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INFLUENCE OF BIOCHAR AND COMPOST AMENDMENT ON THE SORPTION OF ATRAZINE ON SOIL

BY

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DECLARATION

I hereby declare that except for references of other people's work which have been cited and duly acknowledged, this work is the result of my original research conducted under supervision and that this thesis has neither in whole nor in part been presented for an award of a degree elsewhere.

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ABSTRACT

Biochar, the carbonaceous residue from biomass pyrolysis, and compost have been proposed as agricultural soil amendments to improve soil fertility and retain a broad range of environmental contaminants. However, it is not clear how effective and how long this sorption capacity will be maintained after the biochar is applied to the soil. The study, therefore, focused on assessing the potential of differently aged biochars and compost to effectively attenuate the transport of atrazine by using laboratory batch sorption studies. Batch sorption experiments were conducted to study the adsorption of atrazine on unamended soil, soils amended with one-year-old biochar, soils amended with two-year-old biochar, and soils amended with compost. These experiments were conducted to determine the influence of soil amendments, atrazine concentration and pH on the adsorption of atrazine in soils. The study showed that when soil is amended with biochar of different ages and compost, its physicochemical properties are modified. Results from the adsorption studies also revealed that soils when amended with biochar and compost show a high capacity to adsorb atrazine as compared to the unamended soil. Amending the soil with biochar proved to be a much more efficient adsorbent than compost due to different physicochemical properties and adsorption sites. The soil amended with the two-year-old biochar showed the highest sorption capacity owing to a change in properties after going through biogeochemical changes with ageing leading to an increase in sorption sites. Isotherm studies also revealed that the Langmuir model which assumes monolayer adsorption to homogenous surface best describes the interactions between the atrazine and the various adsorbents.

DEDICATION

I dedicate this work to the almighty God, my parents, and my siblings.

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LIST OF ABBREVIATIONS

CEC	Cation Exchange Capacity
CWSA	Community Water and Sanitation Agency
DACT	Diaminochlorotriazine
DDT	Dichloro diphenyl trichloroethane
DEA	Deethyl-atrazine
DIA	Deisopropylatrazine
EDC	Endocrine Disrupting Compound
EPA	Environmental Protection Agency
FAO	Food and Agricultural Organization
GUS	Groundwater Ubiquity Score
IUPAC	International Union of Pure and Applied Chemistry
MoFA	Ministry of Food and Agriculture
NIEHS	National Institute of Environmental Health Sciences
OECD	Organization for Economic Cooperation and Development
POPs	Persistent Organic Pollutants
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

CHAPTER ONE: INTRODUCTION

1.1 Background

The rapid increase in population has led to the continued search for ways to meet global food demands. Agricultural intensification coupled with improved production practices has led to an increase in yield per unit of inputs used (The World Bank, 2018). The increase in agricultural production is characterized by the rise in the use of agrochemical inputs with pesticides as a major component. This has contributed immensely to increased crop and animal production as well as improvements in the quality of produce. These are partly attributed to the drastic reduction in yield losses with a resultant positive impact on farmers' income over the years (Oerke, 2006).

Notwithstanding the numerous benefits of agrochemicals especially pesticides to society, their continued use has raised serious concerns due to the negative impacts on environmental quality. Although pesticides play very important roles in increasing crop and animal productivity as well as the control of diseases and pests, their extensive use over the years has led to widespread environmental contamination. In addition to the contamination of soil, there has been widespread mobility of pesticide residues from points of application to surface and groundwater 'pools' that serve as sources of drinking water due to indiscriminate use. Compounds that are known to be environmentally persistent and highly toxic and are restricted from agricultural use in most developed countries remain popular in developing countries because, they are cheap and easily affordable (Carvalho, 2006). A pre-emergence pesticide like atrazine for instance, which remains popular among cereal and sugarcane farmers in most west African and some south American countries, is noted to be on the list of banned pesticides in the European Union (Bombardi, 2017).

Concerns about contamination of drinking and groundwater sources by the increased application of pesticides have risen in recent years as more farmers rely on the use of these chemical compounds in agricultural production. Numerous reports have ascribed pesticide residue in groundwater to their continued use in agricultural production with studies indicating that pesticide residues were detected in 60% of groundwater samples from agricultural areas of the United States (Gilliom, et al., 2006). In most developed countries of North America, Europe and other Asian countries like Japan, there are well-established legal frameworks for the assessments of environmental risk emanating from pesticide use. Such requirements are mostly non-existent or inadequately implemented in most developing countries, majority of which are located in the humid tropics (Niemeyer et al., 2017; Albuquerque et al., 2016). In this regard, the increase in pesticide use has not been properly followed with studies and the required legislation to assess their environmental effects and inform the enactment of the necessary regulations relating to their use in most developing countries in the tropical regions (Oliveira et al., 2018).

Under certain conditions, some pesticides may be leached to groundwater after normal field applications. A host of factors including land management practices, the chemical properties of the applied pesticide as well as soil properties play a very important role in influencing the transport of pesticide in soil and their eventual leaching to groundwater (Navarro et al., 2007). To understand the mode of transport and reduce the risk of contamination of groundwater from pesticide application, there is the need for an assessment of the factors enumerated above to estimate the potential movement of the applied chemical compound through the soil to groundwater and other sources.

Most tropical soils are highly weathered, with mostly low-activity clays and very low organic carbon content. Generally, the high moisture and temperatures of the humid tropics accelerate the decomposition of added organic material and therefore, render any benefits from the

amendments that may improve the sorption potential of the soils short-lived. As such most tropical soils are prone to leaching of applied pesticides as they are mostly poorly managed. A very important soil management strategy for reducing leaching of applied pesticides in addition to other measures is to manipulate the sorption potential of the soil. Among the numerous strategies that have been observed, incorporating organic amendments in soil is seen as a promising option because of the strong correlation between soil organic carbon content and adsorption of pesticides (Barriuso et. al., 1997; Morillo et. al., 2002). As has been indicated earlier, the high temperatures and moisture within the humid tropics lead to the accelerated decomposition of added organic matter and make their benefits in soil short-lived. Biochar which is obtained by the pyrolysis of organic matter and used as a soil amendment presents a very good means of mitigating the problem of pesticide leaching in tropical soils since it is suggested as being stable to decomposition when compared to other organic amendments in soil (Chaukura et al., 2016; Singh et al., 2014; Kookana et al., 2011). In addition to improving some soil physical properties (bulk density, soil structure, porosity and water holding capacity) and chemical properties including pH, cation exchange capacity, nutrient availability and organic carbon content (Gamage, et al., 2016; Frimpong-Manso et al., 2019), amending the soil with biochar can reduce pesticide leaching due to its adsorption effects (Trinh, et al., 2017; Zhelezova et al., 2017). Additionally, studies point to biochar as having wide ranging effects including reactivity in the soil and longevity in relation to resistance to microbial degradation. Because of its large surface area and high porosity, biochar can non-selectively adsorb different types of organic and inorganic chemical compounds including pesticides (Herath, et al., 2016).

An important factor for the successful use of biochar in the control of pesticide leaching in soil is that its sorption capacity for contaminants is maintained over an extended period once applied (Ren et al., 2018). Some studies suggest that the sorption characteristics of biochar can be altered once applied to the soil environment through short-term or long-term physical,

chemical and biological processes due to a phenomenon known as ageing (Zhang et al., 2018; Jin et al., 2016; Ren et al., 2018). While reports indicate that ageing may have contrasting effects on the adsorption properties of biochar by having access to some of its sorption sites blocked by labile organic compounds, other studies suggest that the process can lead to increased adsorption due to the exposure of oxygen-containing functional groups on the biochar with time (Joseph, et al., 2010). Additionally, there are reports that suggest that the presence of dissolved organic compounds introduced by the oxidation of organic matter in soil have the potential to reduce the adsorption of applied pesticides (Lin et al. 2012). These reports highlight the indication that the effect of biochar application on the sorption of pesticides in soil needs to be investigated further especially, in tropical soils.

1.2 Justification

The agricultural sector constitutes a pivotal sector in Ghana's economy and its dependence on pesticides and other agrochemicals to increase crop yields and protect farm produce has resulted in an increase in demand for agrochemicals (FAO, 2018). The use of pesticides has become an integral part of modern agriculture with herbicides playing a very significant role in weed control during land preparation and in-between planting and harvesting. In combination with irrigation, farmers are able to increase the yield of crops several folds and undertake cropping all year round. Several studies have pointed to increase in crop yields due to the use of pesticides with Kuniuki (2001) indicating a 10% yield loss due to the failure to apply pesticides by farmers.

There are growing concerns however on the dangers of indiscriminate use of pesticides. The presence of residues of pesticides in different environmental compartments has raised concerns about the possible migration of these contaminants into surface and groundwater sources as well as the food chain (Leah, 1996; Botwe et al., 2012). This poses grave danger to

communities that depend on the water source for drinking and other purposes (Botwe et al., 2012). Residues of pesticides have been detected in sediments and water samples by several research works conducted in Ghana. For instance, some studies conducted in a number of vegetable-growing communities in Akumadan and its environs within the Ashanti region of Ghana revealed the detection of organochlorine pesticide residues in water and sediment samples (Ntow, 2001; Ntow, 2005; Darko et al., 2008). Detectable levels of atrazine were also found in groundwater samples in Ejura in the Ashanti Region of Ghana following persistent application of the herbicide for the control of weeds on maize fields (Quaye, 2012). Although a lot of research reports have indicated the detection of pesticide residues in various environmental compartments especially, in rivers, sediments and groundwater sources, not much information is available in literature on management practices that seek to control the mobility of these contaminants from soils into surface and groundwater sources in Ghana.

1.3 Problem Statement

Most Ghanaian soils, especially those found in the northern part of Ghana are characterised as sandy with very low levels of organic matter and cation exchange capacity (Atakora et al., 2019). These soils are farmed yearly for the production of crops to feed the growing population with cereals, particularly maize among the crops cultivated mostly by farmers. Due to inadequate farm labour and convenience, atrazine and atrazine-based herbicides have become very popular among farmers cultivating maize and other cereals as a means of weed control during the cropping season. The popularity of the herbicide is attributed to the fact that it is cheap and easily obtained on the market. The indiscriminate use of atrazine (which is characterized as very mobile) in the highly weathered sandy soils of northern Ghana with very low levels of organic carbon is bound to cause excessive leaching of the pesticide in agricultural soils to drinking and underground water sources. This constitutes a major cause of concern to inhabitants, some of who depend on bore- holes for their potable water. The possible presence

of atrazine in underground water sources is an issue of great health concern since it can be an endocrine disruptor in humans (Lasserre et al., 2009). There is evidence to suggest that atrazine has the potential to interfere with the normal physiological functions associated with hormonal and anti-hormonal activities (Bohn et al., 2011).

Identifying ways to reduce atrazine leaching to groundwater would be a very important means of protecting the environment and human health from the negative impact of the herbicide. Because biochar-amended soils have been used to improve sorption of pesticides to soil, this study sought to employ this principle to examine the impact of biochar amendment on the sorption of atrazine in the sandy soils of Lawra with very low organic carbon content. Although a lot of studies on the adsorption behavior of biochar-amended soil on pesticides have been done lately, the relationship between biochar-mediated increases in adsorption in the presence of other organic soil amendments is still not clear. Additionally, the mechanisms affecting the age of biochar used in amending soil and the adsorption of pesticides on the amended soils have not been fully understood, particularly in highly weathered tropical soils with low levels of organic carbon.

1.4 Objectives of the Study

The general objective of this research therefore was to assess the influence of soil amended with biochar and compost on the sorption of atrazine in soil samples obtained from Lawra in the Upper West Region of Ghana in the quest to prevent or reduce leaching of the agrochemical into underground water.

The specific objectives of this study were to:

1. Identify the source and types of pesticides used by farmers in the study area.
2. Conduct a batch experiment to investigate the influence of biochar and compost amendment on the sorption of pesticides.

3. Investigate the influence of biochar ageing on the sorption of pesticides.
4. Predict the adsorption isotherm that best fits the adsorption mechanism.
5. Investigate the influence of pH on the adsorption process.

CHAPTER TWO: LITERATURE REVIEW

2.1 Definition of Pesticide

The United States Environmental Protection Agency (USEPA) under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) defines pesticide with certain exceptions to mean "(1) any substance or mixture of substances intended for use in preventing, destroying, repelling or mitigating the action or effect of any pest.

(2) any substance or mixture of substances intended for use as a plant regulator, defoliant or desiccant".

Various stakeholder institutions in Ghana such as the Environmental Protection Agency, the Food and Drugs Authority and Ghana Standard Authority all utilize the USEPA definition of pesticide and as such with a view to this study, the USEPA definition of pesticide will be adopted.

2.2 Types of Pesticides

A pesticide is a broad term that is used to describe an array of chemicals. These chemicals differ from each other either by their physical or chemical properties and thus important that they are classified into respective groups for easy study. Pesticides have been classified differently by several authors. Most commonly, they have been classified by mode of entry, pesticide function or the pest organism they attack and based on the chemical composition of the pesticide (Yadav and Devi, 2017).

Pesticides that attack insects are grouped as insecticides, pesticides that attack fungi are grouped as fungicides and pesticides that attack weeds, classified as herbicides. Imidacloprid, carbendazim and atrazine are examples of commonly used insecticides, fungicides and herbicides respectively. Pesticides may also be classified according to their chemical structure.

In this regard, pesticides that are manufactured on products whose molecular structure is carbon-based are termed organic pesticides. Organophosphates, organochlorines, synthetic pyrethroids and carbamates are the most popular classes of organic compounds. Inorganic pesticides on the other hand are mostly obtained from mineral ores and do not contain carbon in their chemical structure. Examples of inorganic pesticides include ferrous sulphate, Sulphur and copper sulphate. (Koranteng, 2015).

2.3 Herbicides

Herbicides are chemicals that are used to destroy weeds with minimum or no injury to the vegetation of interest (Baird and Cann, 2008). They are also sometimes employed in killing weeds on roadsides, railway tracks etc. Some commonly used herbicides include glyphosate, atrazine and 2,4-D (2,4-Dichlorophenoxyacetic acid). The use of herbicide goes as far back as agriculture. Farmers during the early days supplied crops with suitable conditions by physically removing weeds for optimum growth.

The use of chemicals such as rock salts, crushed arsenical ores, copper salts and oil wastes to control weeds is an old practice. These chemicals could not be used on agricultural lands as it was toxic to all plants (non-selective) and also remained toxic for a considerably long time (Vats, 2015).

In 1896 in France, Sinox became the first major organic chemical herbicide to be developed and followed by the synthesization of new herbicides which were products of research conducted during the Second World War in the 1940s (The Editors of Encyclopaedia Britannica, 2019). This instigated the period of "magic" weed killers which saw over 100 new chemicals developed in the space of 20 years. In the same era, great strides were made in the area of weed biology and ecology, which brought to light more understanding of plant competition, weed seed movement in the fecal matter of animals and other important concepts

(Bell, 2015). Pokorny, a chemist in the year 1941 synthesized the 2,4 dichlorophenoxy acetic acid which was later described as a plant regulator without mention of herbicidal prowess (Zimdahl, 2010).

Triazine herbicides were first discovered and produced between the years 1950 and 1970. An idea of a new family of herbicides that supports modern agriculture was conceived and developed by a team of scientists from the chemical company J.R. Geigy, Ltd., which later translated into not only new triazine compounds, but also a new field of weed control research (LeBaron et al., 2008).

2.3.1 Atrazine

Atrazine, (1-chloro-3-ethylamino-5-isopropyl amino-2,4,6-triazine), is a selective pre- and post-emergent weed control agent used to check broadleaf weeds that may attack maize, millet, sorghum, etc. (Bintein and Devillers, 1996). Atrazine remains one of the most heavily utilized herbicides on cereal farms worldwide. Atrazine operates by modifying the growth, enzymatic processes and photosynthetic activities of targeted weeds (Singh, et al., 2018).

As a result of its wide usage for agricultural uses and non-agricultural applications (including weed control along roads and railroads), the environment is extensively contaminated by atrazine through surface runoff and leaching into groundwater. Atrazine causes mutagenicity, genotoxicity, faulty divisions of cells, defective lipid synthesis and hormonal imbalance in aquatic organisms and other non-target animals (Singh, et al., 2018). Atrazine also has injurious effects on soil microbial communities and thus threatens the sustainability of agricultural soils.

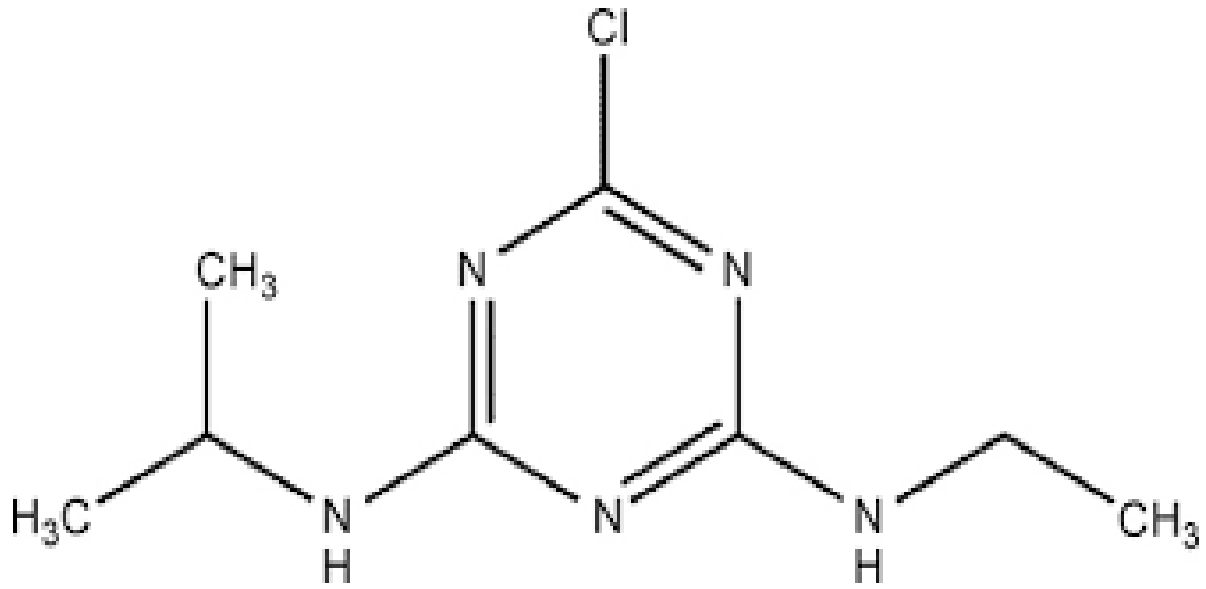

Figure 1: Molecular Structure of Atrazine (Vera Et Al. 2009)

The transformation of atrazine begins immediately after entering the environment and generally follows three main pathways. One degradation process is via the splitting of the triazine ring which is facilitated by microorganisms, N-dealkylation of the ethyl side chain and/or the isopropyl side chain and lastly the hydrolysis of the chlorine-carbon bond (Bintein and Devillers, 1996). The main metabolites of atrazine; hydroxyatrazine, deethyl-atrazine (DEA), deisopropylatrazine (DIA) and diaminochlorotriazine (DACT) are all at present suggested to be of less toxicity than the parent compound.

2.4 Pesticide Use

Growth in world economy especially in the last half of the nineteenth century in both manufacturing and agricultural sectors has led to a steady rise in the production and use of agriculture-based chemicals, frequently having destructive consequences on the environment (Sharma, et al., 2019). It is estimated that 2 million tonnes of pesticides are utilized annually worldwide and projected to reach 3.5 million tonnes by the end of 2020 with China being the major contributing country (Sharma, et al., 2019).

Africa's economy is mainly dependent on agriculture with nearly an estimated 59% of the population making their living from farming (Abate et al., 2000). As a result of increasing population, food demand is projected to increase in the next three decades and thus demand of pesticides is also likely to increase (Snyder et al., 2015). Most governments in Africa in the period of 1970-1990s encouraged the use of pesticides resulting in less monitoring by government (Snyder et al., 2015). In connection with this, inefficient regulatory mechanisms have resulted in importation of banned chemicals across the continent and lack of awareness on the part of farmers with regard to the dangers of indiscriminate pesticide use, has led to poor pesticide practices (PRRP-Ethiopia, 2012). Pesticides in the African market are generally unregulated and do not follow guidelines and code of conducts laid out by Food and Agriculture Organization and thus, most of these pesticides are untested and pose serious risks (Jepson, et al., 2014).

Agriculture remains an important sector in Ghana's economy, contributing about 54% of the Gross Domestic Product (GDP) while it forms 40% of earnings from export and provides more than 90% of the country's food needs (Food and Agriculture Organization, 2019). There is an occurring trend of decrease of agricultural lands resulting from population growth, erosion, reduction of soil fertility, desertification and soil salinization. Intensive utilization of pesticides and other agrochemicals is being adopted to address the increasing need for food (Fianko et al., 2011).

Pesticides have significantly reduced losses and increased the yield of crops like vegetables, cereals and other crops since its introduction. Pesticide usage for fruit, vegetable and cereal production has expanded with regards to quantity and types of chemicals as a result of an increase in the area of cultivation for crops.

In Ghana, pesticide use is more concentrated in the sectors of cocoa, oil palm, cereals, vegetables and fruits. Physical inputs such as agrochemicals, seeds and tools account for less than 30% of the total cost of crop production, however the use of pesticide is becoming increasingly prevalent (Fianko et al., 2011). For example, about twenty-one (21) different kinds of pesticides were imported into the country for agricultural purposes between 1995 and 2000 (FAO, 2004). The use of pesticides has been embraced in local communities who are making a living from the sale of agricultural produce. Among the various classes of pesticides known to farmers, organochlorine pesticides are the most widely used and popular because they are economical and their activities are of a broad spectrum. The pesticide lindane is often employed on cocoa plantations and vegetable farms; cotton growing areas heavily depend on endosulfan (Fianko et al., 2011). Maize growers in Ghana also utilize atrazine to check broadleaf weeds (Voto Mobile Org, 2015).

It is projected that about 87% of farmers in Ghana who apply pesticides apply any of or a combination of organophosphates, carbamates, pyrethroids and organochlorines (Ntow, 2001).

2.5 Fate of Pesticides in the Environment

Understanding the fate of pesticides when introduced into the environment is important for risk assessment of the environment and management decisions. Many processes, directly and indirectly, affect pesticides that are introduced into the environment either via application, disposal or spill (Schnoor, 1992). These processes affect pesticide persistence, movement and ultimate fate and thus influence the effectiveness of the pesticide and its impact on the environment.

Problems arise when pesticides applied move away from their point of application to other non-target regions. Cases of economic loss, ineffective control of pests and more gravely environmental contamination are some of the problems resulting from the indiscriminate use

of pesticides (Tiryaki and Temur, 2010). Groundwater contamination and accumulation of pesticides in the food chain is of serious concern with respect to environmental damage. Nevertheless, the various soil properties (organic matter, sand, clay, pH, etc.), characteristics of the pesticide (solubility in water, water absorptivity, persistence, etc.), climatic factors (wind speed, humidity, precipitation, temperature), method of pesticide application (dusting, spraying, injection, etc.) and ways by which pesticides are handled influence the processes that determine the fate of pesticides in the environment (Braschi et al., 2011). The way pesticides interact with soil, surface and groundwater is complex and controlled by various physical, chemical, and biological reactions occurring simultaneously and/or sequentially. The major processes that govern the fate of pesticides can be categorized into four types: degradation (pesticide breakdown and change of structure), transfer processes (movement of pesticides from point of application), absorption (take-up of pesticides by fauna and flora), and adsorption (attachment of pesticides to soil and other matter).

2.5.1 Degradation

The degradation of pesticides constitutes the breakdown and change of the structure of the pesticide. In most instances, degradation of a pesticide is measured by the half-life. The half-life of the pesticide measures the rate at which it degrades. A half-life is the time it takes for a certain amount of a pesticide to be reduced by half. This occurs as it dissipates or breaks down in the environment. In general, a pesticide will break down to 50% of the original amount after a single half-life (Hanson et al., 2015). A persistent pesticide is one with a long half-life. A persistent pesticide is dangerous for the environment as it increases the possibility of pesticide movement into other environmental compartments (Tiryaki and Temur, 2010). More often than not, degradation products of a pesticide are less toxic than the parent product and thus making degradation environmentally beneficial (Gavrilescu, 2005). This notwithstanding, when a pesticide is broken down before it controls its target pest, degradation becomes a nuisance and

causes economic loss to the applicator. In general, there are three main types of degradation namely biological (microbial), chemical, and photochemical degradation.

Biological degradation is the breakdown of pesticides by bacteria, fungi, algae, actinomycetes, and other microbial strains (Huang, et al., 2018). Pesticide breakdown is frequently via this type of degradation. Biological degradation presents a vital process by which chemicals in the environment are detoxified by soil and/or aquatic microbes (Solaimalai et al., 2004). Nevertheless, there is a possibility that products of biological degradation may be more toxic than the parent chemical. Biological degradation of pesticides usually takes place in the soil and the rate is influenced by temperature, aeration, moisture, organic matter content and pH, most of which directly impact the growth and activity of microbes (Kerle et al., 2007). The regularity of application of a pesticide can also affect biological degradation. When the same pesticide is applied on a field for a long period, organisms' effectiveness to degrade the pesticide increases and thus leads to a more rapid biological degradation process (Solaimalai et al., 2004).

Chemical degradation, also referred to as abiotic degradation of pesticides is the breakdown of pesticides in the absence of living organisms. This occurs via different reaction pathways such as hydrolysis (breaking of bonds in a molecule due to reaction with water), redox (reactions involving the transfer of electrons) and ionization and as such is strongly influenced by pH (Evangelou, 1998). The hydrolytic reaction changes the structure of the pesticide by attacking functional groups that are susceptible. Some of the more hydrolysis-prone functional groups include carbamates, amides, epoxides, carboxylic acid esters, phosphoric acid esters, sulfonic acid esters, and lactones (Neeley, 1985). Redox (reduction-oxidation) reactions are important for the alteration of the oxidation numbers of the available metals and control of their oxidation state leading to change in the structure of the compound (USEPA, 1996). When a chemical

undergoes ionization under environmental conditions, changes in pH will lead to a change in its chemical reactivity and physical properties (Gavrilescu, 2005).

Photochemical degradation is an abiotic process whereby pesticides are dissipated via the excitation of molecules by absorption of light energy which leads to direct or indirect oxidization of a functional group in the pesticide's molecule (Katagi, 2004). Pesticides that are found on leaves, soil, water and the atmosphere can all be denatured by this process. The rate of photochemical degradation is affected by the intensity and spectrum of the sunlight, exposure length, application method, characteristics of the application site and the physical and chemical properties of the pesticide (Kerle et al., 2007).

2.5.2 Transfer Processes

For high efficacious pest control, some pesticides ought to move away from their point of application. However, much movement of pesticides can result in a reduction of the pesticide control action, pollution of surface and groundwater and damage to non-target organisms such as some beneficial organisms and humans (Fishel, 2003). Natural processes such as volatilization, run-off, leaching and absorption can account for pesticide transfer.

Volatilization is the process by which solid and liquid pesticides are converted into the gaseous phase (Frazar, 2000). Once a pesticide undergoes volatilization, air currents can transfer it away from the point of treatment. Henry's Law constant expresses a pesticide's potential to volatilize by the ratio of vapor pressure to its solubility. The higher the value of the constant, the higher the tendency for the pesticide to volatilize and vice versa. Pesticides that have been lost to volatilization can be brought back through the action of rain thereby contaminating other non-target regions (Kloppel and Kordel, 1997). When a pesticide is strongly attached to soil particles or solid matter, there is a relatively lower chance of it undergoing volatilization (Bessin, 2018). Properties of the soil such as moisture and organic matter content can have an

impact on the rate and degree of volatilization of a pesticide (Fishel, 2003). Environmental factors including temperature (high temperature increases volatilization), humidity (low humidity promotes volatilization) and air movement (favors volatilization) influence pesticide volatilization (Gavrilescu, 2005). Highly volatile pesticide compounds with low solubility in water may escape into the atmosphere whereas volatile pesticides with high water solubility may leach and pollute groundwater.

Run-off water carries along contaminants across the surface of the soil as it moves. This occurs when irrigation, rain, or melted snow adds water to the soil surface at a rate faster than it enters the soil (United States Environmental Protection Agency, 2005). Pesticides may be moved along with runoff water if they are dissolved in the water or strongly attached to the soil particles that are carried along. The intensity of runoff of pesticides depends on several factors including soil characteristics, site characteristics and the properties of the pesticide (Gardner, 2016). Soil characteristics such as texture significantly impact runoff as a compacted soil with higher clay content is more susceptible whereas dry sandy soils are less prone. Also, the moisture content of the soil is an important factor as moist soils are more likely to experience runoff than drier soils. The climatic factors of the site such as the amount of rainfall (runoff is high when there is a heavy rainfall after pesticide application) and temperature are also important in predicting the intensity of runoff (Osunbitan et al., 2014). Pesticide Runoff is also dictated by the site characteristics such as the slope of the land (the steeper the slopes the higher the likelihood water along with pesticides will runoff) and the amount and type of vegetation present on site (Gardner, 2016). Reduced-tillage cropping system as well as conservation tillage allows enough vegetation and crop residues on the land which can slow or intercept the movement of runoff water and will hold the pesticides on site. Heavy grass cover also reduces the potential of pesticide runoff. Physico-chemical parameters of the pesticide that influence the degree of pesticide runoff include solubility (highly soluble pesticides may be taken up

with running water), adsorbency (pesticides that are tightly bound to soil particles will remain on site unless the particles are eroded along), persistence (the quicker it degrades, the less it is available to move) and pesticide application method (injected pesticides are likely to remain on site and not removed by runoff water) (Gardner, 2016).

Leaching of pesticides refers to the downward, upward, or sideways movement of water carrying pesticides through the soil (Tiryaki and Temur, 2010). The downward movement is of particular concern as groundwater can be contaminated when pesticides move through the soil profile with infiltrating water to the water table (Kerle et al., 2007). Leaching of pesticides is dependent on the chemical and physical properties of the pesticide such as solubility, adsorption, volatility, degradation and dissociation (Kordel and Kleim, 1992). Pesticides that degrade quickly or are highly volatile have a less tendency to leach into groundwater than pesticide compounds that take a longer time to break down. Soil factors such as the type of soil, texture, moisture content and availability, organic matter, microbial community and soil pH, all affect the leaching of pesticides as a result of their influence on adsorption (Arnold and Briggs, 1990). For example, the porous nature of sandy soil makes it easier for pesticides to leach as compared to clayey soil. The method, rate and time of application also impact the leaching of pesticides. Injected pesticides, frequent applications and applications just before rainfall present a high chance of pesticide leaching. Leaching may be beneficial when the pesticide ought to move to a target pest, too much of it however will result in reduced pest control, possible damage to non-target organisms and contamination of groundwater (Osunbitan et al., 2014).

2.5.3 Absorption

Pesticides can be taken up by plants and/or animals. Also, plants can hold up degradants of the pesticide in their tissues (Gardner, 2016). Environmental conditions such as the physical and chemical characteristics of the pesticide and the soil influence the absorption of pesticides by

both target and non-target organisms. Pesticides after absorption usually break down. The pesticide residues may remain inside the plant or animal and be released back into the environment after the plant or animal dies (Tiryaki and Temur, 2010). Pesticide build-up can cause poisoning in the plant or animal, whereas biomagnification of the pesticide which is the buildup of the pesticide along the food chain can lead to greater risk for organisms higher up the food chain. Pesticide and residues that are taken up by plants and animals are unavailable to cause environmental mayhem such as leaching and runoff (Kerle et al., 2007).

2.5.4 Adsorption

Pesticide adsorption is a surface phenomenon whereby the pesticide attaches itself to soil, vegetation, or other surfaces. Nevertheless, the attraction between soil and pesticides is what is frequently termed as pesticide adsorption (Kerle et al., 2007). The strength of adsorption between the soil and the pesticide impacts the biological activities of the pesticide as well as the degradation, leaching and the distribution of the pesticide through the soil horizon (Fishel, 2003). The soil type and properties such as pH, temperature, particle size distribution and organic matter content are the factors that influence the degree of adsorption in the soil. Pesticide characteristics such as structure, electrical charge, solubility and its concentration in the soil also impact the extent of adsorption (Braschi et al., 2011). Soils that are characterized by high clay and organic matter content have a higher potential to adsorb more pesticides as they tend to have more particle surface area (Fishel, 2003). Wet soils adsorb less than dry soils as water molecules occupy some of the binding sites and reduce the sites available for pesticide binding. Adsorption and the strength of it is an important phenomenon as it influences the availability of pesticides for degradation, uptake and leaching (Fishel, 2003). Pesticides that are weakly adsorbed can be washed away after irrigation or rainfall, contaminating surface water as well as being leached, leading to contamination of groundwater sources.

2.6 Sorption Isotherms

The extent to which an adsorbate varies in terms of amount on an adsorbent is described by a sorption isotherm. The isotherm is a relationship between a substance's concentration in solution and the amount adsorbed in the solid phase when both phases are in equilibrium (Tetteh, 2014).

2.6.1 Quantity adsorbed

At constant temperature, the amount of adsorbate that can be taken up by an adsorbent is given by the general equation:

$$Amount\ adsorbed, q = \frac{(C_o - C_e) \times V}{M} \quad \text{.....2.1}$$

where;

C_o = initial concentrations of chemical (mg/L)

C_e = equilibrium concentrations of chemical (mg/L)

V = volume of solution used (mL)

M= mass of adsorbent (g)

The most common adsorption isotherm utilized for statistical models are the Langmuir and Freundlich isotherms.

2.6.2 Langmuir isotherm

The Langmuir isotherm applies to surfaces that have a finite number of identical sorption sites and thus predict linear adsorption at low adsorption densities and a maximum surface coverage at higher solute concentrations (McMillan, 2018). This model assumes monolayer adsorption

to homogenous surface sites (McMillan, 2018). The equation that describes the Langmuir isotherm is given by:

$$\frac{q_e}{q_m} = \frac{bC_e}{(1+ bC_e)} \quad \text{.....2.2}$$

Where;

q_e = amount of adsorbate per unit mass of adsorbent at equilibrium (mg/kg),

q_m = maximum adsorption capacity (mg/kg),

b = Langmuir constant, relate to the energy of adsorption (L/mg).

C_e = equilibrium concentrations of chemical (mg/L)

2.6.3 Freundlich isotherm

The Freundlich isotherm applies to processes of adsorption which occur on heterogonous surfaces (Ayawei et al., 2015). This expression outlines the heterogeneity of surfaces and the exponential distribution of active sites. The Freundlich isotherm is given by the equation:

$$Q_e = K_F C_e^{\frac{1}{n}} \quad \text{.....2.3}$$

Where;

Q_e = the amount adsorbed per gram of adsorbent at equilibrium (mg/L),

K_F = Freundlich isotherm constant (mg/g),

C_e = equilibrium concentration of adsorbate (mg/L) and

n = adsorption intensity.

2.7 Biochar

Biochar is a substance with charcoal-like characteristics that is obtained by subjecting organic material, usually from agricultural and forestry wastes via a process called pyrolysis (Spears, 2018). Scientists and policy-makers are increasingly recognizing biochar for its potential role in carbon sequestration, greenhouse gas emissions reduction, renewable energy, waste mitigation and as a soil modification (kookana et al., 2011).

2.7.1 Origin and Production

The charcoal technique used to increase the fertility of soils originated in the Amazon basin some 2500 years ago. The region's native Indians would create charcoal and incorporate it into small land plots of 1-80 hectares in size (Biogrow Limited, 2013). As is known in this part of Brazil, Terra Preta (which translates to Black Soil) remains highly fertile even up until today, even with little to no application of fertilizer. Moreover, this is recognized in an area of the world for its very infertile soils. Chars and Ash obtained from cooking fires, and other debris that included manure and bones applied to soil could be traced to the early residents of the Amazon River Basin from 450 to 650 Common Era (Sombroek, 1966). Global interest in biochar has increased considerably in current times as a result of the persistence of observed physical and chemical properties of soil for hundreds to thousands of years (Lehmann, 2007).

Biochar is obtained under low or zero oxygen conditions in a thermochemical process termed as pyrolysis (Duku et al., 2011). Several feedstocks have been proposed as raw materials for the production of biochar. They include biomass ranging from forestry residues, wood waste, agricultural crop residues, organic municipal solid waste and animal manures (Duku et al., 2011). The appropriateness of each type of biomass is hinged on factors such as the chemical composition, properties of the material, environmental, logistics and economic factors (Duku et al., 2011). The physical and chemical properties of biochar are mainly controlled by the pyrolysis conditions and the feedstock type. Biochar is highly persistent in soils, with wood

biochar being recalcitrant in the soils in the range of hundreds to thousands of years. This makes it about 100 times more persistent than most soil organic matter (Verheijen et al., 2010).

Pyrolysis is a Greek word that literally means decomposition by fire. The chemical breakdown of an organic substance via heating in the absence of oxygen is pyrolysis and is the first step in combustion and gasification, as defined by Duku et al (2011). Gasification is the process of subjecting biomass to temperatures above 800 ºC in the presence of oxygen to produce syngas for energy production and a small amount of biochar (Streubel, 2011). The pyrolysis process disintegrates the polymeric building which consists primarily of cellulose, hemicellulose and lignin through processes of depolymerisation, cross-linking and fragmentation at various temperatures (Duku et al., 2011). Three different products are primarily obtained when organic materials are transformed by biomass pyrolysis: gas often referred to as non-condensable volatiles, liquid (bio-oil) often classified as condensable volatiles, and solid in different proportions depending upon both the feedstock and the pyrolysis conditions used (Verheijen et al., 2010).

The product yields of the pyrolysis are largely influenced by process conditions such as heating rates, pressure, temperature, particle size and other factors such as feedstock type, nature, lignin and ash content (Demirbas, 2011). Similarly, the quality of the biochar, characteristics and compositions are heavily influenced by the origin, nature and type of feedstock as well as the pyrolysis process and conditions (Verheijen et al., 2010). An assessment of the yield of biochar from different feedstock revealed that biomass containing high content of lignin produced a greater yield as a result of the stability of lignin in the face of thermal degradation (Demirbas, 2004). Low biochar yield is associated with biomass obtained from crop residues such as maize, rice straw and manures as they are generally characterized by low mechanical strength (Duku et al., 2011).

Pyrolysis may be categorized into slow, intermediate and fast depending on the condition and process of the pyrolysis (Sohi et al., 2009). The energy requirement of the pyrolysis process can be provided through the heat of reaction or by flue gases from the combustion of feedstock and by-products as well as indirectly via heat carriers such as metal spheres and sand (Duku et al., 2011). Fast pyrolysis tends to give higher liquid yields whereas slow and intermediate pyrolysis produces higher biochar yields (Duku et al., 2011). Higher biochar yields are often associated with high lignin, ash and nitrogen contents of biomass, pyrolysis temperature of less than 400 °C (low pyrolysis temperature), long vapour residence and vapour-solid contact, big biomass particle size and enhanced heat integration (Duku et al., 2011; Demirbas, 2004).

Recent research on the production of biochar reveals that herbaceous feedstock such as hulls of peanut, straws and husks of rice produce biochar of lower carbon contents, higher nitrogen contents and higher pHs as compared to biochar produced from woody feedstock (Novak, et al., 2009). The chemical breakdown of the hemicellulose and cellulose influences the pH of the biochar. Organic acids and phenolic substances are produced at pyrolysis temperatures between 300 and 600 °C and alkaline salts are formed, which increase the pH of the biochar (Streubel, 2011). Herbaceous biochar tends to give a higher liming impact per kilogram of biochar applied to soil and thus depending on soil type increasing soil pH by about 1 pH unit. Higher concentrations of calcium and magnesium in biochar are correlated with higher pH as they can act as buffers (Chan and Xu, 2009).

2.7.2 Properties of Biochar

Biochar is exceedingly heterogeneous, with both stable and labile compositions (Verheijen et al., 2010). The feedstock is the primary factor that controls the physical and chemical properties of biochar. Seven biochar properties have been identified and used to evaluate the suitability of biochar for agricultural-related usage. These are, specific surface area, bulk density, pore-volume, water holding capacity, volatile compound content, ash content and pH (Sohi et al.,

2009). Biochar's chemical composition is significantly influenced by the process temperature as well as the residence time of pyrolysis. An increase in the pyrolysis temperature positively correlates with pH and surface area (Lehmann and Joseph, 2009). For example, the carbonization of bagasse at different temperatures of 600 and 700 °C yielded biochar with specific areas 270 m^2/g and 322 m^2/g respectively (Ueno et al., 2008).

The effect of pyrolysis temperature on biochar has led to proposals that biochar prepared at low temperatures are suitable for checking the loss of fertilizer nutrients whereas high temperature biochars are more appropriate for utilization as activated carbon. There is a positive correlation between the porosity of the biochar and its adsorption and water retention capacity (Ogawa et al., 2006). The carbon to nitrogen ratio (C:N) is widely used as a measure of organic substrates' ability to release nutrients when amended to soils. The C:N ratio which has implications for nutrient retention in soils is found to vary widely in biochar ranging from 0.007 to 0.5 (Chan and Xu, 2009).

Biochar elementary analyses showed that the mineral content of the feedstock determines the resulting biochar where their concentrations are magnified as a result of the loss of Carbon, Hydrogen and Oxygen during the pyrolysis process (Amonette and Joseph, 2009). The nitrogen, phosphorus, potassium and sulphur contents of biochar produced from herbaceous biomass are usually greater than that derived from woody feedstocks. Depending on the feedstock, total nitrogen in biochar can vary from 1.8 to 56.4 g/kg^{-1} (Verheijen et al., 2010). During the pyrolysis process as temperature increased from 350 to 600 °C, Streubel observed that majority of the Nitrogen and Sulphur was lost (Streubel, 2011). Also, Shinogi and Kanri observed that during the pyrolysis of rice husks, sugarcane bagasse, cattle manure and sewage sludge, about 60-80% of the Nitrogen was lost (Shinogi & Kanri, 2003). Volatilization occurs during the heating process leading to the condensation of Nitrogen-containing structures (such

as amino acids, amino sugars) in the biochar which culminates in the decrease of Nitrogen concentrations and also into forms that are unavailable for plant usage (Cao and Harris, 2003).

2.7.3 Functions of Biochar

One of the primary reasons why biochar is applied to soil is because of its ability to sequester carbon. Carbon dioxide (CO_2) is released into the environment with the decomposition of organic materials and thus the high stability of organic matter after pyrolysis can lower the release of CO_2 as decomposition is decreased (Sohi et al., 2009).

Incorporation of biochar to soil darkens the color especially for soils that are low in organic matter (Sohi et al., 2009). The darkness of the soil will lead to the high absorption of solar energy and an increase in temperature depending on vegetative cover and water content. The rate of some biological processes and nutrients cycling will all be affected and potentially increase the duration of the growing season (Krull et al., 2009). Although the application of biochar may not necessarily be aimed at achieving higher yield, these three main mechanisms outline how crop production might increase as a result of biochar application (Sohi et al., 2009).

1. Direct modification of soil chemistry through its intrinsic elemental and compositional makeup,

2. Providing chemically active surfaces that modify the dynamics of soil nutrients and

3. Modification of physical characteristics of the soil in a way that benefits root growth and/or nutrient and water retention and acquisition.

Previous works suggest that moderate additions of biochar are normally beneficial with only a few cases producing negative effects. Higher application also seems to hinder plant growth

(Ogawa et al., 2006). However higher biochar application coupled with NPK fertilizer application produced increased crop yield on tropical Amazonian soils (Steiner, et al., 2007).

Increased cation exchange capacity (CEC), surface area, pH and water retention capacity are amongst some of the beneficial characteristics of biochar application. Biochar also has a high affinity for both micro and macronutrients (Lehmann, 2007).

Research also reveals that the amendment of many tropical and subtropical soils with biochar increases exchangeable bases, CEC, availability of nutrients, water holding capacity and reduces soil density (Liang, et al., 2006). Physical properties of soil including structure, texture, bulk density, pore size distribution, water retention and workability can all be altered with the incorporation of biochar (Downie et al., 2009).

2.7.4 Factors affecting adsorption on biochar

The adsorptive capacity of biochar is based on the pyrolysis conditions and the feedstock type which influences the surface area, charged surface and functional groups (Nartey and Zhao, 2014). In recent times, the adsorption of various environmental pollutants by biochar has become a research hotspot in environmental science.

Biochar is used as an adsorbent for heavy metals and this adsorption is achieved via mechanisms such as electrostatic interaction, chemical precipitation, ionic exchange and the complexation with functional groups on the surface of the biochar (Liu and Zhang, 2009). Free functional groups such as phenolic hydroxyl, carboxyl and alcoholic hydroxyl form inner-sphere complex to achieve sorption, as well as co-precipitation or superficial precipitation (Qiu, et al., 2012). The main functional groups that are touted to foster coordination between heavy metals and biochar are the carboxyl and alcoholic hydroxyl (Singh et al., 2010). The solution pH also influences the metal ion speciation and the surface charge density of the adsorbents (Chen et al., 2008).

The mechanism of adsorption of organic pollutants by biochar can be categorized into pore filling, electrostatic attraction, complexes adsorption, spectrometer exchange, partition uncarbonized fraction and π-π electron-donor acceptor interactions (Dai et al., 2019). Adsorption of organic pollutants by biochar increases with an increasing number of oxygen-containing functional groups, owing partially to the presence of π-π electron-donor acceptor interactions. For example, aromatic molecules are efficiently adsorbed with the presence of carboxylic acid, nitro and ketonic groups on the biochar surface acting as electron acceptors (Dai et al., 2019). Ahmed et al, 2018 also proposes that the availability of different types of amine and hydroxyl groups in biochar can also serve as π-electron donor sites. The electrostatic attraction is as a result of negatively charged biochar surfaces and positively charged organic compounds. The extent of this attraction is often dependent on the distance between the two atoms and the charge (Rosales et al., 2017). Biochars with low surface oxidation exhibit hydrophobicity and thus through hydrophobic interactions react with hydrophobic organic pollutants to achieve the purpose of pollutant elimination (Inyang and Dickenson, 2015). Research conducted on the adsorption of methyl orange by ferric oxide biochar nano-composites revealed that complexation helped remove the molecules of the methyl orange in a single solute solution (Chaukura et al., 2017).

Various biochars adsorb via different mechanisms as different types of biochar have different surface-active groups and functional groups. A previous study revealed that ion exchange was the main mechanism at play for the adsorption of organic dye by rice straw (Ji et al., 2016).

2.7.5 Biochar ageing

When biochar is applied to the soil, it undergoes some physical, chemical, and biological changes as it ages and thus affects its ability to adsorb organic contaminants (Cheng and Lehmann, 2009). Volatile organic compounds and aliphatic carbon are mineralized in the soil by microbes leading to the liberation of disjointed aromatic moieties that oxidize to form new

functional groups (Kuzyakov et al., 2014). With the development of functional groups, more interactions with soil minerals and contaminants become possible with the oxidized biochar. The number of functional groups on the oxidized biochar surface, especially carboxylic and phenolic groups, increases with gradual aging. This increase in the number of functional groups results in an increase in sorption capabilities (Mia et al., 2017).

2.8 Compost and adsorption

Composting is the deterioration of organic materials into a humus-like material via a controlled microbial aerobic decomposition process (Negro et al., 1999). Compost is the result of the aerobic biological decomposition of organic matter present in wastes by the activity of mesophilic and thermophilic microorganisms (De Bertoldi *et al*., 1983).

Composts are produced from a variety of by-products and waste materials such as urban and agricultural wastes. The processing of compost is less elaborate and thus can be done at a low economic cost (Food and Agriculture Organization of the United Nations, 2003). Typically, composts are safe stable products, often with neutral or slightly alkaline pH, highly porous and rich in organic matter. Their main applications are in the field of agronomy. The high organic matter content of compost is leveraged as organic amendments in agricultural and horticultural soils (Dominguez *et al*., 2019).

Application of compost enhances the proportion of organic matter and can reduce the bioavailability of organic contaminants through adsorption and by combining with humic substances to form stable complexes (Liua et al., 2009). Composts present a diversity of functional groups that are able to interact with organic and inorganic compounds and contain microorganisms that are able to achieve biodegradation of many organic substances. This often results in a reduction of mobility and bioavailability of pollutants in soils amended with compost, in particular in the case of heavy metals (Smith, 2009). An array of contaminants

such as copper, zinc, colorants and pesticides have been successfully eliminated or drastically reduced in the soil with the treatment with compost (Kazi, et al., 2006).

This ability of compost to interact with different organic and inorganic substances is the basis for another application in environmental remediation: the use of compost as a soil amendment to adsorb pesticide. Compared to other adsorbents, composts present advantages such as their lower cost since they are often produced from wastes and are widely produced and available.

CHAPTER THREE: MATERIALS AND METHODS

3.1 Study Area

The study was carried out in the Lawra District located in the western part of the Upper West Region of Ghana (Figure 2). It shares boundaries in the north with Nandom District, to the east with Lambussie-Karni District and is bounded to the south-west and west by the Republic of Burkina Faso. The district capital is Lawra which is about 85 kilometers away from the regional capital Wa. The 2010 population and housing census put the district's population at 54,889 with females constituting 52 percent and 48 percent males. The major economic activity in the district is agriculture employing about 70 percent of the working population. About 80 percent of the farmers are involved mainly in the cultivation of maize, millet, groundnuts, soya bean and cowpea. Animal production is also undertaken to supplement incomes from crop farming (Ghana Statistical Service, 2014).

Climate and Vegetation

The Lawra district is situated within the Guinea Savannah zone which is characterized by short grasses and few woody plants. Trees common in the district include trees that are resistant to drought and fire such as Acacia, Baobab, Dawadawa and Shea trees.

The vegetation is very suitable for livestock production, which makes significant contributions to household incomes in the district. The prolonged dry season has the greatest impact on the vegetation rendering the grass dry and often leading to bush fires that leave the vegetation patchy and bare. The torrential early rains consequently cause excessive soil erosion at the beginning of the season. The vegetation cover and transpiration is reduced with bush burning and thus impacts the average annual total rainfall. This often leads to low agricultural yields as farmers are heavily dependent on rain-fed agriculture.

The district has an annual mean temperature ranging between 27°C and 36°C with the hottest period occurring between February and April. The only wet season in the year occurs between April and October when the Tropical Maritime air mass blows over the area. The average annual rainfall ranges from 900 to 1,200 mm. (Ghana Statistical Service, 2014).

Relief and Drainage

The land in the area rolls gently with a few hills ranging from 180 to 300 meters above sea level. The area is drained by the Black Volta River to the west marking the boundary between the district and the Republic of Burkina Faso. The Black Volta River has some tributaries in the district, which include the Kamba/Dangbang, Nawer, and Duodaa. These water resources when effectively utilized for irrigation can help to increase the production of food crops in the area as well as provide agro-based employment for the youth who migrate to the south to pursue non-existent jobs in the dry season (Ghana Statistical Service, 2014).

Geology and Soil

The rock formation in the District is basically Birimian with dotted outcrops of granite. The mining potential of the district is largely unexplored. There are references to the existence of minor deposits of manganese, gold and diamond fragments, iron ore and clay. There is a high potential for obtaining groundwater in the District resulting from a well-established pattern of fractures in the rocks, making it suitable for all-year-round farming.

The soils in the district mainly consist of laterite deposits. These are derived from the Birmian and granite rocks that lie beneath the area. Strips of alluvial soils are also present along the Black Volta flood plains as well as the presence of sandy loamy soils along some of its tributaries. There is a persistent shortfall in food production due to low crop production owing

to the generally low fertility nature of the soils, traditional land-use practices, and rainfall patterns.

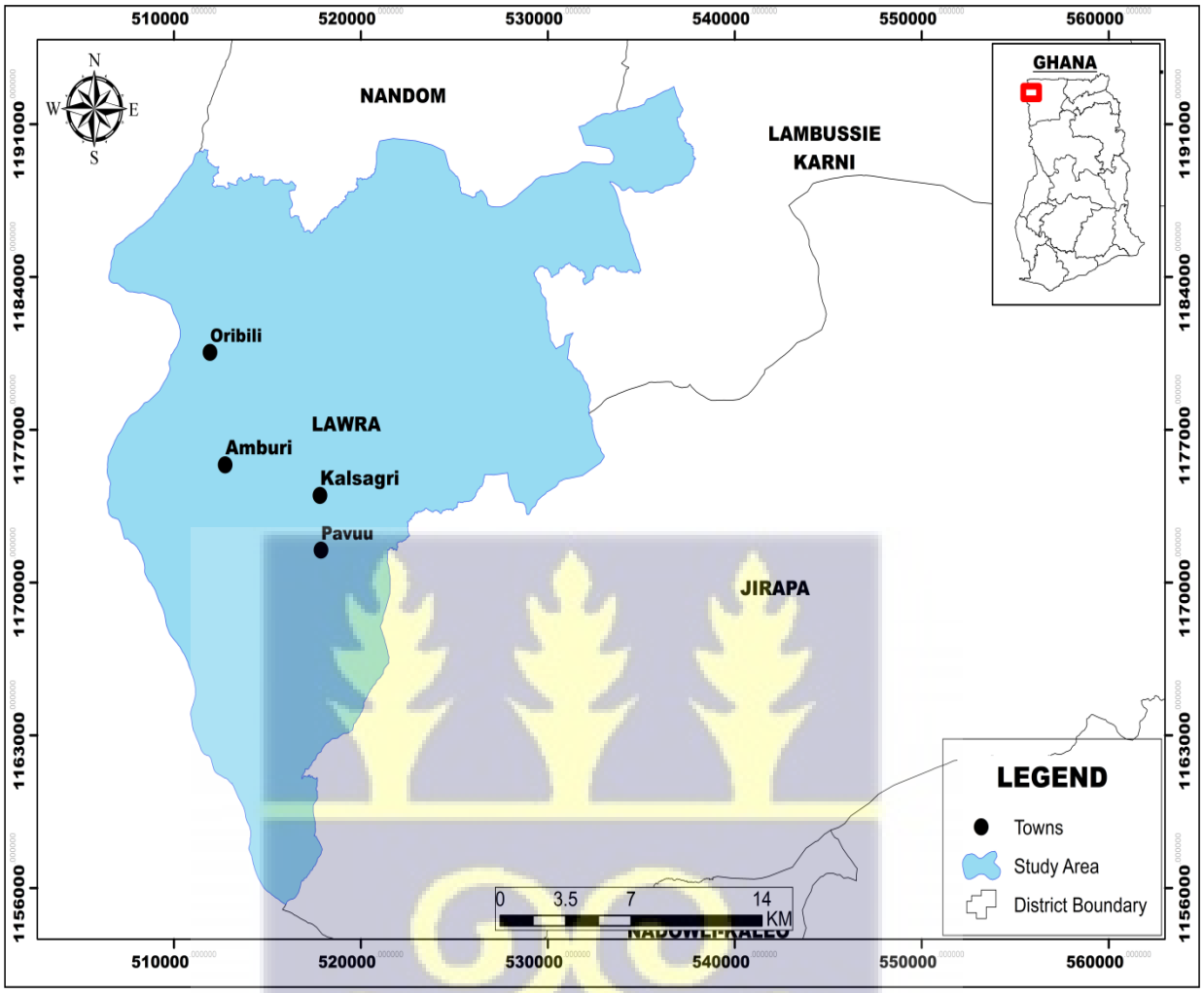

Figure 2 Map of Lawra District

3.2 Selection of sample sites and sampling

The area of study, the Orbili community, was randomly selected from a list of all major farming communities in the district. Soil samples were obtained at site 10°40'44.5" N 02°53'44.1"W. The field was divided into different homogenous units based on visual observation. An auger was driven to a plough depth of about 20 cm to draw the soil sample. Fifteen (15) samples were taken from the different units in a zig-zag pattern to ensure homogeneity. The samples were placed in a bucket and thoroughly mixed. Foreign materials such as twigs, roots, and dry leaves

were removed from the soil, sieved, air dried, stored in well labelled plastic polythene container and transported to the University of Ghana Soil Science Laboratory for routine physico-chemical characterization the subsequent week.

3.3 Farmers' survey

3.3.1 Research design

A mixed analysis approach was chosen to obtain a cross-sectional data of pesticide use pattern in the selected community.

3.3.2 Sampling technique and size

The respondents for this study were farmers within the Lawra district of the Upper West Region of Ghana. A random sampling technique was employed to sample sixty (60) farmers in the Lawra District. Sample size determination is outlined in Appendix C.

3.3.3 Instrument for data collection

The instrument used for the survey was a pre-tested structured questionnaire (Appendix B) which was developed for this study. The structure of questions in the questionnaire included open-ended and close-ended questions. The questionnaire begins with general background information and demographics such as the date of survey, name of the community, farmer's name, age, gender, and educational background. The questionnaire proceeds with questions that seek to identify the source, types and names of pesticides used as well as the proximity of drinking water sources to farms. Other questions on the ability to read pesticide labels, pesticide usage training and the factors that informed decisions in pesticide purchases were also asked in the instrument for the study.

3.4 Preparation of biochar and compost

Biochars were prepared from feedstocks of cow dung, corn cob, maize stalk, maize husk, and groundnut husk. The feedstock was oven-dried at 80ºC overnight and subsequently cut into

smaller pieces. A kiln at the Soil Research Institute of the Council for Scientific and Industrial Research, Kwadaso, Kumasi was used for biochar production at temperatures ranging from 500 to 700ºC. After pyrolysis, the biochar was washed with deionized water, air dried and ground. The ground biochar was then passed through a 2mm sieve and sealed in a sack for use. The biochar used was sourced from the USAID-Ghana/UG Institutional Capacity Building for Agriculture Productivity Project.

The same feedstock was used in the preparation of the compost. The feedstock was piled in layers on a cemented floor in a shaded area. The feedstock was pre-soaked in water except for the manure which was spread directly. The pile was turned over and watered every 3 days for 21 days. The temperature of the pile was kept between 55 to 68 ºC. Samples of the heap were ground and placed in a ziplock bag for routine analysis.

3.5 Physico-Chemical Characterization

3.5.1 Particle Size Analysis

The particle size distribution of the soil was determined using the Bouyoucos Hydrometer method modified by Day (1965). Forty (40) grams of the air-dried, sieved soil was weighed into a beaker and 60 ml of 6% Hydrogen Peroxide (H_2O_2) added to destroy the organic matter present in the soil. A 100 ml portion of 5% Calgon (Sodium hexametaphosphate) solution was added and the suspension was placed on a mechanical shaker for 2 hours. The suspension was completely poured into a graduated sedimentation cylinder and topped up to the 1000 ml mark with distilled water. The suspension was thoroughly mixed with a plunger by moving it up and down several times. Five minutes after the plunger was removed, an ASTM 152H hydrometer was inserted into the suspension and the reading for silt and clay was noted. The reading for clay was taken after 5 hours. The entire content of the sedimentation cylinder was emptied into a 47-micron sieve and the effluent discarded. Tap water was run through the sediments to wash off the fine material until the effluent was clear water. The remaining sand particles on the

sieve were transferred into moisture can of known weight, oven-dried at 105ºC for 24 hours and the dry weight determined. Blank hydrometer readings of sodium hexametaphosphate were recorded during the 5 minute and 5-hour hydrometer reading. The temperatures of the suspensions during the two readings were also taken. The percentage distribution of sand, silt, and clay were calculated as follows:

$$\%Clay\ and\ Silt = \frac{(5\ minute\ reading - correction\ for\ temperature)}{oven\ dry\ mass\ of\ soil\ sample} \times 100\% \quad \text{.....3.1}$$

$$\%Clay = \frac{(5\ hour\ reading - correction\ for\ temperature)}{oven\ dry\ mass\ of\ soil\ sample} \times 100\% \quad \text{.....3.2}$$

$$\%Silt = \%\ (Clay\ and\ Silt) - \%Clay \quad \text{.....3.3}$$

$$\%Sand = \frac{(oven\ dry\ weight\ of\ particles\ retained\ on\ the\ 47\ \mu m\ sieve)}{oven\ dry\ mass\ of\ soil\ sample} \times 100\% \quad \text{.....3.4}$$

The effect of temperature on density was accounted for using the equation by Day (Day, 1965): for every 1 ºC increase in temperature above 19.5 ºC, there is a corresponding 0.3 increase in density of the particles in suspension.

Increase in weight = (T2-T1) × 0.3 = (28-28) × 0.3 = 0

Correction for temperature = blank reading – increase in weight of particles

Therefore, Correction for temperature = blank reading – 0 = blank reading

The soil sample was assigned a textural class using the United States Department of Agriculture textural triangle based on the average proportions of the soil types. The test was conducted in triplicates.

3.5.2 pH Determination

Twenty (20) grams of soil alone, soil mixed with 1 year old biochar, soil mixed with 2-year-old biochar, and soil mixed with compost were weighed in triplicates into 50 mL beakers. Twenty milliliters of distilled water were added to each sample and the soil liquid suspensions

thoroughly stirred for 30 minutes. The suspensions were allowed to stand for 30 minutes to achieve equilibration. An Oakton PC 2700 was calibrated and the electrode inserted into the supernatants of the suspensions to measure the pH of the samples. The pH values were recorded after the stabilization of the readings. The pH of the various soil samples were also determined in 1M KCl using a soil: solution ratio of 1:2 in triplicates.

Additionally, 5 grams of 1 year old biochar, 2-year-old biochar and compost were weighed in triplicates and the pH determined using the above-described procedure in both distilled water and KCl. An adsorbent: solution ratio of 1:3 was used in both instances.

3.5.3 Organic Carbon Determination

The organic carbon content of the soil, biochar and compost was determined by the wet combustion method (Walkley & Black, 1934). A sample weight of 0.5 g each of air-dried and sieved soil sample, soil amended with 1 year old biochar, soil amended with 2-year-old biochar, and soil amended with compost were weighed into conical flasks. Ten millilitres of 0.167 M potassium dichromate ($K_2Cr_2O_7$) and 20 ml of concentrated Sulphuric acid (H_2SO_4) were added to the soil samples in the conical flasks and swirled to ensure full contact. The mixtures were allowed to stand for 30 minutes. The remaining unreduced $K_2Cr_2O_7$ in the solution after the oxidation of the oxidizable organic material in the soil samples were titrated with 0.2 M ferrous ammonium sulphate after adding 10 ml of orthophosphoric acid and 2 ml of barium diphenylamine sulphonate indicator from a dirty brown colour to a bright green endpoint. A standardization titration of the $K_2Cr_2O_7$ with the ferrous ammonium sulphate was done and the amount of oxidizable organic carbon calculated by subtracting the moles of unreduced $K_2Cr_2O_7$ from that of $K_2Cr_2O_7$ present in the standardization titration. The procedure was repeated with

0.02 g of 1 year old biochar, 2-year-old biochar and compost. All experiments were conducted in triplicates and the standard mean calculated.

The percent organic carbon was calculated as follows:

$$\%\ Organic\ Carbon = \frac{(Blank\ Titre - Sample\ Titre) \times Conc.of\ FeSO4 \times 0.39}{Sample\ Weight} \quad \text{.....3.5}$$

3.5.4 Available Phosphorus Determination

The available P of the adsorbents (biochar and compost) was determined using the (Olsen and Watanabe, 1965) method. One gram of 1 year old biochar, 2-year-old biochar and compost were each weighed in triplicates into extraction bottles and 50 ml of sodium bicarbonate solution added and shaken for 30 minutes on a mechanical shaker. Whatman No.42 filter paper was used to filter the mixture afterward. Five millilitres aliquot was taken into a test tube and then in a dropwise manner, 1 ml of 2M H_2SO_4 was added to decoulorise the solution by causing the organic matter in it to settle. It was allowed to cool for a few minutes in a refrigerator. The extracts in the test tube were gently decanted for color development using the (Murphy and Riley, 1962) method. Five mL aliquot of the sample was pipetted into a 50 mL volumetric flask and a drop each of P-nitrophenol and ammonium hydroxide were added. Eight mL of a solution containing ammonium molybdate, ascorbic acid, potassium antimony tartrate and concentrated sulphuric acid were added. The solution was topped up to the 50 mL mark with distilled water. The concentration of phosphorus in the solution was determined using a Cole-Parmer UV/Visible spectrophotometer at a wavelength of 712 nm. The available P content in each sample was calculated as in equation 3.6 below.

$$Available\ P = \frac{(Spectrometer\ reading - blank\ reading) \times volume of\ extract}{Sample\ weight \times volume\ of\ aliquot} \quad \text{.....3.6}$$

The available P of the soil alone, soil amended with 1 year old biochar, soil amended with 2-year-old biochar and soil amended with compost were determined using the Bray 1 method

(Bray and Kurtz, 1945). Five grams of each sample was weighed into a centrifuge bottle in triplicates. Fifty mL of Bray solution consisting of 0.03 M NH_4F and 0.025 M HCl were added (Bray and Kurtz, 1945). The bottles were shaken in a mechanical shaker for 5 minutes. The suspensions were filtered through a No. 42 Whatman filter paper into a 50 ml volumetric flask. The Murphy and Riley method described above was used to determine the phosphorus content in the filtrate. The concentration of phosphorus was then determined using a Cole-Parmer UV/Visible spectrophotometer at a wavelength of 712 nm. Equation 3.6 above was used to determine the available P content in the various soil samples.

3.5.5 Total Nitrogen Determination

The Kjeldahl digestion method as described by Anderson and Ingram (Anderson and Ingram, 1993), was used for the determination of the total nitrogen content of the samples. One gram of soil alone, soil mixed with one year biochar, soil mixed with 2-year-old biochar, soil mixed with compost and 0.5 g each of 1 year old biochar, 2-year-old biochar and compost were weighed in triplicates into a 300 mL Kjeldahl flask and a catalyst in the form of selenium was added. Five mL of concentrated sulphuric acid was added to the sample in each Kjeldahl flask and digested until the digest was clear. The digest was allowed to cool, transferred into a volumetric flask and made up to the 50 mL mark with distilled water. Five mL aliquot of each digest was taken and 5 mL of 40% NaOH were added into a Markham distillation apparatus. The ammonia liberated was trapped in 5 mL of 2% Boric Acid to which had been added three drops of mixed indicators of methylene blue and methyl red. The distillate was back titrated with 0.01M HCl from green color to a purple-reddish endpoint.

The percent nitrogen in each sample was calculated as shown in equation 3.7.

$$\%N = \frac{0.01 \times titre\ volume \times 0.014 \times volume\ of\ extract}{sample\ weight \times volume\ of\ aliquot} \quad \ldots\ldots 3.7$$

3.5.6 Cation Exchange Capacity (CEC) Determination

One gram each of the 1-year-old biochar, 2-year-old biochar and compost was weighed in triplicates into extraction bottles. Five grams of soil alone, soil amended with 1 year old biochar, soil amended with 2-year-old biochar and soil amended with compost were also weighed in triplicates into extraction bottles. Fifty mL of ammonium acetate was added to each bottle and shaken on a mechanical shaker for 30 minutes. A No. 42 Whatman filter paper was used to filter the suspensions and leached twice with 25 mL ethanol to wash off excess ammonium. The residue was further leached twice with 25 ml acidified KCl. Ten mL aliquot of the leachate was pipetted into a Kjeldahl flask and 5 mL of 40% NaOH added. It was then distilled using a Markham distillation apparatus. The distillate was collected into a 5 mL solution of 2% boric acid into which three drops of methyl red and methylene blue indicators had been added. The distillate was back titrated with 0.01 M HCl until the endpoint (color change from green to purple). The CEC was then calculated from the number of moles of HCl consumed in the back titration using equation 3.8.

$$CEC\ (in\ meq/100g\ soil) = \frac{Titre\ value \times Molarity\ of\ HCl \times Vol\ of\ Extract \times 100}{Volume\ of\ filtrate\ for\ distillation \times Sample\ Weight} \quad \text{.....3.8}$$

3.6 Adsorption Experiments

Batch equilibration experiments were conducted to study the adsorption of atrazine on the unamended soil/ soil alone (SA), soils amended with 1 year old biochar (SB1), soils amended with 2-year-old biochar (SB2) and soils amended with compost (SC). These experiments were conducted to determine the influence of soil amendments, atrazine concentration and pH on the adsorption of atrazine. To ensure the ionic strength of the system was kept constant, a background solution of 0.01 M $CaCl_2$ was added to each suspension (Organization for Economic Co-operation and Development, 2000). All experiments were done at laboratory ambient temperature of between 25 and 27 ºC.

3.6.1 Atrazine standards and Calibration Curve

A stock solution of atrazine at a concentration of 100 µg/mL was prepared in methanol. Atrazine standards of 0.5, 1, 2, 4, 6, and 8 µg/mL were prepared from the stock solution and analyzed using a Cole-Parmer UV/Visible spectrophotometer at a wavelength of 222 nm. Preliminary investigations showed that maximum atrazine adsorption occurs at 222 nm. The calibration curve was determined based on the Beer-Lambert law using the relationship between the concentration of atrazine and the absorbance of UV light at 222 nm.

3.6.2 Effect of atrazine concentration on adsorption

Samples of 0.5 g each of SA, SB1, SB2, and SC were weighed into centrifuge bottles. Various amounts (0, 0.5, 1, 2, 4, 6, 10, 15 and 20 ml) of the stock solution of atrazine (100 µg/mL) were pipetted into 100 mL volumetric flasks such that when 1 mL of 1 M $CaCl_2$ was added as background solution (to maintain ionic strength), the atrazine concentrations in the volumetric flask were 0, 0.5, 1, 2, 4, 6, 8, and 10 ug/mL and the concentration of $CaCl_2$ is 10 mM. Thirty (30) mL of the various solutions were added to the centrifuge bottles containing the soil samples and shaken at 200 rpm in a mechanical shaker for 24 hours (OECD, 2000). The bottles were withdrawn after shaking and then centrifuged at 3000 rpm for 15 minutes to obtain a clear solution. All experimental treatments were carried out in triplicates. The supernatants were decanted and further filtered using a No 42 Whatman filter paper. The atrazine concentrations were read on a Cole-Parmer UV/Visible spectrophotometer at wavelength 222 nm. The atrazine adsorbed onto the soil samples was calculated as the difference between the initial and final concentrations as shown in equation 3.9 below.

$$Amount\ adsorbed, q = \frac{(C_o - C_e) \times V}{M} \quad \text{.....3.9}$$

where

C_o, C_e = initial and equilibrium concentrations of atrazine, mg/L

V = volume of solution used, mL

M= mass of adsorbent, g

3.7 Sorption Isotherms

To predict the relationship between the concentration of atrazine in solution and the amount of atrazine adsorbed by the soil alone, soil + 1 year old biochar, soil + 2-year-old biochar and soil + compost, graphs of quantity of atrazine adsorbed were plotted against equilibrium concentration of atrazine to determine the maximum sorption. The linearized forms of the Langmuir and Freundlich isotherms, the two most commonly used models were fitted to the isotherm data to assess their respective fits. The models, equations and the linearized form of each equation are presented in the table below.

Table 1: Models and Equations Fitted to Isotherm Data

Model	**Equation**	**Linearised equation**
Langmuir	$\frac{q_e}{Qm} = \frac{bC_e}{(1 + bC_e)}$	$\frac{1}{q_e} = \frac{1}{Qm} + \frac{1}{Qmb}\frac{1}{C_e}$
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	$\log q_e = \log K_F + \frac{1}{n}\log C_e$

Where C_e = equilibrium concentration, q_e = amount adsorbed, Qm = maximum adsorption capacity, b = Langmuir constant, K_F = Freundlich isotherm constant, and n = adsorption intensity.

The Langmuir isotherm model was determined by plotting $\frac{1}{q_e}$ vs $\frac{1}{C_e}$ with the y-intercept representing $\frac{1}{Qm}$ and the slope, $\frac{1}{Qmb}$.

The Freundlich model was determined by plotting $\log q_e$ vs $\log C_e$ with the y-intercept representing $\log K_F$ and the slope, $\frac{1}{n}$.

Also, the optimum pH for the maximum sorption was obtained from a plot of amount of atrazine adsorbed against equilibrium pH.

3.8 Effect of pH on adsorption

The effect of solution pH on the adsorption of atrazine was studied for pH values 3, 5, 6, 7, 8, 9, and 10. Atrazine concentration of 4 ug/mL was used since it was at this concentration that the highest amount of atrazine was adsorbed on the unamended soil following an initial experiment. The pH of the atrazine solutions containing 0.1 M $CaCl_2$ was adjusted using 0.1 M NaOH and 0.1 M HCl. The adsorption experiment was carried out as described in section 3.6.2. Thirty (30) mL of the various atrazine solutions (pHs 3, 5, 6, 7, 8, 9 and 10) were added to the centrifuge bottles containing the soil samples (0.5 g each of SA, SB1, SB2, and SC) and shaken at 200 rpm in a mechanical shaker for 24 hours (OECD, 2000). The bottles were withdrawn after shaking, and then centrifuged at 3000 rpm for 15 minutes to obtain a clear solution. The supernatants were decanted and further filtered using a No 42 Whatman filter paper. The atrazine concentrations were read on a Cole-Parmer UV/Visible spectrophotometer at wavelength 222 nm. The pH of the atrazine solutions were taken and recorded as equilibrium pH. The atrazine adsorbed onto the soil samples was calculated as the difference between the initial and final concentrations as shown in equation 3.9. All experimental treatments were carried out in triplicates.

3.9 Data analysis

The data obtained from the different experiments undertaken were subjected to analysis of variance (ANOVA) using the Statistical Package for Social Sciences (SPSS) version 22.0 to

establish if there were any significant differences in treatment effects at $p < 0.05$. Mean separations were done using Tukey's Lsd (0.05) where necessary.

CHAPTER FOUR: RESULTS

4.1 Farmers' survey

Results of the survey of farmers within the Lawra district of the Upper West region are presented below. A total of sixty (60) farmers were interviewed during the field survey in the Orbili community of the Lawra district in the Upper West Region of Ghana.

4.1.1 Demographic Profile

The demographic profile of the farmers interviewed is displayed in Table 2 below. About sixty-three percent (63%) of the respondents were males and the remainder (37%), were females. Forty-three percent (43%) of the respondents were in the 25-39 age bracket, 20% in the 40-60 age group while 28% were in the 18-24 age bracket. Only 3.3% of the respondents were below 18 and 5% above 60 years of age. Sixty (60) percent of the respondents had formal education with about (27%) of them receiving formal education up to junior high school level. Fifteen percent of the respondents were educated up to primary school with 5% being educated up to the tertiary level. Forty (40) percent of the respondents had no formal education.

Table 2: Demographic Profile of Respondents

Variable	Description	Percentage (%)
Sex	Male	63.3
	Female	36.7
Age	Less than 18	3.3
	18-24	28.3
	25-39	43.3
	40-60	20
	60 plus	5
Educational level	None	40
	Primary	15
	Junior High School	26.7
	Senior High School	13.3
	Tertiary	5

4.1.2 Types and Sources of pesticides used

Ninety (90) % of the respondents stated that they use pesticides to control weeds and insect pests while 10% stated that they don't apply any form of pesticides on their farms. About 63% of the pesticides used by respondents in the study area were herbicides while insecticides formed 27 % of pesticides used by respondents. All the respondents who applied insecticides during cropping further indicated that they used them only during the fall armyworm outbreak. Atrazine based herbicides formed 90% of the herbicides that were used by the farmers in the study area. While 67% of the respondents stated that they obtained their pesticides from the open market, 17% indicated that they obtained their pesticides from the Ministry of Food and Agriculture with about 7% of respondents purchasing their pesticides from a farming company. Other sources of pesticides including colleague farmers represented 10% of the total respondents. It was also observed that some farms were sited close (less than thirty meters) to boreholes that serve the community.

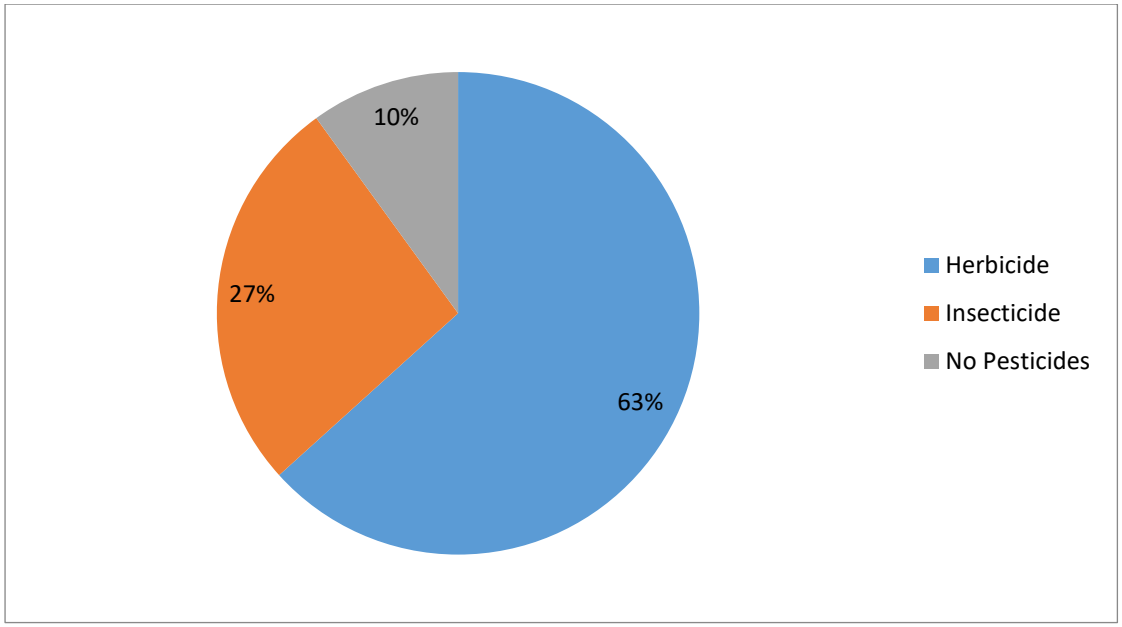

Figure 3: Types of Pesticide Used

4.2 Physico-chemical characterization of the soil

Some physical and chemical properties of the soil used for the study are shown in Table 3 below. The sand fraction of the soil (87.5%) was about 8.7 times more than the clay fraction (10.0%). The soil had a silt fraction of 2.5%, giving it a loamy sand texture using the United States Department of Agriculture textural classification. The soil is strongly acidic with pH in water and KCl being 4.7 and 4.6 respectively.

Table 3: Some Physical and Chemical Properties of The Soil

Parameter	Values
Sand (%)	87.50 ± 0.00
Silt (%)	2.50 ± 0.00
Clay (%)	10.00 ± 0.00
pH (water)	4.74 ± 0.1
pH (1M KCl)	4.62 ± 0.14
Organic C (g/kg)	10.5 ± 0.00
Total N (g/kg)	0.5 ± 0.00
Avail. P (mg/kg)	2.82 ± 0.23
CEC ($cmol_c$/kg)	5.91 ± 0.17

The organic carbon content of 10.5 g/kg was low and very characteristic of tropical soils where high temperatures result in rapid decomposition of added organic matter leading to a reduction in the rate of organic carbon build-up in soils (Dowuona, et al., 2012). Consequently, the total nitrogen and available phosphorus were respectively low at 0.5 g/kg and 2.82 mg/kg (Landon, 1991). The CEC of 5.9 $cmol_c$/kg was also very low and characteristic of soils in northern Ghana.

4.3 Characterization of the soil amendments (biochar and compost)

Some chemical properties of the soil amendments (1-year old biochar, 2-year-old biochar and compost) used for the study are summarized in Table 4. The pH in water of the 1 – year old biochar (1BA) and 2 – year old biochar (2BA) were respectively 9.1 and 8.5 and that of the compost (CA), 8.4. The biochars were thus classified as strongly and mildly alkaline respectively, while the compost was labelled as mildly alkaline according to Verheijen et al, (2010) and Latifah et al, (2018). The pH values determined for the soil amendment in 1M KCl were respectively 8.1 and 7.4 for the 1 – year and 2 – year old biochar and 7.6 for the compost. Since the pH values in the salt (1M KCl) were lower than that in water, the net charges on all the soil amendments were determined as being negative.

The 1 – year old and 2 – year old biochar had organic carbon content of 206.7 g/kg and 205.4 g/kg respectively while that of the compost was 54.5 g/kg. The organic carbon content of the compost was about 73% lower than the values recorded for the biochar samples. With a total nitrogen content of 2.9 g/kg and 4.1 g/kg for 1BA and 2BA respectively, the carbon to nitrogen (C: N) ratios were about 71.3 and 50.1 for the biochars. The total nitrogen content of the compost was 3.9 g/kg giving a C: N ratio of approximately 14.7. The 1 – year and 2 – year biochar had available phosphorus content of 84.2 mg/kg and 110.5 mg/kg respectively with the compost recording an available P content of 38.5 mg/kg. The available P contents of the soil amendments were thus in the order 2BA > 1BA > CA. The 2 – year old biochar and the compost had similar CEC levels at 48.1 $cmol_c$/kg and 48.3 $cmol_c$/kg respectively while that of the 1-year-old biochar was about 20% more at 60.2 $cmol_c$/kg.

Table 4: Some Physical and Chemical Properties of The Soil Amendments

Parameter	1-year-old biochar	2-year-old biochar	Compost
pH (water)	9.05 ± 0.01	8.47 ± 0.01	8.41 ± 0.02
pH (1M KCl)	8.14 ± 0.09	7.40 ± 0.06	7.60 ± 0.01
Organic C (g/kg)	206.70 ± 1.30	205.53 ± 0.60	54.21 ± 2.10
Total N (g/kg)	0.29 ± 0.01	0.41 ± 0.00	0.37 ± 0.00
Avail. P (mg/kg)	84.23 ± 2.72	110.53 ± 5.25	38.47 ± 1.54
CEC ($cmol_c/kg$)	60.23 ± 0.08	48.10 ± 2.95	48.25 ± 2.25

4.4 Effect of amendments on soil chemical properties

The pH of the soil increased with the addition of adsorbents in the order soil + 2-year-old biochar < soil + 1-year-old biochar < soil + compost. Although the soil pH in water, after application of the amendment showed increases compared to the unamended soil in all instances, it was the compost amended soil whose pH increase was more than 0.5 units which, according to Nartey *et al*. (2000) was significant ($p < 0.05$). A similar trend was observed when the pH of the amended soils was determined in 1M KCl.

The organic carbon of the unamended soil was very low at 10.5 g/kg. Amending the soil with the 2-year-old biochar saw a marginal but significant ($p < 0.05$) increase in the organic carbon levels to 12.5 g/kg. The increase in the organic carbon content after amending with the compost and 1-year-old biochar were however not significant.

The available P of the soil was very low at 2.82 mg/kg. Application of the soil amendments saw a significant ($p < 0.05$) 1.9-fold and a 4.6-fold respective increases in the 1-year-old and 2-year-old biochar amended soils while the compost amended soil registered a 3.9-fold increase in the available phosphorus content as indicated in Table 5. Among the amended soils, the available P content was in the order; soil + 1-year-old biochar < soil + compost < soil + 2-year-old biochar.

The total N content of the unamended soil was 0.5 g/kg. When the soil was amended with the biochar, the total nitrogen content increased significantly ($p < 0.05$) by 1.2 and 2.2 folds to 0.6 and 1.1 g/kg for the 1-year-old biochar and 2-year-old biochar respectively. A 1.6-fold increase brought the total N content of the soil to 0.8 g/kg when the compost was amended to the soil. Among the amended soils, the 2-year-old biochar recorded available P levels that were significantly higher than that of the compost which, also recorded significantly higher levels of available P relative to the 1-year-old biochar. Although the CEC of the sampled soil was low, incorporation of the soil amendments did not result in any significant increases in CEC levels.

Table 5: Effects of Amendments on Soil Chemical Properties

Parameter	Soil alone	**S**oil + 1-year-old biochar	**S**oil + 2-year-old biochar	**S**oil + compost
pH (water)	4.74 ± 0.10	5.20 ± 0.05	5.08 ± 0.07	6.34 ± 0.01
pH (1M KCl)	4.62 ± 0.14	5.03 ± 0.05	4.90 ± 0.09	6.06 ± 0.01
Organic C (g/kg)	10.50±0.00a	11.5 ± 0.05ab	12.5 ± 0.03b	11.2 ± 0.03ab
Total N (g/kg)	0.5 ± 0.00a	0.64 ± 0.00b	01.09 ± 0.00d	0.76 ± 0.00c
Avail. P (mg/kg)	2.82 ± 0.23a	5.47 ± 0.20b	13.00 ± 0.54d	10.98±0.18c
CEC ($cmol_c$/kg)	5.91 ± 0.17a	6.09 ± 0.61a	6.12 ± 0.09a	6.17 ± 0.34a

4.5 Adsorption Experiments

4.5.1 Calibration curve

The calibration curve displayed in Figure 4 was obtained by plotting absorbance at 222 nm against atrazine concentration and the curve with a coefficient of determination of 0.9968 illustrates the use of the concentration-dependent 222 nm absorption peak (Sigmon, 2016).

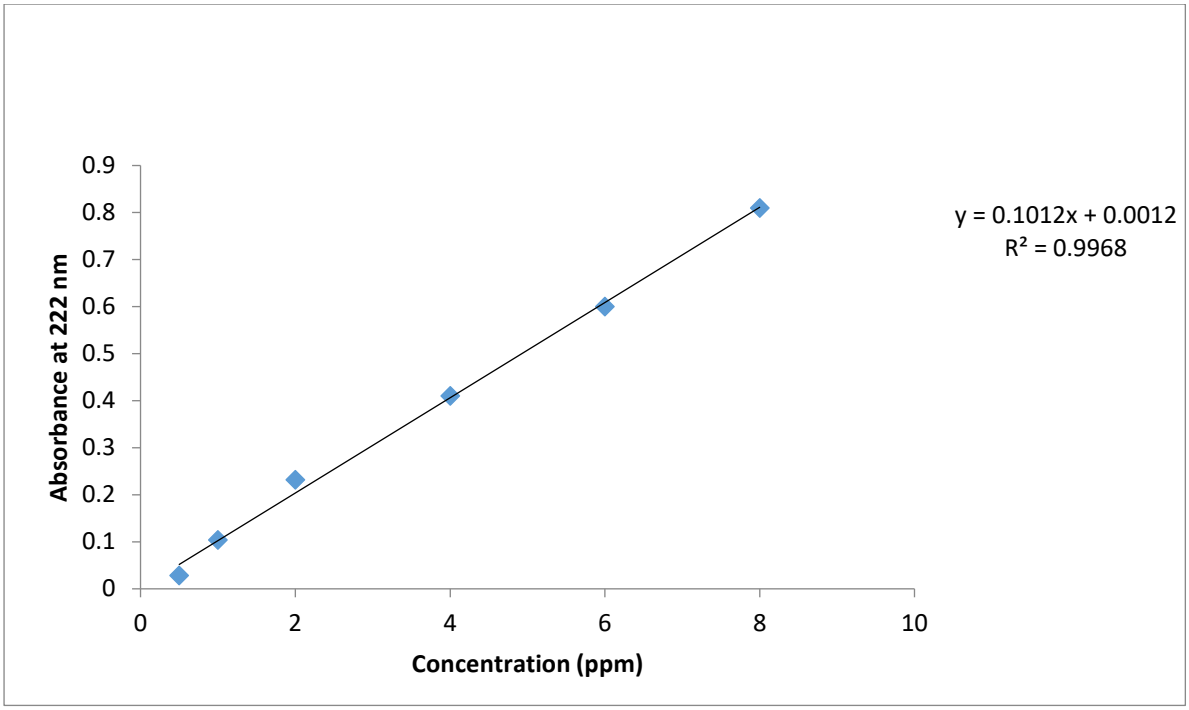

Figure 4:Calibration Curve for Cole-Parmer UV/Visible Spectrophotometer of Atrazine Standards

4.5.2 Effect of atrazine concentration on adsorption

The equilibrium concentration values of atrazine in solution for the various amended soil samples after shaking for 24 hours are displayed in Table 6. The equilibrium concentration values were reduced from the initial concentrations with the most reduction occurring in the soil amended with the 2-year-old biochar except the solution that contained no atrazine. At the end of the adsorption study, the measured concentration of atrazine after equilibrium was attained, generally followed the order S2B<S1B<SC<SA.

Table 6: Equilibrium Concentration of Atrazine After Shaking

Initial Concentration of Atrazine (mg/L)	Equilibrium Concentration of Atrazine (mg/kg)			
	Soil Alone	**Soil + 1-year old biochar**	**Soil + 2-year-old biochar**	**Soil + compost**
0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
0.50	0.41 ± 0.06	0.21 ± 0.03	0.19 ± 0.01	0.32 ± 0.03
1.00	0.82 ± 0.02	0.39 ± 0.06	0.35 ± 0.01	0.64 ± 0.02
2.00	1.60 ± 0.00	0.70 ± 0.08	0.60 ± 0.01	1.20 ± 0.10
4.00	3.48 ± 0.07	1.72 ± 0.14	1.52 ± 0.03	2.96 ± 0.01
6.00	5.73 ± 0.06	2.76 ± 0.08	2.46 ± 0.05	4.80 ± 0.09
8.00	7.73 ± 0.03	3.85 ± 0.02	3.44 ± 0.02	6.56 ± 0.11
10.00	9.74 ± 0.02	5.10 ± 0.09	4.61 ± 0.08	8.5 ± 0.12

The amount of atrazine adsorbed onto the various samples was calculated as the difference between the initial and equilibrium concentrations as shown in equation 4.1 below.

$$Amount\ adsorbed,\ q = \frac{(C_o - C_e) \times V}{M} \quad \text{.....4.1}$$

Where;

C_o, C_e = initial and equilibrium concentrations of atrazine, mg/L

V = volume of solution used, mL

M= mass of adsorbent, g

Table 7: Amount of Atrazine Adsorbed

Initial Concentration of Atrazine (mg/L)	Amount of atrazine adsorbed (mg/kg)			
	Unamended Soil	Soil + 1-year-old biochar	Soil + 2-year-old biochar	Soil + compost
0.00	0.00	0.00	0.00	0.00
0.50	5.40	17.40	18.60	10.80
1.00	10.80	36.60	39.00	21.60
2.00	24.00	78.00	84.00	48.00
4.00	31.20	136.80	148.80	62.40
6.00	16.20	194.40	212.40	72.00
8.00	16.20	249.00	273.60	86.40
10.00	15.60	294.00	323.40	90.00

The amount of atrazine adsorbed increased with increasing concentration for all treatments except for the unamended soil. The amount of atrazine adsorbed reached a maximum of 30.60 mg/kg at 4 mg/L and started decreasing afterwards. The soil amended with the 2-year-old biochar recorded the highest amount of adsorbed atrazine followed in order by soil + 1-year-old biochar, soil + compost and the unamended soil.

4.6 Sorption isotherm

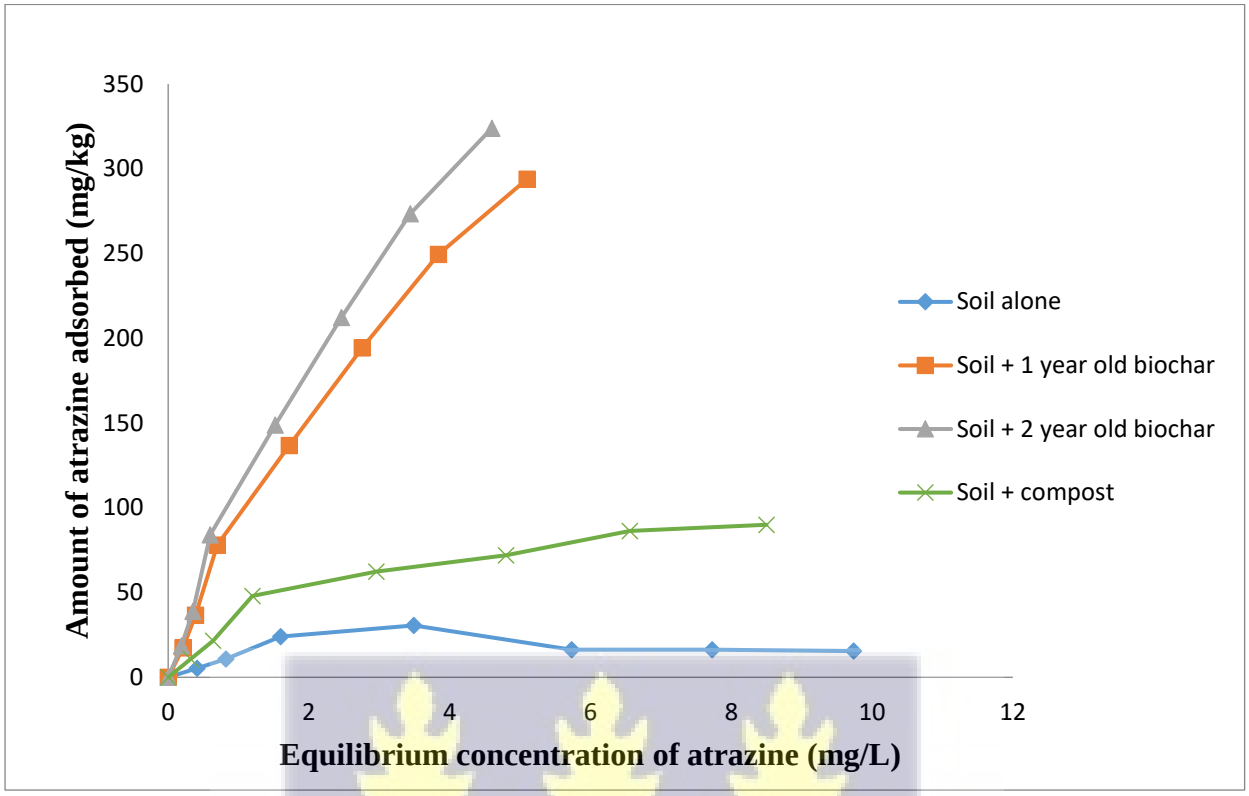

Figure 5:A Graph of Sorption Isotherms of Atrazine for the various treatments

The adsorption isotherms for the various treatments are shown in Figure 5. The relationship between the atrazine in the liquid phase and the atrazine adsorbed on the surface of the adsorbent at equilibrium assuming a constant temperature is represented by the adsorption isotherms. The adsorption data were then fitted to the linearized forms of Freundlich and Langmuir isotherms after which the coefficient of determination was computed to determine which model best described the measured data as shown in Figure 6. The summary of the results are presented in Table 8 below.

Table 8: Isotherms Parameters for Atrazine Sorption

Sample	Freundlich model			Langmuir model		
	$\log K_F$	$\frac{1}{n}$	R^2	$\frac{1}{Qm}$	$\frac{1}{Qmb}$	R^2
SA	0.849	0.500	0.283	0.0305	0.0595	0.820
S1B	1.637	1.00	0.355	0.0007	0.0117	0.999
S2B	1.696	0.929	0.304	0.0006	0.0099	0.999
SC	1.209	0.840	0.419	0.0047	0.0275	0.983

SA= unamended soil; S1B=Soil amended with 1-year-old biochar;

S2B = Soil amended with 2-year-old biochar; SC = Soil amended with compost

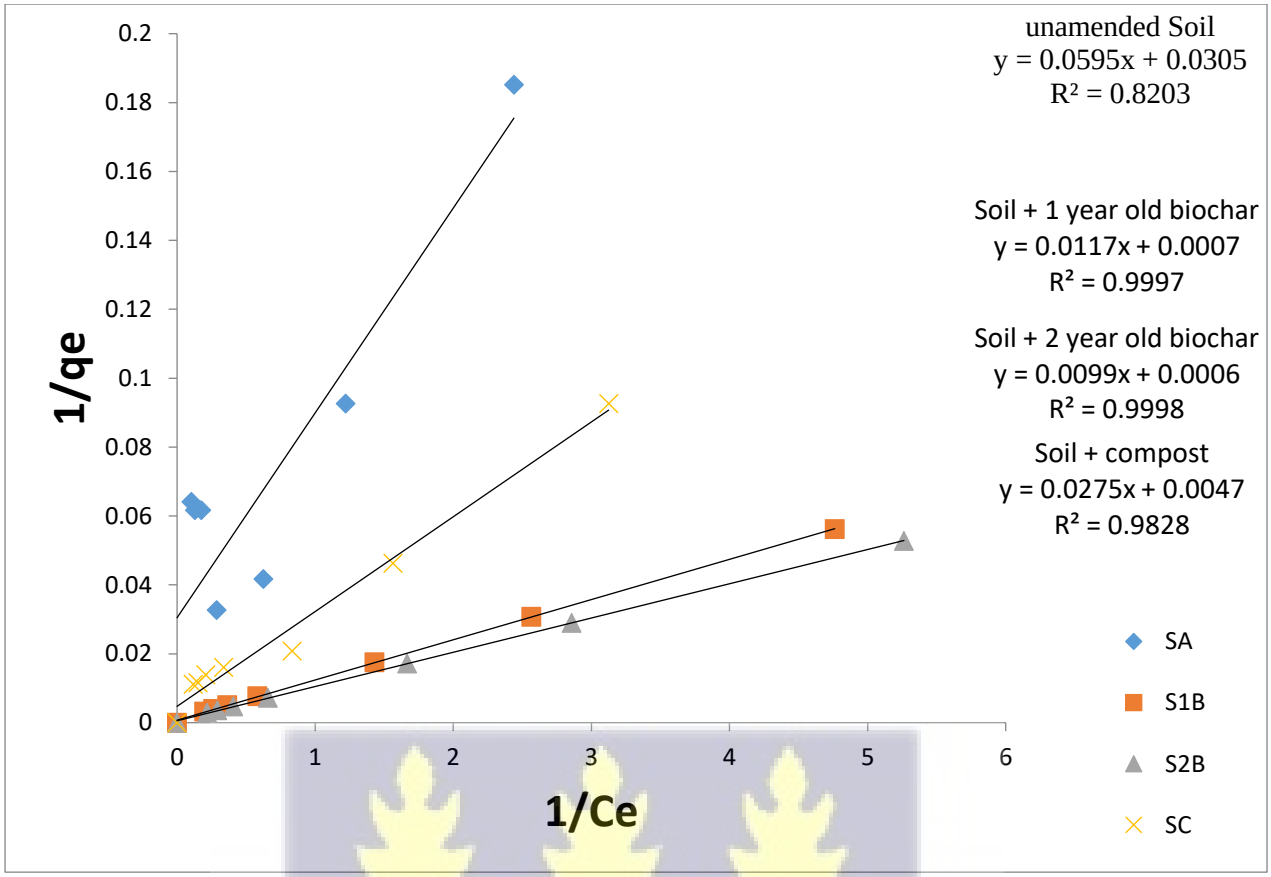

Figure 6:Linearized Langmuir Adsorption Isotherm

4.7 Effects of pH on adsorption

The adsorption of atrazine onto the various treatments was studied over pHs 3, 5, 6, 7, 8, 9, and 10 using atrazine concentration of 4 mg/L. There were changes in pH from the initial values after the adsorption experiment and the new pH value were recorded as the equilibrium pH. From an initial pH value of 3, the equilibrium pH of the unamended soil increased after the adsorption experiment to 4.08 but reduced for all the other treatments with initial pHs (5, 6, 7, 8, 9, and 10) after the adsorption experiment. The equilibrium pH of the amended soils (S1B, S2B and SC) increased after the adsorption experiment for the treatments with initial pH 3 and 5 but reduced for the others with initial pH values 6, 7, 8, 9, and 10.

The adsorption of atrazine onto the various treatments was dependent on initial pH with the maximum adsorption occurring at initial pH 5 for the unamended soil, soil amended with 1 year old biochar and soil amended with 2-year-old biochar. Soil amended with compost saw

the maximum adsorption occurring at initial pH 3. The amount of atrazine adsorbed onto the unamended soil increased from 30.6 mg/kg at an initial pH of 3 to 42 mg/kg for samples set at initial pH 5. The amount of atrazine adsorbed then reduced for initial pHs 6, 7, 8, 9 and 10. Similar trends were observed for the soil amended with 1 year old biochar. The soil amended with 2-year-old biochar followed the same pattern except at initial pHs 6 and 7 where the amount of atrazine adsorbed was constant. The amount of atrazine adsorbed for the soil amended with compost saw a steady reduction from initial pHs 3 to pH 10. At all pHs, the amount of atrazine adsorbed followed the order unamended soil < soil + compost < soil + 1 year old biochar < soil + 2-year-old biochar. The effect of pH on the amount of atrazine adsorbed is displayed in Figures 7-10 indicating the equilibrium pH values.

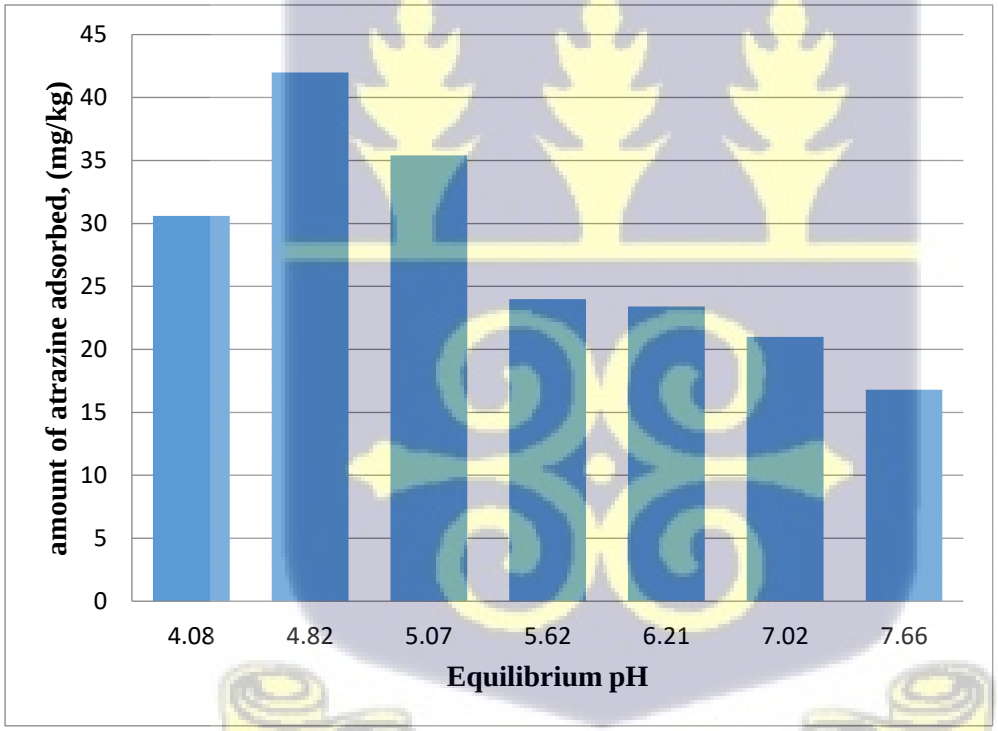

Figure 7: Effect of pH on Adsorption of Atrazine to Unamended Soil

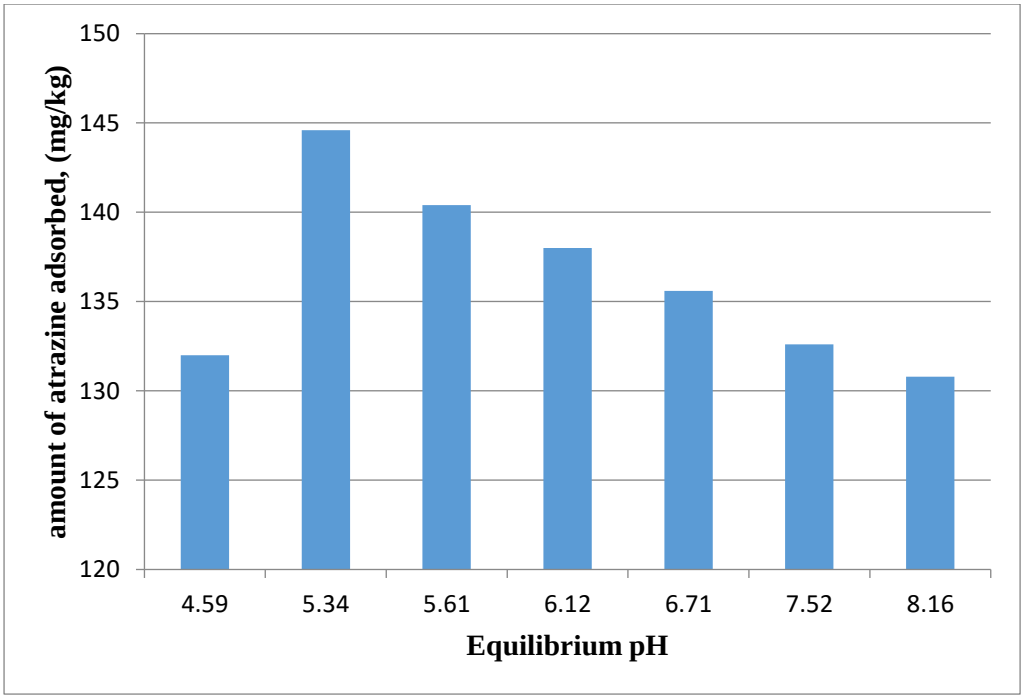

Figure 8: Effect of pH on Adsorption of Atrazine to Soil Amended With 1 Year Old Biochar

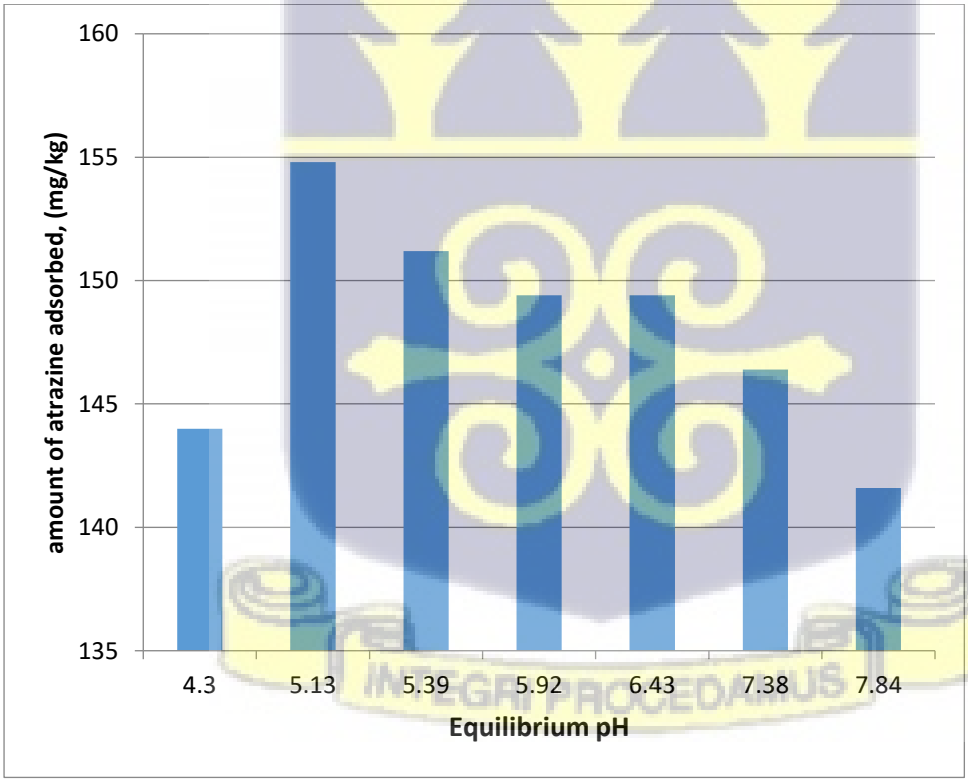

Figure 9: Effect of pH on Adsorption of Atrazine to Soil Amended With 2-Year-Old Biochar

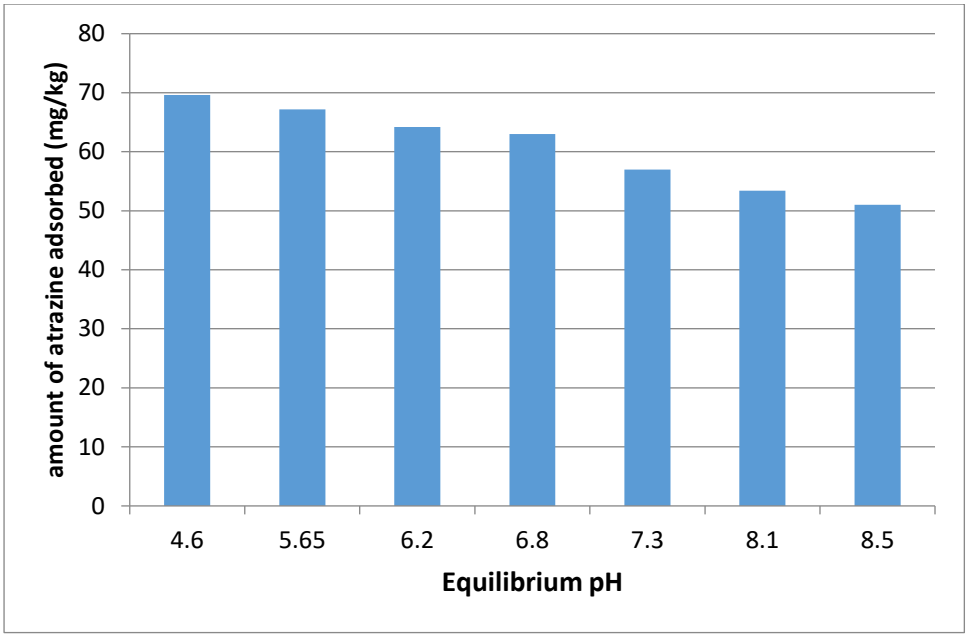

Figure 10: Effect of pH on Adsorption of Atrazine to Soil Amended with Compost

CHAPTER FIVE: DISCUSSION

5.1 Farmers' survey

The results from the demographic studies suggest that males dominate farming in the study area and this is supported by the study of (Anang et al., 2013) which suggests that males are traditionally the heads of households and assets such as lands and farms are controlled by them (Anang et al., 2013). Male farmers often provide more productive labor on the farms as compared to female farmers (Okoffo, 2015). The results also indicate that the farmers in the study area are relatively young with over 70% of them aged between 18 and 40. This result has a positive impact as young farmers are generally open to the adoption of new management practices as compared to an older group (Silva and Broekel, 2016). A substantial proportion (40%) of the farmers interviewed had no formal education and has implications for certain practices such as measurement and mixing of pesticides and calibration of sprayers. Over 90% of the respondents confirmed they used pesticides on their farms and this can lead to an increase in the pesticide residue in soils and groundwater. The close proximity of boreholes to farms and the heavy dependence on boreholes poses a health hazard to farmers' household and communities. The majority of the pesticide users in the study area relied on herbicides to control weeds. Some farmers added that spraying of herbicide was far more economical and practical as compared to hand weeding. Trade names of the herbicides given during the questionnaire assessment and further analysis of used and old pesticide containers in the various households suggest that atrazine-based chemicals account for about 90% of the herbicides used. Atrazine usage is effective in controlling broadleaf weeds before they emerge from the ground or even after they have emerged amongst crops. Atrazine is relatively cheap and can control weeds in maize, sorghum and other narrow-leaf crops. Most of the respondents stated that they obtained their pesticides from chemical shops in and around the communities

which goes to indicate the pesticides are readily available in the open market to be purchased by farmers.

5.2 Physico-chemical characteristics of soil

The high sand fraction and clay content of 87.5% and 10.0% respectively is an indication that the soil used for the study is of loamy sand texture according to the USDA system of classification (Soil Survey Staff, 2003). The texture of the soil, coupled with the low level of organic carbon suggests that the soil would have low water retention capacity and may be prone to erosion. Additionally, the low organic carbon levels and consequently, very low total nitrogen and available phosphorus content of the soil give an indication that the soil is inherently low in fertility and may be prone to leaching of soluble nutrients if subjected to intensive precipitation or irrigation. This is evidenced by the low clay content, which is believed to be mostly of the low activity clay type and the subsequent low CEC levels as indicated by the physico chemical properties of the soil in Table 3. The low pH of the soil is characteristic of the heavily weathered soils in the northern part of Ghana (Nartey, 1994). The soil pH in water is acidic and gives an indication of leaching of basic cations due to the loamy sand texture. The soil pH in water was higher than in KCl resulting in a negative ΔpH (ΔpH = pH in KCl – pH in H_2O). The ΔpH is indicative of the balance of soil charges and negative values indicate a predominantly net negative charge (Nartey, 1997).

The low organic carbon value reported for the soil is as a result of reduced biomass turnover from the grass-dominated vegetative cover, recurring bushfires and generally high ambient temperature which is characteristic of the northern part of Ghana (Gichuru, et al., 2003). As such the contribution of vegetation to organic matter content is low. The low organic carbon content of the soil coupled with the low clay content gives the indication that the soil is inherently poor in fertility. Additionally, the low organic carbon level supports the assertion

that added organic material to the soil may be quickly lost due to rapid decomposition of organic matter as a result of high average temperatures of the area.

Most Ghanaian soils especially those in the northern part are characterized by low nitrogen content with most of it being converted to N_2O as a result of management practices such as tillage, nitrogen fertilizer rate, timing and method of application as well as residue management (Atakora *et al.*, 2019). The soil recorded low levels of available phosphorus as the parent materials from which the soil developed are inherently low in phosphorus bearing minerals and also doesn't possess primary minerals capable of weathering to recharge the nutrients. The almost complete removal of weatherable primary minerals in the predominant tropical climate accounts for the low CEC in the soil (Nartey, 1994). The low available P content and CEC of the soil are consistent with those reported by Senayah *et al*., (2012).

5.3 Characterization of biochar and compost

The high pH values of the two biochar types are as a result of high temperatures of pyrolysis that frees organic acids and phenolic substances via the breakdown of hemicellulose and cellulose. Alkaline salts are formed from the reaction of the released organic acid with basic cations in the feedstocks and thus raise the pH of the biochar (Streubel, et al., 2011). The difference in pH of the two differently aged biochars is as a result of oxidation and accumulation of H^+ ions from the soil solution with the 2-year-old biochar leading to a decrease in pH relative to the 1-year-old biochar (Gul et al., 2015). Similar trends were observed by (Jones *et al*., 2012) in which a pH decrease in a two-year biochar was observed relative to a freshly prepared one. The relatively high pH of the compost can be explained by the exchange of organic anions produced by decomposing compost material and terminal OH of soil minerals leading to the release of OH^- ions which increases the pH (Hue and Van den Berghe, 1999).

Although the feedstock for both the compost and the biochar samples were the same, the organic carbon content of the biochars was at least 4 times higher than that of the compost. The high organic carbon content of the biochar samples can be attributed to high heating rates resulting in a shorter period for dehydration reactions and the formation of few reactive anhydrocellulose, resulting in higher carbon yield (Zanzi, 2001). This is also supported by (Chen *et al*., 2008) who demonstrated that charring increases carbon content. The reduction of the organic carbon content in the two-year-old biochar could be as a result of degradation or natural elimination (Mendes *et al*., 2018).

Volatilization of nitrogen during the pyrolysis of biochar explains the relatively low values of nitrogen in biochar types (Manso, 2017; Cao and Harris, 2003). Also, nitrogen in the compost is oxidized to nitrate in the process of composting and curing and lost to the atmosphere or leached and thus result in the relatively low nitrogen content (Mangan et al., 2020). The available phosphorus in the biochars was higher than that of the compost as organic phosphorus was converted to inorganic forms during the charring process of biochar which eventually combines with calcium to form insoluble phosphorous compounds and increases the phosphorus content.

The high CEC of the biochar samples is a result of the presence of many oxygen-containing functional groups such as hydroxyl and carboxyl groups that deprotonate leading to high CEC values (Mia et al., 2017). The relatively high CEC values for compost can be attributed to the presence of crude humic substances and also high organic matter in the compost (Palanivell et al., 2015).

5.4 Effect of amendments (1-year biochar, 2-year biochar and compost) on soil properties.

Soils amended with biochar showed an increase in pH from that of the unamended soil with the presence of the biochar causing the increment. The addition of compost to the acidic soil

also raised the pH. Similar trends were observed where biochar and compost were added to an acidic soil (Novak, et al., 2019).

Soil amended with the 2-year-old biochar had a slightly higher organic carbon content than the soil amended with 1 year old biochar which may be attributed to the adsorption of soil organic matter onto the surface of the biochar with time as well as the attachment of particles onto the biochar surface leading to an increase in the organic carbon (Ren et al., 2018). The presence of compost which has relatively high organic carbon content also caused an increase in the organic carbon content of the soil amended with the compost. This trend is consistent with the works of Mekki et al. (2019).

Soil amended with the 2-year-old biochar had a higher total nitrogen content as compared to soil amended with 1-year-old biochar and this difference could be attributed to the difference in the total nitrogen between the 1-year-old biochar and the 2-year-old biochar as reported by Lehmann (Lehmann and Rondon, 2006). The compost which was amended with the soil accounted for the relatively high total nitrogen of soil amended with compost as observed by Yang et al. (2019).

The soil amended with the 2-year-old biochar showed a higher available P content and this is as a result of interactions with P containing mineral particles on the surface of the biochar with time and thus increases the available phosphorus content (Ren et al., 2018). Different interactions of biochar and compost with the soil minerals having a net positive surface charge as a result of ligand exchange accounts for the difference in CEC of the soils that were amended with biochars and compost (Mia et al., 2017).

5.5 Adsorption Experiments

5.5.1 Calibration Curve

The calibration curve was obtained using the Beer-Lambert Law. The Beer-Lambert law is a linear relationship between the absorbance and the concentration of a solution. The amount of energy absorbed or transmitted by a solution is proportional to the solution's molar absorptivity and the concentration of solute.

$$A = \varepsilon c l \quad \text{.....5.1}$$

Where A = Absorbance, ε = Molar absorption coefficient, c = molar concentration, l = optical path length

From this equation, the unknown concentration of an analyte could be determined by measuring the amount of light the sample absorbs using a UV/Vis Spectrophotometer (Cheng, 2018). The working curve of absorbance against concentration from the standards gave a coefficient of determination 0.9968, which illustrates the positive correlation between the amount of light absorbed and the concentration of the solution.

5.5.2 Effect of atrazine concentration on adsorption

The influence of the initial concentration plays a major role in adsorption studies. The initial concentration is significant in that it provides an important driving force to surmount the mass transfer resistance of the adsorbate between the aqueous and solid phases (Anbia and Hariri, 2010). From the results in Table 7, it can be observed that amount of atrazine adsorbed increased with increasing initial concentration for all the amended samples except for the unamended soil. The amount of atrazine adsorbed however began to increase at a decreasing rate after initial concentration of 4 mg/L for the amended samples. For the unamended soil, the amount of atrazine adsorbed increased with increasing concentration up to an initial concentration of 4 mg/L and then began to decrease. This shows that there are a finite number

of adsorption sites on the adsorbents and as such, as the concentration increases, more macropores are filled (Mostafapour et al., 2013). The increase in concentration therefore led to competition for the finite/limited adsorption sites. The different adsorption amounts for the different samples are as a result of the different number of macropores and adsorption spots on the samples available for sorption.

5.5.3 Sorption isotherms

To fully elucidate the mechanism of adsorption and the adsorption capacity, adsorption isotherm studies were carried out. The study of isothermal data by matching to various isotherm models is an important step in finding the right model that can be used for design purposes (Langmuir, 1918). The interaction that occurs between the adsorbent and adsorbate is also depicted by isotherm models and thus necessary for adsorption process optimization (Moussavi et al., 2013). This is achieved by the interpretation of what governs the release or retention of substances from an aqueous phase onto a solid phase. The adsorption data of the atrazine on the unamended soil, soil amended with 1 year old biochar, soil amended with 2-year-old biochar and soil amended with compost were analyzed using the Langmuir and Freundlich isotherm. The linearized forms of these models as outlined in Table 1 were used in fitting the adsorption data and the results are presented in Table 8. The coefficient of determination, R^2 was calculated for both models on all the treatments. The R^2 values obtained for the Langmuir (0.820-0.999) were much higher than those obtained for the Freundlich (0.283-0.419). The closer the R^2 value is to 1, the stronger the correlation and the better the adsorption data fit the isotherm model (Baharum, et al., 2020). The Langmuir model describes a type of adsorption where the atrazine is adsorbed at specific binding sites that are on both the unamended and amended soils. This model also emphasizes that the sites for adsorption on each of the adsorbents are identical. The atrazine that is adsorbed forms a monolayer on the adsorbents and

no interactions exists between the adsorbed molecules of atrazine on the surfaces of the unamended soil and the amended soils (Kecili and Hussain, 2018).

The model also depicts the maximum amount of atrazine that can be adsorbed by the various treatments (Qm). This is given by the inverse of the intercept of the linearized Langmuir adsorption equation for each of the soil and the amended soils. From Table 8, the maximum amount of atrazine adsorbed (Qm) are 32.787, 212.766, 1428.571, and 1666.667 mg/kg for the unamended soil (SA), soil amended with compost (SC), soil amended with 1year old biochar (S1B), and soil amended with 2-year-old biochar (S2B) respectively. This suggests a high capability of S2B to adsorb more atrazine than any of the other treatments. Once again, the differences in maximum adsorption for the different adsorbents point to the differences in the number of adsorption sites on these adsorbents.

5.5.4 Effects of pH on the adsorption

It can be observed that, atrazine adsorption generally decreased with increasing pH and is consistent with the works of Abate and Masini, (2005), Tao and Tang, (2004) and Yue, et al., (2017).

Hydrogen bonding at low pH could be the reason for high sorption within this range. Atrazine has five sites capable of accepting H+ ions but only two capable of donating H+ ions (National Institute of Health, 2020). At low pH values, there is abundance of H+ ions on the surface of biochar and composts and since they were amended to the soils they foster the formation of hydrogen bonding with the five H+ accepting sites of atrazine. With the increase of surface pH of the biochar and compost amended soils, the abundance of H+ ions decreases while the abundance of negatively charged functional groups such as $–O^-$ increases, and therefore leads to a reduction in sorption (McMillan, 2018). The relatively low adsorption of atrazine to the

unamended soil at equilibrium pH 4.02 could be as a result of electrostatic repulsion between the cationic form of the atrazine at low pH and the positively charged soil surfaces at low pH.

The difference in sorption capabilities of the 4 different sorbents lies in the difference in abundance of functional groups capable of donating H+ ions for hydrogen bonding leading to adsorption. The aged biochar showed the highest adsorption as a result of oxidation. The number of functional groups on the oxidized biochar surface, especially carboxylic and phenolic, increase with gradual aging, and at the same time benzene polycarboxylic acids liberated possesses a high number of carboxylic groups and thus biochar derived organic materials increases, leading to an increase in sorption capabilities (Mia et al., 2017).

CHAPTER SIX: CONCLUSION AND RECOMMENDATION

6.1 Conclusions

The study showed that when soil is amended with biochar of different ages and compost, its physicochemical parameters are modified.

The field survey revealed that pesticide use is predominant in the study area, chief of them are atrazine-based herbicides. The survey also revealed that they are readily available in the open market as most farmers obtained their chemicals from retail shops. Additionally, it was also observed that farmers and their households depend heavily on boreholes for domestic use.

The results from the adsorption studies also revealed that when soils were amended with biochar and compost, they showed a high capacity to adsorb atrazine. Amending the soil with biochar proved to be a much more effective adsorbent than compost owing to different physico-chemical properties and adsorption sites. The soil amended with the two-year-old biochar showed the highest sorption capacity owing to a change in properties after going through a series of biogeochemical changes. This increase in sorption capacity could be as a result of an increase in surface sorption sites with time. Isotherm studies also revealed that the Langmuir model which assumes monolayer adsorption to homogeneous surface best describes the interactions between the atrazine and the various adsorbents.

A study on the effect of pH on adsorption also showed that the adsorption of atrazine by the various treatments was pH dependent. Increased sorption was observed in the acidic region (pH 3-6) for all the treatments as compared to the alkaline region (pH 8-10). This could be attributed to the fact that atrazine is a weak basic herbicide and thus forms cations in the acidic region, which combine with the negative surfaces of the various soil samples through electrostatic attraction.

6.2 Recommendations

From the findings of this study, the following recommendations are suggested:

1. Further research should be conducted on soils from different areas in Ghana to understand the effect of biochar and compost amendment on soil properties.
2. Further field studies should be conducted to ascertain the transferability of controlled laboratory experiments.
3. Further tests need to be carried out using composts and biochar from different feedstock, different pesticides, and a cocktail of pesticides to understand the different mechanisms.
4. Farmer education on safe pesticide use, as well as biochar and compost preparation, must be intensified to attenuate the mobility of pesticides.
5. Monitoring programs are recommended to be carried out to obtain adequate information on the levels of pesticides in soils and especially groundwater.

REFERENCES

Abate, G., & Masini, J. C. (2005). Adsorption of atrazine, hydroxyatrazine, deethylatrazine, and deisopropylatrazine onto Fe (III) polyhydroxyations intercalculated vermiculite and montmorillonite. *Journal of Agriculture and Food Chemistry*, 1612-1619.

Abate, T., Van Huis, A., & Ampofo, J. K. (2000). Pest Management Strategies in Traditional Agriculture: An Afrian Perspective. *Annual Review of Entomology*, 631-659.

Albuquerque, A. F., Ribeiro, J. S., Kummrow, F., Nogueira, A. J., & Montagner, C. C. (2016). Pesticides in Brazilian freshwaters: a critical review. *Environmental Science Process Impacts*, 779-787.

Amonette, J., & Joseph, S. (2009). Characteristics of Biochar: Micro Chemical Properties. In J. Lehmann, & S. Joseph, *Biochar for Environmental Management: Science and Technology* (pp. 33-52). London.

Anang, B. T., Mensah, F., & Asamoah, A. (2013). Farmers' Assesment of the Government Spraying Program in Ghana. *Journal of Economics and Sustainable Development*, 92-99.

Anbia, M., & Hariri, S. A. (2010). Removal of methylene blue from aqueous solution using nanoporous SBA-3. *Desalination*, 61-66.

Anderson, J. M., & Ingram, J. S. (1993). *Tropical soil biology and fertility, A handbook of methods.* Oxford: Oxford University Press.

Arnold, D. J., & Briggs, G. G. (1990). Fate of pesticides in soils predictive and practical aspect. In D. H. Hutson, & T. R. Roberts, *Environmental fate of pesticide progress in pesticide Biochemistry and Toxicology.* New York: John Wiley and Sons.

Atakora, W. K., Kwakye, P. K., Weymann, D., & Bruggemann, N. (2019). Stimulus of nitrogen fertilizers and soils characteristics on maize yield and nitrous oxide emission from Ferric Luvisol in the Guinea Savanna agro-ecological zone of Ghana. *Scientific African*.

Ayawei, N., Angaye, S. S., Wankasi, D., & Dikio, E. D. (2015). Synthesis, characterization and application of Mg/Al layered double hydroxide for the degradation of congo red in aqueous solution. *Open Journal of Physical Chemistry*, 56-70.

Baharum, N. A., Nasir, H. M., Ishak, M. Y., Isa, N. M., Hassan, M. A., & Aris, A. Z. (2020). Highly efficient removal of diazinon pesticide from aqueous solutions by using coconut shell-modified biochar. *Arabian Journal of Chemistry*, 6106-6121.

Baird, C., & Cann, M. (2008). *Environmental Chemistry.* New York: W. H. Freeman and Company.

Barriuso, E., Houot, S., & Serra-Wittling, C. (1997). Influence of compost addition to soil on the behaviouur of herbicides. *Pesticide Science*, 65-75.

Barriuso, E., Houot, S., & Serra-Wittling, C. (1999). Influence of compost addition to soil on the behavior of pesticides. *Pesticide Science*, 65-75.

Bell, C. (2015). *A Historical View of Weed Control Technology*. Retrieved January 19, 2020, from UC Weed Science Weed Control, management, ecology and minutia: https://ucanr.edu/blogs/blogcore/postdetail.cfm?postnum=17593

Bessin, R. (2018). *Pesticides and the Environment*. Retrieved January 20, 2020, from UK Pesticide Safety Education Program: http://www.uky.edu/Ag/Entomology/PSEP/6environment.html

Bintein, S., & Devillers, J. (1996). Evaluating the Environmental Fate of Atrazine in France. *Chemosphere*, 2441-2456.

Biogrow limited. (2013). *Biochar History*. Retrieved February 2020, from Biochar: https://biochar.co.nz/about-biochar

Bohn, T., Cocco, E., Gourdol, L., Guignard, C., & Hoffmann, L. (2011). Determination of atrazine and degradation products in Luxembourgish drinking water: origin and fate of potential endocrine-disrupting pesticides. *Food Additives and Contaminants*, 1041-1054.

Bombardi, L. M. (2017). *Geography of pesticide use in Brazil and connections with the European Union.* Sao Paulo: FFLCH-USP.

Botwe, B. O., Ntow, W. J., & Nyarko, E. (2012). Pesticide Contamination in Groundwater and Streams Draining Vegetable Plantations. In M. C. Hernandez-Soriano, *Soil Health and Land Use Management* (pp. 51-64). Rijeka: Intech.

Braschi, I., Gessa, C. E., & Blasioli, S. (2011). the Fate of Herbicides in Soil. In A. Kortekamp, *Herbicides and Environment* (pp. 175-191). InTech.

Bray, R. H., & Kurtz, L. T. (1945). Determination of total organic and available forms of phosphorus in soils. *Journal of Soil Science*, 39-45.

Cao, X., & Harris, W. (2003). Properties of dairy manure derived biochar pertinent to its potential use in remediation. *Bioresource Technology*, 241-247.

Carvalho, F. P. (2006). Agriculture, pesticides, food security and food safety. *Environmental Science and Policy*, 685-692.

Chan, K. Y., & Xu, Z. H. (2009). Biochar: Nutrient Properties and Their Enhancement. *Biochar for Environment Management: science and technology*, 67-84.

Chaukura, N., Gwenzi, W., Tavengwa, N. T., & Manyuchi, M. (2016). Biosorbents for the removal of synthetic organics and emerging pollutants: Opportunities and challenges for developing countries. *Environmental Development*, 84-89.

Chaukura, N., Murimba, E. C., & Gwenzi, W. (2017). Synthesis, characterisation and methyl orange adsorption capacity of ferric oxide-biochar nano-composites derived from pulp and paper sludge. *Applied Water Science*, 2175-2186.

Chen, B. L., Zhou, D. D., & Zhu, L. Z. (2008). Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environmental Science and Technology*, 5137-5143.

Cheng, C. H., & Lehmann, J. (2009). Ageing of black carbon along a temperature gradient. *Chemosphere*, 1021-1027.

Cheng, J. W. (2018). *Beer-Lambert Law*. Retrieved August 3, 2020, from National Taiwan University: http://life.nthu.edu.tw/~labcjw/BioPhyChem/Spectroscopy/beerslaw.htm

Dai, Y., Zhang, N., Xing, C., Cui, Q., & Sun, Q. (2019). The adsorption, regeneration and engineering applications of biochar for removal organic pollutants: A review. *Chemosphere*, 12-27.

Darko, G., Akoto, O., & Oppong, C. (2008). Persistent organochlorine pesticide residues in fish, sediments and water from Lake Bosomtwi, Ghana. *Chemosphere*, 21-24.

Day, P. R. (1965). Particle Fractionation and Particle-Size Analysis. In C. A. Black, D. D. Evans, J. L. White, E. L. Ensminger, & F. E. Clark, *Methods of Soil Analysis* (pp. 545-567). Madison: American Society of Agronomy.

De Bertoldi, Vallini, G., & Pera, A. (1983). The biology of composting. *Waste Management Resources*, 157-176.

Demirbas, A. (2004). Adsorption of lead and cadmium ions in acqueous solutions onto modified lignin from alkali glycerol delignication. *Journal of Hazardous Materials*, 221-226.

Demirbas, A. (2011). Carbonization ranking of selected biomass for charcoal, liquid and gaseous products. *Energy Conversion and Management*, 1229-1238.

Dominguez, M., Paradelo, R., Pineiro, J., & Barral, M. T. (2019). Physicochemical and biochemical properties of an acid soil under potato culture amended with municipal solid waste compost. *International Journal of Recycling Organic Wastes in Agriculture*, 171-178.

Downie, A., Crosky, A., & Munroe, P. (2009). Biochar for Environment Management. In J. Lehmann, & S. Joseph, *Biochar for Environment Management.* London: Routledge.

Dowuona, G. N., Atwere, P., Dubbin, W., Nude, P. M., Mutala, B. E., Nartey, E. K., & Heck, R. J. (2012). Characteristics of termite mounds and associated acrisols in the coastal

savanna zone off Ghana and impact on hydraulic conductivity. *Natural Science*, 423-437.

Duku, M. H., Gu, S., Gu, S., & Hagan, E. B. (2011). Biochar production potential in Ghana-A review. *Renewable and Sustainable Energy Reviews*, pp. 3539-3551.

Evangelou, V. P. (1998). *Environmental Soil and Water Chemistry: Principles and Applications.* New York: John Wiley & Sons.

FAO. (2004). Scaling soil nutrient balances. *FAO Fertilizer and Plant Nutrition Bulletin*.

FAO. (2018). *Improving Food and Environmental Security in Ghana.* FAO.

Fianko, J. R., Donkor, A., Lowor, S. T., & Yeboah, P. O. (2011). Agrochemicals and the Ghanaian Environment, a Review. *Journal of Environmental Protection*, 221-230.

Fishel, F. (2003, February). *Pesticides and the Environment*. Retrieved January 12, 2020, from Extension University of Missouri: https://extension2.missouri.edu/g7520

Food and Agriculture Organization. (2002). *International Code of Conduct on the Distribution and USe of Pesticides.* Rome.

Food and Agriculture Organization. (2019). *Ghana at a glance*. Retrieved January 19, 2020, from FAO in Ghana: http://www.fao.org/ghana/fao-in-ghana/ghana-at-a-glance/en/

Food and Agriculture Organization of the United Nations. (2003). *On-Farm Composting Methods.* Rome: FAO.

Frazar, C. (2000). *The Bioremediation and Phytoremediation of Pesticide-Contaminated Sites.* Washington, DC.

Frimpong Manso, E., Nartey, E. K., Adjadeh, T. A., Darko, D. A., Lawson, I. Y., & Amoatey, C. A. (2019). Use of Corn Cob and Rice Husk Biochar as Liming Materials in Acid Soils. *West African Journal of Applied Ecology*, 32-50.

Gamage, D. N., Mapa, R. B., Dharmakeerthi, R. S., & Biswas, A. (2016). Effect of rice-husk biochar on selected soil properties in tropical Alfisols. *Soil Research*, 302-310.

Gardner, R. (2016). *Pesticide Environmental Stewardship*. Retrieved February 17, 2020, from https://pesticidestewardship.org/terms/terminology/

Gardner, R. (2016). *The Problem of Runoff*. Retrieved January` 19, 2020, from Pesticide Environmental Stewardship: https://pesticidestewardship.org/water/runoff/

Gavrilescu, M. (2005). Fate of Pesticides in the Environment and its Bioremediation. *Engineering in Life Sciences*, 497-526.

Ghana Statistical Service. (2014). *Lawra District Analytical Report* . Accra: Ghana Statistical Service.

Gichuru, M. P., Bationo, A., Bekunda, M. A., Goma, H. C., Mafongoya, P. L., Mugendi, D. N., . . . Swift, M. J. (2003). *Soil Fertility Management in Africa: A regional Perspective.* Nairobi: Academy Science Publishers (ASP).

Gilliom, R. J., Barbash, J. E., Crawford, C. G., Hamilton, P. A., Martin, J. D., Nakagaki, N., . . . Wolock, D. M. (2006). *The Quality of our Nation's Waters - Pesticides in the Nation's Streams and Ground Water, 1992-2001.* Virginia: U.S Geological Survey.

Gul, S., Whalen, J. K., Thomas, B. W., & Sachdeva, V. (2015). Physico-chemical properties and microbial responses in biochar-amended soils: Mechanisms and future directions. *Agriculture, Ecosystems and Environment*, 46-59.

Hanson, B., Bond, C., Buhl, K., & Stone, D. (2015, May). *National Pesticide Information Center.* Retrieved from Pesticide Half-life: http://npic.orst.edu/factsheets/half-life.html#:~:text=A%20half%2Dlife%20is%20the,lives%2C%2025%25%20will%20remain.

Herath, I., Kumarathilaka, P., Al-Wabel, M. I., Abduljabbar, A., Ahmad, M., Usman, A. R., & Vithanage, M. (2016). Mechanistic modeling of glyphosate interaction with rice husk derived engineered biochar. *Microporous and Mesoporous Materials*, 280-288.

Huang, y., Xiao, L., Li, F., Xiao, M., Lin, D., Long, X., & Wu, Z. (2018). Microbial Degradation of Pesticide Residues and an Emphasis on the Degradation of Cypermethrin and 3-phenoxy Benzoic Acid: A Review. *Molecular Diversity Preservation*.

Hue, N., & Van den Berghe, C. (1999). Liming Potential of Composts Applied To an Acid Oxisol in Burundi. *Compost Science and Utilization*, 40-46.

Inyang, M., & Dickenson, E. (2015). The potential role of biochar in the removal of organic and microbial contaminants from potable and reuse water: A review. *Chemosphere*, 232-240.

Jepson, P. C., Guzy, M., Blaustein, K., Sow, M., Sarr, M., Mineau, P., & Kegley, S. (2014). Measuring pesticide ecological and health risks in West African agriculture to establish an enabling environment for sustainable intensification. *Philos Trans R Soc Lond B Biol Sci*.

Ji, X., Lu, L., Chen, F., & Yang, C. (2016). Sorption properties and mechanisms of organic dyes by straw biochar. *Acta Scientiae*, 1648-1654.

Jin, J., Kang, M. J., Sun, K., Pan, Z. Z., Wu, F. C., & Xing, B. S. (2016). Properties of biochar-amended soils and their sorption of imidacloprid, isoproturon, and atrazine. *Science of the Total Environment*, 504-513.

Jones, D.L., Rousk, J., Edwards-Jones G., DeLuca T.H. & Murphy D.V. (2012). Biochar mediated changes in soil quality and plant growth in a three-year field trial. *Soil Biology and Biochemistry*, 113-124.

Joseph, S. D., Camps-Arbestain, M., Lin, Y., Munroe, P., Chia, C. H., Hook, J., & Amonette, J. E. (2010). An investigation into the reactions of biochar in soil. *Australian Journal of Soil Research*, 501-515.

Katagi, T. (2004). Photodegradation of pesticides on plant and soil surfaces. *Reviews of Environmental Contamination and Toxicology*, pp. 1-189.

Kazi, T. G., Jamali, M. K., Siddiqui, A., Kazi, G. H., Arain, M. B., & Afridi, H. I. (2006). An ultrasonic assisted extraction method to release heavy metals from untreated sewage sludge samples. *Chemosphere*, 411-420.

Kecili, R., & Hussain, C. M. (2018). Chapter 4 - Mechanism of Adsorption on Nanomaterials. In C. M. Hussain, *Nanomaterials in Chromatography* (pp. 89-115). Elsevier.

Kerle, E. A., Jenkins, J. J., & Vogue, P. A. (2007, April). Understanding pesticide persistence and mobility for groundwater and surface water protection. *Oregon State University Extension Service*.

Kloppel, H., & Kordel, W. (1997, January). Pesticide Volatilization and Exposure of Terrestrial Ecosystems. *Chemosphere*, pp. 1271-1289.

Kookana, R. S., Baskaran, S., & Naidu, R. (1998). Pesticide fate and behaviour in Australian soils in relation to contamination and management of soil and water: a review. *Australian Journal of Soil Research*, 715-764.

kookana, R. S., Sarmah, A. K., Van Zwieten, L., Krull, E., & Singh, B. (2011). Biochar Application to Soil: Agronomic and Environmental Benefits and Unintended Consequences. In D. L. Sparks, *Advances in Agronomy* (pp. 103-143). San Diego: Academic Press.

Koranteng, S. S. (2015). *Pesticides in Environmental Compartments of Afram Arm of the Volta Basin in Ghana*. Accra: University of Ghana.

Kordel, W. M., & Kleim, H. M. (1992). Fetermination of the fate of pesticides in outdoor lysimeter experiment. *Science Total Environment*, 421-434.

Krull, E. S., Baldock, J. A., Skjemstad, J. O., & Smernik, R. J. (2009). Characteristics of biochar: organo-chemical properties. In J. Lehmann, & S. Joseph, *Biochar for environmental management: Science and technology* (pp. 52-65). London: Earthscan.

Kuniuki, S. (2001). Effects of organic fertilization and pesticide application on growth and yield of field-grown rice for 10 years. Japanese Journal of Crop Science, 70(4): 530-540. Retrieved 2008-01-08.

Kuzyakov, Y., Bogomolova, I., & Glaser, B. (2014). Biochar stability in soil: decomposition during eight years and transformation as assessed by compound-specific carbon 14 analysis. *Soil Biology and Biochemistry*, 229-236.

Landon, J. R. (1991). *A Handbook for soil survey and agricultural land evaluation in the tropics and subtropics.* New York: Routledge.

Langmuir, i. (1918). The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *Journal of the American Chemical Society*, 1361-1403.

Lasserre, J.-P., Fack, F., Revets, D., Planchon, S., Renaut, J., Hoffmann, L., & Bohn, T. (2009). Effects of the Endocrine Disruptors Atrazine and PCB 153 on the Protein Expression of MCF-7 Human Cells. *Journal of Preteome*, 5485-5496.

Latifah, O., Ahmed, O. H., & Majid, N. M. (2018). Soil pH buffering capacity and nitrogen availability following compost application in a tropical acid soil. *Compost Science and Utilization*, 1-15.

Leah, L. (1996). *Silent Spring*. Retrieved August 28, 2019, from. The life and Legacy of Rachel Carson: http://www.rachelcarson.org/SilentSpring.aspx

LeBaron, H., McFarland, J., & Burnside, O. (2008). *The Triazine Herbicides 50 years Revolutionalizing Agriculture.* San Diego: Elsevier.

Lehmann, J. (2007). A handful of carbon. *Nature*, 143-144.

Lehmann, J. (2007). Bio-energy in the black. *Frontiers in Ecology and the Environment*, 381-387.

Lehmann, J., & Joseph, S. (2009). *Biochar for Environmental Management.* London: Earthscan.

Lehmann, J., & Rondon, M. (2006). Bio-char soil management on highly weathered soils in the humid tropics. In N. Ed. Uphoff, *Biological Approaches to Sustainable Soil Systems* (pp. 517-530). Boca Raton: CRC Press.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Niell, B., . . . Neves, E. G. (2006). Black Carbon Increases Cation Exchange Capacity in Soils. *Soil Science Society of America Journal*, 1719-1730.

Lin, Y., Munroe, P., Joseph, S. D., & Zwieten, L. V. (2012). Nanoscale organo-mineral reactions of biochars in ferrosol: An investigation using microscopy. *Plant and Soil*, 369-380.

Liu, Z., & Zhang, F. (2009). Removal of lead from water using biochars pepared from hydrothermal liquefaction of biomass. *Journal of Hazardous Materials*, 933-939.

Liua, L., Chena, H., Caia, P., Lianga, W., & Huang, Q. (2009). Immobilization and hytotoxicity of cd in contaminated soil amended with chicken manure compost. *Journal of Hazardous Materials*, 563-567.

Mangan, F., Barker, A., Bodine, S., & Borten, P. (2020, January 17). *Compost Use and Fertility*. Retrieved August 15, 2020, from The Center for Agriculture, Food and the Environment: https://ag.umass.edu/vegetable/fact-sheets/compost-use-soil-fertility

Manso, E. F. (2017). *Biochar as a liming agent and phosphorous source to enhance the growth of soya bean in two acid soils.* Legon: University of Ghana.

McMillan, O. W. (2018). *Characteristics and Mechanisms of atrazine sorption to biochar for land remediation.* Cambridge: University of Cambridge.

McMillan, O. W. (2018). *Characterization and mechanisms of atrzine sorptions to biochar for land remediation.* University of Cambridge.

Mekki, A., Aloui, F., & Sayadi, S. (2019). Influence of biowaste compost amendment on soil organic carbon storage under arid climate. *Journal of the Air and Waste Management Association*, 867-877.

Mendes, K. F., Dias Junior, A. F., Takeshita, V., & Rego, A. J. (2018). Effect of Biochar Amendments on the Sorption and Desorption Herbicides in Agricultural Soil. In S. Edebali, *Advanced Sorption Process Applications.* IntechOpen.

Mia, S., Dijkstra, F. A., & Singh, B. (2017). Chapter One - Long -Term Aging of Biochar: A Molecular Understanding With Agricultural and Environmental Implications. *Advances in Agronomy*, 1-51.

Morillo, E., Maqueda, C., Reinoso, R., & Undabeytia, T. (2002). Effect of two organic amendments on norflurazon retention and release by soils of different characteristics. *Environmental Science Technology*, 4319-4325.

Mostafapour, F. K., Bazrafshan, J., Farzadkia, M., & Amini, S. (2013). Arsenic removal from aqueous solutions by salvadora persica stem ash. *Journal of Chemistry*.

Moussavi, G., Hosseini, H., & Alahabadi, A. (2013). The investigations of diazinon pesticide removal from contaminated water by adsorption onto NH4Cl-induced activated carbon. *Chemical Engineering Journal*, 172-179.

Murphy, J., & Riley, J. P. (1962). A modified single solution for determination of phosphate in natural water. *Acta Journal of Analytical Chemistry*, 31-36.

Nartey, E. (1994, December). *Pedonic changes and phosphorus availability in some soils of northern Ghana.* Retrieved August 15, 2020, from UG Space: http://ugspace.ug.edu.gh/bitstream/handle/123456789/8119/PEDOGENIC%20CHANGES%20AND%20PHOSPHORUS%20AVAILABILITY%20OF%20SOME%20SOILS%20IN%20NORTHERN%20GHANA.pdf?sequence=1&isAllowed=y

Nartey, E., Dowuona, G. N., Ahenkora, Y., Memut, A. R., & Tiessen, H. (1997). Amount of distribution of some forms of phosphorus in ferruginous soils of the interior savannah zone of Ghana. *Ghana Journal of Agricultural Science*, 135-143.

Nartey, E., Matsue, N. & Henns, T. (2000). Adsorptive mechanisms of orthosilicic acid on neoball allophane. *Clay Science 11*, 125-136.

Nartey, O. D., & Zhao, B. (2014). Biochar Preparation, Characterization, and Adsorptive Capacity and Its Effect on Bioavailability of Contaminants: An Overview. *Advances in Materials Science and Engineering*.

National Institute of Health. (2020). *Compound Summary for atrazine*. Retrieved October 28, 2020, from PubChem: https://pubchem.ncbi.nlm.nih.gov/compound/atrazine

Navarro, S., Vela, N., & Navarro, G. (2007). Review. An overview on the environmental behaviour of pesticide residues in soils. *Spanish Journal of Agricultural Research*, 357-375.

Neeley, W. B. (1985). Hydrolysis. In W. B. Neeley, & G. E. Blau, *Environmental Exposure from Chemicals.* Boca Raton: CRC Press.

Negro, M. J., Solano, P. C., Ciria, P., & Carasco, J. (1999). Composting of sweet sorghum bagasse with other wastes. *Bioresource Technology*, 89-92.

NIEHS. (2019, May 23). *Pesticides*. Retrieved October 24, 2019, from National Institute of Environmental Health Sciences: https://www.niehs.nih.gov/health/topics/agents/pesticides/index.cfm

Niemeyer, j. C., Chelinho, S., & Sousa, J. P. (2017). Soil ecotoxicology in Latin America: Current research and perspectives. *Environmental Toxicology and Chemistry*, 1795-1810.

Novak, J. M., Busscher, W. J., Watts, D. W., Laird, D. A., Ahmedna, M. A., & Niandou, M. A. (2009, nOVEMBER 2009). Short-term CO2 mineralization after additions of biochar and switchgrass to a Typic Kandiudult. *Geoderma*, pp. 281-288.

Novak, J. M., Ippolito, J. A., Watts, D. W., Sigua, G. C., Ducey, T. F., & Johnson, M. G. (2019). Biochar compost blends facilitate switchgrass growth in mine soils by reducing Cd and Zn bioavailability. *Biochar 1*, 97-114.

Ntow. (2001). Organochlorine Pesticides in Water, Sediment, Crops, and Human Fluids in a Farming Community in Ghana. *Archives of Environmental Contamination and Toxicology*, 557-563.

Ntow. (2005). Pesticide residues in Volta Lake, Ghana. *Lakes and Reservoirs*, 243-248.

Oerke, E. (2006). Crop Losses to Pests. *The Journal of Agricultural Science.*

Ogawa, M., Okimori, Y., & Takahashi, F. (2006). Carbon sequestration by carbonization of biomass and forestation: three case studies. *Mitigation and Adaption Strategies for Global Change*, 421-436.

Okoffo, E. D. (2015, July). *UG Space.* Retrieved August 12, 2020, from University of Ghana: http://ugspace.ug.edu.gh/handle/123456789/8718

Oliveira, V. B., Bianchi, M. O., & Espindola, E. L. (2018). Hazard assessment of the pesticides KRAFT 36 EC and SCORE in a tropical natural soil using an ecotoxicological test battery. *Environmental Toxicology and Chemistry*, 2919-2924.

Olsen, S. R., & Watanabe, F. S. (1965). Test of an ascorbic acid method of determining phosphorus in water and extracts from the soil. *Journal of Soil Science*, 677-678.

Organization for Economic Co-operation and Development. (2000). *OECD Guideline for the testing oc chemicals.* USEPA.

Osunbitan, J. A., Adekalu, K. O., & Aina, P. O. (2014). Intermittent leaching of copper from copper based fungicide through a saturated soil profile. *Journal of Soil Science and Environmental Management*, 83-90.

Palanivell, P., Ahmed, O. H., Majid, N. M., Jalloh, M. B., & Susilawati, K. (2015). Improving Lowland Rice Plant Growth Variables, Nutrients Uptake, and Nutrients Recovery Using Crude Humic Substances. *The Scientific World Journal*.

PRRP-Ethiopia. (2012). *Sustainability of pesticide management system in Ethiopia.* Addis Ababa.

Qiu, R., Lu, H., Zhang, W., Yang, Y., Huang, X., & Wang, S. (2012). Relative distribution of Pb2+ sorption mechanisms by sludge-derived biochar. *Water Research*, 854-862.

Quaye, F. A. (2012). *Atrazine contamination in groundwater at Ejura in the Ashanti Region of Ghana.* International Nuclear Information System.

Ren, X., Sun, H., Wang, F., Zhang, P., & Zhu, H. (2018). Effect of ageing in field soil on biochar's properties and its sorption capacity. *Environmental Pollution*, 1880-1886.

Ren, X., Sun, H., Wang, F., Zhang, P., & Zhu, H. (2018). Effect of aging in field soil on biochar's properties and its sorption capacity. *Environmental Pollution*, 1880-1886.

Rosales, E., Meijide, J., Pazos, M., & Sanroman, M. A. (2017). Challenges and recent advances in biochar as low-cost biosorbent: From batch assays to continous-flow systems. *Bioresource Technology*, 176-192.

Schnoor, J. L. (1992). Fate of Pesticides and Chemicals in the Environment. In *Environmental Science and Technology* (pp. 1-26). New York: John Wiley & Sons, Inc.

Senyah, J. K., Issaka, R. N., Nketia, K. A., Asamoah, E., & Badu, J. (2012). *Report on soil physical and chemical properties for crop production in three Northern Regions of Ghana.* Kumasi: Council for Scientific and Industrial Research.

Sharma, A., Kumar, V., Shahzad, B., Tanveer, M., Sidhu, G. P., Handa, N., & THukral, A. (2019). Worldwide pesticide usage and its impacts on ecosystem. *SN Applied Sciences*.

Shinogi, Y., & Kanri, Y. (2003). Pyrolysis of plant, animal and human waste: Physical and chemical characterization of the pyrolytic products. *Bioresource Technology*, 241-247.

Sigmon, L. (2016). Photodegradation of Atrazine: A comparison of Anatase and Brookite phases of titanium dioxide. *The National Conference of Undergraduate Research (NCUR)* (pp. 315-323). Asheville: University of North Carolina.

Silva, K., & Broekel, T. (2016). Factors constraining farmers' adoption of new agricultural technology programme in Hambantota District in Sri Lanka: Perceptions of Agriculture Extension Officers. *13th International Conference on Business Management (CBM)*, (pp. 1-21). Sri Jayewardenepura.

Singh, B., Macdonald, L. M., Kookana, R. S., Zwieten, L. V., Butler, G., Joseph, S., . . . Esfandbod, M. (2014). Opportunities and constraints for biochar technology in Australian agriculture: looking beyond carbon sequestration. *Soil, land care and environmental research*, 739-750.

Singh, B., Singh, B. P., & Cowie, A. L. (2010). Characterisation and evaluation of biochars for their application as a soil amendment. *Australian Journal of Soil Research*, 516-525.

Singh, S., Kumar, V., Chauhan, A., Datta, S., Wani, B. A., Singh, N., & Singh, J. (2018). Toxicity, degradation and analysis of the herbicide atrazine. *Environmental Chemistry Letters*, 211-237.

Smith, S. R. (2009). A critical review of the bioavailability and impacts of heavy metals in municipal solid waste composts compared to sewage sludge. *Environmental International*, 142-156.

Snyder, J., Smart, J., Goeb, J., & Tschirley, D. (2015). *Pesticide use in sub-saharan Africa: Estimates, Projections, and implications in the context of food system transformation.*

Sohi, S., Lopez-Capel, E., Krull, E., & Bol, R. (2009). *Biochar, climate change and soil: A review to guide future research.* CSIRO.

Solaimalai, A., Ramesh, R., & Baskar, M. (2004). Environmental contamination and bioreclamation. *Pesticides and environment*, 345-382.

Sombroek, W. G. (1966). *Amazon Soils: a reconnaissance of the soils of the Brazilian Amazon region.* Wageningen: Wageningen University & Research.

Spears, S. (2018, 05 16). *What is Biochar*. Retrieved February 3, 2020, from Regeneration International: https://regenerationinternational.org/2018/05/16/what-is-biochar/

Steiner, C., Teixeira, W. G., Lehmann, J., Nehls, T., Vasconcelos de Macedo, J. L., Blum, W. E., & Zech, W. (2007). Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. *Plant and Soil*, 275-290.

Streubel, J. D. (2011). *Biochar: Its characterization and utility for recovering phosphorus from anaerobic digested dairy effluent.*

Streubel, J. D., Collins, H. P., Garcia-Perez, M., Tarara, J., Granatstein, D., & Kruger, C. E. (2011). Influence of contrasting biochar types on five soils at increasing rates of application. *Soil Science Society of America Journal*, 1402-1413.

Tao, Q. H., & Tang, H. X. (2004). Sorption Behavior of Atrazine onto Natural Sediments under Various Solution Conditions. *Adsorption Science and Technology*, 639-652.

Tetteh, J. L. (2014). *Adsorptive characteristics of phosphorus on four biochar types.* Accra: University of Ghana.

The Editors of Encyclopaedia Britannica. (n.d.). *Britannica*. Retrieved December 19, 2019, from Herbicide: https://www.britannica.com/science/herbicide

Tiryaki, O., & Temur, C. (2010). The Fate of Pesticide in the Environment. *Journal of Biological & Environmental Sciences*, 29-38.

Trinh, B. S., Werner, D., & Reid, B. J. (2017). Application of a fullscale wood gasification biochar as a soil improver to reduce organic pollutant leaching risks. *Journal of Chemical Technology and Biotechnology*, 1928-1937.

Uchimiya, M., Lima, I. M., Klasson, K. T., & Wartelle, L. H. (2010). Contaminant immobilisation and nutrient release by biochar soil amendment roles of organic matter. *Chemosphere*, 935-940.

Ueno, M., Kawamitsu, Y., Komiya, Y., & Sun, L. (2008). Carbonisation and gasification of bagasse for effective utilisation of sugarcane biomass. *International Sugar Journal*, 22-25.

United States Environmental Protection. (2019, July 19). *Basic Information about Pesticide Ingredients*. Retrieved October 10, 2019, from United States Environmental Protection: https://www.epa.gov/ingredients-used-pesticide-products/basic-information-about-pesticide-ingredients

United States Environmental Protection Agency. (2005, March). *Protecting Water Quality from Agricultural Runoff*. Retrieved January 20, 2020, from United States Environmental Protection Agency: https://www.epa.gov/sites/production/files/2015-09/documents/ag_runoff_fact_sheet.pdf

USEPA. (1996). *Product Properties Test Guidelines. Oxidation/Reduction: Chemical Incompatibility.* Washington DC: US EPA.

Vats, S. (2015). Herbicides: History, Classification and Genetic Manipulation of Plants for Herbicide Resistance. In *Sustainable Agriculture Reviews* (pp. 153-192). Cham: Springer International Publishing.

Vera, Y. M., Jose de Carvalho, R., Torem, M. L., & Calfa, B. A. (2009). Atrazine degradation by in situ electrochemically generated ozone. *Chemical Engineering Journal*, 691-697.

Verheijen, F., Jeffery, S., Bastos, A. C., Van der Velde, M., & Diafas, I. (2010). *Biochar Application to Soils.* European Commission.

Verheijen, F., Jeffery, S., Bastos, A. C., Velde, M. V., & Diafas, I. (2010). *Biochar application to soils: a critical scientific review of effects on soil properties, processes and functions.* Luxembourg: European Commission.

Voto Mobile Org. (2015). *A Complete Curriculum and Guide to Maize Production in Ghana.*

Walkley, A., & Black, I. A. (1934). An examination of the Degtjaref method for determioning soilorganic matter, and a proposed modification of the chronic acid titration method. *Journal of Soil Science, 37*, 29-38.

World Health Organization. (n.d.). *Pesticides*. Retrieved October 10, 2019, from World Health Organization: https://www.who.int/topics/pesticides/en/

Yadav, I. C., & Devi, N. L. (2017). Pesticide Classification and its Impact on Human and Environment. In R. Chandra, B. R. Gurjar, & J. N. Govil, *Environmental Science and Engineering* (pp. 140-159). Stadium Press LLC.

Yang, X., Liu, E., Zhu, X., Wang, H., Liu, H., Liu, X., & Dong, W. (2019). Impact of composting methods on nitrogen retention and losses during dairy manure composting. *International Journal of Environmental Research and Public Health*, 3324.

Yue, L., Ge, C., Feng, D., Yu, H., Deng, H., & Fu, B. (2017). Adsorption-desorption behavior of atrazine on agricultural soils in China. *Journal of Environmental Sciences*, 180-189.

Zanzi, R. (2001). *Pyrolysis of biomass.* Stockholm: Kemiteknik.

Zhang, P., Sun, H., Min, L., & Ren, C. (2018). Biochars change the sorption and degradation of thiacloprid in soils: Insights into chemical and biological mechanisms. *Environmental Pollution*, 158-167.

Zhelezova, A., Cederlund, H., & Stenstrom, J. (2017). Effect of biochar amendment and ageing on adsorption and degradation of two herbicides. *Water, Air and Soil Pollution*, 216.

Zimdahl, R. L. (2010). *A History of Weed Science in the United States.* Burlington: Elsevier Inc.

APPENDICES

APPENDIX A

QUESTIONNAIRE

Project: Influence of Biochar Amendment on the Leaching of Pesticides into groundwater

Objectives: To identify the source(s), type(s) and how pesticides are used by farmers

General Information

Date of survey:

City/Town/Village:

Name of farmer:

Age:

Gender:

Educational Level: None __ Primary __ Jnr High School __Snr High School __ Tertiary __

1. What crops do you cultivate? A. Maize B. Groundnut C. Millet D. Beans
   E. Cotton F. yam G. Sorghum H. Rice I. Others (specify)
   ……
2. For how long have you been growing the crop(s)? ___ months/ ___ years
3. Do you apply pesticides on your farm? A. Yes B. No
4. If No, how do you control pests or weeds? _____
5. If Yes, For how long have you been using pesticide(s)? ___ months/ ___ years

6. Where do you get your pesticides from? (Tick any that apply) A. A farming company B. Food and Agriculture Ministry D. Open market E. Others (specify)

   ……..

7. Which is the most important consideration in buying a pesticide? (Tick only one) A. Cost B. Effectiveness C. Recommendation by extension officers D. Recommendation by neighbors E. Others (please specify)

   ……
   …..

8. What type of pesticides do you use most on your farm? A. Herbicides/Weedicides B. Insecticides C. Fungicides D. Others (specify):

   ……
   …

9. Trade name of pesticide(s) used

   ……

10. Do you mix different pesticides together? Yes/No

11. At what stage are the chemicals in 9 above used?

    A. Before cultivation B. During cultivation C. Before harvest D. After harvest Others ……

12. How often in the growing season do you use pesticides on your farm? A. Once B. Twice C. Thrice D. More than thrice

13. Which type of chemical pesticide do you prefer? A. Broad Spectrum B. Pest Specific C. Don't know

    ……

14. Have you ever been educated/trained on how to handle pesticides? A. Yes B. No

15. If yes; by who? A. Farming company B. NGO C. MOFA D. Others specify

16. Do all purchased pesticides contain labels? A. Yes B. No

17. How do you read instructions on the labels? A. Observation of pictures B. Read written instructions C. Both D. None of the above E. Others (specify)

18. If you can't read instructions on the label, or if there are no instructions, how do you decide on the correct quantity to use on an acre? A. Advice from supplier / seller B. Advice from extension agent C. Advice from other farmers
    E. Others (specify) ……..
19. Do you go by the recommended dosage on the label? Yes/No
20. Do you think high dosage gives higher yields? Yes/No
21. If there is pesticide left over, how and where is it disposed? ……
22. How are the containers disposed? Reused/Buried/Sold
23. Are you aware that pesticides can be hazardous? A. Yes B. No
24. If yes, what is the damage? A. To human health B. To animal health C. To wildlife D. To water bodies E. Others (please specify)
25. Do you have a drinking water source at the farm?
    A. Yes B. No
26. If yes; how far is your drinking water source from the farm?
    ……
27. What measures do you take to prevent pesticides from contaminating food and water?
    ……
28. Have you heard of any pesticide poisoning incident happening in the community in the last 48 months? A. Yes B. No
29. In case of any pesticide poisoning incidents whom do you report to? (Tick any that apply) A. Farming Company Officer B. Health officer C. Environmental Protection Agency B. Farmers group C. Others (specify)
30. Please provide any additional information …….

THANK YOU.

APPENDIX B

ANOVA Tables for Physicochemical Characterization

Soil alone and soil and 1 yr old biochar

Summary

Groups	Count	Sum	Average	Variance
Soil alone	3	14.22	4.74	0.0091
Soil alone and 1 year old biochar	3	15.6	5.2	0.0025

ANOVA

Source of variation	SS	df	MS	F	P-value	F crit
Between Groups	0.3174	1	0.3174	54.72414	0.001781	7.708647
Within Groups	0.0232	4	0.0058			
Total	0.3406	5				

Soil alone and soil and 2 yr old biochar

Summary

Groups	Count	Sum	Average	Variance
Soil alone	3	14.22	4.74	0.0091
Soil alone and 2 year old biochar	3	15.24	5.08	0.0049

ANOVA

Source of variation	SS	df	MS	F	P-value	F crit
Between Groups	0.1734	1	0.1734	24.77143	0.007613	7.708647

Within Groups	0.028	4	0.007			
Total	0.2014	5				

Soil alone and Soil and compost

Summary

Groups	Count	Sum	Average	Variance
Soil alone	3	14.22	4.74	0.0091
Soil alone and 2 year old biochar	3	19.01	6.336667	3.33E-05

ANOVA

Source of variation	SS	df	MS	F	P-value	F crit
Between Groups	3.824017	1	3.824017	837.3759	8.49E-06	7.708647
Within Groups	0.018267	4	0.007			
Total	3.842283	5				

Organic Carbon

Soil alone and soil and 1 yr old biochar

Summary

Groups	Count	Sum	Average	Variance
Soil alone	3	3.16	1.053333	0.000633
Soil alone and 1 year old biochar	3	3.44	1.146667	0.000633

ANOVA

Source of variation	SS	df	MS	F	P-value	F crit

Between Groups	0.013067	1	0.013067	20.63158	0.01048	7.708647
Within Groups	0.002533	4	0.000633			
Total	0.0156	5				

Soil alone and soil and 2 yr old biochar

Summary

Groups	Count	Sum	Average	Variance
Soil alone	3	3.16	1.053333	0.000633
Soil alone and 1 year old biochar	3	3.74	1.24667	0.00253

ANOVA

Source of variation	SS	df	MS	F	P-value	F crit
Between Groups	0.005606667	1	0.05607	35.4105	0.004	7.70865
Within Groups	0.006333333	4	0.00158			
Total	0.0624	5				

Soil alone and soil and compost

Summary

Groups	Count	Sum	Average	Variance
Soil alone	3	3.151	1.050333	0.00055
Soil alone and 1 year old biochar	3	3.354	1.118	0.00249

ANOVA

Source of variation	SS	df	MS	F	P-value	F crit
Between Groups	0.00687	1	0.00687	4.51358	0.00101	7.70865
Within Groups	0.00609	4	0.00152			
Total	0.01295	5				

TOTAL NITROGEN

Soil alone and soil and 1 yr old biochar

Summary

Groups	Count	Sum	Average	Variance
Soil alone	3	0.15	0.05	7E-06
Soil alone and 1 year old biochar	3	0.191	0.06367	8.3E-06

ANOVA

Source of variation	SS	df	MS	F	P-value	F crit
Between Groups	0.00028	1	0.00028	4.51358	0.00101	7.70865
Within Groups	3.1E-05	4	7.7E-06			
Total	0.00031	5				

Soil alone and soil and 2 yr old biochar

Summary

Groups	Count	Sum	Average	Variance
Soil alone	3	0.15	0.05	7E-06
Soil alone and 1 year old biochar	3	0.326	0.10867	4.2E-05

ANOVA

Source of variation	SS	df	MS	F	P-value	F crit
Between Groups	0.005162667	1	0.00516	209.297	0.00013	7.70865
Within Groups	9.86667E-05	4	2.5E-05			
Total	0.005261333	5				

Soil alone and soil and compost

Summary

Groups	Count	Sum	Average	Variance
Soil alone	3	0.15	0.05	7E-06
Soil alone and 1 year old biochar	3	0.228	0.076	5.2E-05

ANOVA

Source of variation	SS	df	MS	F	P-value	F crit
Between Groups	0.00101	1	0.00101	34.3729	0.00423	7.70865
Within Groups	0.00012	4	3E-05			
Total	0.00113	5				

AVAILABLE P

Soil alone and soil and 1yr old biochar

Summary

Groups	Count	Sum	Average	Variance

Soil alone	3	8.46	2.82	0.15131
Soil alone and 1 year old biochar	3	16.408	5.46933	0.12534

ANOVA

Source of variation	SS	df	MS	F	P-value	F crit
Between Groups	10.5285	1	10.5285	76.1141	0.00095	7.70865
Within Groups	0.5533	4	0.13832			
Total	11.0817	5				

Soil alone and soil and 2yr old biochar

Summary

Groups	Count	Sum	Average	Variance
Soil alone	3	8.46	2.82	0.15131
Soil alone and 1 year old biochar	3	39.01	13.0033	0.86319

ANOVA

Source of variation	SS	df	MS	F	P-value	F crit
Between Groups	155.5504167	1	155.55	306.655	6.2E-05	7.70865
Within Groups	2.028994667	4	0.50725			
Total	157.5794113	5				

Soil alone and soil and compost

Summary

Groups	Count	Sum	Average	Variance
Soil alone	3	8.46	2.82	0.15131
Soil alone and 1 year old biochar	3	32.948	10.9827	0.09794

ANOVA

Source of variation	SS	df	MS	F	P-value	F crit
Between Groups	99.9437	1	99.9437	801.945	9.3E-06	7.70865
Within Groups	0.49851	4	0.12463			
Total	100.442	5				

CEC

Soil alone and soil and 1 yr old biochar

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	3	17.73	5.91	0.0289
Column 2	3	18.27	6.09	0.7396

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.0486	1	0.0486	0.12648	0.007400	7.708647
Within Groups	1.537	4	0.38425			
Total	1.5856	5				

Soil alone and soil and 2 yr old biochar

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	3	17.73	5.91	0.0289
Column 2	3	18.36	6.12	0.0073

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.06615	1	0.06615	3.654696	0.00128	7.708647
Within Groups	0.0724	4	0.0181			
Total	0.13855	5				

Soil alone and soil and compost

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	3	17.73	5.91	0.0289
Column 2	3	18.51	6.17	0.1123

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.1014	1	0.1014	1.436261	0.002968	7.708647
Within Groups	0.2824	4	0.0706			
Total	0.3838	5				

APPENDIX C

Sample Size Determination

$$Population\ size\ = \frac{n}{1 + \frac{z^2 \times\ p\ (1-p)}{\varepsilon^2\ \times N}}$$

$$n\ = \frac{z^2 \times\ p\ (1-p)}{\varepsilon^2}$$

Where:

z = z score = 1.645 at 90%
p = population proportion = 70% of population estimated to be farmers
ε = margin of error = 10%
N = population size = 54,899

$$n\ = \frac{1.645^2 \times\ 0.70(1-0.70)}{0.10^2}$$

$$n\ = 56.827$$

$$Population\ size\ = \frac{56.827}{1 + \frac{1.645^2 \times\ 0.7\ (1-0.7)}{0.10^2\ \times 54{,}899}}$$

$$Population\ size = 56.768$$

Sample size approximated to **60**