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MANAGING SODIC SOILS: THE ROLE OF ORGANIC AMENDMENTS

BY

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DECLARATION

CANDIDATE'S DECLARATION

I hereby declare that this thesis is the result of my own original research and that no part of it has been presented for another degree in this University or elsewhere.

.... Date 04-04-17

Daniel Kofi Sappor

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SUPERVISORS' DECLARATION

We hereby declare that the preparation and presentation of the thesis were supervised in accordance with the guidelines on supervision of thesis laid down by the University of Cape Coast.

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ABSTRACT

A study was conducted to evaluate the potential of organic amendments in managing sodic soils for crop production. Soils sampled from Cape Coast industrial area, opposite Ameen Sangari Industries Limited, were used in the study. In preliminary studies, wastewater discharged from the soap making industry contained pH of 11.2, EC of 4.37 dS m^{-1} and ESP of 60.4. Soil used in the study had the following properties: pH of 8.7, EC of 3.7dS m^{-1} and ESP of 18.0. A pot experiment was then conducted in which saw dust biochar (SDB), palm fiber biochar (PFB), poultry manure biochar (PMB) and poultry manure (PM) were applied to the sodic soil. Gypsum amendment and a control (soil only) were included for the purpose of comparing results. All amendments were applied at the rate of 4.78 t ha^{-1}. Amended soils were incubated at room temperature. The incubated soil was weekly sampled for 6-weeks for laboratory analysis. From the results, organic based amendments reduced soil pH and electrical conductivity (EC). The same amendments significantly ($P = 0.05$) increased soil Ca^{+2} and Mg^{+2}, with SDB registering the highest increase. Increases soil Na^{+} and K^{+} were marginal and statistically insignificant ($P = 0.05$). PFB recorded the highest CEC at week 6. SDB and PFB reduced soil sodicity below the minimum threshold of ESP 15. SDB recorded the highest OC increase at week 6. PMB released the highest amount of available P. Insignificant ($P = 0.05$) increases were observed for soil NH_4^{+}-N and NO_3^{-}-N. SDB and PFB recorded 90 % and 80 % maize seed germination and also, 10.1 t ha^{-1} and 8.7 t ha^{-1} dry matter yields respectively. No maize seed however germinated in the control and all other amendments.

KEY WORDS

Biochar

Dry matter yield

Exchangeable sodium percentage

Industrial wastewater

Seed germination test

Sodic soils

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DEDICATION

To my wife and children

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CHAPTER ONE

GENERAL INTRODUCTION

1.1 Background of the study

Soil sodicity is one of the extreme soil conditions that hinder the usefulness of soil for crop production. It is basically caused by a high accumulation of sodium at the root zone of plants, making it difficult for roots to access the more important soil nutrients required for plant growth and yield (Waskom, Bauder, Davis & Cardon, 2010). Sodium is a mineral required by plants only in small quantities to help concentrate carbon dioxide and promote metabolism (Waskom, Bauder, Davis & Cardon, 2010). Soil sodium originates from breakdown of rock minerals, application of fertilizers and pesticides; groundwater run-offs as in coastal regions, salty ambient moisture and leaching from shorelines, use of poor quality irrigation water among others (Rogobete, Tarau, Dicu & Bertici, 2013). A sodic soil (sodium-affected soil) is differentiated from saline soils (salt affected soils) by the measure of the presence of sodium and soluble salts. A sodic soil has exchangeable sodium (Na^+) percentage exceeding 15 (ESP 15) with electrical conductivity of the saturation extract bellow 4 dS m^{-1}. This relatively low electrical conductivity of such sodic soils is an indication of the presence of low concentration of soluble salt. The pH of sodic soils usually ranges from 8.2 to 10.5 (Nguyen, 2012). Such high pH values result from the hydrolysis of adsorbed Na^+ in the absence of electrolytes in the soil solution. Physical, chemical and biological degradation of soil results from soil sodicity as well as other extreme soil conditions including soil acidity and alkalinity. These extreme soil conditions adversely impact on crop and pasture production, especially in the arid and semi arid regions of the world (Nguyen, 2012; Rogobete, Tarau, Dicu & Bertici, 2013).

Siyal *et al*., (2013) identified slaking, swelling and dispersion of clay, surface crusting and hard pan setting as the physical processes which destroy the structure of sodic soils. Soil properties which are negatively affected by such soil processes include water and air movement, water holding capacity, root penetration, seedling emergence, runoff and erosion as well as tillage and sowing operations (Srivastava, Gupta, Panday, Singh & Tewan, 2014).

Baric, Kanbolat, Yanik and Rafik (2011); Rogobete, Tarau and Grozav (2011) also indicated that sodium affected soils deteriorate as a result of undesirable changes in soil solution and on the colloidal surfaces including deficiency in several nutrients to high levels of sodium which have a direct impact on the activities of plant roots, soil microbial activity and also on crop growth and yield.

1.2 Justification of the study

The University of Cape Coast land, opposite the Cape Coast Industrial Area, was adopted for this study. This was because a soap making factory located across the road had continuously discharged wastewater on to the land for 43-years. Using sodium hydroxide (NaOH) during the soap making, it was suspected that high levels of exchangeable sodium could be present in the effluent discharged onto the land. The land therefore could no longer sustain the growth of any vegetation and hence remains virtually bare all year round. Farmers who cropped on the land eventually had to stop because yields dwindled to very uneconomic levels. Land was a scarce resource and could not be left wasted. The need to reclaim this land for food crop production was therefore important.

Over the years, researchers had been using different approaches to reclaim sodic soils. These approaches included chemical amendments, phytoremediation (cropping sodium-tolerant plants), land tillage operations, leaching and various combinations of these. Among these, chemicals amendment was the most extensively used (Ali, 2011; Allotey, Asiamah & Nyamekye, 2008). A number of tillage operations such as deep ploughing and sub-soiling had also been used to break up shallow dense sodic clay pans and nitric horizons that occurred within 40 cm depth of soil (Ghafoor, Murtaza, Rehman & Sabir, 2012). The choices of these methods for reclaiming sodic soils were limited by a number of challenges. These included cost and availability of inputs, the level to which sodicity should be reduced per target test crop, the depth of soil that needs to be ameliorated for which crop, nutrient availability status of soil after sodium removal, long term sustainability of an ameliorated soil in terms of agriculture production, environmental implications of the amelioration methods, changes that amelioration would be expected to cause in market value of the land and the user-friendly nature of some of these conventional approaches. Recent research works advocated the use of organic amendments as a more effective means of managing sodium and salt affected soils. This argument stemmed from the fact that organic amendments would not only displace sodium from soil colloidal surface but also improve soil physical conditions for plant growth (Busscher, Novak & Ahmedna, 2011; Brinck & Frost, 2009; Abiven, Manaseri & Chenu, 2009). This assertion forms the basis for this research.

1.3 The Hypothesis

The hypothesis of this study states that: Organic amendments can reduce soil sodicity and restore fertility to sodium affected soils to enhance crop seed germination and crop yield better than the conventional application of gypsum.

1.4 General Objective

The general objective of this study is to determine whether organic amendments could be used to reclaim sodic soils.

1.5 Specific Objectives

The specific objectives of the study are as follows:

- To determine the suitability of effluent from the soap making factory in Cape Coast for use as irrigation water in crop production.
- Determine the impact of soap factory effluent on soil physicochemical properties after 43-year of discharge onto the land.
- Determine the physicochemical properties of prepared types of biochar and poultry manure for use as sodic soil amendments.
- Conduct a pot experiment to determine whether biochar and poultry manure can reduce exchangeable sodium percentage of sodic soil and enhance soil nutrients availability.
- Plant a sodium-sensitive crop on the amended soils and determine the rate of seed germination and dry matter yield.

CHAPTER TWO

LITERATURE REVIEW

2.1 Agricultural Importance of Sodic Soils

Srivastava, Gupta, Panday, Singh and Tewan (2014) postulated that the continuous increase in the human population of the world would eventually lead to the need to cultivate marginal lands for food and fiber production in order to meet human needs. This assertion was complemented by Worku (2015) when he projected that the cultivation of marginal lands for agricultural production would be much more common in the less-developed, arid and semi-arid countries as a result of soil and water quality degradation. Apart from the discharge of industrial effluent onto land, a number of major irrigation schemes have suffered problems of sodicity or salinity which reduced their agricultural productivity and sustainability. According to Singh and Singh (2013), sodic and saline soils occupy at least 20 % of irrigated lands of the world and the economic loss was estimated at $ 12 billion per year. Though no hard data exist, it is a common knowledge that large proportion of sodic and saline soils occur on lands belonging to small holder farmers. This situation poses serious economic threat to the very survival of such class of people.

Conventionally, sodic soil amelioration aims at displacing excess Na^+ from cation exchange sites of soil coloids and leaching out the displaced Na^+ in order to reduce soil sodicity to levels that permit seed emergence and high crop yield. The leaching out of displaced sodium cations, however, generates considerable amounts of saline-sodic drainage water which has negative off-site environmental impacts (Nadeem, Zahif, Naveed & Nawaz, 2013). Besides, leaching out soil sodium is also accompanied by leaching out valuable soil nutrients which could have been useful in crop production. The challenge therefore is how to establish sustainable and environmentally friendly methods of remediating sodic soils for crop production.

Even though every approach adopted to correct soil sodicity would have its own strength and weaknesses, the fact remains that sodic soils are valuable resources which cannot be neglected. Consequently, if the challenges of global food security are to be met, it is important to find ways to improve such soils to ensure that they support productive land use systems.

2.2 Characterization of Effluent from Soap Manufacturing Industries.

Effluent is an inevitable product of an industrial process. It was simply defined by Vimaldeep and Gitanjali (2014) as the wastewater (treated or untreated) that flows out of a treatment plant, sewer or industrial outfall. Effluent may vary in composition depending on the kind of industry or source of production (Omron & Maghraby, 2012). Depending on the source, effluent may contain essential soil nutrients and or toxic substances. The availability of macro and micro nutrients of effluent can increase soil fertility (Sou-Dakoure, 2013). On the other hand, toxic components of effluent can accumulate in soil (Rusan, Hinnawi & Rousan, 2007). The rate of accumulation of nutrients and toxic substances would, however, depend on the duration of exposure of soil to the effluent discharge (Vimaldeep &

Gitanjali, 2014). Production of soap and detergents result in effluent streams and several types of contaminants which are of special concern to the external environment. Synthetic surface active agents in high concentrations can be toxic to living organisms in the receiving medium. Effluents having high levels of nutrients such as nitrogen and phosphorus could be detrimental when discharged into aquatic medium because of their contribution to eutrophication. This, however, could be beneficial if the nutrient-rich effluent is discharged onto a farm land, provided other soil fertility parameters are right (Khurana, 2011). According to Okoye, Obidike and Nduka (2011), soap production leads to effluent with high alkalinity, high salt and high oxygen demand since strong acids and strong alkalies are used in the soap making processes. Accidental spills of raw materials also contribute to high oil and grease levels (Marium, 2013). Soil pH can be very high or very low in soap effluent (Lourenzi *et al*., 2011). In monitoring the quality of wastewater of soap and detergent plants therefore, the following parameters have been classified in literature as very important.

2.2.1 Biochemical oxygen demand (BOD)

Biochemical Oxygen Demand (BOD) is the measure of the oxygen consuming capabilities of organic matter (Arun & Kanjan, 2012). The BOD in itself does not cause harm to soil. Instead, it exerts an indirect effect on soil by depleting its oxygen content following the increase in microbial activities towards decomposing the organic matter (Bitalova & Schwarbauer, 2011). This depletion of oxygen creates an anaerobic condition in the soil (Ahmad, Bajahlan & Hammad, 2008). The continuous decomposition of organic matter under anaerobic conditions leads to the production of noxious gases such as hydrogen sulfide and methane. An effluent of high BOD therefore indicates the presence of decomposing organic matter and subsequent high bacteria counts which degrade its quality and potential uses (Arun & Kanjan, 2012).

2.2.2 Chemical oxygen demand (COD)

Chemical Oxygen Demand (COD) is a measure of the total oxidizable carbon in effluent and relates to the chemically-bound sources of oxygen of the effluent (Yerasi, 2013). Materials exerting COD are not readily biodegradable as is the case for long fatty acids from soap and detergent manufacturing industries (Arun & Kanjan, 2012). As a result, the chemical balance of a receiving medium (soil/land) is altered. Since COD is usually encountered coincidentally with BOD, the combined effect is highly harmful to soil and other receiving media. Chemical oxygen demand (COD) is therefore used as a primary parameter for characterizing effluent from industries because of the need for complete oxidation of oxidizable carbon in the effluent prior to its discharge to the external environment (Tekade, Mohabansi & Patil, 2011).

2.2.3 Total suspended solids (TSS)

Total suspended solids of an industrial effluent could be organic and inorganic. Organic fraction includes materials such as grease, oil, tar, animal and vegetable fats, various fibers, saw dust, hair, and the like. Inorganic components include sand, silt and clay (Ale, Jha & Belbase, 2008).

2.2.4 Oil and grease

Oil is a major raw material in soap making. Though some of the soap making industries depend on already extracted oil from other industries, most of such industries extract their own oil from palm fruits which is then used to manufacture the soap. Effluent from boiling the palm fruit is oil laden. This coupled with oil spills at various production stages (palm oil extraction, storage tanks bust and leakages, etc) enable good percentage of oil into effluent which finds its way into the external environment. Okoye, Obidike and Nduka (2011) estimated that 0.6 – 0.7 % of untreated palm oil mill effluent is basically oil. Besides, some industries fuel and service their vehicles on site. Spilled fuel and dirty oil enter factory effluent into external environment. When discharged onto land, oil and grease can close soil pores and reduce soil aeration and water infiltration. This could create anaerobic soil condition that hinders the activities of soil macro and micro organisms and slow down the rate of decomposition of soil organic matter. A long term effect of oil and grease, however, could be organic matter build-up especially in the soil which could help to improve the physical conditions of soil including aggregate stability, hydraulic conductivity, bulk density, nutrient retention among others (Sumithra, Ankalaias & Janardhana, 2013; Lui-Yen & Heynes, 2010; Khodabakhsh, 2013).

2.2.5 Effluent pH, acidity and alkalinity

Effluent pH, acidity and alkalinity are important quality parameters which must be monitored continually. This is because any acidic or alkaline spill or discharge could upset the normal regimen of soil (Su & Tin, 2014). The impact of industrial effluent discharge on soil pH is very important because soil pH greatly influences the availability of plant soil nutrients. It also regulates the activities of soil macro and micro organism. The discharge of industrial effluent with extreme pH (acidic or alkaline pH) on to agricultural land, therefore, remain an issue of serious concern (Lourenzi *et al*., 2011).

2.3 The Use of Industrial Effluent for Irrigation

Analysis of untreated effluents from some soap industries in the Aba-Abia State of Nigeria was conducted by Okoye, Obidike and Nduka (2011). They sampled water from up and down streams of Eziama-Eziukwu river into which three (3) different soap manufacturing industries discharged their effluent. These industries were Peterson Zochonis Industries Limited (PZ), International Equitable Association Limited (IEAL) and Unilever Brothers Soap Factories (UB). This research was carried because small holder farmers depended on water from this river to irrigate farms during the dry season. They observed that biological oxygen demand (BOD), chemical oxygen demand (COD), oil and grease (OG), sulphides, detergents, and total acidity were within acceptable limits of irrigation water. This was possible due to the dilution effect of the river between the raw factory effluent and the soil. Values obtained for nitrates, nitrite, chlorides, phosphates, hardness, dissolved solids, pH and electrical conductivity (EC), however, exceeded acceptable standards for irrigation water. Values for dissolved oxygen (DO) and turbidity (ntu) were also undesirable for irrigation water. From a similar study, Suo-Dakoure (2013); Omron and Maghraby, (2012); Ahmad, Manderia and Mandria (2012); Gouider (2010) further evaluated the impact of industrial effluent on soil properties of a farm land. Their observations and conclusions were that:

- Irrigation of agricultural lands with industrial wastewater resulted in higher crop yield than fresh water due to the supply of nutrients such as nitrogen, phosphorus and potassium.
- The practice also led to accumulation of sodium and bicarbonates, especially in the top soil, leading to soil pH increase to alkaline values, dramatic collapse of soil structure and pore network, soil compaction and poor water storage ability of soil.
- Effluent with high organic matter content helped sustain soil physical properties including aggregate stability, hydraulic conductivity, water infiltration and nutrient retention.
- Long-term use of industrial effluent as irrigation water for agricultural lands resulted in the build-up of undesirable metals in soil.

Eid, Elgala, Hassan and Ramadan (2008) also carried out an experiment on the effect of industrial effluents on soil chemical properties and faba bean growth. The faba bean was grown on soils irrigated with effluents from ceramic, paper and starch factories in Cairo-Egypt. At the end of 45 days period, effluent from the ceramics factory had increased soil pH from 7.5 to 9.86 and 10.12 in two different soils. Effluent from starch factory had the least effect by increasing soil pH from 7.5 to 7.62 and 7.93 for the two experimental soils respectively. On the average, electrical conductivity increased from 6 dS m^{-1} to 9 dS m^{-1} in the order of ceramics > paper > starch. Effluent from starch factory had the best impact on soil organic matter, followed by paper before ceramics. Improvement on total nitrogen ranged from 31 % to 74 %. The increase in phosphorus values ranged from 9 % to 39 % whilst that of potassium (K) ranged from 11 % to 65 %. The relative increase for iron ranged from 12 % to 67 %, Mn (4 % to 74 %); Zn (210 % to 486 %) and Cu (57 % to 316 %) respectively. The increment for lead (Pb) ranged from 49 % to 193 %, 14 % to 166 % for cadmium (Cd), 220 % to 1,200 % for cobalt (Co) and 162 % to 783 % for nickel (Ni). Most of the parameters measured from the application of starch effluent were within favourable limits but those of ceramic and paper exceeded permissible levels. The application of starch effluent yielded better vegetation of the test crop (faba beans) when compared to the outputs from ceramics and paper effluents. From their findings, it could be concluded that, it was safe to use untreated effluent from starch factory to irrigate crop lands but effluent from ceramic and paper industries must be necessarily treated before use.

2.4 The Impacts of Sodicity on Soil Physical Properties

The clay fraction of soil is an important component of soil matrix because of its charge properties. Its surface area per unit mass is large relative to those of sand and silt. According to Tanji and Wallender (2012), sodicity influences the clay microstructure of soil. Soil degradation mechanisms under sodic conditions proceed through different stages. Initially, dry aggregates are strong and the attractive forces between the clay particles are effective. Hydration reactions, however lead to the establishment of repulsive forces, which reduce the attraction between the clay particles. This mechanism leads to slaking and swelling while continuous hydration results in the liberation of the clay particles contained within aggregates which spontaneously disperse (Pushparaj & Thiyagarajan, 2016).

Slaking refers to the breakdown of macro-aggregates into micro-aggregates upon wetting (Narchuk & Rangasamy, 2011). This process reduces the number and size of large pores found on soil coloidal surface, thereby limiting the infiltration of rain or irrigation water (Patel & Dave, 2011). Dispersion is the release of individual clay platelets from soil aggregates which leads to the creation of unstable soil structure. Both slaking and dispersion have negative impacts on soil's hydraulic properties. Clay particles flocculate when divalent cations such as Ca^{2+} and Mg^{2+} are added through the application of amendments. The resultant osmotic effect causes the clay-water system to dehydrate, thereby reducing the distance separating the particles (Rengasamy, 2014). Improvements observed in the physical properties of sodic soils during amelioration process were, therefore attributed to an increase in the levels of divalent cations, both in the soil solution and on the exchange complex. Such an increase in divalent cations (mostly Ca^{2+} and Mg^{2+}) enhances soil aggregation and reduces crusting, thereby improving the soil's hydraulic properties (Rengasamy, 2014).

2.5 The Impact of Sodicity on Soil Chemical Properties

Sodic soils have relatively low electrical conductivity (EC_e), high exchangeable sodium percentage (ESP) and pH (Rengasamy, 2014). Sodic soils with high pH are generally deficient in plant nutrients; macronutrients such as nitrogen (N), phosphorus (P) and potassium (K) (Nadeem *et al*., 2013) and micro nutrients such as aluminum (Al), iron (Fe), Zinc (Zn), manganese (Mn) and cupper (Cu) (Lakhdar *et al*., 2009). They are also low in organic matter content due to the low inputs of plant biomass and high rates of losses (Worku & Bedadi, 2016). Srivastava, Gupta, Panday, Singh and Tewan (2014) observed that surface crust and sealing caused significant erosive losses of organic matter. They again noted that organic carbon and total nitrogen decreased due to increased soil sodicity which resulted from the use of sodic irrigation water. Worku (2015) also observed that increased dispersion of soil aggregates by sodicity exposed the inaccessible organic matter fixed in soil aggregates to stressed soil microbes and this stimulated faster decomposition of the organic matter. Carbon inputs are generally low in sodic soils due to the decline in vegetation growth as affected by toxicity of micronutrients, deficiency of macronutrients, osmotic stress and degraded soil structure (Wong, Dalal & Greene, 2009). Furthermore, Davis, Waskom and Bauder (2012) noted decreased carbon and nitrogen mineralization rates and enzyme activities at high sodicity levels. It was found in their studies that increased sodicity decreased nitrification rates ranging from 8 to 83 % and promoted ammonia losses through volatilization. Salinity and sodicity were also found to affect nitrification (Davis, Waskom & Bauder, 2012). Similarly, Negim and Mustafa (2016) found that increasing salinity and sodicity reduced nitrogen mineralization and increased gaseous NH_3 losses. The same Authors reported that increasing sodicity and salinity decreased both carbon and nitrogen losses in arid soils treated with organic amendments. Elsevior (2012) reported a decrease in carbon mineralization with increasing salinity but sodicity on the other hand, increased carbon decomposition due to solubilization of organic matter.

2.6 Effects of Sodicity on Soil Microbial Properties

Changes in soil chemistry due to soil sodicity negatively affect soil microbial and biochemical processes that are important for maintaining soil ecological functions (Dodd & Perez-Alfocea, 2012). Increasing sodicity and salinity limit microbial growth and activity by causing osmotic stress, dehydration and lysis of cells (Grover, Ali, Sandhya, Sasul & Venkateswarlu, 2011). In addition to sodium toxicity, accumulation of other ions such as chlorides, carbonates and bicarbonates to toxic levels, nutritional deficiencies like Ca^{2+}, loss of organic matter due to soil structure degradation, all contribute to reducing microbial populations and their activities in sodic soils (Paul, 2012). In a study conducted on a wide range of soils collected from arid regions, Tank and Saraf (2010) found that soil sodicity had a negative effect on soil microbial community. Wichern and Jorgensen (2006) observed that fungal communities are more prone to increasing sodicity than bacterial population. Ali (2011) reported that irrigation induced soil sodicity negatively affected soil microbial and biochemical activities. Microbial biomass carbon was exponentially decreased with increase in soil electrical conductivity whilst a linear decrease in biomass carbon was observed with increasing exchangeable sodium percentage (Allotey, Asiamah & Nyamekye, 2008). Several other studies reported significant decreases in soil microbial biomass and related enzyme activities due to increased salinity and sodicity (Thripathi, Chakraborty & Bandyopadhyay, 2007; Yuan, Li, Lui, Gao & Zhang, 2007). Wong, Dalal and Greene (2008) observed an increase in metabolic quotient (respiration per unit biomas) with increasing sodicity which indicated a more stressed microbial community. Ghollarata and Raiest (2007) also observed an increase in metabolic quotient with simultaneous increase in soil salinity and sodicity, indicating a modification in microbial community with less catabolic activity. Yuan, Li, Lui, Gao and Zhang (2007) reported a shift in soil microbial community with less metabolism, an adaptive mechanism to alleviate salt stress.

2.7 Reclamation of Sodic Soil using Gypsum, Manure and Compost

The chemical formula for gypsum is $CaSO_4.2H_2O$. It is a white mineral of natural deposit. Gypsum contains 23 % calcium and 18 % sulphur. It is relatively soluble in water, making it possible for it to dissolve in soil solution (Sackey, 2015). Change in soil properties which result from the application of gypsum is attributed to ability of the divalent calcium ions (Ca^{2+}) to displace monovalent sodium ions (Na^+) from exchange sites of clay particles (Pushparaj & Thiyagarajan, 2016; Ahmed, 2011).

The role of gypsum in reclaiming sodic soils has been extensively investigated by researchers. In a field experiment conducted by Shabaan, Abid and Abou-Shanab (2013), it was observed that sole application of gypsum to saline-sodic soil decreased soil pH, electrical conductivity and sodium adsorption ratio. The highest decrease in pH was observed with the application of 100 % gypsum requirement. The rate of reduction in soil pH, however, reduced with decreasing rate of gypsum application. The effectiveness of gypsum in improving fertility of sodic soils improved when it was combined with farm yard manure and commercial humic acid. Muhammad and Khattak (2011) also reported that the combined application of gypsum and poultry manure decreased soil pH, electrical conductivity and sodium adsorption ratio of saline-sodic soil. The effects of gypsum in the soil medium could be enhanced when combined with organic amendments.

In a leaching experiment using columns techniques, Mohamed and Abdel-Fattah (2012) evaluated the effectiveness of gypsum, water hyacinth compost (WHC) and rice straw compost (RSC) and their different combinations on amelioration of saline – sodic soils. All sole amendments reduced extractable sodium percentage (ESP), electrical conductivity (EC) and pH of soil to margins that were statistically significant compared to a control. Results of combined amendments, however, showed more efficiency.

Karien, Mateus, Luiz, Richar and Rachel (2008) evaluated the effects of gypsum addition to irrigation water on physical and chemical properties of soils which had different levels of sodicity. They observed that soils leached with gypsum saturated water increased Ca^{2+} and K^+ content whilst soil pH decreased. They also observed a reduction in soil EC, Na^+ and ESP from same amendments. They concluded that the addition of gypsum to irrigation water improved soil physical and chemical properties and should be considered as an alternative in the process of reclaiming sodic soils.

The application of desulfurized gypsum at the rate of 100 % and 200 % of gypsum requirement significantly increased wet stability of macro aggregates (> 0.25 mm), infiltration rate and hydraulic conductivity of sodic soil (Fatemeh, Ali & Najafali 2013). They also found improvement in soil physical properties promoted the leaching of Na^+ which resulted in significant decrease in soil sodicity.

Fatemeh, Ali and Najafali (2013) observed that the application of coarse gypsum showed more efficiency compared to fine gypsum of same rate. Amending the soil with course gypsum resulted in increase in soil hydraulic conductivity over the application of fine gypsum. The credit of this observation was given to the coarse texture of gypsum rather than its chemical properties.

2.8 Use of Biochar as an Organic Soil Amendment

Biochar is a carbon-rich organic product obtained from exothermic slow thermal decomposition (pyrolysis) of biomass at temperatures ≤700 °C under zero or low oxygen conditions (Kwapinsiki *et al.*, 2010; Woolf, Amonette, Street-Perrott, Lehmann & Joseph, 2010). Biochar is perceived as an effective mitigation strategy in combating climate change by successfully sequestering carbon in soil and thus actively withdrawing carbon dioxide from atmosphere to abate global warming effects (Lehmann *et al.*, 2011; Harath,Camps-Arbestain & Hedley, 2013). Apart from being a carbon sink, biochar has also shown to improve soil properties when applied as an organic soil amendment. Literature is abundant with respect to the agronomic benefits of biochar incorporation into soil with many studies demonstrating significant enhancement in overall soil quality by altering soil physical, chemical and biological properties and subsequently increasing plant productivity (Atkinson, Fitzgerald & Hipps, 2010; Jones, Rousk, Edward-Jones, DeLuca & Murphy, 2012; Laird *et al.*, 2010; Lehmann *et al.*, 2011; Solaiman, Blackwell, Abbott & Storer, 2010; Van Zwieten *et al.*, 2010). Most of the studies evaluated the benefits of biochar incorporation in non-saline and non-sodic soils. However, its use for the reclamation of degraded lands especially sodium affected soils is scanty.

Studies involving biochar application to soil have reported enhancement in soil physical properties like bulk density, porosity, water infiltration rate, aggregate stability and hydraulic conductivity (Jien & Wang, 2013; Karhu, Mattila, Bergstrom & Regina, 2011; Lui, Han & Zhang, 2012; Uzoma *et al.*, 2011; Verheijen *et al.*, 2010). Jien and Wang (2013) found an increase in macro aggregation of soil which consequently increased the saturated hydraulic conductivity of a highly weathered soil treated with 5 % biochar. Similarly, Asai *et al.* (2009) reported a two-fold increase in soil hydraulic conductivity when biochar was applied at 16 t ha^{-1}. Harath, Camps-Arbestain and Hedley (2013) also found an increased field saturated hydraulic conductivity due to an increase in macro aggregation of soil amended with biochar. Again, Busscher, Novak and Ahmedna (2011); George, Wagner, Kucke and Rillig (2012); Mukherjee and Lal (2013) reported increased soil aggregation following biochar addition. Improvements in soil physical properties are very important in sodic soil remediation. Moreover, addition of divalent cations such as Ca^{2+} and Mg^{2+} is necessary to offset Na^+ on the cation exchange complex of a sodic soil. Major, Rondon, Molina, Riha and Lehmann (2010) observed increased soil Ca^{2+} and Mg^{2+} availability when biochar was applied at 20 t ha^{-1} to a Colombian savanna oxisol. In an Iowa study, Laird *et al.* (2010) found a significant increase in Ca^{2+} levels when biochar was applied to soil at 20 g kg^{-1} soil. Similarly studies showed that, biochar can significantly increase these divalent cations in soil (Gaskin *et al*., 2010; Novak *et al*., 2009). Per these research findings, therefore, biochar could be a significant source of these cations (Singh & Singh, 2010) and could potentially help in sodic soil remediation. Thus it is important to evaluate if biochar biochar could be an effective organic soil amendment to reclaim a sodium-affected soil.

CHAPTER THREE

GENERAL MATERIALS AND METHODS

3.1 Effluent Sampling and Analysis

Three (3) different effluent samples (12 litres in all) were taken from the discharge point of Ameen Sangari Industries Limited, Cape Coast. Thus 4-litres sampled per day. These samples were taken into clean and dry plastic bottles and stored in an iced-chest stalked with iced-blocks. This was done in order to halt microbial activity in the samples during transportation to the laboratory. Four (4) effluent quality parameters namely: pH, turbidity, temperature and electrical conductivity were determined on the field immediately after sampling. The samples were then transported to Water Research Institute of Council for Scientific and Industrial Research in Accra where sixteen (16) other parameters were determined. These included total dissolved solids (TOD), chemical oxygen demand (COD), biological oxygen demand (BOD), oil and grease (OG), total suspended solids (TSS), exchangeable sodium (Na^+), exchangeable potassium (K^+), exchangeable calcium (Ca^{2+}), exchangeable magnesium (Mg^{2+}), total phosphorus (P), ammonium nitrogen (NH_4^+-N), nitrate nitrogen (NO_3^--N), chlorine (Cl), zinc (Zn), iron (Fe) and copper (Cu). The various analytical methods used in the analysis are presented below:

3.1.1 Temperature and pH

Effluent temperature and pH were measured using the pH meter with an attached thermometer. After calibration, the probe of the meter was thoroughly rinsed with distilled water and dipped into the sample such that the end of the probe was completely immersed into the sample. The sample was gently stirred with the probe to create a homogenous medium. The probe was left in the sample until pH and temperature values stabilized and were recorded (APHA, AWWA & WEF, 2005).

3.1.2 Electrical conductivity (EC) and total dissolved solids (TDS)

Electrical conductivity and total dissolved solids of effluent samples were determined using a conductometer. The probe of this meter is able to measure the two (2) parameters concurrently. Following calibration, the probe was thoroughly rinsed with distilled water. It was then rinsed with a small volume of effluent sample before dipping it into the sample such that the liquid level was above the upper steel band. The probe was used to gently stir the sample to ensure a homogeneous medium. Time was allowed for readings to stabilize. Readings were then recorded (APHA, AWWA & WEF, 2005).

3.1.3 Determination of effluent turbidity

Sample turbidity was determined using turbidimeter. A 20 ml sized vial was adequately rinsed with effluent samples and wiped dry with clean cotton wool. A thin film of silicon oil was then applied on the vial. The vial was filled with 10 ml of effluent sample and covered with a shield cap. The sample vial was then snapped into the sample well and aligned to the material vial (slot on the turbidity meter). After 12 seconds, the turbidity value of the sample was recorded (APHA, AWWA & WEF, 2005).

3.1.4 Chemical oxygen demand (COD) of sample

Chemical oxygen demand (COD) is the measure of the amount of organic matter/pollutants in the wastewater. Three (3) COD vials were arranged and 2.5 ml of effluent were measured into two of the vials. The vial (blank) received 2.5 ml of distilled water. A volume of 1.5 ml of potassium dichromate was added to the content of each vial. This was followed by the addition of 3.5 ml of sulphuric acid. The vials were tightly capped, placed in a block digester (150 °C) and allowed to digest for two hours. The vials were removed from the digester and allowed to cool down to room temperature. The digested samples and blank were each transferred into conical flasks, few drops of ferroin indicator were added and each digest titrated against ferrous ammonium sulphate (APHA, AWWA & WEF, 2005).

Calculation:

$$\text{COD} = \frac{A-B * N * 8 * 1000}{V}$$

Where: A = Volume of ferrous ammonium sulphate for the blank

B = Volume of ferrous ammonium sulphate for the sample

N = Normality of ferrous ammonium sulphate and

V = Volume of sample

3.1.5 Biological oxygen demand (BOD) of sample

The amount of oxygen taken up by micro-organisms which decompose the organic waste matter in effluent is known as biological oxygen demand (BOD). BOD is calculated by keeping a sample of effluent containing a known quantity of oxygen for 5-days at 20 °C. To determine the BOD of the sample, four (4) 300 ml BOD bottles were arranged. Two of the bottles were each filled with 10 ml of sample and the other two filled with distilled water (blanks). The bottles were closed tightly to avoid the influence of external oxygen. One sample and one blank bottle were incubated at 20 °C for five days. A volume of 2 ml of 36.4 % of manganous sulfate ($MnSO_4.H_2O$) solution was added to the samples and blanks respectively. This was followed by the addition of 2 ml of alkali-iodide-azide reagent. After precipitates have settled at the bottom of the bottles, 2 ml of concentrated sulfuric acid was also added and the bottles swelled thoroughly to dissolve the precipitates. The contents were emptied into Erlenmeyer flasks and titrated immediately with 0.025 N sodium thiosulfate solution using starch indicator until blue colour disappeared. The burette readings were recorded (APHA, AWWA & WEF, 2005).

Calculation: BOD mg/l = [B.R. for sample at ($D_o - D_5$) – blank correction]

Where:

B. R. = burette reading

D_o = Initial amount of oxygen of sample

D_5 = Oxygen of sample after day 5 of incubation

3.1.6 Determining total suspended Solids (TSS) in effluent

To determine total suspended solids (TSS) of sample, 75 ml of effluent was piped into a clean crucible of known weight (W1). This was dried in an oven (105 °C) for 2-hours to obtain a constant mass. The container was then cooled in a desiccator. Thereafter, the crucible was weighed again (W2) (APHA, 1975).

Calculation:

Weight of residue (W) = W2 – W1 (g)

$$\text{TSS (g /ml)} = \frac{W1 - W2}{V}$$

Where:

V = Volume of sample (ml)

3.1.7 Determination of oil and grease of effluent.

The determination of oil and grease in effluent followed the method described by Stenstrom, Fam & Silverman (1986). It started with the measurement of 350 ml of sample into a clean 500 ml separatory funnel, followed by the addition of 4 ml of 1:1 hydrochloric acid solution into the separatory funnel. The content was stirred thoroughly to mix well. A volume of 20 ml of n-hexane was added to the separatory funnel and a stopper used to cock the funnel. The funnel was vigorously shaken for 2-minutes and thereafter, allowed to stand for 10 minutes to enable the separation of the lower water layer and the upper solvent layer. The lower water layer was slowly drained from the separatory funnel into a 500 ml volumetric flask. A glass funnel was put in the neck of a distillation flask and a folded 42 No. Whatman filter paper was put in the funnel. A 10 g of anhydrous sodium sulphate was added to the filter paper. The solvent layer was drip-drained into a pre-weighed boiling flask through a funnel that contains the filter paper and 10 g anhydrous sodium sulphate. The separatory funnel was rinsed with three different 5 ml aliquots of fresh hexane to remove oil film that stayed on the funnel walls. The hexane was then distilled off using a hot plate. Hereafter, the distillation flask was put in a desiccator for 30 minutes to cool down to room temperature. The flask was weighed again on an analytical balance.

Calculation:

Oil and Grease (mg/l) = [(A – B) ÷ Sample volume] x 1000

Where:

A = Weight (mg) of residue

B = Weight (mg) of flask

3.1.8 Determination of ammonium nitrogen (NH_4^+-N), in effluent

Determination of ammonium nitrogen in effluent sample followed the procedure defined by APHA, AWWA and WEF (2005). A volume of 100 ml of wastewater sample was measured into a volumetric flask. A 1 ml $ZnSO_4$ solution and 0.5 ml NaOH were added in that order to obtain a pH of 10.5. The content was allowed to stand for 10 minutes to settle after which the supernatant was filtered through 42 No. Whatman filter paper. A drop of EDTA was added to the filtrate and mixed well. A volume of 3 ml Nessler reagent was added and the content was thoroughly mixed. Percent transmission was read after 10 minutes using a spectrophotometer at 410 nm. A blank was also prepared in the same way by taking distilled water instead of effluent sample. The concentration was obtained from a standard graph prepared from a standard ammonium solution (3.819 g of NH_4Cl dissolved in 1 liter of distilled water).

3.1.9 Determination of nitrate nitrogen (NO_3^-N) in effluent

A volume of 100 ml of filtered effluent sample was measured into a beaker and neutralized to pH 7.0 by adding portions of 1 N NaOH. This was evaporated to dryness on water bath. The residue was dissolved using glass rod and 2 ml phenol disulphonic acid reagent. The dissolved residue was diluted with 50 ml distilled water and transferred to a Nessler tube. A volume of 10 ml of 12 N KOH was added to the content and filtered. The volume was then made up to 100 ml using distilled water. A blank was prepared in the same way using distilled water in place of effluent sample. Using a spectrophotometer, the intensity of colour developed was read at 410nm with a light path of 1cm. The concentration of nitrate was obtained from a standard calibration curve prepared from standard nitrate stock solution (0,1,2,4,7,.....15 ml, diluted with distilled water to 50 ml) (APHA, AWWA & WEF 2005).

3.1.10 Determination of sodium (Na^+) and potassium (K^+) in effluent

Ten milliliters (10 ml) of effluent was transferred into a 150 ml conical flask and diluted with distilled water to the 100 ml mark. Sodium and potassium concentrations in the effluent were determined using a flame photometer and the actual value was extrapolated from a standard graph prepared from the flame photometer readings of working standards (0, 2, 4, 6 8 and 10µg/ml) of both K and Na.

3.1.11 Determination of exchangeable calcium (Ca^{2+}) in effluent

Twenty milliliters (20 ml) of effluent sample was transferred into a 50 ml conical flask. A volume of 2 ml of 1 N NaOH was added, followed by the addition of 3-drops of ammonium purple indicator, giving the sample a pink colouration. This was titrated against 0.02 M EDTA solution to a purple end point.

Calculation:

$$Ca^{2+}\ (\text{cmol/l})] = \frac{\text{Volume of EDTA} \times N \times 40.8 \times 1000}{\text{Volume of sample taken}}$$

Where:

N = Normality of EDTA

40.8 = equivalent of calcium

1000 = Conversion to per liter value.

3.1.12 Determination of exchangeable magnesium (Mg^{2+}) in effluent

A pipette was used to transfer 20 ml of effluent sample into a 50 ml conical flask. Hereafter, 2 ml of 1 N lanthanum chloride was added, followed by the addition of 3-drops of ammonium purple indicator. This was titrated against 0.02 M EDTA solution to a purple end point.

Calculation:

$$Mg^{2+} \text{ (cmol/l)} = \frac{\text{Volume of EDTA x N x 39.1 x 1000}}{\text{Volume of sample taken}}$$

Where:

N = Normality of EDTA

39.1 = equivalent of calcium

1000 = Conversion to per liter value.

3.1.13 Determination of available phosphorus (P) in effluent

A pipette was used to transfer 10 ml of effluent into a 25 ml volumetric flask. Following this, 4 ml of vanadate-molybdate reagent was added and sample was diluted to 25 ml mark. A blank was prepared in a similar manner using distilled water. After 10 minutes, absorbance of both sample and blank were measured using a spectrophotometer at 400 nm wavelength. A calibration curve was established from the absorbance of standards (1, 3, 5, 7 ppm) prepared from a phosphorus stock solution of 100 ppm. The concentration of P in the sample was then extrapolated from the standard curve and corrected by the value obtained for the blank (Kennedy, 1984).

Calculation:

$$\text{mgP/l (sample)} = \frac{\text{C x 1000}}{\text{Volume of sample}}$$

Where:

C = ml P/l obtained from the graph

1000 = conversion to per liter.

3.1.14 Determination of chlorine in effluent

Twenty milliliters (20 ml) of effluent was transferred into a 50 ml volumetric flask and 5 ml of potassium dichromate (K_2CrO_4) added as an indicator. This was titrated against 0.0141 N $AgNO_3$ to a brick-red end point.

Calculation:

$$\text{mgCl/l} = \frac{(A - 0.2) \times 0.5 \times 1000}{\text{Sample Volume}}$$

Where:

A = titer value,

0.5 = normality of 0.0141 N $AgNO_3$

1000 = conversion to per liter equivalent

(Balaara, Paintsil & Vitenu, 2008)

3.1.15 Determination of copper (Cu) in effluent

For the determination of copper, 100 ml of effluent sample was transferred into a 250 ml beaker where 1 ml concentrated H_2SO_4 and 5 ml concentrated HNO_3 were added respectively. Four (4) boiling chips were added and substance cautiously evaporated to dense white SO_3 fumes using a hot plate. Beaker was allowed to cool down to room temperature after which 80 ml of distilled water was added. The substance was thoroughly dissolved and filtered into a 100 ml volumetric flask. Hereafter, 5 ml $NH_3OH.HCl$ solution and 10 ml sodium citrate solution were added, and substance mixed thoroughly. Following this, 10 ml neocuproine reagent and 10 ml $CHCl_3$ were added to the sample respectively and the beaker was firmly stopperred and vigorously shook for 30 seconds. This was followed by the extraction of the copper neocuproine complex layer into a 25 ml beaker and made up to the 25 ml mark with additional portions of CH_3OH. After another thorough mixing, absorbance of the extract was measured using spectrophotometer at 457 nm. A blank sample was prepared by carrying 50 ml distilled water through the complete digestion and analytical procedure. A calibration curve prepared from absorbencies of standard stock solution was used to determine final value of copper in the sample. (Gahler, 1954).

3.1.16 Determination of zinc (Zn) in effluent

To determine readily acid extractable total zinc in effluent, 1 ml concentrated HCl was added to 50 ml effluent sample and mixed thoroughly. The sample was filtered and the pH adjusted to 7 by the addition of NaOH. Absorbance of the sample was measured using spectrophotometer and zinc concentration was read from a standard calibration curve prepared from absorbencies of standard stock solution (Platte & Marcy, 1959).

3.1.17 Determination of iron (Fe) in effluent

After a thorough mixing, 50.0 ml of sample was measured into a 125-ml erlenmeyer flask. Five (5) boiling chips were added and the sample was heated on a hot plate to boiling. Boiling was allowed to continue until sample volume reduced to 15 ml. Sample was allowed to cool down to room temperature and then transferred into a 100-ml volumetric flask. Hereafter, 10 ml of $NH_4C_2H_3O_2$ buffer solution and 4 ml of phenanthroline solution were added respectively and sample was diluted with distilled water to the mark. After a thorough mixing iron concentration in sample was determined using a spectrophotometer at 510 nm wavelength. Blank determination was also carried out following the same procedure and its determined value subtracted from that of sample to obtain the actual iron concentration of effluent (Mehlig & Hulett, 1942).

3.2 Study Site, Soil Sampling and Analysis

3.2.1 Site description

Soil samples used for this experiment were collected from an area about 50 m from the premises of Ameen Sangari Industries Limited, Cape Coast where effluent from the soap making factory was discharged for 43 years. The soil belongs to oyibi series (Sodic Solonchak according to the FAO world map legend). The experiments were conducted at the Soil Science Laboratory, School of Agriculture, College of Agriculture and Natural Sciences, University of Cape Coast.

3.2.2 Soil sampling and preparation

Two different soil profiles were excavated, one at the contaminated site and a control profile 1-km away from the contaminated site, but within the same soil series. Each profile was 150 cm X 100 cm X 210 cm length, breadth and depth respectively. Soil was sampled at every 30 cm depth, giving seven soil samples per profile. The basis for the 210 cm sampling depth was to evaluate a universal rooting depth for a wide range of crops, following the impact of 43-years of discharge of soap factory effluent onto the land. The second profile pit was to serve as a control against which the properties of the contaminated soil are compared. Each soil sample was pulverized, thoroughly mixed, air - dried for 7 days, sieved through a 2 mm sieve and used for preliminary soil analyses. The rest of the soil sample from the first 30 cm depth of the contaminated site was later used for the pot experiment.

3.2.3 Determination of particle size distribution of soil

Soil particle size analysis was carried out using the pipette method as described by Rowell (1994). An amount of soil (10g + 0.01) was weighed into a 500 ml beaker. A volume of 20 ml of hydrogen peroxide was added and allowed to stand until frothing ceased. The suspension was then heated to complete the destruction of organic matter, and then allowed to cool. The peroxide-treated soil was quantitatively transferred into a 500 ml plastic bottle, 10 ml of dispersing agent was added, and the soil suspension was made up to 200 ml and shaken overnight. The contents were then transferred quantitatively into a 500 ml measuring cylinder and made up to 500 ml with distilled water.

The suspension was stirred using a plunger for thorough mixing. It was allowed to settle for 40 seconds after which 25 ml was pitetted from 10 cm below the surface into a weighed beaker for the determination of the mass of silt and clay. The suspension was allowed to settle for 5-hours after which 25 ml was pipetted at 10 cm depth into another beaker for the determination of the mass of clay. The pipetted suspensions were dried at 105 °C till constant weight. Supernatant liquids were gently poured off and the sediments were transferred into other beakers.

Sediments were repeatedly washed through stirring, settling and decanting till clear supernatants were obtained. Residues were transferred into weighed beakers and dried at 105°c till constant weight.

Calculations:

$$\text{Percentage sand (m/m)} = \frac{\text{mass of sand}}{\text{mass of oven dry soil}} \times 100$$

$$\text{The total mass of silt in the soil sample} = \text{Mass in 25 ml} \times \frac{500}{25}$$

$$\text{Percentage silt} = \frac{\text{total silt}}{\text{Mass of oven dry soil}} \times 100$$

$$\text{The total mass of clay in the soil sample} = \text{mass in 25 ml} \times \frac{500}{25}$$

$$\text{Percentage clay} = \frac{\text{total clay}}{\text{mass of oven dry soil}} \times 100$$

The textural classes of the soil samples were determined using the USDA textural triangle (Rowell, 1994).

3.2.4 Determination of soil bulk density

Samples were taken horizontally from the surface of soil pits. Sampling cylinders were placed against the soil surface with the driving tools in place. The cylinders were gently hammered into the soil until soil projected a few millimeters out of the cylinders. The cylinders plus soils were excavated leaving extra soils extending from each end of cylinders. The ends of the cylinders were trimmed and caps put at both ends and the samples were sent to the laboratory. In the laboratory the samples were weighed and later dried till constant weight (Rowell, 1994).

Calculation:

$$\text{Bulk density} = \frac{\text{mass of oven dry soil}}{\text{Volume of oven dry soil}}$$

3.2.5 Determination of soil pH

Ten grams (10 g) of the air-dried soil was weighed into plastic bottles with screw cap. Twenty-five milliliters (25 ml) of distilled water was added and agitated on a mechanical shaker for 15 minutes. The electrode of the pH meter was inserted into the soil-water suspension and the pH readings were recorded (Rowell, 1994).

3.2.6 Electrical conductivity of soil

Forty grams (40 g) of air-dried soil was placed in 250 ml plastic bottle and 80 ml of distilled water was added, stoppered and shaken on a reciprocating shaker for 1hour. The suspension was then filtered through whatman No. 1 filter paper. The conductivity meter was calibrated and the electrical conductivity of the filtrate was determined (FAO, 2008).

3.2.7 Soil extraction for the determination of exchangeable cations

Five grams (5 g) of soil sample was weighed into 100 ml extracting bottle and 20 ml of I *M* ammonium acetate solution was added, stirred and allowed to stand overnight. The suspension was then filtered into a 100 ml volumetric flask. The leaching process was continued with successive 20 ml volumes of ammonium acetate allowing the funnel to drain between each addition. The process was continued till nearly 100 ml of filtrate was collected. The filtrate was made up to

100 ml with ammonium acetate solution. Aliquots of the extract were used for the determination of Ca^{2+}, Mg^{2+}, K^+ and Na^+ (Rowell, 1994).

3.2.8 Determination of exchangeable calcium and magnesium in soil

For exchangeable Ca and Mg in soil, aliquots of 25 ml of 1.0 *M* ammonium acetate extract was transferred into 250 ml conical flasks and diluted to 150 ml mark with distilled water. Fifteen mililiters (15 ml) of buffer solution was added to each, followed by 10 drops each of KCN, NH_2OH, HCl, K_4Fe (CN_6) and triethanolamine. After the additions, 20 minutes were allowed to ensure that reactions were completed. Ten drops of Erichrome Black T indicator was added to each of the solutions and titrated against 0.005 *M* Na_2 - EDTA to a blue end point. For exchangeable calcium alone, aliquots of 25 ml of each extract were transferred into 250 ml conical flasks and diluted to 150 ml mark with distilled water. After adding all the reagents mentioned in the determination of calcium, the pH of each solution was adjusted to 12 by the additions of various portions of 10 % NaOH. Five drops of calgon indicator was added to all the samples and then titrated against 0.005 *M* EDTA. The values obtained were subtracted from those of calcium plus magnesium to obtain those of magnesium only (Page, Miller & Keeny, Eds: 1982).

Calculations:

$$\% \text{ Ca} = \frac{0.005 \text{ X } 40.08 \text{ X T}}{\text{Sample weight}}$$

$$\% \text{ Mg} = \frac{0.005 \text{ X } 39.1 \text{ X T}}{\text{Sample weight}}$$

Where T = titre value

3.2.9 Exchangeable potassium and sodium

Potassium and sodium in the digested samples were determined using a flame photometer. In the determination, the following working standards of both K and Na were prepared: 0, 2, 4, 6 8 and 10μg/ml. The working standards as well as the sample solutions were aspirated individually into the flame photometer and their emissions (readings) were recorded. A calibration curve was plotted using the concentrations and emissions of the working standards. The concentrations of the sample solutions were extrapolated from the standard curve using their emissions (Stewarts *et al*. 1974).

Calculation:

$$\mu gK/g = \frac{C \text{ X solution volume}}{\text{Sample weight}}$$

$$\mu g\ Na/g = \frac{C \text{ x solution volume}}{\text{Sample weight}}$$

3.2.10 Soil exchangeable acidity

To determine exchangeable acidity of soil, ten grams of air-dry soil was weighed into a 100 ml beaker. Twenty-five mililiters of 1*M* KCl was added. The content was thoroughly stirred and left to stand for 30 min. It was then filtered through a number 44 Whatman filter paper into 250 ml conical flasks. The residue was further leached with five successive aliquots of 1 *M* KCl. Five drops of phenolphthalein solution was added and the extract was titrated against 0.1 *M* NaOH to the first permanent pink point. The procedure also included a blank determination and the value was used to correct that of the sample.

3.2.11 Determination of organic carbon

A weight of 1.0 g of soil sample was weighed into a 500 ml conical flask and 10 ml of 0.1667M K_2Cr_2O solution and 20 ml concentrated H_2SO_4 were added. A thorough mixing was done and the content allowed 30-minutes for reactions to complete. The content was diluted with 200 ml of distilled water and 10 ml of H_3PO_4 was added. Hereafter, 10 ml of NaF solution and 1ml of diphenylamine indicator were added and titrated against 0.5 *M* ammonium ferrous sulphate solution to a green colour. A blank was determined alongside the sample (FAO, 2008).

Calculation:

$$\%\ \text{organ carbon} = \frac{(B - S) \times \text{molarity of Fe}^{2+} \times 0.003 \times 100}{\text{Weight of sample} \times 77}$$

Where:

B = Blank titre

S = sample titre

3.2.12 Determination of total nitrogen in soil

A weight of 1.0 g of soil sample was placed in a digestion flask and 0.2 g of catalyst and 3 ml of concentrated H_2SO_4 were added. The contents were digested on a block digester at 380 °C for 2 hours. After the digestion, the digest was allowed to cool then diluted to 50 ml with distilled water. An aliquot of 20 ml was pipetted into the reaction chamber of a steam distillation apparatus. Following this, 10 ml of alkali mixture was added and distillation commenced. About 40 ml of distillate was collected in a boric acid indicator. The distillate was titrated against 1/140 HCl from green to a wine colour. Blank determination was carried out alongside (FAO, 2008).

$$\% \text{N} = \frac{(\text{S} - \text{B}) \text{ X solution volume}}{10^2 \text{ X aliquot X sample weight}}$$

Where :

S = Sample titre

B= blank titre

3.2.13 Determination of ammonium and nitrate nitrogen of soil

Twenty milliliters (20 ml) of fresh soil sample was extracted with 100 ml of 2 *M* KCl. The mineral nitrogen content of the extract was determined by steam distillation.

Ammonium–N was determined by introducing 20 ml of the extract into the reaction chamber and adding 0.2 g MgO. The extract was distilled and about 40 ml of distillate was collected in boric acid indicator and titrated for ammonium nitrogen. At this point, 0.2 g of devardas alloy was added to the content in the reaction chamber and another 40 ml of distillate was collected in a new flask. The second distillate collected was titrated for the determination of nitrate-N (Rowell, 1994).

Calculation:

$$\text{N (Kg}^{-1}\text{)} = 2.8\,\frac{\text{x corrected titration volume (ml) x total liquid volume}}{\text{Oven- dry soil mass}}$$

3.2.14 Determination of available phosphorous in soil

Available phosphorus in soil was determined by the Bray number 1 method as described by Bray and Kurtz (1945). Extraction was done using 0.3 *M* ammonium fluoride in 0.5 *M* hydrochloric acid. This was followed by the estimation of the quantity of available phosphorus, using the ascorbic acid method. Available phosphorus was read using the spectronic 20 spectrophotometer at 880 nm.

Calculations:

If C = µgP/ml obtained from the graph, then $\mu\text{gP/g (sample)} = \frac{\text{C x dilution factor}}{\text{Weight of sample}}$

3.2.15 Determination of micronutrients

The micronutrients were extracted using diethylene triamine pentaacetic acid (DTPA). Ten grams (10 g) of soil sample was placed in polypropylene bottle and 20 ml of DTPA extracting solution was added. The bottle was stoppered and shaken for 2 hours. The content was then filtered. The extract obtained was used for determination of different micronutrients using the Atomic Absorption Spectrophotometer (FAO, 2008).

Standard solutions of 1, 2 and 5µg/ml solutions of Fe, Cu, and Zn were prepared. The standard solutions were aspirated into the atomic absorption spectrophotometer (AAS) and the respective calibration curves were plotted on the AAS. As the sample solutions were aspirated their respective concentrations were recorded (Stewarte *et al.* 1974).

Calculations:

$$\text{Fe } (\mu g/g) = \frac{\text{C X solution volume}}{\text{Sample weight}}$$

$$\text{Cu } (\mu g/g) = \frac{\text{C X solution volume}}{\text{Sample weight}}$$

$$\text{Zn } (\mu g/g) = \frac{\text{C X solution volume}}{\text{Sample weight}}$$

Where C = concentration obtained from AAS

3.2.16 Determination of gypsum requirement for the contaminated soil

In determining the gypsum requirement of the contaminated soil, 0.5 g of air-dry soil was weighed into a 250 ml conical flask and 100 ml of saturated gypsum solution was added. The flask was firmly stoppered and shaken in a mechanical shaker for 5 minutes. The content was then filtered through a no.42 Whatman filter paper into another flask. An aliquot of 5 ml of the filtrate was transferred into a 100 ml porcelain dish where 1 ml of ammonium hydroxide – ammonium chloride buffer solution was added as well as 3-drops of EBT indicator. The content was then titrated against 0.01 N EDTA (versanate solution) to a sky-blue end point. A blank determination was also done following same procedure.

Calculation:

Gypsum requirement (GR)/ha = (A-B) X N X 382

Where:

A = Volume of EDTA (versanate solution) used for blank titration (ml)

B = Volume of EDTA (versanate solution) used for soil extraction (ml)

N = Normality of EDTA solution

(FAO, 2008).

3.3 Preparation of Biochar

Saw dust, palm fiber, and poultry manure were gathered from various sources for the preparation of biochar. Saw dust was collected from Cobosco Enterprise, Abura-Cape Coast, palm fiber from Solidaridad Oil Mills, Nfuom in the Twifo Hemang-Lower Denkyira District of Central Region and poultry manure from the Teaching and Research Farm, College of Agriculture and Natural Sciences, University of Cape Coast. These waste-stocks were sun-dried and loaded into Lucia biomas pyrolytic stoves – Top Lift-up Draft made of zinc alloy sheet, fabricated by the Cape Coast Technical Institute. The primary components of the pyrolyser comprised a combustion chamber, ventilation outlet and a lid. A fueling material was prepared by thoroughly mixing melted candle sticks with well-dried saw dust. A dry waste-stock was fed into the stove, a piece of lighting material placed on the waste-stock and lit with matches to start the fire. After the fire got intense, the lid was closed. The initial yellow collour of the flames turned to black smoke after some time, indicating the completion of charring of the waste-stock. The fire was then put off. The Charring temperature ranged between 350 °C and 450 °C and each session lasted between 40 minutes to 1 hour. The char produced was milled using Brook Crompton Series 2000 Mill to pass through a 2 mm sieve.

3.4 Characterization of Biochar

The prepared types of biochar and un-chared sample of the poultry manure were analyzed for sixteen (16) parameters important for improving soil fertility. These were pH, electrical conductivity (EC), exchangeable calcium (Ca^{+2}), exchangeable magnesium (Mg^{+2}), exchangeable potassium (K^{+}), exchangeable sodium (Na^{+}), exchangeable acidity (EA), effective cation exchange capacity (ECEC) and exchangeable sodium percentage (ESP). The others include total organic carbon (OC), total nitrogen (N), total phosphorus (P), iron (Fe), Cupper (Cu), Zinc (Zn), and carbon-nitrogen ratio (C:N).

The analytical methods used were the same as those in soil analysis reported earlier in this chapter.

3.5 Soil Amendments

All amendments were applied at the rate of total gypsum requirement of soil. These were:

- Control (Soil only - 5 kg soil/pot)

- Gypsum only at full gypsum requirement rate of 4.78 t ha^{-1} (11.95g/5kg soil/pot)
- Saw dust biochar only at 4.78 t ha^{-1} (11.95g/5kg soil/pot)
- Palm fiber biochar only at 4.78 t ha^{-1} (11.95g/5kg soil/pot)
- Poultry manure biochar only at 4.78 t ha^{-1} (11.95g/5kg soil/pot) and
- Poultry manure only at 4.78 t ha^{-1} (11.95g/5kg soil/pot)

3.6 Soil Sampling and Analysis

Amendments were applied and thoroughly mixed with soil. Each amendment was replicated 5-times. The amended soils were incubated for the period of six weeks during which soil sampling was done weekly for laboratory analysis. Soil in each pot was thoroughly stirred and about 150 g sampled for analysis. Periodic watering of soil was done in order to keep moisture level at field capacity.

Soil properties monitored during the six weeks were soil pH, electrical conductivity (EC), exchangeable sodium (Na^+), exchangeable calcium (Ca^{+2}), exchangeable magnesium (Mg^{+2}), exchangeable potassium (K^+), cation exchange capacity (CEC), exchangeable sodium percentage (ESP), organic carbon (OC), nitrate nitrogen (NH_4^+-N), ammonium nitrogen (NO_3^- -N) and available phosphorus (P).

The analytical methods used were the same as those in soil analysis reported earlier in this chapter.

3.7 Seed germination test and determination of dry matter yield

After the six weeks of monitoring, a sodium sensitive crop (***Zea mays L***) was planted on the amended soils. The local Obatanpa variety was planted. The rate of seed germination was monitored and also, dry matter yield of above ground portion at day 45 after seed germination.

3.8 Statistical Analysis

The GenStat discovery software (2016) was used to determine the level of significance for measured parameters of soil.

CHAPTER FOUR

ASSESSMENT OF THE SUITABILITY EFFLUENT FROM A SOAP MAKING FACTORY IN CAPE COAST FOR USE AS IRRIGATION WATER FOR CROP PRODUCTION

4.1 Introduction

Effluent is an inevitable by-product of most processing industries. Though various countries enact laws that make it mandatory for industries to treat effluent prior to discharge into the external environment (rivers, ponds, lakes, sea, land, etc), the relatively large volumes of effluent generated on daily basis make it difficult for them to comply. Consequently volumes of untreated effluents are discharged into the external environment without any proper treatment (Hillebrand, Musallam, Scherer, Nodler & Licha, 2013; Ternes, Joss & Oehlmann, 2015). As an alternative measure to this problem, some countries have adopted the use of industrial effluent to irrigate farmlands especially during the dry season, enabling farmers to produce food crops all year round (Loos *et al*., 2013; Mills *et al*., 2014). This was against the background that some industrial effluents are nutrients rich and could provide substantial amount of plant nutrients. Major set-backs identified from the practice, however, include the build-up of toxic elements such as Boron (B) Lead (Pb) and Molybdenum (Mo), which hinder crop production. (Ahmad, Manderia & Mandria, 2012; Ahmad, Anawar, Chowdhury & Ahmad, 2011; Ali, 2011; Arun & Kanjan, 2012). Sodium build-up also impose soil sodicity and alkalinity, which destroy soil structure and leads to poor soil aeration and water infiltration, high bulk density, low microbial activity among others (Gatta *et al*., 2014; Petrie, Barden & Kasprzyk-Hordern, 2014; Gardner *et al*., 2013; Gardner *et al*., 2012). The need to carefully evaluate the quality of industrial effluent before applying to crop land is therefore very necessary in order to achieve desirable crop yields.

Ameen Sangari Industries Limited in Cape Coast is one of such industries. The industry extracts palm oil from palm fruits and combines this with alkali (NaOH) to produce soap. The effluent generated from this production process was discharged onto a nearby land for 43 years. The land has gradually lost its ability to support plant growth. As a result, farmers who used to crop on the land eventually stopped as their yields dwindled to un-economic levels. It was assumed that the effluent discharged by the industry onto the land could have deleterious substances which have destroyed the soil's fertility. This study was therefore designed to evaluate the quality of the effluent discharged onto the land as compared to the standards prescribed by the Environmental Protection Agency of Ghana. The findings from this study would inform the Management of the industry about the need to adopt a more efficient way to manage their effluent and also, enable the land owners to fashion out suitable approaches to reclaim the affected land.

4.2 Materials and Methods

In this study, effluent samples were collected from the discharge point into plastic bottles with necessary precautions for laboratory analysis. Physicochemical properties such as pH, Turbidity, Temperature and Electrical Conductivity (EC) were immediately determined on site after sampling (APHA, AWWA & WEF, 2005). Determination of parameters such as Total Dissolved Solids (TDS), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Oil and Grease (OG), Total Suspended Solids (TSS), Sodium (Na^+), Potassium (K^+), Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Phosphorus (P), Ammonium Nitrogen (NH_4^+-N), Nitrate Nitrogen (NO_3^--N), Chlorine (Cl), Zinc (Zn), Iron (Fe) and Copper (Cu) were carried out in the laboratory of Water Research Institute of Council for Scientific and Industrial Research, Accra. Effluent temperature and pH were measured using a pH meter which also has a thermometer. Sample turbidity was determined using turbidimeter. Electrical conductivity (EC) and Total Dissolved Solids (TDS) were determined by the aid of a conductometer (USEPA, 1979). Total Suspended Solids (TSS) was measured by ratio of weights of known volume of effluent and residues left behind after evaporation (APHA, 1975), whilst Chemical Oxygen Demand (COD) was determined by the dichromate digestion method. Biological Oxygen Demand (BOD) was determined by the dilution method (APHA, 1975). Determination of Oil and Grease (OG) was by the method described by Stenstrom, Fam & Silverman (1986), whist Sodium (Na^+) and Potassium (K^+) were determined using a flame photometer. Calcium (Ca^{+2}) and Magnesium (Mg^{+2}) determination were by EDTA titration whilst Ammonium Nitrogen (NH_4^+-N) and Nitrate Nitrogen (NO_3^--N) of effluent were determined by spectrophotometry at 410 nm. Available phosphorus (P) was measured using a spectrophotometer at 400 nm wavelength (Kennedy, 1984) and

Chlorine (Cl) was determined by $AgNO_3$ titration (Balaara, Paintsil & Vitenu, 2008). Copper (Cu) was determined by spectrophotometry at 457 nm (Gahler, 1954) and Zinc (Zn) by a spectrophotometer method defined by Platte and Marcy (1959). Determination of iron (Fe) in effluent was by the spectrophotometer method at 510 nm wavelength (Mehlig & Hulett, 1942). The data obtained was compared to the standards of the Environmental Protection Agency of Ghana.

4.3 Results and Discussions

4.3.1 Effluent temperature, pH, electrical conductivity and micro nutrients

Table 1 shows the results of the physicochemical properties of the effluent from the soap manufacturing industry located in Cape Coast industrial area. Effluent temperature is a very important parameter because it can influence the physical, chemical and biological properties of a receiving medium. In the soil, temperature is known to influence seed germination, nutrient availability, plant root and fruit development, microbial activities and organic matter decomposition among others (Martias & Musil, 2012; Nwankwo & Ogugurue, 2012). The temperature of the effluent was 36.80 °C as against the EPA recommended temperature of < 30 °C. This suggested that some effluent was discharged right from source without any temporary holding for treatment (EPA, 2012).

Effluent pH was 11.19 as against the standard range of 6.0 - 9.0. The discharge of such an effluent onto agricultural land could negatively influence the soil regime. Soil pH directly affects the life and growth of plants because it affects the availability of all plant nutrients in the soil. Between pH 6.0 and 6.5, most plant nutrients are in their most available state (Muamar *et al*., 2014). An effluent with such a high pH could increase soil pH to alkaline conditions. Under alkaline soil condition, the availability of phosphorus and most micro nutrients are adversely affected.

Electrical conductivity of the effluent is a measure of its capability to pass electrical flow (Perlman, 2014). This ability relates to the concentration of ions in the effluent, derived from dissolved inorganic materials such as alkalis, chlorides, sulfides, and carbonate compounds (Lourenzi *et al*., 2011; EPA, 2012). A high conductivity depicts the presence of more dissolved ions and vice versa. The effluent sample registered a relatively low electrical conductivity of 4.37 dS m^{-1} compared to an approved standard of 1,500.0 dS m^{-1} for discharge into the external environment. This gives a 34,324 % lower value when compared to the standard hence could be described as negligible. This reflected in the relatively low values obtained for all the micronutrients namely Copper (1.73 mg/l), Zinc (0.59 mg/l), Chlorine (0.39 mg/l) and Iron (0.79 mg/l) as against standards of 10.0 mg/l, 5.0 mg/l, 250.0 mg/l and 10.0 mg/l respectively. Despite the low levels of these ions, continuous discharge of this effluent onto land for a long term could lead to their build-up in soil to levels which could be detrimental to plant growth (Lourenzi *et al*., 2011; EPA, 2012). The use of such effluent for irrigation may be beneficial at the onset but yields may dwindle over time as these micronutrients build-up in the soil and negatively impact on crop growth and yield (Lourenzi *et al*., 2011; EPA, 2012).

4.3.2 Total suspended solids, chemical and biological oxygen demands

Total suspended solids (TSS) is a measure of organic and inorganic solid materials in an effluent. It positively correlates with effluent turbidity (T). The organic components of suspended solid of soap industrial effluent include palm fiber, oil and grease (O&G) whilst the inorganic fraction comprise mainly of sand, silt and clay (Ale, Jha & Belbase, 2008). The values obtained for TSS, T and O&G for the soap factory effluent were 2,090 ppm, 959 NTU and 159 mg/l respectively as against the EPA standards of 50 ppm, 75 NTU and 5.0 mg/l in that order (Table 1). These represented 4,180 %, 1,278 % and 19,180 % increase over the standards. Even though the discharge of such an effluent into water bodies could negatively impact water quality; its discharge onto farm land over time could lead to accumulation of organic matter in soil (Czuba *et al.*, 2011). Soil organic matter improves soil aggregate stability, aeration, water infiltration, water holding capacity, nutrient retention and release to soil solution for plant roots absorption, etc. The sand, silt and clay fractions of effluent may come from erosion of the banks and base of drains that conduct the effluent (Czuba *et al.*, 2011).

The biological oxygen demand (BOD) of the effluent sample measured was 805 mg/l compared to the EPA standard value of 50 mg/l (Table 1). This represented a 1,161 % increase over the standard. Chemical oxygen demand (COD) of the effluent was 6,090 mg/l as against a standard value of 250 mg/l, giving a 2,436 % deviation from the standard. BOD and COD make a common demand on the soil regime by depleting soil oxygen.

Table 1: *Effluent quality parameters of Ameen Sangari Industries Limited*

Parameter	**Value**	**Standards (EPA-Ghana)**
pH	11.19 ± 0.020	6.0 – 9.0
Temperature (°C)	36.80 ± 0.220	< 30°C
Electrical Conductivity (dS m^{-1})	4.37 ± 0.015	1,500.0
Total Dissolved Solids (ppm)	5.87 ± 0.010	1,000.0
Turbidity (NTU)	959 ± 0.0186	75.0
Chemical Oxygen Demand (COD, mg/l)	6,090 ± 4.92	250.0
Biological Oxygen Demand (BOD, mg/l)	805 ± 0.166	50.0
Oil and grease (ml/l)	159 ± 0.225	5.0
Total Suspended Solids (ppm)	2,090 ± 0.567	50.0
Sodium [Na^+ (cmol/l)]	26.44 ± 0.045	-
Potassium [K^+ (cmol/l)]	16.36 ± 0.010	-
Calcium [Ca^{2+} (cmol/l)]	0.70 ± 0.05	-
Magnesium [Mg^{2+} (cmol/l)]	0.3 ± 0.005	-
Phosphorus [P (mg/l)]	111.57 ± 3.953	2.0
CEC (cmol/l)	43.8 ± 1.901	-
ESP (%)	60.4 ± 3.936	-
Ammonium Nitrogen [NH_4^+-N (mg/l)]	19.1 ± 0.110	1.0
Nitrate Nitrogen [NO_3^--N (mg/l)]	17.4 ± 0.010	50.0
Zinc [Zn (mg/l)]	0.59 ± 0.040	10.0
Copper [Cu (mg/l)]	1.73 ± 0.007	5.0
Chlorine [Cl (mg/l)]	0.39 ± 0.049	250.0
Iron [Fe (mg/l)]	0.79 ± 0.009	10.0

BOD indirectly depletes soil oxygen following the increase in microbial activity towards the decomposition of organic matter (Botalova & Schwarbauer, 2011; Ahmad, Bajahlan & Hammad, 2008), whilst COD demands soil oxygen in order to oxidize long fatty acids, typical of palm oil and soap manufacturing industries (Arun & Kanjan, 2012).

The combined effect of BOD and COD in soil therefore could create anaerobic condition that would slow down microbial activity, organic matter decomposition and also increase gaseous loss of some soil-plant nutrients, notably ammonium and nitrate nitrogen (Arun & Kanjan, 2012).

4.3.3 Sodium, calcium and magnesium

Exchangeable Sodium (Na^+) in effluent sample was 26.44 cmol/l, calcium (Ca^{+2}) recorded 0.70 cmol/l and magnesium (Mg^{+2}), 0.30 cmol/l (Table 1). The relatively high value for Na^+ in effluent could be as the result of the use of NaOH as alkali for soap production by the industry (Arun & Kanjan, 2012). The exchangeable forms of sodium (Na^+), calcium (Ca^{+2}) and magnesium (Mg^{+2}) are very important parameters which must be monitored in any form of wastewater intended for application to farm land. This is because sodium accumulation in soil is known to be the lead cause of sodicity, an undesirable soil condition which destroys soil structure, aggregate stability, water infiltration and hydraulic conductivity, microbial activity and nutrient supply (Arun & Kanjan, 2012). Ca^{+2} and Mg^{+2} on the other hand enable the formation of salts [$CaCO_3$, $MgCO_3$, $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$], which cause soil salinity (Arun & Kanjan, 2012).

4.3.4 Potassium, phosphorus, ammonium and nitrate nitrogen

Potassium (K^+), phosphorus (P), ammonium nitrogen (NH_4^+-N) and nitrate nitrogen (NO_3^--N) are effluent properties desirable for soil fertility and plant nutrition. The effluent sample recorded 16.36 cmol/l, 111.57 ml/l, 19.1 ml/l, and 17.4 ml/l for K^+, P, NH_4^+-N and NO_3-N respectively. The value obtained for P has exceeded the standard by 5,478.5 %, that for NH_4^+-N exceeded by 1,901 % whilst the value for NO_3-N (17.4 ml/l) was lower than the standard of 50 ml/l. The discharge of such an effluent into water bodies could cause eutrophication and a significant degradation of aquatic life (Botalova & Schwarbauer, 2011; Ahmad, Bajahlan & Hammad, 2008). Discharging it onto a farm land, however, could be a source of major plant nutrients (Botalova & Schwarbauer, 2011; Ahmad, Bajahlan & Hammad, 2008). The impact of the other physical and chemical properties of the effluent, however, would have to be considered alongside.

4.4 Conclusion

The purpose of this study was to assess the suitability of effluent from the Ameen Sangari Industries Limited, Cape Coast for crop production. The study showed that seven (7) out of twenty (22) effluent properties were within acceptable limits. These are nitrate-nitrogen, electrical conductivity, total dissolved solids, chlorine, iron, copper and zinc. Nine (9) effluent properties exceeded quality guidelines. These include pH, temperature, turbidity, chemical oxygen demand, biological oxygen demand, oil and grease, total suspended solids, phosphorus and ammonium nitrogen. Effluent potential was relatively high for improving soil

CEC. On the basis of nitrogen, potassium and phosphorus concentrations which were adequate and the low micro nutrients (Fe, Cu, Zn) concentrations, the effluent has the potential for use as irrigation water. Effluent ESP and EC, however, may pose the challenge of soil sodicity and salinity which could erode the economic benefits of any gain a farmer may make from applying this effluent to farmland. There is therefore the need to fashion out an effluent treatment system which could adequately reduce effluent ESP and EC. The following chapter therefore evaluates the impact of the industrial effluent on physicochemical properties of the receiving soil.

CHAPTER FIVE

IMPACT OF SOAP FACTORY EFFLUENT ON SOIL PHYSICOCHEMICAL PROPERTIES: A STUDY OF CAPE COAST INDUSTRIAL AREA

5.1 Introduction

The need to produce food crops all year round has made it necessary to explore alternative sources of water to irrigate farm lands. One potential alternative sources of irrigation water is industrial effluent. Industrial effluent is a common by-product of most industrial processes whose containment, treatment and disposal add to the production cost of industries. The composition of industrial effluent may vary from one industry to the other due to the differences in raw materials processed and chemical substances involved in different industrial activities. Depending on the chemical composition of an effluent, its application to farm lands could either enhance soil fertility or render it infertile. On one hand, effluent irrigation has been reported to increase crop yield compared to irrigation with fresh water due to the supply of nutrients such as nitrogen, phosphorus and potassium contained in the effluents (Vimaldeep & Gitanjili, 2014; Liu & Haynes, 2010). On the other hand, physico-chemical analysis of soil irrigated with effluent usually indicate sodium and bicarbonates accumulation and pH increase to alkaline values especially in the top soil horizons of farmlands (Sou, 2013; Khurana, 2012). Shrinkage analysis has shown that the structural pore network of such soils collapse dramatically, resulting in compact layers with poor water storage capacity (Omron & Maghraby, 2012). Besides, alkanization induces organic matter dissolution, which leads to the formation of black alkali on top of the soil (Rusan, Hinnawi & Rousan, 2007). The build-up of soil micro nutrients such as iron, copper, chlorine, boron, zinc among others to toxic levels and the subsequent detrimental effects on seed germination and plant growth were also reported (Khodabakhsh, 2013; Marium, 2013). The study site for this research is a land situated opposite Cape Coast industrial area onto which effluent from a soap factory has been discharged for 43-years. The industry extracts palm oil from palm fruits and thereafter, use the palm oil as a raw material to manufacture soap, with sodium hydroxide (NaOH) as alkali. Over the years, most other plant species have died, leaving virtually one grass specie (guinea grass – *Magathysus maximus*). All farming activities have also ceased on the land as farmers harvested no crop to compensate for their toils. The objective of this study therefore was to conduct profile analysis of physicochemical properties of the soil as influenced by soap factory effluent for 43 year.

5.2 Materials and Method

Two different soil profiles were excavated, one at the contaminated site (Figure 1) and a control profile, 1-km away from the contaminated site, but within the same soil series. Each profile was 150 cm X 100 cm X 210 cm length, breadth and depth respectively. Soil was sampled at every 30 cm depth, giving seven soil samples per profile (designated PL1-PL7). The basis for the 210 cm sampling depth was to evaluate a universal rooting depth for a wide range of crops, following the impact of 43-years of discharge of soap factory effluent onto the land. The second profile pit was to serve as a control against which the properties of the contaminated soil are compared. Each soil sample was pulverized, thoroughly mixed, air- dried for 7 days, sieved through a 2 mm sieve and used for preliminary soil analyses. Sixteen (16) physicochemical parameters of soil were investigated. These were soil, pH, electrical conductivity, sodium and exchangeable sodium percentage, calcium, magnesium and potassium, ammonium and nitrate nitrogen, available phosphorus, organic carbon, iron, zinc, and gypsum requirement, bulk density and textural class. These parameters were informed by an earlier study of the physicochemical properties of the effluent from the industry.

Soil pH determination was done using the pH meter and soil to water ratio of 1:2.5, electrical conductivity was determined by using a conductivity meter and sample to water ratio of 1:2. Ca^{+2} was determined by titrating aliquot of ammonium acetate extract against 0.005 M Na_2-EDTA, using Erichrome Black T as indicator whilst Mg^{+2} determination followed a similar process but with calgon indicator. Potassium and sodium were determined by use of a flame photometer (FAO, 2008) and available nitrogen forms were determined by the Kjeldahl distillation method. For exchangeable acidity, soil was extracted with 1M KCl (soil to extractant ratio of 1:2.5) and titrated against 0.1 M NaOH with phenolphthalein as indicator. Organic carbon determination followed the potassium dichromate digestion method. The digest was then titrated against 0.5 M ammonium ferrous sulphate solution, using diphenylamine as indicator. Available phosphorus determination was by the use of a spectrophotometer at a wavelength of 882 nm whilst the micro nutrients were determined using the Atomic Absorption Spectrophotometer (AAS) after 10 g of soil was extracted with 20 ml of diethylene triamine pentaacetic acid (DTPA). Textural class determination was by the hydrometer method described by Rowel (1994) and soil bulk density was by the use of sampling cylinder. The GenStat discovery software (2016) was used to determine the level of significance for measured parameters of soil.

Figure 1: An excavated soil profile at the contaminated site

5.3 Results and Discussion

5.3.1 Soil pH

Presents in table Table 2 are the results of the physicochemical properties of the effluent contaminated soil profile as against the control profile. Values of the soil pH exhibited significant ($p = 0.05$) differences inter and intra soil profiles. The pH values of both contaminated and control sites were relatively high in PL1 but steadily declined with depth. The contaminated soil exhibited a general alkaline soil pH up the profile, which gradually declined to slightly acidic pH with depth. These were, however, different from the control profile whose pH was slightly acidic in PL1 but declined to acidic pH values with depth. This difference could be the impact of the industrial effluent (of pH 11.2) on the contaminated soil. The relatively lower soil pH (≤ 8.7) as compared to that of the effluent (Table 2) could be attributed to the acidifying effect of decomposing oil and grease of effluent and soil acidity. Similar observations were made by Sou (2013); Ensink, Mahmood and Dalsgaard (2007); Rusan, Hinnawi and Rousan (2007) where the application of industrial wastewater to land resulted in increase soil pH. Contrary situations were however reported by Vimaldeep and Gitanjili (2014) where the application of industrial wastewater to farmlands increased soil acidity. This suggested that the impact of industrial effluent on soil fertility, therefore, would depend largely on the source and composition.

5.3.2 Electrical conductivity and exchangeable cation

Values obtained for electrical conductivity (EC) of the soils are reported in Table 2. Electrical conductivity (EC) of soil is a measure of the total concentration of ionized substances in soil solution. It affects crop yield, crop sustainability, plant nutrients availability, activity of soil microorganisms and also provides the basis for diagnoses of soil sodicity and salinity (Meethu & Jaya, 2015; Sonawane, Lawande, Gaikwad & Kuchekar, 2010). Analysis of variance indicated significant ($p = 0.05$) difference in EC values obtained for the contaminated site as against that of the control. Even though EC of the control were below detection limit, EC of contaminated soil increased with depth and the values ranged between 3.67 and 5.2 dS m^{-1} (Table 2).These values predict a sodic top soil and slightly saline soils from PL2 (US Salinity Laboratory Staff, 1954).

Values obtained for exchangeable sodium (Na^+) exhibited significant ($p = 0.05$) differences among the contaminated profile depths (Table 2). PL1 of contaminated soil showed a high amount of Na^+ but the Na^+ concentration reduced 3 fold throughout the other depths. Profile depths of the control site did not show any significant sodium concentration. The accumulation of exchangeable sodium in soil of farm lands is of a particular interest because it is not required in high concentration by most crops (Tanji & Wallender, 2012). Besides sodium has a dispersive influence on the clay component of soil. By the processes of slaking and swelling, soil clay particles disperse in a process that affect aggregate stability, break down soil structure, seal soil pores and reduce water infiltration (Rengasamey, 2014). Sou (2013) observed sodium accumulation in the top soil of plots irrigated with recycled effluent. This resulted in a dramatic collapse of structural pore network of the soil and led to the formation of compact soil layers with poor water storage ability (Marium, 2013; Khurana *et al.* (2012).

Calcium (Ca^{+2}), magnesium (Mg^{+2}) and potassium (K^{+}) are all important plant nutrients whose build up in soil through the application of industrial effluent is desirable. Ca^{+2} exhibited moderately high concentration in PL1 of the contaminated soil and followed by a fourfold decrease in PL2, and thereafter, remained constant with depth. A similar trend was observed for Mg^{+2} and K^{+}. Sonawane, Lawande, Gaikwad and Kuchekar (2010) observed accumulation of Ca^{+2}, Mg^{+2} and K^{+}, in soil after the continuous discharge of industrial effluent onto soil at Kurkumbh Industrial area in india. A similar observation was made by Okwute and Isu (2007) after they studied the physicochemical properties of soil as influenced by the discharge of palm oil mill effluent onto farmlands at Anyigba, Kogi State of Nigeria. After five years of irrigating farm land with industrial effluent from a tyre factory, however, Dastorani, Hakimzadeh and Kalantari (2008) did not observe any significant change in the value of soil K^{+}. Vimaldeep and Gitanjili (2014) stated that land application of wastewater can increase the level of soluble and exchangeable forms of potassium in soil more rapidly than with conventional inorganic fertilizers and that, most of the potassium in industrial effluent is immediately available. They added that, elements such as Ca^{+2} and Mg^{+2} needed for plant growth can accumulate in soil and improve soil pH especially in acidic soils.

Cation exchange capacity (CEC) of soil is a measure of the quantity of readily exchangeable cations neutralizing negative charges in the soil. It therefore serves as the buffer against the development of extreme acidic soil conditions which are detrimental to microbial activity and availability of soil-plant nutrients (Dastorani, Hakimzadeh & Kalantari, 2008). The CEC was moderate in the PL1 of contaminated soil but generally low in all sub layers examined. Analysis of variance showed significant ($p = 0.05$) differences in values for CEC within sampling levels of contaminated soil and also with the control.

5.3.3 Exchangeable sodium percentage

Exchangeable sodium percentage of soil is often used as a measure of the amount of sodium which can cause soil structure deterioration (Fatemeh, Ali & Najafali, 2013; Sackey, 2015). The exchangeable sodium percentage (ESP) of the contaminated soil exceeded the minimum threshold of 15 % through the entire sampled depth. With a corresponding EC of < 4 dS m^{-1}, PL1 is classified as sodic (US Salinity Laboratory Staff, 1954). Sodicity increased with soil depth with values significantly ($p = 0.05$) different from values of corresponding depths of the control. Soil permeability decreased with increased ESP and decreased soil solution electrolyte concentration as a result of swelling and or dispersion of clay (Meethu & Jaya, 2015). Blockade of soil pores as a result of clay dispersion and movement has been identified as the main mechanism controlling soil permeability when soils of low ESP values are leached with dilute salt solutions whereas swelling is recognized as the dominant mechanism at high ESP values (Rengasamey, 2014). The impact of the industrial effluent on the soil was thus significant as ESP was higher that 15 %. Even the widely accepted ESP 15 % as the critical level beyond which soil structure could be deleteriously affected has also been considered too high by some authors. Nearly 40 years back, Mclntyre (1979) proposed an ESP of 5 % as more appropriate for identifying sodic soil in Australia. Shainberg and Letey (1984) also reported soil dispersion with resulting decrease in hydraulic conductivity at ESP close to zero in a soil medium of low electrolyte concentration. Aylmore and Quirk (1959); Shainberg and Caiserman (1971) also observed that swelling of clay is not generally appreciable unless ESP exceeds 25 or 30 %. Besides, climatic variability and soil factors such as texture and mineralogy, bulk density, aggregate binding agents such as iron and aluminum oxide, organic matter and mechanical stress to which soil is subject to have also been identified as variables which could affect the ESP at which soil structure deterioration could arise. These arguments therefore bring afore a new dawn of soil research in order to establish a universal ESP which is applicable in our day.

5.3.4 Organic carbon, nitrogen and phosphorus

Values obtained for organic carbon (OC), nitrate nitrogen (NO_3^--N) and ammonium nitrogen (NH_4^+-N) and also available phosphorus (P) are presented in Table 3. Values for OC were significantly ($p = 0.05$) different within the contaminated soil profile and also, with the control. The OC at PL1 translates to a moderate level of soil organic matter. A fourfold decreased value was, however, observed from PL2 which remained constant down the profile (Table 3). Contrary to this trend, NO_3^-N and NH_4^+-N of the contaminated soil registered generally high values throughout the soil profile, relative to the control. Probably for its immobility in soil (Karen, Joshua, Chad & Ray, 2012), available phosphorus (P) accumulated to a very high level in PL1 of contaminated site, followed by a six times decrease in the P value of the next sampling level. Organic matter content strongly affects soil fertility by increasing the availability of plant nutrients, improving soil structure and water holding capacity and also acting as the accumulation phase for toxic heavy metals in the soil environment. For this reason, the recycling of organic effluent through their application to the soil can be an important promising activity for agriculture (Meethu & Jaya, 2015; Brejda & Moormann, 2011; Charanjit & Syed, 2011).

The application of palm oil mill effluent to farm land over time resulted in the build-up of soil organic matter, nitrogen and phosphorus (Okwute & Isu, 2007). The assessment of the physicochemical properties of soil at Kurkumbh Industrial Area of india also revealed a similar trend of moderate accumulation of OC, N and P in soils onto which industrial effluent was dumped over time (Sonawane, Lawande, Gaikwad & Kuchekar, 2010). A contrary situation was, however, reported by Dastorani, Hakimzadeh and Kalantari (2008) whereby the application of effluent from a tyre factory at Yazd, Iran, resulted in decreases in soil OC, N and P as compared to the use of ground water for irrigation. It therefore holds that the use of industrial effluent for farmland irrigation would always require a thorough assessment of the source.

Table 2: *Chemical properties of wastewater contaminated soil and control site*

PL (cm)	Soil pH		EC (dS m^{-1})		Na^+(cmol kg^{-1})		Ca^{+2}(cmol kg^{-1})		Mg^{+2} (cmol kg^{-1})		K^+(cmol kg^{-1})		CEC(cmol kg^{-1})		ESP	
	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S
PL1	6.5	8.7	0.0	3.7	0.1	3.1	2.2	9.3	0.6	6.5	0.3	0.8	3.1	19.6	1.5	16.0
PL2	6.4	8.0	0.0	4.5	0.0	1.3	0.7	2.1	0.4	3.9	0.1	0.2	1.1	7.4	1.7	17.2
PL3	6.4	7.3	0.0	5.0	0.0	1.3	0.4	2.1	0.4	3.3	0.0	0.1	0.8	6.7	1.6	18.5
PL4	6.4	7.2	0.0	5.2	0.0	1.3	0.3	1.9	0.4	3.7	0.1	0.1	0.7	7.0	1.2	18.4
PL5	6.1	6.6	0.0	4.6	0.0	1.1	0.3	1.9	0.4	2.9	0.1	0.1	0.8	6.0	2.0	18.3
PL6	5.4	6.5	0.0	3.8	0.0	1.0	0.2	1.9	0.4	3.1	0.1	0.1	0.7	6.2	3.1	16.8
PL7	5.2	6.1	0.0	3.8	0.0	0.8	0.2	2.1	0.4	3.3	0.1	0.1	0.7	6.3	3.5	15.4
LSD	0.1955		0.0615		0.0596		0.0111		0.1827		0.0054		0.6947		0.9860	

Where PL = Profile Level, C = Control and S = Sample

The contaminated soil exhibited generally high bulk density throughout the profile when compared to the control (Table 3). This corresponded to a textural class of clay loam, as against a constant textural class of sandy loam throughout the control profile. A clayey soil with such a high bulk density is characterized by compact layers, poor porosity, low rate of water infiltration and poor hydraulic conductivity (Vimaldeep & Gitanjili, 2014). Such a soil would inhibit seeds emergence and root penetration (Meethu & Jaya, 2015). The best management option for such a soil may be an organic based amendment which has the tendency of reducing soil bulk density, improving aeration, hydraulic conductivity among other things.

5.3.5 Micro nutrients

Figures 2 and 3 show the level of iron (Fe) and Zinc (Zn) in the contaminated soil as against the control soil. Even though Fe concentration in the industrial effluent was relatively negligible, the 43-years of continuous discharge onto the land has resulted in over 107 times increase of iron in the contaminated soil with a linear decrease with soil depth.

Zinc build-up in contaminated soil was 11- times that of the industrial effluent and statistically significant (($p = 0.05$) from values of the control soil. Fe and Zn are essential plant micro nutrients whose tolerance level varies widely among plants. Their toxicity in plants are evident in the form of leaf chlorosis, stunted growth, shorter root length and narrow leaves (Ho *et al.*, 2012).

Table 3: *Some Macro plant nutrients and physical properties of effluent affected soil*

PL	OC (%)		NH_4^+(mgN kg^{-1})		NO_3^- (mgN kg^{-1})		P (mgkg^{-1})		BD (gcm^3)		texture	
	C	S	C	S	C	S	C	S	C	S	C	S
PL1	0.4	1.2	1.5	26.8	2.5	18.2	10.3	42.5	1.1	1.4	SL	CL
PL2	0.3	0.3	1.3	16.7	1.4	16.7	5.7	5.7	1.1	1.6	SL	SCL
PL3	0.1	0.2	0.8	19.6	1.2	17.0	2.8	3.9	1.1	1.6	SL	CL
PL4	0.3	0.2	1.1	19.5	1.4	17.0	4.9	1.4	1.1	1.6	SL	CL
PL5	0.1	0.2	0.8	23.3	2.2	24.9	1.6	2.3	1.1	1.7	SCL	CL
PL6	0.2	0.2	0.9	25.7	1.7	23.7	1.8	4.8	1.1	1.6	SCL	CL
PL7	0.1	0.2	0.9	25.6	1.2	21.4	12.8	1.5	1.1	1.6	SCL	CL
LSD	0.0513		2.164		2.775		0.675		0.0568			

Where PL = Profile Level, C = Control and S = Sample, SL = Sandy Loam, CL = Clay Loam, SCL = Sandy Clay Loam.

Long term use of industrial effluent on agricultural lands generally leads to the build-up of heavy metals in soil (Vimaldeep & Gitanjili, 2014). Sewage irrigation for 20-years resulted in significant build-up of Fe (170 %) and Zn (208 %) in

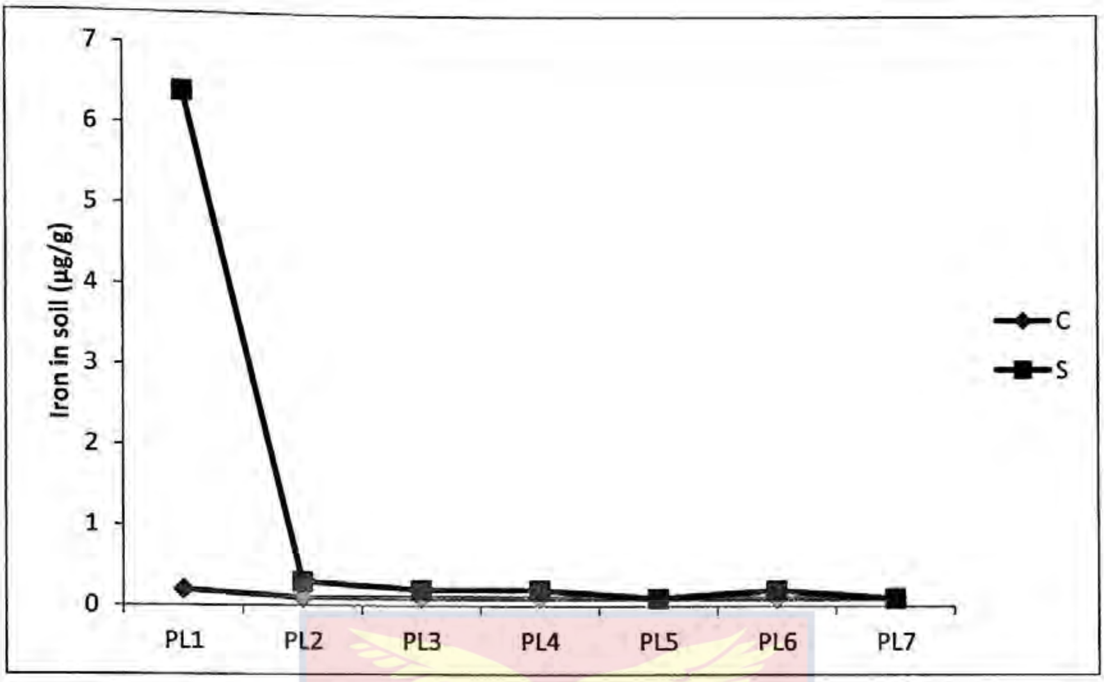

Figure 2: Iron (Fe) concentration across soil profile

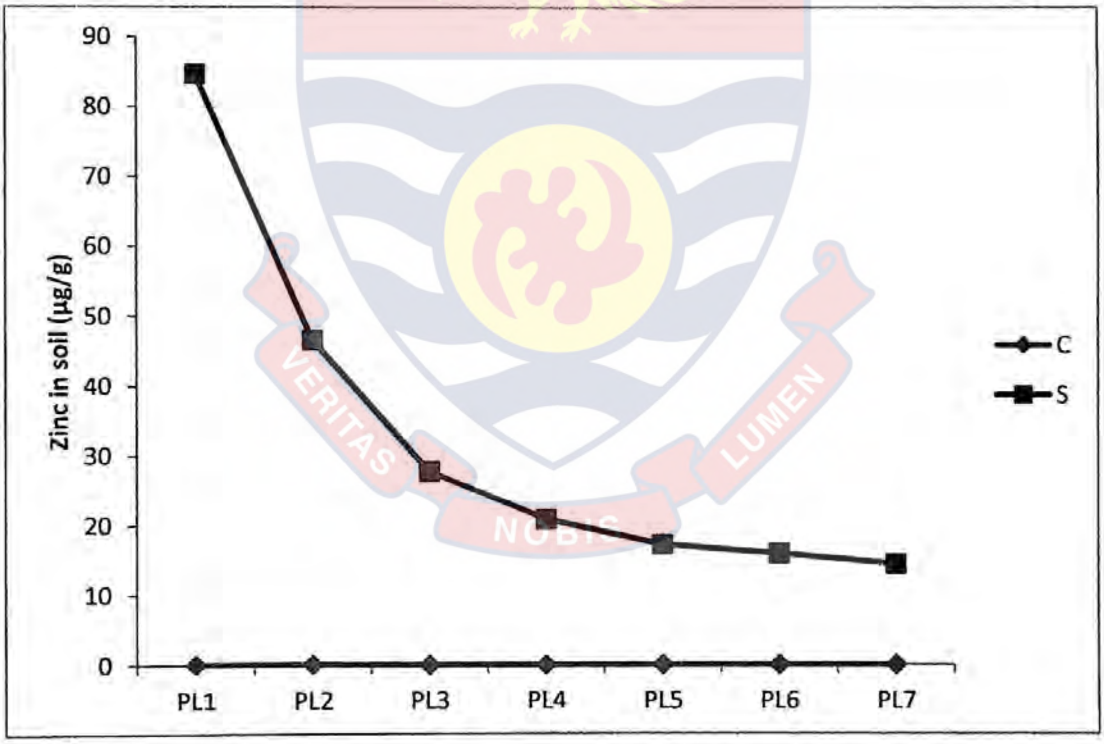

Figure 3: Zinc (Zn) concentration across soil profile

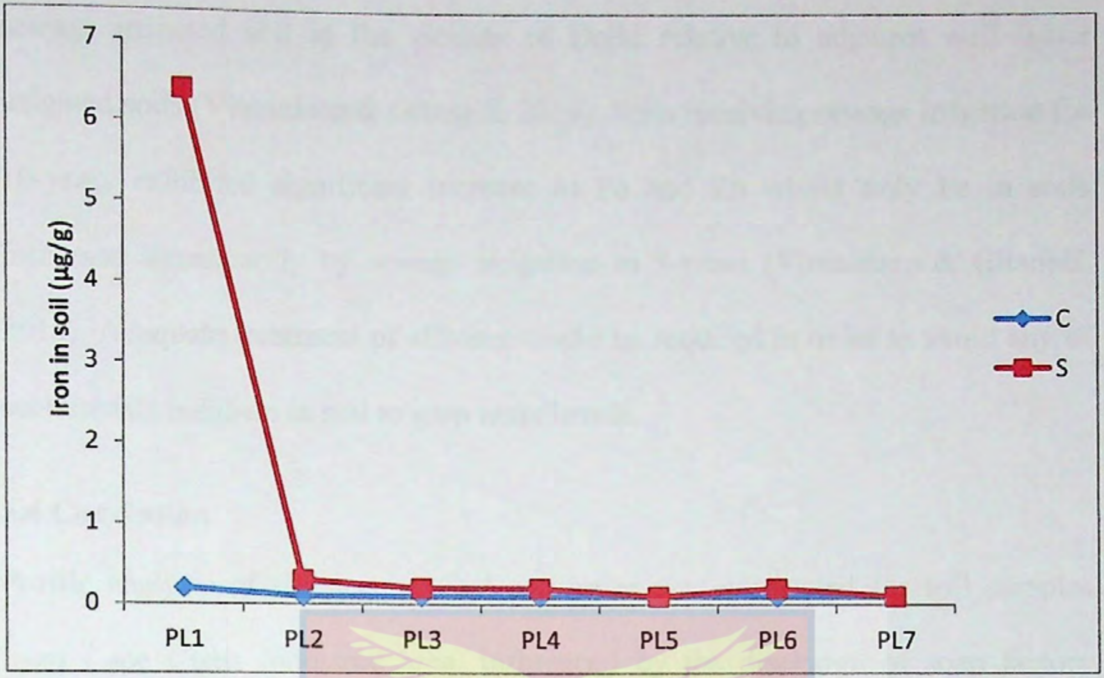

Figure 2: Iron (Fe) concentration across soil profile

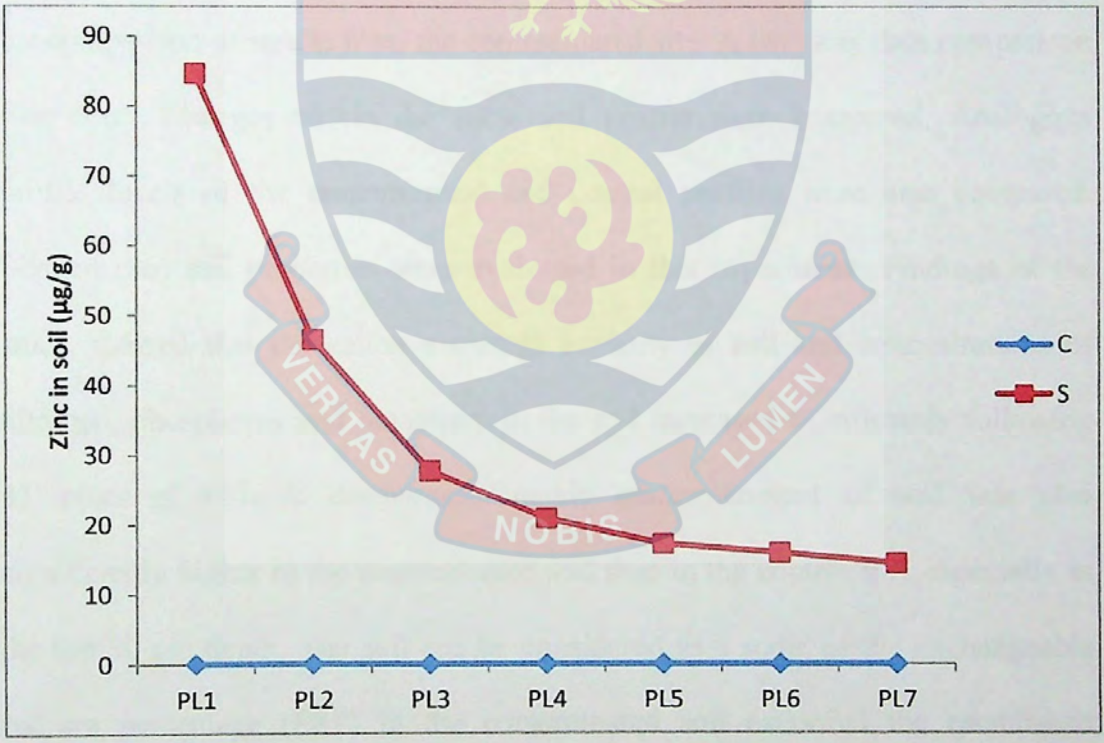

Figure 3: Zinc (Zn) concentration across soil profile

sewage irrigated soil in the vicinity of Delhi relative to adjacent well water irrigated soils (Vimaldeep & Gitanjili, 2014). Soils receiving sewage irrigation for 10-years exhibited significant increase in Fe and Zn whilst only Fe in soils increased significantly by sewage irrigation in 5-years (Vimaldeep & Gitanjili, 2014). Adequate treatment of effluent would be required in order to avoid any of such metals build-up in soil to crop toxic levels.

5.4 Conclusion

Profile analysis of physicochemical properties was conducted for soil samples from Cape Coast Industrial area, influenced by the discharge of soap factory effluent for 43 years. A control profile excavated 1 km away provided the basis for comparison of results from the contaminated site. A two-way data comparison was done. Changes within the same soil profile were compared. Analogous profile levels of the contaminated and control profiles were also compared. Sixteen (16) soil properties were evaluated in this experiment. Findings of the study showed that the cation exchange capacity of soil and concentrations of nitrogen, phosphorus and potassium in the soil increased significantly following 43 years of effluent discharge. Organic matter content of soil was also significantly higher in the contaminated soil than in the control soil, especially in the top 30 cm depth. The soil can be considered as a sodic as the exchangeable sodium percentage (ESP) in the contaminated soil exceeded the established minimum threshold of 15 % while the electrical conductivity (EC) in the same soil was less than 4 dS m^{-1}. The impact of the sodic condition on soil structure (dispersion and slacking of clay soil particle) resulted in the development of compact soil of high bulk density throughout the soil profile.

In the following chapter, biochars were prepared from saw dust, palm fiber and poultry manure. These, together with un-charred poultry were evaluated for their potentials to ameliorate sodic soils for crop production.

CHAPTER SIX

PHYSICOCHEMICAL STUDY OF BIOCHAR AND POULTRY MANURE FOR SOIL AMENDMENT

6.1 Introduction

Though poultry manure is much known for its ability to improve soil fertility, the term "biochar" is a relatively recent occurrence in soil fertility management. Biochar is simply defined as a highly porous charcoal produced from incomplete combustion processes. Biochar is perceived as a multi-purpose material. Apart from its role as a source of energy/fuel (Kwapinski *et al.*, 2010), biochar has also been identified as a sequester of carbon (Matovic, 2016) which could help in reversing the spate of climate change (Woolf, Amonette, Street-Perrott, Lehmann & Joseph, 2010). In the soil regime, biochar was identified as a source of organic matter which improves soil physical properties and also, an alternative to inorganic fertilizers in terms of supplying plant nutrients (Joseph *et al.*, 2013; Jeffery, Verheijen, van der Velde & Bastos, 2011; Gaskin *et al.*, 2010; Bruun *et al.*, 2011). It also proved to be an adsorbent of soil pollutants (Graber, Tsechansky, Gerstl & Lew, 2011; Graber, Tsechansky, Khanukov & Oka, 2011; Wang, Lin, Hou, Richardson & Gan, 2010). Biochar is found in soils around the world as a result of vegetation fires and the traditional farming practice of slash and burn. Conscious research to identify and quantify the impact of biochar in the soil regime, however, dates recent (Woolf, Amonette, Street-Perrott, Lehmann & Joseph, 2010). Even though the production of biochar has now been modernized and produced through pyrolysis, the choice of feedstock, together with burning temperature could influence yield and physicochemical properties of the product. The intended use of the biochar could also influence the choice of feedstock. For soil amendment, it is always important to characterize every substance prior to application so that changes in soil properties and plant behavour could be interpreted. Biochar characterization could also help in preventing the application of hazardous substances. The objective of this study therefore was to produce and characterize biochar from three (3) readily available industrial and agricultural waste materials namely, palm fiber, saw dust and poultry manure for soil application.

6.2 Materials and Method

The saw dust used in this experiment was collected from Cobosco Enterprise, Abura-Cape Coast. Palm fiber was collected from Solidaridad Oil Mills, Nfuom in the Twifo Hemang-Lower Denkyira District of Central Region and poultry manure from the Teaching and Research Farms, College of Agriculture and Natural Resources, University of Cape Coast. Each material was sun-dried for seven days to considerably reduce moisture. They were then prepared into biochar using the Lucia biomas pyrolytic stoves at charring temperature of 450 °C. The chars produced were milled using Brook Crompton Series 2000 Mill to pass through a 2 mm sieve. These, together with un-chared sample of the poultry manure were analyzed for sixteen (16) parameters important for improving soil fertility. These were pH, Total organic carbon (OC), total nitrogen (N), total phosphorus (P), exchangeable calcium (Ca^{+2}), exchangeable magnesium (Mg^{+2}), exchangeable potassium (K^+), exchangeable sodium (Na^+), exchangeable acidity (EA), electrical conductivity (EC), iron (Fe), Cupper (Cu), Zinc (Zn), carbon-nitrogen ratio (C:N), effective cation exchange capacity (ECEC) and exchangeable sodium percentage (ESP).

The determination of pH was done using the pH meter (sample to water ratio of 1:2.5) and electrical conductivity (EC) by the use of a conductivity meter and sample to water ratio of 1:2. For Ca^{+2} and Mg^{+2}, 5 g biochar and manure were extracted with ammonium acetate and aliquots titrated against 0.005 M Na_2 – EDTA, using Erichrome Black T and calgon indicators respectively. Potassium and sodium were determined by the use of a flame photometer (FAO, 2008) and available nitrogen forms determined by Kjeldahl distillation method. For exchangeable acidity, samples were extracted with 1M KCl (soil to extractant ratio of 1:2.5) and titrated against 0.1 M NaOH, with phenolphthalein as indicator. Organic carbon determination followed the potassium dichromate digestion method and the digest titrated against 0.5 M ammonium ferrous sulphate solution, using diphenylamine as indicator. Available phosphorus determination was by the use of spectrophotometer at a wavelength of 882 nm. For micro nutrients, 10 g of each sample was extracted using 20 ml of diethylene triamine pentaacetic acid (DTPA). The Atomic Absorption Spectrophotometer (AAS) was then used to measure their concentrations. The C:N ratios, effective cation exchange capacities (ECEC) and exchangeable sodium percentages (ESPs) were variously extrapolated from earlier stated properties of samples. Samples of the biochar prepared are displayed in Figure 4.The GenStat software was used to conduct analysis of variance (ANOVA) to determine the level of differences for measured parameters of biochars and manure samples.

Figure 4: Biochar prepared from saw dust (top), palm fiber (right) and poultry manure (left)

6.3 Results and Discussion

6.3.1 pH, and electrical conductivity

Properties of the types of biochar [saw dust biochar (SDB), palm fiber biochar (PFB) poultry manure biochar (PMB)] and poultry manure are presented in Table 4. The materials differed (P = 0.01) much in their characteristics. The pH values ranged from neutral to alkaline. The observed order of increase in pH was SDB<PFB<PM<PMB. Biochar pH could impact soil pH which would in turn

influence soil nutrient availability and microbial activity. SDB and PFB registered neutral pH and therefore could be suitable for application to a wide range of agricultural soils. The pH for PMB and PM were alkaline. Their application would therefore be more suitable in acid soils (Joseph *et al*., 2013; Jeffery, Verheijen, van der Velde & Bastos, 2011; Gaskin *et al*., 2010; Bruun *et al*., 2011).

SDB registered the lowest value for electrical conductivity (EC) as against the highest value for PMB. The order of increase in EC is SDB<PFB=PM<PMB. Being the indicator for salt load, SDB poses the least threat of soil salinity, followed by PFB and PM in that order. The application of PMB to soil may pose the challenge of soil salinity over time. This would, however, depend on the salinity status of the receiving soil and also, the rate of application of the biochar (Joseph *et al*., 2013; Jeffery, Verheijen, van der Velde & Bastos, 2011; Gaskin *et al*., 2010; Bruun *et al*., 2011)..

6.3.2 Organic carbon, C:N ratio and phosphorus.

Generally high levels of organic carbon (OC) were registered for all materials characterized in this study though the values were not statistically significant (P = 0.01) from each other. PM registered the highest OC value whilst PMB was the lowest. The pyrolysis of PM resulted in nearly 10 % loss of OC. The carbon content of biochar is of prime importance because of its role in carbon sequestration and the subsequent potential to reduce climate change (Sohi, 2012; Enders, Hanley, Whitman, Joseph & Lehman, 2012). Unlike the carbon in biomass which degrades easily and release CO_2 into the atmosphere (Lee, Eum, Park, Jung & Hyun, 2013; Lee *et al.*, 2010), the pyrogenic carbon formed during charring of biomas is recalcitrant to degradation and therefore remains in soil for long periods (Lee, Eum, Park, Jung & Hyun, 2013; Lee *et al*, 2010).

Table 4: *Physicochemical properties of biochars and poultry manure*

PROPERTIES /MATERIALS	**SDB**	**PFB**	**PMB**	**PM**	**LSD**
pH (Biochar : water)	7.2	7.4	10.0	8.7	0.14
EC (dS m^{-1})	0.5	3.2	10.0	3.2	1.35
Total Organic Carbon (%)	25.3	29.9	23.5	33.1	ns
Total Nitrogen (%)	0.5	1.9	2.0	2.2	0.12
Total Phosphorus (%)	0.1	0.4	1.0	0.7	0.27
C: N	47: 1	17: 1	12: 1	15: 1	
Calcium (cmol kg^{-1})	20.5	40.8	32.4	72.5	12.05
Magnesium (cmol kg^{-1})	1.7	23.8	69.8	29.1	13.61
Potassium (cmol kg^{-1})	7.1	14.5	25.2	27.1	2.13
Sodium (cmol kg^{-1})	4.0	8.0	14.8	14.6	1.12
Ex. Acidity	0.9	1.7	1.4	4.2	1.02
ECEC (cmol kg^{-1})	34.5	67.7	143.6	144.5	11.62
ESP (%)	11.6	11.8	10.3	10.1	ns
Fe (µg g^{-1})	6.2	12.5	5.7	6.9	3.64
Cu (µ g g^{-1})	7.6	24.8	8.6	24.2	7.09
Zn (µg g^{-1})	1.6	2.62	6.0	19.4	1.27

SDB = Saw dust Biochar

PFB = Palm fiber Biochar

PMB = Poultry Manure Biochar and

PM = Poultry manure

ns = not significant at P = 0.01

By modeling, the vitality of biochar in soil was projected to last for centuaries and even to millennia (Lehmann *et al*., 2011). In agronomy, soil organic carbon enhances soil physical conditions by reducing soil bulk density, enhancing soil porosity, and water and nutrients retention and also improves activity of soil microbes (Lehmann *et al*., 2011).

The application of SDB to soil could result in a net immobilization of nitrogen. This is derived from its high C:N ratio (Table 4). The remaining materials, however, exhibited low C:N ratios in the order of PMB<PM<PFB which explains the ability of these materials to enhance soil nitrogen supply to plants.

The level of phosphorus (P) recorded by all materials were high and could enhance soil P levels for crop production. PMB registered the highest percentage of P whereas SDB recorded the lowest (Table 4). This coupled with the presence of nitrogen and potassium would enable the materials to improve the ability of soil to supply major plant nutrients.

6.3.3 Exchangeable cations

A number of plant available nutrients exist in the form of cations. Common among them is calcium (Ca^{+2}), magnesium (Mg^{+2}) potassium (K^{+}) and sodium (Na^{+}). Ca^{+2}, Mg^{+2}, and K^{+} are absorbed in relatively high quantities but the utilization of Na^+ is usually small by most crops (Lehmann *et al*., 2011). All the materials characterized in this study exhibited high cation exchange capacity. Ca^{+2} increased in the order of SDB<PMB<PFB<PM, Mg^{+2} by SDB<PFB<PM<PMB, K^+ of SDB<PFB<PMB<PM and Na^+ of SDB<PFB<PMB<PM (Table 4). The effective cation exchange capacities (ECEC) of the materials were also statistically significant ($P < 0.01$) from each other Table 4. Exchangeable sodium percentage (ESP) recorded by all samples were below sodicity threshold of ESP ≥ 15 (US Salinity Laboratory Staff, 1954).

6.3.4 Micro nutrients in biochar and poultry manure

Generally low values were recorded for micro plant nutrients namely iron (Fe), copper (Cu) and zinc (Zn). Values for Fe were not significant ($P = 0.01$) for SDB, PMB and PM. The three were, however, significant ($P = 0.01$) when compared to PFB (Table 4). Values of Cu increased in the order of SDB<PMB<PM<PFB. These values were significant ($P = 0.01$) from each other. SDB and PMB did not differ statistically from each other. Zn was relatively high in PM. Its concentration in SDB, PFB and PMB were, however, low (Table 4).

6.4 Conclusion

Four organic materials were evaluated for their potential to enhance soil fertility. These materials were saw dust biochar (SDB), palm fiber biochar (PFB), poultry manure biochar (PMB) and poultry manure (not charred). The study assessed the materials ability to enhance soil organic carbon (OC), cation exchange capacity (CEC), enhancement of soil macro and micro plant nutrients supply and their potentials for soil salinity and sodicity. All materials exhibited high potential for OC as values ranged from 23.5 % to 33.1 %. The potential for CEC improvement was high for all the materials studied. PM exhibited the highest potential for CEC improvement whilst SDB registered the lowest. PM proved to be a better source for plant major nutrients (NPK) as against the potentials of PMB, PFB and SDB in that order. All the materials could also supply some plant micro nutrient namely, Fe, Cu and Zn, though their supply potentials were on the low side. The materials recorded generally low values for electrical conductivity which is the measure for salt load. Exchangeable sodium percentage (ESP) for all materials was also below sodicity threshhold of ESP ≥ 15. All the materials showed high potentials for soil fertility improvement. SDB and PFB proved suitable for all manner of agricultural soils. PMB and PM would, however, be more suitable for acidic soils.

In the next chapter, a pot experiment was conducted. The sodic soil was amended with the three different biochars and the un-charred poultry manure. The impacts of the amendments on sodic soil reclamation were evaluated.

CHAPTER SEVEN

RECLAIMING SODIUM AFFECTED SOIL: THE ROLE OF ORGANIC AMENDMENTS

7.1 Introduction

From the agricultural point of view, sodic soils are soils which contain excess exchangeable sodium that adversely affects the growth of most crop plants (Srivastava, Gupta, Panday, Singh & Tewan, 2014). The exchangeable sodium percentage (ESP) of such soils usually exceeds 15 (US Salinity Laboratory Staff, 1954). Adverse effects of soil sodicity include the degradation of soil physical and nutritional properties with consequent reduction in crop growth, significantly or entirely (Nguyen, 2012; Singh & Singh, 2013). Sodic soils usually exhibit electrical conductivity (EC) values below 4 dS m^{-1} and pH ranges of 8.2 to 10.5 (US Salinity Laboratory Staff, 1954). The fundamental principle which governed the reclamation of sodic soils was the removal of part or most of the exchangeable sodium and its replacement by calcium ions and other preferred cations such as magnesium and potassium in the root zone of crops. This involved the use of soluble calcium salts such as gypsum, calcium chloride, acids or acid forming substances, including sulphuric acid, iron sulphate, aluminium sulphate, lime-sulphur, sulphur, pyrite, and calcium salts of low solubility like ground limestone (Ali, 2011; Allotey, Asiamah & Nyamekye, 2008). Organic manures have long been known to facilitate the reclamation of sodic soils (Busscher, Novak & Ahmedna, 2011; Brinck & Frost, 2009; Abiven, Manaseri & Chenu, 2009). The mechanisms involved and the precise reasons for observed responses have, however, remained unclear. The option of phyto-remediation has also been long exploited but found to be the slowest in terms of removing excess sodium from soil (Busscher, Novak & Ahmedna, 2011; Brinck & Frost, 2009; Abiven, Manaseri & Chenu, 2009). The use of chemicals in remediation of sodic soils was not without challenges. Apart from their relative high cost, most of such chemicals were not readily available in the market. A number of them are also not user friendly (Busscher, Novak & Ahmedna, 2011; Brinck & Frost, 2009; Abiven, Manaseri & Chenu, 2009). The chemicals approach to reclaiming sodic soils also was largely accompanied by leaching with water, the cost of which may not be bearable in terms of reclaiming large acreages of farm land (Nadeem, Zahif, Naveed & Nawaz, 2013). The leachates also pose the challenge of off-site pollution (Nadeem, Zahif, Naveed & Nawaz, 2013). Leaching may also wash away important soil-plant nutrients. The time has therefore come for researchers to come up more sustainable and environmentally friendly methods of addressing soil sodicity. The objective of this research therefore was to evaluate the potential of biochars and poultry manure for the reclamation of sodium affected soils without leaching.

7.2 Materials and Method

The soil sample used in this experiment was that top soil (≤ 30 cm depth) of a Sodic Solonchak sampled from the land opposite Cape Coast industrial area and polluted with soap industrial effluent for 43-years. The physicochemical properties of the soil were, pH (8.7), EC (3.7 dS m-1), Na^+ (3.1 cmol kg^{-1}), Ca^{+2} (9.3 cmol kg^{-1},) Mg^{+2} (6.5 cmol kg^{-1}), K^+ (0.8 cmol kg^{-1}), CEC (19.6 cmol kg^{-1}), ESP (18.0), OC (1.2 %), NH_4^+(26.8 mgN kg^{-1}), NO_3^- -N (18.2 mgN kg^{-1}), P (42.35 mg kg^{-1}), BD (1.4 gcm^3) and texture (clayey loam).

A pot experiment was conducted to evaluate the potential of four (4) different organic based amendments to correct the sodicity status of the soil without the conventional leaching. The applied amendments included saw dust biochar (SDB), palm fiber biochar (PFB), poultry manure biochar (PMB) and poultry manure (PM). The general properties of these materials are reported in Table 4. The performances of these treatments were compared to those of conventional gypsum and a control soil (soil anly). The rates of application were:

- Control (Soil only - 5 kg soil/pot)
- Gypsum only at full gypsum requirement rate of 4.78 t ha^{-1} (11.95g/5kg soil/pot)
- Saw dust biochar only at 4.78 t ha^{-1} (11.95g/5kg soil/pot)
- Palm fiber biochar only at 4.78 t ha^{-1} (11.95g/5kg soil/pot)
- Poultry manure biochar only at 4.78 t ha^{-1} (11.95g/5kg soil/pot) and
- Poultry manure only at 4.78 t ha^{-1} (11.95g/5kg soil/pot)

The completely randomized design was used to assign the amendments to experimental pots. The amendments were applied and thoroughly mixed with soil. Each amendment was replicated 5-times. The amended soils were incubated for a period of six weeks during which soil sampling was done weekly for laboratory analysis. Periodic watering of soil was done in order to keep soil moisture level at field capacity (about 60 % moisture content).

Soil properties monitored during the six weeks were, soil pH, electrical conductivity (EC), exchangeable sodium (Na^+), exchangeable calcium (Ca^{+2}), exchangeable magnesium (Mg^{+2}), exchangeable potassium (K^+), cation exchange capacity (CEC), exchangeable sodium percentage (ESP), organic carbon (OC), nitrate nitrogen (NH_4^+-N), ammonium nitrogen (NO_3^- -N) and available phosphorus (P).

The pH determination was done using the pH meter (soil to water ratio of 1:2.5), electrical conductivity by use of conductivity meter and (sample to water ratio of 1:2). Ca^{2+} was determined by titrating aliquot of ammonium acetate soil extract against 0.005 M Na_2 – EDTA, and Erichrome Black T used as indicator whilst Mg^{2+} determination followed a similar process but with calgon indicator. Potassium and sodium were determined using the flame photometer (FAO, 2008) and available nitrogen forms determined by Kjeldahl distillation method. For exchangeable acidity, soil was extracted with 1M KCl (soil to extractant ratio of 1:2.5) and titrated against 0.1 M NaOH with phenolphthalein as indicator. Organic carbon determination was by the potassium dichromate digestion method. The digest was titrated against 0.5 M ammonium ferrous sulphate solution, using diphenylamine as indicator.

After the six weeks of monitoring, a sodium sensitive crop (***Zea mays L***) was planted on these soils. The local obatanpa variety was used. The rate of seed germination was monitored and also, dry matter yield of above ground portion at day 45 after seed germination.

The GenStat discovery software (2016) was used to perform analysis of variance (ANOVA) in order to determine the effects of the amendments on soil properties. This enabled the determination of the level of differences for measured parameters of soil samples.

7.3 Results and Discussion

7.3.1 Soil pH and electrical conductivity

The results of soil pH and electrical conductivity (EC) following the application of treatments and weekly sampling for six weeks are presented in Tables 5 and 6. The application of gypsum resulted in a marginal increase in soil pH in week 1. The margin of increase was, however, not statistically significant (P = 0.05) from that of the control. This marginal increase in soil pH was constant for the six weeks period. The increase in soil pH after the application of gypsum could be the result of the formation of calcium salts [$CaCO_3$, and Ca $(HCO_3)_2$] (Brinck & Frost, 2009). All the organic based amendments, however, resulted in significant (P = 0.05) decrease in soil pH. The average decrease in soil pH was in the order of PM<PFB<SDB<PMB. Poultry manure biochar was the least effective in reducing soil pH when compared to the other organic based amendments. Soil pH was relatively constant for SDB and PMB throughout the sampling period (Table 5). In the case of PFB, however, reduction in soil pH was gradual in the first two weeks but the value stabilized from week 3. The general decrease in soil pH

following the application of biochars and poultry manure could be attributed to the release of cations from the ash component of these biochars and also, the decomposition of poultry manure (Brinck & Frost, 2009). This might have resulted in the reduction in the amount of anions on soil colloidal surface. Soil pH influences the availability of plant nutrients. The decrease in soil pH following the application of biochars and poultry manure contradicts the findings of Bayu, Tadesse and Amsalu (2015); Nicole (2013); Abebe, Endalkachew, Mastarwesha and Gebermedihin (2012), all of whom recorded increased pH after the application of biochar and compost. It is, however, worth to note that the impact of biochar/manure application on soil pH could be much influenced by the properties of the feedstock from which they are prepared. There was a general increase in soil EC following the application of all the organic based amendments (Table 6). The percentages of increase were, however, not statistically significant (P = 0.05) for all amendments.

7.3.2 Exchangeable calcium, magnesium, potassium and sodium

Values obtained for Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} are presented in Figures 5, 6, 7 and 8 respectively. Increased calcium levels were observed following the application of all amendments. The differences in Ca^{2+} values were significantly (P = 0.05) different from each other. The application of gypsum recorded the highest Ca^{+2} values in week 4. Ca^{+2} release in biochar amendments increased gradually with time and assumed the highest values at week 6 (Figure). The peak Ca^{+2} value for poultry manure was, however, observed at week 5, followed by a significant decrease in availability of same in week 6 (Figure 5).

Table 5: *Soil pH of amended soils*

Weeks	Amendments					
	CT	GP	SDB	PFB	PMB	PM
Wk1	8.6	8.9	7.8	8.1	7.3	8.0
Wk2	8.7	8.9	7.9	8.1	7.1	8.3
Wk3	8.7	8.8	7.9	7.6	7.0	8.2
Wk4	8.6	8.7	7.9	7.6	7.1	8.3
Wk5	8.7	8.8	7.7	7.6	7.0	8.2
Wk6	8.7	8.8	7.7	7.6	7.1	8.1

LSD (0.05): 0.2146

Where CT = Control, GP = Gypsum, SBD = Saw Dust Biochar, PFB = Palm Fiber Biochar, PMB = Poultry Manure Biochar and PM = Poultry Manure

Table 6: *Electrical Conductivity (EC dS m^{-1}) of amended soil*

Weeks	Amendments					
	CT	GP	SDB	PFB	PMB	PM
				dS m^{-1}		
Wk1	3.7	10.2	4.2	5.8	8.1	8.6
Wk2	3.7	10.3	3.8	5.8	8.1	8.6
Wk3	3.6	9.6	3.8	3.9	7.4	8.8
Wk4	3.7	26.4	3.8	3.6	7.1	8.9
WK5	3.7	10.0	3.5	3.6	7.1	10.9
Wk6	3.7	12.0	3.5	3.6	7.1	12.7

LSD (0.05): 9.560

In comparison to the control, the differences in Ca^{+2} values for all amendments were statistically significant (P = 0.05) at week 6. The amendments were, however, not significant (P = 0.05) against each other at week 6. Gypsum is a calcium concentrate and known for its ability to readily increase soil Ca^{+2} levels when applied. The gradual release of Ca^{+2} by the biochars and the poultry manure to almost the same level of gypsum provided the basis that these organic amendments could replace gypsum in terms of calcium supply in soil.

Significant (P = 0.05) decrease in soil Mg^{+2} was observed after the application of gypsum (Figure 6). The values for same amendment, however, increased gradually in biochars and manure amendments over time, with highest values recorded in week 6. At week 6, Mg^{+2} release was highest for PFB, followed by saw dust biochar.

All organic based amendments increased soil K^+ values by an average of 0.33 cmol kg^{-1} in week 1 (Figure 7). This increase was, however, not statistically significant (P = 0.05) from that of the control. Soil K^+ levels, however, declined from week 2 through to week 6. This could be attributed to microbial immobilization for decomposition of applied organic matter.

Marginal increase in soil Na^+ was observed following the application of all amendments (Figure 8). The margin of increment was also not significant (P = 0.05) from the control. Calcium plays a crucial role in soil nutrition and plant root development. Magnesium is also the central element of chlorophyll. Potassium plays crucial role in plant reproduction and considered second to nitrogen.

Sodium, though required in relatively small quantities, also plays important role in plant growth. Major, Rondon, Molina, Riha and Lehmann (2010) observed increased soil Ca^{2+} and Mg^{2+} availability when biochar was applied at 20 t ha^{-1} to a Colombian savanna oxisol. In an Iowa study, Laird *et al.* (2010) found a significant increase in Ca^{2+} levels when biochar was applied to soil at 20 g Kg^{-1} soil. Bayu, Tadesse and Amsalu (2015); Nicole (2013); Abebe, Endalkachew, Mastarwesha and Gebermedihin (2012) also observed significant increase in the levels of Ca^{+2}, Mg^{2+}, K^{+} and Na^{+} following the application of biochar and compost. Per these research findings, therefore, biochar could be a significant source of these cations (Singh, Singh & Cowie, 2010) and could potentially help in sodic soil remediation.

7.3.3 Cation exchange capacity and exchangeable sodium percentage

Cation exchange capacity (CEC) represents the total amount of positively charged ions that a soil can hold (Nicole, 2013). A higher CEC indicates the capacity of the soil to adsorb and hold nutrients and therefore, higher nutrient availability in soil. The soil analysis showed that the biochar and poultry manure amendments significantly ($P = 0.05$) increased soil CEC compared to the control and gypsum (Table 7). Organic amendments exhibited gradual increase in soil CEC over time, with PFB recording the highest CEC at week 6. The order of increase in CEC at week 6 was CT<GP<PM<PMB<SDB<PFB (Table 7). All biochar amendments improved soil CEC better that non-biochar amendments (Table 7). Literature explains that biochar is a variably charged organic material with high surface area and highly porous.

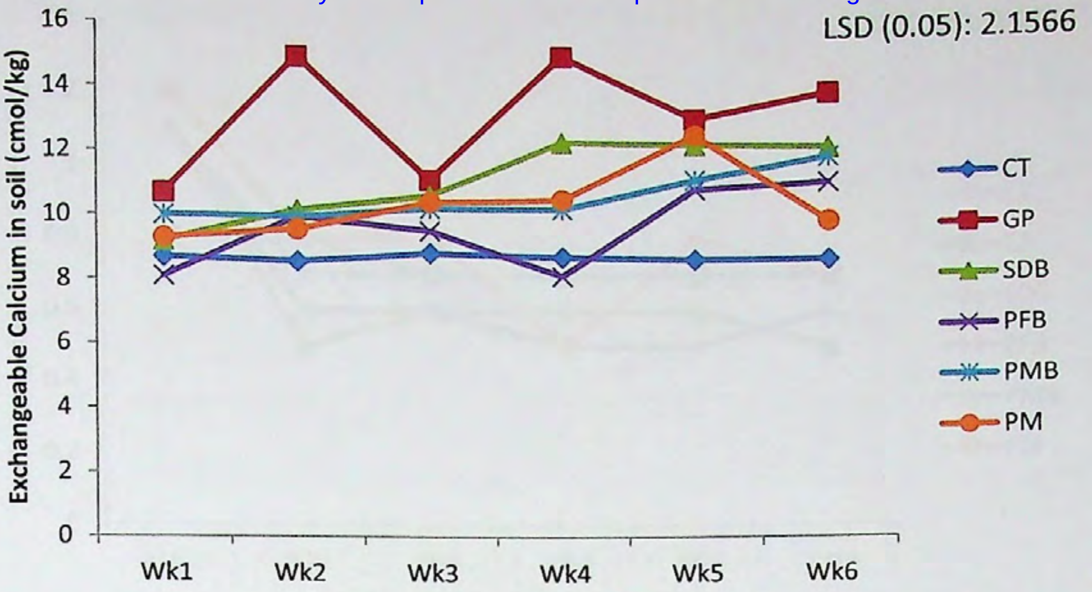

Figure 5: Exchangeable calcium dynamics in soil after amendments were applied.

Where CT = Control, GP = Gypsum, SBD = Saw Dust Biochar, PFB = Palm Fiber Biochar, PMB = Poultry Manure Biochar and PM = Poultry Manure

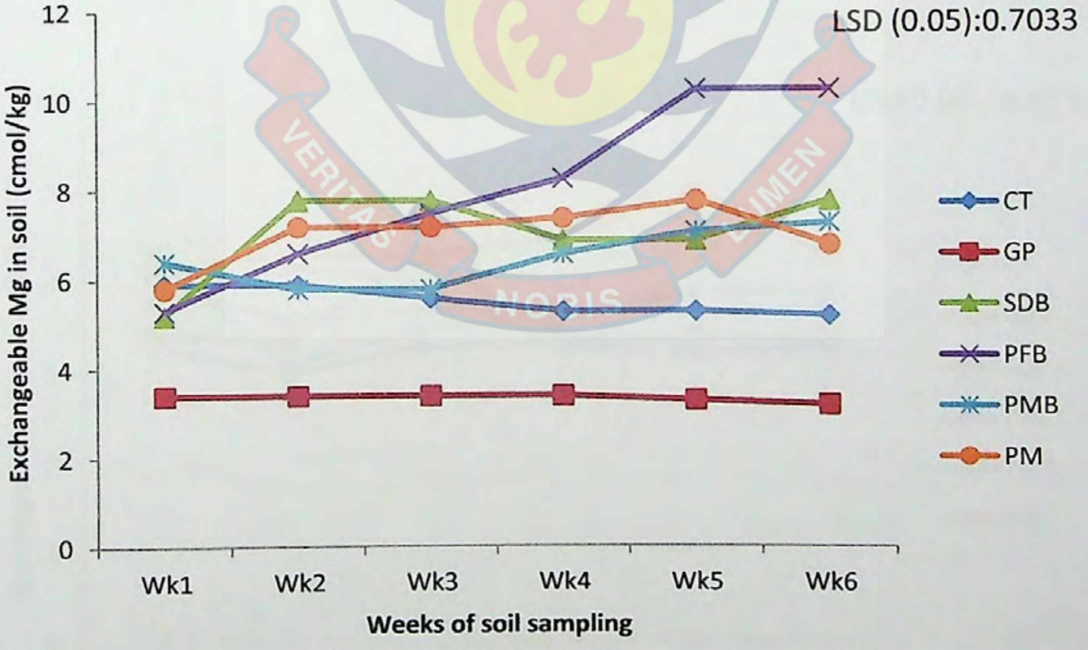

Figure 6: Exchangeable magnesium dynamics in soil after amendments were applied.

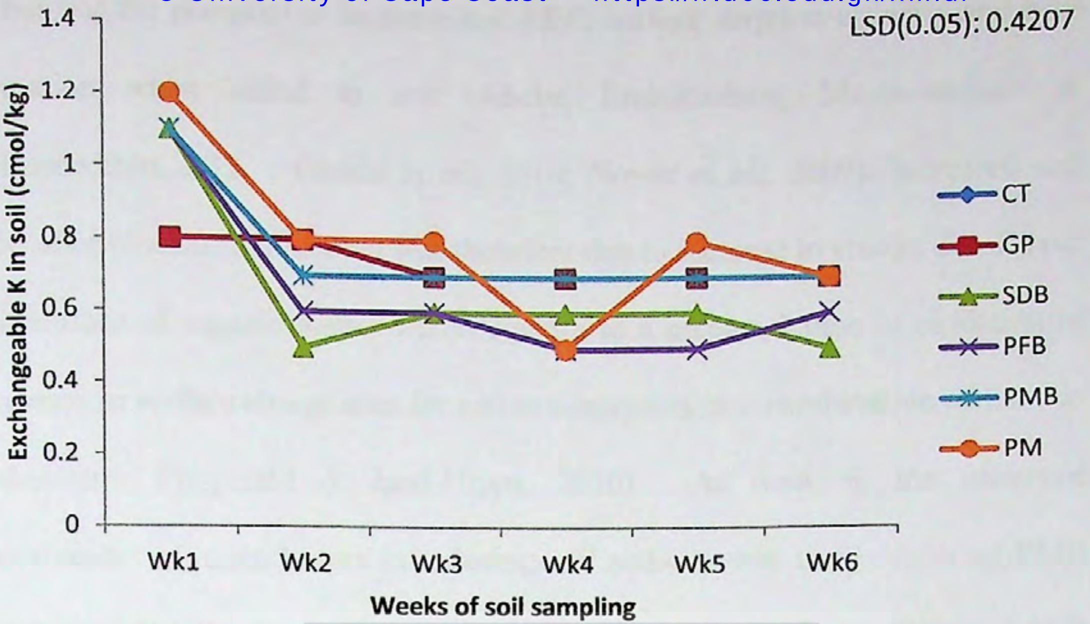

Figure 7: Exchangeable potassium dynamics in soil after amendments were applied.

Where CT = Control, GP = Gypsum, SBD = Saw Dust Biochar, PFB = Palm Fiber Biochar, PMB = Poultry Manure Biochar and PM = Poultry Manure

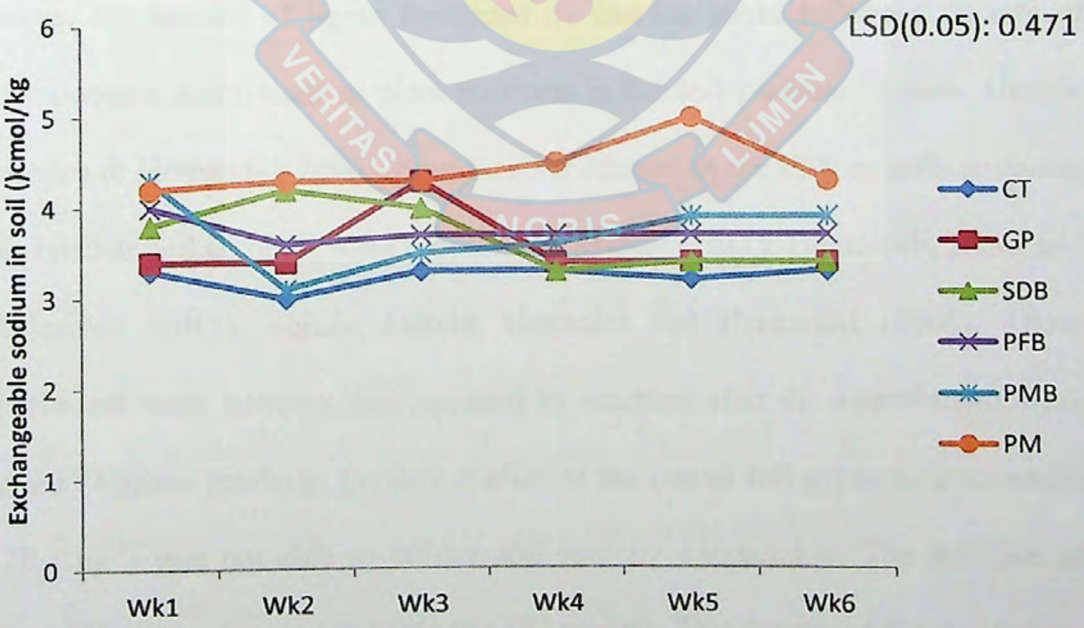

Figure 8: Exchangeable sodium dynamics in soil after amendments were applied.

It thus has the potential to increase soil CEC, surface sorption capacity and base saturation when added to soil (Abebe, Endalkachew, Mastarwesha & Gebermedihin, 2012 ; Gaskin *et al.*, 2010; Novak *et al.*, 2009). Increased soil CEC after biochars application was therefore due to increase in charge density per unit surface of organic matter which equates to a greater degree of oxidation or increases in surface charge area for cation adsorption or a combination of the two (Atkinson, Fitzgerald & Jand-Hipps, 2010). At week 6, the observed effectiveness of amendments in reducing soil sodicity was in the order of PMB (9.3 %) < GP (12.6 %) < SDB (21.9) = PFB (21.9 %) (Table 8). SDB and PFB reduced soil sodicity below the minimum threshold of ESP 15 (Table 8). PMB, however, could not. It is worth stating that SDB and PFB exhibited relatively high Ca^{+2} and Mg^{+2} values at week 6 (Figures 5 & 6). The sum of the divalent cations to the total cation concentration of those amendments had therefore increased, leading to the reduction in the percentage soil colloidal surface occupied by Na^{+}. Besides, the amount of lignin contained by biochar could influence its rate of decomposition and release of plant nutrients in the soil medium (Tejada, Garcia, Gonzales & Hernandel, 2006). Significant reduction in the ESP of soils amended with biochar and compost were reported by Mahdy (2011); Gharaibeh, Eltaif and Albalasmeh (2011); Tejada, Garcia, Gonzales and Hernandel (2006). Those experiments were however accompanied by leaching after the amendments were applied .Without leaching; gypsum applied at the rate of full gypsum requirement (4.78 t ha^{-1}) was not able to reduce soil sodicity appreciably. The addition of gypsum introduced more Ca^{+2} into the soil regime. This increased the percentage

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7.3.4 Soil organic carbon and available phosphorus after the application of amendments

Results obtained for soil organic carbon (OC) after the application of amendments are reported in Table 9. All the organic based amendments resulted in an increased soil OC. Most of the OC increases were, however, not statistically significant (P = 0.05) from each other. Saw dust biochar (SDB) recorded the highest value for OC at week 6; an increase which was statistically significant (P = 0.05) over the control.

Table 7: *Cation exchange capacity (cmol kg^{-1}) of amended soil*

Weeks	Amendments					
	CT	GP	SDB	PFB	PMB	PM
	cmol kg^{-1}					
Wk1	18.5	18.2	19.2	18.6	22.0	20.7
Wk2	18.2	21.8	22.4	20.6	19.4	21.9
Wk3	18.5	18.7	22.4	21.4	20.4	22.8
Wk4	18.1	22.4	23.2	22.7	21.1	23.0
Wk5	18.0	20.7	22.8	25.4	22.9	26.4
Wk6	18.0	21.4	24.0	25.6	23.8	21.7
LSD (0.05): 2.180						

Where CT = Control, GP = Gypsum, SBD = Saw Dust Biochar, PFB = Palm Fiber Biochar, PMB = Poultry Manure Biochar and PM = Poultry Manure

Table 8: *Exchangeable sodium percentage (%) of amended*

Weeks	Amendments					
	CT	GP	SDB	PFB	PMB	PM
	%					
Wk1	18.0	18.6	19.4	21.9	19.7	20.3
Wk2	17.0	15.8	18.4	17.4	16.2	19.8
Wk3	18.0	18.5	18.0	17.1	17.2	19.8
Wk4	18.0	16.0	14.4	16.5	17.2	19.6
Wk5	18.2	17.0	14.9	14.5	16.5	19.1
Wk6	18.3	16.0	14.3	14.3	16.3	20.0
LSD (0.05): 2.518						

The relative OC increases from the application of the biochars and poultry manure could be from the presence of high amount of OC in the feed stocks. The highest value of OC from a biochar amended soil indicated the recalcitrance and high stability of C-organic in biochar. High OC in soils amended with biochar were also reported by Abebe, Endalkachew, Mastarwesha and Gebermedihin (2012); Novak, Busscher, Laird, Ahmedna, Watts and Niandou (2009); Mukherjee and Lal (2013); Lakhdar, Rabhi, Ghnaya, Montemurro, Jedidi and Abdelly (2009); Brennam, Fenton, Rodgers and Healy (2011). Increased OC level of soil could be very valuable in restoring degraded soil physical properties of agricultural soils.

The impacts of amendments on soil available phosphorus (P) are presented in Table 10. SDB, PFB and PM all recorded no insignificant ($P = 0.05$) increases in soil available P over the control soil. PMB, however, did recorded significant ($P = 0.05$) increase in available P over the control in weeks 4, 5, and 6. Peak P availability was observed in week 4 (Table 10). It is worth to note that, PMB exhibited the highest percent of total P when the amendments were characterized (Table 4).

The application of gypsum rather resulted in the depletion of soil available P. This could be attributed to fixation following the introduction of calcium divalent cations into the soil medium (Karen, Joshua, Chad & Ray 2012; Brennan, Fenton, Rodgers & Healy, 2011).

Table 9: *Organic carbon (%) of amended*

Weeks	Amendments					
	CT	**GP**	**SDB**	**PFB**	**PMB**	**PM**
	%					
Wk1	0.8	0.9	0.8	0.9	0.9	1.0
Wk2	0.8	0.9	0.9	0.9	0.8	1.0
Wk3	0.8	0.9	0.9	0.9	0.8	0.9
Wk4	0.8	0.8	0.8	0.8	0.7	1.0
Wk5	0.9	0.9	0.8	0.9	1.0	1.0
Wk6	0.7	0.9	1.1	0.9	0.9	1.0

LSD (0.05): 0.3846

Where CT = Control, GP = Gypsum, SBD = Saw Dust Biochar, PFB = Palm Fiber Biochar, PMB = Poultry Manure Biochar and PM = Poultry Manure

Table 10: *Available phosphorus (mg kg^{-1}) after of amended soils*

Weeks	Amendments					
	CT	**GP**	**SDB**	**PFB**	**PMB**	**PM**
	mg kg^{-1}					
Wk1	29.6	22.6	27.4	25.6	38.9	31.2
Wk2	30.1	22.4	26.7	24.9	36.4	30.5
Wk3	30.9	22.4	26.8	24.9	38.2	30.5
Wk4	28.4	20.7	27.5	24.9	43.6	24.4
Wk5	23.8	19.2	27.4	27.2	37.1	27.1
Wk6	28.9	19.4	29.5	16.7	39.4	24.6

LSD (0.05): 11.143

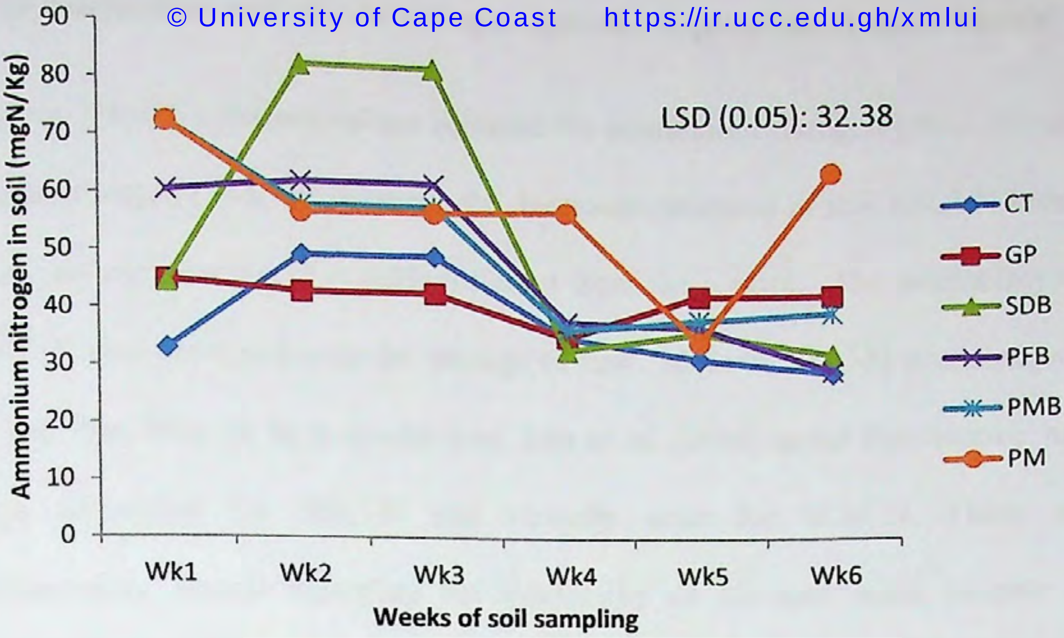

Figure 9: Ammonium Nitrogen (NH_4^+-N) after application of amendments

Where CT = Control, GP = Gypsum, SBD = Saw Dust Biochar, PFB = Palm Fiber Biochar, PMB = Poultry Manure Biochar and PM = Poultry Manure

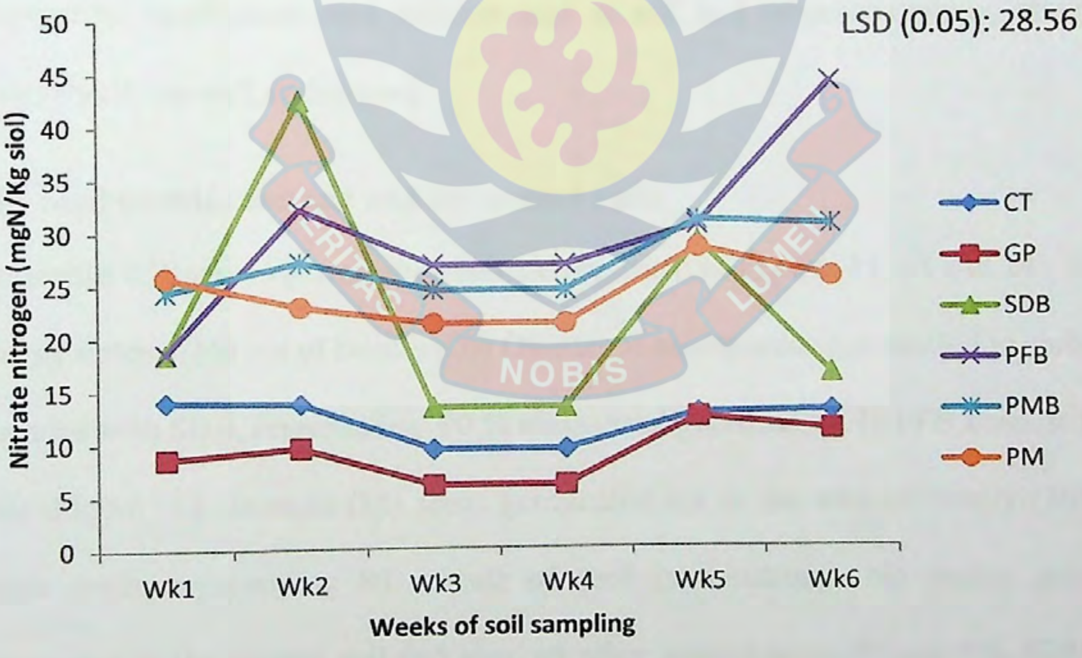

Figure 10: Nitrate Nitrogen (NO_3^--N) after application of amendments

7.3.5 Ammonium and nitrate nitrogen after the application of amendments

Figures 7 and 8 represent values obtained for ammonium nitrogen (NH_4^+-N) and nitrate nitrogen (NO_3^--N) respectively. Increases observed in soil NH_4^+-N levels were not significantly ($P = 0.05$) different from the control. The availability of NH_4^+-N also decreased with the passage of time. More of NH_4^+-N was observed in soil than NO_3^--N. In a similar trial, Lou *et al*. (2016) noted that biochar had high adsorption for NH_4^+-N and virtually none for NO_3^--N. There are contradictory reports regarding the availability of nitrogen when biochar is applied. Some researchers reported N-increase, some, N-decrease and others, no effect (Blackwell, Riethmuller & Collings (2009); Clough, Condron, Kammann & Muller (2013); Bai *et al*., 2015b; Xu *et al*., 2015). To explain these dynamics, however, the role of factors such as composition of feedstock, pyrolytic temperature, application rates, resident time in soil, soil properties among other things should be well understood.

7.3.6 Seed germination test and dry matter yield

The results of the seed germination test are presented in Figures 11, 13 and 14. A total of sixteen (16) out of twenty (20) Obantanpa maize seeds germinated in soils amended with SDB, representing 90 % maize seed germination. In PFB amended soils (Figure 11), fourteen (14) seeds germinated out of the total of twenty (20) maize seeds, representing 80 % rate of seed germination. No maize seed germinated in the control soil and also, all other amendments (Figure 15). SDB amended soils yielded 10.1 t ha^{-1} dry matter as against 8.7 t ha^{-1} for PFB (Figure 12).

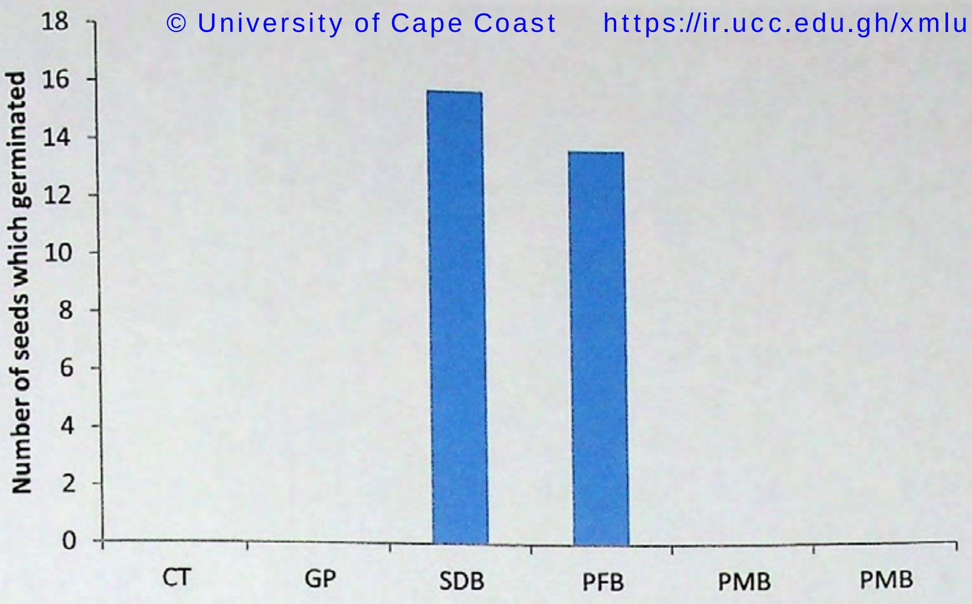

Figure 11: Rate of seed germination per type of soil amendment

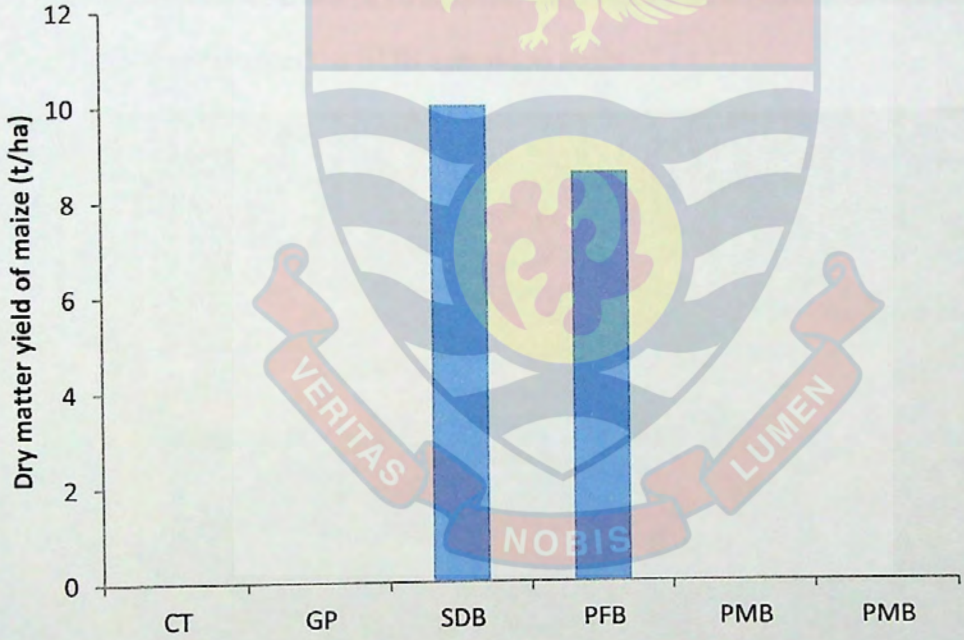

Figure 12: Dry matter yield of maize (t ha^{-1})

Figure 13: Maize planted in SDB amended soils

Figure 14: Maize planted in PFB amended soils

Figure 15: Pots amended with GP, PMB and PM where no maize germinated

7.4 Conclusion

A study was conducted to evaluate the potential of organic amendments in managing sodic soils for crop production without conventional leaching. In doing this, a pot experiment was conducted in which saw dust biochar (SDB), palm fiber biochar (PFB), poultry manure biochar (PMB) and poultry manure (PM) were applied to sodic soil sampled from Cape Coast industrial area. Gypsum amendment and a control were included for the purpose of comparing results. All amendments were applied at the rate of 4.78 t ha^{-1} which was the full gypsum requirement rate for the soil. Amended soils were incubated and weekly sampled for 6-weeks for laboratory analysis. Periodic watering was done to keep moisture at field capacity. From the results, organic based amendments marginally reduced soil pH and electrical conductivity (EC). The same amendments significantly ($P = 0.05$) increased soil Ca^{+2} and Mg^{+2}, with SDB registering the highest increase. The increases in the levels of Na^{+} and K^{+} were marginal and statistically insignificant ($P = 0.05$). PFB recorded the highest CEC at week 6. SDB and PFB reduced soil sodicity below the minimum threshold of ESP 15. All the organic based amendments recorded marginal increase in soil OC but SDB recorded the highest value for OC at week 6. PMB released the highest amount of available P, with peak availability observed in week 4. Insignificant ($P = 0.05$) increases were also observed for soil NH_4^{+}-N and NO_3^{-}-N. SDB and PFB recorded 90 % and 80 maize seed germination and also, 10.1 t ha^{-1} and 8.7 t ha^{-1} dry matter yields respectively. No maize seed, however, germinated in the control and all other amendments as ESP levels remain high. The hypothesis is therefore accepted because SDB and PFB were able at reduce exchangeable sodium percentage below threshold of 15 % and maize seeds germinated in soils amended with these materials.

CHAPTER EIGHT

SUMMARY, CONCLUSION AND RECOMMENDATION

8.1 Summary and Conclusions

In experiment 1, the suitability of wastewater from Ameen Sangari Industries Limited for crop production was assessed. The study showed that seven (7) out of twenty (22) effluent properties were within acceptable limits. These are nitrate-nitrogen, electrical conductivity, total dissolved solids, chlorine, iron, copper and zinc. Nine (9) effluent properties exceeded quality guidelines. These include pH, temperature, turbidity, chemical oxygen demand, biological oxygen demand, oil and grease, total suspended solids, phosphorus and ammonium nitrogen. Effluent potential was relatively high for improving soil CEC. On the basis of nitrogen, potassium and phosphorus concentrations which were adequate and the low micro nutrients (Fe, Cu, and Zn) concentrations, the effluent has the potential for use as irrigation water. Effluent ESP and EC, however, may pose the challenge of soil sodicity and salinity which could erode the economic benefits of any gain a farmer may make from applying this effluent to farmland. There is therefore the need to fashion out an effluent treatment system which could adequately reduce effluent ESP and EC.

In experiment 2, profile analysis of physicochemical properties was conducted for soil samples from Cape Coast Industrial area, influenced by discharge of soap factory effluent for 43 years. A control profile excavated 1 km away provided the basis for comparison of results from the contaminated site. A two-way data comparison was done. Changes within the same soil profile were compared.

Analogous profile levels of the contaminated and control profiles were also compared. Sixteen (16) soil properties were evaluated in this experiment. Findings of the study showed that the cation exchange capacity of soil and concentrations of nitrogen, phosphorus and potassium in the soil increased significantly following 43 years of effluent discharge. Organic matter content was also significantly higher in the contaminated soil than in the control soil, especially in the top 30 cm depth. The soil can be considered as a sodic soil as the exchangeable sodium percentage (ESP) in the contaminated soil exceeded the established minimum threshold of 15 % for sodic soils while the electrical conductivity (EC) in the same soil was less than 4 dS m^{-1}. The impact of the sodic condition on soil structure (dispersion and slacking of clay soil particle) resulted in the development of compact soil of high bulk density throughout the soil profile.

In experiment 3, saw dust biochar (SDB), palm fiber biochar (PFB), poultry manure biochar (PMB) and poultry manure (not charred) were evaluated for their potential to enhance soil fertility. The study assessed the potential of these materials to enhance soil organic carbon (OC), cation exchange capacity (CEC), supply of macro and micro plant nutrients and the potentials to cause soil salinity and sodicity. All materials exhibited high potential for OC as values ranged from 23.5 % to 33.1 %. The potential for CEC improvement was high for all the materials studied. PM exhibited the highest potential for CEC improvement whilst SDB registered the lowest. PM proved a better source for major plant nutrients (NPK) as against the potentials of PMB, PFB and SDB in that order. All the materials could also supply some micro plant nutrients namely, Fe, Cu and Zn though their supply potentials were on the low side. The materials recorded generally low values for electrical conductivity which is the measure for salt load. Exchangeable sodium percentage (ESP) for all materials was also below sodicity limit of ESP $\geq$ 15. All the materials showed high potentials for soil fertility improvement. SDB and PFB proved suitable for all manner of agricultural soils. PMB and PM would, however, be more suitable for acidic soils.

In experiment 4, therefore, a pot experiment was conducted in which saw dust biochar (SDB), palm fiber biochar (PFB), poultry manure biochar (PMB) and poultry manure (PM) were applied to sodic soil sampled from Cape Coast industrial area. The purpose of this experiment was to evaluate the potential of these organic amendments in managing sodic soils for crop production. Gypsum amendment and a control were included for the purpose of comparing results. All amendments were applied at the rate of 4.78 t ha^{-1} which was the full gypsum requirement rate for the soil. Amended soils were incubated and weekly sampled for 6-weeks for laboratory analysis. Periodic watering was done to keep soils moisture at field capacity. From the results, organic based amendments marginally reduced soil pH electrical conductivity (EC). The same amendments significantly ($P = 0.05$) increased soil Ca^{+2} and Mg^{+2}. SDB registered the highest increase. The increases in the levels of Na^{+} and K^{+} were marginal and statistically insignificant ($P = 0.05$). PFB recorded the highest CEC at week 6 and SDB and PFB reduced soil sodicity below the minimum threshold of ESP 15. All organic based amendments recorded marginal increase in soil OC but SDB recorded the highest value for OC at week 6. PMB released the highest amount of available P, with peak availability observed in week 4. Insignificant ($P < 0.05$) increases were also observed for soil NH_4^+-N and NO_3^--N. SDB and PFB recorded 90 % and 80 maize seed germination and also, 10.1 t ha^{-1} and 8.7 t ha^{-1} dry matter yields respectively. No maize seed however germinated in the control and all other amendment. SDB and PFB were able at reduce exchangeable sodium percentage below threshold of 15 % and maize seeds germinated in soils amended with these materials. The hypothesis is therefore accepted.

8.2 Recommendations

Further studies should be conducted into the usefulness of industrial wastewater for crop production, including wastewater from other types of industries. Periodic investigation of the influence of industrial wastewater on soil fertility and plant nutrition should also be carried out such that maximum benefits could be derived from the practice.

The potentials of saw dust biochar and palm fiber biochar in managing sodium affected soils should be further studied. Field experiments should also be conducted to consolidate the potential of these amendments in reclaiming sodic soils for crop production.

The useful period of biochar in soil after application should be further investigated.

Cost : benefit analysis should also be done to consolidate the economic benefits of biochar in managing sodic soils.

The Ministry of Trade and Industry, Ministry of Food and Agriculture and the Ministry of Environment, Science, Technology and Innovations should unite efforts in research aimed at making industrial wastewater an important agricultural resource.

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APPENDICES

Appendix A

A1: Iron (Fe) and Zinc (Zn) in Effluent Affected Soil Profile

PL (cm)	Fe (μgg^{-1})		Zn (μgg^{-1})	
	C	S	C	S
PL1	0.1	84.7	0.2	6.4
PL2	0.1	46.6	0.1	0.3
PL3	0.0	27.7	0.1	0.2
PL4	0.0	20.9	0.1	0.2
PL5	0.0	17.2	0.1	0.1
PL6	0.0	15.9	0.1	0.2
PL7	0.0	14.4	0.1	0.1

A2: Exchangeable Calcium (Ca^{+2} in cmol kg^{-1}) after amendments were applied.

Weeks/treatments	**CT**	**GP**	**SDB**	**PFB**	**PMB**	**PM**
Wk1	8.7	10.7	9.2	8.1	10.0	9.3
Wk2	8.6	15.0	10.2	10.0	10.0	9.6
Wk3	8.9	11.2	10.7	9.6	10.3	10.5
Wk4	8.8	15.1	12.4	8.2	10.3	10.6
Wk5	8.7	13.1	12.3	10.9	11.2	12.6
Wk6	8.7	13.9	12.2	11.1	11.9	9.9
LSD (0.05): 2.1566						

A3: Exchangeable magnesium dynamics in soil after amendments were applied.

Weeks/treatments	CT	GP	SDB	PFB	PMB	PM
Wk1	5.9	3.4	5.2	5.3	6.4	5.8
Wk2	5.9	3.4	7.8	6.6	5.8	7.2
Wk3	5.6	3.4	7.8	7.5	5.8	7.2
Wk4	5.3	3.4	6.9	8.3	6.6	7.4
Wk5	5.3	3.3	6.9	10.3	7.1	7.8
Wk6	5.2	3.2	7.8	10.3	7.3	6.8

LSD (0.05): 0.7033

A4: Exchangeable Potassium (K^+ in cmol kg^{-1}) after amendments were applied

Weeks/treatments	CT	GP	SDB	PFB	PMB	PM
Wk1	0.8	0.8	1.1	1.1	1.1	1.2
Wk2	0.8	0.8	0.5	0.6	0.7	0.8
Wk3	0.7	0.7	0.6	0.6	0.7	0.8
Wk4	0.7	0.7	0.6	0.5	0.7	0.5
Wk5	0.7	0.7	0.6	0.5	0.7	0.8
Wk6	0.7	0.7	0.5	0.6	0.7	0.7

LSD (0.05): 0.4207

A5: Exchangeable Sodium (Na^+ in cmol kg^{-1}) dynamics in soil after amendments were applied.

Weeks/treatments	CT	GP	SDB	PFB	PMB	PM
Wk1	3.3	3.4	3.8	4.0	4.3	4.2
Wk2	3.0	3.4	4.2	3.6	3.1	4.3
Wk3	3.3	3.4	4.0	3.7	3.5	4.3
Wk4	3.3	3.4	3.3	3.7	3.6	4.5
Wk5	3.2	3.4	3.4	3.7	3.9	5.0
Wk6	3.3	3.4	3.4	3.7	3.9	4.3
LSD (0.05): 0.471						

A6: Ammonium Nitrogen (NH_4^+-N) after application of amendments

Weeks/treatments	CT	GP	SDB	PFB	PMB	PM
Wk1	32.9	44.8	44.4	60.4	72.3	72.3
Wk2	49.5	43.1	82.7	62.3	58.2	57.0
Wk3	49.6	43.1	82.6	62.3	58.3	57.2
Wk4	35.6	35.7	33.4	38.4	37.0	57.8
Wk5	31.9	43.1	36.5	37.5	38.8	34.9
Wk6	29.3	43.1	32.6	29.7	40.0	64.9
LSD (0.05): 32.38						

A7: Nitrate Nitrogen (NO_3^--N) after application of amendments

Weeks/treatments	CT	GP	SDB	PFB	PMB	PM
Wk1	14.0	8.6	18.6	18.6	24.4	25.8
Wk2	13.8	9.6	42.6	32.2	27.2	23.0
Wk3	9.4	6.0	13.4	27.0	24.6	21.4
Wk4	9.4	6.0	13.4	27.0	24.6	21.4
Wk5	12.8	12.4	29.2	30.8	31.2	28.6
Wk6	13.0	11.2	16.6	44.4	30.8	25.8

LSD (0.05): 28.56

Appendix B

B1: pH IN BIOCHARS AND POULTRY MANURE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	0.007717	0.003858	1.80	
Reps.*Units* stratum					
Treatmts	3	14.983567	4.994522	2326.04	<.001
Residual	6	0.012883	0.002147		
Total	11	15.004167			
LSD:		0.1403			

B2: EXCHANGEABLE ACIDITY OF BIOCHARS AND POULTRY MANURE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	0.1751	0.0876	0.78	
Reps.*Units* stratum					
Treatmts	3	20.2193	6.7398	59.80	<.001
Residual	6	0.6763	0.1127		
Total	11	21.0707			
LSD:		1.0163			

B3: ELECTRICAL CONDUCTIVITY OF BIOCHARS AND POULTRY MANURE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	0.5835	0.2917	1.47	
Reps.*Units* stratum					
Treatmts	3	148.1059	49.3686	248.22	<.001
Residual	6	1.1933	0.1989		
Total	11	149.8827			
LSD:		1.350			

B4: EXCHANGEABLE CALCIUM IN BIOCHARS AND POULTRY MANURE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	4.80	2.40	0.15	
Reps.*Units* stratum					
Treatmts	3	5537.49	1845.83	116.56	<.001
Residual	6	95.02	15.84		
Total	11	5637.31			
LSD:		12.05			

B5: EXCHANGEABLE MAGNESSIUN IN BIOCHARS AND POULTRY MANURE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	92.09	46.04	2.28	
Reps.*Units* stratum					
Treatmts	3	7268.42	2422.81	119.86	<.001
Residual	6	121.29	20.21		
Total	11	7481.79			
LSD:		13.61			

B6: EXCHANGEABLE POTASSIUM IN BIOCHARS AND POULTRY MANURE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	1.1222	0.5611	1.13	
Reps.*Units* stratum					
Treatmts	3	662.8784	220.9595	446.62	<.001
Residual	6	2.9685	0.4947		
Total	11	666.9691			
LSD:		2.129			

B7: EXCHANGEABLE SODIUM IN BIOCHARS AND POULTRY MANURE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	0.8269	0.4134	3.01	
Reps.*Units* stratum					
Treatmts	3	239.2002	79.7334	581.15	<.001
Residual	6	0.8232	0.1372		
Total	11	240.8503			
LSD:		1.121			

B8: EFFECTIVE CATION EXCHANGE CAPACITY OF BIOCHARS AND POULTRY MANURE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	43.34	21.67	1.47	
Reps.*Units* stratum					
Treatmts	3	26739.91	8913.30	604.71	<.001
Residual	6	88.44	14.74		
Total	11	26871.69			
LSD:		11.62			

B9: EXCHANGEABLE SODIUM PERCENTAGE OF BIOCHARS AND POULTRY MANURE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	0.3365	0.1682	0.18	
Reps.*Units* stratum					
Treatmts	3	7.6522	2.5507	2.76	0.134
Residual	6	5.5539	0.9257		
Total	11	13.5426			
LSD:		2.912			

B10: TOTAL NITROGEN IN BIOCHARS AND POULTRY MANURE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	0.029717	0.014858	9.21	
Reps.*Units* stratum					
Treatmts	3	5.088092	1.696031	1050.90	<.001
Residual	6	0.009683	0.001614		
Total	11	5.127492			
LSD:		0.1216			

B11: ORGANIC CARBON IN BIOCHARS AND POULTRY MANURE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	4.79	2.39	0.16	
Reps.*Units* stratum					
Treatmts	3	172.62	57.54	3.85	0.075
Residual	6	89.69	14.95		
Total	11	267.10			
LSD:		11.70			

B12: TOTAL PHOSPHORUS IN BIOCHARS AND POULTRY MANURE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	2221803.	1110902.	1.43	
Reps.*Units* stratum					
Treatmts	3	180642850.	60214283.	77.29	<.001
Residual	6	4674379.	779063.		
Total	11	187539032.			

B13: COPPER IN BIOCHARS AND POULTRY MANURE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	7.326	3.663	0.67	
Reps.*Units* stratum					
Treatmts	3	814.787	271.596	49.47	<.001
Residual	6	32.938	5.490		
Total	11	855.051			
LSD		7.092			

B14: IRON IN BIOCHARS AND POULTRY MANURE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	1.884	0.942	0.65	
Reps.*Units* stratum					
Treatmts	3	89.154	29.718	20.48	0.001
Residual	6	8.704	1.451		
Total	11	99.742			
LSD:		3.646			

B15: ZINC IN BIOCHARS AND POULTRY MANURE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	0.4617	0.2309	1.32	
Reps.*Units* stratum					
Treatmts	3	607.6525	202.5508	1158.89	<.001
Residual	6	1.0487	0.1748		
Total	11	609.1629			
LSD:		0.341			

Appendix C

C1: pH OF SOIL PROFILE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	0.13190	0.06595	3.04	
Reps.Treatmt stratum					
Treatmt	1	12.48595	12.48595	576.27	0.002
Residual	2	0.04333	0.02167	1.92	
Reps.Treatmt.Depth stratum					
Depth	6	14.33143	2.38857	211.20	<.001
Treatmt.Depth	6	1.62571	0.27095	23.96	<.001
Residual	24	0.27143	0.01131		
Total	41	28.88976			
LSD:		0.1934			

C2: ELECTRICAL CONDUCTIVITY OF SOIL PROFILE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	0.004286	0.002143	1.00	
Reps.Treatmt stratum					
Treatmt	1	200.648571	200.648571	93636.00	<.001
Residual	2	0.004286	0.002143	0.22	
Reps.Treatmt.Depth stratum					
Depth	6	3.641429	0.606905	62.94	<.001
Treatmt.Depth	6	3.641429	0.606905	62.94	<.001
Residual	24	0.231429	0.009643		
Total	41	208.171429			
LSD:		0.0615			

C3: EXCHANGEABLE CALCIUM OF SOIL PROFILE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	21.51	10.76	1.06	
Reps.Treatmt stratum					
Treatmt	1	20.15	20.15	1.99	0.294
Residual	2	20.22	10.11	0.99	
Reps.Treatmt.Depth stratum					
Depth	6	333.76	55.63	5.43	0.001
Treatmt.Depth	6	3.37	0.56	0.05	0.999
Residual	24	246.04	10.25		
Total	41	645.05			
LSD		4.222			

C4: EXCHANGEABLE MAGNESIUM OF SOIL PROFILE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	0.45194	0.22597	11.94	
Reps.Treatmt stratum					
Treatmt	1	113.83078	113.83078	6013.50	<.001
Residual	2	0.03786	0.01893	0.40	
Reps.Treatmt.Depth stratum					
Depth	6	14.34504	2.39084	50.92	<.001
Treatmt.Depth	6	13.51473	2.25245	47.97	<.001
Residual	24	1.12685	0.04695		
Total	41	143.30719			
LSD:		0.1827			

C5: EXCHANGEABLE POTASSIUM OF SOIL PROFILE

```
                  Analysis of Variance Table

Source of variation      d.f.        s.s.        m.s.      v.r.   F pr.

Reps stratum               2   0.0002333   0.0001167      7.00

Reps.Treatmt stratum
Treatmt                    1   0.1000595   0.1000595   6003.57   <.001
Residual                   2   0.0000333   0.0000167      0.15

Reps.Treatmt.Depth stratum
Depth                      6   0.9617286   0.1602881   1479.58   <.001
Treatmt.Depth              6   0.3257571   0.0542929    501.16   <.001
Residual                  24   0.0026000   0.0001083

Total                     41   1.3904119
LSD:                             0.00542
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C6: EXCHANGEABLE SODIUM OF SOIL PROFILE

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                  Analysis of Variance Table

Source of variation      d.f.        s.s.        m.s.      v.r.   F pr.

Reps stratum               2    0.005776    0.002888      1.43

Reps.Treatmt stratum
Treatmt                    1   19.968610   19.968610   9901.79   <.001
Residual                   2    0.004033    0.002017      0.23

Reps.Treatmt.Depth stratum
Depth                      6    5.295514    0.882586     98.89   <.001
Treatmt.Depth              6    5.086924    0.847821     95.00   <.001
Residual                  24    0.214190    0.008925

Total                     41   30.575048
LSD:                              0.0596
```

C7: CATION EXCHANGE CAPACITY OF SOIL PROFILE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	0.0728	0.0364	0.13	
Reps.Treatmt stratum					
Treatmt	1	529.7311	529.7311	1935.09	<.001
Residual	2	0.5475	0.2738	2.47	
Reps.Treatmt.Depth stratum					
Depth	6	294.1399	49.0233	442.16	<.001
Treatmt.Depth	6	157.2704	26.2117	236.41	<.001
Residual	24	2.6610	0.1109		
Total	41	984.4227			
LSD:		0.6947			

C8: EXCHANGEABLE SODIUM PERCENTAGE OF SOIL PROFILE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	1.2780	0.6390	1.16	
Reps.Treatmt stratum					
Treatmt	1	2393.5010	2393.5010	4340.30	<.001
Residual	2	1.1029	0.5515	0.88	
Reps.Treatmt.Depth stratum					
Depth	6	9.5439	1.5906	2.55	0.047
Treatmt.Depth	6	33.8809	5.6468	9.06	<.001
Residual	24	14.9630	0.6235		
Total	41	2454.2698			
LSD:		0.986			

C9: ORGANIC CARBON OF SOIL PROFILE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	0.006765	0.003382	2.27	
Reps.Treatmt stratum					
Treatmt	1	0.161324	0.161324	108.13	0.009
Residual	2	0.002984	0.001492	0.43	
Reps.Treatmt.Depth stratum					
Depth	6	1.924457	0.320743	91.66	<.001
Treatmt.Depth	6	0.693961	0.115660	33.05	<.001
Residual	24	0.083984	0.003499		
Total	41	2.873475			
LSD:		0.05129			

C10: AVAILABLE PHOSPHORUS OF SOIL PROFILE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	0.117	0.058	0.23	
Reps.Treatmt stratum					
Treatmt	1	227.688	227.688	880.07	0.001
Residual	2	0.517	0.259	0.25	
Reps.Treatmt.Depth stratum					
Depth	6	2799.885	466.647	445.08	<.001
Treatmt.Depth	6	1373.961	228.994	218.41	<.001
Residual	24	25.163	1.048		
Total	41	4427.331			
LSD:		0.675			

C11: AMMONIUM NITROGEN OF SOIL PROFILE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	4.256	2.128	0.80	
Reps.Treatmt stratum					
Treatmt	1	4839.875	4839.875	1822.14	<.001
Residual	2	5.312	2.656	0.36	
Reps.Treatmt.Depth stratum					
Depth	6	143.185	23.864	3.24	0.018
Treatmt.Depth	6	127.042	21.174	2.87	0.030
Residual	24	176.981	7.374		
Total	41	5296.652			
LSD:		2.164			

C12: NITRATE NITROGEN OF SOIL PROFILE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	8.21	4.11	0.94	
Reps.Treatmt stratum					
Treatmt	1	3821.72	3821.72	874.96	0.001
Residual	2	8.74	4.37	0.40	
Reps.Treatmt.Depth stratum					
Depth	6	364.55	60.76	5.55	0.001
Treatmt.Depth	6	291.32	48.55	4.43	0.004
Residual	24	262.84	10.95		
Total	41	4757.38			
LSD:		2.775			

C3: SOIL BULK DENSITY OF SOIL PROFILE

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Reps stratum	2	0.003654	0.001827	1.00	
Reps.Treatmt stratum					
Treatmt	1	1.990344	1.990344	1089.48	<.001
Residual	2	0.003654	0.001827	1.00	
Reps.Treatmt.Depth stratum					
Depth	6	0.059936	0.009989	5.47	0.001
Treatmt.Depth	6	0.064164	0.010694	5.85	<.001
Residual	24	0.043845	0.001827		
Total	41	2.165596			
LSD:		0.05675			

Appendix D:

D1: SOIL pH AFTER AMENDMENTS

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Subject stratum					
Treatmt	5	60.25133	12.05027	602.51	<.001
Residual	24	0.48000	0.02000	0.76	
Subject.Time stratum					
d.f. correction factor 0.6402					
Time	5	0.28733	0.05747	2.20	0.091
Time.Treatmt	25	2.36933	0.09477	3.62	<.001
Residual	120	3.14000	0.02617		
Total	179	66.52800			
LSD:		0.2146			

D2: ELECTRIVAL CONDUCTIVITY OF SOIL AFTER AMENDMENTS

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Subject stratum					
Treatmt	5	2194.02	438.80	12.39	<.001
Residual	24	849.80	35.41	0.93	
Subject.Time stratum					
d.f. correction factor 0.2009					
Time	5	142.19	28.44	0.75	0.396
Time.Treatmt	25	1054.16	42.17	1.11	0.382
Residual	120	4565.72	38.05		
Total	179	8805.88			
LSD:		9.560			

D3: EXCHANGE CALCIUM OF SOIL AFTER AMENDMENTS

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Subject stratum					
Treatmt	5	337.982	67.596	11.96	<.001
Residual	24	135.598	5.650	3.52	
Subject.Time stratum					
d.f. correction factor 0.4570					
Time	5	91.883	18.377	11.44	<.001
Time.Treatmt	25	133.687	5.347	3.33	0.001
Residual	120	192.792	1.607		
Total	179	891.943			
LSD:		2.1566			

D4: EXCHANGE MAGNESIUM OF SOIL AFTER AMENDMENTS

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Subject stratum					
Treatmt	5	412.1922	82.4384	289.66	<.001
Residual	24	6.8305	0.2846	1.04	
Subject.Time stratum					
d.f. correction factor 0.6771					
Time	5	43.2602	8.6520	31.63	<.001
Time.Treatmt	25	108.3645	4.3346	15.85	<.001
Residual	120	32.8260	0.2735		
Total	179	603.4733			
LSD:		0.7033			

D5: EXCHANGEABLE POTASSIUM OF SOIL AFTER AMENDMENTS

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Subject stratum					
Treatmt	5	38.221	7.644	1.05	0.412
Residual	24	174.647	7.277	1.00	
Subject.Time stratum					
d.f. correction factor 0.2003					
Time	5	37.312	7.462	1.02	0.322
Time.Treatmt	25	190.181	7.607	1.04	0.415
Residual	120	874.647	7.289		
Total	179	1315.009			
LSD:		4.207			

D6: EXCHANGEABLE SODIUM OF SOIL AFTER AMENDMENTS

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Subject stratum					
Treatmt	5	25.80653	5.16131	24.71	<.001
Residual	24	5.01245	0.20885	2.16	
Subject.Time stratum					
d.f. correction factor 0.5442					
Time	5	1.02293	0.20459	2.12	0.112
Time.Treatmt	25	9.14133	0.36565	3.78	<.001
Residual	120	11.59907	0.09666		
Total	179	52.58232			
LSD:		0.4719			

D7: CATION EXCHANGE CAPACITY OF SOIL AFTER AMENDMENTS

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Subject stratum					
Treatmt	5	436.369	87.274	19.03	<.001
Residual	24	110.066	4.586	2.15	
Subject.Time stratum					
d.f. correction factor 0.6032					
Time	5	216.414	43.283	20.27	<.001
Time.Treatmt	25	281.383	11.255	5.27	<.001
Residual	120	256.258	2.135		
Total	179	1300.490			
LSD:		2.180			

D8: ESP OF SOIL AFTER AMENDMENTS

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Subject stratum					
Treatmt	5	187.054	37.411	6.08	<.001
Residual	24	147.591	6.150	2.00	
Subject.Time stratum					
d.f. correction factor 0.7126					
Time	5	201.986	40.397	13.11	<.001
Time.Treatmt	25	223.342	8.934	2.90	<.001
Residual	120	369.729	3.081		
Total	179	1129.701			
LSD:		2.518			

D9: SOIL ORGANIC CARBON AFTER AMENDMENTS

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Subject stratum					
Treatmt	5	0.50697	0.10139	1.83	0.146
Residual	24	1.33205	0.05550	0.88	
Subject.Time stratum					
d.f. correction factor 0.2325					
Time	5	0.51429	0.10286	1.63	0.215
Time.Treatmt	25	1.62066	0.06483	1.03	0.428
Residual	120	7.58155	0.06318		
Total	179	11.55552			
LSD:		0.3846			

D10: SOIL AVAILABLE PHOSPHORUS AFTER AMENDMENTS

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Subject stratum					
Treatmt	5	5486.29	1097.26	3.72	0.012
Residual	24	7083.10	295.13	18.93	
Subject.Time stratum					
d.f. correction factor 0.4183					
Time	5	189.06	37.81	2.42	0.096
Time.Treatmt	25	803.06	32.12	2.06	0.044
Residual	120	1871.17	15.59		
Total	179	15432.69			
LSD:		11.543			

D11: AMMONIUM NITROGEN OF SOIL AFTER AMENDMENTS

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Subject stratum					
Treatmt	5	7286.4	1457.3	2.14	0.096
Residual	24	16372.4	682.2	1.67	
Subject.Time stratum					
d.f. correction factor 0.2782					
Time	5	15878.9	3175.8	7.76	0.004
Time.Treatmt	25	15458.5	618.3	1.51	0.198
Residual	120	49099.3	409.2		
Total	179	104095.5			
LSD:		32.38			

D12: AMMONIUM NITROGEN OF SOIL AFTER AMENDMENTS

Analysis of Variance Table

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Subject stratum					
Treatmt	5	10673.5	2134.7	1.47	0.236
Residual	24	34847.3	1452.0	7.21	
Subject.Time stratum					
d.f. correction factor 0.5119					
Time	5	2109.2	421.8	2.09	0.119
Time.Treatmt	25	3761.7	150.5	0.75	0.709
Residual	120	24179.1	201.5		
Total	179	75570.8			
LSD:		28.56			