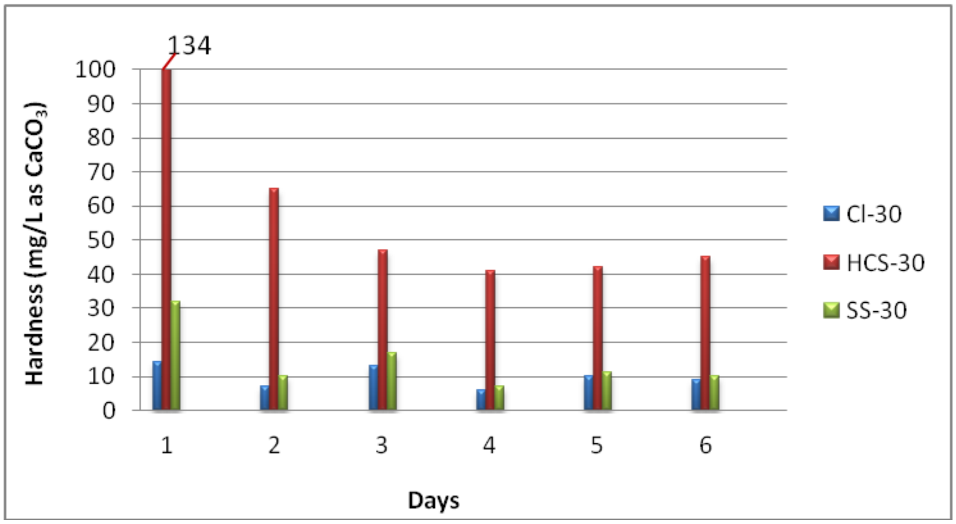


Figure 20. Hardness of sub soil controls

Hardness results obtained from CAA control columns of 20 cm in length had higher hardness levels in comparison with columns of 10 cm (Figure 21). Both columns CAA-10 and CAA-20 showed very high hardness values during the first days of sampling, however the last sampling days these values decreased to the category of slightly hard. For the last day of sampling from CAA columns of 10 and 20 cm the hardness values were 38 and 48 mg/L as $CaCO_3$, respectively. This is a good result because it shows that quickly as days passed aggregates can decrease the hardness to acceptable levels. Hardness values for CAA controls values were higher than the values measured for top soils and sub soils as observed in Figure 21. For a CAA-10 decreases the first three days, after third day continue to decrease but at a slower rate. For CAA-20 during the first three days decreases at a slower rate and after third day decreases at a higher rate.

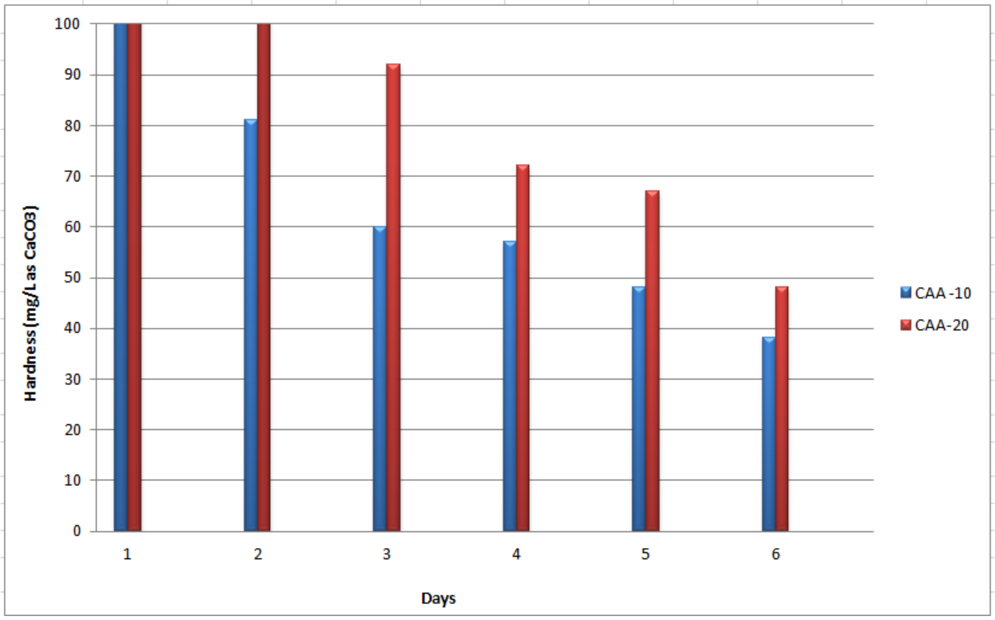


Figure 21. Hardness of CAA controls

5.2. **Statistical Analysis**

A factorial statistical analysis was performed in line with the factorial design of the experiment. The experiment was designed as a 3^3 factorial and the three factors were: top soil, top soil/CAA ratio, and sub soil. Each factor had three levels, top soil levels were highly organic soil, medium organic soil, and inorganic sand. Sub soil levels were clayey soil, sandy soil, and high calcium soil. The three levels used for top soil/CAA ratio factor were: 2:1, 1:2, and 1:1. From the factorial analysis residuals plots, p-values of factors, main effects plot and interaction plot were obtained. This analysis was made for the parameters of: turbidity, conductivity, pH, and hardness.

A code was used in order to easily identify all the 27 combinations of ternary columns. The code identified three levels from 1 to 3. Table 22 shows the codes per level and factors. For ternary columns, combinations of three numbers were used: the first number for top soil, second number for top soil/CAA ratio, and the third for sub soil (Table 23). This code was used in the following plots of ternary columns and for main effects and interaction plots in the next section.

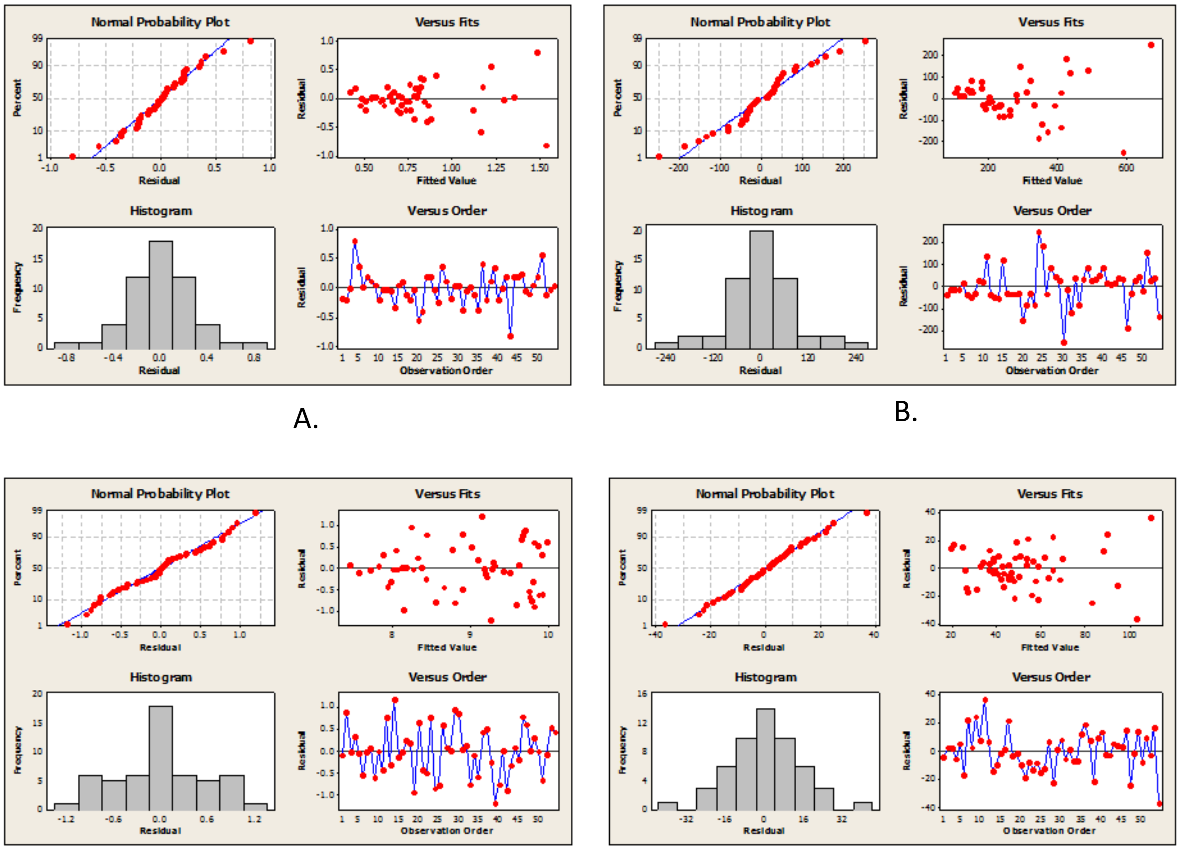
Table 22. Code number for identification of levels

Code Number	Top Soil	Top Soil/CAA Ratio	Sub Soil
1	HOS	2:1	Cl
2	MOS	1:2	SS
3	IS	1:1	HCS

Table 23. Coded levels for ternary combinations

Combination Code	Top Soil	Top Soil/CAA Ratio	Sub Soil
111	HOS	2:1	Cl
112	HOS	2:1	SS
113	HOS	2:1	HCS
121	HOS	1:2	Cl
122	HOS	1:2	SS
123	HOS	1:2	HCS
131	HOS	1:1	Cl
132	HOS	1:1	SS
133	HOS	1:1	HCS
211	MOS	2:1	Cl
212	MOS	2:1	SS
213	MOS	2:1	HCS
221	MOS	1:2	Cl
222	MOS	1:2	SS
223	MOS	1:2	HCS
231	MOS	1:1	Cl
232	MOS	1:1	SS
233	MOS	1:1	HCS
311	IS	2:1	Cl
312	IS	2:1	SS
313	IS	2:1	HCS
321	IS	1:2	Cl
322	IS	1:2	SS
323	IS	1:2	HCS
331	IS	1:1	Cl
332	IS	1:1	SS
333	IS	1:1	HCS

Examples of residual plots for turbidity, conductivity, pH, and hardness obtained from the last-day samples (i.e., Day 6) are shown in Figure 22. Residual plots are necessary to confirm that the model agrees with the assumptions of the statistical analysis, normal distribution, constant variance, and independence. Normal distribution is shown in normal probability plot and this plot should roughly follow a straight line. From this plot, the presence of outliers, non-normality, and skewness can be identified. Histogram of residuals makes a distribution of residuals and this plot provides information on the data as skewness or outliers. A histogram with a bell shape is an indication that the model agrees with the assumptions. For constant variance residuals versus fitted values should show scattered randomly about zero. Plots of residuals versus order of observations are useful when the order of the observation could influence results when data is collected in sequence, this type of plots should fluctuate in a random pattern around zero. The residual plots shown in Figure 22 show a good pattern to meet these requirements.



A.

B.

C.

D.

Figure 22. Residual plots for water quality parameters at Day 6:

A. Turbidity, B. Conductivity, C. pH, D. Hardness

5.2.1. Significant Factors

The purpose of the statistical test performed during this study was to verify if CAAs amendment to different soils influences statistically water quality parameters. This analysis illustrated that ternary interaction of soils with CAA is not significant to water quality parameters with a reliable test. From the output generated by the test, p-values provide valuable information regarding the factors or interactions between that factors are statistically significant. If the p-value is less than or equal to the confidence level (α-level), the effect is significant. If p-value is greater than α-level, the effect is not significant. The α-level used for the factorial analysis is 0.05. This means that the factors with p-value less than or equal to 0.05 provide statistically significant impact on the response variables, in this case, water quality parameters.

Table 24 shows a summary of the water quality parameters which obtained significant p-values. Turbidity parameter was not included because factors and interactions doesn't resulted with significant p-values. For conductivity, the sub soil factor and top soil*TS/CAA ratio interaction had significant p-values only at days 5 and 6. For hardness, factors of TS/CAA ratio at days 1 to 3 and sub soil at day 2 showed significant effects; and also binary interactions of top soil*TS/CAA ratio and top soil*sub soil. The pH parameter had more significant values, top soil and sub soil factors had significant values at days 1 and 1 to 6, respectively. Also all three binary interactions had significant impacts but only at day 1.

Table 24. Water quality parameter which obtained significant p-values

		Variables					
		Conductivity	**Day**	**pH**	**Day**	**Hardness**	**Day**
Factors	Top Soil			x	1		
	TS/CAA Ratio					x	2, 3, 4
	Sub Soil	x	5, 6	x	1 to 6	x	2
Interactions	Top Soil*TS/CAA Ratio			x	4	x	1
	Top Soil*Sub Soil	x	5, 6	x	3	x	4
	TS/CAA Ratio*Sub Soil			x	1		
	Top Soil*TS/CAA Ratio*Sub Soil						

Only the factor of sub soil on the pH parameter was constantly significant for all the six sampling days during experimentation. On the contrary, the other factors showed p-values lower than 0.05 only for 1 or 3 days. The sub soil resulted a significant factor for this experiment, it is that depending on the type of sub soil pH values varied significantly. Another important observation is that no ternary interactions had significant results.

5.2.2. Mean Plot of Ternary Columns

Mean results were plotted for a better representation of the levels by factor. From each parameter were plotted three different graphs based on factors (top soil, sub soil, top soil to CAA ratio), each plot represents all the ternary combination that used each level. For example, the blue bars in Figure 23 corresponded to the mean values of all combinations that used the highly organic soil as top soil. As mentioned earlier, a total of 9 combinations were experimented in replicate. Therefore, the data in Figure 23 are the mean values of 18 samples.

For turbidity no difference was observed between factors and their respective levels through all the sampling days (see Figures 23 to 25), values were ranging from 0.7 – 1.3 NTU. This shows again that no factors influenced significantly on this variable.

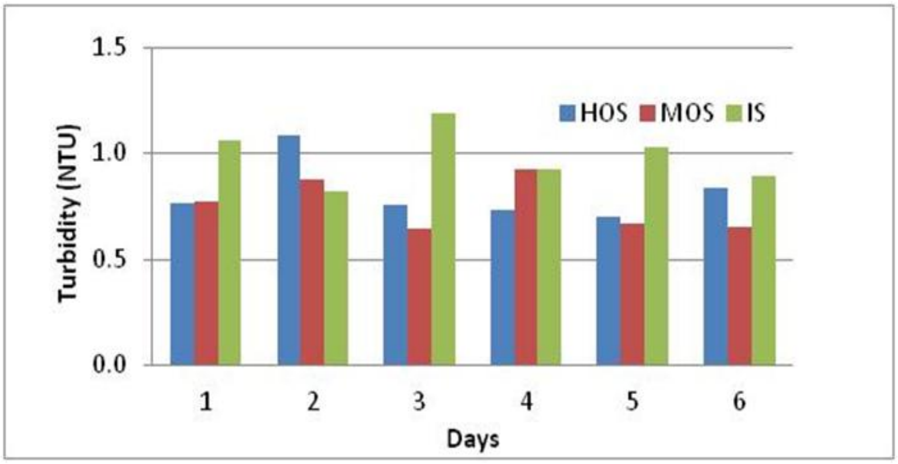


Figure 23. Mean values for turbidity with respect to top soil factor

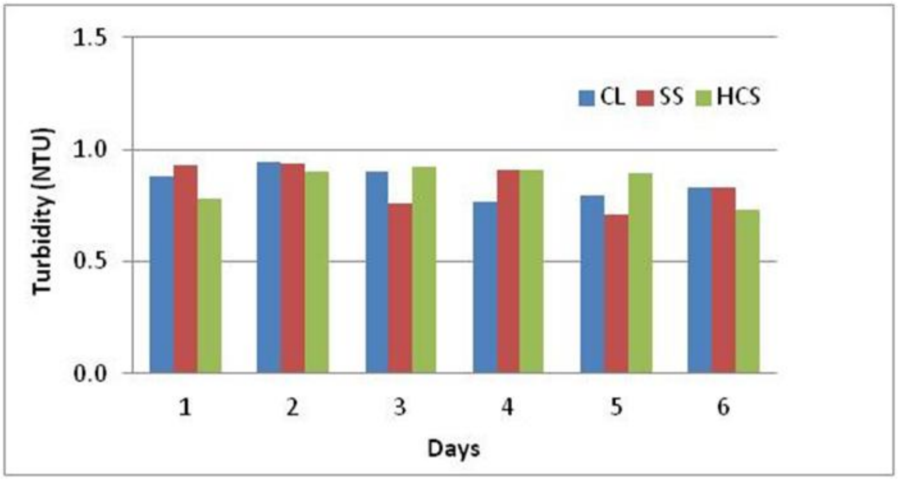


Figure 24. Mean values for turbidity with respect to sub soil factor

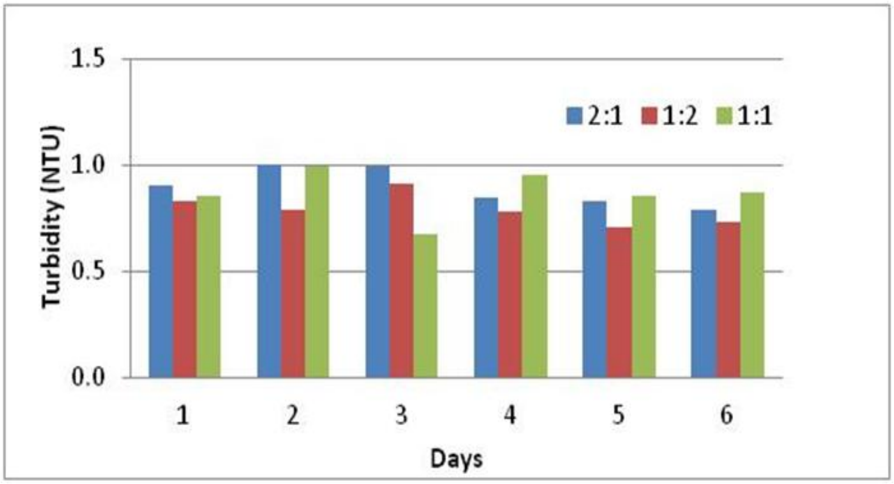


Figure 25. Mean values for turbidity with respect to

TS/CAA Ratio factor

For conductivities, the mean values by factor (Figures 26 to 28) columns showed that at the first day values, were higher of 700 µS/cm but decreased considerably afterwards. Values from days 2 to 6 were 500 µS/cm or lower after amendment, and no difference between factors was found. In Figure 28, there was noticeable that the level of 1:2 top soil to CAA ratio showed higher values at mean values that included all combinations that used this ratio.

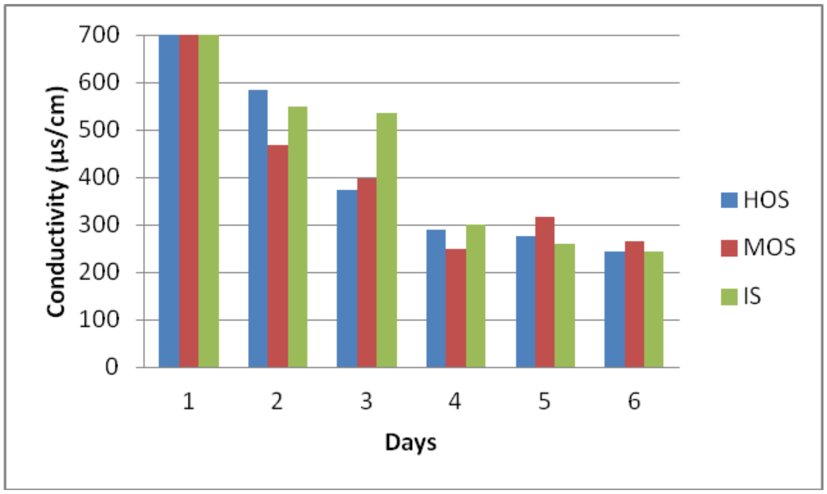


Figure 26. Mean values for conductivity with respect top soil factor

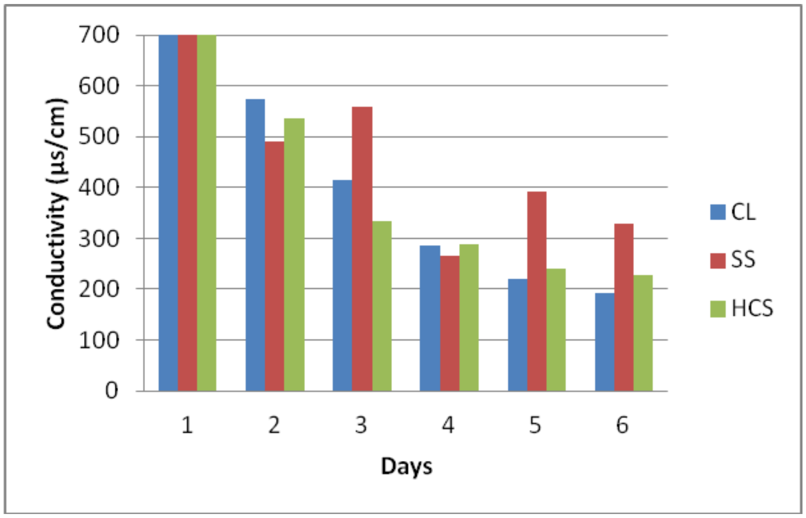


Figure 27. Mean values for conductivity with respect sub soil factor

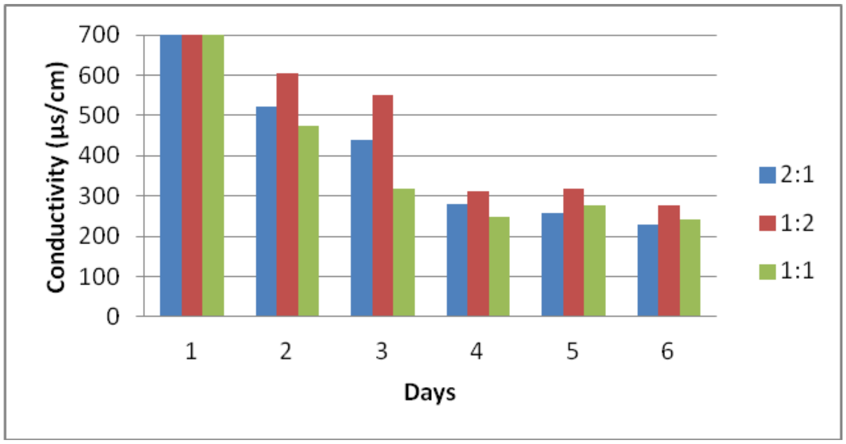


Figure 28. Mean values for conductivity with respect TS/CAA ratio factor

In contrast to conductivity, the pH plots showed opposite results; at the first days lower pH values were obtained and then values increased afterwards. At the last three days of experimentation, steady pH values were observed (Figures 29 to 31). In top soil plot (Figure 29), combinations with highly and medium organic soil had pH values lower than 9, and inorganic soil combination had the higher pH values of above 9. Sub soil plot (Figure 30) shows a clear pattern in which values were lower to higher in the following order: clayey soil, sandy soil and high calcium soil. Sandy soil and high calcium soil had pH values higher than 9 which were not plausible results based on drinking water standards. Based on this plots (sub soil) clayey seems to be the only sub soil that should be utilized. This plot shows that pH depended on the type of sub soil used and that Top Soil/CAA ratio did not produce the same results.

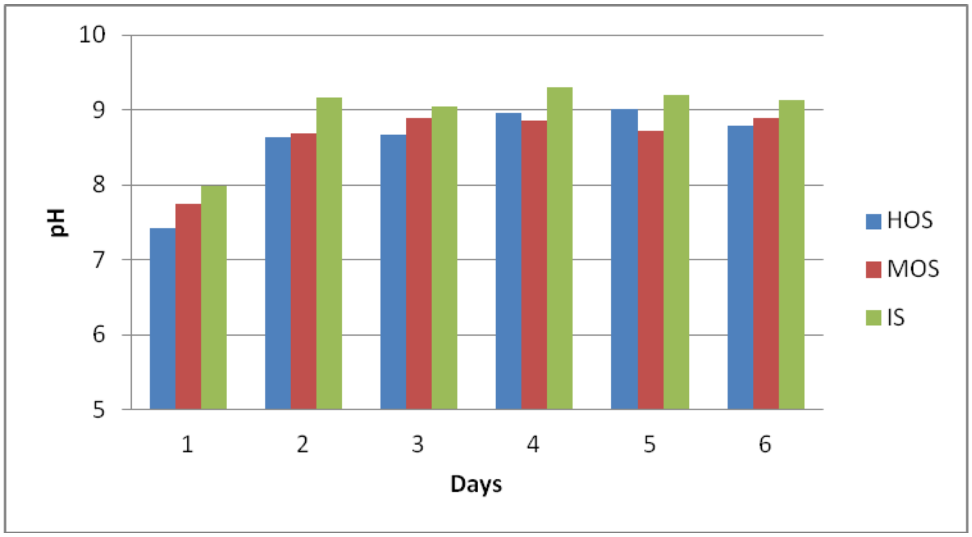


Figure 29. Mean values for pH with respect top soil factor

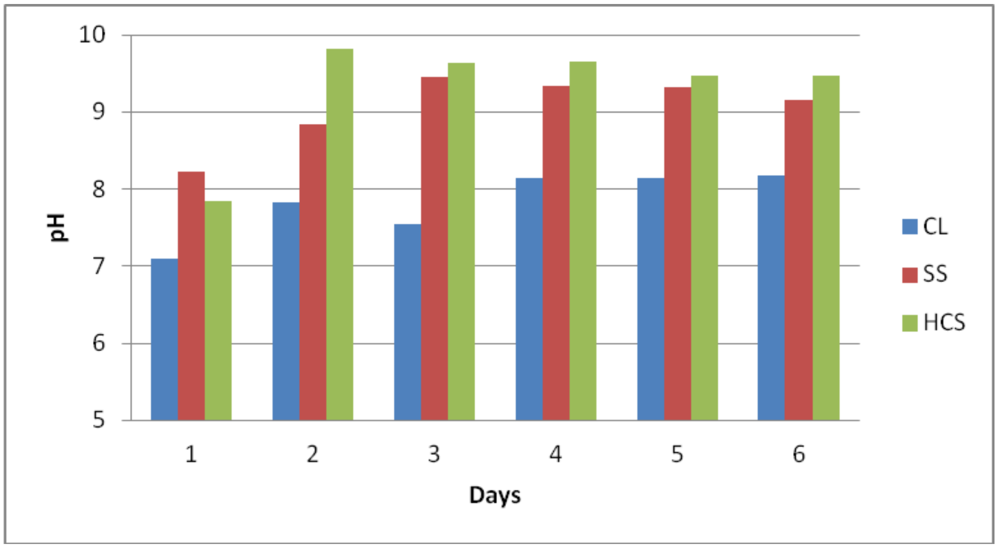


Figure 30. Mean values for pH with respect sub soil factor

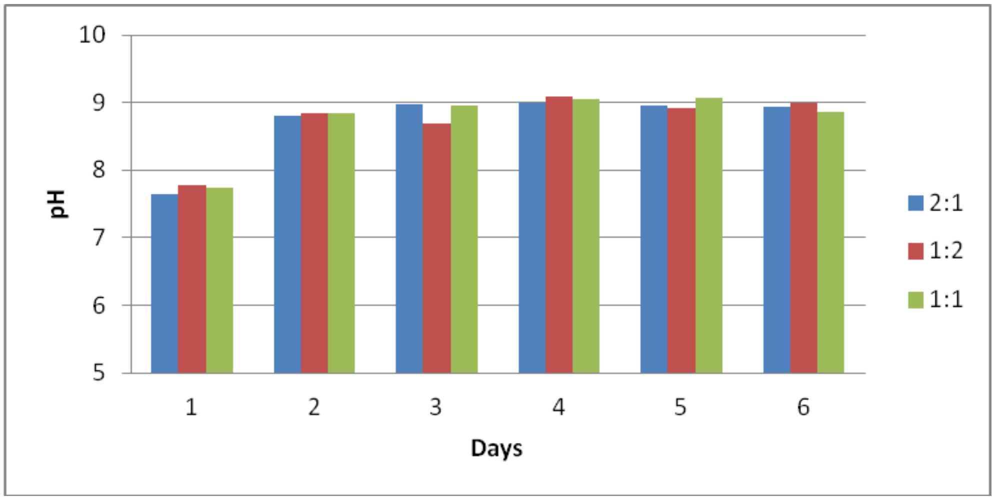


Figure 31. Mean values for pH with respect TS/CAA soil factor

Figures 32 to 34 obtained from hardness showed that the mean harness values were in the same descending trend as days passed. For top soil to CAA ratio plot (Figure 34), higher values were obtained at combinations with 1:2 ratio at all days. Larger amount of CAAs application results in higher pH in water as seen at CAA control columns.

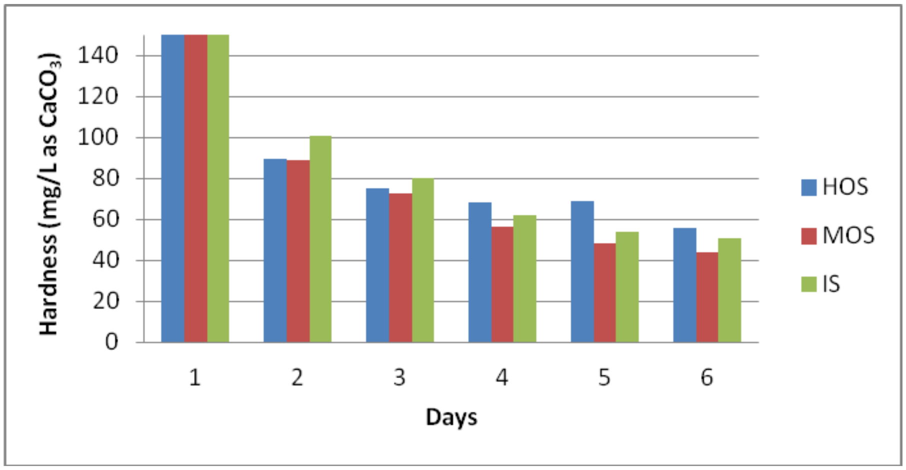


Figure 32. Mean values for hardness with respect top soil factor

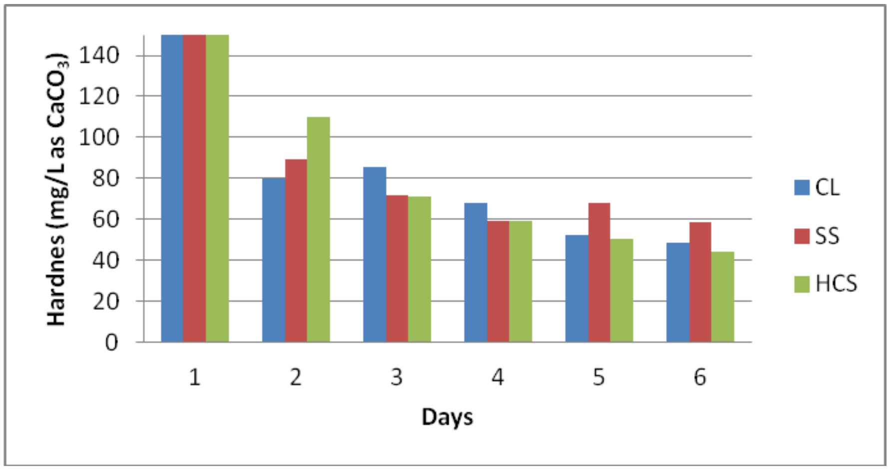


Figure 33. Mean values for hardness with respect sub soil factor

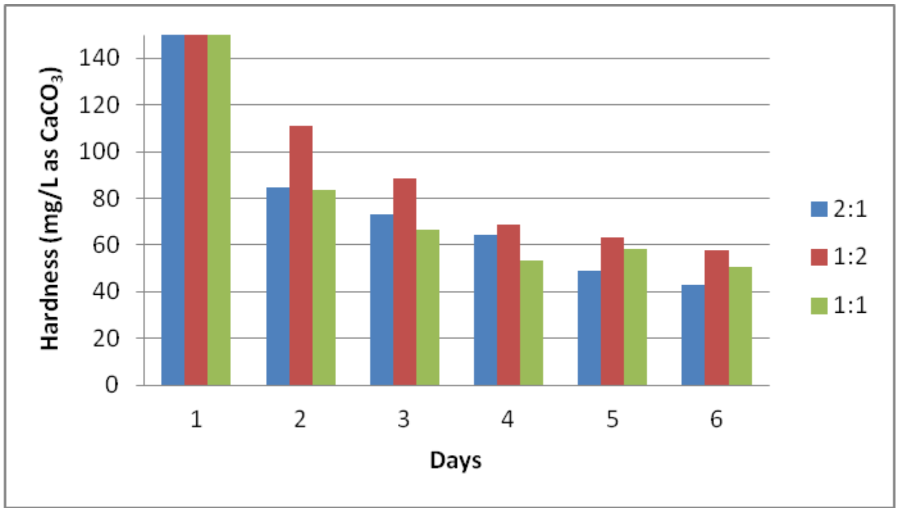


Figure 34. Mean values for hardness with respect TS/CAA soil factor

5.2.3. Main Effects and Interaction

When different levels affect a response, there is a main effect present on a factorial analysis. A main effects plot connects with a line the mean values of a response indentifying levels of factors. Interpretation of plots is important to know if there is main effect of level or not. Below are clues to identify a main effect:

- No main effect present = When connected points create a horizontal line to the x-axis, factor levels have the same effect on the response or a very similar.

- Main effect present = Connected point doesn’t create a horizontal line to the x-axis; levels of this factor affect the response. Higher slope of the line means a greater main effect.

Interaction plots help to visualize interaction of levels between factors; no interaction is indicated with parallel lines. This type of plots can’t indicate if interaction is statistically significant but shows a great summary of means. Main effects and interaction plots were used to present another way to understand the combination from the 3^3 factorial design used. This plots also used the code of levels presented in Table 23 and numbers on axis and legend correspond to Table 22. Main effects and interaction plots help to better understand the extent of effects caused by the factors of different soils and ratios used. Comparison between the level differences and finding which level or combinations are better are made. For each parameter, both plots are included and observation from them is discussed below.

For the main effects and interaction plots of turbidity (Figures 35 and 36), the ranges were plotted close to 0.5 - 1.1 NTU. So, the lines created by the points connected appear to be greater than real. Also this parameter is not in concern according to turbidity level results. On the other hand, the main effects were seen more significantly for top soils with a greater slope of lines.

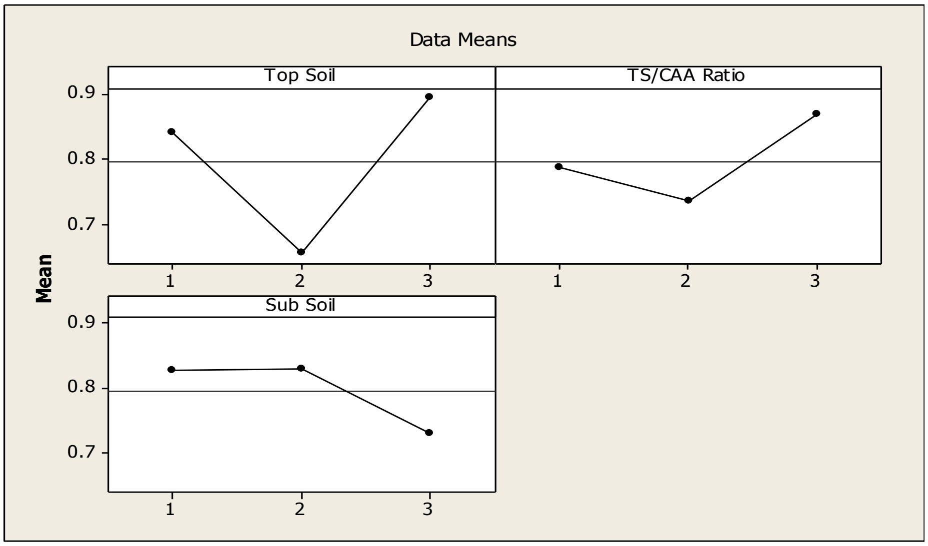


Figure 35. Main effects plot for turbidity Day 6

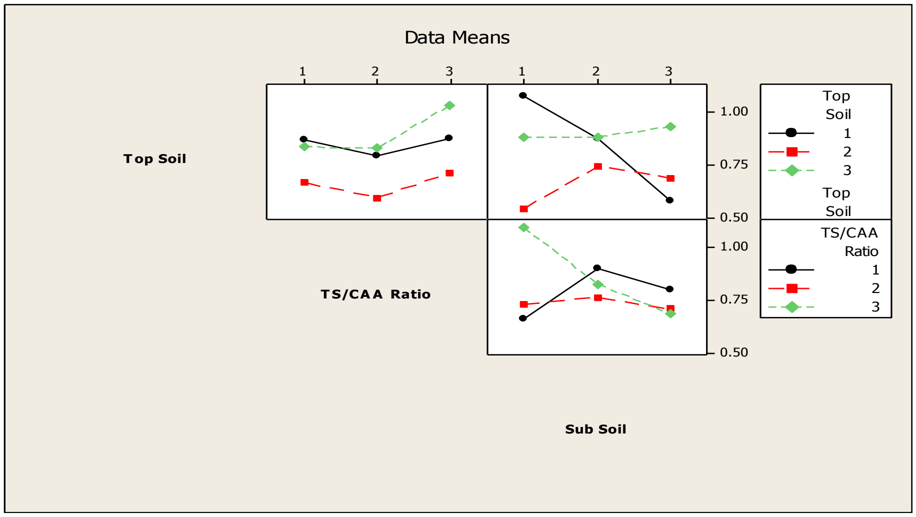


Figure 36. Interaction plot for turbidity Day 6

Greater main effects on conductivity (Figure 37) were seen for sub soil, whereas top soil showed less main effect for conductivity. Interaction plot (Figure 38) showed that there was interaction present and medium organic soil (top soil), sandy soil (sub soil) and top soil to CAA ratio 1:2 produced the higher conductivity values. Lower values were obtained when highly organic soil and inorganic sand (top soils) were combined with top soil to CAA ratio of 2:1 and 1:1, and clayey soil and high calcium soil as sub soils.

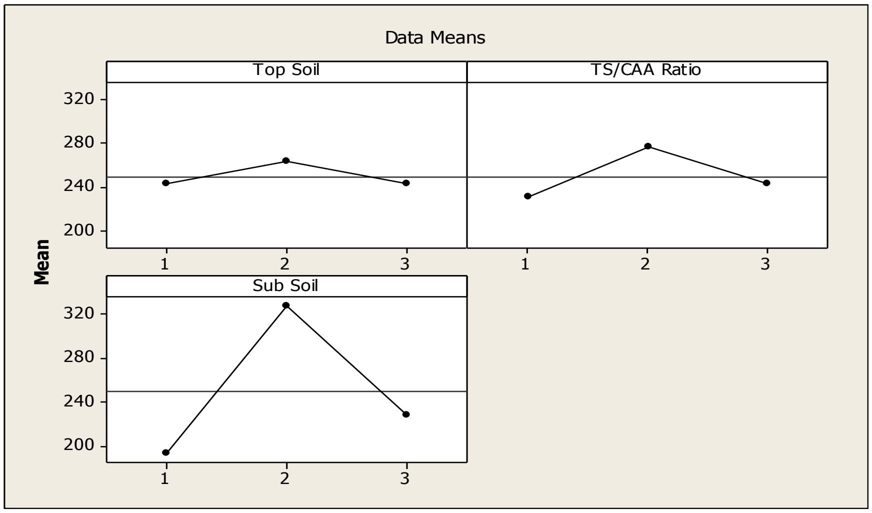


Figure 37. Main effects plot for conductivity Day 6

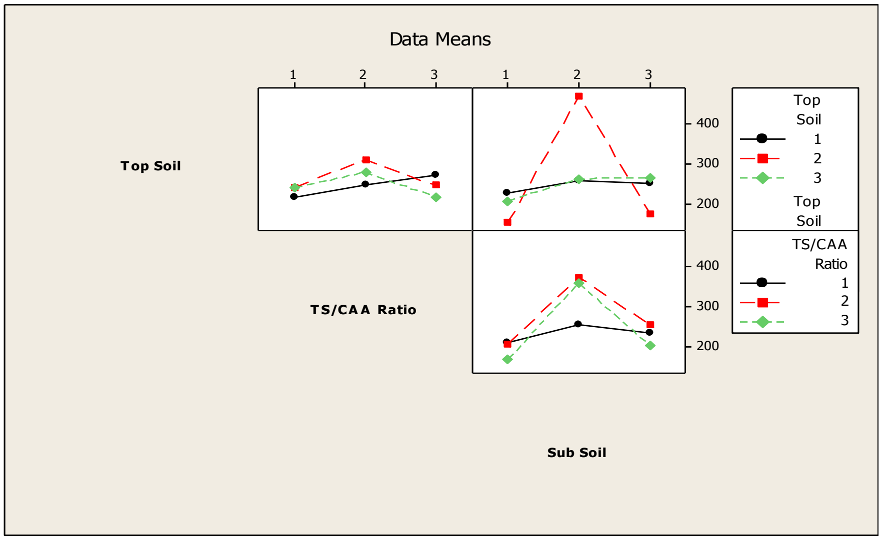


Figure 38. Interaction plot for conductivity Day 6

As shown in Figure 39, sub soil produced a main interaction for pH parameter. Top soil and top soil/CAA ratio showed main effect but lower in comparison to sub soil. The lower pH values were obtained with highly organic soil as top soil, top soil to CAA ratios of 2;1 and 1:1, and clayey as sub soil (Figure 40). The pH parameter is very important and the clayey soil was the only one that showed the values of 7.5 from the controls columns and after amendments this sub soils increased the pH values but no higher than 8.5 which is the high end level for drinking water standard set by EPA.

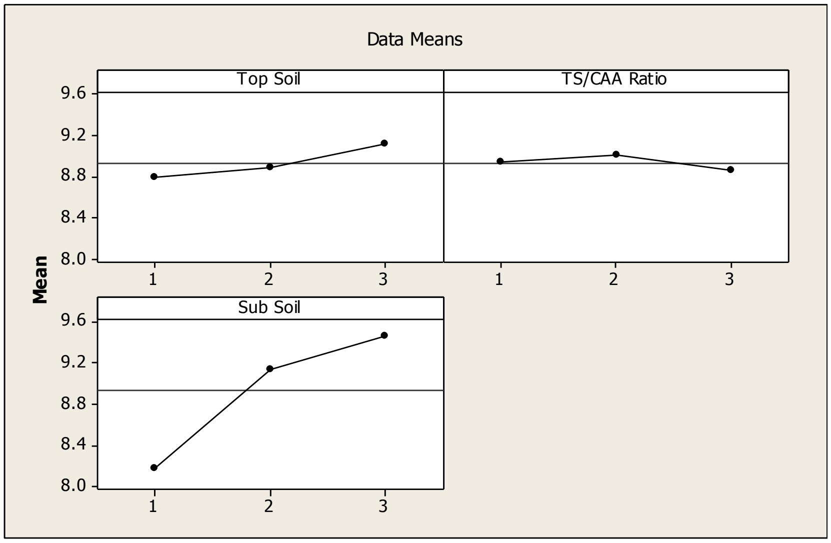


Figure 39. Main effects plot for pH Day 6

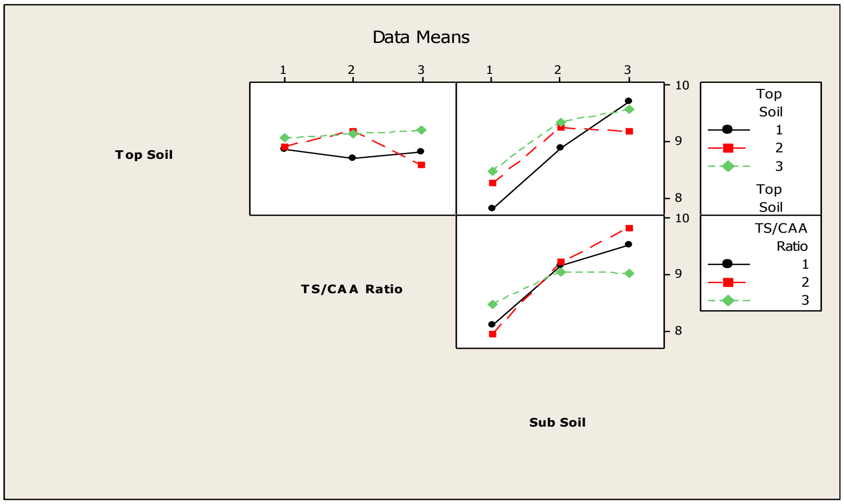


Figure 40. Interaction plot for pH Day 6

Figures below show that all level and factors had main effects and interaction on hardness. In the main effect plot (Figure 41), levels of 1:2 of top soil to CAA ratio showed higher levels. Top soil (1,2,3) in combination with 2:1 ratio showed lower hardness levels, which was the same results observed in Figures previously shown. Also, as shown on the right bottom of Figure 41, all sub soils in combination with ratio 2:1 showed lower hardness levels in comparison to other levels.

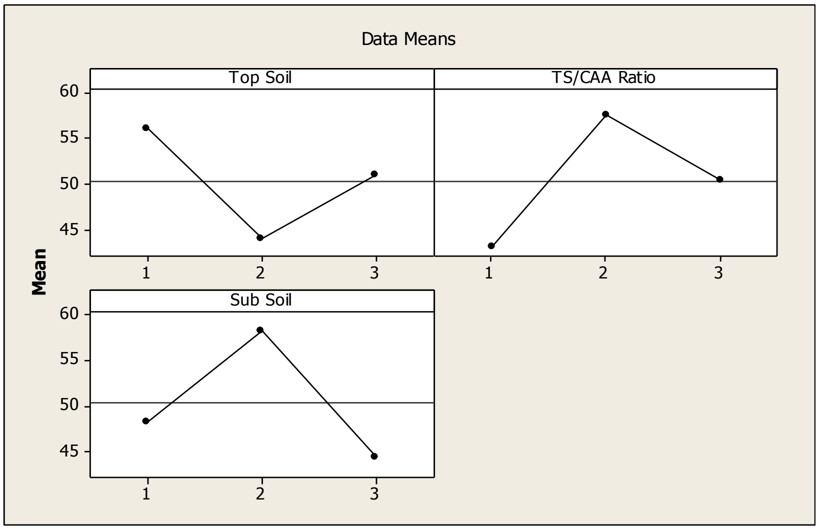


Figure 41. Main effects plot for hardness Day 6

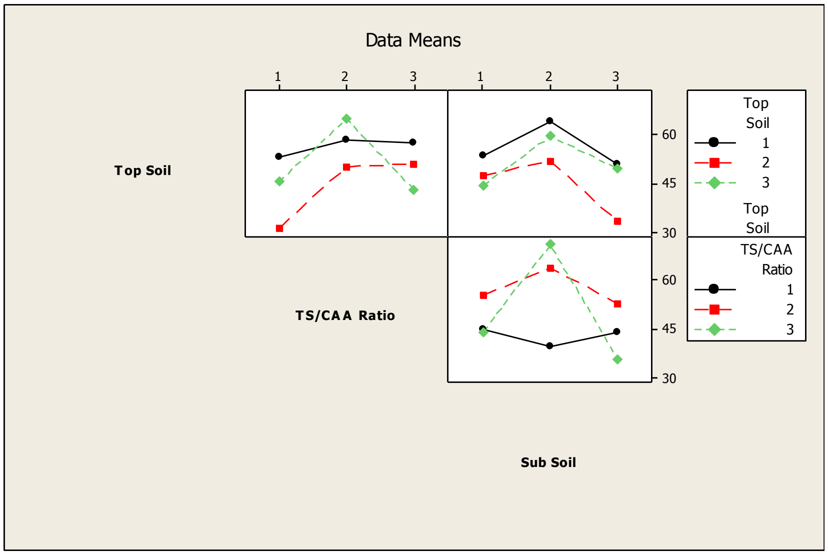


Figure 42. Interaction plot for hardness Day 6

5.3. **Toxicity Assessment**

Based on the type of sample (water) and the toxic elements suspected (heavy metals) the 45% Basic Test is the recommended following the guidelines from Microtox. This test was performed for some samples and results detected hormesis. With the detection of hormesis it recommends a re-test, however, the same results were obtained again. This result is considered that the sample tested has low concentrations of toxic substance and for this reason toxicity can’t be detected. Microtox doesn’t take hormesis responses reliable and doesn’t use them to estimate toxicity (Christofi et al., 2001)

To increase the initial concentration, the 81.9% Basic Test was used to see if this method detects toxicity in the samples. This test was made in duplicate for all combinations of binary and ternary columns for CAA and sub soil samples. Also CAA control columns were tested. Despite this effort, the results from all samples detected hormesis again and it was unable to make a regression to calculate EC_{50} value. A Table with all results of samples was included in Appendix A.

According with García, M.L. (2004) hormesis is the stimulatory effect of low concentrations of toxic chemicals on organism metabolism and it is common in luminescent bioassay. Shen et al. (2009) studied the effects of Cu (II), Zn (II), Cd (II) and Cr (VI) on luminescence at low concentrations and hormesis was observed in all analyzed metals. Based on studies mentioned before, it is construed that the water samples analyzed were not toxic at acute concentrations.

5.4. **Heavy Metal Analysis**

Coal ash aggregates were assessed for its potential of leaching heavy metals during the experiments. Samples were collected from every sampling ports throughout the experimental period, stored in the refrigerator prior to the analysis, and analyzed to make sure that heavy metal concentrations in the percolated water were safe in terms of groundwater quality. Controls (CAA and soil) and ternary columns were analyzed to make sure that heavy metal concentrations from any combinations do not exceed water quality standards. Heavy metals analyzed were chromium (Cr), arsenic (As), selenium (Se), cadmium (Cd), barium (Ba), and lead (Pb). Drinking water standards for these heavy metal were summarized in Table 25.

Table 25. Drinking water standards for heavy metals from US EPA, 2012

Heavy Metal	Standard for Concentration (ppb)
Cr	< 100
As	< 10
Se	< 50
Cd	< 5
Ba	< 2000
Pb	< 15

For controls of top soils and CAAs, the columns of 10 and 20 cm in length were use. For sub soils, 30-cm long columns were used. Measurements from days 1, 3, 5 and 6 were analyzed by ICP-MS. The maximum concentrations of Cr, As, Se, Cd, Ba, and Pb for all samples (controls, binary and ternary columns) were below drinking water standard set by EPA. The concentrations of Cr and Cd in all samples were under the detection limit (1 ppb). For As, Se and Pb, the concentrations were some cases under the detection limit.

Table 26 shows values of heavy metal analysis for the control columns at sampling day 6. The concentration Cr and Cd were under the detection limit as mentioned before. For better visualization, Figure 43 to 46 were plotted using results presented in Table 26. Only plots for As, Se, Ba, and Pb were made because Cr, and Cd results were all below the detection limit.

Table 26. Heavy metal concentration for controls columns Day 6

Identification			Concentration (ppb)					
			Cr	As	Se	Cd	Ba	Pb
CONTROLS	Highly Organic Soil	10	UDL	UDL	UDL	UDL	325.8	1.1
		20	UDL	UDL	1.5	UDL	139.8	5.9
	Medium Organic Soil	10	UDL	UDL	1.7	UDL	230.0	8.7
		20	UDL	UDL	1.9	UDL	240.4	8.7
	Inorganic Sand	10	UDL	1.1	1.1	UDL	324.6	8.9
		20	UDL	1.7	1.2	UDL	206.0	9.6
	Clayey	30	UDL	UDL	UDL	UDL	97.9	UDL
	High Calcium Soil	30	UDL	2.7	1.1	UDL	71.7	UDL
	Sandy Soil	30	UDL	2.8	4.1	UDL	57.3	1.7
	CAA	10	UDL	1.3	5.5	UDL	176.6	3.3
		20	UDL	1.5	8.2	UDL	169.0	1.3

UDL- Under Detection Limit, less than 1 ppb

Also plots were made for every heavy metals detected at levels higher than the detection limit. Plots of control columns of day 6 were included for the purpose to demonstrate which sources were leaching more concentrations of metals. This is useful because in general the same trend was obtained at control plots during 4 sampling days.

From the plot of arsenic (Figure 43), it can be seen that major concentrations were detected in the percolated water from the columns of SS and HCS. CAA and IS were the only other controls that had results higher than the detection limit. As shown in Figure 45 for barium and Figure 46 for lead, top soils were the sources for those higher concentrations. The only heavy metal whose concentration was higher from CAAs than the soils was selenium (Figure 44). From these four Figures, it can be said that the percolated water from the natural soils had the concentrations of Cr, As, Se, Cd, Ba, and Pb higher than that from CAAs in most cases.

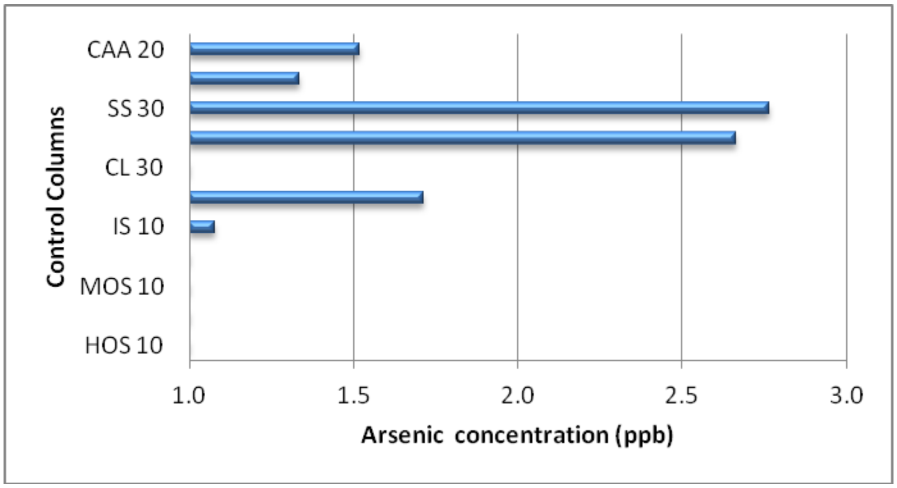


Figure 43. Arsenic concentration for control column at Day 6

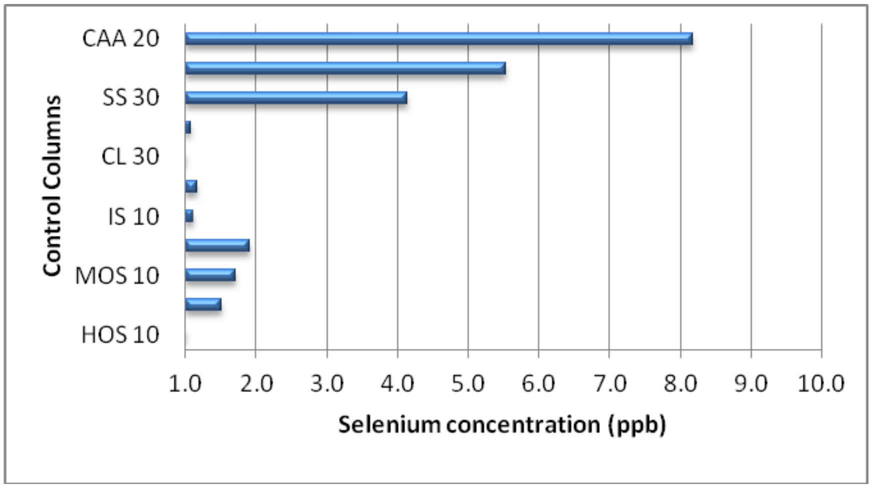


Figure 44. Selenium concentration for control column at Day 6

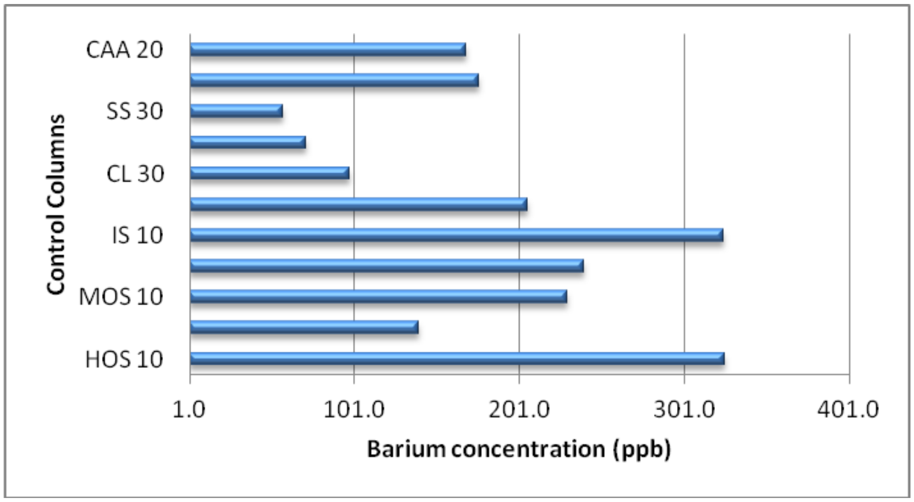


Figure 45. Barium concentration for control column at Day 6

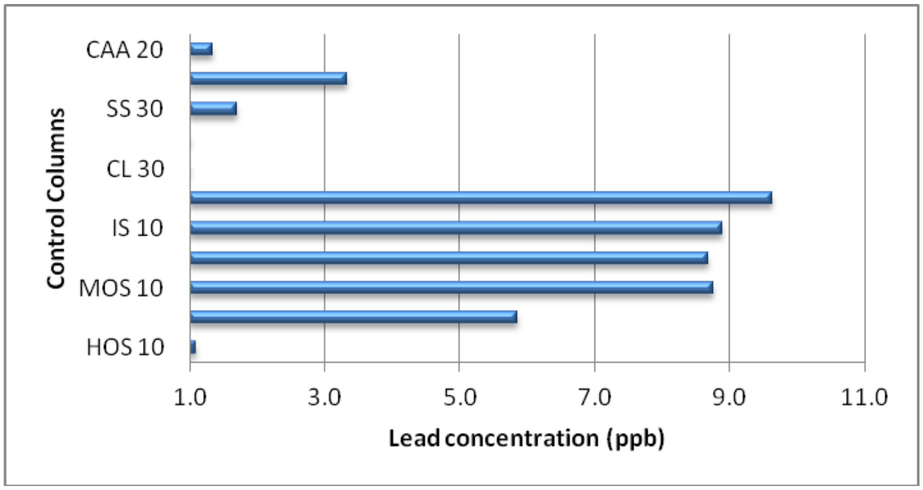


Figure 46. Lead concentration for control column at Day 6

Figure 47 presents that SS and HCS with IS 20 had higher As concentrations than CAA. For CAAs, the highest As concentration was detected in the percolated water from 20-cm CAA column. In contrast, SS and HCS produced As concentrations higher than 2.5 ppb. For other soils, As concentrations decreased slightly on days 5 and 6. On the other hand, CAA controls showed higher Se concentration as shown in Figure 48. Soils showed low Se concentrations in the beginning but as days passed the concentrations decreased close to the detection limit.

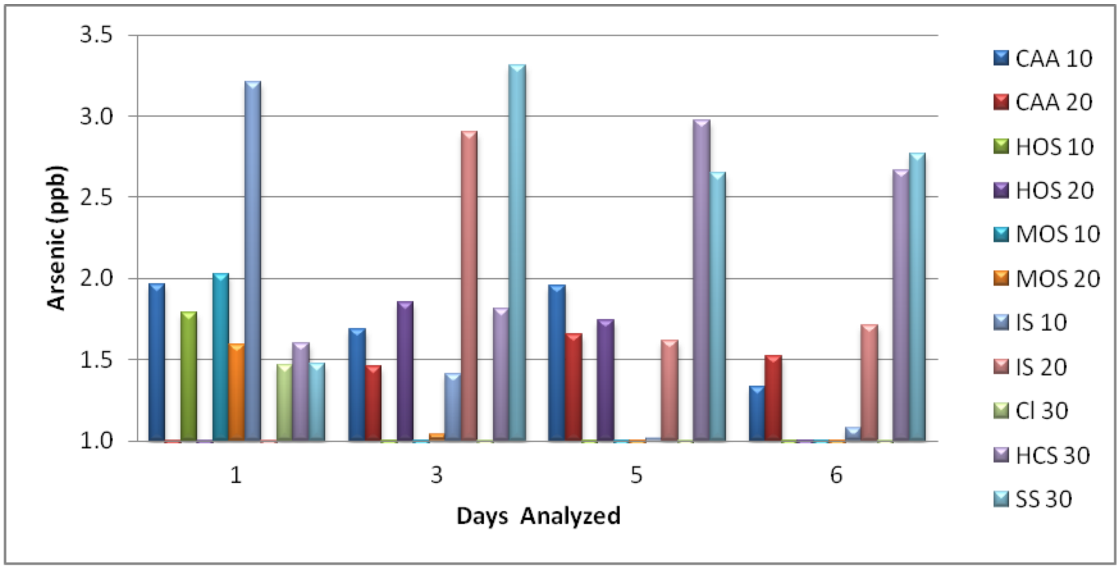


Figure 47. Arsenic concentration for control column

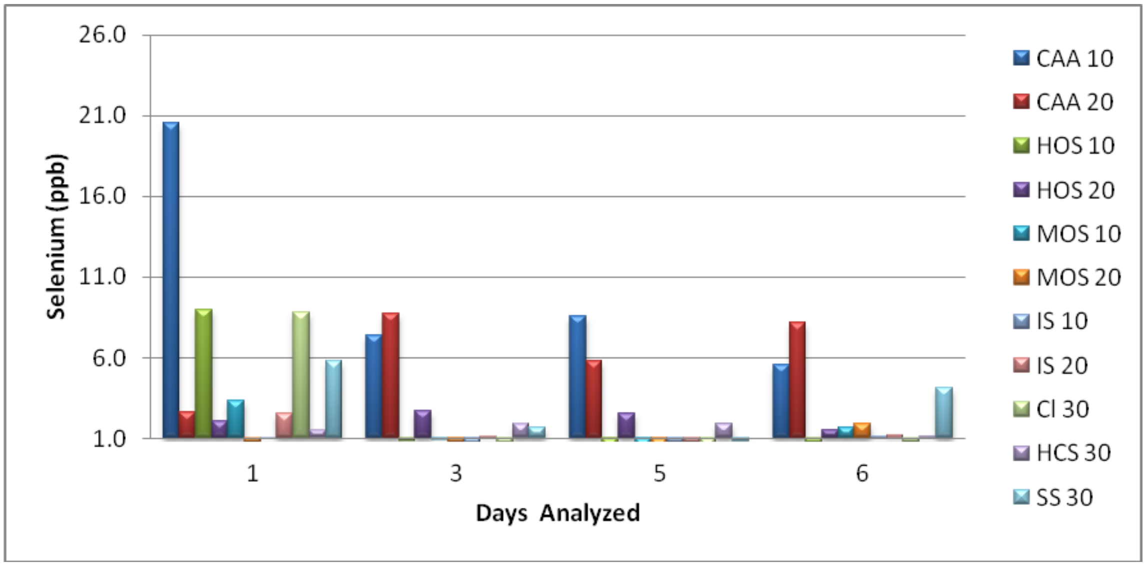


Figure 48. Selenium concentration for control column

Barium showed increases in concentrations as days passed. For soils, there were some fluctuations. However, an increasing trend was observed for CAAs (Figure 49). Higher Ba concentration was shown for IS's 10 and 20, and results were consistent during the experiment. Also, as shown in Figure 50, IS's 10 and 20 showed more consistent higher concentrations than other controls. The highest Pb concentration was 14.9 ppb for IS 20 at day 1. This concentration is close to the MCL set by EPA (15 ppb).

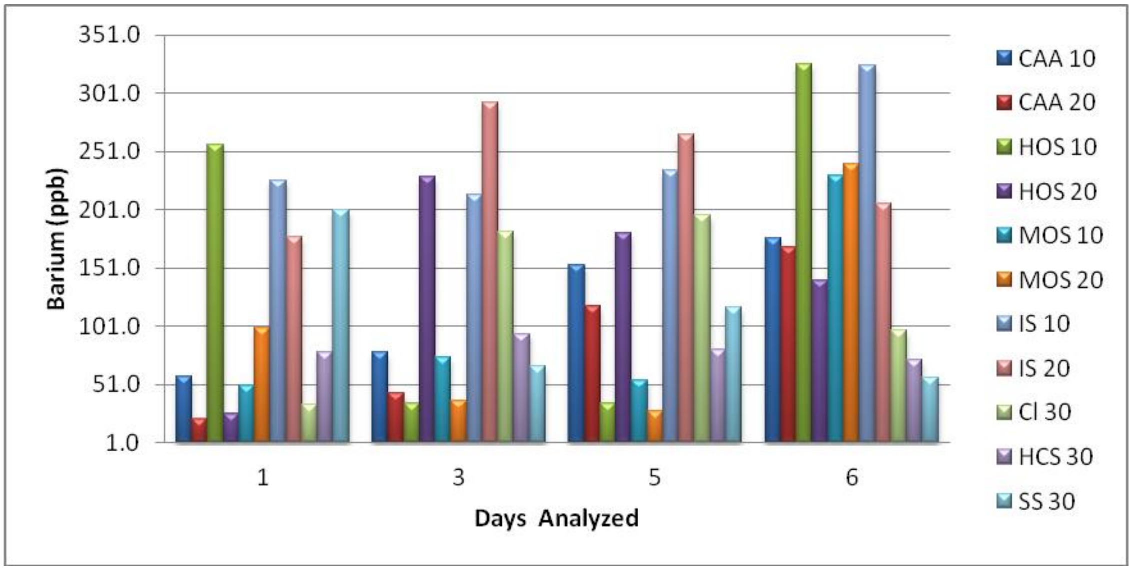


Figure 49. Barium concentration for control column

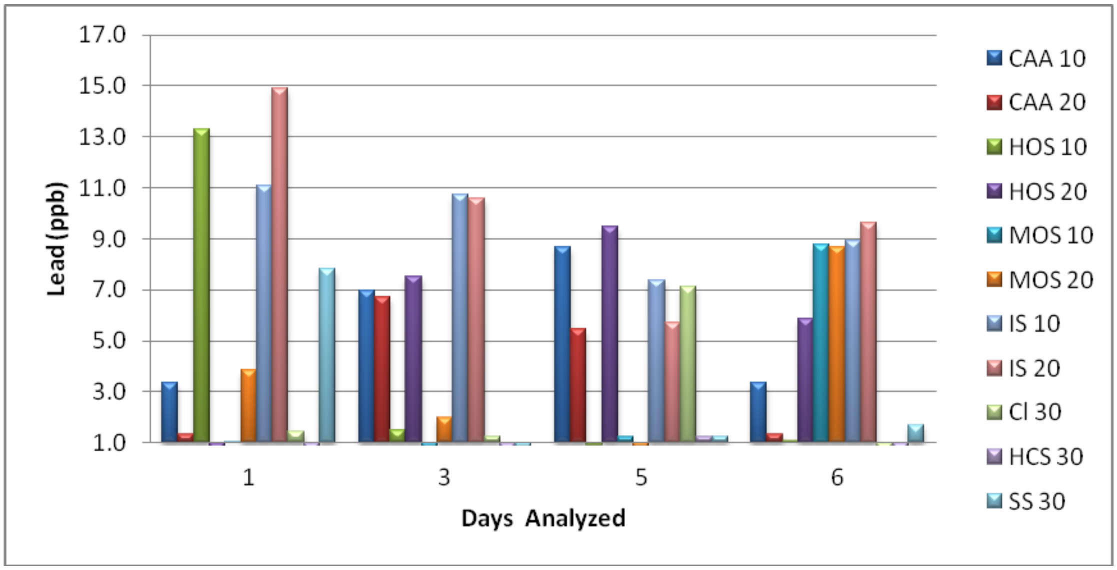


Figure 50. Lead concentration for control column

From heavy metal assessment, it was found that the percolated water from the soils had Ar, Se, Ba, and Pb concentration above 1 ppb. In some cases, concentrations of As, Ba and Pb were greater in the percolated water from the soils than CAAs. Inorganic soil 20 cm was the soil that consistently showed high concentrations of As, Ba and Pb. Also this sub soil was the only one produced Pb concentration near the drinking water standard limit. CAA showed higher concentrations of selenium up to 8 ppb. With the exclusion of IS 20 for Pb, all other heavy metal concentrations were below drinking water standards.

5.5. **Worst and Best Scenarios**

In order to provide engineering recommendation by which CAAs can be applied for land restoration without producing any detrimental impacts on resulting water quality, the best-case restoration scenario was determined. Also, the worst case scenario was assessed to compare the results from the best case scenario. The three factors used for the design of this experiment, top soil, top soil to CAA ratio and sub soil were analyzed individually for this purpose.

Following the analysis for water quality parameters, toxicity, and heavy metals, no problem was found with the last two studies mentioned. For pH water quality , the values exceeded the standard limit for drinking water. So pH was the parameter which limits the use of all combinations. According with USEPA (2012), pH values for drinking water can't be higher than 8.5. With this in mind, combinations were limited with those that resulted in pH values lower than 8.5 in water collected from column amendment after subsoil port. (Other parameters as turbidity, conductivity, and hardness ratio were not critical for the decision to recommend the combinations). For this reason, comparisons for best and worst cases were plotted with pH values obtained from the ternary column settings. Based on the pH comparison between the combinations, those showing good results are compared and assessed with the other water quality parameters.

5.5.1. pH Assessment

In Figures shown below, the y-axis represents every sampling ports from the ternary columns. The first port was located at the water tank identified as inlet, which was used for simulation of rain water. The second was after top soil section, the third after CAA, and last one after sub soil section (see Figure 8 for schematic views of the column setting). The plots were created to help to understand how the water quality parameters changed through the columns, and to see whether CAAs application influenced resulting water quality or not. The red line in Figures below corresponds to the pH value of 8.5.

Figure 51 shows a comparison of three top soils (highly organic soil, medium organic soil, and inorganic sand) with top soil to CAA ratio of 2:1 and clayey soil as sub soil. Inlet water had an average pH value of 8.0 and the percolated water from top soil ranged from 8.0 to 9.0. The ascending order from lowest to highest pH values for top soils were highly organic soil, inorganic sand, and medium organic soil. The values of pH from the CAA port were the highest, showing 9.5 to 9.8. After sub soil port, pH values decreased. For example, pH values from clayey subsoil port was in the range of 7.5 to 8.3.

Figure 51 also shows interaction between the different types of top soils, having the same type of sub soil and the same ratio of top soil to CAA. Different combinations of top soils had different interaction between levels and pH values. As expected from the results of controls columns of top soils, the highly organic soil had the lowest pH values and resulting water also had the lowest pH values. Medium organic soil and inorganic sand had higher pH value but not higher than the standard (pH 8.5).

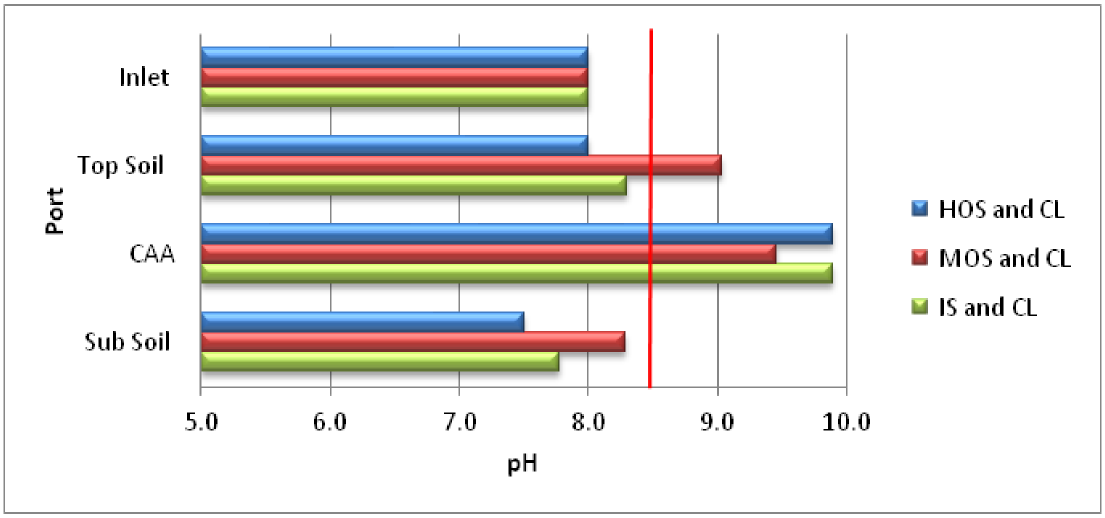


Figure 51. Comparison of Top soil pH values with clayey soil and

Figures 52 and 53 shows different comparison of top soil to CAA ratio factor. This comparison was made using the same top soil (HOS) and subsoil (Cl). From CAA port, it can be seen that values were around pH 10 and that 1:2 ratio showed higher pH value. But after water passed through Cl sub soil pH decreased below 8.5. The lowest pH value was 7.5 at 2:1 ratio and the values for other ratios were 8.0 and 8.1 for 1:2 and 1:1, respectively. Therefore, this combination of top soil HOS above CAAs and sub soil Cl below CAAs turned out to be the best case scenarios because pH values were lower than 8.5 regardless of TS/CAA ratios.

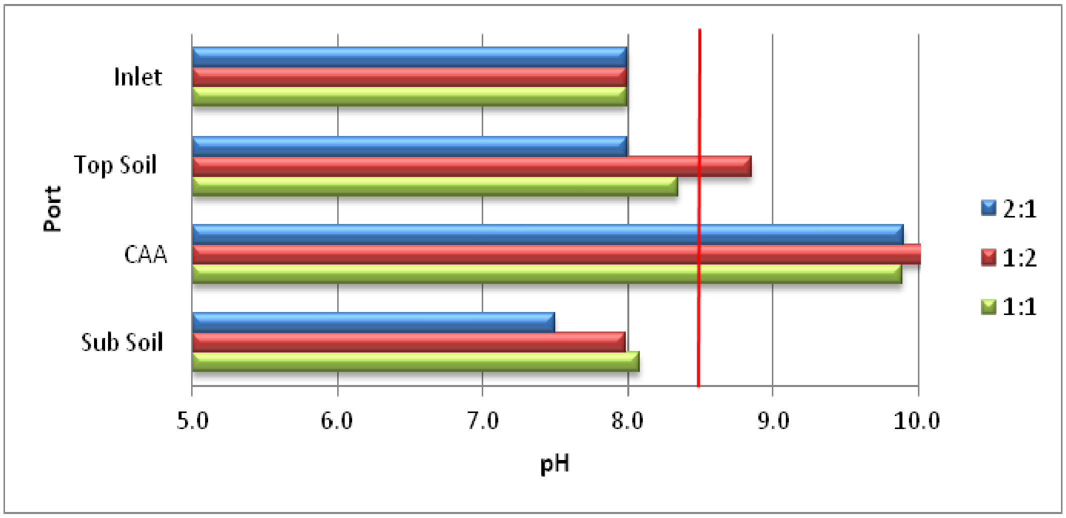


Figure 52. pH by port at treatment HOS and Cl at Day 6

On the other hand, the combinations of HOS (top soil) and HCS (sub soil) at all TS/CAAs ratios produced pH values above the limit (Figure 53). At TS/CAA ratio of 2:1, 1:2 and 1:1 pH values were 9.4, 9.9 and 9.8, respectively. These pH values are so high that HCS is not recommended as sub soil. Also, it can be seen again that the TS/CAAs ratio of 2:1 produced lower pH values than the ratios of 1:2 and 1:1.

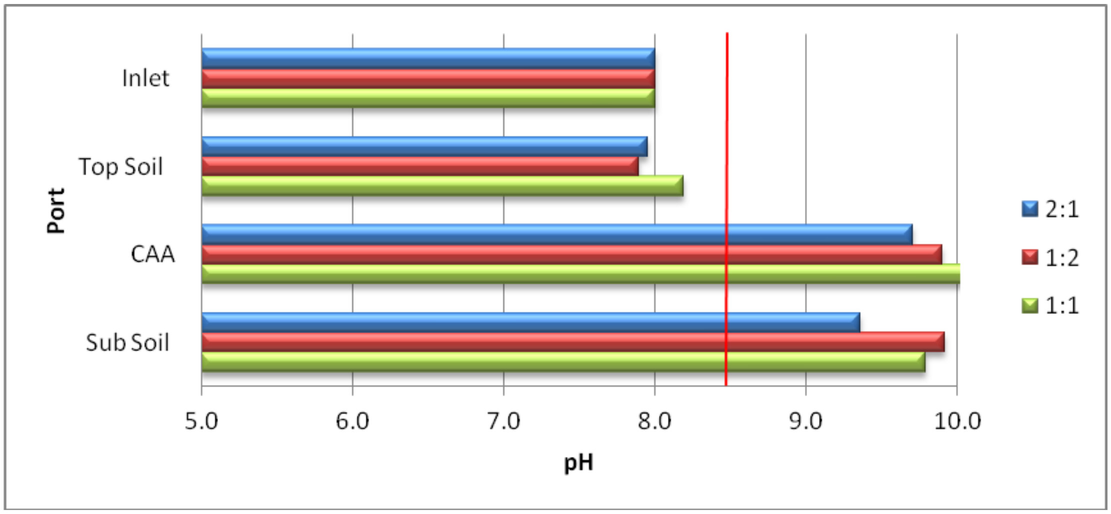


Figure 53. pH by port at treatment HOS and HCS at Day 6

Comparisons among sub soil types are is important because potentially high pH water percolated through the CAAs may be buffered through the sub soils and the pH can reduce to plausible ranges. Figure 54 shows a comparison of pH values in the percolated water from the combinations of the same HOS as top soil and the same 2:1 TS/CAA ratio but with three different sub soils. As shown, the only combination that didn't exceed pH 8.5 was the one that used Cl as subsoil. Combinations with SS and HCS did not meet the pH requirement.

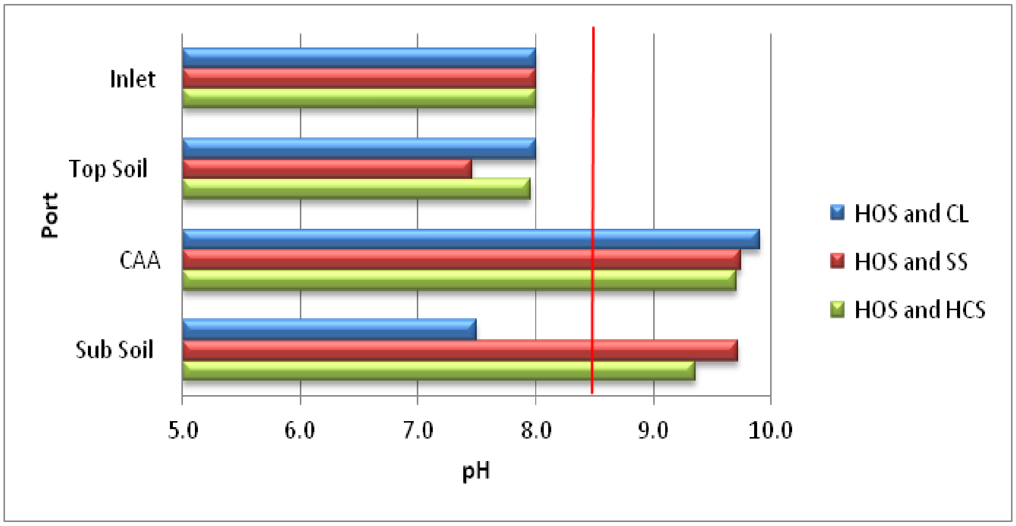


Figure 54. Comparison of sub soil pH values with highly organic soil

Figure 55 shows a comparison of different top soils and sub soils with the same TS/CAA ratio of 2:1. The values of pH measured from the sub soil port were used for this case. It is clear that the combinations of top soils only with Cl sub soil did not exceed pH 8.5.

Also, Figures 56 and 57 show comparisons of top soils with sub soils at TS/CAA ratios of 1:2 and 1:1. As shown, top soils HOS and MOS in combination with Cl sub soil produced pH values within the required range. All other combinations with sub soils SS and HCS were not suitable to be used according to this analysis.

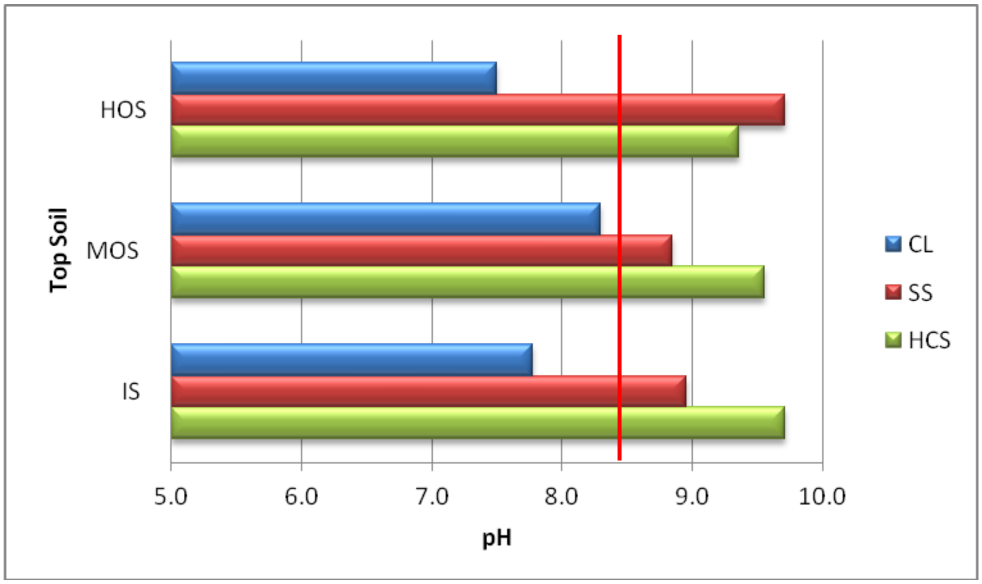


Figure 55. Comparison of sub soil 2:1 at Day 6

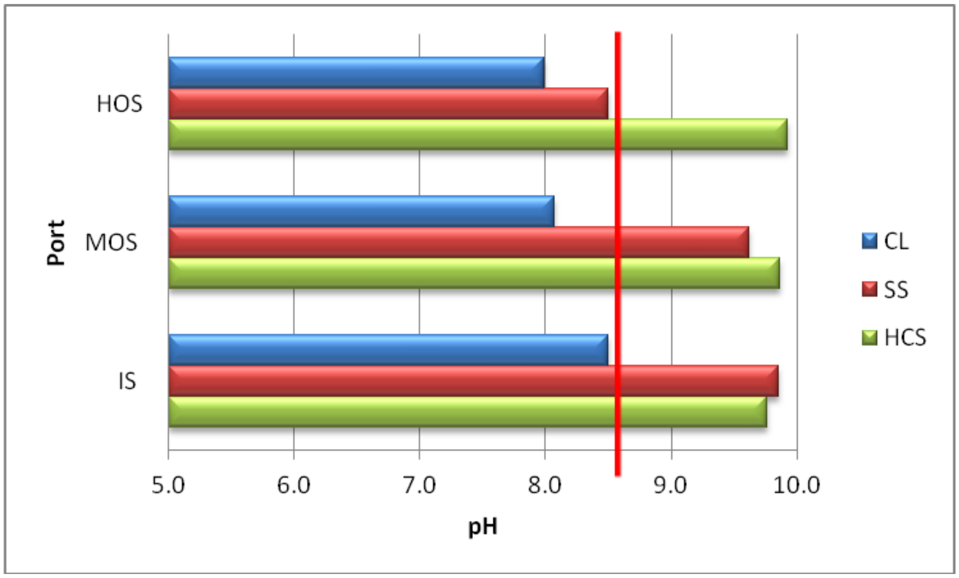


Figure 56. Comparison of sub soil 1:2 at Day 6

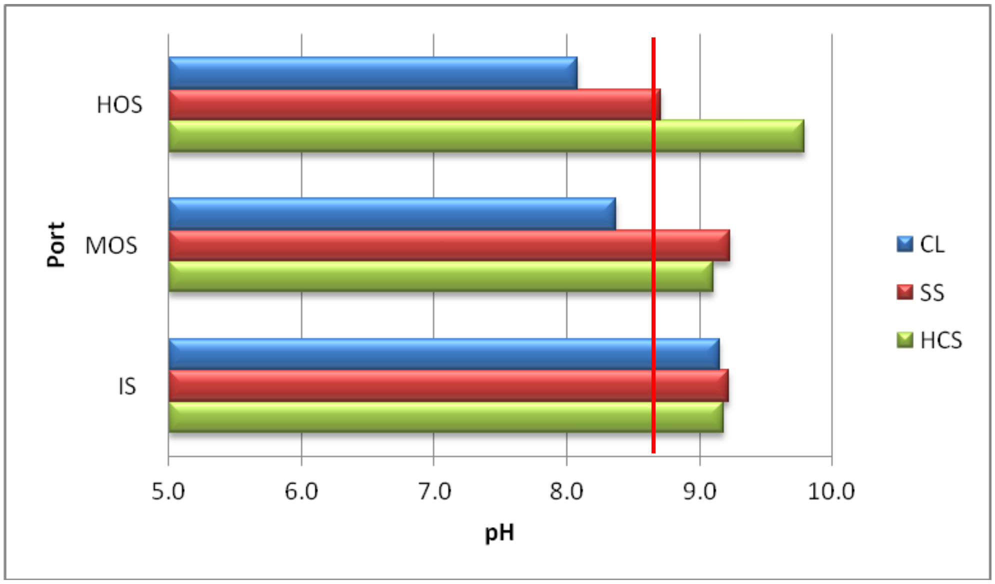


Figure 57. Comparison of sub soil 1:1 at Day 6

5.5.2. Best and Worst Cases Comparison

After analyzing all 27 combinations, two best and two worst combinations were selected to show differences on pH result. Table 27 summarizes all the pH values at day 6 from all combinations. It can be seen that only combinations with Cl sub soil and the pH values lower than 8.5. Two best combinations were HOS or MOS top soils with Cl sub soil; also 2:1 and 1:2 TS/CAA ratio. Two worst combinations were MOS or IS top soils with HCS as sub soil; and 1:2 TS/CAA ratio. Figure 58 shows the best cases (HOS/Cl, MOS/Cl) and worst cases (MOS/HCS, IS/HCS). Table 28 summarizes all combinations that values were below 8.5. Those combinations are: HOS or MOS with Cl as sub soil at all TS/CAA ratios, and IS with Cl only at 2:1 ratio.

Table 27. Summary of pH value of all combinations of ternary columns at Day 6

Top Soil	**Top soil to CAA ratio and Sub soil**								
	2:1			**1:2**			**1:1**		
	Cl	**SS**	**HCS**	**Cl**	**SS**	**HCS**	**Cl**	**SS**	**HCS**
HOS	7.5	9.7	9.4	8.0	8.5	9.9	8.1	8.7	9.8
MOS	8.3	8.8	9.6	8.1	9.6	9.9	8.4	9.2	9.1
IS	7.8	9.0	9.7	8.5	9.9	9.8	9.1	9.2	9.2

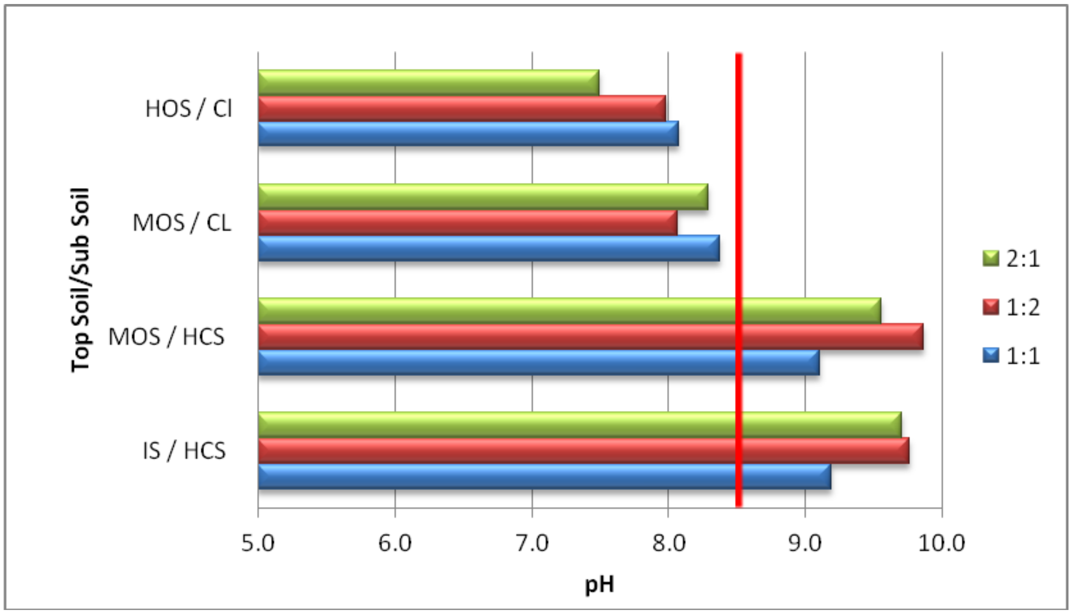


Figure 58. Comparison of best and worst scenarios at Day 6

Table 28. Best combinations and pH values

Top Soil	Clayey Soil Sub Soil		
	Top Soil to CAA Ratio		
	2:1	1:2	1:1
HOS	7.5	8.0	8.1
MOS	8.3	8.1	8.4
IS	7.8		

Combinations shown in Table 28 were assessed for other water quality parameters and heavy metal concentrations to ensure that the results from 7 best combinations were met the standards. Figure 59 shows hardness results for all sampling days; only the first sampling values were higher and classified as very hard (Table 20). But as days passed the results from all combinations were on slightly hard (17-120 mg/L $CaCO_3$) and soft (0-17 mg/L $CaCO_3$). Harness in the range of 75 - 120 mg/L $CaCO_3$ is practically accepted as the limit for hardness. In general, the percolated water was very hard at the beginning due to initial flushing of hardness causing ions (calcium and magnesium) from soils and CAA. However, from the second sampling, hardness was lower than 100 mg/L $CaCO_3$. For this reason, the results obtained from the percolated water at days 2 to 6 were used.

Similar phenomena to hardness were observed for conductivity (Figure 60). The first conductivity values were above 500 µS/cm; the standard for conductivity classified as inland fresh waters. But later on conductivity decreased considerably to a level below 500 µS/cm.

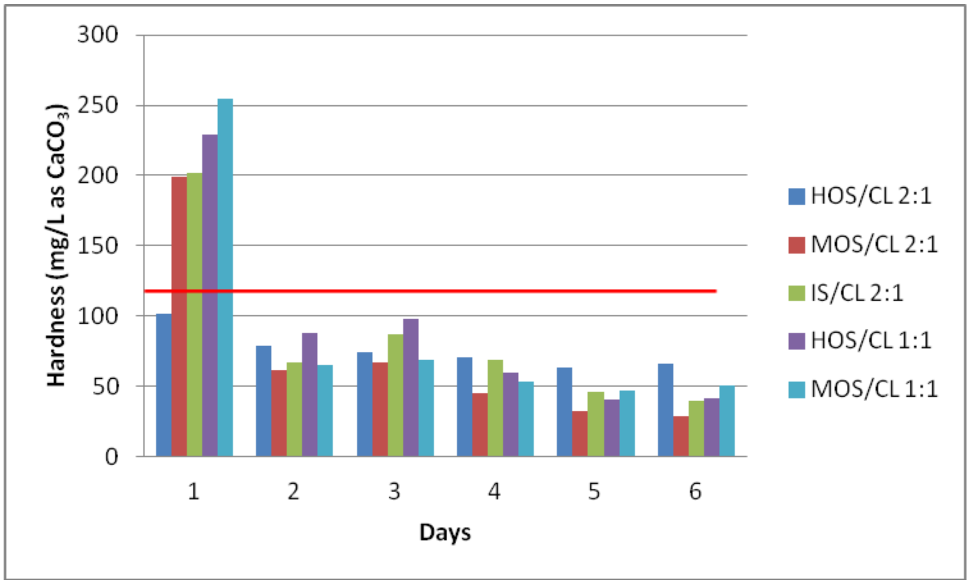


Figure 59. Comparison of hardness for best ternary combinations

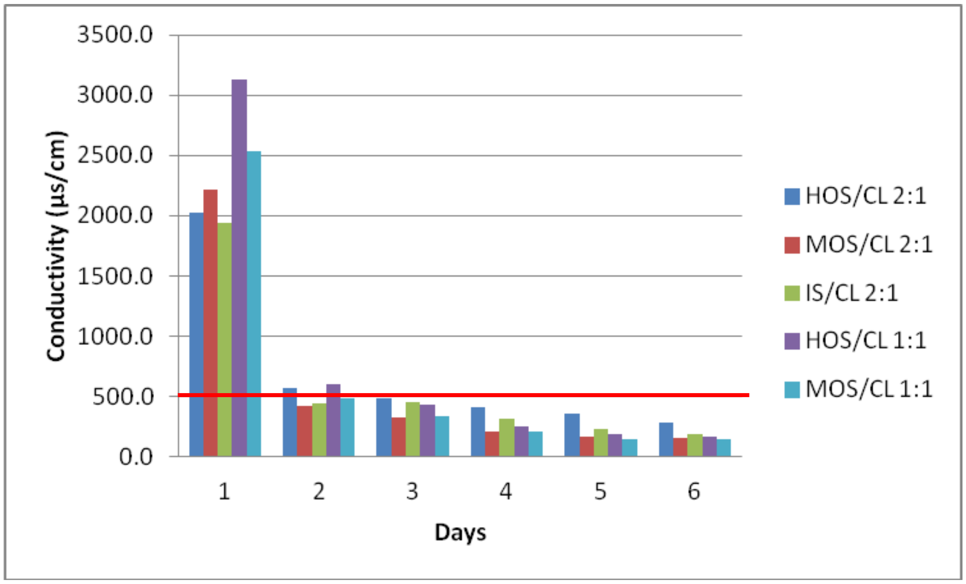
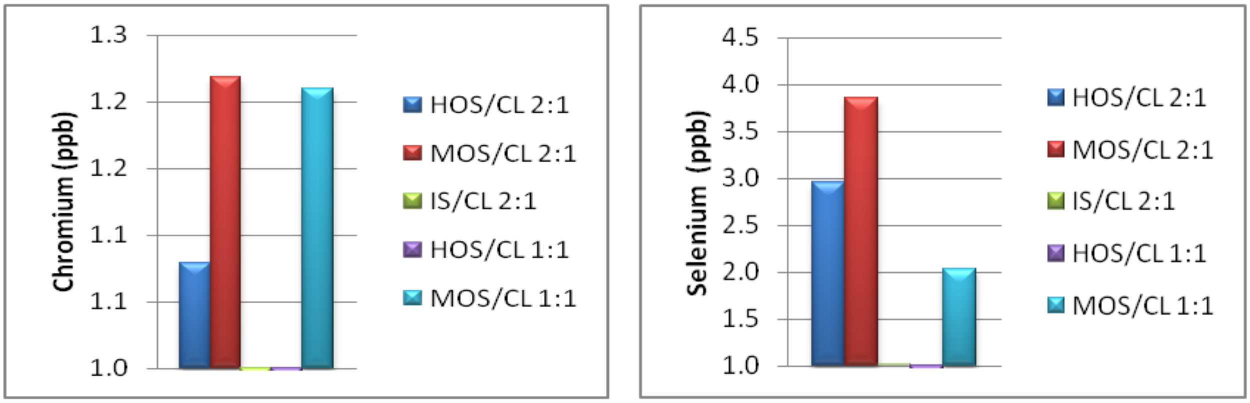


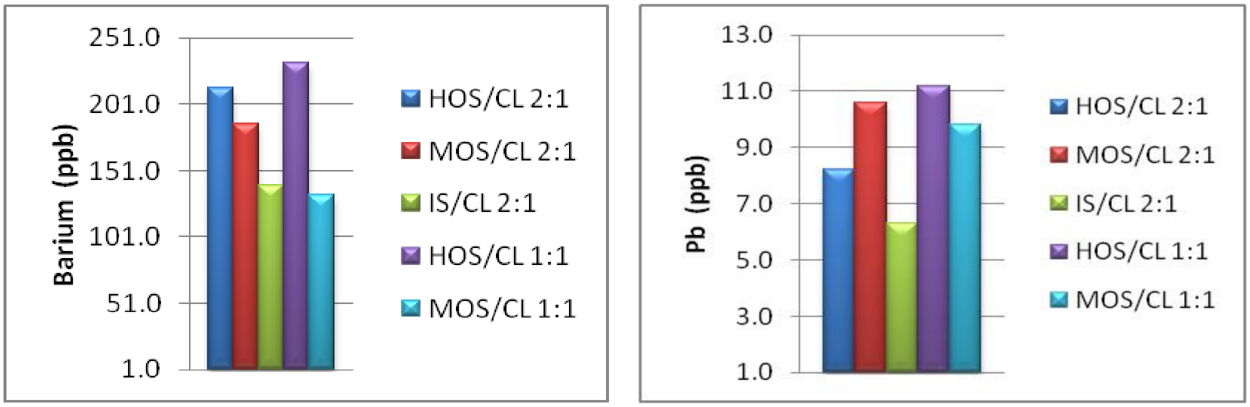
Figure 60. Comparison of conductivity for best ternary combinations

Figure 61 show the results from heavy metal analysis, concentrations of heavy metals Cr, Se, Ba and Pb were detected from the combinations selected (Table 28). Arsenic concentrations were also detected but below detection limit and, therefore, As plot was not included. No heavy metals were detected above the MCLs established by EPA (Table 25). Therefore, it is construed that all combinations met water quality standards in terms of heavy metal.



A. Chromium

B. Selenium



C. Barium

D. Lead

Figure 61. Heavy metal concentration from best combination at Day 6

6. CONCLUSIONS AND RECOMMENDATIONS

All the established objectives were successfully completed. The 3^3 factorial experimental design demonstrated how combination factors of soils types and CAA volume in open pit restoration could affect water quality parameters. Results showed that the limiting water quality parameter for CAAs application was the pH. When Cl was used as a sub soil, the lowest pH (7.4) was obtained from the percolated water, compared with the pH values from HCS and SS sub soils. Consequently, Cl was able to buffer the high pHs (9.5-10.5) in the percolated water from CAAs. The combination of any top soils with Cl sub soil and 2:1 TS/CAA ratio produced the best results in terms of pH. Also the top soils HOS and MOS with 1:2 and 1:1 ratios showed the pH values below 8.5. The statistical analysis confirmed that the selection of the sub soil is an important decision for CAA applications when used for land restoration.

Toxicity analysis did not show any presence of acute toxicity in the percolated water collected from any combinations due to the substances leached out of CAAs. Moreover, the analysis of heavy metals showed low concentrations of Se, Cd, Cr, Ar, Pb, and Ba for the tested combinations and controls. No samples revealed higher concentrations that MCLs set by EPA for drinking water quality. In addition, it was shown that the percolated water from natural soils had background heavy metal concentrations; in some cases, greater than that from CAAs. Only Se was found higher in the percolated water from CAAs than the soils.

Although the plausible results were obtained from this study, it is suggested to further corroborate the findings and data with the following recommended works:

- Utilization of rain water instead of DI water for simulation of rain activity. Also different percolation flow rates stemmed from actual precipitation rate, because the amount of water which infiltrates the soils will produce varying results (i.e., turbidity).

- Field testing under natural environment, with real temperature conditions. Temperature would affect dissolution rates and extent of substances from the soils and CAAs.

- Larger scale experiments where actual soils and CAAs can be tested, not dried and crushed ones used to accommodate lab-scale experiments. It is important to evaluate ground water quality in larger scale that is typically very different from a lab-scale to ensure applicability of CAAs.

- Long-term monitoring to observe time-dependent changes and stabilities in responses.
- Consider mutual influence between surface vegetation and CAAs application. Rhizosphere will affect heavy metal dissolutions from soils and CAAs. And, at the same time, the components from CAAs might increase plant growth and rhizospheric microbial activities.

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APPENDIX A. MICROTOX RESULTS

To ensure that groundwater quality is not affected by CAA amendment, water samples were evaluated by toxicological tests. Microtox was used to help monitor possible contamination in samples wash columns with CAA. In the following tables are the results for each of the analyzed samples. Samples were analyzed CAA controls, binary and ternary combinations.

Table 29. Toxicity results from CAA controls

Control	Column Length (cm)	Result
CAA	10	Detected Hormesis
	10	Detected Hormesis
	20	Error
	20	Detected Hormesis

Table 30. Toxicity results from binary combinations: top soil/CAA

Top Soil/CAA Combination	Top Soil/CAA Ratio	Result
High Organic Soil/CAA	2/1	Detected Hormesis
	2/1	Detected Hormesis
	1/2	Invalid confidence factor
	1/2	Detected Hormesis
	1/1	Detected Hormesis
	1/1	Detected Hormesis
Inorganic Sand/CAA	2/1	Detected Hormesis
	2/1	Detected Hormesis
	1/2	Detected Hormesis
	1/2	Detected Hormesis
	1/1	Detected Hormesis
	1/1	Invalid confidence factor
Medium Organic Soil/CAA	2/1	Detected Hormesis
	2/1	Detected Hormesis
	1/2	Detected Hormesis
	1/2	Detected Hormesis
	1/1	Detected Hormesis
	1/1	Detected Hormesis

Table 31. Toxicity results from binary combinations: CAA/sub soil

CAA/Sub Soil Combination	CAA/Sub Soil Ratio	Result
CAA/Clayey	2/1	Detected Hormesis
	2/1	Detected Hormesis
	1/2	Detected Hormesis
	1/2	Detected Hormesis
CAA/High Calcium Soil	2/1	Detected Hormesis
	2/1	Detected Hormesis
	1/2	Detected Hormesis
	1/2	Detected Hormesis
CAA/Sandy Soil	2/1	Detected Hormesis
	2/1	Detected Hormesis
	1/2	Detected Hormesis
	1/2	Detected Hormesis

Table 32. Toxicity results from ternary combinations with clayey soil

Top Soil/CAA/Clayey Soil Combination	Top Soil/CAA Ratio	Result
High Organic Soil/CAA/Clayey Soil	2/1	Detected Hormesis
	2/1	Detected Hormesis
	1/2	Detected Hormesis
	1/2	Detected Hormesis
	1/1	Detected Hormesis
	1/1	Detected Hormesis
Medium Organic Soil/CAA/Clayey Soil	2/1	Detected Hormesis
	2/1	Detected Hormesis
	1/2	Detected Hormesis
	1/2	Detected Hormesis
	1/1	Detected Hormesis
	1/1	Detected Hormesis
Inorganic Soil/CAA/Clayey Soil	2/1	Detected Hormesis
	2/1	Detected Hormesis
	1/2	Detected Hormesis
	1/2	Detected Hormesis
	1/1	Detected Hormesis
	1/1	Invalid confidence factor

Table 33. Toxicity results from ternary combinations with sandy soil

Top Soil/CAA/Sandy Soil Combination	Top Soil/CAA Ratio	Result
High Organic Soil/CAA/Sandy Soil	2/1	Detected Hormesis
	2/1	Detected Hormesis
	1/2	Detected Hormesis
	1/2	Invalid confidence factor
	1/1	Detected Hormesis
	1/1	Detected Hormesis
Medium Organic Soil/CAA/Sandy Soil	2/1	Cannot calculate regression
	2/1	Detected Hormesis
	1/2	Cannot calculate regression
	1/2	Detected Hormesis
	1/1	Detected Hormesis
	1/1	Detected Hormesis
Inorganic Soil/CAA/Sandy Soil	2/1	Detected Hormesis
	2/1	Detected Hormesis
	1/2	Detected Hormesis
	1/2	Detected Hormesis
	1/1	Detected Hormesis
	1/1	Detected Hormesis

Table 34. Toxicity results from ternary combinations with high calcium soil

Top Soil/CAA/High Calcium Soil Combination	Top Soil/CAA Ratio	Result
High Organic Soil/CAA/High Calcium Soil	2=1	Detected Hormesis
	2=1	Invalid confidence factor
	1=2	Detected Hormesis
	1=2	Detected Hormesis
	1=1	Detected Hormesis
	1=1	Detected Hormesis
Medium Organic Soil/CAA/High Calcium Soil	2=1	Detected Hormesis
	2=1	Detected Hormesis
	1=2	Detected Hormesis
	1=2	Detected Hormesis
	1=1	Detected Hormesis
	1=1	Detected Hormesis
Inorganic Soil/CAA/High Calcium Soil	2=1	Detected Hormesis
	2=1	Detected Hormesis
	1=2	Detected Hormesis
	1=2	Error
	1=1	Detected Hormesis
	1=1	Detected Hormesis

APPENDIX B. ANALYSIS OF HEAVY METALS

HHeavy metal analysis was performed to ensure that our experimental design meets the concentration limits for heavy metals: chromium (Cr), arsenic (Ar), selenium (Se), cadmium (Cd), barium (Ba), and lead (Pb). Results ternary combinations of columns with the last day of sampling were summarized in the following tables. Also heavy metal analysis was made for controls reactors for days 1,3,and 5 to find data trends. Table 12 shows the summary of all data collected.

Table 35. Heavy metal concentration of binary combinations of top soil/CAA

Identification			Concentration (ppb)					
			Cr	**As**	**Se**	**Cd**	**Ba**	**Pb**
TOP SOIL /CAA	High Organic Soil / CAA	2/1	0.8	2.5	8.3	0.0	192.4	10.3
		1/2	0.5	0.9	4.1	0.0	120.1	10.0
		1/1	0.5	1.6	4.2	0.0	178.4	1.4
	Inorganic Sand / CAA	2/1	1.2	1.1	7.8	0.0	177.6	7.2
		1/2	1.6	1.3	14.6	0.0	145.5	7.2
		1/1	1.6	1.4	7.8	0.2	160.5	7.9
	Medium Organic Soil / CAA	2/1	1.0	1.9	6.4	0.2	340.8	7.9
		1/2	1.7	1.3	15.6	0.1	133.6	9.5
		1/1	0.9	1.3	8.6	0.0	197.5	4.8

Table 36. Heavy metal concentration of binary combinations of CAA/sub soil

Identification			Concentration (ppb)					
			Cr	**As**	Se	**Cd**	**Ba**	**Pb**
CAA/SUB SOIL	CAA / Clayey	2/1	2.0	1.1	2.8	0.2	275.7	14.2
		1/2	1.4	0.1	2.1	0.2	159.3	6.1
	CAA / High Calcium Soil	2/1	0.7	1.1	9.6	0.0	75.4	0.6
		1/2	0.6	1.3	6.3	0.0	31.5	0.6
	CAA / Sandy Soil	2/1	1.6	2.8	23.8	0.1	137.5	12.1
		1/2	0.6	2.9	6.9	0.0	193.0	12.9

Table 37. Heavy metal concentration of ternary combinations with clayey soil

Identification			Concentration (ppb)					
			Cr	As	Se	Cd	Ba	Pb
TOP SOIL /CAA/CLAYEY	High Organic Soil/CAA/Clayey	2/1	1.1	0.2	3.0	0.5	213.7	8.2
		1/2	1.2	0.4	1.9	0.5	149.5	9.9
		1/1	0.8	0.5	0.5	0.4	232.5	11.2
	Medium Organic Soil/CAA/Clayey	2/1	1.2	2.4	3.9	0.2	185.9	10.6
		1/2	1.1	2.2	5.8	0.3	181.3	9.5
		1/1	1.2	0.4	2.0	0.6	132.3	9.8
	Inorganic Soil/ CAA/ Clayey	2/1	0.9	0.3	1.0	0.4	140.3	6.3
		1/2	1.3	0.5	6.6	0.4	213.4	5.6
		1/1	1.2	0.3	1.2	0.4	163.4	6.2

Table 38. Heavy metal concentration of ternary combinations with sandy soil

Identification			Concentration (ppb)					
			Cr	As	Se	Cd	Ba	Pb
TOP SOIL /CAA/SANDY SOIL	High Organic Soil/CAA/Sandy Soil	2/1	0.8	5.5	6.8	0.2	226.4	0.7
		1/2	1.1	1.0	4.7	0.4	186.6	1.3
		1/1	1.7	3.0	23.0	0.4	163.6	6.3
	Medium Organic Soil/CAA/Sandy Soil	2/1	0.9	0.9	7.1	0.2	140.9	2.8
		1/2	2.0	2.8	28.4	0.3	122.6	4.9
		1/1	0.8	2.0	9.7	0.3	50.7	2.7
	Inorganic Soil/ CAA/Sandy Soil	2/1	1.5	3.2	22.4	0.3	219.5	8.5
		1/2	0.8	3.8	12.0	0.2	129.0	0.8
		1/1	1.5	3.0	23.2	0.2	170.4	7.8

Table 39. Heavy metal concentration of ternary combinations with sandy soil

Identification			Concentration (ppb)					
			Cr	**As**	**Se**	**Cd**	**Ba**	**Pb**
TOP SOIL /CAA/HIGH CALCIUM SOIL	High Organic Soil/CAA/High Calcium Soil	2/1	1.0	2.8	8.4	0.2	91.1	1.0
		1/2	0.9	1.8	10.2	0.4	97.8	5.1
		1/1	0.7	2.4	7.2	0.2	101.9	0.8
	Medium Organic Soil/CAA/High Calcium Soil	2/1	0.3	0.9	4.8	0.2	74.4	0.6
		1/2	0.8	1.3	8.6	0.2	107.3	0.9
		1/1	0.8	1.9	6.5	0.2	48.7	0.8
	Inorganic Soil/CAA/High Calcium Soil	2/1	0.8	1.6	7.3	0.3	59.0	**1.7**
		1/2	0.7	1.7	7.3	0.2	37.2	0.9
		1/1	0.5	1.8	6.6	0.2	42.9	0.8

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Table 40. Heavy metal concentration for CAAs and top soils control

		Concentration (ppb)					
Column Type and Length	**Day**	**Cr**	**As**	**Se**	**Cd**	**Ba**	**Pb**
CAA 10	1	0.0	2.0	6.5	0.0	57.4	3.3
	3	0.0	1.7	7.3	0.0	78.4	6.9
	5	0.0	2.0	8.6	0.0	153.6	8.7
	6	0.0	1.3	5.5	0.0	176.6	3.3
CAA 20	1	0.0	0.9	2.6	0.4	21.2	1.3
	3	0.0	1.5	8.7	0.3	43.9	6.7
	5	0.0	1.7	5.8	0.3	118.6	5.5
	6	0.0	1.5	8.2	0.0	169.0	1.3
HOS 10	1	0.0	1.8	8.9	0.4	256.4	13.3
	3	0.0	0.9	0.8	0.3	34.7	1.5
	5	0.0	0.7	0.2	0.4	34.5	0.9
	6	0.0	0.3	0.7	0.0	325.8	1.1
HOS 20	1	0.0	0.9	2.1	0.3	25.6	0.6
	3	0.0	1.9	2.7	0.4	229.3	7.5
	5	0.0	1.7	2.5	0.3	180.4	9.5
	6	0.0	0.7	1.5	0.0	139.8	5.9
MOS 10	1	0.0	2.0	3.3	0.3	50.2	1.0
	3	0.0	0.7	0.9	0.3	74.5	0.8
	5	0.0	0.6	0.0	0.3	54.4	1.2
	6	0.0	0.4	1.7	0.0	230.0	8.7
MOS 20	1	0.0	1.6	0.7	0.3	99.2	3.8
	3	0.0	1.0	0.7	0.4	37.3	2.0
	5	0.0	0.8	0.3	0.3	28.1	0.8
	6	0.0	0.7	1.9	0.5	240.4	8.7
IS 10	1	0.0	3.2	0.9	0.4	226.0	11.1
	3	0.0	1.4	0.6	0.3	213.8	10.7
	5	0.0	1.0	0.7	0.3	234.7	7.4
	6	0.0	1.1	1.1	0.0	324.6	8.9
IS 20	1	0.0	0.6	2.5	1.1	177.5	14.9
	3	0.0	2.9	1.1	0.5	293.4	10.6
	5	0.0	1.6	0.7	0.4	265.0	5.7
	6	0.0	1.7	1.2	0.0	206.0	9.6

Table 41. Heavy metal concentration for CAAs and sub soils control

		Concentration (ppb)					
Column Type and Length	**Day**	**Cr**	**As**	**Se**	**Cd**	**Ba**	**Pb**
Cl 30	1	0.0	1.5	8.8	0.4	33.9	1.5
	3	0.0	0.7	0.6	0.4	182.1	1.2
	5	0.0	0.7	0.4	0.3	196.0	7.1
	6	0.0	0.1	0.7	0.0	97.9	0.6
HCS 30	1	0.0	1.7	2.3	0.4	83.8	0.6
	3	0.0	1.8	1.9	0.3	94.5	0.7
	5	0.0	3.0	1.9	0.4	80.6	1.2
	6	0.0	2.7	1.1	0.0	71.7	0.6
SS 30	1	0.0	1.5	5.8	0.4	201.1	7.8
	3	0.0	3.3	1.7	0.3	66.4	0.8
	5	0.0	2.6	0.8	0.3	117.1	1.3
	6	0.0	2.8	4.1	0.0	57.3	1.7

APPENDIX C. OUTPUT FROM FACTORIAL STATISTICAL ANALYSIS

A 3^3 factorial design was perform for the experiments, the three factors were: top soil, top soil/CAA ratio, and sub soil. From the factorial analysis p-values of factors were included. This analysis was made for the parameters of: turbidity, conductivity, pH, and hardness. Output from Minitab as p-values and least means square are included below for the six days of experimentation.

APPENDIX C. 1 Turbidity

Turbidity Day 1

```
Analysis of Variance for Turbidity_Day_1, using Adjusted SS for Tests

Source                           DF   Seq SS   Adj SS   Adj MS     F      P
Blocks                            1   0.0868   0.0868   0.0868  0.36  0.555
Top Soil                          2   0.9950   0.9950   0.4975  2.05  0.149
TS/CAA Ratio                      2   0.0517   0.0517   0.0259  0.11  0.899
Sub Soil                          2   0.2191   0.2191   0.1096  0.45  0.642
Top Soil*TS/CAA Ratio             4   0.1810   0.1810   0.0452  0.19  0.943
Top Soil*Sub Soil                 4   0.1960   0.1960   0.0490  0.20  0.935
TS/CAA Ratio*Sub Soil             4   0.4737   0.4737   0.1184  0.49  0.745
Top Soil*TS/CAA Ratio*Sub Soil    8   0.6917   0.6917   0.0865  0.36  0.934
Error                            26   6.3134   6.3134   0.2428
Total                            53   9.2084


Least Squares Means for Turbidity_Day_1

Top Soil                           Mean  SE Mean
1                                0.7669   0.1161
2                                0.7717   0.1161
3                                1.0572   0.1161
TS/CAA Ratio
1                                0.9075   0.1161
2                                0.8342   0.1161
3                                0.8542   0.1161
Sub Soil
1                                0.8828   0.1161
2                                0.9331   0.1161
3                                0.7800   0.1161
Top Soil*TS/CAA Ratio
1        1                       0.8417   0.2012
1        2                       0.6758   0.2012
1        3                       0.7833   0.2012
2        1                       0.8358   0.2012
2        2                       0.6850   0.2012
2        3                       0.7942   0.2012
3        1                       1.0450   0.2012
3        2                       1.1417   0.2012
```

```
3        3                      0.9850   0.2012
Top Soil*Sub Soil
1        1                      0.8125   0.2012
1        2                      0.8675   0.2012
1        3                      0.6208   0.2012
2        1                      0.7083   0.2012
2        2                      0.8042   0.2012
2        3                      0.8025   0.2012
3        1                      1.1275   0.2012
3        2                      1.1275   0.2012
3        3                      0.9167   0.2012
TS/CAA Ratio*Sub Soil
1            1                  1.0483   0.2012
1            2                  0.9792   0.2012
1            3                  0.6950   0.2012
2            1                  0.6992   0.2012
2            2                  0.9875   0.2012
2            3                  0.8158   0.2012
3            1                  0.9008   0.2012
3            2                  0.8325   0.2012
3            3                  0.8292   0.2012
Top Soil*TS/CAA Ratio*Sub Soil
1        1            1         0.8150   0.3484
1        1            2         1.0075   0.3484
1        1            3         0.7025   0.3484
1        2            1         0.5900   0.3484
1        2            2         0.8300   0.3484
1        2            3         0.6075   0.3484
1        3            1         1.0325   0.3484
1        3            2         0.7650   0.3484
1        3            3         0.5525   0.3484
2        1            1         1.1550   0.3484
2        1            2         0.7550   0.3484
2        1            3         0.5975   0.3484
2        2            1         0.3350   0.3484
2        2            2         0.9600   0.3484
2        2            3         0.7600   0.3484
2        3            1         0.6350   0.3484
2        3            2         0.6975   0.3484
2        3            3         1.0500   0.3484
3        1            1         1.1750   0.3484
3        1            2         1.1750   0.3484
3        1            3         0.7850   0.3484
3        2            1         1.1725   0.3484
3        2            2         1.1725   0.3484
3        2            3         1.0800   0.3484
3        3            1         1.0350   0.3484
3        3            2         1.0350   0.3484
3        3            3         0.8850   0.3484
```

Turbidity Day 2

```
 Analysis of Variance for Turbidity_Day_2, using Adjusted SS for Tests

Source                          DF   Seq SS  Adj SS  Adj MS     F      P
Blocks                           1   1.0724  1.0724  1.0724  3.70  0.065
Top Soil                         2   0.6723  0.6723  0.3362  1.16  0.329
TS/CAA Ratio                     2   0.5289  0.5289  0.2644  0.91  0.414
Sub Soil                         2   0.0159  0.0159  0.0080  0.03  0.973
Top Soil*TS/CAA Ratio            4   0.8743  0.8743  0.2186  0.75  0.564
Top Soil*Sub Soil                4   2.6447  2.6447  0.6612  2.28  0.087
TS/CAA Ratio*Sub Soil            4   0.6035  0.6035  0.1509  0.52  0.721
Top Soil*TS/CAA Ratio*Sub Soil   8   0.6525  0.6525  0.0816  0.28  0.966
Error                           26   7.5304  7.5304  0.2896
Total                           53  14.5949


Least Squares Means for Turbidity_Day_2

Top Soil                          Mean  SE Mean
1                               1.0831   0.1268
2                               0.8789   0.1268
3                               0.8236   0.1268
TS/CAA Ratio
1                               1.0017   0.1268
2                               0.7886   0.1268
3                               0.9953   0.1268
Sub Soil
1                               0.9456   0.1268
2                               0.9350   0.1268
3                               0.9050   0.1268
Top Soil*TS/CAA Ratio
1        1                      1.3758   0.2197
1        2                      0.7300   0.2197
1        3                      1.1433   0.2197
2        1                      0.8792   0.2197
2        2                      0.8433   0.2197
2        3                      0.9142   0.2197
3        1                      0.7500   0.2197
3        2                      0.7925   0.2197
3        3                      0.9283   0.2197
Top Soil*Sub Soil
1        1                      1.2525   0.2197
1        2                      1.0450   0.2197
1        3                      0.9517   0.2197
2        1                      0.5983   0.2197
2        2                      0.7742   0.2197
2        3                      1.2642   0.2197
3        1                      0.9858   0.2197
3        2                      0.9858   0.2197
3        3                      0.4992   0.2197
TS/CAA Ratio*Sub Soil
1            1                  1.0392   0.2197
1            2                  1.0000   0.2197
1            3                  0.9658   0.2197
2            1                  0.6242   0.2197
2            2                  0.8308   0.2197
2            3                  0.9108   0.2197
3            1                  1.1733   0.2197
3            2                  0.9742   0.2197
3            3                  0.8383   0.2197
Top Soil*TS/CAA Ratio*Sub Soil
```

```
1        1             1          1.6500   0.3805
1        1             2          1.4125   0.3805
1        1             3          1.0650   0.3805
1        2             1          0.4800   0.3805
1        2             2          0.7150   0.3805
1        2             3          0.9950   0.3805
1        3             1          1.6275   0.3805
1        3             2          1.0075   0.3805
1        3             3          0.7950   0.3805
2        1             1          0.5650   0.3805
2        1             2          0.6850   0.3805
2        1             3          1.3875   0.3805
2        2             1          0.4675   0.3805
2        2             2          0.8525   0.3805
2        2             3          1.2100   0.3805
2        3             1          0.7625   0.3805
2        3             2          0.7850   0.3805
2        3             3          1.1950   0.3805
3        1             1          0.9025   0.3805
3        1             2          0.9025   0.3805
3        1             3          0.4450   0.3805
3        2             1          0.9250   0.3805
3        2             2          0.9250   0.3805
3        2             3          0.5275   0.3805
3        3             1          1.1300   0.3805
3        3             2          1.1300   0.3805
3        3             3          0.5250   0.3805
```

Turbidity Day 3

```
Analysis of Variance for Turbidity_Day_3, using Adjusted SS for Tests

Source                          DF   Seq SS   Adj SS  Adj MS     F      P
Blocks                           1   1.6380   1.6380  1.6380  3.43  0.075
Top Soil                         2   2.9478   2.9478  1.4739  3.09  0.063
TS/CAA Ratio                     2   1.0301   1.0301  0.5151  1.08  0.355
Sub Soil                         2   0.2743   0.2743  0.1371  0.29  0.753
Top Soil*TS/CAA Ratio            4   1.9721   1.9721  0.4930  1.03  0.409
Top Soil*Sub Soil                4   2.3646   2.3646  0.5912  1.24  0.319
TS/CAA Ratio*Sub Soil            4   1.0098   1.0098  0.2524  0.53  0.715
Top Soil*TS/CAA Ratio*Sub Soil   8   1.3831   1.3831  0.1729  0.36  0.931
Error                           26  12.4066  12.4066  0.4772
Total                           53  25.0265


Least Squares Means for Turbidity_Day_3

Top Soil                          Mean  SE Mean
1                               0.7528   0.1628
2                               0.6428   0.1628
3                               1.1842   0.1628
TS/CAA Ratio
1                               0.9953   0.1628
2                               0.9142   0.1628
3                               0.6703   0.1628
Sub Soil
1                               0.8983   0.1628
2                               0.7600   0.1628
3                               0.9214   0.1628
Top Soil*TS/CAA Ratio
1        1                      0.8742   0.2820
1        2                      0.6142   0.2820
1        3                      0.7700   0.2820
2        1                      0.7608   0.2820
2        2                      0.5783   0.2820
2        3                      0.5892   0.2820
3        1                      1.3508   0.2820
3        2                      1.5500   0.2820
3        3                      0.6517   0.2820
Top Soil*Sub Soil
1        1                      1.0967   0.2820
1        2                      0.6292   0.2820
1        3                      0.5325   0.2820
2        1                      0.6208   0.2820
2        2                      0.6733   0.2820
2        3                      0.6342   0.2820
3        1                      0.9775   0.2820
3        2                      0.9775   0.2820
3        3                      1.5975   0.2820
TS/CAA Ratio*Sub Soil
1            1                  1.1342   0.2820
1            2                  0.9283   0.2820
1            3                  0.9233   0.2820
2            1                  0.7433   0.2820
2            2                  0.7667   0.2820
2            3                  1.2325   0.2820
3            1                  0.8175   0.2820
3            2                  0.5850   0.2820
3            3                  0.6083   0.2820
```

Top Soil*TS/CAA Ratio*Sub Soil

1	1	1	1.2925	0.4885
1	1	2	0.7850	0.4885
1	1	3	0.5450	0.4885
1	2	1	0.6925	0.4885
1	2	2	0.6150	0.4885
1	2	3	0.5350	0.4885
1	3	1	1.3050	0.4885
1	3	2	0.4875	0.4885
1	3	3	0.5175	0.4885
2	1	1	0.8125	0.4885
2	1	2	0.7025	0.4885
2	1	3	0.7675	0.4885
2	2	1	0.5250	0.4885
2	2	2	0.6725	0.4885
2	2	3	0.5375	0.4885
2	3	1	0.5250	0.4885
2	3	2	0.6450	0.4885
2	3	3	0.5975	0.4885
3	1	1	1.2975	0.4885
3	1	2	1.2975	0.4885
3	1	3	1.4575	0.4885
3	2	1	1.0125	0.4885
3	2	2	1.0125	0.4885
3	2	3	2.6250	0.4885
3	3	1	0.6225	0.4885
3	3	2	0.6225	0.4885
3	3	3	0.7100	0.4885

Turbidity Day 4

```
Analysis of Variance for Turbidity_Day_4, using Adjusted SS for Tests

Source                           DF   Seq SS  Adj SS  Adj MS     F      P
Blocks                            1   0.3585  0.3585  0.3585  1.68  0.206
Top Soil                          2   0.4655  0.4655  0.2327  1.09  0.351
TS/CAA Ratio                      2   0.2901  0.2901  0.1450  0.68  0.516
Sub Soil                          2   0.2592  0.2592  0.1296  0.61  0.553
Top Soil*TS/CAA Ratio             4   0.9296  0.9296  0.2324  1.09  0.383
Top Soil*Sub Soil                 4   0.2297  0.2297  0.0574  0.27  0.895
TS/CAA Ratio*Sub Soil             4   1.1199  1.1199  0.2800  1.31  0.292
Top Soil*TS/CAA Ratio*Sub Soil    8   1.0234  1.0234  0.1279  0.60  0.770
Error                            26   5.5530  5.5530  0.2136
Total                            53  10.2288


Least Squares Means for Turbidity_Day_4

Top Soil                           Mean  SE Mean
1                                0.7300   0.1089
2                                0.9264   0.1089
3                                0.9275   0.1089
TS/CAA Ratio
1                                0.8481   0.1089
2                                0.7789   0.1089
3                                0.9569   0.1089
Sub Soil
1                                0.7633   0.1089
2                                0.9086   0.1089
3                                0.9119   0.1089
Top Soil*TS/CAA Ratio
1        1                       0.9567   0.1887
1        2                       0.5075   0.1887
1        3                       0.7258   0.1887
2        1                       0.7058   0.1887
2        2                       0.9758   0.1887
2        3                       1.0975   0.1887
3        1                       0.8817   0.1887
3        2                       0.8533   0.1887
3        3                       1.0475   0.1887
Top Soil*Sub Soil
1        1                       0.6708   0.1887
1        2                       0.8042   0.1887
1        3                       0.7150   0.1887
2        1                       0.7550   0.1887
2        2                       1.0575   0.1887
2        3                       0.9667   0.1887
3        1                       0.8642   0.1887
3        2                       0.8642   0.1887
3        3                       1.0542   0.1887
TS/CAA Ratio*Sub Soil
1            1                   0.7050   0.1887
1            2                   0.9492   0.1887
1            3                   0.8900   0.1887
2            1                   0.7217   0.1887
2            2                   0.5792   0.1887
2            3                   1.0358   0.1887
3            1                   0.8633   0.1887
3            2                   1.1975   0.1887
3            3                   0.8100   0.1887
```

```
Top Soil*TS/CAA Ratio*Sub Soil
1        1             1         0.8425   0.3268
1        1             2         1.2100   0.3268
1        1             3         0.8175   0.3268
1        2             1         0.5225   0.3268
1        2             2         0.2000   0.3268
1        2             3         0.8000   0.3268
1        3             1         0.6475   0.3268
1        3             2         1.0025   0.3268
1        3             3         0.5275   0.3268
2        1             1         0.5625   0.3268
2        1             2         0.9275   0.3268
2        1             3         0.6275   0.3268
2        2             1         0.9850   0.3268
2        2             2         0.8800   0.3268
2        2             3         1.0625   0.3268
2        3             1         0.7175   0.3268
2        3             2         1.3650   0.3268
2        3             3         1.2100   0.3268
3        1             1         0.7100   0.3268
3        1             2         0.7100   0.3268
3        1             3         1.2250   0.3268
3        2             1         0.6575   0.3268
3        2             2         0.6575   0.3268
3        2             3         1.2450   0.3268
3        3             1         1.2250   0.3268
3        3             2         1.2250   0.3268
3        3             3         0.6925   0.3268
```

Turbidity Day 5

```
Analysis of Variance for Turbidity_Day_5, using Adjusted SS for Tests

Source                          DF   Seq SS  Adj SS  Adj MS     F      P
Blocks                           1   0.2275  0.2275  0.2275  1.03  0.320
Top Soil                         2   1.4089  1.4089  0.7045  3.18  0.058
TS/CAA Ratio                     2   0.2269  0.2269  0.1134  0.51  0.605
Sub Soil                         2   0.3138  0.3138  0.1569  0.71  0.502
Top Soil*TS/CAA Ratio            4   0.5268  0.5268  0.1317  0.59  0.670
Top Soil*Sub Soil                4   1.0464  1.0464  0.2616  1.18  0.343
TS/CAA Ratio*Sub Soil            4   0.8383  0.8383  0.2096  0.95  0.454
Top Soil*TS/CAA Ratio*Sub Soil   8   0.4714  0.4714  0.0589  0.27  0.972
Error                           26   5.7624  5.7624  0.2216
Total                           53  10.8225



Least Squares Means for Turbidity_Day_5

Top Soil                          Mean  SE Mean
1                               0.6997   0.1110
2                               0.6697   0.1110
3                               1.0264   0.1110
TS/CAA Ratio
1                               0.8300   0.1110
2                               0.7083   0.1110
3                               0.8575   0.1110
Sub Soil
1                               0.7922   0.1110
2                               0.7086   0.1110
3                               0.8950   0.1110
Top Soil*TS/CAA Ratio
1        1                      0.8717   0.1922
1        2                      0.5000   0.1922
1        3                      0.7275   0.1922
2        1                      0.5350   0.1922
2        2                      0.6292   0.1922
2        3                      0.8450   0.1922
3        1                      1.0833   0.1922
3        2                      0.9958   0.1922
3        3                      1.0000   0.1922
Top Soil*Sub Soil
1        1                      0.7933   0.1922
1        2                      0.7567   0.1922
1        3                      0.5492   0.1922
2        1                      0.7117   0.1922
2        2                      0.4975   0.1922
2        3                      0.8000   0.1922
3        1                      0.8717   0.1922
3        2                      0.8717   0.1922
3        3                      1.3358   0.1922
TS/CAA Ratio*Sub Soil
1            1                  0.7750   0.1922
1            2                  0.9342   0.1922
1            3                  0.7808   0.1922
2            1                  0.7108   0.1922
2            2                  0.6375   0.1922
2            3                  0.7767   0.1922
3            1                  0.8908   0.1922
3            2                  0.5542   0.1922
3            3                  1.1275   0.1922
```

```
Top Soil*TS/CAA Ratio*Sub Soil
1        1            1         0.9025   0.3329
1        1            2         1.2625   0.3329
1        1            3         0.4500   0.3329
1        2            1         0.5700   0.3329
1        2            2         0.4525   0.3329
1        2            3         0.4775   0.3329
1        3            1         0.9075   0.3329
1        3            2         0.5550   0.3329
1        3            3         0.7200   0.3329
2        1            1         0.4825   0.3329
2        1            2         0.6000   0.3329
2        1            3         0.5225   0.3329
2        2            1         0.6825   0.3329
2        2            2         0.5800   0.3329
2        2            3         0.6250   0.3329
2        3            1         0.9700   0.3329
2        3            2         0.3125   0.3329
2        3            3         1.2525   0.3329
3        1            1         0.9400   0.3329
3        1            2         0.9400   0.3329
3        1            3         1.3700   0.3329
3        2            1         0.8800   0.3329
3        2            2         0.8800   0.3329
3        2            3         1.2275   0.3329
3        3            1         0.7950   0.3329
3        3            2         0.7950   0.3329
3        3            3         1.4100   0.3329
```

Turbidity Day 6

```
Analysis of Variance for Turbidity _Day 6, using Adjusted SS for Tests

Source                           DF  Seq SS  Adj SS  Adj MS     F      P
Blocks                            1  0.0414  0.0414  0.0414  0.28  0.601
Top Soil                          2  0.5700  0.5700  0.2850  1.93  0.166
TS/CAA Ratio                      2  0.1638  0.1638  0.0819  0.55  0.581
Sub Soil                          2  0.1187  0.1187  0.0593  0.40  0.674
Top Soil*TS/CAA Ratio             4  0.0638  0.0638  0.0160  0.11  0.979
Top Soil*Sub Soil                 4  0.7538  0.7538  0.1885  1.27  0.306
TS/CAA Ratio*Sub Soil             4  0.5789  0.5789  0.1447  0.98  0.437
Top Soil*TS/CAA Ratio*Sub Soil    8  1.2554  1.2554  0.1569  1.06  0.419
Error                            26  3.8468  3.8468  0.1480
Total                            53  7.3926



Least Squares Means for Turbidity _Day 6

Top Soil                           Mean  SE Mean
1                                0.8397  0.09066
2                                0.6542  0.09066
3                                0.8942  0.09066
TS/CAA Ratio
1                                0.7864  0.09066
2                                0.7339  0.09066
3                                0.8678  0.09066
Sub Soil
1                                0.8289  0.09066
2                                0.8294  0.09066
3                                0.7297  0.09066
Top Soil*TS/CAA Ratio
1        1                       0.8650  0.15703
1        2                       0.7867  0.15703
1        3                       0.8675  0.15703
2        1                       0.6633  0.15703
2        2                       0.5908  0.15703
2        3                       0.7083  0.15703
3        1                       0.8308  0.15703
3        2                       0.8242  0.15703
3        3                       1.0275  0.15703
Top Soil*Sub Soil
1        1                       1.0700  0.15703
1        2                       0.8708  0.15703
1        3                       0.5783  0.15703
2        1                       0.5383  0.15703
2        2                       0.7392  0.15703
2        3                       0.6850  0.15703
3        1                       0.8783  0.15703
3        2                       0.8783  0.15703
3        3                       0.9258  0.15703
TS/CAA Ratio*Sub Soil
1            1                   0.6625  0.15703
1            2                   0.8992  0.15703
1            3                   0.7975  0.15703
2            1                   0.7308  0.15703
2            2                   0.7625  0.15703
2            3                   0.7083  0.15703
3            1                   1.0933  0.15703
3            2                   0.8267  0.15703
3            3                   0.6833  0.15703
```

```
Top Soil*TS/CAA Ratio*Sub Soil
1        1             1         0.8300  0.27199
1        1             2         1.3200  0.27199
1        1             3         0.4450  0.27199
1        2             1         0.8750  0.27199
1        2             2         0.7625  0.27199
1        2             3         0.7225  0.27199
1        3             1         1.5050  0.27199
1        3             2         0.5300  0.27199
1        3             3         0.5675  0.27199
2        1             1         0.5050  0.27199
2        1             2         0.7250  0.27199
2        1             3         0.7600  0.27199
2        2             1         0.4750  0.27199
2        2             2         0.6825  0.27199
2        2             3         0.6150  0.27199
2        3             1         0.6350  0.27199
2        3             2         0.8100  0.27199
2        3             3         0.6800  0.27199
3        1             1         0.6525  0.27199
3        1             2         0.6525  0.27199
3        1             3         1.1875  0.27199
3        2             1         0.8425  0.27199
3        2             2         0.8425  0.27199
3        2             3         0.7875  0.27199
3        3             1         1.1400  0.27199
3        3             2         1.1400  0.27199
3        3             3         0.8025  0.27199
```

APPENDIX C.2 Conductivity

Conductivity Day 1

```
Analysis of Variance for Conductivity_1, using Adjusted SS for Tests

Source                           DF    Seq SS    Adj SS   Adj MS     F       P
Blocks                            1   5420727   5420727  5420727  4.39  0.046
Top Soil                          2   5431352   5431352  2715676  2.20  0.131
TS/CAA Ratio                      2   1976555   1976555   988277  0.80  0.460
Sub Soil                          2   1014168   1014168   507084  0.41  0.668
Top Soil*TS/CAA Ratio             4  10313513  10313513  2578378  2.09  0.111
Top Soil*Sub Soil                 4   1093547   1093547   273387  0.22  0.924
TS/CAA Ratio*Sub Soil             4  10084711  10084711  2521178  2.04  0.118
Top Soil*TS/CAA Ratio*Sub Soil    8   7839872   7839872   979984  0.79  0.613
Error                            26  32122237  32122237  1235471
Total                            53  75296682


Least Squares Means for Conductivity_1

Top Soil                            Mean  SE Mean
1                                 2808.0    262.0
2                                 2272.9    262.0
3                                 2052.7    262.0
TS/CAA Ratio
1                                 2135.1    262.0
2                                 2602.6    262.0
3                                 2396.0    262.0
Sub Soil
1                                 2549.3    262.0
2                                 2213.9    262.0
3                                 2370.5    262.0
Top Soil*TS/CAA Ratio
1        1                        2109.4    453.8
1        2                        2853.8    453.8
1        3                        3460.7    453.8
2        1                        2411.8    453.8
2        2                        2096.7    453.8
2        3                        2310.3    453.8
3        1                        1883.9    453.8
3        2                        2857.4    453.8
3        3                        1416.8    453.8
Top Soil*Sub Soil
1        1                        3043.9    453.8
1        2                        2379.4    453.8
1        3                        3000.7    453.8
2        1                        2413.7    453.8
2        2                        2292.8    453.8
2        3                        2112.3    453.8
3        1                        2190.3    453.8
3        2                        1969.3    453.8
3        3                        1998.5    453.8
TS/CAA Ratio*Sub Soil
1            1                    2062.4    453.8
1            2                    2210.0    453.8
1            3                    2132.8    453.8
2            1                    3259.8    453.8
2            2                    1610.8    453.8
2            3                    2937.3    453.8
3            1                    2325.7    453.8
```

```
3            2                 2820.8    453.8
3            3                 2041.4    453.8
Top Soil*TS/CAA Ratio*Sub Soil
1        1            1        2029.0    786.0
1        1            2        1556.8    786.0
1        1            3        2742.5    786.0
1        2            1        3977.5    786.0
1        2            2        1301.5    786.0
1        2            3        3282.5    786.0
1        3            1        3125.2    786.0
1        3            2        4280.0    786.0
1        3            3        2977.0    786.0
2        1            1        2219.3    786.0
2        1            2        3459.5    786.0
2        1            3        1556.7    786.0
2        2            1        2484.5    786.0
2        2            2        1321.0    786.0
2        2            3        2484.5    786.0
2        3            1        2537.2    786.0
2        3            2        2098.0    786.0
2        3            3        2295.7    786.0
3        1            1        1939.0    786.0
3        1            2        1613.8    786.0
3        1            3        2099.0    786.0
3        2            1        3317.5    786.0
3        2            2        2209.8    786.0
3        2            3        3045.0    786.0
3        3            1        1314.5    786.0
3        3            2        2084.5    786.0
3        3            3         851.5    786.0
```

Conductivity Day 2

```
Analysis of Variance for Conductivity_2, using Adjusted SS for Tests

Source                            DF   Seq SS   Adj SS  Adj MS     F      P
Blocks                             1     1678     1678    1678  0.04  0.842
Top Soil                           2   129239   129239   64620  1.57  0.227
TS/CAA Ratio                       2   158098   158098   79049  1.92  0.167
Sub Soil                           2    60541    60541   30271  0.74  0.489
Top Soil*TS/CAA Ratio              4   176066   176066   44017  1.07  0.391
Top Soil*Sub Soil                  4   325727   325727   81432  1.98  0.127
TS/CAA Ratio*Sub Soil              4   130592   130592   32648  0.79  0.540
Top Soil*TS/CAA Ratio*Sub Soil     8   369881   369881   46235  1.12  0.380
Error                             26  1069520  1069520   41135
Total                             53  2421342



Least Squares Means for Conductivity_2

Top Soil                            Mean  SE Mean
1                                  585.1    47.80
2                                  467.8    47.80
3                                  547.9    47.80
TS/CAA Ratio
1                                  523.3    47.80
2                                  604.4    47.80
3                                  473.1    47.80
Sub Soil
1                                  573.8    47.80
2                                  491.8    47.80
3                                  535.1    47.80
Top Soil*TS/CAA Ratio
1        1                         651.6    82.80
1        2                         578.8    82.80
1        3                         524.8    82.80
2        1                         425.2    82.80
2        2                         520.5    82.80
2        3                         457.7    82.80
3        1                         493.0    82.80
3        2                         713.8    82.80
3        3                         436.7    82.80
Top Soil*Sub Soil
1        1                         749.2    82.80
1        2                         401.7    82.80
1        3                         604.2    82.80
2        1                         454.9    82.80
2        2                         481.4    82.80
2        3                         467.1    82.80
3        1                         517.2    82.80
3        2                         592.3    82.80
3        3                         534.2    82.80
TS/CAA Ratio*Sub Soil
1            1                     646.0    82.80
1            2                     453.1    82.80
1            3                     470.8    82.80
2            1                     563.5    82.80
2            2                     614.0    82.80
2            3                     635.7    82.80
3            1                     511.8    82.80
3            2                     408.3    82.80
3            3                     499.0    82.80
```

```
Top Soil*TS/CAA Ratio*Sub Soil
1        1            1         1072.2   143.41
1        1            2          464.5   143.41
1        1            3          418.0   143.41
1        2            1          577.2   143.41
1        2            2          368.8   143.41
1        2            3          790.5   143.41
1        3            1          598.2   143.41
1        3            2          372.0   143.41
1        3            3          604.0   143.41
2        1            1          420.5   143.41
2        1            2          390.7   143.41
2        1            3          464.5   143.41
2        2            1          461.0   143.41
2        2            2          639.5   143.41
2        2            3          461.0   143.41
2        3            1          483.2   143.41
2        3            2          414.0   143.41
2        3            3          475.7   143.41
3        1            1          445.2   143.41
3        1            2          504.0   143.41
3        1            3          529.8   143.41
3        2            1          652.2   143.41
3        2            2          833.8   143.41
3        2            3          655.5   143.41
3        3            1          454.0   143.41
3        3            2          439.0   143.41
3        3            3          417.2   143.41
```

Conductivity Day 3

```
Analysis of Variance for Conductivity_3, using Adjusted SS for Tests

Source                           DF   Seq SS   Adj SS  Adj MS     F      P
Blocks                            1   157972   157972  157972  1.69  0.205
Top Soil                          2   277868   277868  138934  1.49  0.244
TS/CAA Ratio                      2   493281   493281  246641  2.64  0.090
Sub Soil                          2   461677   461677  230838  2.47  0.104
Top Soil*TS/CAA Ratio             4   321872   321872   80468  0.86  0.500
Top Soil*Sub Soil                 4   842928   842928  210732  2.26  0.090
TS/CAA Ratio*Sub Soil             4   261551   261551   65388  0.70  0.599
Top Soil*TS/CAA Ratio*Sub Soil    8   558524   558524   69816  0.75  0.650
Error                            26  2426727  2426727   93336
Total                            53  5802401



Least Squares Means for Conductivity_3

Top Soil                            Mean  SE Mean
1                                  373.2    72.01
2                                  397.9    72.01
3                                  536.2    72.01
TS/CAA Ratio
1                                  439.6    72.01
2                                  550.8    72.01
3                                  316.8    72.01
Sub Soil
1                                  415.3    72.01
2                                  557.8    72.01
3                                  334.1    72.01
Top Soil*TS/CAA Ratio
1        1                         370.2   124.72
1        2                         403.6   124.72
1        3                         345.7   124.72
2        1                         313.2   124.72
2        2                         566.3   124.72
2        3                         314.2   124.72
3        1                         635.5   124.72
3        2                         682.5   124.72
3        3                         290.5   124.72
Top Soil*Sub Soil
1        1                         487.7   124.72
1        2                         259.7   124.72
1        3                         372.1   124.72
2        1                         339.0   124.72
2        2                         567.8   124.72
2        3                         286.8   124.72
3        1                         419.3   124.72
3        2                         845.8   124.72
3        3                         343.3   124.72
TS/CAA Ratio*Sub Soil
1            1                     454.0   124.72
1            2                     573.8   124.72
1            3                     291.0   124.72
2            1                     457.9   124.72
2            2                     779.7   124.72
2            3                     414.8   124.72
3            1                     334.2   124.72
3            2                     319.8   124.72
3            3                     296.3   124.72
```

```
Top Soil*TS/CAA Ratio*Sub Soil
1        1            1          584.3   216.03
1        1            2          245.8   216.03
1        1            3          280.5   216.03
1        2            1          442.6   216.03
1        2            2          231.5   216.03
1        2            3          536.8   216.03
1        3            1          436.2   216.03
1        3            2          301.7   216.03
1        3            3          299.0   216.03
2        1            1          321.5   216.03
2        1            2          372.2   216.03
2        1            3          245.8   216.03
2        2            1          356.0   216.03
2        2            2          986.8   216.03
2        2            3          356.0   216.03
2        3            1          339.5   216.03
2        3            2          344.5   216.03
2        3            3          258.5   216.03
3        1            1          456.2   216.03
3        1            2         1103.5   216.03
3        1            3          346.8   216.03
3        2            1          575.0   216.03
3        2            2         1120.7   216.03
3        2            3          351.8   216.03
3        3            1          226.8   216.03
3        3            2          313.3   216.03
3        3            3          331.5   216.03
```

Conductivity Day 4

```
Analysis of Variance for Conductivity_4, using Adjusted SS for Tests

Source                          DF  Seq SS  Adj SS  Adj MS     F      P
Blocks                           1   10426   10426   10426  1.66  0.209
Top Soil                         2   27427   27427   13714  2.19  0.133
TS/CAA Ratio                     2   35026   35026   17513  2.79  0.080
Sub Soil                         2    5937    5937    2969  0.47  0.628
Top Soil*TS/CAA Ratio            4   23987   23987    5997  0.96  0.448
Top Soil*Sub Soil                4   51198   51198   12799  2.04  0.118
TS/CAA Ratio*Sub Soil            4   50887   50887   12722  2.03  0.120
Top Soil*TS/CAA Ratio*Sub Soil   8   92156   92156   11520  1.84  0.115
Error                           26  163157  163157    6275
Total                           53  460201


Least Squares Means for Conductivity_4

Top Soil                          Mean  SE Mean
1                                289.2    18.67
2                                248.5    18.67
3                                301.2    18.67
TS/CAA Ratio
1                                280.4    18.67
2                                310.5    18.67
3                                248.1    18.67
Sub Soil
1                                286.4    18.67
2                                264.8    18.67
3                                287.7    18.67
Top Soil*TS/CAA Ratio
1        1                       328.6    32.34
1        2                       295.6    32.34
1        3                       243.5    32.34
2        1                       220.2    32.34
2        2                       288.1    32.34
2        3                       237.3    32.34
3        1                       292.5    32.34
3        2                       347.7    32.34
3        3                       263.4    32.34
Top Soil*Sub Soil
1        1                       344.8    32.34
1        2                       220.9    32.34
1        3                       302.0    32.34
2        1                       228.6    32.34
2        2                       273.9    32.34
2        3                       243.1    32.34
3        1                       285.8    32.34
3        2                       299.8    32.34
3        3                       318.1    32.34
TS/CAA Ratio*Sub Soil
1            1                   347.4    32.34
1            2                   230.2    32.34
1            3                   263.6    32.34
2            1                   284.3    32.34
2            2                   321.8    32.34
2            3                   325.3    32.34
3            1                   227.4    32.34
3            2                   242.5    32.34
3            3                   274.3    32.34
```

```
Top Soil*TS/CAA Ratio*Sub Soil
1        1             1         511.3    56.01
1        1             2         225.5    56.01
1        1             3         249.0    56.01
1        2             1         268.5    56.01
1        2             2         202.9    56.01
1        2             3         415.5    56.01
1        3             1         254.8    56.01
1        3             2         234.3    56.01
1        3             3         241.5    56.01
2        1             1         213.1    56.01
2        1             2         222.0    56.01
2        1             3         225.5    56.01
2        2             1         260.3    56.01
2        2             2         343.8    56.01
2        2             3         260.2    56.01
2        3             1         212.5    56.01
2        3             2         256.0    56.01
2        3             3         243.5    56.01
3        1             1         318.0    56.01
3        1             2         243.3    56.01
3        1             3         316.3    56.01
3        2             1         324.3    56.01
3        2             2         418.8    56.01
3        2             3         300.0    56.01
3        3             1         215.0    56.01
3        3             2         237.3    56.01
3        3             3         338.0    56.01
```

Conductivity Day 5

```
Analysis of Variance for Conductivity_5, using Adjusted SS for Tests

Source                          DF   Seq SS  Adj SS  Adj MS     F      P
Blocks                           1   174780  174780  174780  5.31  0.029
Top Soil                         2    30714   30714   15357  0.47  0.632
TS/CAA Ratio                     2    34561   34561   17280  0.53  0.598
Sub Soil                         2   316014  316014  158007  4.80  0.017
Top Soil*TS/CAA Ratio            4    59179   59179   14795  0.45  0.772
Top Soil*Sub Soil                4   440921  440921  110230  3.35  0.024
TS/CAA Ratio*Sub Soil            4    83234   83234   20809  0.63  0.644
Top Soil*TS/CAA Ratio*Sub Soil   8   272187  272187   34023  1.03  0.437
Error                           26   855526  855526   32905
Total                           53  2267116



Least Squares Means for Conductivity_5

Top Soil                         Mean  SE Mean
1                               276.4    42.76
2                               317.0    42.76
3                               260.4    42.76
TS/CAA Ratio
1                               258.9    42.76
2                               319.0    42.76
3                               275.9    42.76
Sub Soil
1                               220.4    42.76
2                               392.1    42.76
3                               241.4    42.76
Top Soil*TS/CAA Ratio
1        1                      252.5    74.05
1        2                      253.5    74.05
1        3                      323.2    74.05
2        1                      285.7    74.05
2        2                      374.5    74.05
2        3                      290.9    74.05
3        1                      238.4    74.05
3        2                      329.0    74.05
3        3                      213.7    74.05
Top Soil*Sub Soil
1        1                      262.3    74.05
1        2                      298.2    74.05
1        3                      268.7    74.05
2        1                      163.0    74.05
2        2                      604.9    74.05
2        3                      183.2    74.05
3        1                      235.8    74.05
3        2                      273.2    74.05
3        3                      272.2    74.05
TS/CAA Ratio*Sub Soil
1            1                  252.9    74.05
1            2                  297.6    74.05
1            3                  226.1    74.05
2            1                  235.6    74.05
2            2                  438.5    74.05
2            3                  282.9    74.05
3            1                  172.6    74.05
3            2                  440.3    74.05
3            3                  215.0    74.05
```

```
Top Soil*TS/CAA Ratio*Sub Soil
1        1            1         355.3   128.27
1        1            2         185.6   128.27
1        1            3         216.5   128.27
1        2            1         248.5   128.27
1        2            2         137.0   128.27
1        2            3         375.0   128.27
1        3            1         183.1   128.27
1        3            2         572.0   128.27
1        3            3         214.5   128.27
2        1            1         170.0   128.27
2        1            2         501.5   128.27
2        1            3         185.6   128.27
2        2            1         169.8   128.27
2        2            2         784.0   128.27
2        2            3         169.8   128.27
2        3            1         149.3   128.27
2        3            2         529.2   128.27
2        3            3         194.2   128.27
3        1            1         233.5   128.27
3        1            2         205.6   128.27
3        1            3         276.3   128.27
3        2            1         288.5   128.27
3        2            2         394.5   128.27
3        2            3         304.0   128.27
3        3            1         185.4   128.27
3        3            2         219.5   128.27
3        3            3         236.2   128.27
```

Conductivity Day 6

```
Analysis of Variance for Conductivity_Day 6, using Adjusted SS for Tests

Source                          DF   Seq SS  Adj SS  Adj MS     F      P
Blocks                           1    87721   87721   87721  5.88  0.023
Top Soil                         2     5253    5253    2626  0.18  0.840
TS/CAA Ratio                     2    20255   20255   10127  0.68  0.516
Sub Soil                         2   176487  176487   88244  5.91  0.008
Top Soil*TS/CAA Ratio            4    17898   17898    4475  0.30  0.875
Top Soil*Sub Soil                4   218425  218425   54606  3.66  0.017
TS/CAA Ratio*Sub Soil            4    46186   46186   11547  0.77  0.552
Top Soil*TS/CAA Ratio*Sub Soil   8   204294  204294   25537  1.71  0.143
Error                           26   387938  387938   14921
Total                           53  1164458



Least Squares Means for Conductivity_Day 6

Top Soil                         Mean  SE Mean
1                               242.5    28.79
2                               263.7    28.79
3                               243.0    28.79
TS/CAA Ratio
1                               230.7    28.79
2                               276.3    28.79
3                               242.2    28.79
Sub Soil
1                               192.9    28.79
2                               327.9    28.79
3                               228.4    28.79
Top Soil*TS/CAA Ratio
1        1                      215.1    49.87
1        2                      244.0    49.87
1        3                      268.5    49.87
2        1                      239.7    49.87
2        2                      307.5    49.87
2        3                      243.8    49.87
3        1                      237.2    49.87
3        2                      277.4    49.87
3        3                      214.3    49.87
Top Soil*Sub Soil
1        1                      223.3    49.87
1        2                      255.3    49.87
1        3                      249.1    49.87
2        1                      150.3    49.87
2        2                      468.3    49.87
2        3                      172.4    49.87
3        1                      205.0    49.87
3        2                      260.2    49.87
3        3                      263.7    49.87
TS/CAA Ratio*Sub Soil
1            1                  208.4    49.87
1            2                  252.1    49.87
1            3                  231.5    49.87
2            1                  203.0    49.87
2            2                  373.6    49.87
2            3                  252.3    49.87
3            1                  167.1    49.87
3            2                  358.2    49.87
3            3                  201.4    49.87
```

```
Top Soil*TS/CAA Ratio*Sub Soil
1        1             1         280.0    86.37
1        1             2         177.5    86.37
1        1             3         187.8    86.37
1        2             1         220.8    86.37
1        2             2         142.2    86.37
1        2             3         369.0    86.37
1        3             1         169.0    86.37
1        3             2         446.2    86.37
1        3             3         190.4    86.37
2        1             1         157.3    86.37
2        1             2         384.5    86.37
2        1             3         177.5    86.37
2        2             1         147.0    86.37
2        2             2         628.5    86.37
2        2             3         147.0    86.37
2        3             1         146.7    86.37
2        3             2         392.0    86.37
2        3             3         192.6    86.37
3        1             1         188.0    86.37
3        1             2         194.2    86.37
3        1             3         329.3    86.37
3        2             1         241.2    86.37
3        2             2         350.0    86.37
3        2             3         241.0    86.37
3        3             1         185.8    86.37
3        3             2         236.3    86.37
3        3             3         221.0    86.37
```

APPENDIX C.3 pH

pH Day 1

```
Analysis of Variance for pH_1, using Adjusted SS for Tests

Source                          DF   Seq SS   Adj SS  Adj MS      F      P
Blocks                           1   0.0143   0.0143  0.0143   0.06  0.805
Top Soil                         2   2.9066   2.9066  1.4533   6.37  0.006
TS/CAA Ratio                     2   0.1944   0.1944  0.0972   0.43  0.658
Sub Soil                         2  11.9535  11.9535  5.9768  26.18  0.000
Top Soil*TS/CAA Ratio            4   0.5988   0.5988  0.1497   0.66  0.628
Top Soil*Sub Soil                4   0.7854   0.7854  0.1964   0.86  0.501
TS/CAA Ratio*Sub Soil            4   3.0970   3.0970  0.7742   3.39  0.023
Top Soil*TS/CAA Ratio*Sub Soil   8   4.7046   4.7046  0.5881   2.58  0.062
Error                           26   5.9353   5.9353  0.2283
Total                           53  30.1900

Least Squares Means for pH_1

Top Soil                         Mean  SE Mean
1                               7.425   0.1126
2                               7.749   0.1126
3                               7.992   0.1126
TS/CAA Ratio
1                               7.641   0.1126
2                               7.785   0.1126
3                               7.740   0.1126
Sub Soil
1                               7.096   0.1126
2                               8.230   0.1126
3                               7.841   0.1126
Top Soil*TS/CAA Ratio
1        1                      7.408   0.1951
1        2                      7.320   0.1951
1        3                      7.548   0.1951
2        1                      7.544   0.1951
2        2                      7.896   0.1951
2        3                      7.809   0.1951
3        1                      7.973   0.1951
3        2                      8.139   0.1951
3        3                      7.864   0.1951
Top Soil*Sub Soil
1        1                      6.854   0.1951
1        2                      7.872   0.1951
1        3                      7.550   0.1951
2        1                      6.895   0.1951
2        2                      8.382   0.1951
2        3                      7.971   0.1951
3        1                      7.539   0.1951
3        2                      8.437   0.1951
3        3                      8.000   0.1951
TS/CAA Ratio*Sub Soil
1            1                  6.792   0.1951
1            2                  8.420   0.1951
1            3                  7.712   0.1951
2            1                  6.947   0.1951
2            2                  8.258   0.1951
2            3                  8.150   0.1951
3            1                  7.549   0.1951
```

```
3            2                  8.013   0.1951
3            3                  7.659   0.1951
Top Soil*TS/CAA Ratio*Sub Soil
1        1            1         6.163   0.3378
1        1            2         8.620   0.3378
1        1            3         7.442   0.3378
1        2            1         7.097   0.3378
1        2            2         7.201   0.3378
1        2            3         7.663   0.3378
1        3            1         7.303   0.3378
1        3            2         7.795   0.3378
1        3            3         7.545   0.3378
2        1            1         6.806   0.3378
2        1            2         8.251   0.3378
2        1            3         7.574   0.3378
2        2            1         6.625   0.3378
2        2            2         8.410   0.3378
2        2            3         8.652   0.3378
2        3            1         7.255   0.3378
2        3            2         8.484   0.3378
2        3            3         7.688   0.3378
3        1            1         7.407   0.3378
3        1            2         8.390   0.3378
3        1            3         8.121   0.3378
3        2            1         7.121   0.3378
3        2            2         9.162   0.3378
3        2            3         8.135   0.3378
3        3            1         8.088   0.3378
3        3            2         7.758   0.3378
3        3            3         7.745   0.3378
```

pH Day 2

```
Analysis of Variance for pH_2, using Adjusted SS for Tests

Source                          DF   Seq SS   Adj SS   Adj MS      F      P
Blocks                           1   0.3628   0.3628   0.3628   0.73  0.399
Top Soil                         2   2.9513   2.9513   1.4756   2.99  0.068
TS/CAA Ratio                     2   0.0219   0.0219   0.0110   0.02  0.978
Sub Soil                         2  35.4735  35.4735  17.7368  35.94  0.000
Top Soil*TS/CAA Ratio            4   1.4953   1.4953   0.3738   0.76  0.562
Top Soil*Sub Soil                4   3.9542   3.9542   0.9886   2.00  0.124
TS/CAA Ratio*Sub Soil            4   2.1104   2.1104   0.5276   1.07  0.392
Top Soil*TS/CAA Ratio*Sub Soil   8   3.7048   3.7048   0.4631   0.94  0.503
Error                           26  12.8329  12.8329   0.4936
Total                           53  62.9071


Least Squares Means for pH_2

Top Soil                          Mean  SE Mean
1                                8.638   0.1656
2                                8.692   0.1656
3                                9.158   0.1656
TS/CAA Ratio
1                                8.801   0.1656
2                                8.847   0.1656
3                                8.840   0.1656
Sub Soil
1                                7.827   0.1656
2                                8.848   0.1656
3                                9.812   0.1656
Top Soil*TS/CAA Ratio
1        1                       8.514   0.2868
1        2                       8.552   0.2868
1        3                       8.847   0.2868
2        1                       8.605   0.2868
2        2                       8.992   0.2868
2        3                       8.479   0.2868
3        1                       9.285   0.2868
3        2                       8.996   0.2868
3        3                       9.194   0.2868
Top Soil*Sub Soil
1        1                       7.492   0.2868
1        2                       8.316   0.2868
1        3                      10.106   0.2868
2        1                       7.581   0.2868
2        2                       8.950   0.2868
2        3                       9.545   0.2868
3        1                       8.410   0.2868
3        2                       9.279   0.2868
3        3                       9.787   0.2868
TS/CAA Ratio*Sub Soil
1            1                   7.676   0.2868
1            2                   8.742   0.2868
1            3                   9.986   0.2868
2            1                   7.830   0.2868
2            2                   8.697   0.2868
2            3                  10.013   0.2868
3            1                   7.976   0.2868
3            2                   9.105   0.2868
3            3                   9.439   0.2868
```

```
Top Soil*TS/CAA Ratio*Sub Soil
1        1            1          7.135   0.4968
1        1            2          8.454   0.4968
1        1            3          9.954   0.4968
1        2            1          7.766   0.4968
1        2            2          7.382   0.4968
1        2            3         10.508   0.4968
1        3            1          7.574   0.4968
1        3            2          9.111   0.4968
1        3            3          9.856   0.4968
2        1            1          7.272   0.4968
2        1            2          8.695   0.4968
2        1            3          9.847   0.4968
2        2            1          7.602   0.4968
2        2            2          9.435   0.4968
2        2            3          9.939   0.4968
2        3            1          7.869   0.4968
2        3            2          8.720   0.4968
2        3            3          8.848   0.4968
3        1            1          8.620   0.4968
3        1            2          9.077   0.4968
3        1            3         10.157   0.4968
3        2            1          8.124   0.4968
3        2            2          9.275   0.4968
3        2            3          9.591   0.4968
3        3            1          8.486   0.4968
3        3            2          9.485   0.4968
3        3            3          9.612   0.4968
```

pH Day 3

```
Analysis of Variance for pH_3, using Adjusted SS for Tests

Source                          DF   Seq SS   Adj SS   Adj MS      F      P
Blocks                           1   0.1336   0.1336   0.1336   0.23  0.637
Top Soil                         2   1.2521   1.2521   0.6261   1.07  0.358
TS/CAA Ratio                     2   0.8726   0.8726   0.4363   0.75  0.484
Sub Soil                         2  48.2500  48.2500  24.1250  41.23  0.000
Top Soil*TS/CAA Ratio            4   4.4838   4.4838   1.1209   1.92  0.138
Top Soil*Sub Soil                4   9.4889   9.4889   2.3722   4.05  0.011
TS/CAA Ratio*Sub Soil            4   4.6116   4.6116   1.1529   1.97  0.129
Top Soil*TS/CAA Ratio*Sub Soil   8   1.1037   1.1037   0.1380   0.24  0.980
Error                           26  15.2124  15.2124   0.5851
Total                           53  85.4086

Least Squares Means for pH_3

Top Soil                          Mean  SE Mean
1                                8.677   0.1803
2                                8.893   0.1803
3                                9.048   0.1803
TS/CAA Ratio
1                                8.976   0.1803
2                                8.693   0.1803
3                                8.948   0.1803
Sub Soil
1                                7.540   0.1803
2                                9.446   0.1803
3                                9.631   0.1803
Top Soil*TS/CAA Ratio
1        1                       8.873   0.3123
1        2                       8.105   0.3123
1        3                       9.052   0.3123
2        1                       8.921   0.3123
2        2                       9.227   0.3123
2        3                       8.531   0.3123
3        1                       9.133   0.3123
3        2                       8.749   0.3123
3        3                       9.262   0.3123
Top Soil*Sub Soil
1        1                       6.738   0.3123
1        2                       9.310   0.3123
1        3                       9.981   0.3123
2        1                       7.438   0.3123
2        2                       9.743   0.3123
2        3                       9.498   0.3123
3        1                       8.444   0.3123
3        2                       9.285   0.3123
3        3                       9.414   0.3123
TS/CAA Ratio*Sub Soil
1            1                   7.598   0.3123
1            2                   9.623   0.3123
1            3                   9.706   0.3123
2            1                   6.909   0.3123
2            2                   9.324   0.3123
2            3                   9.846   0.3123
3            1                   8.113   0.3123
3            2                   9.391   0.3123
3            3                   9.341   0.3123
Top Soil*TS/CAA Ratio*Sub Soil
1        1            1          6.943   0.5409
```

```
1        1             2           9.781   0.5409
1        1             3           9.894   0.5409
1        2             1           5.633   0.5409
1        2             2           8.767   0.5409
1        2             3           9.914   0.5409
1        3             1           7.639   0.5409
1        3             2           9.382   0.5409
1        3             3          10.135   0.5409
2        1             1           7.442   0.5409
2        1             2           9.672   0.5409
2        1             3           9.650   0.5409
2        2             1           7.515   0.5409
2        2             2          10.003   0.5409
2        2             3          10.164   0.5409
2        3             1           7.358   0.5409
2        3             2           9.555   0.5409
2        3             3           8.680   0.5409
3        1             1           8.410   0.5409
3        1             2           9.416   0.5409
3        1             3           9.573   0.5409
3        2             1           7.581   0.5409
3        2             2           9.204   0.5409
3        2             3           9.462   0.5409
3        3             1           9.342   0.5409
3        3             2           9.237   0.5409
3        3             3           9.208   0.5409
```

pH Day 4

```
Analysis of Variance for pH_4, using Adjusted SS for Tests

Source                          DF   Seq SS   Adj SS   Adj MS      F      P
Blocks                           1   0.1239   0.1239   0.1239   0.23  0.638
Top Soil                         2   1.9577   1.9577   0.9788   1.79  0.187
TS/CAA Ratio                     2   0.0862   0.0862   0.0431   0.08  0.925
Sub Soil                         2  23.2651  23.2651  11.6326  21.23  0.000
Top Soil*TS/CAA Ratio            4   8.3994   8.3994   2.0998   3.83  0.014
Top Soil*Sub Soil                4   0.4966   0.4966   0.1241   0.23  0.921
TS/CAA Ratio*Sub Soil            4   5.9113   5.9113   1.4778   2.70  0.053
Top Soil*TS/CAA Ratio*Sub Soil   8   2.0032   2.0032   0.2504   0.46  0.875
Error                           26  14.2447  14.2447   0.5479
Total                           53  56.4881


Least Squares Means for pH_4

Top Soil                          Mean  SE Mean
1                                8.964   0.1745
2                                8.862   0.1745
3                                9.308   0.1745
TS/CAA Ratio
1                                8.997   0.1745
2                                9.095   0.1745
3                                9.043   0.1745
Sub Soil
1                                8.135   0.1745
2                                9.342   0.1745
3                                9.658   0.1745
Top Soil*TS/CAA Ratio
1        1                       9.014   0.3022
1        2                       8.664   0.3022
1        3                       9.215   0.3022
2        1                       8.848   0.3022
2        2                       9.567   0.3022
2        3                       8.172   0.3022
3        1                       9.128   0.3022
3        2                       9.053   0.3022
3        3                       9.742   0.3022
Top Soil*Sub Soil
1        1                       8.021   0.3022
1        2                       9.120   0.3022
1        3                       9.752   0.3022
2        1                       7.976   0.3022
2        2                       9.192   0.3022
2        3                       9.419   0.3022
3        1                       8.406   0.3022
3        2                       9.715   0.3022
3        3                       9.802   0.3022
TS/CAA Ratio*Sub Soil
1            1                   7.624   0.3022
1            2                   9.861   0.3022
1            3                   9.505   0.3022
2            1                   8.257   0.3022
2            2                   9.037   0.3022
2            3                   9.989   0.3022
3            1                   8.523   0.3022
3            2                   9.129   0.3022
3            3                   9.478   0.3022
Top Soil*TS/CAA Ratio*Sub Soil
```

```
1        1             1           7.620   0.5234
1        1             2           9.999   0.5234
1        1             3           9.421   0.5234
1        2             1           7.883   0.5234
1        2             2           8.019   0.5234
1        2             3          10.090   0.5234
1        3             1           8.560   0.5234
1        3             2           9.341   0.5234
1        3             3           9.745   0.5234
2        1             1           7.621   0.5234
2        1             2           9.549   0.5234
2        1             3           9.375   0.5234
2        2             1           8.794   0.5234
2        2             2           9.726   0.5234
2        2             3          10.180   0.5234
2        3             1           7.514   0.5234
2        3             2           8.302   0.5234
2        3             3           8.701   0.5234
3        1             1           7.630   0.5234
3        1             2          10.034   0.5234
3        1             3           9.719   0.5234
3        2             1           8.094   0.5234
3        2             2           9.367   0.5234
3        2             3           9.697   0.5234
3        3             1           9.494   0.5234
3        3             2           9.743   0.5234
3        3             3           9.988   0.5234
```

pH Day 5

```
Analysis of Variance for pH_5, using Adjusted SS for Tests

Source                           DF   Seq SS   Adj SS  Adj MS      F      P
Blocks                            1   0.0019   0.0019  0.0019   0.00  0.954
Top Soil                          2   2.1143   2.1143  1.0571   1.89  0.171
TS/CAA Ratio                      2   0.2089   0.2089  0.1044   0.19  0.831
Sub Soil                          2  18.9191  18.9191  9.4596  16.94  0.000
Top Soil*TS/CAA Ratio             4   1.4382   1.4382  0.3595   0.64  0.636
Top Soil*Sub Soil                 4   1.2282   1.2282  0.3071   0.55  0.701
TS/CAA Ratio*Sub Soil             4   1.9909   1.9909  0.4977   0.89  0.483
Top Soil*TS/CAA Ratio*Sub Soil    8   1.1592   1.1592  0.1449   0.26  0.974
Error                            26  14.5219  14.5219  0.5585
Total                            53  41.5824



Least Squares Means for pH_5

Top Soil                          Mean  SE Mean
1                                9.012   0.1762
2                                8.724   0.1762
3                                9.205   0.1762
TS/CAA Ratio
1                                8.953   0.1762
2                                8.921   0.1762
3                                9.066   0.1762
Sub Soil
1                                8.148   0.1762
2                                9.314   0.1762
3                                9.478   0.1762
Top Soil*TS/CAA Ratio
1        1                       9.133   0.3051
1        2                       8.701   0.3051
1        3                       9.201   0.3051
2        1                       8.742   0.3051
2        2                       8.846   0.3051
2        3                       8.583   0.3051
3        1                       8.985   0.3051
3        2                       9.216   0.3051
3        3                       9.414   0.3051
Top Soil*Sub Soil
1        1                       8.148   0.3051
1        2                       9.217   0.3051
1        3                       9.670   0.3051
2        1                       7.693   0.3051
2        2                       9.240   0.3051
2        3                       9.238   0.3051
3        1                       8.605   0.3051
3        2                       9.485   0.3051
3        3                       9.526   0.3051
TS/CAA Ratio*Sub Soil
1            1                   8.066   0.3051
1            2                   9.392   0.3051
1            3                   9.401   0.3051
2            1                   7.898   0.3051
2            2                   9.110   0.3051
2            3                   9.755   0.3051
3            1                   8.481   0.3051
3            2                   9.440   0.3051
3            3                   9.278   0.3051
```

```
Top Soil*TS/CAA Ratio*Sub Soil
1        1             1         8.261   0.5285
1        1             2         9.575   0.5285
1        1             3         9.561   0.5285
1        2             1         7.747   0.5285
1        2             2         8.483   0.5285
1        2             3         9.873   0.5285
1        3             1         8.437   0.5285
1        3             2         9.592   0.5285
1        3             3         9.576   0.5285
2        1             1         7.834   0.5285
2        1             2         9.279   0.5285
2        1             3         9.114   0.5285
2        2             1         7.407   0.5285
2        2             2         9.435   0.5285
2        2             3         9.696   0.5285
2        3             1         7.837   0.5285
2        3             2         9.007   0.5285
2        3             3         8.904   0.5285
3        1             1         8.105   0.5285
3        1             2         9.323   0.5285
3        1             3         9.528   0.5285
3        2             1         8.540   0.5285
3        2             2         9.411   0.5285
3        2             3         9.697   0.5285
3        3             1         9.170   0.5285
3        3             2         9.720   0.5285
3        3             3         9.353   0.5285
```

pH Day 6

```
Analysis of Variance for pH_Day 6, using Adjusted SS for Tests

Source                          DF   Seq SS   Adj SS  Adj MS      F      P
Blocks                           1   0.1636   0.1636  0.1636   0.27  0.610
Top Soil                         2   1.0493   1.0493  0.5246   0.85  0.437
TS/CAA Ratio                     2   0.1908   0.1908  0.0954   0.16  0.857
Sub Soil                         2  16.2752  16.2752  8.1376  13.24  0.000
Top Soil*TS/CAA Ratio            4   1.0441   1.0441  0.2610   0.42  0.789
Top Soil*Sub Soil                4   1.9253   1.9253  0.4813   0.78  0.546
TS/CAA Ratio*Sub Soil            4   2.8168   2.8168  0.7042   1.15  0.357
Top Soil*TS/CAA Ratio*Sub Soil   8   6.2481   6.2481  0.7810   1.27  0.301
Error                           26  15.9807  15.9807  0.6146
Total                           53  45.6937


Least Squares Means for pH_Day 6

Top Soil                          Mean  SE Mean
1                                8.790   0.1848
2                                8.886   0.1848
3                                9.122   0.1848
TS/CAA Ratio
1                                8.939   0.1848
2                                9.002   0.1848
3                                8.857   0.1848
Sub Soil
1                                8.179   0.1848
2                                9.149   0.1848
3                                9.470   0.1848
Top Soil*TS/CAA Ratio
1        1                       8.862   0.3201
1        2                       8.699   0.3201
1        3                       8.810   0.3201
2        1                       8.904   0.3201
2        2                       9.178   0.3201
2        3                       8.575   0.3201
3        1                       9.050   0.3201
3        2                       9.130   0.3201
3        3                       9.187   0.3201

Top Soil*Sub Soil
1        1                       7.809   0.3201
1        2                       8.871   0.3201
1        3                       9.690   0.3201
2        1                       8.253   0.3201
2        2                       9.235   0.3201
2        3                       9.170   0.3201
3        1                       8.474   0.3201
3        2                       9.342   0.3201
3        3                       9.550   0.3201
TS/CAA Ratio*Sub Soil
1            1                   8.110   0.3201
1            2                   9.169   0.3201
1            3                   9.537   0.3201
2            1                   7.943   0.3201
2            2                   9.222   0.3201
2            3                   9.841   0.3201
3            1                   8.483   0.3201
3            2                   9.056   0.3201
3            3                   9.032   0.3201
```

```
Top Soil*TS/CAA Ratio*Sub Soil
1        1             1          7.515   0.5544
1        1             2          9.714   0.5544
1        1             3          9.358   0.5544
1        2             1          7.987   0.5544
1        2             2          8.188   0.5544
1        2             3          9.922   0.5544
1        3             1          7.927   0.5544
1        3             2          8.711   0.5544
1        3             3          9.791   0.5544
2        1             1          8.316   0.5544
2        1             2          8.844   0.5544
2        1             3          9.553   0.5544
2        2             1          8.069   0.5544
2        2             2          9.625   0.5544
2        2             3          9.841   0.5544
2        3             1          8.373   0.5544
2        3             2          9.235   0.5544
2        3             3          8.117   0.5544
3        1             1          8.500   0.5544
3        1             2          8.949   0.5544
3        1             3          9.701   0.5544
3        2             1          7.773   0.5544
3        2             2          9.854   0.5544
3        2             3          9.761   0.5544
3        3             1          9.149   0.5544
3        3             2          9.223   0.5544
3        3             3          9.187   0.5544
```

APPENDIX C.4 Hardness

Hardness Day 1

```
Analysis of Variance for Hardness_Day1, using Adjusted SS for Tests

Source                           DF   Seq SS  Adj SS  Adj MS     F      P
Blocks                            1   277092  277092  277092  8.25  0.008
Top Soil                          2    39752   39752   19876  0.59  0.560
TS/CAA Ratio                      2   223393  223393  111696  3.33  0.052
Sub Soil                          2   190273  190273   95136  2.83  0.077
Top Soil*TS/CAA Ratio             4   444540  444540  111135  3.31  0.026
Top Soil*Sub Soil                 4   207042  207042   51760  1.54  0.219
TS/CAA Ratio*Sub Soil             4    94924   94924   23731  0.71  0.594
Top Soil*TS/CAA Ratio*Sub Soil    8   483502  483502   60438  1.80  0.123
Error                            26   872756  872756   33568
Total                            53  2833275

Least Squares Means for Hardness_Day1

Top Soil                          Mean  SE Mean
1                                324.0    43.18
2                                380.9    43.18
3                                322.7    43.18
TS/CAA Ratio
1                                295.0    43.18
2                                433.4    43.18
3                                299.1    43.18
Sub Soil
1                                260.6    43.18
2                                367.8    43.18
3                                399.2    43.18
Top Soil*TS/CAA Ratio
1        1                       262.3    74.80
1        2                       267.7    74.80
1        3                       442.0    74.80
2        1                       356.3    74.80
2        2                       556.3    74.80
2        3                       230.0    74.80
3        1                       266.3    74.80
3        2                       476.3    74.80
3        3                       225.3    74.80
Top Soil*Sub Soil
1        1                       187.7    74.80
1        2                       335.0    74.80
1        3                       449.3    74.80
2        1                       248.7    74.80
2        2                       486.3    74.80
2        3                       407.7    74.80
3        1                       345.3    74.80
3        2                       282.0    74.80
3        3                       340.7    74.80
TS/CAA Ratio*Sub Soil
1            1                   167.7    74.80
1            2                   297.3    74.80
1            3                   420.0    74.80
2            1                   401.0    74.80
2            2                   430.3    74.80
2            3                   469.0    74.80
3            1                   213.0    74.80
```

```
3            2                  375.6    74.80
3            3                  308.7    74.80
Top Soil*TS/CAA Ratio*Sub Soil
1        1            1         102.0   129.55
1        1            2         234.0   129.55
1        1            3         451.0   129.55
1        2            1         232.0   129.55
1        2            2         140.0   129.55
1        2            3         431.0   129.55
1        3            1         229.0   129.55
1        3            2         631.0   129.55
1        3            3         466.0   129.55
2        1            1         199.0   129.55
2        1            2         411.0   129.55
2        1            3         459.0   129.55
2        2            1         292.0   129.55
2        2            2         857.0   129.55
2        2            3         520.0   129.55
2        3            1         255.0   129.55
2        3            2         190.9   129.55
2        3            3         244.0   129.55
3        1            1         202.0   129.55
3        1            2         247.0   129.55
3        1            3         350.0   129.55
3        2            1         679.0   129.55
3        2            2         294.0   129.55
3        2            3         456.0   129.55
3        3            1         155.0   129.55
3        3            2         305.0   129.55
3        3            3         216.0   129.55
```

Hardness Day 2

```
Analysis of Variance for Hardness_Day2, using Adjusted SS for Tests

Source                          DF   Seq SS   Adj SS  Adj MS     F      P
Blocks                           1      0.0      0.0     0.0  0.00  0.999
Top Soil                         2   1528.7   1528.7   764.3  0.84  0.444
TS/CAA Ratio                     2   8613.5   8613.5  4306.7  4.72  0.018
Sub Soil                         2   8237.3   8237.3  4118.7  4.52  0.021
Top Soil*TS/CAA Ratio            4   6146.2   6146.2  1536.5  1.69  0.184
Top Soil*Sub Soil                4   4058.7   4058.7  1014.7  1.11  0.372
TS/CAA Ratio*Sub Soil            4   1424.5   1424.5   356.1  0.39  0.813
Top Soil*TS/CAA Ratio*Sub Soil   8   8515.9   8515.9  1064.5  1.17  0.355
Error                           26  23705.6  23705.6   911.8
Total                           53  62230.4



Least Squares Means for Hardness_Day2

Top Soil                          Mean  SE Mean
1                                89.43    7.117
2                                89.11    7.117
3                               100.56    7.117
TS/CAA Ratio
1                                84.78    7.117
2                               110.88    7.117
3                                83.44    7.117
Sub Soil
1                                80.10    7.117
2                                89.33    7.117
3                               109.67    7.117
Top Soil*TS/CAA Ratio
1        1                       85.67   12.327
1        2                       93.63   12.327
1        3                       89.00   12.327
2        1                       68.33   12.327
2        2                      110.67   12.327
2        3                       88.33   12.327
3        1                      100.33   12.327
3        2                      128.33   12.327
3        3                       73.00   12.327
Top Soil*Sub Soil
1        1                       92.63   12.327
1        2                       72.33   12.327
1        3                      103.33   12.327
2        1                       68.00   12.327
2        2                       93.33   12.327
2        3                      106.00   12.327
3        1                       79.67   12.327
3        2                      102.33   12.327
3        3                      119.67   12.327
TS/CAA Ratio*Sub Soil
1            1                   81.00   12.327
1            2                   77.00   12.327
1            3                   96.33   12.327
2            1                   89.63   12.327
2            2                  112.33   12.327
2            3                  130.67   12.327
3            1                   69.67   12.327
3            2                   78.67   12.327
3            3                  102.00   12.327
```

```
Top Soil*TS/CAA Ratio*Sub Soil
1        1            1         114.00   21.351
1        1            2          69.00   21.351
1        1            3          74.00   21.351
1        2            1          75.90   21.351
1        2            2          72.00   21.351
1        2            3         133.00   21.351
1        3            1          88.00   21.351
1        3            2          76.00   21.351
1        3            3         103.00   21.351
2        1            1          62.00   21.351
2        1            2          68.00   21.351
2        1            3          75.00   21.351
2        2            1          77.00   21.351
2        2            2         135.00   21.351
2        2            3         120.00   21.351
2        3            1          65.00   21.351
2        3            2          77.00   21.351
2        3            3         123.00   21.351
3        1            1          67.00   21.351
3        1            2          94.00   21.351
3        1            3         140.00   21.351
3        2            1         116.00   21.351
3        2            2         130.00   21.351
3        2            3         139.00   21.351
3        3            1          56.00   21.351
3        3            2          83.00   21.351
3        3            3          80.00   21.351
```

Hardness Day 3

```
Analysis of Variance for Hardness_Day3, using Adjusted SS for Tests

Source                           DF   Seq SS   Adj SS  Adj MS     F      P
Blocks                            1    785.9    785.9   785.9  1.57  0.222
Top Soil                          2    515.1    515.1   257.6  0.51  0.604
TS/CAA Ratio                      2   4732.0   4732.0  2366.0  4.72  0.018
Sub Soil                          2   2299.1   2299.1  1149.6  2.29  0.121
Top Soil*TS/CAA Ratio             4   2588.9   2588.9   647.2  1.29  0.299
Top Soil*Sub Soil                 4   4303.1   4303.1  1075.8  2.14  0.104
TS/CAA Ratio*Sub Soil             4    791.6    791.6   197.9  0.39  0.811
Top Soil*TS/CAA Ratio*Sub Soil    8   5883.6   5883.6   735.4  1.47  0.217
Error                            26  13040.1  13040.1   501.5
Total                            53  34939.3


Least Squares Means for Hardness_Day3

Top Soil                           Mean  SE Mean
1                                 75.33    5.279
2                                 72.78    5.279
3                                 80.22    5.279
TS/CAA Ratio
1                                 73.11    5.279
2                                 88.78    5.279
3                                 66.44    5.279
Sub Soil
1                                 85.33    5.279
2                                 71.78    5.279
3                                 71.22    5.279
Top Soil*TS/CAA Ratio
1        1                        74.67    9.143
1        2                        78.67    9.143
1        3                        72.67    9.143
2        1                        70.33    9.143
2        2                        82.00    9.143
2        3                        66.00    9.143
3        1                        74.33    9.143
3        2                       105.67    9.143
3        3                        60.67    9.143
Top Soil*Sub Soil
1        1                        97.00    9.143
1        2                        55.33    9.143
1        3                        73.67    9.143
2        1                        70.00    9.143
2        2                        78.67    9.143
2        3                        69.67    9.143
3        1                        89.00    9.143
3        2                        81.33    9.143
3        3                        70.33    9.143
TS/CAA Ratio*Sub Soil
1            1                    88.33    9.143
1            2                    62.00    9.143
1            3                    69.00    9.143
2            1                    93.67    9.143
2            2                    89.33    9.143
2            3                    83.33    9.143
3            1                    74.00    9.143
3            2                    64.00    9.143
```

```
3            3                   61.33    9.143
Top Soil*TS/CAA Ratio*Sub Soil
1        1            1         111.00   15.836
1        1            2          55.00   15.836
1        1            3          58.00   15.836
1        2            1          82.00   15.836
1        2            2          52.00   15.836
1        2            3         102.00   15.836
1        3            1          98.00   15.836
1        3            2          59.00   15.836
1        3            3          61.00   15.836
2        1            1          67.00   15.836
2        1            2          70.00   15.836
2        1            3          74.00   15.836
2        2            1          74.00   15.836
2        2            2          97.00   15.836
2        2            3          75.00   15.836
2        3            1          69.00   15.836
2        3            2          69.00   15.836
2        3            3          60.00   15.836
3        1            1          87.00   15.836
3        1            2          61.00   15.836
3        1            3          75.00   15.836
3        2            1         125.00   15.836
3        2            2         119.00   15.836
3        2            3          73.00   15.836
3        3            1          55.00   15.836
3        3            2          64.00   15.836
3        3            3          63.00   15.836
```

Hardness Day 4

```
Analysis of Variance for Hardness_Day4, using Adjusted SS for Tests

Source                           DF   Seq SS  Adj SS  Adj MS     F      P
Blocks                            1     90.7    90.7    90.7  0.36  0.556
Top Soil                          2   1308.2  1308.2   654.1  2.57  0.096
TS/CAA Ratio                      2   2244.3  2244.3  1122.1  4.40  0.023
Sub Soil                          2    917.0   917.0   458.5  1.80  0.185
Top Soil*TS/CAA Ratio             4   2049.1  2049.1   512.3  2.01  0.122
Top Soil*Sub Soil                 4   5159.4  5159.4  1289.9  5.06  0.004
TS/CAA Ratio*Sub Soil             4   2720.8  2720.8   680.2  2.67  0.055
Top Soil*TS/CAA Ratio*Sub Soil    8   5032.8  5032.8   629.1  2.47  0.039
Error                            26   6623.7  6623.7   254.8
Total                            53  26146.0



Least Squares Means for Hardness_Day4

Top Soil                           Mean  SE Mean
1                                 68.22    3.762
2                                 56.17    3.762
3                                 62.30    3.762
TS/CAA Ratio
1                                 64.51    3.762
2                                 68.73    3.762
3                                 53.44    3.762
Sub Soil
1                                 68.06    3.762
2                                 59.44    3.762
3                                 59.19    3.762
Top Soil*TS/CAA Ratio
1        1                        82.00    6.516
1        2                        71.67    6.516
1        3                        51.00    6.516
2        1                        50.00    6.516
2        2                        65.17    6.516
2        3                        53.33    6.516
3        1                        61.53    6.516
3        2                        69.37    6.516
3        3                        56.00    6.516
Top Soil*Sub Soil
1        1                        92.67    6.516
1        2                        51.33    6.516
1        3                        60.67    6.516
2        1                        53.33    6.516
2        2                        61.67    6.516
2        3                        53.50    6.516
3        1                        58.17    6.516
3        2                        65.33    6.516
3        3                        63.40    6.516
TS/CAA Ratio*Sub Soil
1            1                    84.00    6.516
1            2                    54.00    6.516
1            3                    55.53    6.516
2            1                    66.50    6.516
2            2                    73.00    6.516
2            3                    66.70    6.516
3            1                    53.67    6.516
3            2                    51.33    6.516
3            3                    55.33    6.516
```

```
Top Soil*TS/CAA Ratio*Sub Soil
1        1            1         138.00   11.286
1        1            2          57.00   11.286
1        1            3          51.00   11.286
1        2            1          80.00   11.286
1        2            2          52.00   11.286
1        2            3          83.00   11.286
1        3            1          60.00   11.286
1        3            2          45.00   11.286
1        3            3          48.00   11.286
2        1            1          45.00   11.286
2        1            2          52.00   11.286
2        1            3          53.00   11.286
2        2            1          62.00   11.286
2        2            2          74.00   11.286
2        2            3          59.50   11.286
2        3            1          53.00   11.286
2        3            2          59.00   11.286
2        3            3          48.00   11.286
3        1            1          69.00   11.286
3        1            2          53.00   11.286
3        1            3          62.60   11.286
3        2            1          57.50   11.286
3        2            2          93.00   11.286
3        2            3          57.60   11.286
3        3            1          48.00   11.286
3        3            2          50.00   11.286
3        3            3          70.00   11.286
```

Hardness Day 5

```
Analysis of Variance for Hardness_Day5, using Adjusted SS for Tests

Source                           DF   Seq SS   Adj SS  Adj MS     F      P
Blocks                            1   1896.3   1896.3  1896.3  2.51  0.125
Top Soil                          2   4057.9   4057.9  2029.0  2.69  0.087
TS/CAA Ratio                      2   1795.4   1795.4   897.7  1.19  0.321
Sub Soil                          2   3373.6   3373.6  1686.8  2.23  0.127
Top Soil*TS/CAA Ratio             4   1671.2   1671.2   417.8  0.55  0.699
Top Soil*Sub Soil                 4    323.6    323.6    80.9  0.11  0.979
TS/CAA Ratio*Sub Soil             4   5027.5   5027.5  1256.9  1.66  0.189
Top Soil*TS/CAA Ratio*Sub Soil    8  14050.6  14050.6  1756.3  2.32  0.050
Error                            26  19646.7  19646.7   755.6
Total                            53  51842.8



Least Squares Means for Hardness_Day5

Top Soil                            Mean  SE Mean
1                                  68.67    6.479
2                                  48.11    6.479
3                                  53.78    6.479
TS/CAA Ratio
1                                  49.17    6.479
2                                  63.06    6.479
3                                  58.33    6.479
Sub Soil
1                                  52.50    6.479
2                                  67.94    6.479
3                                  50.11    6.479
Top Soil*TS/CAA Ratio
1        1                         57.33   11.222
1        2                         70.67   11.222
1        3                         78.00   11.222
2        1                         40.17   11.222
2        2                         51.83   11.222
2        3                         52.33   11.222
3        1                         50.00   11.222
3        2                         66.67   11.222
3        3                         44.67   11.222
Top Soil*Sub Soil
1        1                         63.00   11.222
1        2                         79.67   11.222
1        3                         63.33   11.222
2        1                         44.83   11.222
2        2                         62.50   11.222
2        3                         37.00   11.222
3        1                         49.67   11.222
3        2                         61.67   11.222
3        3                         50.00   11.222
TS/CAA Ratio*Sub Soil
1            1                     47.17   11.222
1            2                     46.67   11.222
1            3                     53.67   11.222
2            1                     66.33   11.222
2            2                     70.83   11.222
2            3                     52.00   11.222
3            1                     44.00   11.222
3            2                     86.33   11.222
3            3                     44.67   11.222
```

```
Top Soil*TS/CAA Ratio*Sub Soil
1        1             1           63.00   19.438
1        1             2           43.00   19.438
1        1             3           66.00   19.438
1        2             1           85.00   19.438
1        2             2           47.00   19.438
1        2             3           80.00   19.438
1        3             1           41.00   19.438
1        3             2          149.00   19.438
1        3             3           44.00   19.438
2        1             1           32.50   19.438
2        1             2           52.00   19.438
2        1             3           36.00   19.438
2        2             1           55.00   19.438
2        2             2           71.50   19.438
2        2             3           29.00   19.438
2        3             1           47.00   19.438
2        3             2           64.00   19.438
2        3             3           46.00   19.438
3        1             1           46.00   19.438
3        1             2           45.00   19.438
3        1             3           59.00   19.438
3        2             1           59.00   19.438
3        2             2           94.00   19.438
3        2             3           47.00   19.438
3        3             1           44.00   19.438
3        3             2           46.00   19.438
3        3             3           44.00   19.438
```

Hardness Day 6

```
Analysis of Variance for Hardness_Day 6, using Adjusted SS for Tests

Source                           DF   Seq SS   Adj SS  Adj MS     F      P
Blocks                            1    581.5    581.5   581.5  1.53  0.227
Top Soil                          2   1297.6   1297.6   648.8  1.71  0.201
TS/CAA Ratio                      2   1874.9   1874.9   937.5  2.47  0.104
Sub Soil                          2   1859.2   1859.2   929.6  2.45  0.106
Top Soil*TS/CAA Ratio             4   1381.2   1381.2   345.3  0.91  0.473
Top Soil*Sub Soil                 4    560.5    560.5   140.1  0.37  0.829
TS/CAA Ratio*Sub Soil             4   2665.2   2665.2   666.3  1.75  0.169
Top Soil*TS/CAA Ratio*Sub Soil    8  10701.4  10701.4  1337.7  3.52  0.007
Error                            26   9879.0   9879.0   380.0
Total                            53  30800.6

Least Squares Means for Hardness_Day 6

Top Soil                           Mean  SE Mean

1                                 56.01    4.594
2                                 44.06    4.594
3                                 51.00    4.594
TS/CAA Ratio
1                                 43.12    4.594
2                                 57.56    4.594
3                                 50.39    4.594
Sub Soil
1                                 48.34    4.594
2                                 58.33    4.594
3                                 44.39    4.594
Top Soil*TS/CAA Ratio
1        1                        52.70    7.958
1        2                        58.00    7.958
1        3                        57.33    7.958
2        1                        31.33    7.958
2        2                        50.00    7.958
2        3                        50.83    7.958
3        1                        45.33    7.958
3        2                        64.67    7.958
3        3                        43.00    7.958
Top Soil*Sub Soil
1        1                        53.37    7.958
1        2                        64.00    7.958
1        3                        50.67    7.958
2        1                        47.33    7.958
2        2                        51.67    7.958
2        3                        33.17    7.958
3        1                        44.33    7.958
3        2                        59.33    7.958
3        3                        49.33    7.958
TS/CAA Ratio*Sub Soil
1            1                    45.03    7.958
1            2                    40.00    7.958
1            3                    44.33    7.958
2            1                    55.67    7.958
2            2                    64.00    7.958
2            3                    53.00    7.958
3            1                    44.33    7.958
3            2                    71.00    7.958
3            3                    35.83    7.958
```

```
Top Soil*TS/CAA Ratio*Sub Soil
1        1            1           66.10   13.783
1        1            2           50.00   13.783
1        1            3           42.00   13.783
1        2            1           52.00   13.783
1        2            2           36.00   13.783
1        2            3           86.00   13.783
1        3            1           42.00   13.783
1        3            2          106.00   13.783
1        3            3           24.00   13.783
2        1            1           29.00   13.783
2        1            2           28.00   13.783
2        1            3           37.00   13.783
2        2            1           62.00   13.783
2        2            2           65.00   13.783
2        2            3           23.00   13.783
2        3            1           51.00   13.783
2        3            2           62.00   13.783
2        3            3           39.50   13.783
3        1            1           40.00   13.783
3        1            2           42.00   13.783
3        1            3           54.00   13.783
3        2            1           53.00   13.783
3        2            2           91.00   13.783
3        2            3           50.00   13.783
3        3            1           40.00   13.783
3        3            2           45.00   13.783
3        3            3           44.00   13.783
```

APPENDIX D. PLOTS FOR TERNARY COMBINATIONS

Plots for water quality parameters monitored with all 27 ternary combinations were included in Figures 25 to 28. Values plotted represent the water quality data from water samples collected after the port at subsoil section. Each plot includes average values for each ternary combination and data collected from all sampling days.

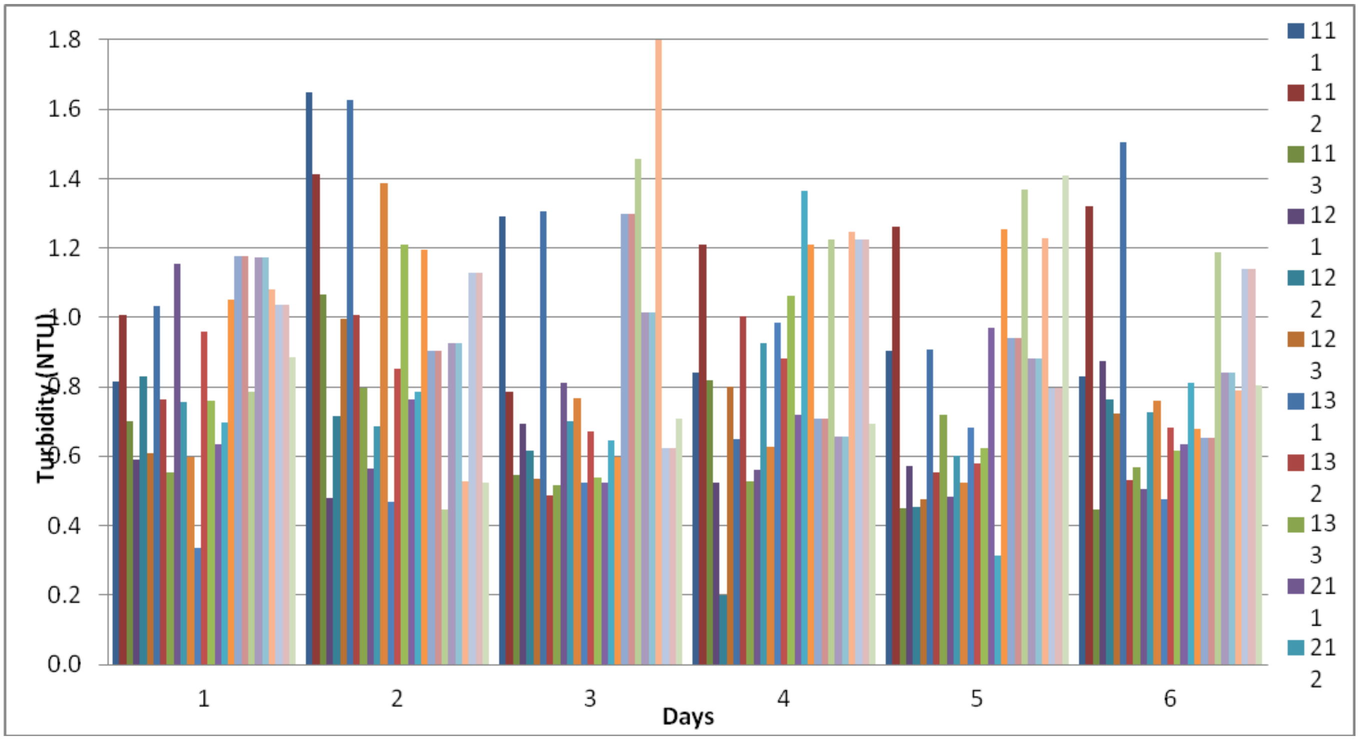

Figure 62. Mean values for turbidity for all ternary combinations

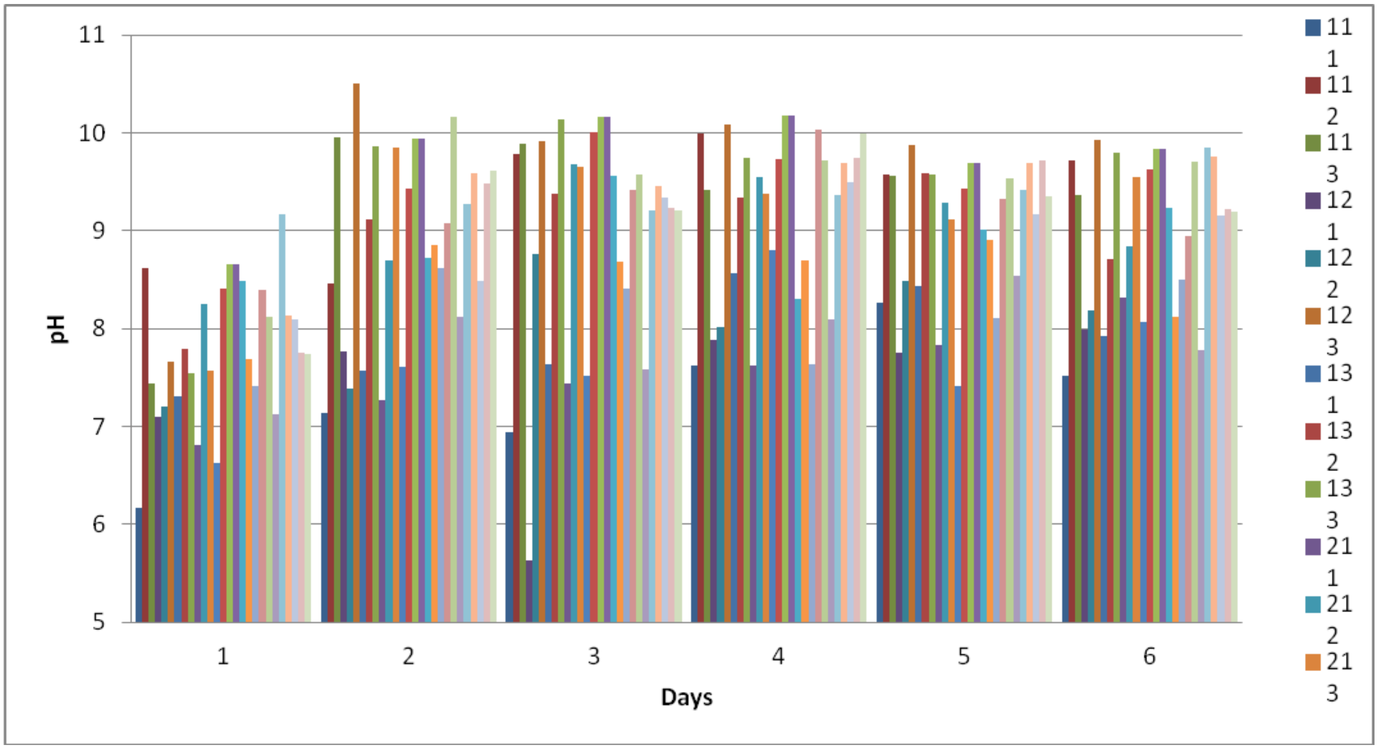

Figure 63. Mean values for pH for all ternary combinations

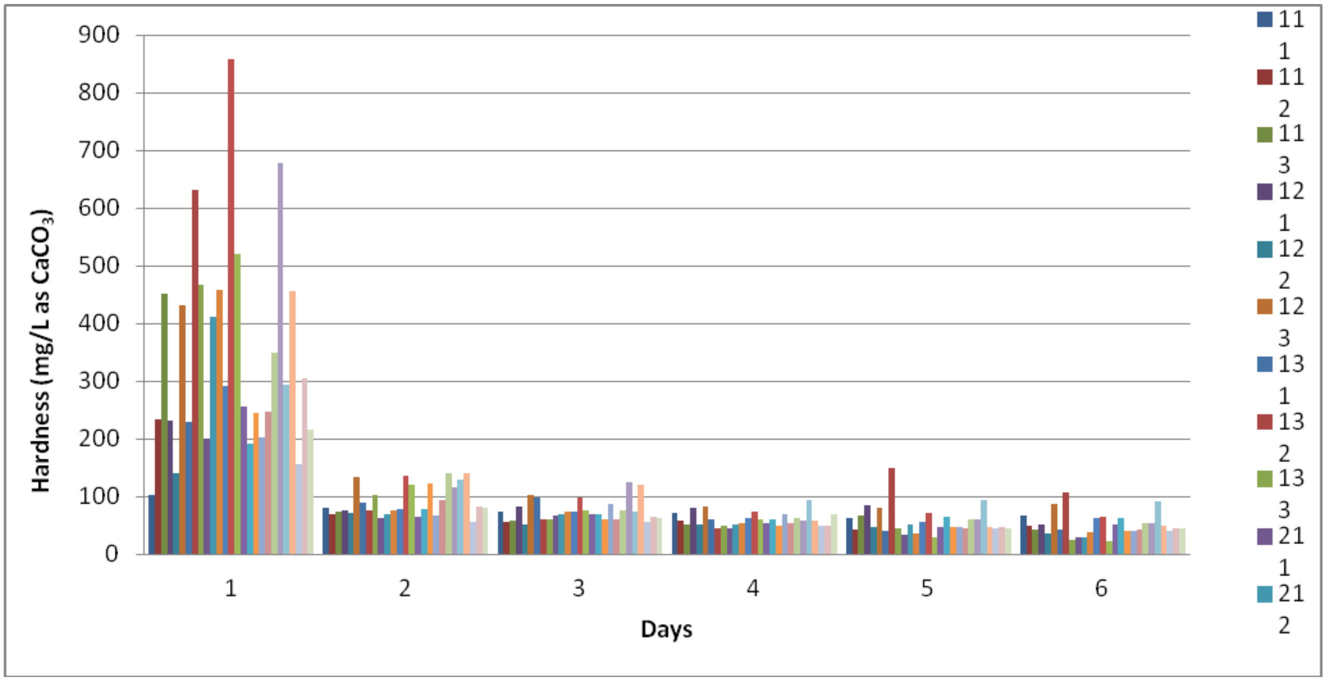

Figure 64. Mean values for hardness for all ternary combinations