

SOIL NUTRIENT AVAILABILITY PROPERTIES OF BIOCHAR

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ABSTRACT

Soil Nutrient Availability Properties of Biochar

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Biochar's high porosity and negative surface charge allows for numerous soil and plant benefits such as increased water retention, high nutrient availability, and plant growth.

By analysing biochar's effect of all of these factors, a system can be put in place in which soils can be remediated with the proper soil amendments. This report discusses and tests the effects of varying rates of biochar on pH levels, cation exchange capacity, and nutrient exchangeability (of calcium, magnesium, sodium, and potassium) in soil.

Corn plants were also grown in soils of varying amendment types and analysed for plant growth and germination to determine soil effects on the plant.

Testing showed significant differences between treatment types in all areas tested except plant germination. A 2:1 ratio of biochar to compost produced the best overall results for the soil used in testing. This treatment maintained acceptable levels of exchangeable nutrients while raising pH and cation exchange capacity, and also raised the plant growth in the soil by 30%. However, for added soil health, gypsum or calcium fertilizer should be added to the soil to remediate low calcium exchangeability. This testing confirmed that biochar does have a strong positive influence on soil and plant health when used in combination with compost.

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Chapter 1: Introduction

Dating back as early as 2000 years ago, biochar has been used along the Amazon Basin by natives as a soil amendment for soil with poor nutrient retention. This soil is referred to as *terra preta* or “dark earth” and is commonly sold as potting soil in Brazilian markets due to its high nutrient content. Anthropologists believe *terra preta* was a result of cooking fires and intentional placement of charcoal in the soil (1).

Biochar is classified as a fine-grained, highly porous charcoal formed from biomass (2). The internal structure is composed primarily of an amorphous carbon phase with a small percentage of graphene sheets interspersed within the material (3). These two structural components in biochar allow for innovative applications in soil science and sustainability efforts.

Biochar has the potential to increase nutrient availability in many types of soil, particularly when used in combination with compost. The intent of this study is to further determine the extent of soil nutrient availability improvement based on biochar application to soil with and without compost.

1.1 What is Biochar?

Biochar is produced by thermal decomposition of organic material under a limited supply of oxygen at relatively low temperatures (<700C). This process mirrors the production of charcoal. Biochar distinguishes itself from charcoal in that it is produced with the intent to be applied to soil to improve soil productivity, carbon (C) storage, or water filtration.

Burning biomass in a fire creates ash, which mainly contains minerals such as calcium (Ca) or magnesium (Mg) and inorganic carbonates. A small portion of vegetation is only partially burned in areas of limited oxygen supply, which becomes char (3).

The defining property of biochar is the organic portion with a high carbon content, which mainly comprises so-called aromatic compounds characterized by rings of 6 carbon atoms linked together without oxygen or hydrogen. If these rings were arranged in perfect stacks, the structure would be referred to as graphite. Under temperatures used for biochar production, graphite does not form to any significant extent. Instead, much more irregular arrangements of carbon form, containing oxygen, hydrogen and minerals, depending on the feedstock. Biochar has avoided intense characterization up to this point due to its complexity and extreme variability. Efforts to characterize biochar began in the 1920's by John D. Bernal and are ongoing to this day (3).

'Activated charcoal' is a term used for biochar-type substances, as well as for coal, that have been 'activated' in various ways using, for example, steam or chemicals, often at high temperatures (>700C). This process is intended to increase the surface area for use in industrial processes such as filtration (3).

In 1927, Morley writes in the first issue of *The National Groundskeeper* that 'charcoal acts as a sponge in the soil, absorbing and retaining water, gases and solutions. As a purifier of the soil and an absorber of moisture, charcoal has no equal.' (3).

Paring and burning, where soil is heaped onto organic matter (often peat) after setting it on fire, produces significant increases in farm revenue. A common practice in China involves waste biomass being mixed and covered with soil, and set on fire to burn over several days until a black earth is produced, which reportedly improved plant vigor.

Despite early descriptions and research, global interest in biochar only began in the past few years (3).

Research found that biochar-type substances are the explanation for high amounts of organic carbon and sustained fertility in the Amazonian Dark Earths known as Terra Preta de Indio.

Unequivocal proof has become available showing that biochar is not only more stable than any other amendment to soil and increases nutrient availability beyond a fertilizer effect, but that these basic properties of stability and capacity to hold nutrients are more effective than those of other organic matter in soil. This ability is rooted in specific chemical and physical properties, such as the negative surface charge that allows cations to attach to biochar's surface, resulting in much greater nutrient retention (3).

1.2 Pyrolysis

Pyrolysis is the direct thermal decomposition of biomass in the absence of oxygen to obtain an array of solid (biochar), liquid (bio-oil) and gas (syngas) products. Pyrolysis techniques can be altered to achieve higher energy outputs or higher biochar production. When biochar is used as a soil amendment, it is slowly oxygenated and transformed in a physically stable manner, leading to interesting chemical properties such as cation exchange capacity and reduction of soil acidity (4).

As the pyrolysis material is broken down, it releases gas. This is the first step in the combustion or gasification of biomass. All the processes involved in pyrolysis, gasification, and combustion can be seen in a match. The flame provides heat for pyrolysis, and the resulting gases and vapors burn in a process called flaming combustion, leaving behind char. When the match is put out, the remaining wood continues to bake, or pyrolize, releasing a smoke composed of tar droplets as it cools (3, Figure 1).

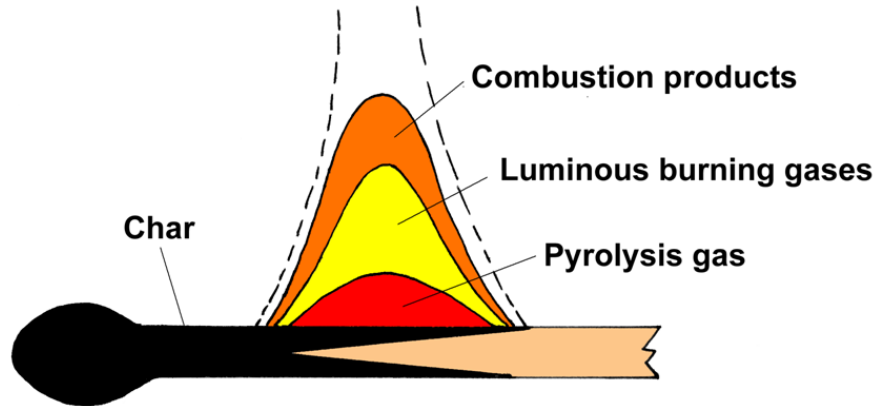


Figure 1: A match details the pyrolysis process (4).

Pyrolysis systems use kilns and retorts and other specialized equipment to contain the baking biomass while excluding oxygen. The reaction vessel is vented, to allow pyrolysis gases to escape. Pyrolysis gases are often called “syngas”. The process becomes self-sustaining as the syngas produced is combusted, and heat is released (5).

There are two types of pyrolysis systems in use today: fast pyrolysis and slow pyrolysis. Fast pyrolysis tends to produce more oils and liquids while slow pyrolysis produces more syngas. The type of pyrolysis used is chosen based on which output should be optimized (5).

1.3 Stoves

To those who live in the developed world, it may come as a surprise to learn that more than two billion people still cook and heat their homes with primitive stoves or open fires. These inefficient technologies emit air pollution that can exacerbate global warming. People struggle to gather enough biomass fuels to meet their needs. And in many cases, the demand for wood accelerates deforestation.

For nearly two decades a small group of researchers and development advocates has worked to improve household biomass energy technologies. Now concerns over global

warming have added a new reason to accelerate the transition to cleaner biomass energy use in the developing world. New stove technologies can produce both heat for cooking and biochar for carbon sequestration and soil building. Limited testing indicates that these stoves are much more efficient and emit less pollution (5).

The UN Environment Program now recognizes that Atmospheric Brown Clouds (ABCs) are a major contributor to climate change. ABCs are caused by particulate emissions from combustion of biomass and fossil fuels such as black particles (soot) that heat the atmosphere by absorbing sunlight, and white particles that reflect sunlight and contribute to cooling (6).

Black carbon has a significant effect on global warming, second only to carbon dioxide. However, the atmospheric residence time of black carbon is only a few weeks, while CO₂ emissions stay in the atmosphere anywhere from 30-95 years. This means that we have an opportunity for immediate action to decrease environmental breakdown by reducing black carbon emissions (6).

Biochar-producing stoves are not yet a mature technology, and indeed, the emissions from the few designs that have been developed have not yet been systematically tested. However, there are good reasons to believe that they will be as clean as or cleaner than other gasifier stoves that do not retain the biochar, but combust it (5).

The two main stove types used for pyrolysis are the TLUD stove and the anila stove. The TLUD operates as a gasifier by creating four basic zones within the stove: raw biomass, flaming pyrolysis, charcoal and gas combustion. Fan-forced TLUD stoves retain the charcoal layer without burning it more easily, but charcoal can also be retained by a naturally draft TLUD if it is properly timed and quenched (5, Figure 2).



Figure 2: The TLUD stove breaks down into 4 pyrolysis zones for a proper burn (5).

Anila-type stoves use two concentric cylinders of different diameters (Figure 3). Biomass fuel is placed between the two cylinders and a fire is lit in the center. Heat from the central fire pyrolyzes the concentric ring of fuel. The gasses escape to the center where they add to the cooking flame as the ring of biomass turns to char (5).

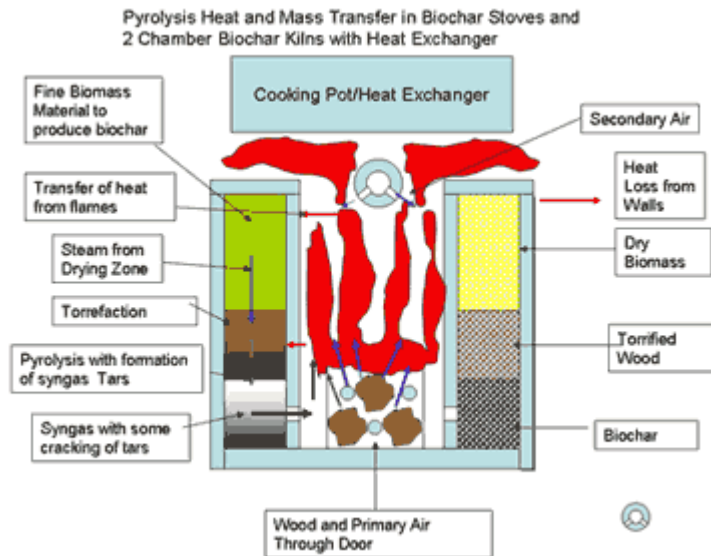


Figure 3: The Anila stove uses concentric rings around a fire to pyrolyze biomass (5).

1.4 Deforestation

The current method used in deforestation is called slash and burn, in which trees are cut down and then burn to make way for fields. Only 3% of the carbon from organic material is left in the soil using the slash and burn technique (1). Switching from slash and burn to slash and char techniques in rainforests can decrease both deforestation and carbon dioxide emission, as well as increase the crop yield.

Switching to slash and char can sequester up to 50% of the carbon that would be released into the atmosphere due to decomposition (6). Additionally, the many benefits of biochar to the soil would allow for sustainable agriculture production, compared to non-amended soils, which become quickly depleted and unusable. Additionally, the biochar produced can be applied by the currently used tillage machinery or equipment used to apply fertilizer (2).

1.5 Climate

Fossil fuels are carbon-positive, meaning they produce carbon dioxide and release it into the atmosphere. Ordinary biomass fuels are carbon neutral and their carbon footprint technically does not exist. Sustainable biochar systems can be carbon negative because they hold a substantial portion of the carbon dioxide in soil. The result is a net reduction of carbon dioxide in the atmosphere. Biochar-producing stoves have lower emissions of harmful greenhouse gases, making biochar a viable candidate to sequester carbon in soils, and reduce the use of fossil-fuel based fertilizers (5).

In the natural carbon cycle, plant matter decomposes rapidly after the plant dies, emitting carbon dioxide; the overall natural cycle is carbon neutral. Instead of allowing the plant matter to decompose, pyrolysis can be used to sequester some of the carbon

in a much more stable form. Biochar thus removes circulating carbon dioxide from the atmosphere, making it a carbon-negative process, as shown in Figure 1 (5).

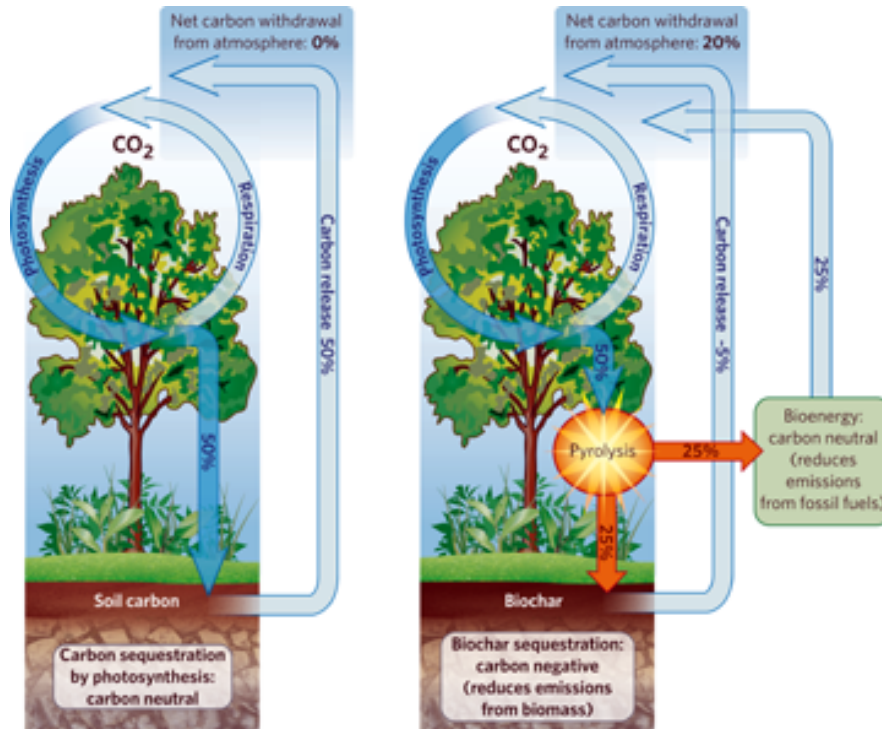


Figure 4: Carbon neutral processes in plants recycle released carbon by photosynthesis (left). Biochar uses pyrolysis and carbon capture to reduce emissions, making the process carbon negative (5).

Agricultural waste that already remains unused can be pyrolyzed and used to improve the soil and reduce greenhouse gas emissions. The use of pyrolysis also provides an opportunity for the processing of municipal waste into useful clean energy rather than increased problems with land space for storage. Estimates place residence time of carbon sequestration anywhere between 100-10,000 years (7). Lab experiments confirm a decrease in the rate of CO₂ release with increasing temperature, so carefully controlled charring of plant matter can increase the soil residence time of the biochar C (4). According to a study by the International Biochar Initiative, counting only the impacts of biochar burial in soil, and without considering the displacement of energy from fossil

fuels, we can conservatively offset one quarter of a gigaton of carbon annually by 2030 (5). Optimistically, we could achieve one gigaton of offsets annually before 2050 (Figure 5).

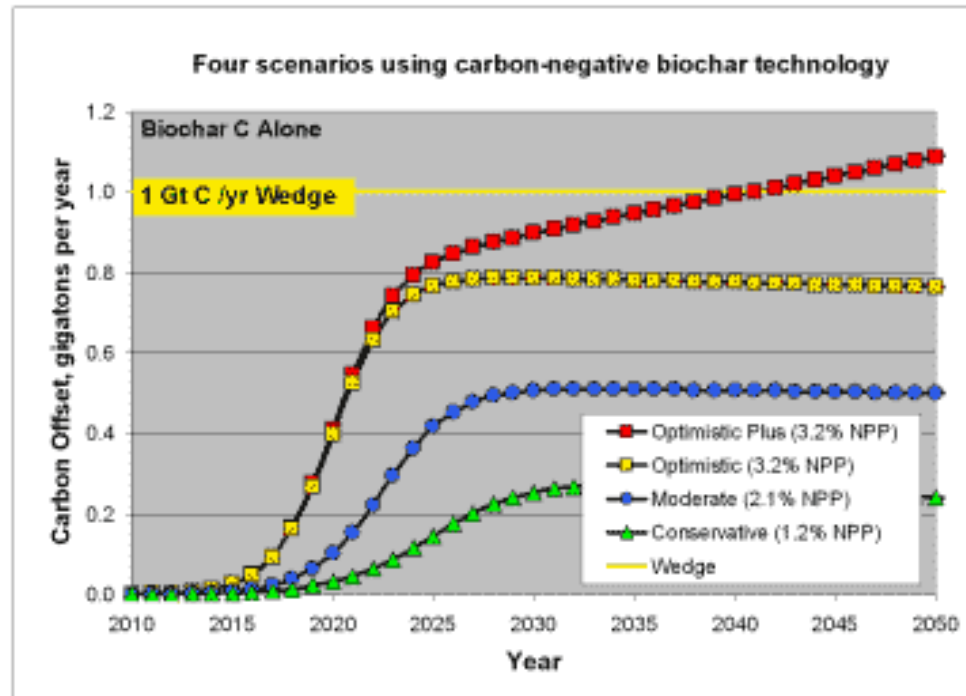


Figure 5: Carbon offset estimates using biochar technology can offset carbon emissions by 1 gigaton before the year 2050 (5).

1.6 Soil Enhancement

Biochar as a soil amendment increases the Cation Exchange Capacity (CEC) of the soil, which represents the soil's ability to retain nutrients in the soil to be taken up by plants. This increased CEC allows for more active microbes and nutrients, leading to improved soil fertility. This increase in microbial growth also allows for better moderation of soil acidity, which can prevent toxic effects to the plants. The porous surface of biochar enables the soil to retain water more efficiently and reduce the release of nitrogen into the ground water, improving water quality (6). Soil aeration is also drastically improved due to macroporosity of biochar (3). Utilizing biochar can improve nearly any type of soil,

particularly soils with low nutrient levels and low rainfall (6). In fact, based on recent research, biochar is more stable than any other soil amendment and its ability to retain nutrients is more effective than that of any other organic matter used in soil (3).

The composition of biochar depends on the feedstock used and the duration and temperature of pyrolysis. As an example, biochar produced from feedstocks with high potassium levels often have higher potassium contents than those with lower potassium levels in the original feedstock. However, pyrolysis conditions greatly affect nutrient properties contents and so it is crucial to test small portions of biochar to check for ideal properties based on soil needs (5).

1.6.1 Nutrient Availability

Nutrient availability will differ depending on the soil type and environmental conditions present in the soil. There are 3 levels of nutrient availability in all soil types. Unavailable nutrients are found in crystalline structures of feldspars, clay minerals and micas, which are part of the soil (Figure 6). Plants cannot use nutrients in these insoluble forms. However, these minerals eventually break down with time, and small quantities of nutrients are released to the soil solution through this process (8).

Fixed Nutrients become slowly available to plants over the growing season. During wetting and drying of the soil, nutrients become trapped between mineral layers (Figure 6). Once the soil gets wet, some of the trapped ions are released to the soil solution (8). The slowly available nutrients are not usually measured in regular soil testing and this testing does not include fixed nutrients.

Exchangeable nutrients are readily available nutrients, which plants can easily absorb (Figure 6). These nutrients are held on the surface of clay particles and organic matter in soil and are easily released when plants absorb nutrients from the soil solution (8).

Exchangeable nutrients are measured in most soil testing and are the focus of this experiment.

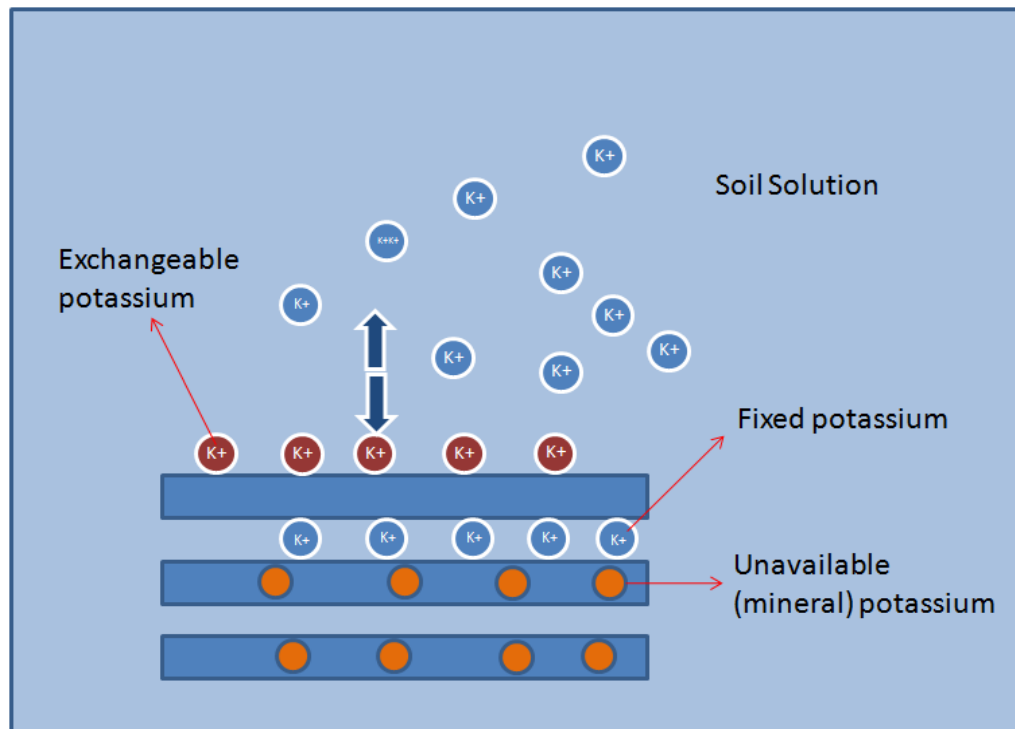


Figure 6: Available nutrients are easily accessible to plants while unavailable and fixed nutrients are difficult to release for plant use. The above is an example of available and unavailable potassium in soil (8).

1.6.2 pH Effects

The pH scale (Figure 6) ranges from 0-14, with values greater than 7 considered basic (or alkaline), and values less than 7 considered acidic. A pH of 7 is considered neutral and is neither acidic nor alkaline. An acid is defined as a proton donor that increases the concentration of positively charged ions, forming acidic soil with a pH value less than 7. A base is a proton acceptor, which reduces the concentration of positively charged ions in the soil, which causes a pH above 7 (9).

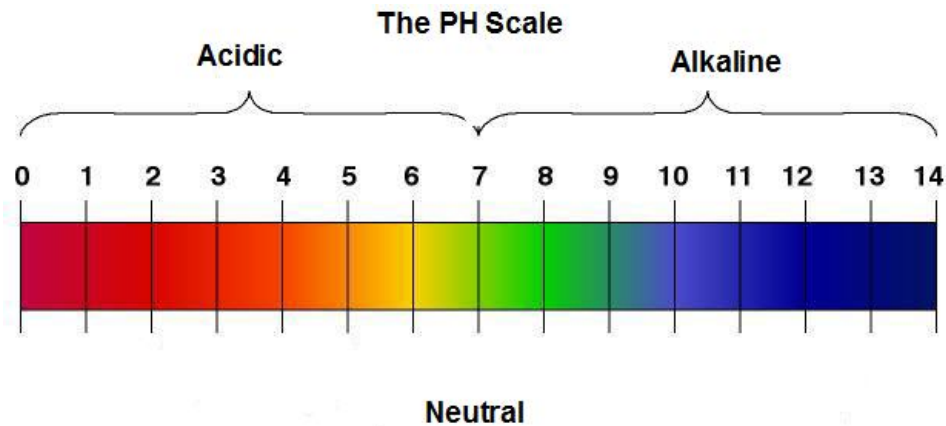


Figure 7: The pH scale is split by acidic vs. alkaline. Soil is ideally between 6-7 on the pH scale (10).

In terms of soil quality, there is little intrinsic value of pH to soil. Many plants can adapt to a large range of pH values with no negative effect on plant growth. However, pH is commonly used as a proxy to evaluate nutrient availability and potential toxicity of various ions, as these soil characteristics strongly alter soil pH levels. Soil pH also strongly affects both plant availability of most nutrients and the potential toxicity of various ions in the soil (11).

Previous biochar research reveals a trend of increasing pH with biochar application. This is due to organic matter such as biochar having a negative charge on the surface, increasing the alkaline composition in the soil. This also implies that compost, another form of organic matter, will also increase soil pH (3).

Evidence suggests that raising soil pH may be biochar's most important documented contribution to improved soil quality. Soil pH mostly influences the relative availability of nutrients. Aluminum toxicity is a common problem at low pH levels that causes damage to plant growth. Aluminum toxicity is widespread problem in soil, and biochar can be an easily available solution to combat it (3).

pH can measure only the concentration of hydrogen ions in the soil solution, or 'active' hydrogen ions. Acidic soils contain only a small fraction of the total hydrogen in the soil solution at any one time. Most of the hydrogen ions are adsorbed to the surface of the clay and organic matter within the soil, and is referred to as non-active or 'reserve' hydrogen ions (9).

1.6.3 Calcium

Calcium plays a crucial role in proper soil nutrition and plant development. Appropriate Calcium levels are necessary for decent root integrity (12). Without good root integrity, plants can have a difficult time reaching nutrients and water vital for healthy plant growth. Calcium also promotes proper cell elongation. This strengthens cell walls, giving stability and binding cells together. Strong cell walls also help protect the plant against diseases that impair plant cell walls. Plants with sufficient Calcium levels also benefit from protection against heat stress because it improves stomata function and assists with induction of heat shock proteins (12).

Calcium also helps to stabilize soil structure. Adsorbed sodium might cause the soil to crack when dry and swell up when wet, but replacing sodium ions with calcium prevents this problem (12).

Calcium plays a balancing act with other positively charged ions, such as sodium (Na^+), potassium (K^+), and magnesium (Mg^{+2}). Applying too much of these other positively charged ions may decrease calcium uptake by plants. Sodium ions can also replace the adsorbed calcium, damaging soil structure and decreasing calcium availability.

Another common issue occurs when free calcium accumulates in the soil solution (e.g. when soil pH is high), in which calcium can form insoluble compounds with phosphorous, causing a decrease in both calcium and phosphorous availability in soil.

The optimal range for exchangeable calcium in soil is 65-85% (11). The percentage of exchangeable calcium represents ratio of exchangeable calcium compared with all other nutrients in the soil. The exchangeable percentage of all nutrients together will total 100%. Calcium deficiency in soil can lead to curling of young leaves or shoots scorching or spotting on young leaves, poor growth, leaf tip burn, stunted roots, and damage to fruit (12).

Calcium deficiency is commonly remedied by adding gypsum or a calcium fertilizer to acid soils, aiming at a pH of 6.5, unless the subject plants specifically prefer acidic soil (10). Organic matter should be added to the soil to improve its moisture-retaining capacity. However, due to the root cause of deficiency being poor transport of calcium within plants, the problem cannot generally be cured by directly applying calcium to roots (12).

1.6.4 Magnesium

Magnesium is essential for many critical plant functions, such as photosynthesis (Mg is the central element of chlorophyll), enzyme activation, sugar synthesis, nutrient uptake control, and many others. Magnesium also aids in carrying phosphorus in the plant and forming plant oil and fat (10).

Soil pH is a strong indicator of exchangeable magnesium in soil, as low soil pH decreases magnesium availability and high soil pH increases availability. Low CEC soils (soils that do not retain exchangeable nutrients well) hold less magnesium, while high CEC soils can hold much more magnesium. However, if a high CEC soil does not happen to have strong levels of magnesium, it will tend to release less of the magnesium that it holds to the crop. Manganese has also proven to directly reduce magnesium levels in soil. Cation competition plays a large role in the magnesium levels in soil. High levels of potassium or calcium in soil tend to provide less magnesium for plants (10).

High application rates of other cations, especially potassium, can reduce the uptake of magnesium by soil. This is most common on grasses, and corn seems to be the most sensitive to this process (10).

Soil has an ideal range of 6-12% exchangeable magnesium, however exchangeability of magnesium can increase to 40% without adverse effect on crop production (11).

1.6.5 Sodium

Sodium is critical to healthy soil and plant growth, but only in small amounts. The presence of excessive amounts of exchangeable sodium causes soil aggregates to disperse into their constituent individual soil particles. This is known as deflocculation and occurs in sodic soil (soil above 6% exchangeable sodium).

Deflocculation occurs because unlike the polyvalent cations of calcium and aluminum, sodium is monovalent. When sodium is adsorbed onto negatively charged particles, it cannot form a bridge between the particle it is attached to and any nearby particles. This means the two particles will repel each other and create a dispersed soil condition (11).

Sodium imbalances in soil attribute mostly to the physical properties of soil and result in poor soil structure, causing issues with both germination and plant growth. Poor soil structure also leads to slow water uptake in the soil as well as poor soil drainage.

A sodic soil contains a high level of sodium relative to the other exchangeable cations (i.e. calcium, magnesium and potassium). A soil is considered "sodic" when the Exchangeable Sodium Percentage (ESP) is 6% or greater. The ideal exchangeability range for sodium is between 1-6%. ESP above 6% is considered sodic and can lead to poor soil structure and many physical issues in the soil structure (11).

1.6.6 Potassium

Potassium is an essential plant nutrient and is required for proper growth and reproduction of plants. Potassium is considered second only to nitrogen, when it comes to nutrients needed by plants. It affects the plant shape, size, color, taste and other measurements attributed to healthy produce (13).

In Photosynthesis, potassium regulates the opening and closing of stomata, and therefore regulates CO₂ uptake. It triggers activation of enzymes and is essential for production of Adenosine Triphosphate (ATP), an important energy source for many chemical processes within plants. Potassium also plays a large role in the regulation of water in plants and is known to improve drought resistance (13).

Potassium assists in the activation of many growth-related enzymes in plants, and therefore aids in proper plant growth. Any potassium deficiency in soils can cause abnormalities in plants (usually related to plant growth).

The first symptom of potassium deficiency is commonly Chlorosis, shown in plants as scorching of plant leaves with yellowing of the margins of the leaf. Slow or stunted growth can also occur, as potassium is an important growth catalyst in plants.

Poor potassium uptake will also result in less water circulation in the plant, making it more susceptible to drought and temperature changes. Defoliation can also occur in potassium-deficient soils. This results in plants losing their leaves sooner than they should (13).

Several factors can affect the ability of plant to absorb potassium from soil, such as oxygen level, which is necessary for proper root function and uptake of potassium. High moisture levels also ease the ability for plants to absorb potassium.

Although the ideal range for exchangeable potassium is low (2-5%), potassium is considered non-toxic even when much higher than the ideal range of potassium exchangeability. Although, soils rarely contain greater than 10% potassium because it is

slow to weather out of soil minerals and 90-98% of soil potassium is locked up in minerals and is not exchangeable in the soil (11).

1.6.7 Ca:Mg Ratio

Evidence suggests that proper Ca:Mg ratios will improve soil structure, reduce weed populations, and improve forage quality. Most importantly, an appropriate Ca:Mg ratio can reduce leaching of other plant nutrients and improve the balance of most soil nutrients. This ratio has proven to be important to nutrient balances within soil because both calcium and magnesium have a strong effect on the exchangeability of many other ions in the soil (14).

The Ca:Mg ratio should be much greater than 1:1, and the ideal Ca:Mg ratio is considered to be 5:1. Many California soils have serpentinite, which leads to high Magnesium levels and lowers the Ca:Mg ratio. For soils with low Ca:Mg ratios, the best method of remediation is adding gypsum or calcium fertilizers to increase calcium levels and counteract the excessive magnesium levels (11).

1.6.8 Cation Exchange Capacity

The Cation Exchange Capacity (CEC) represents the total amount in meq/100 g soil of positively charged exchangeable ions that the soil can hold. The unit meq/100 g soil is the standard unit used to measure CEC and measures all nutrients based on their atomic weight to give a more accurate measurement of the true volume of nutrients in the soil. A higher CEC indicates a higher capacity of the soil to adsorb and hold nutrients, and therefore higher nutrient availability (15). Biochar is expected to increase CEC due to its ability to raise nutrient levels and nutrient availability in soil (3). Many local soils contain high clay and organic matter, leading to CEC of >30meq./100 g soil. Sandy soils near the coast are low in clay and organic matter <10meq./100 g soil (11).

1.6.9 Cation Interactions

Many of the major cations such as calcium, magnesium, potassium, sodium, ammonium, iron, and aluminum are in competition with each other. In other words, if any of these cations are found in large quantities in the soil, the exchangeability of other cations will be reduced and can lead to an imbalance of ions in the soil. For example, potassium is a strong competitor with magnesium and whenever the soil potassium level is higher than desired, plant magnesium levels are often reduced. This effect occurs sooner and more severely in grasses, especially corn, than in other crops (16).

For many years, there have been a few people who claim that there is an "Ideal" ratio of the three principal soil cation nutrients (K, Ca, and Mg). This concept probably originated from New Jersey work by Bear in 1945, stating the ideal ratio of principal cations is 65% Ca, 10% Mg, and 5% K (11).

Chapter 2: Procedure

This experiment is intended to show trends in soil nutrient availability based on various application rates of biochar and compost. Corn plants were grown in 5 soil treatment types and compared based on germination and plant growth. pH levels of each treatment type were compared to determine whether soil amendments cause a significant change in soil acidity. The nutrient analysis includes trends in Calcium, Magnesium, Sodium, and Potassium, all of which are vital to plant growth. Nutrient values were then converted to calculate Cation Exchange Capacity in each soil treatment to note any changes in CEC based on treatment type.

2.1 Set-up

In order to determine soil properties, this experiment used 5 treatment types of various soil amendment applications. Treatment 1 is considered the control group, as it is purely soil with no amendments added. Treatment 2 incorporates purely compost with no biochar additive. Treatment 3 involves combining compost and biochar in a 2:1 ratio. Next, a 2:1 ratio of biochar to compost was formed to create Treatment 4. Treatment 5 uses only biochar as a soil amendment with no compost added. Treatments 3 and 4 were measured in ratios to allow this procedure to transfer well into soil practices. Most people that apply soil amendments will not have a way to measure the volume of their soil in comparison to their soil amendment. I have chosen ratios to make this amendment process simple for those who would like to apply this practice on a larger scale than I used for this experiment.

Each of these treatments was placed in what is referred to as a “torpedo tube.” These torpedo tubes are long, thin planters that are shaped like a torpedo. Each torpedo tube is approximately 9 inches long and 3 inches in diameter at the opening. Due to the size

and shape of these tubes, only one plant is grown per tube. Planting more than one seed in each tube could impede growth due to lack of room for proper root growth and could skew the data in this experiment. To ensure reliable data, 5 samples of each treatment type were created. With 5 samples of 5 treatments, this brings the total number of samples to 25.

In addition to the original experimental design, a smaller experiment to analyze germination based on treatment type was also set up. In order to test germination, 5 clay pots were prepared with each of the 5 formerly mentioned treatments, bringing the total to 5 pots for this testing. Each clay pot contained 10 corn seeds, which were left to grow over the next 6 weeks. At the end of 6 weeks, the number of properly germinated corn plants was recorded for each treatment.

Both of the experiments performed used corn seeds as the growth medium due to its quick plant growth and ideal planting season. Corn receives the most benefit from planting in mid-May, which is when this 6-week experiment was planned to run (17)

2.2 Germination Measurement

Checking plant germination is a simple procedure in this case. After the 6 week growing stage for the corn seeds, each treatment was checked for the number of corn stalks grown in each treatment. Since 10 corn seeds were placed in each clay pot, relative germination capabilities can be determined based on percentage of plants that achieved proper germination. Treatments were then compared using ANOVA statistical analysis to determine whether any significant differences in germination were observed.

2.3 Plant Growth Measurement

All plants used in these experiments were uprooted after 6 weeks, at which point all samples growing individually in torpedo tubes were measured for plant height. Each corn stalk was measured starting from the base of plant roots, along the stem, to the top of the highest leaf. All leaves on each plant were gathered together along the stem to give accurate length measurement. These values were then analyzed using ANOVA statistics to evaluate differences in plant length based on treatment.

2.4 pH Determination

Several different methods have been developed to determine soil pH. Most existing measurement methods represent differences in the ratio of soil to water. Common examples are a saturated paste, which is most common in California, and a 1:1 and a 1:2 ratio of soil to water. The saturated paste soil:water ratio varies with the soil texture and is generally about 1 to 0.5 to 1 to 0.8. In general, the soil pH tends to rise as the soil sample is diluted. This is true because the concentration of hydrogen ions is being diluted with more water.

In addition, some laboratories use 0.01 molar calcium chloride instead of water to test the soil pH. This solution reduces the salt effect due to the fertilizer because the calcium chloride is a salt. Soil pH values determined with 0.01 molar calcium chloride are usually 0.5 to 1.0 pH units lower than pH values on the same soil with water only (11).

The measurement of pH is easy to miscalculate due to the many factors that must be considered when measuring pH. A standard buffer solution must be used to standardize the pH meter before any soils are analyzed. Soil pH can be more accurate than the accuracy of the buffers used to standardize the instrument. The National Bureau of

Standards (NBS) has established several strong buffer solutions that will resist a change in pH. Most soil investigations use buffer pH 7 for any pH testing (11).

Preparation for testing pH begins by weighing 10 g of soil with any amendments and transferring it to a clean 50 mL plastic beaker. 20 mL of deionized water is added to the soil and stirred with a clean spatula. The suspension is stirred frequently for the next 15 minutes.

A beaker of fairly strong acid (about 1 normal) is used to rinse the electrodes on the pH meter. This rinsing removes any lime film or other foreign substances remaining on the electrodes from any previous testing. The electrodes are then removed from the acid and placed in a beaker of deionized water for about a minute to allow hydrogen ions to diffuse out of the interstices of the glass. The electrodes are then rinsed with deionized water and placed into the buffer solution to calibrate the pH meter according to NBS standards (11).



Figure 8: The pH meter uses an electrode dipped in the soil suspension to determine soil pH.

Electrodes are transferred from the buffer solution to deionized water, and rinsed to remove any buffer solution remaining on the electrodes. Electrodes are then rinsed with deionized water and placed in the soil suspension. The pH meter will jump in value until it reaches the appropriate pH measurement, at which the number will remain steady for 10 seconds. Once a pH value is reached, the electrodes are removed from the soil suspension, rinsed and placed in deionized water. This process is repeated for all 25 samples to determine pH values (11).

2.5 Magnesium, Calcium, Sodium, and Potassium

The process of measuring nutrients in soil begins by placing 4 g of $\leq 2\text{mm}$, air-dried soil in a 50 mL centrifuge tube. 20 mL of 1 M Ammonium Acetate is added to the centrifuge tubes and shaken for 30 minutes on a reciprocating shaker to mix the suspension. Samples are then placed in a centrifuge and spun at 2000 rpm for 10 minutes to allow full mixing of the suspension.

Once properly mixed, the supernatant is filtered via a funnel through Whatman No. 1 filter paper into a 50mL volumetric flask, which is rinsed with 1 M Ammonium Acetate. An additional 20 mL of 1 M Ammonium Acetate is added to the soil “pellet” at the bottom of the centrifuge tube.

The extract is then brought up to volume with 1 M Ammonium Acetate. This solution is diluted by 20x (Figure 9) and used to determine cation concentrations using the Atomic Absorption Spectrophotometer (AAS) (11).

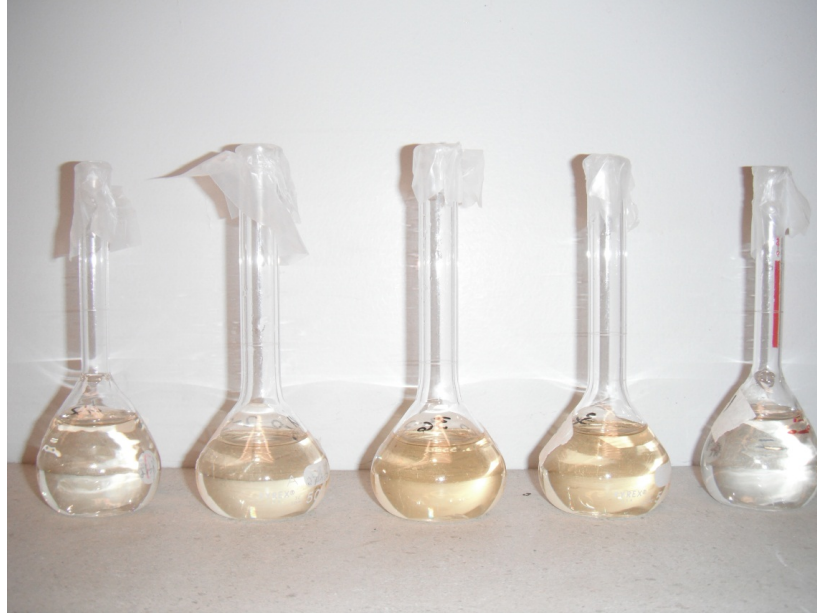


Figure 9: 20x dilutions are made of all soil treatments for nutrient analysis using Atomic Absorption Spectrophotometry

To prepare the AAS for analysis of basic cations, it is first calibrated with at least three standards for each element. Standards are made up in neutral 1 N NH_4OAc .

After calibration, an initial calibration verification checks the calibration curve. The external standard should be between $\pm 5\%$ of its known concentration in order for the analysis to continue. Duplicates are run periodically to ensure the AAS analyzes repeat samples within 5% of their original value. A calibration check occurs every 10th sample as well to verify samples are recorded within 5% of their actual concentration.

All concentrations are recorded in parts per million (ppm) (11).

2.6 Cation Exchange Capacity/ % Saturation

The values recorded in ppm for each cation are then converted to meq./100 g dry soil using the conversions in Figure 10 for each element. CEC is calculated using the sum of all cations in meq./100 g dry soil. The exchangeability of each cation (or % saturation) can also be calculated as the meq./100g dry soil of the cation, divided by the Cation Exchange Capacity. This will give the % exchangeability of the cation (11).

$$\begin{aligned}1 \text{ ppm Na}^+ &= \frac{0.1 \text{ mg Na}^+}{100 \text{ g soil}} \times \frac{1 \text{ meq Na}^+}{22.989 \text{ mg Na}^+} = \frac{0.00435 \text{ meq. Na}^+}{100 \text{ g dry soil}} \\1 \text{ ppm K}^+ &= \frac{0.1 \text{ mg K}^+}{100 \text{ g soil}} \times \frac{1 \text{ meq K}^+}{38.098 \text{ mg K}^+} = \frac{0.00256 \text{ meq. K}^+}{100 \text{ g dry soil}} \\1 \text{ ppm Mg}^{2+} &= \frac{0.1 \text{ mg Mg}^{2+}}{100 \text{ g soil}} \times \frac{1 \text{ meq Mg}^{2+}}{12.153 \text{ mg Mg}^{2+}} = \frac{0.00822 \text{ meq. Mg}^{2+}}{100 \text{ g dry soil}} \\1 \text{ ppm Ca}^{2+} &= \frac{0.1 \text{ mg Ca}^{2+}}{100 \text{ g soil}} \times \frac{1 \text{ meq Ca}^{2+}}{20.04 \text{ mg Ca}^{2+}} = \frac{0.00499 \text{ meq. Ca}^{2+}}{100 \text{ g dry soil}}\end{aligned}$$

Figure 10: Conversion factors are used for cations to determine nutrient exchangeability (11).

2.7 Atomic Absorption Spectrophotometry

The Atomic Absorption Spectrophotometer (AAS) is operated by a computer program, which allows the operator to select the desired element to be analyzed. Only one element can be analyzed at a time. The AAS and the special lamps for Calcium and Magnesium must be warmed about 10 minutes prior to analysis. Once the operator selects the desired element, the instrument must be calibrated against standard solutions with known concentrations. The AAS is highly sensitive and can measure as little as 0.01 parts per million of the element being analyzed (11).

The AAS uses a special burner that contains a mixture of acetylene and air. The liquid from samples is pulled into the burner with very fine tubing (Figure 11). The solution is

then vaporized and mixed with the acetylene and air, and the mixture of gases passes into the flame.

In the hottest part of the flame, the element becomes excited and momentarily loses an electron. This electron has a very characteristic wavelength that exists in the absorption phase, when the correct amount of energy has been absorbed to excite the electron (11).



Figure 11: The AAS uses a fine tube to pull in the sample for analysis via emission and absorption.

As the gases rise higher in the flame, the temperature drops and the electron returns to its orbital level in the electron. This causes a specific wavelength of light to be emitted. This is the emission phase and occurs when the excited atom returns to its ground state. Calcium and Magnesium are analyzed with the absorption mode by using a lamp containing pure Calcium and Magnesium. The lamp provides a heat source to excite these elements so that they emit the characteristic wavelength of light for each element. The proper wavelength must be adjusted for each element. The wavelength for both the absorption and the emission process is identical for a given element (11).

The AAS has a light beam, which is split during the absorption phase. Half of the lamp's light goes directly to a photoelectric tube where its intensity is measured. It also has a "chopper" which hides half of the light from the original lamp while it allows the light from the flame to reach the photoelectric tube.

The other half of the light from the lamp passes through the flame. There the light excites the atom as it absorbs the light energy and emits the electron. As the light continues after passing through the flame, it contains less light intensity because some light energy is absorbed by atoms in the flame (11).

Potassium and Sodium are analyzed using the emission mode. In this process, no lamp is used. The light emitted from the atom as it moves upward in the cool flame is measured directly by the photoelectric tube.

The process described above was used to test calcium, magnesium, and sodium.

However, potassium levels were in high concentration in the soil samples tested and were unable to be recorded using the initial dilution. This required a second 20:1 dilution to be made for all treatment types (11). To account for this additional dilution, results for potassium were all multiplied by 20 to properly represent potassium levels in ppm.

2.8 Analysis Method

To visualize the variance between treatment types, boxplots were charted for each test. Boxplots can show a clear trend occurring between treatments to support any statistical analysis. Analysis of Variance (ANOVA) tests were performed on each treatment type to determine average soil nutrient levels and identify significant differences between treatment types. The two key identifiers for statistical differences in this testing method are the F-statistic and P-value. The F statistic shown in ANOVA analysis represents the variance between treatments. In other words, high F statistics imply a large variance

between treatments and can verify the conclusion that there is a significant difference between treatments.

The other significant number to observe is the P-value, which shows whether there is a significant difference between treatments. P-values represent the percent chance a test statistic (in this case, the F statistic) as extreme as the value observed could be achieved with a true null hypothesis. A p-value less than 0.05 means there is less than 5% chance that the same result would occur if the null hypothesis were true. In this case, the null hypothesis states there is no significant difference between treatments.

Chapter 3: Results

3.1 Germination

Out of the 5 treatment types tested, only 1 treatment type failed in reaching full germination of all 10 corn plants. The control soil (treatment 1) had one seed fail to germinate, but the soil did still reach 90% germination with no soil amendments. While it is possible that the failed germination was caused by poor soil conditions in the control soil, it cannot be conclusively stated without more samples of each treatment type to compare. For the experiment at hand, a significant difference between treatments cannot be assumed. Therefore, all treatment types are assumed to have equal germination.

3.2 Plant Growth

Application rates of biochar and compost proved to have a significant effect on plant growth. The control soil showed the smallest plant growth of all 5 treatments, only reaching an average height of 23.4 inches. A jump in growth occurs once compost is added to the soil, increasing plant growth by 25% (to 29.4 inches). All treatments using soil amendments achieved plant growth well above the control soil. Treatment 4, using a 2:1 ratio of biochar to compost, had the strongest effect on plant growth and increased plant growth from the control soil by 30% (Figure 13).

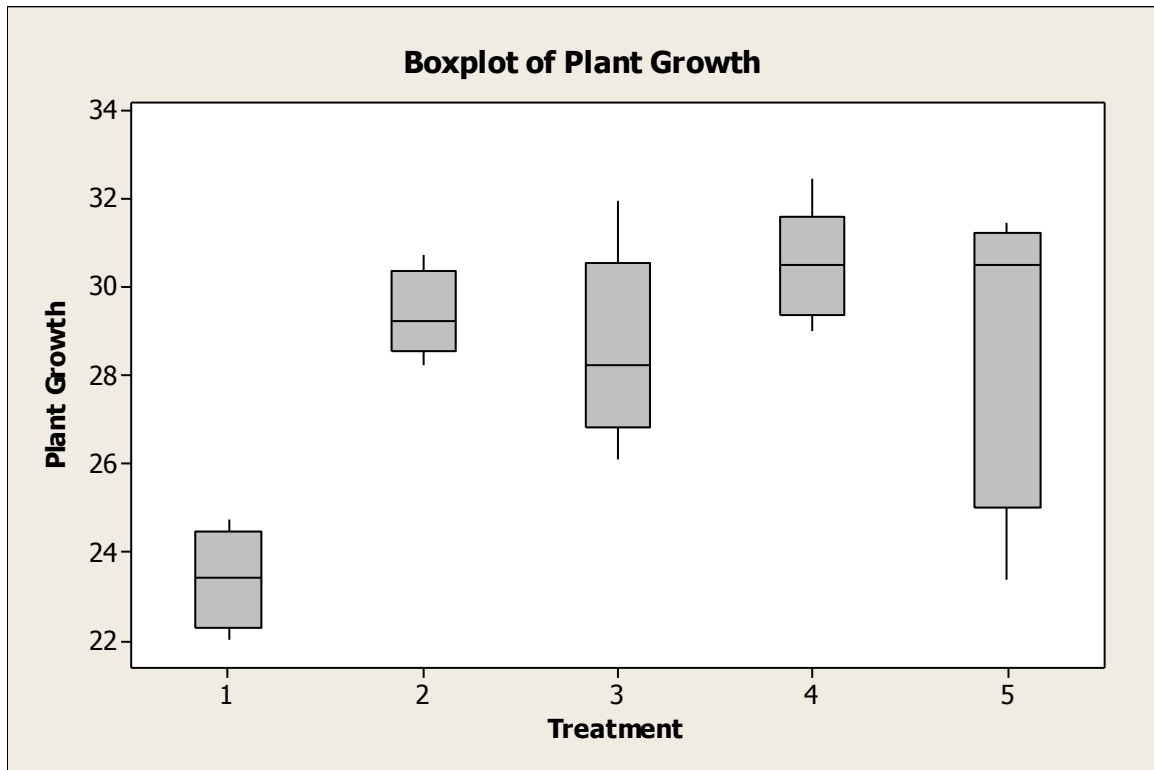


Figure 12: Boxplot of plant growth by soil treatment type (in inches)

As expected, there is a clear difference between treatments according to ANOVA analysis (Table 1). With a conclusive F-statistic (7.33) and p-value (0.001), it is safe to say that soil amendments do cause an increase in plant growth. For this soil, treatment 4 (2:1 biochar to compost) proves to be most beneficial for plant growth, followed closely by treatment 2 (compost only).

Table 1: ANOVA Analysis of plant growth by soil treatment type

Source	DF	SS	MS	F	P
Treatment	4	127.84	31.96	7.33	0.001
Error	20	82.83	4.36		
Total	24	210.66			
S = 2.088		R-Sq = 60.68%		R-Sq(adj) = 52.41%	

3.3 Soil pH

Data received regarding pH values for each treatment shows a clear trend of increasing soil pH based on treatment type (Figure 14). pH values range from a minimum of 6.334 to a maximum of 7.454. All pH results were close to neutral on the pH scale and were in an acceptable range for optimum plant growth.

Another notable characteristic of this test is the relation to pH of biochar and compost on their own. The pH shown for compost soil amendments is significantly lower than the pH level for biochar soil amendments. By using average values achieved for each treatment, biochar has the capability of raising the pH of soil by 18% compared to soil with no amendments added.

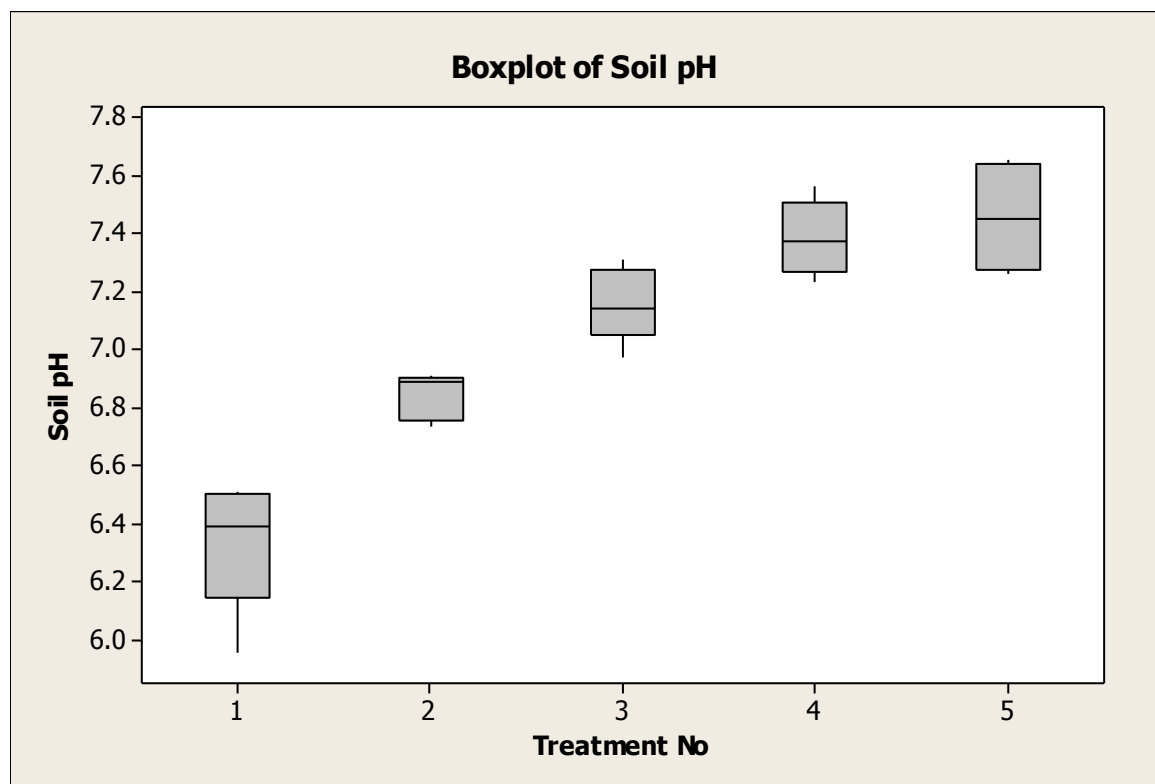


Figure 13: Boxplot of Soil pH by soil treatment type

In the case of pH values, the resulting F statistic of 42.53 would be considered high and gives more support to the hypothesis that pH values do change significantly when biochar is added (Table 2). The p-value for pH based on treatment is 0.000, showing there is essentially no probability that the null hypothesis is acceptable.

All pH values recorded are within a reasonable range for healthy soil and all treatments show a significant improvement in soil pH from the control soil. However, the clear trend shown by biochar suggests that acidic soils should be treated with higher levels of biochar to produce a more alkaline soil.

Table 2: Analysis of Variance for Soil pH

Source	DF	SS	MS	F	P
Treatment	4	4.1977	1.0494	42.52	0.0000
Error	20	0.4936	0.0247		
Total	24	4.6913			
S = 0.157105		R-Sq = 89.48%		R-Sq(adj) = 87.37%	

3.4 Calcium

All soil amendments show a jump in calcium compared to the control soil. While the addition of compost increased calcium by 60% compared to standard soil, the largest spike occurs with the addition of biochar to the soil, which caused a calcium increase of 101% compared to soil with only compost added. All treatment types with biochar remained at levels much higher than those treatments without biochar (Figure 15).

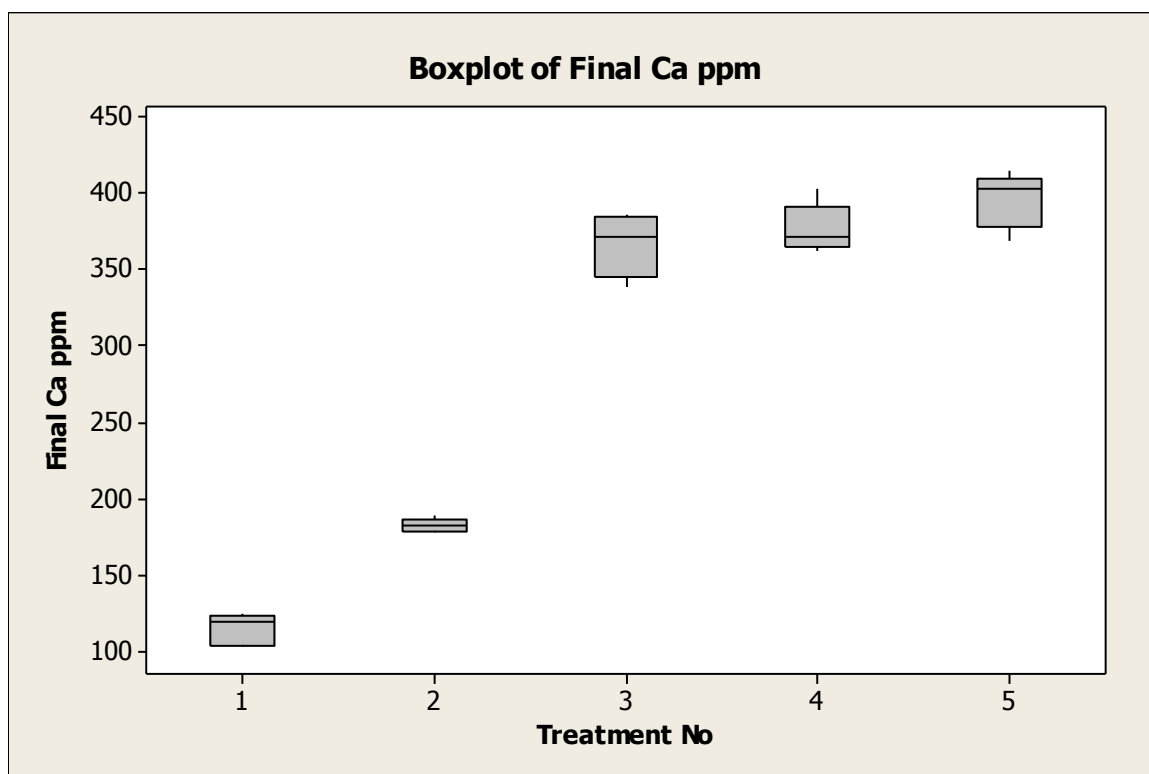


Figure 14: Boxplot of calcium by soil treatment type (in ppm)

ANOVA analysis of calcium levels in the soil showed a significant difference in calcium between soil treatments. The F statistic from the ANOVA analysis is high at 375.12, meaning the null hypothesis of having equal values based on treatment is incorrect. The p-value of 0.0000 also concludes that it is highly unlikely that there is no difference in calcium based on treatment type (Table 3).

Based on this analysis, biochar has a significant impact on the amount of calcium retained in soil. While compost created a spike in calcium levels in the control soil, biochar caused the most drastic rise in calcium in the soil.

Table 3: Analysis of Variance for Ca ppm

Source	DF	SS	MS	F	P
Treatment	4	334728	83682	375.12	0.0000
Error	20	4462	223		
Total	24	339189			
S = 14.9358		R-Sq = 98.68%		R-Sq(adj) = 98.42%	

The exchangeable percentage of Calcium in CEC was at its highest level of 49% in the control soil. Once compost was added, there was a large drop to 26% exchangeable percentage, which then increased with added biochar up to 40.1% (Figure 16).

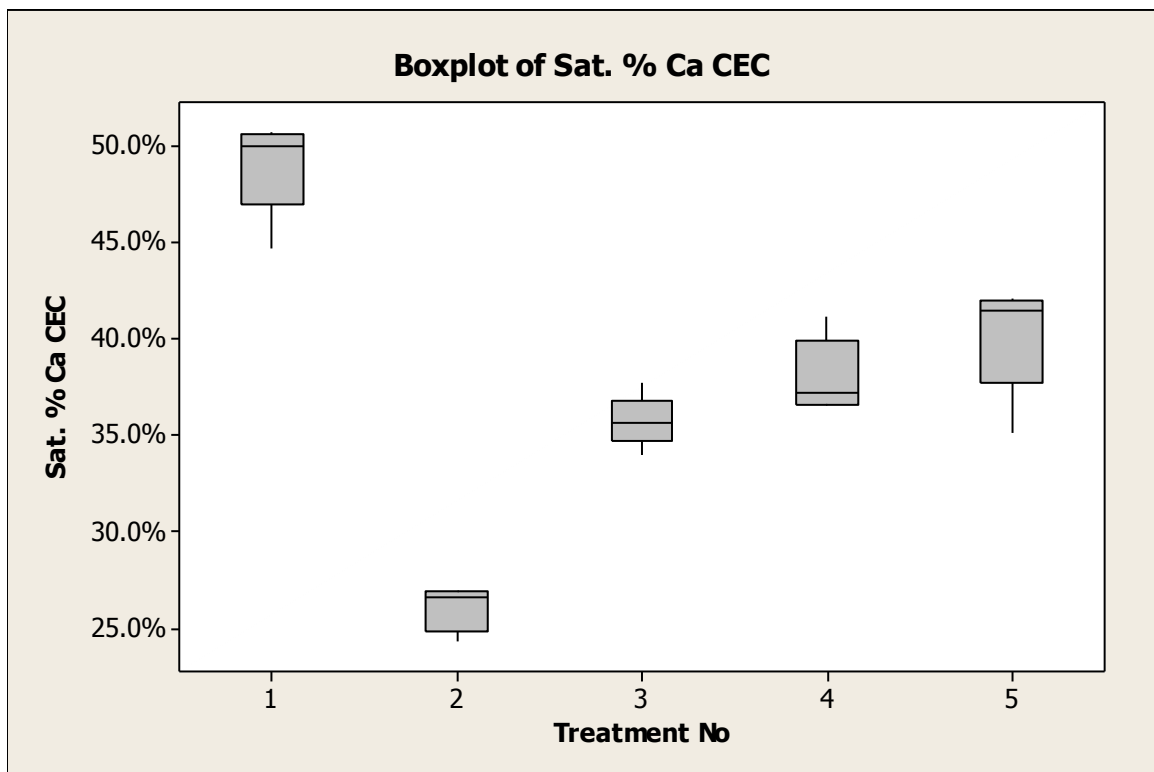


Figure 15: Boxplot of Exchangeable percentage of calcium by soil treatment type

The high F-value of 79.63 and low p-value of 0.0000 both confirm that there is clearly a significant difference between treatment types (Table 4). Overall, this soil is low on exchangeable calcium for all treatment types. This means the best soil treatments for exchangeable calcium are the control soil, soil with only biochar applied, and the 2:1 ratio biochar to compost application. Fortunately, though calcium levels are low in this soil even with soil treatments, calcium can be easily remediated in soil using gypsum or a calcium fertilizer (11).

Table 4: Analysis of Variance for Sat. % Ca

Source	DF	SS	MS	F	P
Treatment	4	0.137075	0.034269	79.63	0.0000
Error	20	0.008607	0.000430		
Total	24	0.145682			
S = 0.0207450		R-Sq = 94.09%		R-Sq(adj) = 92.91%	

3.5 Magnesium

The magnesium levels in soil had a significant increase when compost and biochar were introduced, with biochar producing the most substantial spike in magnesium content at 90.2 ppm. However, the initial spike in Magnesium decreases with additional biochar until 65.3 ppm is reached with only biochar added to the soil (Figure 17).

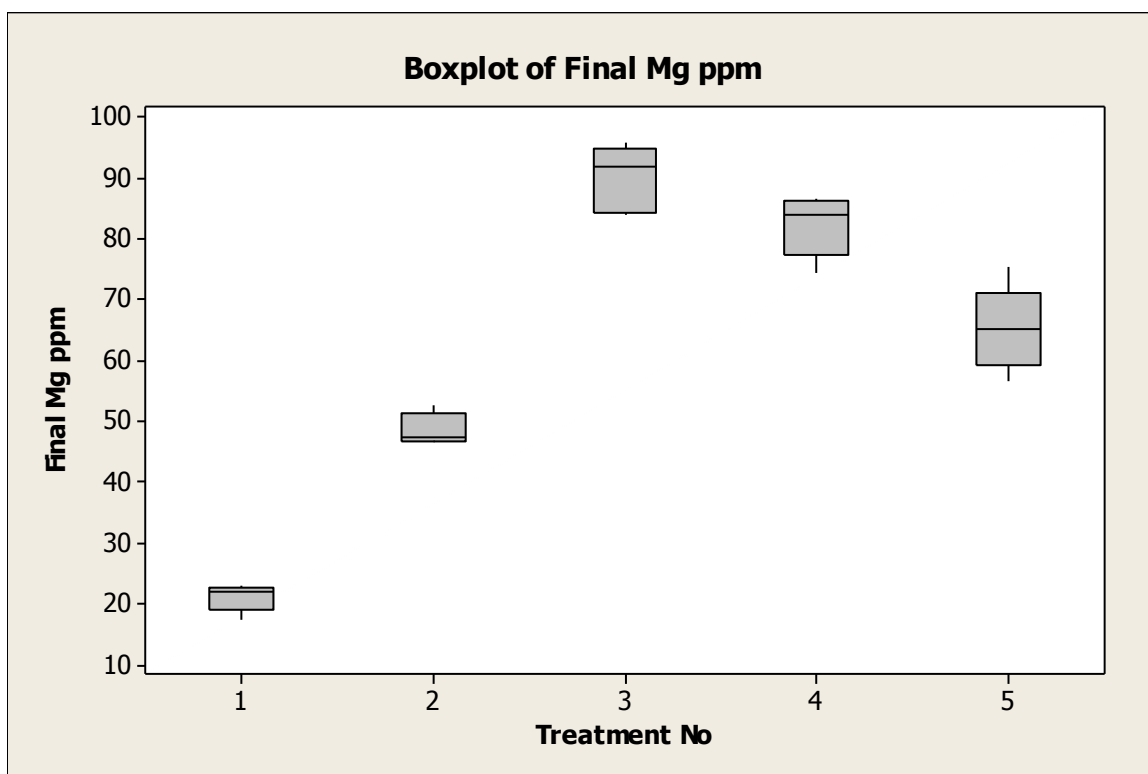


Figure 16: Boxplot of magnesium by soil treatment type (in ppm)

The ANOVA analysis achieved an F-value of 166.09 and a P-value of 0.000, leading to the conclusion that there is a clear significant difference between soil treatments based on Magnesium content (Table 5).

Table 5: Analysis of Variance for Mg ppm

Source	DF	SS	MS	F	P
Treatment	4	15343.7	3835.9	166.09	0.0000
Error	20	461.9	23.1		
Total	24	15805.6			
S = 4.80583		R-Sq = 97.08%		R-Sq(adj) = 96.49%	

Analysis of exchangeable percentage of magnesium in CEC revealed a sudden 3.3% drop in exchangeable magnesium when compost is added, followed by a 3% spike when biochar is added along with compost. The two treatments with both compost and biochar keep a high exchangeable percentage of magnesium, but decreases again to 10.9% saturation when only biochar is applied to the soil (Figure 18). In this case, the treatments closest to the ideal range for magnesium availability are Treatment 2 (only compost applied) and Treatment 5 (only biochar applied). However, magnesium toxicity is extremely rare and none of the plants grown in this experiment showed signs of severe toxicity. Since all 5 treatments are relatively close to the ideal range of exchangeable magnesium, it is safe to say that any of these treatments will achieve acceptable magnesium levels.

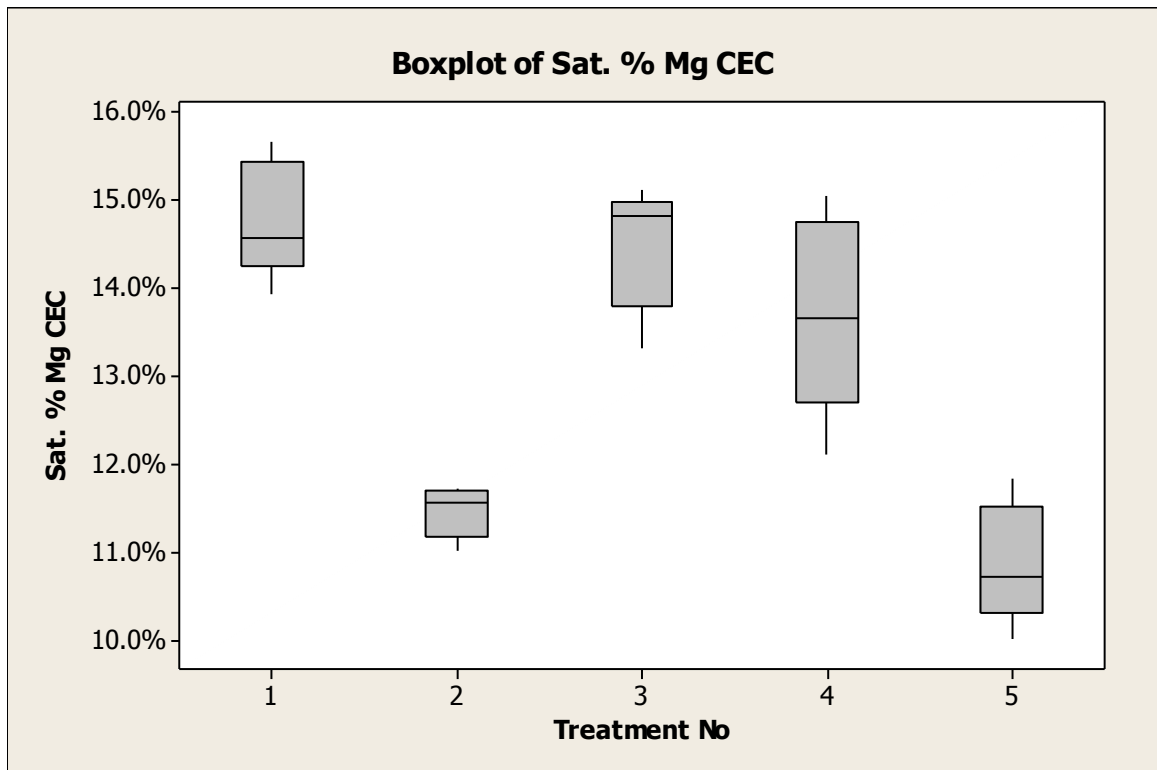


Figure 17: Boxplot of exchangeable percentage of magnesium by soil treatment type

The relatively high F-value of 28.68 supports the hypothesis that there is a significant difference in magnesium saturation percentage based on treatment type. This hypothesis is also supported by the P-value of 0.0000, proving that at least one treatment had a significant effect on saturation levels of magnesium in the soil (Table 6).

Table 6: Analysis of Variance for Sat. % Mg

Source	DF	SS	MS	F	P
Treatment	4	0.0063728	0.0015932	28.68	0.0000
Error	20	0.0011109	0.0000555		
Total	24	0.0074837			
S = 0.00745278		R-Sq = 85.16%		R-Sq(adj) = 82.19%	

3.6 Sodium

Similar to the results shown for magnesium (Figure 17), sodium reaches a maximum level of 45.4 ppm with a 1:2 ratio of biochar to compost soil amendments, followed by a sharp drop in sodium levels as biochar is added.

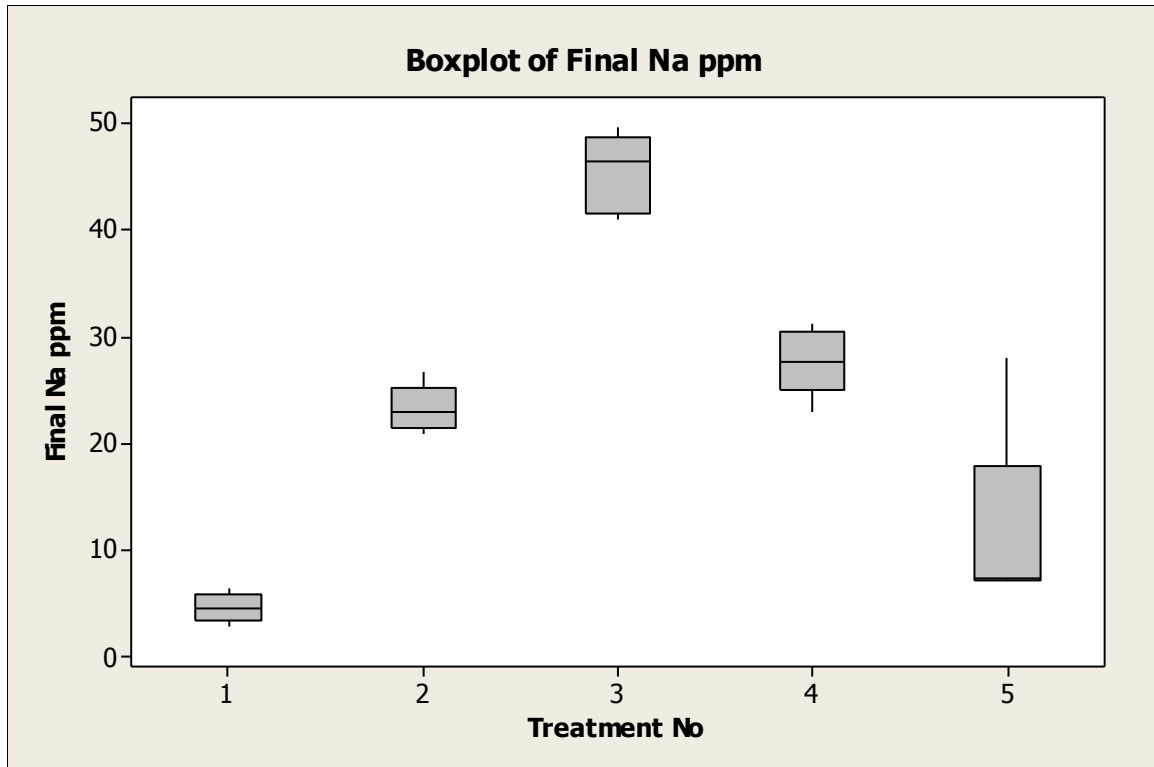


Figure 18: Boxplot of sodium by soil treatment type (in ppm)

Significant differences between treatment types are observed based on the high F-value and low p-value recorded as 53.94 and 0.000, respectively (Table 7). It is apparent from these results that biochar caused an increase in sodium, but additional biochar stunted the sodium levels in the soil.

Table 7: Analysis of Variance for Na ppm

Source	DF	SS	MS	F	P
Treatment	4	4966.1	1241.5	53.94	0.0000
Error	20	460.4	23		
Total	24	5426.5			
S = 4.79767		R-Sq = 91.52%		R-Sq(adj) = 89.82%	

The results for exchangeable sodium in the soil follow a similar pattern as that of sodium ppm in the soil (Figure 19). The exchangeable percentage starts in the control soil at a low of 1.7%, then rises gradually when compost and biochar are added. Exchangeable percentage reaches a maximum of 3.8% when a 1:2 ratio of biochar to compost is used on the control soil, and drops gradually until only biochar is added to the soil, which reaches the minimum saturation of 1%.

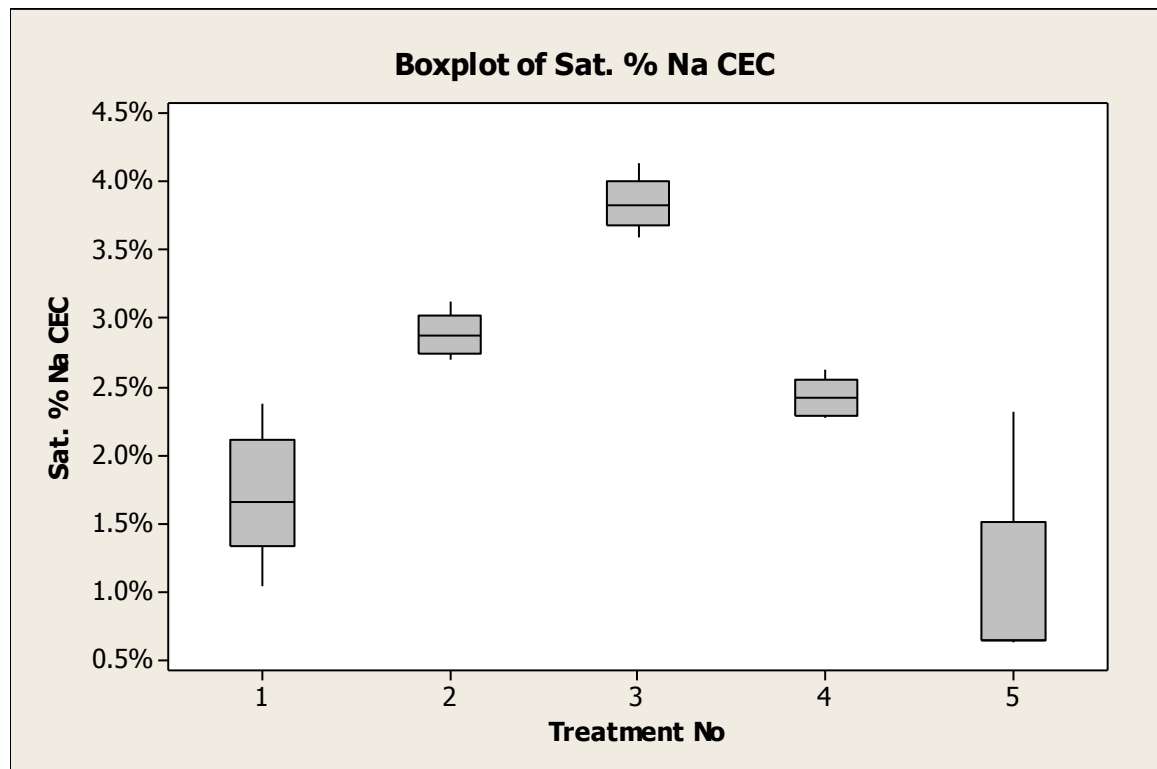


Figure 19: Boxplot of exchangeable percentage of sodium by treatment type

The ANOVA analysis provides proof that soil treatments cause a significant difference of exchangeable percentage of sodium. The high F-statistic of 34.37 and the low p-value of 0.0000 both support the conclusion that soil treatments caused a clear change in exchangeable percentage of sodium in the soil (Table 8). All treatment types in this experiment achieved ideal exchangeable sodium levels in the soil, meaning any of these application rates of compost or biochar will provide acceptable sodium levels for this soil.

Table 8: Analysis of Variance for Sat. % Na

Source	DF	SS	MS	F	P
Treatment	4	0.00240054	0.00060013	34.37	0.0000
Error	20	0.00034922	0.00001746		
Total	24	0.00274975			
S = 0.00417861		R-Sq = 87.30%		R-Sq(adj) = 84.76%	

3.7 Potassium

The ANOVA analysis of Potassium based on soil treatments shows a clear pattern in potassium levels. There is a jump in Potassium of 73% when compost is added to plain soil, and potassium levels remain high with increased biochar levels (Figure 21). This implies that any addition of organic matter will greatly increase potassium levels in soil.

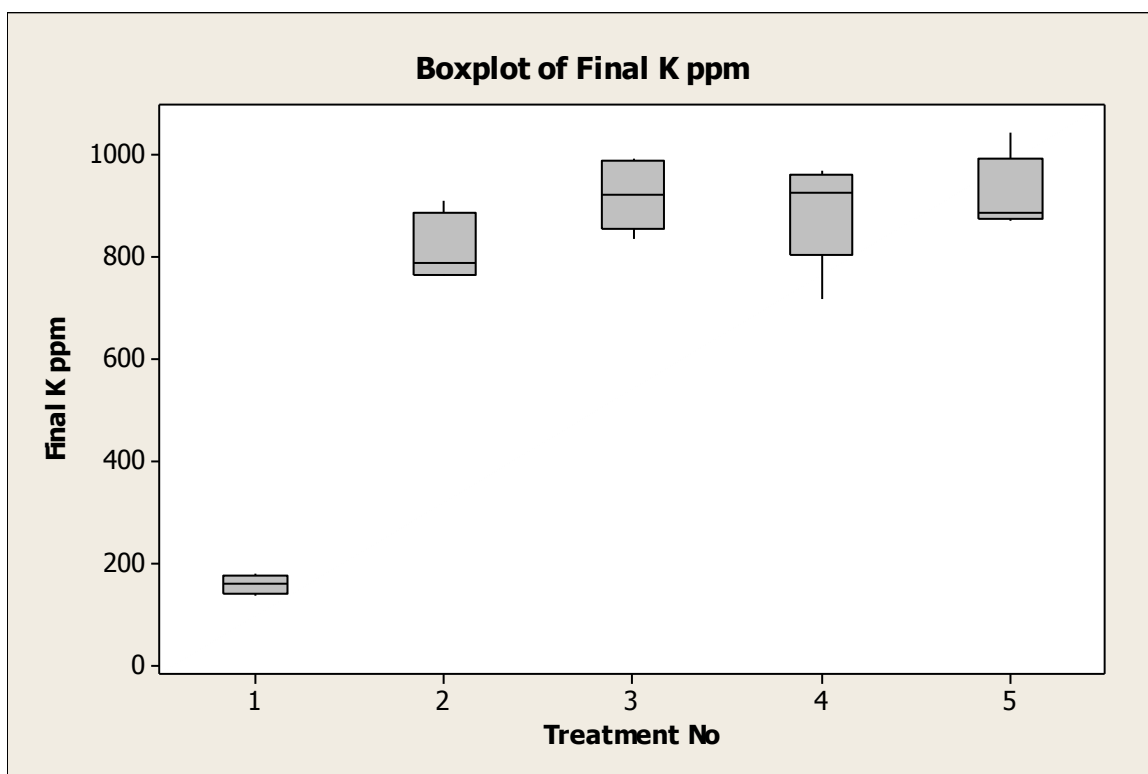


Figure 20: Boxplot of potassium by soil treatment type (in ppm)

The F-statistic 109.44 and p-value 0.0000 calculated during ANOVA analysis both conclude that there is a significant difference between at least 2 of the soil treatments tested (Table 9). In this case, it is safe to say that the soils with any amendments have significantly higher levels of potassium than the control soil.

Table 9: Analysis of Variance for K ppm

Source	DF	SS	MS	F	P
Treatment	4	2178767	544692	109.44	0.0000
Error	20	99546	4977		
Total	24	2278313			
S = 70.5498		R-Sq = 95.63%		R-Sq(adj) = 94.76%	

The exchangeable percentage of potassium starts at a low of 34.5% in the control soil and has a jump to 59.7% when compost is added. The 3 soil treatments using biochar have an exchangeable percentage in between the first 2 treatments with saturations of 46%, 45.8%, and 48% (Figure 22).

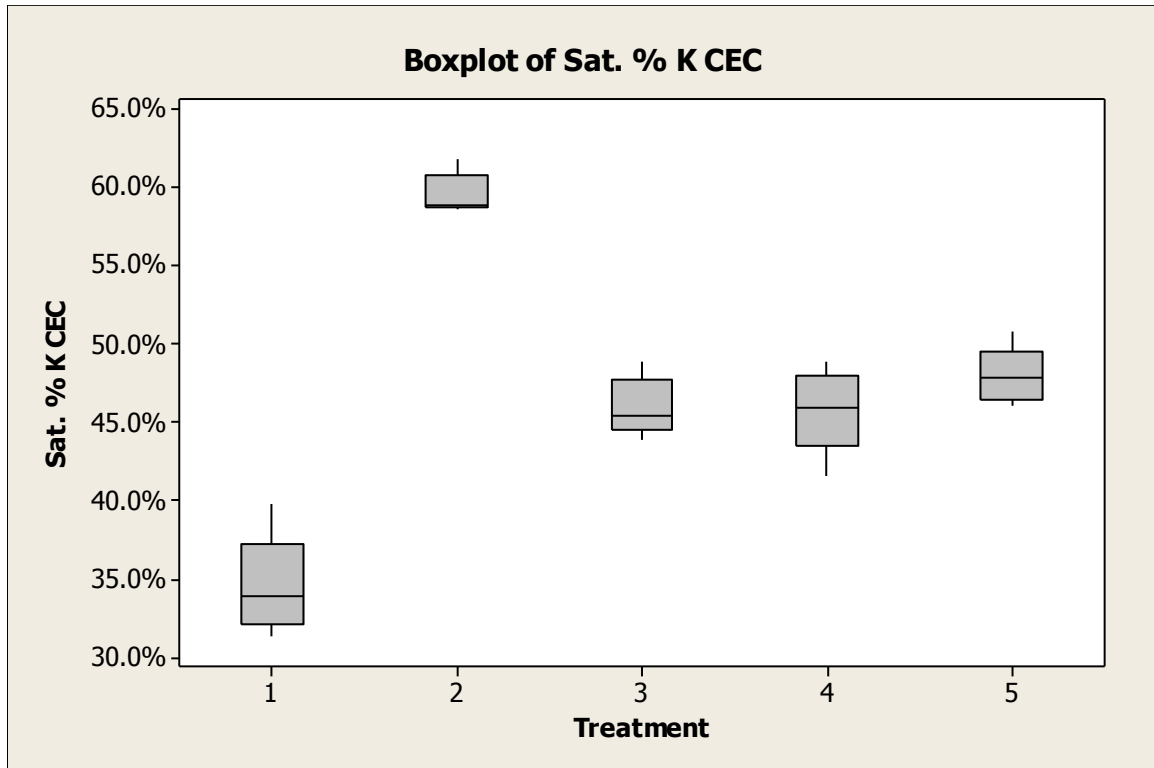


Figure 21: Boxplot of exchangeable percentage of potassium by soil treatment type

The F-statistic (76.45) and p-value (0.0000) both indicate a significant difference between treatment types, proving that soil amendments do have an effect on exchangeable potassium in the soil (Table 10).

All treatment types have high exchangeable potassium levels (the ideal value for exchangeable potassium is 5%). This could be a cause for alarm for other ions, but potassium does not cause any toxicity problems even at levels much higher than the ideal exchangeable potassium range (11). For this reason, the control soil and

treatments with biochar added are a closer fit to ideal soil composition for potassium, although any of the treatment types can be used without a negative effect on plants.

Table 10: Analysis of Variance for Sat. % K

Source	DF	SS	MS	F	P
Treatment	4	0.159617	0.039904	76.45	0.0000
Error	20	0.010439	0.000522		
Total	24	0.170056			
S = 0.0228464		R-Sq = 93.86%		R-Sq(adj) = 92.63%	

3.8 Ca:Mg Ratio

The Ca:Mg ratio found based on treatment types had a significant drop (from 5.5:1 to 3.7:1) when compost was added to the control soil, with a gradual increase as biochar was added to the soil. The Ca:Mg ratio reaches a maximum of 6.1:1 when only biochar is applied to the control soil. The trend shows an overall increase to the Ca:Mg ratio as more biochar is applied to the soil (Figure 23).

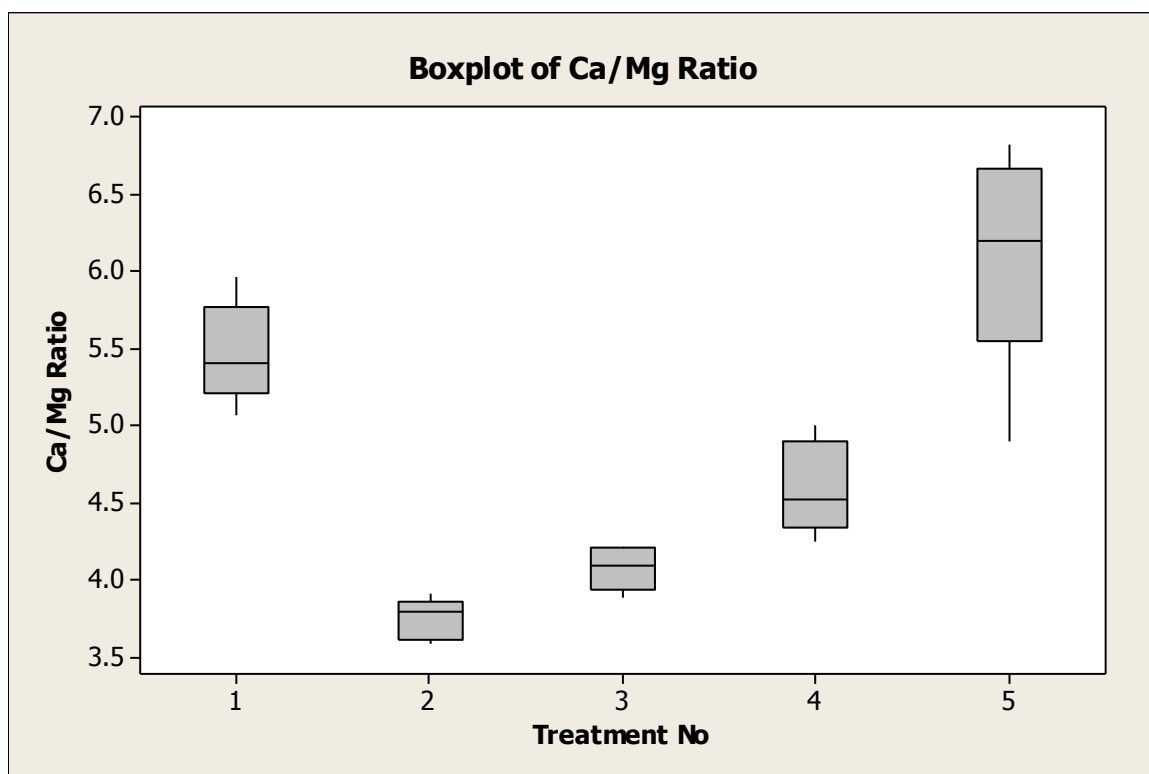


Figure 22: Boxplot of Ca:Mg Ratio

ANOVA analysis shows an F-statistic of 31.12 and a p-value of 0.0000, meaning the trend shown in this analysis is significant (Table 11). All Ca:Mg ratios recorded were within an acceptable range for soil. For this soil, biochar is unnecessary to reach an acceptable Ca:Mg ratio, but for soils with low Calcium or high Magnesium levels, biochar should be considered to stabilize this ratio.

Table 11: Analysis of Variance for Ca:Mg Ratio

Source	DF	SS	MS	F	P
Treatment	4	19.4421	4.8065	31.12	0.0000
Error	20	3.1238	0.1562		
Total	24	22.5659			
S = 0.395208		R-Sq = 86.16%		R-Sq(adj) = 83.39%	

3.9 Cation Exchange Capacity

Data reveals a dramatic rise in Cation Exchange Capacity with the addition of compost (from 1.2 to 3.5) and another increase to 5.1 when biochar was added to the soil.

Additional biochar kept CEC at relatively the same level, so there was no added benefit to increasing the rate of biochar application (Figure 24).

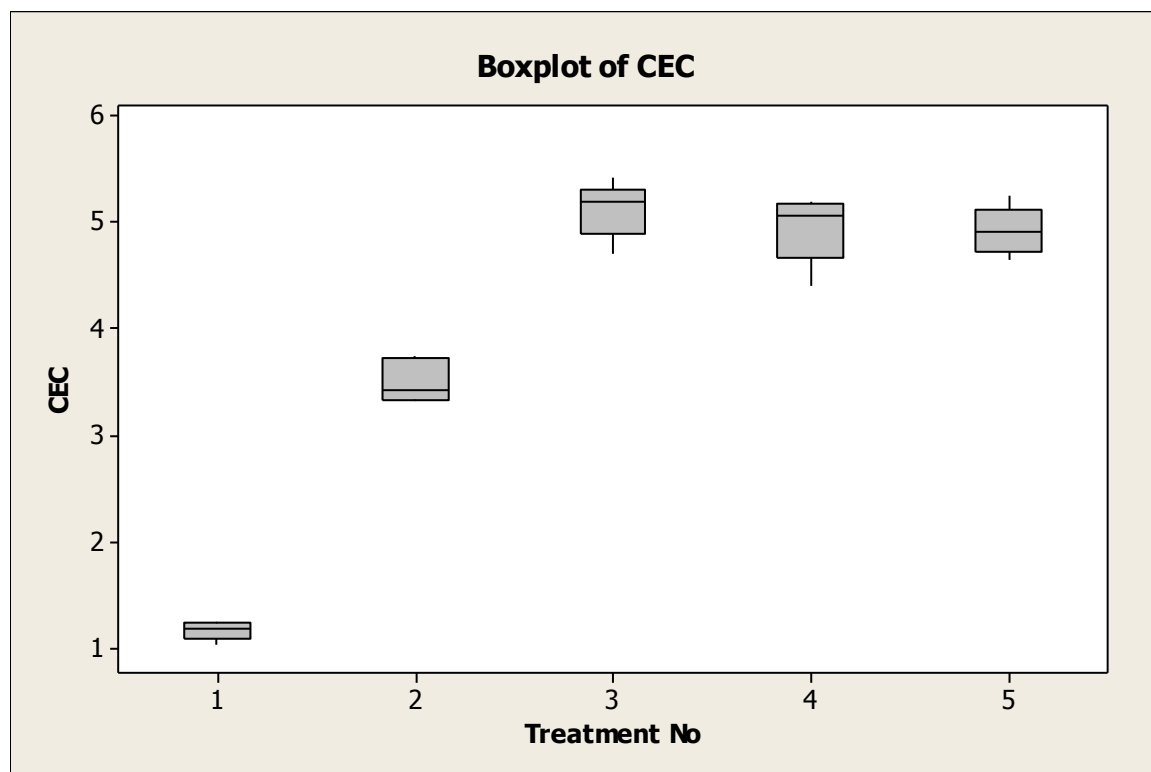


Figure 23: Boxplot of Cation Exchange Capacity (in meq./100 g)

The F-value of 253.87 and P-value of 0.000 also confirm the conclusion that there is a significant difference in CEC between at least two soil treatments. All recorded CEC values were below the ideal range of CEC for soil, and the best option in this case for soil was treatment 3, with the 1:2 ratio of biochar to compost. This treatment brought CEC the closest to the ideal CEC range (Table 12).

Table 12: Analysis of Variance for CEC

Source	DF	SS	MS	F	P
Treatment	4	56.479	14.120	253.87	0.0000
Error	20	1.112	0.056		
Total	24	57.591			
S = 0.235832		R-Sq = 98.07%		R-Sq(adj) = 97.68%	

Chapter 4: Discussion

4.1 Germination

Although ANOVA analysis showed no significant change in germination based on treatment type, the soil treatment using biochar only reached 90% germination. There are external factors that could cause stunted germination in this instance. First, it is possible there was a faulty seed that would be incapable of germinating, or at least have a difficult time doing so. Also, receiving too much or too little water can reduce seed germination. Another cause of changes in seed germination could be the biochar itself. Biochar can contain traces of phytotoxic compounds, which cause toxicity in the plant and inhibit seed germination (18).

Considering the results of this experiment, it is unlikely that the biochar is causing germination problems since a pattern would be seen in the other 2 treatments using biochar. Since water was evenly dispersed across all treatments, the most likely reason for a decline in seed germination is simply due to a faulty seed. For future testing, multiple samples could be made of each treatment type to observe any outliers such as a faulty seed to verify that any change in germination was not due to the treatment itself.

4.2 Plant Growth

The design of this experiment was intended to randomize results as much as possible and avoid any false trends occurring due to experiment incongruences, but any plant testing can be prone to error due to environmental factors. The greenhouse where the samples were grown may have warm or cool spots that can affect plant growth, although the samples were organized randomly to minimize this risk. The weather is also uncontrollable, so the plant growth could also be stunted by non-ideal weather conditions. The tubes each sample was grown in may have inhibited root growth due to

size constraints. In a field study of corn plants under the same conditions, this experiment could have produced drastically different results by allowing plants more room to grow. All of these factors combined could create skewed results. However, every effort is made to ensure consistency among all treatment groups to avoid any false conclusions from any external forces.

In this study, plant growth has been used as a proxy for soil health under the assumption that healthier soil will lead to healthier plants and better plant growth. There are many factors that contribute to plant growth, and only a few of those factors were measured. Micronutrients and microbes within the soil also have a strong effect on plant growth, but the scope of this experiment did not allow for these to be measured. Without this data to confirm, there is no conclusive evidence stating plant growth directly relates to soil health. However, the data we did collect implies that added soil amendments increase

4.3 Soil pH

Research suggests that pH increases when biochar is added to soil due to the negative charge that forms on biochar's surface. This negative charge buffers soil acidity, causing a jump in pH. Organic matter has the same acidity buffering effect, which explains why the pH level of the soil rises with only compost added in treatment 2 (5). As biochar and organic matter are added to the soil, there is an increase in pH level and therefore a decrease in soil acidity. The results from this experiment match up appropriately with the underlying theory of organic matter's negative charge buffering soil acidity.

4.4 Calcium

Calcium levels in the soil behaved as expected when varying soil treatments were implemented. As biochar is added, calcium becomes increasingly available in the soil.

This reaction is caused by the negative surface charge of biochar, which attracts more positively charged ions to its surface and keep ions available to plants (3). Adding compost also produced an increase in calcium, which can be attributed to direct calcium additions made by the compost. However, calcium in all soil treatments is still considered low for soil. The best method for remediation is to apply gypsum or calcium fertilizer to the soil in addition to compost or biochar (11).

4.5 Magnesium

The drop in magnesium when compost is added to the control soil can be attributed to a large spike in potassium (Figure 21). The high exchangeable potassium content when soil amendments are used has caused the exchangeability of competing ions to decrease, including magnesium and calcium. This jump in exchangeable potassium leads to a corresponding decrease in exchangeable magnesium. However, when biochar is added along with compost, the exchangeable magnesium increases. This makes sense since biochar is shown to increase nutrient levels, such as magnesium. Magnesium levels increase as biochar is added, so the percent of exchangeable magnesium naturally increases relative to the cation exchange capacity.

4.6 Sodium

Sodium levels were shown to increase when compost and biochar are added initially, which is expected due to the nutrient retention properties of biochar. However, as the volume of biochar increased, sodium began to decrease in the soil. This is a common problem with adding high amounts of biochar to soil. Biochar can often reach a point of diminishing returns, where adding excessive biochar can cause nutrient properties to quickly return to their original levels from before biochar was introduced to the soil (6).

However, excess sodium is more damaging to plant growth than deficient sodium levels (11). In this testing, all treatments were within an acceptable range and would not cause any deficiencies or toxicities in plants.

4.7 Potassium

The increase in potassium as compost is added to the control soil is a clear shift in nutrient levels due to soil additions. Potassium found in compost is completely available to soil and plants, which will show a clear increase in exchangeable potassium when added to soil (19). Once biochar is applied to the soil, exchangeable potassium levels decrease, but remain above the control soil. Biochar is not shown to have a significant effect on exchangeable potassium, which would explain the decrease in exchangeable potassium as biochar begins to replace compost in the soil (3).

4.8 Ca:Mg Ratio

The Ca:Mg ratio is directly effected by the change in calcium (in ppm) and the change in magnesium (in ppm). The most notable change in Ca:Mg is the jump starting when biochar is introduced to the soil. As biochar was added into the soil, magnesium decreased due to ion competition with potassium. Since calcium levels remained steady once biochar was introduced to the soil, the decreasing magnesium levels caused a steady rise in Ca:Mg ratio. The treatments that produce the most ideal Ca:Mg ratios are treatments 5, 1, and 4 respectively.

4.9 Cation Exchange Capacity

The CEC increase that occurs when compost and biochar are added to the soil makes a clear statement that soil amendments do have an effect on the nutrient availability in soil.

Increases in cation exchange capacity imply that the amount of readily available nutrients in the soil has increased, which provides a healthier soil and a better environment for plant health (5). This increase in CEC can be attributed to many factors, such as the simple addition of available nutrients coming directly from biochar and compost. But the most noticeable jump in CEC occurred once biochar was added to the soil. This increase is due to the porosity of biochar that holds onto nutrients better than soil alone, while also keeping those nutrients accessible for plant uptake. The negative surface charge of biochar also attracts cations to its surface, allowing for better nutrient retention in the soil (3).

Chapter 5: Conclusions and Recommendations

When determining the most effective soil additions for this experiment, all nutrient levels and plant health that were tested in this experiment must be considered to eliminate any soil treatments causing toxicity or deficiency in the soil. First, CEC levels are considered because the CEC of soil represents the overall health of the soil and the relative amount of available nutrients for plants. The control soil and the soil with only compost added have severely low CEC values, and are taken out of consideration for the ideal soil treatment type. The 3 treatments using biochar remain and will be analyzed based on nutrient levels and plant health to determine the best possible treatment for this soil. All pH levels for the 3 treatment types remaining are within an acceptable range and achieve a close-to-neutral soil pH.

The next step in choosing the best soil treatment is reviewing exchangeability of calcium, magnesium, potassium, and sodium. Calcium for all remaining treatment types is low, and gypsum or calcium fertilizer should be considered to raise calcium exchangeability and improve the nutrient balance for this soil. However, considering all the remaining treatment types are low in calcium, all treatment types can still be considered as the best amendment method for this soil.

Magnesium is slightly high for the 2 treatment types with the most added biochar, and the treatment with 1:2 ratio of biochar to compost is within the ideal range of magnesium exchangeability. All 3 treatments are still considered due to the small difference in exchangeability and the fact that all 3 treatments would not cause any toxicity issues to the plants.

Sodium is within an acceptable range for all treatment types and all amendments form a non-sodic soil, leading to the conclusion that all amendments allow for a healthy soil structure.

Potassium is considered extremely high for all 3 treatment types, but potassium also does not cause toxicity, even well above the ideal potassium range for soil. Therefore, none of the 3 treatment types will be deemed bad for the soil.

The last factor to consider when determining the best treatment type possible for this soil is plant health. Since germination did not produce any significant difference between treatment types, the deciding factor for the best soil treatment is plant growth. Between the 3 treatments left, the most plant growth is seen with a 2:1 ratio of biochar to compost applied to the soil. This treatment caused the corn plants to grow an average of 30% more than the control soil. For this reason, treatment 4 is considered the best soil amendment tested, and a 2:1 ratio of biochar to compost will produce the healthiest soil and plants for soil similar to the soil analyzed in this experiment. To optimize plant growth, gypsum or calcium fertilizer should also be considered along with biochar to improve calcium levels in the soil.

For future testing, a germination test should be developed with multiple samples of each treatment type to allow for proper ANOVA analysis. Also, gypsum or calcium fertilizer could be added to Treatment 4 to see if any increase in exchangeable calcium occurs. Adding this treatment type to testing would show if adding gypsum or calcium fertilizer, biochar, and compost will be effective in remediating the soil without causing imbalances in other cations. The soil amendments can also be tested for nutrient properties to know precisely the quantity of nutrients that are being added to the soil with each treatment type. This can reveal which nutrient differences are caused by directly adding nutrients or are caused by the material properties of the soil amendments.

References

1. Glaser, Bruno, Johannes Lehmann and Wolfgang Zech. "Ameliorating Physical and Chemical Properties of Highly Weathered Soils in the Tropics with Charcoal - a Review." Biology and Fertility of Soils (2002).
2. Lehmann, Johannes. "A Handful of Carbon." Garnaut Climate Change Review (2011).
3. Lehmann, Johannes and Stephen Joseph. Biochar for Environmental Management: Science and Technology. Sterling: Earthscan, 2009.
4. Gill, Jock. Improved Biomass Cooking Stoves. 15 January 2011
<<http://bioenergylists.org/taxonomy/term/124>>.
5. International Biochar Initiative. 21 September 2011 <<http://www.biochar-international.org>>.
6. Lehmann, Johannes, John Gaunt and Marco Rondon. "Biochar Sequestration in Terrestrial Ecosystems - A Review." Mitigation and Adaptation Strategies for Global Change (2006).
7. Shinogi, Y., et al. Basic Characteristic of Low-temperature Carbon Products from Waste Sludge. 2003.
8. "Potassium in Soil." Smart Fertilizer. 20 April 2013 <<http://www.smart-fertilizer.com/articles/potassium-in-soil>>.
9. McMillan, Gregory and Robert Cameron. Advanced pH Measurement and Control. Vol. 3. Research Triangle Park: ISA, 2005.
10. Moon, G.E. The Acid-Alkaline pH Scale. 20 April 2013
<<http://www.abundanthealthcenter.com/blog/the-acid-alkaline-ph-scale>>.
11. Dickson, Bruce A., et al. SS 221: Fertilizers and Plant Nutrition. San Luis Obispo: Cal Poly State University, 1990.
12. Lal, Rattan, ed. Encyclopedia of Soil Science. 2nd Edition. Vol. 1. Boca Raton: CRC Press, 2006.
13. UMI Microform. Characterization of Soil Potassium Availability and Plant Uptake by Rice Grown on a Flooded Dewitt Silt Loam. Ann Arbor: ProQuest LLC, 2008.
14. Fageria, N.K. The Use of Nutrients in Crop Plants. Boca Raton: CRC Press, 2009.
15. Mengel, David. Fundamentals of Soil Cation Exchange Capacity (CEC). West Lafayette: Purdue University, n.d.
16. Manahan, Stanley. Environmental Chemistry. 8th Edition. Boca Raton: CRC Press, 2005.

17. Smith, C. Wayne, Javier Betran and E.C.A. Runge. Corn: Origin, History, Technology, and Production. Hoboken: John Wiley & Sons, Inc., 2004.
18. Rogovska, N., et al. Germination Tests for Assessing Biochar Quality. Ames: American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, 2012.
19. Paulin, Bob and Peter O'Malley. Compost Production and Use in Horticulture. Western Australian Agriculture Authority, 2008.

Appendices

A: Soil nutrient data

Treatment	Sample	pH	Ca ppm	Mg ppm	Na ppm	K ppm	Ca/Mg Ratio
1	1	6.49	103.4	20.4	2.8	180	5.07
1	2	6.51	119.4	22.4	6.4	144	5.33
1	3	6.39	103.8	17.4	4	136	5.97
1	4	6.33	122.4	22	4.6	168	5.56
1	5	5.95	124.2	23	5.2	160	5.40
2	1	6.91	189	52.8	26.6	868	3.58
2	2	6.89	182.8	50.2	23.8	908	3.64
2	3	6.89	183.6	47	23	788	3.91
2	4	6.78	177.6	46.8	22	768	3.79
2	5	6.73	179.4	47.4	20.8	764	3.78
3	1	7.31	353.2	84	46.4	992	4.20
3	2	7.23	338.4	85	41	836	3.98
3	3	7.14	385.8	92	42.2	876	4.19
3	4	7.12	384.8	94.2	47.8	988	4.08
3	5	6.97	372.2	95.8	49.6	920	3.89
4	1	7.56	371.8	74.4	26.8	968	5.00
4	2	7.37	379.4	86	31.2	956	4.41
4	3	7.3	368.6	86.8	27.6	888	4.25
4	4	7.45	403	84	29.6	924	4.80
4	5	7.23	362.8	80.4	23	716	4.51
5	1	7.65	403.8	62	7.2	880	6.51
5	2	7.62	403.6	65.2	7.4	944	6.19
5	3	7.45	386.2	56.6	7.6	872	6.82
5	4	7.29	415.2	67	7.2	888	6.20
5	5	7.26	369.6	75.6	28	1044	4.89

B: CEC data

Treatment No	Sample No	CEC	Sat. % Ca CEC	Sat. % Mg CEC	Sat. % Na CEC	Sat. % K CEC
1	1	1.156	44.6%	14.5%	1.0%	39.8%
1	2	1.176	50.7%	15.6%	2.4%	31.3%
1	3	1.026	50.5%	13.9%	1.7%	33.9%
1	4	1.242	49.2%	14.6%	1.6%	34.6%
1	5	1.241	49.9%	15.2%	1.9%	33.0%
2	1	3.713	25.4%	11.7%	3.1%	59.8%
2	2	3.751	24.3%	11.0%	2.8%	61.9%
2	3	3.418	26.8%	11.3%	2.9%	59.0%
2	4	3.331	26.6%	11.6%	2.9%	59.0%
2	5	3.33	26.9%	11.7%	2.7%	58.7%
3	1	5.193	33.9%	13.3%	3.9%	48.9%
3	2	4.705	35.9%	14.9%	3.8%	45.4%
3	3	5.106	37.7%	14.8%	3.6%	43.9%
3	4	5.43	35.4%	14.3%	3.8%	46.5%
3	5	5.214	35.6%	15.1%	4.1%	45.1%
4	1	5.06	36.7%	12.1%	2.3%	48.9%
4	2	5.182	36.5%	13.7%	2.6%	47.2%
4	3	4.945	37.2%	14.4%	2.4%	45.9%
4	4	5.194	38.7%	13.3%	2.5%	45.5%
4	5	4.403	41.1%	15.0%	2.3%	41.6%

5	1	4.807	41.9%	10.6%	0.6%	46.8%
5	2	4.997	40.3%	10.7%	0.6%	48.3%
5	3	4.656	41.4%	10.0%	0.7%	47.9%
5	4	4.926	42.1%	11.2%	0.6%	46.1%
5	5	5.258	35.1%	11.8%	2.3%	50.8%