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Evaluating the Potential of Biochars and Composts as Organic Amendments to Remediate a Saline-Sodic Soil Leached with Reclaimed Water

**Author**
Chaganti, Vijayasatya Nagendra

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# Evaluating the Potential of Biochars and Composts as Organic Amendments to Remediate a Saline-Sodic Soil Leached with Reclaimed Water

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

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in

Soil and Water Sciences

by

Vijaya Satya Nagendra Chaganti

March 2014

Dissertation Committee:
- Dr. David M. Crohn, Chairperson
- Dr. David E. Crowley
- Dr. Jiri Simunek

The Dissertation of Vijaya Satya Nagendra Chaganti is approved:

Committee Chairperson

University of California, Riverside

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# DEDICATION

I dedicate this dissertation to my beloved parents, Chaganti Gandhi and Chaganti Sambrajyam, who provided their stanch support, encouragement, and blessings all through my life. Thanks for always being there for me, Mom and Dad.

# ABSTRACT OF THE DISSERTATION

## Evaluating the Potential of Biochars and Composts as Organic Amendments to Remediate a Saline-Sodic Soil Leached with Reclaimed Water

by

Vijaya Satya Nagendra Chaganti

Doctor of Philosophy, Graduate Program in Soil and Water Sciences
University of California, Riverside, March 2014
Dr. David M. Crohn, Chairperson

Use of organic amendments in lieu of more expensive inorganic amendments is increasingly seen as a sustainable alternative for reclaiming salt-affected soils. Moreover, due to the scarcity of fresh waters for agricultural irrigation, alternatives such as use of low quality reclaimed waters and drainage waters are encouraged. The main objectives of this dissertation were (1) to evaluate whether composts and/or biochars can be used to reclaim a saline sodic soil in conjunction with reclaimed water, (2) to understand and quantify the relative contribution of physiochemical and biological factors that aid in saline-sodic soil reclamation, and (3) to evaluate the specific effects of temperature on soil respiration, aggregate stability, hydraulic conductivity, and other chemical properties of a saline-sodic soil amended with composts and biochar.

Laboratory incubation and column leaching experiments were used in this research. Organic amendments included, a biosolids co-compost, a greenwaste compost, a woodchip biochar and a dairy manure biochar. Soil properties including wet aggregate stability and saturated hydraulic conductivity were analyzed in relation to cumulative leachate losses of $Na^+$, $Ca^{2+}$, and $Mg^{2+}$. Chemical properties such as CEC, $EC_e$, pH, SAR, ESP, and exchangeable cations were quantified for soils before and after leaching. Results showed that soil aggregate stability and hydraulic conductivity improvements were greatest with composts. Biochars did not significantly affect soil aggregate stability but increased soil hydraulic conductivity relative to untreated soils. Organic amendments significantly increased $Na^+$ leaching with corresponding decreases in leaching times. Cumulative losses of $Ca^{2+}$ and $Mg^{2+}$ were greatest from composts followed by biochars, indicating their potential to contribute divalent cations. Only composts significantly affected soil pH and CEC. Mode of action by biochars was determined to be physiochemical. Composts offer a comprehensive advantage since physiochemical and biological factors act synergistically in those materials. Temperature only significantly affected the soil physical but not chemical properties, and these effects were associated only with compost treated soils. Finally, this work showed that simultaneous use of reclaimed water and organic amendments can successfully leach and reclaim a saline-sodic soil.

## TABLE OF CONTENTS

## LIST OF TABLES

# LIST OF FIGURES

## LIST OF EQUATIONS

# 1. INTRODUCTION

## Soil Salinization

Since ancient times, soil degradation due to salinization is one of the major environmental concerns, threatening the sustainability of world’s agricultural production and is prevalent in arid and semi-arid regions (Manchanda and Garg, 2008). Soil salinization is generally referred to as the accumulation of salts in the soil root zone to the extent that depresses plant growth (Rengasamy, 2006). Associated agricultural production losses were estimated to be close to $12 billion per year (Pitman and Läuchli, 2002) due to soil salinization. Globally, salt affected soils are distributed across all continents and about 100 countries all over the world face this menace (Rengasamy, 2006). In addition, approximately 831 M ha of land is estimated to be salt affected across different countries (Martinez-Beltran and Manzur, 2005), while about a third of the irrigated land in United States was reported to be salinized (Wichelns, 1999). Also, In California, approximately half of the total cultivated land (~ 4.5 million acres) is salinized and is mostly concentrated in the major irrigated areas of imperial and western San Joaquin Valley’s (Letey, 2000).

Salt affected soils are generally formed due to either or both, primary and secondary soil salinization processes. Primary soil salinization includes those soils which naturally have high inherent salts due to rock weathering, sea water intrusions etc. (Rengasamy, 2006). Secondary salinization process is human induced and is predominantly caused by prolonged irrigation with salt-rich water without adequate leaching, concentrating salts in the root zone (Ghassemi et al., 1995). Furthermore, irrigation with poor quality waters, shallow ground water tables with poor drainage, and excessive evaporation than precipitation exacerbate salt accumulation in the surface horizon (Brinck and Frost, 2009; Rhoades, 1987; Smedema and Shiati, 2002). Overgrazing, indiscriminate chemical fertilizer use and deforestation are some of the other minor contributors for soil salinization (Pessarakli, 2002). Amassing soil salts will not only affect plant growth but also deteriorate soil health by altering the soil physical, chemical and biological properties (Bernstein, 1975; Lakhdar et al., 2009; Manchanda and Garg, 2008).

Salt affected soils are generally characterized by having high concentrations of dissolved mineral salts, primarily composed of chlorides, sulfates, carbonates, and bicarbonates of Sodium ($Na^+$), Calcium ($Ca^{2+}$), and Magnesium ($Mg^{2+}$) (Manchanda and Garg, 2008; Qadir et al., 2000). Spatial variations in the concentrations and proportions of these salts are commonly observed. General classification of salt affected soils is based on their electrical conductivity of saturated paste extracts ($EC_e$), soil sodium adsorption ratio (SAR), and exchangeable sodium percentage (ESP) (Richards, 1954). Based on these properties, soils are classified as saline, sodic or saline-sodic. Saline soils are characterized by having high $EC_e$ values ($> 4$ dS $m^{-1}$) while saline-sodic soils have both high $EC_e$ ($> 4$ dS $m^{-1}$) and SAR ($>13$) of the saturation extract and/or an ESP $> 15$. Sodic soils are those which have low $EC_e$ ($< 4$ dS $m^{-1}$) but have high SAR's ($>13$) and/or ESP $>$ 15 (Richards, 1954). Soils which exhibit salinity and sodicity (saline-sodic) together are considered to be the most degraded due to their combined effects of salinity and sodicity on plant growth and soil properties (Rengasamy, 2002).

## Salinity and Sodicity Effects on Soil Physical Properties

Soils having elevated levels of $Na^+$, both in solution and on exchangeable sites, are generally poor in soil-water and soil-air relations due to structural deteriorations (Rengasamy and Olsson, 1991). Soil hydraulic properties like infiltration rate and hydraulic conductivity are more negatively affected by sodicity than by salinity due to aggregate breakdown. The principle mechanisms involved in the aggregate breakdown of sodic soils are slaking, clay swelling, and dispersion (Rengasamy and Sumner, 1998). Slaking breaks individual aggregates during wetting when entrapped air expands. Clay swelling shrinks pore sizes, but increased swelling beyond the attractive forces of the clay particles results in spontaneous dispersion into individual clay particles (Frenkel et al., 1978; Rengasamy and Sumner, 1998). Soil structural stability and thus the pore systems are influenced by the attractive and repulsive forces due to intermolecular and electrostatic interactions between soil particles and soil solution, as explained by diffuse double layer (DDL) theory (Quirk, 1994; Rengasamy and Olsson, 1991). Increasing soil sodium increases inter particulate distances by increasing repulsive forces and therefore causes dispersion, which consequently results in undesirable soil structure (Oster and Shainberg, 2001). While swelling is a reversible process, dispersion is irreversible and can result in permanent blockage of water conducting pores due to translocation of individual soil particles (Sumner, 1993). Thus, swelling and dispersion are the two mechanisms by which soil infiltration and hydraulic conductivity are decreased in soils dominated by sodium salts. Clay swelling and dispersion are also influenced by the total electrolyte concentration (TEC) of soil solution (salinity) and irrigation water. High electrolyte concentrations of soil solution generally favor soil flocculation but low salinity and high soil ESP result in significant reduction of infiltration and hydraulic conductivity by inducing swelling or dispersion (Dikinya et al., 2006; Frenkel et al., 1978; McNeal et al., 1968; Quirk, 2001; Quirk and Schofield, 1955; Shainberg and Lety, 1984; Shainberg et al., 1981). Therefore, at higher salinity levels there is a positive effect in terms of providing soil aeration and improving permeability but high levels of soil salinity negatively affect plant growth. Hence, the salinity of the soil cannot be increased to improve poor soil structure as consideration must be given to the impacts of soil salinity on plant growth.

Surface soils are more sensitive to sodicity and electrolyte concentration, with low electrolyte concentration and high soil ESP causing aggregate breakdown by mechanical slaking and dispersion (Shainberg and Lety, 1984; Shainberg et al., 1992). Consequently, due to rearrangement of individual soil particles during such processes, a thin layer of high shear strength is formed upon soil drying known as a ‘surface crust’ (Agassi et al., 1981). These surface crusts generally seal the soil surface and drastically reduce water infiltration rate, thus making the surface soil prone to excessive erosion and potentially cause water logged conditions (Moore and Singer, 1990; Shainberg et al., 1992). Another important characteristic of soils with high sodium is the incidence of ‘hard setting’, which is similar in function to soil crusts but the process continues to occur at relatively lower soil depths rather than at the soil surface increasing the bulk density of the soil (Qadir and Schubert, 2002). Increase in soil sodicity therefore results in the formation of dispersed soils due to loss of soil structure, which manifests as reduced ability of a soil to transmit air and water. This leads to the formation of bulky, high strength, poorly aerated, waterlogged soil, which consequently causes problems such as poor seedling emergence, their establishment, and root growth, decreasing the overall potential of that soil to support plant growth (Nelson et al., 1998).

### Salinity and Sodicity Effects on Soil Chemical Properties

Soils high in salinity and sodicity generally have high soil $EC_e$, ESP, and SAR. Also, saline and sodic soils are generally high in carbonates and bicarbonate salts, which result in high soil pH (Abrol et al., 1988). Salt affected soils with high pH are generally deficient in nutrients, with pH effects more detrimental on the availability of micronutrients such as Al, Fe, Zn, Mn, Cu (Pessarakli and Szabolcs, 1999). Salt affected soils are also highly deficient in their nitrogen (N), phosphorus (P), and potassium (K) contents (Lakhdar et al., 2009). Soils with high salinity and sodicity are low in organic matter content due to its low inputs and high rates of losses (Qadir et al., 1997). Surface crusts and sealing can cause significant erosive losses of organic matter (Nelson and Oades, 1998). Chander et al. (1994) found that organic carbon and total N decreased due to increased soil sodicity when irrigated with sodic waters. Adu and Oades, (1978) further proposed that increased dispersion of soil aggregates by sodicity exposes the inaccessible organic matter fixed in soil aggregates to stressed microbes and stimulates its decomposition. Carbon (C) inputs are generally lower in salt-affected soils due to a decline in vegetation growth as affected by salt toxicity, differences in osmotic potential and degraded soil structure (Wong et al., 2009). Furthermore, McClung and Frankenberger, (1985) found decreased C and N mineralization rates and enzyme activities at high salinity levels. It was found in their studies that increasing salinity up to an $EC_e$ of 20 dS $m^{-1}$ decreased nitrification rates ranging from 8 to 83 % and promoted ammonia losses through volatilization. The source of salinity (e.g., NaCl, $Na_2SO_4$) also affects nitrification with NaCl salts strongly inhibiting nitrification (McClung and Frankenberger, 1987). Similarly, Gandhi and Paliwal (1976) found that increasing salinity reduced N mineralization and increased gaseous $NH_3$ losses. Pathak and Rao (1998) also reported that increasing salinity and alkalinity decreased both C and N mineralization in arid soils treated with organic amendments. Whereas, Nelson et al. (1996) reported a decrease in C mineralization with increasing salinity but sodicity on the other hand, increased C decomposition due to solubilization of organic matter. Frankenberger and Bingham (1982) reported that increasing salinity decreased the activities of soil enzymes which had a role in N, C, P and S cycles.

### Salinity and Sodicity Effects on Soil Microbiological Properties

Changes in soil chemistry negatively affect soil microbial and biochemical processes important for maintaining soil ecological functions (Rietz and Haynes, 2003). Increasing salinity limits microbial growth and activity by causing osmotic stress, dehydration, and lysis of cells (Oren, 1999; Wichern et al., 2006). In addition to $Na^+$ toxicity, accumulation of other ions such as chloride, carbonate and bicarbonate ions to toxic levels, nutritional deficiencies like $Ca^{2+}$, loss of organic matter due to soil structural degradation, all contribute for reducing microbial populations and their activities in soils affected by salinity and sodicity (Nelson and Oades, 1998; Zahran, 1997). Several studies have reported soil salinity effects on microbial growth and dynamics (Chander et al., 1994; García et al., 1994; Sardinha et al., 2003; Wong et al., 2008). Garcia et al. (1994) also found that increasing the soluble salts in soil had a negative effect on soil microbial community composition in a wide variety of soils collected from arid regions of SE Spain. Wichern et al. (2006) further proposed that fungal communities are more prone to increasing salts than bacterial populations. Rietz and Haynes (2003) reported that irrigation induced soil salinity and sodicity negatively affected soil microbial and biochemical activity. Microbial biomass C was exponentially decreased with increase in soil $EC_e$ while a linear decrease in biomass C was observed with increasing ESP and SAR. Various biochemical enzyme activities were also evaluated in the same study and it was found that increasing $EC_e$, ESP, and SAR linearly decreased enzyme activities (Rietz and Haynes, 2003). Several other studies have also reported significant decreases in soil microbial biomass and related enzyme activities due to increased salinity and sodicity (Chander et al., 1994; García and Hernández, 1996; Tripathi et al., 2007; Tripathi et al., 2006; Yuan et al., 2007). Rietz and Haynes (2003) and Wong et al. (2008) showed an increase in metabolic quotient (respiration per unit biomass) with increasing salinity and sodicity, indicating a more stressed microbial community. Ghollarata and Raiesi (2007) also observed an increase in metabolic quotient with simultaneous increase in soil salinity, signifying a modification in microbial community with less catabolic activity. Similarly, Yuan et al. (2007) also reported a shift in soil microbial community with less metabolism, an adaptive mechanism to alleviate salt stress. Soil microbial and biochemical activities play a very important role in maintaining the soil ecological functions and are also considered central for the formation and stabilization of soil aggregates to enhance soil structure (Six et al., 2004).

## Reclamation of Saline-Sodic Soils

### Chemical Reclamation

Salinity and sodicity have different reclamation processes. Saline soils are relatively easy to manage if good quality water is available to leach salts down. Leaching of soil and providing adequate drainage are the two major processes by which salinity is reduced (Qadir et al., 2000). Though scraping salts from the soil is sometime possible, leaching by far is the most commonly used method for salt removal (Abrol et al., 1988). Effective leaching is accomplished by infiltrating good quality water and providing adequate drainage to carryout leached salts away from the reclaimed area. However, remediating a saline-sodic soil requires a two-step protocol; first to substitute $Na^+$ from the exchange sites with divalent cations such as $Ca^{2+}$ and promote soil flocculation to increase permeability, followed by salt leaching (Gupta and Abrol, 1990). Gypsum is the most common inorganic amendment used as a $Ca^{2+}$ supplier and its effectiveness as an ameliorant for saline-sodic soil reclamation is extensively studied (Armstrong and Tanton, 1992; Choudhary et al., 2004; Ghafoor et al., 2001; Gharaibeh et al., 2010; Gharaibeh et al., 2009; Ilyas et al., 1997; Lebron et al., 2002; Mace and Amrhein, 2001; Oster et al., 1999; Qadir et al., 2001b). Other inorganic amendments commonly used for saline-sodic soil remediation include elemental sulfur and sulfuric acid, which upon application, dissolve native calcium carbonate in calcareous soils and increase soil $Ca^{2+}$ levels (Amezketa et al., 2005; Niazi et al., 2001; Sadiq et al., 2007; Vance et al., 2008).

## Phyto-Reclamation

The concept of a plant-assisted approach or *Phytoremediation/Vegetative bioremediation* of sodic and saline-sodic soils was considered as early as in 1937 when Kelly (1937) first experimented the sodic soil amelioration with Bermuda grass. Since then, many studies have evaluated the potential of crop based approaches in remediating sodic and saline-sodic soils (Ahmad et al., 2006; Ammari et al., 2008; Gharaibeh et al., 2011; Qadir et al., 2001a; Qadir et al., 1996; Qadir et al., 2002; Robbins, 1986). However, most of the crop based experiments have signified the presence of native calcite in order to achieve reclamation in sodic and/or saline-sodic soils. Qadir et al. (2007) reported several mechanisms by which phyto-remediation takes place in calcareous saline-sodic soils that include; increase in partial pressure of $CO_2$ ($P_{CO2}$) in the root zone, which forms carbonic acid and help solubilize native calcite to yield $Ca^{2+}$ into soil solution; physical effects of roots and root penetration, which form channels aiding in improved drainage and leaching, and finally, salt uptake by plant accumulation (Qadir et al., 2007).

## Reclamation by Organic Amendment Application

Another method to ameliorate sodium saturated soils is to apply organic matter. Different types of organic matter can act at different scales within the soil structure but the common effect is to bind soil particles in to aggregates (Nelson and Oades, 1998). Large organic poly-anions formed by de-protonation of humic and fulvic acids can bind clay particles together into stable micro-aggregates by forming a "*[(Cl-P-OM)x]y*" complex, where Cl is the clay particle, P is polyvalent cation and OM is the organic anion (Edwards and Bremner, 1967; Tisdall and Oades, 1982). Sodic and saline-sodic soils are generally depleted in organic matter due to their relatively low productivity and associated low organic matter inputs. Any organic matter that they contain has relatively high vulnerability to losses through erosion or decomposition by microbes (Nelson and Oades, 1998). Reclamation of a saline-sodic soil thus requires application of amendments to replace exchangeable sodium and enhance soil structure stabilization. Improved soil structure increases soil hydraulic conductivity which facilitates leaching of salts from the soil profile (Abrol et al., 1988). Also, an increase in organic matter in the soil surface layer can help to absorb the energy of raindrop impacts and facilitate water movement into the soil reducing surface runoff and erosion and accelerate salt leaching (Jordan, 1998). Composts can have beneficial effects in two ways; (1) improving the soil structure and permeability to enhance salt leaching, and (2) reducing the surface evaporation and inhibit salt accumulation in the upper profiles from shallow ground water tables (Lakhdar et al., 2009). Though extensive research has not been conducted with respect to saline-sodic soils, some of the researchers have found that organic materials could be used to improve soil properties in salt affected soils through organic matter additions and stimulate microbial activity by providing energy substrates (Ghosh et al., 2010; Hanay et al., 2004; Lax et al., 1994; Makoi and Ndakidemi, 2007; Ros et al., 2003; Tejada et al., 2006; Wahid et al., 1998). The chemical properties of composts vary according to the feedstocks from which they are made and can have a different scale of effect on soil properties. So, their use and the mechanisms by which they remediate a saline-sodic soil need study. Also, most of the studies ascribe the beneficial effects of organic amendment applications to the added organic matter and subsequent improvement in microbial activity, which facilitate structural enhancements. However, the physiochemical properties of composts can also aid in reclamation. For example, Walker and Bernal (2008) reported that the cation exchange sites were saturated with $Ca^{2+}$ and $Mg^{2+}$ when poultry manure and olive and cotton waste compost were applied to a saline soil. Additional literature also suggests that composts can be significant sources of divalent cations like $Ca^{2+}$ and $Mg^{2+}$ when applied to normal soils (Bulluck Iii et al., 2002; Hargreaves et al., 2008). Therefore, it is important to examine the relative importance of physiochemical factors that aid in saline-sodic soil remediation when composts are used as amendments.

### Effect of Organic Matter and Microbial Activity on Soil Structure

Soil structure plays a key role in maintaining the functions of soil and its ability to support flora and fauna. Soil structure influences soil water movement, water retention, erosion, nutrient cycling, crop growth, root penetration, and gas exchanges (Bronick and Lal, 2005). Formation of soil aggregates and their stability during wetting and drying cycles are generally considered as direct indicators of good structure. Factors influencing soil aggregate stability and structure include; soil texture, clay mineralogy, organic matter, microbial activity, and land management practices (Kay et al., 1998). Aggregates are secondary particles formed by the combination of mineral particles with organic and inorganic binding agents and are grouped in to micro ($< 250$ µm) and macro aggregates ($> 250$ µm) (Oades, 1984). Several authors have proposed different theories with regards to soil aggregate formation due to organic matter additions (Edwards and Bremner, 1967; Emerson, 1959; Tisdall and Oades, 1982), of which, the mechanisms discussed by Tisdall and Oades (1982) are most commonly agreed by the scientific community. Tisdall and Oades, (1982) reported that the important mechanism of interaction between clay and soil organic matter (SOM) include the bridging of polyvalent cations between the clay surface and the hydroxyl polymers and ligand groups of organic amendments. It was postulated that different organic binding agents (temporary vs. transient vs. persistent) were responsible at different stages of aggregate formation. While most of the micro-aggregates are formed by the persistent humic fractions of organic matter, macro-aggregates are formed by the exudates and sticky mucilages by roots and microbes (Tisdall and Oades, 1982). The role of microbes in soil aggregate formation and stability has been extensively reviewed (Amezketa, 1999; Degens, 1997; Kandeler and Murer, 1993; Lynch and Bragg, 1985; Oades, 1993; Roberson et al., 1995). Microbial derived exo-polysaccharides are major agglutinants for soil aggregates (Bronick and Lal, 2005). Bacterial exudates can form a polysaccharide capsule around which clay particles are aligned to form aggregates. Fungal hyphae and hyphal secretions (Glomalin) are some of the other major binding agents influencing the soil aggregate formation and their stability (Six et al., 2004). It is understood that application of organic materials provides an energy substrate (C) for microbes to thrive, decompose, and release these by-products. Carbon in composts is relatively more labile and is readily available for microbial use. Conversely, even though an organic amendment like biochar contains high C, it is highly refractory and is not readily available for microbial decomposition.

## Use of Biochar as an Organic Soil Amendment

Biochar is a carbon (C) rich organic product obtained during the exothermic, slow thermal decomposition (pyrolysis) of biomass at temperatures ≤ 700 °C under zero oxygen or low oxygen conditions (Kwapinski et al., 2010; Lehmann and Joseph, 2009).

In addition to biochar, pyrolysis of biomass also offers a tool to increase the production of bioenergy through generation of syngas and bio-oils with different energy values (Gaunt and Lehmann, 2008). Research interest in biochar production and use has gained importance in recent times due to increasing concerns regarding global warming and irreversible climate shift as a result of enhanced anthropogenic $CO_2$ emissions (Woolf et al., 2010). Biochar has been perceived as an effective mitigation strategy in the context of combating climate change by successfully sequestering C into soil and thus actively withdrawing carbon dioxide from atmosphere to abate continuing global warming effects (Lehmann, 2007b). Apart from being a C sink, biochar was 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 enhancements in overall soil quality upon biochar addition by altering soil physical, chemical, and biological properties and subsequently increasing plant productivity (Asai et al., 2009; Atkinson et al., 2010; Chan and Xu, 2009; Jones et al., 2012; Laird et al., 2010; Lehmann et al., 2011; Rondon et al., 2007; Solaiman et al., 2010; Spokas et al., 2009; Thies and Rillig, 2009; Van Zwieten et al., 2010). Till date most of the studies evaluated the benefits of biochar incorporation in non-saline soils. However, research concerning its use for the reclamation of degraded lands, especially salt affected soils such as a saline-sodic soil, is scant.

Studies involving biochar applications to soil have reported enhancements in soil physical properties like bulk density, porosity, water holding capacity, aggregate stability, and hydraulic conductivity (Asai et al., 2009; Jien and Wang, 2013; Karhu et al., 2011;

Liu et al., 2012; Uzoma et al., 2011; Verheijen et al., 2010). For e.g., Jien and Wang (2013) found an increase in macro aggregation of soils, which consequently increased the saturated hydraulic conductivity ($K_s$) of a highly weathered soil treated with 5 % biochar. Similarly, Asai et al. (2009) reported a two fold increase in soil $K_s$ when biochar was applied at 16 t $ha^{-1}$. In a more recent study, Hardie et al. (2013) also found an increase in field saturated hydraulic conductivity due to an increase in macro aggregation of soils treated with biochar. Busscher et al. (2011), George et al. (2012), and Mukherjee and Lal (2013) also reported increased soil aggregation upon biochar additions. Furthermore, Piccolo et al. (1996) and (1997) demonstrated that coal derived humic substances are the primary binding agents responsible for increasing soil aggregation. Soil macro-aggregate stability improvements ranged between 20-130 % when coal derived humic substances were added to four different soils in Southern Nigeria (Piccolo et al., 1997).

Improvements in such soil physical properties are deemed highly essential with respect to a saline-sodic soil remediation. Moreover, addition of divalent cations such as $Ca^{2+}$ and $Mg^{2+}$ is necessary to offset $Na^+$ on the exchange sites in a saline-sodic soil. Major et al. (2010) observed increased soil $Ca^{2+}$ and $Mg^{2+}$ availability when biochar was applied at 20 t $ha^{-1}$ to a Columbian savanna oxisol. In an Iowa study, Laird et al. (2010) found a significant increase in soil $Ca^{2+}$ levels, when an oak derived biochar was applied to a Midwestern agricultural soil at 20 g $Kg^{-1}$ of soil. Similarly, some other studies have also shown that biochar can significantly increase these divalent cation concentrations in the soil (Chan et al., 2008a; Gaskin et al., 2010; Novak et al., 2009). Therefore, biochar can perhaps be a significant source of these cations (Gaskin et al., 2008; Singh et al.,

2010) and could potentially help in saline-sodic soil remediation. Thus, it is important to evaluate if biochar can be an impending organic soil amendment to reclaim a salt affected soil. Also, it is imperative to understand the mechanism of biochar functioning when applied to a salt affected soil, either physiochemical or biological, given its high recalcitrant C content.

### Irrigation with Poor Quality Waters

Maintaining the sustainability of the dwindling water resources is an international priority to meet the demands of future population. Exploding population growth and increased urbanization has levied an unprecedented pressure on finite fresh water resources (Levine and Asano, 2004), forcing the current and future generations to efficiently use available scant water resources. This resulted in reduced allocation of fresh waters for agricultural irrigation (Qadir and Oster, 2004). However, maintaining agricultural productivity is very important to meet the food demands of continuing population growth and therefore, reducing the acreage under irrigation is not an option as already considerable amount of land is lost due to various land degradation problems. Due to this fact, alternatives to using potable water resources for irrigation have received increased attention. As a consequence, treated waste waters from municipal treatment plants (reclaimed water), agricultural drainage waters, agricultural and urban runoff are often considered as viable options for using as irrigation waters or to meet other non-potable water demands (Corwin and Bradford, 2008; Oster, 1994). These waters are generally referred to as “Degraded Waters” due to their deterioration in physical, chemical, and biological properties (O'Connor et al., 2008). Reuse of such waters also helps to reduce and prevent their discharge into rivers, lakes and other water bodies, thus reducing their degradation effects on receiving environments (Grattan et al., 2008; Toze, 2006).

In much of the western United States, mainly in California, reuse of agricultural drainage and reclaimed waters is highly adopted to irrigate agricultural lands (Kinney et al., 2006; Wu et al., 2009). However, when such waters are diverted for agricultural irrigation, the chemical constituents, importantly salts, can lead to their accumulation and cause soil degradation, especially those relating to soil structure and permeability (Stevens et al., 2003). Constraints involved using these low quality waters are with respect to their salinity and sodicity (SAR) (Suarez et al., 2006). While salinity is a problem with crop growth due to ion toxicities, high SAR deteriorates soil structure (Ayers and Westcot, 1985). Application of waters with high salinity and sodicity and their consequential effects on soil properties have been long studied and are well documented (Beltrán, 1999; Chander et al., 1994; Choudhary et al., 2011; Emdad et al., 2004; Ganjegunte et al., 2008; Grattan and Oster, 2003; Grattan and Rhoades, 1990; Qadir and Oster, 2004; Rietz and Haynes, 2003; Smedema and Shiati, 2002; Suarez et al., 2006). While most of the studies evaluated the effects of high SAR (> 15) waters on soil properties, the use of relatively moderate SAR (< 8) (Mace and Amrhein, 2001; Mandal et al., 2008) water such as reclaimed water, has been less investigated, especially when used to leach a salt affected soil. Understanding its effect on soil properties while using to leach a saline-sodic soil treated with organic amendments is important with respect to soil management and therefore warrants study. Any benefits obtained when reclaimed water and organic amendments are conjunctively used to leach and ameliorate a saline-sodic soil, will not only offer farmers a cheaper and sustainable alternative to remediate such soils but also reduce their reliance on freshwater and expensive inorganic amendments.

Therefore, the overall goal of this research was to evaluate the potential of organic amendments such as composts and biochar to reclaim a saline-sodic soil when used in conjunction with reclaimed water as a leaching solution.

# 2. LEACHING AND RECLAMATION OF A BIOCHAR AND COMPOST AMENDED SALINE-SODIC SOIL WITH MODERATE SAR RECLAIMED WATER

## Abstract

Remediating saline-sodic soils with organic amendments is increasingly seen as a cheaper and sustainable alternative to inorganic materials. The reclamation potential of biochar, biosolids and green waste composts applied to a saline-sodic soil was evaluated in a laboratory leaching experiment using moderate SAR reclaimed water. Treatments included biochar, biosolids co-compost, and greenwaste compost (all applied at a rate of 75 t $ha^{-1}$), gypsum (50 % gypsum requirement), biochar + gypsum, biosolids + gypsum, greenwaste + gypsum, and a non-amended control. All treatments were subjected to a one month incubation after which, the soils were filled in columns and leached using reclaimed water until 7 PV of water had passed. Cumulative leachate $Na^+$, $Ca^{2+}$, and $Mg^{2+}$ losses were evaluated in addition to soil properties after leaching. Results show that leaching with moderate SAR water was effective in reducing the soil salinity and sodicity in all soils. However, incorporation of organic amendments significantly increased $Na^+$ leaching compared to gypsum and the control due to increases observed in soil aggregation and saturated hydraulic conductivity. Also, biochar and composts were found to be significant sources of divalent cations ($Ca^{2+}$ and $Mg^{2+}$), which helped to displace $Na^+$ on the exchange sites more efficiently than gypsum and the control. After leaching, soil analyses indicate that organic amendments significantly lowered soil $EC_e$, ESP and SAR and saturated the exchange complex with $Ca^{2+}$. Soil pH and CEC were significantly

affected only when soils were treated with composts. Gypsum addition to organic amendments had a significant effect in most cases and could have a supplementary benefit of accelerating the reclamation process.

## Introduction

Soil salinization is defined as an excessive accumulation of salts within the soil profile to the extent that it decreases plant growth. It has been one of the major environmental problems threatening agricultural productivity since ancient times (Rengasamy, 2006). Salt affected soils are in general classified as; saline, sodic or saline-sodic, based on their respective electrical conductivity ($EC_e$) and sodium adsorption ratio (SAR) of the saturated paste extracts or the sodium on the exchange sites (Exchangeable Sodium Percentage, ESP) (Richards, 1954). Saline soils are characterized by having high $EC_e$ values ($> 4$ dS $m^{-1}$) while saline-sodic soils have both high $EC_e$ ($> 4$ dS $m^{-1}$) and SAR ($> 13$) of the saturation extract and an ESP $> 15$. Sodic soils are those which have low $EC_e$ ($< 4$ dS $m^{-1}$) but have high SAR's ($> 13$) or ESP $> 15$ (Richards, 1954). Saline-sodic soils can be considered to be the highly degraded and least productive due to their simultaneous effect of salinity and sodicity on soil physical, chemical, and biological properties. High salinity retards plant growth by creating osmotic imbalances and specific ion toxicities. On the other hand, sodicity deteriorates soil physical structure by clay swelling and dispersion due to high concentrations of $Na^+$ in the soil solution or at the exchange phase, forming dispersed soils (Rengasamy and Olsson, 1991). Dispersed saline-sodic soils are compacted and have reduced water infiltration and hydraulic conductivity which play a major role in water, air, and solute movement through the soil profile (Shainberg and Lety, 1984; Suarez et al., 2006). In addition to physical effects, chemical, biological, and biochemical property deteriorations have been well reported in literature for saline and sodic soils (García and Hernández, 1996; Ghollarata and Raiesi, 2007; McClung and Frankenberger, 1985; Pathak and Rao, 1998; Rietz and Haynes, 2003; Setia et al., 2012; Wong et al., 2008).

Reclamation of saline-sodic soils requires a two-step procedure, which involves the removal of sodium from exchange sites into soil solution by other divalent cations ($Ca^{2+}$ more importantly), which then promote soil flocculation. Subsequently, salts are leached from the profile (Abrol et al., 1988). Extensive research has been conducted over decades with respect to use of chemical amendments to provide $Ca^{2+}$ to replace $Na^{+}$ on the exchange sites (Brinck and Frost, 2009; Qadir et al., 2002). Gypsum ($CaSO_4.2H_20$) is the most commonly used chemical amendment and its efficiency as a supplier of $Ca^{2+}$ to offset $Na^{+}$ on exchange sites has been long studied and is an established technology to remediate saline-sodic soils (Ghafoor et al., 2001; Mace and Amrhein, 2001; Oster et al., 1999). Other chemical amendments such as sulfur and sulfuric acid have also been used to remediate saline-sodic soils by facilitating native calcite dissolution to release required calcium into soil solution (Amezketa et al., 2005; Sadiq et al., 2007; Zia et al., 2007). Alternatively, phyto-remediation technique has gained attention as a less expensive alternative to chemical amendments (Qadir et al., 2001b). This technique works on the same principle of native calcite dissolution to supply soluble calcium by facilitating changes in root zone partial pressure of $CO_2$ by plants and thus helps to remediate calcareous saline-sodic soils (Qadir et al., 2007; Qadir and Oster, 2004). Organic amendments have long been studied for their effectiveness in improving soil properties like structure, aggregate stability, hydraulic conductivity, and other chemical and biological properties (Giusquiani et al., 1995; Haynes and Naidu, 1998; Ros et al., 2003; Tejada et al., 2009) when applied to degraded lands. Several studies have also reported the benefits of using organic materials to remediate salt affected soils by improving their physical, chemical, and biological properties (Lax et al., 1994; Liang et al., 2005; Tejada et al., 2006; Wahid et al., 1998; Walker and Bernal, 2008). Composts differ in their physiochemical properties based on the feedstocks from which they are made and could influence soil properties differently when used for reclamation (Lakhdar et al., 2009). This study evaluates the effects of two different composts; biosolids and greenwaste composts used to reclaim a saline-sodic soil. Moreover, the benefits of combined applications of these composts and gypsum during the process of saline-sodic soil remediation and their effects on specific soil processes like hydraulic conductivity and aggregate stability have been seldom studied. Besides, the effect of extremely stable organic materials, such as biochar, on the reclamation of saline-sodic soils has not been investigated.

Biochar, a carbonaceous organic material, is produced by slow pyrolysis of biomass under zero or limited oxygen conditions in a closed furnace at temperatures $\leq$ $700^{o}$C (Lehmann and Joseph, 2009). Interest in biochars is more recent with its use mainly focused to combat global climate change by sequestering atmospheric $CO_2$ into soil C (Chan et al., 2008a). In addition to the C sequestration value, beneficial aspects of improved soil quality, nutrient enhancement, and plant growth have also been reported when biochar is used as an organic soil conditioner (Glaser et al., 2002; Lehmann et al., 2006). However, the use of biochar as a potential soil amendment for salt affected soils, in particular saline-sodic soils, has never been evaluated. Biochar was shown to improve soil physical properties like bulk density, porosity, aggregate stability, and saturated hydraulic conductivity (Herath et al., 2013; Laird et al., 2010). Moreover, recent studies have reported that biochars can be rich in nutrients like $Ca^{2+}$ and $Mg^{2+}$ (Tsai et al., 2012) and may enhance their availability in soil when added as amendments (Laird et al., 2010; Rajkovich et al., 2012). So addition of biochar to a saline-sodic soil could aid in its remediation by adding $Ca^{2+}$ and $Mg^{2+}$, improve aggregate stability, hydraulic conductivity, and potentially might enhance $Na^{+}$ leaching.

Degraded water, defined as “that water which has suffered chemical, physical or microbiological degeneration in quality”, (O'Connor et al., 2008) like agricultural drainage water, municipal treated waste water, water from animal and feed operations, are increasingly seen as alternative sources of irrigation water due to an augmented demand for high quality potable water by cities (Corwin and Bradford, 2008). In California and much of the western United States, agricultural drainage and municipal treated wastewater, termed as ‘reclaimed water’, are used mainly for agricultural irrigation to supplement the scarcity of fresh canal water and as an alternative for their disposal (Mandal et al., 2008; Wu et al., 2009). The chemical characteristics that determine the suitability of these marginal quality waters for irrigation are same as those of fresh waters as given by Ayers and Westcot (1985). Important issues that constrain the use of these low quality waters for irrigation are the salinity, sodicity, and specific ion toxicities. Salinity ($EC_{iw}$) and Sodicity (SAR) of the irrigation water are the principle water quality properties that determine the extent of soil degradation. Many studies have evaluated the effects of irrigation water salinity and sodicity on soil structure deterioration by clay dispersion and subsequent reduction in hydraulic conductivity (Frenkel et al., 1978; Grattan and Rhoades, 1990; Mace and Amrhein, 2001; McNeal and Coleman, 1966; McNeal et al., 1968; Quirk and Schofield, 1955). Reclaimed water from municipal treatment plants may contain higher EC and SAR values (Wu et al., 2009) than other fresh water resources. While the effects of water with high SAR's (> 13) on soil properties have been well studied (Grattan and Oster, 2003; Jalali et al., 2008; Murtaza et al., 2006), the use of moderate SAR waters (< 8), especially to leach a saline-sodic soil treated with organic amendments for reclamation, is questionable and warrants study.

The main objective of this research was to compare and evaluate the effects of organic amendments (biochar and composts) and gypsum as individual and conjunctive applications on the reclamation potential of a saline-sodic soil when leached with marginal quality reclaimed water. Our hypothesis is that the combined applications of gypsum and organic amendments and subsequent leaching with reclaimed water will accelerate the reclamation process beyond what is achieved when they are used separately. Moreover, the negative chemical effects of reclaimed water use on soil structure degradation will be negated due to structural stability enhancements offered by organic matter additions.

## Materials and Methods

### Soil Sampling

Bulk saline-sodic soil samples (0-20 cm) were collected from an agricultural farm located on the west side of San Joaquin valley, California (36°22’57.2”N, 120°13’50.8” W). These soils had a history of being previously irrigated with saline-sodic drainage water as part of Integrated on Farm Drainage Management (IFDM) and were abandoned without any crop cultivation for more than a year due to poor soil performance. The soil has a clay loam texture and belongs to the Ciervo soil series (Fine, smectitic, thermic Vertic Haplocambids). Bulk soils were air dried and crushed to pass through a 2 mm sieve and were homogenized by thorough mixing. Sub samples were randomly collected from bulk soils to analyze for their physical and chemical properties. Soil particle size analysis was conducted using hydrometer method (Gavlak et al., 2003). Soil $EC_e$ and pH measurements were made on saturated paste extracts following the method given by Richards (1954), using Oakton CON 6 conductivity meter (Oakton Instruments, IL) and Thermo Scientific Orion 3 star bench top pH meter (Thermo Scientific, Inc. MA). Soluble cations were analyzed on the same extracts by Inductively Coupled Plasma Optical Emission Spectrophotometry (ICP-OES) using a Perkin Elmer Optima 7300DV spectrophotometer (PerkinElmer, Inc. MA). Soil Cation Exchange Capacity (CEC) was estimated by following the Bower method of $Na^+$ saturation using 1M sodium acetate solution (pH 8.2), followed by ethanol rinsing and replacing adsorbed $Na^+$ by $NH_4^+$ using 1M ammonium acetate solution. Exchangeable cations were measured by rinsing soils with excess of 1M ammonium acetate solution (buffered at pH 7) as given by Richards

(1954). Calcium carbonate equivalent was calculated following the calcimeter method, which measures the pressure developed by soil reaction with concentrated hydrochloric acid (Loeppert and Saurez, 1996). Important soil physical and chemical characteristics are presented in Table 2.1.

### Amendments and Irrigation Water

Wood chip biochar, greenwaste compost, and biosolids co-compost were used as organic amendments. In addition to these, 98% pure laboratory grade gypsum was used as an inorganic amendment. Greenwaste and biosolids composts were collected from local STA (Seal of Testing Assurance) affiliated compost producers. Greenwaste compost was produced using turned windrows while biosolids co-compost was produced in aerated static piles. Greenwaste composts consisted of mostly roadside landscaping green material and biosolids compost was made as co-compost with municipal biosolids and horse stable beddings. Wood chip biochar was procured from a local biochar producer (Western Environmental Inc. Mecca, CA). The feed stock was charred at 500 °C for about an hour under oxygen free conditions in an industrial furnace. Compost materials had passed through a 0.25-inch (< 6.35mm) sieve while biochar had passed through a 2 mm sieve. Composts were analyzed for their properties using methods outlined in TMECC (TMECC, 2001), while biochar was analyzed following the methods outlined in International Biochar Initiative (IBI, 2013). Some important properties of the organic materials used are presented in Table 2.2. Irrigation/leaching water used was the reclaimed water collected from a local farm with its primary source from Eastern Municipal Water District (EMWD), Southern California. Chemical properties of the reclaimed water are given in Table 2.3. According to Mace and Amrhein (2001), this water can be classified as “moderate SAR” water.

## Soil Treatments and Incubation

Three hundred grams of air-dried base soil samples were treated with organic and gypsum treatments. Organic amendments were applied at a rate of 75 t $ha^{-1}$ on a dry weight basis (~ 5 % w/w) and gypsum was applied at 50 % gypsum requirement (GR). The high organic amendment application rate was chosen to simulate a one-time application and long term effects of addition of these amendments. Reduced gypsum rate was to simulate reduced usage of an inorganic amendment and to test its effects when applied at half of its recommended dosage. A total of 8 treatments were used in this experiment: Control (no amendment), gypsum (G), greenwaste compost (GWC), biosolids compost (BSC), biochar (BC), biochar + gypsum (BCG), biosolids compost + gypsum (BSCG), and greenwaste compost + gypsum (GWCG). The combined treatments had the same 5 % application rate and 50 % GR. All the amendments were thoroughly mixed into the soil and were incubated for a month in mason jars maintained at 60% water-filled pore space (WFPS) and room temperature (25 ± 1°C). WFPS was calculated using Eq. 1.

$$\text{WFPS (\%)} = \frac{\theta_g \times \rho}{\left(1 - \frac{\rho}{2.65}\right)} \text{ x } 100 \qquad (1)$$

where, $\theta_g$ is the gravimetric water content, $\rho$ is the soil bulk density and *2.65* is the particle density. This incubation was done in order to stabilize the microbial activity and evaluate the wet aggregate stability improvements after the organic amendment additions.

Also, soils maintained at 55- 60 % WFPS have been shown to have higher microbial activity (Doran et al., 1990). Increased microbial activity was shown to increase aggregate development and stability (Kandeler and Murer, 1993; Tisdall et al., 1978). After a month of incubation, treated soils were carefully emptied from the mason jars, were air dried, and gently crushed to pass through a 2 mm sieve.

**Leaching Experiment**

Leaching columns consisted of acrylic tubes with an internal diameter of 5 cm and a length of 20 cm. The acrylic columns were filled with acid washed #12 silica sand at the bottom (to a height of 1.5 cm) and incubated soils were added in batches with simultaneous tapping to achieve a uniform bulk density and avoid any air pockets. Soils were packed close to a field bulk density of 1.23 g $cm^{-3}$. Final mean bulk densities after packing into columns were calculated to be 1.24 g $cm^{-3}$ for the control and gypsum treatments, and 1.20 g $cm^{-3}$ for all other organic amendment treated soils. Soil filled columns were initially subjected to wetting from the bottom in order to remove any air pockets developed during the packing process. After complete saturation from bottom, the direction of the flow was reversed by maintaining a 5 cm constant head on top of the soil using a Mariotte bottle setup. For every treatment, three replicates were used and were setup in a completely randomized experimental design.

The pore volume of each soil column was calculated using volume of the soil in the column ($V_s$) and its associated porosity ($\phi_s$) and is given as ($PV = V_s * \phi_s$) (Kirkham, 2004). Organic amendment treated soil columns had a mean pore volume of 148 $cm^3$ while the control and gypsum treated soils had 126 $cm^3$ as one pore volume. All soil columns were leached with approximately seven pore volumes of moderate SAR reclaimed water. Leachate samples were collected for every one third pore volume in centrifuge tubes. Saturated hydraulic conductivity measurements were made after every one pore volume of leaching solution had passed through the column. Saturated hydraulic conductivity ($K_s$) was calculated using the standard Darcy's law as given in Eq. 2.

$$K_S\ (\text{cm hr}^{-1}) = \frac{V * L}{\left[A * t * \left(H_2 - H_1\right)\right]} \qquad (2)$$

where, $L$ is the length of the soil in the column, $V$ is the volume of leachate collected within a time interval $t$, flowing through an area $A$. $H_2$ & $H_1$ are the respective pressure heads at the top and bottom of the soil column (Kirkham, 2005). Leachate was analyzed for $Na^+$, $Ca^{2+}$, and $Mg^{2+}$ ions using ICP analysis. Cumulative amounts of cations leached were calculated using Eq. 3.

$$Q_L = \sum\left(C_l - C_{ls}\right)V_j \qquad (3)$$

where, $Q_L$ is the cumulative amount of a cation in the leachate, $C_l$ and $C_{ls}$ are the respective cation concentrations in the leachate and leaching solution and $V_j$ is the volume of the leachate collected in the $j^{th}$ interval of time (Jalali and Ranjbar, 2009). After the completion of leaching phase, all the columns were allowed to drain freely. Soils from the columns were carefully removed, air-dried and crushed to pass through a 2- mm sieve. These air-dried soil samples were analyzed as post-leaching soil samples to determine their respective chemical properties including $EC_e$, SAR, CEC, soluble, and exchangeable cations. Wet aggregate stability measurements were also conducted on base (before amendment application) soils, soils after incubation, and on post-leaching soils.

Percent wet aggregate stability was measured on 1-2 mm soil aggregates using wet sieving apparatus following the method given by Nimmo and Perkins (2002).

### Data analysis

Two-way factorial analysis of variance was conducted using SPSS V.20 software to test the effects of gypsum addition to the organic amendments. Where there was no effect of gypsum, data were analyzed using one-way anova to separate the means. Significant differences between the treatment means were analyzed using Tukey's test in SPSS at 95 % significance ($P < 0.05$).

## Results and Discussion

### Leachate EC

Breakthrough curves for mean leachate EC for various treatments during the leaching process are presented in Fig. 2.1. For all the treatments, EC initially increased reaching a high after approximately 1 PV. EC values then decreased gradually with further leaching. This trend may be attributed to the movement of soluble salts to the upper part of the soil column along with the wetting front while the columns were initially saturated from the bottom. Thus, the soil in the column was likely not uniform with respect to its salt concentration all along its profile as opposed to leaching a dry soil with a uniform salt profile. Therefore, the first sample of leachate had a low salt concentration followed by increasing concentration due to the movement of the accumulated salts downward from the top of the profile. This was followed by a continuous decrease in EC due to additional leaching of salts until equilibrium was reached between the EC's of the leaching and soil solutions. All treatments had significantly higher mean leachate EC's at about 1 PV compared to the control (Fig. 2.1) demonstrating that amendments increased the salt concentration of the leachate. BSCG had the highest leachate EC followed by other amendments. Addition of gypsum to organic amendments significantly ($P < 0.05$) increased leachate EC of the combined applications at 1 PV. This can be ascribed to added $Na^+$ from irrigation water and also its increased replacement from exchange sites into the soil solution by the combined applications. As leaching progressed, gypsum alone treatment (G) continued to have a higher leachate EC followed by GWC and GWCG until about 4.7 PV of water had passed. Increase in leachate EC by organic amendments during the initial stages of leaching was also observed by Jalali and Ranjbar (2009) when sheep and poultry manure were applied to a degraded soil. The high initial leachate EC's in the biosolids compost treated soils was also likely due to the high electrical conductivity of the biosolids material compared to the green waste compost and biochar materials.

## Cumulative Leachate Losses of $Ca^{2+}$, $Mg^{2+}$, and $Na^+$

### *Cumulative $Ca^{2+}$*

Cumulative leachate losses of $Ca^{2+}$ are presented in Fig. 2.2. Organic amended soils lost significantly higher ($P < 0.05$) amounts of total $Ca^{2+}$ than gypsum (G) and the control soils. Gypsum (G) and the control soils lost statistically similar amounts of $Ca^{2+}$. Although, $Ca^{2+}$ losses were higher from the combined applications than the sole applications of composts and biochar, the differences were not statistically significant ($P > 0.05$). Between composts, biosolids compost produced greater $Ca^{2+}$ losses as this amendment had higher calcium content than the green waste compost though the differences were not statistically significant. Average leachate losses of $Ca^{2+}$ were 12, 17, and 11 % higher from biochar, biosolids, and green waste compost treated soils relative to the control soils. These results concur with those reported by Jalali and Ranjbar (2009), where soils amended with sheep and poultry manure lost greater amounts of $Ca^{2+}$ through leachate when leached with different SAR waters.

### ***Cumulative $Mg^{2+}$***

The breakthrough curves showing cumulative leachate losses of $Mg^{2+}$ from different treatments during different stages of leaching are presented in Fig. 2.3. It is evident that soils amended with organic amendments significantly ($P < 0.01$) lost greater amounts of $Mg^{2+}$ through leachate than gypsum (G) and the control soils. Gypsum had no significant effect ($P > 0.05$) when combined with organic amendments. Also, cumulative $Mg^{2+}$ losses from composts were significantly higher ($P < 0.05$) than from the biochar treatments. Cumulative $Mg^{2+}$ losses from the control and gypsum (G) soils were not significantly different. Mean cumulative losses were 11, 39, and 37 % more from soils treated with biochar, biosolids, and green waste composts relative to the unamended control. These results indicate that organic amendments can be a significant source of divalent cations such as $Ca^{2+}$ and $Mg^{2+}$ in the soil solution. However, leachate losses of $Mg^{+2}$ from composts were much higher than their respective $Ca^{2+}$ losses which can be due to the preferential exchange of $Ca^{2+}$ over $Mg^{2+}$ by the soil exchange complex.

### ***Cumulative $Na^{+}$***

Mean cumulative leachate losses of $Na^{+}$ for different treatments are shown in Fig. 2.4. All amended soils lost significantly higher ($P < 0.01$) amounts of $Na^{+}$ compared to the unamended control. At 37.89 meq, control soils lost the least amount of $Na^+$. Gypsum addition had a significant effect ($P < 0.05$) in increasing the cumulative losses of $Na^+$ from compost treated soils. BSCG and GWCG lost significantly higher $Na^+$ compared to BSC and GWC treatments. Differences between BC and BCG were not significant ($P > 0.05$), however. On average, combined applications leached 33 % more total $Na^+$ relative to the control, while the sole organic amendment applications leached 26 % more cumulative $Na^+$ from the soil. High $Ca^{2+}$ releases from the organic amendments preferentially exchanged $Na^+$ and facilitated its release into soil solution where it was leached subsequently. Additional $Ca^{2+}$ availability from gypsum enhanced this exchange rate and thus released more $Na^+$ into the solution when soils were treated with both gypsum and composts together. $Na^+$ loss from soil treated with gypsum (G) at 50% GR was significantly higher than the untreated control but less than that observed from the compost and biochar amended soils. These results indicate that application of organic amendments lead to the efficient replacement of $Na^+$ on the exchange sites by adding significant amounts of divalent cations and also prevented the entry of $Na^+$ onto the exchange phase when low SAR water was used as a leaching solution. Similar results of enhanced $Na^+$ leaching were observed in other studies when saline-sodic soils were treated with various amendments (Ahmad et al., 2006; Ghafoor et al., 2012; Gharaibeh et al., 2011; Gharaibeh et al., 2010; Jalali and Ranjbar, 2009).

Cumulative $Na^+$ leaching times were also significantly reduced ($P < 0.01$) by gypsum (G) and organic amendments (Fig. 2.5). The control soils lost less $Na^+$ in significantly more time compared to organic amendment and the gypsum treated soils, which lost more $Na^+$ in significantly less time (Fig. 2.5). Adding gypsum to biosolids and biochar further reduced their $Na^+$ leaching times relative to their individual applications. Increased $Na^+$ leaching from the soil profile in relatively shorter times would mean faster reclamation of these soils in the presence of organic amendments like composts and biochar.

### Soil Aggregate Stability

Mean soil wet aggregate stability measurements at three different stages of the experiment are presented in Fig. 2.6. Before amendment application, mean wet aggregate stability of the base soils ranged from a low of 33.11 % to a high of 34.92 % and the differences were not statistically significant. After 30 day incubation, marked differences were observed between treatments. Soils treated with compost amendments exhibited significantly higher ($P < 0.01$) mean soil aggregate stability compared to gypsum (G), biochar, and unamended control soils. Adding gypsum to composts or biochar did not significantly affect ($P > 0.05$) the soil aggregate stability relative to their sole applications. On average, compost applications increased the soil wet aggregate stability by 41 and 32 % relative to the control and gypsum (G) after incubation (Fig. 2.6). These results are consistent with Wahid et al. (1998), who reported increases in water stable soil aggregates when manure, clover hay, and wheat straw were applied at 3 % to a highly saline soil in Pakistan. Furthermore, in a long term field study, Tejada et al. (2006) found significant increases in soil structural stability following the incorporation of cotton gin crushed compost and poultry manure into a semi-arid Mediterranean soil. They determined that humic fractions of organic matter and chelation of $Ca^{2+}$ and $Mg^{2+}$ by organic matter contributed to the structural stability of the soil. Many other studies have also reported similar increases in aggregate stability following compost applications (Aggelides and Londra, 2000; Annabi et al., 2007; Caravaca et al., 2001; Lax et al., 1994). In addition, increased biological activity and their release of soil agglutinants such as exo-polysaccharides likely contributed to the increase of soil aggregate stability (Roberson et al., 1995).

Soil aggregate stabilities of BC and BCG treatments were 5.5 and 6 % higher than the control after 30 day incubation but the differences were not statistically significant ($P > 0.05$). Literature with respect to biochar effects on soil aggregate stability is rather minimal and conclusions are mixed. Piccolo et al. (1996) demonstrated that highly stable humic substances from oxidized charcoal can significantly increase the aggregate stability of soils. More recently, Herath et al. (2013) reported increases in aggregate stability in two different soils when biocharred corn stover was applied. They explained that longer incubation of biochar treated soils facilitated the release of microbial exudates which glued soil particles and lead to the formation of macro aggregates. This was confirmed with Scanning Electron Microscope (SEM) images showing increased concentration of fungal hyphae and other microbial products within the pores of biochar (Herath et al., 2013). Contrastingly, in China, Peng et al. (2011) reported no significant increase in aggregate stability when biochar from rice straw was applied to an ultisol. It appears that the properties of a feedstock used to produce the biochar likely determine the ability of that biochar to affect the soil aggregate stability. Gypsum (G) applied at 50 % GR also increased the soil aggregate stability but the difference was not statistically significant compared to the control treatment. Soil aggregate stability increased for all treatments including the control, post leaching (Fig. 2.6). At 41.4 %, control had the least soil aggregate stability followed by gypsum (G) with 47 % stability. Stability measurements ranged from 52 to 55 % for soils treated with organic amendments. Combined applications of gypsum and organic amendments did not significantly differ from their individual applications in increasing the soil aggregate stability post leaching. Overall, biosolids compost, green waste compost and biochar increased the soil aggregate stability by an average of 58, 56, and 61 %, respectively, compared to their respective initial measurements. Also, a 25 and 37 % increase in soil aggregate stability was observed in the control and gypsum (G) soils compared to their respective initial stabilities. This was likely because of $Na^+$ leaching from all treatments which helped the soils to flocculate. Stability increases were more pronounced and significant in soils that received organic amendments, which also had significantly higher $Na^+$ losses relative to gypsum (G) and the control soils.

### Saturated Hydraulic Conductivity ($K_s$)

Mean saturated hydraulic conductivity ($K_s$) measurements are provided in Fig. 2.7. All organic amendments significantly increased ($P < 0.01$) the mean $K_s$ of soils. Mean $K_s$ of all the treatments stayed relatively constant throughout the leaching process indicating that soils reached steady state immediately after leaching started. Hydraulic conductivity of the control soils were the lowest and gradually decreased over time as leaching progressed (Fig. 2.7), which was likely due to some exchange of $Na^+$ occurring between the leaching solution and soil exchange sites. Decrease in soil $K_s$ was also observed by Mace and Amrhein (2001) when moderate SAR water was used to leach a clay loam soil and attributed this effect to increased swelling and dispersion by $Na^+$ adsorption onto exchange sites. Similar processes likely dominated in our system and reduced the $K_s$ of the control soil over time. Factorial analysis revealed that combined applications of organic amendment and gypsum produced a significant and interactive effect on soil $K_s$. Gypsum additions significantly increased ($P < 0.05$) the $K_s$ of all the organic amendment treated soils compared to the soils treated with just organic materials (Fig. 2.7). Statistically, the order of soil $K_s$ observed for various treatments during leaching was; BSCG > BSC > GWCG > GWC > gypsum (G) ≥ BCG > BC > control. High $Na^+$ leaching observed from the soils with combined applications contributed for their increased $K_s$ than their individual applications. Also, addition of gypsum likely increased the electrolyte concentration of the leaching solution and therefore helped to increase soil $K_s$ (McNeal and Coleman, 1966; Quirk and Schofield, 1955).

On average, combined applications of composts increased the soil $K_s$ by 346 % and 63 % relative to the control and gypsum (G) treatments, respectively. Individual applications of both biosolids and Greenwaste composts also significantly increased ($P < 0.01$) the soil $K_s$ (Fig. 2.7). Mean soil $K_s$ of BSC and GWC was 287 and 210 % higher than the control and 42 and 14 % higher than the gypsum (G) treatment. This can be attributed to increased soil aggregate stability by organic amendments (Fig. 2.7), which directly helped to increase the porosity of the soil and therefore improved soil permeability. Addition of organic amendments was shown to significantly increase the soil hydraulic conductivity in other studies (Aggelides and Londra, 2000; Felton and Ali, 1992). Biochar on the other hand, performed better than the control but was not efficient in increasing soil $K_s$ when compared to the gypsum (G) (Fig. 2.7). Mean conductivities of BC and BCG treated soils were 127 and 155 % higher than the control soil but were 16 & 6.5 % less than that of the gypsum (G) treated soil. Similar improvements in $K_s$ of the top soil were observed by Asai et al. (2009) when biochar was applied to rice fields in northern Laos. Also in a more recent study in New Zealand, Herath et al. (2013) reported 50-139 % increase in soil $K_s$ after corn stalk biochar was applied at 11 t $ha^{-1}$ to silt loam soils and attributed this effect to increased soil aggregate stability and porosity. In this study we observed significantly higher improvements in soil $K_s$ with an application rate of 75 t $ha^{-1}$.

### Soil CEC

Cation exchange capacities of different treatments at the end of the experiment are presented in Fig. 2.8. The initial soil CEC's, before amendment applications, ranged from 25.86 to 27.44 meq/100g. Significant differences were observed between treatments at the end of the experiment. Addition of composts significantly increased ($P < 0.01$) soil CEC compared to biochar, gypsum, and the control soils (Fig. 2.8). However, no statistical significance ($P > 0.05$) was observed between biosolids and green waste compost amended soils. Also, gypsum addition to organic amendments did not have any significant effect ($P > 0.05$) in altering the soil CEC when compared to their individual applications. BSC and GWC increased soil CEC by an average of 15 and 16 % relative to the control; by 16 and 17 % relative to gypsum and by 14.5 and 15 % compared to biochar. Percent changes compared to their initial values were also significantly higher for green waste and biosolids composts, relative to gypsum and the control (Fig. 2.8). BSC and GWC increased soil CEC by an average of 17 and 19 % than their initial CEC. Previous studies have also reported similar increases in soil CEC after addition of organic amendments like composts (Aggelides and Londra, 2000; Ouédraogo et al., 2001). CEC of biochar-amended soils on the other hand, did not significantly differ from gypsum and the control soils at the end of the experiment. However, addition of biochar nominally increased the soil CEC by an average of 3.2 % when compared to an initial mean soil CEC of 26.47 meq/100g. Laird et al. (2010) observed CEC increases ranging from 4 to 30 % when hardwood biochar was incorporated at different rates after a 500 day incubation. In our study, wood chip biochar did not significantly increase the soil CEC after 30 day incubation. A longer incubation might be necessary to facilitate adequate abiotic or microbial oxidation of the char (Cheng et al., 2008; Liang et al., 2006).

### Soil pH and $EC_e$

The initial and final soil pH of different treatments is presented in Fig. 2.9. Base soils pH ranged from a low of 8.05 to a high of 8.12. Reductions in soil pH were observed in all treatments after leaching, when compared to their respective initial values. Also, analysis of post-leaching soils revealed significant differences between treatments. Biochar, gypsum, and the control had significantly higher ($P < 0.01$) soil pH values, respectively, compared to the compost treatments. No significant differences among the two composts were observed, however. Applying composts significantly decreased ($P < 0.01$) soil pH after incubation and leaching (Fig. 2.9). Addition of gypsum to the organic amendments did not further reduce soil pH. Mahdy, (2011) also reported similar results of reduced soil pH when a saline sodic soil was leached after amending with a compost made out of animal and plant residues. However, in the same study, anthracite coal powder did not significantly alter the soil pH, which concurs with our results. Reductions in soil pH were also reported by other researchers when organic amendments were applied to soils (Li and Keren, 2009; Makoi and Ndakidemi, 2007; Wong et al., 2009). It is possible that addition of composts likely increased the $P_{\mathrm{CO2}}$ due to increased microbial activity during incubation and/or leaching followed by both inorganic and organic acid formation, which led to greater pH reductions in the compost soils (Nelson and Oades, 1998; Qadir et al., 2001b; Wong et al., 2009). Biochar on the other hand, did not increase soil pH but in fact reduced it (Fig. 2.8). These results contrast with Chan et al. (2008a) and Laird et al. (2010), who reported increases in soil pH with biochar additions. It is likely that leaching of $Na^+$ salts from biochar amended soils contributed to reductions in soil pH relative to their initial pH.

Soil $EC_e$ differences among various treatments are shown in Fig. 2.10. Post leaching, all treatments achieved significant reductions in soil $EC_e$ compared to their respective initial $EC_e$'s, a consequence of salt removal through leaching. Gypsum (G) and GWC significantly differed ($P < 0.01$) from the control in reducing the soil $EC_e$. Other treatments were not significantly different from either gypsum (G) or GWC (Fig. 2.9). Except the control, all other treatments reduced the soil $EC_e$ levels close to the saline soil threshold of 4 dS $m^{-1}$. Gypsum addition to organic materials had no significant effect in decreasing soil $EC_e$ when compared to their respective individual applications. Similar reductions in soil $EC_e$ were reported by Ghafoor et al. (2001) & (2012) and Tejada et al.

(2006) when organic manures and composts were added to saline soils. Overall, addition of organic amendments decreased soil $EC_e$ by an average of 79.4 % while the soil $EC_e$ of gypsum (G) and the control soils were reduced by 77 and 73 % respectively, when compared to their initial readings.

### Soil SAR

The Sodium Adsorption Ratio (SAR) is determined as the relative concentration of $Na^+$ over the square root of mean $Ca^{2+}$ and $Mg^{2+}$ concentrations in soil solution. A decrease in soil SAR could be interpreted as the decrease in $Na^+$ concentration in soil solution relative to the $Ca^{2+}$ and $Mg^{2+}$ concentrations or a relative increase in $Ca^{2+}$ and $Mg^{2+}$ concentrations. Sodium adsorption ratios of different treatments before and after leaching are presented in Fig. 2.11. Initial soil SAR's ranged from a low of 27.39 to a high of 29.33 before amendment applications, respectively. After soil leaching, reduction in soil SAR was observed in all treatments due to salt removal through leaching (Fig. 2.11). However, soils treated with gypsum (G) and organic amendments had significantly lower ($P < 0.01$) SAR relative to the control soils, with the lowest SAR in GWCG treatment. Factorial analysis revealed the significant effect ($P < 0.05$) of gypsum, with combined applications significantly reducing soil SAR more than that of the individual compost applications (Fig. 2.11). Gypsum addition to biochar did not have any significant effect compared to biochar alone treatment in reducing soil SAR. Also, BSCG was not significantly different from BC and BCG. Increased $Ca^{2+}$ and $Mg^{2+}$ release by organic amendments increased their concentrations in soil solution and helped to replace $Na^+$ on exchange sites into soil solution and facilitated its leaching, thus causing reductions in soil SAR. Also, additional $Ca^{2+}$ availability from gypsum in combined applications (BSCG and GWCG) enhanced the $Na^+$ displacement from exchange sites into soil solution and its subsequent leaching helped to reduce soil SAR in these treatments in much greater proportions. It is evident that organic amendments can be a significant source of $Ca^{2+}$ and $Mg^{2+}$ and can significantly increase their concentration in soil solution. Percent SAR reductions for different treatments, compared to their initial respective values, ranged from a low of 83 % in the control soils to a high of 93 % in GWCG soils and were in the order; GWCG > BCG> BSCG > BC > BSC = GWC = G > control. These results concur with those observed by Shaaban et al. (2013) and Tazeh et al. (2013), who also reported significant reductions in SAR after leaching soils amended with gypsum and organic amendments.

### Soil ESP

Soil exchangeable sodium percentages of different treatments are given in Fig. 2.12. All treatments were effective in reducing the soil ESP to values less than 15 after leaching with 7 pore volumes of reclaimed water including the control. Koo et al. (1990) and Gharaibeh et al. (2011) reported similar results with saline-sodic soil being reclaimed with just irrigation water and attributed this effect to ‘valence dilution’ (Reeve and Doering, 1966), where adsorption of divalent cations is preferred at the expense of monovalent cations when soil solution is diluted by added water. In addition, high inherent exchangeable $Ca^{2+}$ relative to exchangeable $Na^+$ seen in the control soil (Table 2.1) may have prevented the fast exchange of $Na^+$ in the leaching solution onto the soil exchange sites and thus helped not to further increase it’s ESP. However, ESP reductions were still significantly greater ($P < 0.01$) in soils amended with organic amendments than the control and gypsum (G) soils (Fig. 2.12).

Conjunctive applications of composts (BSC and GWC) and gypsum (G) were highly effective ($P < 0.01$) in reducing soil ESP compared to their individual applications (Fig. 2.12). BC and BCG were statistically equally effective in reducing the soil ESP. Gypsum (G) alone reduced soil ESP considerably but was not statistically different from the control. Gypsum was added at a reduced dosage (50% gypsum requirement) which could not enhance $Ca^{2+}$ availability in soil solution to meet the $Na^{+}$-$Ca^{2+}$ exchange demand. On the other hand, factors such as 1) high $Ca^{2+}$ release from the organic amendments (Table 2.2), 2) $Ca^{2+}$ contributions from native calcite dissolution by composts, and 3) addition of gypsum to these amendments, enhanced the $Na^{+}$-$Ca^{2+}$ exchange rate with the soil solution, therefore producing greater ESP reductions in these soils compared to the control soils. Reductions in soil ESP were also reported by previous studies with gypsum and other organic amendment applications (Gharaibeh et al., 2011; Jalali and Ranjbar, 2009; Qadir et al., 1996; Qadir et al., 2002; Tejada et al., 2006). Percent reductions of soil ESP compared to their respective initial ESP's were also significantly higher in soils that received both gypsum and organic amendments. The ESP reclamation provided by different treatments was in the order; BSCG > GWCG > BCG > BC > BSC > GWC > gypsum > control.

### Soil Exchangeable $Na^{+}$, $Ca^{2+}$, and $Mg^{2+}$

Exchangeable $Ca^{2+}$, $Mg^{2+}$ and $Na^{+}$ concentrations for soils before and after leaching are presented in Table 2.4. Significant differences were found between various treatments with respect to exchangeable $Ca^{2+}$ concentrations. All treatments had significantly ($P < 0.01$) higher ($P < 0.01$) exchangeable $Ca^{2+}$ relative to the control. Although combined applications of organic amendments and gypsum resulted in higher soil exchangeable $Ca^{2+}$ than their individual applications, the differences were not statistically significant ($P > 0.05$). On the other hand, gypsum (G) applied at 50 % GR also had significantly higher ($P < 0.05$) soil exchangeable $Ca^{2+}$ (12 %) than the control but was not different from organic amendment treatments. Among the organic amendments, biosolids compost had the highest increase in soil exchangeable $Ca^{2+}$ than the green waste compost and biochar (Table 2.4). This can be attributed to its very high *in situ* $Ca^{2+}$ levels (Table 2.2). On average, exchangeable $Ca^{2+}$ concentrations were 16, 21, and 12 % higher in biochar, biosolids compost and green waste compost treated soils respectively, relative to the control. When compared to their respective initial measurements, gypsum (G) and organic amendments augmented soil exchangeable $Ca^{2+}$. Average increases were 5, 12, 12, and 9 % for soils treated with gypsum (G), biochar, biosolids, and green waste composts, respectively. This increase in soil exchangeable $Ca^{2+}$ levels by organic amendments likely increased the displacement of $Na^{+}$ from exchange sites and enhanced its leaching from the soil profile, thus helping the soils to be remediated at a much faster rate. Similar observations were made by Jalali and Ranjbar (2009), who reported increases in soil exchangeable $Ca^{2+}$ after leaching a saline sodic soil treated with gypsum, sheep, and poultry manure. Also, Walker and Bernal (2008) reported increased sodium leaching due to the saturation of soil exchange sites with $Ca^{2+}$ when olive mill waste compost was applied to a highly saline soil. Similarly, Laird et al.

(2010) reported significant increases in soil extractable $Ca^{2+}$ when soils were treated with different rates of oak biochar. The controls on the other hand lost $Ca^{2+}$ (Table 2.4), which was perhaps due to non-availability of an additional source to replenish it.

Significant differences between treatments were not observed in after-leaching soils with respect to their soil exchangeable $Mg^{2+}$ levels (Table 2.4). However, when compared to their respective initial measurements, all treatments had lower soil exchangeable $Mg^{2+}$ concentrations. This can be partly attributed to the increased $Ca^{2+}$ concentrations in soil solution which favored its adsorption onto the soil exchange sites than $Mg^{2+}$ (Jalali and Ranjbar, 2009) and led to the leaching of $Mg^{2+}$ in gypsum and organic amendment treated soils. Decreased $Mg^{2+}$ levels are considered good with respect to the soil structure as some studies have shown that elevated soluble or exchangeable $Mg^{2+}$ could be deleterious in maintaining the soil permeability (Mahmoodabadi et al., 2013).

Initial and after-leaching soil exchangeable $Na^{+}$ concentrations are given in Table 4. Post-leaching soil analysis revealed significant differences among treatments with the control having significantly higher ($P < 0.01$) soil exchangeable $Na^{+}$ than amendments (Table 2.4). Gypsum addition to composts and biochar had a significant effect ($P < 0.05$) in reducing the soil exchangeable $Na^{+}$ than compost and biochar alone. Enhanced availability of $Ca^{2+}$ from combined applications facilitated higher displacement of $Na^{+}$ from the exchange complex. Organic amendments by themselves were also very effective in reducing soil exchangeable $Na^{+}$ compared to the control and gypsum (G) treatments due to their release of excess amounts of $Ca^{2+}$. Therefore, application of composts and biochar helped to reduce high exchangeable $Na^+$ by saturating the exchange complex with $Ca^{2+}$. Overall, biochar, biosolids compost and greenwaste compost amendments reduced soil exchangeable $Na^+$ by 80, 77, and 72 % relative to the control. Gypsum reduced the same by 32 %. When compared to their initial respective exchangeable $Na^+$ levels, the same trend was observed where decreases were more prominent in soils with combined and individual organic amendment applications than gypsum (G) and the control treatments. Percent reductions relative to initial measurements were between 93-94 % for combined applications while the individual organic amendments had percent reductions ranging between 86-92 %.

## Conclusions

This study has evaluated the reclamation potential of woodchip biochar and two composts (biosolids and green waste) when applied as individual or conjunctive applications with gypsum, to remediate a saline-sodic soil leached with moderate SAR water. Biochar and compost treated soils lost significantly greater amounts of $Na^+$ compared to gypsum soil and an unamended control. Losses were more prominent from compost amended soils when combined with gypsum. Cumulative losses of $Ca^{2+}$ and $Mg^{2+}$ were also higher from the organic amendment treated soils, which indicate the potential of these materials to significantly contribute divalent cations to the soil solution. Soil saturated hydraulic conductivity ($K_s$) was significantly improved by both biochar and composts. Gypsum had a significant interactive effect on soil $K_s$ with combined applications of composts improving $K_s$ by 346 % compared to the $K_s$ of an untreated control soil. Biochar was also effective in increasing $K_s$ by as much as 188 % than the control but had soil $K_s$ less than that of the gypsum treatment. Soil wet aggregate stability measurements revealed the superiority of organic amendments with average soil stability increases ranging from 8 to 41 % after incubation and 58 to 61 % post leaching, when compared to their initial soil aggregate stability. Gypsum addition to amendments offered no performance advantage in improving the soil aggregate stability.

Soil cation exchange capacity was significantly increased by composts but not by biochar during the study period. Thirty days may not have sufficiently oxidized the biochar material. Organic amendments had a significant effect in reducing soil pH and $EC_e$ post leaching. Composts exhibited greater reductions in soil pH than other treatments, which can be attributed to their formation of both organic and inorganic acids. Biochar on the other hand did not significantly alter the soil pH. Reductions in soil $EC_e$ were observed in all treatments, including the control, due to salt leaching. However, post leaching, gypsum and organic amendment treated soils had significantly lower soil $EC_e$ compared to the control. When compared with their respective initial soil $EC_e$'s, mean reductions were 79, 77, and 73 % for organic amendments, gypsum, and the control soils.

Reductions in soil SAR and ESP were also more prominent in organic amendment treated soils than gypsum and the control. Gypsum had a significant effect only when added to composts, with combined applications producing greater reductions in soil SAR and ESP. This is due to their enhanced $Na^+$ leaching potential. Exchangeable $Na^+$ was also significantly reduced by compost and biochar applications compared to gypsum and the control after leaching. At the end of the experiment, exchangeable $Ca^{2+}$ concentrations were significantly higher in organic amendments when compared to the control and gypsum treated soils. No significant differences existed between treatments with respect to post-leaching exchangeable $Mg^{2+}$ levels. However, when compared to the initial measurements, exchangeable $Mg^{2+}$ concentrations decreased after leaching.

It should be noted that in most cases, significant differences were not found among the two composts in altering the soil properties. Also, gypsum addition to biochar did not improve its performance when compared to sole biochar application. Overall, results from this laboratory study indicate that biochar and composts can be significant sources of divalent cations like $Ca^{2+}$ and $Mg^{2+}$ in addition to their structural improvements offered due to organic matter additions. Hence, these can be successfully used for desalinization and desodification of a saline sodic soil even when leached with moderate SAR water. Adding gypsum to these amendments can provide a supplementary benefit of accelerating the reclamation process.

Table 2.1. Soil physical and chemical characteristics.

| **Soil characteristic** | **Value** |
|---|---|
| Sand (%) | 43 |
| Silt (%) | 18 |
| Clay (%) | 39 |
| Texture | Clay Loam |
| Bulk density (g $cc^{-1}$) | 1.23 |
| Organic Matter % | 0.6 |
| CEC (meq/100g) | 27.78 |
| pH | 8.26 |
| $EC_e$ (dS $m^{-1}$) | 23.37 |
| Soluble Na (meq $L^{-1}$) | 177.64 |
| Soluble Ca (meq $L^{-1}$) | 47.25 |
| Soluble Mg (meq $L^{-1}$) | 15.28 |
| Exchangeable Na (meq/100g) | 7.23 |
| Exchangeable Ca (meq/100g) | 78.91 |
| Exchangeable Mg (meq/100g) | 4.8 |
| SAR | 31.78 |
| ESP (%) | 26.03 |
| CCE (%) | 3.85 |

Table 2.2. Physical and chemical characteristics of composts and woodchip biochar.

| **Characteristic** | **Woodchip Biochar** | **Biosolids compost** | **Greenwaste compost** |
|---|---|---|---|
| Total C (%) | 63 | 24.4 | 23 |
| Total N (%) | 0.74 | 3.8 | 0.99 |
| Org. C (%) | 83.9 | 32 | 33.2 |
| C:N ratio | 85.1 | 6.42 | 23.2 |
| Organic Matter % | – | 61.4 | 56 |
| pH[1] | 8.55 | 7.38 | 6.36 |
| EC[1] (dS $m^{-1}$) | 0.56 | 12.8 | 2.75 |
| Stability indicator (mg $CO_2$-C OM $g^{-1}$ $day^{-1}$) | – | 2.3 | 0.66 |
| Total Elements (%) | | | |
| Ca | 1.68 | 2.84 | 1.47 |
| Mg | 0.41 | 0.48 | 0.37 |
| Na | 0.46 | 0.16 | 0.09 |
| K | 0.53 | 0.55 | 0.73 |

[1] pH and EC of composts were measured on 1:5 water extracts (TMECC, 2001), and that of biochar were measured on 1:20 water extracts (IBI, 2013).

Table 2.3. Chemical composition of reclaimed water.

| **Characteristic** | **Value** |
|---|---|
| $EC_w$ (dS $m^{-1}$) | 0.96 |
| pH | 7.2 |
| $Na^+$ (meq $L^{-1}$) | 5.21 |
| $Ca^{2+}$ (meq $L^{-1}$) | 2.09 |
| $Mg^{2+}$(meq $L^{-1}$) | 1.12 |
| SAR | 4.11 |
| $Cl^-$ (meq $L^{-1}$) | 5.4 |
| $SO_4^{2-}$ (meq $L^{-1}$) | 1.8 |
| $HCO_3^- + CO_3^{2-}$ (meq $L^{-1}$) | 1.5 |

Table 2.4. Soil exchangeable $Na^+$, $Ca^{2+}$, and $Mg^{2+}$ concentrations (Mean ± s.e.) (meq/100g) for different treatments before and after leaching.

| Treatment | $Na^+$ | | $Ca^{2+}$ | | $Mg^{2+}$ | |
|---|---|---|---|---|---|---|
| | Initial | Final | Initial | Final | Initial | Final |
| Control | 6.73±0.15 a* | 2.46±0.14 a | 78.72±0.65 a | 75.61±5.63 a | 4.80±0.33 a | 3.69±0.52 a |
| Gypsum | 6.89±0.63 a | 1.68±0.10 b | 80.69±4.07 a | 84.94±5.36 b | 4.93±0.38 a | 3.92±0.42 a |
| BC | 6.54±0.31 a | 0.53±0.07 cd | 78.23±1.35 a | 83.22±1.81 b | 4.57±0.26 a | 2.79±0.28 a |
| BSC | 6.51±0.44 a | 0.78±0.16 c | 77.91±1.45 a | 90.67±3.82 b | 4.21±0.23 a | 3.76±0.33 a |
| GWC | 6.80±0.28 a | 0.92±0.07 c | 79.92±2.04 a | 83.86±1.66 b | 4.59±0.23 a | 3.60±0.42 a |
| BCG | 6.74±0.32 a | 0.47±0.05 d | 77.69±3.24 a | 91.67±1.11 b | 4.10±0.24 a | 3.05±0.12 a |
| BSCG | 6.61±0.38 a | 0.37±0.11 d | 78.59±3.02 a | 92.16±5.81 b | 4.34±0.29 a | 2.43±0.17 a |
| GWCG | 6.91±0.19 a | 0.46±0.02 d | 75.69±3.39 a | 85.59±2.86 b | 4.88±0.18 a | 3.10±0.10 a |

*Same letters within a column indicate no significant differences between treatments ($P < 0.05$), Tukey's test).

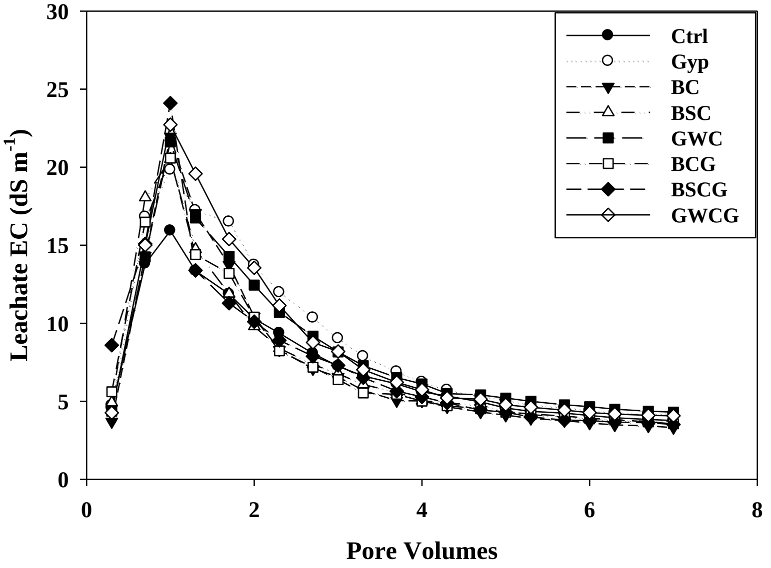

Fig. 2.1. Mean leachate electrical conductivity (EC) for different treatments.

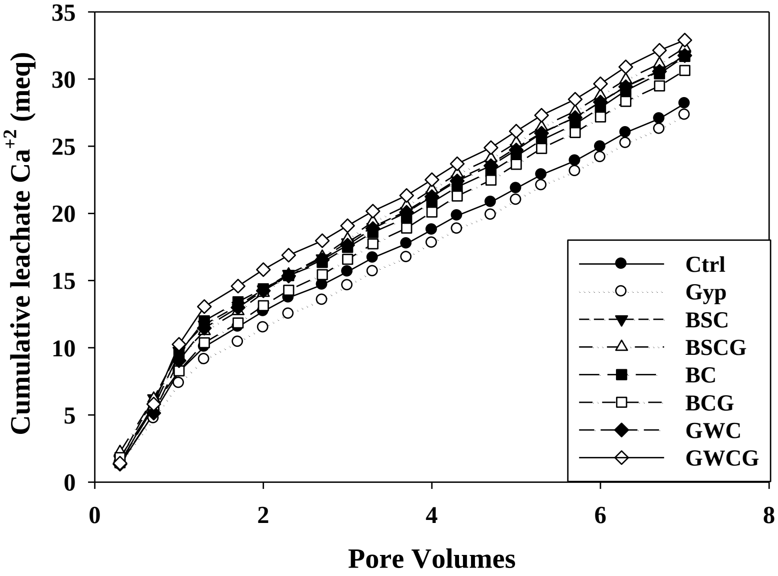

Fig. 2.2. Mean cumulative leachate losses of $Ca^{2+}$ from soils of different treatments.

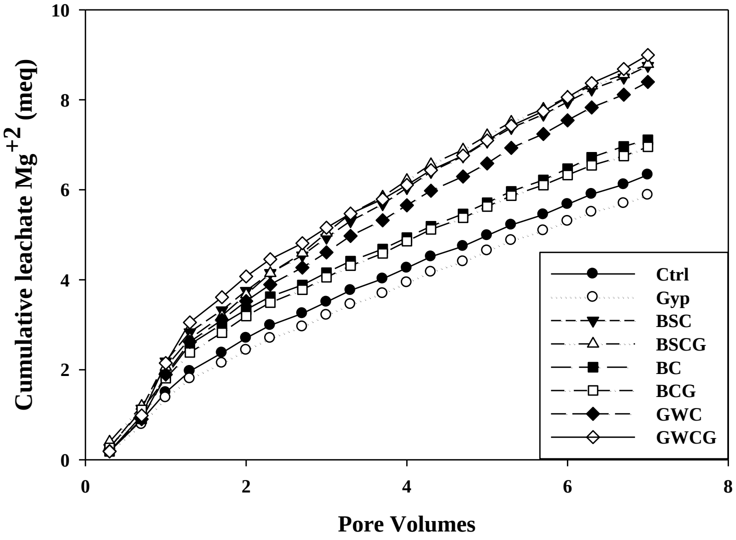

Fig. 2.3. Mean cumulative leachate losses of $Mg^{2+}$ from soils of different treatments.

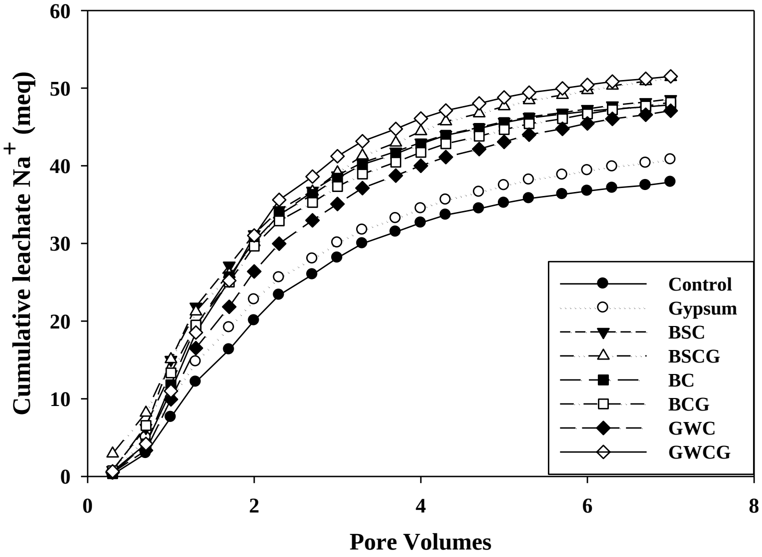

Fig. 2.4. Mean cumulative leachate losses of $Na^{+}$ from soils of different treatments.

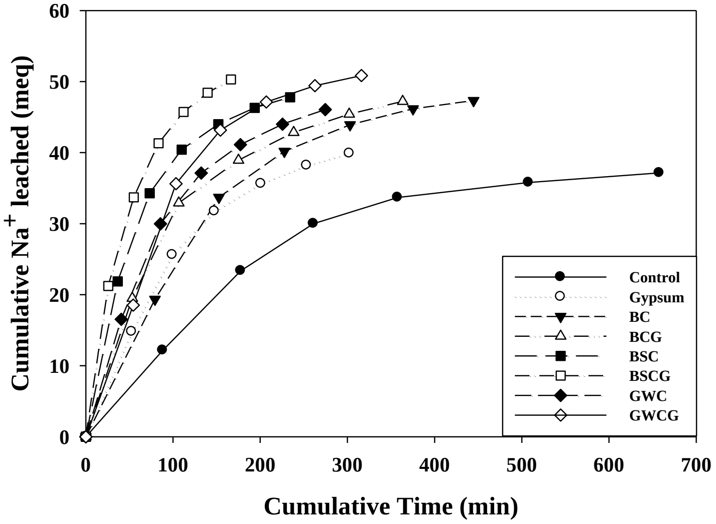

Fig. 2.5. Mean cumulative Na$^+$ leached from soils of different treatments with respect to time.

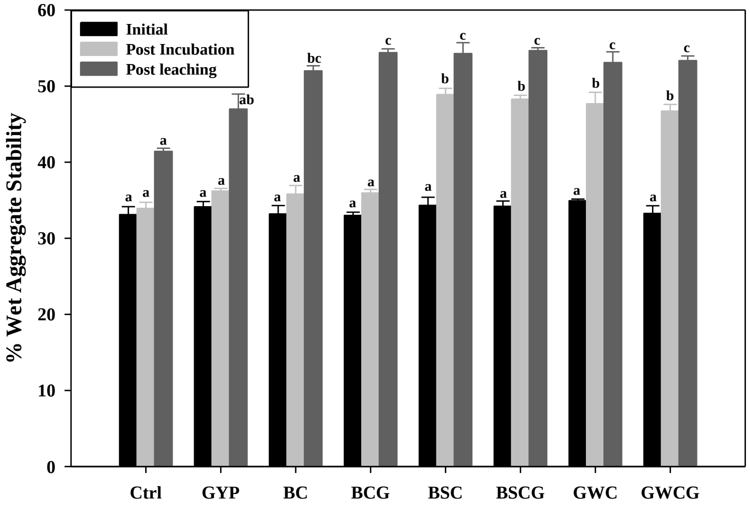

Fig. 2.6. Soil wet aggregate stability (%) (Mean ± s.e.) for different treatments. Same letters in a column series indicate no significant differences among treatments ($P < 0.05$, Tukey's test).

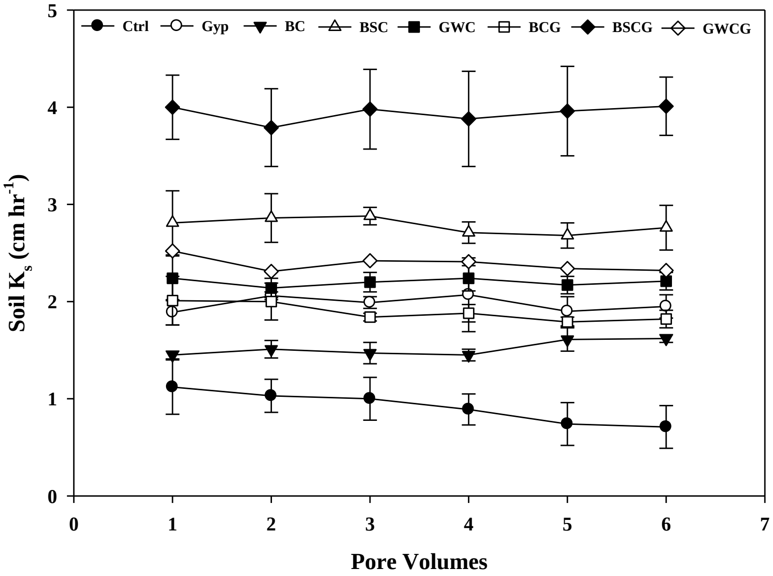

Fig. 2.7. Soil saturated hydraulic conductivity ($K_s$) (Mean ± s.e.) for different treatments during leaching.

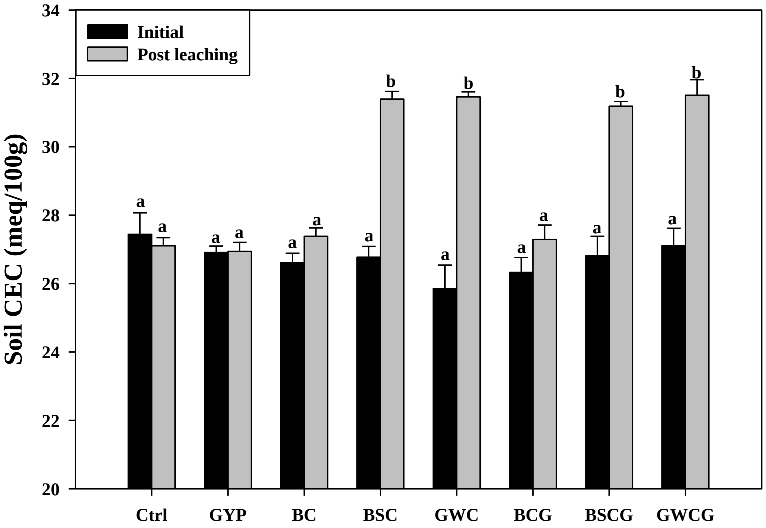

Fig. 2.8. Soil cation exchange capacity (Mean ± s.e.) before and after leaching for different treatments. Same letters in a column series indicate no significant differences among treatments ($P < 0.05$, Tukey's test).

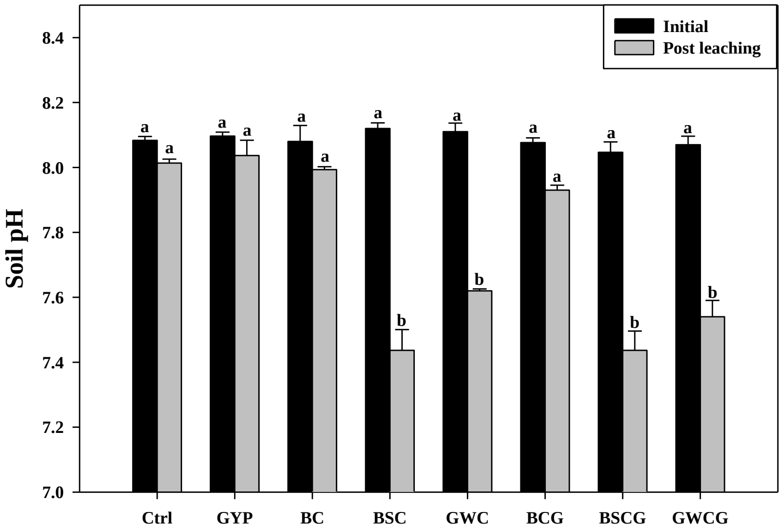

Fig. 2.9. Soil pH (Mean ± s.e.) for different treatments before and after leaching. Same letters in a column series indicate no significant differences among treatments ($P < 0.05$, Tukey's test).

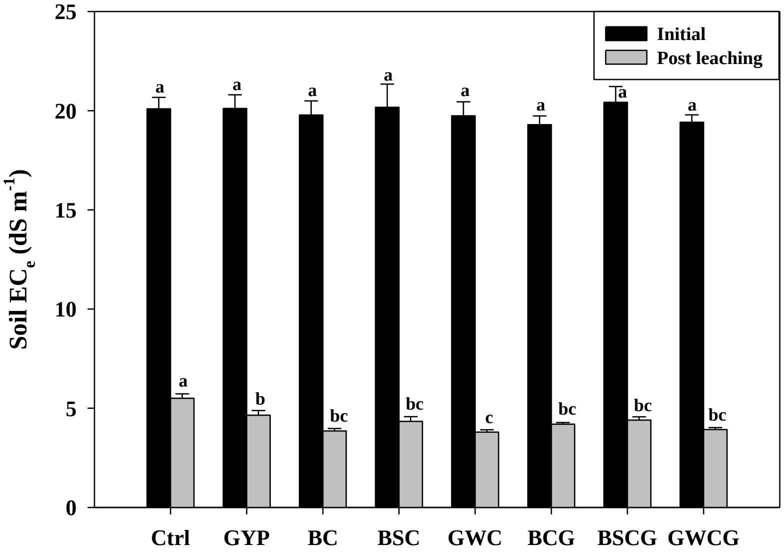

Fig. 2.10. Electrical conductivity (Mean ± s.e.) of saturation paste extracts of soils before and after leaching for different treatments. Same letters in a column series indicate no significant differences among treatments ($P < 0.05$, Tukey's test).

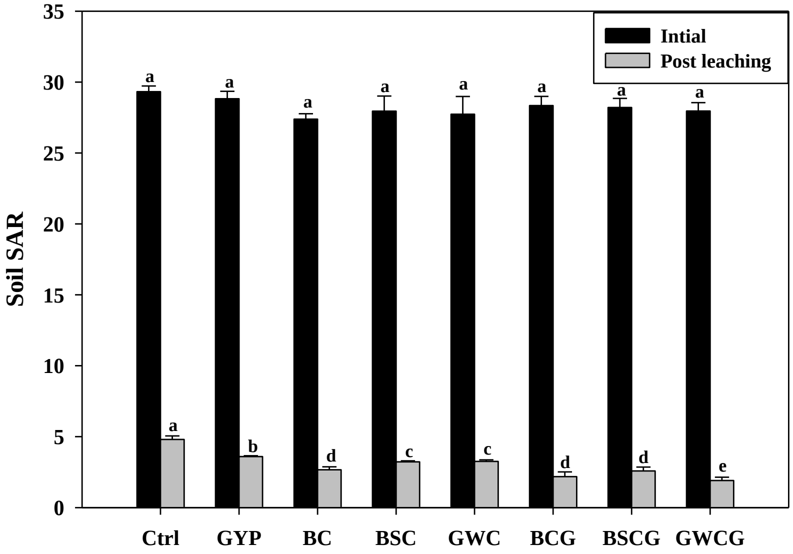

Fig. 2.11. Sodium adsorption ratio (Mean ± s.e.) of soils before and after leaching for different treatments. Same letters in a column series indicate no significant differences among treatments (P < 0.05, Tukey's test).

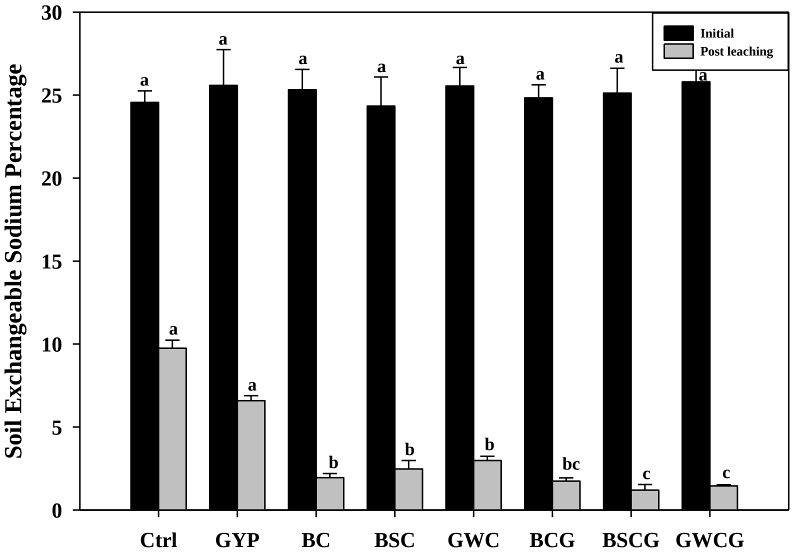

Fig. 2.12. Exchangeable sodium percentage of soils (Mean ± s.e.) before and after leaching. Same letters in a column series indicate no significant differences among treatments (P < 0.05, Tukey's test).

# 3. EVALUATING THE RELATIVE CONTRIBUTION OF PHYSIOCHEMICAL AND BIOLOGICAL FACTORS IN AMELIORATING A SALINE-SODIC SOIL AMENDED WITH COMPOSTS AND BIOCHAR AND LEACHED WITH RECLAIMED WATER

## Abstract

Organic amendments are increasingly considered as a cheaper and sustainable alternative to remediate salt affected soils. In this experiment, the relative importance of biological and physiochemical mechanisms by which biosolids and greenwaste composts and woodchip biochar aid in reclamation of physical and chemical properties of a saline-sodic soil was evaluated. Sterilized and unsterilized soil and composts/biochar mixtures were used to test the effects of biological and physiochemical factors. Sterilization was achieved by subjecting soils and amendments to autoclaving and gamma sterilization. Amendments were applied at a rate of 75 t ha$^{-1}$ and treated soils were incubated for a month and then leached with reclaimed water. Soil physical and chemical characteristics such as wet aggregate stability, saturated hydraulic conductivity; cumulative amounts of $Na^+$, $Ca^{2+}$, and $Mg^{2+}$ leached, soil pH, SAR, $EC_e$, and ESP were analyzed. Results indicate that sterilization significantly affected soil physical properties such as aggregate stability and hydraulic conductivity only in compost treated soils. Unsterilized compost-treated soils had significantly higher soil aggregate stability and saturated conductivity than sterilized soils. Soil pH was significantly lower in unsterilized soils that received composts, but other chemical properties were not affected by sterilization. On the other

hand, no significant effect of sterilization was observed in biochar treated soils in remediating their physical and chemical properties. Irrespective of sterilization, all organic amendments were successful in remediating a saline-sodic soil leached with reclaimed water. It seems that the mode of action of biochar is mostly physiochemical while composts support reclamation with biological and physiochemical factors together.

## Introduction

Soil salinity and sodicity are the two major environmental concerns leading to land degradation in irrigated areas of arid and semi-arid regions across the world (Mahmoodabadi et al., 2013). Saline-sodic soils belong to an important category of salt affected soils characterized with both high $EC_e$ and SAR/ESP (Richards, 1954). Saline-sodic soils are degraded both by the negative effects of salinity on plant growth and of sodicity on soil structure deterioration. These soils are high in both soluble and exchangeable sodium, which causes soil swelling and dispersion that leads to poor structure, thus limiting the soil infiltration and permeability capabilities (Gharaibeh et al., 2010; Yu et al., 2010). In addition to structural losses, chemical and biological properties are also negatively affected by high salinity and sodicity (Frankenberger and Bingham, 1982; Ganjegunte et al., 2008; García and Hernández, 1996; Rietz and Haynes, 2003; Wichern et al., 2006; Wong et al., 2008).

Successful amelioration of a saline-sodic soil involves a two-step protocol; 1) application of a $Ca^{2+}$ source to displace $Na^{+}$ on clay surfaces, which promotes soil flocculation and 2) subsequent leaching of salts from the profile (Gupta and Abrol, 1990). Gypsum is widely accepted as a significant source of $Ca^{2+}$ to soils and its use has been long studied as the most important remediation strategy for saline-sodic soils. Many studies have evaluated the potential of gypsum and established it as a primary chemical reclamation method (Abrol et al., 1988; Armstrong and Tanton, 1992; Ghafoor et al., 2001; Oster et al., 1999; Qadir et al., 2001b). Other chemical reclamation strategies include elemental S and sulfuric acid applications, which solubilize native calcite and provide required $Ca^{2+}$ to offset $Na^{+}$ on the exchange sites (Amezketa et al., 2005; Gupta and Abrol, 1990; Sadiq et al., 2007).

However, due to increased costs of chemical amendments, phytoremediation with salt tolerant crops has been increasingly adopted, especially in developing countries, as a cheaper alternative to chemical amendments. This technique works on the same principle of native calcite dissolution by building up the partial pressure of $CO_2$ ($P_{CO2}$) in the rhizosphere (Qadir et al., 2007). Use of organic amendments has been presented as an alternative for remediating salt affected soils (Lax et al., 1994). Organic amendments represent an another alternative for reclaiming a variety of degraded soils and significant improvements have been reported with respect to soil physical, chemical, and biological characteristics after organic matter incorporations (Epstein et al., 1976; Ghosh et al., 2010; Giusquiani et al., 1995; Liang et al., 2005; Piccolo and Mbagwu, 1990; Tejada et al., 2006). Contributions towards soil structure development by aggregation and aiding in salt leaching is of prime importance in saline soil amelioration (Lakhdar et al., 2009; Wahid et al., 1998).

While gypsum provides chemical reclamation, the reclamation potential of organic amendments applied to soils has been mostly attributed in the literature to the added organic matter, which improves soil structure by enhancing the soil microbial activity (Albiach et al., 2001; García-Orenes et al., 2005; Roldán et al., 1996). Addition of organic amendments promotes soil aggregation and offers significant structural enhancements due to organic matter inputs. Increased soil aggregation helps increase soil porosity and therefore increase soil infiltration and permeability (Haynes and Naidu, 1998). Soil microbial activity is often reported to increase drastically after organic matter additions due to the increased availability of energy substrates. Soil microbiological activity is an important factor controlling organic matter turnover that positively influences soil aggregation, in addition to physical (alternate wetting and drying, freezing and thawing, mechanical action of flora and fauna) and chemical ($Ca^{2+}$and other multivalent cations) factors that help in the formation and stabilization of soil aggregates (Amezketa, 1999; Oades, 1993). Aggregates are formed when microbial derived exo polysaccharides (Kandeler and Murer, 1993) and glyco-protein glomalin from mycorrhizal fungi (Wright and Upadhyaya, 1998), act as strong soil agglutinants. These are termed as transient binding agents by Tisdall and Oades (1982), which promote soil aggregate stability. The importance of increased microbial activity in facilitating soil aggregation and stabilization has been well documented (Degens, 1997; Lynch and Bragg, 1985; Six et al., 2004). Improvements in soil aggregation in turn help to improve soil hydraulic conductivity. It is a combination of physiochemical and biological properties of these organic amendments that help in soil remediation, but the relative significance and effect of each of these properties contributing towards saline-sodic soil reclamation have not been characterized.

The physiochemical effects of organic amendments on reclaiming saline-sodic soils, including soil structure stabilization, hydraulic conductivity and $Na^+$ leaching has received little attention. Ascribing benefits solely to improved biological activity may be inappropriate given that many physiochemical properties of these materials can also assist in remediation. For example, Walker and Bernal (2008) reported that application of olive mill waste compost and poultry manure to remediate a saline soil in Spain, resulted in saturation of exchange sites with $Ca^{2+}$ and $Mg^{2+}$. Similarly, Jalali and Ranjbar (2009) also found that sheep and poultry manure helped to increase $Ca^{2+}$ and $Mg^{2+}$ concentrations in soil solution and on exchange sites. Tejada et al. (2006) demonstrated that high molecular weight humic acids from the organic amendments were key in improving the aggregation of soil particles. Additionally, organic anions from these amendments form cationic bridges with negatively charged clay particles and multivalent cations, thus helping in soil aggregation and improving the conductivity of soil (Tisdall and Oades, 1982). Also, the individual particles of these organic materials are likely large enough to physically create channels in otherwise structure-less saline-sodic soils and thus help improve the soil permeability and leach $Na^+$ from the soil profile (Lakhdar et al., 2009).Therefore, assigning proper credit to the inorganic constituents of various organic materials is important and may help identify products most suitable for remediation programs.

Though, like compost, biochar is an organic amendment, it is more recalcitrant than compost and is therefore less likely to directly support microbial growth. Biochar may improve saline-sodic soils chemically, since it can be a source of elements such as

$Ca^{2+}$ and $Mg^{2+}$ (Laird et al., 2010) which aid in $Na^+$ exchange (Lehmann et al., 2006). Its use for saline-sodic soil reclamation has not been studied yet. This study aimed at specifically evaluating the effect of excluding biological activity on soil aggregation, hydraulic conductivity, $Na^+$ leaching, and the overall reclamation potential of compost and biochar applied to a saline-sodic soil. Two different composts (biosolids and greenwaste) and a woodchip biochar were evaluated in this study.

## Materials and Methods

### Soil Sampling

Bulk saline-sodic soils were collected from a local farm located on the west side of the San Joaquin Valley. Detailed descriptions of the soil sampling location, sampling methodology, soil classification, and soil analyses used to determine different physical and chemical properties, are discussed in chapter 2. Important soil physical and chemical characteristics are presented in Table 2.1.

### Amendments and Leaching Solution

Wood chip biochar (WBC), greenwaste compost (GWC), and biosolids co-compost (BSC) were used as organic amendments. Sources, production techniques, and characteristics of these organic amendments are described in chapter 2. Some properties of the organic materials are given in Table 2.2. Irrigation/leaching water used was the reclaimed water collected from a local farm with its primary source from Eastern Municipal Water District (EMWD) located in Southern California. Chemical properties of the reclaimed water are given in Table 2.3.

### Soil and Compost Sterilization

In order to study the influence of biological activity, we prepared two different batches of soil and compost mixtures. One batch had unsterilized soil and compost while the other batch had soil and compost mixture completely sterilized to eliminate the biological activity. It was therefore assumed that any remediation in sterile soils was purely due to the physiochemical effect of the organic amendments while in unsterilized soils, it was a combination of physical, chemical, and biological effects. Compost and biochar were sterilized twice using high intensity $Cs^{140}$ $\gamma$-irradiation. Compost and biochar samples were placed in a sealed plastic bag and were placed in an irradiator for 72 h the first time, and 48 h for the second time, exposing them to a total radiation dose of 15 KGy (Yun et al., 2007). Gamma radiation was selected for sterilization as it does not significantly affect the physiochemical properties of the treated material (Trevors, 1996). Samples were transported back to the laboratory in a sealed container at 5 °C to prevent contamination and were stored at 5 °C until mixed with soil. Soil samples were sterilized using an autoclave, as the irradiator was of low capacity and could not accommodate large quantities of soil. Soils were spread on a metal tray to a depth of 2 cm and were autoclaved twice using a dry cycle at 121 °C for 20 min each. All the equipment used to handle the soil, composts, and biochar were also autoclaved prior to use.

### Soil Treatments and Incubation

A total of 8 treatments were used in this study which includes:

1. Unsterilized control soil (USC)
2. Unsterilized soil + unsterilized WBC (UWBC)

3. Unsterilized soil + unsterilized BSC (UBSC)
4. Unsterilized soil + unsterilized GWC (UGWC)
5. Sterilized control soil (SC)
6. Sterilized soil + sterilized WBC (SWBC)
7. Sterilized soil + sterilized BSC (SBSC)
8. Sterilized soil + sterilized GWC (SGWC)

Sterilized soil and amendment mixtures were incubated in a low temperature incubator set at 4 ± 1°C in order to reduce microbial activity. Unsterilized soil and amendment mixtures were stored at normal room temperature (25 ± 1 °C). Moisture contents were maintained in all jars on a gravimetric basis. Soil respiration, an indirect measurement for microbial activity, was monitored by measuring the $CO_2$ evolution for all treatments at regular intervals. Jars were sealed for 3 hours and the accumulated gas in the head space was sampled and analyzed for $CO_2$ concentration using a portable EGM 4 infra-red gas analyzer for $CO_2$ (PP Systems, Amesbury, MA). Cumulative $CO_2$-C evolution was calculated over the entire incubation period by linear interpolation of measurements made at different sampling dates. Emissions between the sampling intervals were assumed to be the average of measurements made at the beginning and the end of that interval. After a month of incubation, treated soils were carefully emptied from the mason jars and were air dried and gently crushed to pass through a 2 mm sieve.

### Leaching Experiment and Post Leaching Soil Analyses

Soil leaching, leachate analysis, and post-leaching soil analyses were conducted similar to those described in chapter 2.

### Wet Aggregate Stability

Wet aggregate stability measurements were conducted on base soils (before incubation), soils after incubation and soils after leaching. Percent wet aggregate stability was measured on 1-2 mm soil aggregates using wet sieving apparatus and following the method given by Nimmo and Perkins (2002).

### Data analysis

Univariate analysis of variance was conducted using SPSS V.20 software. Two-way factorial analysis of variance was used to test the effects of sterilization and treatments on soil properties. Where there was no significant effect of sterilization, data was analyzed using one-way ANOVA for both normal and sterilized soils to separate the means. Significant differences between the treatment means were separated using Tukey's multiple comparison tests at 95 % significance level ($P < 0.05$).

## Results and Discussion

### $CO_2$ Evolution

Cumulative $CO_2$ evolution rates from unsterilized and sterilized soils are presented in Fig 3.1, for different treatments. Sterilization had a very significant effect ($P < 0.01$) in reducing the soil respiration rates. Cumulative $CO_2$ emissions from sterilized soils ranged from 17-37 mg $CO_2$-C $kg^{-1}$ with the control (SC) and biochar (SWBC) having significantly lower ($P < 0.05$) $CO_2$ emissions than composts (SBSC and SGWC). Autoclaving and gamma radiation were successful in inhibiting the biological activity in both soil and composts thus decreasing the respiration rates. However, two weeks into the incubation, the effects of sterilization started to wear off and respiration rates increased steadily (Fig. 3.1), a pattern likely due to the rejuvenation of the microbial activity by contamination of soils during moisture adjustments and $CO_2$ samplings. Also, autoclaving of soil may not have completely killed the microbial spores, which likely contributed for microbial biomass revival upon their germination (Tuominen et al., 1994). Increases in soil respiration were greater in compost treated soils (Fig. 3.1) as microbes had instant access to the energy substrates upon their revival. At the same time, continuous incubation at a very low temperature (3-5 °C) after sterilization helped to keep the microbial activity at a minimum compared to normal unsterilized soils.

Cumulative $CO_2$ emissions from unsterilized soils were most pronounced ranging from 208-1327 mg $CO_2$-C $kg^{-1}$ and were 12-36 times higher than the sterilized soils (Fig. 3.1). The control (USC) and biochar (UWBC) soils had significantly lower ($P < 0.01$) cumulative $CO_2$-C emissions than the compost (UBSC and UGWC) treatments, a trend similar to that observed in sterilized soils. Carbon dioxide emissions from soils treated with biosolids compost (UBSC) were lower than those treated with greenwaste compost (UGWC) but the differences were not significant ($P > 0.05$), however (Fig 3.1). Wong et al. (2009) also reported similar increases in $CO_2$ fluxes from an alkaline saline-sodic soil treated with kangaroo grass after a 12 week incubation. It was asserted that readily available energy substrates from organic matter inputs re-activate the dormant microbial community and subsequently increase their biomass and activity in such salt affected soils (Wong et al., 2009). It is likely that a similar process dominated in our system with composts providing readily available C substrates for starving soil microbes, which facilitated its rapid decomposition. Thus, higher $CO_2$ evolutions were observed from compost treatments. Similarly, Tejada et al. (2006) observed significantly higher cumulative $CO_2$ losses from poultry manure and cotton gin compost treated saline soils and attributed this effect to the presence of labile C in these amendments. On the other hand, cumulative $CO_2$ evolution rates from biochar amended soils were significantly ($P < 0.01$) lower than the soils with composts and was comparable to the control soils (Fig. 3.1). The C in biochar is mostly recalcitrant and is unlikely to be a source of energy for microbes (Thies and Rillig, 2009). Therefore, it was not readily available for microbial decomposition (Lehmann et al., 2011).

### Leachate EC

No significant effect of sterilization was found with respect to leachate EC. Regardless of sterilization, all soils treated with organic amendments had significantly higher ($P < 0.05$) leachate EC's compared to the control soils after the addition of first pore volume of water, with the exception of UBSC (Fig. 3.2). The initial leachate EC of UBSC soil was low compared to the other organic amendments and was comparable to that of the control soils. However, it continued to have a higher leachate EC until about 2 PV than the control and other organic amendment soils (Fig. 3.2). No significant differences ($P > 0.05$) existed between biochar, greenwaste and biosolids compost treated soils with respect to their leachate EC. Higher leachate EC observed in organic amendment treated soils was likely due to the enhanced salt leaching facilitated by the addition of organic amendments. Moreover, efficient $Na^+$ exchange by the organic amendments from the exchange sites and its release into the soil solution contributed for increases in their leachate EC. As leaching progressed, leachate EC declined for all treatments after 6 PV of reclaimed water has passed through the soil profile. These results concur with those reported by Jalali and Ranjbar (2009) and Li and Keren (2009), who also observed similar increases in leachate EC during the very early stages of leaching when soils were amended with different organic amendments.

## Cumulative Leachate Losses of $Ca^{2+}$, $Mg^{2+}$, and $Na^{+}$

### *Leachate $Ca^{2+}$*

Cumulative losses of $Ca^{2+}$ through leachate for both sterilized and unsterilized treatments are given in Fig. 3.3. Sterilization as a factor, had a significant effect ($P < 0.01$) in the amounts of $Ca^{2+}$ lost through leachate with significantly higher losses found in unsterilized biosolids compost (UBSC) and greenwaste compost (UGWC) treatments than their sterilized counterparts (SBSC and SGWC). Also, cumulative losses of $Ca^{2+}$ from UWBC were significantly higher than SWBC. No effect of sterilization was found with respect to $Ca^{2+}$ losses from the control soils (USC and SC). $Ca^{2+}$ losses from SBSC, SGWC and SWBC were 15, 10, and 19 % lower than UBSC, UGWC, and UWBC treatments, respectively. But irrespective of sterilization, composts had significantly higher $Ca^{2+}$ losses than control soils, with biosolids having the highest losses. Cumulative $Ca^{2+}$ losses from biochar were not significantly different form either composts or the control. On average, respective cumulative $Ca^{2+}$ losses from biosolids compost, greenwaste compost, and biochar were 20, 14, and 10 % higher than that of control soils.

### *Leachate $Mg^{2+}$*

Sterilization significantly ($P < 0.05$) and negatively affected the cumulative $Mg^{2+}$ losses from organic amendments (Fig. 3.4). No effect of sterilization was observed between sterilized and unsterilized control soils. Losses of $Mg^{2+}$ were 13, 11, and 10 % lower in SWBC, SBSC, and SGWC treatments respectively, relative to their corresponding unsterilized treatments. Regardless of sterilization, composts significantly ($P < 0.01$) lost greater amounts of $Mg^{2+}$ than the control. Also, cumulative leachate losses of $Mg^{2+}$ from biosolids compost were significantly higher than the greenwaste compost. On the other hand, losses from biochar amended soils were not significantly different from that of the control soils. Average cumulative leachate losses of $Mg^{2+}$ were 5, 60, and 41 % higher from biochar, biosolids, and greenwaste compost treated soils respectively, compared to the unamended control soils.

### ***Leachate $Na^+$***

Cumulative leachate losses of $Na^+$ from both sterilized and unsterilized treatments are presented in Fig. 3.5. Sterilization had a significant effect ($P < 0.05$) on $Na^+$ leachate losses only with respect to the biosolids treatment. Sterilization lowered the $Na^+$ losses from SBSC treated soil by 8 % compared to its corresponding unsterilized treatment (UBSC). It was likely that increased $Ca^{2+}$ availability in unsterilized biosolids treatment facilitated higher $Na^+$ removal than sterilized biosolids compost treatment. However, cumulative $Na^+$ losses from the control, biochar, and greenwaste compost soils were not significantly ($P > 0.05$) affected when subjected to sterilization. Nevertheless, regardless of sterilization, soils amended with organic amendments significantly ($P < 0.01$) lost greater amounts of $Na^+$ through leachate than the control soils. Differences between various organic amendment treatments were not statistically significant, however.

Cumulative leachate $Na^+$ losses were 12, 17, and 14 % higher from biochar, biosolids compost, and greenwaste compost treated soils, respectively, relative to untreated soils.

Sterilization significantly increased ($P < 0.01$) cumulative $Na^+$ leaching times in compost treated soils only (Fig. 3.6). The time it took to leach $Na^+$ was significantly lower in both unsterilized biosolids and greenwaste compost treated soils compared to their corresponding sterilized treatments. Leaching times of biochar and the control soils were not affected ($P > 0.05$) by sterilization. Therefore, it can be premised that microbial activity also has a role in reducing $Na^+$ leaching times, which might be due to its direct effect on soil aggregation and hydraulic conductivity. Regardless of sterilization, organic amendments performed better and lost higher amounts of $Na^+$ in significantly less time ($P < 0.01$) compared to the control, which lost less $Na^+$ in relatively more time (Fig. 3.6). Quicker leaching times reduce the duration of standing water on soil surface, which can significantly reduce its evaporative losses. Fields can also get back into production more quickly.

Leachate losses of $Ca^{2+}$, $Mg^{2+}$, and $Na^+$ were significantly higher from organic amendment treated soils which indicate the potential of these materials to supply divalent cations such as $Ca^{2+}$ and $Mg^{2+}$, needed to displace $Na^+$ from soil exchange sites. On the other hand, leachate $Na^+$ could potentially originate from both the remediated soil and the added amendments. However, the introduction of exchangeable $Na^+$ by the organic amendments would likely be small compared to their $Ca^{2+}$ and $Mg^{2+}$ contributions (Table 2.2). Hence, it could be assumed that most of the $Na^+$ lost through leachate from organic amendment treated soils came from soil exchange sites.

Sterilization significantly affected the losses of $Ca^{2+}$ and $Mg^{2+}$ from organic amendments, especially from compost treated soils. This indicates that microbial activity mineralizes $Ca^{2+}$ and $Mg^{2+}$ to soluble forms at rates exceeding the exchange capacity of the soil (Jalali and Ranjbar, 2009). Interestingly, $Ca^{2+}$ and $Mg^{2+}$ losses from soils treated with SWBC were lower than those from UWBC, even though both biochars were quite recalcitrant and $CO_2$ evolution rates were low and similar for both SWBC and UWBC. It is known that soil exchange sites have a higher affinity for $Ca^{2+}$ than $Mg^{2+}$ (Fletcher et al., 1984) and as expected, $Mg^{2+}$ losses were much more prominent than $Ca^{2+}$ losses in this study, especially from compost treated soils.

### Soil Wet Aggregate Stability

Mean soil Wet Aggregate Stability (WAS) measurements for different treatments at pre incubation, post incubation and post leaching are shown in Fig. 3.7. Wet aggregate stabilities averaged at 31 % for all treatments before incubation and amendment application. Analysis of soils after incubation revealed that suppression of microbial activity significantly affected ($P < 0.01$) the aggregate stabilities of compost amended soils, with higher aggregate stabilities found in corresponding unsterilized compost treated soils. Wet aggregate stabilities were lowered by 28 and 25 % respectively, in SBSC and SGWC compared to UBSC and UGWC treatments. These results demonstrate the role of biological activity in increasing the stability of soil aggregates upon organic matter additions as opposed to its absence due to sterilization. Similar results were reported by Tisdall et al. (1978), where the stability of soil aggregates was reduced when microbial activity was restricted by soil irradiation. Soil microbes have been found to play a major role in soil aggregation and stabilization by releasing microbial exudates such as exo-polysaccharides, which act as agglutinants (Abiven et al., 2007; Degens, 1997). In our study, reduced biological activity likely inhibited the formation of such products during incubation and therefore did not significantly increase the soil aggregate stability in sterilized compost treated soils compared to their unsterilized soils, when tested after incubation. Though the differences were not statistically different, SBSC and SGWC treatments also had a 7 and 8 % increase in soil stability when compared to the sterilized control (SC) soil, respectively, after incubation (Fig. 3.7). This could be attributed to the physiochemical effect of these amendments wherein, aromatic humic and fulvic fractions of organic matter helped in clay-organic complex formation, thereby increasing soil aggregate stability (Amezketa, 1999; Piccolo and Mbagwu, 1990). Sterilization did not show an effect on the post incubation aggregate stabilities of biochar and control soils. No significant differences were found between USC, SC, UWBC, and SWBC treatments. However, slight increases in stability measurements were observed in both UWBC (by 9 %) and SWBC (by 6 %) soils compared to USC and SC after incubation, indicating that the effect of biochar on aggregate stability is not likely due to the biological activity but merely a physiochemical phenomenon (Piccolo et al., 1996).

Overall, UBSC and UGWC soils had significantly higher aggregate stabilities compared to all other treatments (Fig. 3.7) after incubation. Percent increases ranged from 39-51 % for UBSC and 34-47 % for UGWC when compared to all other treatments, respectively. Previous studies also reported similar increases in soil aggregate stabilities due to organic amendment incorporations (Aggelides and Londra, 2000; Piccolo and Mbagwu, 1990; Tejada et al., 2006; Wahid et al., 1998).

Aggregate stabilities increased for all treatments post leaching (Fig. 3.7), a likely consequence of $Na^+$ leaching observed from all treatments, which promoted soil flocculation. Sterilization as a factor did not have any significant effect on soil wet aggregate stabilities post leaching. Addition of organic amendments resulted in significantly higher ($P < 0.05$) soil wet aggregate stabilities than untreated soils. Biosolids and greenwaste composts amended soils had the highest stabilities followed by biochar amendment. Nevertheless, statistically significant differences were not found between the two composts. Biosolids and greenwaste composts increased soil aggregate stability by an average of 47 and 44 % relative to the control soil and by 32 and 29 % relative to the biochar treated soil, respectively. Biochar treated soils had an aggregate stability 11 % higher than the untreated soils. Final mean aggregate stabilities increased by 76, 72, and 35 % for soils treated with biosolids compost, greenwaste compost, and biochar, respectively, while a 22 % increase was seen in the unamended control soils, when compared to their respective initial stabilities.

### Saturated Hydraulic Conductivity ($K_s$)

Mean soil saturated hydraulic conductivities of all treatments were relatively constant throughout the leaching experiment. Soil and compost sterilization significantly ($P < 0.01$) and negatively affected the hydraulic conductivity of compost amended soils (Fig. 3.8). An average decrease of 35 % in soil $K_s$ was observed for sterilized biosolids (SBSC) and greenwaste composts (SGWC) when compared to their corresponding unsterilized treatments (UBSC and UGWC). This phenomenon was likely due to lower soil aggregation and associated stabilities in sterilized compost treatments, which decreased the relative number of conducting pores, as opposed to their unsterilized soils. Increasing soil structure and its stability was shown to strongly influence the pore formation, their sizes and distribution, which play a vital role in water transmission (Pagliai et al., 2004). On the other hand, no effect of sterilization was found with respect to $K_s$ of the control and biochar treated soils. Regardless of sterilization, organic amendments significantly ($P < 0.01$) increased $K_s$ relative to the control soils with the highest values observed in UBSC followed by UGWC soils. Mean saturated hydraulic conductivities of different treatments followed the order; UBSC > UGWC > SBSC = SGWC > WBC = SWBC > SC = USC, based on their statistical significance. Hydraulic conductivities of SBSC, SGWC, UWBC, and SWBC soils were significantly higher than untreated soils, a difference that can be attributed solely to the physiochemical action of these amendments (Fig. 3.8). Nominal increases in soil aggregation by these treatments may have contributed to an increase in soil $K_s$ and the particles of these materials make have physically created channels in the soil profile, which facilitated water movement. More importantly, release of cations like $Ca^{2+}$ and $Mg^{2+}$ from these amendments and enhanced $Na^+$ displacement from soil exchange sites and its subsequent leaching helped the soils to flocculate, which increased their hydraulic conductivity.

Overall, amending with biosolids compost, greenwaste compost, and biochar increased soil $K_s$ by an average of 390, 305, and 180 %, relative to the untreated soil. Several other studies have also reported similar improvements in soil hydraulic conductivities when different organic amendments were incorporated into soils for reclamation (Aggelides and Londra, 2000; Asai et al., 2009; Hanay et al., 2004; Herath et al., 2013; Obi and Ebo, 1995). Finally, it is clearly evident from these results that when soils were treated with organic amendments, the resultant increase in biological activity played a very important role in improving hydraulic conductivity by directly influencing soil aggregation. Also, it should be noted that in the absence of biological activity, the physiochemical contributions of these amendments were also significant enough to improve the soil saturated hydraulic conductivity.

### Soil CEC

Soil CEC increases after organic amendment applications are mostly attributed to the addition of humic fractions which contain oxidizable functional groups (Adani et al., 2006). Abiotic or biotic oxidation of such functional groups increase carboxylic, phenolic, hydroxyl forms, which consequently increase the cation exchange capacity of a soil (Cheng et al., 2006). Mean soil cation exchange capacities of different treatments before and after leaching are presented in Fig. 3.9. Before leaching, soil CEC ranged from 23.90 to 25.46 meq/100 g, irrespective of sterilization. After amendment application, incubation and subsequent to leaching, marked differences between treatments were observed. Sterilization did not have any significant effect ($P > 0.05$) in altering the CEC of post-leaching soils indicating that any increase in soil CEC was mostly due to abiotic chemical oxidation of added humic fractions. Regardless of sterilization, compost addition significantly increased ($P < 0.01$) the soil CEC relative to the control and biochar soils. Differences between biochar and the control and between the two composts were non-significant ($P > 0.05$). CEC was increased by 21 and 22 % in greenwaste compost and biosolids compost treated soils relative to the control soils after leaching. Also, composts significantly increased soil CEC when compared to their respective initial values. Average increases were 21 and 22 % for biosolids and greenwaste compost amended soils, relative to their initial soil CEC's. Similar increases in soil CEC were reported by previous studies when organic amendments were incorporated into soils (Aggelides and Londra, 2000; Bulluck Iii et al., 2002). On the other hand, CEC increases in biochar treated soils were not significantly different from that of the control. These results contrast with reports by Liang et al. (2006) and Laird et al. (2010), who reported increases in soil CEC when biochar was applied to soil in an extended study. Longer incubation facilitates biotic and abiotic oxidation of charred materials, which increase the relative percentage of carboxyl groups and thus help to increase the soil exchange capacity (Cheng et al., 2008). In this study, biochar treated soils were incubated for just 30 days, which may explain why CEC values of biochar treated soils were not significantly higher due to non-aging of the added material (Lehmann, 2007a).

### Soil pH and $EC_e$

Soil pH measurements for soils before and after leaching are presented in Fig. 3.10. Initial pH readings ranged from 8.08 to 8.15 before amendments were applied. Soil pH was not significantly changed when soils were subjected to sterilization before amendment application. After leaching, soil analysis revealed that pH decreased for all treatments, which can be attributed to the leaching of sodium from all the treatments

(Chorom and Rengasamy, 1997). Sterilization had a significant effect in compost treated soils only. Unsterilized compost treatments had significantly lower ($P < 0.01$) soil pH than their corresponding sterilized treatments. pH of biochar and the control soils was not affected by sterilization. Regardless of sterilization, compost amended soils had significantly lower ($p < 0.01$) soil pH than the control and biochar treatments. Similar results were reported by Mahdy, (2011) and Wong et al. (2009), where soil pH was reduced when soils were treated with different organic amendments. No significant differences existed between biochar and the control soils, however. It is possible that increased microbial activity due to compost additions, enhanced soil $P_{CO2,}$ which when combined with water formed inorganic carbonic acid (Qadir et al., 2005). In addition, increases in organic acid concentrations upon compost decomposition, together facilitated pH reduction in unsterilized compost amended soils (Wong et al., 2009). It was likely that the above processes were inhibited when microbial activity was excluded by sterilization, therefore no pH reductions were observed in sterilized compost treatments. Nevertheless, when compared with respective initial values, pH reductions were more pronounced in compost amended soils than unamended control soils and those treated with biochar due to enhanced salt leaching observed in compost treated soils.

Initial electrical conductivities ($EC_e$) of soils ranged from 22.19 dS $m^{-1}$ to 25.55 dS $m^{-1}$ before amendment applications. Post-leaching soil analysis revealed that soil salinity was significantly reduced by all treatments due to the successful leaching of salts form the soil profile (Fig. 3.11). No significant effect of sterilization ($P > 0.05$) was observed with respect to soil $EC_e$ in any of the treatments after leaching. It is true that salt leaching is mostly a function of improvements in soil hydraulic conductivity, which facilitates salt removal through water movement and therefore, is not directly related to microbial processes. Regardless of sterilization, soils with organic amendments had significantly lower ($P < 0.01$) $EC_e$ relative to the control soils. Differences between organic amended soils were not statistically significant, however. Treating with biochar, biosolids compost, and greenwaste compost reduced post-leaching soil $EC_e$ by 26, 24, and 25 %, respectively, relative to the unamended soils. A similar trend was observed in soil $EC_e$ reductions when compared to their respective initial soil salinities, with organic amendment applications reducing soil $EC_e$ in greater proportions than the control. Biochar, biosolids, and greenwaste composts treated soils decreased soil salinity by an average of 84, 83, and 82 %, respectively, while a 76 % decrease in soil salinity was observed in control soils. Other studies have reported similar reductions in soil $EC_e$ when different organic amendments were applied to reclaim salt affected soils (Hanay et al., 2004; Jalali and Ranjbar, 2009; Tejada et al., 2006).

### Soil SAR

SAR is the defined as the relative concentration of $Na^+$ over the $Ca^{2+}$ and $Mg^{2+}$ concentrations in soil solution. Decrease in soil solution $Na^+$ with simultaneous increase in $Ca^{2+}$ and $Mg^{2+}$ concentrations will reduce soil SAR. Initial soil SAR measurements ranged from 29.37 to 31.61 (Fig. 3.12). Post leaching, SAR decreased for all treatments due to leaching of $Na^+$ (Fig 3.5). Sterilization did not have any significant effect ($P > 0.05$) either on initial or after-leaching soil SAR. Amended soils had significantly lower ($P < 0.01$) SAR compared to the control soils after leaching. This can be attributed to the increased $Na^+$ leaching observed from organic amendment treated soils (Fig. 3.5) and also the chemical enrichment of soil solution by $Ca^{2+}$ and $Mg^{2+}$ by these materials, both affecting soil solution chemistry. Therefore, biological activity is not expected to be a significant factor directly affecting soil SAR reductions. Thus, no significant effect of sterilization was seen. Adding organic amendments reduced the soil SAR by an average of 51 %, relative to the control after leaching. Significant differences between biochar, greenwaste, and biosolids compost treatments were not observed ($P > 0.05$). Similarly, application of organic amendments decreased soil SAR at a higher rate than the control, when compared to their respective initial measurements. Initial SAR was decreased by an average of 94 % by organic amendment application while SAR in the control soil was reduced by 85 % after leaching. These findings are consistent with those reported by Harris and Rengasamy, (2004), Mahmoodabadi et al. (2013) and Shaaban et al. (2013), who found that application of organic amendments decreased soil SAR due to a decrease in the concentrations of solution $Na^+$ and enhanced supply of $Ca^{2+}$.

### Soil ESP

Exchangeable sodium percentages for different treatments before and after leaching are presented in Fig. 3.13. Irrespective of soil sterilization, initial ESP's ranged from 23.26 to 25.55 before leaching. As expected, analysis of soils after leaching revealed that sterilization had no effect on soil ESP for all treatments. Relative changes in soil exchangeable $Na^+$ are purely dependent on the chemical exchange reactions taking place between soil 'solution' and 'exchange' phases due to changes in chemical concentrations of monovalent and divalent cations. Therefore, these chemical reactions are mostly independent of soil biology. Nevertheless, all treatments successfully reduced the soil ESP to less than the sodicity threshold value of 15. Organic amendment treated soils had significantly lower ($P < 0.01$) soil ESP relative to the control after leaching with 6 pore volumes of reclaimed water. Treating soils with biochar, biosolids compost, and greenwaste compost reduced ESP by 83, 86, and 83 % respectively, when compared to the control after leaching. However, differences between various organic amendments were not statistically significant ($P > 0.05$). Reclamation efficiencies of soil ESP by different organic amendments were also much higher than the control when compared against their initial numbers. Biochar, biosolids, and greenwaste composts had an average reclamation efficiency of 95 %, whereas the reclamation efficiency of the control was only 71 %. These results are in accord with the findings reported in chapter 2 and those reported in literature (Hanay et al., 2004; Jalali and Ranjbar, 2009; Walker and Bernal, 2008).

### Soil Exchangeable $Ca^{2+}$, $Mg^{2+}$, and $Na^{+}$

Soil exchangeable cations ($Ca^{2+}$, $Mg^{2+}$, and $Na^{+}$) before amendment application (initial) and after leaching with reclaimed water (final) are given in Table 3.1. No significant ($P > 0.05$) effect of sterilization was found with respect to soil exchangeable $Ca^{2+}$, $Mg^{2+}$ and $Na^{+}$ concentrations before and after leaching. Increase or decrease of an exchangeable cation concentration is dominated by constant chemical exchange reactions taking place between soil solution and exchange phase. These chemical reactions are dependent on the equilibrium chemistry as affected by relative concentrations of different cations in soil solution (Oster and Frenkel, 1980) and are directly not related to soil biology. When analyzed regardless of sterilization, exchangeable $Ca^{2+}$, $Mg^{2+}$, and $Na^{+}$ concentrations followed a similar pattern as observed in chapter 2. Amended soils had significantly higher soil exchangeable $Ca^{2+}$ levels compared to the control soils. On average, exchangeable $Ca^{2+}$ concentrations were 26, 36, and 28 % higher in biochar, biosolids compost, and greenwaste compost treated soils, respectively, than in the control soils. When compared to their respective initial concentrations, organic amendments increased soil exchangeable $Ca^{2+}$. Percent increases were 8, 16, and 11 % for biochar, biosolids compost, and greenwaste compost treated soils.

Post leaching, exchangeable $Mg^{2+}$ concentrations did not statistically differ between treatments although soils that received organic amendments had relatively higher concentrations than the control soils (Table 3.1). However, when compared to their initial concentrations, all treatments significantly had lower exchangeable $Mg^{2+}$ concentrations. But the ability to retain $Mg^{2+}$ was higher in compost treatments as they lost less $Mg^{2+}$ compared to the biochar and control soils. Losses averaged at 21 % for composts treated soils while the control and biochar soils lost about 30 % of their initial exchangeable $Mg^{2+}$ after leaching.

Soil exchangeable $Na^{+}$ concentrations were significantly lower ($P < 0.05$) in organic amendment treated soils than the controls, after leaching (Table 3.1). Application of biochar and composts lowered soil exchangeable $Na^{+}$ by an average of 79 and 83 % respectively, relative to the control. Similarly, organic amendments reduced exchangeable $Na^{+}$ in greater proportions than the control when compared against their initial levels. Treating with organic amendments reduced soil exchangeable $Na^{+}$ by an average of 95 %, while the untreated soil lost 71 % of its initial exchangeable $Na^+$ due to leaching. Leaching with reclaimed water did not increase exchangeable $Na^+$ in any of the treatments, a result consistent with that observed in chapter 2. It can be understood that, organic amendments increased divalent cation concentrations and therefore did not allow $Na^+$ in the leaching solution to be exchanged with soil. On the other hand, high initial soil exchangeable $Ca^{2+}$ concentration (Table 2.1) and additional $Ca^{2+}$ supply through reclaimed water (Table 2.3), preferentially excluded $Na^+$ from entering onto the exchange sites in the control soils.

## Conclusions

This study evaluated the relative importance of biological and chemical mechanisms by which composts and biochar aid in the reclamation of physical and chemical properties of a saline-sodic soil. To study the effect of biological factor, microbial activity was excluded by subjecting the soil and organic amendments to autoclaving and $\gamma$-sterilization. Inhibiting microbial activity by sterilization significantly affected the soil physical properties including soil wet aggregate stability and saturated hydraulic conductivity of only those soils that were treated with biosolids and greenwaste composts. Both soil aggregate stability and saturated hydraulic conductivity were significantly reduced by an average of 27 and 35 % in sterilized compost treatments than their corresponding unsterilized treatments. Also, sterilization reduced the losses of divalent cations from compost treatments, which elucidates that microbial breakdown of these materials, could solubilize fixed $Ca^{2+}$ and $Mg^{2+}$ ions and supplement the dissolved ionic concentrations. Cumulative $Na^+$ losses were not affected by sterilization with the exception of biosolids compost treatment, where sterilization reduced $Na^+$ losses. Unsterilized compost treated soils had significantly lower sodium leaching times than sterilized compost treated soils, which can be ascribed to increased soil aggregation and hydraulic conductivity in the presence of microbial activity. Irrespective of sterilization, all organic amendments leached more $Na^+$ in significantly less time compared to the control soil. Achieving high $Na^+$ leaching rates will facilitate a faster reclamation in the presence of such amendments rather than just leaching an unamended soil.

Soil pH was also affected by sterilization with unsterilized compost treatments having significantly lower soil pH than sterilized treatments. Other chemical properties such as $EC_e$, SAR, ESP, and exchangeable cations were not affected by sterilization in compost treated soils, which indicates that these properties were influenced more by the chemistry of the material rather than the microbiology. This is conclusive evidence that the chemical characteristics of composts are as important as that of biological factor in their potential for reclamation. In order to achieve a comprehensive physical and chemical amelioration of a saline-sodic soil, it is critical that both biological and chemical factors act synergistically. On the other hand, sterilization did not significantly alter soil physical and chemical properties of biochar treated soils. Therefore, it can be concluded that reclamation provided by biochar was purely a physiochemical phenomenon. Overall, irrespective of sterilization, biosolids compost, greenwaste compost and biochar significantly improved physical and chemical properties of a saline-sodic soil even when leached with moderate SAR reclaimed water.

Table 3.1. Soil exchangeable $Na^+$, $Ca^{2+}$, and $Mg^{2+}$ concentrations (meq/100g) (Mean ± s.e.) before and after leaching for different treatments.

| Treatment | $Na^+$ | | $Ca^{2+}$ | | $Mg^{2+}$ | |
|---|---|---|---|---|---|---|
| | Initial | Final | Initial | Final | Initial | Final |
| USC | 6.19±0.41 a* | 1.73±0.10 a | 72.33±1.62 a | 60.89±1.57 a | 3.81±0.04 a | 2.65±0.06 a |
| UWBC | 5.65±0.55 a | 0.23±0.07 b | 71.06±1.53 a | 76.81±2.33 b | 3.95±0.17 a | 2.94±0.14 a |
| UBSC | 6.22±0.31 a | 0.26±0.04 b | 70.27±0.91 a | 83.03±3.85 b | 3.92±0.18 a | 3.42±0.53 a |
| UGWC | 6.21±0.03 a | 0.39±0.17 b | 70.25±1.93 a | 79.37±1.57 b | 4.00±0.10 a | 3.91±0.22 a |
| SC | 5.76±0.29 a | 1.76±0.13 a | 70.76±2.80 a | 59.89±1.81 a | 3.88±0.16 a | 2.73±0.31 a |
| SWBC | 5.94±0.18 a | 0.38±0.09 b | 69.89±0.99 a | 75.53±2.63 b | 3.99±0.17 a | 2.68±0.15 a |
| SBSC | 6.02±0.28 a | 0.33±0.05 b | 70.59±2.79 a | 80.80±0.68 b | 3.96±0.05 a | 2.59±0.21 a |
| SGWC | 5.81±0.36 a | 0.33±0.07 b | 69.74±1.53 a | 75.48±2.28 b | 4.15±0.39 a | 2.63±0.24 a |

*Same letters within a column indicate no significant differences between treatments ($P < 0.05$, Tukey's test).

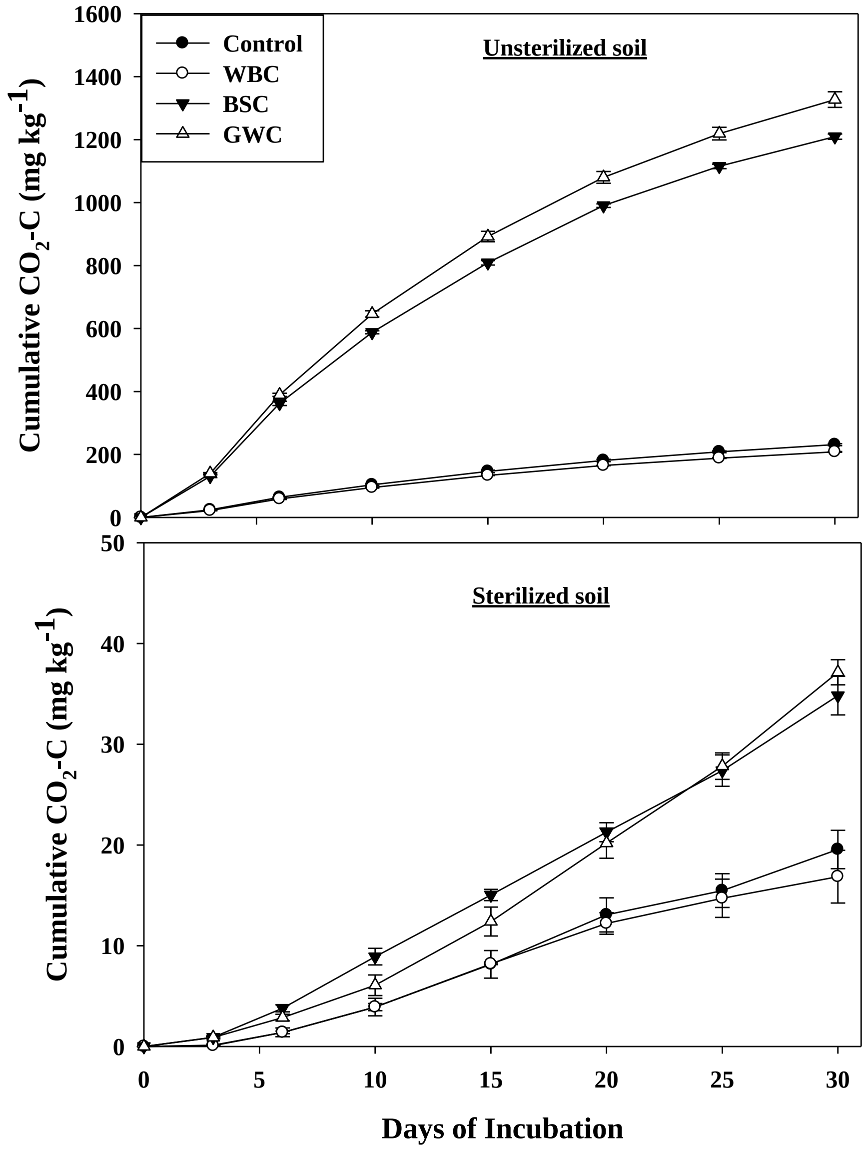

Fig. 3.1. Cumulative $CO_2$-C emissions (Mean ± s.e.) for different treatments from unsterilized and sterilized soils.

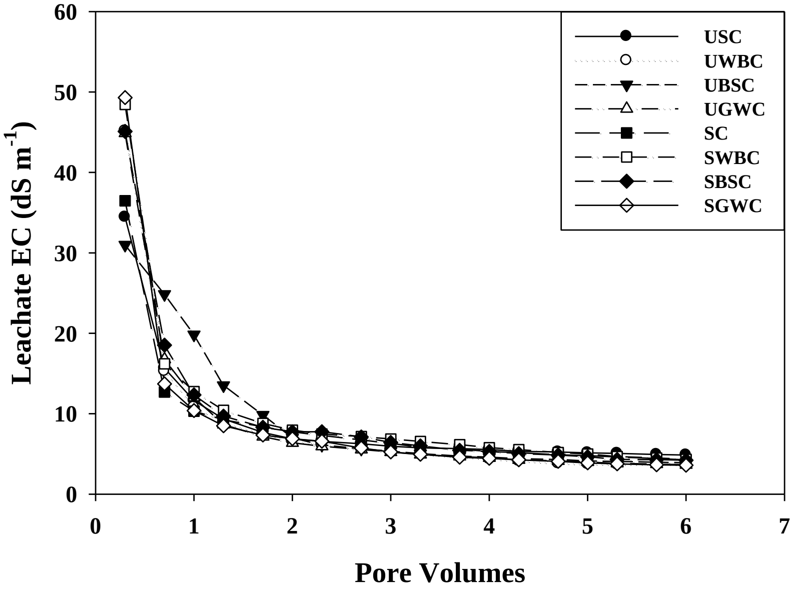

Fig. 3.2. Mean leachate electrical conductivity (EC) for different treatments.

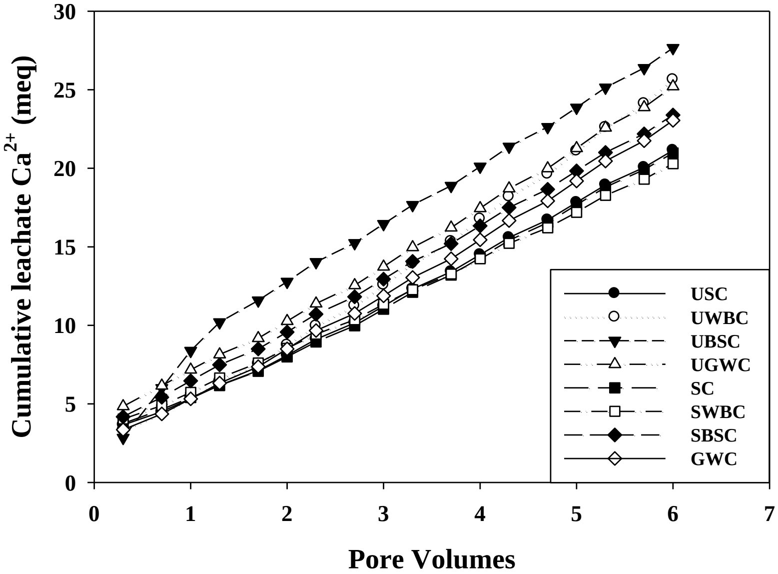

Fig. 3.3. Mean cumulative leachate losses of $Ca^{2+}$ from soils of different treatments.

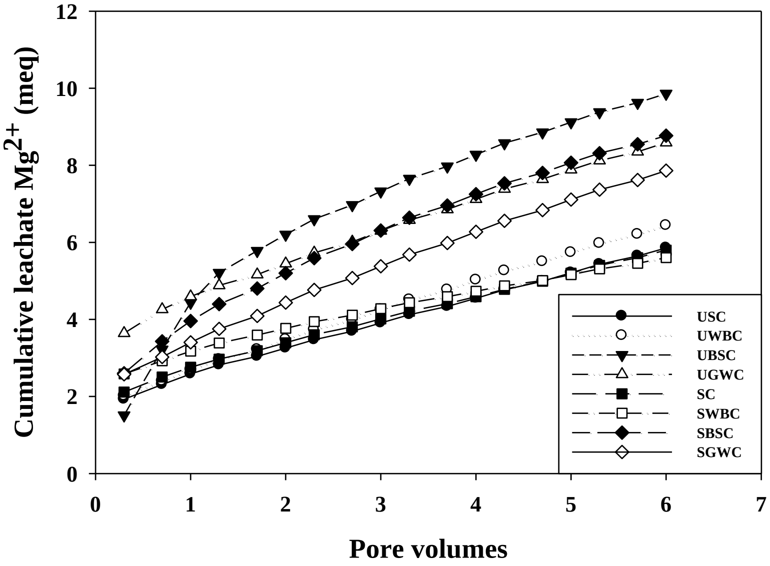

Fig. 3.4. Mean cumulative leachate losses of $Mg^{2+}$ from soils of different treatments.

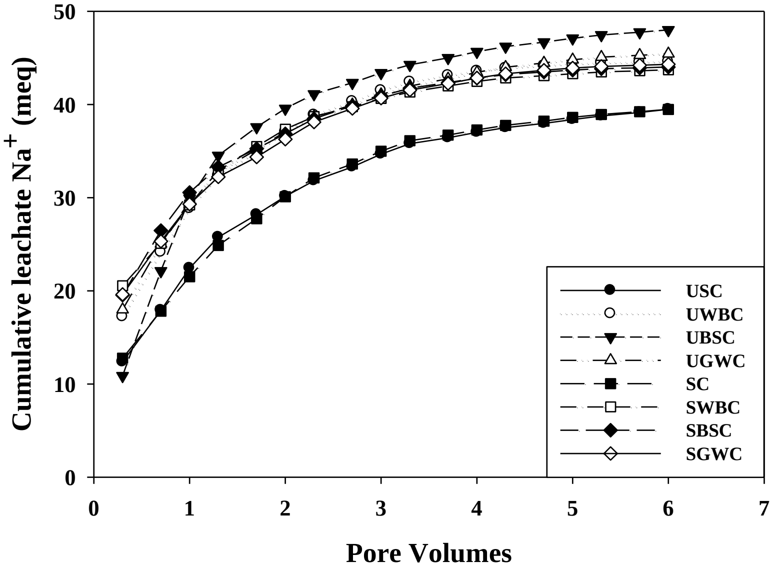

Fig. 3.5. Mean cumulative leachate losses of $Na^{+}$ from soils of different treatments.

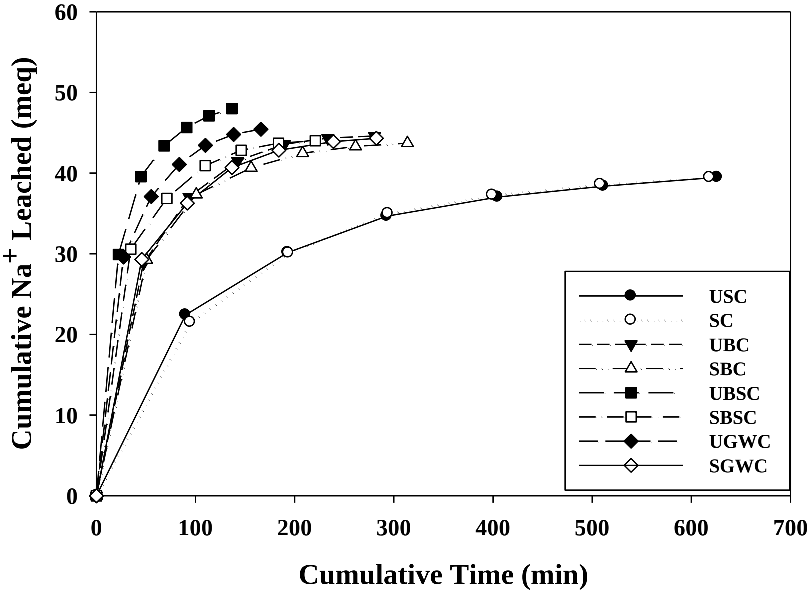

Fig. 3.6. Mean cumulative $Na^+$ lost through leachate from soils of different treatments with respect to time.

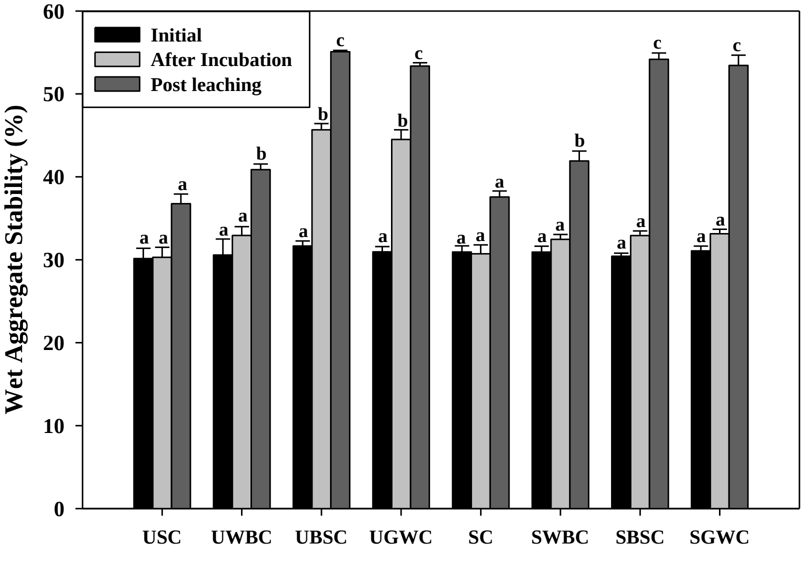

Fig. 3.7. Soil wet aggregate stability (%) (Mean ± s.e.) for different treatments. Same letters within a column series indicate no significant differences between treatments ($P < 0.05$, Tukey's test).

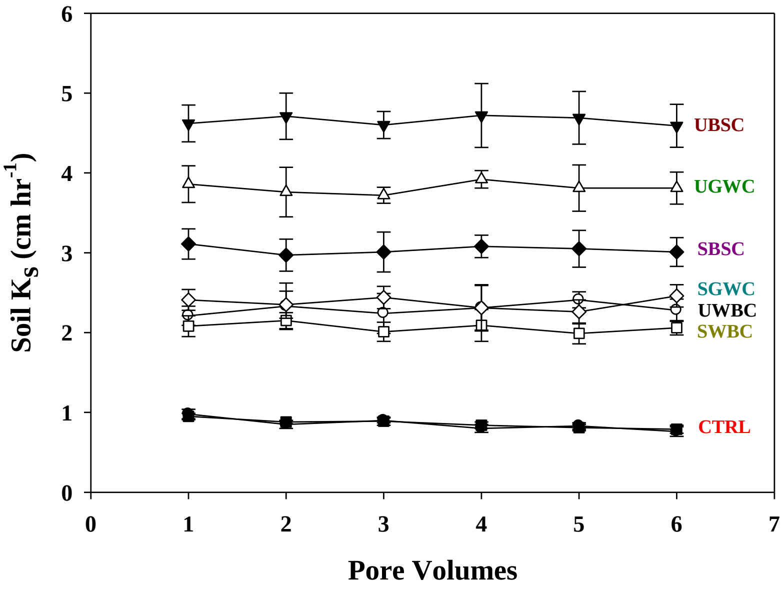

Fig. 3.8. Soil saturated hydraulic conductivity ($K_s$) (Mean ± s.e.) of different treatments during leaching.

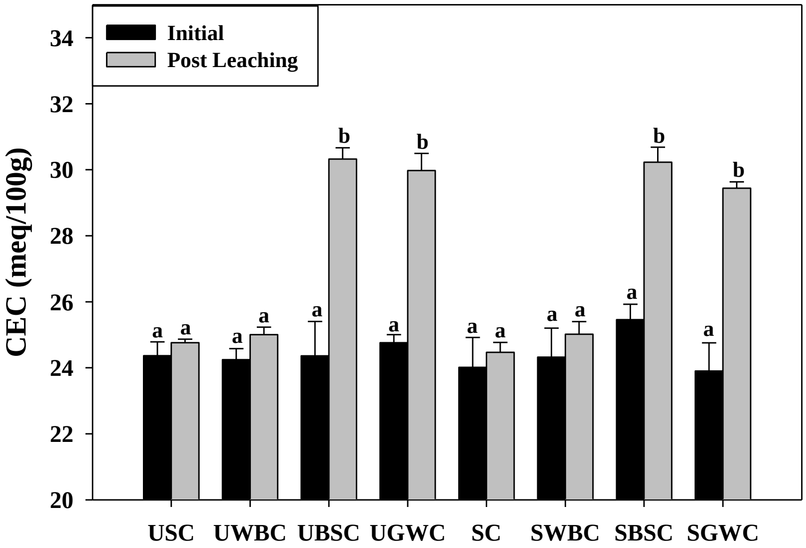

Fig. 3.9. Cation exchange capacity (Mean ± s.e.) of soils before and after leaching for different treatments. Same letters within a column series indicate no significant differences between treatments ($P < 0.05$, Tukey's test).

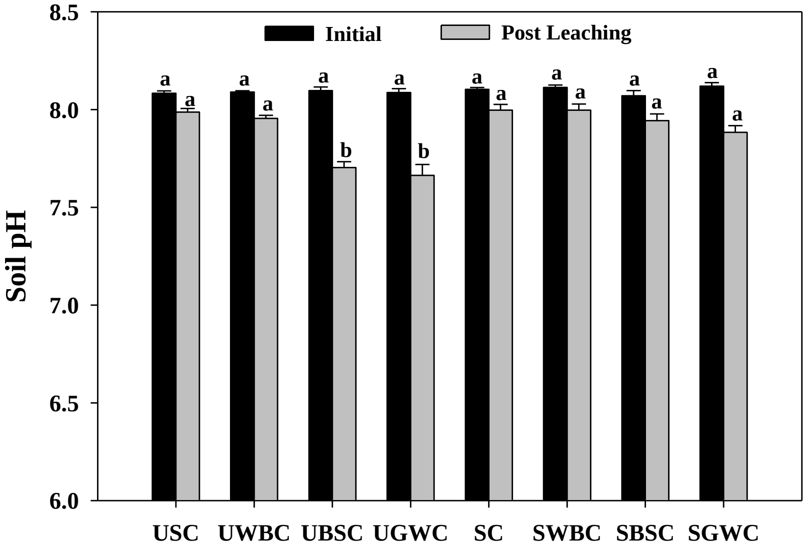

Fig. 3.10. Soil pH (Mean ± s.e.) for different treatments before and after leaching. Same letters within a column series indicate no significant differences between treatments (P < 0.05, Tukey's test).

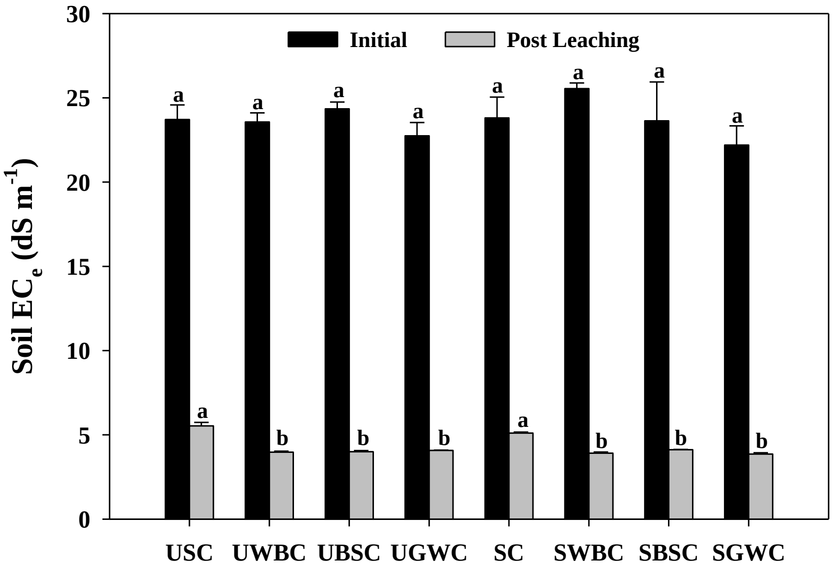

Fig. 3.11. Electrical conductivity (Mean ± s.e.) of saturation paste extracts of soils before and after leaching for different treatments. Same letters within a column series indicate no significant differences between treatments (P < 0.05, Tukey's test).

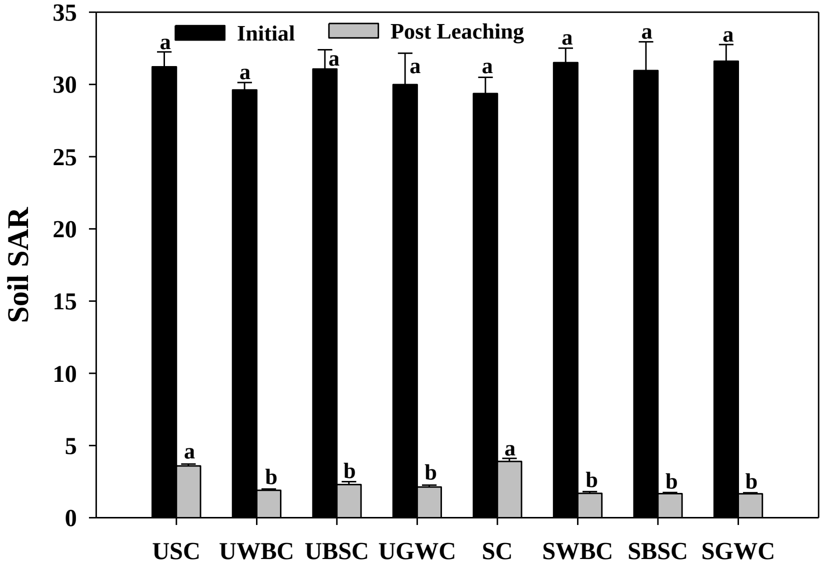

Fig. 3.12. Sodium adsorption ratio (Mean ± s.e.) of soils before and after leaching for different treatments. Same letters within a column series indicate no significant differences between treatments ($P < 0.05$, Tukey's test).

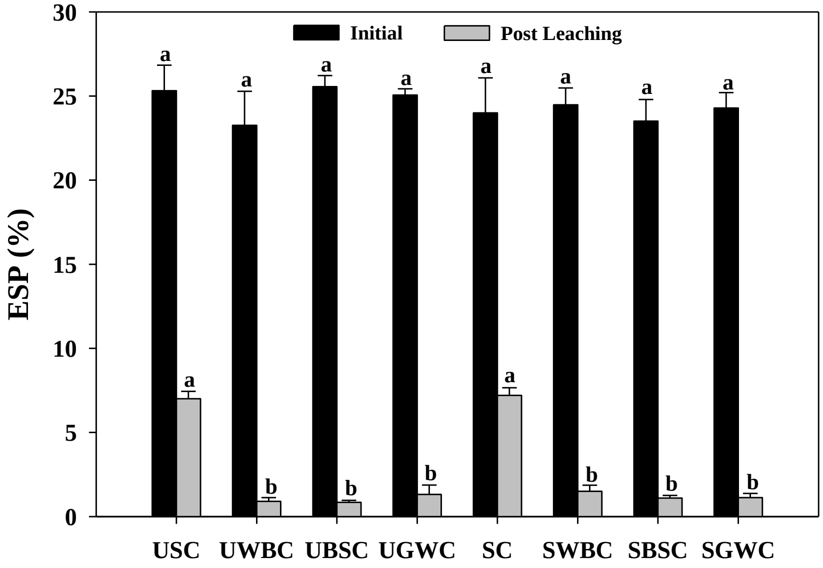

Fig. 3.13. Exchangeable sodium percentage (Mean ± s.e.) of soils before and after leaching for different treatments. Same letters within a column series indicate no significant differences between treatments ($P < 0.05$, Tukey's test).

# 4. INFLUENCE OF TEMPERATURE ON SOIL RESPIRATION, WET AGGREGATE STABILITY, SATURATED HYDRAULIC CONDUCTIVITY, AND OVERALL RECLAMATION OF A SALINE-SODIC SOIL TREATED WITH BIOCHAR, COMPOST, AND GYPSUM

## Abstract

Soil temperature is one of the important factors influencing soil respiration ($CO_2$-C evolution) by regulating microbial activity. Also, literature is abundant relating microbial activity to soil aggregate stability. This laboratory study investigated the influence of temperature on soil respiration and aggregate stability dynamics during 60 day incubation when biochars and composts were applied as amendments to remediate a saline-sodic soil. Subsequent improvements in saturated hydraulic conductivity ($K_s$), leachate losses of $Ca^{2+}$, $Mg^{2+}$ and $Na^+$, and the overall reclamation potential of these amendments were quantified for soils incubated at 15, 25, and 35 °C after leaching with reclaimed water. Treatments included: greenwaste and biosolids composts, woodchip and dairy manure biochar, applied at 75 t $ha^{-1}$, gypsum at 100 % GR and an unamended control. Increasing temperature increased soil respiration and soil wet aggregate stability in compost amended soils only. Similarly, soil $K_s$ was significantly higher in only compost treated soils incubated at higher temperatures. Gypsum and biochars also increased $K_s$ relative to the control but were not affected by temperature fluctuations. Cumulative leachate losses of $Ca^{2+}$ and $Mg^{2+}$ were significantly higher from compost treatments set at 25 and 35 °C. All amendments leached more $Na^+$ in significantly less time compared to the control. Temperature did not affect total $Na^+$ losses from most of

the treatments but higher temperatures significantly decreased sodium leaching times in compost amended soils. Temperature did not significantly affect soil chemical properties when treated with composts, biochars, or gypsum. Thus, temperature seems to indirectly affect soil physical properties more than chemical properties by influencing soil microbial activity and these effects are specific to soils treated with composts.

## Introduction

Soil salinization is a growing concern in arid and semi-arid areas reducing the agricultural productivity of these regions (Qadir et al., 2000). Extent of soil salinization is increasing both in its magnitude and intensity with time (Qadir et al., 2000). Soil salinization can occur both naturally and/or anthropogenically (Rengasamy, 2006). Irrigation is one of the key factors affecting the soil salinization process. High evaporation rates, low precipitation, continuous irrigation without proper leaching and drainage, and irrigation with poor quality waters are all the important factors leading to soil salinization in these dry climates (Ayars et al., 1999; Ghassemi et al., 1995; Makoi and Ndakidemi, 2007).

Soil salinity and sodicity are the two major concerns negatively influencing plant production and soil physical, chemical, and biological properties (Rietz and Haynes, 2003). Saline-sodic soils demonstrate both high $EC_e$ ($> 4$ dS $m^{-1}$) and SAR/ESP (SAR $>$ 13 or ESP $>$ 15) values (Richards, 1954) dominated by sodium salts. In addition to high salinity, which retards the plant growth in these soils (Rengasamy, 2006), excess $Na^+$ concentrations, both in the solution and exchange phases, deteriorate soil structure due to enhanced clay dispersion (Rengasamy and Sumner, 1998; So and Aylmore, 1993).

Dispersed soils are generally characterized by having poor soil aggregation, low infiltration rates and reduced hydraulic conductivity (Shainberg and Lety, 1984). Chemical reclamation of saline-sodic soils involves supplementing excess $Na^+$ with $Ca^{2+}$ on the exchange sites, thus reducing dispersion. This promotes soil flocculation and salts are leached subsequently (Gupta and Abrol, 1990). Gypsum is the most commonly used $Ca^{2+}$ source and its use for saline-sodic soil reclamation has been extensively studied (Brinck and Frost, 2009; Ghafoor et al., 2001; Lebron et al., 2002; Qadir et al., 2001b). Alternative reclamation strategies include sulfuric acid applications (Amezketa et al., 2005) and phytoremediation techniques (Qadir et al., 2007), which work on the principle of native calcite dissolution to supply needed $Ca^{2+}$. Additionally, biological amelioration includes application of different kinds of organic amendments.

Organic amendments were shown to improve soil properties, more importantly soil aggregation and structure (Bronick and Lal, 2005; Epstein et al., 1976; Le Bissonnais and Arrouays, 1997; Tisdall and Oades, 1982). Addition of organic amendments to salt affected soils was studied as a cheaper alternative to chemical amendments due to the structural enhancements offered by the organic matter incorporations (Lax et al., 1994). Some studies have evaluated the effects of organic amendment applications to saline-sodic soils and their salt leaching efficiency. Tejada et al. (2006) demonstrated that both cotton gin compost and poultry manure significantly reduced soil $EC_e$ and ESP due to increases in soil structural stability, when evaluated under field conditions in Spain. Another study in Pakistan showed that addition of FYM, clover hay and wheat straw improved the water stable aggregates (WSA) and WHC of both saline and a saline-sodic soil, when applied at rate of 3 % w/w (Wahid et al., 1998). Increased soil aggregation enhanced salt leaching and thus was shown to reduce the $EC_e$ of soils (Wahid et al., 1998). Soil aggregate development and structural buildup by organic matter additions can be considered as the two key factors affecting the reclamation efficiency of these soils. Organic matter influence on soil aggregation is attributed to the action of different organic binding agents (Tisdall and Oades, 1982). Three different organic binding agents were said to affect the formation and stability of soil aggregates, which include 1) transient 2) temporary and 3) persistent binding agents. Transient agents are composed of carbohydrates with plant and microbial derived polysaccharides acting as soil agglutinants. Temporary agents include plant roots and fungal hyphae, entangling soil particles to form aggregates. Finally, persistent binding agents include aromatic humic and fulvic acids forming metal cationic bridges between clay particles and thus promoting their aggregation (Tisdall and Oades, 1982).

Microbial derived exo-polysaccharides, though transient, can produce stable soil aggregates (Roberson et al., 1995). The degree of formation of these transient binding agents depends on the extent of microbial activity taking place in the soil which in turn influences the production of highly stable soil aggregates (Kandeler and Murer, 1993). Microbial activity is negatively affected by salinity and sodicity (Rietz and Haynes, 2003; Sardinha et al., 2003; Wong et al., 2008). Moreover, saline-sodic soils are generally low in organic matter due to plant growth restrictions in these degraded soils. Organic amendment applications to these soils act as energy substrates by providing carbon (C) and thus help to revive the microbial biomass and increase their activity (Tejada et al., 2006; Tejada et al., 2009).

Soil respiration, quantified as $CO_2$ evolution, is considered as one of the immediate indicators of increased microbial activity following organic matter additions (Setia et al., 2012). Increased temperatures are known to accelerate microbial activity and associated soil respiration rates (Pietikåinen et al., 2005; Yiqi and Zhou, 2010; Zak et al., 1999). Increasing temperature accelerates microbial activity as heated molecules more frequently meet needed activation energy requirements for reactions (Davidson and Janssens, 2006). Neither the effects of different temperatures on microbial activity as evidenced by soil respiration rates, nor the associated influence of temperature on soil aggregate stability measures, have been evaluated in saline-sodic soils, however. Substrate properties also influence microbial activity (Wang et al., 2003). While both composted and un-composted organic materials contain labile materials suitable as microbial substrates, biochar is recalcitrant (Spokas et al., 2009). The use of biochar for saline-sodic soil reclamation and its effect on soil respiration and aggregate stability at different temperatures has not been explored yet.

This study considers the use of different organic amendment (greenwaste compost, biosolids compost, dairy manure, and woodchip biochars) applications on soil respiration ($CO_2$ evolution) and aggregate stability at three (15, 25, and 35 °C) different soil temperatures using laboratory incubation for 60 days in a saline-sodic soil. Hydraulic conductivity improvements and $Na^+$ leaching potential were quantified for these treated soils and their reclamation efficiency was evaluated. We hypothesized that soils incubated at a higher temperature and treated with composts will have higher soil respiration rates due to increased microbial activity, and will thus have higher soil aggregate stability measurements compared to those at lower temperatures and treated with biochars. Consequently, due to increased soil aggregate stability, improvements in hydraulic conductivity would be more pronounced in compost treated soils incubated at higher temperatures.

## Materials and Methods

### Soil Collection and Analysis

Soils used in this study were same as those used in chapters 2 and 3. Detailed description of soil collection, processing and analyses is given in chapter 2. Some physical and chemical characteristics of soils are presented in Table 2.1.

### Amendments

Two Biochars and two composts made from different feedstocks were used as organic amendments. Product description about the two composts (biosolids and greenwaste composts) and the wood chip biochar is presented in chapter 2. Manure biochar was made using dairy manure biomass as feedstock and was prepared at University of California, Riverside campus. Dairy manure was collected from a local dairy farm and was oven dried in the laboratory for a 24 hour period. Oven dried feedstock material was then loaded into small crucibles covered with lids, and was combusted at 400 °C pyrolysis temperature for 1 hour in a muffle furnace purged with nitrogen to facilitate oxygen free conditions. Biochars were analyzed for their properties following the methods outlined in International Biochar Initiative (IBI) (IBI, 2013).

Composts were passed through a 0.25 inch (< 6.35mm) sieve while biochars were passed through a 2 mm sieve to achieve a uniform particle size. Important characteristics of the organic materials used in this study are given in Table 4.1. Agricultural grade (90% pure) gypsum was also used to compare the effects between organic and inorganic amendments.

### Irrigation Water

"Moderate SAR" (Mace and Amrhein, 2001) reclaimed water collected from a local farm with its primary source from Eastern Municipal Water District (EMWD) located in Southern California, was used as irrigation/leaching water. Important chemical properties of the reclaimed water are given in Table 2.3.

### Soil Treatments and Incubation

Treatments for this study included an unamended control (Control), agricultural grade gypsum applied at 100 % GR (Gypsum), woodchip biochar (WBC), dairy manure biochar (MBC), biosolids co-compost (BSC), and greenwaste compost (GWC). All organic amendments were applied at a rate of 75 t $ha^{-1}$ (~ 5 % w/w) on dry weight basis. Three hundred grams of saline-sodic soil was treated with different amendments, thoroughly mixed and was packed to a 1.25 g $cc^{-1}$ bulk density in each 1L mason jars. The control, gypsum, and organic amendment treated soils were subjected to laboratory incubation for a 60 day period at three different temperature regimes set at 15±1 °C, 25±1 °C, and 35±1 °C. Three replicates of each treatment were setup at each temperature. Laboratory incubation chambers were used to incubate jars at 15 and 35 °C, while jars at 25 °C were set on a laboratory bench. During incubation, water content in all jars was maintained at 60% water filled pore space (WFPS) calculated using Eq. 1 given in chapter 2.

Soil respiration was monitored by measuring the $CO_2$ evolution for all treatments on day 2, 6, 11, 16, 22, 28, 35, 42, 50, and 60 from the start of incubation. $CO_2$ measurement methodology and cumulative $CO_2$-C calculations are discussed in Chapter 3. Additionally, 10-12 g of soil sample was collected on the same day of $CO_2$ analysis from each of the jars set at different temperatures to determine their wet aggregate stability. Percent wet aggregate stability was measured on air dried 1-2 mm soil aggregates using wet sieving apparatus and following the method given by Nimmo and Perkins (2002). Soil samples collected on each day of $CO_2$ sampling were allowed to air dry followed by gentle separation of 1-2 mm aggregates by sieving through 2 and 1 mm sieves. Approximately 4 g of these 1-2 mm aggregates were added into numbered sieves, having a screen size of 0.25 mm, and were subjected to slow wetting. The sieves containing wet aggregates were first sieved into aluminum cups filled with distilled water for 3 min ± 5s using wet sieving apparatus. These cups contain soil from unstable aggregates. Later, these cups were replaced with a second set of aluminum cups containing 0.2 % sodium hexametaphosphate solution (dispersing agent) and sieving was continued for an additional 5 min ± 5s until all soil has been sieved, leaving behind only sand and other particles larger than the sieve opening. These second set of cups contain soil from stable aggregates. Both set of cans were oven dried for 24 hours and the dry weight of the materials in the cups was determined.

Soil wet aggregate stability (WAS) was calculated by,

$$\text{WAS (\%)} = \frac{\text{weight of soil in the dispersing solution cup X 100}}{\text{sum of weights of soils in both distilled water cups and dispersing solution cups}}$$

## Leaching Experiment

After 60 days of incubation, treated soils from three different temperatures were carefully emptied from the mason jars and were air dried and gently crushed to pass through a 2 mm sieve. Soils were filled in acrylic columns and were leached using moderate SAR reclaimed water until about 6 pore volumes of water had passed through each of the columns. Soil $K_s$, cumulative leachate losses of cations, and post-leaching soil analyses followed the methods given in chapter 2.

## Data Analysis

Univariate analysis of variance was conducted using SPSS V.20 software. Two-way factorial analysis of variance was used to assess the effects of temperature and amendments on soil respiration, aggregate stability, hydraulic conductivity, and other soil chemical properties. Significant differences between different temperature levels and amendments were separated using Tukey's HSD multiple comparison tests at a significance level of 95 % ($P < 0.05$). Where there was no effect of temperature, data across all three temperatures was combined to differentiate the significant differences between means of various treatments using Tukey's test.

## Results and Discussion

## Soil Respiration ($CO_2$ evolution)

Increasing temperature significantly increased ($P < 0.01$) cumulative $CO_2$ emissions from compost treated soils with highest emissions observed at 35 °C, followed by 25 and 15 °C (Fig. 4.1). This suggests that incubation at higher temperatures enhanced soil microbial activity, which increased the decomposition of added substrate. Cumulative $CO_2$ emissions were 2 and 2.6 times higher from the biosolids compost treated soils set at 25 and 35 °C relative to those at 15 °C. Greenwaste compost increased soil respiration rates by an average of 3 times for soils incubated at 25 and 35 °C compared to 15 °C. Differences between the two compost treatments in terms of their $CO_2$ evolutions were not statistically significant at any temperature, however. Addition of composts to soils significantly increased ($P < 0.01$) their soil respiration with significantly higher cumulative $CO_2$ evolutions observed in compost treated soils (Fig. 4.1) than gypsum, WBC, MBC, and the control soils at all three temperatures. Increased availability of labile C from composts likely contributed to the high rates of soil respiration from compost treated soils compared to other treatments (Chaoui et al., 2003). Similar increases in soil respiration rates with compost addition were reported by Borken et al. (2002), Cox et al. (2001), and Moreno et al. (Moreno et al., 1999). Moreover, Ros et al. (2003) demonstrated increased soil respiration in a semi-arid soil when treated with composted and uncomposted urban waste and attributed this effect to the increased microbial activity and decomposition of readily available energy substrates. In a more recent study, Yazdanpanah et al. (2013) reported similar increases in soil respiration rates upon addition of decomposed cattle manure and pistachio residue to a saline-sodic soil. Increases in soil respiration rates in salt affected soils, after incorporation of easily decomposable organic amendments, were also reported by several other authors (Liang et al., 2005; Setia et al., 2012; Wong et al., 2009). This increase was mostly attributed to the rejuvenation of a dormant microbial community in such soils upon addition of nutrient and energy substrates (Wong et al., 2009). Unlike our study, most of the above studies measured soil respiration at constant temperature conditions. Our results assert that temperature is a significant factor in driving the microbial dynamics when composts are applied to salt affected soils. Nevertheless, average cumulative $CO_2$ emissions from composts were 6 and 4 times higher than woodchip and dairy manure biochars, and 5 times that of gypsum and unamended control soils, across all temperatures.

Manure biochar treated soils had significantly higher ($P < 0.01$) respiration rates at 25 and 35 °C compared to 15 °C (Fig. 4.1). Differences in $CO_2$ evolutions from soils at 25 and 35 °C were not statistically significant ($P > 0.05$), however. Cumulative $CO_2$ evolution was increased by an average of 2.4 times from manure biochar treated soils at 25 and 35 °C compared to 15 °C. Also, cumulative $CO_2$ emissions from soils treated with dairy manure char were significantly higher ($P < 0.05$) than soils treated with woodchip biochar, gypsum, and the control at all three temperatures (Fig. 4.1). This contradicts the premise that C in biochar is mostly inert and is not subjected to biotic decomposition (Lehmann et al., 2006). However, several authors have reported that there could be a short term increase in soil respiration ($CO_2$ evolution) due to the presence of small quantities of readily available C in certain biochars (Bruun et al., 2011; Jones et al., 2011; Smith et al., 2010). For example, Smith et al. (2010) demonstrated that application of biochar produced from slow pyrolysis of switch grass at 500 °C for 2 h, increased cumulative soil $CO_2$ flux at the initial stages of incubation when applied to two silt loam soils. This was ascribed to the availability of the labile C pool in biochar which facilitated its decomposition by microbes. Additionally, Jones et al. (2011) hypothesized several reasons for increased soil respiration in soils treated with biochar and finally concluded that increased soil respiration was mainly due to the contributions from the breakdown of labile C in biochar by microbes and release of inorganic C from mineral carbonates contained in the biochar.

Our results are close to those reported by Zimmerman et al. (2011), who found a 'positive priming' effect with increased cumulative $CO_2$ production during the first 90 days of incubation due to application of chars made at temperatures close to 400 °C to soils with low initial C content; while a 'negative priming' was seen with chars made out of hard woods and at temperatures $\geq$ 500 °C. It was hypothesized that more labile components existed in biochars made at lower temperatures and thus facilitated their decomposition. The manure biochar in our study was prepared at a similar pyrolysis temperature of 400 °C and likely contained labile C fractions, which enhanced soil respiration. It is also possible that existing soil aggregates were dispersed (indicated by reduced soil aggregate stability, Fig. 4.2) by manure char addition, making available previously inaccessible organic matter (Adu and Oades, 1978) in these soils. Furthermore, the decomposition of available C in biochar increases at higher temperatures. Most of the above studies did not measure soil respiration from biochar treated soils along a temperature gradient. This could have an implication on biochar degradation in certain climatic regions were warmer temperatures prevail during summers such as in California.

Respiration rates of WBC, gypsum, and the control treatments followed the same pattern with significantly higher ($P < 0.05$) soil respiration rates at 25 and 35 °C compared to 15 °C (Fig. 4.1), which can be solely attributed to the enhanced microbial activity at higher temperatures. It has been well established in the literature that increases in soil temperature increase soil $CO_2$ production due to changes in activities of soil microorganisms (Schaufler et al., 2010; Smith et al., 2003). Drobnik (1962) demonstrated that increases in temperature increase soil respiration, irrespective of substrate availability, due to enhanced soil enzyme activation at higher temperatures. In that study, soil respiration rates were significantly higher from soils set at 38 and 48 °C, compared to those set at 8, 18, and 28 °C (Drobnik, 1962). Other studies have also reported increases in soil respiration rates with increase in soil temperature (Davidson et al., 1998; Fang and Moncrieff, 2001; Kirschbaum, 1995). WBC, gypsum, and the control treatments were not significantly ($P > 0.05$) different from each other with respect to their cumulative $CO_2$ evolutions at any of the three temperatures (Fig. 4.1). This is expected as there were no additional C inputs in gypsum and untreated soils (Celis et al., 2013), whereas C added with wood chip biochar made at 500 °C was likely more recalcitrant and hence was not accessible for microbial degradation (Zimmerman et al., 2011), as opposed to manure biochar. The feedstock and the temperature at which a biochar is made strongly influence the physical and chemical characteristics of that material (Keiluweit et al., 2010) and it is therefore not surprising that WBC and MBC performed differently.

**Soil Wet Aggregate Stability**

Effect of temperature on aggregate stability was found to be significant ($P < 0.01$) only with respect to compost treated soils all through the incubation period. Wet aggregate stabilities were significantly higher for both greenwaste and biosolids compost treated soils at 25 and 35 °C than those at 15 °C (Fig. 4.2). However, differences in stabilities of compost treated soils at 25 and 35 °C were not statistically significant ($P > 0.05$). Between composts, stability differences were not statistically significant at any temperature, either. Average wet aggregate stability increases were 14 % and 16 % between 15-25 °C and 15-35 °C for greenwaste compost treated soils. Biosolids compost treated soils had stabilities increased by an average of 21 and 30 % at 25 and 35 °C relative to those set at 15 °C. Soils that received greenwaste and biosolids composts had significantly higher ($P < 0.01$) wet aggregate stabilities throughout the incubation period compared to the control, gypsum, and the two biochar (Fig. 4.2) soils at 15, 25, and 35 °C. It should be noted that the wet aggregate stability increased immediately after compost application and the onset of incubation, at any given temperature (Fig. 4.2). This suggests that addition of these materials drastically increased the microbial activity and facilitated the release of by-products such as exo-polysaccharides, which glued soil particles together (Lynch and Bragg, 1985) and therefore, contributed for immediate increases in soil stability. This increase was perhaps higher in soils at 25 and 35 °C than at 15 °C, as temperature directly affected the rate of microbial activity, which in turn influenced the polysaccharide production. After the initial increase, aggregate stabilities varied, though not significantly over time. This is expected due to fluctuations in the concentrations of these agglutinants over time, as these substances are transient in nature (Degens, 1997). Nevertheless, irrespective of temperature, biosolids compost increased soil aggregate stabilities by an average of 52, 46, 51, and 62 % relative to the control, gypsum, WBC, and MBC soils, respectively, while greenwaste compost increased the same by an average of 45, 39, 44, and 55 %, respectively. These results are consistent with those observed in chapters 2 and 3, where compost applications significantly increased soil wet aggregate stability.

On the other hand, temperature did not significantly ($P > 0.05$) affect the aggregate stabilities of the control, gypsum, WBC, and MBC soils during incubation. In addition, at any given temperature, differences between these treatments were not significant during the early stages of incubation. However, approximately 20 days into the incubation, differences started to emerge between gypsum and manure biochar treatments. Gypsum treated soils had significantly higher ($P < 0.05$) aggregate stabilities than MBC treated soils and this trend was commonly observed at all three temperatures (Fig. 4.2). Soil stabilities of the untreated control and WBC soils were not statistically different from either gypsum or MBC soils at all three temperatures. Increases in soil stability in gypsum treated soils can be attributed to the addition of $Ca^{2+}$ which promoted soil flocculation. This result is in accordance with Muneer and Oades (1989), who demonstrated that incubating soils treated with gypsum, increased the proportion of water stable aggregates due to soil flocculation. Whereas, lower soil aggregate stabilities observed in soils treated with manure biochar were possibly due to $Na^{+}$ supplemented by the amendment (Table 4.1), which caused soils to disperse (Haynes and Naidu, 1998).

Biochar applications did not significantly increase soil aggregate stability compared to the control soils at any temperature, a result consistent with those found in chapters 2 and 3. Moreover, it is important to understand that the chemical characteristics of the materials, for example in our case, high $Na^+$ in dairy manure biochar, may have a deleterious effect on soil aggregate stability by increasing soil dispersion.

Analysis of post-leaching soils revealed that temperature did not have any significant effect on soil wet aggregate stabilities but regardless of temperature, the stabilities of all treatments increased due to $Na^+$ leaching (Fig. 4.3). However, significant differences ($P < 0.01$) existed between treatments with compost treated soils having the highest soil stabilities. Based on statistical significance, the wet aggregate stabilities observed for various treatments were in the order; BSC = GWC > MBC > gypsum = WBC > control. After leaching, irrespective of temperature, aggregate stabilities were on an average 50 % higher in compost treated soils, 14 % higher in biochar treated soils and 2.5 % higher in gypsum treated soils relative to the untreated controls, respectively. When compared against their respective initial soil aggregate stabilities (Fig. 4.3), a similar trend was observed wherein, compost amendments increased soil stabilities in greater proportions than the two biochars and gypsum. An average 100% increase in wet aggregate stability was found in compost treated soils, while woodchip and manure biochar increased stability by an average of 58.5 %, respectively, when compared to their before amendment soil aggregate stabilities. Increases in aggregate stabilities for the control and gypsum treated soils averaged at 37 and 52 %, respectively.

### Relationship between Soil Respiration and Wet Aggregate Stability

In order to assess the relationship between soil respiration ($CO_2$-C) and wet aggregate stability, simple correlations and regression fits were performed. It was found that soil respiration and wet aggregate stability were significantly ($P < 0.01$) and positively correlated at all three temperatures (Fig. 4.4). Corresponding Pearson correlation coefficients were 0.68, 0.67, and 0.70 for 15, 25, and 35 °C soils. Significant correlations between $CO_2$-C and aggregate stability have been reported in other studies (Abiven et al., 2009). Soil respiration accounted for approximately 50 % of the variability in soil wet aggregate stability at 15, 25, and 35 °C ($0.46 < r^2 < 0.50$; $P < 0.01$; Fig. 4.4). Physiochemical factors independent of biological activity likely account for much of the remaining variability.

### Saturated Hydraulic Conductivity ($K_s$)

Temperature only had a significant effect ($P < 0.05$) on saturated hydraulic conductivity of compost treatments during the leaching process (Fig. 4.5). The highest $K_s$ was observed in compost treated soils at 35 °C and declined with temperature, though differences between 35 °C and 25 °C compost treatments were not statistically significant. Higher $K_s$ in compost treated soils at 25 and 35 °C are likely associated with the corresponding higher soil aggregation and related stabilities observed in the compost treated soils (Fig. 4.2) set at higher temperatures. It can be understood that changes in temperature affected the conductivity of compost treatments specifically, while no effect of temperature was seen on $K_s$ of gypsum, WBC, MBC, and the control soils, whose aggregation was similarly unaffected by temperature during incubation. Also, at any given temperature, saturated hydraulic conductivity was significantly higher ($P < 0.01$) in BSC, GWC, WBC, MBC, and gypsum treated soils relative to the unamended control soil (Fig. 4.5). Statistically, soil $K_s$ followed the order; BSC > GWC > WBC = MBC = gypsum > control, at each of the three temperatures. BSC increased soil $K_s$ by 4, 6, and 7 fold and GWC increased the same by 4, 5, and 5 fold at 15, 25, and 35 °C. An average 2 fold increases in $K_s$ was observed in gypsum, MBC, and WBC treated soils at any given temperature.

Our results are consistent with those found in previous chapters (2 and 3), where composts had the highest soil $K_s$, followed by biochar and gypsum. Increases in soil $K_s$ in compost amended soils may have occurred due to: 1) increases in soil aggregation and stability during incubation, 2) efficient exchange of $Na^+$ and its leaching, 3) increases in electrolyte concentrations and additional soil flocculation through $Ca^{2+}$ and $Mg^{2+}$ supply. With respect to biochars, dramatic increases in aggregate stability were not observed during the 60 day incubation (Fig. 4.2). Therefore, we assume that soil flocculation achieved through $Ca^{2+}$ addition and $Na^+$ leaching in biochar treated soils could be the principle mechanism by which these materials increased soil $K_s$. These results concur with those reported by Oguntunde et al. (2008), Asai et al. (2009), and Githinji, (2013), where soil hydraulic conductivity was shown to increase upon biochar addition. The mode of action of gypsum in improving the hydraulic conductivity is already well known (Amezketa et al., 2005; Armstrong and Tanton, 1992; Gharaibeh et al., 2009; Ilyas et al., 1997; Mace and Amrhein, 2001; Qadir et al., 1996; Zia et al., 2007).

### Cumulative Leachate Losses of $Ca^{2+}$, $Mg^{2+}$, and $Na^+$

Cumulative leachate losses of $Ca^{2+}$ and $Mg^{2+}$ were significantly ($P < 0.01$) higher from compost treated soils set at 25 and 35 °C than at 15 °C (Fig. 4.6 & 4.7). Differences with respect to cumulative $Ca^{2+}$ and $Mg^{2+}$ losses between 25 and 35 °C compost treated soils were however, not significant. Also, the two composts did not statistically differ from each other with respect to their divalent cation losses at any of the three temperatures. Cumulative losses of $Ca^{2+}$ and $Mg^{2+}$ were on an average 26 and 37 % higher from biosolids compost and 11 & 16 % higher from greenwaste compost treated soils set at 25 and 35 °C than from those set at 15 °C. With respect to leachate $Na^+$, cumulative losses from biosolids compost treatment were not significantly different ($P > 0.05$) between the three temperatures (Fig. 4.8). However, losses from greenwaste compost were significantly higher ($P < 0.05$) from soils at 35 °C than at 15 °C (Fig. 4.8). Losses of $Na^+$ from greenwaste compost treated soils set at 25 °C did not differ from either 35 or 15 °C soils. Losses of cations, especially $Ca^{2+}$ and $Mg^{2+}$ from compost treated soils at higher temperatures was likely due to increased microbial mineralization of these materials that released fixed forms of these cations, which consequently increased their concentrations in soil solution (Ranjbar and Jalali, 2011). It can be assumed that the concentrations of these divalent cations were above the $Na^+$-$Ca^{2+}$ exchange demand of the soil exchange complex, which caused a net excess of these cations in the solution. On the other hand, the control, biochars and gypsum treated soils did not significantly ($P > 0.05$) differ from each other with respect to their cumulative losses of $Ca^{2+}$ and $Mg^{2+}$ at any of the three temperatures (Fig. 4.6 & 4.7). Also, increasing temperature did not significantly increase their cumulative divalent cation losses. But cumulative $Na^+$ losses were significantly higher ($P < 0.05$) from WBC treated soils at 25 and 35 °C compared to 15 °C soils. On the other hand, temperature did not significantly ($P > 0.05$) affect total $Na^+$ losses from other treatments (MBC, gypsum and the control) (Fig. 4.8). In chapter 3, when microbial activity was eliminated by sterilization, cumulative losses of $Ca^{2+}$ and $Mg^{2+}$ were significantly reduced in sterilized compost treated soils. This suggests that microbial mineralization is an important process, which releases these cations from composts. In this study, increasing temperature increased the divalent cation losses, which further elucidates that microbial activity and its rate, as influenced by temperature, play an important role with respect to cation release and their subsequent losses when composts are applied to soils. This effect cannot be generalized for biochars as they are less prone to microbial decomposition.

Regardless of temperature, addition of both organic and inorganic amendments significantly increased cumulative losses of, $Ca^{2+}$, $Mg^{2+}$, and $Na^+$ through leachate, relative to the control soils (Fig. 4.6, 4.7, & 4.8). Statistically, cumulative losses of $Ca^{2+}$ followed the order; BSC > MBC > GWC ≥ WBC > gypsum > control. Similarly, cumulative losses of $Mg^{2+}$ for various treatments was in the order; BSC > MBC > GWC > WBC ≥ gypsum ≥ control. Peak losses of $Ca^{2+}$ and $Mg^{2+}$ from BSC and MBC treatments could be attributed to their very high inherent $Ca^{2+}$ and $Mg^{2+}$ levels (Table 4.1) compared to WBC and GWC treatments. Relative to the control, average cumulative leachate losses of $Ca^{2+}$ were 27.5 and 17 % higher, while $Mg^{2+}$ losses were 69 and 41 % higher from composts and biochar, respectively, across all temperatures. At the same time, cumulative losses of $Ca^{2+}$ and $Mg^{2+}$ from gypsum treatments were increased nominally by 7 and 8 % than that observed from the control soils. On the other hand, cumulative leachate losses of $Na^+$ were also significantly higher ($P < 0.01$) from soils treated with both organic and inorganic amendments, regardless of temperature (Fig. 4.8). Cumulative losses of $Na^+$ through leachate from various treatments followed the order; MBC > BSC = GWC = WBC = gypsum > control. It could be possible that increased losses of $Na^+$ from MBC treatments could be due to high *in situ* $Na^+$ concentrations found in this material relative to other organic amendments (Table 4.1), which when combined with that released from exchange sites, resulted in much higher losses. Overall, irrespective of temperature, treating soils with manure biochar, woodchip biochar, biosolids compost, greenwaste compost, and gypsum increased $Na^+$ leaching by an average of 36, 23, 25, 25, and 27 % respectively, relative to the control.

### $Na^+$ Leached vs. Cumulative Time

Temperature significantly affected the actual time taken to leach $Na^+$ in both biosolids ($P < 0.01$) and greenwaste compost ($P < 0.05$) treated soils. Compost amended soils lost $Na^+$ in relatively lesser time when incubated at 25 and 35 °C than at 15 °C (Fig. 4.9). Increasing temperature decreased the time needed to leach $Na^+$ when soils were treated with composts. In our previous study (chapter 3), we found that unsterilized compost treatments had significantly lower $Na^+$ leaching times relative to their sterilized treatments. We proposed that increase in soil aggregation and hydraulic conductivity in the presence of microbial activity accelerated $Na^+$ leaching. The results from this present study substantiate that premise with lower leaching times at higher temperatures, consequent to increased microbial activity and associated increases in soil aggregation and hydraulic conductivities in compost treated soils. On the other hand, sodium leaching time was not significantly affected ($P > 0.05$) by temperature for all other treatments (gypsum, WBC, MBC, and the control). When compared between treatments irrespective of temperature, significant differences were found with respect to time required to leach $Na^+$. At any given temperature, compost amended soils took the least amount of time followed by biochars and gypsum treatments. The controls on the other hand, took significantly longer time and lost less $Na^+$ compared to organic and gypsum amendments (Fig. 4.9). This highlights the role of amendments to accelerate the $Na^+$ exchange rate by readily supplying necessary $Ca^{2+}$ as opposed to the control, which did not have a source that delivered $Ca^{2+}$ immediately. Decreased leaching times would translate into faster soil reclamation and prevent evaporative losses of leaching water, especially when a remediation program is scheduled during summer seasons.

### Cation Exchange Capacity (CEC)

Temperature did not have any significant effect ($P > 0.05$) on soil CEC for any of the treatments. Regardless of temperature, post leaching soil analysis revealed that compost and biochar amendments significantly ($P < 0.01$) increased soil CEC's compared to the control and gypsum soils (Fig. 4.10). Soil CEC observed for different treatments after leaching follows the order; BSC > GWC > MBC > WBC > gypsum = control. Biosolids and greenwaste composts increased soil cation exchange capacities by an average of 27 and 24 %, while woodchip and manure biochars increased the same by 12 and 17 %, respectively, relative to the control. At the same time, when compared to their respective initial CEC’s, a similar trend was observed where composts and biochars increased soil CEC significantly (Fig. 4.10). Biosolids and greenwaste composts increased soil CEC by 30 and 26 % and biochars increased the same by 14 and 21 %, relative to their unamended base soils. Increases in soil CEC after compost application can be attributed to the increases in humic and oxidizable C fractions (Madejón et al., 2001). These results follow those reported in chapters 2 and 3. In chapter 3 where soil CEC was not affected by sterilization, it was hypothesized that abiotic oxidation of added humic fractions was the likely dominant process that contributed for any significant CEC increases. No significant effect of temperature observed in this study confirms that hypothesis and therefore, CEC increases are a likely result of abiotic oxidation of added humic fractions. However, contributions from biotic oxidation cannot be ruled out, though may not be significant enough.

Interestingly, both woodchip and dairy manure biochar resulted in significant increase in soil CEC after treated soils were incubated for 60 days. These results are contrasting to the findings in our previous studies (chapters 2 and 3) where significant increases in soil CEC were not found when woodchip biochar was added. However, the soils in those experiments were incubated only for a period of 30 days. It is likely that increased duration of incubation facilitated some degree of biotic and abiotic oxidation of woodchip biochar in this study (Schmidt and Noack, 2000). In addition, our results are close to those reported by Cheng et al. (2006), who also demonstrated increases in soil CEC after 120 day incubation and attributed this effect mostly to the surface oxidation of biochar particles mediated by abiotic processes such as chemisorption of oxygen. On the other hand, increases in CEC of soils treated with manure biochar were greater than those that received woodchip biochar. This difference may be related to the increased microbial decomposition (Fig. 4.1) that facilitated some biotic oxidation in addition to abiotic oxidation processes, which caused an increase in relative number of carboxyl groups, thus enhancing the soil cationic exchange capacity (Cheng et al., 2008) of dairy manure treated soils compared to soils amended with woodchip biochar. Similar increases in soil CEC by biochar addition have been noted in other studies (Chan et al., 2008a; Liang et al., 2006; Van Zwieten et al., 2010).

### Soil pH and $EC_e$

Initial soil pH ranged between a low of 8.04 to a high of 8.21 for all soils. Incubating amended soils at 15, 25, and 35 °C did not significantly affect ($P > 0.05$) their pH. Nevertheless, regardless of temperature, pH of post leaching soils differed significantly between treatments (Fig. 4.11). Soil pH was significantly reduced by both biosolids and greenwaste composts compared to the control and gypsum. On the other hand, addition of MBC significantly ($P < 0.05$) decreased soil pH but woodchip biochar addition did not cause any significant changes. Overall, soil pH observed for various treatments after leaching was in the order; BSC = GWC < MBC < WBC = Gypsum = control. At the same time, soil pH was reduced in all treatments including the control compared to their initial values (Fig. 4.11), which was due to leaching of $Na^+$ and its associated salts like carbonates and bicarbonates (Nelson and Oades, 1998). However, significantly greater reductions in pH were observed in soils that were treated with composts. On average, compost applications reduced soil pH by 0.7 units while biochars reduced the same by 0.4 units, respectively. Reductions in pH for the control and gypsum treated soils averaged at 0.2 units. Similar to the findings in chapter 2 and 3, larger pH reductions were observed in compost treated soils which can be attributed to the increased production of organic and inorganic acids during the microbial breakdown of the added organic matter (Wong et al., 2009). In chapter 3, unsterilized compost treated soils had significantly lower soil pH than their sterilized counterparts. Microbial activity seemed to play an important role there in reducing soil pH by producing organic and inorganic acids, in addition to $Na^+$ leaching. It can be hypothesized that increase in microbial activity would increase such acid production in compost treated soils. In this study, even though microbial activity increased with increasing temperature in compost treated soils, their soil pH was not significantly affected. This contrasts our hypothesis and the understanding for this result is not clear as the concentrations of such acids were not measured definitively. The only assumption that can be made is that the production rate of such acids was not significantly increased with increasing temperatures that could produce a significant change in soil pH. On the other hand, decreases in soil pH observed in biochar treated soils can be purely ascribed to their increased $Na^+$ leaching efficiency and its associated salts.

Soil salinity ($EC_e$) ranged between 18.28 dS $m^{-1}$ to 25.22 dS $m^{-1}$ for all soils before amendment application. Post leaching, reduction in soil salinity was observed in all treatments due to leaching of salts but no significant effect of temperature ($P > 0.05$) was detected (Fig. 4.12). However, gypsum and organic amendments decreased soil salinity significantly ($P < 0.01$) relative to the control because of their increased salt leaching potential. Differences between gypsum, composts, and biochars were not statistically significant ($P > 0.05$), however. In short, $EC_e$ of post leaching soils treated with organic amendments and gypsum was lowered by 29 and 30 % relative to the control soils. Similarly, reductions in soil salinity were greater for soils treated with gypsum, composts, and biochars than those of the control soils, when compared against their respective initial soil $EC_e$'s. Reductions in soil $EC_e$ averaged at 82 and 83 % for organic and gypsum amendments. The control had a 76 % reduction in initial soil salinity when leached with reclaimed water (Harker and Mikalson, 1990). These results further confirm those observed in chapter 2 and 3, where organic amendments produced significant reductions in soil salinity due to their potential to increase salt leaching efficiency as a consequence of increased hydraulic conductivity.

### Soil SAR

Post leaching, sodium adsorption ratio of all treatments decreased to values less than the threshold of 13 (Richards, 1954), with no significant differences between soils of different treatments set at 15, 25, and 35 °C ($P > 0.05$) (Fig. 4.13). Decrease in soil SAR values could be attributed to the leaching of $Na^+$ observed in all treatments, including the control. However, regardless of temperature, SAR values of soils treated with gypsum and organic amendments were significantly ($P < 0.01$) lower than that of the control soils (Fig. 4.13). Statistically, post leaching soil SAR followed the order; GWC = MBC < Gyp = BSC = WBC < control. Greater decreases in soil SAR observed in gypsum and organic amended soils were due to both increased $Na^+$ leaching, and higher concentrations of $Ca^{2+}$ and $Mg^{2+}$ in the soil solution. Overall, relative to the control, SAR reductions averaged at 46 and 47 % for biochars and compost treated soils, respectively. At the same time, gypsum lowered soil SAR by 42 % over the control. Similarly, initial SAR's were also reduced at higher rates when soils were treated with gypsum and organic amendments than that of the control (Fig. 4.13). Gypsum and organic amendments decreased initial soil SAR by an average of 94 and 93 % respectively, while the SAR in the control soils was reduced by 88 % after leaching. Mahmoodabadi et al. (2013) reported that leaching a saline-sodic soil by itself could significantly reduce the soil SAR due to salt removal. However, in the same study, addition of different amendments like gypsum and pistachio residue increased the potential to reduce SAR greater than that of the control, a finding similar to this study.

### Soil ESP

Initial soil ESP's ranged between a low of 20 and a high of 27.85 for all treatments, irrespective of temperature (Fig. 4.14). Significant effect of temperature was not found ($P > 0.05$) with respect to the ESP of post leaching soils. Exchangeable sodium percentage of all treatments reduced to values less than the threshold of 15 (Richards, 1954) after leaching with 6 pore volumes of reclaimed water (Fig. 4.14). But relative to the control, ESP reductions were more prominent in soils treated with gypsum, composts and biochar ($P < 0.01$). Differences between gypsum and other organic amendments were statistically not significant, however. When compared to the control, compost and biochar application reduced soil ESP by an average of 80 and 75 %, respectively. Gypsum addition on the other hand, reduced soil ESP by 76 %, relative to the unamended control. A similar trend was observed when compared against the initial ESP measurements, with gypsum, composts, and biochar treated soils producing greater reductions in soil ESP than the untreated control (Fig. 4.14). Corresponding reclamation efficiencies were 92, 92, and 93 % for soils amended with gypsum, biochars, and composts, respectively, while the reclamation efficiency of the control was only 65 %. Importantly, this study showed that organic amendments like composts and biochars could perform similar to that of gypsum, a common ameliorant used for saline-sodic soil reclamation. Also, it should be noted that the soil used in this study could be self-reclaiming upon provision of adequate leaching, even when 'moderate' SAR water is used. This effect was ascribed to the "valence dilution" principle explained in detail by Qadir et al. (2001b). Additionally, Reeve and Doering (1966) explained that when the ratio (R) of sum of $Ca^{2+}$ and $Mg^{2+}$ concentrations ($C_{Ca^{2+}} + C_{Mg^{2+}}$, meq $L^{-1}$) to the total cation concentration ($C_{TC}$) of a leaching solution is at least 0.3, successful amelioration of a saline-sodic soil can be achieved just by leaching and without any amendment application. The leaching solution in this study has an R value of 0.34, which is just above the threshold of 0.3 (Reeve and Doering, 1966) and therefore aided in ESP reduction even in the control soils, albeit it's moderate SAR.

Likewise, significant reductions in ESP of saline-sodic soils amended with organic materials like composts and traditional gypsum were reported in our previous chapters (2 and 3) and by other studies (Ahmad et al., 2006; Amezketa et al., 2005; Armstrong and Tanton, 1992; Choudhary et al., 2004; Gharaibeh et al., 2010; Hanay et al., 2004; Mahdy, 2011; Niazi et al., 2001; Qadir et al., 2001b; Tejada et al., 2006).

### Soil Exchangeable $Ca^{2+}$, $Mg^{2+}$, and $Na^{+}$

Before and after-leaching concentrations of soil exchangeable $Ca^{2+}$, $Mg^{2+}$ and $Na^{+}$ for different treatments are presented in Table 4.2. Initial concentrations ranged between 64.7-73.5 meq/100g for $Ca^{2+}$, 3.23-4.66 meq/100g for $Mg^{2+}$, and 4.99-6.85 meq/100g for $Na^{+}$. Post leaching, temperature was found to have no significant effect ($P > 0.05$) on exchangeable $Ca^{2+}$, $Mg^{2+}$, and $Na^{+}$ concentrations, whose changes are mostly driven by the chemical exchange reactions taking place between soil solution and exchange phases. After leaching, final soil exchangeable cation concentrations of various treatments ranged between 0.26-2.77 meq/100g for $Na^{+}$, 51.3-98.7 meq/100g for $Ca^{2+}$ and 1.91-4.43 meq/100g for $Mg^{2+}$. Nevertheless, regardless of temperature, significant differences ($P < 0.01$) were detected between the control and other treatments with respect to their exchangeable $Na^{+}$, $Ca^{2+}$, and $Mg^{2+}$ concentrations. Gypsum, WBC, MBC, BSC, and GWC treatments had significantly higher ($P < 0.01$) soil exchangeable $Ca^{2+}$ concentrations with corresponding increases ranging between 34-36 %, relative to the control soils. On the other hand, post-leaching soil exchangeable $Na^{+}$ concentrations were significantly lower ($P < 0.01$) in soils treated with gypsum, composts, and biochars when compared against the control soils. This can be attributed to increased $Ca^{2+}$ levels due to the addition of these amendments, which facilitated efficient $Na^{+}$ displacement from the exchange sites. Gypsum and composts were equally effective and reduced exchangeable $Na^{+}$ concentrations by 76 % while biochars reduced the same by an average of 73 % relative to the control.

Exchangeable $Mg^{2+}$ concentrations in dairy manure biochar treated soils were significantly higher ($P < 0.05$) than the control and gypsum soils (Table 4.2). This was likely due to the higher intrinsic $Mg^{2+}$ levels measured in dairy manure biochar (Table 4.1) compared to other organic amendments. Akin to our study, Chan et al. (2008b) observed similar increases in soil exchangeable $Mg^{2+}$ levels when treated with poultry litter biochar applied at 50 t $ha^{-1}$. However, exchangeable $Mg^{2+}$ concentrations of BSC, GWC, and WBC treated soils were not statistically different from either the control and gypsum soils or manure biochar soil.

When compared to their initial levels, it was found that exchangeable $Ca^{2+}$ levels were significantly increased for soils treated with gypsum, biochars, and composts, after leaching (Table 4.2). As expected, highest increase in exchangeable $Ca^{2+}$ was facilitated by gypsum (16 %), which was applied at 100 % GR, followed by biosolids compost (14 %), dairy manure biochar (13 %), greenwaste compost (11 %), and woodchip biochar (9 %). The controls on the other hand lost approximately 10 % of their initial $Ca^{2+}$ when leached with reclaimed water (Table 4.2). Similar increases in soil exchangeable $Ca^{2+}$ when treated with composts and biochars were reported in previous studies (Jalali and Ranjbar, 2009; Novak et al., 2009; Walker and Bernal, 2008; Warman and Termeer, 2005). Simultaneously, soil exchangeable $Mg^{2+}$ concentrations decreased for all treatments relative to their initial concentrations, with enhanced reduction seen in gypsum and the control soils. Reductions in initial exchangeable $Mg^{2+}$ concentrations averaged at 24, 17, 30, and 29 % for composts, biochars, gypsum, and the control soils, respectively. It should be observed here that losses of $Mg^{2+}$ were more pronounced in the control and gypsum treated soils than composts and biochar. This indicates the ability of both composts and biochar to retain divalent cations better than untreated soils, even when leached with reclaimed water.

Contrastingly, losses of initial exchangeable $Na^+$ were more pronounced in gypsum, composts, and biochar treated soils than in the control (Table 4.2). Soils treated with gypsum, biosolids and greenwaste composts, woodchip and dairy manure biochars, lost an average of 92, 91, and 90 % of their initial sodium, respectively, while the unamended controls lost only 64 % of their initial sodium after leaching. It can be understood that increased $Ca^{2+}$ availability from all amendments significantly increased their potential to displace more $Na^+$ from the exchange sites than that of the control. Also, with respect to the control soils, it is critical to observe that $Na^+$ losses were much higher than the losses of divalent cations. It is due to the fact that divalent cations are more preferred than monovalent cations by the soil exchange complex (Qadir et al., 2001b), which likely resulted in two simultaneous processes; 1) displacement of $Na^+$ from the exchange complex by $Ca^{2+}$ in irrigation water and 2) preferential exclusion of $Na^+$ in the irrigation water from entering exchange sites by high soil exchangeable $Ca^{2+}$ (Table 2.1).

## Conclusions

This laboratory incubation study specifically evaluated the effect of temperature on soil respiration and aggregate stability dynamics when woodchip biochar, dairy manure biochar, biosolids compost, greenwaste compost, and gypsum were applied to reclaim a saline-sodic soil. Subsequently, improvements in saturated hydraulic conductivity, total leachate losses of $Na^{2+}$, $Ca^{2+}$, and $Mg^{2+}$ and the overall reclamation efficiencies with respect to soil chemical properties such as pH, CEC, $EC_e$, SAR, ESP, and exchangeable cation concentrations were also quantified for soils treated with different amendments and incubated at different temperatures. In general, soil respiration significantly increased with increasing temperatures for compost treated soils. Significantly higher cumulative $CO_2$-C evolutions were observed in compost treated soils due to their higher labile C contents and increased microbial decomposition at 25 and 35 °C compared to 15 °C. In addition, dairy manure biochar had higher soil respiration rates compared to woodchip biochar at all temperatures. It is possible that this was a short term positive priming effect ascribed due to the availability of labile C in manure biochar. Respiration rates of the control and gypsum soils were higher at 25 and 35 °C, but still were significantly lower than MBC and compost treated soils due to lack of energy substrates. Temperature increased soil wet aggregate stability but the increase was significant only for compost treated soils. Soils amended with both biosolids and greenwaste composts had significantly higher aggregate stabilities compared to other treatments, at all temperatures. Excessive $Na^+$ contents in organic amendments can however, decrease aggregate stability by promoting soil dispersion, as evident from reduced aggregate stabilities in manure biochar treated soils. Hydraulic conductivities of compost treated soils were higher at 25 and 35 °C than at 15 °C but no effect of temperature was observed with respect to hydraulic conductivities of biochar and gypsum treated soils. Therefore, higher temperatures preferentially help hasten the reclamation by increasing soil aggregation and hydraulic conductivity when composts are applied as amendments to remediate salt affected soils. Also, this finding is critical with respect to scheduling a remediation program. For example, applying composts during summer time would facilitate much faster soil reclamation than scheduling during a winter season when soil temperatures are at their lowest. Hydraulic conductivities of biochar and gypsum were also significantly higher than the control at any given temperature. This result is a further confirmation that the effect of biochars on soil hydraulic conductivity is a physiochemical phenomenon as observed in chapter 3 and is independent of microbial activity and temperature.

Cumulative leachate losses of $Ca^{2+}$ and $Mg^{2+}$ were elevated in compost treated soils at 25 and 35 °C compared to 15 °C. This suggests that increased microbial breakdown of these materials could release divalent cations in substantial amounts but when unreacted with soil exchange complex, could potentially increase their leaching. Cumulative losses of divalent cations from gypsum and biochars did not increase with increasing temperature but were comparatively higher than the control at any given temperature. $Na^{+}$ losses were on the other hand, not affected by temperature in most cases but both inorganic and organic soil amendments increased its leaching relative to the control. Also, $Na^{+}$ leaching times were significantly lowered by amendment application. Moreover, compost application significantly lowered $Na^{+}$ leaching times at higher temperatures indicating an indirect role of microbial activity and its rate, which influences soil aggregation and hydraulic conductivity. Soil properties such as CEC, pH, $EC_e$, SAR, ESP, and exchangeable cation concentrations were not affected by temperature for any of the treatments. Results are consistent with those observed in chapters 2 and 3 with respect to the effects of both composts and biochars on soil chemical properties. It is therefore, critical to understand that complex interactive reactions taking place between various soil factors and the chemistry of different organic amendments influence the means by which these amendments aid in the reclamation of physical and chemical properties of a saline-sodic soil.

Table 4.1. Chemical characteristics of biochars and composts.

| **Characteristic** | **Woodchip Biochar** | **Dairy Manure Biochar** | **Biosolids compost** | **Greenwaste compost** |
|---|---|---|---|---|
| Total C (%) | 63 | 22.8 | 24.4 | 23 |
| Total N (%) | 0.74 | 1.5 | 3.8 | 0.99 |
| Org. C (%) | 83.9 | 62.1 | 32 | 33.2 |
| C:N ratio | 85.1 | 15.2 | 6.42 | 23.2 |
| Organic Matter % | – | – | 61.4 | 56 |
| pH[1] | 8.55 | 10.4 | 7.38 | 6.36 |
| EC[1] (dS $m^{-1}$) | 0.56 | 7.55 | 12.8 | 2.75 |
| Total Elements (%) | | | | |
| Ca | 1.68 | 2.99 | 2.84 | 1.47 |
| Mg | 0.41 | 1.46 | 0.48 | 0.37 |
| Na | 0.46 | 1.37 | 0.16 | 0.09 |
| K | 0.53 | 5.38 | 0.55 | 0.73 |

[1] pH and EC of composts were measured on 1:5 water extracts (TMECC, 2001), and that of biochars were measured on 1:20 water extracts (IBI, 2013).

Table 4.2. Soil exchangeable $Na^+$, $Ca^{2+}$, and $Mg^{2+}$ concentrations (Mean ± s.e.) (meq/100g) for different treatments before and after leaching.

| Treatment | $Na^+$ | | $Ca^{2+}$ | | $Mg^{2+}$ | |
|---|---|---|---|---|---|---|
| | Initial | Final | Initial | Final | Initial | Final |
| Control | 5.91±0.06 a* | 2.15±0.14 a | 69.91±0.73 a | 62.56±2.24 a | 4.00±0.12 a | 2.83±0.26 a |
| Gypsum | 5.97±0.08 a | 0.52±0.06 b | 68.87±0.75 a | 79.51±2.99 b | 3.92±0.08 a | 2.73±0.15 a |
| WBC | 6.09±0.14 a | 0.51±0.06 b | 69.39±0.33 a | 75.30±2.47 ab | 3.78±0.10 a | 2.91±0.13 ab |
| MBC | 6.08±0.14 a | 0.64±0.04 b | 70.73±0.74 a | 80.25±2.38 b | 3.93±0.09 a | 3.46±0.29 b |
| BSC | 5.99±0.22 a | 0.58±0.04 b | 69.47±0.41 a | 79.80±2.90 b | 3.96±0.11 a | 3.04±0.16 ab |
| GWC | 5.96±0.10 a | 0.46±0.04 b | 70.13±0.70 a | 77.87±2.34 b | 3.86±0.08 a | 2.93±0.17 ab |

*Same letters within a column indicate no significant differences between treatments ($P < 0.05$, Tukey's test).

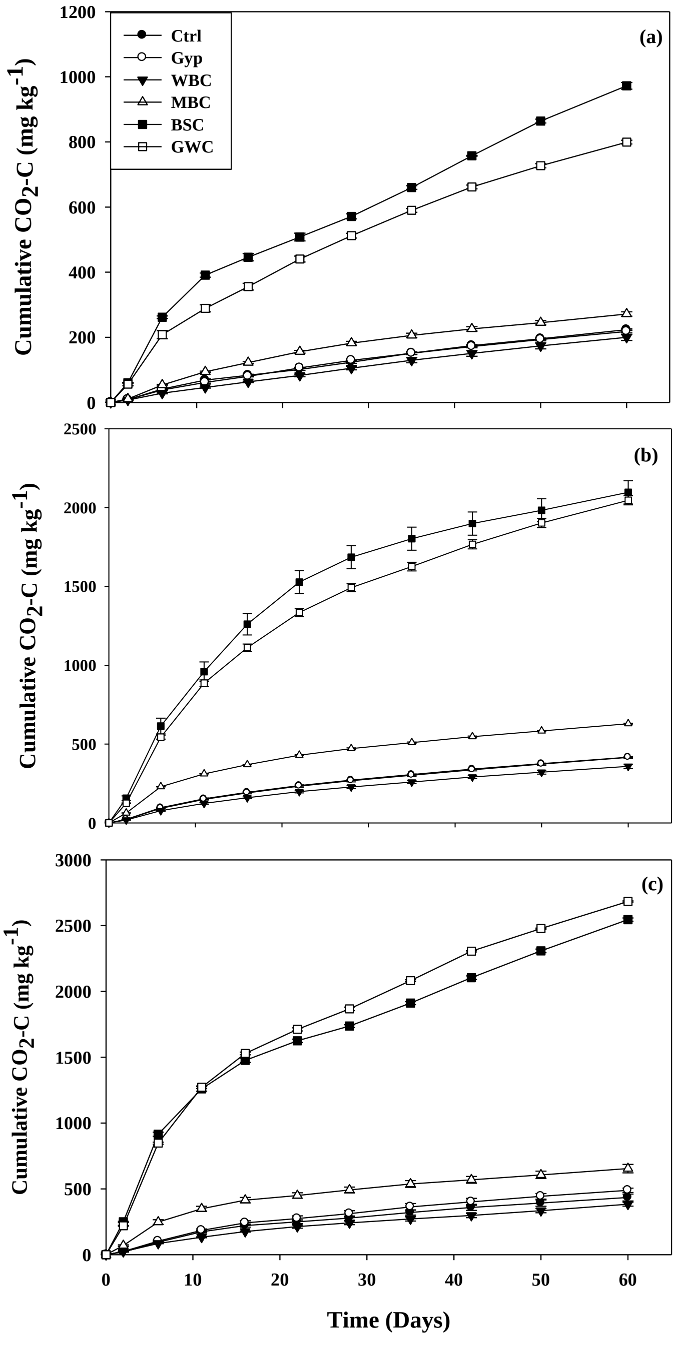

Fig. 4.1. Cumulative $CO_2$-C (Mean ± s.e.) evolution from soils of different treatments incubated at (a) 15 °C, (b) 25 °C, and (c) 35 °C.

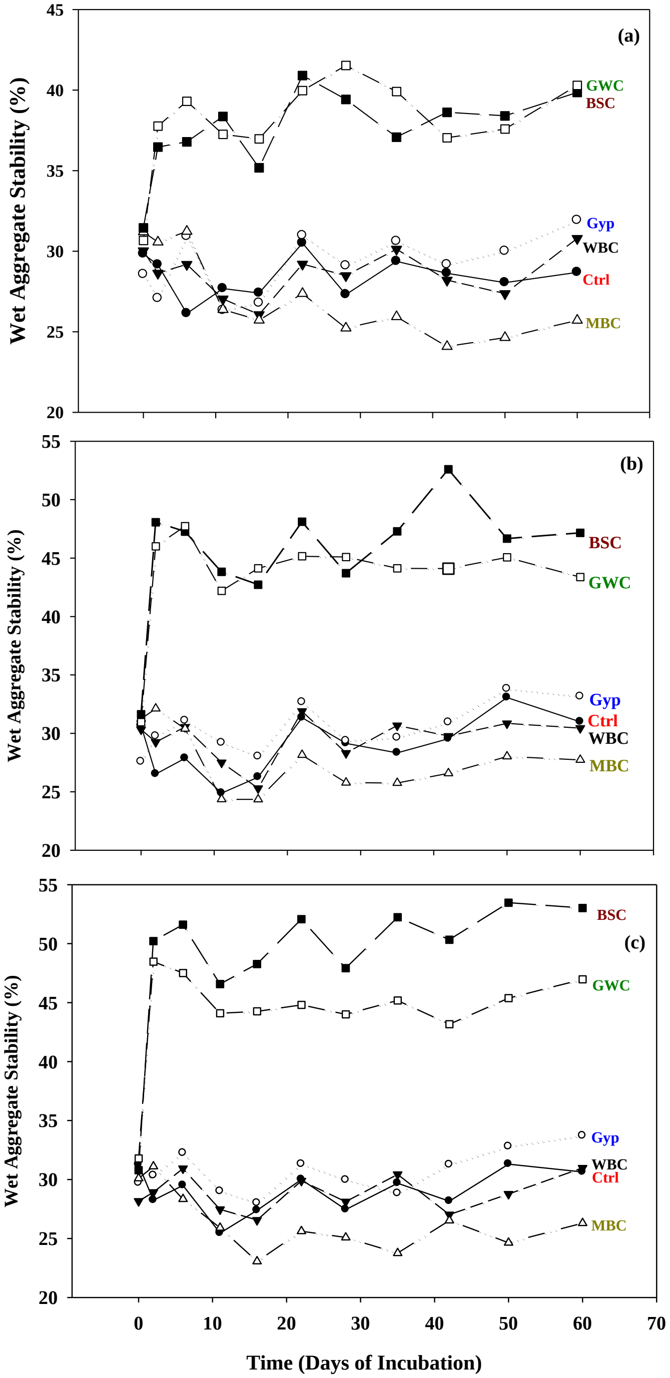

Fig. 4.2. Wet aggregate stability (%) of soils of different treatments incubated at (a) 15 °C, (b) 25 °C, and (c) 35 °C.

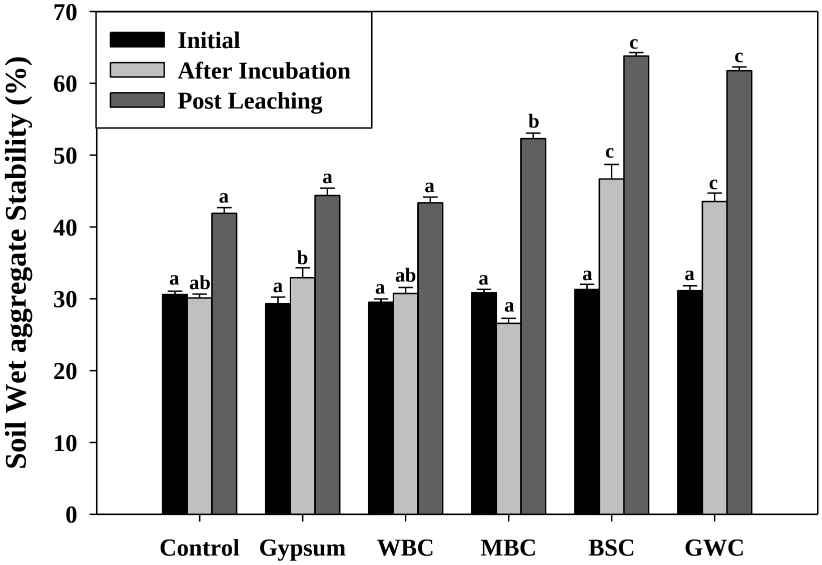

Fig. 4.3. Wet aggregate stability (%) (Mean ± s.e.) of soils before incubation, after incubation, and post leaching for different treatments. Same letters within a column series indicate no significant differences between treatments ($P < 0.05$, Tukey's test).

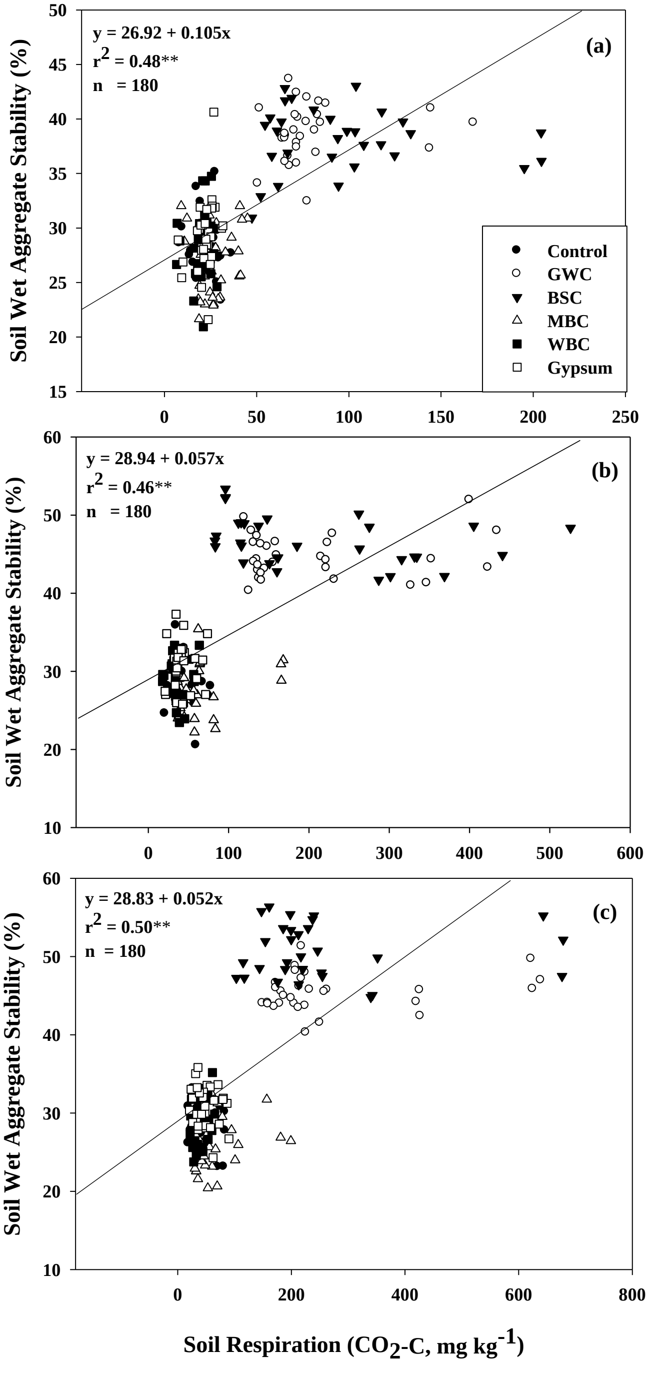

Fig. 4.4. Linear regression fits between soil respiration and soil aggregate stability for different treatments at (a) 15 °C, (b) 25 °C, and (c) 35 °C. **, indicates significance at P < 0.01.

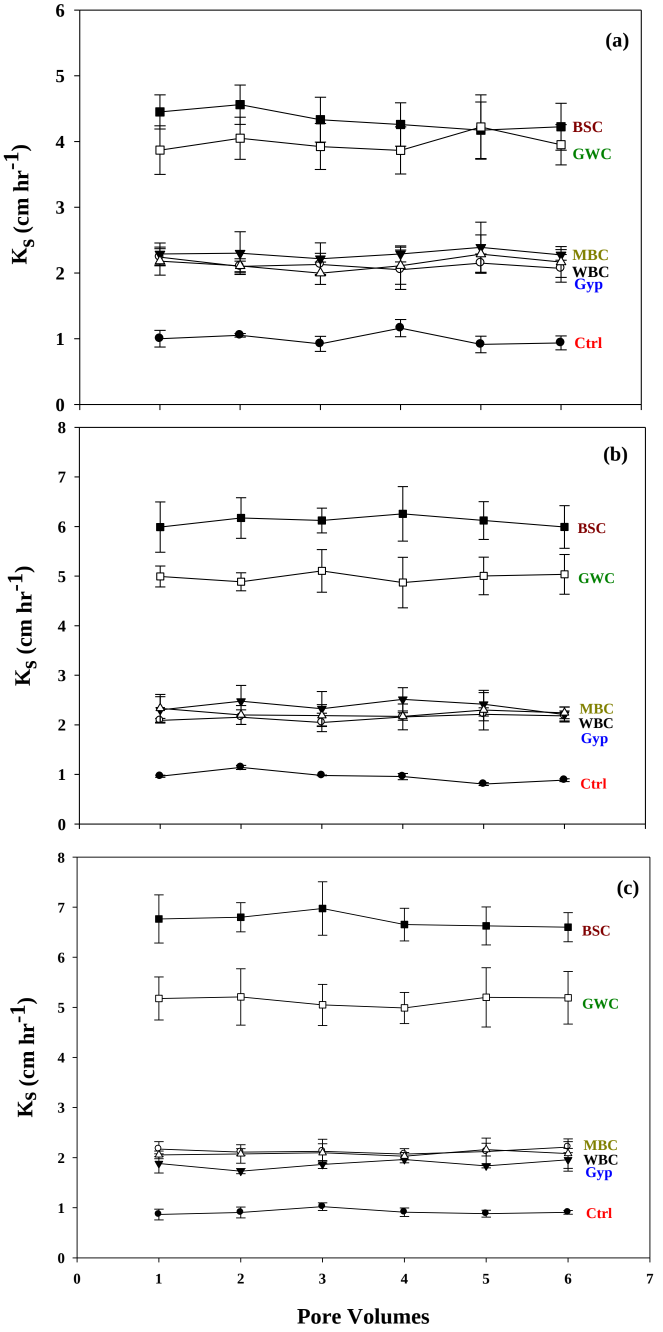

Fig. 4.5. Saturated hydraulic conductivity ($K_s$) (Mean ± s.e.) of different treatments during leaching of soils incubated at (a) 15 °C, (b) 25 °C, and (c) 35 °C.

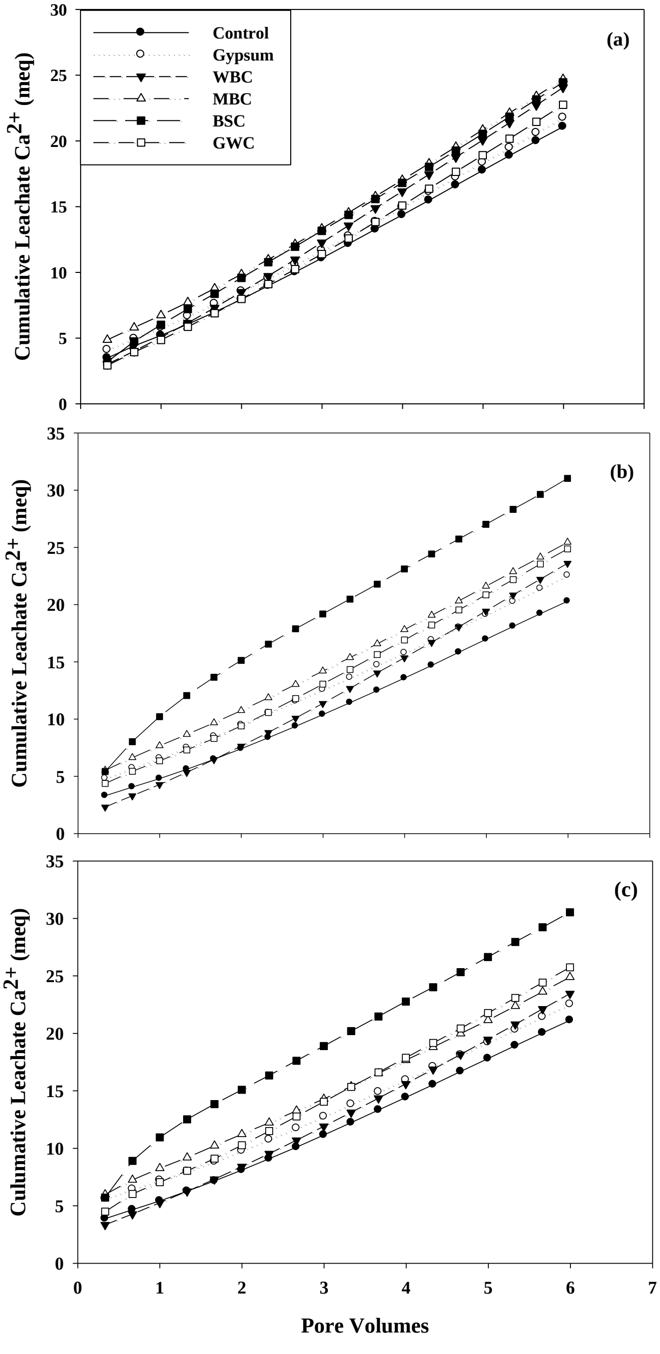

Fig. 4.6. Mean cumulative leachate losses of Ca$^{2+}$ from soils of different treatments incubated at (a) 15 °C, (b) 25 °C, and (c) 35 °C.

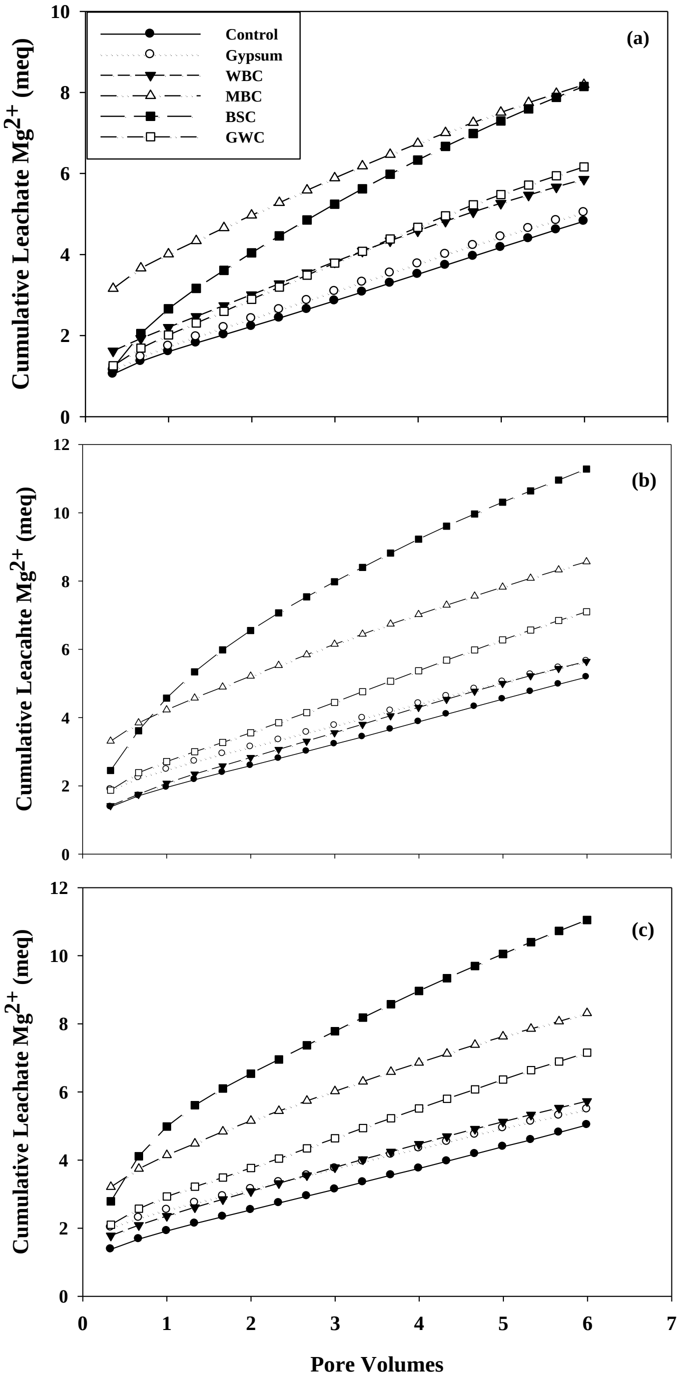

Fig. 4.7. Mean cumulative leachate losses of Mg$^{2+}$ from soils of different treatments incubated at (a) 15 °C, (b) 25 °C, and (c) 35 °C.

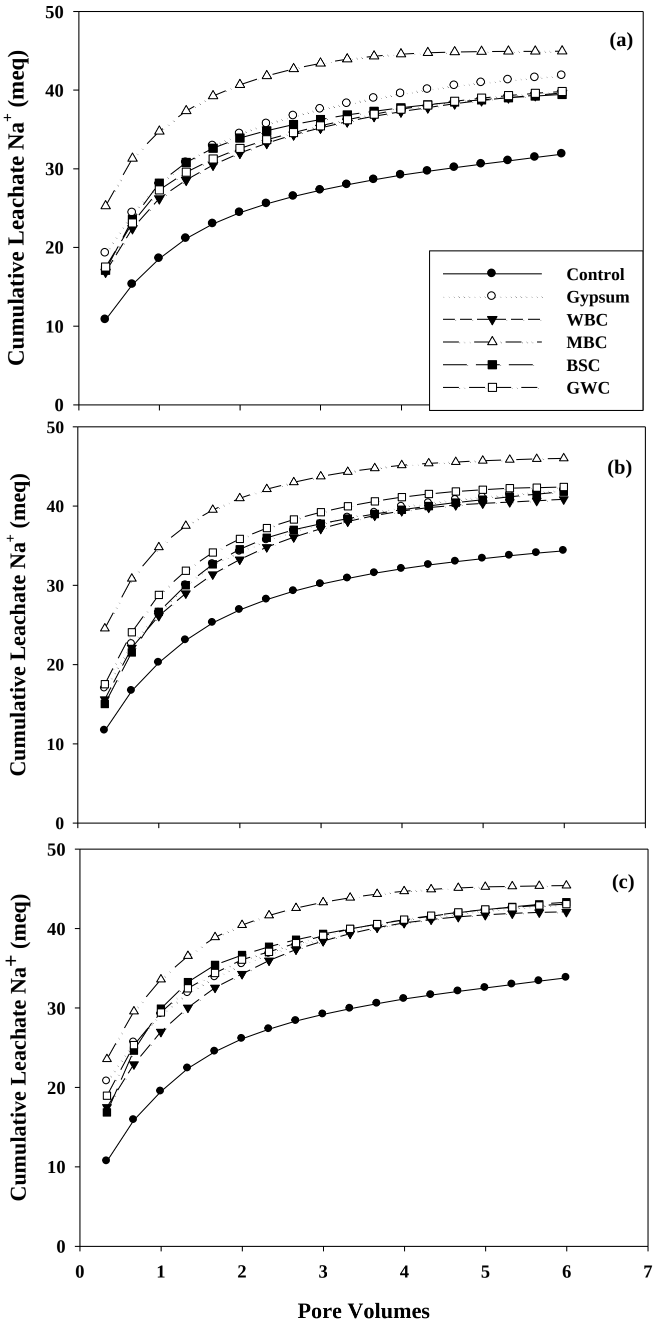

Fig. 4.8. Mean cumulative leachate losses of $Na^+$ from soils of different treatments incubated at (a) 15 °C, (b) 25 °C, and (c) 35 °C.

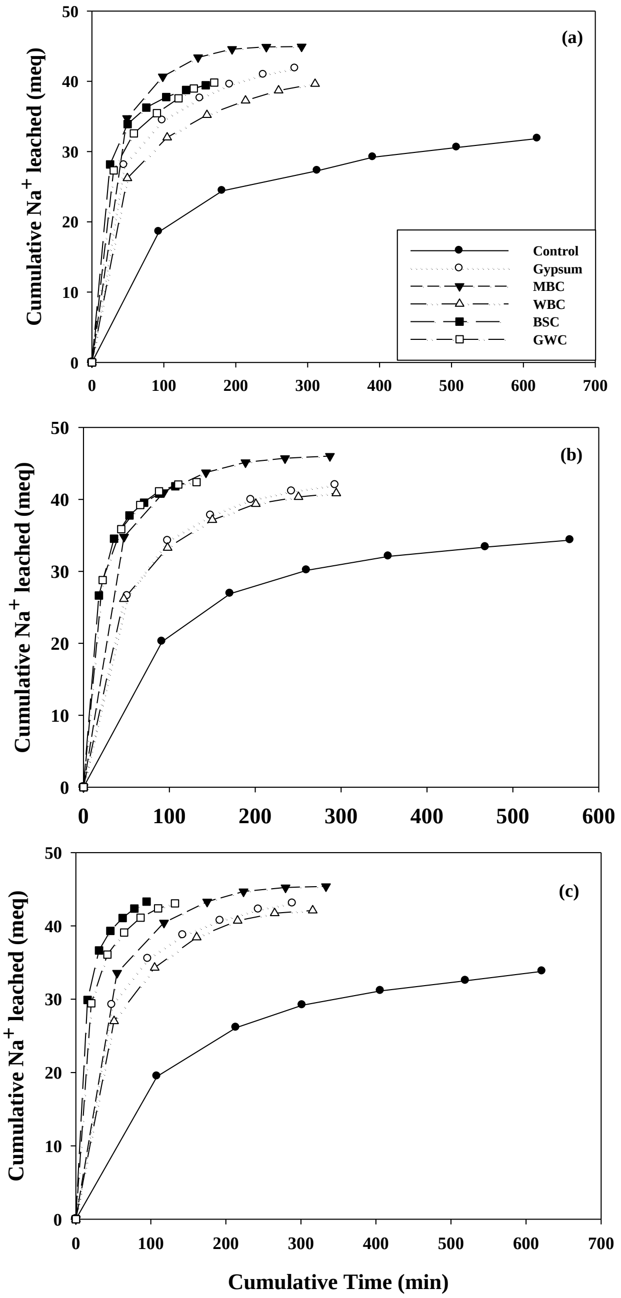

Fig. 4.9. Mean cumulative Na$^+$ lost through leachate from soils of different treatments incubated at (a) 15 °C, (b) 25 °C, and (c) 35 °C with respect to actual time.

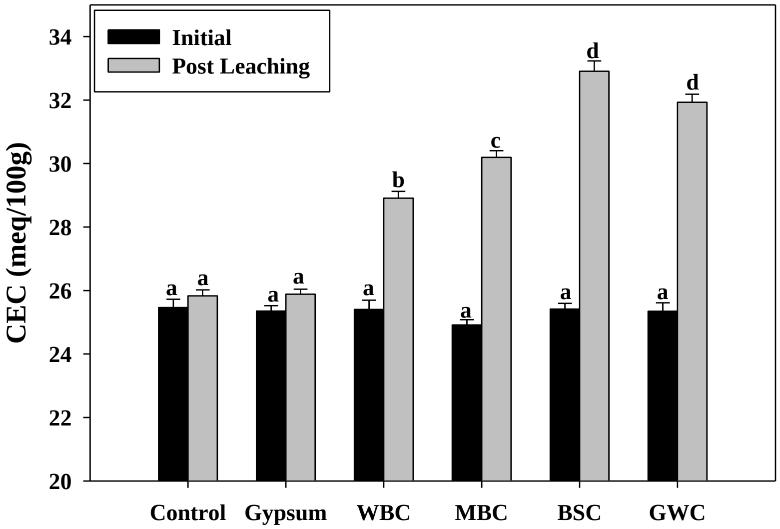

Fig. 4.10. Cation exchange capacity (Mean ± s.e.) for soils before and after leaching for different treatments. Same letters within a column series indicate no significant differences between treatments (P < 0.05, Tukey's test).

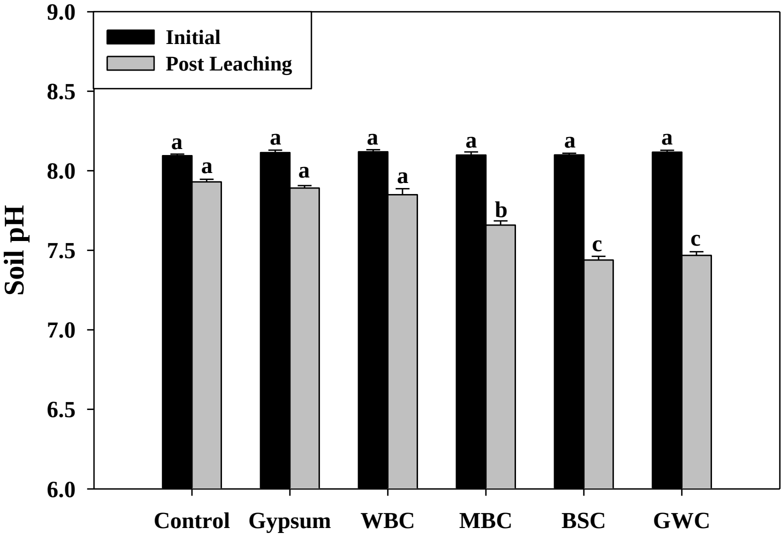

Fig. 4.11. Soil pH (Mean ± s.e.) before and after leaching for different treatments. Same letters within a column series indicate no significant differences between treatments (P < 0.05, Tukey's test).

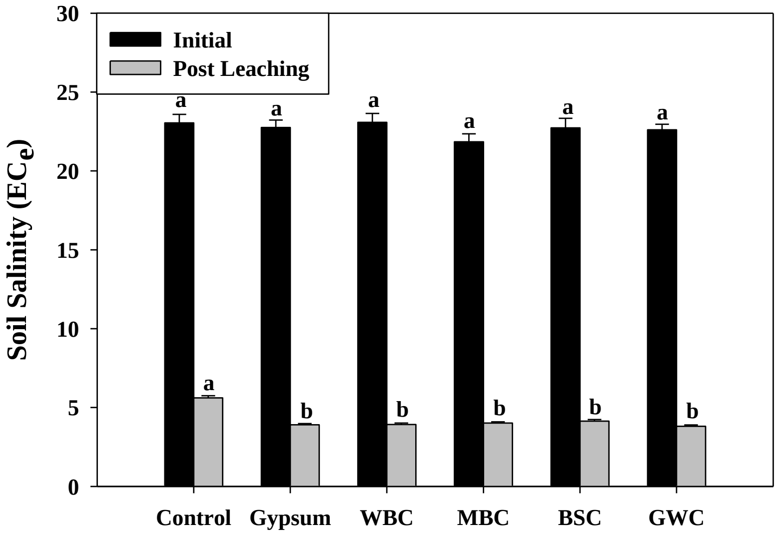

Fig. 4.12. EC (Mean ± s.e.) of soil saturated paste extracts before and after leaching for different treatments. Same letters within a column series indicate no significant differences between treatments ($P < 0.05$, Tukey's test).

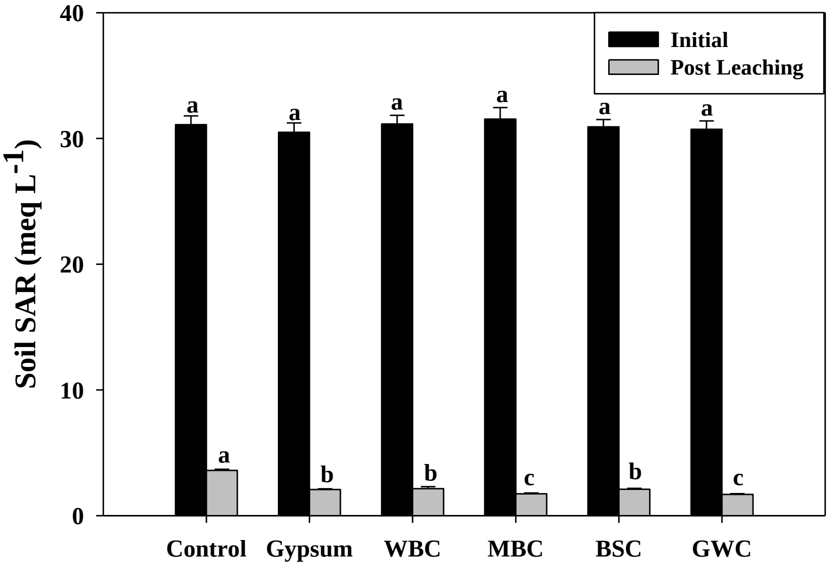

Fig. 4.13. Sodium adsorption ratio (Mean ± s.e.) of soils before and after leaching for different treatments. Same letters within a column series indicate no significant differences between treatments ($P < 0.05$, Tukey's test).

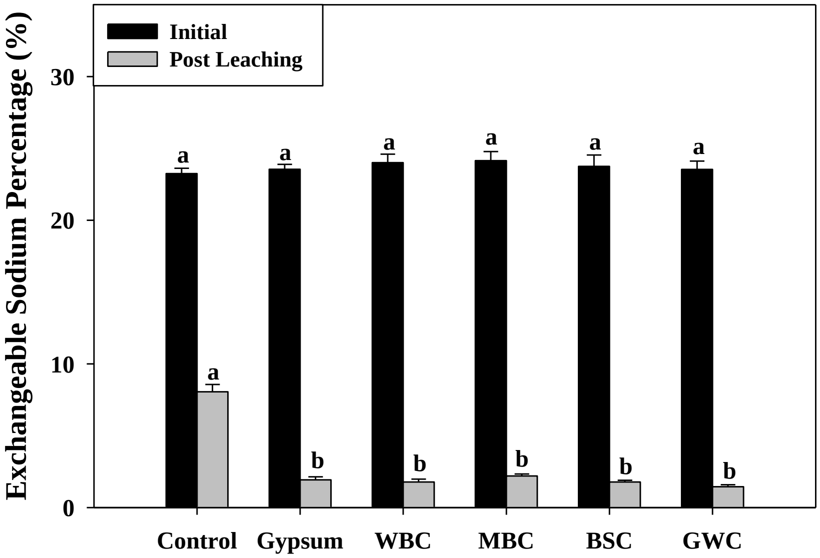

Fig. 4.14. Exchangeable sodium percentage (Mean ± s.e.) of soils before and after leaching for different treatments. Same letters within a column series indicate no significant differences between treatments ($P < 0.05$, Tukey’s test).

# 5. OVERARCHING CONCLUSIONS

The overall goal of this research was to assess the reclamation potential of biochar and composts as organic amendments when used in conjunction with reclaimed water to leach a saline-sodic soil. To summarize, both composts and biochars significantly improved physical and chemical properties of a saline-sodic soil. Also, their performance was statistically equal to that of gypsum when compared. Nevertheless, combined applications of composts and gypsum significantly improved properties directly related to $Na^+$ remediation including hydraulic conductivity, leachate losses of $Na^+$, soil SAR, ESP, and after-leaching soil exchangeable $Na^+$ concentrations, than their individual applications.

Due to their high labile C content relative to biochars, respiration rates were highest in compost treated soils. At the same time, $CO_2$ evolutions were also significantly affected by temperature and sterilization in compost treated soils. Respiration of woodchip biochar treated soils was not significantly different from controls and neither temperature nor sterilization significantly affected its respiration rates. However, $CO_2$ evolution from dairy manure biochar was significantly higher from that of woodchip biochar treatment. More labile C in manure char relative to wood chip biochar may have facilitated this short term ‘positive priming’ effect. Increasing temperature further increased this effect. Both biosolids and greenwaste composts significantly increased soil wet aggregate stability after incubation while the effect was negligible in biochar treated soils. This was likely due to the increased microbial activity following addition of easily degradable organic materials (composts), which facilitated the production of soil agglutinants such as microbial exo-polysaccharides and growth of fungi, which produce abundant hyphae that binds soil particles together. In this research, the actual polysaccharide production was not evaluated but sterilization reduced the soil aggregate stability of compost treated soils as compared to their corresponding unsterilized compost amended soils. This is an indirect demonstration that microbes are principal agents of soil aggregation. Moreover, increased aggregation was observed at higher temperatures in compost treated soils (25 and 35 °C than at 15 °C), which further explains that the rate of microbial activity determines the production of polysaccharides and thus affects the formation and stabilization of soil aggregates accordingly. Biochars on the other hand, did not cause significant changes in soil aggregate stability, an effect that can be attributed to its high recalcitrant C that did not support microbial growth. This was evident by a similar performance of biochars either in sterilized or unsterilized environments. As a further confirmation, temperature did not affect the aggregate stability of biochar treated soils. Aggregate stability of manure biochar treated soils was significantly lower relative to gypsum treated soils during the 60-day incubation. This can be ascribed to the higher $Na^+$ content of the manure biochar, which likely caused soil dispersion. Therefore, the feedstock from which the biochar was made could have a deleterious effect on soil aggregate stability. At the same time, aggregate stabilities of control or woodchip biochar treated soils were not different from either manure biochar or gypsum treated soils. Post leaching, soil aggregate stabilities generally increased for all treatments but these increases were greatest in compost and biochar treated soils.

Hydraulic conductivity improvements were highest for compost treatments followed by biochar. Both sterilization and temperature significantly affected hydraulic conductivity of only the compost treated soils. Unsterilized compost treated soils and those set at 25 and 35 °C had higher soil hydraulic conductivities. This highlights the role of microbiology in soil aggregation and associated improvements in hydraulic conductivity. At the same time, the hydraulic conductivity of the biochar treated soils was not affected by either sterilization or temperature, although their hydraulic conductivities were always significantly higher than control soils.

Cumulative leachate losses of $Ca^{2+}$ and $Mg^{2+}$ were significantly higher from compost treated soils relative to both biochars and untreated soils. Losses of these cations were affected by both sterilization and temperature in compost treated soils, specifically. Higher losses were observed in unsterilized soils and those set at 25 and 35 °C. Also, losses were greater from biosolids compost treated soils than greenwaste compost treated soils. This is conclusive evidence that microbial mineralization of these materials releases fixed cations and supplements the existing dissolved ion concentrations. Both biochars (woodchip and dairy manure biochar) increased the concentrations of these cations in the leachate, independent of sterilization and temperature. However, dairy manure biochar leached significantly more $Mg^{2+}$ than woodchip char, which can be attributed to its high initial $Mg^{2+}$ content.

Both composts and biochars had significantly higher cumulative $Na^{+}$ leachate losses relative to unamended control, which reflects their higher $Na^{+}$ leaching potential. Cumulative $Na^{+}$ losses were always highest from compost treated soils followed by biochars with the only exception of dairy manure biochar, which had relatively higher $Na^+$ losses compared to other materials. Elevated losses from the dairy manure biochar was likely due to higher initial $Na^+$, which when combined with that released from exchange sites increased its losses by leaching from soils treated with manure biochar. In general, cumulative sodium losses were not significantly affected by either sterilization or temperature in both compost and biochar treated soils. Cumulative time required for leaching $Na^+$ significantly decreased with compost and biochar applications. Soils treated with composts and biochars lost relatively higher $Na^+$ in significantly less time compared to control soils. Sterilization and temperature effects on cumulative time were statistically significant only when soils were amended with composts but not when treated with biochars. Cumulative times were significantly lower in unsterilized compost treated soils and those incubated at higher temperatures (25 and 35 °C). This demonstrates the importance of microbial activity in reducing leaching times by directly enhancing soil aggregation and hydraulic conductivity when salt affected soils are amended with composts. Decreased leaching times would mean faster reclamation offered by organic amendment applications.

Soil chemical properties including CEC, soil salinity ($EC_e$), SAR, ESP, and exchangeable $Ca^{2+}$, $Mg^{2+}$, and $Na^+$ concentrations were in general, not affected by either sterilization or temperature in any of the amended and unamended soils. Soil pH in general, was reduced in all treatments after leaching due to leaching of $Na^+$ salts. Reductions in soil pH were significantly greater in soils amended with composts, relative to other treatments. Effects of sterilization on soil pH were however, specific to compost treated soils only, with significantly lower soil pH measures observed in unsterilized soils compared to sterilized compost treated soils. This can be related to microbial releases of organic and inorganic acids. Temperature variations did not cause any significant changes in soil pH in the same compost treated soils, however. CEC increases were highest in compost treated soils irrespective of 30 or 60 day incubation. Duration of incubation was relevant in biochar treated soils, where CEC values increased only after a 60-day incubation. Leaching facilitated reductions in soil salinity, SAR, and ESP for all treatments. Adding composts and biochars produced a greater reduction in these parameters relative to the control soils.

Exchangeable $Ca^{2+}$ concentrations increased for both compost and biochar treated soils after leaching while controls lost $Ca^{2+}$, instead. Exchangeable $Mg^{2+}$ concentrations decreased after leaching for all treatments. Exchangeable $Na^{+}$ concentrations also decreased for all treatments but addition of composts and biochars facilitated much greater reductions. This result can be attributable to the release of significant amounts of $Ca^{2+}$ and $Mg^{2+}$ from organic amendments, which accelerated the displacement of $Na^{+}$ from exchange sites relative to the unamended control soils.

Use of moderate SAR reclaimed water did not affect the reclamation process. Both soluble and exchangeable $Na^{+}$ concentrations were reduced upon leaching with reclaimed water for all treatments. It is true that providing just adequate leaching helped to remove $Na^{+}$ from untreated soils. This effect could be partly attributed to the high exchangeable $Ca^{2+}$ intrinsic to the soils used in this research. However, it could be a prolonged reclamation process due to low hydraulic conductivity of untreated soils compared to those, which are treated either with composts or biochar. This will have an implication both with respect to time and water requirements in order to achieve reclamation without any amendment application. Moreover, using this water for extended periods of time could possibly result in soil degradation, due to absence of an amendment that could alleviate $Na^+$ accumulation over time by supplying divalent cations. In short, this research has found evidence to support important conclusions which are:

1. Composts and biochars can be significant sources of divalent cations like $Ca^{2+}$ and $Mg^{2+}$ and increase $Na^+$ leaching in a salt affected soil.
2. Biological activity is key in improving soil aggregate stability and hydraulic conductivity while reclamation of chemical properties is driven by material chemistry.
3. Soil temperature enhances the rate at which physical properties can be reclaimed by directly influencing microbial activity.
4. Labile C content in organic amendments largely determines their efficiency to significantly improve soil physical properties by influencing microbial activity.
5. Reclamation by biochar is physiochemical while composts provide a better and comprehensive remediation when both physiochemical and biological factors act together.

These laboratory studies were conducted in controlled conditions greatly reducing the variability. Out in the field, variability is inevitable and performance of these materials could differ. Also, field studies are generally setup to run for extended periods of time which could possibly help us understand the effects of leaching with reclaimed water on a long term basis in the presence of such amendments. Therefore, future studies should focus on testing these materials under field conditions. Additionally, it would be interesting to evaluate the effects of composts and biochars in soils with varying textures, as soil texture is known to considerably influence soil aggregation and hydraulic conductivity. Furthermore, it is worth investigating the effects of active vs. cured composts, as we found in this research that labile C content would essentially govern the potential of such amendments in improving soil physical properties due to differences in microbial mineralization of added substrates and subsequent release of soil agglutinants. Biochars made from different feedstocks at different temperatures could also be tested, as feedstock and pyrolysis temperature largely determine the physical and chemical characteristics of a biochar.

Finally, this research has shown that simultaneous use of organic amendments such as composts and biochars with reclaimed water can successfully remediate a saline-sodic soil. This therefore, offers farmers a low cost method to remediate salt affected soils and reduce their dependence on scarce fresh waters and expensive inorganic amendments. Moreover, the benefits associated with biochar application to degraded soils can strike two goals at once, their reclamation and an additional sink to sequester atmospheric carbon.

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