

**AKENTEN APPIAH-MINKA UNIVERSITY OF SKILLS TRAINING AND
ENTERPRENEURIAL DEVELOPMENT**

**ASSESSMENT OF PESTICIDE RESIDUES IN SOILS AND CROPS GROWN
IN THE ASANTE-AKYEM CENTRAL MUNICIPALITY OF THE ASHANTI
REGION OF GHANA AND THEIR ASSOCIATED HEALTH RISKS**

MOHAMMED OSMAN

MAY, 2024

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BY

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**A thesis submitted to the School of Graduate Studies, Akenten Appiah-Menka
University of Skills Training and Entrepreneurial Development in partial
fulfillment of the requirements for the award of a Master of Philosophy degree in
Chemistry Education**

MAY, 2024

DECLARATION

Candidate's Declaration

I hereby declare that this thesis is the result of my own original work and no part of it has been presented for another degree at this university or elsewhere

Mohammed Osman

Signature:..... **Date:**.....

Supervisors' Declaration

We hereby declare that, the preparation and presentation of this thesis was supervised in accordance with the guidelines for supervision of thesis as laid down by the University of Education, Winneba.

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ABSTRACT

Pesticides applications on crops production have contributed immensely to crops' yield. Nevertheless, their applications on vegetables could have adverse effects on the health status of consumers. This study was therefore intended to determine pesticide residues in soils and crops (cocoyam tubers and leaves, cassava and maize) and their associated health risks. The crops were analysed for organochlorine (OC), organophosphate (OP) and carbamate (CM) pesticides. Pesticides residues were extracted using Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) mini multi-residue procedure and their levels analysed by Gas Chromatography-Mass Spectrometry (GC-MS) equipped with 1.0 mL/min flow detector. OCPs levels in crops ranged from 0.001 to 0.086 mg/kg, OPPs levels in soils ranged from 0.004 to 7.446 mg/kg whilst that of carbamates ranged from 0.040 to 0.192 mg/kg. Concentrations of Chlordane, Dieldrin, Endosulfan, Endrin and Heptachlor (OCs), carbamates (Carbofuran and Carbaryl) and OPPs except Profenofos in the crops were above the maximum residual limits (MRLs) recommended by United State Environmental Protection Agency and European Union. These high levels of pesticides residues in the crops could affect the health status of consumers. Positive and negative correlations existed between moisture contents, exchangeable cations, pH, organic matter, sand, silt and clay contents of the soils and some pesticides levels in the crops. These imply that soil properties influenced distributions of pesticides levels in the crops. Even though, computed Hazard Indexes (HIs) and Hazard Quotients (HQs) of pesticide residues were below 1, continuous consumption of the crops could cause certain health risks in consumers due to bioaccumulation in tissues. I recommend that agriculture extension officers should educate farmers on proper handling and how to use approved pesticides in the right proportions during application on crops.

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DEDICATION

This thesis is dedicated to my wife Mrs. Zainab Mohammed, and my children (Nazeefat Mohammed, Abdul Hameed Mohammed) and the entire Osman family especially Mrs. Nansata Osman, Rkayatu Osman and Abdul Wahab Osman.

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CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Across the globe, Cocoyam (*Xanthosoma sagittifolium*) is considered as one of the six vital root and tuber crops (FAO, 2012). Cocoyam originated from Central and South America (Ramanatha *et al.*, 2010) where the specie was domesticated from the wild (Bermejo and Leon, 1994). Cocoyam can be cultivated in many tropical areas and therefore has also been domesticated in several societies in Oceania, Africa, and Asia (Ramanatha *et al.*, 2010). Globally, it provides nourishment for over 400 million people (Onokpise *et al.*, 1999; Vaneker & Slaats, 2013). Currently, the highest producer of cocoyam is Africa (Onyenka, 2014). Over 60% of Africa's total cocoyam production is obtained from Ghana, Nigeria and Cameroon (Onyenka, 2014). This indicates significance of the crop to the regional food security.

Although cocoyam is produced in large quantities and has better storage abilities compared to other tropical root and tuber crops (Boakye *et al.*, 2018), agricultural policies put in place across the African continent do not consider cocoyam production (Onyeka, 2014). In French Polynesia, Florida, Galapagos Island Puerto Nico and Costa Rica, *Xanthosoma species* are regarded as invasive. *Xanthosoma* is referred to as “new cocoyam” in West Africa (Bammite *et al.*, 2021). In the 16th and the 17th centuries, Amadi (2012) traced its origin to West Africa whilst Wright (1930) traced its introduction to Ghana in the 19th century (1843) by the West Indian missionaries.

Generally, all the parts of cocoyam plant are comestible (Green & Oguzor 2009). The usage of cocoyam varies from location to location, due to its wide spread in different cultures and geographical regions (Vaneke *et al.*, 2013). The crop is used mainly as food whilst, the other parts are also used as silage (Nanbol *et al.*, 2019). The leaves are used as an anti-poisonous agent against scorpions, snakes and tarantula bites (Nanbol *et al.*, 2019). No part of the plant is consumed raw due to its acidity content (Ramanatha *et al* 2010).

Boiling, baking, roasting and frying are the most notable traditional cooking methods for cocoyam (Boakye *et al.*, 2018). Cocoyam tubers are used as meals and also in preparation of special dishes (mpotompoto) for babies between 1 to 2years old (Ponka, *et al.*, 2016). According Falade & Okafor (2014), significant similarities exist in the use of cocoyam roots and tubers across in West African countries.

Cocoyam unlike other root and tuber staples have superior nutritional value such as protein digestibility and minerals (Ekwe & Nwachuku, 2009; Lim 2016). Cocoyam is considered as an important source of energy, proteins and vitamins (Opara 2003) and has high potassium, Zinc and nicotinic acid contents. Cocoyam also has ability to slowly inhibit trypsin compared to other comestible aroids (Temesgen & Retta 2015). Cocoyam leaves are heart shaped and grow well in tropical and subtropical areas (Sharma *et al.*, 2020). The cocoyam tuber has moderate starch root content (Odeku, 2013). The leaves are also used in various cuisines (Chukwu 2015). Although the leaves contain several nutrients such as iron, calcium potassium, folate, vitamin C and A, phosphorus, magnesium, calcium, Iron, Protein (Daniel Prieto, 2020), they could be poisonous when eaten raw

(Otekunrin *et al.*, 2021). Due to its high fiber content and low calories, cocoyam leaves offer a nutritional complement to a well-balanced diet (Apata, & Babalola 2012). The high nutrient contents of cocoyam leaves help prevent diseases such as rickets, scurvy and serves as healthy addition to a balanced diet and function to boost heart health (Okechukwu *et al.*, 2020).

Cassava was first planted around the coast by the Portuguese who brought them from Brazil, the country of its origin (Emperaire, & Peroni, 2007). Cassava became the most widely grown and used crop by the people of the coastal plain in the middle of the 18th century (Rostain, 2008). Cassava is very significant root crop in Ghana, before yam and cocoyam (Apata, & Babalola, 2012, Sanful, & Darko 2010). It was later spread to all parts of Ghana and remains the most useful root tuber in the country (Robert, *et al.*, 2016). In Africa cassava accounts for about 30% of tropical staple food crops for over 200 million people (El-Sharkawy, 2004).

Cassava became a well-established crop in most areas in Ghana after 1982 -1983 when other crops failed completely (Andoh, 2010, Manu-Aduening *et al.*, 2006). The crop is cultivated as monocrop or intercropped with other crops such as cocoyam, maize (Adekunle *et al.*, 2014, Nchanji *et al.*, 2016). Today in Ghana, cassava is a popular food used in the preparation of many dishes, such as Gari, fufuo, Konkonte, Tuo Zaafi among others (Annor *et al.*, 2016). Not only as a staple food crop, but also used as raw material in the production of ethanol and starch (Shanavas, *et al.*, 2011, Ssiroth *et al.*, 2010).

Several varieties of cassava are cultivated in Africa (Patil & Fauquet 2009). In Ghana cassava has been researched to improved varietal development (Acheampong, *et al.*, 2013). The National Agricultural Research System (NARS) in Ghana has released improved varieties of cassava which are resistant to pest and diseases, mature early and have high yield (Okogbenin *et al.*, 2007). Some improved varieties of cassava cultivated in Ghana are; Ampong, Buroni bankye, Sika bankye, and Otuhia among others (Essegbey, & MacCarthy, 2020, CSIR, CRI, 2010).

It is estimated that over 32 million acres of land are used in cassava cultivation globally (Ikuemonisan, *et al.*, 2020, Babalola & Olayemi, 2013). Of these more than 70% are in Africa and Asia (EL-Sharkawy 2003). Over 500 million people depend on cassava as the main source of carbohydrate (Balagopalan, 2001). These are nutritionally variable part depending on geographical location, age and variety of the cassava (Tewa and Iutaladio 2004).

Although, cassava is known to contain high amounts of carbohydrate, it also provides essential nutrients (protein, lipid, dietary fiber, thiamin, riboflavin, ascorbic acid) when the leaves are consumed (Bayata, 2019). Cassava roots upon consumption provide calcium, phosphorus, iron, potassium, copper, zinc sodium and manganese (Burtrago 2002). Cassava root is a high energy content food and produces over 250000 calories per hectare (Bayata, 2019).

Energy content of cassava root is above that of maize, rice, sorghum and wheat (Montagnac, *et al.*, 2009). Cassava root is rich in calcium, iron, copper, zinc, manganese, potassium and magnesium compared to leguminous crops (Uarrota *et al.*, 2019). Calcium content of cassava root depending on the variety ranged between 15 – 35mg per 100g of the edible portions whilst vitamin C content ranged between 15 – 45mg per 100g of the edible part (Salvador, 2015, Charles *et al.*, 2004). Generally, minerals and vitamins contents are less in cassava root than in sorghum and maize (Gil and Buitrago, 2002).

In Ghana, maize production is predominantly done during raining seasons by poorly resourced small farmers (Darfour, & Rosentrater, 2016). Report indicates that maize has overtaken sorghum and millet as traditional staple crop in Northern Ghana (SRID-MoFA, 2011). Maize contributes over 50% of Ghana's total cereal production.

In an attempt to reduce crop damage and meet the world's growing food demands, pesticides have been employed in farming activities for years (Shang, *et al.*, 2019). It is estimated that, if farmers worldwide suddenly stop using pesticides, 78% (fruits), 54% (vegetables) and 32% (grains) would be lost to pests and diseases (Cai, 2008). Globally, pesticides production has increased by 11% (annually), from 0.2 million tons in 1950's to 5 million tons in 2000 (Carvalho, 2017). In 2012, an average, of 3.8 million tons of pesticides were applied to agricultural lands (FAO, 2020). This amounted over 40 billion US dollars (Pimentel, 2009). As a consequence of pesticide use, over two million people, mainly residing in developing nations, are at an elevated risk of the negative health effects linked to pesticides (Hicks, 2019).

Extensive use of pesticides for farming has increased soil pollution (Bisht & Chauhan 2020). Despite the benefits of using pesticides to improve food safety environmental and health risks of pesticides have increased (Özkara, *et al.*, 2016, Williams & Hammitt, 2001). Soil plays a crucial role in fate, behaviour and dispersas of pesticides and their degradable products which might negatively affect different food webs (Lewis *et al.*, 2016, Zhang *et al.*, 2006).

Most pesticides are intended to protect plants or crops from weeds, fungi and insects among others (Zotti. *et al.*, 2018). In their attempt to save money and maximize profits farmers use pesticides to prevent crop loses to insect and other pests (Kellogg *et al.*, 2002). Pesticides application has increased over the last ten decades due to increased farming activities and farmers effort to obtain higher crop yield (Asare, 2010).

Overdependence on pesticide by farmers could cause irreparable change and long-standing health problems to the environment, humans and other living organisms (Zacharia, 2011). Organic phosphates, carbamates and synthetic pyrethroids pesticides are being used on large scale by farmers (Abubakar, *et al.*, 2020). Lack of proper training for farmers on the use of pesticides has been the reason of inappropriate pesticides application on crops (Rijal *et al.*, 2018). Excessive use of pesticides can cause pesticides build up in foods and this could exert serious public health hazard when the foods are consumed (Alavanja, Hoppin, & Kamel, 2004).

In Ghana, inadequate training for agrochemical sellers have led to sale of pesticides that are not recommended for use on crops in Ghana (Aniah *et al.*, 2021, Onwona *et al.*, 2019). Recently, Ghanaian farmers have become over reliant on the use of pesticide (Ehiakpor, *et al.*, 2016).

Due to numerous health hazards and challenges posed by pesticides, developed nations have put measures in place to monitor pesticide residues levels in food to curtail their effects on the exposed population (Handford, *et al.*, 2015). In developing countries several banned pesticides are still being used and these pesticides continue to cause health and environmental problems (Leoci, & Ruberti, 2021). In some developing countries, farmers use pesticides as substitutes for fertilizers (Rahman, 2003). Hence, it is very necessary to educate farmers on integrated pest management (IPM) is very necessary.

1.2 Statement of Problem

Pesticides are considered to be vital for adequate crop cultivation for an ever-increasing world population (Pirzada *et al.*, 2020, Nishimoto 2019). They are also used to control insect – borne diseases (Van Den Berg, *et al.*, 2012), hence, the rapid rise in global demand for pesticides (Carvalho, 2017, Ejobi *et al.*, 1996). Although alternative methods such as the use of bio pesticides, developing pest resistant crop varieties and the transgenic approaches among others to control crop loss due to pest attacks, the use of chemical pesticides remain preferred choice (Kouser, & Qaim, 2013). The over 3 billion kilograms of pesticides used annually, worldwide (Sharma *et al.*, 2019), 47.5% are herbicides, insecticides (29.5%), fungicides (17.5%) and others (5.5%), (De *et al.*, 2014).

Pesticides pose threat to humans due to their persistent nature and their high toxic properties (Yoder, 2003). In living organisms, pesticides hinder normal functioning of endocrine and reproductive systems (Tiemann, 2008; Vos *et al.*, 2000). Pesticides (dichlorodiphenyltrichloroethane (DDT), chlordane, aldrin, dieldrin, endrin, mirex, heptachlor and hexachlorobenzene) have lethal effects on human health and environment at even reduced doses (Barhoumi, 2014; UNEP 2001). African economy is largely dependent on agriculture and about 59% of Africans population make their living from farming (Abate, *et al.*, 2000). Due to increasing global population, food demand has been projected to increase at a rapid rate in the next three decades (Eickhout *et al.*, 2006) and thus, demand of pesticides, herbicides, fungicides among others are also likely to increase (Sharma *et al.*, 2019).

In Ghana, approximate 87% of farmers apply varieties of pesticides on vegetables (Mohammed & Boateng 2017). Of these 41% are pyrethroids, organophosphates (37%) and the remaining 9% for carbamates and others (Ntow *et al.*, 2006). Farmers apply cocktails of pesticides in their attempt at increasing their potency (Abrokwah *et al.* 2019). Majority of these pesticides used by Ghanaian farmers are employed in the forest areas of Ashanti, Bono, Ahafo, Bono East, Western and Eastern Regions (Koch *et al.*, 2016).

Lack of pesticides education for farmers has contributed to the application of inappropriate pesticides on crops (Paarlberg 2009). Lack of access to agricultural extension services has deprived farmers of making informed choices and decisions in pesticides use (Tandi *et al.*, 2014, Ngowi, 2007). Though pesticides are helpful in controlling pest diseases in order to

increase crop yield, they persist in crops and soil (Donkor *et al.*, 2016). Cases of residual pesticides in food crops above recommended maximum limits permitted by Regulatory Agencies to be in crops and soils (Syed *et al.*, 2014).

Globally, annual pesticide poisoning cases are estimated to be about 1-5 million leading to about 20,000 deaths in agricultural workers, and a most of this is recorded in developing countries (WHO, 2004). Also, about 99% of the global minimum of 300,000 death cases related to pesticides poisoning annually are believed to occur in developing countries (WHO, 2008). The World Health Organization estimates that 20,000 unintentional deaths in humans and 3 million poisoning cases are caused by pesticides misuse in developing countries, due to farmers' application of pesticides without using protective clothing (Wumbei, 2019). Some farming communities in developing countries uses pesticides cans as drinking cups (Miyinzi 2016). Some farming families consume treated seeds during lean periods (Litchfield, 2005).

Studies have suggested possible negative correlations between residual pesticide levels in food and human health (Bhattacharjee *et al.*, 2012, Berrada *et al.*, 2010). Humans, diseases such as headaches and nausea were found to be acute symptoms of pesticide exposure (Nazir *et al.*, 2021). Cancers, reproductive defects, developmental impairment, immunotoxicity birth defects and endocrine disruption are also associated symptoms of human exposure to pesticides (Yilmaz *et al.*, 2020). About 849,000 human deaths that occurred globally in 2001 were due to exposure to high levels of pesticides (WHO 2002). In the last few decades, inappropriate use of pesticides in most developing countries. This

endangers lives of farmers, the environment and the entire population, (Augustine *et al.*, 2016).

Despite the fact that data on levels of pesticides residues in farm products exist for many years in Ghana, the information is very scanty (Donkor *et al.*, 2016). Many governments of African countries do not have pesticides monitoring programme to check levels of pesticides in crops and soils (Bempah *et al.*, 2011; Osei Fosu *et al.*, 2014). Thus, there appear to be no work done on pesticide levels in maize, cassava and cocoyam, cocoyam leaves and in the soils on which they are cultivated. In view of the numerous negative health issues linked to pesticides, there is the need to investigate pesticides residues in soils and food crops cultivated in the Asante Akyem municipality in the Ashanti Region of Ghana.

1.3 Objective of the Study

The main objective of this study is to access levels of pesticides in soil and selected food crops cultivated in the Asante Akim central municipality of the Ashanti region of Ghana.

To achieve this, specific objectives of the study are to determine:

- 1 Physio-chemical properties of soils where food crops are cultivated during the time of the study.
- 2 Organochlorine, organophosphate and carbamate pesticides levels in the soil where food crops are grown during the study.
- 3 Organochlorine, organophosphate and carbamate pesticides levels in food crops (maize, cassava, cocoyam and cocoyam leaves) harvested from farmlands where soil are sampled for the study.

- 4 Health issues likely to be suffered by consumers of the food crops cultivated on the farms included in the study.
- 5 Compare pesticides levels in food crops (maize, cassava, cocoyam, and cocoyam leaves) to the recommended maximum residue limits permitted by United State Environmental Protection Agency (USEPA) and European Union (EU).
- 6 Correlation between soil properties and level of pesticides in soil and selected food crops.

1.4 Significance of the Study

The study would create the necessary awareness on levels of pesticides in food crops, maize, cassava, cocoyam and cocoyam leaves “kontomire, being consumed by people in the Asante Akim central municipality and beyond. The results of this study would assist regulatory authorities to set maximum residues limits and also take relevant measures to cut back on levels of pesticides in food crops. This study would further help to understand correlations between pesticides residues in soils and food crops from the study area.

1.5 Justification of the Study

Carbamates, organochlorine and organophosphate pesticides are of great importance in health and agricultural sectors (Nicolopoulou-Stamati *et al.*, 2016). Globally, massive use of pesticides in recent time has increased crop production. Crops such as maize and cassava, production have gradually increased over the years, due to the use of approved chemicals. Pesticides assist farmers to decrease production costs, risks, and to survive in a

highly competitive market (Sanjay Choudhary, 2018).

In spite of these, pesticides can contaminate soil, water, and vegetation (Meena & Mishra 2020). Organochlorine pesticides are found to be the most extensively used pesticides by farmers due to the fact that they cost effective and have broad-spectrum activity (Özkara et al., 2016). However, pesticides are highly toxic and persistent in the environment for extended period (Bempah *et. al.*, 2011).

Pesticides act as endocrine disruptors and also cause reproductive defects as well as immune dysfunction (Damstra, *et. al.*, 2000). Several pesticides affect gonads and reproductive development (Lintelmann, *et al.*, 2002). Evidence available indicates that, there is a decline in the functioning of reproductive organs in human and some wild life population due to exposure to pesticides (Petrelli *et al.*, 2003). Even at low dosages organochlorine pesticides disrupt the endocrine system of human (Smith and Gangolli, 2002).

Pesticides may also modulate the human immune system leading to homeostasis, reproductions, development and behavioural alterations (Asare, 2011). Pesticides have also been found to have further negative effects on humans and other mammals (Karalliede *et al.*, 2003). Example, organophosphate pesticides have been found to affect the central nervous system through inhibition of acetylcholinesterase (Karalliede *et al.*, 2003). Inhibition of neuromuscular enzymes as well as glandular tissues where acetylcholinesterase plays a key role in cell to cell communications are caused by acute

poisoning of the nervous system by organophosphate compounds (Karallie *et al.*, 2003).

Being exposed to pesticides as a result of food and water consumption have dire consequences on nervous system, normal functioning of thyroid, low sperm counts in males, birth defects, increased testicular cancer, reproductive and immune system malfunctioning, (emerging from endocrine disruption phenomenon), immune-toxicity, neurobehavioural and developmental disorders among others (Cocco *et al.*, 2013; Gill & Garg, 2014).

Data available indicate that interaction between some extragenetic dieldrin, endosulfan, toxaphene, and chlordane cause synergistic increase in their estrogenic potency (Xavier *et al.*, 2004). Experimental and epidemiological evidence indicate that extensive uses of pesticides are immunosuppressive (Asare, 2011). Studies have linked childhood cancers to pesticides exposure (Zahm, *et al.*, 1997). Pesticides residues on consumable commodities could affect health status (Claeys *et al.*, 2011, Fothergill & Abdelghani 2013, Chauhan *et al.*, 2014, Maguire *et al.*, 2019). Dietary intake of pesticides residues on agricultural products are toxins and hence it is recommended to reduce these residues in food (Zawiyah, *et al.*, 2007).

Due to their response, availability and ease of application, pesticides use has become dispensable in increasing yield of crops such as maize and cassava (Noort *et al.*, 2022) Indiscriminate pesticides use has resulted in cases where enough attention has not been paid to pesticides use and toxicity (Mahmood *et al.*, 2016). Though pesticides have been

recognized as solution to food quality and safety, use of pesticides by farmers has become so prevalent that farmers see it as a way to improving their income from farming.

A critical review of poor performance of agricultural sector has revealed that problems in the sector viz: insufficient extension staff- farmer ratio, high rate of attrition of trained staffs, weak research extensions farmer linkage, lack of reliable statistical data for decision making, weak agro-business system, poor access to communication among others have hinder the growth of the sector (MoFA 2002).

The Asante Akim central municipality is among districts in Ghana known for cassava cocoyam and maize cultivation (Sakyi, Appiah-Adjei, Asare, & Asante (2022). However, limited data on pesticides residues on crop cultivation in the municipality available.

In view of public health issues that characterize pesticides residues in diets and the long-term effects upon exposure to even low dosages of pesticides and the environment, it is essential that pesticides residues in food crops, soils and other agricultural produce are thoroughly investigated. The generated data would provide information for policy makers to institute needed regulations to protect human lives.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This chapter looks at necessary literature on works done on pesticides, origin and history of the selected staple crops (cocoyam, cassava and maize), their taxonomy, nomenclature, nutritional importance and their productions in Ghana. The chapter also looks at definitions and classification of pesticides, chemistry of organochlorine, organophosphate and carbamate pesticides. The chapter finally reviews pesticide toxicity in foods and the need to reduce pesticide residues in food.

Farm sizes for cocoyam production are small compared to those for other crops cultivated in Ghana (Quaye *et al.*, 2010). Cocoyam productivity remains low, with average yields of 6tons/ha (Acheampong, *et al.*, 2014). Thirty percent of cocoyam produced in Ghana are consumed by producers and the remaining (70%) sold (Acheampong *et al.*, 2014). Twelve million eight hundred and thirty-eight thousand six hundred and sixty-four (12,838,664) tones of cocoyam were produced in 2020 (Otekunrin *et al.*, 2021). World production of cocoyam fluctuated substantially in recent years (Ifeanyi-obi, *et al.*, 2016). It is however intended to increase through 1971 - 2020 period ending at 12.8 million tonnes in 2020 (Akem, & Pemunta 2020, Phommasack, 2014).

Nigeria is ranked first in the production of cocoyam in the world (Otekunrin *et al.*, 2021). Production of taro (cocoyam) in Nigeria was 3.21 million tonnes in 2020 (Osahon, & Ekwe,

2020). That accounted for 24.89% of the world's cocoyam production in 2020. Ethiopia, China, Cameroon and Ghana (2,327,972, 1,924,942, 1,815,246 and 1,251,998) are ranked second, third, fourth and fifth highest producers of cocoyam respectively (Oladimej *et al.*, 2022). The world's total production of taro (cocoyam) was estimated at 12.9 million tonnes in 2020 (Dietz *et al.*, 2020).

2.2 Health and Nutritional Importance of Cocoyam

Cocoyam has superior nutritional value (Calcium, Phosphorous and Magnesium) compare to other major root and tuber crops of West Africa (Chukwu *et al.*, 2008; Ekwe *et al.*, 2008; Opara, 2003). Almost every part of cocoyam such as cormels, petioles, leaves, and inflorescence cocoyam plant are comestible (Vaneker & Slaats, 2013). Due to global widespread of cocoyam into diverse areas and societies, its usage varies from one area to another (Vaneker & Slaats, 2013). Cocoyam's roots are used mostly as food whiles the other plant parts are used as forage, medicine, and antipoisonous agents against bites of scorpion, tarantula and snake (Wachamo 2018, Nanbol & Namo 2019).



Plate 1: An image of cocoyam tubers

Generally, *Xanthosoma sagittifolium* is considered as a significant source of dietary energy, proteins, and vitamins (Opara 2003). Again, it is believed to have high levels of potassium, zinc, nicotinic acid but low quantities of trypsin compared to other comestible aroids (Temesgen *et al.*, 2015).

2.2.1 Nutritional and Health Benefits of Cocoyam Leaves

Cocoyam leaves are mainly used as vegetable in many countries including Ghana, Nigeria, Cameroon, and Côte d'Ivoire where they are cultivated (Onyeka, 2014). The term vegetable is usually used for desirable soft edible plant products that may be eaten raw or cooked, either alone or with other preparation (Odedeji *et al.*, 2014, Khalid *et al.*, 2021). Vegetables are seasoned and highly described due to their high moisture contents, soft, high rate of physiological activities within their cells and delicate tissues. (Odedeji *et al.*, 2007).

Cocoyam leaves have substantial levels of antioxidants, vitamins, and dietary fiber (Okechukwu *et al.*, 2020). However, food and pharmaceutical industries have been able to explore these health benefits of cocoyam leaves much (Okechukwu *et al.*, 2020). Aside adding variety to menu, cocoyam leaves are valuable sources of nutrients (Taiwo *et al.*, 2007). The leaves contribute substantial amounts of protein, mineral, vitamins, fibre and additional nutrients which are normally lacken in daily diets (Taiwo *et al.*, 2007).

The leaves have no cholesterol and contribute only 1% of total fat. Thus, cocoyam leaves are good to reducing cholesterol as indicated by (Mitharwal *at el.*, (2022), Shekade *et al.*, 2018). Due to dietary fibre and methionine contents of cocoyam leaves, they bind and break down fat and cholesterol especially triglycerides (Mitharwal *et al.*, 2022, Mante, 2019).



Plate 2: An image of cocoyam leaves

2.3 Historical Origin of Cassava, and Its Production

Cassava has its genetic, geographical and agricultural origin in Latin America (Isendahl 2011). Its domestication began 5000 – 7000 years BC in the Amazon, Brazil (Isendahl 2011). Cassava was spread to the other parts of the globe by Europeans (Henry & Hershey, 2002). Cassava (*Manihot Esculenta*) is a perennial, root tuber crop and belongs to the family Euphorbiaceae (Onyenwoke, & Simonyan, 2014). It is a woody shrub and drought-tolerant crops (Onyenwoke, & Simonyan, 2014). It is the major food in developing countries (Tonukari, 2004). Cassava is produced in all tropical and subtropical counties of the globe (Onwueme 2001).

Globally, 268 million tonnes of cassava tubers were produced in 2014 (Tope *et al.*, 2019). Nigeria is the world largest producer of cassava (Awerije, 2014). The country produces about 55 million tonnes of world total (Tope *et al.*, 2019) and Awerije (2014). More than half of the total global cassava production is from Africa (Otekunrin, & Sawicka, 2019). Cassava production in Nigeria reached the highest level with an estimated amount of 59 million (Uzochukwu *et al.*, 2021). This value constituted for 20.4% of the global share production in 2017 (Uzochukwu *et al.*, 2021). Brazil and Indonesia are ranked second and third respectively with production amounting to 25.3 million and 24 million metric tons respectively (Onyenwoke & Simonyan, 2014). The only African nation ranked among the top ten highest cassava exporter in the globe is Egypt (Otekunrin *et al.*, 2019). Egypt cassava export value is \$20.7million (Adetunji, 2022). Again, Egypt is the highest cassava exporter in Africa even though it is not among the highest producers of cassava in the world (Adetunji, 2022).

In Ghana, cassava was introduced in the 16th century (Andoh, 2010). Since its introduction, the crop has substantially contributed to livelihood of the populace (Manu-Aduening *et al.*, 2005). Cassava is an important root crop in Ghana (Adjebeng-Danquah *et al.*, 2016). About 1,027,755 hectares of land is for production of cassava and in 2019, fresh cassava produced was estimated to be 22 million metric tons (Usman 2011).

Over 70% of farmers in Ghana cultivate cassava and that contribute about 22% of Agricultural GDP (Oppong *et al.*, 2020). Initially, cassava production was obscure and neglected (Fischer & Connor, 2018). However, in recent time growing interest in the crop has resulted in realization of its potential as food security and emergence crop (Fischer & Connor, 2018). Cassava production also could contribute to employment for the rural poor and foreign exchange (Fischer & Connor, 2018).

2.3.1 Nutritional and Health Benefits of Cassava

Raw uncooked cassava consists of about 60% water, 38% carbohydrate and 1% protein (Arya *et al.*, 2022, Tewe, 2004). The remaining constituent are dietary fiber, vitamins and negligible fat content (Arya *et al.*, 2022, Tewe, 2004).

Hundred grams of raw cassava provide 670 kilojoules of food energy per serve and 25% of daily value of vitamin C (Page 2019). Cassava has high carbohydrate, fiber and vitamins contents (Bayata 2019). The roots provide about 250,000 calories of energy per hector per day (Onyenwoke & Simonyan 2014). This energy is above that provided by same quantity of maize, sorghum and wheat (Montagnac *et al.*, 2009). Small amounts of sucrose, glucose,

fructose, and maltose are also contained in cassava (Tewe 2004). Amino acids contents of cassava are very low while arginine, glutamic acid and aspartic acid contents are in abundance (Gil & Buitrago, 2002).

Cassava root has 50% crude protein, 50% free amino acids (dominated by glutamic acid and aspartic acid) and non-protein components (nitrate, nitrite and cyanogenic compounds) (Bataya, 2019). The root also has high levels of calcium, iron, magnesium, copper, potassium, zinc and manganese (Bayata 2019). Calcium, potassium, iron, copper, zinc magnesium and manganese contents in cassava root ranges between 15 to 45 mg per 100g edible portions (Broadley & White 2010, Bayata 2019). Vitamins contents of cassava roots are very small and ranges between 6.80 - 8.28mg per 100g of edible portion (Mégnanou *et al.*, 2009, Onyenwoke & Simonyan 2014).



Plate 3: An image of cassava tuber

2.4 Historical Origin of Maize and Its Production

Maize (*Zea Mays*) originated from southwest United States (Da Fonseca *et al.*, 2015). However, available archaeological data suggest that maize has either coastal or highland route of diffusion (Da Fonseca *et al.*, 2015). According to Da Fonseca *et al.* (2015) maize spread into southwest United States was about 4,000 years ago and is likely to have occurred via highland route. This was followed by gene flow from lowland coastal maize at least 2,000 years ago (Da Fonseca *et al.*, 2015).

In 2020, global maize production was 1.162 billion tonnes ((Shafiq *et al.*, 2022). Maize production increased worldwide from 313 million tonnes in 1971 to 1.16 billion tonnes in 2020 (Shafiq *et al.*, 2022). The annual rate of maize growing is approximately 3.06% (Abbade, 2020). Globally, the highest producer of maize is the United States of America (Dowswell *et al.*, 2019).

Maize production in the United States of America was 360 million tonnes and that accounted for 34.28% of the world's maize production in 2020 (Aye *et al.*, 2021). Maize produced by 5 countries (USA, China, Brazil, Argentina, and Ukraine) accounted for 74.86% of global maize production. Total global maize produced in 2020 was estimated at 1.05 billion tonnes in 2020 (Nicol *et al.*, 2011). Africa accounts about 7% (49 metric tonnes) of global (736 metric tonnes) maize production (Pardey & Greyling 2019, Jacob 2014).

Cultivation of maize in Africa is increasing faster (2.8% per annum) compare to world cultivation (2.5% per annum) (Dowswell *et al.*, 2019, Oyakhilomen *et al.*, 2012). In 2020, Ghana's maize production was 3 million tonnes (Mwambo *et al.*, 2020). Maize production in Ghana has increased from 384 thousand tonnes in 1971 to 3 million tonnes in 2020. During that period, maize production in Ghana grew at an average annual rate of 8.79% (Munyabarenzi 2014).

Maize cultivation in Ghana began over a century ago (Darfour & Rosentrater 2016). Its cultivation is mostly done under rain-fed environments by not well-resourced farmers (Makate *et al.*, 2017, Derkyi *et al.*, 2016). Agro-ecological zones for maize production in Ghana is categorized into four; viz, forest zone, transition zone, Coastal savannah zone and Guinea savannah zone (Wongnaa & Awunyo-Vitor 2019). In Ghana, maize accounts for about 50% of total cereal production (Darfour & Rosentrater 2016). Postharvest maize losses have been reported to be between 5 – 70% (Darfour & Rosentrater 2016). Maize is second most important staple food in Ghana, next to cassava (Appiah-Twumasi *et al.*, 2020).

Stored maize are attacked by over 20 different species of insect pests such as maize weevil, *sitophilus*, among others (Darfour & Rosentrater 2016). There are traditional techniques (drying in the field, special platform built above fire on bare dry ground among other) are used to stored maize. Modern methods such as using metal silos, solar dryers, chemical, hermetic and Purdue Improved Drying Stove are also used to stored maize (Darfou & Rosentrater 2016). Pesticides application to store maize has been one of the old methods

used in Ghana to preserve maize, before, during, and after harvest (Adu *et al.*, 2014, Gitonga *et al.*, 2013).

2.4.1 Health and Nutritional Benefits of Maize

Edible maize grain is nutritive part of the plant (Rouf Shah *et al.*, 2017). It contains vitamins (C, E, K, B1 (Thiamine), B2 (Niacin), B3 (Riboflavin), B5 (Pantothenic acid), B6 (Pyridoxine), folic acid, selenium, N-p-coumaryl tryptamine, and N-ferrulyl tryptamine (Saritha *et al.*, 2020). Potassium is also a major nutrient in maize (Kumar *et al.*, 2022).

Maize germ contains about 45 – 50% oil that is processed via wet milling or into cooking. (Orthofer *et al.*, 2003). Unrefined maize oil approximately has 14% saturated fatty acids, 30% monounsaturated fatty acids, and 56% polyunsaturated fatty acids whilst refined maize oil has about 54 – 60% (linoleic acid), 25 – 31% (oleic acid), 11–13% (palmitic acid), 2 – 3% and (stearic acid) (Silka 2017). Maize oil also has about 21.3 – 94.1mg γ -tocopherol per 100g of maize (Sen, Khanna, & Roy, 2006).

Maize silk is rich in compounds such as maizenic acid, fixed oils, resin, sugar, mucilage, salt, and fibers) which are vital for human diet (Rouf Shah *et al.*,2016). Maize has several health benefits (Friedman 2018). Vitamin B-complex in maize is good for skin, hair, brain health heart and proper digestion (Huma *et al.*, 2019). These vitamins also prevent symptoms of rheumatism because they improve joint motility (Huma *et al.*, 2019). The vitamins A, C, and K, carotenoid and selenium in maize help to improve normal functioning of the thyroid gland and the immune system (Issa *et al.*, 2006).

Maize silk also has several health benefits. In India, China, Spain, France and Greece maize silk is used to treat kidney stones, urinary tract infections, jaundice, and fluid retention (Rouf Shah *et al.*, 2016, Mada *et al.*, 2020). The silk also helps to improve blood pressure, support liver functioning, and bile production (Mada *et al.*, 2020). It is good emollient for wounds, swelling, and ulcers (Huma *et al.*, 2019, Rouf Shah *et al.*, 2016). Maize roots, leaves and silk decoction are good for treatment of bladder issues, nausea, and vomiting, while cob decoction is also good treatment of stomach issues (Kumar & Jhariya, 2013).



Plate 4: An image of maize

2.5 Definition and Classification of Pesticides

Pesticides are chemical compounds that are used to kill pests, insects, rodents, fungi and unwanted plants (Poudel *et al.*, 2020, Abubakar *et al.*, 2020). Pesticides are classified according to the type of pest the chemical was developed to kill (Yadav & Devi, 2017). Pesticides are also classified based on the active ingredients, chemical structure, mode of action and toxicity (Botitsi *et al.*, 2017). They can further be classified either as organic or inorganic (Patinha *et al.*, 2018). Organic pesticides can be natural pesticides from plants and animals or synthetic pesticides (Biondi *et al.*, 2012; Cantrell *et al.*, 2012).

United States Department of Agriculture (USDA, 2015) further classified pesticides according to Chemical classes (organophosphates, organochlorines, synthetic pyrethroids and carbamates), degree of hazard (extremely hazardous, moderately hazardous, slightly hazardous and non-hazardous) and linked to their active ingredients against target organism (insects, herbs, fungi, nematodes, molluscsc, bacteria).

2.5.1 Organochlorine Pesticides (OCPs)

Organochlorine pesticides (OPCs) are a group of chlorinated compounds widely used to kill pests (Borshi *et al.*, 2016). They are persistent organic pollutants (POPs) and persist in the environment for a longer period (Tieyu *et al.*, 2005). Organochlorines pesticides were used successfully to control malaria and typhus (Edwards 2013).

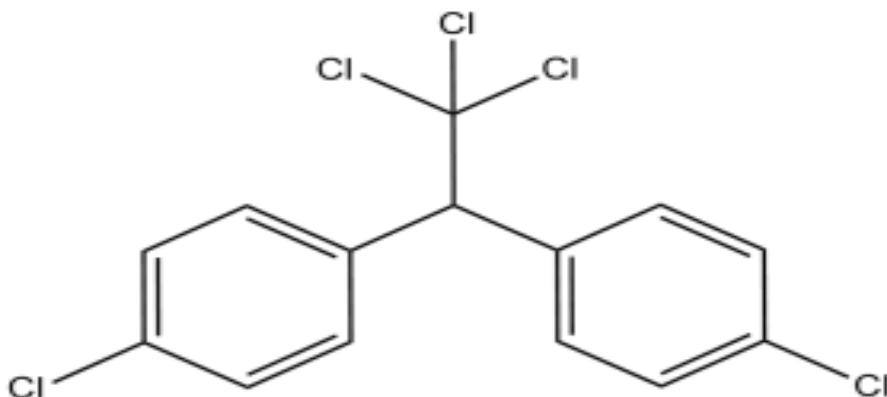


Figure 2.1: An image showing the structure of DDT, an example of organochlorine pesticide

Data on the application of various classes of pesticides indicate that organochlorine compounds constituted about 40% of pesticides used (Gupta, 2004; FAO, 2005). Due to their less cost and efficacy against several pests, OCPs are commonly used in developing nations (FAO, 2005; Gupta, 2004).

2.5.2 Organophosphate Pesticides (OPPs)

Organophosphate pesticides (OPPs) are esters of phosphoric acid (Eto & Zweig, 2018). The organophosphate pesticides (OPP) exert their effects via irreversible inactivation of the enzyme acetylcholinesterase, vital for nerve functioning in humans, insects and other animals (Ansari *et al.*, 2021). OPPs are rapidly hydrolysed on exposure to light, air and soil (Rose *et al.*, 2007). However, their residues in food and water can be detected (Amoako, 2010). Organophosphate pesticides (OPPs) include; Parathion, Profenofos, Malathion, Chlorpyrifos, Diazinon and Pirimiphos, Fonofos, Fenitrothion, Methamidophos, Chlorfenvinphos, Ethoprophos and Dimethoate (Osman *et al.*, 2019). Organophosphorus compounds cause neurotoxic effects (cholinergic syndrome, delayed polyneuropathy and neuropsychiatric disorder) in humans (Jokanović 2018). Epidemiological evidence exist for a long-term health effects on human exposure to OPPs (Costa, 2018). OPPs bind to and inactivate the enzymes acetylcholinesterase (AChE) (Bajgar 2004). This induce high produce of the neurotransmitter acetylcholine (ACh) and this lead to an acute cholinergic syndrome (Greig *et al.*, 2005, Anand *et al.*, 2012). Human exposure to OPPs are much common and it has led to situation of examining their potential health effects (Bajgar 2004). Annually, there are about 10,000 cases of OPPs poisoning in the United States (Morris 2006).

Pesticides are applied over vast area of land and have great effect on humans and the environment (Rani *et al.*, 2021). Study has shown that more than 95% of herbicides and more than 98% of insecticides do not reach targeted pests (Sharma *et al.*, 2012). This is because pesticides are applied over large tracts of land and carried away by wind and water

runoff (Pazikowska-Sapota 2020). As these chemicals travel to other areas, they affect plants, animals and the environment (Bonney & Jaber 2011). Production, storage and transportation of pesticides allow some quantities of pesticides to be introduced into the environment (Bonney & Jaber 2011).

Impacts of pesticides on the environment is varied and has increased over the last few decades (Benbrook, 2016). Due to high toxicity levels of using organophosphate pesticides and carbamate, United States and the European Union have stopped using those pesticides (Blum *et al.*, 2019).

Organophosphate pesticides are widely used to control weeds, diseases, and crop pests (Mulla *et al.*, 2020). Synthetic pesticides including organophosphates pesticides are very toxic and hazardous to a variety of organisms such as living soil biota, valuable arthropods, fish, birds, human beings, animals, and plants (Mulla *et al.*, 2020, Yadav & Devi 2017).

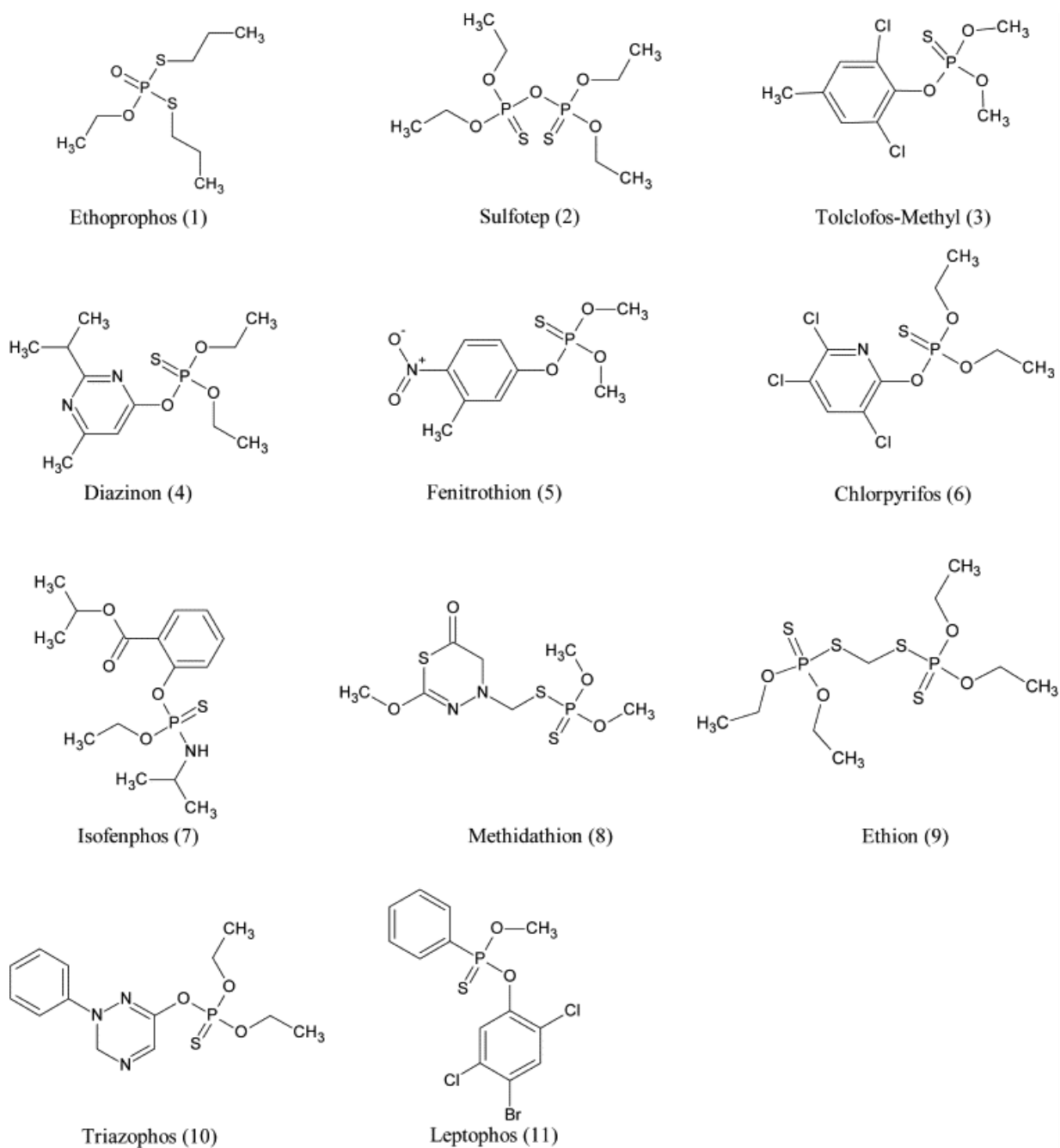


Figure 2.2: An image showing structures of some examples of organophosphate pesticide

Organophosphate pesticides decontaminate rapidly through hydrolysis on exposure to biosphere (Zhang *et al.*, 2020). The rapid hydrolysis is responsible for significant influence

they on abiotic and/or biotic factors (Zhang *et al.*, 2020). Bacterial cultures isolated from various places in the environment have distinctive ability to break down different organophosphate pesticides (Kumar *et al.*, 2021).

2.5.3 Carbamates

Carbamates are organic compound derivatives of carbamic acid (NH_2COOH) (Karachaliou, *et al.*, 2017). They are use as insecticides and nematicides (Malhotra, 2021). The functional group of ccarbamatess are carbamate esters (Grzyb & Batey, 2008). Carbamates include carbaryl, carbofuran and Benomyl among others (Oliveira *et al.*, 2020).

Carbamates are environmentally ubiquitous due to their use as insecticides and nematicides (Vandergragt *et al.*, 2020). Though carbamates have persistence than OPPs, they less toxic to humans and animals than OPPs (Khan *et al.*, 2021). Their mechanism of action is by reversible inactivation of acetylcholinesterase (Colovic *et al.*, 2013). Carbamates persist in the environment for a short period, usually within weeks or months (Goel & Aggarwal, 2007). They were introduced in 1956 to modern agriculture (Padmarasu, 2016). Esters of methyl and dimethylcarbamic acid (CH_3HNCOOH and $(\text{CH}_3)_2\text{NCOOH}$) have been used for many years as parasymphomimetic agents (Vikash *et al.*, 2018). Carbamates are derivative of carbamic acid (Colovic *et al.*, 2013). They cause carbamylation of acetylcholinesterase at neuronal synapses and neuromuscular junctions (Colovic *et al.*, 2013). While carbamates have similar mechanism of action as that of organophosphates, they bind reversibly to acetylcholinesterase (Bartolini *et al.*, 2007). Hence carbamates

possess similar toxicological profile to OPPs poisonings (King & Aaron, 2015). Typically, duration of carbamates toxicity is less than 24 hours (King & Aaron, 2015). Common examples of carbamate are aldicarb, carbofuran, carbaryl, ethinenocarb, fenobucarb, oxamyl, methomyl, pirimicarb, propoxur, and trimethacarb (Šabacký, 2021).

Acetylcholinesterase (AChE) usually hydrolyses acetylcholine to acetic acid and choline (Silberman & Taylor 2018). This leads to cessation of neurotransmitter signaling (Amenta & Tayebati, 2008; Silberman & Taylor, 2018). Carbamates cause reversible inhibition of acetylcholinesterase enzyme present at parasympathetic and sympathetic ganglia, parasympathetic muscarinic terminal junctions, sympathetic fibers located in sweat glands, and nicotinic receptors at skeletal neuromuscular junction (Kaur *et al.*, 2019). Persistent high levels of acetylcholine levels as a result of AchE inhibition lead to increased neurotransmitter signaling (Pope *et al.*, 2005).

High levels of acetylcholine lead to central nervous system symptoms such as confusion, delirium, hallucinations, tremor, and seizures (Hlusicka *et al.*, 2019). Increased levels of acetylcholine in the autonomic nervous system upsurge sympathetic and parasympathetic activity (Koopman *et al.*, 2017; Silberman & Taylor 2018).

Metabolism of Carbamates occurred via hydrolysis, conjugation and hydroxylation (Landmark *et al.*, 2012). Ninety percent of the metabolized products of carbamates are renally excreted within days (Landmark *et al.*, 2012). Central nervous depression is a common symptom in pediatric exposure to carbamates (Noble *et al.*, 2019). The

carbamation product formed from acetylcholinesterase undergoes spontaneous hydrolyses (Silberman & Taylor, 2018).

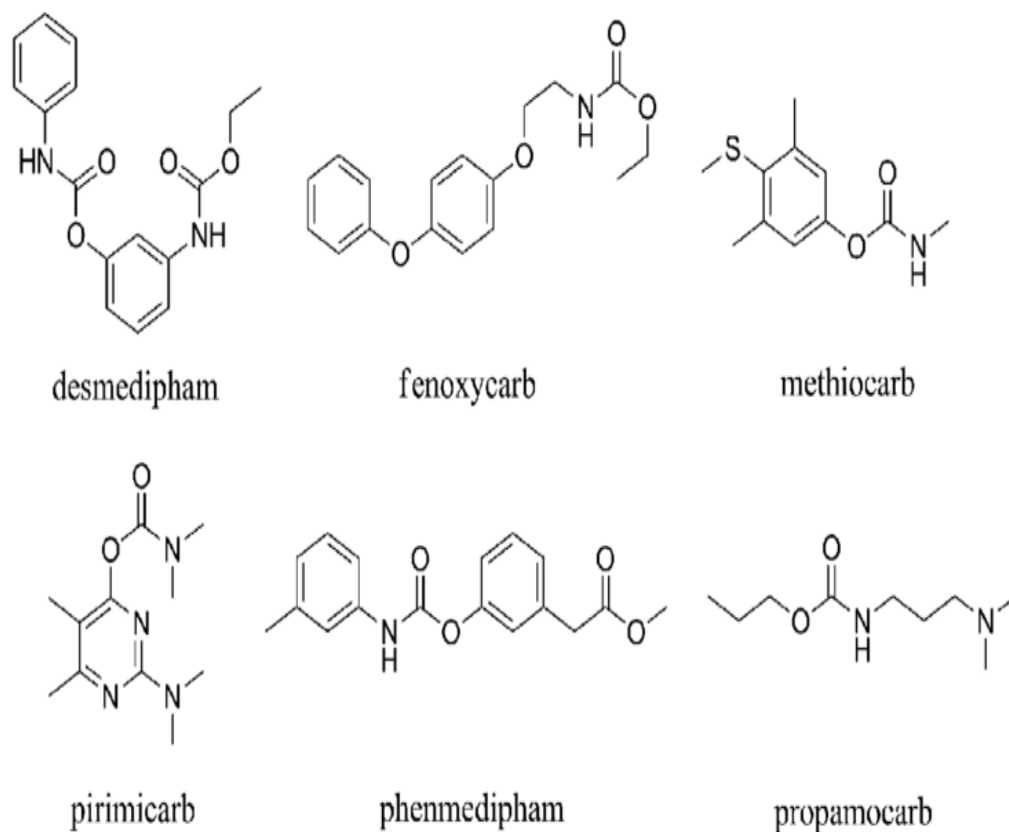


Figure 2.3: An image showing the structures of some examples of carbamates pesticides

Human exposure to carbamates can cause headaches, dizziness, weakness, nausea, convulsion, stomach cramps, diarrhoea, sweating, skin rashes and even death (Debnath & Khan, 2017). Data collected by American Association of Poison Control Centers (AAPCC) between 2002 and 2006, indicated that carbamate poisonings amounted to 14,000 reported of exposures with 10 to 20% fatality rate (Szponar, 2021).

2.6 Pesticides Use in Crop Production

Pesticides use in agriculture has been high due to increasing human population (Carvalho, 2017). Global population has been projected to reach 8.5 billion by 2030 (Zhang, 2008). This has trigger fear for the impact population explosion would have on food security (Seck, *et al.*, 2012).

The highest consumers of pesticides is Europe followed by China (Zhang *et al.*, 2011). China also uses high percentage of pesticides produce globally than the United States of America (Zhang *et al.*, 2011). African consumes averagely 25% global pesticides (Mwabulambo *et al.*, 2018). This estimated value is mostly use for vegetable cultivation (De Bon *et al.*, 2014). One prominent reason for using pesticides on agricultural farmlands is crop protection from pests in order to, boost yield and productivity (Ngowi *et al.*, 2007). Generally, pesticides are applied in agriculture to control weeds, disease causing organisms, and pests that have capacity to damage plants (Tudi *et al.*, 2021). Thus, pesticides are biocidal in nature when humans become through various agriculture activities (Das, 2013).

Globally, over 1000 pesticides are used to avoid foods destruction by pests (Pimentel & Burgess, 2014). Toxicity of a pesticide depends on its function, its form, its innate chemical activity, dosage, route of exposure, among others (Damalas & Koutroubas, 2016). Same pesticides can have diverse impacts at 33hown33ent quantity, route of exposure (such as swallowing, inhaling, or direct contact with the skin) and more toxic in one organism than

other (Damalas & Koutroubas, 2016). For example, insecticides are more toxic to humans than plants (Grdiša & Gršić, 2013).

Pesticides authorized for international trade for use on food are not genotoxic (not damaging to DNA), non-mutagenic or non-cancerous (Nohmi, 2018). Adverse effects of pesticides mostly occur above levels deemed safe for human exposure (Nohmi, 2018). Human exposure to high levels of pesticide could lead to acute poisoning or longstanding health impacts, on reproduction and other vital organism (Damalas & Eleftherohorinos, 2011).

2.7 Pesticide Residues Distribution in Foods

Various research works have reported that for some cereal grains' pesticide residues build up on outer covers of the grain (Padaliya *et al.*, 2020). Thus, processing methods such as milling could reduce pesticide residues contents (Padaliya *et al.*, 2020).

Normally before storage, cereal crops are sprayed with insecticides to ensure longer period preservation (Dammer & Adamek, 2012). For lipophilic pesticides, their residues often remain on coat of seeds although small amounts could move to portions with high triglycerides contents such as the germ (Inobeme *et al.*, 2020, Bajwa & Sandhu, 2014).

Generally, it is not possible to remove residues of some pesticides (deltamethrin and cypermethrin among others) by cooking or washing stored grains (Bajwa & Sandhu 2014, Amvrazi, 2011). This implies that pesticides could penetrate inside of grains (Kaushik *et*

al., 2009). For examples, high levels of cypermethrin have been found in seed coats (Lai & Dikshit, 2000).

2.7.1 Toxicity of Pesticides Residues in Foods

Various diseases have been reported to be linked to consumption of plants and animal products contaminated with pesticides residues contents above daily maximum residue limits (MRLs) allowed by internal regulatory bodies such as European Union, World Health Organization and Food and Agriculture Organization. Process of monitoring and institution of allowable limits for pesticide residues in different products and foods helps to efficiently control pesticides for human safety (Neme & Satheesh, 2016).

Some health effects associated with human exposure to pesticides include vomiting, headache, dizziness, irritation of skin, neurological diseases, difficulty in breathing, among others (Joko, *et al.*, 2020). Intense pesticides poisoning could cause cancer and death (Zikankuba *et al.*, 2019).

Nearly 25 million agricultural workers in developing nations are exposed to pesticides annually (Kesavachandran *et al.*, 2009). The World Health Organization (WHO) has estimated that about 3 million serious pesticide poisoning episodes occur every year. About 300,000 of the people exposed to pesticide poisoning die (Gunnell & Eddleson, 2003). Nearly 99% (297,000) of these cases occur in low and middle income nations (Gunnell & Eddleson, 2003).

Developing countries use about 20% of agrochemicals produced globally. Though this is minimal, they experience 99% of deaths from pesticides poisoning (Hashemi *et al.*, 2014). Annually, about 400,000 tonnes of pesticides are used by Japanese farmers. In the early 2000s, application of pesticides lead to about 1,000 deaths annually. (Kesavachandran *et al.*, 2009; Nagami *et al.*, 2005).

Production, distribution, and application of pesticides require strict regulation and control due to their toxic nature (Lebelo *et al.*, 2021). Some pesticides are not degraded by microorganisms in the environment (Bonmatin *et al.*, 2015). Thus, they persist in the environment for decades (Bonmatin *et al.*, 2015). Such pesticides are capable of bioaccumulating due to their prolong half-life in human tissue and the environment (Bonmatin *et al.*, 2015).

Infertility in humans has recently been identified as a social challenge that is linked to pesticides residues in agricultural products (Inobeme *et al.*, 2020). Research has shown that quality and quantity of human sperms have declined following introduction of pesticide use for agricultural processes (Martenies & Perry, 2013). A number of factors to affect pesticides toxicity due to their usage in agriculture (Damalas & Eleftherohorinos, 2011). For instance, insecticides are more toxic to humans compared to herbicides (Mesnage *et al.*, 2014). Doses of pesticides, route of exposure also determine toxic effects of pesticides in exposed population (Kim *et al.*, 2017). Most of pesticides allowed by monitoring and other regulatory agencies for use have no genotoxic effect and adverse effects only occur beyond recommended level (Triacchini, 2020).

CHAPTER THREE

METHODOLOGY

3.1 Description of the Study Area

This study was conducted in the Asante Akyem Central municipality of Ghana. The Asante Akim Central Municipality is one of the forty-three (43) Districts in the Ashanti Region. It was created by Legislative Instrument (L.I) 2056 and it has Konongo – Odumasi as its twin Capital Town (GSS, 2014). The municipality was carved out of the then Asante Akim District Council in 1988 and was elevated to Municipality status by L.I 1907 in November 2007 (GSS, 2014). Until July 2012, it was Asante Akim North Municipality (GSS, 2014). However, with the carving out of the Asante Akim North District, the municipality was renamed Asante Akim Central (GSS, 2014).

The Municipality is located in the eastern part of the Ashanti Region. It lies between latitude 60 30' North and 70 30' North and longitude 00 15' West and 10 20' West (GSS, 2014). There are five districts in which the municipality share boundaries within the Ashanti region, viz Asante Akim North in the North, Asante Akim South in the South-East, Ejisu-Juaben and Sekyere East in the West and Bosome-Freho in the south-western part (Fig. 1). The land size of the Municipality is approximately 1,160 square kilometres (km²) (GSS, 2014). The geology of the Municipality is categorized by various underlying rock materials such as granite, biotite, muscovite among others (GSS, 2014). According to the 2021 Population and Housing Census, population of the municipality is 91,673. Half of the population (50.0%) in the municipality are into agriculture (GSS, 2014).

DISTRICT MAP OF ASANTE AKIM CENTRAL

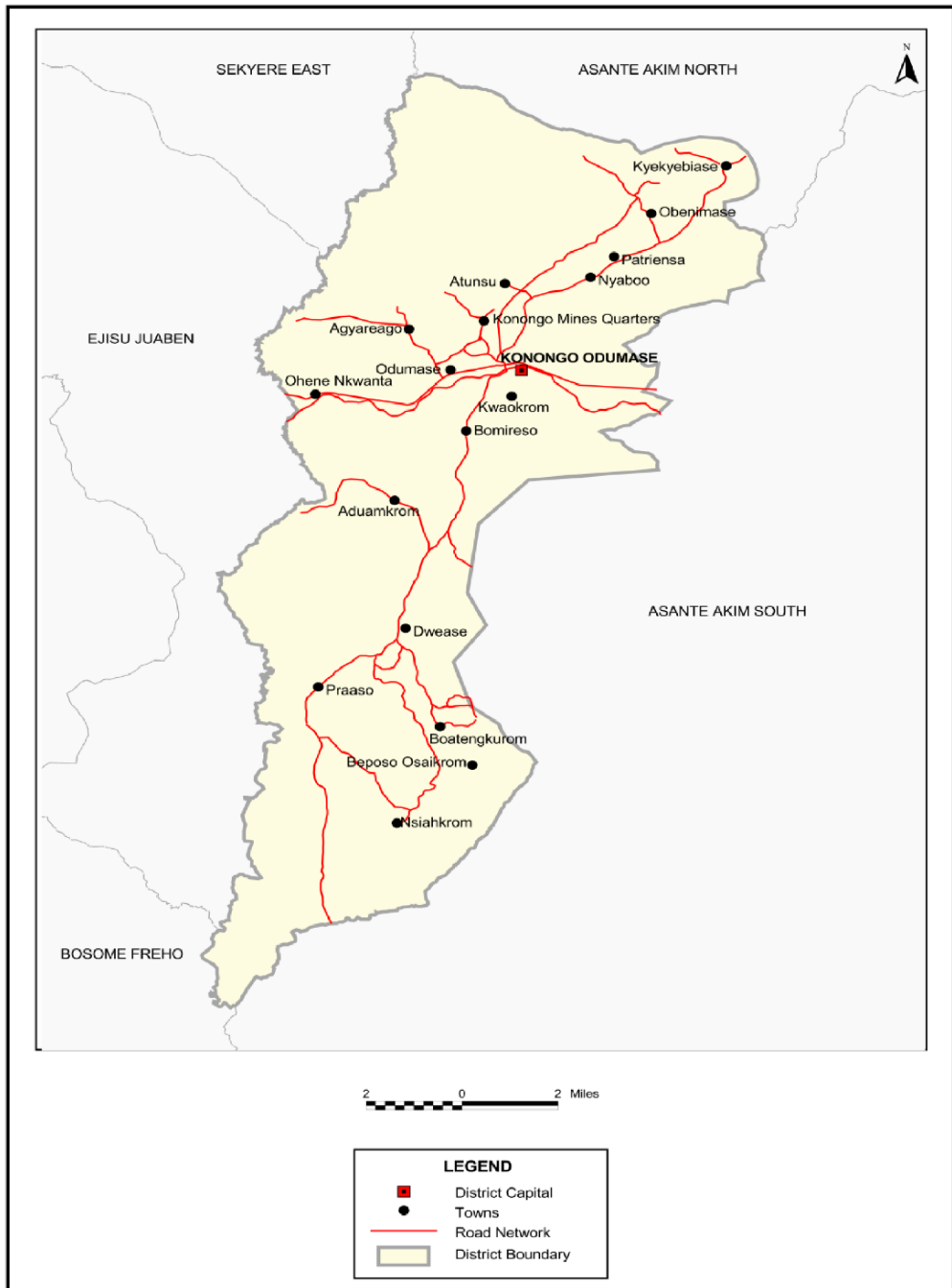


Figure 3.1: Map of the study area indicating sampling locations

In the rural localities, seven out of ten households (75.1%) are agricultural households while in the urban localities, 39.3 percent of households are into agriculture (GSS, 2014). The total land area of the municipality is 1,160 square kilometers (Ghana Statistical Service [GSS], 2014). The Municipality lies within the semi-equatorial belt annum (Meteorological Service Department, 2021). The climate is the wet semi equatorial type with temperatures generally high and averaging 26°C (MoFA, 2022). The first rainy season is from May to July and the second from September to November annum (Meteorological Service Department, 2021). The dry harmattan season occurs between December and April and is associated with drought conditions annually (Meteorological Service Department, 2021).

3.2 Sampling Method, Sampling Area and Sampling Size

Major food crops producing areas in the Asante Akyem Central municipality in the Ashanti Region of Ghana were selected for the study. A Complete Randomized Design (CRD) was used in this study. Four different crops (cocoyam and cocoyam leaves, cassava and maize) were investigated.

A total of twelve (12) farms were randomly selected from eighteen (18) different farms initially investigated within the Asante Akyem Central municipality. The twelve (12) farms were selected due to their large sizes (about 3 acres each). This initial survey indicated that the selected farms were suitable for the study. The farms included four (4) cocoyam farms, four (4) cassava farms, and four (4) maize farms. This investigation was carried out over a four month period (May and August, 2021).

Thirty soil samples were randomly collected from the farms at 0 to 20 cm depth using an auger. The auger was pushed and twisted into the soil to a depth of 20 cm and soils adhering to the auger sampler were carefully transferred into a stainless steel bucket and then mixed thoroughly to form a composite sample described by Dick *et al.* (1997). The depth (0 to 20 cm) was taken because nutrients uptake by plants are reported to be within 0 to 20 cm deep (Aiyesanmi & Idowu, 2012). 30 soil samples collected were sealed into glass bottles and then labeled with unique sample identity, Farm A (soil from cocoyam farms), Farm B (soil from cassava farms) and Farm C (soil from maize farm).

A total of 80 crop samples were collected, consisted of 20 cocoyam heads, 20 cocoyam leaves, 20 cassava and 20 maize were collected from 12 different farms in Asante-Central Akyem municipality. The minimum sample size was 2 kg for small and medium sized crops (cocoyam, cocoyam leaf, and maize) whilst the maximum weight of crop for large size crop (cassava) was 4 kg. The sample size was determined using Codex Alimentarius Commission (2000) protocol for determining sample size. For each crop samples, twenty (20) were randomly selected from different farms. Crop samples from the farms were collected the same date soil samples were obtained. Crop samples from the farms were labelled A1, A2, A3, A4 and A5 (cocoyam), B1, B2, B3, B4 and B5 (cocoyam leaves), C1, C2, C3, C4 and C5 (cassava) and D1, D2, D3, D4 and D5 (maize).

The labelled samples were put into glass containers, sealed, stored in an iced chest at 4 °C and then transported to the Pesticide Residues Laboratory of Ghana Atomic Energy Commission for pesticides residues extraction, Accra, where samples were extracted and

analyzed for pesticide residues. Pesticides residues were extracted from the soils and the edible portions of each type of crops used in the study.

In the pesticide residues laboratory, the samples were kept in a refrigerator at 5 °C at sample preparation (pesticides extraction) and instrumental analysis. Physico-chemical parameters including; particle size, bulk density, pH, organic carbon, moisture content, total nitrogen, phosphorus, calcium and magnesium contents of the soil samples were also determined.

3.3 Reagents Used in Pesticides Residues Extraction

Acetonitrile (AcN), and ethyl acetate (EtOAc) (Sigma Aldrich, USA) were of analytical grade. The Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) absorbent primary-secondary amine, polypropylene (PP) kits and salt pouches (magnesium sulphate, sodium chloride, trisodium citrate dehydrate, selenium mixture, and disodium hydrogen citrate sesquehydrate) (Altmann Analytik, USA) were used as described by Suleiman *et al.* (2020) and Anastassiades *et al.* (2003). Other reagents included formic acid (98% purity), polyethylene glycol (Fluka, USA) and standard pesticides were obtained from Sigma Aldrich, USA.

3.3.1 Reagents Used to Determine Physico-Chemical Properties of Soil

The physico-chemical properties of the soil samples were determined using sodium hexamethaphosphate (dispersing agent), buffer solutions (pH 4, 7 and 10), potassium dichromate solution, 98 % concentrated sulphuric acid, ferrous sulphate solution, sodium hydroxide solution, boric acid, 36 % hydrochloric acid and bromocresol green indicator.

Other chemicals used were Bray-1 solution, ammonium fluoride, ammonium molybdate, ammonium acetate, ammonium chloride buffer solution, triethanolamine buffer, potassium cyanide solution, Eriochrome Black T indicator solution, ethylene diamine tetraacetic acid, ammonium acetate (NH_4OAC) solution and potassium chloride.

3.3.2 Preparation of 0.1 M Sodium Hydroxide and 0.2 M Potassium Chloride Solutions

To prepare 0.1 M sodium hydroxide, 40 g of sodium hydroxide pellets was weighed into a 250 mL beaker. Hundred millilitres (100 mL) of distilled water was added and the mixture was stirred gently to ensure dissolution of the pellets. The solution was transferred into a 1 L volumetric flask and the beaker was rinsed thrice and added to the solution. Enough distilled water was then added to make the 1 L mark.

To prepare 0.2 M potassium chloride solution, 12 g of potassium chloride crystals was weighed into a 100 mL beaker. This was dissolved with 50 mL distilled water. The mixture was poured into a 1 L volumetric flask and enough distilled water was then added to make the 1 L mark.

3.3.3 Preparation of 1.0 M Iron (II) Sulphate and 0.1667 M Potassium Dichromate Solutions

To prepare 1.0 M iron (II) sulphate solution, 278 g of iron (II) sulphate crystals was weighed into a 250 mL beaker. Twenty milliliters of 98% concentrated Tetraoxosulphate (VI) acid was added. The mixture was stirred gently and then transferred into a 1 L

volumetric flask. The beaker was rinsed thrice with distilled water and added to the solution. Enough distilled water was then added to make the 1 L mark. The solution was prepared freshly to prevent oxidation of iron (II) to iron (III).

The 0.166 M potassium chromate solution was also prepared by weighing 49.05 g of an analytical grade potassium chromate crystals into a 250 mL beaker. Twenty millilitres distilled water was added and the mixture was stirred gently with a clean stirring rod to ensure uniform solution. The solution was poured into a 1 L volumetric flask. The beaker was rinsed thrice with distilled water and added to the solution. Enough distilled water was then added to make the 1 L mark.

3.3.4 Preparation of Soil Dispersing Agent

To prepare dispersing agent (a mixture of 4% sodium hexametaphosphate and 1 % soda), 40.0 g of sodium hexametaphosphate and 10.0 g of Soda were weighed and dissolved in a 250 mL Erlenmeyer flask with 150 mL distilled water. The mixture was stirred with stirring rod to ensure that the solutes dissolve. The solution was poured into a 1 L volumetric flask and then made to the mark with distilled water. Enough distilled water was then added to make the 1 L mark.

3.3.5 Preparation of 0.02 M Ethylene Diamine Tetra Acetic Acid (Edta) and 0.1% Bromocresol Green Solutions

In the preparation of EDTA solution, 7.44 g of disodium salt of EDTA was weighed into a 100 mL beaker. The salt was dissolved with 50 mL of distilled water, stirred glass rod to

ensure dissolution. The mixture was poured into a 1 L volumetric flask. Enough distilled water was added to make exactly 1 L mark. The solution was put into a stoppered plastic bottle and stored for use.

The 0.1% bromocresol green solution was prepared by dissolving 0.1 g of bromocresol green in 75 mL of ethyl alcohol. The mixture was stirred with a glass rod to ensure complete dissolution of solute. The solution was then diluted to 100 mL with distilled water.

3.3.6 Preparation of pH 4 Potassium Hydrogen Phthalate and pH 7 Potassium Phosphate Mono Basic Buffer Solutions

To prepare potassium hydrogen phthalate (pH 4), 5.0 g of potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$) was dissolved in 250 mL of deionized water. The solution was transferred into a 500 mL volumetric flask and 0.5 mL of 0.1 M HCl aqueous solution added. The solution was then diluted to make the 500 mL mark.

The 0.10 M potassium phosphate mono basic (KH_2PO_4) buffer solution (pH 7) was prepared by dissolving 3.40 g of KH_2PO_4 in 250 mL of deionized water. The 0.20 M sodium hydroxide solution was also prepared separately by dissolving 0.8 g of sodium hydroxide pellets in 100 mL of deionized water. Two hundred and fifty millilitres (250 mL) 0.10 M potassium phosphate solution and 73 mL of 0.2 M sodium hydroxide solution were added. The mixture was swirled gently to obtain uniform solution and then diluted with deionized water to 500 mL mark of the neck of flask.

3.3.7 Preparation of Ammonium Chloride Buffer Solution (pH 10)

To prepare ammonium chloride buffer solution (pH 10), 5.4 g of ammonium chloride crystals was dissolved in 20 mL of distilled water. Thirty-five milliliters (35 mL) of 10 M ammonia solution was added. The mixture was shaken thoroughly and then diluted with distilled water to make 100 mL. To prepare 10 M ammonium acetate solution, 770 g of ammonium acetate was dissolved in 800 mL of H₂O. The solution was poured into 1 L volumetric flask. Enough distilled water was added to make 1 L of ammonium acetate solution.

3.3.8 Preparation of Ammonium Molybdate Reagent and (5%) Methanoic Acid Solution

Ammonium molybdate [(NH₄)₆Mo₇O₂₄.4H₂O] reagent was prepared by dissolving 4.5 g of (NH₄)₆Mo₇O₂₄.4H₂O crystals in 0.88 M ammonia solution and deionized water (2:3 v/v). The resulted solution was added to 12 g of ammonium nitrate and the resultant mixture was diluted with deionized water to 100 mL. The solution was acidified with 1.5 mL of 63 % concentrated trioxonitrate(V) acid per very 10 mL of ammonium molybdate solution prior to it use.

To prepare 5% Methanoic acid solution, 500 mL of 90% concentrated methanoic acid was pipetted into a 1 L volumetric flask. This was diluted to 1 L mark with deionized water. The flask was corked, inverted and then shaken vigorously to ensure thorough mixing.

3.3.9 Preparation of 1.0 M Ammonium Acetate and 0.05 M Sulphuric Acid Solution

To prepare 1.0 M ammonium acetate solution, 77.7 g of ammonium acetate was put into a 250 mL beaker. Fifty milliliters (50 mL) of distilled water was added and then stirred continuously to ensure dissolution. The resultant solution was poured into 1 L volumetric flask and then made to the mark by adding deionized water.

To prepare 0.05 M sulphuric acid solution, 2.8 mL of 98 % sulphuric acid was measured into a 1 L volumetric flask half-filled with deionized water. The solution was thoroughly shaken to obtain uniform solution and then made to the 1 L mark by adding enough deionized water.

3.3.10 Preparation of 1.0 M Ammonium Fluoride Hydrochloric Acid Extracting Solution

To prepare this solution, 37 g of ammonium fluoride was dissolved in 1 L of distilled water to form 1.0 M ammonium fluoride (NH_4F) solution. The solution was stored in a polyethylene bottle. To prepare 0.5 M hydrochloric acid solution, 40.40 mL of (36%) concentrated HCl was measured into a 1 L volumetric flask half filled with distilled water. Thirty millilitres (30 mL) of 1M NH_4F solution was added to 50 mL of 0.5 M HCl solution and the mixture shaken thoroughly to ensure complete dissolution. Deionized water was then added to the solution to make 1 L of HCl solution to obtain 0.03 M NH_4F and 0.025 M HCl.

3.3.11 Preparation of 1.0 M Triethanolamine Buffer (pH 7.5) and 1% Alcoholic Phenolphthalein Indicator Solutions

To prepare 1.0 M triethanolamine buffer (pH 7.5) solution, 14.9 g of triethanolamine was dissolved in 50 mL of deionized water. The pH of the solution was adjusted to 7.5 by dropwise addition of 30 mL 2M HCl. Enough deionized water was then added to the resultant solution to make 100 mL of solution. pH of the resultant solution was checked with a glass electrode to ensure that it is 7.5 as attained.

To prepare 1% alcoholic phenolphthalein solution, 1 g of phenolphthalein powder was dissolved in 50 mL of 95 % ethyl alcohol. The mixture was stirred gently to ensure a uniform dissolution of the phenolphthalein. The resultant solution was poured into 100 mL flask and then diluted to the mark with 95% ethyl alcohol.

3.3.12 Preparation of Bray's No. 1 and Eriochrome black T indicator

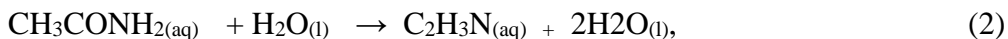
To prepare Bray's No. 1 solution, 2.22 g of ammonium fluoride (NH_4F) was dissolved in deionised water. The solution was poured into 2 L volumetric flask, 5 mL of 36 % concentrated hydrochloric acid was added. The resultant mixture was shaken thoroughly and then diluted with deionised to make 2 L of solution.

To prepare Eriochrome Black T indicator solution, 1.0 g of Eriochrome Black T powder was put into a 250 mL beaker, eighty milliliter (80 mL) of 95% ethanol was then added. The resultant mixture was stirred gently until the powder dissolved and then made to 100 mL with 95% ethanol.

3.3.13 Preparation of Dilute Acetonitrile (C₂H₃N) Solution

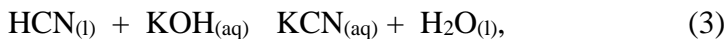
To prepare this solution, 25 mL of acetic acid was neutralized by adding 75 mL of ammonia solution to generate ammonium acetate solution. The resultant ammonium acetate solution was mixed with gaseous ammonia (2 mL) and mixture heated at 320 °C. The heated mixture was forced through a fixed bed reactor filled with ammonium oxide to generate acetonitrile mixed gas.

To obtain pure acetonitrile, the mixed gas was stirred using magnetic stirrer. One milliliter (1 mL) calcium hydride was added to remove the remaining water. The mixed acetonitrile gas was completely dried when effervescence of hydrogen was ceased. The dried mixed acetonitrile gas was then distilled in an all-glass apparatus under a high reflux ratio of phosphorus pentoxide. The distillate was protected from atmospheric moisture with a drying tube filled with anhydrous magnesium perchlorate. First 5 % of the distillate was discarded and the rest collected. The distillate was refluxed over calcium hydride (5 g per litre) for one hour, and then further distilled gradually under maximum reflux ratio (b.p. 81.6°C) and 5 to 90 % fraction was collected. Reactions involve in the preparation of acetonitrile are as follows:



3.3.14 Preparation of Dilute Potassium Cyanide and 0.5% Diphenylamine Indicator Solution

To prepare dilute potassium cyanide solution, 318 mL of hydrogen cyanide was reacted with 182 mL of aqueous potassium hydroxide. The chemical reaction involved in the preparation is indicated by equation 3.



To prepare 0.5% diphenylamine indicator solution, 90 mL of 98% concentrated sulphuric acid was added to 10 mL of deionized water. The solution was stirred continuously for 2 minutes and then added in drops to 0.5 g of diphenylamine. Extreme caution was taken when adding the acid to water since substantial quantities of heat were generated during the dilution.

3.4 Soil Samples Physical Properties Determination

Soil samples were sent to Ghana Atomic Energy Commission, Accra, for soil particle size, bulk density, moisture content, pH, organic carbon and total nitrogen contents determination. Other physico-chemical parameters determined included phosphorus contents, porosity, bulk density and texture of the soil samples.

3.4.1 Determination of pH and Conductivity of Soil Samples

pH of the soil samples was measured using pH meter (EUTECH 510). Prior to its use, the pH meter was calibrated by 3 points calibration with Orion. Standard buffer solutions (pH 4, 7 and 10) supplied by thermos scientific. To calibrate the pH – meter, the pH probe was

inserted into buffer solutions (pH 4, 7 and 10). In each case, the control knob of the pH – meter was adjusted to read pH of the corresponding buffer solution. The readings were considered stable and recorded when pH values read by the pH – meter did not change by 0.2 pH unit.

To determine pH of the soil samples, 30 g of each soil was put into a different 100 mL beaker. Thirty milliliters of deionized water was added. The soil – deionized mixtures were allowed to stand for an hour. The calibrated pH – meter was inserted into upper portion of soil solution and the pH read and recorded. Electrical conductivity meter was also immersed into the upper portion of the soil – deionized mixtures and the electrical conductivity determined and recorded.

pH and electrical conductivity of the soil samples were determined simultaneously. Prior to determination of electrical conductivity of the soil samples, the electrical conductivity meter (EC – meter) was also calibrated. To calibrate the EC – meter, EC – meter probe was inserted into 25 mL of 0.01M KCl standard solution. The EC – meter was adjusted to read 1413 $\mu\text{s}/\text{m}$ for the 0.01M KCl solution. The reading was saved on the instrument. The electrode was removed, washed with deionized water and the re – inserted into the standard KCl solution before the reading.

3.4.2 Soil Moisture Content Determination

Moisture contents of the soil samples were determined using the Gardner gravimetric test (Gardner *et al.*, 2000). Hundred grams (100 g) of each of the soil sample was put into a

pre-weighed leak-proof stainless container and then labelled. The container containing the soil sample was weighed (M_1) and then dried in the oven at a temperature of 105 °C until a constant mass was attained. After drying, the container with soil the sample were reweighed (M_2). Mass of water in the sample was obtained from the difference between the masses (M_1 and M_2). Gravimetric moisture was then calculated using Equation (4):

$$\theta_g = \frac{M_1 - M_2}{M_2} \times 100, \quad (4)$$

Where: θ_g is the soil is gravimetric moisture content, M_1 is the weight of the soil before oven drying and M_2 is the weight of soil after oven-drying.

3.4.3 Determination of Soil Particle Size

Hydrometer procedure as described by Huluka & Miller (2014) was used to determine soil particle size. The soil samples were dried using temperature controlled oven method as described by Naveena *et al.* (2015). The soil samples were kept in electric oven at 30°C and allowed to dry for 2 hours. The temperature was increased to 40°C and the soil samples were further dried for an hour. To ensure thorough drying, the temperature was again increased progressively to 50°C and the soil samples were further dried for additional one hour.

After thorough drying, the soil samples were kept in a desiccator and then allowed to cool to 25°C. Fifty grams (50 g) of the oven dried soil sample was put into a 250 mL flat bottom flasks, 50 mL of 5 % sodium hexamethaphosphate added and the flask was placed onto a Stuart flask shaker (SSL2) and operated at 350 rpm for 30 minutes. The resultant soil

suspension was transferred to a 1 L measuring cylinder. This made to the mark with distilled water.

A hydrometer was inserted in the soil suspensions and the cylinders agitated vigorously to ensure that soil particles were uniformly distributed in the soil suspension. A thermometer was also inserted into the soil suspension to measure that read temperature of the soil suspension whilst recording the hydrometer readings for every 40 seconds for 3 hours. Percentage sand, silt and clay components of soil samples were calculated using Equations 5, 6 and 7 below:

$$\% \text{ Sand} = 100 - \left(\frac{A}{W} \times 100 \right), \quad (5)$$

$$\% \text{ Clay} = \left(\frac{B}{W} \times 100 \right) \quad (6)$$

$$\% \text{ Silt} = 100 - (\% \text{ Sand} \times \% \text{ Clay}) \quad (7)$$

Where A is hydrometer reading for 40 seconds, B is hydrometer reading for 3 hours and W is weight of soil sample used.

3.4.4 Determination of Soil Organic Carbon Contents

Walkley-Black wet oxidation technique described by Da Silva *et al.* (2013) was used to determine organic carbon contents of the soil. One gram (1 g) of the soil sample was put into a 250 mL conical flask. Ten millilitres (10 mL) of 0.16 M aqueous solution of potassium dichromate ($K_2Cr_2O_7$) was added. Twenty millilitres (20 mL) of 98% concentrated sulphuric acid was also added in dropwise via a burette to the soil-potassium dichromate mixture. The mixture was swirled gently, allowed to stand for 30 minutes before 250 mL of distilled water was added. Ten millilitres (10 mL) of 98% concentrated

phosphoric acid was further added in drops, mixture was swirled gently and then allowed to cool to room temperature. One millimeter (1 mL) of diphenylamine indicator solution was added and then titrated with 1.0 M ferrous sulphate solution. The colour changes from green to violet at the endpoint. Soil organic carbon contents were calculated using Equation (8).

$$\text{Organic carbon (\%)} = \left(\frac{M \times 0.39 \times \text{MCF} (V_1 - V_2)}{W} \right), \quad (8)$$

Where, M is molarity of the solution used (mol dm^{-3}), V_1 is the volume of sulphate solution used for blank titration (mL), V_2 is the volume of sulphate solution used for sample titration (mL), W(g) is the weight of air – Dry sample (grams) and MCF is the moisture correcting factor $(100 + \% \text{ moisture}) / 100$. The MCF was used to convert analytical results of air-dried soil to dry weight on the basis of oven-dry soil. Percentage of organic matter was determined using the Equation (9):

$$\% \text{ Organic Matter (OM)} = \% \text{ Organic carbon} \times 1.724, \quad (9)$$

Where $1.724 = \frac{100}{58}$, because, 58% of mass of organic matter exists as carbon.

3.4.5 Determination of Total Nitrogen Contents of Soil Sample

Total nitrogen contents of the soil sample were determined using the Kjeldahl digestion and distillation process as described in Soil Laboratory Staff by Searle (1984). Ten grams (10 g) of the soil sample was placed into a digestion flask and 5 mL of distilled water was added. Five millilitres (5.0 mL) of 98 % concentrated sulphuric acid and 2.5 g of selenium mixture consisting of selenium, copper sulphate and potassium sulphate in the ratio 1:6:100 (w/w) respectively were added to the mixture then digested at 375 °C for three hours. Fifty

millilitres (50 mL) of deionized water was added to the digested soil sample and the mixture was allowed to cool to room temperature.

After cooling, 25 mL of the digested soil sample was put into the reaction chamber of the Kjeldahl apparatus, 10 mL of 40 % NaOH solution was added and the solution was distilled. The distillate was collected into a 50 mL flask containing 2% of boric acid. The distillate-boric mixture was swirled gently to ensure a uniform mixture. The mixture was then titrated against 0.02 M HCl solution using bromocresol green indicator until endpoint was established. At the endpoint the colour of the distillate-boric acid bromocresol indicator mixture changed from yellow to blue. Blank distillation and titration were also done using the procedure as described for the soil samples. The blank samples were used to track traces of nitrogen in the reagents used. The proportions of nitrogen in the soil samples were calculated using Equation (10).

$$\text{Nitrogen (\%)} = \frac{M(a-b) \times 1.4 \times \text{MCF} \times V}{W \times t}, \quad (10)$$

Where M is concentration of HCl solution used (mol dm^{-3}), a is the volume (mL) of HCl used in the sample titration, b is the volume (mL) of HCl used in the blank titration, V is the weight (g) of air-dry sample used, MCF is moisture correction factor $(100 + \% \text{ moisture})/100$ and t is the total weight (g) of soil sample used. The MCF was used to convert analytical results on air-dried soil to dry weight of an oven-dried soil.

3.4.6 Determination of Phosphorus Contents of Soil Samples

Bray's No. 1 solution (2.22 mL of 0.03 M NH_4F and 5 mL of 0.025 M HCl) as outlined by Gee & Bauder (1986) was used to extract phosphorus contents of the soil. Five grams (5.0

g) of the soil was put into a 50 mL flat bottom flask and 35 mL of Bray-1 solution added. The mixture was vortexed for 10 minutes and then filtered through Whatman No. 42 filter paper. Five millilitres (5 mL) of the filtrate was pipetted into a 25 mL flask and then 10 mL of 0.23 M ammonium molybdate added. Phosphorus contents of the soils were recorded at 600 nm wavelength on UV spectrometer (Spectronic 21D).

Phosphorus contents of the soil samples were calculated using Equation (11):

$$P \text{ (mg kg}^{-1} \text{ soil)} = \frac{(a-b) \times 35 \times 15 \times \text{MCF}}{W} \quad (11)$$

Where, 'a' is P (phosphorus) content in the soil sample extract, 'b' is phosphorus content of the volume of blank extracting solution (35mL), 15mL is the final volume of sample solution, MCF is moisture correcting factor and W is the weight (g) of soil sample used.

3.5 Soil Preparation for Extraction of Exchangeable Bases Contents of Soil Samples

Ten grams (10 g) of each soil sample was weighed into 500 mL flat bottom flask and 250 mL of 1.0 M ammonium acetate solution buffered (pH 7) was added. The mixture was shaken at 250 rpm on a Stuart flask shaker (SSL2) for 90 minutes after which it was filtered under vacuum through Whatman No. 42 filter paper. The exchangeable bases in the soil samples (calcium, magnesium, potassium and sodium) were determined from the filtrate.

3.5.1 Determination of Calcium and Magnesium Contents of Soil Samples

Ten milliliters (10 mL) of the prepared filtrate was put into a 100 mL conical flask. Five milliliters (5 mL) of ammonium chloride buffer solution was added followed by 1 mL of 1.0 M triethanolamine buffer solution, 1 mL of 2.0 % potassium cyanide solution and 0.2 mL of Eriochrome Black T solution. The mixture was swirled gently and then titrated to a turquoise blue colouration with 0.02 M EDTA (ethylenediamine tetraacetic acid). The titre value was noted and then recorded. The main reaction involved in the titration are presented in Equations 12, 13 and 14:



Indicator reaction (ErioT is blue and ErioT-Mg is pink)



The titre value for calcium was calculated using Equation 15:

$$T_A = \frac{V_1 + V_2 + V_3 + \dots + V_n}{n} \quad (15)$$

Where: T_A is the average titre volume (V_1 , V_2 and V_3) for 1st, 2nd and 3rd titrations respectively and n is the number of titre values.

3.5.2 Determination of Calcium Content of Soil

Ten milliliters (10 mL) of the filtrate was put into a 100 mL conical flask, 10 mL of 10 % potassium hydroxide solution, 1 mL triethanolamine, 1 mL of 2.0 % potassium cyanide solution, and 3 drops of cal-red indicator were added and the mixture was mixed thoroughly. The resulted red coloured mixture was titrated to a pure blue colour with 0.02

M EDTA solution. Calcium contents of the soil samples were calculated using Equation (16):

$$\text{Ca + Mg (or Ca) (cmol+ kg}^{-1}\text{ soil)} = \frac{0.02 \times (V_s - V_b) \times 1000}{W} \quad (16)$$

Where W is weight (g) of air-dry soil used, V_a is volume (mL) of EDTA solution used in sample titration, V_b is volume (mL) of EDTA used in blank titration, 0.02 M is concentration of EDTA solution and 1000 is the conversion factor from g to cmol+kg^{-1} .

3.5.3 Determination of Exchangeable Potassium and Sodium Contents of Soil Samples

Exchangeable potassium and sodium contents of the filtrate produced from soil samples were determined by flame photometry. Standard solutions of potassium hydroxide (1M) and sodium hydroxide (1M) were prepared by transferring 25mL each of 1000 mg/L standard solution of potassium and sodium into separate 100mL volumetric flasks. Each solution was diluted with ammonium acetate to 100 mL mark.

Different volumes (5, 10, 15, 20 and 25 mL) of 250 mL standard solutions of potassium and sodium were transferred into different 250 mL volumetric flasks. Hundred millilitres (100 mL) of 1 M NH_4OAC (ammonium acetate) solution was added to each flask, the mixture was swirled gently and then made to the volumes with distilled water to produce 2.5, 5.0, 7.5, 10.0 mg/L and 0, 2.5, 5.0, 7.5, 10.0 mg/L working solutions of potassium and sodium respectively. Required volumes of 0, 5, 10, 15, 20 mL of potassium and sodium working solutions were aspirated in the preparation of calibration graphs. Potassium and sodium contents in the soil samples were determined by flame photometry at wavelengths

of 766.5 and 589.0 nm respectively. Exchangeable potassium and sodium contents of the soil samples were then calculated using Equations 17 and 18 respectively.

$$\text{Exchangeable K (cmol+ kg}^{-1}\text{ soil)} = \frac{(a-b) \times 250 \times \text{mcf}}{10 \times 39.1 \times w} \quad (17)$$

$$\text{Exchangeable Na (cmol+ kg}^{-1}\text{ soil)} = \frac{(a-b) \times 250 \times \text{mcf}}{10 \times 23 \times w} \quad (18)$$

Where a (mg L⁻¹K) is the filtrate used b (mg L⁻¹K) is the volume of blank filtrate, used, W is weight (g) of air-dry soil sample and MCF is moisture correcting factor used.

3.6 Preparation of Soil Samples for Pesticides Residues Extraction

Soil samples were collected from study farms that had food crops cultivated on them at the time of the study. Laboratory analysis of the samples (soil and crops) for pesticides residues were conducted at the Ghana Atomic Energy Commission, Accra. The Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) mini multi-residue method for extracting multi pesticides residues as described by Suleiman *et al.* (2020) & Anastassiades *et al.* (2003) was used. Composite samples comprising soils collected from farmlands cultivated with cocoyam, cassava and maize at the time of the study. Representative portions of the soil samples were air-dried at 40 °C as described and then sieved through a 2 mm mesh size. The sieved soil samples were stored at room temperature (25 °C) for pesticides extraction and analysis.

3.6.1 Multi Pesticides Residues Extraction from Soil Samples

The soil samples were grinded into fine particles using a previously acid washed and oven dried at 105 °C. The grinded soil samples were sieved using 2 µm mesh size. Thirty grams (30 g) of each soil sample was put into a thimble and then inserted into 500 mL quick fit

Soxhlet extraction apparatus. Two hundred and fifty milliliters (250 mL) of extraction solvent (3:1v/v n-hexane-acetone mixture) was added to each sample in the Soxhlet apparatus and sample extracted repeatedly for 16 hours. One milliliter (1 mL) of isooctane was added and the mixture shaken vigorously using a flask shaker at 300 rpm for 30 minutes. Rotary evaporator (Model, SD -RE524, China) was used to concentrate the extracts to 2 mL. The concentrated extracts were cleaned – up using silica gel mounted chromatographic columns.

3.6.2 Clean-up of Multi Pesticides Residues Extract

The clean – up method described by Jaoven – Madoublet *et al.*, (2000) was adopted. Chromatographic columns for the sample clean – up were mounted as described for cassava and cocoyam (leaves and tubers). Concentrated crude pesticides extracts were introduced to the head of the columns for cleaning. Columns were eluted with 150 mL of n-hexane-diethyl ether mixture (3:1 v/v) and the eluent collected at flow rate of 1 mL/minute into a 200 mL round bottom flask. The eluents were concentrated into 1 mL, put into a 1 mL glass vessels and then analysed using high resolution chromatographic instrument (Varian CP – 3800) equipped with Pulse Flame Photometric Detector (PFPD) for quantities of pesticides present in the samples.

3.7 Extraction of Pesticides Residues from Cocoyam (Leaves and Tubers) and Cassava Tubers

Edible portions of cassava and cocoyam tubers were peeled with stainless steel knife whilst the cocoyam leaves were chopped into pieces using domestic knife. The samples were homogenized separately using Binatone blender (Model, BLG 555 MK2).

Fifty grams (50 g) each of the homogenized samples was put into flat bottom flasks and 100 mL of acetonitrile added. The mixtures were shaken continuously at 500 rpm for 72 hours using rotary flask shaker (Model, PLT-207) to extract enough pesticides. The extracts of the samples were filtered by suction. Two grams of sodium chloride and 50 mL of 0.5 M phosphate buffer solution (pH 7.0) were then added. These were allowed to stand at room temperature in 500 mL separating funnels till mixtures were separated into clear layers. The layers were carefully separated and the aqueous portions discarded.

3.7.1 Clean – up of Pesticides Extracts

A graphite carbon – silica gel (1:1 w/w) mini chromatographic (2.0 mm diameter) were filled with 2g of silica gel previously activated at 120 °C. Twenty milliliters (20g) each of acetonitrile – toluene mixture (1:1 w/w) was used to condition the columns. The extracts (previously reduced to 1mL) were introduced into the column head. The columns were eluted with 100 mL of acetonitrile – toluene mixture (3:1 v/v) and the eluents collected into 100 mL round bottom flask at flow rate of 1 mL/minute. The eluates were collected and concentrated to dryness at 76 °C using rotary evaporator (Buchi Rotary evaporator, Model

2199A, India). The extracts were reconcentrated with 50 mL of acetonitrile – toluene (3:1 v/v) and then reconcentrated to 1 mL for HPLC analysis.

3.8 Extraction of Pesticide Residue from Dry Maize

The husks of the maize were removed and the maize separated from the comb. The maize samples were milled into fine powder using mini corn grinder mill (MY-M6FFC 20190117). Twenty grams each of the milled samples was put into 500 mL flat bottom flasks. The flasks were put onto a shaker operated at 500 rpm for 72 hours. After shaken, the samples were filtered by suction using Ahlstrom Muncksjo filter paper grade 615. The filtrates were transferred into 500 mL measuring cylinders and 4 g of anhydrous magnesium sulphate (previously oven dried at 100 °C for 5 hours), trisodium citrate dihydrate (1 g), disodium hydrogen citrate sesquihydrate (0.5g) and 20 mL of 0.2 M aqueous sodium chloride solution added. The mixtures were shaken cautiously at 500 rpm for 24 hours and then filtered through Ahlstrom Muncksjo filter paper grade 615 by suction into 500 mL separating funnels. The filtrates were allowed to stand till the aqueous and the organic layers were clearly separated. The two layers were carefully separated and the aqueous portion discarded.

3.9 Gas Chromatographic Determination of Pesticides Residues

Shimadzu GC-2010 equipped with ⁶³Ni electron capture detector (ECD) was employed for the determination of pesticides contents of the samples. Injector and detector temperature were set at 280 °C and 300°C respectively. A fused silica ZB-5 (30mm × 0.25 mm, 0.25 µm film thickness) column was used at 60°C initial temperature. The temperature was

adjusted to 180°C and then further adjusted to 220°C for 3 minutes at 73.33°C/minute. Again, the temperature was further increased to 300°C for additional 3 minutes at 100°C/minute. Carrier gas used was nitrogen at a flow rate of 1.0 mL/min. Sample (1.0 µL) was injected into the GC for analysis.

The final pesticides extracts were analyzed using gas chromatography (Varian CP-3800) equipped with autosampler and pulse flame photometric detector (PFPD). The GC conditions and the detector response were adjusted to match relative retention times and detector response as described by Syoku-An (2006). GC conditions for the analysis were fused silica capillary column with 30 m × 0.25 mm internal diameter and 0.25 µm film thickness. The injector and detector-PFPD temperatures were set at 270°C and 280 °C respectively whilst oven conditions were held at temperature 70°C for 2 minutes, and then ramped at 25°C to 200°C, for a minute. The oven temperature was finally ramped at 200°C to 250°C for another minute. Samples were injected at 2.0 µL in a split less mode for 15 minutes total run time.

3.10 High Performance Liquid Chromatography (HPLC) Determination of Carbamates

High Performance Liquid Chromatography spectrometer (Shimadzu, LC-10 from Japan) equipped with Photo Diode Array Detector (PDAD), Reverse Phase Alltech analytical column (250 × 4.6 mm), and Rotary vacuum evaporator (Type - 350, USA) were used to determine carbamate contents of the samples.

Sample injections into HPLC instrument were done by micro syringe. The HPLC instrument was operated at 282nm wavelength, column temperature (30°C), sample injection volume (2.0µL) and 10 minutes run time. Quantification of carbamate was done using standard curves calibration of freshly prepared carbofuran and carbaryl standard pesticides. Carbofuran and carbaryl standards were analysed using HPLC fitted with PDAD.

3.11 Estimation of Hazard Quotients (HQ) of Detected Pesticides

To estimate the risk of the detected pesticides on the health of consumers, estimated daily intakes (EDI) of each pesticide was divided by its corresponding acceptable daily intake (ADI) as expressed in Equation (19), Hossain *et al.*, (2015) and Bhandari *et al.* (2019).

$$HQ = \frac{\text{Estimated daily intakes (EDI)}}{\text{Acceptable daily intake (ADI)}}, \quad (19)$$

Hazard quotient (HQ) above unity indicates unacceptable risk to consumers as reported in similar studies by Akoto *et al.*, (2015), Hossain *et al.*, (2015) and Bhandari *et al.* (2019).

The estimated daily intake (EDI) was also calculated using Equation (20)

$$EDI = C_p \times CR_p / B_{wc} \quad (20)$$

Where, EDI is the estimated daily intake of pesticides (mg/kg), CR_p is the consumption rate of pesticides via crop (mg/kg), C_p is the mean concentration of pesticides residues in the food crop samples and B_{wc} is the average body weight (kg) of consumers.

3.11.1 Estimation of Hazard Indices of the Pesticides Detected

The combined health quotients of the organochlorines, organophosphate and carbamate in the food crop samples were estimated by adding the hazard quotients (HQs) of the various pesticides detected in the food crop samples using Equation (21):

The health risk indices (HIs) of the organochlorines, organophosphate and carbamates in the food crop samples were computed using Equation (21):

$$HI = \sum(HQS_{(OC)} + HQS_{(OP)} + HQS_{(CB)}), \quad (21)$$

Hazard indices above 1 indicate that mixture of pesticides in a given food crop is above the maximum acceptable risk. Thus, consumers may suffer health issues linked to the pesticides when the food crops are consumed overtime as reported in similar studies by (Akoto *et al.* 2015; Hossain *et al.* 2015).

3.12 Quality Assurance Process Adopted in This Study

The standard pesticides solution (10 µg/mL) containing 10 µg of pesticides in 99 % n-hexane was used. Working standard pesticide solutions (1 - 100 µg/mL) were prepared by diluting (1, 2, 5, 10, and 50 µg/mL) of the mixed pesticides standard solution with 2mL of 99% n-hexane and concentrations confirmed in recovery study. Prior to analysis, the extracts were kept frozen until quantification was done. Blank and samples extracts were analysed in duplicates. Recalibration of the instrument was done intermittently. The efficiency of the analytical method employed was determined by percentage recoveries of the standards pesticide solution. The percentage recoveries were used to check reproducibility of the analytical results obtained.

3.13 Quantification and Limit of Detection of Pesticides

Levels of pesticides were quantified by the external standard method using peak area. The peak areas with retention times corresponding with that of the pesticide standards used were extrapolated on corresponding calibration curves to obtain the concentrations. The limit of detection for pesticides in soil samples was 0.001 mg/kg.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

This chapter looks at results obtained in the study. It also presents and discusses data generated for physico – chemical properties of the investigated soils as well as the levels of pesticides in soil and food crops samples studied.

4.2 Recovery Study

Recoveries of various pesticides (OPs, OCs and CBs) at 0.010 mg/kg fortification from soils and crop samples are shown in the Tables 4.1, 4.2 and 4.3 below. The obtained recoveries were within the acceptable percentage range of 70.0 - 120.0 % (Wang *et al.*, 2015; Kolberg *et al.*, 2011; Kovacicova *et al.*, 1975). Limits of detection (LOD) and limits of quantification for the pesticides (OP, OC and CB) residues detected in both soil and crop samples were 0.001 mg/kg and 0.003 mg/kg respectively.

Table 4.1: Percentage of organophosphorus pesticides recovered from spiked samples

Pesticide	Mean %	Standard Deviation
Methamidophos	98.16	0.110
Dimethoate	99.30	0.001
Chlorpyrifos	99.55	0.009
Parathion-methyl	99.55	0.007
Chlorfenvinphos	98.51	0.124
Malathion	100.73	0.003
Phorate	98.90	0.105
Profenofos	99.09	0.010
Ethoprophos	99.27	0.008
Diazinon	98.45	0.107

LOD = 0.001 mg/kg; LOQ = 0.003 mg/kg

Table 4.2: Percentage of carbamates pesticides recovered from spiked samples

Pesticide	Mean %	Standard Deviation
Carbofuran	98.64	0.104
Carbaryl	100.02	0.001

LOD = 0.001 mg/kg; LOQ = 0.003 mg/kg

Table 4.3: Percentage of organochlorine pesticides recovered from spiked samples

Pesticides	Mean %	Standard deviation
Aldrin	98.09	0.100
Chlordane	99.27	0.005
DDT	99.45	0.008
Dieldrin	100.82	0.001
Endosulfan	98.05	0.103
Endrine	98.05	0.107
Heptachlor	99.56	0.002
Lindane	99.51	0.004
Methoxychlor	99.50	0.010

LOD = 0.001 mg/kg; LOQ = 0.003 mg/kg

4.3 Physical Properties of Soil from Selected Farms in the Asante Akyem Central Municipality

Soil samples from twelve (12) different farms, viz Farm A (cocoyam and cocoyam leaves), farm B (cassava) and farm C (maize) were investigated. The twelve farms were made of four cocoyam farms, four cassava farms and four maize farms. Physicochemical properties of soil were computed statistically and data presented (Tables 4.4, 4.5, and 4.6).

Mean soil moisture content (%) were 4.84 ± 1.03 for Farm A and ranged (4.0 – 7.0), farm B has mean 4.68 ± 1.49 and ranged (2.70 – 6.14), 6.94 ± 1.88 was recorded in farm C with a range (5.41 – 9.11). Maize farm (farm C) recorded highest soil moisture contents whilst farm B (cassava farm) recorded the least soil moisture content. uThe range of soil moisture

contents (6.35 - 13.56%) recorded in this study were below range of moisture content indicated by Bentum *et al.* (2006) in similar study.

According to Kumar and Philip (2015), pesticides retention and its availability in soil depend on soil moisture content. Lower soil moisture contents have huge influence on activities of soil microorganism as indicated by Abera *et al.* (2012). The activities of many soil microorganisms are halted at very low soil moisture (Brockett *et al.*, 2012). Reduction in rates of pesticide molecules are as linked to inactiveness of some soil microorganisms. Consequently, pesticides accumulate and adsorb onto soil particles for longer periods (Asare, 2011). The soil moisture contents recorded in this study is low. Hence favour pesticides retention, availability and adsorption onto soil particle.

Particles size distribution analysis of soil taken from the study were sand (65.5 – 81.1%) > silt (28.6 – 50.4%) > clay (4.0 – 10.9%) for farm A, (cocoyam farms), sand (20.9– 60.2%) > silt (27.6 – 58.5%) > clay (15.0 – 32.9 %) for farm B, (cassava farm). Whilst in maize farm, (farm C) soil particle size distributions were sand (50.0 – 73.0%) > silt (35.5 – 70.3%) > clay (11.5 – 20.9%).

From the results, it is clear that the soils have high proportions of sand. Mean percentage of soil particle size distribution were cocoyam farm (farm A) sand ($74.52 \pm 7.04\%$) > silt ($39.55 \pm 10.01\%$) > clay ($7.95 \pm 3.00\%$) (Table 4.4). The cassava farm (Farm B) had sand ($46.70 \pm 17.73\%$) > silt ($38.63 \pm 13.65\%$) > clay ($24.43 \pm 7.65\%$). Whilst in the maize farm (Farm C), mean percentage soil particle size distributions were sand ($60.78 \pm 9.86\%$) > silt

(55.85 ± 14.62%) > clay (16.38 ± 4.13%). The observed low clay contents suggest that adsorption of pesticides molecules onto soil might be low. Thus, pesticides molecules could persist in the soil for short period as reported by Laabs *et al.* (2002). The findings agreed favourably with that reported by Asare (2011). According to Asare (2011), low clay contents of soils decrease capabilities of soils to bind and retain pesticides molecules due to reduced cation exchange capacity sites on clay. Soil bulk densities are the dry weight of soils per unit volume of soil. They were determined by both solids and pore soil space as indicated by Cresswell & Hamilton (2002). Soil bulk densities of the soil samples ranged from 0.80 - 1.70 g/cm³. Soil bulk density of the farms ranged from 1.00 – 1.60 g/cm³ (Farm A), 0.90 – 1.70 g/cm³ (Farm B) and 0.80 – 1.30 g/cm³ (Farm C). Mean soil bulk densities of the soil were 1.30 ± 0.26 g/cm³ (Farm A), 1.37 ± 0.34g/cm³ (farm B) and 1.07 ± 0.26 g/cm³ (Farm C).

Table 4.4: Mean Values of Physical Properties of Soil from Asante Akyem Central

Soil characteristic	Farm A Mean ± SD	Farm B Mean ± SD	Farm C Mean ± SD
Moisture (%)	4.85 ± 1.03	4.68 ± 1.49	6.94 ± 1.88
Sand (%)	74.52 ± 7.04	46.70 ± 17.72	60.78 ± 9.86
Silt (%)	39.55 ± 10.01	38.63 ± 13.65	55.85 ± 14.62
Clay (%)	7.95 ± 3.00	24.43 ± 7.65	16.38 ± 4.13
Bulk density (g/cm ³)	1.30 ± 0.26	1.38 ± 0.34	1.08 ± 0.26
Soil porosity	0.65 ± 0.13	0.70 ± 0.08	0.77 ± 0.11
Texture	Sand-loam	Sand-loam	Sand- loam

The bulk density was found to be inversely related to soil porosity as reported by Fuentes *et al.*, (2004), Horn & Smucker, (2005). The bulk densities were low and this suggest that, soils structures were porous as indicated in similar studies by Fuentes *et al.* (2004), Horn

& Smucker (2005). These observations were reaffirmed by low clay contents of the soils. The, relatively low average bulk densities obtained in this study do not support high adsorption of pesticides molecules. Thus, pesticides could be short-lived in the soils of the investigated farms.

4.3.1 Chemical Properties of Soil from the Asante Akyem Central Municipality

Soil pH values recorded in the study farms ranged from 5.09 – 6.60 across all farms. Mean soil pH of cocoyam farm (farm A) was 5.52 ± 0.72 , whilst that of cassava farm (farm B) and maize farm (Farm C) were 5.71 ± 0.64 and 5.83 ± 0.77 respectively. Based on the pH values recorded, soils were weakly acidic. Thus, it is expected that availability of pesticides molecules as well as their adsorption onto soil particles would be relatively high. In an acidic soil medium ($\text{pH} < 7$) pesticides molecules adsorbed onto soil particles dissolve and become part of the soil solution for subsequent adsorption by plants via their root hairs (Fosu – Mensah *et al.*, 2016). pH range recorded in this study were slightly below $5.89 \pm 0.47 - 7.09 \pm 0.24$, reported by Asare (2011) when studies were conducted on some soils of Nsadwire in Komenda-Edina-Eguofo-Abirem district of the central region of Ghana. However, soil pH data reported in this study corresponded with $4.80 \pm 0.17 - 5.82 \pm 0.62$ documented in similar research by Fosu – Mensah *et al.* (2016). Low pH values recorded in this study could be attributed to acidic cations detected in soil samples. This observation compares favourably with study by Kortatsi (2007).

Table 4.5: Mean values of chemical properties of soil from Asante Akyem Central

Soil characteristic	Farm A Mean \pm SD	Farm B Mean \pm SD	Farm C Mean \pm SD
pH	5.52 \pm 0.72	5.71 \pm 0.64	5.83 \pm 0.77
Conductivity (mS/m)	462.38 \pm 53.34	545.06 \pm 126.65	566.04 \pm 119.86
Organic carbon (%)	1.19 \pm 0.19	1.69 \pm 0.54	1.02 \pm 0.34
Organic matter (%)	2.05 \pm 0.34	2.91 \pm 0.93	1.75 \pm 0.58
Total Nitrogen (%)	0.04 \pm 0.03	0.13 \pm 0.07	0.10 \pm 0.09
Total Phosphorus (%)	1.86 \pm 0.62	2.86 \pm 1.99	3.64 \pm 1.20

Soil electrical conductivity (mS/s) ranged from 343.03 – 723.01 mS/m across the study farms. Mean soil conductivities were 462.38 \pm 53.34 mS/m (Farm A), 545.06 \pm 126.65 mS/m (Farm B) and 566.04 \pm 119.86 mS/m (Farm C). (Table 4.5). Soil electrical conductivities were generally low and that could be due to low concentration of ions in the investigated soils (Table 4.4).

Mean organic matter contents were 2.05 \pm 0.34% (Farm A), 2.91 \pm 0.93% (Farm B) and 1.75 \pm 0.34 (Farm C) (Table 4.5). Generally, no significant differences ($P > 0.05$) existed in mean values of organic matter contents of the soil (Table 4.5). The apparent differences in the organic matter contents might be due to errors during sampling and sample preparation. Mean organic matter contents followed the order 1.09 \pm 0.59% (Farm B) > 1.69 \pm 0.54% (Farm A) > 1.02 \pm 0.34% (Farm C). Total nitrogen contents of the soil samples were 0.13 \pm 0.07% (Farm B) > 0.1 \pm 0.09% (Farm C) > 0.04 \pm 0.03% (Farm A) (Table 4.5). Total phosphorus contents of the soil samples were 3.64 \pm 1.20% (Farm C) > 2.86 \pm 1.99% (Farm B) > 1.86 \pm 0.62% (Farm A).

Organic matter, organic carbon total nitrogen and total phosphorus contents of the soils were generally low Denkyi *et al.*, (2014). Thus, it is expected that adsorption of pesticides molecules onto soil particles would also be low. The relatively low percentage of organic matter, organic carbon, total nitrogen and phosphorus contents would course pesticides molecules to be part of soil solution for easily absorption by plants as indicated by Denkyi *et al.*, (2014). The organic matter contents (1.12 – 3.55%) recorded in this study was below (2.40 – 24.60%) recorded in similar study by Asare (2011). Total nitrogen contents (0.01 – 0.23%) generally agreed with 0.17 – 0.25% reported by Fosu –Mensah *et al.*, (2016). Organic carbon contents (0.65 – 2.06%) reported in this work also agreed with 1.38 – 1.78% indicated in a study by Fosu-Mensah *et al.*, (2016).

Table 4.6: Mean values of exchangeable cations, CEC (cmolckg⁻¹) of Asante Akyem

Soil

Soil characteristic	Farm A Mean ± SD	Fram B Mean ± SD	Farm C Mean ± SD
CEC	6.84 ± 0.83	6.48 ± 1.23	6.63 ± 0.92
Ca ²⁺	1.96 ± 0.62	1.95 ± 0.72	2.14 ± 1.09
Mg ²⁺	0.29 ± 0.13	0.58 ± 0.28	0.54 ± 0.31
Na ⁺	0.04 ± 0.02	0.03 ± 0.02	0.04 ± 0.02
K ⁺	0.08 ± 0.07	0.07 ± 0.06	0.13 ± 0.07

Soil exchangeable capacity, is a good indicator of the ability of soil to store nutrients and other chemicals such as pesticides. CEC of soil also indicates its ability to alter pesticides molecules that accumulated in the soil.

Mean CEC of the soils ranged from 6.48 ± 1.23 (Farm B) – 6.84 ± 0.83 (Farm A). Mean Ca^{2+} contents of the soils ranged from 1.95 ± 0.72 (Farm B) - 2.14 ± 1.09 (Farm C), whilst Mg^{2+} contents ranged from 0.29 ± 0.13 (Farm A) – 0.58 ± 0.28 (Farm B). Sodium ion (Na^+) contents also ranged from 0.03 ± 0.02 (Farm B) - 0.04 ± 0.02 (Farm A). Potassium ion (K^+) contents of soils also ranged from 0.07 ± 0.07 (Farm B) - 0.13 ± 0.07 (Farm C) (Table 6). Mean CECs were in order, Farm A (6.84 ± 0.83) > Farm C (6.63 ± 0.92) > Farm B (6.48 ± 1.23).

Farm C had the highest mean value of CEC for (2.14 ± 1.09) Ca^{2+} , whilst Farm B had the lowest mean value of CEC (1.95 ± 0.72) for the same ion (Ca^{2+}). Highest mean value of Mg^{2+} (0.58 ± 0.28) occurred in the soils from farm B whilst lowest mean of Mg^{2+} (0.29 ± 0.13) occurred in soils from farm A. Mean Na^+ content (0.03 ± 0.02) was low in the soil from farm B whilst highest occurred in the soils of farm A and farm C. Potassium ion (K^+) contents of the soil were 0.13 ± 0.07 (Farm C) > 0.08 ± 0.07 (Farm A) > 0.07 ± 0.06 (Farm B).

Cation exchange capacities (CEC), recorded in this study 6.48 - 6.84 cmol/kg were above (2.35 - 3.80 cmol/kg) reported by Asare (2011) and (2.91 - 3.61 cmol/kg) reported by Denkyi *et al.*, (2014). These CECs (6.48 to 6.84 cmol/kg) recorded in this work fell within ($2 - 16 \text{ cmolckg}^{-1}$) reported by IPNI (2011), to be a characteristic of a sandy soil. These low CECs values also indicate that the soils of the investigated farms would allow pesticides molecules to leach and become a component of soil solution for absorption by

plants via their root hairs. Thus, pesticides adsorption and persistence in the soils are expected to be low as indicated in a report by Afrane & Ntiamoah (2011).

4.4 Levels of Pesticides in the Soil Sample from Asante Akyem Central

The soil samples collected from investigated farms were analyzed for pesticides residue. Nine (9) different organochlorine pesticides, 10 different organophosphate pesticides and 2 different carbamates were detected in all samples. Mean concentration, standard deviation, minimum and maximum levels of each class of the pesticides were determined statistically with Microsoft Excel (2016 version). The mean level recorded for each class of pesticides was compared with the USEPA and the European Union (EU) permitted pesticides residue levels in soil (Tables 4.7 – 4.18).

Table 4.7: Organochlorine Pesticides Level (mg/kg) in Soil Samples from Farm A (cocoyam) in the Asante Akyem Central Municipality

Pesticides	Min. conc.	Max. conc.	Mean conc.	SD	USEPA/EU
Aldrin	0.014	0.022	0.018	0.004	0.02
Chlordane	0.013	0.045	0.029	0.015	0.25
D D T	0.018	0.046	0.035	0.013	0.05
Dieldrin	0.023	0.055	0.036	0.015	0.02
Endosulfan	ND	ND	ND	ND	0.05
Endrin	0.133	0.655	0.391	0.225	0.04
Heptachlor	0.016	0.079	0.045	0.027	0.03
Lindane	0.003	0.025	0.011	0.009	0.04
Methoxychlor	7.240	10.605	8.833	1.751	0.05

ND = Not Detected.

4.4.1 Organochlorine Pesticides Level (mg/kg) in Soil Samples from Farm A Analysis

(Table 4.7) showed that organochlorine pesticides levels ranged from (ND) – 10.605 mg/kg (Methoxychlor). Mean level of Methoxychlor (8.833 ± 1.751 mg/kg), Dieldrin (0.036 ± 0.015 mg/kg), Endrin (0.391 ± 0.225 mg/kg), and Heptachlor (0.045 ± 0.027 mg/kg) were above levels recommended by USEPA (2009) & EU (2013) (Table 4.7). Mean level of Chlordane (0.029 ± 0.015 mg/kg), DDT (0.035 ± 0.013 mg/kg), and Lindane (0.011 ± 0.009 mg/kg) were below recommended maximum residual limit set by USEPA/EU (Table 4.7). Lindane level was above 0.002 mg/kg recorded in study done in Ilawe, Ekiti, state in Nigeria by Olayinka (2013). Mean level of Lindane in soil samples from the cocoyam farm (Farm A) was below 8.60 mg/kg indicated by Bentum *et al.* (2006), 0.257 mg/kg by Aiyesanmi & Idowu, (2012) and 0.04 mg/kg by Fosu–Mensah *et al.* (2016). Dieldrin (0.036 ± 0.015 mg/kg) and DDT (0.035 ± 0.013 mg/kg) occurred in soil samples from the cocoyam farm was above Dieldrin (0.02 mg/kg) and DDT (0.03 mg/kg) reported by Fosu – Mensah *et al.* (2016). The differences in Dieldrin and DDT levels recorded in this work and the one recorded by Fosu-Mensah *et al.* (2016) could be due to different geographical location of the studies.

Table 4.8: Organochlorine pesticide levels (mg/kg) in the soil samples from farm B (cassava) in the Asante Akyem Central Municipality

Pesticides	Min. conc.	Max. conc.	Mean conc.	SD	USEPA/EU
Aldrin	0.000	0.025	0.010	0.012	0.02
Chlordane	0.025	0.045	0.036	0.009	0.25
D D T	0.015	0.045	0.031	0.012	0.05
Dieldrin	0.019	0.072	0.041	0.023	0.02
Endosulfan	0.000	0.024	0.010	0.012	0.05
Endrin	0.158	0.950	0.495	0.342	0.04
Heptachlor	0.005	0.085	0.036	0.039	0.03
Lindane	0.008	0.036	0.025	0.013	0.04
Methoxychlor	0.000	10.165	5.366	5.035	0.05

ND = Not Detected

4.4.2 Levels of Organochlorine Pesticides in Soil from Farm B

Levels of organochlorine pesticides in the soil samples collected from the cassava farm (Farm B) were analyzed and data presented (Table 4.8). Levels of organochlorine pesticides recorded ranged from ND – 10.165 mg/kg (Table 4.8). Levels of the organochlorine pesticides were Methoxychlor (5.366 ± 5.035 mg/kg) > Endrin (0.495 ± 0.342 mg/kg) > Dieldrin (0.041 ± 0.023 mg/kg) > Chlordane (0.036 ± 0.009 mg/kg) > DDT (0.031 ± 0.012 mg/kg) > Lindane (0.025 ± 0.013) > Endosulfan (0.010 ± 0.012 mg/kg).

In farm B mean levels organochlorine pesticides were Chlordane (0.036 ± 0.009 mg/kg), Dieldrin (0.041 ± 0.023 mg/kg), Endrin (0.495 ± 0.342 mg/kg), Heptachlor (0.036 ± 0.039 mg/kg), and Methoxychlor (5.366 ± 5.035 mg/kg). These exceeded recommended maximum limits for (0.25) Chlordane, (0.02) Dieldrin and (0.05) Methoxychlor set up by USEPA/EU. However, Mean levels of Aldrin (0.010 ± 0.012 mg/kg), DDT (0.031 ± 0.012 mg/kg) and Endosulfan (0.010 ± 0.012 mg/kg) were below (0.02) Aldrin, (0.05) DDT and

(0.05) Endosulfan levels allowed by USEPA/EU (Table 8). Mean level of Lindane recorded (0.025 ± 0.013 mg/kg) in the soil samples from Farm B was above 0.002 mg/kg reported by Agyen (2011) and 0.005 mg/kg documented Asare (2011). Lindane level was however below 0.04, 0.257 and 8.60 mg/kg reported in similar works by Fosu-Mensah *et al.* (2016), Aiyesanmi *et al.* (2012) and Bentum *et al.*, (2006) respectively. Mean level of Dieldrin (0.041 ± 0.023 mg/kg) and DDT (0.031 ± 0.012 mg/kg) in the soil samples from the cassava farm (Farm B) were above 0.007 mg/kg (Dieldrin) and 0.003 mg/kg (DDT) reported by Olayinka (2013) and Agyen (2011) respectively.

Table 4.9: Organochlorine pesticide levels (mg/kg) in soil sample from farm C (maize) in the Asante Akyem Central Municipality

Pesticides	Min. conc.	Max. conc.	Mean conc.	SD	USEPA/EU
Aldrin	ND	0.025	0.013	0.014	0.02
Chlordane	0.018	0.080	0.047	0.031	0.25
D D T	0.010	0.049	0.033	0.018	0.05
Diedrin	0.016	0.088	0.039	0.034	0.02
Endosulfan	ND	0.028	0.009	0.013	0.05
Endrin	0.285	0.762	0.439	0.221	0.04
Heptachlor	0.028	0.050	0.044	0.011	0.03
Lindane	0.005	0.025	0.014	0.009	0.04
Methoxychlor	2.911	12.317	7.864	3.882	0.05

ND = Not Detected

4.4.3 Levels of Organochlorine Pesticides in the Soil Samples from the Maize Farm

The samples of soils from the maize farm (Farm C) were also analyzed for organochlorine pesticides. The data recorded is presented (Table 4.9).

Organochlorine pesticides levels detected in the soil samples from Farm C ranged from ND (Aldrin) – 12.317 mg/kg (Methoxychlor). The levels were Methoxychlor ($7.864 \pm$

3.882 mg/kg) > Endrin (0.439 ± 0.221 mg/kg) > Chlordane (0.047 ± 0.031 mg/kg) > Heptachlor (0.044 ± 0.011 mg/kg) > Dieldrin (0.039 ± 0.034 mg/kg) > DDT (0.033 ± 0.018 mg/kg) > Lindane (0.014 ± 0.009 mg/kg) > Aldrin (0.013 ± 0.014 mg/kg) > Endosulfan (0.009 ± 0.013 mg/kg). Though Aldrin, DDT, Endosulfan and Lindane contents of the soil were below acceptable maximum limits of 0.02, 0.05, 0.05 and 0.04 mg/kg set by USEPA (2009) EU (2013) whilst Methoxychlor, Endrin, Chlordane, Heptachlor and Dieldrin contents were however above the acceptable limit of 0.05, 0.04, 0.25, 0.03 and 0.02 mg/kg respectively set by USEPA (2009) and EU (2013).

Mean levels of Dieldrin (0.039 ± 0.034 mg/kg) and dichloro-diphenyl-trichloroethane (DDT) (0.033 ± 0.018 mg/kg) in the soils from farm C were above 0.0032 and 0.02 mg/kg indicated in similar studies by Agyen (2011) & Fosu – Mensah *et al.* (2016) respectively. Mean levels of DDT (0.033 mg/kg) was also above 0.003 and 0.007 mg/kg documented by Agyen (2011) and Olayinka (2013) respectively. Mean level of DDT (0.033 mg/kg) in the soil samples from maize farm however agreed with 0.03 mg/kg reported by Fosu – Mensah *et al.* (2016).

Level of Lindane recorded in Farm C was below 0.04, 0.257, and 8.60 mg/kg reported in works by Fosu – Mensah *et al.* (2016), Aiyesanmi *et al.* (2012) & Bentum *et al.* (2006) respectively. Lindane level recorded in this study also agreed with 0.005 mg/kg detected in some soil samples from Nsadwir in the Central Region by Asare (2011).

4.4.4 Comparison of Organochlorine Pesticides Residues Contents from the Investigated Farms

The results presented (Tables 4.7 – 4.9), showed that, Methoxychlor was high across all farms (Farm A – C). The cocoyam farm A had the highest level of Methoxychlor (8.833 ± 1.751 mg/kg) followed by the farm D (7.864 ± 3.882 mg/kg). Minimum level of Methoxychlor (5.366 ± 5.035 mg/kg) occurred in the soil sampled from the cassava farm (Farm B). Methoxychlor content was above USEPA (2009) and EU (2013) recommended residual Methoxychlor level.

The high level of Methoxychlor recorded in this work could be attributed to its persistent nature just as many organochlorines. Dieldrin, Endrin, and Heptachlor levels recorded across all the farms (Tables 4.7 – 4.9) were also above recommended levels by USEPA (2009) and EU (2013). High levels of organochlorines in the soil samples investigated may be due to frequent application coupled with their reduced rates of degradation by soil micro-organisms and sunlight as reported by Horgarh, (2014). Reduced rate of leaching could have enabled these pesticides to persist in the soils at depth (0 – 20 cm).

Aldrin, Endosulfan and Lindane levels were low across all the farms. Aldrin level had the order farm A (0.018 ± 0.004 mg/kg) > farm C (0.013 ± 0.014 mg/kg) > farm B (0.010 ± 0.012 mg/kg). Endosulfan level was farm B (0.012 ± 0.013 mg/kg) > farm C (0.009 ± 0.013 mg/kg) > farm C (ND) whilst Lindane level was farm B (0.025 ± 0.013 mg/kg) > farm C (0.014 ± 0.009 mg/kg) > farm A (0.011 ± 0.009 mg/kg). Low levels of Aldrin,

Endosulfan and Lindane recorded could be ascribed to higher rate of leaching from soil surface to deeper depth than (0 – 20 cm) at which soil samples were collected.

4.4.5 Organophosphate Pesticides Levels (mg/kg) in Soil Samples from Farm A

Organophosphate pesticides (OPPs) concentrations in the soil samples were detected and the data presented (Table 10). OPPs concentrations in soil samples from the cocoyam farm (Farm A) ranged between 0.007 (Diazinon) - 1.485 mg/kg (Dimethoate) (Table 4.10). Mean levels of the OPPs were Dimethoate (1.165 ± 0.237 mg/kg) > Chlorfenvinphos (0.710 ± 0.343 mg/kg) > Parathion (0.577 ± 0.351 mg/kg) > Chlorpyrifos (0.529 ± 0.233 mg/kg) > Profenofos (0.431 ± 0.262 mg/kg) > Phorate (0.324 ± 0.196 mg/kg). Diamethoate, Chlorfenvinphos, Parathion, Chlorpyrifos, Profenofos and Phorate levels exceeded recommended by USEPA (2009) and EU (2013) to be safe in soil whilst Diazinon, Methamidofos, Ethoprophos and Malathion levels were within acceptable by USEPA (2009) and EU (2013) (Table 4.10). Dimethoate, Chlorpyrifos, Phorate, and Profenofos in the soil samples from Farm A was also above that reported by Asare (2011) for some OPPs in soils sampled from watermelon farms in Nsadwir in the Komenda Edina Eguafo Abirim (KEEA) Municipality of the Central Region. The OPP levels (0.007 – 1.485 mg/kg) recorded in this work were generally above (0.520 – 0.97 mg/kg) reported in a study by Mahmud *et al.* (2015) in some soils sampled from Gashua, Bade local government area, Yobo state, Nigeria.

Mean level of profenofos (0.527 ± 0.367 mg/kg) obtained in this study was above (0.03 ± 0.001 mg/kg) reported by Fosu – Mensah *et al.* (2016) in a similar work. The difference

between profenofos level recorded in this work and that reported by Fosu – Mensah *et al.* (2016) could be due to difference in geographical locations and extent to which soils were contaminated.

Table 4.10: Organophosphate pesticides levels (mg/kg) in soil samples from Farm A (cocoyam) in the Asante Akyem Central Municipality

Pesticides	Min. conc.	Max. conc.	Mean conc.	SD	USEPA/EU
Methamidofos	0.019	0.030	0.025	0.006	0.03
Dimethoate	0.966	1.485	1.165	0.237	0.03
Chlorpyrifos	0.255	0.805	0.529	0.233	0.03
Parathion	0.102	0.910	0.577	0.351	0.04
Chlorfenvinphos	0.017	0.803	0.710	0.343	0.05
Malathion	0.027	0.079	0.045	0.024	0.05
Phorate	0.105	0.565	0.324	0.196	0.05
Profenofos	0.128	0.750	0.431	0.262	0.05
Ethoprophos	0.005	0.065	0.037	0.026	0.05
Diazinon	0.007	0.039	0.021	0.014	0.03

Table 4.11: Organophosphate pesticides levels (mg/kg) in soil samples from farm B (cassava) in the Asante Akyem Central Municipality

Pesticides	Min. conc.	Max. conc.	Mean conc.	SD	USEPA/EU
Methamidofos	0.008	0.088	0.029	0.040	0.03
Dimethoate	0.559	1.480	0.917	0.431	0.03
Chlorpyrifos	0.196	0.530	0.402	0.153	0.03
Parathion-methyl	0.058	0.856	0.495	0.343	0.04
Chlorfenvinphos	0.085	0.900	0.514	0.335	0.05
Malathion	0.030	0.088	0.708	0.026	0.05
Phorate	0.299	0.607	0.420	0.148	0.05
Profenofos	0.025	0.499	0.194	0.220	0.05
Ethoprophos	0.014	0.050	0.038	0.016	0.05
Diazinon	0.008	0.044	0.024	0.017	0.03

4.4.6 Organophosphate Levels in Soils from the Cassava Farm

OPPs levels in the soils sampled from farm B ranged from 0.008 – 1.480 mg/kg). The levels were Dimethoate (0.917 ± 0.431 mg/kg) > Malathion (0.708 ± 0.026 mg/kg) > Chlorfenvinphos (0.514 ± 0.335 mg/kg) > Parathion (0.495 ± 0.343 mg/kg) > Phorate (0.420 ± 0.148 mg/kg) > Chorpyrifos (0.402 ± 0.153 mg/kg) > Ethoprophos (0.038 ± 0.016 mg/kg) > Methamidofos (0.029 ± 0.040 mg/kg) > Diazinon (0.024 ± 0.017 mg/kg). Diazinon, Malathion, Profonofos, Chlorfenvinphos, Parathion, Phorate, and Chlorpyrifos contents of the soil samples from farm B were above (0.03), (0.05), (0.05), (0.05), (0.04), (0.05), and (0.03) respectively by the USEPA (2009) and EU (2013) recommended to be in soil. Profenofos contents of soil were also above 0.03 ± 0.001 mg/kg recorded by Fofu-Mensah *et al.* (2016). The difference in pesticides levels could be attributed to different geographical locations where soil samples were collected for each of the studies. However, mean levels Diazinon, Methamidofos, and Ethoprophos detected in soil samples from in farm B were below (0.03), (0.03) and (0.05) respectively recommended by USEPA (2009) and EU (2013) (Table 4.11). Generally, levels of the investigated OPPs in the soil samples from farm B were above those documented for the same OPPs in a research work by Supriyadi *et al.* (2015). This suggests that, cassava farmers in the Asante Akyem Central Municipality use OPPs extensively in farming to maximize crop yield and revenue.

4.4.7 Organophosphate Levels in Soils from the Maize Farm

OPPs levels in the soil sampled from 0 – 20cm depth in the maize farms (Farm C) were statistically treated and the data reported (Table 4.12). The levels of OPPs obtained in soil samples ranged from 0.0070 – 1.302 mg/kg (Table 4.12).

Table 4.12: Organophosphate pesticides level (mg/kg) in soil samples from farm C (maize) in the Asante Akyem Central Municipality

Pesticides	Min. conc.	Max. conc.	Mean conc.	SD	USEPA/EU
Methamidofos	0.010	0.046	0.032	0.018	0.03
Dimethoate	0.676	1.302	0.993	0.264	0.03
Chlorpyrifos	0.055	0.955	0.444	0.460	0.03
Parathion-methyl	0.285	0.505	0.438	0.104	0.04
Chlorfenvinphos	0.124	0.750	0.447	0.269	0.05
Malathion	0.004	0.030	0.018	0.012	0.05
Phorate	0.034	0.552	0.510	0.351	0.05
Profenofos	0.034	0.852	0.510	0.351	0.05
Ethoprophos	ND	0.050	0.031	0.024	0.05
Diazinon	0.006	0.050	0.026	0.020	0.03

ND = Not detected

The OPPs levels were Dimethoate (0.993 ± 0.264 mg/kg) > Phorate (0.510 ± 0.351 mg/kg) and Profenofos (0.510 ± 0.351 mg/kg) > Chlorfenvinphos (0.447 ± 0.269 mg/kg) > Chlorpyrifos (0.444 ± 0.460 mg/kg) > Parathion (0.438 ± 0.104 mg/kg) > Methamidofos (0.032 ± 0.018 mg/kg) > Ethoprophos (0.031 ± 0.024 mg/kg) > Malathion (0.018 ± 0.012 mg/kg). Although Methamidofos, Ethoprophos and Malathion levels were within USEPA/EU recommended maximum residue limits in soil, Dimethoate, Phorate, Profenofos, Chlorfenvinphos, Chlorpyrifos, and Parathion levels in the soil samples were above USEPA/EU recommended levels (Table 4.12). Mean Diazinon, Ethoprophos, Methamidofos, and Malathion contents of the soil samples were also below (0.018 ± 0.012 , 0.026 ± 0.020 , 0.031 ± 0.024 mg/kg) respectively detected in some soil samples from Nsadwir in the Central Region by Asare (2011).

4.4.8 Comparison of Organophosphate Pesticides Levels Between Soil Samples from the Study Farms

Comparison of the OPPs levels recorded for the soils sampled from the study farms showed that, Dimethoate contents were very high in soils of the farms were very high. Dimethoate levels across the farms were, farm A (1.16 ± 0.237 mg/kg) > farm C (0.993 ± 0.460 mg/kg) > farm B (0.917 ± 0.431 mg/kg). Paration, Chlorfenvinphos, Chlorpyrifos, Profenofos and Phorate levels were also high in farm A and farm C. Farm B had high level of Malathion (0.708 ± 0.026 mg/kg).

Reported levels were above USEPA (2009) and EU (2013) recommended maximum residue limits (Table 4.12). Elevated levels of Dimothoate, Parathion, Chlorfenvinphos, Chlorpyrifos, Profenofos and Phorate recorded could be attributed to their continuous use by farmers. Also, according to Asare (2011) the presence could be due to their strong binding ability to soil particles.

Dimethoate, Chlorpyrifos, Profenofos and Phorate reported for the investigated soil samples were above those reported by Asare, (2011). There were lower levels of Methamidofos, Diazinon and Ethoprophos across all the investigated farms. Mean Diazinon levels were cassava farm B (0.029 ± 0.040 mg/kg) > maize farm (Farm C) (0.026 ± 0.020 mg/kg) > (0.021 ± 0.006 mg/kg) cocoyam farm (Farm A). Malathion levels recorded across all investigated farms were cassava farm (Farm B) (0.708 ± 0.026 mg/kg) > cocoyam farm (Farm A) (0.045 ± 0.024 mg/kg) > maize farm (farm C) (0.018 ± 0.012 mg/kg).

Ethoprophos levels recorded across soils in farms investigated were cassava farm (farm B) (0.038 ± 0.016 mg/kg) cocoyam farm (A) (0.037 ± 0.026 mg/kg) maize farm (C) (0.031 ± 0.024 mg/kg) maize Farm (C). Mean levels of Methamidofos were Farm C (0.032 ± 0.018 mg/kg) > Farm A (0.031 ± 0.242 mg/kg) > Farm B (0.029 ± 0.040 mg/kg). Diazinon, Malathion, Ethoprofos and Methamidofos contents in the soils of the investigated farms were less than USEPA (2009) and EU (2013) recommended maximum residual limits (Table 4.12). The low levels of Diazinon, Malathion, Ethoprofos and Methamidofos pesticides could be ascribed to their limited application by farmers in the study area and their higher rate of decay. Faster rates of their degradation by sunlight could also explain their low levels recorded as ascribed by Asare (2011).

4.4.9 Carbamate Levels in Soil Sample from the Farm A (cocoyam)

Carbamate pesticides levels in soil samples taken at a depth 0 – 20 cm were determined and the results presented (Table 4.13). Carbamate levels in the soil samples from Farm A ranged from 0.054 (Carbaryl) – 0.900 mg/kg (Carbofuran) (Tables 4.13, 4.14 and 4.15).

Table 4.13: Carbamate Levels (mg/kg) in Soil Samples from Farm A (cocoyam) in the Asante Akyem Central Municipality

Pesticides	Min. conc.	Max. conc.	Mean conc.	SD	USEPA/EU
Carbofuran	0.055	0.900	0.413	0.373	0.030
Carbaryl	0.054	0.650	0.354	0.256	0.030

Carbamate levels in the soil samples from the farm A were Carbofuran (0.413 ± 0.373 mg/kg) > Carbaryl (0.354 ± 0.256 mg/kg). The Carbofuran and Carbaryl levels that occurred in the soil sampled from farm A were less than recommended maximum limits

set by the USEPA (2009) and EU (2013), (Table 4.13). The mean values of carbamates reported herein were above 0.335 mg/g (Carbofuran) and 0.296 mg/g (Carbaryl) reported by Rosmalina *et al.* (2019) in a similar study.

4.4.10 Carbamate Levels in Soil Sample from Farm B (cassava)

Carbamate levels in the soil samples from farm B ranged from 0.026 (Carbaryl) – 0.0551 mg/kg (Carbofuran) (Table 4.14). Levels of carbamate in the soil from farm B were Carbaryl (0.402 ± 0.310 mg/kg) > Carbofuran (0.366 ± 0.223 mg/kg). Carbofuran and Carbaryl levels that occurred in the soil of the cocoyam farm (farm B) were below recommended maximum limits set by USEPA (2009) and EU (2013) (Table 4.14). These mean values were above 0.335 mg/g (Carbofuran) and 0.2956 mg/g (Carbaryl) recorded by Rosmalina *et al.* (2019) in a similar work.

Table 4.14: Carbamate pesticides levels (mg/kg) in soil sample from farm B (cassava) from Asante Akyem Central Municipality

Pesticides	Min. conc.	Max. conc.	Mean conc.	SD	USEPA/EU
Carbofuran	0.055	0.551	0.366	0.223	0.030
Carbaryl	0.026	0.754	0.402	0.310	0.030

4.4.11 Carbamate Levels in Soil Sample from Farm C

Carbamate levels recorded for soil samples from farm C ranged from 0.035 (Carbaryl) – 0.597 mg/kg (Carbofuran) (Table 4.15). Mean of carbamate levels in the soil sampled from farm C were Carbofuran (0.308 ± 0.218 mg/kg) > Carbaryl (0.293 ± 0.220 mg/kg). Mean levels of Carbofuran and Carbaryl recorded for the soil samples in the farms C were below recommended limits set by the USEPA (2009) and EU (2013) (Table 15). Levels of

Carbofuran and Carbaryl detected herein were above 0.000335 mg/g (Carbofuran) and 0.000296 mg/g (Carbaryl) reported by Rosmalina *et al.* (2019) in a similar work.

Table 4.15: Carbamate Levels (mg/kg) in the Soil Samples from Farm C (maize) in the Asante Akyem Central Municipality

Pesticides	Min. conc.	Max. conc.	Mean conc.	SD	USEPA/EU
Carbofuran	0.105	0.597	0.308	0.218	0.020
Carbaryl	0.035	0.550	0.293	0.220	0.020

4.4.12 Comparison of Carbamate Pesticides Levels Between the Soils from the Various Farms Used in the Study

Levels of Carbofuran in soil sampled from the farms investigated were farm A (0.413 ± 0.373 mg/kg) > farm B (0.366 ± 0.223 mg/kg) > farm C (0.308 ± 0.218 mg/kg). The results indicated that, means of Carbaryl were farm B (0.402 ± 0.354 mg/kg) > farm A (0.354 ± 0.256 mg/kg) > farm C (0.293 ± 0.220 mg/kg).

High levels of Carbofuran recorded suggest that carbofuran resist degradation than Carbaryl, hence its elevated levels. The recorded high levels of carbamate (Carbofuran and Carbaryl) in the soil sample collected from the investigated farms could be ascribed to an excessive application of these pesticides by farmers on crops. Generally, levels of Carbofuran and Carbaryl in the soil samples studied were above levels of Carbofuran and Carbaryl reported by Rosmalina *et al.* (2019). The differences observed in the levels of Carbofuran and Carbaryl recorded in this study and those reported in Rosmalina *et al.*, (2019) could be ascribed to difference in geographical locations for the two studies. The rate at which Carbofuran and Carbaryl were used by farmers in the Asante – Akyem Central

Municipality of the Ashanti region might have led to difference in high levels of Carbofuran and Carbaryl in the soils sampled.

4.5 Levels of Organochlorine, Organophosphate, and Carbamate Pesticides in Selected Food Crops from Various Farms

Selected crops (cocoyam, cocoyam leaves, cassava and maize) samples collected from investigated farms at Konongo, Ohene Nkwanta, Adumkrom and Nyaaboo in the Asante Akyem Central Municipality were also analyzed for pesticides residue. Nine (9) different organochlorine pesticides, ten (10) organophosphate pesticides and two (2) different carbamates were detected in the selected crop samples. Levels of pesticides detected in selected food crops were determined statistically with Microsoft Excel (2016 version) and the results presented (Figure 4.1 – 4.8 and Table 4.16 – 4.19). The mean levels of organochlorine, organophosphate and carbamate pesticides determined were compared with the United State Environmental Protection Agency (USEPA) and European Union (EU) recommended maximum residual levels.

4.5.1 Levels of Organochlorine Pesticides (OCPs), in Cocoyam Tubers

Cocoyam samples collected were analyzed for organochlorine pesticide residue. Detected mean levels of OCPs were presented (Figure 4.1) and compared with USEPA and EU levels. Mean concentrations of organochlorine pesticides (OCPs) in cocoyam the farms were computed and the results presented graphically (Figure 4.1). Levels of OCPs in cocoyam samples ranged Aldrin (0.001 ± 0.002 mg/kg) to Methoxychlor (0.049 ± 0.004 mg/kg). Organochlorine pesticides recorded in cocoyam crops investigated were

Methoxychlor (0.049 ± 0.004 mg/kg) > Endrin (0.038 ± 0.064 mg/kg) > Dieldrin (0.026 ± 0.003 mg/kg) > Endosulfan (0.011 ± 0.009 mg/kg) > Lindane (0.004 ± 0.005 mg/kg) > Heptachlor (0.003 ± 0.006 mg/kg) > Chlordane (0.002 ± 0.001 mg/kg) > Aldrin (0.001 ± 0.002 mg/kg). Mean levels of Methoxychlor, Endrin and Dieldrin recorded in cocoyam samples were higher than the recommended maximum residue limits of reported by USEPA (2009) and EU (2013). High levels of Methoxychlor, Endrin and Dieldrin in the cocoyam could be attributed to the shorter duration from the time of application of these pesticides to the time of harvesting of the crops for the analysis, which indicates that, there have not been any significant loss through leaching and degradation. Levels of Methoxychlor, Endrin and Dieldrin recorded were above mean levels of Aldrin (0.00828 mg/kg), Dieldrin (0.0056 mg/kg) and Heptachlor (0.0038 mg/kg) reported by Asare (2011) in watermelon fruits from Nsadwir in the Central Region.

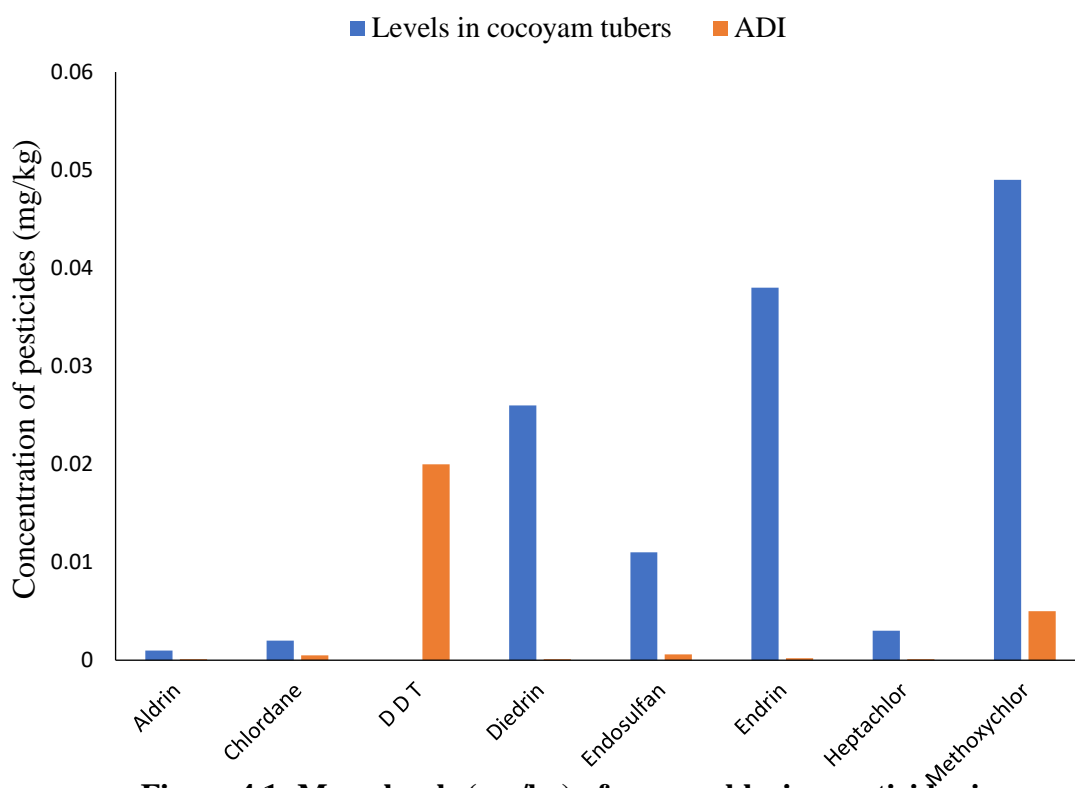


Figure 4.1: Mean levels (mg/kg) of organochlorine pesticides in cocoyam heads

Levels of Aldrin, Chlordane, Heptachlor, Lindane, and Endosulfan recorded were less than recommended maximum residue limits reported by the USEPA (2009) and the EU (2013). The low levels might be due to quick metabolism of organochlorine pesticides in cocoyam plants as report by Horská *et al.* (2020) and Asare (2011). Low levels of OCPs could also be that farmers applied them at lower levels than recommended by manufactures or at early stage in the development of the crops as indicated by Asare (2011) and Kocourek *et al.* (2017).

Table 4.16: Organophosphate pesticides levels (mg/kg) in cocoyam from the Asante – Akyem Central Municipality

Pesticides	Min. conc.	Max. conc.	Mean conc.	SD	USEPA/EU
Methamidofos	ND	0.019	0.005	0.006	0.01
Dimethoate	ND	0.028	0.005	0.008	0.01
Chlorpyrifos	0.002	0.220	0.028	0.049	0.01
Parathion	ND	0.054	0.006	0.012	0.01
Chlorfenvinphos	0.011	0.208	0.073	0.062	0.01
Malathion	1.658	7.504	4.870	1.489	0.02
Phorate	0.020	0.224	0.078	0.061	0.01
Profenofos	ND	0.060	0.008	0.037	0.01
Ethoprofos	0.004	0.045	0.016	0.012	0.01
Diazinon	0.002	0.050	0.016	0.011	0.01

4.5.2 Levels of Organophosphate Pesticides (OPPs) in Cocoyam Tubers

Cocoyam samples obtained from the farms were analyzed for organophosphate pesticides residues. Levels of OPPs were reported in the form of Mean \pm standard deviation and results graphically represented (Table 4.16) and then compared with acceptable levels of OPPs in foods.

Levels of organophosphate pesticides (OPPs) in cocoyam samples ranged from 0.005 \pm 0.006 mg/kg (Methamidofos) – 4.870 \pm 1.489 mg/kg (Malathion). Mean concentration of Malathion (4.870 \pm 1.489 mg/kg) > Phorate (0.078 \pm 0.061 mg/kg) > Chlorfenvinphos (0.073 \pm 0.062 mg/kg) > Chlorpyrifos (0.028 \pm 0.049 mg/kg) > Profenofos (0.008 \pm 0.037 mg/kg) > Ethoprofos and Diazinon (0.016 mg/kg) > Parathion (0.006 mg/kg) > Methamidofos and Dimethoate (0.005 mg/kg). Levels of Malathion, Phorate, Chlorfenvinphos, Chlorpyrifos, Ethoprofos, and Diazinon recorded in this study were above recommended maximum residue limits reported by the USEPA (2009) and EU

(2013). The high levels of Malathion, Phorate, Chlorfenvinphos, Chlorpyrifos, Ethoprophos, and Diazino could be due to over application of these pesticides and the inability of crops to breakdown the pesticides more quickly, leading to their buildup in the food (Asare 2011). Concentration of Methamidophos, Dimethoate, Parathion and Profenofos (0.005 ± 0.006 mg/kg, 0.005 ± 0.008 mg/kg, 0.006 ± 0.012 mg/kg and 0.008 ± 0.037 mg/kg) respectively recorded were less than recommended maximum residue limits reported by the USEPA (2009) and the EU (2013) (Figure 4.2).

Levels of Ethoprophos (0.016 ± 0.012 mg/kg), Phorate (0.078 ± 0.061 mg/kg), Diazinon (0.016 ± 0.011 mg/kg), Chlorpyrifos (0.028 ± 0.049 mg/kg), Chorfenvinphos (0.073 ± 0.062 mg/kg) and Dimethoate (0.005 ± 0.008 mg/kg) recorded fall below levels of Ethoprophos, Phorate, Diazinon, Chlorpyrifos, Chlorfenvinphos and Dimethoate (1.134 mg/kg, 0.678 mg/kg, 0.029 mg/kg, 0.041 mg/kg, 0.315 mg/kg and 0.043 mg/kg) respectively reported by Armah (2011) in cabbage cultivated in Cape Coast, Ghana. However, levels of same OPPs (Table 4.16) recorded in this study were above levels of Methamidophos (0.00498 mg/kg), Ethoprophos (0.00395 mg/kg), Phorate (0.00935 mg/kg), Diazinon (0.00575 mg/kg), Dimethoate (0.0219 mg/kg), Parathion (0.0088 mg/kg), Profenofos (0.00665 mg/kg), Malathion (0.0122 mg/kg) and Chlorfenvinphos (0.0077 mg/kg) reported by Asare (2011) in watermelon fruit in the Central Region of Ghana. The difference could be due to difference in geographical location for the study site.

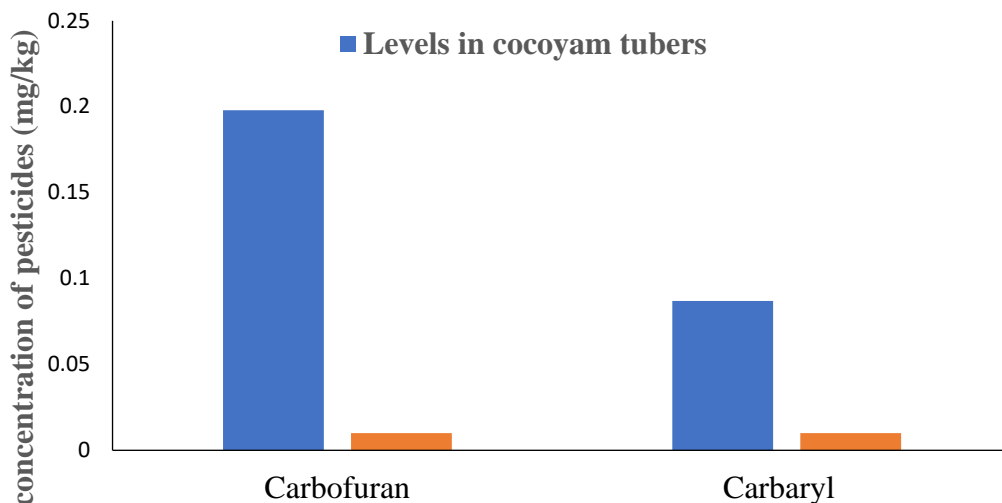


Figure 4.2: Mean levels (mg/kg) of carbamate pesticides in cocoyam tubers

4.5.3 Levels of Carbamate Pesticides in Cocoyam Tubers

Mean concentrations of carbamate pesticides detected in the cocoyam were also computed, graphed and compared with USEPA and the European Union recommended maximum residual levels (Figure 4.2).

Results of carbamate pesticides in cocoyam samples as presented (Figure 4.3) showed ranged of 0.087 ± 0.103 mg/kg (Carbofuran) – 0.198 ± 0.088 mg/kg (Carbaryl). Mean concentration of Carbaryl (0.198 ± 0.088 mg/kg) > Carbofuran (0.087 ± 0.103 mg/kg). Levels of Carbaryl and Carbofuran reported in this study were all above the recommended MRLs reported by the USEPA (2009) and the EU (2013) (Figure 4.2).

4.5.4 Levels of Organochlorine Pesticides (OCPs) in Cocoyam Leaf Samples

Organochlorine pesticides levels in cocoyam leave samples were detected and result analyzed and presented graphically (Figure 4.3). The levels of organochlorine pesticides

ranged from 0.002 ± 0.001 mg/kg (Aldrin) – 0.086 mg/kg (Endosulfan). The levels of OCPs recorded in the cocoyam leaf samples from the farms were Endosulfan (0.086 ± 0.008 mg/kg) > Endrin (0.034 ± 0.051 mg/kg) > Lindane (0.006 ± 0.003 mg/kg) > Methoxychlor and Heptachlor (0.005 ± 0.003 mg/kg) > Dieldrin and DDT (0.003 ± 0.001 mg/kg) > Aldrin and Chlordane (0.002 ± 0.001 mg/kg). The levels of Endosulfan and Endrin reported were above recommended maximum residue limits reported by the USEPA (2009) and EU (2013) (Figure 4.3). Mean levels of Aldrin, Chlordane, DDT, Dieldrin, Heptachlor, Lindane and Methoxychlor recorded in cocoyam leaf were less than the recommended MRLs reported by the USEPA (2009) and the EU (2013).

Low levels of Aldrin, Chlordane, DDT, Dieldrin, Heptachlor, Lindane and Methoxychlor in the cocoyam leaf samples could be ascribed to quick breakdown of these pesticides in the crops (Asare 2011). Low rate of applications of these pesticides could also be a factor of their minimum levels reported.

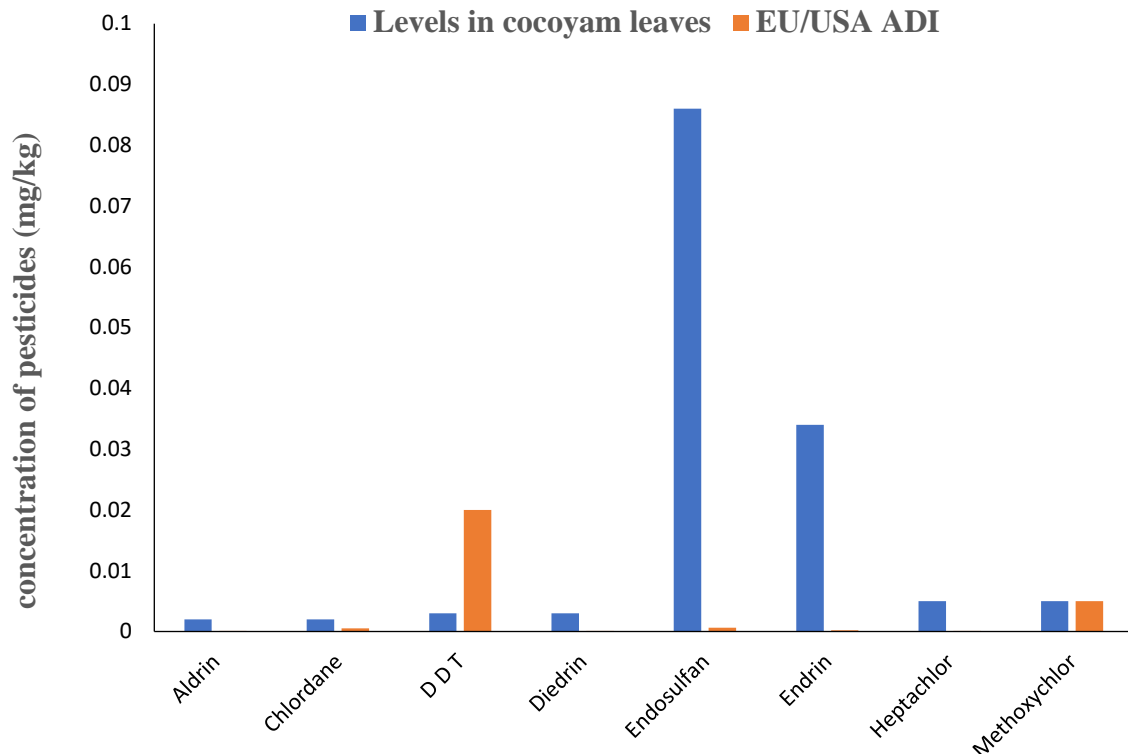


Figure 4.3: Mean levels of organochlorine pesticides in cocoyam leaves

Recorded levels of Aldrin, Chlordane, DDT, Dieldrin, Heptachlor, Lindane and Methoxychlor collaborated well with levels of 0.0056 mg/kg (Aldrin), 0.0068 mg/kg (DDT), 0.0038 mg/kg (Dieldrin), 0.0082 mg/kg (Heptachlor), 0.00713 mg/kg (Lindane) and 0.00646 mg/kg (Methoxychlor) reported by Asare (2011) in watermelon from Nsadwir, in the Central region. The results of OCPs were below mean concentrations of Heptachlor (0.323 ± 0.048 mg/kg), Aldrin (0.391 ± 0.065 mg/kg), Dieldrin (1.465 ± 0.875 mg/kg), and Endrin (0.351 ± 0.371 mg/kg) reported by Kocourek *et al.* (2019) in leafy vegetables grown in South – Western Nigeria. The differences in the levels could be as a result of different geographical location for the study. Organophosphate pesticide residue. Levels of OPPs were statistically treated and result reported graphically (Figure 9) and compared with acceptable levels of OPPs in foods/vegetables.

Table 4.17: Organophosphate pesticides levels (mg/kg) in cocoyam leaves from the Asante Akyem Central Municipality

Pesticides	Min. conc.	Max. conc.	Mean conc.	SD	USEPA/EU
Methamidofos	0.001	0.015	0.004	0.005	0.01
Dimethoate	0.002	0.015	0.005	0.004	0.01
Chlorpyrifos	0.003	0.309	0.025	0.068	0.01
Parathion	0.001	0.092	0.009	0.020	0.01
Chlorfenvinphos	ND	0.200	0.059	0.065	0.01
Malathion	ND	6.900	2.683	2.235	0.02
Phorate	0.009	0.224	0.070	0.063	0.01
Profenofos	ND	0.072	0.007	0.016	0.01
Ethoprophos	0.003	0.050	0.015	0.013	0.01
Diazinon	0.003	0.052	0.017	0.013	0.01

Levels of organophosphate pesticides detected in cocoyam leaves ranged from 0.004 ± 0.005 mg/kg (Methamidophos) to 2.683 ± 2.235 mg/kg (Malathion). Concentrations of OPPs recorded in cocoyam leaves were Malathion (2.683 ± 2.235 mg/kg) > Phorate (0.070 ± 0.063 mg/kg) > Chlorfenvinphos (0.059 ± 0.065 mg/kg) > Chlorpyrifos (0.025 ± 0.068 mg/kg) > Diazinon (0.017 ± 0.013 mg/kg) > Ethoprophos (0.015 ± 0.013 mg/kg) > Parathion (0.009 ± 0.020 mg/kg) > Profenofos (0.007 ± 0.016 mg/kg) > Dimethoate (0.005 ± 0.004 mg/kg) > Methamidophos (0.004 ± 0.005 mg/kg).

Mean concentration of Malathion, Phorate, Chlorfenvinphos, Chlorpyrifos, Diazinon, and Ethoprophos reported were higher than the recommended maximum residue limits reported by the USEPA (2009) and EU (2013) (Table 4.17). These high levels of Malathion, Phorate, Chlorfenvinphos, Chlorpyrifos, Diazinon, and Ethoprophos recorded could be due to the fact that they were applied to the cocoyam few weeks prior to harvest or inability of

the cabbage to breakdown the pesticides more quickly as reported by Asare (2011) and Glotfelty *et al.* (1989).

Levels of Methamidophos (0.004 ± 0.005 mg/kg), Dimethoate (0.005 ± 0.004 mg/kg), Parathion (0.009 ± 0.020 mg/kg), and Profenofos (0.007 ± 0.016 mg/kg) were below recommended maximum residue limits reported by the USEPA (2009) and EU (2013).

The levels of Diazinon, Dimethoate and Chlorpyrifos (0.017 ± 0.013 mg/kg, (0.005 ± 0.004 mg/kg and 0.025 ± 0.068 mg/kg) respectively were below the levels of Diazinon (0.085 mg/kg), Dimethoate (0.081 mg/kg) and Chlorpyrifos (0.084 mg/kg) reported by Asare (2011) in watermelon fruits grown in Nsawri in the Central Region and levels of Dimethoate (0.07 mg/kg), Chlorpyrifos (0.4 mg/kg) in cabbage samples in Accra, Ghana of reported by Achiri *et al.* (2016).

4.5.5 Levels of Carbamate Pesticides in Cocoyam Leave Samples

Cocoyam leaves heads from five different farms located in Nyaboo, Ohene – Nkwanta, Odumasi, Konongo and Adumkrom were included in this study. Mean concentrations of carbamate pesticides in the cocoyam leaves heads were presented graphically (Figure 4.6) below.

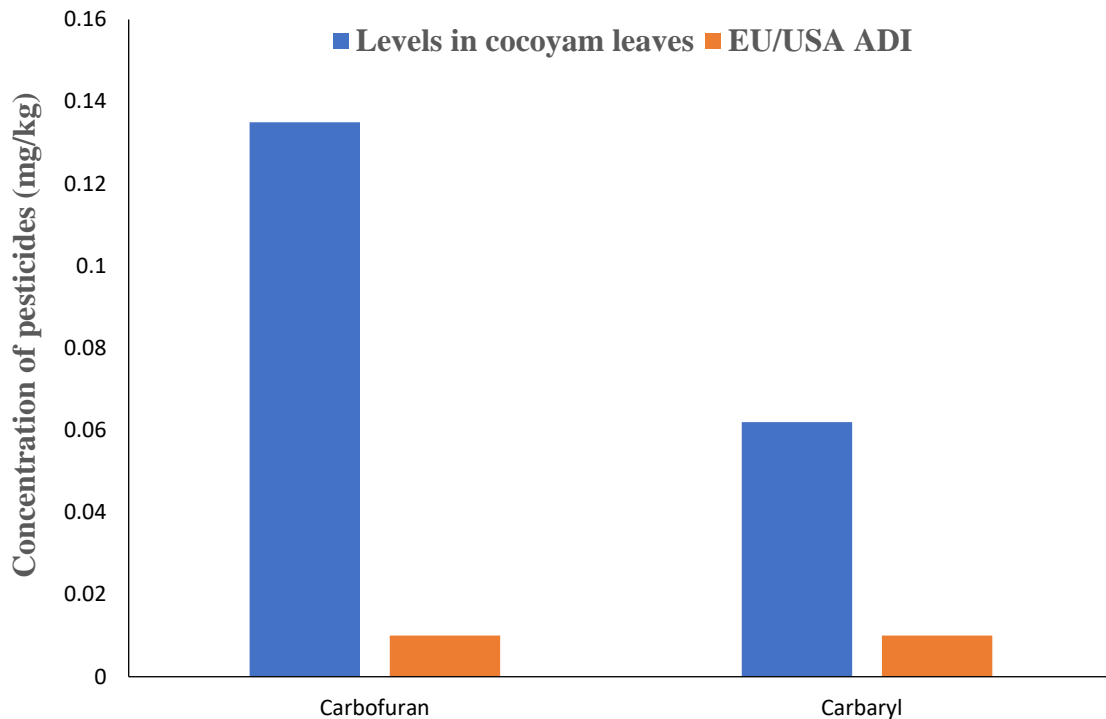


Figure 4.4: Mean levels (mg/kg) of carbamate pesticides in cocoyam leaves

In cocoyam leaves samples, two carbamate pesticides determined were Carbaryl and Carbofuran. The results presented (Figure 4.4) showed that levels of Carbofuran (0.135 ± 0.059 mg/kg) > Carbaryl (0.062 ± 0.063 mg/kg). Levels of carbofuran and carbaryl recorded were above recommended maximum residue limits reported by the USEPA (2009) and EU (2013).

Higher levels of Carbofuran and Carbaryl in cocoyam leaf samples could be attributed to their excessiv or repeated use by farmers as reported by Asare (2013). Periods between the last application on these pesticides and the harvesting time could also be a factor to be considered when discussing the high levels of carbofuran and carbaryl pesticides reported in this study.

4.5.6 Levels of Organochlorine Pesticides (OCPs) in Cassava Samples

Organochlorine pesticides (OPCs) levels were analysed in cassava sampled obtained from the selected farms in the Asante Akyem Municipal. The results obtained were treated statistically at 95% confidence level and mean levels of OCPs in the cassava sample graphically presented (Figure 4.5).

Organochlorine pesticides levels ranged from 0.002 ± 0.002 mg/kg (DDT) to 0.215 ± 0.013 mg/kg (Endosulfan). Mean concentrations of OCPs in cassava samples recorded from highest to the lowest were Endosulfan (0.215 ± 0.013 mg/kg), Methoxychlor (0.010 ± 0.006 mg/kg), Heptachlor (0.006 ± 0.008 mg/kg), Endrin (0.005 ± 0.004 mg/kg), Aldrin (0.005 ± 0.003 mg/kg), Chlordane (0.004 ± 0.002 mg/kg), Dieldrin (0.003 ± 0.003 mg/kg) and D D T (0.002 ± 0.002 mg/kg). Levels of Methoxychlor, Heptachlor, Endrin, Aldrin, Chlordane, Dieldrin, D D T recorded were below recommended maximum residual limits (0.0050, 0.0001, 0.0002, 0.0001, 0.0005, 0.000 and 0.0200 mg/kg) documented by USEPA (2009) and EU (2013).

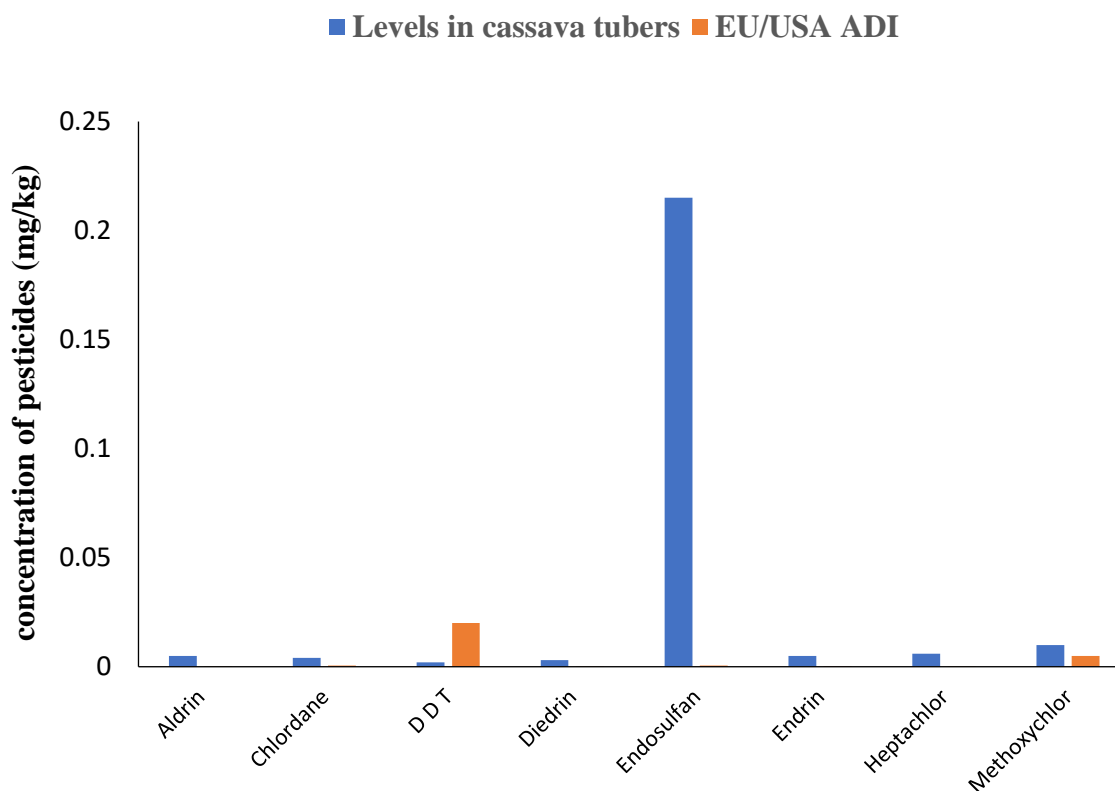


Figure 4.5: Mean levels (mg/kg) of organochlorine pesticides in cassava tubers

Low levels of Methoxychlor, Lindane, Heptachlor, Endrin, Aldrin, Chlordane, Dieldrin, DDT could be attributed to the ban imposed on the use of some of the above pesticide for agricultural purposes in Ghana, Lindane for example was sold in Ghanaian markets as Gammalin 20 and was commonly used until 2007 as a result of its persistence and toxicity to non-target organisms (Agbeve *et al.*, 2014). Level of Lindane observed was less than the mean concentration of 0.01 mg/kg reported by Frimpong *et al.*, (2012). Mean levels of Endrin, Endosulfan and Dieldrin observed in this study collaborated with the mean levels of 0.007, 0.022 and 0.008 mg/kg reported by Ogah *et al.* (2011) in maize grain, for Endrin, Endosulfan and Dieldrin respectively.

4.5.7 Levels of Organophosphate Pesticides (OPPs) in Cassava Samples

Cassava samples from the farms in the Asante Akyem Municipality were analyzed for levels of organophosphate pesticides. Results of OPPs obtained were treated and presented graphically (Table 4.18). Methamidophos, Dimethoate, Chlorpyrifos, Parathion, Chlorfenvinphos, Malathion, Phorate, Ethoprophos and Diazinon were detected in cassava sample for this study. Levels of OPPs ranged from not detected ND (Profenofos) to 7.210 ± 2.282 mg/kg (Malathion). Average levels of OPPs detected in cassava samples were Malathion (7.210 ± 2.282) > Phorate (0.119 ± 0.094) > Chlorfenvinphos (0.071 ± 0.050) > Chlorpyrifos (0.026 ± 0.036) > Ethoprophos (0.023 ± 0.015) > Diazinon (0.021 ± 0.014) > Dimethoate (0.015 ± 0.014) > Parathion (0.008 ± 0.017) > Methamidophos (0.007 ± 0.005 mg/kg). Levels of Malathion, Dimethoate, Chlorpyrifos, Chlorfenvinphos, Phorate, Ethoprophos and Diazinon recorded were above USEPA/EU recommended maximum residue limits (MRLs) (Table 4.18). Elevated levels of these OPPs in cassava samples could be ascribed to the fact that cassava roots absorbed more pesticides from the soil due to high pesticides accumulation in the soil due excessive used of pesticides by farmers as reported by Öztaş *et al.* (2018). Continuous farming on the same piece of land as reported by Wongnaa *et al.* (2019) could also be a contributing factor to the high levels of organophosphate pesticides detected as cassava roots would be continually absorbing accumulated undegraded pesticides molecules from soils. Levels of Methamidophos and Parathion recorded in this study were within USEPA (2009) and EU (2013) recommended maximum residue limits (MRLs) (Table 4.18).

Table 4.18: Organophosphate pesticides levels (mg/kg) in cassava from the Asante Akyem Central Municipality

Pesticides	Min. conc.	Max. conc.	Mean conc.	SD	USEPA/EU
Methamidofos	0.001	0.020	0.007	0.005	0.01
Dimethoate	ND	0.050	0.015	0.014	0.01
Chlorpyrifos	ND	0.150	0.026	0.036	0.01
Parathion	ND	0.070	0.008	0.017	0.01
Chlorfenvinphos	0.009	0.209	0.071	0.050	0.01
Malathion	4.000	10.910	7.210	2.282	0.02
Phorate	0.016	0.268	0.119	0.094	0.01
Profenofos	ND	ND	ND	ND	0.01
Ethoprophos	0.006	0.055	0.023	0.015	0.01
Diazinon	0.004	0.050	0.021	0.014	0.01

Levels of Chlorpyrifos (0.026 ± 0.036 mg/kg) and Parathion (0.008 ± 0.017 mg/kg) observed in this study were below concentrations of Chlorpyrifos (0.049 mg/kg) and Parathion (0.043 mg/kg) indicated by Akoto *et al.* (2013) in similar study. However, level of Malathion (7.210 ± 2.282 mg/kg) recorded herein was above 1.567 mg/kg (Malathion) reported by Akoto *et al.* (2013). (2013. Also, Methamidophos (0.007 ± 0.005 mg/kg) observed agreed to Methamidophos (0.0086 mg/kg) reported by Asare (2011) whilst levels of Ethoprophos (0.023 ± 0.015 mg/kg), Phorate (0.119 ± 0.094 mg/kg), Diazinon (0.021 ± 0.014 mg/kg), and Chlorfenvinphos (0.071 ± 0.050 mg/kg) were above 0.0077 mg/kg, 0.0767 mg/kg, 0.005 mg/kg, and 0.006 mg/kg for Ethoprophos, Phorate, Diazinon, and Chlorfenvinphos respectively reported by Asare (2011) in similar studies. The differences in the levels of OPPs reported could be due to different geographical location for the studies.

4.5.8 Levels of Carbamate Pesticides in Cassava Samples

Carbamate pesticides levels were also determined in cassava samples obtained from the farms in the study sites. Analysis of results of carbamate pesticides level recorded in cassava samples were presented graphically (Figure 4.9).

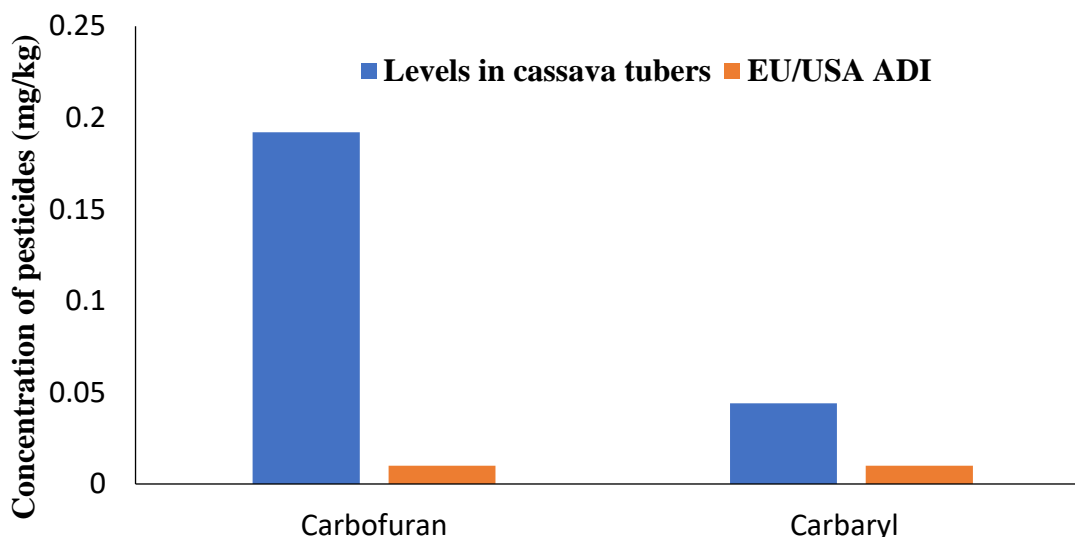


Figure 4.6: Mean levels (mg/kg) of carbamate pesticides in cassava tubers

Mean levels of carbamate pesticides levels in cassava sample ranged from 0.044 ± 0.06 (Carbaryl) – 0.192 ± 0.148 mg/kg (Carbofuran). Carbofuran levels (0.192 ± 0.148) > Carbaryl (0.044 ± 0.065 mg/kg). Levels of Carbofuran and Carbaryl observed were higher than the recommended MRLs reported by the USEPA (2009) and the EU (2013). Levels of Carbaryl (0.044 ± 0.065 mg/kg) recorded in the study were in agreement to the level of 0.038 mg/kg (Carbaryl) indicated by Ogah *et al.* (2012) in Nigeria, however, levels of Carbofuran (0.192 ± 0.148 mg/kg) reported in this study exceeds levels of Carbofuran (0.0841 mg/kg) indicated by Ogah *et al.*, (2012).

4.5.9 Levels of Organochlorine Pesticides (OCPs) in Maize Samples

Maize heads from different farms from Ohene – Nkwanta, Odumasi, Konongo and Nyaboo in the Asante Akyem Central Municipal of Ghana were analyzed for organochlorine pesticides (OCPs). The levels of OCPs detected were treated statistically and data presented (Figure 4.7). Mean levels OCPs in maize samples determined were compared with standard maximum residue limits documented by the USEPA (2009) and the EU (2013).

Mean levels of organochlorine pesticides recorded in maize samples ranged from 0.0001 ± 0.0003 (Aldrin) to 0.037 ± 0.029 mg/kg (Endosulfan). Levels of OCPs recorded in maize samples were Endosulfan (0.037 ± 0.029) > Methoxychlor (0.022 ± 0.011) > Endrin (0.011 ± 0.007) > D D T (0.009 ± 0.001) > Heptachlor (0.004 ± 0.002) > Chlordane (0.004 ± 0.002) > Dieldrin (0.003 ± 0.002) > Lindane (0.002 ± 0.002) > Aldrin (0.0001 ± 0.0003 mg/kg). Levels of Methoxychlor and Endrin recorded in the maize samples from the farms in this study were above recommended maximum residual limits permitted by the USEPA (2009) and the EU (2013) (Figure 4.7). Levels of Aldrin, Chlordane, DDT, Dieldrin, Endosulfan, Heptachlor, and Lindane were 0.0001 ± 0.0003 , 0.004 ± 0.002 , 0.009 ± 0.001 , 0.003 ± 0.002 , 0.037 ± 0.029 , 0.004 ± 0.002 mg/kg, and 0.002 ± 0.002 respectively. These were within the United State Environmental Protection Agency, 2009 and the European Union, 2013 documented recommended MRLs.

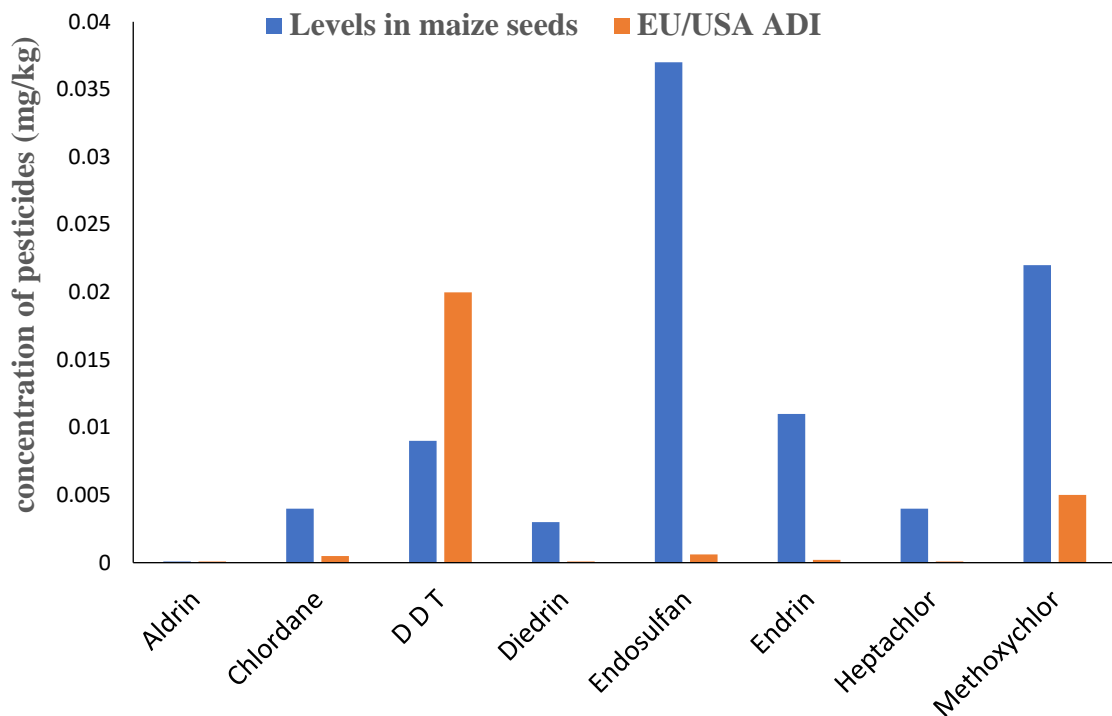


Figure 4.7: Mean levels (mg/kg) of organophosphate pesticides in maize seeds

Low levels of Aldrin, Chlordane, DDT, Dieldrin, Endosulfan, Heptachlor, and Lindane could be due to the ability of crops to breakdown of the pesticides more rapidly (Asare, 2011), hence their minimal levels in the crops. Ban imposed on some of these organochlorine pesticides might have also contributed to their low levels, because these pesticides would be unavailable in several shops in the country.

Levels of Methoxychlor (0.022) and Lindane (0.002 mg/kg) observed in this work were below levels of 0.02 (Methoxychlor) and 0.04 mg/kg (Lindane) reported by Okoffo *et al.* (2016) in cocoa beans produced in Ghana. Endosulfan and Endrin levels observed in this study were above 0.020 and 0.008 mg/kg indicated by Ogah *et al.* (2011) for Endosulfan and Endrin respectively in maize samples from markets in Lagos state, Nigeria. Also,

observed levels of Endrin, Dieldrin, Heptachlor, Lindane, Methoxychlor and DDT in maize sample (Figure 4.7) in this study were below 1.17 ± 0.03 (Methoxychlor), 1.00 ± 0.01 (Lindane), 0.02 ± 0.04 (Heptachlor), 0.018 ± 0.01 (Endrin), 0.005 ± 0.06 (Dieldrin) and 0.008 ± 0.02 mg/kg (D D T) in maize samples studied by Anzene *et al.* (2014). The differences in levels of these OCPs in maize could be attributed different location for the studies.

4.5.10 Levels of Organophosphate Pesticides (OPPs) in Maize Samples

Mean concentrations of Organophosphate pesticides (OPPs) detected in the maize were also computed, graphed and compared with USEPA (2009) and EU (2013) recommended maximum residual limits (Table 4.19). Mean levels OPPs. Organophosphate pesticides detected in maize sample ranged from 0.006 ± 0.006 (Methamidophos) to 7.226 ± 3.382 mg/kg (Malathion). Mean levels of OPPs recorded in maize sample were Malathion (7.226 ± 3.382) > Phorate (0.148 ± 0.105) > Chlorfenvinfos (0.103 ± 0.056) > Profenofos (0.039 ± 0.031) > Chlorpyrifos (0.033 ± 0.023) > Parathion (0.029 ± 0.015) > Ethoprofos (0.027 ± 0.020) > Dimethoate (0.017 ± 0.008) > Diazinon (0.008 ± 0.007) > Methamidophos (0.006 ± 0.006 mg/kg).

Levels of Methamidophos (0.006 ± 0.006) and Diazinon (0.008 ± 0.007 mg/kg) recorded in the maize samples were below the USEPA (2009) and EU (2013) recommended maximum residual limits. Low levels of Methamidophos and Diazinon in maize samples could be due to rapid metabolism of the pesticides by the maize plants as indicated by Horska *et al.* (2020). Besides, low levels could be attributed to the fact that the farmers

might have applied these pesticides either at lower levels than required or at initial stage of the maize crops growth as reported by Kocourek *et al.* (2019), Wongnaa *et al.* (2017) and Asare (2011). Methamidophos (0.006 ± 0.006) and Diazinon (0.008 ± 0.007 mg/kg) levels observed in this study agrees with 0.0049 (Methamidophos) and 0.0057 mg/kg (Diazinon) indicated by Asare (2011) in similar study.

There were high levels of Malathion (7.226 ± 3.383), Phorate (0.148 ± 0.105), Chlorfenvinphos (0.103 ± 0.056), Profenofos (0.039 ± 0.031), Chlorpyrifos (0.033 ± 0.010), Parathion (0.029 ± 0.015), Ethoprophos (0.027 ± 0.010), and Diamethoate (0.017 ± 0.008) in the maize sample than USEPA (2009) and the EU (2013) recommended maximum residual limits. The high levels of OPPs could be ascribed to the shorter period between the time of application of these pesticides and the harvesting of the crops for analysis, which shows that, there have not been any significant loss of the chemicals through leaching and degradation.

Levels of OPPs recorded in this study for Chlorpyrifos, Diazinon, and Parathion were below Chlorpyrifos (0.049), Diazinon (0.021), and Parathion (0.043 mg/kg) reported in maize samples studied by Ogah *et al.* (2012) in Nigeria. However, levels of Malathion (7.226 ± 3.382 mg/kg) detected in this study was above 1.565 mg/kg indicated by Ogah *et al.* (2012).

Table 4.19: Organophosphate pesticides levels (mg/kg) in maize from the Asante Akyem Central Municipality

Pesticides	Min. conc.	Max. conc.	Mean conc.	SD	USEPA/EU
Methamidofos	ND	0.020	0.006	0.006	0.01
Dimethoate	0.004	0.032	0.017	0.008	0.01
Chlorpyrifos	0.002	0.073	0.033	0.023	0.01
Parathion	0.008	0.067	0.029	0.015	0.02
Chlorfenvinphos	0.023	0.224	0.103	0.056	0.01
Malathion	2.845	12.350	7.226	3.382	8.00
Phorate	0.032	0.380	0.148	0.105	0.05
Profenofos	ND	0.094	0.039	0.031	0.01
Ethoprofos	ND	0.062	0.027	0.020	0.01
Diazinon	ND	0.025	0.008	0.007	0.01

4.5.11 Levels of Carbamate Pesticides in Maize Samples

The results obtained for the analysis of carbamate pesticides in the studied maize sampled from were recorded and the data plotted (Figure 4.8) from Ohene-Nkwanta, Nyaboo, Odumasi and Konongo in Asante Akyem Central Municipality.

Two detected carbamate pesticides were Carbaryl and Carbofuran. Mean level of carbamate recorded were Carbaryl (0.056 ± 0.034) > Carbofuran (0.040 ± 0.026) mg/kg). Though levels of Carbofuran exceeded USEPA (2009) and EU (2013) recommended maximum residue limits, that of Carbaryl were within recommended maximum residue limits reported by USEPA (2009) and EU (2013) (Figure 4.8).

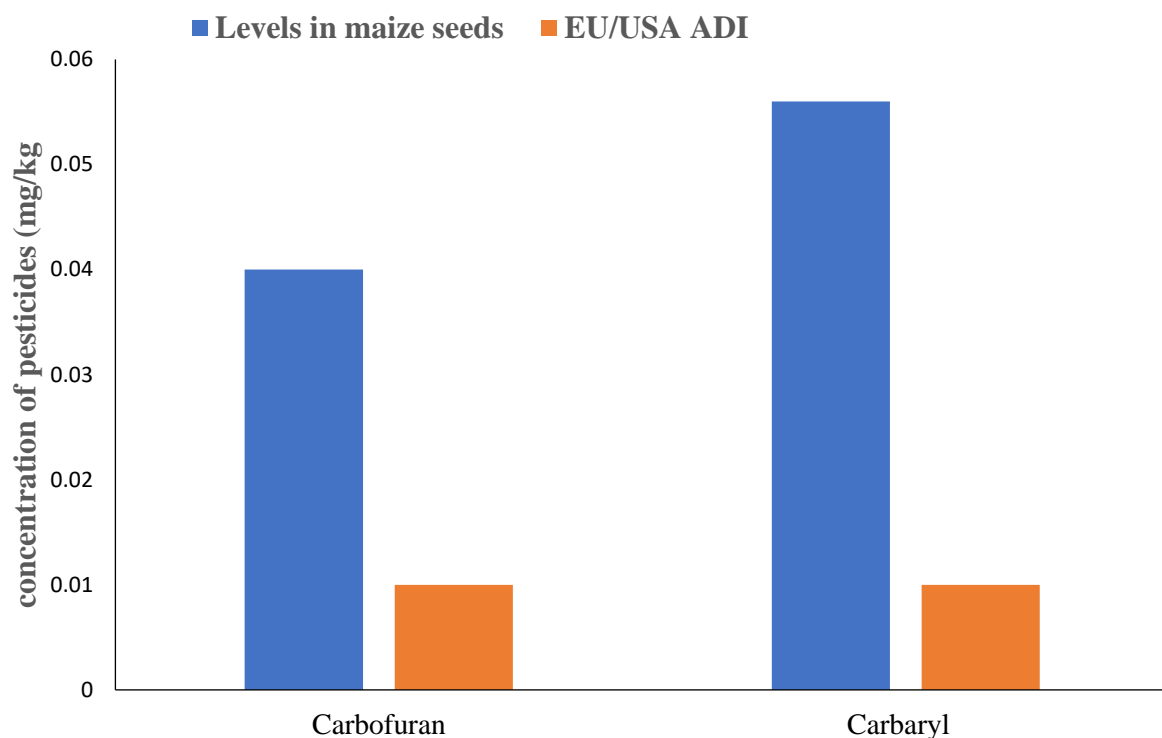


Figure 4.8: Mean levels (mg/kg) of carbamate pesticides in maize seeds

These results recorded for analysis of carbamate in the maize samples were above 0.038 mg/kg (Carbaryl) than indicated by Ogah *et al.* (2012) and Carbofuran (0.084 mg/kg) reported by Ogah *et al.* (2012). This study recorded substantial levels of Carbofuran (0.040 ± 0.026 mg/kg) compared to Carbofuran (Below Detection Limit) reported by Hossain *et al.* (2013) in investigated vegetables in Dhaka Bangladesh. However, levels of Carbaryl (0.056 ± 0.034) detected herein was below Carbaryl (0.127 mg/kg) reported by Hossain *et al.* (2013).

4.6 Correlation of Soil Properties with Levels of Pesticides in the Selected Crops

In order to find out how soil properties influence concentrations of pesticides in cocoyam leaves, cocoyam crops, cassava tubers and maize seeds, correlation analysis

between physico-chemical properties of the soil and the concentrations of pesticides in the crops were done and the results presented (Table 4.20 to 4.31).

4.6.1 Correlation Analysis Between Soil Properties and Organophosphate Pesticides in Cocoyam Leaves

Correlation between Ca^{2+} , Mg^{2+} , K^+ , Na^+ , N^+ , sand and silt and the organophosphate pesticides (Chlorpyrifos, Chlorfenvinphos, Diazinon, Dimethoate, Malathion, Methamidophos, Parathion methyl, Phorate and Profenofos) levels in the cocoyam leaves were not significant at the indicated P-value ($P < 0.05$) (Table 4.16). These imply that levels and distributions of the aforementioned pesticides in the cocoyam leaves are not influenced by the physico-chemical properties of the soils. The non-significant correlations observed between the physico-chemical properties (Ca^{2+} , Mg^{2+} , Na^+ and silt) of the soils and the organophosphate pesticides were at variance with that observed by Chaudhari, *et al.* (2013) and Copaja *et al.* (2021) where negative correlations existed between soil properties (Ca^{2+} , Mg^{2+} , Na^+ and silt) and organophosphate pesticides levels in investigated vegetables.

Table 4.20: Correlations of soil properties with organophosphate pesticides in cocoyam leaves

Soil properties	CHLO	CHLOF	DIAZ	DIME	MALA	METH	PARA	PHOR	PROF
Ca ²⁺	0.120	0.001	0.065	-0.199	0.009	0.038	0.058	0.149	0.047
K ⁺	-0.825	-0.136	-0.021	-0.200	-0.010	-0.068	-0.980	0.385	0.213
Mg ²⁺	0.014	-0.180	-0.067	-0.332	-0.038	-0.013	0.047	-0.137	-0.364
Na ⁺	-0.919	0.835	-0.421	0.139	0.027	0.086	-0.643	-0.660	0.232
N ⁺	-0.162	-0.090	-0.085	0.142	0.029	-0.086	-0.111	0.325	-0.129
pH	-0.120	-0.067	0.054*	-0.078	-0.011	0.017	-0.127	-0.067	-0.061
CEC	0.073	0.120	-0.032	0.171	0.079	-0.076	-0.090	0.043*	0.199
Soil moisture (%)	-0.062	-0.467	0.094*	-0.013	-0.076	0.078	0.017*	-	-0.006
Organic matter	0.155	0.186*	-0.127	0.052	0.091*	0.041	-0.082	0.033*	-0.042
Sand (%)	-0.026	-0.022	0.014	-0.243	0.039	0.016	-0.013	-0.021	-0.028*
Silt (%)	0.049	0.038	0.069	-0.161	-0.056	-0.014	0.023	-0.026	0.011
Clay (%)	-0.331	0.022*	-0.003	0.296	-0.038	-0.013*	0.023	0.033	0.025
Bulk density (Mg/m ³)	-0.281	-0.306	-0.041*	0.134	0.039	0.027	-0.292	-0.234	-0.337

*Correlation is significant at the 0.05 level CHLO = Chlorpyrifos; CHLOF = Chlorfenvinphos; DIAZ = Diazinon; DIME = Dimethoate; MALA

= Malathion; METH = Methamidophos; PARA = Parathionmethyl M; PHOR = Phorate; PROF = Profenofos

pH of the soil samples had significant positive correlation ($r = 0.054$; $P < 0.05$) with Diazinon levels in the cocoyam leaves whilst CEC showed positively correlated ($r = 0.043$; $P < 0.05$) with Phorate levels in the cocoyam leaves. Clay contents of the soil showed positive correlation ($r = 0.022$; $P < 0.05$) with Chlorfenvinphos and negatively correlated ($r = - 0.013$; $P > 0.05$) with Malathion contents of the soil. Moisture contents of the soils also showed positive correlation ($r = 0.094$; $P < 0.05$) with Diazenon and Parathion ($r = 0.017$; $P < 0.05$) but correlated negatively ($r = - 0.033$; $P > 0.05$) with Phorate levels of the soil.

The positive correlations observed between soil pH and Diazinon, CEC and Phorate and moisture contents and Diazenon indicate that, the soil properties have significant influence on the distributions and levels of these pesticides in the cocoyam leaves. This implies that as those soil properties increase, the levels of these organochlorines in the cocoyam leaves also increase and vice versa. The positive correlation between soil pH and Diazenon was at variance with that indicated by Fosu-Mensah *et al.* (2016) where soil pH (> 7) led to reduction of pesticides uptake by crops. Again, the positive correlation between soil moisture and Diazenon disagreed with that reported by Asare (2011) where soil moisture contents made soil organisms unable to breakdown pesticides molecules. This according to Asare (2011), this contributed to elevated levels of pesticides in watermelon fruits. However, the positive correlation observed between clay contents and Chlorfenvinphos agreed favourably with that reported by Copaja *et al.* (2021) & Barriuso (2021) where increased in clay contents led to increased pesticides uptake by crops due to strong adsorption of pesticides molecules onto soil particles.

Negative correlations were observed between sand contents of the soils and Profenofos ($r = - 0.028$; $P > 0.05$) and between soil bulk density and Diazinon ($r = - 0.041$; $P > 0.05$). These show that, as the quantities of the soil properties increased, the concentrations of respective pesticides decreased in the cocoyam leaves. The negative correlation existed between sand contents and Profenofos levels in the cocoyam leaves agreed favourably with that reported by Fosu-Mensah *et al.* (2016). The researchers indicated that rate of pesticides leaching is high in sandy soil and that could be responsible for the negative correlations observed between sand contents of the soil and Profenofos contents of investigated food crops.

4.6.2 Correlations of Physico-Chemical Properties of Soil with Organochlorines Pesticides

Correlations between physico-chemical properties of the soils sampled from the cocoyam farms and organochlorine pesticides levels in the cocoyam crops were also investigated and reported (Table 4.21).

Correlations that existed between K^+ , Mg^{2+} , Na^+ and N^+ contents of the soils and organochlorine pesticides (Chlordane, Lindane, Heptachlor, Aldrin, Dieldrin, Methoxychlor, Endrin) contents of the soil were non-significant. These indicate that physico-chemical properties of the soils had little to no influence on the concentrations of organochlorines in the cocoyam leaves.

Table 4.21: Correlations of soil properties with organochlorines pesticides in cocoyam leaves

Soil properties	CHLO	LIN	HEPTA	ALD	DIEL	DDT	MET	END
Ca ²⁺	-0.940	0.003	0.103	-0.223*	-0.158	0.053	0.622	0.185
K ⁺	0.144	-0.040	0.095	0.174	0.021	-0.074	-0.091	-0.750
Mg ²⁺	-0.016	0.016	-0.025	-0.057	0.0304	0.047	-0.056	-0.213
Na ⁺	-0.919	0.105	0.595	-0.107	0.165	0.368	0.461	-0.919
N ⁺	-0.792	0.0409	-0.144	-0.133	0.051	0.070	0.066	-0.120
pH	-0.994	-0.212*	0.011	0.081	0.012	-0.109	0.194	-0.052
CEC	0.012	-0.005	0.092	0.063	0.359*	-0.151	0.272	-0.014*
Soil moisture (%)	0.044	0.029	-0.072*	0.070	0.083*	-0.533	0.092	-0.103
Organic matter	0.009	0.217	0.012*	-0.033	0.013	-0.003	0.091	0.095
Sand (%)	-0.046	-0.012	0.068	0.015	-0.187	-0.073	0.161*	-0.040
Silt (%)	-0.853	-0.108	0.089	0.095	0.101	-0.003	0.721	-0.408
Clay (%)	-0.926	0.080*	-0.387	-0.047	-0.039	0.156	0.067	-0.042
Bulk density (Mg/m ³)	-0.0171	-0.011*	0.009	0.422	-0.001	0.014	0.081	-0.115

*Correlation is significant at the 0.05 level; CHLO = Chlordane; LIN = Lindane; HEPTA = Heptachlor; ALD = Aldrin; DIEL = Dieldrin; MET =

Methoxychlor; END = Endrin

The negative correlations that existed between Ca^{2+} and Aldrin, pH and Lindane, CEC and Endrin, soil bulk density and Lindane and soil moisture content and Heptachlor imply that, increasing physico-chemical properties of the soils would result in decreasing contents of the organochlorines in the cocoyam leaves. The negative correlation existed between pH and Lindane agreed favourably with that reported by Chadwick *et al.* (2001) where pH of soils had negative correlations with pesticides in the soils. The observed negative correlation between CEC and Endrin is also at variance with that reported by Asare (2011) where positive correlation ($r = 0.559$; $P < 0.05$) was existed between CEC and Methoxychlor levels of soils. However, the negative correlation between soil moisture and Heptachlor corroborated well with that documented by Asare (2011) who indicated that as soil moisture contents increase, soil microorganisms become more active and breakdown pesticides in the soil more rapidly. Hence less pesticides would be available in the soil to be absorbed by the cocoyam leaves.

Organic matter, sand and clay contents correlated positively and significantly with Heptachlor ($r = 0.012$; $P > 0.05$), Methoxychlor ($r = 0.161$; $P > 0.05$) and Lindane ($r = 0.080$; $P > 0.05$) respectively. These observations imply that as organic matter, sand and clay contents of the soils increase, Heptachlor, Methoxychlor and Lindane levels of the cocoyam leaves from the cocoyam farms also increase. Thus high concentrations of Heptachlor, Methoxychlor and Lindane were available in the soils to be absorbed by the cocoyam leaves. The observed correlations between Organic matter Heptachlor and clay contents and Methoxychlor agreed favourably with that of Copaja *et al.* (2021) and Barriuso (2021) where increased in organic matter and clay contents resulted in increased pesticides molecules uptake by plants and led to high accumulation of

pesticides molecules in some fruits and vegetables. Thus Heptachlor and Methoxychlor appear to be freely available for uptake by the cocoyam leaves due to the apparent inability of the pesticides molecules to be absorbed onto the organic carbon contents of the soils due to apparent sufficient active absorption sites on the organic carbon compounds as indicated by Akoto *et al* (2013).

4.6.3 Correlations of Soil Properties with Carbamate Pesticides in Cocoyam Leaves

The correlations between physico-chemical properties of the soils from the cocoyam farms and carbamate pesticides were investigated and reported (Table 4.22).

Table 4.22: Correlations of soil properties with carbamate pesticides in cocoyam leaves

Soil chemical properties	Carbaryl	Carbofuran
Ca ²⁺	-0.023	-0.058
K ⁺	-0.600	-0.825
Mg ²⁺	-0.236	0.039*
Na ⁺	-0.86	-0.919
CEC	0.024	0.078*
Soil moisture (%)	-0.936*	-0.037
Organic matter	0.192*	0.063
Sand (%)	0.027	0.016
Silt (%)	0.083	0.037
Clay (%)	0.008*	-0.051
Bulk density (Mg/m ³)	0.109	0.285

*Correlation is significant at the 0.05 level

The results obtained indicate no significant correlations existed between Ca²⁺, K⁺, Na⁺, sand, silt and bulk density and the detected carbamate pesticides (Carbaryl and Carbofuran) in the cocoyam leaves. Thus, Ca²⁺, K⁺, Na⁺, sand, silt and bulk density contents of the soils had no effect on Carbaryl and Carbofuran levels of the cocoyam leaves. Hence increase or decrease in the contents of the physico-chemical properties

of the soils from the cocoyam farms will not affect the levels of the identified carbamates in the cocoyam leaves.

Significant positive correlations were existed between Mg^{2+} contents of the soils and Carbofuran ($r = 0.039$; $P < 0.05$) levels in the cocoyam leaves, CEC and Carbofuran ($r = 0.078$; $P < 0.05$), organic matter and Carbaryl ($r = 0.192$; $P < 0.05$) and clay contents and Carbaryl ($r = 0.008$; $P < 0.05$). The positive correlations existed between the aforementioned physico-chemical properties of the soils from the cocoyam farms and the carbamate pesticides indicate that the concentrations of the carbamates (Carbofuran and Carbaryl) in the cocoyam varied directly with their corresponding physico-chemical properties of the soils. Thus, as the levels of the physico-chemical properties of the soils from the cocoyam farms increase, the concentrations of the Carbofuran and Carbarayl in the cocoyam leaves also increase.

The observed correlations between organic matter contents and also Carbaryl and clay contents of the soil and levels of Carbaryl corroborated well with that of Khalid *et al.* (2020) & Akoto *et al.* (2013) who indicated that the high clay or organic matter contents in the soil, the more it absorbs pesticides and hence high absorption by cabbage plants. However, the positive correlation observed between CEC and Carbofuran corroborated well with that of Asare (2011) where positive correlation ($r = 0.559$; $P < 0.05$) existed between CEC and Methoxychlor levels of soils of water melon farm from Nsadwir in the Central Region of Ghana.

4.6.4 Correlations of Soil Properties with Organophosphates Pesticides in Cocoyam Crops

The correlations between physico-chemical properties of the soils from the cocoyam farms and organophosphate pesticides of the cocoyam tubers were computed and presented (Table 4.23). The correlation between K^+ ions, N^+ ions, sand and silt contents of soils and the detected organophosphate pesticides were not significant at the indicated P-value (Table 23). The observed correlation means that K^+ ions, N^+ ions, sand and silt contents of soils had little to no influence on their respective organophosphate pesticides in the in the cocoyam tubers.

Calcium ions (Ca^{2+}) and Na^+ ions had significant positive correlation between Malathion ($r = 0.165$; $P < 0.05$) and Chloropyrifos ($r = 0.690$; $P < 0.05$) respectively. The positive correlations detected indicate that as the contents of Ca^{2+} and Na^+ ions in soils increase, the levels of Malathion and Chloropyrifos in the cocoyam also increase. The positive correlations detected for Malathion and Chloropyrifos suggested that both pesticides did not degrade rapidly as Ca^{2+} and Na^+ ions contents of the soils increase due to high pH since Ca^{2+} and Na^+ ions are basic ions as reported by Asare (2011).

The pH of soils correlated significantly negative with Chlorfenvinphos ($r = - 0.041$; $P < 0.05$) but positive with Malathion ($r = 0.281$; $P < 0.05$). Soil moisture contents also had positive correlation with Chlorfenvinphos ($r = 0.002$; $P < 0.05$) but correlated negatively with Profenofos ($r = - 0.005$; $P < 0.05$). Organic matter correlated positively with Diazinon ($r = 0.026$; $P < 0.05$).

Table 4.23: Correlations of soil properties with organophosphate pesticides in Cocoyam crops

Soil properties	CHLO	CHLO	DIAZ	DIME	MALA	METH	PARA	PHOR	PROF
Ca ²⁺	0.640	-0.056	-0.021	0.001	0.165*	0.002	0.115	0.004	0.029
K ⁺	-0.014	0.146	-0.039	0.032	-0.151	-0.003	0.003	-0.015	0.004
Mg ²⁺	-0.021	-0.024*	0.011	0.006	0.104	-0.042	-0.056	0.015	-0.003
Na ⁺	0.023	0.690*	-0.032	-0.011	0.898	-0.011	-0.007	0.173	0.002
N ⁺	-0.023	0.684	0.055	0.043	-0.147	-0.071	0.004	-0.086	0.006
pH	-0.041*	0.022	0.002	-0.065	0.281*	0.019	-0.009	0.012	-0.002
CEC	0.379	0.043	-0.073	0.001	0.149*	-0.004	0.020	-0.003	0.092
Moisture (%)	0.746	0.002*	0.016	0.076	-0.076	-0.055	-0.023	0.079	-0.005*
Organic matter	0.758	0.024	0.026*	-0.035	0.156	0.001	-0.022	0.004	-0.003
Sand (%)	0.698	0.994	-0.094	-0.001	-0.085	0.019	0.001	0.031	-0.013
Silt (%)	0.652	0.696	0.014	0.043	0.016	-0.013	-0.003	0.383	-0.006
Clay (%)	0.902	0.819	0.034	0.042	-0.035*	-0.008	0.097	-0.003	0.054
Bulk density (Mg/m ³)	0.994	0.073	-0.009	-0.007*	-0.467	0.001	-0.001	0.006	-0.002

*Correlation is significant at 0.05 level; CHLOP = Chlorpyrifos; CHLOF = Chlorfenvinphos; DIAZ = Diazinon; DIME = Dimethoate; MALA =

Malathion; METH = Methamidophos; PARA = Parathionmethyl M; PHOR = Phorate; PROF = Profenofos

The positive and negative significant correlations between pH and Chlorfenvinphos and Malathion respectively, mean that at the indicated P-value, soils pH has significant influence on distributions and levels of these pesticides in the cocoyam tubers. Thus at high pH, levels of Chlorfenvinphos could be low in cocoyam but levels of Malathion could be high in cocoyam. The negative correlation existed between pH and Chlorfenvinphos corroborated favourably with that of Fosu-Mensah *et al.* (2016) where soil pH above 7 (high pH) led to reduced pesticides uptake by crops.

Moisture contents correlated positively and significantly with Chlorfenvinphos ($r = 0.002$; $P < 0.05$) but had negative correlation with Phorate ($r = - 0.005$; $P < 0.05$) whilst positive correlation existed between organic matter and Diazinon ($r = 0.026$; $P < 0.05$). The observed positive correlations imply that as the contents of the physico-chemical properties of the soil increase, the levels of the corresponding pesticides increase. The positive correlation existed between soil moisture contents and Chlorfenvinphos levels in the cocoyam tubers indicates that at high soil moisture contents, cocoyam tubers take up high levels of Chlorfenvinphos. Hence, it is expedient that in cases where Chlorfenvinphos are used during cultivation of cocoyam, farmers reduce irrigation rates to decrease Chlorfenvinphos levels that would be accessible by the cocoyam crops. This finding was in contrary to that of Asare (2011) where soil moisture contents made soil organisms unable to breakdown pesticides molecules low. This according to Asare (2011), led to elevated levels of pesticides in watermelon fruit. However, the negative correlation existed between soil moisture contents and Phorate agreed favourably with that of Asare (2011) indicating that as soil moisture contents increase, soil microorganisms become more active to breakdown pesticides easily leading low levels of Phorate to be absorbed by cocoyam tubers.

The positive correlation between organic matter and Diazinon implies organic matter contents of the soils from the cocoyam farms had significant influence on distributions and levels of Diazinon in the cocoyam tubers. Thus, increased in organic matter contents could result in increased in the levels of cocoyam tubers from the cocoyam farms. The positive correlations between organic matter contents of the soils and Diazinon levels in the cocoyam tubers corroborated favourably with that reported by Fosu-Mensah *et al.* (2016). Hence, Diazinon levels would persist in the cocoyam tubers for long time as the quantities of organic matter of the soils increase.

Soils clay contents exhibited positive correlation with Parathion. This correlation shows that as the clay contents of the soils surge, levels of the Parathion in the cocoyam tubers also become high. The observation between clay contents and Parathion levels in the cocoyam tubers corresponded favourably with that of Copaja *et al.* (2021) and Barriuso (2021) where increased in clay contents resulted in increased pesticides uptake by crops due to high adsorptivity of the soil particles to the pesticides molecules

4.6.5 Correlations of Soil Properties with Levels of Organochlorine Pesticides in Cocoyam Crops

The correlations between physico-chemical properties of the soils from the cocoyam farms and organochlorine pesticides in the cocoyam tubers were investigated and presented (Table 4.24). The correlation results showed no significant between soil properties Ca^{2+} , Mg^{2+} , Na^+ , pH and organic matter and the detected organochlorine pesticides in cocoyam tubers. This implies that the aforementioned physicochemical properties of the soils had little to no impact on the concentrations of organochlorines in the soils.

Table 4.24: Correlations of soil properties with organochlorines pesticides in cocoyam crops

Soil properties	CHLO	LIN	HEPTA	ALD	DIEL	DDT	MET	END
Ca ²⁺	-0.001	-0.003	-0.001	-0.002	0.013	-0.026	-0.001	0.006
K ⁺	0.008	0.026*	-0.023	0.003	0.012	-0.008	-0.016	0.368
Mg ²⁺	0.001	0.003	-0.015	0.002	0.042	-0.087	0.003	0.104
Na ⁺	-0.026	0.005	0.201	-0.015	0.015	-0.142	-0.014	0.200
N ⁺	0.008	-0.037	0.035	0.006	-0.002	-0.016	0.007*	0.729
pH	-0.026	0.004	-0.005	0.003	-0.007	-0.066	0.067	-0.025
CEC	-0.004	0.001	0.004*	-0.007	-0.062	-0.018	-0.005	0.022
Moisture (%)	0.001	0.007	-0.002	0.005	-0.002	0.065	0.038*	0.012
Organic matter	-0.037	-0.008	0.004	-0.001	-0.007	-0.011	0.065	0.006*
Sand (%)	0.006	0.024	-0.003	-0.001*	-0.002	0.005	-0.007	-0.015
Silt (%)	0.003	0.011	-0.002	0.001	-0.025	-0.007	0.004	0.011
Clay (%)	-0.001	-0.008	0.001	-0.006	0.012	0.055	-0.002*	0.004*
Bulk density (Mg/m ³)	0.001	0.002	0.0023	-0.002	-0.002	-0.007	0.006	-0.087

*Correlation is significant at the 0.05 level: CHLO = Chlordane; LIN = Lindane; HEPTA = Heptachlor; ALD = Aldrin; DIEL = Dieldrin; MET =

Methoxychlor; END = Endrin

Potassium ions had positive correlation with Lindane ($r = 0.026$; $P < 0.05$), N^+ ions exhibited positive correlation with Methoxychlor ($r = 0.007$; $P < 0.05$) whilst CEC showed significant positive correlation with Heptachlor ($r = 0.001$; $P < 0.05$). The observed positive correlations indicate the contents of K^+ ions, N^+ ions and CEC in the soils from the cocoyam farms could directly influence the levels Methoxychlor, Lindane and Heptachlor respectively in the cocoyam tubers. Thus, as the contents of K^+ ions, N^+ ions and CEC in the soils increase, the levels of their corresponding pesticides increase accordingly. The observed correlation between CEC and Heptachlor corroborated well with that of Asare (2011) where positive correlation ($r = 0.559$; $P < 0.05$) was reported between CEC and Methoxychlor levels of soils however disagreed favourably with that of Fosu-Mensa *et al.* (2016) who reported negative correlation between CEC and Lindane ($r = -0.492$; $P < 0.05$).

Soils moisture and organic matter contents exhibited significant positive correlation with Methoxychlor and Endrin respectively. These observations show that increasing moisture and organic matter contents of the soil could lead to an increase in levels of Methoxychlor and Endrin in the cocoyam tubers and vice versa. The positive correlation existed between moisture contents and Methoxychlor is at variance with that reported by Asare (2011) who reported that as the moisture contents of soil increase, soil microorganisms become more active and hence breakdown pesticides readily leading to low levels of pesticides available in the soils to be absorbed by the plants. However, positive correlation existed between organic matter and Endrin corroborated favourably with of Fosu-Mensah *et al.* (2016) who reported significant positive correlation between organic matter and Dieldrin ($r = 0.998$; $P < 0.05$) and HCH ($r = 0.936$; $P < 0.05$). This implies that the Dieldrin concentrations in the cocoyam

tubers are related to high organic matter contents of the soils and could be ascribed to pesticide molecules having high propensity of binding to organic matter in soil, like fats or lipids of plants and animals as indicated by Bentzen *et al.* (2008).

Negative correlation was observed between sand contents of the soils and Aldrin ($r = -0.001$; $P < 0.05$). This observation shows that an increase in sand contents of soils led to a corresponding decrease in Aldrin and vice versa. This agreed favourably with that of Fosu-Mensah *et al.* (2016) who recorded negative correlation between sand content and HCH and DDT. The researchers indicated that sandy soils are believed to enhance leaching and hence low availability of pesticides in the soils to be absorbed by plants.

Besides, positive correlation existed between clay contents of soils and Endrin ($r = 0.004$; $P < 0.05$) and negative correlation with Methoxychlor ($r = 0.002$; $P < 0.05$) show that an increase in soil clay contents led to an increased levels of Endrin whilst an increase in soil clay contents led to a decreased level of Methoxychlor. The negative correlation observed between clay contents of soil and Methoxychlor indicates that clay has significant influence on the distribution of pesticides in soils. This observation agreed favourably with that of Fosu-Mensah *et al.* (2016) and Copaja *et al.* (2021) but contrary to that of Aiyesanmi and Idowu (2012). However, the positive correlation corroborated well with that of Fosu-Mensah *et al.* (2016) and Copaja *et al.* (2021) but at variance with that of Aiyesanmi and Idowu (2012). The researchers (Fosu-Mensah *et al.*, 2016) and Copaja *et al.* (2021) reported that clayey soils help in accumulation of pesticides in the soils through colloid formation and hence would be available to be absorbed by crops.

4.6.6 Correlations of Soil Properties with Levels of Carbamate Pesticides in Cocoyam Crops

The correlations between physico-chemical properties of the soils from the cocoyam farms and carbamate pesticides detected in cocoyam tubers were computed and presented (Table 4.25). Calcium (Ca^{2+}), K^+ , Mg^{2+} , Na^+ , CEC, organic matter, sand and bulk density contents of soils had no significant correlation with the detected carbamate pesticides (Carbaryl and Carbofuran). This observation shows that the aforementioned soil properties had little to influence on the levels of Carbaryl and Carbofuran in the cocoyam tubers.

Table 4.25: Correlations of soil properties with levels of carbamate pesticides in cocoyam crops

Soil chemical properties	Carbaryl	Carbofuran
Ca^{2+}	0.013	0.023
K^+	0.194	0.407
Mg^{2+}	-0.009	0.005
Na^+	0.565	0.930
pH	-0.074*	0.067
CEC	0.052	-0.007
Soil moisture (%)	-0.048	-0.012*
Organic matter	0.033	0.018
Sand (%)	0.137	0.243*
Silt (%)	0.665	0.727
Clay (%)	0.002*	0.011
Bulk density (Mg/m^3)	-0.134	0.095

*Correlation is significant at the 0.05 level

However, pH of soils exhibited significant negative correlation with Carbaryl ($r = -0.074$; $P < 0.05$) whilst soil moisture contents had significant negative correlation with Carbofuran ($r = -0.012$; $P < 0.05$). Besides, sand and clay contents of the soils

correlated significantly and positively with Carbofuran ($r = - 0.243$; $P < 0.05$) and Carbarayl ($r = - 0.002$; $P < 0.05$) respectively (Table 4.21).

The negative correlations between pH of soils and Carbarayl and also between moisture contents and Carbofuran imply that high contents of soil pH and moisture led to a decreased concentrations of their respective carbamate pesticides and vice versa. The negative correlation existed between soil pH and Carbaryl corroborated well with a similar study by Bentum *et al.* (2006) which indicated significant negative correlations between soil pH and Lindane and Propoxur but at variance with that of Aiyesanmi and Idowu (2012), which reported no significant ($p > 0.05$) correlations between soil pH and organochlorines concentrations detected in soil sampled from cocoa farms in Ondo State Central District in Nigeria.

The positive correlation existed between sand contents and Carbofuran as well as that of clay contents and Carbaryl indicate that an increase in sand and clay contents of soils led to an increased levels of Carbofuran and Carbaryl accordingly and vice versa. The positive significant correlation between sand contents of the soils and Carbofuran levels in cocoyam tubers indicates that high sand levels of the soils could not absorbed the Carbofuran molecules in the soil and that led to high absorption rate of Carbofuran molecules by cocoyam tubers. This observation was contrary to that of Fosu-Mensah *et al.* (2016) where high sand contents of soils resulted in reduced adsorption of pesticide onto soil particles. Moreover, the positive correlation existed between clay contents and Carbaryl corroborated well with that of Copaja *et al.* (2021) and Barriuso (2021) where increased in clay contents led to an increased pesticides molecules uptake

by plants and hence high accumulation of pesticides molecules in some fruits and vegetables.

4.6.7 Correlations of Soil Properties with Organophosphate Pesticides in Cassava Tubers

The correlations between physico-chemical properties of the soils from the cassava farms and organophosphate pesticides detected in cassava tubers were computed and presented (Table 4.26). The correlation results revealed that there was no significant correlation between Ca^{2+} , Mg^{2+} , N^+ , organic matter, silt and bulk density contents in the soil and organophosphate pesticides levels detected in cassava tubers (Table 4.26). The non-significance difference between the physico-chemical properties of the soils from the cassava farms and organophosphates pesticides levels in the cassava tubers implies that the aforementioned physico-chemical properties of the soils have little to no influence on the levels and distributions of the organophosphate pesticide levels in the cassava tubers.

Table 4.26: Correlations of soil properties with organophosphate pesticides in cassava tubers

Soil properties	CHLO	CHLOF	DIAZ	DIME	MALA	METH	PARA	PHOR	PROF
Ca ²⁺	0.002	0.007	-0.006	-0.006	0.116	0.002	0.011	0.004	-0.001
K ⁺	-0.005	0.120*	-0.018	0.058	0.282	0.009	0.099	-0.080	-0.007
Mg ²⁺	-0.004	-0.043	0.016	-0.026	0.340	-0.040	0.042	-0.028	-0.080
Na ⁺	0.258	0.031	-0.204	-0.070	0.170*	0.071	-0.396	0.396	0.077
N ⁺	0.079	-0.204	0.066	-0.117	0.199	0.094	-0.025	-0.265	-0.036
pH	-0.004*	0.014	-0.002	0.006	-0.225	-0.003	0.009	0.013*	0.029
CEC	0.005	0.006	-0.003	0.002	0.192	0.002	-0.013	-0.004	0.001
Moisture (%)	-0.001	-0.004	0.003	-0.001	0.045	-0.065	0.007*	-0.005	-0.064
Organic matter	0.005	-0.018	0.008	-0.004	0.404	0.001	0.003	0.007	-0.098
Sand (%)	-0.002	0.003	-0.001	0.001	-0.045	-0.002*	-0.030	0.039	0.076
Silt (%)	-0.001	-0.001	0.005	-0.002	0.028	-0.001	0.029	-0.011	0.068
Clay (%)	0.001	-0.008	0.001	-0.003	0.014	0.001*	-0.001	-0.003	-0.063
Bulk density (Mg/m ³)	-0.012	-0.002	-0.009	0.029	-0.207	-0.001	-0.059	0.027	0.004

*Correlation is significant at 0.05 level; CHLO = Chlorpyrifos; CHLOF = Chlorfenvinphos; DIAZ = Diazinon; DIME = Dimethoate; MALA =

Malathion; METH = Methamidophos; PARA = Parathionmethyl M; PHOR = Phorate; PROF = Profenofos

K⁺ and Na⁺ ions contents of the soil exhibited significant positive correlations with Chlorfenvinphos ($r = 0.120$; $P < 0.05$) and Malathion ($r = 0.170$; $P < 0.05$) levels in cassava tubers respectively. The positive correlation indicate that as the levels of K⁺ and Na⁺ ions contents of the soil increase, levels of Chlorfenvinphos and Malathion increase respectively.

Soil pH had significant negative correlation with Chlorpyrifos ($r = - 0.004$; $P < 0.05$) but significant positive correlation with Phorate ($r = 0.013$; $P < 0.05$) whilst moisture contents of the soil had significant positive correlation with Paraathion ($r = 0.007$; $P < 0.05$). Sand contents of the soil recorded significant negative correlation with Methamidophos ($r - 0.002$; $P < 0.05$) whilst clay contents of the soil had significant positive correlation with Methamidophos ($r - 0.001$; $P < 0.05$).

The significant negative correlations existed between soil pH and sand contents and levels of respective pesticides in the cassava tubers, imply that decreased in soil pH and sand contents of the soil led to an increased in levels of Chlorpyrifos and Methamidophos in the cassava tubers. The negative correlation between pH and Chlorpyrifos levels in the cassava tubers agreed favourably with that of Akoto et al (2013). (2015) where reduction in soil pH (less than 7) led to mobility of pesticides molecules, less adsorption onto soil particles and increased in the rates of pesticides uptake by crops which could led to high levels in crops. However, the observed positive significant correlations between moisture and clay contents and Parathion and Methamidophos respectively mean that these soil properties significantly influenced the distributions and the levels of the organophosphate pesticides in the cassava tubers. Thus levels of pesticides in the cassava tubers increase as the contents of the physico-

chemical properties of the soil increase. This result is at variance with that of Bentzen *et al.* (2008) and Chaudhari *et al.* (2013) where increased clay contents of soils led to a reduced uptake of pesticides by crops. This could be ascribed to the fact that high clay contents of soil present massive active absorption sites for pesticides molecules. The positive correlation between moisture contents and Methamidophos levels was also at variance with that of Asare (2011) who reported that low soil moisture contents rendered most soil organisms inactive and made it difficult for them to facilitate in breakdown of the pesticides molecules. He added that this could led to high pesticides accumulation due to firm adsorption of pesticides molecules onto soil particles.

4.6.8 Correlations of Farm Crops with Organochlorines Pesticides in Cassava Tubers

Correlations between physico-chemical properties of the soils sampled from the cassava farms and organochlorine pesticides were computed and reported (Table 4.27). The results (Table 4.27) showed no significant correlation between Ca^{2+} , K^+ , Na^+ , N^+ , CEC, sand and clay contents of the soil from cassava farms and the organochlorines levels in the cassava tubers. This result indicate the physico-chemical properties of the soil had little to no influence on the levels of the organochlorines in the cassava tubers. The non-significant correlation observed between CEC and the organochlorine pesticides was variance with that of Asare (2011) where positive correlation ($r = 0.559$; $P < 0.05$) existed between CEC and Methoxychlor levels of soils.

However, Mg^{2+} ions in the soil significantly correlated positively with the levels of Dieldrin ($r = 0.017$; $P < 0.05$) whilst pH of the soil had significant positive correlation with Lindane ($r = 0.003$; $P < 0.05$) levels in the cassava tubers. Soil moisture had

significant positive correlation with Endrin ($r = 0.001$; $P < 0.05$) and organic matter significant negative correlation with Dieldrin ($r = - 0.001$; $P < 0.05$). Silt and bulk density of the soil correlated significantly negative with Lindane ($r = - 0.003$; $P < 0.05$) and Aldrin ($r = - 0.024$; $P < 0.05$) respectively.

Table 4.27: Correlations of farm crops with organochlorines pesticides in cassava tubers

Soil properties	CHLO	LIN	HEPTA	ALD	DIEL	DDT	MET	END
Ca ²⁺	0.009	-0.001	-0.002	-0.019	0.003	0.007	-0.009	-0.004
K ⁺	0.015	0.008	-0.024	0.007	0.032	-0.005	-0.006	-0.020
Mg ²⁺	-0.002	-0.009	-0.012	0.052	0.004	0.017*	0.003	-0.006
Na ⁺	-0.024	0.058	0.290	-0.026	-0.049	0.046	0.047	0.313
N ⁺	-0.002	-0.041	0.094	0.021	0.018	0.011	0.025	0.165
pH	-0.002	0.003*	-0.005	-0.001	-0.005	0.007	0.007	-0.004
CEC	-0.069	0.091	0.007	0.021	-0.003	0.004	0.007	0.008
Soil moisture (%)	-0.006	-0.009	-0.001	0.011	0.002	-0.009	0.068	0.001*
Organic matter	-0.001	0.001	0.005	-0.026	-0.001*	0.006	0.022	0.008
Sand (%)	0.001	0.015	-0.001	-0.002	-0.005	-0.006	-0.023	-0.002
Silt (%)	-0.008	-0.003*	-0.013	-0.004	0.001	0.003	0.004	-0.001
Clay (%)	0.001	-0.012	0.001	0.015	0.002	-0.001	-0.024	0.002
Bulk density (Mg/m ³)	-0.002	0.012	-0.004	-0.024*	-0.007	-0.001	0.024	-0.004

*Correlation is significant at 0.05 level; CHLO = Chlordane; LIN = Lindane; HEPTA = Heptachlor; ALD = Aldrin; DIEL = Dieldrin; MET =

Methoxychlor; END = Endrin

The significant positive correlation between Mg^{2+} ions in the soil and Dieldrin, pH of the and Lindane as well as that between soil moisture and Endrin indicate that as soil properties (Mg^{2+} ions, pH and moisture) increase, levels of the respective organochlorines in the cassava tubers from the cassava farms also increase.

The positive correlation between soil pH and Lindane was contrary to that recorded by Fosu-Mensah *et al.* (2016) where soil pH higher than 7 led to decreased pesticides uptake by crops. The positive correlation between soil moisture contents and Endrin was not in agreement with that reported by Asare (2011) where low soil moisture contents made soil organisms unable to breakdown pesticides molecules. This according to Asare (2011), led to elevated levels of pesticides in watermelon fruit crop as moisture contents decrease.

The negative significant correlations existed between organic matter and Dieldrin also implies that as the organic matter contents of the soil increase, the levels of Dieldrin in the cassava tubers decrease. This result was at variance with that of Fosu-Mensah *et al.* (2016) who indicated positive significant correlation between organic matter and Heptachlor, Aldrin and Beta HCH levels in vegetables.

4.6.9 Correlations of Soil Properties with Levels of Carbamate Pesticides in Cassava Tubers

The correlations between physico-chemical properties of the soils from the cassava farms and synthetic carbamate pesticides of the carrot roots were computed and presented (Table 4.28).

Table 4.28: Correlations of soil properties with levels of carbamate pesticides in cassava tubers

Soil properties	Carbaryl	Carbofuran
Ca ²⁺	-0.017*	0.016
K ⁺	-0.016	0.693
Mg ²⁺	0.234	0.112
Na ⁺	-0.870	0.660
pH	0.003	-0.018*
N ⁻	-0.003	0.865
CEC	-0.002	0.031
Soil moisture (%)	0.006*	0.001
Organic matter	0.013	0.033
Sand (%)	-0.002	-0.001
Silt (%)	0.003	0.008
Clay (%)	0.004*	-0.008
Bulk density (Mg/m ³)	-0.077	-0.061

*Correlation is significant at 0.05 level

Correlations that existed between K⁺, Mg²⁺, Na⁺, N⁻, CEC, organic matter, sand, silt and bulk density and Carbaryl and Carbofuran levels in the cassava tubers were insignificant at P < 0.05.

However, Ca²⁺ ions contents of the soil from cassava farms had significant negative correlation with Carbaryl ($-r = -0.017$; $P < 0.05$) whilst pH of the soil correlated negatively and significantly with Carbofuran ($r = -0.018$; $P < 0.05$). There were also significant positive correlations existed between soil moisture and Carbaryl ($r = -0.004$; $P < 0.05$) and clay contents and Carbaryl. ($r = -0.004$; $P < 0.05$).

The negative correlation between Ca²⁺ ions contents and Carbaryl pH of the soil and Carbofuran, suggests that as Ca²⁺ ions contents and pH of the soils increased, Carbaryl and Carbofuran levels in the soil rapidly degrades and hence Carbaryl and Carbofuran levels available in the soil for uptake by the cassava tubers becomes reduced and thus

very small amount of Carbaryl and Carbofuran would be absorbed by the cassava tubers. This observation agreed favourably with that of Fosu-Mensah *et al.* (2016). The significant positive correlation existed between soil moisture and Carbaryl and clay contents and Carbaryl show that the aforementioned soil properties have direct influence on the levels of the respective pesticides (Carbofuran and Carbaryl). Thus as the levels of the physico-chemical properties of the soil increase, their corresponding pesticides' levels also increase and vice versa. This observation corroborated well with that of Copaja *et al.* (2021) and Barriuso (2021) where high clay contents led to an increased pesticides molecules uptake by plants and resulted in high accumulation of pesticides molecules in some fruits and vegetables.

4.6.10 Correlations of Soil Properties with Organophosphate Pesticides in Maize Seeds

The correlations between physico-chemical properties of the soils from maize farms and organophosphate pesticides detected in maize seeds were computed and presented (Table 4.29). Correlations between physico-chemical properties (K^+ , Na^+ , N^+ , sand and silt) were insignificant at $P < 0.05$. These imply the aforementioned physico-chemical properties of the soil have little to no influence on the distribution and levels of the organophosphates detected in the maize seeds.

Table 4.29: Correlations of soil properties with organophosphate pesticides in maize seeds

Soil properties	CHLOP	CHLO	DIAZ	DIME	MALA	METH	PARA	PHOR	PROF
Ca ²⁺	0.024	-0.003	-0.004	0.006	-0.680*	-0.006	0.059	0.006	0.006
K ⁺	0.016	-0.099	-0.013	0.055	-0.467	-0.011	0.008	-0.082	-0.007
Mg ²⁺	-0.043	0.018	0.008	0.013	0.124	-0.003	0.011	-0.046	0.016
Na ⁺	0.689	0.259	-0.101	-0.238	0.214	0.029	0.062	-0.045	0.084
N ⁺	-0.097	0.048	0.028	-0.060	0.152	0.011	0.097	-0.332	0.127
pH	0.005*	0.009	-0.006	0.007	0.142	-0.001	-0.002	0.006*	-0.008
CEC	0.013	0.016	-0.001	-0.005	0.534*	0.815	0.002	-0.009	0.025
Moisture (%)	-0.007	0.003	0.001	-0.003	0.026	0.422	0.167	-0.007	0.072
Organic matter	0.026	0.008*	0.004	-0.003	0.658	0.001	0.002*	0.007	0.003
Sand (%)	0.001	-0.001	-0.005	0.005	-0.023	0.052	-0.024	0.077	-0.004
Silt (%)	0.005	0.001	0.003	-0.003	0.033	0.518	0.011	-0.005	-0.001
Clay (%)	-0.015*	-0.006	0.006	0.007	0.026	0.374	0.011	-0.003	0.293
Bulk density (Mg/m ³)	-0.043	-0.002	-0.003	-0.005	0.030	0.087	-0.012	0.044	-0.026

*Correlation is significant at 0.05 level; CHLOP = Chlorpyrifos; CHLOF = Chlorfenvinphos; DIAZ = Diazinon; DIME = Dimethoate; MALA

= Malathion; METH = Methamidophos; PARA = Parathionmethyl M; PHOR = Phorate; PROF = Profenofos

The correlation results (Table 4.29) again show that Ca^{2+} ion contents had significant negative correlation with Malathion ($r = - 0.680$; $P < 0.05$) whilst pH of the soil had significant positive correlations with Chlorpyrifos ($r = 0.005$; $P < 0.05$) and Phorate ($r = 0.006$; $P < 0.05$). CEC of the soils from maize had significant positive correlation with Malathion ($r = 0.534$; $P < 0.05$). Again, organic matter contents significantly correlated positively with Chlorfenvinphos ($r = 0.008$; $P < 0.05$) and Parathion ($r = 0.002$; $P < 0.05$) whilst clay contents of the soil correlated significantly and negatively with Chlorpyrifos ($r = - 0.015$; $P < 0.05$).

The positive correlations detected show these soil properties (pH, CEC and organic matter contents) have substantial influence on distributions and levels of Chlorpyrifos, Malathion, Chlorfenvinphos and Parathion in the maize seeds. Thus an increase in the contents of the physico-chemical properties of the soils from maize farms could result in high levels of the respective pesticides in the cassava tubers which could be harmful to consumers of maize seeds. The observed correlations between organic matter Chlorfenvinphos and Parathion agreed favourably with that indicated by Khalid *et al.* (2020) and Akoto *et al.* (2013). (2013) who indicated that, the higher the organic matter contents in the soil, the more it absorbs pesticides and hence high absorption by maize seeds. However, the observed positive correlation between pH and Chlorpyrifos levels in the cassava tubers was at variance with that indicated by Fosu-Mensah *et al.* (2016) where soil pH above 7 led to reduced pesticides uptake by crops.

The negative correlation existed between Ca^{2+} and Malathion and clay contents and Chlorpyrifos show that at high contents of Ca^{2+} and clay, levels of Malathion and Chlorpyrifos in the cassava tubers would be low. This observation is in contrary to that

of Khalid *et al.* (2020) and Akoto et al (2013). (2013) who indicated that, the higher the clay contents in the soil, the more it absorbs pesticides and hence high absorption by maize seeds.

4.6.11 Correlations of Farm Crops with Organochlorine Pesticides in Maize Seeds

The correlations between physico-chemical properties of the soils from the maize farms and organochlorine pesticides were computed and reported (Table 4.30). The results obtained indicate that no significant correlations existed between K^+ , Na^+ , N^+ ions, soil moisture and silt contents at the indicated P-value ($P < 0.05$). This implies K^+ , Na^+ , N^+ ions, soil moisture and silt contents had no influence on levels of Chlordane, Lindane, Heptachlor, Aldrin, Dieldrin, Methoxychlor and Endrin. This finding was at variance with that of Fosu-Mensah *et al.* (2016), Akoto et al (2013). (2013) and Sarkar *et al.* (2020) where soil properties were reported to contribute greatly to synthetic pyrethroid pesticides levels in the vegetables collected from some vegetable farms.

Table 4.30: Correlations of farm crops with organochlorine pesticides in maize seeds

Soil properties	CHLO	LIN	HEPTA	ALD	DIEL	DDT	MET	END
Ca ²⁺	0.013*	0.009	-0.001	0.064	0.006	0.004	-0.002	-0.001
K ⁺	0.007	-0.005	-0.011	0.037	0.014	0.005	0.014	-0.007
Mg ²⁺	0.005	-0.002	-0.007	0.015*	0.007	-0.001	0.022	0.001
Na ⁺	-0.093	0.048	0.104	0.011	-0.017	0.022	-0.036	-0.099
N ⁺	-0.018	-0.002	-0.009	0.039	0.023	0.005	0.089	0.002
pH	-0.013	-0.008*	-0.006	-0.002	0.003*	-0.004	0.001	-0.001
CEC	-0.017	0.006	0.002	-0.028	-0.003	0.003	-0.001	-0.005*
Moisture (%)	0.057	-0.007	-0.008	0.015	0.007	-0.002	0.003	0.005
Organic matter	-0.002	0.003	0.004*	0.013	0.004	0.004	0.048*	-0.009
Sand (%)	-0.073	-0.003	-0.002	-0.019*	-0.007	0.001	-0.001	0.002
Silt (%)	-0.068	-0.002	-0.002	-0.062	0.006	-0.00	0.013	-0.003
Clay (%)	0.098*	0.003	0.004	-0.033	0.001	-0.005	-0.006	0.003
Bulk density (Mg/m ³)	-0.027	-0.003	-0.001	-0.092*	-0.004	0.008	0.002	0.004

*Correlation is significant at 0.05 level; CHLO = Chlordane; LIN = Lindane; HEPTA = Heptachlor; ALD = Aldrin; DIEL = Dieldrin; MET = Methoxychlor; END = Endrin

However, Ca^{2+} and Mg^{2+} ions contents of the soils from maize farms had significant positive correlation with Chlordane ($r = 0.013$; $P < 0.05$) and Aldrin ($r = 0.013$; $P < 0.05$) respectively. pH of the soils had negative and positive correlations with Lindane ($r = -0.008$; $P < 0.05$) and Dieldrin ($r = 0.003$; $P < 0.05$) respectively. Again CEC had significant negative correlation with Endrin ($r = -0.005$; $P < 0.05$) but organic matter contents had positive correlation with Heptachlor ($r = 0.004$; $P < 0.05$) and Methoxychlor ($r = 0.048$; $P < 0.05$). Both sand and bulk density contents of the soils from maize farms had significant negative correlation with Aldrin ($r = -0.019$; $P < 0.05$) and ($r = -0.092$; $P < 0.05$) respectively.

Positive correlations existed between Ca^{2+} ions and Chlordane, Mg^{2+} ions and Aldrin, pH of soil and Lindane and organic matter and Heptachlor show that as the contents of the physico-chemical properties increase in the soils, levels of respective pesticides in the maize seeds also increase. The observed correlations between Ca^{2+} ions and Chlordane, Mg^{2+} ions and Aldrin and pH of soil and Lindane were at variance with that of Fosu-Mensah *et al.* (2013) and Asare (2011) where Ca^{2+} Mg^{2+} ions pH correlated negatively and significantly with Cyfluthrin Deltamethrin, Allethrin and Cypermethrin levels in some vegetables and fruits.

However, negative correlations observed between CEC and Endrin, sand and bulk density contents with Aldrin indicate that as CEC, sand and soil bulk density increase, concentrations of Endrin and Aldrin in the maize seeds from the maize farms also decrease. For instance, the negative correlation existed between sand contents of the soil and Aldrin levels of maize seeds implies that Aldrin levels of between maize seeds are expected to decrease as sand contents of the soils increase. This result corroborated with

that of Fosu-Mensah *et al.* (2016) who stated that sandy soils speed up leaching of pesticides and hence low levels of pesticides in the maize were expected at high sand contents in the soil since at high sand contents low levels of pesticides would be available for absorption by plants.

4.6.12 Correlations of Soil Properties with Levels of Carbamate Pesticides in Maize Seeds

Correlations between physico-chemical properties of the soils from the maize farms and the carbamate pesticides were assessed and presented (Table 4.31). Results obtained indicated that correlations between Ca^{2+} , Mg^{2+} , pH, N^+ , organic matter, sand, clay and bulk density contents of the soils and Carbaryl and Carbofuran were not significant at the indicated P-value ($P < 0.05$). Thus Ca^{2+} , Mg^{2+} , pH, N^+ , organic matter, sand, clay and bulk density contents of the soils from maize farms had no significant influence on the levels of Carbaryl and Carbofuran in the maize seeds. These findings disagreed with that reported by Fosu-Mensah *et al.* (2016) who detected significant negative correlation between Ca^{2+} , Mg^{2+} and pH Cyfluthrin Deltamethrin, Allethrin and Cypermethrin levels in some vegetables and fruits.

Potassium ions (K^+) correlated significantly and positively with Carbaryl ($r = 0.129$; $P < 0.05$) whilst Na^+ ions recorded positive correlation with Carbofuran ($r = 0.293$; $P < 0.05$). Again soil moisture contents had significant positive correlation with Carbaryl ($r = 0.092$; $P < 0.05$) whilst significant negative correlation was observed for CEC and silt with Carbofuran ($r = 0.002$; $P < 0.05$) and Carbaryl ($r = 0.021$; $P < 0.05$) respectively. The observed positive correlations existed between K^+ and Carbaryl, Na^+ ions and Carbofuran as well as that between moisture contents and Carbaryl imply that increased

in K^+ , Na^+ and moisture contents of soils from maize farms could result in increased in the levels of the respective pesticides in the maize seeds from the carrot farms. The positive correlation existed between moisture content and Carbaryl was at variance with that of Kumar and Philip (2006) and Asare (2011) where low soil moisture contents were reported to make most soil organisms less active and hence less ability to break down pesticides molecules. According to the researchers, that leads to high pesticides accumulation due to firm adsorption of pesticides molecules onto soil particles.

Table 4.31: Correlations of soil properties with levels of carbamate pesticides in maize seeds

Soil properties	Carbaryl	Carbofuran
Ca^{2+}	0.014	-0.016
K^+	0.129*	-0.179
Mg^{2+}	0.069	-0.055
Na^+	-0.118	0.293*
pH	-0.018	0.007
N^+	0.146	-0.240
CEC	-0.017	-0.002*
Soil moisture (%)	0.092*	-0.087
Organic matter	-0.016	0.059
Sand (%)	-0.043	0.009
Silt (%)	-0.021*	-0.002
Clay (%)	0.049	-0.061
Bulk density (Mg/m^3)	-0.054	0.081

*Correlation is significant at 0.05 level

However, the negative significant correlation existed between CEC and Carbofuran and silt Carbaryl showed that increasing CEC contents of the soils would lead to reduction in levels of the respective Carbaryl in the maize seeds. This observation corroborated well with that of Fosu-Mensah *et al.* (2016) where significant negative correlation was detected between exchangeable cation and Lindane ($r = - 0.492$; $P < 0.05$).

4.7 Health Quotient of Organochlorines, Organophosphate and Carbamates Pesticides in Food Crops Form the Study Area

It is expected that, the levels of pesticides residue in food crops and other consumable crops should not be above the maximum residue levels documented by both the local and international organization such as the Ghana Standard Authority (GSA), Ghana Food and Drugs Authority (FDA), Environmental Protection Agency, Ghana (EPA), World Health Organization (WHO), United State Environmental Protection Agency (USEPA), and European Union (EU) etc. Maximum Residue Limit is the maximum permissible level of remain of pesticides (usually expressed in mg/kg), recommended by the Codex Alimentarius Commission and other organizations to be permitted legally and toxicologically permitted in foods as well as animal feeds (WHO, 2013). Ensuring good agricultural practices (GAP) by the farmers will be the best way to decrease the pesticides residues in food crops below the maximum residue limits as recommended by the United State Environmental Protection Agency (USEPA) and European Union (EU) for human consumption. (Mebdoua, 2018) attributed the existence of higher pesticides residue in food crops to the violation of GAP. Also, the unauthorized use of some ban pesticides by the farmers on the crops in their farms are part of the contributing factors. These residues of pesticides on crops are often found in food which can cause chronic effect on the health of living organism including humans who consumed such products. Some of the associated health implications on the consumption of food contaminated with pesticide residue include headaches, nausea, various cancers, reproductive complications as well as the disruption to the endocrine system (Berrada *et al.*, 2010; Gilden *et al.*, 2010).

Table 4.32: Health quotient of organochlorines pesticides in cocoyam heads

Pesticides	Mean level (mg kg⁻¹)	ADI (mg kg⁻¹d⁻¹)	EDI (mg kg⁻¹d⁻¹)	HQ
Aldrin	0.001	0.0001	2.28E-06	2.28E-02
Chlordane	0.002	0.0005	4.57E-06	9.14E-03
D D T	ND	0.0200	2.28E-03	1.14E-01
Dieldrin	0.026	0.0001	5.94E-05	5.94E-01
Endosulfan	0.011	0.0006	2.51E-05	4.18E-02
Endrin	0.038	0.0002	8.68E-05	4.34E-01
Heptachlor	0.003	0.0001	6.85E-06	6.85E-02
Methoxychlor	0.049	0.0050	1.11E-04	2.22E-02

4.7.1 Health quotient (HQ) for Organochlorine Pesticides in the Cocoyam

Health quotient (HQ) for organochlorine pesticides obtained from the cocoyam in the cocoyam farms were calculated and presented in the (Table 4.19) above. The health quotients (HQ) recorded for organochlorine chlorine pesticides in cocoyam ranges from 9.14E-03 (Chlordane) – 5.94E-01 (Dieldrin). The health quotient (HQ) recorded were Dieldrin (5.94E-01) > Endrin (4.34E-01) > D D T (1.14E-01) > Heptachlor (6.85E-02) > Endosulfan (4.18E-02) > Aldrin (2.28E-02) > Methoxychlor (2.22E-02) > Chlordane (9.14E-03). All the health quotients (HQ) recorded for organochlorine pesticides in the cocoyam were below 1, which indicates that consumers of cocoyam at the time of study are at no risk as indicated by EU (2013), USEPA (2009), Akoto *et al.* (2013) and Hossain *et al.* (2015). The health quotient as reported in (Table 19) above shows no health risk to consumers, however, continuous consumption of these food crop could lead to accumulation of pesticides in the fatty tissues and would later result in some chronic health effects such as cancers (Barnhoorn *et al.*, 2015) etc. to the consumers since the mean concentration of some of the organochlorines, examples methoxychlor dieldrin, and endrin (0.049 mg/kg, 0.026 mg/kg, 0.038 mg/kg) respectively were all above their respective maximum residue limits by USEPA, 2009 and EU 2013.

Table 4.33: Health quotient of organochlorines pesticides in cocoyam leaves (taro leaves) heads

Pesticides	Mean level (mg kg ⁻¹)	ADI, (mg kg ⁻¹ d ⁻¹)	EDI (mg kg ⁻¹ d ⁻¹)	HQ
Aldrin	0.002	0.0001	4.57E-06	4.57E-02
Chlordane	0.002	0.0005	4.57E-06	9.14E-03
D D T	0.003	0.0200	6.85E-06	3.43E-04
Dieldrin	0.003	0.0001	1.96E-05	1.96E-01
Endosulfan	0.086	0.0006	7.76E-05	1.29E-01
Endrin	0.034	0.0002	1.14E-05	5.70E-02
Heptachlor	0.005	0.0001	1.14E-05	1.14E-01
Methoxychlor	0.005	0.0050	6.85E-06	1.37E-03

4.7.2 Hazard Quotient (HQ) for Organochlorine Pesticides in the Cocoyam Leaves

Health quotient (HQ) for organochlorine pesticides obtained from the cocoyam leaves in the farms of study area were computed and presented (Table 4.20). The range for health quotients (HQ) recorded for organochlorine chlorine pesticides in cocoyam leaves is 3.43E-04 (D D T) – 1.96E-01 (Dieldrin). Dieldrin (1.96E-01) was the highest followed by Endosulfan (1.29E-01), Heptachlor (1.14E-01), Endrin (5.70E-02), Aldrin (4.57E-02), Chlordane (9.14E-03), Methoxychlor (1.37E-03) and D D T (3.43E-04). Just as in the cocoyam all health quotient (HQ) recorded for organochlorine pesticides in cocoyam leaves were below 1. This implies that consumers of cocoyam leaves from the study area are at no risk as indicated by EU (2013), USEPA (2009), Akoto *et al.* (2013), 2015 and Hossain *et al.* (2015). The health quotient as reported in (Table 20) above shows no health risk to consumers. However, continuous consumption of these food crop could lead to the accumulation of the in the fatty tissues and would later result in some chronic health effects such as cancers (Barnhoorn *et al.*, 2015) etc. to the consumers since the mean concentration of some of the organochlorine pesticides,

examples endosulfan and endrin (0.086, and 0.034) mg/kg respectively were above their respective maximum residue limits by USEPA (2009) and EU (2013).

Table 4.34: Health quotient of organochlorines pesticides in cassava tubers

Pesticides	Mean level (mg kg⁻¹)	ADI (mg kg⁻¹d⁻¹)	EDI (mg kg⁻¹d⁻¹)	HQ
Aldrin	0.005	0.0001	1.14E-05	1.14E-01
Chlordane	0.004	0.0005	9.13E-06	1.82E-02
D D T	0.002	0.0200	4.57E-06	2.29E-04
Dieldrin	0.003	0.0001	6.85E-06	6.85E-02
Endosulfan	0.215	0.0006	4.91E-04	8.18E-01
Endrin	0.005	0.0002	1.14E-05	5.70E-02
Heptachlor	0.006	0.0001	1.37E-05	1.37E-01
Methoxychlor	0.010	0.0050	2.28E-05	4.56E-03

4.7.3 Health Quotient (HQ) for Organochlorine Pesticides in the Cassava Tubers

In table 21, health quotients (HQ) for organochlorine pesticides pesticide calculated for cassava were presented. The calculated health quotient for organochlorine pesticides for cassava ranged from D D T (2.29E-04) – Endosulfan (8.18E-01). HQs recorded were 8.18E-01, 1.37E-01, 1.14E-01, 6.85E-04, 5.70E-02, 1.82E-02, 4.56E-03, 2.29E-04 for Endosulfan, Heptachlor, Aldrin, Dieldrin, Endrin, Chlordane Chlordane, methoxychlor and D D T respectively. None of the health quotients recorded for organochlorine pesticides in cassava exceeded or equal to 1. This is an indication that, consumptions of these food crops do not pose any serious risk as indicated by EU (2013), USEPA (2009), Akoto *et al.* (2013), 2015 as well as Hossain *et al.*, 2015). However, due to the bioaccumulation nature of these pesticides the continuous consumption of these food crops could later resulting in some chronic health effects such as cancers (Barnhoom *et al.*, 2015) to consumers because of the higher mean concentrations of some of the organochlorine pesticides such as endosulfan

(0.215mg/kg) which exceeds the maximum residue limits by USEPA (2009) and EU (2013).

Table 4.35: Health quotient of organochlorines pesticides in maize seeds

Pesticides	Mean level (mg kg⁻¹)	ADI (mg kg⁻¹d⁻¹)	EDI (mg kg⁻¹d⁻¹)	HQ
Aldrin	0.0001	0.0001	2.28E-07	2.28E-03
Chlordane	0.004	0.0005	9.13E-06	1.83E-02
D D T	0.009	0.0200	2.06E-05	1.03E-03
Dieldrin	0.003	0.0001	6.85E-06	6.85E-02
Endosulfan	0.037	0.0006	8.45E-05	1.41E-01
Endrin	0.011	0.0002	2.51E-05	1.26E-01
Heptachlor	0.004	0.0001	9.13E-06	9.13E-02
Methoxychlor	0.022	0.0050	5.02E-05	1.00E-02

4.7.4 Health Quotient (HQ) for Organochlorine Pesticides in the Maize Seeds

Health quotients (HQs) for organochlorine pesticides in maize crops investigated from the maize farms were estimated and data presented (Table 4.22). The highest health quotient (HQ) in the maize crops were recorded by Endosulfan (1.41E-01). HQs recorded in maize farms ranged from 1.03E-03 (D D T) – 1.41E-01 (Endosulfan). Health quotients recorded in maize farm were Endosulfan (1.41E-01) > Endrin (1.26E-01) > Heptachlor (9.13E-02) > Dieldrin (685E-02) > Chlordane (1.83E-02) > Methoxychlo (1.00E-02) > Aldrin (2.28E-03) > D D T (1.03E-03).

Table 4.36: Health quotient of organophosphate pesticides in cocoyam tubers

Pesticides	Mean level (mg kg⁻¹)	ADI (mg kg⁻¹d⁻¹)	EDI (mg kg⁻¹d⁻¹)	HQ
Methamidofos	0.005	0.0010	1.75E-06	1.75E-03
Dimethoate	0.005	0.0020	1.75E-06	8.75E-04
Chlorpyrifos	0.028	0.0100	9.80E-06	9.80E-04
Chlorfenvinphos	0.073	0.0005	2.56E-05	5.12E-01
Malathion	4.870	0.0300	1.70E-03	5.67E-02
Profenofos	0.008	0.0300	2.80E-06	9.33E-05
Diazinon	0.016	0.0050	5.60E-06	1.12E-04

None of the health quotients recorded for organochlorine pesticides in maize exceeded or equal to 1. This is an indication that, consumptions of these food crops do not pose any serious risk as indicated by EU (2013), USEPA (2009), Akoto *et al.* (2013), 2015 and Hossain *et al.* (2015). However, due to the bioaccumulation nature of these pesticides the continuous consumption of these food crops could later resulting some chronic health effects such as cancers (Barnhoom *et al.*, 2015) to the consumers because the mean concentration of methoxychlor (0.022 mg/kg) of the organochlorine pesticide exceeds the respective maximum residue limits by USEPA (2009) and EU (2013).

4.7.5 Health Quotient of Organophosphate Pesticides in Cocoyam Tubers

Table 4.36 above shows health quotients (HQs) determined for organophosphate pesticides (OPPs) in cocoyam crops from cocoyam farms in the study area. The calculated health quotients (HQs) ranges from Profenfos (9.33E-05) – Chlorfenvinphos (5.12E-01). Health quotients of OPPs recorded in cocoyam crops were Chlorfenvinphos (5.12E-01) > Malathion (5.67E-02), > Methamidofos (1.75E-03) > Chlorpiryfos (9.80E-04) > Dimethoate (8.75E-04) > Diazinon (1.12E-04) > Profenofos (9.33E-05). All the health quotients recorded for organophosphate pesticides in the cocoyam exceeded or equal to 1. This is an indication that, consumptions of these food crops do not pose any serious health risk as indicated by (EU (2013), USEPA (2009), Akoto *et al.* (2013), 2015 and Hossain *et al.* (2015). However, due to the bioaccumulation nature of these pesticides the continuous consumption of these food crops could later result in some chronic health effects such as cancers (Barnhoom *et al.*, 2015) to the consumers because the mean concentration of some of the organophosphorus pesticides example Chlorpyrifos (0.028mg/kg), Chlorfenvinphos (0.073 mg/kg), Malathion (4.870 mg/kg),

Diazinon (0.016 mg/kg) were above their respective maximum residue limits by USEPA (2009) and EU (2013).

Table 4.37: Health quotient of organophosphate pesticides in cocoyam leaves (taro leaves) heads

Pesticides	Mean level (mg kg⁻¹)	ADI (mg kg⁻¹d⁻¹)	EDI (mg kg⁻¹d⁻¹)	HQ
Methamidofos	0.004	0.0010	1.40E-06	1.40E-03
Dimethoate	0.005	0.0020	1.75E-06	8.75E-04
Chlorpyrifos	0.025	0.0100	8.75E-06	8.75E-04
Chlorfenvinphos	0.059	0.0005	2.07E-05	4.14E-02
Malathion	2.683	0.0300	9.39E-04	3.03E-02
Profenofos	0.007	0.0300	2.45E-06	8.17E-05
Diazinon	0.017	0.0050	5.95E-06	1.19E-03

4.7.6 Health Quotient of Organophosphate Pesticides in Cocoyam Leaves

Health quotients (HQs) for organophosphate pesticides in cocoyam leaves from the farms were also estimated and data reported (Table 4.37). The health quotients (HQs) estimated for organophosphate pesticides were < 1. The ranged of recorded health quotients (HQs) was 8.17E-05 (Profenofos) 4.14E-02 (Chlorfenvinfos). HQs of organophosphate pesticides were 4.14E-02 (Chlorfenvinfos) > 3.03E-02 (Malathion) > 1.40E-03 (Methamidofos > 1.19E-03 (Diazinon) > 8.75E-04 (Diamethoate and Chlorpiryfos) > 8.17E-05 (Profenofos).

The health quotients (HQs) recorded for organophosphate pesticides in the cocoyam leaves did not exceed 1, which suggests that, consumption of these food crops do not pose any serious health risk as indicated by EU (2013), USEPA (2009), Akoto *et al.* (2013), 2015 as well as Hossain *et al.* (2015). However, due to the bioaccumulation nature of these pesticides continuous consumption of these food crops could later

resulting some chronic health effects such as cancers (Barnhoom *et al.*, 2015) to the consumers because the mean concentration of chlorpyrifos (0.025 mg/kg), chlorfenvinfos (0.059 mg/kg), Malathion (2.683 mg/kg) and Diazinon (0.017mg/kg) were above the MRLs by USEPA (2009) and EU (2013).

Table 4.38: Health quotient of organophosphate pesticides in cassava tubers

Pesticides	Mean level (mg kg⁻¹)	ADI (mg kg⁻¹d⁻¹)	EDI (mg kg⁻¹d⁻¹)	HQ
Methamidofos	0.007	0.0010	2.45E-06	2.45E-03
Dimethoate	0.015	0.0020	5.25E-06	2.63E-03
Chlorpyrifos	0.026	0.0100	9.10E-06	9.10E-04
Chlorfenvinphos	0.071	0.0005	2.49E-05	4.98E-02
Malathion	7.210	0.0300	2.52E-03	8.40E-02
Profenofos	ND	0.0300	3.50E-04	1.17E-02
Diazinon	0.021	0.0050	7.35E-06	1.47E-03

4.7.7 Health Quotient of Organophosphate Pesticides in Cassava Tubers

Health quotient (HQ) for organophosphate pesticides in cassava crops investigated were also computed and data tabulated (Table 4.38). All the estimated health quotients for OPPs were below 1. HQs recorded ranged from 9.10E-04 (Chlorpyrifos) – 8.40E-02 (Malathion). The recorded health quotients were Malathion (8.40E-02) > Chlorfenvinphos (4.98E-02) > Profenofos (1.17E-02) > Dimethoate (2.63E-03) > Methamidofos (2.45E-03) > Diazinon (1.47E-03) > Chlorpyrifos (9.10E-04). None of the health quotients recorded for the organophosphate pesticides in cassava exceeded or equal to 1. This is an indication that people who consume these food crops are not exposed to any serious health risk as indicated by EU (2013), USEPA (2009), Akoto *et al.* (2013) and Hossain *et al.* (2015). However, due to the bioaccumulation nature of these pesticides the continuous consumption of these food crops could later resulting some chronic health effects such as cancers (Barnhoom *et al.*, 2015) to the consumers because mean concentrations of dimethoate, chlorpyrifos, chlorfenvinfos, malathion

and Diazinon (0.015 mg/kg, 0.026 mg/kg, 0.071 mg/kg, 7.210 mg/kg and 0.021 mg/kg) respectively exceeded the maximum residue limits by USEPA, 2009 and EU 2013.

Table 4.39: Health quotient of organophosphate pesticides in maize seeds

Pesticides	Mean level (mg kg⁻¹)	ADI (mg kg⁻¹d⁻¹)	EDI (mg kg⁻¹d⁻¹)	HQ
Methamidofos	0.006	0.0010	2.10E-06	2.10E-03
Dimethoate	0.017	0.0020	5.95E-06	2.98E-03
Chlorpyrifos	0.033	0.0100	1.16E-05	1.16E-03
Chlorfenvinphos	0.103	0.0005	3.61E-05	7.22E-02
Malathion	7.226	0.0300	2.53E-03	8.43E-02
Profenofos	0.039	0.0300	1.37E-05	4.57E-04
Diazinon	0.008	0.0050	2.80E-06	5.60E-04

4.7.8 Health Quotient of Organophosphate Pesticides in Maize Seeds

Health quotient (HQ) for organophosphate pesticides (OPPs) in maize crops from the farms were estimated and the results presented (Table 4.39). The health quotient values recorded were not up to 1, which suggest that people who consume maize crops from the study area might not suffer any health issue related to the pesticides in the maize crops. Seven different organophosphate pesticides health quotients were detected, the highest health quotients recorded were Malathion (8.43E-02), followed by Chlorfenvinphos (7.22E-02), Dimethoate (2.98E-03), Methamidofos (2.10E-03), Chlorpyrifos (1.16E-03), Diazinon (5.60E-04) and the least health quotient was Profenofos (4.57E-04).

None of the health quotients recorded for the organophosphate pesticides in the maize exceeded 1, which is an indication that, consumptions of these food crops do not pose any serious risk as indicated by EU (2013), USEPA (2009), Akoto *et al.* (2013), 2015 and Hossain *et al.* (2015). However, due to the bioaccumulation nature of these

pesticides the continuous consumption of these food crops could later result in some chronic health effects such as cancers (Barnhoom *et al.*, 2015) to consumers since mean concentration of some of Dimethoate, Chlorpyrifos, Chlorfenvinfos, and Malathion (0.017, 0.033, 0.103, 7.226) mg/kg respectively exceeded the maximum residue limits by USEPA (2009) and EU (2013).

Health quotients of carbamate pesticides (carbofuran and carbaryl) in food crops used in the study were estimated and recorded (Tables 4.27, 4.28, 4.29 and 4.29).

Table 4.40: Health quotient of carbamate pesticides in cocoyam tubers

Pesticides	Mean level (mg/kg)	ADI (mg kg⁻¹d⁻¹)	EDI	HQ
Carbofuran	0.198	0.0100	4.54E-04	4.54E-02
Carbaryl	0.087	0.0100	1.98E-04	1.98E-02

4.7.9 Health Quotient of Carbamate Pesticides in Cocoyam Tubers

In table 4.40, health quotients for carbofuran and carbaryl in the cocoyam tubers were presented. Carbaryl recorded a value (1.98E-02) < carbofuran (4.54E-02). However, none of the recorded health quotients exceeded for carbofuran and carbaryl in cocoyam exceeded 1, which is an indication that, consumptions of these food crops do not pose any serious risk as indicated by EU (2013), USEPA (2009), Akoto *et al.* (2013) and Hossain *et al.* (2015). However, due to the bioaccumulation nature of these pesticides the continuous consumption of these food crops could later result in some chronic health effects such as cancers (Barnhoom *et al.*, 2015) to the consumers since the mean concentration of carbofuran (0.198 mg/kg) and carbaryl (0.087 mg/kg) were above the MRLs by USEPA (2009) and EU (2013).

Table 4.41: Health quotient of carbamate pesticides in cocoyam leaves heads

Pesticides	Mean level (mg/kg)	ADI (mg kg⁻¹d⁻¹)	EDI	HQ
Carbofuran	0.135	0.0100	3.08E-04	3.08E-02
Carbaryl	0.062	0.0100	1.42E-04	1.42E-02

4.7.10 Health Quotient of Carbamate Pesticides in Cocoyam Leaves

The health quotient carbofuran and carbaryl recorded in cocoyam leaves estimated were presented (Table 4.41). The health quotients values recorded were not greater or equal to 1 which suggests that consumers of cocoyam leaves from the study area may not suffer any serious health implications as indicated by EU (2013), USEPA (2009), Akoto *et al.* (2013) and Hossain *et al.* (2015). Recorded health quotients were 1.42E-02 and 3.08E-02 for carbaryl and carbofuran respectively in cocoyam leaves. Due to the bioaccumulation nature of these pesticides the continuous consumption of these food crops could later result in some chronic health effects such as cancers (Barnhoom *et al.*, 2015) to the consumers since the mean concentration of carbofuran (0.135 mg/kg) and carbaryl (0.062 mg/kg) were above the MRLs by USEPA (2009) and EU (2013).

Table 4.42: Health quotient of carbamate pesticides in cassava tubers

Pesticides	Mean level (mg/kg)	ADI (mg kg⁻¹d⁻¹)	EDI	HQ
Carbofuran	0.192	0.0100	4.38E-04	4.32E-02
Carbaryl	0.044	0.0100	1.00E-04	1.00E-02

4.7.11 Health Quotient of Carbamate Pesticides in Cassava Tubers

In cassava crops used for the study, health quotient for carbaryl and carbofuran estimated were tabulated (Table 4.29). The highest health quotients 4.32E-02 was estimated for carbofuran with 1.00E-02 for carbaryl. Again, estimated health quotients in maize crop were less than 1. This is an indication that, consumptions of these food

crops do not pose any serious risk as indicated by EU (2013), USEPA (2009), Akoto *et al.* (2013) and Hossain *et al.* (2015). However, due to the bioaccumulation nature of these pesticides, the continuous consumption of cassava from the study area could later result in some chronic health effects such as cancers (Barnhoom *et al.*, 2015) to the consumers because the mean concentration of the carbofuran and carbaryl (0.192 and 0.044) mg/kg respectively which were above the MRLs by USEPA (2009) and EU (2013).

Table 4.43: Health quotient of carbamate pesticides in maize seeds

Pesticides	Mean level (mg/kg)	ADI (mg kg ⁻¹ d ⁻¹)	ED I	HQ
Carbofuran	0.040	0.0100	9.13E-05	9.13E-03
Carbaryl	0.056	0.0100	1.29E-04	1.29E-03

4.7.12 Health Quotient of Carbamate Pesticides in Maize Seeds

Table 4.43 above shows health quotients for carbofuran and carbaryl estimated in maize crops in the study area. Carbofuran (9.13E-03) > Carbaryl (1.29E-03). Recorded health quotients do not exceed 1 for carbofuran and carbaryl in maize, which show that consumptions of these food crops do not pose any serious risk as indicated by EU (2013), USEPA (2009), Akoto *et al.* (2013), 2015 and Hossain *et al.* (2015). However, due to the bioaccumulation nature of these pesticides the continuous consumption of these food crops could later resulting in some chronic health effects such as cancers (Barnhoom *et al.*, 2015) to the consumers since the mean concentration of carbofuran (0.04 mg/kg) exceeded the maximum residue limit by USEPA, 2009 and EU 2013.

Table 4.44: Combined Health quotient (CHQ), hazard indices (CHI) and health risk (HR) of pesticides in some food crops (cocoyam, cocoyam leaves, cassava and maize) samples from Asante Akyem Central Municipality.

Food crops	Pesticides	CHQ	CHI	HR
Cocoyam	Organochlorines	1.310	1.948	Yes
	Organophosphates	5.73E-01		
	Carbamates	6.50E-02		
Cocoyam leaves	Organochlorines	5.53E-01	6.74E-01	No
	Organophosphates	7.60E-02		
	Carbamates	4.50E-02		
Cassava	Organochlorines	1.217	1.423	Yes
	Organophosphates	1.53E-01		
	Carbamates	5.30E-02		
Maize	Organochlorines	4.58E-01	6.32E-01	No
	Organophosphates	1.64E-01		
	Carbamates	1.04E-02		

4.7.13 Combined Health Quotient (CHQ), Hazard Indices (CHI) and Health Risk (HR) of Pesticides in Cocoyam, Cocoyam Leaves, Cassava and Maize

The combined health quotients and corresponding combined hazard indices as well as the health risk assessment for systematic association with organochlorines, organophosphorus and carbamates pesticides residues encountered in cocoyam, cocoyam leaves, cassava and maize are summarized (Table 4.44). The combined health quotient (CHQ) values determined were 1.310 (organochlorines pesticides) > 5.73 x 10⁻⁰¹ (organophosphate pesticides) > 6.50 x 10⁻⁰² (carbamates pesticides). The CHQ value obtained for organochlorine pesticides pose a serious health treat for human consumption, unlike CHQ values recorded for organophosphate pesticides and carbamate pesticides that pose no serious health risk. Usually, a health quotient of less than 1 (HQ < 1) indicates that the consumers (people who eat such foods) are safe from the potential adverse health effects, whereas health quotients greater than 1 (HQ > 1) suggest that there are detrimental health effects to the exposed consumers. However,

continuous intake of these foods for a longer period may lead to adverse health risk, since these pesticides are able to accumulate in the adipose tissue for so long, no matter how small the intake may be. The combined health indices calculated for the pesticides in the cocoyam food is above 1 which shows a possible health risk for the consumers of cocoyam in the study areas.

In cocoyam leaves combined health quotients (CHQ) organochlorine pesticides were (5.53×10^{-1}) > organophosphate pesticides (7.60×10^{-2}) > carbamate pesticides (4.50×10^{-2}). Unlike in cocoyam, the combined health quotients (CHQ) determined in cocoyam leaves were below 1, which suggests no health risk linked with the intake of cocoyam leaves, provided the prolong intake of these foods are avoided since these pesticides can be accumulated in the tissues of consumers for longer periods. The combined health index recorded was less than 1 (CHI < 1), which also confirm the minimal or no health risks for the consumers.

Combined health quotients (CHQs) determined for pesticides in cassava foods showed a higher CHQ for organochlorines (1.217), followed by organophosphorus (1.53×10^{-1}) and then carbamate (5.30×10^{-2}). High CHQ recorded for organochlorines in cassava indicates that consumers of cassava from the study area are at health risk. Unlike the organochlorine pesticides, the CHQs recorded for organophosphorus and carbamates pesticides posed no negative health implications. The health index as indicated in table 4.44 (1.423) is greater than 1 which is as a result of higher CHQ recorded by the organochlorine. Therefore, consumptions of cassava in the study area may pose a serious health implication.

Combined health quotients (CHQ) recorded in maize was organochlorine pesticides (4.58×10^{-1}) > organophosphate pesticides (1.64×10^{-1}) carbamate pesticides (1.04×10^{-2}). None of these combined health quotients pose any health treat, since they all fall below 1. Their combined health risk also falls below 1, (6.32×10^{-2}) which confirms minimal or no health implications for the consumers of maize at the time of study. However, as indicated in this write up already, these pesticides have bio accumulative properties and hence are able to stay in the tissues for a longer period and may cause long term health effects.

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 Summary

This chapter deals with summary, conclusion from the study and the recommendations made.

Foods provide necessary nutrients for body growth, repair of tissues and boost the immune system London (2010). Staple crops dominate the major part of human diet and supply energy and nutrient needed by the body Requier *et al.* (2015). These nutrients are carbohydrates, protein, vitamins and minerals. They help to improve the functions of the body, boost the immune system and promote healthy living among mammals (Yahia *et al.*, 2019). Foods provide nutrients that are vital to energy requirements, body building and general health of humans (Wu 2016). Hence pesticides accumulation in food should be of a concern because it could lead to ingestion of pesticides by humans and may be detrimental to their health.

This study looked at the levels of pesticides namely organochlorine, organophosphate and carbamates in cocoyam tubers, cocoyam leaves, cassava tubers and maize cultivated in the Asante Akyem Central Municipality of the Ashanti Region of Ghana. The study again investigated correlation between pesticides levels in the food crops investigated from selected farmlands and their associated physico-chemicals parameter. Also, the health quotient (HQ) and health index (HI) were investigated.

Complete Randomized Design method of sampling was employed in collecting soil and food crop samples. In all, ten (10) crop farms were randomly selected from fifteen (15) identified farms between April, 2021 and November, 2021. The ten (10) farms selected were as a result of their large size as well as the crops availability compared to the five (5) that were not included in this study. The average farm size where food crops and soil samples were collected were about 1.6 ha and observed were below 1.0 ha. Soil samples and food crops from the ten (12) farms were collected on the August 16, 2021.

Physical and chemical properties of the soil samples in addition to the organochlorine, organophosphate and carbamate pesticides levels were determined. Fresh and healthy cocoyam, cocoyam leaves, cassava and dried maize obtained from the farms in the Asante Akyem Central Municipality were analyzed for their levels of pesticides. The results obtained from laboratory were statistically treated using one-way ANOVA to determine the difference in properties of the soils. Pesticides levels of the soil and the food crops were reported in the form of mean and standard deviation of the mean using GenStat (Version 11.10) and the data obtained reported.

The soil samples were taken at depth 0 to 20cm from the ten (10) farms (namely cocoyam, cocoyam leaves, cassava, and maize farms) for the physical properties, chemical properties, and exchangeable cations analysis. pH of soil samples used for the experiments ranged from 5.09 to 6.60. Soil conductivity on the other hand ranged from 343.03 to 723.01 mS/m, whilst organic carbon content ranged from 0.65 to 2.06%, soil organic matter recorded ranged from 1.12 to 3.55%, total nitrogen content ranged from 0.01 – 0.23%, and the total phosphorus content ranged from 1.18 to 5.81%. Cation exchange capacity (CEC) of the soil recorded ranged from 6.84 ± 1.23 to 6.84 ± 0.83

cmol/kg, exchangeable Ca^{2+} ions ranged from 1.01 to 3.66 cmol/kg, exchangeable Mg^{2+} ions also from 0.10 to 1.14 cmol/kg, Na^+ exchangeable ions recorded from 0.01 to 0.06 cmol/kg and the exchangeable K^+ ions from 0.01 –to 0.18 cmol/kg.

Ca^{2+} , Mg^{2+} , Na^+ , and K^+ ions recorded were low. That shows the reduction of number of active sites by the soil. Therefore, pesticides adsorption onto the soil particles was minimal and weak. As a result, pesticides persisted for a longer period in the soils. This was expected because the pesticides molecules could easily leach into soil solution (Asare, 2011). Moisture contents of the soil ranged from 2.70 to 9.11%, sand content ranged from 20.90 to 81.10%, silt content on the other hand ranged from 27.60 to 70.30% and the clay content ranged from 4.00 to 32.90%. Soil porosity density in gcm^{-3} ranged from 0.80 –to 1.70, soil porosity ranged from 0.50 to 0.90.

Mean levels of organochlorine pesticides contents of soil from the farms ranged from 0.006 ± 0.009 to 10.053 ± 3.608 mg/kg. Chlordane contents of soils ranged from 0.029 ± 0.015 to 0.047 ± 0.031 mg/kg, Dieldrin levels ranged from 0.033 ± 0.026 to 0.041 ± 0.023 mg/kg, Endrin levels ranged 0.439 ± 0.221 to 0.543 ± 0.176 mg/kg, Heptachlor levels also ranged 0.036 ± 0.039 to 0.057 ± 0.031 mg/kg and the Methoxychlor levels ranged from 5.366 ± 5.035 to 10.053 ± 3.608 mg/kg. The mean levels were all above the levels recommended by USEPA/EU to be acceptable for soils. Organophosphate pesticides content of the soils ranged from 0.018 ± 0.012 to 0.993 ± 0.264 mg/kg. Methamidofos levels in the soil ranged from 0.029 ± 0.040 to 0.032 ± 0.018 mg/kg, Dimethoate 0.917 ± 0.431 to 0.993 ± 0.264 mg/kg, Chlorpyrifos levels ranged from 0.305 ± 0.262 – 0.444 ± 0.460 mg/kg, Parathion 0.315 ± 0.194 to 0.495 ± 0.343 mg/kg, Chorfenvinfos levels also range 0.312 ± 0.242 to 0.514 ± 0.335 mg/kg, Phorate 0.345

± 0.342 to 0.510 ± 0.351 mg/kg, and Profenofos content levels in the soil ranged from 0.194 ± 0.229 to 0.527 ± 0.36 mg/kg. These concentrations of organophosphates recorded were higher than the maximum recommended levels in the soil set by USEPA/EU. These high levels of organophosphates may be due to the continuous use of the pesticides on the same soil and agreed with that of Asare (2011). Mean levels of carbamate pesticides in the soil ranged from 0.293 ± 0.220 to 0.694 ± 0.142 mg/kg. Carbofuran content levels in the soil from 0.308 ± 0.218 to 0.694 ± 0.142 mg/kg and that of Carbaryl from 0.293 ± 0.220 to 0.577 ± 0.354 mg/kg.

Aldrien, Chlordane, Endosulfan, Heptachlor, Lindane contents of cocoyam heads from the crop farm were 0.001 ± 0.002 mg/kg, 0.002 ± 0.001 mg/kg, 0.011 ± 0.009 mg/kg, 0.003 ± 0.006 mg/kg and 0.004 ± 0.005 mg/kg. These mean values were below the acceptable limits permitted by USEPA and EU. However, the mean levels recorded for Dieldrin, Endrin and Methoxychlor 0.026 ± 0.003 mg/kg, 0.038 ± 0.064 mg/kg and 0.049 ± 0.004 mg/kg respectively from the cocoyam were above the maximum residue limits (0.01 mg/kg) recommended by the USEPA and the EU for Dieldrin, Endrin and Methoxychlor.

Mean contents of Methamidofos, Dimethoate, Parathion and Prefenofos of cocoyam obtained from the farms were 0.005 ± 0.006 mg/kg, 0.005 ± 0.008 mg/kg, 0.006 ± 0.012 mg/kg and 0.008 ± 0.037 mg/kg respectively. These values recorded in the cocoyam were below the value 0.01 mg/kg set by USEPA and UE in 2013. Chlorpyrifos (0.028 ± 0.049 mg/kg), Chlorfenvinfos (0.073 ± 0.062 mg/kg), Malathion (4.870 ± 1.489 mg/kg), Phorate (0.078 ± 0.061 mg/kg), Enthoprofos (0.016 ± 0.012 mg/kg) and Diazinon (0.016 ± 0.011 mg/kg). The mean values recorded for Chlorpyrifos,

Chlorfenvinfos, Malathion, Phorate, Ethoprophos and Diazinon exceed the USEPA and EU, (2013) maximum limits.

Levels of Carbofuran and Carbaryl of cocoyam heads from the farms were $(0.198 \pm 0.088 \text{ mg/kg})$ and $(0.087 \pm 0.103 \text{ mg/kg})$. These values were above the (0.002 mg/kg) and (0.001 mg/kg) for Carbofuran and Carbaryl respectively set by the USEPA (2009) and EU in (2013).

Aldrin, Chlordane, D D T, Dieldrin, Heptachlor, Lindane and Methoxychlor contents of cocoyam leaves heads from the farm were $0.002 \pm 0.001 \text{ mg/kg}$, $0.002 \pm 0.001 \text{ mg/kg}$, $0.003 \pm 0.001 \text{ mg/kg}$, $0.003 \pm 0.003 \text{ mg/kg}$, $0.005 \pm 0.003 \text{ mg/kg}$, $0.006 \pm 0.003 \text{ mg/kg}$ and $0.005 \pm 0.003 \text{ mg/kg}$ respectively. These values recorded in the cocoyam leaves were below the value 0.01 mg/kg set by USEPA (2009) and EU (2013). The mean contents of cocoyam leaves heads from the farm Endosulfan (0.086 ± 0.008) and Endrin ($0.034 \pm 0.051 \text{ mg/kg}$) exceeded the maximum residue limits set by the USEPA (2009) and the EU (2013).

Levels of organophosphate pesticides detected in cocoyam leaves ranged from $0.004 \pm 0.005 \text{ mg/kg}$ (Methamidophos) to $2.683 \pm 2.235 \text{ mg/kg}$ (Malathion). Concentrations of OPPs recorded in cocoyam leaves were Malathion (2.683 ± 2.235) > Phorate (0.070 ± 0.063) > Chlorfenvinfos (0.059 ± 0.065) > Chlorpyrifos (0.025 ± 0.068) > Diazinon (0.017 ± 0.013) > Ethoprophos (0.015 ± 0.013) > Parathion (0.009 ± 0.020) > Profenofos (0.007 ± 0.016) > Dimethoate (0.005 ± 0.004) > Methamidophos ($0.004 \pm 0.005 \text{ mg/kg}$).

Mean concentration of Malathion, Phorate, Chlorfenvinphos, Chlorpyrifos, Diazinon, and Ethoprophos reported were higher than the recommended maximum residue limits reported by the USEPA (2009) and EU (2013).

Levels of Methamidophos (0.004 ± 0.005 mg/kg), Dimethoate (0.005 ± 0.004 mg/kg), Parathion (0.009 ± 0.020 mg/kg), and Profenofos (0.007 ± 0.016 mg/kg) were below recommended maximum residue limits reported by the United State Environmental Protection Agency (USEPA) 2009, and European Union (2013).

Carbofuran (0.135 ± 0.059 mg/kg) and Carbaryl (0.062 ± 0.063 mg/kg) occurred in cocoyam leaves heads from the farm and were above the mean values (0.002 mg/kg) for Carbofuran and (0.010 mg/kg) for Carbaryl recommended by the USEPA (2009) and European Union (2013).

Levels of Aldrien, Chlordane, D D T, Dieldrin, Endrin, Heptachlor, and Lindane of cassava farm were 0.005 ± 0.003 mg/kg, 0.004 ± 0.002 mg/kg, 0.002 ± 0.002 mg/kg, 0.003 ± 0.003 mg/kg, 0.005 ± 0.004 mg/kg, 0.006 ± 0.008 mg/kg and 0.007 ± 0.056 mg/kg respectively and were below the recommended maximum residue limits by the USEPA (2009) and the UE (2013). Levels of Endosulfan (0.215 ± 0.013 mg/kg) and Methoxychlor (0.010 ± 0.006 mg/kg) recorded in the cassava crops exceed the (0.05 mg/kg) Endosulfan and (0.01 mg/kg) for Methoxychlor recommended by the USEPA (2009) and the EU (2013).

Methamidofos (0.007 ± 0.005 mg/kg) and Parathion (0.008 ± 0.017 mg/kg) occurred in cassava heads from the farm were less than the 0.010 mg/kg recommended by USEPA

(2009) and EU (2013). Dimethoate (0.015 ± 0.014 mg/kg), Chlorpyrifos (0.026 ± 0.036 mg/kg), Chlorfenvinfos (0.071 ± 0.050 mg/kg), Malathion (7.210 ± 2.282 mg/kg), Phorate (0.119 ± 0.094 mg/kg) Ethoprophos (0.023 ± 0.015 mg/kg), and Diazimnon (0.021 ± 0.014 mg/kg) determined in the cassava heads from the farm were above the 0.010 mg/kg recommended by the USEPA (2009) and the EU (2013).

Carbofuran (0.192 ± 0.148 mg/kg) and Carbaryl (0.044 ± 0.065 mg/kg) occurred in the cassava taken from the farm were above the 0.002 mg/kg and 0.01 mg/kg set USEPA (2009) and EU (2013) for Carbofuran and Carbaryl respectively.

Levels of Aldrin, Chlordane, D D T, Dieldrin, Endosulfan, Heptachlor and Lindane detected in maize were 0.0001 ± 0.0003 mg/kg, 0.004 ± 0.002 mg/kg, 0.009 ± 0.001 mg/kg, 0.003 ± 0.002 mg/kg, 0.027 ± 0.029 mg/kg, 0.004 ± 0.002 mg/kg, 0.002 ± 0.002 mg/kg respectively. These levels were below 0.01 mg/kg for Aldrien, Dieldrin, Heptachlor, Lindane and 0.02 mg/kg for Chlordane and 0.05 mg/kg for D D T and Endosulfan recommended by the USEPA (2009) and EU (2013) to be safe for human health. Endrin and Methoxychlor levels in the maize were 0.011 ± 0.001 mg/kg and 0.022 ± 0.011 mg/kg respectively. The recommended maximum concentration by the USEPA (2009) and UE (2013) for Endrin and Methoxychlor is 0.01 mg/kg which show higher concentrations of Endrin and Methoxychlor in the maize from the farm.

In the maize farms only Methamidophos (0.006 ± 0.006 mg/kg) and Diazinon (0.008 ± 0.007 mg/kg) levels were below the 0.010 mg/kg recommended by the USEPA (2009) and UE (2013). The levels for Dimethoate (0.017 ± 0.008 mg/kg), Chorpyrifos (0.033 ± 0.023 mg/kg), Parathion (0.029 ± 0.015 mg/kg), Chlorfenvinfos (0.103 ± 0.056

mg/kg), Malathion (7.226 ± 3.382 mg/kg), Phorate (0.148 ± 0.105 mg/kg), Profeninfos (0.039 ± 0.031 mg/kg), and Ethoprophos (0.027 ± 0.020 mg/kg) in the maize were above the 0.010mg/kg recommended by the USEPA (2009) and EU (2013) to be the maximum residue limits.

Carbofuran and Carbaryl contents in the maize were 0.040 ± 0.045 mg/kg and 0.056 ± 0.034 mg/kg respectively, and were all above the USEPA (2009) and EU (2013) recommended maximum residue limits of 0.010 mg/kg and 0.500 mg/kg for Carbofuran and Carbaryl in that other.

Cocoyam, cocoyam leaves, cassava and maize cultivated in the Asante Akyem Central Municipality at the period of this study appeared not to pose serious health risk issues linked to organophosphate, organochlorine and carbamate pesticides on consumption. This was confirmed in the estimated HQs which were below 1 for each class of the pesticides investigated herein. However, the combined health index value above 1 calculated showed health risk in cocoyam and cocoyam and cassava in the study area. Cocoyam leaves and maize did not show any combined health risk because value obtained was less than 1. Twenty-one (21) pesticides detected in this study, only few are currently approved for used by the European Union (EU pesticides approval list 2015). These were Malathion, Pirimiphos, Carbofuran, and Carbaryl. Ghana EPA however, have approved in the following pesticides for use in Ghana. They were Diazinon, Dimethoate, Chlorpyrifos, Malathion, Pirimiphos, Profenofos, Carbofuran and Carbaryl. None of the organochlorine pesticides detected herein has received approval for used by European Union and Ghana EPA. Hence, people who consume foods contaminated with organochlorine pesticides at the time of this study were likely

to endure some health issues associated with organochlorines.

5.2 Conclusion

The results of this study indicate that cocoyam, cocoyam leaves, cassava and maize growers in the Asante Akyem Central Municipality of the Ashanti Region apply pesticides (authorized and unauthorized) on crops they grow. Farmers in the municipality quest to control pests, diseases and to obtain high produce led to application of high quantities of pesticides on cocoyam, cocoyam leaves, cassava and maize grown in the municipality.

This study identified organochlorine, organophosphate, and carbamate pesticides as commonly used for cocoyam, cocoyam leaves, cassava, and maize cultivation. These pesticides were found in soils samples taken at depth 0 to 20 cm below the soil surface. Organochlorines, organophosphate and carbamate pesticides levels in the soils ranged from ND to 12.317 mg/kg (organochlorines pesticides), 0.007 to 1.485 mg/kg (organophosphate pesticides), and 0.026 to 0.900 mg/kg (carbamate pesticides). Levels of Methoxychlor, Dieldrin, Endrin, Heptachlor (organochlorines) recorded in the study were above recommended levels set by USEPA (2009) and the EU (2013). Likewise, Chlorpyrifos, Chlorfenvinphos, Phorate, Profenofos, Parathion (organophosphate pesticides) and the levels of Carbofuran and Carbaryl (carbamate pesticides) were all above the maximum recommended residual limits by USEPA (2009) and the EU (2013). This shows that food crops which absorb nutrients from 0 to 20cm within the soil surface are likely to be contaminated by pesticides.

Levels of soil pH ranged from 5.09 to 6.60, conductivity ranged from 343.03 to 723.01 mS/m, whilst organic carbon content ranged from 0.65 to 2.06%. Soil organic matter recorded ranged from 1.12 to 3.55%, total nitrogen ranged from 0.01 to 0.23%, and total phosphorus ranged from 1.18 to 5.81%. Cation exchange capacity (CEC) of the soil recorded ranged from 6.84 ± 1.23 to 6.84 ± 0.83 cmol/kg, exchangeable Ca^{2+} ions ranged from 1.01 to 3.66 cmol/kg, exchangeable Mg^{2+} ions ranged from 0.10 – 1.14 cmol/kg, Na^+ exchangeable ions from 0.01 to 0.06 cmol/kg and exchangeable K^+ ions ranged from 0.01 to 0.18 cmol/kg.

The results recorded from the experimental farms indicated that, cocoyam, cassava and maize farmers in the Asante Akyem Central Municipality use almost similar pesticides on the crops. Chlorfenvinphos was present in all the food crops at a concentration which ranged from 0.059 ± 0.065 mg/kg to 0.103 ± 0.056 mg/kg. Levels of Chlorfenvinphos recorded were 0.073 ± 0.012 mg/kg (Cocoyam), 0.059 ± 0.065 mg/kg (cocoyam leaves), 0.071 ± 0.050 mg/kg (cassava farm) and 0.103 ± 0.045 mg/kg (maize farm). Carbofuran was also recorded in all food crops and ranged from 0.040 ± 0.045 mg/kg to 0.198 ± 0.088 mg/kg. Levels of carbofuran were cocoyam (0.198 ± 0.088 mg/kg), cocoyam leaves (0.135 ± 0.059 mg/kg), cassava (0.192 ± 0.148 mg/kg) and cassava (0.040 ± 0.045 mg/kg). When pesticides levels in all food crops were compared with the USEPA and EU, it was envisaged that mean levels of the Methoxychlor, Endrin, dieldrin, Endosulfan, (organochlorine pesticides), Chlorfenvinphos, Malathion, Phorate, Diazinon, Ethoprofos (organophosphorus pesticides) and Carbofuran, Carbaryl (Carbamates) were above recommended levels by the USEPA (2009) and EU (2013).

The findings in the study confirm that cocoyam tubers, cocoyam leaves, cassava tubers and maize cultivated in the Asante-Akyem Municipality of the Ashanti Region are contaminated with organophosphate, organochlorine and carbamates pesticides. Cocoyam, cocoyam leaves, cassava and maize farmers and consumers could have elevated levels of pesticides in their blood tissues and organs. Hence, it is important that the farmers in the Asante-Akyem are educated on handling and application of pesticides. If farmers continue to use pesticides at high levels, consumers would likely experience negative effects associated with the pesticide's intake.

5.3 Recommendations

Based on the discoveries from this study, it is recommended that Environmental Protection Agency (EPA), Food and Drug Authority (FDA) and Ghana Standard Authority (GSA) should:

- 1 Intensify their supervision and monitoring on the importation of pesticides to ensure that unapproved pesticides would not get into the hands of farmers.
- 2 Educate farmers on proper usage of approved pesticides for crop production
- 3 Educate farmers on adverse health effects associated with the use of pesticides for crop production.
- 4 Finally, further studies should be done to determine pesticides levels in plantain, yam and banana which are also consumed by majority of people living in the Asante-Akyem municipality of the Ashanti Region.

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