UNIVERSITY OF EDUCATION, WINNEBA

HEALTH RISKS ASSOCIATED WITH PESTICIDES RESIDUES IN VEGETABLES AND SOILS

JOB DONKOR

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DECLARATION

STUDENT'S DECLARATION

I, Job Donkor, hereby declare that this thesis, with the exception of quotations and references contained in published works which have all been identified and duly acknowledged, is entirely my own original work, and it has not been submitted, either in part or whole, for another degree elsewhere.

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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DEDICATION

This thesis is dedicated to Pamela Obed Donkor (Mrs), Mr. Theophilus Asamoah Donkor and Reverend Paul Akwasi Annor of Assemblies of God, Ghana.

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ABSTRACT

Applications of pesticides help to increase agricultural productivity. However, their applications on vegetables can be detrimental to the health of consumers. In view of this, the study was conducted to investigate pesticides residues in soils and vegetables and their associated health risks. Cabbage heads, carrot roots, green pepper fruits and lettuce leaves and soils from the vegetable farms were analysed for organophosphates (OPP), organochlorines (OCP) and synthetic pyrethroids (SPP) pesticides. The Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) mini multi-residue method for extracting multi pesticides residues was used and pesticides levels determined using Gas Chromatography-Mass Spectrometry (GC-MS). Correlation between physico-chemical properties of soils and pesticide residues levels were determined. OPPs, OCPs and SPPs occurred in all samples. OPPs levels in soils ranged from 0.016 ± 0.01 to 0.059 ± 0.007 mg/kg. OCPs levels in soils ranged from 0.013 ± 0.006 to 0.052 ± 0.002 mg/kg whilst that of SPPs ranged from 0.022 ± 0.005 to 0.074 ± 0.039 mg/kg. Pesticides levels in vegetables ranged from 0.002 ± 0.001 to 0.042 ± 0.004 mg/kg (OPPs), 0.002 ± 0.001 to 0.059 ± 0.002 mg/kg (OCPs) and 0.003±0.001 to 0.064 ± 0.008 mg/kg (SPPs). However, levels of some of the OPPs (Diazinon, Pirimiphos, and Dimethoate), OCPs (Aldrin, Beta Endosulfan, and Dieldrin) were above MRLs sanctioned by USEPA and European Union. The high levels of the pesticides detected indicate that vegetables were contaminated based on the USEPA and EU acceptable maximum residue limits. OPPs (Diazinon, Pirimiphos, Malathion and Dimethoate) and OCPs (Aldrin, Beta Endosulfan, Dieldrin, P'P' DDE and Methoxychlor) detected in soils and the vegetables are banned for use or not registered for use by USEPA and European Union or Ghana EPA. Positive correlations existed between pH, H^+, exchangeable cations, clay, moisture contents, organic carbon, bulk density, and total nitrogen, available phosphorus of soils and pesticides levels in vegetables. Thus, soil properties influenced the distributions and levels of pesticides in vegetables. The HQs and HIs of pesticides were below 1. However, continuous consumption of the vegetables could lead to development of certain health risks in consumers due to bioaccumulation in tissues. It is recommended that farmers should be educated on prpper handling and use of approved pesticides and should be educated on negative health issues linked to pesticides application.

CHAPTER ONE

INTRODUCTION

This chapter presents the background to the study, statement of the problem, justification of the study, significance of the study and the research objectives.

1.1 Background to the Study

Pesticides are utilized by health officials, gardeners and farmers to control the activities of pathogens (Grube *et al*., 2011; FAO, 1989). Pesticides are chemical substances that derive their names from the French word “Peste”, which means pest or plague and the Latin word “caedere”, which also means to kill (Akunyili and Ivbijaro, 2006).

Application of pesticides is justifiable since they help increase agricultural productivity (Gianessi, 2014). For instance, Clarke *et al.* (1997) reported that about 40 to 75% of crops grown in tropical countries such as Ghana got lost due to pest infestation. Pesticides used in agriculture have played crucial role in reducing crop losses before and after harvest (Kumar *et al*., 2017; Maksymiv, 2015).

Pesicides applications have resulted in improved crop yield, quality of produce as well as customer appeal (Ogwuik *et al.,* 2014; Cooper and Dobson 2007). High rates of pesticides application in vegetables (cabbage, carrot, green pepper and lettuce) production have negative environmental and human health effects (Musah, 2018). Pesticides are potentially toxic to humans and can have both acute and chronic health effects, depending on the quantities and route of exposure (WHO, 2018). Thus, pesticides application on crops can be detrimental to the health of consumers.

Soil is an important resource for agriculture and has an ability to retain agro-chemicals (Bhattarai, 2010). Soil contamination causes the presence of xenobiotics from industrial activity and improper disposal of waste agricultural chemicals to build up in the soil (Bożena *et al.*, 2017). The presence of pesticides in soils may have originated from different sources including direct application, accidental spillage of pesticides, surface runoff from plants and incorporation of pesticide contaminated plant materials into compost (Rashid *et al.*, 2010).

Pesticides application to soil could have an impact on non-target crops, non-target organisms and damage the metabolism required for soil fertility and pesticide degradation (Asare, 2011; Rani *et al*., 2021). Although organochlorine pesticides are banned from sale, and use in Ghana, evidence exist of their presence in the ecosystem due to continuous use (Darko and Acquah, 2007). Continuous application of organochlorine pesticides on farms can lead to deterioration of soil flora and fauna through physical and chemical destruction (Rani and Dhania, 2014).

Vegetables are highly consumed among Ghanaians (Abdulai *et al.*, 2017). They provide nutrients which help improve human immune system and promote healthy living among consumers (Hanif *et al.*, 2006). Vegetables contain active compounds such as terpenoids, carotenoids, phenolics, phytosterols, and glucosinolates that can reduce the effect of cardiovascular diseases in humans (Boateng, 2018). High intake of vegetables (80 g per day) has been found not only to prevent ailments of vitamin deficiency but also reduce the incidences of major diseases such as cancer, cardiovascular diseases and obesity (Albani *et al.*, 2017; Castejon and Casado 2011). Although, vegetables have high immune importance, their consumption can be a source of exposure to pesticides from residues in ingested vegetables (Amoah *et al.*, 2006). Ingestion of pesticide residues on vegetables could cause diseases and other negative effects (Parrón *et al.*, 2014; Lemos *et al.*, 2016). Due to their persistence and lipophilicity, pesticides may concentrate in the adipose tissues (La Merrill *et al.*, 2013) and in blood serum of mammals from their persistence in the environment and via food chain (Darko and Acquah, 2007; Wilson *et al.*, 2007).

Globally, use of pesticides is estimated to be 4.2 million metric tons/year (Fernández, 2021). About 69% of pesticides is used by Europe whilst the remaining 31% is consumed by USA and the rest of the world (Abhilash and Singh, 2009). Pesticides application on food crops has increased rapidly in low- and middle-income countries over the last decades (Praneetvatakul *et al.*, 2013). This could be due to increased availability of these chemicals on the markets (Kumari and John, 2019) and their availability has increased the problems in humans and environment (Ashburner and Friedrich, 2001). Hence effects of pesticides in humans and the environment need to be addressed (National Research Council, 2000). In Ghana, pesticides use has increased rapidly (Dankyi *et al.*, 2018) and thus has contributed to the production of high-value cash crops and vegetables (Gerken *et al.*, 2001).

1.2 Statement of the Problem

Pesticides application to control pests in vegetable production cause pesticides residues to persist in vegetables and soils where the vegetables are cultivated (Donkor *et al.*, 2016). The levels of these residues can be below the maximum residue limit (MRL) allowed by some international regulatory bodies if good agricultural practices are observed. However, pesticide residues have been found in vegetables and soils at levels far exceeding the recommended maximum residue limits (Syed *et al.*, 2014; Fosu *et al.*, 2017). These elevated pesticide residues in vegetables and soils indicate that in most farming settings good agricultural practices are violated (Ripley *et al.*, 2000). Again, there is increasing export of synthetic pesticides banned for use by the European Union (EU) to developing countries (Sarka *et al.*, 2021) which Ghana is no exception.

In a work done in Chile, 65% of the vegetables had two or more active pesticides compounds in them (Sebastian *et al.*, 2017). Twenty-seven percent (27%) of the samples had pesticides residues above the maximum limits (Sebastian *et al.*, 20217). In another work by Osei-Fosu *et al*. (2014), 810 samples of 5 different vegetables from Central, Volta, Greater Accra, Ashanti, Eastern Regions, and neighbouring country (Togo), 82% of the vegetables were found to contain pesticides residues. Of these, 20% of them had residues levels above MRLs set by EU (Osei-Fosu *et al.*, 2014) whilst only 18% had residue levels below detection limit of the method used (Osei-Fosu *et al.*, 2014).

Exposure to pesticides has effects on human nervous system, normal thyroid functioning, low sperm count, birth defects, increased testicular cancer, reproductive and immune system malfunctioning and developmental disorders among others (Mesnage *et al*., 2010; Tanner *et al.*, 2011; Cocco *et al.*, 2013; Gill and Garg, 2014).

Most pesticides, particularly the organochlorines, can persist in the environment or soil for long period of time without losing their toxicity (Gill and Garg, 2014) and thus can destroy soil organisms such as earthworms and microbes that act as decomposers (Al-Nasir *et al.*, 2020). Destruction of these soil organisms decreases soil microbial biomass and affects their activities (reproduction, behaviour and metabolism of the organism) and impairs their interactions in the ecosystem (Aktar *et al.*, 2009; Gill and Garg, 2014).

Study conducted by Praneetvatakul *et al.* (2013) indicates that pesticides application in Ghana has increased over time due to their use in the production of high-value cash crops and vegetables. However, issues of environmental pollution caused by pesticides application in developing countries including Ghana is not well documented (Saeed *et al.*, 2001). Vegetables sold in the local markets usually contain pesticide residues due to their overuse in vegetable cultivation (Chowdhury *et al.*, 2011). A review by Donkor *et al.* (2016) suggested that misuse and overuse of pesticides in the last few decades particularly in developing countries are primarily due to lack of farmer education. This has endangered lives of farmers, environment and the entire population (Donkor *et al.*, 2016).

Despite the negative effects of pesticides, inadequate data on pesticides levels in farm produce exist in many areas in Ghana particularly, in the Asante-Mampong Municipality where vegetables are cultivated on a large scale (Donkor *et al.*, 2016). This has resulted in the absence of effective monitoring programme for pesticides use and their contamination in vegetables, water and other food crops (Donkor *et al.*, 2016). Most governments in Africa do not have proper pesticides regulatory systems to monitor pesticide residues in vegetables, water soils and other food crops (Essumang *et al.,* 2008; Bempah *et al.*, 2011; Osei-Fosu *et al.,* 2014). Few data are available on pesticide residues in only vegetables (Bempah and Donkor, 2011) whilst studies on pesticides levels in soils in Ghana are very limited (Fianko *et al.,* 2011).

In the Asante-Mampong Municipality of the Ashanti Region of Ghana, works done so far on pesticides are just on levels of organochlorines in fruits (Forkuo *et al.*, 2018). Hence, there is the need to investigate pesticide residues in soils and in vegetables cultivated in the Mampong municipality of the Ashanti Region of Ghana.

1.3 Justification of the Study

The Asante-Mampong Municipality of the Ashanti Region is one of the areas in Ghana known to have several farms for vegetable cultivation especially carrot (Asiedu *et al.,* 2020). The municipality also has a booming market for the vegetables cultivated there. Thus, traders from outside the regional capital (Kumasi) purchase large quantities of vegetables from the Asante-Mampong Municipality (Abunyuwah *et al*., 2019).

Among the local inhabitants of Asante-Mampong, the perception is that vegetables produced in the municipality are safe and hygienic compared to those grown elsewhere (Keraita and Drechsel, 2015). This perception emerged from the fact that vegetables farmers within the municipality use safe water to irrigate their crops (Dwumfour, *et al.*, 2018). However, pesticide application in the municipality has progressively increased over the years especially in the production of cash crops and vegetables (Gerken *et al*., 2001). Though, there is increase usage of pesticides in the

Asante-Mampong Municipality in vegetable farmers, little is known about levels of pesticides residues in vegetables and the soils on which the vegetables are cultivated (Forkuoh *et al.,* 2018). For instance, work done by Forkuoh *et al.* (2018) on pesticide residues in the municipality was on the levels of organochlorine pesticides in oranges and pinneaples. Limited research has been done on pesticides residues in vegetables and soils in the municipality. Thus, it is imperative that investigations on pesticides residues in food crops and soils are conducted in order to safe guard the health of consumers.

In view of public health issues associated with pesticides coupled with the uncertainty regarding long term effects of exposure to low dosages of pesticides on human and the environment, it is very vital that pesticides in vegetables and the soils within the municipality are thoroughly investigated to provide data for policy makers to institute effective pesticides monitoring scheme in order to protect the lives of people.

In Ghana, there have been increase rates of pesticides applications by farmers in order to maximize productivity and profits (Akomea-Frempong *et al*., 2017). Pesticides application in Ghana has increased over time due to their use in the production of high-value cash crops and vegetables (Gerken *et al.*, 2001). Amoabeng *et al.* (2017) reported that 87% of vegetable farmers in Ghana use different classes of pesticides. Of these clsses, 41% are pyrethroids, 37% are organophosphates and the remaining 22% are carbomates and organochlorines. It has also been reported that more than 80% of Ghanaian farmers use pesticides in their farming activities (Akoto *et al.,* 2015; Bempah *et al.*, 2011; Fosu *et al.*, 2017). Amoabeng *et al.* (2017) has further reported that some farmers apply cocktails of various pesticides on crops in order to increase their effectiveness. Amoabeng *et al.* (2017) has again reported that farmers lack agricultural extension service in order to apply the right proportions of pesticides on vegetables. Thus, applications of pesticides on vegetables are likely to result in high pesticides levels in crops and soil. In Ghana, much works have not been done on assessing pesticides levels in vegetables and soils where the vegetables are cultivated and no such study has been carried out in the Asante-Mampong Municipality of the Ashanti Region of Ghana.

In Ghana, the Environmental Protection Agency (GEPA) is responsible for quality checks of pesticides products on the market (Yeboah, 2014). Even though some organochlorine and organophosphate pesticides have been banned for use in Ghana, they are still being used in many parts of the country due to lack of supervision by the GEPA (Ntow *et al*., 2006). Work done by Bempah *et al.* (2021) on market basket survey for some pesticides residues in fruits and vegetables from Ghana detected organochlorine, organophosphate and synthetic pyrethroid pesticides in fruits and vegetables. Fruits and vegetables were sampled from both rural and urban markets in the country and their work considered only vegetables and fruits on the markets. Besides, their work also did not take into consideration pesticides residues in the soils where the vegetables and the fruits were cultivated. Their study also did not take into account the possible health implications on consumers due to the pesticides levels in fruits and vegetables.

A study by Yakubu Fusheini (2018) on levels of pesticide in soil and water samples from Waanpu Dam in the Bimbilla District of Ghana did not consider pesticides levels in crops cultivated on those soils. The work did not classify the pesticides detected.

1.4 Objectives of the Study

The main objective of this study is to assess pesticides levels in soils and vegetables grown in the Asante-Mampong Municipality of the Ashanti Region of Ghana and determine presence of unregulated pesticides in the vegetables. The specific objectives of the study are to determine:

1 Physico-chemical properties and exchangeable cations of soils where vegetables are cultivated.

2 Organochlorines (OCs), organophosphates (OPs) and synthetic pyrethroids (SPs) residues in soils where vegetables are cultivated

3 Organochlorines, organophosphorus and pyrethroids residues in vegetables (cabbage, green pepper, carrot and lettuce) grown on these soils.

4 Estimate health risk indices of OCs, OPs and SPs pesticides to predict possible health issues likely to be suffered by consumers.

1.5 Significance of the Study

This study would create awareness of pesticides levels in vegetables that are consumed by people in the Asante-Mampong Municipality and beyond. The results of this study could be used by regulatory bodies to set maximum residue limits (MRLs) and could also provide data for risk assessment exercises. Furthermore, this study would assist academics to understand correlations that exist between pesticides residues in soils and vegetables from the study area.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This chapter looks at studies done related to this current study. This includes vegetables and their production in Ghana, nutritional and health benefits of some selected vegetables, pesticides definition and classification, pesticides applications, effects of pesticides applications and factors affecting pesticides residues in the soil.

2.2 Vegetables

Vegetables are the fresh and edible portions of herbaceous plants and include edible roots, stems, leaves, fruits or seeds (Adeniyi *et al.*, 2012). They also include flowers, stems, bulbs and leaves (Boateng, 2018). Vegetable crops include but not limited to carrots, cabbage, pepper, onion, garlic, and garden eggs (Grubben *et al.*, 2914). They are important sources of minerals (Ca, Mg, I, Zn, Se, Fe, Cu, and Si) and vitamins (vitamins B, C, K). Vegetables are cultivated and consumed by people globally (Yahia *et al.*, 2019; Drechsel and Keraita, 2014).

Vegetables contribute minerals, vitamins, and fiber to the diet of consumers depending on quantity consumed per day (Yahia *et al.*, 2019). Vegetables when added to food provide a balance diet and also serve as an excellent source of fibre or roughage which enhances digestion by helping to move food through the digestive system (Ambuja and Rajakumar, 2018).

According to works done by Abdulai *et al.* (2017) and Boateng (2018) vegetables such as cabbage, carrots, onion among others can be consumed raw or cooked. To health, growth and development, it is recommended that large quantities of vegetables are consumed regularly (Sebastian *et al.*, 2017).

Although vegetables have numerous health benefits, they can be a major source of pesticides contaminants and hence the need to determine pesticides residues in vegetables. Among vegetables, cabbage, green pepper, carrot and lettuce are the most important vegetable crops commercially grown within the Asante-Mampong municipality due to their high consumer acceptance and demand (Adinku, 2014).

2.1.1 Vegetables production in Ghana

Vegetables are produced globally with high acceptability and demand (Henchion *et al*., 2017) and China is the largest producer of vegetables (Diop and Jaffee, 2005). Vegetable production ranges from small scale farming to commercial farming depending on consumer preferences and acceptability (Sebastian *et al.*, 2017.

In Ghana, there is high demand for vegetables (Duedu *et al.*, 2014). However, production levels remain low as compared to other African countries such as Kenya and Togo (Amoah *et al*., 2016). Vegetable production system in Ghana is categorised into commercial and truck farming systems whereby vegetables are produced in the rural areas from where they are purchased by middlemen or contractors and sent to cities. The other category of vegetable production system is small scale/backyard farming system (Amofa and Ali, 2020). Most of the vegetables (cocoyam leaves, pepper, cabbage, carrot, okro, garden eggs and tomato) consumed in Ghana are locally produced whilst some vegetables (cabbage, carrot, cucumber, lettuce, and spring onion) are imported due to climatic requirement for such crops (Boateng*et al*., 2016).

According to Boateng *et al*. (2016) huge sums of money are spent annually to import vegetables into the country. Vegetables that are mostly grown in Ghana include: tomato (*Lycopersicon esculentum*), onion (*Allium cepa*), shallots (*Allium escalonicum*), okro (*Hibiscus esculentus*), eggplant (*Solanum melongena*), spinach (*Amaranthus spp*), sweet and chill pepper (*Capsicum annuum*) and hot pepper (*Capsicum frutescens*) (Amoah *et al*., 2016). These vegetables have ready markets not only in the cities but also in the rural areas (Torkpo *et al*., 2006). Lettuce is a popular vegetable in the cities and does extremely well almost throughout the year (Fosu-Mensah *et al*., 2016). Other vegetables which are gaining popularity (cucumber and green pepper) (Fosu-Mensah *et al*., 2016) are currently cultivated by vegetable farmers in the Asante-Mampong Municipality. Other vegetables cultivated by vegetable farmers in the Asante-Mampong Municipality are carrot, cabbage, lettuce and green pepper.

Several factors affect vegetable production in Ghana and these include: financial constraints among farmers, shortage of seeds at the required time, inadequate extension officers, high prices of inorganic fertilizers and pesticides, unreliable rain fall pattern, inadequate irrigation facilities and poor marketing systems (Boateng *et al*., 2016). The Ministry of food and Agriculture (MoFA) and the USAID are the two principal sources from which viable seeds are obtained. However, a few departmental stores sometimes sell seeds in small packets to farmers (Sperling *et al*., 2021). Vegetable seeds sold in such departmental stores are often not been tested in Ghana by Crop Research Institute and as a result, most of them do not perform well (Mariyono, 2018). In addition, these seeds are often purchased by individuals who take up gardening as a part-time interest. Thus, hardly any seed available for growers interested in large scale vegetable cultivation (Wongnaa *et al*., 2019).

2.3 Origin and Distribution of Cabbage

Cabbage (*Brassica oleracea*) is a leafy vegetable which originated from the Mediterranean area, Germany, France among other countries (Ahmad and Akhtar, 2013). Recently, cabbage is grown in commercial quantities in countries like Indonesia, Malaysia, China, Central, East and West America (Ahmad and Akhtar, 2013). Cabbage was domesticated in Europe before 1000 BC and became a prominent part of European cuisine (Langgut *et al*., 2013). Currently, cabbage has been distributed across the globe and can be prepared in different ways for consumption (Owusu-Boateng and Amuzu, 2013). Cabbage can be pickled, fermented steamed, stewed, sautéed, braised, or eaten raw (Mouritsen, and Styrbæk, 2020). It is a good source of vitamin K, vitamin C and dietary fibre (Tanongkankit *et al*., 2010). World production of cabbage and other brassicas was estimated to be 69 million tons in 2018, with China accounting for 48 % of the total production (Biondi *et al*., 2021).

Weight of cabbage head ranges from 500 to 1000 grams (Amofa and Ali, 2020) and under favourable environmental conditions, cabbage can grow quite large. In 2012, the world recorded heaviest cabbage head of 4 kilograms (Abed *et al*., 2015). Cabbage is prone to several nutrient deficiencies, as well as to multiple pests, and bacterial and fungal diseases and these conditions require serious attention (Owusu-Boateng and Amuzu, 2013).

2.3.1 Botany of cabbage

Cabbage crops have thin taproot and cordate (heart-shaped) cotyledons. The first leaves produced are ovate (egg-shaped) with a lobed petiole (Tomkins and Williams, 1990). The height of cabbage crops ranges from 40 to 60 cm tall at maturity (Tomkins and Williams, 1990). During the flowering stage, height of cabbage crops ranges from 1.5 to 2.0 m (Ahmad and Akhtar, 2013). Average cabbage heads range between 0.5 and 4 kg. Fast-growing, earlier-maturing varieties however produce smaller heads at maturity (Davy *et al.*, 2006). Most cabbage crops have thick, alternating leaves, with margins that range from lobed to highly dissected (Davy *et al.*, 2006).

Some varieties of cabbage crops have waxy bloom on the leaves and have fibrous and shallow root systems (Fang *et al.*, 2004). About 90 % of the root mass of cabbage is in the upper 20 to 30 cm of soil (Owusu-Boateng and Amuzu, 2013) and lateral roots which penetrate to approximately 2 m deep into soil (Owusu-Boateng and Amuzu, 2013).

Cabbage takes between 60 and 100 days to mature Torres *et al.* (2017). However, cabbage crops which are intended for seed production are allowed to grow for two years and are kept separate from other crops to prevent cross-pollination (Sharma *et al.*, 2017). Cabbage crops have many shapes, colours and leaf textures depending on the variety (Owusu-Boateng and Amuzu, 2013).

Report by Arce-Lopera *et al.* (2013) indicates that twelve (12) types of cabbage (White, Red, Green, Pointed, Cannaball, Danish, Savoy, Choy, Choy Sum, January, King and Tuscan cabbage) exist and colour spectrum of cabbage crops (white, different shapes of green and purple) also exist (Matysiak and Kowalski, 2019). Cabbage crops have been selectively bred for head weight, morphological characteristics (resistant varieties, frost hardiness, fast growth) and storage ability (Opfer and McGrath, 2013).

The development of cabbage heads is important in selective breeding. Cabbage varieties are bred for shape, colour, firmness and other physical characteristics such as height of cabbage head, stem, and length of cabbage heads and for high yield (Van Bueren and Struik, 2017). Breeding objectives in cabbage production focused on increasing resistance to various pests, diseases and improved nutritional contents (Opfer and McGrath, 2013).

2.3.2 Nutritional and health benefits of cabbage

Cabbage has several nutritional and health benefits to consumers (Dekker *et al*., 2000). The crop contains vitamin A and B6, iron, folate and riboflavin which are important for metabolic processes (Martin and Li, 2017) and normal functioning of the nervous system (Munthali and Tshegofatso, 2014). Cabbage also has high fibre contents and powerful antioxidants (polyphenols and sulphur compounds) (Kaur and Kapoor, 2001).

Antioxidant in cabbage protects human body from damage caused by free radicals (Suleman, *et al.,* 2019). These free radicals are highly unstable due to the present of high amount of electrons in them (Hines and Hutchison, 2013). When levels of free radicals in humans become very high they cause damage body cells (Adwas *et al.,* 2019). Cabbage also contains high levels of vitamin C and a potent antioxidant that protect humans against heart disease, certain cancers and vision loss (Opfer and McGrath, 2013). The human body system relies on inflammatory responses to protect humans against infections or accelerate healing process and also reduce inflammation (Chen *et al.,* 2018). Research shows that consumption of diets containing vitamin C rich foods lower risk of certain cancers (Wongnaa *et al*., 2019).

Cabbage again contains insoluble fibre which serves as fuel for normal functioning of beneficial bacteria in the gut and it also promotes regular bowel movements (Opfer and McGrath, 2013). The crop further has powerful pigments (anthocyanins) which reduce the risk of heart disease (Khoo *et al.,* 2017). High blood pressure affects more than one billion people worldwide and is a major risk factor for heart disease and stroke among people (Wongnaa *et al*., 2019). Cabbage contains potassium which is an important mineral and electrolyte require for normal body function (Broadley and White, 2010). Potassium contents of cabbage also help regulate blood pressure by counteracting the effects of sodium in the body (Mariyono, 2018). Potassium in cabbage further helps excrete excess sodium through urine (Sussman *et al.*, 2020) and also relaxes blood vessel walls to lower blood pressure (Widiyanto *et al.*, 2021).

2.4 Origin and Distribution of Carrot

Carrot is a member of *Apiaceae* family. It produces edible leaves, taproot and seeds for propagation (Appiah *et al*., 2017). Carrot is a native of Afghanistan in the Mediterranean region before the Christian era and later established as a food crop in India, China and Japan by the 13th century (Fritz, 2013). The Greeks and the Romans knew the plant during early civilization and their early use were mainly medicinal, to cure stomach pains, treat wounds, ulcers, and liver and kidney ailments (Goswami and Ram, 2017).

According to a report by Appiah *et al*. (2017), carrot plant is extensively grown throughout the temperate zones. World production of carrots has significantly increased by 133% from 2001 to 2010 and amounted to 19.4 million metric tons. In 2010, China was the global highest (26%) producer of carrot in the world, followed by the United States of America (10%), Russia (8%), Poland (5%) and United Kingdom (4%) (Dipendra *et al*., 2019).

In Ghana, production is gradually partly due to its high demand in urban centres and also exported for income (Appiah *et al*., 2017: Dipendra *et al*., 2019). The greatest development and improvement of the original carrot that had thin, long roots took place in France (Downham and Collins, 2000). Carrots are now popular vegetable and are grown globally (Appiah *et al*., 2017: Dipendra *et al*., 2019).

2.4.1 Botany of carrot

Carrot is erect in nature and cultivated throughout the year among vegetable farmers (Poku Snr *et al*., 2020). The plant grows up between 20 and 100 cm tall and has compound pinnate leaves (Gadekar *et al.*, 2010). The stems are so short, barely visible, somewhat round rods and has small diameter of about 1 to 1.5 cm (Drechsel and Keraita, 2014). In general, the carrot plant has dark green and unbranched stems and has fibrous root system (Amofa and Ali, 2020; Ilyas *et al*., 2022).

The growth of the taproot changes the shape and function to storage of food reserves (Rossato *et al.*, 2001). The taproots develop and become round and elongated until it reaches a length of about 30 cm and a diameter of about 6 cm (Poku Snr *et al*., 2020). However, different varieties of carrot have different lengths and roots diameter values (Poku Snr *et al*., 2020). The carrot plant produces white or pale pink flowers with double umbrella-shaped at the end of the crop. Carrot plants that had experienced carrot flower pollination produce viable seeds and furry (Abdulai *et al*., 2017).

2.4.2 Nutritional and health benefits of carrot

Globally, carrots are consumed either in their raw state, cooked or in combination with other vegetables as ingredients of soup, dishes, sauces, juices and in dietary compositions (Tanveer *et al*., 2015). Carrot is a low-calorie vegetable which provides essential dietary fibre with low cholesterol levels, vitamin A and many other minerals needed to keep vision at its best and prevent nutritional deficiencies (Mariyono, 2018).

The taproot of carrots contains more than 88 percent water by weight, which makes them an excellent addition to human diet (Yamaguchi, 2012). Carrot has low fat content, and consuming a low-fat diet may also help to prevent prostate cancer in men (Mariyono, 2018).

According to the Institute of Medicine, men need 30 to 38 grams of fibre daily whilst women need 21 to 25 grams (Mariyono, 2018, 2014). Getting enough fibre in the body helps maintain proper digestion, may prevent colon cancer, and also aid in maintaining healthy cholesterol levels (Mariyono, 2018). Furtheremore, high-fibre diet may also aid in weight loss and help prevent obesity (Willoughby *et al.*, 2018). Carrot plants are very good sources of vitamins such as vitamin A, vitamin C, vitamin B6, vitamin K1 and minerals such as, calcium, iron, biotin and potassium (Akram *et al.*, 2020).

The most recognized vitamin contribution from carrots comes in the form of vitamin A. Vitamin A is needed for proper vision, immune function, reproductive health, cell formation and cell communication (Appiah*et al*., 2017: Dipendra *et al*., 2019). In the body, carrot also functions as an antioxidant which helps to prevent cellular damage from free radicals (Devasagayam *et al.*, 2004).

Carrots also help to protect against cardiovascular disease such as atherosclerosis and heart attack because of their deep orange colour, which comes from precursors to vitamin A called carotenoids found in carrots (Dipendra *et al*., 2019). Carrots also contain calcium, iron, magnesium, phosphorus, potassium, copper and manganese which help maintain bone and tooth health, proper muscle function and a healthy nervous system Appiah *et al*., 2017: Dipendra *et al*., 2019). Furthermore carrots also help with energy metabolism, protein synthesis, fluid balance and red blood cell formation (Appiah *et al*., 2017: Dipendra *et al*., 2019).

Evidence from different research suggests that eating more antioxidant-rich carrots can help reduce the risks of cancer and cardiovascular disease (Dipendra *et al*., 2019). According to the report of Mariyono (2018), there is a possible link between diets rich in carotenoids and a lower risk of prostate cancer.

In India, carrots are used as salad or as vegetables added to spicy rice and other dishes. Carrot juice is also widely marketed especially, as a health drink, either stand-alone or blended with fruits and other vegetables (Dipendra *et al*., 2019). The beta carotene in carrots is a powerful antioxidant effective in fighting against some forms of cancer, especially lung cancer (Zeb and Mehmood, 2004). Nutritional value per 100 g of carrots produce 173 KJ of energy, 9 g of carbohydrate, 5 g of sugars, dietary 3 g of fibre, 0.2 g of fat and 1 g of protein (Dipendra *et al*., 2019).

2.5 Origin and Distribution of Green Pepper

Capsicum annuum which is commonly called Green Pepper is an exotic vegetable crop and belongs to the *Solanacae* family (Olatunji and Afolayan, 2018). The crop is known to have originated from Tropical America (Dagnoko *et al.*, 2013). The fresh, large square fruits have thick walls that surround the seeds and they are picked when green (Occhiuto *et al.*, 2014). The leaves are glabrous and lanceolate.

The mature green pepper fruits are used more as a vegetable than as a spice (Bosland, 2012). They are used either raw in salads or stuffed with meat or rice and cooked (Katz, 2009). Green pepper can also be dried and ground to produce a red condiment, and the fruits are rich in vitamin C (Dias *et al.*, 2013).

According to the report of Dagnoko *et al.* (2013) the cultivation of green pepper is confined to the urban areas and cities. It is only in recent years that efforts have been made by some newly established agencies to export few quantities to some European countries (Jaffee and Masakure, 2005).

2.5.1 Botany of green pepper

Green pepper belongs to the night shades family (*solanaceae)*. Most peppers are varieties of the species *capsicum annuum* (FAOSTAT, 2011). According to the statement of FAOSTAT (2011), green pepper is an annual or short-lived perennial herb and it up to 1.5 m in height. It has a well-developed tap root system with many lateral roots. The leaves of green pepper vary in size and are mainly oval with pointed tips (Csilléry, 2006). Also the flowers of green pepper are borne singly and arise terminally but appear to be axillary (Dagnoko *et al.*, 2013).

Dagnoko *et al.* (2013) submitted that, the calyx of green pepper plant is ribbed and usually enlarges to enclose the base of the fruit. The fruit is a berry and varies in size, shape, colour and pungency. Dias *et al.* (2013) is of the view that green pepper is an autogamous species, but the level of cross pollination varies from 20% to 40%, depending on insect activity. The seeds are small (to 200 g), hairless, reniform and white to yellow in colour and unaffected by photoperiod (Garcia and Lopez, 2020).

2.5.2 Nutritional and health benefits of green pepper

Green pepper is an important vegetable crop used as spices and provides nutrients for humans (Nowak *et al.*, 2020). Green pepper is also used medicinally for the treatment of fever and cold (Dagnoko *et al.*, 2013). The crop contains vitamins A and C, mixture of antioxidants notably carotenoids, ascorbic acid, flavonoids and polyphenols (Campos *et al.*, 2013). Green pepper is an important constituent of food and is also capable of adding flavour, colour and pungency (Campos *et al.*, 2013). The crop can be used in whole, chopped or in various forms including fresh, dried, ground into powder or as an extract (Dias *et al.*, 2013).

In some countries, green pepper can be processed into paste and packaged nicely for sale (Olayemi *et al.*, 2010). However, in Ghana green pepper is used for the preparation of *shito* popularly used among students and for export. When consumed, green pepper is a rich source of vitamins A, C, B6, folic acid, beta-carotene and antioxidant compounds which protect human body from oxidative damage induced by free radicals (Kumar, 2009) and helps to reduce the risk of cardiovascular (asthma, sore throat and headache among others) (FAOSTAT, 2011).

2.6 Origin and Distribution of Lettuce

Lettuce (*Lactuca sativa*) is a cool season crop which originated from Minor or Middle East of Asia, North Africa and across Europe and subsequently to all other countries in the world (Khoshkam, 2016). Study by Smitha and Sunil (2016) indicated that lettuce was domesticated 4500 years ago and now is grown extensively in China, Taiwan, Malaysia, Vietnam and Ghana due to high consumer demand and acceptability.

2.6.1 Botany of lettuce

Lettuce (*Lactuca sativa*) is grown purposely for it leaves, which are consumed raw as salad. Lettuce is an annual leaf vegetable and belongs to the family *Asteraceae*. The plant has a fibrous root system with wide range of colours, from shades of green to deep red and purple (Nabhan *et al.*, 2015). It can be grown on any type of soil structure with good fertility and good water holding capacity (Hernández *et al.*, 2016). The plant do well on slightly alkaline sandy-loamy soils (Nabhan *et al.*, 2015) and the plant is mostly harvested prior to flowering as the size of the flower reduces leaves.

Lettuce (*Lactuca sativa*) required adequate water especially during the dry season as compared to the rainy season (Nabhan *et al.*, 2015). The cos, leaf and butter head types are mostly cultivated at a moderate temperature (15 to 20 °C) (Konstantopoulou *et al*., 2010). In the tropics, lettuce plants perform better in the highlands and during rainy season in the lowlands (Niam and Suhardiyanto, 2019). High temperatures above (28 °C) cause loose heads, bolting and dry leaves (Nabhan *et al.*, 2015).

2.6.2 Nutritional and health benefits of lettuce

Lettuce has several health benefits due to its low calories level, high water content and several vitamins and minerals (Kim *et al.*, 2016). Regular intake of lettuce provides maximum amounts of nutrients required by the body (Du-Toit, 2012). The crop contains antioxidants, including flavaonoids and tannins, which prevent the accumulation of harmful free radicals and reduce the risk of chronic diseases (Zhang *et al*., 2010).

Lettuce is composed of about 95% water, which may increase hydration (Nabhan *et al.*, 2015). Because lettuce contains about 95% water, they are especially effective at promoting hydration, reducing blood sugar levels and preventing some complications of diabetes (Sandrou and Arvanitoyannis, 2000). Lettuce is low in c alories, high in water and can be used as a low-calorie topping for several dishes (Morquecho-Campos *et al*., 2020). And it contains high quanties of fibre (Du-Toit, 2012). The fibre and water contents in lettuce may help prevent constipation and increase regularity (Du-Toit, 2012). Lettuce also contains vitamin A for improved vision and reduced risk of cataracts (Abdel-Aal *et al*., 2013).

2.7 Pesticide Definition and Classification

United State Department of Agriculture (USDA, 2015) definition of pesticides is broad term and it takes into consideration synthetic or organic chemicals used for controlling or preventing unwanted activities of insects, weeds and diseases which affect crop yield. Pesticides are chemical substances or mixture of chemical substances intended for preventing, destroying, repelling, or mitigating the effects of pests on plants and animals (Cox and Surgan, 2006). There are hundreds of pesticides and they are classified depending on the type of pests and disease against which they are effective to control such as fungi, bacteria, weeds, mites, snails, nematodes, slugs and rodents (Yadav and Devi, 2017).

Some pesticides are organism-specific and have particular mode of action to kill the pests (Pandya, 2018). There are different types of pesticides and they include herbicides, insecticides, rodenticides, fungicides, molluscides, nematicides, avicides, acaricides, repellents and attractants (Yadav and Devi, 2017). These are used in agriculture, public health and food storage systems to control or kill pests (Nornu and Ukamaka, 2019). Insecticides are different class of pesticides examples of which are the organochlorines, organophosphates, carbamates, synthetic pyrethroids and plants derived pesticides (Zacharia, 2011).

Pesticides are also classified depending on the active ingredients, chemical structure, mode of action and toxicity (Botitsi *et al.*, 2017). They can further be classified as organic and inorganic pesticides (Patinha *et al.*, 2018). Organic are usually carbon based and can be either natural pesticides (from natural occurring materials) or synthetic pesticides (Biondi *et al.*, 2012; Cantrell *et al.*, 2012). The World Health

Organization (2010) also classified pesticides as acute oral and dermal toxicity to rat as the standard toxicology procedure, (presented as LD50). United State Department of Agriculture (USDA, 2015) further classified pesticides into/depending:

1 Chemical classes (carbamates, organochlorines, organophosphates and pyrethroids).
2 Active ingredients according to the degree of hazards (extremely hazardous, moderately hazardous, slightly hazardous and not hazardous).
3 Effectiveness against particular type of pest or diseases which include insecticides, fungicides, herbicides, nematicides, acaricides, molluscicides, bactericides and rodenticides, desiccants, insect growth regulators, mothballs, ovicides, pheromones, repellents, among others.

2.7.1 Carbamates

Carbamates are derivatives of carbonic acid which contains insecticides and nematicides (Malhotra, 2021). Carbamates were introduced into modern agriculture in 1956 (Padmarasu, 2016). They consist of insecticides and nematicides (Aldicarb, Benomyl and Carbofuran) which are more persistent than the organophosphate pesticides which are highly toxic to humans and animals (Khan *et al.*, 2021). However, fungicides such as Mencozeb and Maneb are not acutely toxic (Padmarasu, 2016) whilst the carbamate insecticides kill insects by inactivating the enzyme acetylcholinesterase (Colovic *et al.*, 2013). Human exposure to carbamate can lead to headaches, dizziness or weakness, nausea, convulsion, stomach cramps, diarrhoea and sweating as well as skin rash (Debnath and Khan, 2017).

2.7.2 Organochlorine (OC) pesticides

Organochlorine pesticides are organic compounds containing at least one covalently bonded atom of chlorine that has an effect on the chemical behaviour of the molecule (Zimmermann *et al.*, 2020). Organochlorine pesticides contain chemicals such as Beta- HCH, Delta- HCH, Lindane, Heptachlor, Aldrin, Gamma Chlordane, P’P’-DDE, Dieldrin, Endrin, Alpha- Endosulfan, Beta – Endosulfan, Endosulfan – sulphate, P’ P’ – DDT, P’P’ – DDE, Methoxychlor among others. Organochlorine pesticides were not discovered until 1930’s and was found to be unduly toxic to both man and animals (Halldorsson, 2012). The chemicals belong to the class of persistent organic pollutants and have high persistence in the environment (Aktar *et al*., 2009). These were successfully used in the control of malaria and typhus (Malla *et al*., 2021). However these were banned in most of the developed countries due to their high toxicity and long persistent in the environment (Aktar *et al*., 2009). These chemical compounds are capable of controlling pest slowly and persistent for long periods in soils (Amoako, 2010). Hence there is the need to determine their presence in vegetables and soils where the vegetables are cultivated. Hence determination of organochlorine pesticides levels in vegetables and soils in the Asante-Mampong Municipality of the Ashanti Region where lots of vegetables are cultivated is very necessary as it will provide data on levels of pesticides in vegetables and soils and it would be used in monitoring process to ensure pesticides levels in vegetable meet the recommended maximum residue limits for human consumption. The DDT, an organochlorine pesticides works on the peripheral nervous system whilst exposure to chlorinated cyclodienes type leads to depressed central nervous system (CNS) activity, followed by hyperexcitability, tremors, and seizures (Vikash *et al*., 2018).

2.7.3 Organophosphate (OP) pesticides

Organophosphates the general name for esters of phosphoric acid (Eto and Zweig, 2018). Organophosphate pesticides consist of chemicals of chemicals such as Parathion, Profenofos, Malathion, Chlorpyrifos, Diazinon and Pirimiphos, Fonofos Fenitrothion, Methamidophos, Chlorfenvinphos Ethoprophos and Dimethoate (Osman *et al.*, 2019). These compounds have been in existences since 1940's with high acute mammalian toxicity (Amoako, 2010). They are easily broken and hence are much less persistent in the soil than organochlorine pesticides (Amoako, 2010). Organophosphate pesticide pesticides irreversibly inactivate acetylcholinesterase, which is essential to nerve functioning in insects, humans, and many other animals (Agrawal and Sharma, 2010). Thus, it is prudent to determine organophosphate pesticides levels in vegetables and soils where the vegetables are cultivated.

2.7.4 Synthetic pyrethroids

Pyrethroids are very effective in controlling pest and diseases in vegetable production (Khan *et al*., 2017). These chemical compounds have low persistence, moderate toxic to human and animals and have very high acute effects on aquatic organisms (Amoako, 2010). Examples of such synthetic pyrethroids include Fenvalerate, Allethrin, Bifenthrin, Fenpropathrin, Lambda – Cyhalothrin, Permethrin, Cyfluthrin, Cypermethrin and Deltamethrin (Zhan *et al.*, 2020). They are axonic excitoxins, the toxic effects of which are mediated through prevention of the closure of the voltage-gated sodium channels in the axonal membranes (Khan *et al*., 2017). According to (Vikash *et al.*, 2018) person developed Parkinson's disease after six months of daily exposure to Fenpropathrin. No work so far done in the municipality on the levels of synthetic pyrethroids in the soil and vegetables and there is the need to establish levels of these chemicals in veetables and soils on which these vegetables are cultivated in the Asante-Mampong Municipality.

2.8 Pesticides Applications

Pesticides are generally applied for the destruction of insects, weeds, fungi, bacteria, among others (Oerke, 2006). The methods used for the applications depend on factors such as the nature and habits of the target pest, characteristics of the target site, and properties of the pesticide formulation (Dhananjayan *et al.*, 2020). Other factors include appropriateness of the application equipment, cost, and efficacy of alternative methods of application (Dhananjayan *et al.*, 2020). Methods of pesticides applications include band method which involves applying pesticide in parallel strips rather than evenly over the entire field (Calliera *et al.*, 2021). A basal application have low-pressure spray of pesticide is directed to the lower portions of the trunk of vegetable plant (from the ground up to 20 inches).

Foliar applications are by far the most common type of pesticides application method used in a grove (Gertsis and Karampekos, 2021). This technique directs the pesticide to the foliage of the tree and is very susceptible to drift (Gertsis and Karampekos, 2021). A much targeted, low-volume of pesticide application is the rope-wick or wiper treatment where pesticide is released onto a wick that is wiped onto the target plant (Ozkan, 2017).

When a pesticide is applied uniformly to an area or a field, it is termed a broadcast application (Hunter III *et al.*, 2019). Soil injection is the application of a pesticide under pressure beneath the soil surface and may be done with or without a plastic covering, depending on the pesticide properties (Dusek *et al*., 2010). Space treatment is the application of a pesticide to an enclosed area and this type of application is used on bins of fruit to control pests that might move with the fruit (Parker and Popenoe, 2008).

Types of equipment used for pesticides application include dusters, sprayers, agricultural aircrafts, granule applicators, soil injectors, among others (Meissle *et al.*, 2010). Dusters are used to distribute dust formulations and they may be manually operated or power operated (Dhananjayan *et al.*, 2020). A sprayer is an appliance which atomizes the spray fluid, which may be a suspension, an emulsion or a solution (Mlkvik *et al.*, 2015). The atomised pesticide fluid is ejected with enough force for proper distribution (Mlkvik *et al.*, 2015). The use of an aircraft in pesticide application enables coverage of vast areas very speedily, timely and economically (Tsouros *et al.*, 2019).

Miscellaneous pesticide application machine machinery includes granule applicator and soil injectors (Matthews and Thornhill, 2019). Granule applicator involves placement of insecticidal granules in the whorls of crops such as maize, jowar and others and is effective for controlling stem borers (Maiti and Kumari, 2016). Most soil fumigants are liquids and are applied with soil injectors (Austerweil *et al.,* 2006). They further added that handheld soil injectors with a capacity of 2-3 litres are commonly used to inject fumigants up to a depth of 15-22 cm, to control soil insects and nematodes.

2.8.1 Global pesticides application

Globally, about 1.8 billion people are into agriculture and most of them use pesticides in one way or the other for economic management of crops and animals (Sharma *et al.*, 2019).

The application of large volumes of pesticides for agricultural purposes is a prevalent practice for controlling pests, diseases and weeds globally (Meissle *et al.*, 2010). Globally, more than 1000 different types of pesticides are used to prevent damage and destruction of food by pests (Pimentel, D. and Burgess, 2014). Global consumption of pesticides for agricultural purposes showed a steady increase from 1990 to 2019 (Fernández, 2021).

In 2019, the amounts of pesticides usage stood at 4.2 million metric tons, and these represented an increase of more than 80% when compared to 1990 Sharma, *et al.*, 2019). The leading countries in consumption of pesticides for agricultural purpose in 2019 were China (1,763 metric tons), United States (407.78 metric tons), Brazil (377.18 metric tons) and Argentina (204.56 metric tons) (Fernández, 2021). About 3.5 million tons of pesticides are used annually (Sharma, *et al.*, 2019). Of these 47.5% (1.66 million tons) are herbicides, 29.5% (1.03 million tons) are insecticides, 17.5% (0.61 million tons) are fungicides and 5.5% (0.20 million tons) are other pesticides (Sharma *et al.*, 2019). According to a report by Pimentel (2009), annual global pesticide application is about 3 million tons, market value is USD 40 billion. In 2019 global pesticide market was approximately 84.5 billion USD (Adeola, 2020). This has increased at an annual growth rate of 4.2% since 2015, and it is likely to reach 11.5% with an estimated value of approximately 130.7 billion USD by 2023 (Adeola, 2020).

The European Union (EU) has approved approximately 500 new active substances for use in pesticides (EC, 2016) and these would had an estimated annual sales of 374,000 tons from 2011 to 2016 for the EU-28 (Silva *et al.*, 2019). In 2011, the USEPA reported over 10 billion pounds worth of pesticides usage. Global agricultural sector also recorded over 700 million pounds worth of pesticides active ingredient application in farming (Lah, 2011).

2.8.2 Pesticides application in Africa

According to a report by Shen *et al*. (2005), most governments in Africa advocated for usage of pesticides since 1970 and in 1990s. Their advocacy resulted in non-monitoring of pesticides by authorised bodies. As a result, more influx of pesticides occurred from informal channels and that caused an enhanced usage of pesticides (Shen *et al*., 2005) and that led to an increased import value by 261% from 2000 to 2010 (Shen *et al*., 2005). In Africa, quantities of pesticides applied for agricultural purposes have increased over the years by more than a quarter (26%) between 1990 and 2017 with a total volume of about 4.1 million tons (Pernet and Ribi, 2019).

In South Africa alone, over 700 pesticides active ingredients are presently available on the market (Fuhrimann *et al.*, 2020). Only 2-4% of the global pesticides usage is in Africa (Sharma *et al*, 2019). However, demand for pesticides is expected increase in the continent due to population growth and local markets expansion for pesticides (Sharma *et al*, 2019). Global projections for pesticides application until 2027 suggest a further increase in pesticide use due to continued growth in agricultural activities in sub-Saharan Africa (OECD and FAO, 2018). Even though the EU is much concerned about the export of banned pesticides by firms within the union, overall application of banned pesticides is becoming rampant in developing countries including Africa (Sarka *et al.*, 2021).

2.8.3 Importance of pesticides applications on crops

Remarkable benefits have been obtained from application of pesticides in forestry, public health and the domestic sphere as well as in agriculture (Dhananjayan *et al.*, 2020). Pesticides have been used in agriculture for years in the effort to reduce crop loss and to meet the world's growing food demands (Stephenson *et al*., 2001).

About one-third of agricultural commodities are produced using chemical pesticides (Zhang *et al.*, 2011). If farmers globally decide not to apply pesticides, crop losses to pests would increase by 78% (fruit), 54% (vegetable) and 32% (grains) (Cai, 2008). Thus pesticides play a vital role in sustainable development by helping farmers to save money, time, and also increase their productivity.

Pesticides are widely applied for grains and vegetables before and after harvest to protect them from loss damage (Grewal, 2017). Pesticides applied to crops enable farmers to obtained huge yield on small land (Shah and Wu, 2019). Pesticides are also important for controlling invasive species and harmful weeds (Weidenhamer and Callaway, 2010). The use of pesticides on stored agro products can prolong the shell life of the produce by preventing huge post-harvest losses due to pests and diseases (Bradford *et al.*, 2020). Pesticides levels in vegetables and soil can be detrimental to the environment and human health and there is the need to assess their levels in vegetables and soils (Alengebawy *et al.*, 2021). Though few works on pesticides residues in agro-products have been done in some areas in Ghana, more has not been done in Asante-Mampong Municipality.

2.8.4 Effect of soil properties on pesticides residues

The fate of pesticides in soil depends on several processes responsible for their mobility and persistence (Durães *et al.,* 2018; Børgensen *et al*., 2015). When a pesticide is applied to soil, it adheres to soil particles (mainly organic matter and clays), become degrade by soil micro-organisms or move through soil with water (Holland and Sinclair, 2003). Pesticides are retained in soil at different rates depending on the rate of application, soil type and pesticides properties (Khalid *et al.*, 2020). Akoto *et al.* (2013) reported that pesticides residue in soil is influenced by soil organic carbon and organic matter. They further reported that the larger the organic matter content in soil, the more it absorbs pesticides and the smaller the organic matter content, the lesser it absorbs pesticides.

Soils with high clay or organic matter contents tend to have more stable soil structures than those containing mostly sand and or silt (Chaudhari, *et al.*, 2013). Sheng *et al.* (2001) reported that the extent of pesticides absorption and adsorption depends on various soil properties, such as organic matter, amounts and type of clay, ion exchange capacity and pH.

As the amount of H^+ ion increases, the concentration of basic cations decreases during ecosystem development and increase H^+ ion is also inversely proportional to the increase in pH (Chadwick and Chorover, 2001). An increase in clay contents result to increasing adsorption of pesticides (Copaja and Gatica-Jeria, 2021; Barriuso *et al.,*

2021) while increasing in sand content results in a corresponding decrease in adsorption of pesticide (Fosu-Mensah *et al.*, 2016). They also stated that sandy soils speed up leaching whereas clayey soils enhance accumulation of pesticides through colloid formation

According to Yang *et al.* (2019) indicated a higher correlation exist between adsorption and clay contents of soils than exist between organic matter contents. Synthetic pyrethroids persist longer in soil and sediments due to their higher affinity for organic carbon and clay in soils despite their shorter half-life compare to the other classes of pesticides (Oros and Werner, 2005). Clay addition to soil, increases the adsorption capacity of soil resulting in an increased in the amounts of pesticides retained therein (Copaja and Gatica-Jeria, 2021).

Pesticides levels in soil is also affected by cation exchange capacity of soil and the ability of soil to hold positively charged ions in an exchangeable form (Sarkar *et al.*, 2020). Soil Exchangeable cations are known to influence the dynamics and behaviour of pesticides molecules in soils (Fosu-Mensah *et al.*, 2016).

Soil moisture plays a significant role in pesticides retention, pesticides availability in soil and adsorption of pesticide onto soil particles (Kumar and Philip, 2006). Low soil moisture contents render most soil organisms inactive and make it difficult for them to break down pesticides molecules (Asare, 2011). The reduced ability of soil micro-organisms to function led to high pesticides accumulation and adsorption onto soil particles and their persistence in soil (Asare, 2011). Increasing pesticides residues in soil decreases soil pH and total nitrogen and reduced the levels of bacteria and fungi in soil (Akoto *et al.,* 2013).

Plants depend on bacteria, fungi and other microorganisms to convert atmospheric nitrogen into nitrates to be used by the plants for development (Dellagi *et al.,* 2020). However, high levels of pesticides affect soil microbial biomass and inhibit and disrupt activities of these microbes (Arora Sahni, 2016) Soil micro-organisms in some instances are killed depending on the rate of application of pesticides and their levels in soil (Akoto *et al.,* 2015).

As soil pH decreases (below 7) pesticides availability, adsorption onto soil particles and persistence in soils are expected to be considerably high (Fosu-Mensah *et al*., 2016). Thus as soil pH decreases (below 7) concentration of hydrogen ions in soil solution increases making pesticides molecules more available in soil and thus become available in the soil for easy absorption by roots of plants (Fosu-Mensah *et al*., 2016). They further reported that as soil pH's increase (above 7) most of pesticides maintain neutral charges and thus are less tightly adsorbed onto soil particles and become more available to plant roots for absorption.

2.8.5 Factors affecting pesticides levels in soils and vegetables

The use of pesticides over the years has led to the contamination of various environmental compartments such as soil, ground and surface waters air as well as numerous agricultural food products (Mensah *et al.,* 2011). More than 95% of sprayed insecticides and herbicides reach a destination other than their target species (Cooper and Dobson, 2007).

The excessive use of pesticides over recent years is now of considerable environmental concern due to the release of mobile and/or persistent pollutants into the environment, and their possible accumulation of these toxic substances in soils, water and even air and these are likely to end up in food crops (Silva *et al.*, 2019; Hveˇzdová *et al.*, 2018). Contamination of agricultural soils with pesticides could lead to changes in their chemical and biological properties and thus affect their quality which in turn results in negative impacts on crop yields (Al-Ahmadi *et al.*, 2019). Organic amendments increase soil OC contents which is the most relevant factor that influence the adsorption process and affinity of hydrophobic pesticides by soils (Zolgharnein *et al.*, 2011; Garrido *et al.*, 2015).

Adsorption-desorption directly or indirectly determines availability of pesticides to be transported to surface waters by runoff, leached into ground waters, dispersed into air by volatilization, degraded/transformed by microbial attack, or to be taken up by plants (Gavrilescu, 2005; Zhang *et al.*, 2010). Thus, weak adsorption and/or strong desorption of pesticides enhances leaching, run-off, volatilization, biodegradation and even ecotoxicological impacts on non-target organisms while strong adsorption prevents losses of pesticides by leaching, run-off, volatilization and biodegradation (Jiang *et al.*, 2016). Thus, adsorption-desorption influences levels of pesticides in soils and vegetables and hence there is the need to determine pesticides levels in soils and vegetables grown in the Asante-Mampong Municipality to ensure consumers safety.

Pesticides can accumulate up through the food chain and they have been detected in breast milk (Ferronato *et al.*, 2018). Present of pesticides in breast milk is dangerous for suckling babies. Some pesticides are very slow to break down (the organochlorines) and can be subjected to long-range transport into soil, water, air and food crops (Olatunji, 2019). The persistence of pesticides in various media depends on physical and chemical properties (partition coefficients, degradation rates, deposition rates) and characteristics of the environment (Arias-Estévez *et al.*, 2008). Climate characteristics also play a role in persistence (Devi, 2020). Pesticide residues could move from nearby fields through water and wind and be deposited in surrounding environments and crops (Dan *et al.*, 2012) and become accumulated at higher levels in topsoil (about 1 to 2 cm) than deeper soil (Dan *et al.*, 2012).

Pesticide residues in food and crops can also be a direct result of the application of pesticides to crops and to a lesser extent from pesticide residues remaining in soil (Puri, 2014). Again presence of pesticides in soils may have originated from different sources such as direct application, accidental spillage of pesticides, surface runoff from plants, or from incorporation of pesticide contaminated plant materials into compost among others (Rashid *et al.*, 2010).

Pesticides can run off from fields or leach into ground water resources and also absorb by food crops (Tiryaki and Temur, 2010). Application of pesticides on crops and soils can also result in pesticides residues on farm produce (Afrane and Ntiamoah, 2011). Hence, there is need to determine pesticides levels in vegetables and soils in areas of massive agriculture activities.

2.8.6 Pesticides effects on humans and the environment

Different pesticides have different properties and different toxicological effects (Costa, 2008). USAD (2015) reported over 30,000 unintentional deaths and over 3 million food poisoning caused by over pesticides used in the third world countries each year. This is due to inadequate knowledge and awareness of pesticides used among farmers, inappropriate applications of pesticides by farmers to crops without wearing protective clothing and dangerous combination of pesticides by some farmers (Okoffo *et al.*, 2016).

The world-extensive deaths and persistent sicknesses are mostly because of pesticide poisoning which account for over 1 million death every (Sebastian *et al.*, 2017). People most likely to be exposed to hazards of pesticides include pesticides manufacturing employees, pesticides formulators, sprayers, mixers, loaders and agricultural farm employees (Aktar *et al.*, 2009).

In commercial settings, employees are at elevated risk because they manage numerous poisonous chemical compounds which include pesticides, poisonous solvents and inert carriers (Amoabeng *et al.*, 2017). Pesticides can cause death, negative systemic effects, neurological, developmental, endocrine, and immunological toxicities in humans and animals (Sabra and Mehana, 2015). High rate of complicated illnesses nausea and cancers in humans are recognized to be acute signs due to pesticides exposure (Sebastian *et al.*, 2017). Organophosphates, organochlorines and related pesticides act by binding to the enzyme acetyl cholinesterase, disrupting nerve functioning, leading to paralysis and possibly death (Lushchak *et al*, 2018). Exposure to those pesticides may lead to acute effects such as meiosis, urination, diarrhoea, diaphoresis, lacrimation, excitation of central nervous system, salivation among others (Grewal, 2017). Neurotic and behavioural effects of pesticides can be experienced as a result of chronic exposure to them (Ecobichon, 2020).

Specific effects of pesticides can include cancers, allergies and hypersensitivities, damage to the central and peripheral nervous systems, reproductive disorders and disruption of the immune system (Tahir *et al*., 2009). Therefore, there is an urgent need to ensure that people do not consume vegetables that contain pesticides residues above recommended levels allowed by WHO, the EU, amnong other world bodies. One of the ways to ensure this is to assess concentrations of pesticides in vegetables and soils where the vegetables are planted.

Pesticides easily contaminate air and water when they run off from agricultural fields, leak from storage tanks, not discarded properly, and especially when they are sprayed aerially (Geyikçi, 2011). During the Vietnam War, United States naval forces internationally sprayed almost 19 million gallons of herbicide on about 3.6 million acres of Vietnamese and Laotian lands to get rid of wooded area cover, damage crops, and clean plants from the sides of their base (Amoabeng *et al*., 2017).

Application of pesticides could also lead to contamination of soil, water, lawn, and other vegetation (Choudhary *et al*., 2018). In addition to killing pests, pesticides can be toxic to a host of other organisms including birds, fish, beneficial insects, and non-target plants.

2.9 Health Effects of Pesticides on Vegetables Consumers

Globally, people are unduly exposed to pesticides through food (Huan *et al*., 2016). As a consequence of pesticide use, over two million people (0.029%), mainly residing in developing nations, are at an elevated health risks (Khan *et al*., 2021). Studies have reported presence of pesticides in food commodities such as cereals among others (Akoto *et al*., 2013), fish water and sediments ((Khan *et al*., 2021), in watermelon fruits (Asare, 2011), in vegetables (Akoto *et al*., 2015; Darko and Akoto 2008) and in the atmosphere (Huan *et al*., 2016). Most of these studies in Ghana, detected the levels of pesticides in vegetables sold on the markets (Akoto *et al*., 2015; Bempah *et al*., 2016).

Several researches validated weak correlation among pesticides residues and human health (Sebastian *et al*., 2017; Akoto *et al*., 2013). Pesticides residues are present in all areas of agro-ecosystems and the risk to human is high and mostly through consumption of pesticides contaminated foods such as vegetables, fruits, fish among others (Bempah *et al*., 2012). Hence, this work is to investigate levels of pesticides in vegetables and soils where vegetables are cultivated especially in the Asante-Mampong Municipality where no such work has been done is very important.

Concentrations of pesticide in vegetables have been found to be harmful to the health status of humans, mostly when they are freshly consumed (Baig *et al*., 2009; Chen *et al*., 2011). Developmental impairment, immunotoxicities and endocrine disruption are related signs and symptoms affecting so many people through consumption of vegetables containing pesticides residues (Bempah *et al*., 2016).

Atieno *et al*. (2014) reported that pesticides residues in vegetables are potentially dangerous to humans and animals health as well as the environment. According to Amoabeng *et al*. (2017), in 2001, pesticides toxicities led to the death of approximately 849,000 individuals globally. Human exposure to pesticides may lead to both acute and chronic effects (Blair *et al.*, 2015). Acute effects include meiosis, urination, diarrhoea, diaphoreses, lacrimation, excitation of central nervous system and salivation whilst chronic exposure can lead to neurotic and behavioural effects (Blair *et al.*, 2015). However specific effects of pesticides include cancers, allergies and hypersensitivities, damage to the central and peripheral nervous systems, reproductive disorders and disruption of the immune system (Tahir *et al.*, 2009).

2.9.1 Effect of pesticides residues on the quality of vegetables produced

The consumption of vegetables promotes good health due to the high levels of nutrients in them (Schreinemachers *et al.*, 2018). However, vegetables are mostly affected by pest and diseases resulting in most farmers (80 %) using different types of pesticides to fight diseases and control activities of pests (Bempah *et al*., 2016). The process of controlling pests, result in killing non-targeted plants whilst other plants also suffer sublethal effects of applied (Saha *et al.*, 2020).

Some farmers' right after application of pesticides on the vegetables proceed to harvest and sell them on the market making the crops unsafe for consumption (Jallow *et al.*, 2017). According to Akoto *et al.* (2013), exposure of plants to glyphosate severely reduces seed quality and shelf life whilst Atieno *et al*. (2014) reported that exposure of tomatoes, cabbage and lettuce to clopyralid can reduce yields and shelf life.

2.9.2 Maximum and minimum residue limits for pesticides

Pesticide residue refers to any specified substance in food, agricultural commodities or animal feed resulting from the use of a pesticide (Zikankuba *et al*., 2019). The term includes any derivatives of pesticides which result from conversion products, metabolites, reaction products and impurities considered to be of toxicological significance. Thus, the amounts of pesticides remained in crops and vegetables after harvest are known as pesticides residues (Keikotlhaile and Spanoghe, 2011).

Maximum Residue Limit (MRL) is the maximum permissible concentration of a pesticide residues (expressed as mg/kg), recommended by the Codex Alimentarius Commission to be legally permitted and toxicological accepted on or in food commodities and animal feeds (FAO, 2013). MRLs are also seen as the highest levels of residues expected to be in the food when the pesticide is applied according to the approved agricultural practices (Keikotlhaile and Spanoghe, 2011).

The USEPA (2009) and the EU (2013) have acceptable and unacceptable levels of pesticides residues in food commodities and were established by local and international authorities or organizations (Amoabeng *et al*., 2017). Residue levels above MRLs, Aceptable Daily Intake (ADI) and/or Acute Reference Dose (ARfD) are taken into consideration to assess risk of pesticides to consumers to determine the existence of possible chronic or acute health risks (FAO, 2015; and WHO, 2017).

Hazard quotient (HQ) and hazard index (HI) are used globally for health risk assessment and they are mainly based on concentrations of pesticides in consumable items (Hu *et al*., 2014; Sun *et al*., 2016; Pan *et al*., 2018). Hazard quotient (HQ) is the ratio of the potential exposure to a toxic substance and the level at which no adverse effects whilst hazard index (HI) is the sum of hazard quotients for toxicants that affect the same target organ or organ system (US EPA, 2006). Since different toxicants can result in similar adverse health effects, hazard quotients for different toxicants are combined (US EPA, 2006).

CHAPTER THREE

METHODOLOGY

3.1 Introduction

This chapter presents description of the study area, experimental design equipment and reagents used in the study. This chapter also looks at soils and vegetables samples collection and the protocols used in the determination of physico-chemical properties of soil. This chapter further gives a detailed description of the method used to determine pesticides levels in soils and vegetables.

3.2 Description of the Study Area

This study was conducted in the Asante-Mampong municipality of the Ashanti Region of Ghana. Asante-Mampong is the capital of the Mampong Municipality (GSS, 2010). The Municipality is located 60 km North-East of Kumasi on the Kumasi - Ejura road (GSS, 2010). It lies in the transitional zone between the savanna zone of the north and the tropical rain forest of the south of Ghana (GSS, 2010).

Asante-Mampong Municipality is situated at latitude 07^{o} 04’ degrees north and longitude 01^{o} 24’ degrees west at 457 m above sea level (GSS, 2010). Annual temperatures of the municipality ranged between 21.9 and 30.1^{o}C (Meteorological Service Department, 2021). Rainfall pattern in the municipality is bimodal, and it occurs from April to July (major rainy season) and August to November (minor rainy season) and has about 1224 mm of rain per annum ((Meteorological Service Department, 2021). The dry season starts from December and ends in March. The vegetation is transitional savanna woodland and its supports vegetable production.

3.2.1 Soil type and vegetation in Ashanti Mampong Municipality

The soil belongs to the Bediase series with the characteristics of deep yellowish red sandy loam, free from concretion and stones (Richard *et al*., 2015). It drains quite well, it is friable and has satisfactory ochrosol formed from Voltaian sand stone with a thin layer of organic matter (Adu and Mensah-Ansah, 1995). The pH of the soil ranges from 6.0 to 6.5 (Richard *et al*., 2015). The farmlands are used to cultivate vegetables such as tomatoes, onion, sweet and hot pepper, cabbage, carrot and garden eggs (Richard *et al*., 2015)

The farmlands are left to fallow for about six months before commencement of new cropping season (Richard *et al*., 2015). The vegetation is predominantly Savannah and it abounds with weed species such as *Pennisetum, conyzoides, Imperata cylindrical, purpureum, Cyperus spp, Eleusine indica, Ageratum Rottboelia exaltata* and *Panicum maximum* among others (Richard *et al*., 2015).

3.3 Experimental Design and Selection of Experimental Sites

A Complete Randomized Design (CRD) was used in this study. Four different vegetables (cabbage, green pepper, carrot and lettuce) were investigated in this study. Each of the vegetables was analysed in triplicate. An initial field investigation was done to assess the nature of the study farms. This investigation was carried out over a two month period (January and February, 2021).

A total of twelve (12) vegetable farms were randomly selected from twenty in the Asante-Mampong municipality. The twelve (12) farms were selected due to their large sizes and also the frequency at which the farmlands have been cultivated with vegetables over the last five years. The total land size for the 12 farms was 36 acres. This initial survey indicated that the selected farms were suitable for the study and they included three (3) cabbage farms, three (3), green pepper farms, three (3), carrot farms (3) and three (3) lettuce farms. The farms were labelled A1, A2 and A3 (cabbage farms), B1, B2 and B3 (carrot farms), C1, C2, C3 (green pepper farms) and D1, D2 and D3 (lettuce farms).

3.4 Equipment and Reagents

3.4.1 Instruments used for pesticides analysis and physico-chemical properties of the soil

Gas Chromatography-Mass Spectrometer (GC-MS) (Varian CP-3800 GC-ECD, made in Germany) with a combiPAL Autosampler was used for the organophosphates, organochlorines and synthetic pyrethroids. The column used was 30 ± 10 EZ Guard x 0.25 mm. The internal diameter of the column was fused with silica capillary coated with VF-5ms (0.25 µm film) and was supplied by Varian Inc. The injector and detector temperature were set at 270 and 300 °C respectively. The oven temperature was programmed as follows: 70 °C held for 2 min, ramp at 25 °C/min to 180 °C, held for 1 min, and finally ramp at 5 °C/min to 300 °C. The flow rates for the nitrogen carrier gas were 1 mL/min at a constant flow and 29 mL/min.

Other instruments used were Homogenizer - FOSS 2096 based on Tecator Technology, a Sartorius weighing balance (Model LE632P), ZhongFan test tube, a 250 mL JOAN glass separating funnel, Sino Sonics® sonicator/vortexer, Centrifuge - CRi multifunction from Thermo Electron Industries SAS, (France), a 2 mL vial, 250 mL Aldrich® single-neck round-bottom flask of 250 mL capacity (Model Z414506) and Rotary vacuum evaporator (Büchi RE-200, Labortechnic AG, Postfach, Switzerland).

Equipment used in the determination of physico-chemical properties of soils were glass bottle (1 L), Cole-Parmer Stuart reciprocal shaker (Model GZ-51900-63), Mettler Toledo Digital Hydrometer infrared/RS-232 adapter, measuring cylinder (500 mL), Gardner gravimetric test, oven and Garden Spiral Hole Drill Planter Augar. Others included EUTECH pH 510 meter, Pyrex Kjeldahl nitrogen distilling apparatus (Model CLS3340500), conical flasks (250 mL), Whatman No. 42 filter paper, Laser technik spectrometer (ARYELLE 200, Germany) and a thermometer.

3.4.2 Reagents used in pesticides residues extraction

Acetonitrile (AcN), and ethyl acetate (EtOAc) were of analytical grade (Sigma Aldrich City, USA). Ouick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) absorbent PSA, (primary-secondary amine), polypropylene (PP) kits and pouches of salts (magnesium sulphate, sodium chloride, trisodium citrate dehydrate, selenium mixture, and disodium hydrogen citrate sesquehydrate) (Altmann Analytik, USA) were used. Other reagents included formic acid (98% purity), polyethylene glycol supplied by Fluka (USA) and standard pesticides (purity for all standards >95%) were obtained from Dr. Ehrenstofer GmbH (Germany).

3.4.3 Reagents used to determine physico-chemical properties of soil

Reagents used in the determination of physico-chemical properties of soil were sodium hexamethaphosphate (dispersing agent), buffer solutions (pHs 4 and 7), 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.

3.5 Collection of Soil and Vegetable Samples

Soils were sampled from twelve (12) different vegetable farms whilst vegetables were sampled from twelve (12) different farms and twelve (12) different markets.

2.5.1 Sampling of soil samples

Soil samples from the selected farms were collected on 20th March, 2021 and then transported to the Pesticide Residues Laboratory of Ghana Standard Authority, Accra and Soil Research Institute, Kwadaso-Kumasi for determination of levels of pesticides and physico-chemical properties of soils respectively. At each of the twelve (12) experimental sites, twenty-five (25) soil samples were collected along the four arms of the ‘W’ pattern (Figure 1) using an auger. “W” pattern was used to give a fair representation of the study fields. 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 and Idowu, 2012). Samples were labelled A1, A2 and A3 (cabbage farms), C1, C2 and C3 (carrot farms), E1, E2 and E3 (preen pepper farms) and G1, G2 and G3 (lettuce farms).

The composite soil samples were then kept in well-labelled glass bottles, placed into iced chest box and then transported to the laboratory for analysis. For pesticides residues analysis, soil samples were sent to the Pesticide Residues Laboratory of the Ghana Standard Authority, Accra whilst physico-chemical properties of soil were determined in the laboratory of Soil Research Institute at Kwadaso in Kumasi, Ghana.

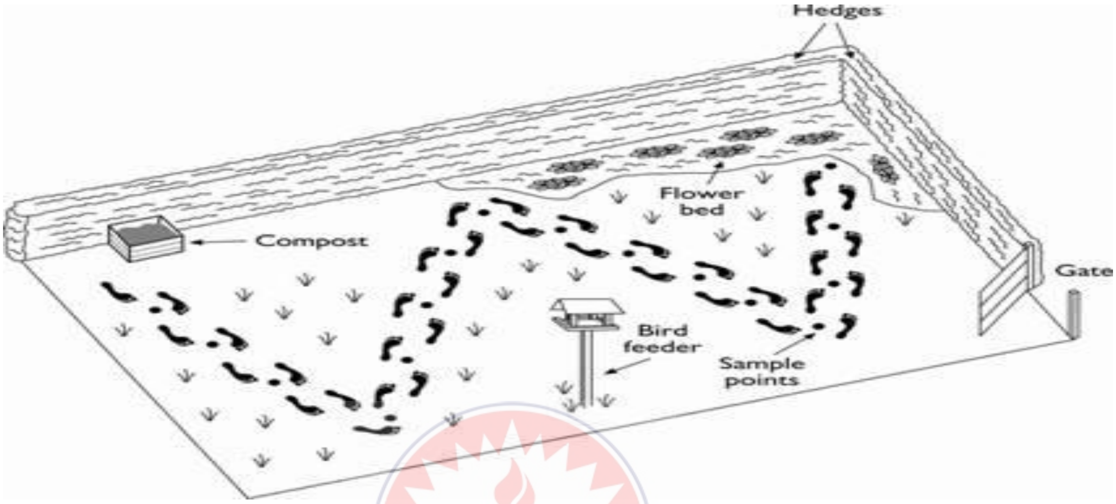

Plate 1: 'W' Pattern used in soil sample collection

Source: www.huttonsoils.com/soilsampling.html

3.5.2 Sampling of vegetables from farms and markets

A total of 120 fresh vegetable samples consisted of 30 cabbage heads, 30 carrot roots, 30 green pepper fruits and 30 lettuce leaves were collected from 12 different vegetable farms and 12 different vegetable markets within the Asante-Mampong municipality. The maximum sample size was 1 kg for small and medium sized vegetables (lettuce, carrot and green pepper) whilst the minimum weight of vegetable for large size vegetable (cabbage) was 2 kg. The sample size was determined using Codex Alimentarius Commission (2000) protocol for determining sample size. For each vegetable samples, thirty (30) were randomly selected from different farms and markets. Vegetable samples from the farms were collected the same date soil samples were obtained and those fro markets were purchased the next day.

Samples from the farms were labelled A1, A2 and A3 (cabbage farms), C1, C2 and C3 (carrot farms), E1, E2 and E3 (preen pepper farms) and G1, G2 and G3 (lettuce farms) whilst those from the markets were also labelled as B1, B2 and B3 (cabbage markets), D1 D2 and D3 (carrot markets), E1, E2 and E3 (green pepper markets) and G1, G2 and G3 (lettuce markets). The samples were put into glass containers, sealed, properly labelled, stored in an iced chest at 4 ^{o}C and then transported to the Pesticide Residues Laboratory of the Ghana Standard Authority for pesticides residues extraction. Samples labelled with a unique sample identities, stored in brown paper boxes, and then transported to the Pesticide Residues Laboratory of the Ghana Standard Authority Accra, where samples were extracted and analyzed for pesticide residues. Pesticides residues were extracted from only the edible portions of each type of vegetable used in the study.

3.6 Laboratory Analytical Methods for Soil Samples

Soil samples were sent to Soil Research Institute Kwadaso Kumasi, Ghana, for soil particle size, bulk density, moisture content, pH, organic carbon and total nitrogen contents determination. Other physico-chemical parameters determined included phosphorus contents, exchangeable bases (calcium and magnesium contents, exchangeable potassium and sodium), exchangeable acidity (Al^{3+} and H^{+}) and cation exchange capacity of the soil samples.

3.6.1 Soil particle size determination

Soil particle size determination was performed using the hydrometer procedure outlined by Huluka and Miller (2014). Soil samples were dried using temperature controlled oven method as described by Naveena *et al*. (2015). The soil samples were kept in oven and allowed to dry at 30 ^{o}C initial temperatures for 2 hours. The temperature was increased to 40 ^{o}C and the soil samples were further dried at this temperature for an hour. The temperature of the oven was again increased progressively to 50 ^{o}C and the soil samples were again dried for additional one hour to ensure thorough drying.

After thorough drying, soil samples were kept in a dessiccator and allowed to cool to room temperature. Fifty grams (50 g) of the oven dried sample was put into 250 mL flat bottom flasks, 50 mL of 5% sodium hexamethaphosphate (dispersing agent) was added and the flask placed onto a Stuart flask shaker (SSL2) and operated at 350 rpm for 30 minutes. The resultant suspension was transferred to 1 L measuring cylinder and made to the mark with distilled water.

A hydrometer was placed in the soil suspensions and the cylinders agitated vigorously to ensure that soil particles were uniformly distributed in the soil suspension. Thermometer was inserted into the suspension to measure its' temperature whilst hydrometer readings were taken every 40 seconds for 3 hours. Percentage sand, silt and clay components of soil samples were calculated using Equations 2, 3 and 4 below:

$$\%\ \text{Sand} = 100 - \left(\frac{A}{W} \times 100\right) \qquad (4)$$

$$\%\ \text{Clay} = \left(\frac{B}{W} \times 100\right) \qquad (5)$$

% Silt = 100 – (% Sand × % Clay) (6)

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

3.6.2 Soil bulk density determination

The core method used (Rai *et al.*, 2017) was adopted and used for determining bulk density of soil. The soil samples were collected using a sharp-edged cylindrical auger of 5 cm internal diameter. The auger was driven carefully into the soil at a depth of 20 cm to ensure negligible compaction. Soil samples were weighed on site, labelled and then sent to Soil Science Research Institute laboratory, Kwadaso-Kumasi for soil parameters determination.

In the laboratory, soil samples were oven dried at 105 °C until constant weights were achieved. Bulk densities of soils were determined using Equation (7) expressed mathematically as:

$$\text{Bulk density (g cm}^{-3}\text{)} = \frac{W}{V}, \qquad (7)$$

Where W is weight of soil sample used and V is volume of soil sample suspension used.

3.6.3 Soil moisture content determination

Moisture contents were determined using the Gardner gravimetric test (Gardner *et al.*, 2000). Hundred grams (100 g) of each soil sample was put into a pre-weighed leak-proof seamless container and then labelled. The container together with soil sample was weighed (M1) and then oven dried at 105 °C until a constant mass was obtained. After drying, the container with soil sample were reweighed (M2) and the mass of water in the sample was obtained from the difference between the masses (M1 and M2). Gravimetric moisture was calculated using Equation (8):

$$(\theta g) = \frac{(M1-M2}{M2} \times 100 \qquad (8)$$

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

3.6.4 Soil pH determination

Soil pH was determined using pH meter (EUTECH 510). Twenty-five grams (25 g) of soil was put into a 100 mL measuring cylinder and 50 mL of deionized water was added. The soil-water mixture was stirred continuously for 30 minutes using magnetic stirrer (Variomag Poly 15, CN48043) to constitute a uniform soil suspension. The suspension was allowed to stand for 30 minutes. The pH meter was adjusted to 2 points within a range of 4.0 and 7.0 using pH 4 potassium hydrogen phthalate and pH 7 potassium phosphate mono basic buffer solutions respectively (Rubinson (2017).

In adjusting the pH meter, its electrode was first rinsed with deionized water and then inserted into potassium phosphate mono basic buffer solution of pH 7, reading was allowed to stabilize until it read pH 7.0. The electrode was then removed from the pH 7 buffer solution and then rinsed with copious amounts of deionized water. The electrode was further inverted into potassium hydrogen phthalate buffer solution of pH 4 and waited for the meter reading to stabilize until it read pH 4. pH of soil samples was taken by immersing the electrode of the pH meter (EUTECH 510) into the upper part of the soil suspension. The procedure was repeated until soil samples wet exhausted. The pH meter was rinsed with copious amounts of distilled water before and after it was used in determining pH of each soil sample.

3.6.5 *Soil organic carbon determination*

To assess organic carbon (OC) contents of soil samples, the modified Walkley-Black wet oxidation technique as describe by Da Silva *et al.* (2013) was used. One gram (1 g) of soil sample was put into a 250 mL conical flask and 10 mL of 0.16 M aqueous solution of potassium dichromate was added. Twenty milliliters (20 mL) of 98% concentrated sulphuric acid was added to the soil-potassium dichromate dropwise from a burette. The mixture was swirled gently, allowed to stand for 30 minutes and the (250 mL) of distilled water was added. Ten millitres (10 mL) of (98%) concentrated phosphoric acid was further added in drops, mixture 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 and the colour changes from green to violet. The organic carbon contents of the soil were calculated using Equation 9.

$$\text{Organic carbon (\%)} = \left(\frac{\mathrm{M} \times 0.39 \times \mathrm{MCF}\ (\mathrm{V1} - \mathrm{V2}}{\mathrm{W}}\right) \qquad (9)$$

Where, M is the molarity of the solution used (moldm^{-3}),V1 is the volume of sulphate solution for blank titration (mL), V2 is the volume of sulphate solution for sample titration (mL) and W is the weight of air – Dry sample (grams) and MCF is the moisture correcting factor (100 + % moisture) / 100. The MCF was used to convert analytical results of air-dried soil to dry weight on the basis of oven-dry soil.

3.6.6 *Determination of total nitrogen contents of soil*

Total nitrogen contents of soils ware determined using the Kjeldahl digestion and distillation process as described in Soil Laboratory Staff (1984). Ten grams (10 g) of soil 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 soil mixture. The mixture was digested at 375 °C for three hours. Fifty millilitres (50 mL) of distilled water was added to the digested sample and then the mixture was allowed to cool to room temperature.

After cooling, 25 mL of digested sample was put into the reaction chamber of the Kjeldahl apparatus, 10 mL of 40% NaOH solution was added and the mixture was distilled. The distillate was collected into a 50 mL flask containing 2% of boric acid, swirled gently to ensure a uniform mixture. The mixture was then titrated with 0.02 M HC1 solution using bromocresol green indicator until end-point was established and the colour change was 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.

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

Where M is concentration of HCl solution used (moldm^{-3}), a is the volume of HCl used in the simple titration, b is the volume of HCl used in the blank titration, V is the weight (g) of air–dry sample used, MCF is the moisture correcting factor (100 + % 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 the dry weight of oven-dry soil.

3.6.7 Determination of available phosphorus

Bray’s No. 1 solution (2.22 mL of 0.03 M NH_4F and 5 mL of 0.025 M HCl) was used to extract soil available phosphorus (Gee and Bauder, 1986). Five grams (5.0 g) of soil was put into a 50 mL flat bottom flask and 35 mL of Bray-1 solution was 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 pippeted into a 25 mL flask and then 10 mL of 0.23 M ammonium molybdate added. Phosphorus contents of soils were recorded at 600 nm wavelength on spectrometer (Spectronic 21D).

The available phosphorus contents of soils were calculated using Equation 11:

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

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

3.6.8 Filtrate preparation for extraction of exchangeable bases

Ten grams (10 g) of soil sample was weighed into a 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 at rpm on a Stuart flask shaker (SSL2) for 90 minutes after which it was filtered under vacuum through Whatman No. 42 filter paper. The filtrate was used to determine the exchangeable bases (calcium, magnesium, potassium and sodium) in soil samples.

3.6.9 Determination of calcium and magnesium

Ten milliliters (10 mL) of the filtrate prepared (**under section 3.7.5**) 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, 1 mL of 2.0% potassium cyanide solution and 0.2 mL of Eriochrome Black T solution. The mixture was titrated to a turquoise blue colouration with 0.02 M EDTA (ethylenediamine tetraacetic acid) and the titre value recorded. The main reaction is presented in Equation 12, 13 and 14.

$Ca^{2+} + EDTA^{4-} \rightarrow [Ca\text{-}EDTA]^{2-}$ (12)

Back titration $EDTA^{4-} + Mg^{2+} \rightarrow [Mg\text{-}EDTA]^{2-}$ (13)

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

$ErioT + Mg^{2+} \rightarrow ErioT\text{-}Mg$ (14)

The titre value for calcium was calculated using Equation 15:

$$T_A = \frac{V1+V2+V3+ \ldots\ldots\ldots\ldots Vn}{n} \qquad (15)$$

Where: T_A is the average titre volume (V1, V2 and V3) for 1st, 2nd and 3rd titrations respectively and n is the number of titre values.

3.6.10 Determination of calcium content of soil

Ten milliliters (10 mL) of the filtrate obtained 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 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).

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

Where w is weight (g) of air-dry soil used, Va is volume (mL) of EDTA solution used in sample titration, Vb 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}.

3.6.11 Determination of exchangeable potassium and sodium

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

Different volumes (5, 10, 15, 20 and 25 mL) of 250 mL standard solution 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 soil samples were determined by flame photometry at wavelengths of 766.5 and 589.0 nm respectively. Exchangeable potassium and sodium contents of soil samples were then calculated using Equations 17 and 18 respectively.

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

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

Where a (mg L^{-1}K) filtrate used b (mg L^{-1}K) is the volume of blank filtrate and w is weight (g) of air-dry soil sample and mcf is moisture correcting factor.

3.6.12 Exchangeable acidity (Al^{3+} and H^{+}) determination

Five grams (5 g) of soil sample was weighed into a 200 mL plastic bottle and 100 mL of 1.0 M KCl solution was added. The mixture was shaken vigorously on Stuart's shaker (SSL2) at 250 rpm for 2 hours after which it was filtered using Whatman No. 42 filter paper. In determining Al^{3+} contents of soil, 50 mL of the filtrate obtained from soil was measured into a 250 mL Erlenmeyer flask, 100 mL of distilled water added, followed by 3 drops of phenolphthalein indicator solution. The mixture was swirled gently and then titrated against 25 mL of 0.05 MNaOH to a permanent pink colour and then the volume titre value was recorded.

To the titrated mixture, 25 mL of 0.05 MHCl was added to change the initial pink colour back to a colourless mixture. Ten millilitres of 0.95 M sodium fluoride (NaF) was added and then titrated further against 0.05 MHCl to a colourless end point. The titre value of Al^{3+} obtained in the first titration was subtracted from the second end point value to obtain the final required titre value for H^{+}. The exchangeable acidity was then calculated using Equation 19.

$$\text{Exchangeable acidity (cmol/kg soil)} = \frac{(a-b)\times M\times 2\times 100\times mcf}{w} \qquad (19)$$

Where, a (mL) is the volume of NaOH used in titration against the sample, b (mL) is the volume of NaOH used to titrate against the blank sample, M is the concentration of NaOH solution used, w (g) is the weight of air-dry soil sample used, 2 = 100/50 (filtrate/pipetted volume) and mcf is the moisture correcting factor (100 + % moisture)/100.

3.6.13 Effective cation exchange capacity (ECEC) determination

Effective cation exchange capacity was calculated as the summation of the exchangeable bases (Ca^{2+}, Mg^{2+}, K^+ and Na^+) and exchangeable acidity (Al^{3+}, H^+) using the Equation 20.

$$ECEC = E_{Ca}{}^{2+} + E_{Mg}{}^{2+} + E_K{}^{+} + E_{Na}{}^{+} + E_{Al}{}^{3+} + E_H{}^{+} \qquad (20)$$

Where $E_{Ca}{}^{2+}$, $E_{Mg}{}^{2+}$, $E_K{}^{+}$, $E_{Na}{}^{+}$, $E_{Al}{}^{3+}$ and $E_H{}^{+}$ represent the exchangeable calcium, magnesium, potassium, sodium, aluminium and hydrogen respectively.

3.7 Soil Samples Preparation for Pesticides Residues Extraction

Composite samples comprising soils collected from farmlands cultivated with cabbage, green pepper, carrot and lettuce at the time of the study. Representative portions of soil sample was 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 for pesticides extraction and analysis.

3.7.1 Extraction of pesticides residues from soil samples

Ten grams (10 g) of homogenized soil sample was put into a 100 mL separating flask. Ten millilitres (10 mL) of acetonitrile was added and then sonicated for 2 hours. After sonication, 10 mL of acetonitrile was further added to the content of the separating flask, the flask was corked and then placed onto a flask shaker and shaken continuously for 30 minutes at 350 rpm. The mixture was allowed to stand for 30 minutes to separate into two layers. Ten millilitres (10 mL) of the organic phase (top layer) was pippeted into a 50 mL round-bottomed flask and then evaporated at 35 °C to 2 mL vial for purification. The pesticides extraction procedure was repeated for all the soil samples.

3.7.2 Purification of extract using silica (Catalog no. 60)

A silica cartridge (catalog no. 60) consisting of 100 mg/mL of silica and a 1 cm thickness layer of anhydrous magnesium sulphate on top was conditioned with 10 mL of acetonitrile. Conditioning was done with 6 to 10 mL of acetonitrile after which extracts of the samples were loaded onto the cartridge bed. Two millitres (2 mL) of extracts were loaded onto the head of the cartridge and the eluates were collected at 1 mL/minute into a 50 mL round bottom flask. The cartridges were eluted with 10 mL of acetonitrile and then the eluates were concentrated at 35 ^{o}C to 1 mL on rotary evaporator (Buchi Rotary evaporator, Model 2199A, India). The eluates were re-dissolved in 1 mL ethyl acetate stored in 2 mL vials and then refrigerated at 4 ^{o}C for analysis using GC instrument coupled with an electron capture detector (GC-ECD).

3.8.1 Extraction and clean-up of pesticides residues extracted from various vegetable samples

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) and Anastassiades *et al*. (2003) was used. Vegetables were cut into smaller pieces with a knife and then homogenised using a warring blender (Foss Homogeniser, model. 2096). Ten grams (10 g) of each of the homogenized vegetable type (cabbage, green pepper, carrot and lettuce) was placed into a separate 50 mL centrifuge tube and cap screwed. Ten milliters (10 mL) of acetonitrile was added to each sample and then samples were vortexed for 3 minutes.

Mixture of 4 g of anhydrous magnesium sulphate, 1 g of sodium chloride, 1 g of trisodium citrate dehydrate and 0.5 g disodium hydrogen citrate sesquehydrate was added to the samples and then vortexed further for another 3 minutes. The samples were centrifuged at 3000 rpm for 5 minutes. Six millilitres (6 mL) of the centrifuged extract of the various vegetables was put into polypropylene single used centrifugation tube containing 150 mg primary-secondary amine (methyl amine and dimethyl amine) mixture and 900 mg of anhydrous magnesium sulphate. These samples were further vortexed for additional 3 minute and then centrifuged at 3000 rpm for another 5 minutes.

Four millilitres of each of the extract was put into a round bottom flask, acidified with 40 mL of 5 % formic acid in acetonitrile, mixed thoroughly by gentle shaken and then concentrated to 1 mL using a rotary evaporator (Buchi Rotary evaporator, India). The various extracts were reconstituted in 20 uL of ethyl acetate and then transferred into 2 mL auto sampler vials. Pesticides residues determination was done using a gas chromatography technique on Varian CP-3800. The procedure was repeated for all the vegetables.

3.8.2 Spiked samples preparation

To ascertain the effectiveness of the QUECHERS method of extraction, the method was optimized and validated by spiking 10% of the sample (n=10) with 1.0 µg/mL standard mixture before analysis to evaluate the recovered levels of the pesticides. Spiked samples of both soil and vegetable were prepared by adding 1 mg/mL of standard pesticide spiking solution to 10.0 g of soil and 10.0 g of vegetable extracts respectively. A stock solution of the pesticides containing 1.0 µg/mL of the pesticides in ethyl acetate was used for the preparation of the spiked samples.

The spikes were prepared at the time pesticide residues were being extracted from soil and vegetable samples. The same extraction and clean-up processes as described for the vegetable sample types were used in the preparation of the spike samples. Samples were spiked with 0.1 mL of the 1.0 µg/mL standard pesticides to investigate efficiency of the extraction procedure. The percentage recoveries of the pesticides were determined by using Equation (21).

$$\text{Recovery percent} = \frac{\text{conc of pesticide residue recoverd from the fortified sample}}{\text{concentration of pesticides added to the sample}} \times 100 \qquad (21)$$

3.9 Gas Chromatography Analysis

Extracts of soil and vegetable samples were analysed using a Varian CP-3800 gas chromatograph (Varian Association Inc. Germany) equipped with combiPAL Autosampler and 63Ni electron capture detector. The sample extracts were injected onto the inlet port. The samples were vapourised in the hot inlet pot and turned into gases. The mobile phase (nitrogen gas) carried the vapourised samples through the column (stationary phase). Different pesticides in the samples interact differently with the column's stationary phase, depending on their volatility. This caused them to travel through the column at different speeds and hence separated.

The separated pesticides then left the column one after the other, and enter a detector (mass spectrometer). The time required for each pesticide to travel through the column is called its retention time. The GC produced a graph called a chromatogram, where each separated pesticide was represented by a peak. The number of peaks indicated the number of separated pesticides in the sample extracts. The position of each peak indicated the retention time for each pesticide.

3.9.1 Conditions for the analysis

The conditions for the GC were capillary column coated with VF-5 (30 m + 10 m EZ guard column × 0.25 mm internal diameter, 0.25 µm film thickness). Temperatures for injector and detector were set at 270 and 300 °C respectively. The oven temperature was also set as follows: 70 °C held for 2 min, ramp at 25 °C/min to 180 °C, held for 1 min, and finally ramp at 5 °C/min to 300 °C. The GC conditions and the detector response were adjusted in order to match the relative retention times and response as spelt out by the Japanese analytical methods for agricultural chemicals (Syoku-An 2006). Nitrogen gas was used as carrier at a flow rate of 1.0 ml/min and detector make-up gas of 29 mL/min. The injection volume of the GC hiwas 1.0 mL.

3.10 Determination of Health Quotients (HQ) of Detected Pesticides

To estimate the risk of pesticides on the health of consumers, the estimated daily intakes (EDI) of each pesticide was divided by its corresponding acceptable daily intake (ADI) as expressed in Equation (22).

$$\text{HQ} = \frac{\text{Estimated daily intakes (EDI)}}{\text{Acceptable daily intake (ADI)}} \qquad (22)$$

Hazard quotient (HQ) greater than 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 (23)

$$\text{EDI} = \text{Cp} \times \text{CRp/Bwc} \qquad (23)$$

Where, EDI is the estimated daily intake of pesticides (mg/kg), CRp is the consumption rate of pesticides via vegetables (mg/kg), Cp is the mean concentration of pesticides residues in vegetables samples and Bwc is the average body weight (kg) of consumers.

3.11 Estimation of Health Indices of the Detected Pesticides

The combined health quotients (health indices) of organochlorines, organophosphate and pyrethriods in vegetable samples were estimated by adding the hazard quotients (HQs) of the various pesticides detected in the vegetables using Equation (24).

$$HI = \sum(HQs_{(OP)} + HQs_{(OC)} + HQs_{(SP)}) \qquad (24)$$

Hazard indices above 1 indicate that mixture of pesticides in a given vegetable is above the maximum acceptable risk and consumers may suffer health issues when vegetables are consumed (Akoto *et al.* 2015; Hossain *et al.* 2015).

Acceptable daily intake of organochlorines, organophosphates and synthetic pyrethroids in various vegetables

Acceptable daily intake (ADI) (mg/kg/day) and maximum residue limit of organochlorine pesticides, OCs (Lindane, Heptachlor, Aldrin, Beta Hexachlorocyclohexane (HCH), Dichlorodiphenyldichloroethylene (P'P'- DDE), Dieldrin, Endrin, Methoxychlor and Beta – Endosulfan) are shown in Appendix 2 (Akoto *et al.,* 2015; Hossain *et al.*, 2015). Whilst that of organophosphate pesticides (Parathion, Diazinon, Malathion, Chlorpyrifos, Profenofos, Dimethoate and Pirimiphos) and synthetic pyrethroid pesticides (Fenvalerate, Allethrins, Permethrin, Cyfluthrin, Cypermethrin and Deltamethrin) are reported in Appendices 3 and 4 (Akoto *et al.*, 2015; Hossain *et al.*, 2015).

CHAPTER FOUR

RESULTS AND DISCUSSION

This chapter deals with results and discussion on chemical properties (pH, organic carbon, total nitrogen, and phosphorus, exchangeable cations such as calcium, magnesium, potassium, sodium, aluminum and hydrogen) and physical properties (moisture, sand, silt, clay, soil texture and bulk density) of soil samples investigated and pesticides levels in soils and vegetables (cabbage, carrot, green pepper and lettuce grown) in the Asante-Mampong municipality. This chapter also discussed HQ and HI values of each type of pesticide and also discusses the possible health issues likely to be suffered by consumers.

4.1 Quality Control

Recoveries of various pesticides (OPs, OCs and SPs) at 0.010 mg/kg fortification from soils and vegetable samples are shown in the Tables 1, 2 and 3 below. The obtained recoveries were within the acceptable percentage range of 70.0 - 120.0% (Kovacicova *et al.*, 1975). Limits of detection (LOD) and limits of quantification for the pesticides (OP, OC and SP) residues detected in both soil and vegetable samples were 0.001 mg/kg and 0.003 mg/kg respectively.

Table 1: Percentage of orgnophosphate pesticides recovered from standard pesticide spiking solution

Pesticides	**Mean (%)**	**Standard Dewviation**
Diazinon	84.50	0.006
Dimethoate	80.50	0.010
Pirimiphos	86.50	0.010
Chlorpyrifos	83.50	0.011
Parathion	84.00	0.007
Profenofos	79.00	0.023
Malathion	81.00	0.006

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

Table 2: Percentage of organochlorine pesticides recovered from standard pesticide spiking solution

Pesticides	Mean (%)	Standard Deviation
Lindane	82.00	0.009
Heptachlor	78.00	0.009
Aldrin	82.00	0.009
P’P’- DDE	79.00	0.006
Dieldrin	76.50	0.009
Beta Endosulfan	77.00	0.010
Beta HCH	78.00	0.010
Endrin	80.00	0.006
Methoxychlor	78.00	0.010

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

Table 3: Percentage of synthetic pyrethroids pesticides recovered from standard pesticide spiking solution

Pesticides	Mean (%)	Standard Deviation
Allethrins	79.50	0.010
Permethrin	83.00	0.006
Cyfluthrin	83.50	0.009
Cypermethrin	82.50	0.004
Fenvalerate	82.50	0.008
Deltamethrin	86.50	0.007

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

4.2.1 Soil chemical analysis at the experimental sites

Soil samples investigated for exchangeable cations and physico-chemical properties were taken from a depth of 0 to 20 cm from 12 different vegetable farms within the Asante-Mampong Municipality of the Ashanti Region of Ghana. Data obtained for soil physico-chemical properties were treated statistically and the results presented (Tables 4, 5 and 6). The pH of soil across the experimental farms ranged from 5.78 to 6.27 (Table 4). The analysis of variance showed that significant differences ($P<0.05$) existed in pH of the soil across vegetable farms investigated.

Soil samples taken from the cabbage farms had the highest soil pH (6.27 ± 0.32) followed by that from lettuce farms (6.19 ± 0.24), green pepper (6.04 ± 0.31) farms and carrot farms (5.78 ± 0.12). These observed pH data indicate that pesticides availability, adsorption onto soil particles and persistence in soils were expected to be considerably high. Fosu-Mensah *et al*. (2016) reported that as soil pH decreases below 7 (acidic conditions), concentration of hydrogen ions in soil solution increases making pesticides molecules more available in soil and easily absorbed by roots of plants.

Although the pH range (5.78 ± 0.12 to 6.27 ± 0.32) observed in this study is comparable to that (5.89 ± 0.47 to 7.09 ± 0.42) reported by Asare (2011) and far below those (7.56 to 8.49) reported by Fosu-Mensah *et al*. (2016), the differences in pH reported herein and that reported by Asare (2011) and Fosu-Mensah *et al*. (2016) could be attributed to differences in geographical locations where soils were sampled for these investigations and soil compositions.

Soil organic carbon contents ranged from 0.76 to 0.87%, total nitrogen contents ranged from 0.08 to 0.10% and available phosphorus contents ranged from 10.51 to 11.06 (Table 4). No significant differences existed between soil organic carbon, total nitrogen and available phosphorus contents of soils. High organic carbon (0.87 ± 0.09), total nitrogen (0.10 ± 0.03) and available phosphorus (11.06 ± 1.22) contents were observed for soil samples taken from the lettuce farms followed by that from green pepper farms, carrot farms and cabbage farms (Table 4).

In general, organic carbon, total nitrogen and available phosphorus contents of soils were below that reported in a similar study by Emiru and Gebrekidan (2013). These indicate that adsorption of pesticide molecules onto soil particles was expected to be low since high organic matter content in soil would absorbs pesticides molecules than soil particles. This deduction corresponded well with a report by Khalid *et al.* (2020) who reported that smaller organic matter content of soil means lesser pesticides by organic matter contents and higher pesticides absorption into soil particles. Rate of leaching and run-off of pesticides molecules from soil surfaces were also expected to be high as reported in a similar study by Owusu-Boateng and Amuzu (2013). According to Dankyi *et al.* (2014) as soil organic carbon, total nitrogen and available phosphorus contents decrease, solubility of pesticides increases whilst binding onto soil particles decreases. Soil organic carbon (0.76 to 0.87%) and total nitrogen contents (0.08 to 0.10%) recorded herein corroborated well with organic carbon (0.71 to 0.91%) and total nitrogen (0.07 to 0.15%) contents reported by Dankyi *et al.* (2014) and were below (1.38 to 1.78%) and (0.17 to 0.25%) for organic carbon and total nitrogen contents respectively reported by Fosu-Mensah *et al*. (2016).

Table 4: Mean values of chemical properties of soil from the vegetable farms

Soil chemical properties	Cabbage	Carrot	Green pepper	Lettuce	LSD	P-value
Soil pH (1:1)	6.27 ± 0.32^{a}	5.78 ± 0.12^{c}	6.04 ± 0.31^{b}	6.19 ± 0.24^{ab}	0.26	0.002
Organic carbon (%)	0.76 ± 0.09	0.78 ± 0.12	0.84 ± 0.29	0.87 ± 0.09	0.20	0.495
Total N (%)	0.07 ± 0.03	0.08 ± 0.02	0.09 ± 0.03	0.10 ± 0.03	0.06	0.500
Available P (mg/kg)	10.51 ± 1.00	10.62 ± 1.23	11.03 ± 0.69	11.06 ± 1.22	1.71	0.599

^{abc}= Means bearing different superscripts in the same column are significantly different

4.2.2 Exchangeable cations contents in soil from vegetable farms

Soil Exchangeable cations are known to influence dynamics and behaviour of pesticides molecules in soils (Fosu-Mensah *et al.,* 2017). Analysis of soil samples taken from different vegetable farms for exchangeable cations showed that cation exchange capacity (CEC) of the soils ranged from 2.86 ± 1.47 to 3.94 ± 1.01cmol/kg. Calcium ions (Ca^{2+}) contents of soil ranged from 4.40 to 5.14 cmol/kg, Mg^{2+} 1.05 to 1.28 cmol/kg, K^{+} 0.45 to 0.56 cmol/kg, Na^{+} 0.23 to 0.49 cmol/kg, Al^{3+} 0.12 to 0.17 cmol/kg and H^{+} contents 0.16 to 0.19 cmol/kg (Table 5). Highest cation exchangeable capacity was in the order $Ca^{2+} > Mg^{2+} > K^{+} > H^{+} > Al^{3+}$ (Table 5). Generally, no significant differences (P>0.05) existed in mean values of Ca^{2+}, Mg^{2+}, K^{+}, Al^{3+} and H^{+} among CEC of soils sampled from the various vegetable farms (Table 5).

The order of CEC in soil was green pepper farms (3.94 ± 1.01) > lettuce farms (3.71 ± 2.31) > cabbage farms (3.29 ± 1.56) > carrot farms (2.86 ± 1.47). High proportions of Mg^{2+} (1.28 ± 0.44), K^{+} (0.56 ± 0.21) and H^{+} (0.19 ± 0.02) were recorded for soil samples from green pepper farms whilst those from lettuce farms had high proportions of Ca^{2+}, (5.14 ± 0.56), Na^{+} (0.49 ± 0.25) and Al^{3+} (0.17 ± 0.15).

Cation exchangeable capacity (CEC) measures quantity of active adsorptive sites available in soil (Solly *et al.*, 2020) and it influences binding capacities of pesticides molecules onto soil particles as reported by Zhang *et al.* (2020). The results obtained (Table 5) showed that the soil samples from the various farms investigated have small available active adsorption site for pesticides adsorption onto soils sampled from the various vegetable farms.

However, adsorption of pesticides molecules onto soil particles and their subsequent persistence in the soils were expected to be small and short since they would be easily leached into soil solution as reported by Asare (2011). The range of CEC (2.86 ± 1.47 to 3.94 ± 1.01) reported herein is similar to 2.35 ± 1.14 to 3.80 ± 0.93 cmol/kg reported in 2011 by Asare and 2.91 ± 0.77 to 3.61 ± 0.88 reported in 2018 by Dankyi *et al*. The results (Table 5) further showed that soil samples from various vegetable farms also have low Ca^{2+} (4.40 ± 0.74 to 5.14 ± 0.56), Mg^{2+} (1.05 ± 0.46 to 1.28 ± 0.44), K^{+} (0.45 ± 0.30 to 0.56 ± 0.21), Na^{+} (0.23 ± 0.08 to 0.49 ± 0.25), Al^{3+} (0.12 ± 0.03 to 0.17 ± 0.15) and H^{+} (0.16 ± 0.01 to 0.19 ± 0.02).

The reduction observed for Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} contents of the various soils shows that pesticides retention and availability in the soils were expected to be high whilst the reduction seen in Al^{3+} and H^{+} contents of the soils also indicates that pesticides retention and their availability in the soils were expected to be low and the findings corroborated well with that of Akoto *et al.* (2013) and Fosu-Mensah *et al.* (2016).

Thus, low levels of acidic cations (Al^{3+} and H^{+}) could mean that the levels of pesticides in soil solutions were low since exchangeable acidic cations are directly related to levels of pesticides in soil. This finding also corroborated well with that reported in 2011 by Asare. According to reports by Afrane and Ntiamoah (2011), Agyen (2011) and Owusu-Boateng and Amuzu (2013) amounts of pesticides molecules that go into soil solution decreases as cations exchange capacity of soil decreases. Hence, small amounts of pesticides were expected to be available in the soil samples because they may have leached into soil solution.

Table 5: Mean values (cmol/kg) of soil exchangeable cations of soils from the vegetable farms

Exchangeable cations	Cabbage	Carrot	Green pepper	Lettuce	LSD	P-value
CEC	3.29 ± 1.56^{c}	2.86 ± 1.47^{b}	3.94 ± 1.01^{a}	3.71 ± 2.31^{a}	0.19	0.010
Ca^{2+}	4.89 ± 1.02	4.62 ± 0.96	4.40 ± 0.74	5.14 ± 0.56	2.16	0.521
Mg^{2+}	1.24 ± 0.48	1.22 ± 0.26	1.28 ± 0.44	1.05 ± 0.46	1.10	0.684
K^{+}	0.47 ± 0.14	0.54 ± 0.09	0.56 ± 0.21	0.45 ± 0.30	0.29	0.612
Na^{+}	0.23 ± 0.08^{c}	0.36 ± 0.15^{b}	0.36 ± 0.09^{b}	0.49 ± 0.25^{a}	0.44	0.011
Al^{3+}	0.15 ± 0.07	0.12 ± 0.03	0.16 ± 0.06	0.17 ± 0.15	0.15	0.691
H^{+}	0.17 ± 0.01	0.16 ± 0.01	0.19 ± 0.02	0.17 ± 0.02	0.03	0.807

Means bearing different superscripts (a, b, c) in the same column are significantly different at indicated p - value; LS.D = Least significance difference.

4.1.3 Physical properties of soil at the experimental farms

The results presented (Table 6) are the physical properties for soil samples investigated herein. Moisture contents of the soil range from 4.24 ± 1.23 to 6.41 ± 2.31 %, sand contents (79.11 to 81.78%), silt contents range from 18.22 to 20.89%, clay range between 9.56 to 10.67% whilst soil bulk densities were between 1.23 to 1.27 Mg/m^3. The analysis of variance showed that significant differences (LSD = 0.19, $P<0.05$) existed in moisture contents of soils across the investigated vegetable farms. However the other physical properties showed no significant differences in physical parameters of soil investigated across the various vegetable farms at the indicate p-value ($p > 0.05$).

Soil samples from green pepper and lettuce farms had high similar moisture contents (6.14 ± 2.71% and 6.41 ± 2.31% respectively) when compared to 4.24 ± 1.23% and 5.74 ± 1.77% of soils taken from cabbage and carrot farms respectively. Proportions of sand contents in the soils were carrot farms (81.78 ± 2.53%) > green pepper farms (80.67 ± 3.74 %) > cabbage farms (80.22 ± 3.93%) > lettuce farms (79.11 ± 4.59 %) whilst silt contents were carrot farms (20.89 ± 4.60) > green pepper farms (19.93 ± 3.71%) > cabbage farms (19.78 ± 3.91%) > lettuce farms (18.22 ± 4.54 %).

Clay contents of soil were also in order carrot farms (10.67 ± 4.47%) > green pepper farms (10.22 ± 2.73%) > cabbage farms (10.00 ± 3.61%) > lettuce farms (9.56 ± 2.71 %) whilst bulk densities were also in order lettuce farms (1.27 ± 0.06 Mg/m^3) > carrot farms (1.26 ± 0.07 Mg/m^3) > green pepper farms (1.24 ± 0.06 Mg/m^3) > cabbage (1.23 ± 0.08 Mg/m^3) farms.

Soil moisture plays a significant role in pesticides retention, availability in soil and pesticides molecules adsorption onto soil particles as indicated by (Kumar and Philip, 2006). Soil moisture contents recorded herein favour pesticides molecules retention and availability in soil as indicated in a similar study by Olayinka (2013). Results of this study also agreed favourably with a report by Asare (2011) that indicated that low soil moisture contents inactive soil micro-organisms and make it difficult for them to breakdown pesticides molecules which lead to high pesticides accumulation in soils, high adsorption rates onto soil particles and long persistence in soil. Texture of soils was found to be sandy-loamy (SL) when soil classification system as indicated by the United States Department of Agriculture (1987) was used.

Table 6: Mean values of physical properties of soils from various vegetable farms

Physical properties	Cabbage	Carrot	Green pepper	Lettuce	LSD	P-value
Soil moisture (%)	4.24 ± 1.23^{c}	5.74±1.7^{b}	6.14± 2.71^{a}	6.41± 2.31^{a}	1.56	0.020
Sand (%)	80.22 ± 3.93	81.78±2.3	80.67±3.74	79.11±4.59	6.53	0.520
Silt (%)	19.78 ± 3.91	20.89±4.0	19.93±3.71	18.22±4.54	6.51	0.121
Clay (%)	10.00 ± 3.61	10.67±4.7	10.22±2.73	9.56 ± 2.71	4.61	0.934
Bulk density(Mg/m^{3})	1.23 ± 0.08	1.26 ±0.07	1.24 ± 0.06	1.27 ± 0.06	0.16	0.767
Soil texture	S.L	S.L	S.L	S.L		

Means bearing different superscripts (a, b, c) in the same column are significantly different at indicated p-value; LS.D = Least significance difference

4.3.1 Levels of organophosphate pesticides in the soil samples

The soil analysis results (Figure 2) showed that mean levels of organophosphate pesticides (OPPs) in soil samples ranged from 0.016 ± 0.001 to 0.059 ± 0.004 mg/kg. Mean levels of Dimethoate, Pirimiphos, Parathion and Profenofos ranged from 0.032 ± 0.003 to 0.043 ± 0.002 mg/kg, 0.032 ± 0.006 to 0.040 ± 0.012 mg/kg, 0.033 ± 0.004 to 0.053 ± 0.003 mg/kg and 0.051 ± 0.004 to 0.059 ± 0.004 mg/kg respectively. These were above recommended maximum residual levels set by the USEPA (2009) and EU (2013) (Figure 2).

Dimethoate (0.043 ± 0.002 mg/kg) and Profenofos (0.059 ± 0.004 mg/kg) mean levels were higher in soil samples collected from the cabbage farms. However, Dimethoate (0.032 ± 0.003 mg/kg) and Profenofos (0.051 ± 0.004 mg/kg) were low in soil samples taken from the green pepper farms whilst Parathion (0.053 ± 0.003 mg/kg) and Malathion (0.035 ± 0.012 mg/kg) were also higher in soils collected from the cabbage farms. Parathion (0.033 ± 0.004 mg/kg) and Malathion (0.019 ± 0.003 mg/kg) were low in soils taken from the green pepper farms.

Dimethoate (0.032 ± 0.003 to 0.043 ± 0.002 mg/kg), Pirimiphos (0.032 ± 0.007 to 0.040 ± 0.004 mg/kg), Parathion (0.033 ± 0.001 to 0.053 ± 0.003 mg/kg) and Profenofos (0.051 ± 0.005 to 0.059 ± 0.007 mg/kg) were high in the investigated soils. These high levels could be attributed to the frequent use of the pesticides (Silva *et al*., 2019; Asare, 2011) and lack of knowledge about these pesticides among vegetable farmers as reported by Aktar *et al.* (2018). These imply that continuous application of these pesticides led to their accummulation in the soils. These observations corroborated well with findings by Asare (2011) who reported higher levels of Dimethoate (0.040 mg/kg), Pirimiphos (0.034 mg/kg) and Profenofos (0.073 mg/kg) in soils sampled from watermelon farms at Nsadwir in the central region of Ghana. Asare (2011) attributed the higher levels of Dimethoate, Pirimiphos and Profenofos in the Nsadwir soils to lower rate of pesticides leaching into soil solution and the ability of pesticides molecules to bind tightly to soil particles leading to their higher accumulation and longer persistence in the soil. Again findings of this study corresponded favourably with report by Ofori *et al.* (2014) which indicated that vegetable growers have low knowledge of the toxic effects of pesticides and hence apply higher doses than recommended on crops.

Mean values of Diazinon (0.016 ± 0.005 to 0.022 ± 0.002 mg/kg), Chlorpyrifos (0.016 ± 0.005 to 0.037 ± 0.011 mg/kg) and Malathion (0.019 ± 0.03 to 0.035 ± 0.012 mg/kg) that occurred in soils from various vegetable farms (Figure 2) were below 0.03 mg/kg recommended by both USEPA (USEPA, 2009) and European Union (EU, 2013) for Diazinon and Chlorpyrifos and 0.05 mg/kg for Malathion. The low levels of Diazinon, Chlorpyrifos, and Malathion recorded herein could be attributed to rapid removal of pesticides from soils through run-off, leaching and faster rate of degradation as reported in a similar study by Owusu-Boateng *et al.* (2013). The low levels of Diazinon, Chlorpyrifos and Malathion in almost all the soil samples could also be due to high rates of uptake by both vegetable plants and bodies of soil invertebrates as reported by Asare (2011). Asare (2011) recorded lower levels of Diazinon (0.0051 mg/kg) and Malathion (0.009 mg/kg) in soil samples from watermelon farms at Nsadwir in Central region of Ghana and reported that this could be attributed to fast rates of pesticides leaching and surface run-off.

Pesticide levels in soils could again lead to toxicity in plants and their products and also contaminate the food chain when absorbed by plants roots (Fosu-Mensah *et al.*, 2016; Silva *et al*., 2019). Study by Wang *et al*. (2002) on effects of organophosphates pesticides toxicity on soil organisms reported that soil organisms are sensitive to organophosphate toxicity and affects species and quantities of soil organisms. The authors further reported that the organophosphate pesticides have deadly effects on earthworms, and their toxicity affect respiration systems of soil micro-organisms and their toxicities increase with increasing concentrations and prolong exposure time. Thus, high levels of Parathion, Dimethoate, Pirimiphos and Profenofos recorded herein could have serious consequences on activities of soil organisms which could lead to reduced soil fertility.

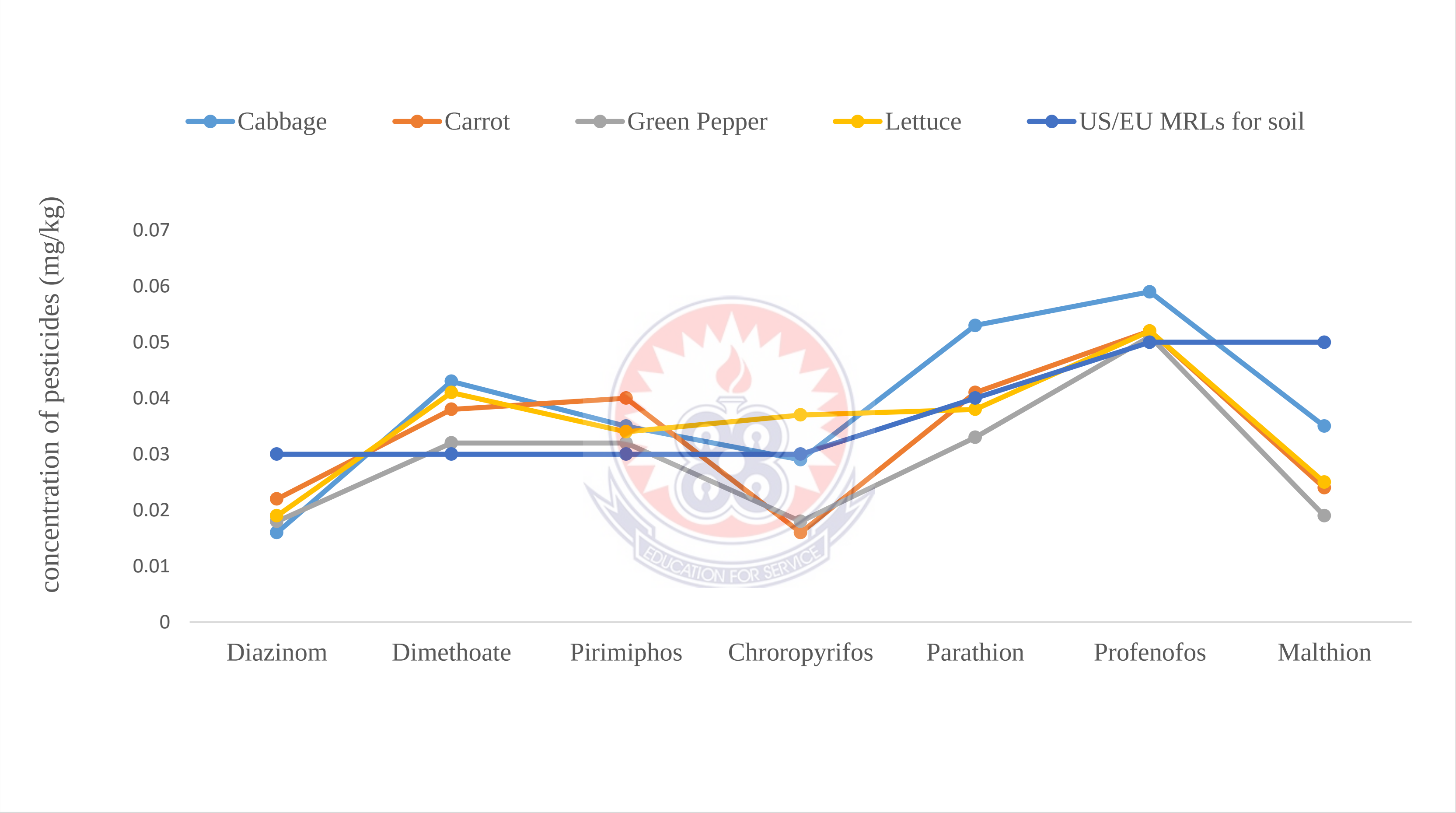

Figure 2: Mean levels of organophosphate pesticides in soil from difference vegetable farms

4.3.2 Levels of organochlorine pesticides in soil samples

The results obtained herein (Figure 3) showed that organochlorine pesticides (OCPs) in soil samples from the different vegetable farms had mean concentrations ranging from 0.013 ± 0.002 mg/kg (Endrin) to 0.054 ± 0.002 mg/kg (P'P DDE). The levels of Lindane ranged from 0.042 ± 0.002 to 0.050 ± 0.004 mg/kg, Dichlorodiphenyldichloroethylene (P'P'- DDE) ranged from 0.041 ± 002 to 0.054 ± 0.002 mg/kg, Beta Endosulfan ranged from 0.044 ± 0.005 to 0.052 ± 0.003 mg/kg and Beta Hexachlorocyclohexane (HCH) ranged from 0.039 ± 0.006 to 0.048 ± 0.007 mg/kg in soil samples were above recommended maximum residual levels (0.04, 0.04, 0.04 and 0.03 mg/kg) permitted by the USEPA and EU (USEPA, 2009; EU, 2013).

Lindane, Dieldrin and Beta Endosulfan levels (0.050 ± 0.006, 0.024 ± 0.003 and 0.052 ± 0.002 mg/kg respectively) were high in soil samples from the lettuce farms and low (0.042 ± 0.004, 0.018 ± 0.003 and 0.045 ± 0.004 mg/kg respectively) in soil samples taken from the green pepper farms. Though, P'P'- DDE level (0.054 ± 0.002 mg/kg) was high in soil samples from the green pepper farms, it was low (0.041 ± 0.006) in soil samples from the cabbage farms.

The high levels of Lindane (0.042 ± 0.002 to 0.050 ± 0.004 mg/kg), P'P'- DDE (0.041 ± 0.002 to 0.054 ± 0.002 mg/kg), Beta Endosulfan (0.044 ± 0.005 to 0.052 ± 0.003 mg/kg) and Beta Hexachlorocyclohexane (HCH) (0.039 ± 0.06 mg/kg to 0.048 ± 0.007 mg/kg) could be due to application of high concentrations of pesticides than recommended by the pesticides manufactures onto soils as reported by Asare (2011) which subsequently led to the build-up of pesticides molecules in the soils.

Continuous applications of pesticides onto vegetables as reported by Olayinka (2013) could also be a contributing factor to the high levels of pesticides found in the soil samples. High persistent naure of organochlorine pesticides could again be a reason for their high levels in the soil (Thiombane *et al.*, 2018).

The high levels of Lindane (0.042 ± 0.002 to 0.050 ± 0.004 mg/kg), P'P'- DDE (0.041 ± 0.002 to 0.054 ± 0.002 mg/kg), Beta Endosulfan (0.044 ± 0.005 to 0.052 ± 0.003 mg/kg) and Beta HCH (0.039 ± 0.06 mg/kg to 0.048 ± 0.007 mg/kg) could also be attributed to the relatively high clay contents in soil samples. Clay contents in the soils have large reactive surface area for pesticide adsorption as reported by Copaja and Gatica-Jeria (2021) and Zhang *et al.* (2021). Thus the ability of pesticides molecules to bind to soil particles and accumulate in soil might have contributed to the elevated levels of pesticides in the soils. Highe levels of pesticides residues in the soils could lead to off-site transport of pesticides to places where humans and non-target organisms would be exposed to high levels of pesticides as reported by FAO and ITPS and (2017) Silva *et al.* (2019).

Mean concentration of Heptachlor ranged from 0.029 ± 0.003 to 0.033 ± 0.006 mg/kg, Aldrin (0.022 ± 0.026 to 0.039 ± 0.013 mg/kg) and Endrin (0.013 ± 0.006 to 0.033 ± 0.012 mg/kg) were all below recommended maximum residual levels (0.04 mg/kg) allowed by the USEPA and the European Union. Low levels of these organochlorine pesticides could be attributed to high pesticides uptake by plants and also into bodies of soil organisms as reported by Asare (2011) and Owusu-Boateng and Amuzu, 2013).

The high levels of Lindane (0.042 ± 0.002 to 0.050 ± 0.004 mg/kg), P’P’- DDE (0.041 ± 0.002 to 0.054 ± 0.002 mg/kg), Beta Endosulfan (0.044 ± 0.005 to 0.052 ± 0.003) and Beta HCH (0.039 ± 0.006 to 0.048 ± 0.007 mg/kg) detected herein could affect soil organisms since they have long period of persistence in the environment as reported by Jayaraj *et al.* (2016). Study by AL-Ahmadi (2019) on pesticides use, misuse and their impacts in the environment indicated that contamination of agricultural soils with pesticides could lead to changes in their chemical and biological properties of soil, affect their quality and cause negative impacts on crops production. Baxter and Cummings (2008) and Arora *et al.* (2019) have also reported that pesticides residues in soils impair soil microbial biodiversities and enzymatic activities and degrade soil organic matter.

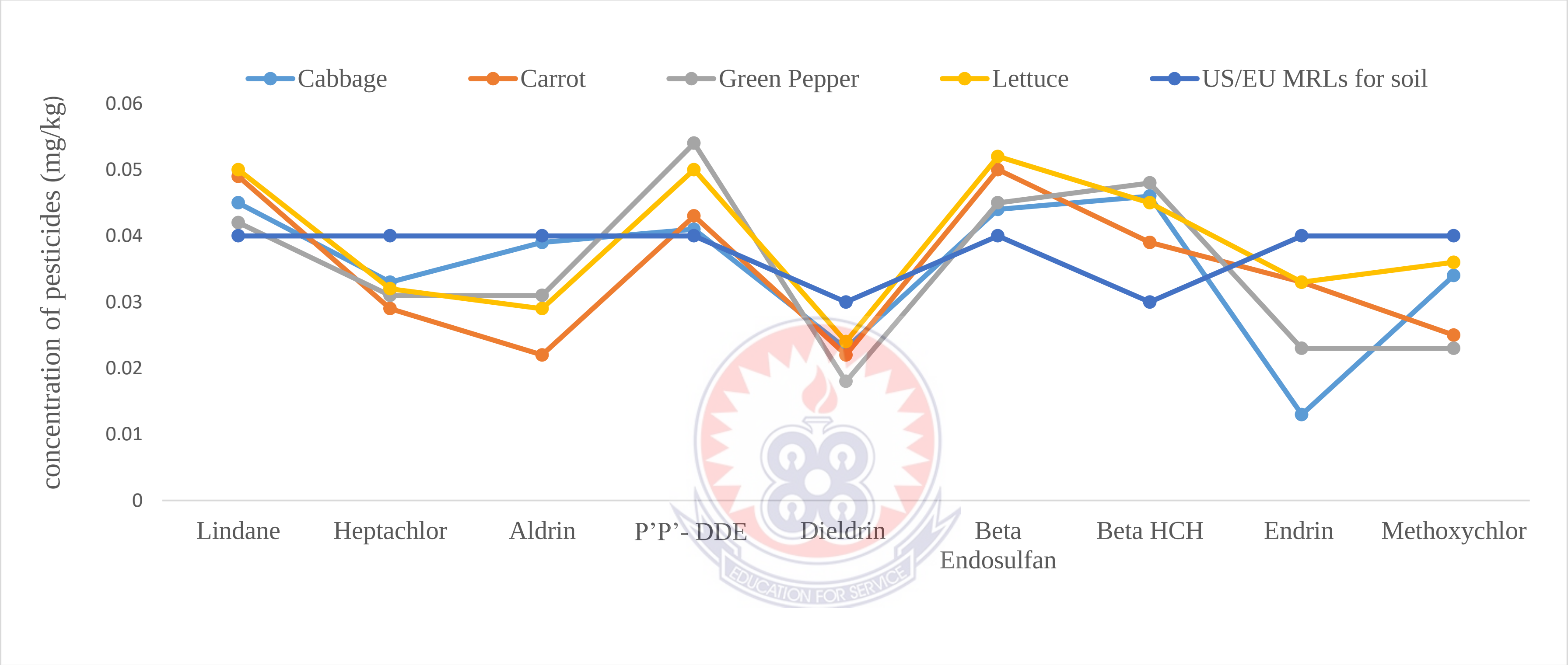

Figure 3: Mean levels (mg/kg) of organochlorine pesticides in soils from different vegetable farms

4.3.3 Levels of synthetic pyrethroid pesticides in soil samples

Levels of synthetic pyrethriod pesticides (SPPs) in the soil samples from the vegetable farms were computed and presented graphically. Mean levels of synthetic pyrethriod pesticides in soils samples ranged from 0.022 ± 0.006 mg/kg (Fenvalerate) to 00.074 ± 0.040 mg/kg (Permethrin). Allethrin mean concentrations (0.052 ± 0.004 to 0.060 ± 0.006 mg/kg) and Cypermethrin (0.052 ± 0.002 to 0.072 ± 0.010 mg/kg) were above recommended maximum residual level (0.05 mg/kg) allowed by the USEPA (2009) and the European Union (2013) for both pesticides. Mean concentrations of Allethrin (0.060 ± 0.006 mg/kg) and Cypermethrin (0.072 ± 0.010 mg/kg) in soils samples were high in soils from the green pepper farms whilst low Allethrin (0.052 ± 0.004 mg/kg) and Cypermethrin (0.052 ± 0.033 mg/kg) were observed in those from the cabbage farms. The high mean levels of Allethrin (0.060 ± 0.006 mg/kg) and Cypermethrin (0.052 ± 0.033 mg/kg) in the soil samples suggest that they tightly bind to soil particles and they have reduced rate of leaching as reported by Fosu-Mensah *et al*. (2016).

These observations corroborated well with the findings of similar works conducted by Cycoń *et al.* (2016) and Lah (2011). These researchers recorded high levels of Cypermethrin (0.059 ± 0.033 mg/kg) in soil samples and attributed the high levels to strong binding capability of the pesticides to soil particles which in turn make it difficult for the pesticide to leach from the soil. Similar report by Aiyesanmi *et al.* (2012) also suggested strong binding capabilities of synthetic pyrethroid pesticides to be responsible for their persistence in soil.

Permethrin (0.036 ± 0.012 to 0.074 ± 0.040 mg/kg), Cyfluthrin (0.058 ± 0.005 to 0.062 ± 0.003), Fenvalerate (0.022 ± 0.006 to 0.024 ± 0.004 mg/kg) and Deltamethrin (0.022 ± 0.017 to 0.043 ± 0.009 mg/kg) were below recommended maximum residual levels suctioned by the USEPA/EU (0.10, 0.15, 0.03 and 0.05 mg/kg respectively). These observed low mean concentrations could be attributed to a fastest rate of leaching from soil surfaces and plant uptake as indicated by Owusu-Boateng *et al.* (2013).

Similarly, the observed low levels of Permethrin, Cyfluthrin, Fenvalerate and Deltamethrin could also be attributed to their rapid uptake by soil organisms that incorporate them into their bodies as reported by Asare, (2011).

Levels of Allethrin (0.052 ± 0.004 to 0.060 ± 0.006 mg/kg) and Cypermethrin (0.052 ± 0.002 to 0.072 ± 0.010 mg/kg) were above MRLs suctioned by the USEPA/EU. These elevated Allethrin and Cypermethrin levels in soils could leach to water sources through run-off from soil and might be detrimental to aquatic organisms as reported by Martínez *et al.* (2005). Even though synthetic pyrethroids were developed purposely to be selective to insects, pyrethroids are extremely toxic to aquatic organisms including fish as indicated in a report by Martínez *et al.* (2005). Pyrethroids could also pose health risks to humans through food chain and direct contact because of their presence in aquatic organisms, surface water resources and soils.

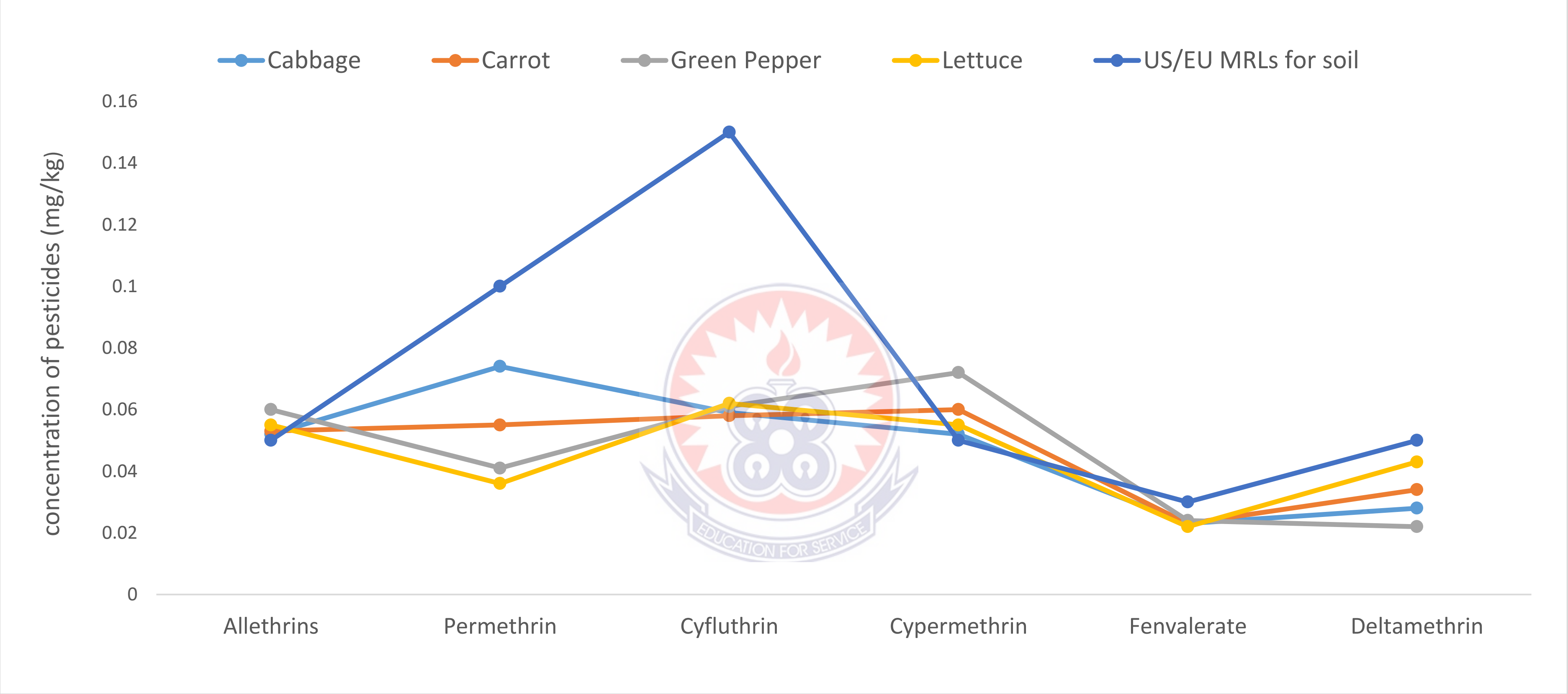

Figure 4: Mean levels (mg/kg) of synthetic pyrethroids in soil ssamples from various farms

4.4.1 Levels of organophosphate pesticides in cabbage head from various farms and markets

Cabbage heads from three different farms located in Asante-Mampong Municipality, Kofiase and Kyiremfaso and vegetable markets also in Mampong, Kofiase and Yonso were included in this study. The mean concentrations of organophosphate pesticides were calculated and compared with USEPA/EU recommended maximum residual levels in vegetables (Figure 5).

The mean levels of Parathion (0.032 ± 0.011 mg/kg), Profenofos (0.004 ± 0.002 mg/kg) and Malathion (0.013 ± 0.007 mg/kg) were in cabbage heads from the farms whilst cabbage heads bought from the markets had Parathion (0.018 ± 0.008 mg/kg), Profenofos (0.004 ± 0.001 mg/kg) and Malathion (0.015 ± 0.001 mg/kg) (Table 5). These mean concentrations of Parathion, Profenofos and Malathion in cabbage heads (both farms and markets) were below USEPA (USEPA, 2009) and European Union (EU, 2013) recommended maximum residual levels in cabbage.

The mean concentrations of Diazinon (0.041 ± 0.004 mg/kg), Dimethoate (0.040 ± 0.008), Pirimiphos (0.041 ± 0.008 mg/kg), and Chlorpyrifos (0.021 ± 0.002 mg/kg) were in cabbage heads from the farms whilst those which occurred in cabbage heads bought from the various markets were Diazinon (0.040 ± 0.007 mg/kg), Dimethoate (0.038 ± 0.007), Pirimiphos (0.038 ± 0.009 mg/kg), and Chlorpyrifos (0.015 ± 0.002 mg/kg). The residues in the cabbage heads from the farms were slightly above those purchased from the markets. Mean concentrations of organophosphate pesticides were above 0.01 mg/kg USEPA/EU recommended maximum residual levels for Diazinon, Dimethoate, Pirimiphos and Chlorpyrifos.

These high mean levels of Diazinon (0.041 ± 0.004 and 0.040 ± 0.007 mg/kg for farms and markets respectively), Dimethoate (0.040 ± 0.008 and 0.038 ± 0.007 mg/kg), Pirimiphos (0.041 ± 0.008 and 0.038 ± 0.009 mg/kg) and Chlorpyrifos (0.021 ± 0.002 and 0.015 ± 0.002 mg/kg) could be due to the fact that they were applied to the cabbage few weeks prior to harvest or failure of the cabbage to metabolize the pesticides as reported by Asare (2011) and Glotfelty, *et al.* (1989). The findings of this study corroborated well with that of Asare (2011). Asare (2011) reported high levels of Diazinon (0.085 mg/kg), Dimethoate (0.081 kg/mg) and Chlorpyrifos (0.084 kg/kg) in watermelon fruits grown in Nsadwri in the Central Region of Ghana. Similar findings were also reported by Achiri *et al*. (2016) where they indicated high levels of Dimethoate (0.07 mg/kg), Chlorpyrifos (0.4 mg/kg) in cabbage samples in Accra, Ghana.

Study by Berrada *et al*. (2010) indicated possible health issues associated with pesticide residues in the environment, crops, humans and animals. In humans, OPPs could cause acute headaches and nausea as indicated by Chowdhury *et al.* (2012) as well as cancers and reproductive defects (Bassil *et al.*, 2007), developmental impairment, immunotoxicity (Berrada *et al.*, 2010), birth defects and disrupt the endocrine system (Kalliora *et al.*, 2018).

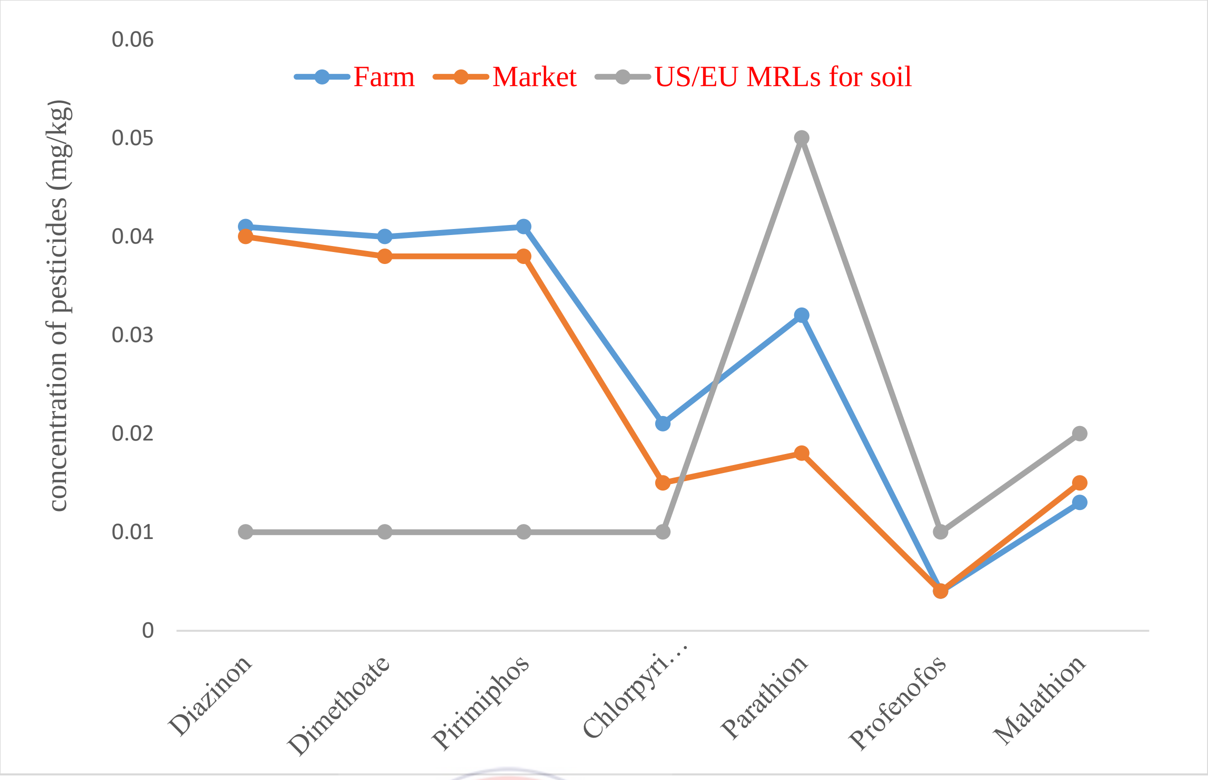

Figure 5: Mean levels (mg/kg) of organophosphate pesticides in cabbage from farms and markets

4.4.2 Levels of organochlorines pesticides in cabbage head from various farms and markets

Cabbage heads from three different farms located in Mampong, Kofiase and Kyiremfaso and vegetable markets also in Mampong, Kofiase and Yonso were included herein. The cabbage heads were analysed for organochlorines pesticides (OCPs) and the mean levels presented graphically (Figure 6). The mean concentrations of OCPs were also compared with USEPA/European Union recommended maximum residual levels in vegetables. Mean levels of Beta Endosulfan, Beta Hexachlorcyclohexane (HCH) and Methoxychlor in cabbage from the farms were (0.040 ± 0.007 mg/kg), (0.003 ± 0.002 mg/kg) and (0.007 ± 0.002 respectively whilst those found in cabbage heads purchased from the various markets had Beta Endosulfan (0.028 ± 0.008 mg/kg), HCH (0.002 ± 0.001 mg/kg) and Methoxychlor (0.006 ± 0.002 mg/kg). These means were below 0.01 mg/kg

USEPA/EU recommended maximum residual level in cabbage. However, the mean concentrations of Lindane (0.023 ± 0.008 mg/kg) (farms), Heptachlor (0.019 ± 0.008 mg/kg) (farms), Aldrin (0.033 ± 0.005 mg/kg) (farms), Dieldrin (0.034 ± 0.007 mg/kg) (farms) and Endrin (0.025 ± 0.007 mg/kg) (farms) and Lindane (0.020 ± 0.004 mg/kg) (markets), Heptachlor (0.018 ± 0.006 mg/kg) (markets), Aldrin (0.019 ± 0.007 mg/kg) (markets), Dieldrin (0.032 ± 0.005 mg/kg) (markets) and Endrin (0.015 ± 0.002 mg/kg) (markets) were above 0.01 mg/kg USEPA/European Union recommended maximum residual levels (USEPA, 2009; EU, 2013).

These observed elevated levels of Lindane, Heptachlor, Aldrin, Dieldrin and Endrin levels in cabbage heads from the farms and the markets could apparently be attributed to their accumulation in the soil for rapid absorption by the roots of cabbage plants and also could be due to failure of the cabbage plants to metabolize them and thus leading to high levels found. These findings herein agreed favourably with that reported by Owusu-Boateng *et al*. (2013) where high levels of Lindane (0.02 ± 0.01 mg/kg), Beta HCH (0.02 ± 0.01 mg/kg), Beta Endosfsn (0.31 ± 0.03 mg/kg) and P'P'-DDE (0.23 ± 0.01 mg/kg) were found in cabbage heads from farms along the Oyansia River, Accra-Ghana. However, the findings were at variance with that of Asare (2011) where low levels of Heptachlor (0.007 mg/kg), Aldrin (0.003 mg/kg), Dieldrin (0.002 mg/kg) and Endrin (0.001 mg/kg) were reported in watermelon fruits in a study conducted on watermelon farms in Nsadwir village in the Central Region of Ghana.

Pesticide residues in soils have potential to contaminate plants, plant products and food chain when absorbed by roots of plants as indicated by (Fosu-Mensah *et al*., 2016). According to Wu *et al.* (2017 and Akomea-Frempong *et al.* (2017) pesticide residues above MRLs pose a possible health risk to consumers. The health risks may include acute neurological toxicity, disturbances in the immune and reproductive system among others (Landrigan *et al.*, 2015). Organochlorine pesticides are less expensive, effective against various pests, have long persistent in the environment, they are able to bioaccumulate and are potentially toxic to humans and wildlife (Fosu *et al.*, 2017; Rahmawati *et al.*, 2017).

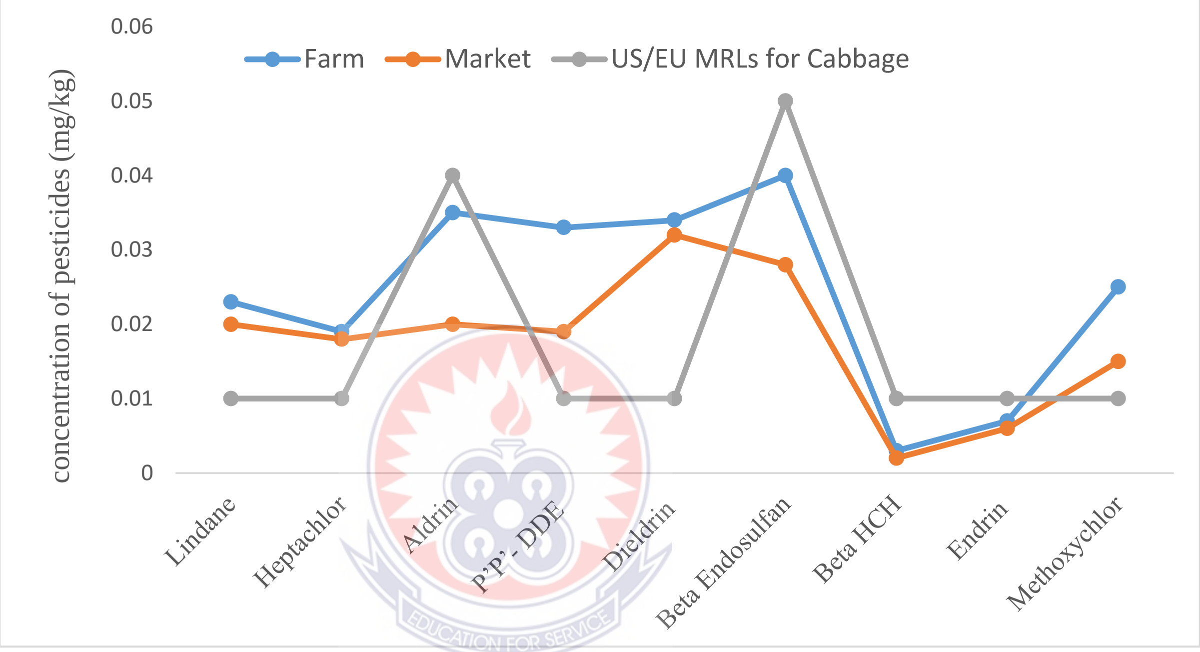

Figure 6: Mean levels (mg/kg) of organochlorine pesticides in cabbage from farms and markets

4.3.3 Levels of synthetic pyrethroid pesticides in cabbage heads from farms

Cabbage heads from three different farms located in Mampong, Kofiase and Kyiremfaso and vegetable markets also in Mampong, Kofiase and Yonso were included in this study. Mean concentrations of synthetic pyrethroids pesticides in the cabbage heads were presented graphically (Figure 7) and also compared with USEPA/European Union recommended maximum residual levels.

Mean concentration of Allethrin (0.006 ± 0.002 mg/kg), Permethrin (0.037 ± 0.003 mg/kg), Cyfluthrin (0.010 ± 0.03 mg/kg), Cypermethrin (0.039 ± 0.001 mg/kg) and Deltamethrin (0.051 ± 0.009 mg/kg) were in cabbage heads from the farms whilst those which occurred in cabbage heads purchased from the various markets were Allethrin (0.004 ± 0.003 mg/kg), Permethrin (0.026 ± 0.008 mg/kg), Cyfluthrin (0.023 ± 0.001 mg/kg), Cypermethrin (0.031 ± 0.006 mg/kg) and Deltamethrin (0.061 ± 0.005 mg/kg). These levels were below 0.01 mg/kg, 0.05 mg/kg, 0.03 mg/kg, 1.0 mg/kg and 0.10 mg/kg levels set by USEPA/European Union recommended maximum residual levels for Allethrin, Permethrin, Cyfluthrin and Deltamethrin respectively (Figure 7). However, mean level of Fenvalerate (0.027 ± 0.004 mg/kg) occurred in cabbage heads from the farms highly than Fenvalerate (0.024 ± 0.005 mg/kg) occurred in those from the markets. Mean concentration of Fenvalerate in cabbage samples were above 0.02 mg/kg recommended maximum residual level set by USEPA/European Union (Figure 7).

These observed high levels could be attributed partly to failure of cabbage plants to metabolize the pesticides or partly due to the fact that the cabbage plants could not release absorbed pesticides more rapidly into the soil and thus led to their accumulation in the cabbage heads as reported by Asare (2011) and Owusu-Boateng *et al*. (2013). Exposure to certain synthetic pyrethroids including fenvalerate could cause reproductive dysfunction, developmental impairment, and certain cancer through hormonal pathways (Garey and Wolff, 1998).

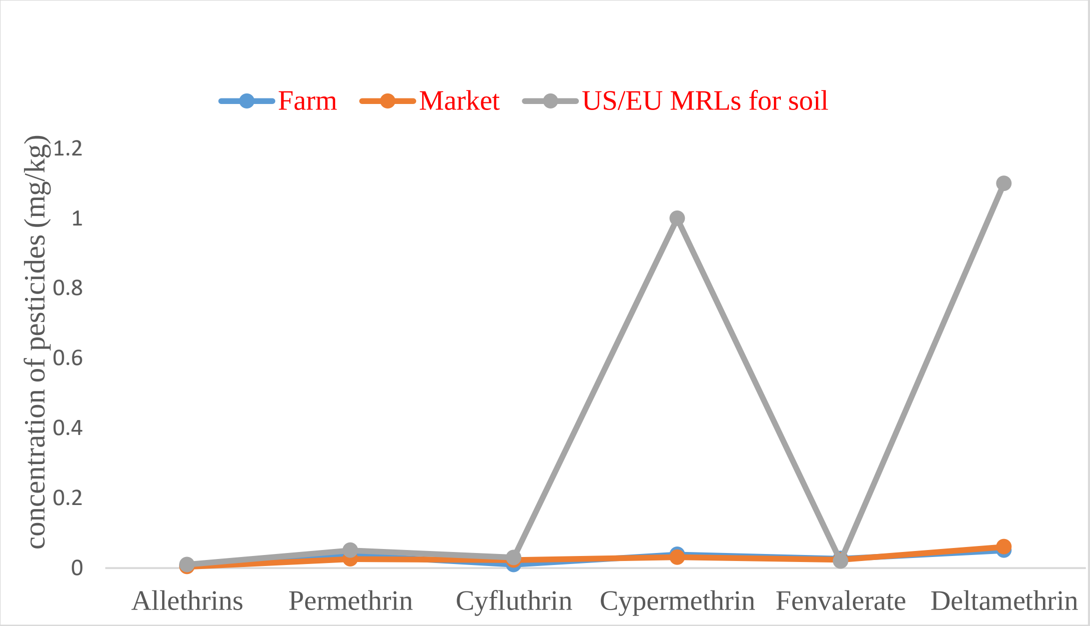

Figure 7: Mean levels (mg/kg) of synthetic pyrethroid pesticides in cabbage from farms and markets

4.4.4 Levels of organophosphate pesticides in carrot roots from farms and markets

The mean concentrations of organophosphate pesticides in carrot roots from the farms and the markets were also represented graphically and again compared with USEPA/European Union recommended maximum residual levels (Figure 8). Chlorpyrifos recorded a mean level of 0.007 ± 0.003 mg/kg for farms and 0.005 ± 0.002 mg/kg for markets, Parathion, 0.023 ± 0.004 mg/kg for farms and 0.016 ± 0.003 mg/kg for markets, Profenofos, 0.008 ± 0.011 mg/kg for farms and 0.003 ± 0.002 mg/kg for markets and Malathion had 0.010 ± 0.004 mg/kg for farms and 0.008 ± 0.001 mg/kg for markets. Organophosphate pesticides levels were below 0.01 mg/kg recommended maximum residual levels for carrot (Figure 8).

Diazinon recorded a mean level of 0.036 ± 0.007 mg/kg for farms and 0.035 ± 0.006 mg/kg for markets, Dimethoate, 0.039 ± 0.006 mg/kg for farms and Pirimiphos had 0.042 ± 0.004 mg/kg for farms and 0.039 ± 0.005 mg/kg for markets. Mean levels of Diazinon, Dimethoate and Pirimiphos in carrot roots from farms were slightly above those purchased from the markets. The mean concentrations of Diazinon (0.036 ± 0.007 mg/kg) (farms), Dimethoate (0.039 ± 0.006 mg/kg) (farms) and Pirimiphos (0.042 ± 0.004 mg/kg) (farms), Diazinon (0.035 ± 0.006 mg/kg) (markets), Dimethoate (0.032 ± 0.010 mg/kg) (markets) and Pirimiphos (0.039 ± 0.005 mg/kg) (markets) were above 0.01 mg/kg limit recommended by USEPA and European Union. The elevated levels of Diazinon, Dimethoate and Pirimiphos observed in carrot roots from both the farms and markets could be due to the fact that carrot roots absorbed more pesticides from the soil due to high pesticides accumulation in the soil as a result of excessive application 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 carrot roots would be continually absorbing accumulated undegraded pesticides molecules from soils. Consumers of vegetables contaminated with high levels of Pirimiphos could suffer from reproductive health issues as reported by Ngoula *et al*. (2007) when they conducted a study on the effects of Pirimiphos on fertility of adult male rats.

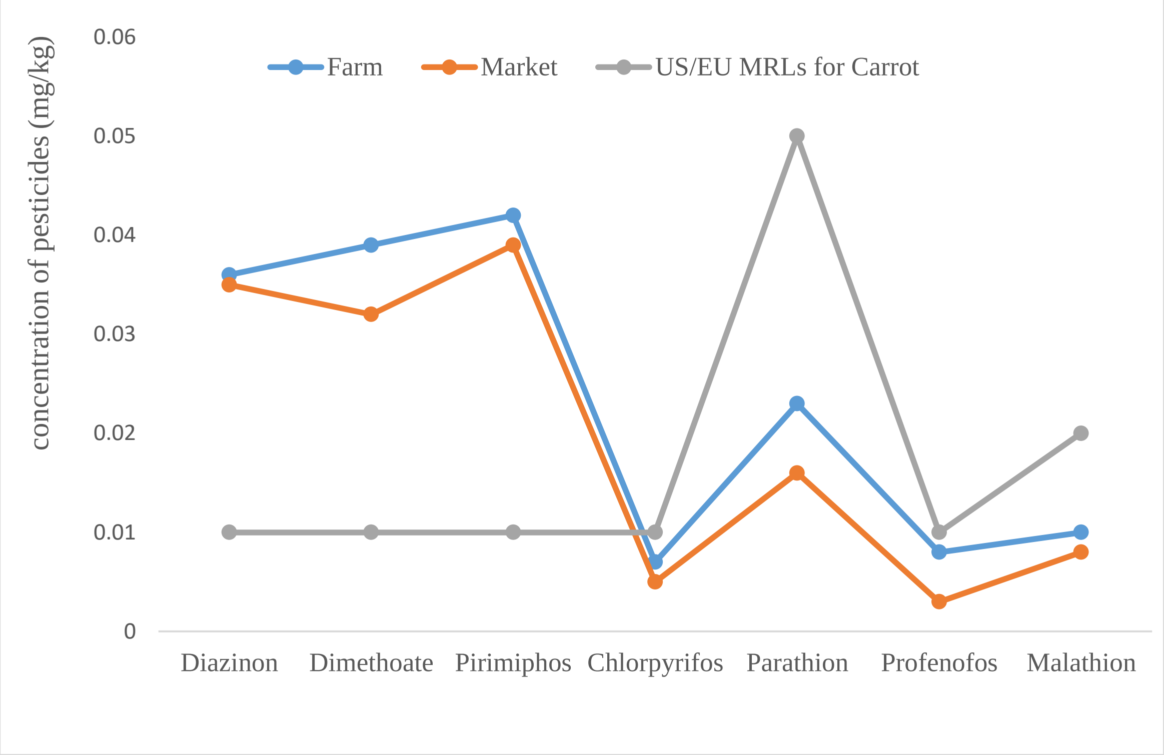

Figure 8: Mean levels (mg/kg) of organophosphate pesticides in carrot roots from farms and markets

4.4.5 Levels of organochlorine pesticides in carrot roots from farms and markets

Mean concentrations of organochlorine pesticides detected herein were graphically presented and compared with USEPA/European Union recommended maximum residual levels (Figure 9). Lindane recorded mean levels of 0.007 ± 0.003 mg/kg for farms and 0.006 ± 0.004 mg/kg for markets, Heptachlor, 0.007 ± 0.004 mg/kg for farms and 0.003 ± 0.001 mg/kg for markets, P'P'- DDE, 0.027 ± 0.002 mg/kg for farms and 0.021 ± 0.003 mg/kg for markets, Beta Endosulfan, 0.055 ± 0.014 for farms and 0.054 ± 0.007 for markets Beta HCH, 0.005 ± 0.001 mg/kg for farms and 0.003 ± 0.002 mg/kg for markets and Methoxychlor had 0.006 ± 0.003 mg/kg for farms and 0.005 ± 0.003 mg/kg for markets. Levels of aforementioned OCPs were below 0.01 mg/kg USEPA/European Union recommended maximum residual levels (Figure 9). However, Aldrin (0.032 ± 0.004 mg/kg) (farms), Dieldrin (0.025 ± 0.007 mg/kg) (farms) and Endrin (0.029 ± 0.007 mg/kg) (farms) and Aldrin (0.047 ± 0.008 mg/kg) (markets), Dieldrin (0.026 ± 0.003

mg/kg) (markets) and Endrin (0.023 ± 0.004 mg/kg) (markets) were above the USEPA/European Union recommended maximum residual levels (Figure 9).

The high organochlorine pesticides levels detected herein could be attributed to high accumulation and persistence of elevated levels of OCPs in the soil. Continuous cultivation of carrots on the same piece of land and failure of carrot plants to metabolize absorbed pesticides as reported by Asare (2011) could also be the cause of the high levels of organochlorine pesticides found in the carrot roots. The findings of this study agreed favourably with that reported by Ekevwe *et al*. (2021) where elevated levels of Aldrin (5.86 mg/kg), Dieldrin (3.23 mg/kg), Heptachlor (6.89 mg/kg) and Endrin (8.17 mg/kg) were detected in carrot roots.

Organochlorine pesticides as reported by Akan *et al*. (2013) and Agbeve *et al*. (2014) have ability to accumulate and increase their levels in the food chain. The elevated organochlorines pesticides in the food chain have been reported by Akan *et al*. (2013) and Agbeve *et al*. (2014) to pose serious human health risks. Exposure to pesticide residues through food and drinking water consumption affect normal thyroid functioning, cause low sperm counts in adults, birth defects and contribute to increase testicular cancer (Mesnage *et al*., 2010), immune malfunctioning (Tanner *et al*., 2011), endocrine system disruption, certain cancers, immunotoxicity (Cocco *et al*., 2013), neuro behavioural and developmental disorders, among others (Gill and Garg, 2014).

The levels of the organochlorine pesticides in the carrot roots ranged from 0.003 ± 0.001 mg/kg (Heptachlor) to 0.055 ± 0.005 (Beta Endosulfan) (Figure 9). Levels of Beta Endosulfan (0.055 ± 0.005 mg/kg and 0.054 ± 0.003 mg/kg) were recorded for carrot roots obtained from the farms and markets respectively. Here the order of OCPs in the carrot roots were Aldrin (0.032 ± 0.004 mg/kg, farms) and (0.029 ± 0.004 mg/kg, markets) > Endrin (0.029 ± 0.006 mg/kg, farms) and (0.023 ± 0.008 mg/kg, markets) > P'P-DDE (0.027 ± 0.010 mg/kg, farms) and (0.021 ± 0.010 mg/kg, markets) > Dieldrin 0.025 ± 0.005 mg/kg, farms) and (0.013 ± 0.006 mg/kg, markets).

Lindane, Heptachlor, Methoxychlor and Beta HCH had the least mean levels (0.007 ± 0.001 mg/kg, farms) and (0.006 ± 0.005 mg/kg, markets), (0.007 ± 0.006 mg/kg, farms) and 0.003 ± 0.002 mg/kg, markets), (0.006 ± 0.004 mg/kg (farms) and (0.005 ± 0.004 mg/kg, markets), (0.005 ± 0.001 mg/kg, farms) and (0.003 ± 0.002 mg/kg, markets) respectively were also present in the carrot roots sampled from the various vegetable farms and market within the Asante-Mampong Municipality.

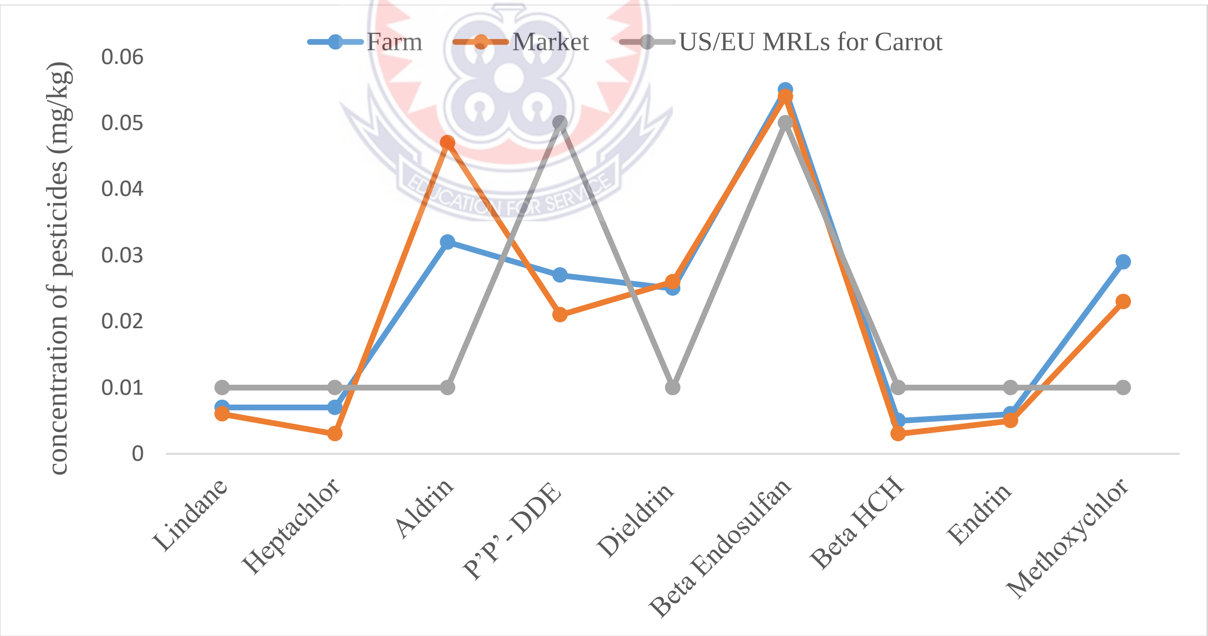

Figure 9: Mean levels (mg/kg) of organochlorine pesticides in carrot roots from farms and markets

4.4.5 Levels of synthetic pyrethroids in carrot roots from farms and markets

Mean concentrations of synthetic pyrethroids pesticides (SPPs) detected in the carrot roots were also computed, graphed and compared with USEPA and the European Union recommended maximum residual levels (Figure 10). The mean values of the SPPs ranged from 0.003 ± 0.001 mg/kg (Allethrin) to 0.023 ± 0.009 mg/kg (Permethrin). The mean levels detected in carrot roots from the farms were Allethrin (0.003 ± 0.001 mg/kg), Permethrin (0.023 ± 0.009 mg/kg), Cyfluthrin (0.014 ± 0.002 mg/kg), Cypermethrin (0.021 ± 0.010 mg/kg), Fenvalerate (0.018 ± 0.003 mg/kg) and Deltamethrin (0.013 ± 0.002 mg/kg) whilst those which occurred in carrot roots purchased from the various markets were Allethrin (0.007 ± 0.003 mg/kg), Permethrin (0.011 ± 0.008 mg/kg), Cyfluthrin (0.010 ± 0.001 mg/kg), Cypermethrin (0.021 ± 0.001 mg/kg), Fenvalerate (0.019 ± 0.003 mg/kg) and Deltamethrin (0.017 ± 0.003 mg/kg). The mean concentrations of SPPs in carrot roots from the farms and the markets were below the USEPA and the European Union's recommended residue levels (Figure 10).

The low concentrations of SPPs found in the carrot roots could be attributed to a possible rapid metabolisation of the SPPs by carrot plants as reported by Asare (2011) and Hoska *et al*. (2020). The observed low levels could also be due to the fact that farmers might applied the SPPs at lower concentrations than prescribed by the manufacturer(s) of the SPPs as reported by Kocourek *et al.* (2019) and Wongnaa *et al.* (2019). Application of the SPPs at the early stage of the carrot plants as reported by Asare (2011) could also account for the low SPPs detected in the carrot roots.

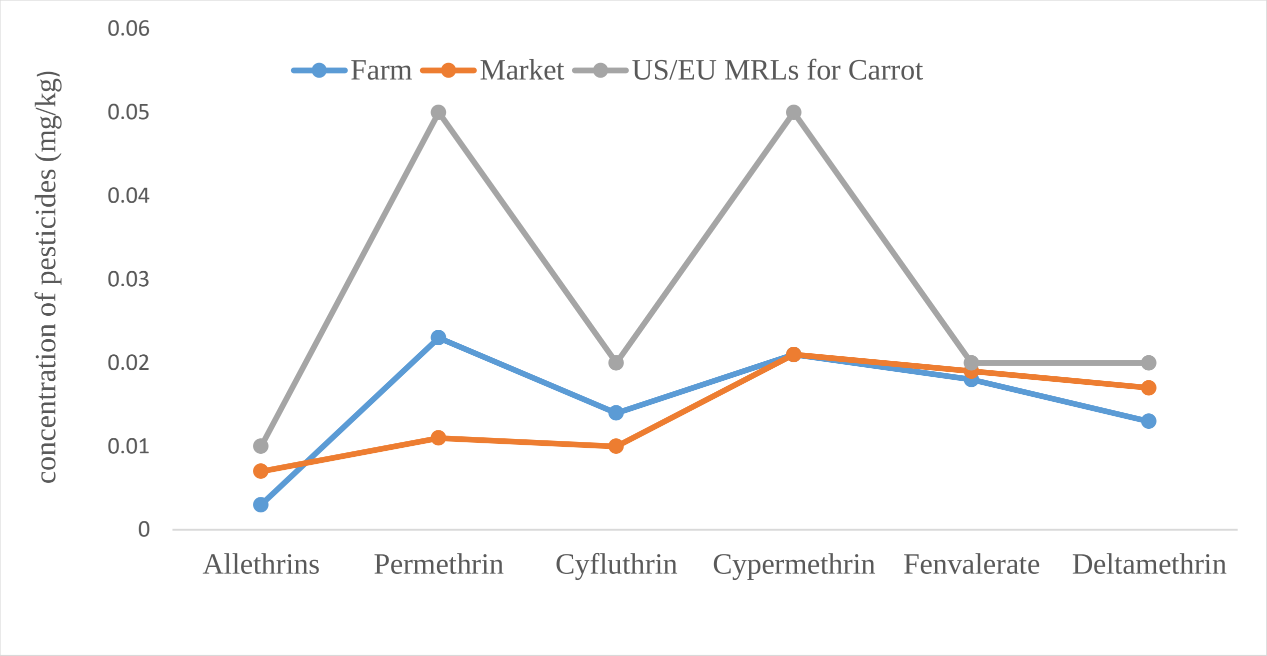

Figure 10: Mean levels (mg/kg) of synthetic pyrethroid pesticides in carrot from farms and markets

4.4.6 Levels of organophosphate pesticides in green pepper fruits from farms and markets

Concentrations of organophosphate pesticides (OPPs) in green pepper from the farms and the markets were treated statistically and the mean values plotted (Figure 11). The mean values of OPPs in green pepper fruits from the farms were Diazinon (0.038 ± 0.004 mg/kg), Dimethoate (0.040 ± 0.005 mg/kg), Chlorpyrifos (0.002 ± 0.001 mg/kg), Parathion (0.025 ± 0.006 mg/kg), Malathion (0.014 ± 0.002 mg/kg), Pirimiphos (0.020 ± 0.001 mg/kg) and Profenofos (0.021 ± 0.002 mg/kg) whilst those in green pepper fruits bought from the markets were Diazinon (0.021 ± 0.004 mg/kg), Dimethoate (0.030 ± 0.008 mg/kg), Chlorpyrifos (0.006 ± 0.002 mg/kg), Parathion (0.020 ± 0.005 mg/kg), Malathion (0.014 ± 0.002 mg/kg), Pirimiphos (0.018 ± 0.002 mg/kg) and Profenofos (0.022 ± 0.004 mg/kg) (Figure 11). The OPPs levels in the green pepper fruits from the farms and the markets were below MRLs set by USEPA and European Union (Figure 11) except that of Pirimiphos and Profenofos. Pirimiphos (0.020 ± 0.001 mg/kg) was slightly high in the green pepper fruits from the farms than (0.018 ± 0.002 mg/kg) in those from markets. However, Profenofos levels in green pepper fruits from the farms (0.021 ± 0.002 mg/kg) were similar to (0.022 ± 0.004 mg/kg) in those bought from the markets.

The high levels of Pirimiphos and Profenofos recorded could be due to the fact that they were applied either few weeks prior to the harvest of the green pepper as reported by Tereza *et al*. (2020) and Wongnaa *et al*. (2019) or were high for the green pepper plants to metabolize them as reported by Asare (2011). Continuous application of Pirimiphos and Profenofos to the green pepper plants could also explain their levels detected in the green pepper fruits. Those pesticides might have accumulated in the soils and absorbed by the crops as stated by Wongnaa *et al*. (2019) and Asare (2011).

Exposure to high levels of Profenofos above MRL could lead to over stimulation of the nervous system and could lead to nausea, dizziness, confusion, respiratory paralysis and even death as reported by Abdollahi (2011). A report by Greish *et al*. (2011), risk of Profenofos to human indicated that as dosage of Profenofos is increased, liver and kidney damage were high in research animals.

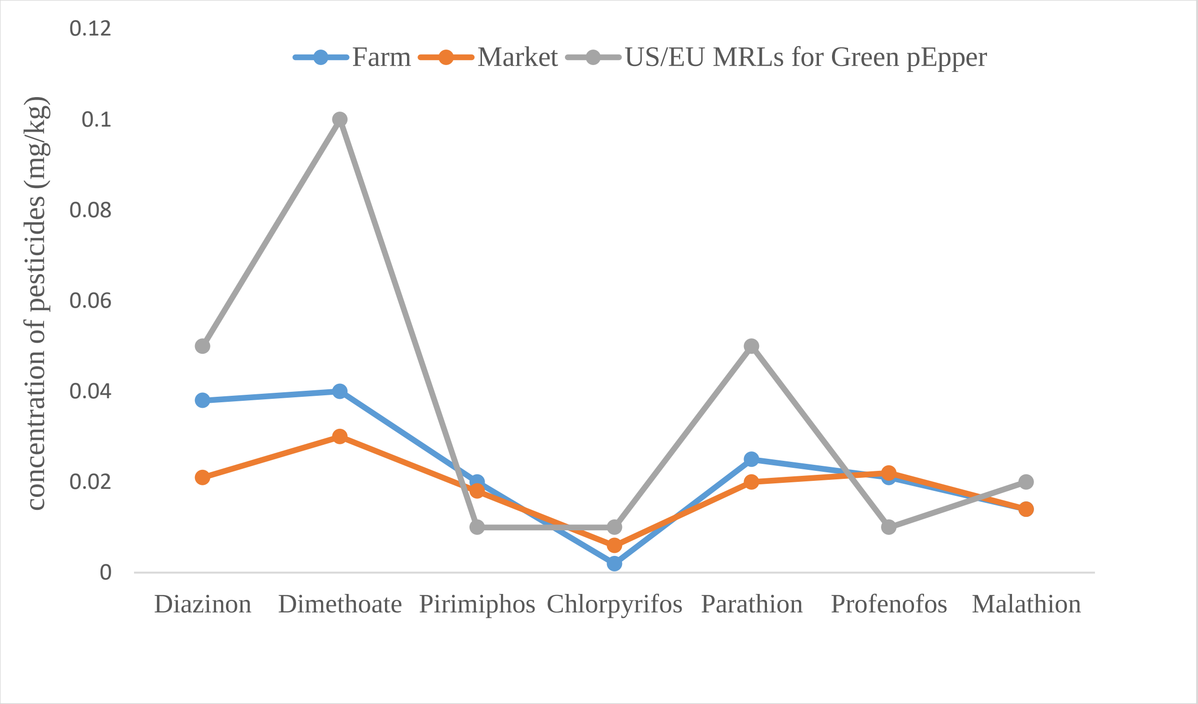

Figure 11: Mean levels (mg/kg) of organophosphate pesticides in green pepper from farms and markets

4.4.7 Levels of organochlorines in green pepper from farms and markets

Mean concentrations of organochlorines pesticides in gree pepper fruits detected herein were graphically presented and compared with USEPA (USEPA, 2013) and European Union (EU, 2009) recommended maximum residual levels (Figure 12). The mean values of the OCPs identified ranged from 0.002 ± 0.001 mg/kg (Methoxychlor) to 0.059 ± 0.002 mg/kg (Beta Endosulfan). High levels (0.030 ± 0.004 mg/kg and 0.059 ± 0.002 mg/kg) were recorded for Beta Endosulfan in green pepper fruits from the markets and the farms respectively whilst low levels (0.002 ± 0.001 mg/kg, farms and 0.005 ± 0.001 mg/kg, markets) were recorded for Methoxychlor. Green pepper samples taken from the farms and the markets had similar concentrations of Heptachlor and Aldrin.

The mean levels (0.023 ± 0.003 and 0.021 ± 0.060 mg/kg) were recorded for Heptachlor in green pepper fruits taken from farms and the markets respectively whilst Aldrin (0.033

± 0.005 mg/kg and 0.031 ± 0.005 mg/kg) were recorded for the green pepper fruits from the farms and the markets respectively (Figure 12).

Lindane, Beta HCH, Methoxychlor and Endrin mean concentrations were below USEPA/European Union MRLs of 0.01 mg/kg. P’P’- DDE also had a mean level below the MRLs of 0.05 mg/kg. However, the mean concentrations of Heptachlor (0.023 ± 0.003 mg/kg, farms), (0.021 ± 0.001 mg/kg, markets), Aldrin (0.033 ± 0.005 mg/kg, farms) (0.031 ± 0.005 mg/kg, markets) and Dieldrin (0.022 ± 0.002 mg/kg, farms), (0.017 ± 0.002 mg/kg, markets) were above (0.01 mg/kg) USEPA/European Union MRLs (Figure 12).

The higher concentrations of Heptachlor, Aldrin and Dieldrin observed (Figure 12) could be attributed to either high levels of the OCPs in the soils for absorption by the green pepper plants or failure or inability of the plants to effectively metabolize them. Hence, the plants absorbed the high OCPs levels recorded. These findings agreed favourably with that of a similar study which reported high levels of Aldrin (22.66 ± 0.15 mg/kg) and Methoxychlor (165.21 ± 12.65 mg/kg) in some lettuce sold in Kumasi (Bolor *et al*., 2018). In a study by Asare (2011) high levels of Heptachlor (8.28 µg/kg), Aldrin (5.60 µg/kg) and Dieldrin (3.8 µg/kg) were detected in some watermelon fruits grown in Nsadwir in the Central Region of Ghana.

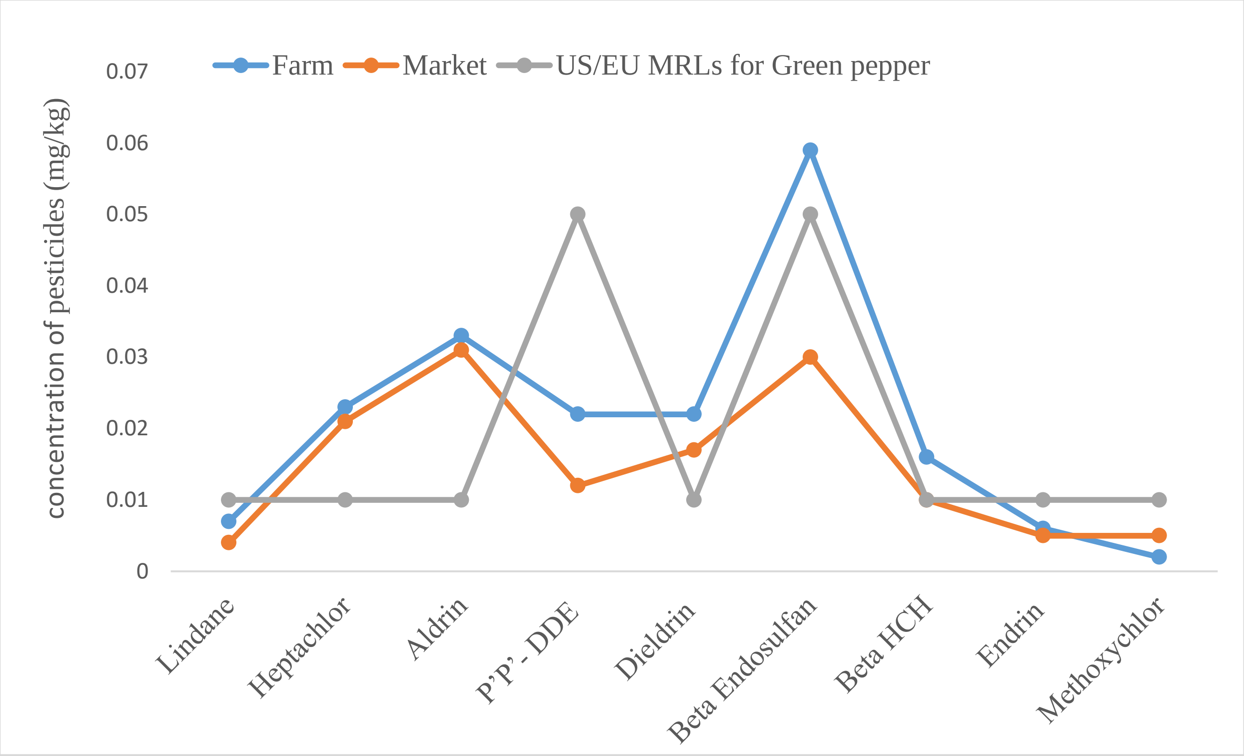

Figure 12: Mean levels (mg/kg) of organochlorine pesticides in green pepper from farms and markets

4.4.8 Levels of synthetic pyrethroid pesticides in green pepper fruit from farms and markets

Mean concentrations of the synthetic pyrethroid pesticides detected in green pepper samples taken from the farms and the markets were computed, results presented graphically and compared with the USEPA/European Union MRLs (Figure 13). Allethrin (0.005 ± 0.002 mg/kg and 0.006 ± 0.002) were recorded in the green pepper fruits from the farms and markets respectively. Permethrin (0. 022 ± 0.005 mg/kg), Cyfluthrin (0.029 ± 0.007 mg/kg), Cypermethrin (0.019 ± 0.007 mg/kg) and Fenvalerate (0.020 ± 0.002 mg/kg) occurred in the green pepper fruits from the farms whilst 0.026 ± 0.006 mg/kg (Permetgrin), 0.026 ± 0.003 mg/kg (Cyfluthrin), 0.017 ± 0.008 mg/kg (Cypermethrin) and 0.018 ± 0.002 mg/kg (Fenvalerate) occurred in those bought from the markets. Mean levels of synthetic pyrethroids in grren pepper fruits from the farms and the markets were below USEPA's (USEPA, 2013) and the European Union's (EU,

2009) MRLs (Figure 13). The low levels of the synthetic pyrethroids in the green pepper could be attributed to rapid metabolism of the pesticides by the green pepper plants as reported by Horska *et al*. (2020).

The low levels of synthetic pyrethroids detected could also be due to the fact that the farmers might have applied these pesticides either at lower levels than required or at early stage of the green pepper crop development as reported by Kocourek *et al.* (2019), Wongnaa *et al.* (2017) and Asare (2011). However, Deltamethrin levels in green pepper fruits from the farms (0.062 ± 0.004 mg/kg) and the markets (0.050 ± 0.013 mg/kg) were above USEPA/European Union recommended MRLs. This could be due to that fact that the pesticides were applied at high concentrations than recommended as reported by Amin and Hashem (2012).

Study by Sharma *et al.* (2014) had indicated that exposure to Deltamethrin at elevated levels could cause significant reduction in weight of male reproductive organs, reduction in sperm count, sperm motility, serum testosterones, follicle stimulating hormones in testis and kidney and liver failure. The report further added that a dose of 6 mg/kg causes a serious effect on kidney and liver.

Order of synthetic pyrethroids in the green pepper fruits from the farms was Deltamethrin (0.062 ± 0.004 mg/kg) > Cyfluthrin (0.029 ± 0.007 mg/kg) > Permethrin (0.022 ± 0.005 mg/kg) > Fenvalerate (0.020 ± 0.002 mg/kg) > Allethrin (0.005 ± 0.002 mg/kg) whilst that of those bought from the markets, the synthetic pyrethroids was Deltamethrin (0.050 ± 0.004 mg/kg) > Cyfluthrin (0.026 ± 0.003 mg/kg) > Permethrin

(0.026 ± 0.006 mg/kg) > Fenvalerate (0.018 ± 0.002 mg/kg) > Allethrin (0.006 ± 0.002 mg/kg).

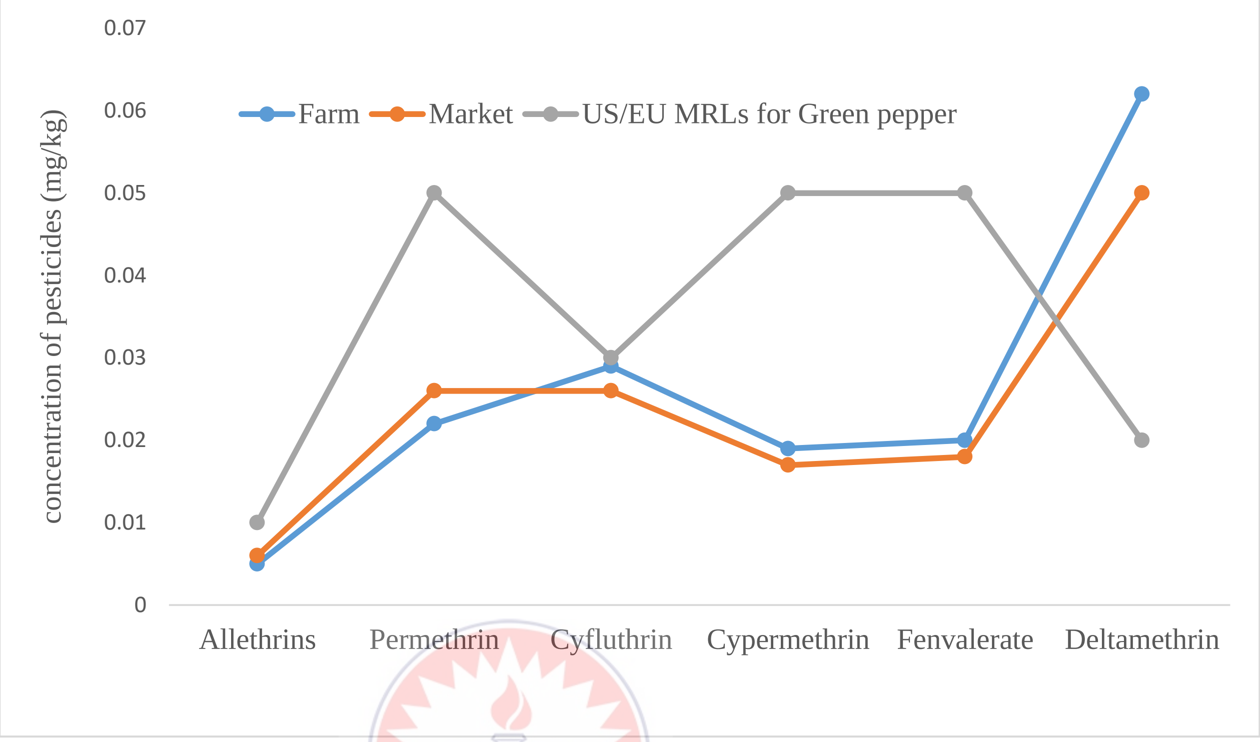

Figure 13: Mean levels (mg/kg) of pyrethroid pesticides in green pepper from farms and markets

4.4.9 Levels of organophosphate pesticides in lettuce from sampling sites

Lettuce from the farms and the markets were analysed for organophosphate pesticides. The results were treated statistically, the mean levels reported in the form mean ± standard deviation and then compared with USEPA (USEPA, 2013) and European Union (EU, 2009) recommended MRLs (Figure 14). Mean levels of Parathion (0.027 ± 0.004 mg/kg), Profenofos (0.007 ± 0.004 mg/kg) and Malathion (0.029 ± 0.005 mg/kg) occurred in lettuce from the farms whilst Parathion (0.018 ± 0.002 mg/kg), Profenofos (0.004 ± 0.002 mg/kg) and Malathion (0.022 ± 0.002 mg/kg) were present in those purchased from the markets. The Parathion, Profenofos and Malathion levels in lettuce from the farms and the markets were below recommended maximum residual levels set by USEPA (USEPA, 2013) and European Union (EU, 2009) (Figure 14).

Order of mean levels of OPPs in the lettuce from the farms were Diazinon (0.034 ± 0.003 mg/kg) > Pirimiphos (0.032± 0.004 mg/kg) > Dimethoate (0.029 ± 0.004 mg/kg) > Malathion (0.029 ± 0.005 mg/kg) > Parathion (0.027 ± 0.004 mg/kg) > Chlorpyrifos (0.017 ± 0.005 mg/kg) > Profenofos (0.007 ± 0.004 mg/kg) whilst that in those bought from the markets were Diazinon (0.031 ± 0.002 mg/kg) > Pirimiphos (0.031 ± 0.008 mg/kg) > Dimethoate (0.025 ± 0.006 mg/kg) > Malathion (0.022 ± 0.002) > Parathion (0.018 ± 0.002 mg/kg) > Chlorpyrifos (0.014 ± 0.005 mg/kg) > Profenofos (0.004 ± 0.002 mg/kg).

Mean levels of the OPPs which ranged from Diazinon (0.031 ± 0.002 to 0.034 ± 0.003 mg/kg), Dimethoate (0.025 ± 0.006 to 0.029 ± 0.004 mg/kg), Pirimiphos (0.025 ± 0.006 to 0.032 ± 0.004 mg/kg) and Chlorpyrifos (0.014 ± 0.005 to 0.017 ± 0.005 mg/kg) were above USEPA/European Union recommended maximum residual levels (0.01 mg/kg).

These observed high levels of Diazinon, Dimethoate, Pirimiphos and Chlorpyrifos could be due to the fact that the pesticides were applied late on the lettuce prior to harvest and the observation agreed favourably with that made by Asare (2011). High levels of Diazinon, Dimethoate, Pirimiphos, and Chlorpyrifos could also be attributed to inability of lettuce crop to metabolize the pesticides as reported by Glotfelty, *et al.* (1989 and Asare (2011). The high levels could also be attributed to that fact that pesticides were applied at high concentrations than recommended as reported in a study by Amin and Hashem (2012). These findings corroborated well with that of a similar report by Asare (2011) in which high levels of Diazinon (5.75 ± 3.71 µg/kg), Dimethoate (19.0 ± 2.00 µg/kg) and Chlorpyrifos (1123.7 ± 10.0 µg/kg) were detected in watermelon fruits cultivated at Nsadwir in the Central Region of Ghana.

Vegetables which contain pesticides levels above recommended MRLs could pose a health risk to consumers (Fillion *et al.*, 2000; Sinha *et al.*, 2012). Thus high mean levels of Diazinon (0.034 ± 0.003 mg/kg), Dimethoate (0.029 ± 0.004 mg/kg), Pirimiphos (0.032 ± 0.004 mg/kg) and Chlorpyrifos (0.017 ± 0.005 mg/kg) in the lettuce could lead to unwanted health issues among consumers. For instance, exposure to Dimethoate and Chlorpyrifos could cause headache, profuse sweating, nausea, vomiting, diarrhoea, loss of coordination, muscle twitching, death, (Meshram *et al.*, 2014) mutation and damage to developing fetus (Silva *et al*., 2021). Exposure to low levels of Diazinon could cause mild skin and eye irritation (García *et al.*, 2016).

Low mean levels of Parathion (0.027 ± 0.004 mg/kg), Profenofos (0.007 ± 0.004 mg/kg) and Malathion (0.029 ± 0.005 mg/kg) could also be due to the fact that farmers applied these pesticides at low levels than required or at limited frequencies at the early stage of the lettuce crop development as indicated by Kocourek *et al.* (2019) and Asare (2011).

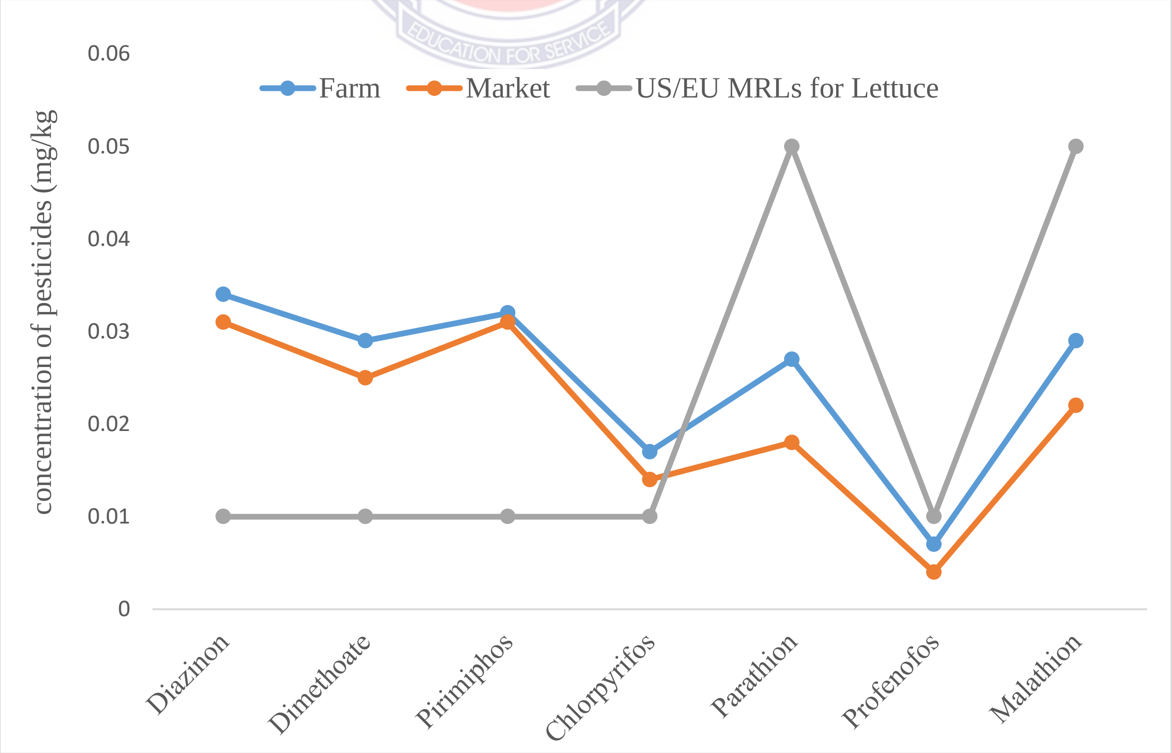

Figure 14: Mean levels (mg/kg) of organophosphate pesticides in lettuce from farms and markets

4.4.10 Levels of organochlorine pesticides in lettuce from sampling sites

Levels of OCPs in lettuce were also reported in the form mean ± standard deviation. The data were plotted (Figure 15) and compared with acceptable levels of OCPs in vegetables as set by USAEPA (USAEPA, 2013) and European Union (EU, 2009).

Lindane, Heptachlor, Aldrin, P'P'- DDE, Dieldrin, Beta Endosulfan, Beta HCH, Methoxychlor, and Endrin levels in lettuce collected from the farms were 0.005 ± 0.001 mg/kg, 0.006 ± 0.002 mg/kg, 0.036 ± 0.004 mg/kg, 0.026 ± 0.001 mg/kg, 0.026 ± 0.005 mg/kg, 0.057 ± 0.008 mg/kg, 0.006 ± 0.004 mg/kg, 0.004 ± 0.002 mg/kg and 0.004 ± 0.001 mg/kg respectively. OCPs levels in lettuce bought from the markets were Lindane (0.007 ± 0.003 mg/kg), Heptachlor (0.006 ± 0.002 mg/kg), Aldrin (0.027 ± 0.003 mg/kg), P'P'- DDE (0.022 ± 0.004 mg/kg), Dieldrin (0.025 ± 0.005 mg/kg), Beta Endosulfan (0.052 ± 0.004 mg/kg), Beta HCH (0.008 ± 0.002 mg/kg), Methoxychlor (0.005 ± 0.003 mg/kg) and Endrin (0.006 ± 0.002 mg/kg). Except Aldrin (0.036 ± 0.004 mg/kg) and Dieldrin (0.026 ± 0.005 mg/kg) which were above recommended maximum residual levels of the OCPs in the lettuces collected from the farms and markets were below USEPA and the European Union's recommended levels. For example, Lindane, Heptachlor, Beta Endosulfan, Methoxychlor and Endrin levels were below 0.01 mg/kg recommended by USEPA and the European Union. P'P'-DDE and Beta HCH levels were also below 0.05 mg/kg permissible by USEPA and the European Union (Figure 15).

The elevated levels of Aldrin and Dieldrin in the lettuce from various sampling sites could be attributed to frequency of their application, time of pesticides application and growth stage of the crop at which the pesticides were applied as indicated by Asare (2011). Inability of lettuce crops to metabolize the pesticides might as well be a contributing factor to the high levels of Aldrin and Dieldrin detected as reported by Asare (2011).

In a similar study by Kocourek *et al*. (2019), assessment of OCPs in two leafy vegetables grown in South-western Nigeria also reported high levels of Heptachlor (0.323 ± 0.048 mg/kg), Aldrin (0.391 ± 0.065 mg/kg), Dieldrin (1.465 ± 0.879 mg/kg) and Endrin (0.351 ± 0.371 mg/kg). The results herein also corroborated well with that of a study by Bempah *et al*. (2016) on OCPs levels in vegetables purchased from some markets in the Greater Accra Region of Ghana. The study also reported high levels of Lindane (0.100 ± 0.004 mg/kg), Methoxychlor (0.023 ± 0.008 mg/kg) in lettuce, (0.023 ± 0.008 mg/kg) in cabbage, Dieldrin (0.035 ± 0.013 mg/kg) in cabbage and Endrin (0.040 ± 0.03 mg/kg) in lettuce. The elevated levels of Lindane, Methoxychlor, Aldrin and Dieldrin in this study could bioaccumulate in the blood and tissues of consumers from long time ingestion of the lettuce. Thus consumers are likely to brain and spinal cord problems and liver and kidney damages as indicated by Sharma *et al.* (2017).

The mean levels of OCPs in the lettuce ranged from 0.004 ± 0.002 mg/mg (Methoxychlor) to 0.057 ± 0.008 mg/kg (Beta Endosulfan). Beta Endosulfan (0.057 ± 0.008 mg/kg) was the highest mean level in the lettuce from the farms. The lettuce bought from the markets also had Beta Endosulfan occurring at elevated levels (0.052 ± 0.004m g/kg).

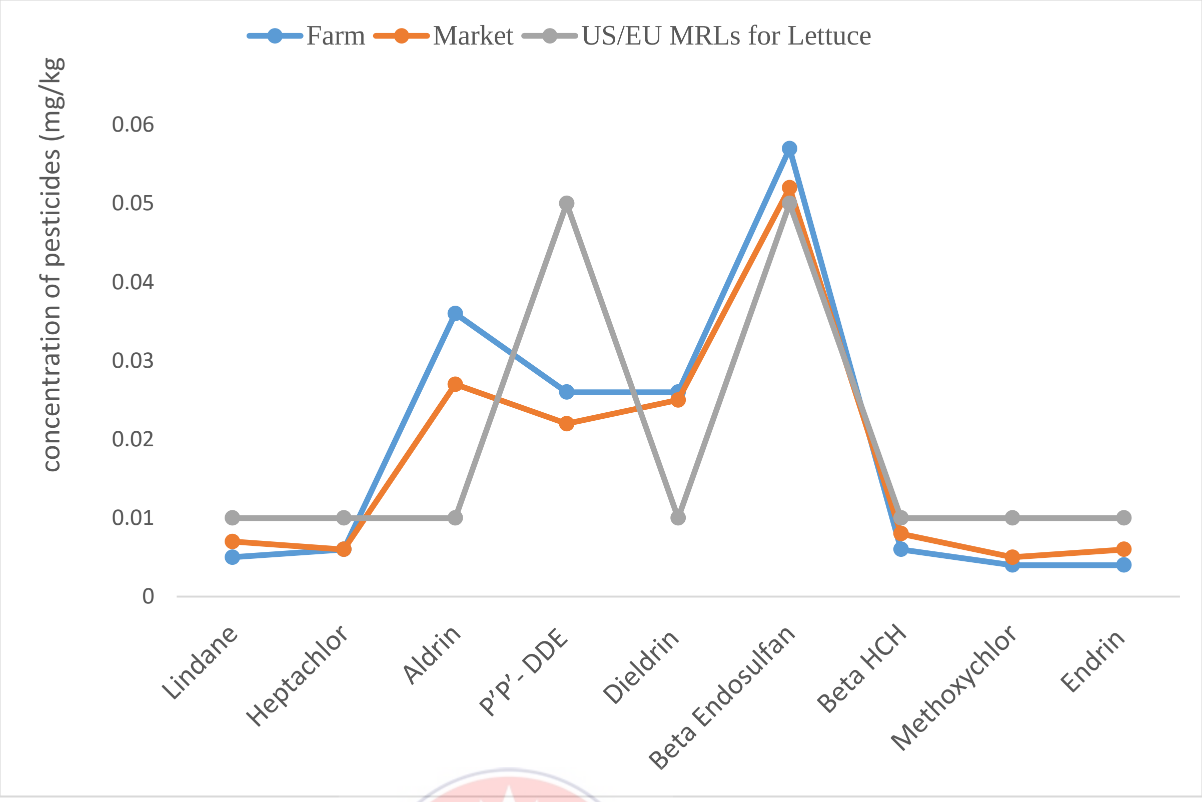

Figure 15: Mean levels (mg/kg) of organochlorine pesticides in lettuce from farms and markets

4.3.11 Levels of pyrethroid pesticides in lettuce from various sampling sites

Mean concentrations of synthetic pyrethroids in lettuce from the farms and markets were computed and the results presented graphically (Figure 16). Allethrin, 0.005 ± 0.002 mg/kg occurred in lettuce from the farms whilst 0.004 ± 0.001 mg/kg was present in those bought from the markets. Although Allethrin was slightly high in lettuce from the farms, its level was below USEPA/EU recommended maximum residual levels (Figure 16). Mean concentration of Permethrin in lettuce from the farms was 0.026 ± 0.004 mg/kg whilst that in those from the markets was 0.013 ± 0.004 mg/kg.

Cyfluthrin, recorded a mean levels of 0.064 ± 0.008 mg/kg for farms and 0.036 ± 0.008 mg/kg for markets, Cypermethrin, (0.044 ± 0.004 mg/kg) for farms and (0.034 ± 0.007 mg/kg) for makets, Fenvalerate, (0.019 ± 0.003 mg/kg) for farms and (0.016 ± 0.003

mg/kg) for markets and Deltamethrin had 0.026 ± 0.006 mg/kg for farms and 0.040 ± 0.004 mg/kg for markets. SPPs levels were below USEPA and EU recommended maximum residual levels (Figure 16).

The low levels could be attributed to rapid metabolism of synthetic pyrethroids in lettuce plants as report by Horská *et al*. (2020) and Asare (2011). The low levels of SPPs could also be due to the fact 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).

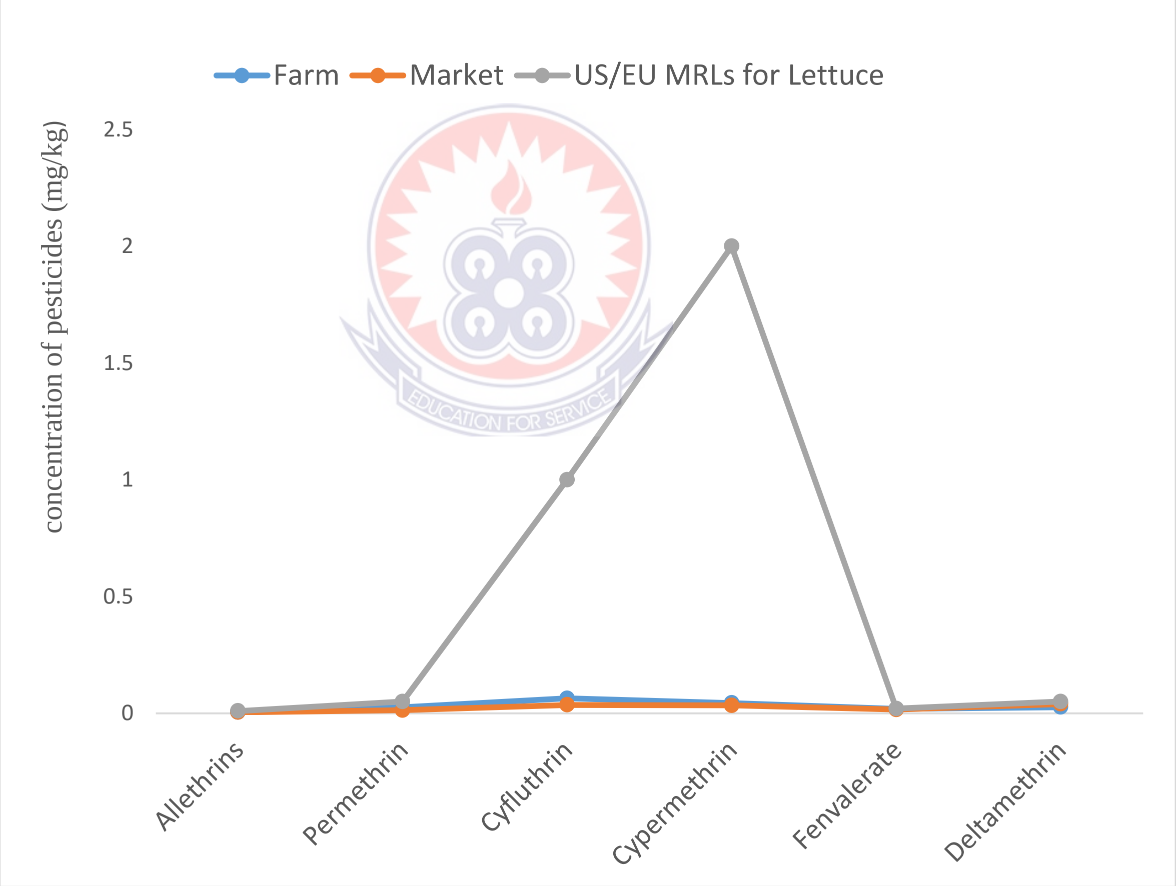

Figure 17: Mean levels (mg/kg) of synthetic pyrethroid pesticides in lettuce from farms and markets

4.5 Correlation of Soil Properties with Levels of Pesticides in the Vegetable Crops

In order to investigate how the soil properties contributed to the levels of pesticides in the vegetables, correlation analysis was done to establish the relationship between physico-chemical properties of the soil and the levels of pesticides in the vegetables. The results obtained for the correlation were treated statistically and the data presented (Table 7 to 18).

Table 7: Correlations of soil properties with organophosphorus pesticides in cabbage

Soil chemical properties	Dia	Dime	Piri	Chlo	Para	Prof	Mala
Soil pH	0.511**	-3.320*	0.531	0.341	-0.520	0.222*	-0.533
Organic carbon (%)	0.361*	0.306*	0.311*	0.439	0.477	0.325	0.369*
Total N (%)	0.371*	-0.420	-0.346	0.337*	0.321	-0.391	0.348
Available P (mg/kg soil)	-0.236	0.183*	-0.327	-0.381	-0.321	0.351	0.216*
Exchangeable cations							
CEC	-0.428*	-0.523	0.544	-0.482	-0.611	0.572	0.439
Ca^{2+}	0.230**	-0.271	0.274	0.325	-0.412*	0.271*	0.216*
Mg^{2+}	0.124*	0.187	-0.129	0.328	0.195	0.261*	0.291*
K^{+}	0.132*	-0.137	0.165	-0.284	-0.137	0.268	0.138
Na^{+}	0.029	0.151*	-0.054	0.146*	0.071*	0.097	-0.048
Al^{3+}	0.081	0.112	0.086	0.028*	0.032	0.048	-0.125*
H^{+}	0.151*	0.321	0.189	0.184	-0.138	-0.280	-0.141
Physical properties							
Soil moisture (%)	-0.374*	-0.214*	0.389	0.371	0.568	0.410	-0.381
Sand (%)	-0.652	-0.451	-0.470	-0.467	-0.332	0.551	0.491
Silt (%)	-0.417	0.622	0.429	0.416	0.415	0.337	0.512
Clay (%)	0.129	0.417*	5.316	3.4148	3.612	5.511*	-4.522
Bulk density (Mg/m^3)	0.546	0.333	0.226*	0.311*	0.371*	0.306*	-0.406*
Soil texture	0.502	-0.436	0.479	-0.514	0.381	0.374	0.390

*Correlation is significant at 0.05 level and **Correlation is significant at 0.01 level; Dia = Diazinon; Dime = Dimethoate; Piri = Pirimiphos M; Chlo = Chlorpyrifos; Para = Parathion; Prof = Profenofos; Mala = Malathion

4.5.1 Correlation analysis between soil properties and organophosphate pesticides in cabbage heads

The correlations between physico-chemical properties of the soils samples from the cabbage farms and the organophosphate pesticides levels in cabbage samples were computed and presented (Table 7). Correlation assessment between pH of the soil samples from the cabbage farms and the pesticides levels (Table 7) showed that pH of soils from the cabbage farms had a positive significant ($P<0.05$) correlation at the indicated P-value with the levels of Diazinon ($r = 0.411$) and Profenofos ($r = 0.222$; $P < 0.05$). However, a negative significant correlation ($P<0.05$) existed between Dimethoate levels in cabbage and pH of the soils ($r = -3.320$; $P<0.05$). No significant correlation existed between pH of the soil samples and Pirimiphos, Chlorpyrifos, Parathion and Malathion levels at the indicated P-value ($P > 0.05$) (Table 7).

The positive correlation observed between soil pH, Profenofos and Diazinon indicates that as pH of soils (cabbage farms) increases concentrations of Profenofos and Diazinon also increase. This observation did not corresponded to that made by Akoto *et al.* (2013) and Sheng *et al.* (2001) where the researchers reported that increasing pesticides residues in soil decreases with soil pH. The negative correlation that existed between Dimethoate and soil pH implies that as pH decreases, concentration of Dimethoate increases. This finding corresponded well to that reported by Akoto *et al*. (2013) and Sheng *et al.* (2001). This observed correlation may be attributed to the higher quantities of clay and organic matter contents of the soil as stated by Yang *et al.*, (2019).

According to Yang *et al.* (2019) higher correlations exist between pesticides adsorption and clay contents of soils when compared with that between pesticides and organic matter contents. The non-significant correlations ($P>0.05$) that existed between pH of the soils and Pirimiphos, Chlorpyrifos, Parathion and Malathion depict that pH of the soils from the various vegetable farms did not contribute to the concentration of Pirimiphos, Chlorpyrifos, Parathion and Malathion in the cabbage heads of the farms investigated herein. This means that as pH of the soil increases, Pirimiphos, Chlorpyrifos, Parathion and Malathion levels decrease. Thus, pH of the soil must be kept at a lower level in order to decrease their levels in the cabbage heads.

The organic carbon contents showed significant positive correlation with Diazinon ($r = 0.361$; $P<0.05$), Dimethoate ($r = 0.306$, $P<0.05$), Pirimiphos ($r = 0.311$; $P<0.05$) and Malathion ($r = 0.369$; $P<0.05$). However, non-significant positive correlations existed between organic carbon contents of the soils and Chlorpyrifos ($r = 0.439$, $P>0.05$), Parathion ($r = 0.477$, $P>0.05$) and Profenofos ($r = 0.325$, $P>0.05$) (Table 7) at the indicated P-value. Thus strong positive correlation that existed between organic carbon contents of the soils and Diazinon, Dimethoate, Pirimiphos and Malathion levels indicates that increase in organic carbon contents of soil would result in corresponding increase in concentrations of Diazinon, Dimethoate, Pirimiphos and Malathion and vice versa. This observation corresponded favourably with that reported by Asare (2011), Khalid *et al.*, (2020) and Akoto *et al.* (2013).

A strong positive correlation that existed between organic matter contents of soil and Diazinon, Dimethoate, Pirimiphos and Malathion levels indicate that the high levels of Diazinon, Dimethoate, Pirimiphos and Malathion in the cabbage heads were due to their strong attachments to the organic matter contents of the soils. Thus, the high levels of

Diazinon, Dimethoate, Pirimiphos and Malathion could be due to their strong adherance onto the organic matter contents as reported by Bentzen *et al.* (2008).

The total nitrogen contents of the soils exhibited significant positive correlation with Diazinon ($r = 0.371$; $P<0.05$) and Chlorpyrifos ($r = 0.337$; $P<0.05$) and hence an increase in nitrogen contents of the soil would result in an increase in the concentrations of the pesticides. This result did not correspond well with that of Fosu-Mensah *et al.* (2016) where negative correlations existed between nitrogen contents of soil and levels of Lindane and Beta-HCH in it. Although total nitrogen contents of the soils exhibited negative correlation with Dimethoate ($r = -0.420$; $P<0.05$), Pirimiphos ($r = -0.346$; $P<0.05$) and Profenofos ($r = -0.391$; $P<0.05$) (Table 1), the correlation was not significant at the reported P-values.

Phosphorous contents of the soil also showed significant positive correlation with Dimethoate ($r = 0.183$; $P<0.05$) and Malathion ($r = 0.216$; $P<0.05$). However, correlation that existed between phosphorus contents of soils and profenofos ($r = 0.351$; $P<0.05$) though positive was not significant at the reported P-value. The non-significant correlation that existed between total nitrogen contents of soils and Dimethoate, Pirimiphos and Profenofos levels in the cabbage implies that the total nitrogen contents of the soil appear to have no influence on concentrations of Dimethoate, Pirimiphos and Profenofos in the cabbage. This observation was contrary to a report by Akoto *et al.* (2013) in which pesticides residues in soil decrease soil pH and total nitrogen contents of soils.

The positive correlation observed between available phosphorous contents of soil and Dimethoate and Malathion levels in the cabbage indicates that the phosphorus contents of soils appear to significantly influence the levels and distributions of Dimethoate and Malathion in the cabbage. Hence, an increase in levels of phosphorus resulted in a corresponding increase in Dimethoate and Malathion residues contents of the cabbage. However, available phosphorous contents of the soils correlated negatively with Diazinon ($r = -0.236$; $P<0.05$), Pirimiphos ($r = -0.327$; $P<0.05$), Chlorpyrifos ($r = -0.381$; $P<0.05$) and Parathion ($r = -0.321$; $P<0.05$) (Table 7). Hence as the phosphorus contents of the soil increased, the levels of Diazinon, Pirimiphos, Chlorpyrifos and Parathion decreased in the cabbage. The positive correlations existed between phosphorus contents of the soils and of Dimethoate and Malathion levels in the cabbage agreed with findings of a similar work done by Fosu-Mensah *et al.* (2016). These researchers reported significant positive correlation ($r = 0.864$; $P<0.05$) between phosphorus contents of soil and Lindane levels in soils.

Cation exchange capacity (CEC) of the soil showed significant ($P<0.05$) negative correlation ($r = -0.428$; $P<0.05$) with Diazinon levels in the cabbage. This suggests that CEC of soils negatively influenced Diazinon levels and distribution in the cabbage. Thus, an increased in CEC of soils resulted in a corresponding decreased in levels of Diazinon in the cabbage heads. This finding corresponded favourably with that of Sheng *et al.* (2001) and Fosu-Mensah *et al.* (2016). The researchers reported that pesticides adsorption onto soil particles to be a function of cation exchange capacity of soil. Conversely, CEC had a non-significant positive correlation with Pirimiphos ($r = 0.544$; $P>0.05$), Profenofos ($r = 0.572$; $P>0.05$) and Malathion ($r = 0.439$; $P>0.05$) and non-significant negative correlation with Dimethoate ($r= -0.523$; $P>0.05$), Chlorpyrifos (r = -

0.482; $P>0.05$) and Parathion ($r = - 0.611$; $P>0.05$) (Table 7). The non-significant correlations indicate that CEC had no influence on the levels of the pesticides in the cabbage heads.

Soil calcium (Ca^{2+}) had high significant positive correlation with Diazinon levels ($r = 0.230$; $P<0.01$) levels in the cabbage heads whilst that between Profenofos ($r = 0.271$; $P<0.05$) and Malathion ($r = 0.216$; $P<0.05$) levels in the cabbage were positive and moderately correlated. Calcium (Ca^{2+}) ions also had a non-significant positive correlation ($P<0.05$) with Pirimiphos ($r = 0.274$; $P>0.05$) and Chlorpyrifos ($r = 0.325$; $P>0.05$) levels of cabbage. The observed correlation between calcium (Ca^{2+}) contents of soils and Diazinon, Profenofos, Malathion and Pirimiphos levels in the cabbage heads show that calcium (Ca^{2+}) contents of the soils affected Diazinon, Profenofos, Malathion and Pirimiphos levels in the cabbage. Hence, increased in calcium (Ca^{2+}) contents of the soil resulted in an increased in Diazinon, Profenofos and Malathion levels in the cabbage heads.

Magnesium (Mg^{2+}) contents of the soils had significant positive correlation ($P<0.05$) with Diazinon ($r = 0.124$; $P<0.05$), Profenofos ($r = 0.261$; $P<0.05$) and Malathion ($r = 0.291$; $P<0.05$) levels of cabbage and a non-significant positive correlation with Dimethoate, Pirimiphos, Chlorpyrifos and Parathion levels of the cabbage at the indicated P-value. The observed correlation between Mg^{2+} contents of the soil and Diazinon, Profenofos and Malathion levels of the soil indicate that levels of Diazinon, Profenofos and Malathion levels would increase in the cabbage heads whenever Mg^{2+} contents of the soil increased. Positive correlation between Mg^{2+} contents of soils and Diazinon, Profenofos and Malathion were at variance with that of Fosu-Mensa *et al.*

(2016) where negative correlation ($r = -0.492$; $P>0.05$) existed between cation exchangeable capacity and Lindane.

Potassium ion (K^+) contents of the soils had a significant positive correlation with Diazinon ($r = 0.132$; $P<0.05$) levels of the cabbage. Hence an increased in K^+ contents would increased Diazinon levels in the cabbage. However, non-significant correlation existed between K^+ contents of the soils and Dimethoate ($r = -0.137$; $P>0.05$), Pirimiphos ($r = 0.165$; $P>0.05$), Profenofos ($r = 0.268$; $P>0.05$), Malathion ($r = 0.138$; $P>0.05$) and Parathion ($r = -0.137$; $P>0.05$) levels in the soils (Table 7). The non-significant correlation observed between K^+ contents of the soils and Dimethoate, Pirimiphos, Profenofos, Malathion and Parathion levels in the cabbage means that K^+ would not impact the levels of these pesticides in the cabbage. The positive correlation between K^+ contents and Diazinon agreed favourably with that of Fosu-Mensah *et al* (2016) where positive correlations were observed between K^+ contents and Lindane ($r = 0.923$; $P<0.01$), Diedrin ($r = 0.851$; $P<0.05$) and HCH ($r = 0.925$; $P<0.01$).

Sodium ion (Na^+) contents of the soil showed a significant positive correlation between Dimethoate ($r = 0.151$; $P<0.05$), Chlorpyrifos ($r = 0.146$; $P<0.05$) and Parathion ($r = 0.071$; $P<0.05$) levels in the cabbge heads whilst a non-significant correlation exist between Diazinon ($r = 0.029$; $P>0.05$), Profenofos ($r = 0.097$; $P>0.05$), Pirimiphos ($r = -0.054$; $P>0.05$) and Malathion ($r = -0.048$; $P>0.05$) levels in the soils (Table 7). The non-significant correlation between total Na^+ contents of the soil Diazinon, Pirimiphos, Malathion and Profenofos levels in the cabbage means that Na^+ contents of the soil had no influence on the levels Diazinon, Pirimiphos, Malathion and Profenofos levels in the cabbage.

Significant positive correlation existed between Chlorpyrifos ($r = 0.028$; $P<0.05$) and Aluminium ions (Al^{3+}) contents of the soils whilst that between Malathion ($r = - 0.125$; $P<0.05$) levels in the cabbage was negative and significant. However, non-significant correlation existed between Al^{3+} contents of the soils and Diazinon ($r = 0.081$; $P>0.05$), Dimethoate ($r = 0.112$; $P>0.05$), Pirimiphos ($r = 0.086$; $P>0.05$), Parathion ($r = 0.032$; $P>0.05$) and Profenofos ($r = 0.048$; $P>0.05$) levels in the cabbage (Table 7).

Hydrogen ions (H^+) contents of the soils showed a significant positive correlation with Diazinon ($r = 0.151$; $P<0.05$) levels of cabbage heads whilst non-significance correlation existed between H^+ contents of the soils and Dimethoate ($r = 0.321$; $P>0.05$), Pirimiphos ($r = 0.189$; $P>0.05$), Chlorpyrifos ($r = 0.184$; $P>0.05$), Parathion ($r = - 0.138$; $P>0.05$), Profenofos ($r = - 0.280$; $P>0.05$) and Malathion ($r = - 0.141$; $P>0.05$) levels of the soil (Table 7).

The positive correlation that existed between Na^+ contents of the soils and Dimethoate, Chlorpyrifos and Parathion levels, Al^{3+} and Chlorpyrifos and H^+ and Diazinon levels of cabbage means that these exchangeable cations would significantly influence the levels and distribution of respective pesticides levels in cabbage. Hence, increase in contents of respective exchangeable cations of the soils would result in increased in the levels of the corresponding pesticides. The positive correlation observed between H^+ and Diazinon levels and Al^{3+} and Chlorpyrifos levels in the cabbage agreed with that reported by Fosu-Mensah *et al*. (2016) where pH below 7 was found to have resulted in high H^+ ions in soil solutions. This according to Fosu-Mensah *et al*. (2016), made pesticides molecules more available in the soils. The non-significant correlation that observed between total Na^+ contents of the soil and Diazinon, Pirimiphos, Malathion and Profenofos levels of the soils means that Na^+ contents of the soil would not affect Diazinon, Pirimiphos, Malathion and Profenofos levels in the cabbage. However, this finding is at variance with that reported by Kantachote *et al*. (2004) that addition of sodium ion to soil significantly increased dissolved organic carbon levels, anaerobic bacterial numbers and amounts of DDT residues in soil solution.

Soil moisture content showed a significant negative correlation with Diazinon (r = - 0.374; P<0.05) and Dimethoate (r = - 0.214; P<0.05) levels of cabbage. These mean that as soil moisture contents increased, Diazinon and Dimethoate levels in the cabbage decreased. This observation corresponded favourably with that made by Asare (2011) where low soil moisture contents rendered most soil organisms inactive. This made it difficult for soil micro-organisms to breakdown pesticides molecules and that led to elevated pesticides accumulation, firm adsorption of pesticides onto soil particles, hence subsequent persistence of pesticides in the cabbage.

Bulk density (Mg/m^3) of the soil showed a significant positive correlation with Pirimiphos (r = 0.226; P<0.05), Chlorpyrifos (r = 0.311; P<0.05), Parathion (r = 0.371; P<0.05) and Profenofos (r = 0306; P<0.05) levels in the cabbage. However, negative significant correlation existed between Malathion (r = - 0.406; P<0.05) and soil bulk density contents. Clay contents of the soils had a significant positive correlation between Dimethoate (r = 0.417; P<0.05) and Profenofos (r = 5.511; P<0.05) levels in the cabbage. However, sand contents of the soil and silt did not show any significant correlation (P>0.05) between them and the organophosphates pesticides levels in the cabbage heads.

The non-significant correlation that observed between sand and silt contents of the soil and the organophosphates levels of cabbage heads means that sand and silt contents of the soil would not affect organophosphates levels in the cabbage. However, the positive correlation existed between bulk density and the levels of Pirimiphos, Chlorpyrifos, Parathion and Profenofos levels of the cabbage and also between clay contents of the soils and of Dimethoate and Profenofos levels of the cabbage indicate that bulk density and clay contents of the soils have significant positive effect on distribution of the respective pesticides levels in the cabbage. Thus, increased in bulk density and clay contents of the soils would result in a corresponding increase in Pirimiphos, Chlorpyrifos, Parathion, Profenofos and Dimethoate levels in the cabbage. These observations agreed with that made by Fosu-Mensah *et al.* (2016), Ahmad (2013) and Copaja *et al*. (2021). Similarly, positive correlation ($P<0.05$) existed between soil clay contents and Diazinon and Dimethoate levels of the soils. Negative correlation existed between bulk density and Malathion ($r = 0.406$; $P<0.05$) levels in the cabbage also implies that increased in the bulk density of the soils would cause a reduction in Malathion levels of the cabagge.

4.5.2 Correlations of soil properties with organochlorine pesticides in cabbage heads

The correlations between physico-chemical properties of soils sample from the cabbage farms and the organochlorine pesticides were investigated and presented (Table 8). Correlations that existed between soil pH, CEC, soil moisture, sand and silt contents and Lindane, Heptachlor, Aldrin, Dieldrin, Beta Endosulfan, Beta-HCH, Methoxychlor and Endrin levels of cabbage heads were not significant (Table 8). These means that soil pH, CEC, soil moisture and silt contents of the soils have little to no effect on Lindane, Heptachlor, Aldrin, Dieldrin, Beta Endosulfan, Beta-HCH, Methoxychlor and Endrin levels in cabbage heads from the cabbage farms. This affirms the finding of Bentum *et al*. (2006) and Aiyesanmi and Idowu (2012) in similar studies where they reported no significant correlations ($P>0.05$) between soil physico-chemical properties and Lindane and Propoxur levels in soil samples from cocoa growing areas in five districts in the Central Region of Ghana and cocoa farms in Ondo State in the Central District of Nigeria respectively. However, the findings herein were at variance with that of Fosu-Mensah *et al*. (2016) where negative correlation ($P<0.05$) existed between exchangeable cations, total nitrogen, organic matter, nitrate ion, sand, caly and silt contents of soils and Lindane, Dieldrin, Beta HCH and DDT levels in soil.

Significant positive correlations existed between organic carbon contents of the soils and Heptachlor ($r = 0.476$; $P<0.05$) and Aldrin ($r = 0.291$; $P<0.05$) levels in the cabbage heads. Nitrogen contents of the soils had significant positive correlation with Dieldrin ($r = 0.522$; $P<0.05$) levels in cabbage heads. Soil calcium (Ca^{2+}) ion contents of soils showed significant positive correlation with Beta HCH ($r = 0.202$; $P<0.05$) and Methoxychlor ($r = 0.517$; $P<0.05$) levels in the cabbage heads, Mg^{2+} ion contents of soils also showed a significant positive correlation with Methoxychlor ($r = 0.238$; $P<0.05$) whilst Na^{+} ions contents of the soils showed a significant positive correlation ($P<0.05$) with Heptachlor ($r = 0.156$ $P<0.05$), Dieldrin ($r = 0.145$; $P<0.05$) and Beta Endosulfan ($r = 0.025$; $P<0.05$) levels in the cabbage heads.

Table 8: Correlations of soil properties with organochlorines pesticides in cabbage heads

Soil chemical properties	Lin	Hept	Ald	Diel	Beta E	Beta H	Meth	End
Soil pH	0.331	0.490	-0.471	-0.481	0.310	0.324	-0.103	0.244
Organic carbon (%)	0.218	0.476*	0.291*	0.415	-0.367	0.182	0.242	0.192
Total N (%)	-0.425	-0.380	0.466	0.522*	-0.281	-0.801	0.355	0.173
Available P (mg/kg soil)	-0.386	-0.273*	0.317	0.271	0.491	-0.222	0.206	-0.165
Exchangeable cations								
CEC	-0.620	0.526	-0.164	0.411	0.612	0.519	0.429	-0.433
Ca^{2+}	-0.310	0.275	-0.173	0.105	-0.433	0.202*	0.517*	0.231
Mg^{2+}	0.194	-0.173	0.141	0.138	-0.141	0.241	0.238*	0.162
K^{+}	0.177	-0.141	0.169	-0.124	0.107	0.160	0.121	0.53*
Na^{+}	0.058	0.156*	0.1.21	0.145*	0.025*	0.045	-0.078	0.124
Al^{3+}	0.089	0.122	0.082	0.033*	0.088	-0.081	-0.124	0.141
H^{+}	0.157	-0.327	-0.184	-0.122	0.117	0.270	-0.143	0.131*
Physical properties								
Soil moisture (%)	-0.314	0.314	0.339	-0.271	-0.368	0.312	-0.283	-0.276
Sand (%)	0.102	0.451	0.370	-0.417	-0.134	0.251	0.391	-0.258
Silt (%)	0.312	-0.321	0.329	0.316	0.110	-0.037	0.211	-0.318
Clay (%)	-0.149	-0.457	-1.216	3.421	1.217	1.210*	-1.221	0.294
Bulk density (Mg/m^{3})	-0.246	0.133	0.126*	0.201*	0.270*	0.217*	-0.412	0.341
Soil texture	0.401	0.236*	-0.276	0.204	0.285	0.254	0.291	0.212

*Correlation is significant at 0.05 level and **Correlation is significant at 0.01 level; Lin = Lindane; Hept = Heptachlor; Ald = Aldrin; Diel = Dieldrin; Beta E = Beta Endosulfan; Beta H = Beta HCH; Meth = Methoxychlor; End = Endrin.

H^{+} ions content of soils showed a significant positive correlation with Endrin ($r = 0.131$; $P<0.05$) levels in the cabbage heads, clay content of soils also showed a significant positive correlation ($P<0.05$) with Beta HCH ($r = 1.210$; $P<0.05$) levels in the cabbage heads, soil bulk density showed a significant positive correlation ($P<0.05$) with Aldrin ($r = 0.126$; $P<0.05$), Dieldrin ($r = 0.201$; $P<0.05$), Beta Endosulfan ($r = 0.270$; $P<0.05$) and Beta HCH ($r = 0.217$; $P<0.05$) levels of the cabbage heads, whilst soil texture showed a significant positive correlation with Heptachlor ($r = 0.236$; $P<0.05$) levels in the cabbage heads (Table 8).

The positive correlations observed indicate that these soil properties (organic carbon, nitrogen, clay, Ca^{2+}, Mg^{2+}, Na^{+}, H^{+}, bulk density and soil texture contents) have significant influence on distributions and levels of Heptachlor, Aldrin, Dieldrin, Methoxychlor, Beta Endosulfan and Beta HCH levels in the cabbage heads. Hence an increase in the contents of organic carbon, nitrogen, clay, Ca^{2+}, Mg^{2+}, Na^{+}, H^{+}, bulk density and soil texture in the soils could result in a corresponding increase in the levels of respective pesticides in the cabbage heads. For example, as bulk density of soil increases, Aldrin, Dieldrin Beta Endosulfan and Beta HCH also increase and that led to high accumulation in vegetables as reported by Ahmad and Akhtar (2013). The observed correlations also corroborated well with that of Khalid *et al.* (2020) and Akoto *et al.* (2013) who reported that the high clay or organic matter contents in the soil, the more it absorbs pesticides and hence high absorption by cabbage plants.

The positive correlations between soil organic carbon and Heptachlor and Aldrin levels in cabbage heads, between H^{+} ions and Endrin, clay contents and Beta HCH levels, soil bulk density and Aldrin, Dieldrin, Beta Endosulfan, and Beta HCH levels and soil texture and Heptachlor levels in the cabbage heads agreed with that of Copaja and *et al.* (2021) and Sheng *et al.* (2001). However, the positive correlations that existed between soil calcium (Ca^{2+}) ions contents and Beta HCH and Methoxychlor levels in the cabbage heads, Mg^{2+} ions contents and Methoxychlor levels and Na^{+} ions contents and Heptachlor, Dieldrin and Beta Endosulfan levels in the cabbage heads were at variance with that reported by Fosu-Mensah *et al*., (2016).

Available phosphorus contents showed significant negative correlations with Heptachlor ($r = - 0.273; P<0.05$) levels in the cabbage heads. This observation implies that increased in P contents of the soils could lead to reduced levels of Heptachlor in the cabbage. This observation agreed favourably with that of Bentum *et al.* (2006) where they reported that Lindane levels of cocoa were found to decrease with increased in available phosphorus contents of soils. This observation also means Heptachlor could have shorter persistence period in the cabbage heads as available phosphorous contents of the soils increases. This contributed to a corresponding reduction in the levels of Heptachlor in the cabbage heads. The faster rates of Heptachlor degradation in the cabbage heads could mean that morphologically, Heptachlor was well developed for cabbage crops as reported by Montgomery *et al.* (2017).

4.5.3 Correlations of soil properties with synthetic pyrethroids pesticides in cabbage

The correlations between physico-chemical properties of the soils from the cabagge farms and the synthetic pyrethroid pesticides were assessed and presented (Table 9). Correlations existed between organic carbon, total nitrogen, available phosphorous, exchangeable cations, soil moisture contents and soil texture of the soils from cabbage farms and Allethrin ($r = - 0.341; P>0.05$), Permethrin ($r = - 0.319; P>0.05$), Cyfluthrin ($r = - 0.372; P>0.05$), Fenvalerate ($r = - 0.358; P>0.05$) and Deltamethrin ($r = - 0.415; P>0.05$) levels in the cabbage heads (Table 9) were insignificant. These indicate that these soil properties have very little to no influence on the levels of the respective pesticides in the cabbage heads. These observations were at variance to that Oros *et al*. (2005) where organic carbon, clay, moisture and total nitrogen contents of soil correlated positively in the levels in some synthetic pyrethroids in some selected vegetables. The observations made herein between the above mentioned soil properties and Allethrins, Permethrin, Cyfluthrin, Fenvalerate, and Deltamethrin levels in the cabbage heads could be attributed to faster rates of degradation of the synthetic pyrethroids which resulted in shorter persistence and subsequent low levels in the cabbage heads as reported by Le Goff *et al*. (2019).

Soil pH showed significant positive correlations with Allethrins ($r = 0.55$; $P<0.05$), Cyfluthrin ($r = 0.567$; $P<0.05$) and Deltamethrin ($r = 0.521$; $P<0.05$) levels in the cabbage heads whilst soil moisture contents showed a significant positive correlation with Cypermethrin ($r = 0.237$; $P<0.05$) levels in the cabbage heads. These mean that at the indicated P-value, soils pH has significant influence on distributions and levels of these pesticides in the cabbage heads. This finding was at variance with that reported by Fosu-Mensah *et al.* (2016) where soil pH above 7 led to reduced pesticides uptake by crops. The positive correlation between soil moisture contents and Cypermethrin levels in the cabbage heads indicates that at high soil moisture contents, cabbage crops take up high levels of Cypermethrin. Thus, it is prudent that in cases where Cypermethrin are used on cabbage crops, farmers reduced irrigation rates to cutback Cypermethrin levels that would be accessible by the cabbage crops. This finding was at variance with that of Asare (2011) where soil mosture contents made soil organisms unable to breakdown pesticides molecules. This according to Asare (2011), led to elevated levels of pesticides in watermelon fruit crop.

Sand contents of the soil also showed significant positive correlation with Allethrin (r = 0.522; P<0.05) and Cyfluthrin (r = 0.519; P<0.05) levels in the cabbage heads whilst clay contents of soils showed a significant positive correlation with Permethrin (r = 0.276; P<0.05) levels in the cabbage heads. These imply that sand and clay contents of the soils from the cabbage farms had significant influence on distributions and levels of respective pesticides in the cabbage heads. Thus, increased in sand and clay contents could result in increased in the levels of the respective pesticides in the cabbage heads from the cabbage farms. The observation between clay contents and Permethrin levels in the cabbage heads 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 strong adsorption of pesticides molecules onto soil particles. However, observation between sand contents and Allethrin and Cyfluthrin was at variance with that made by Fosu-Mensah *et al.* (2016) where increased sand contents of soils led to low pesticides uptake by crops due to reduced pesticides adsorption onto soil particles.

Soil bulk density had significant positive correlation with Deltamethrin (r = 0.592; P<0.05) levels in the cabbage heads. This indicated that bulk density of the soils contributed to distributions and levels of Deltamethrin in the cabbage heads. Hence increase soil's bulk density could increase Deltamethrin uptake by cabbage crops as reported by Ahmad and Akhtar (2013).

Table 9: Correlations of soil properties with synthetic pyrethroids pesticides in cabbage heads

Soil chemical properties	Alle	Perm	Cyfl	Cyper	Fen	Delta
Soil pH	0.55**	0.421	0.567**	-0.371	0.325	0.521**
Organic carbon (%)	0.273	-0.286	0.342	0.311	0.324	-0.211
Total N (%)	-0.421	0.231	-0.285	-0.156	-0.231	0.432
Available P (mg/kg soil)	-0.332	0.261	0.342	0.211	-0.422	-0.211
Exchangeable cations						
CEC	0.038	-0.045	-0.051	0.023	-0.028	0.011
Ca^{2+}	-0.087	0.064	0.052	0.041	-0.073	-0.039
Mg^{2+}	-0.126	-0.157	0.291	-0.271	0.310	-0.211
K^+	0.321	-0.319	0.275	-0.358	0.234	0.321
Na^+	0.421	0.322	-0.311	0.372	0.329	-0.415
Al^{3+}	-0.325	0.321	0.337	0.381	0.370	0.399
H^+	0.731	-0.231	-0.351	-0.324	-0.281	-0.361
Physical properties						
Soil moisture (%)	-0.132	0.183	-0.211	0.237*	0.581	-0.217
Sand (%)	0.522**	-0.493	0.519**	-0.497	0.532	-0.516
Silt (%)	0.276	-0.201	0.505**	-0.321	-0.245	0.381*
Clay (%)	-0.324	0.276*	0.394	-0.366	-0.251	0.432
Bulk density (Mg/m^3)	0.131	-0.136	0.183	0.174	0.257	0.592**
Soil texture	-0.341	0.262	-0.372	0.281	-0.304	-0.221

*Correlation is significant at 0.05 level and **Correlation is significant at 0.01 level; Alle = Allethrins; Perm = Permethrin; Cyfl = Cyfluthrin; Cyper = Cypermethrin; Fen = Fenvalerate; Delta = Deltamethrin.

4.5.4 Correlations of soil properties with organophosphate pesticides in carrot roots

The correlations between physico-chemical properties of the soils from the carrot farms and organophosphate pesticides in the carrot roots were investigated and presented (Table 10). The correlation between total nitrogen, available phosphorou, CEC, K^+ ions, soil moisture contents, sand, and soil texture and Diazinon, Dimethoate, Pirimiphos, Chlorpyrifos, Parathion, Profenofos and Malathion levels in the carrot roots were not significant at the indicated P-value (Table 10). These indicate that available phosphorus, nitrogen, CEC, K^+ ions, soil moisture sand contents, and soil texture had no influence on levels of respective organophosphate pesticides in the carrot roots. These observations agreed favourably with that made by Sheng *et al.* (2001) and Sarkar *et al.*, 2020) where non-significant correlations were observed between phosphorus, nitrogen, CEC, K^+ ions, soil moisture sand contents, and soil texture and Diazinon, Dimethoate, Pirimiphos, Chlorpyrifos, Parathion, Profenofos and Malathion levels in soils.

pH showed significant negative correlations with Diazinon ($r = -0.581$; $P<0.05$) and Dimethoate ($r = -4.921$; $P<0.05$) levels in the carrot roots and a significant positive correlation with Profenofos ($r = 0.277$; $P<0.05$) levels in the carrot roots. The negative correlation between pH and Diazinon and Dimethoate levels in the carrot roots implies that as pH of the soil decreased, the H^+ ion contents of the soils also increased resulting in increased rates of pesticides uptake by the carrot roots due to high mobility of pesticides molecules at low soil pH. However, the finding herein agreed favourably with that of Fosu-Mensah *et al.* (2016) where low soil pH below 7 was reported to increase mobility of pesticide molecules and hence high uptake by the carrot roots and hence high Diazinon and Dimethoate levels in the carrot roots. However, the positive correlation between pH and Profenofos indicated that increased in pH of soil could lead to increased Profenofos levels in the carrot roots which are at variance with that of Fosu-Mensah *et al.* (2016).

Soil organic carbon had significant positive correlation with Diazinon ($r = 0.264$; $P<0.05$) and Dimethoate ($r = 0.303$; $P<0.05$) levels in the carrot roots. Ca^{2+} ions contents of the soil also had significant positive correlation with Diazinon ($r = 0.212$; $P<0.05$) and Profenofos ($r = 0.176$; $P<0.05$) levels in the carrot roots whilst Mg^{2+} ions contents of the soils had significant positive correlation with Diazinon ($r = 0.103$; $P<0.05$) and Profenofos ($r = 0.162$; $P<0.05$) levels in the carrot roots and a negative significant correlation with Malathion (r = - 0.271; $P<0.05$) levels in the carrot roots. Na^+ ions contents of soils also had significant positive correlation with Chlorpyrifos (r = 0.139; $P<0.05$) levels in the carrot roots. Al^{3+} ions contents of the soils also had significant positive correlation with Chlorpyrifos (r = 0.018; $P<0.05$) and Malathion (r = 0.136; $P<0.05$) levels in the carrot roots. These imply that organic carbon, Ca^{2+}, Mg^{2+} and Al^{3+} contents of the soils from the carrot farms had significant influence on distributions and levels of the respective pesticides in the carrot roots. Thus, increased in organic carbon, Ca^{2+}, Mg^{2+}, Na^+, and Al^{3+} contents could result in increased in the levels of the respective pesticides in the carrot roots from the carrot farms.

The observed positive correlation between organic carbon and Al^{3+} contents and levels of respective pesticides in the carrot roots agreed favourably with that observed by Chaudhari, *et al.* (2013) and Copaja *et al.* (2021) where positive significant correlations were observed between organic carbon contents of soil and Diazinon and Dimethoate and Al^{3+} and Chlorpyrifos and Malathion. However, the positive correlations between Ca^{2+} ions contents, Diazinon and Profenofos levels, Mg^{2+} ions contents and Diazinon and Profenofos levels, Na^+ ions and Chlorpyrifos levels, silt and Diazinon and Dimethoate levels in the carrot roots were at variance with observation made by Chaudhari, *et al.* (2013) and Copaja *et al.* (2021) where negative correlation were observed between the soil properties and the respective pesticides levels in the carrot roots.

H^+ ions contents of soils showed significant positive correlation with Diazinon (r = 0.144; $P<0.05$) levels in the carrot roots whilst silt had significant positive correlation with Diazinon (r = 0.429; $P<0.05$) and Dimethoate (r = 0.532; $P<0.05$) levels in the carrot roots. Soil bulk density showed a significant negative correlation with Diazinon (r

= - 0.517; ($P<0.05$) levels in the carrot roots and positive correlation with Pirimiphos ($r = 0.219$; $P<0.05$), Chlorpyrifos ($r = 0.308$; $P<0.05$), Parathion ($r = 0.301$; $P<0.05$), Profenofos ($r = 0.246$; $P<0.05$) and Malathion ($r = 0.328$' $P<0.05$) levels in the carrot roots (Table 10).

The observed positive correlations indicate that as soil properties (H^+ ions and silt) increase, concentrations of the respective organophosphate pesticides in the carrot roots from the carrot farms also increase whilst negative correlations indicate that as soil property (soil's bulky density) increase, concentrations of the respective organophosphate pesticides in the carrot roots from the carrot farms also decrease. The observed correlation between silt and Diazinon and Dimethoate agreed favourably with that of Fosu-Mensah *et al.* (2016) where positive correlation was observed between silt contents of soil and Dieldrein and Beta HCH.

Table 10: Correlations of soil properties with organophosphorus pesticides in carrot

Soil chemical properties	Diaz	Dime	Piri	Chlo	Para	Prof	Mala
Soil pH (1:1)	-0.581*	-4.921*	0.471	-0.322	0.610	0.277*	0.551
Organic carbon (%)	0.264**	0.303*	0.304	0.414	0.461	0.317	0.336
Total N (%)	0.311	0.403	0.337	0.366	0.231	0.290	0.341
Available P (mg/kg soil)	-0.207	0.101	-0.218	-0.321	-0.314	0.302	0.108
Exchangeable cations							
CEC	0.578	0.613	0.547	0.413	-0.551	0.524	-0.448
Ca^{2+}	0.212*	0.189	0.236	0.316	-0.406	0.176*	-0.346
Mg^{2+}	0.103*	0.117	0.121	0.317	0.196	0.162*	-0.271*
K^+	0.112	0.133	0.155	0.187	-0.129	0.188	0.127
Na^+	0.027	0.054	0.034	0.139*	0.084	0.077	0.066
Al^{3+}	0.089	0.106	0.082	0.018*	0.022	0.079	0.136*
H^+	0.144*	0.304	0.181	0.181	0.181	0.181	0.181
Physical properties							
Soil moisture (%)	0.384	0.203	0.386	0.481	0.264	0.311	0.327
Sand (%)	-0.621	-0.471	-0.422	-0.461	-0.312	0.456	-0.293
Silt (%)	0.429*	0.532*	0.319	0.326	0.325	0.238	0.418
Clay (%)	-0.128	0.411	5.318	3.314	3.302	5.219	4.617
Bulk density (Mg/m^3)	-0.517*	0.312	0.219*	0.308*	0.301*	0.246*	0.328*
Soil texture	-0.310	-0.419	0.410	0.507	0.324	0.465	0.380

*Correlation is significant at 0.05 level and **Correlation is significant at 0.01 level; Dime = Dimethoate; Piri = Pirimiphos M; Chlo = Chlorpyrifos; Para = Parathion; Prof = Profenofos; Mala = Malathion

4.5.5 Correlations of soil properties with organochlorine pesticides in carrot roots

The correlations between physico-chemical properties of the soils from the carrot farms and organochlorine pesticides levels were evaluated and presented (Table 11).

Table 11: Correlations of soil properties with organochlorines pesticides in carrot roots

Soil chemical properties	Lin	Hepta	Ald	Diel	Beta E	Beta H	Meth	End
Soil pH (1:1)	-0.231	0.340*	0.322	0.271	-0.211	-0.381	0.203	-0.334
Organic carbon (%)	-0.211	0.371*	0.301*	0.433	0.227	0.146	0.219	-0.442
Total N (%)	-0.324	0.322	-0.162	0.512*	0.321	0.821	-0.322	0.213
Available P (mg/kg soil)	-0.226	0.143*	-0.327	0.246	-0.453	0.276	-0.271	0.065
Exchangeable cations								
CEC	0.124	0.421	0.261	-0.433	-0.321	-0.501	0.433	0.183
Ca^{2+}	0.300	-0.328	0.103	-0.119	-0.411	0.221*	0.588*	0.311
Mg^{2+}	0.101	-0.271	-0.101	-0.128	0.221	-0.261	0.214	-0.102
K^{+}	-0.207	0.431	-0.229	0.134	0.141	-0.182	0.189	0.549
Na^{+}	-0.144	0.250*	-0.145	0.141*	0.125*	0.073	0.018	-0.364
Al^{3+}	0.1.08	0.223	0.124	0.022*	0.071	0.161	-0.134	0.141
H^{+}	0.124	0.421	-0.334	0.342	-0.142	0.222	-0.173	0.231
Physical properties								
Soil moisture (%)	0.217	-0.213	0.321	0.221	0.268	0.351	0.281	-0.211
Sand (%)	0.161	-0.257	0.338	-0.237	-0.148	0.282	0.322	0.252
Silt (%)	-0.242	-0.281	-0.317	-0.327	-0.121	0.091	-0.237	-0.331
Clay (%)	-0.247	0.317	-1.206	3.426	1.232	1.271*	-1.281	0.228
Bulk density (Mg/m^{3})	0.213	0.238	0.111*	0.191*	0.226*	0.281*	0.401	0.371
Soil texture	0.452	0.411*	0.116	-0.214	-0.248	-0.261	0.281	-0.243

*Correlation is significant at 0.05 level and **Correlation is significant at 0.01 level; Lin = Lindane; Hepta = Heptachlor; Ald = Aldrin; Diel = Dieldrin; Beta E = Beta Endosulfan; Beta H = Beta HCH; Meth = Methoxychlor; End = Endrin.

The results obtained (Table 11) showed that no significant correlation (P>0.05) existed between CEC, Mg^{2+}, K^{+},H^{+}, soil moisture, sand and silt contents of soils and Lindane, Heptachlor, Aldrin, Dieldrin, Beta Endosulfan, Beta Hexachlorocychlorhane, Methoxychlor and Endrin levels in the carrot roots. These indicate that these soil properties have little to no influence contribution to the Lindane, Heptachlor, Aldrin, Dieldrin, Beta Endosulfan, Beta Hexachlorocychlorhane, Methoxychlor and Endrin levels in the carrot roots from the carrot farms. The non-significant correlations observed were at variance with that of Sheng *et al.* (2001) where organochlorine pesticides levels in some vegetables correlated significantly with organic matter, amounts and type of clay, cation exchange capacity and pH of soils.

The results (Table 11) showed that pH of the soil correlated significantly and positively with Heptachlor ($r = 0.340$; $P<0.05$) levels in the carrot roots. Organic carbon contents of the soils significantly and positively correlated with the levels of Heptachlor ($r = 0.371$; $P<0.05$) and Aldrin ($r = 0.301$; $P<0.05$) in the carrot roots. Total nitrogen contents also significantly and positively correlated with Dieldrin ($r = 0.512$; $P<0.05$) levels in the carrots whilst available phosphorous had a significant positive correlation with Dieldrin ($r = 0.143$; $P<0.05$) levels in the carrot roots. Calcium (Ca^{2+}) ions contents of the soils correlated significantly and positively with Beta HCH ($r = 0.221$; $P<0.05$) and Methoxychlor ($r = 0.588$; $P<0.05$) levels of the carrot roots. Na^{+} ions contents of the soils also correlated positively with Heptachlor ($r = 0.250$; $P<0.05$), Dieldrin ($r = 0.141$; $P<0.05$) and Beta Endosulfan ($r = 0.125$; $P<0.05$) levels in the carrot roots whilst Al^{3+} ions contents of the soils positively and significantly correlated with Dieldrin ($r = 0.022$; $P<0.05$) levels in the carrot roots. Clay contents of the soils also significantly and positively correlated with Beta HCH ($r = 1.271$; $P<0.05$) levels in the carrot roots. Soil bulk density significantly and positively correlated with Pirimiphos ($r = 0.111$; $P<0.05$), Chlorpyrifos ($r = 0.191$; $P<0.05$), Parathion ($r = 0.226$; $P<0.05$) and Profenofos ($r = 0.281$; $P<0.05$) (Table 11) levels in the carrot roots. Soil texture exhibited significant and positive correlation with Heptachlor ($r = 0.411$; $P<0.05$) in the carrot roots whilst correlations between CEC, Mg^{2+}, K^{+}, H^{+}, soil moisture contents, sand contents and silt contents of the soils from the carrot farms and Lindane, Heptachlor, Aldrin, Dieldrin, Beta Endosulfan, Beta HCH, Methoxychlor and Endrin levels in the carrot roots were statistically insignificant at the indicated P-value. These indicate that these soil properties have little to no influence on the levels of Lindane, Heptachlor, Aldrin, Dieldrin, among others in the carrot roots sampled from the carrot farms.

The positive correlations between some of the soil properties and some organochlorine pesticides indicate that these soil properties significantly influenced the distributions and the levels of the organochlorine pesticides in the carrot roots. Hence increase in quantities of these soil properties could result in increase in the levels of the respective organochlorine pesticides in the carrot roots.

The positive correlations between organic matter contents of the soils and Heptachlor and Aldrin levels in the carrot roots, clay contents and Beta HCH levels in the carrot roots, soil texture and Heptachlor levels in the carrot roots corresponded favourably with that reported by Fosu-Mensah *et al*. (2016). Hence, Heptachlor, Aldrin and Beta HCH levels would persist in the carrot roots from the carrot farms for long time as the quantities of physico-chemical properties of the soils surge. This observation might have contributed to the high levels of the pesticides in the carrot roots as reported by Ahmad *et al.* (2013). However, the positive correlation between pH and Heptachlor levels in the carrot roots were at variance with that of Akoto *et al.* (2015) where reduction in soil pH (below 7) resulted in mobility of pesticides molecules, reduced adsorption onto soil particles and increase in the rates of pesticides uptake by crops and leading to considerably high levels in crops.

4.5.6 Correlations of soil properties with synthetic pyrethroids pesticides in carrot samples

The correlations between physico-chemical properties of the soils from the carrot farms and synthetic pyrethroid pesticides of the carrot roots were computed and presented (Table 12). Correlations between soil organic carbon contents, total nitrogen, available phosphorous, the exchangeable cations, soil texture and Allethrin, Permethrin, Cyfluthrin, Cypermethrin, Fenvalerate and Deltamethrin levels in the carrot roots were statistically insignificant (Table 12). This means that these physico-chemical properties of the soil had no effect(s) on levels of the synthetic pyrethroids in the carrot roots from carrot farms. This finding is at variance with that of Chaudhari *et al.* (2013), Sheng *et al.* (2001), Copaja *et al*. (2021) and Akoto *et al.* (2013) where soil properties contributed significantly to pesticides levels in vegetables.

For instance, Akoto *et al.* (2013) reported that pesticides residues in some vegetables were influenced by quantities of organic carbon and organic matter contents of soils. Sheng *et al.* (2001) also reported that extent of pesticides accumulation in vegetables depend on soil properties, such as organic matter contents, amounts and type of clay and cation exchange capacity of soils.

Table 12: Correlations of soil properties with synthetic pyrethroids levels in carrot roots

Soil chemical properties	Alle	Perm	Cyfl	Cyper	Fen	Delta
Soil pH	0.562**	-0.403	0.516**	0.321	0.304	0.538**
Organic carbon (%)	-0.313	0.342	-0.207	0.309	-0.310	-0.202
Total N (%)	0.307	0.246	-0.371	0.254	0.272	-0.361
Available P (mg/kg soil)	0.314	-0.209	0.318	-0.227	0.319	0.218
Exchangeable cations						
CEC	0.042	0.037	0.058	0.047	0.040	0.066
Ca^{2+}	0.063	0.069	0.048	0.050	-0.052	0.043
Mg^{2+}	-0.121	-0.207	0.201	0.231	-0.214	-0.317
K^{+}	-0.319	-0.322	0.218	0.327	0.265	0.329
Na^{+}	0.317	-0.337	0.302	-0.324	0.334	0.361
Al^{3+}	0.421	0.372	-0.303	-0.412	0.220	-0.217
H^{+}	0.520	0.217	-0.281	0.254	0.318	-0.253
Physical properties						
Soil moisture (%)	0.176	0.241	-0.416	0.281*	0.401	-0.311
Sand (%)	0.512**	0.372	0.501**	0.391	0.501	-0.522
Silt (%)	-0.352	0.237	0.564**	0.337	0.320	0.326*
Clay (%)	-0.201	0.241*	0.232	-0.300	-0.217	0.328
Bulk density (Mg/m^3)	0.230	0.231	0.197	-0.182	-0.179	0.541**
Soil texture	0.270	0.182	0.276	0.321	-0.421	0.231

*Correlation is significant at 0.05 level and **Correlation is significant at 0.01 level; Alle = Allethrins; Perm = Permethrin; Cyfl = Cyfluthrin; Cyper = Cypermethrin; Fen = Fenvalerate; Delta = Deltamethrin.

The pH of soil correlated significantly and positively (Table 12) with Allethrin (r = 0.562; $P<0.05$), Cyfluthrin (r = 0.516; $P<0.05$) and Deltamethrin (r = 0.538; $P<0.05$) levels in the carrot roots. Soil moisture contents also correlated significantly and positively with Cypermethrin (r = 0.281; $P<0.05$) levels in the carrot roots. Positive correlations observed between pH and Allethrin, Cyfluthrin, and Deltamethrin levels in the carrot roots and soil moisture contents and Cypermethrin indicate that as soil pH and soil moisture contents increase, the levels of the respective pesticides also increase. The observed correlation between soil pH and Allethrin, Cyfluthrin, and Deltamethrin is at variance with that of (Fosu-Mensah *et al*., 2016) where soil pH correlated negatively to pesticides levels in vegetables.

Sand contents of the soils also correlated significantly and positively with Allethrin (r = 0.512; P<0.05) and Cyfluthrin (r = 0.501; P<0.05) levels in the carrot roots. Clay contents correlated significantly and positively with Permethrin (r = 0.241; P<0.05) in the carrot roots whilst soil bulk density correlated significantly and positively with Deltamethrin (r = 0.541; P<0.05) levels in the carrot roots. These imply that sand and bulk density of the soils from the carrot farms had significant influence on distributions and levels of the respective pesticides in the carrot roots. Thus, increased in sand and bulk density could result in increased in the levels of respective pesticides in the carrot roots.

A positive correlation was observed between clay contents of the soil and Permethrin levels in the carrot roots at P<0.05. This indicates that pesticides levels in the carrot roots will increase with clay contents of the soils. Hence, pesticides molecules have tendency to be uptaken by carrot roots. This finding is at variance with that of Bentzen *et al.* (2008) and Chaudhari *et al.* (2013) where increased clay contents of soils resulted in reduced uptake of pesticides by crops. This was attributed to the fact that high clay contents of soil present massive active absorption sites for pesticides molecules adsorption. This led to reduced levels of free pesticides molecules in soils for plants to assimilate.

4.5.7 Correlations of physico-chemical properties of soil with organophosphate pesticides in green pepper fruits

Correlations between physico-chemical properties of soils from the green pepper farms and organophosphate pesticides were investigated and reported (Table 13).

Correlations that existed between soil moisture, clay contents and soil texture and Diazinon, Dimethoate, Pirimiphos, Chlorpyrifos, Parathion, Profenofos and Malathion levels in the green pepper were insignificant at $P<0.05$. However, soil pH had a significant negative correlation with Chlorpyrifos ($r = -0.372$; $P<0.05$) levels in the green pepper fruits. This suggests that as pH of the soils increased, Chlorpyrifos levels in the soil rapidly degrades and hence Chlorpyrifos levels available in the soil for uptake by the green pepper plant becomes reduced and thus very small quantity of Chlorpyrifos would be assimilated by the green pepper plant. This observation agreed favourably with that of Fosu-Mensah *et al.* (2016). The rapid degradation of Chlorpyrifos which led to low Chlorpyrifos in the green pepper fruits could also be attributed to availability and nature of soil organisms which may have provided effective biochemical pathway for efficient and rapid degradation of Chlorpyrifos in the green pepper fruits as reported by Asare (2011).

pH of the soil also showed significant positive correlations with levels of Pirimiphos ($r = 0.551$; $P<0.05$) and Profenofos ($r = 0.387$; $P<0.05$) levels in the green pepper fruits. The correlations indicate that as pH of the soil increased, Profenofos and Pirimiphos levels in the green pepper fruits also increased (Table 13). These observations disagreed favourably with that of Chadwick *et al.* (2001) where pH of soils had negative correlations with of pesticides in the soils. However, they agreed favourably with that of

Fosu-Mensah *et al.* (2016) who indicated that soil pH could have enhanced the adsorption of the pesticides. The observations herein were expected since high soil pH positively affects pesticides levels in soil. These increase pesticides levels in soil are uptaken by crops resulting in high pesticides levels in crops.

Organic carbon contents of the soil also showed a more significant negative correlation with Diazinon ($r = -0.211$; $P<0.05$) levels in the green pepper fruits. This also suggests that as organic carbon contents of the soil are increased, Diazinon levels in the green pepper fruits decreased. This finding disagreed well with that of Khalid *et al.* (2020) and Akoto *et al.* (2013) where significant positive correlation existed between organic carbon contents of soil and some organophosphate pesticides contents of some soil at $P<0.05$.

CEC exhibited a significant negative correlation with Diazinon ($r = -0.522$; $P<0.05$) levels in the green pepper fruits, significant positive correlations with Pirimiphos ($r = 0.644$; $P<0.05$), Pirimiphos ($r = 0.548$; $P<0.05$) and Profenofos ($r = 0.552$; $P<0.05$) levels in the green pepper fruits (Table 13). Ca^{2+} ions in the soils showed a significant negative correlations with Chlorpyrifos ($r = -0.611$; $P<0.05$) and a significant positive correlation with Malathion ($r = 0.442$; $P<0.05$) levels in the green pepper vegetables (Table 13). Mg^{2+} ions contents of the soil also showed significant positive correlation with Malathion ($r = 0.279$; $P<0.05$) levels in the green pepper vegetables whilst Na^{+} ions contents of the soils also exhibited significant positive correlation with Chlorpyrifos ($r = 0.057$; $P<0.05$) and Profenofos ($r = 0.057$; $P<0.05$) levels of the green pepper fruits investigated. The observed positive correlations indicate that as soil properties (CEC, $Ca^{2+,}$ Mg^{2+} and Na^{+} ions) increase, levels of the respective organophosphate pesticides in the green pepper fruits from the green prpper farms also increase whilst negative correlations imply that as soil properties (CEC, Ca^{2+}) increase, concentrations of the respective organophosphate pesticides in the green pepper fruits from the green pepper farms also decrease. These observations corroborated well with that of Asare (2011) where positive correlation ($r = 0.559$; $P<0.05$) was observed between CEC and Methoxychlor levels of soils.

Al^{3+} ions in the soils showed a significant negative correlations with Malathion ($r = -0.241$; $P<0.05$) and significant positive correlations with Diazinon ($r = 0.077$; $P<0.05$), Pirimiphos ($r = 0.089$; $P<0.05$) and concentration of Parathion ($r = 0.118$; $P<0.05$) levels in green pepper fruits. H^+ ions contents of the soil also showed a significant positive correlation with Diazinon ($r = 0.134$; $P<0.05$) and Chlorpyrifos ($r = 0.098$; $P<0.05$) levels in the green pepper fruits. Sand contents also correlated significantly and positively with Diazinon ($r = 0.526$; $P<0.05$) levls in the green pepper fruits. Silt contents of soils also correlated significantly and positively with Diazinon ($r = 0.432$; $P<0.05$) and Profenofos ($r = 0.418$; $P<0.05$) levels in the green pepper fruits. Soil bulk density exhibited significant negative correlation with levels of Diazinon ($r = - 0.413$; $P<0.05$), Chlorpyrifos ($r = - 0.417$; $P<00.05$) and Parathion ($r = - 0.406$; $P<0.05$) levels whilst positive correlations exhibited between bulk density of soils and Dimethoate ($r = 0.377$; $P<0.05$), Pirimiphos ($r = 0.316$; $P<0.05$), Profenofos ($r = 0.301$; $P<0.05$) and Malathion ($r = 0.326$; $P<0.05$) levels of the green pepper vegetables (Table 13). The positive correlations observed indicate that Al^{3+}, H^+, sand, silt and bulk density contents of soils significantly influenced the distribution of Diazinon, Pirimiphos, Parathion, Chlorpyrifos, Profenofos and Malathion in the soils as well as in the green pepper. Hence increased in quantities of Al^{3+}, H^+, sand, silt and bulk density contents of the soils would increase levels of Diazinon, Pirimiphos, Parathion, Chlorpyrifos, Profenofos and Malathion in the green pepper fruits. Thus, Diazinon, Pirimiphos, Parathion, Chlorpyrifos, Profenofos and Malathion would persist for longer period in the green pepper vegetables as soil Al^{3+}, H^{+}, sand, silt and bulk density contents of the soils increase. Therefore longer persistence in the soils would result in elevated Diazinon, Pirimiphos, Parathion, Chlorpyrifos, Profenofos and Malathion in green pepper fruits. These observations agreed favourably with that of Ahmad and Akhtar (2013) where increased in some soil properties led to high pesticides uptake by crops due to reduced pesticides adsorption onto soil particles.

The negative correlations also suggest that Al^{3+} and bulk density contents of the soils would decrease Malathion, Diazinon, Chlorpyrifos and Parathion levels of the soils and green pepper vegetables as these properties increase. The negative correlation between Al^{3+} contents of soils agreed favourably with that of Fosu-Mensah *et al*., (2016) who reported that as the soil pH decreases below 7, acidic cations increase and hence pesticides availability, adsorption onto soil particles and their persistence in the soils are expected to be considerable high.

Table 13: Correlations of soil properties with organophosphate pesticides in green pepper

Soil chemical properties	Diaz	Dime	Piri	Chlo	Para	Prof	Mala
Soil pH (1:1)	-0.461	0.623	0.551*	-0.372*	0.517	0.387*	-0.544
Organic carbon (%)	-0.211**	0.318	0.317	0.329	-0.481	-0.314	0.321
Total N (%)	0.382	0.417*	0.365	0.382	-0.274*	0.398	0.369
Available P (mg/kg soil)	0.276*	0.118	-0.213	0.326	0.319	-0.317	-0.116*
Exchangeable cations							
CEC	-0.522*	0.644*	0.548*	0.462	-0.657	0.552*	0.471
Ca^{2+}	-0.283	0.281	0.432	-0.611*	0.510	0.182	0.442*
Mg^{2+}	0.117	0.105	0.129	-0.306	0.206	0.202	0.279*
K^{+}	0.132*	0.144	-0.161	0.189	0.148	0.137*	-0.141
Na^{+}	0.044	0.057*	0.036	0.141	-0.066	0.057*	-0.069
Al^{3+}	0.077*	0.143	0.089*	0.118*	0.071	0.171	-0.241*
H^{+}	0.134*	0.502	0.186	0.098*	0.149	0.287	0.177
Physical properties							
Soil moisture (%)	-0.483	0.217	0.358	0.387	-0.361	0.371	0.331
Sand (%)	0.526*	-0.521	0.523	0.422	-0.462	0.437	0.319
Silt (%)	0.432*	0.541	-0.362	0.428	0.723	0.418*	0.422
Clay (%)	0.139	0.407	-2.302	3.618	3.705	4.232	4.510
Bulk density (Mg/m^3)	-0.413*	0.377*	0.316*	-0.417*	-0.406*	0.301*	0.326*
Soil texture	0.411	-0.339	0.477	-0.321	0.614	0.429	0.471

*Correlation is significant at 0.05 level and **Correlation is significant at 0.01 level; Diaz= Diazinon; Dime = Dimethoate; Piri = Pirimiphos; Chlo = Chlorpyrifos; Para = Parathion; Prof = Profenofos; Mala = Malathion.

4.5.8 Correlations of soil properties with organochlorine pesticides in green pepper samples

The correlations between physico-chemical properties of the soils from the green pepper farms and organochlorine pesticides detected in green pepper fruits were computed and presented (Table14). Results showed that CEC, Mg^{2+}, soil moisture, sand and silt contents had no correlation with Lindane, Heptachlor, Aldrin, Dieldrin, Beta Endosulfan, Beta HCH, Methoxychlor and Endrin in the green pepper samples. These observations were at variance with that reported by Sheng *et al.* (2001) and Asare (2011) in which extent of pesticides adsorption depended on organic matter, amounts of clay and type, ion exchange capacity and moisture contents of soils.

However, soil pH correlated positively and significantly with Heptachlor ($r = 0.400$; $P<0.05$) levels of green pepper vegetable and organic carbon components of the soil exhibited a significant positive correlation with Heptachlor ($r = 0.201$; $P<0.05$) levels in the green pepper vegetable. Total nitrogen also correlated positively and significantly with Dieldrin ($r = 0.540$; $P<0.05$) levels in the green pepper fruits. The positive significant correlations exhibited between soil pH and Heptachlor, organic carbon contents and Heptachlor and total nitrogen and Dieldrin indicate that increase in soil pH, organic carbon and total nitrogen contents would result in increase in levels of the respective pesticides in the green pepper fruits. The positive correlation existed between organic carbon contents of the soil and Heptachlor levels of the green pepper agreed with that reported by Copaja *et al.* (2021) and Sheng *et al.* (2001). This could be ascribed to pesticide molecules having high affinity for organic matter in soil, similar to fats or lipids of plants and animals as indicated by Bentzen *et al.* (2008). However, correlation between total nitrogen and Dieldrin was at variance with that of Fosu-Mensah *et al.*, (2016).

Table 14: Correlations of soil properties with organochlorine pesticides in green pepper

Soil chemical properties	Lin	Hepta	Ald	Diel	Beta E	Beta H	Meth	End
Soil pH	-0.438	0.400*	0.127	0.331	-0.118	0.415	-0.301	0.410
Organic carbon (%)	0.371	0.201*	0.221	-0.232	-0.236	0.226	0.213	0.321
Total N (%)	0.429	0.321	-0.367	0.540*	-0.422	-0.220	0.317	0.217
Available P (mg/kg soil)	-0.327	0.343*	0.428	-0.222	0.357	-0.373	0.246	-0.019
Exchangeable cations								
CEC	0.133	0.472	0.367	-0.437	0.281	0.409	0.419	-0.280
Ca^{2+}	0.381	0.148	-0.223	0.229	-0.317	0.127*	0.524*	0.378
Mg^{2+}	0.176	0.179	-0.310	0.318	-0.331	0.368	0.271	0.177
K^{+}	-0.245	-0.371	0.127	0.184	0.241	0.281	0.122	0.524*
Na^{+}	-0.167	-0.154*	0.135	0.111*	0.227*	0.074	-0.185	0.329
Al^{3+}	0.188	0.120	0.224	0.029*	0.131	-0.165	-0.166	0.147
H^{+}	0.133	0.281	0.364	0.423	0.165	0.241	-0.124	0.261*
Physical properties								
Soil moisture (%)	-0.427	-0.277	-0.324	0.231	-0.242	0.366	-0.283	-0.281
Sand (%)	-0.176	-0.351	-0.332	-0.336	-0.241	0.281	0.329	-0.351
Silt (%)	-0.256	0.441	0.328	-0.417	0.281	-0.094	0.238	-0.337
Clay (%)	-0.517	0.227	1.276	2.601	1.244	1.375*	-1.217	0.241
Bulk density (Mg/m^3)	0.273	-0.261	0.122*	0.297*	0.233*	0.313*	-0.422	0.370
Soil texture	0.351	0.221*	-0.166	-0.311	0.229	0.321	0.251	0.252

*Correlation is significant at 0.05 level and *Correlation is significant at 0.01 level; Lin = Lindane; Hepta = Heptachlor; Ald = Aldrin; Diel = Dieldrin; Beta E = Beta Endosulfan; Beta H = Beta HCH; Meth = Methoxychlor; End = Endrin.

Available phosphorous exhibited significant positive correlation with Heptachlor ($r = 0.343$; $P<0.05$) levels in the pepper fruits. Ca^{2+} ions contents correlated positively and significantly with Beta HCH ($r = 0.127$; $P<0.05$) and Methoxychlor ($r = 0.524$; $P<0.05$) levels in the green pepper. K^{+} ions contents also correlated positively and significantly with Endrin ($r = 0.524$; $P<0.05$) levels and Na^{+} ions contents also correlated positively and significantly with Dimethoate ($r = 0.111$; $P<0.05$) and Pirimiphos ($r = 0.227$; $P<0.05$) levels in the green pepper investigated. However Na^{+} ions contents of the soil correlated negatively with Heptachlor ($r = - 0.154$; $P<0.05$) levels in the green pepper (Table 14). Al^{3+} ions contents of the soils had significant positive correlation with

Dieldrin ($r = 0.029$; $P<0.05$) levels in the green pepper. H^+ ions contents of the soils also had significant positive correlation with Endrin ($r = 0.261$; $P<0.05$) levels in the green pepper. Soil bulk density correlated positively and significantly with Aldrin ($r = 0.122$; $P<0.05$), Dieldrin ($r = 0.297$; $P<0.05$), Beta Endosulfan ($r = 0.233$; $P<0.05$) and Beta Hexachlorocychlorhexane ($r = 0.313$; $P<0.05$) levels in the green pepper. Texture of the soil also correlated positively and significantly with Heptachlor ($r = 0.221$; $P<0.05$) levels in the green pepper (Table 14).

The positive correlations observed indicate that phosphorus, Ca^{2+}, K^+, Na^+ and H^+ contents of the soils positively affected levels of the respective organochlorine pesticides in the green pepper whilst the negative correlation existed between Na^+ ions contents and Heptachlor implies that as Na^+ ions increase in the soil, Heptachlor levels of the green pepper decrease. Furthermore, as bulk density of soil increases, Aldrin, Dieldrin Beta Endosulfan and Beta HCH levels of the green pepper also increase. This observation would mean that soil bulk densities poorly absorb Aldrin, Dieldrin Beta Endosulfan and Beta HCH molecules. Thus pesticides molecules were free in the soils for easy uptake by green pepper plants as reported by Akhtar (2013). However, positive correlations between H^+ ion Methoxychlor and between Al^{3+} contents of the soils and Dielrin levels of the green pepper agreed favourably with that reported by Akoto *et al.* (2013) and Fosu-Mensah *et al*. (2016). The researchers reported that increased in Al^{3+} and H^+ contents of the soils also increased pesticides retention and their availability in the soils and hence high absorption by plants.

4.5.9 Correlations of soil properties with synthetic pyrethroids in green pepper samples

The correlations between physico-chemical properties of the soils from the green pepper farms and synthetic pyrethroids pesticides were investigated and reported (Table 15). The results obtained indicate that no significant correlations existed between soil organic carbon, total nitrogen, available phosphorous, exchangeable cations and soil texture and Allethrin, Permethrin, Cyfluthrin, Cypermethrin, Fenvalerate and Deltamethrin levels of the green pepper. Thus, organic carbon, total nitrogen, available phosphorous, exchangeable cations and texture contents of the soils had no effect on Allethrin, Permethrin, Cyfluthrin, Cypermethrin, Fenvalerate and Deltamethrin levels of the green pepper. These findings were at variance with that of Fosu-Mensah *et al.* (2016), Akoto *et al*. (2013) and Sarkar *et al*. (2020) where soil properties were reported to contribute significantly to synthetic pyrethroid pesticides levels in the vegetables collected from some vegetable farms.

However, pH of the soils had significant high positive correlations with Cyfluthrin ($r = 0.522$; $P<0.05$) and Deltamethrin ($r = 0.566$; $P<0.05$) levels of the green pepper (Table 15). This means that Cyfluthrin and Deltamethrin levels of in the green pepper would increase as pH of the soils increases. This observation however was at variance with that made by Akoto *et al.* (2013) and Sheng *et al.* (2001) who reported positive correlation between soil properties and pesticides levels.

Table 15: Correlations of soil properties with synthetic pyrethroids pesticides in green pepper samples

Soil chemical properties	Alle	Perm	Cyfl	Cyper	Fen	Delta
Soil pH	-0.431	0.473	0.522**	0.344	-0.317	0.566**
Organic carbon (%)	-0.217	0.343	0.216	0.345	-0.371	0.239
Total N (%)	0.412	0.348	0.326	-0.357	0.319	0.327
Available P (mg/kg soil)	0.220	0.215	-0.217	-0.320	0.324	-0.315
Exchangeable cations						
CEC	-0.067	-0.081	-0.049	-0.045	0.046	0.069
Ca^{2+}	-0.082	-0.057	0.062	-0.041	0.041	-0.061
Mg^{2+}	-0.170	-0.218	0.205	0.138	0.241	-0.418
K^{+}	0.405	-0.371	0.326	0.300	-0.321	0.311
Na^{+}	0.324	-0.232	0.374	0.311	-0.359	0.325
Al^{3+}	0.372	0.322	0.324	0.426	0.200	0.213
H^{+}	0.511	0.246	0.321	0.358	0.321	0.312
Physical properties						
Soil moisture (%)	-0.226	-0.273	-0.319	0.203*	0.407	0.321
Sand (%)	0.502**	0.321	-0.551**	-0.241	0.423	-0.442
Silt (%)	0.262	0.207	0.513**	-0.312	0.321	0.321*
Clay (%)	0.331	0.221*	0.234	0.320	0.212	0.221
Bulk density (Mg/m^3)	0.220	0.242	-0.231	0.212	0.171	0.640**
Soil texture	-0.172	0.129	0.233	-0.372	-0.331	-0.241

*Correlation is significant at 0.05 level and **Correlation is significant at 0.01 level; Alle = Allethrins; Perm = Permethrin; Cyfl = Cyfluthrin; Cyper = Cypermethrin; Fen = Fenvalerate; Delta = Deltamethrin.

Soil moisture contents also had significant positive correlation with Cypermethrin (r = 0.203; P<0.05) levels of the green pepper. Thus high soil mixture contents would increase Cypermethrin levels of the soils for subsequent absorption by the green pepper plants. This observation was at variance with that of Kumar and Philip (2006) and Asare (2011) where low soil moisture contents were reported to render most soil organisms inactive and made it difficult for them to aid in breakdown of the pesticides molecules. According to the researchers that leads to high pesticides accumulation due to firm adsorption of pesticides molecules onto soil particles. Hence lower pesticides levels were detected in some vegetables and watermelon fruits.

Sand contents of the soils showed significant positive correlation with Allethrin ($r = 0.502$; $P<0.05$) levels of the green pepper fruits and significant negative correlation with Cyfluthrin ($r = - 0.551$; $P<0.05$) levels of the green pepper. The positive significant correlation between sand contents of the soils and Allethrin level of the green pepper indicates that high sand levels of the soils could not absorbed the Allethrin molecules in the soil and that led to high absorption rate of Allethrin molecules by the green pepper plants, hence the high Allethrin levels detected in the green pepper fruits. This observation disagreed with that of Fosu-Mensah *et al*. (2016) where high sand contents of soils resulted in reduced adsorption of pesticide onto soil particles. The negative correlation between sand contents of the soil and Cyfluthrin levels of green pepper means that Cyfluthrin levels of green pepper are expected to decrease as sand contents of the soils increase. This finding agreed with that reported by Fosu-Mensah *et al*. (2016).

Clay contents correlated positively and significantly with Permethrin ($r = 0.221$; $P<0.05$) levels of the green pepper which implies green pepper plants are expected to absorb high levels of Permethrin when the clay contents of the soils are increased. This observation agreed favourably with that of Copaja *et al.* (2021) and Barriuso (2021) where increased in clay contents resulted in increased pesticides molecules uptake by plants and led to high accumulation of pesticides molecules in some fruits and vegetables. Bulk densities of the soils also showed more significant positive correlation with Deltamethrin ($r = 0.640$; $P<0.05$) levels in the green pepper fruits (Table 15). The significant positive correlation between soil bulk density and Deltamethrin also indicates that Deltamethrin levels of grern pepper increase with high bulk densities of the soils. This observation disagreed favourably with that of Ghosh (2020) who reported that increased bulk density of soil decreased rate of pesticide vapourisation from a buried soil layer.

4.5.10 Correlations of soil properties with organophosphate pesticides in lettuce samples

Correlations between physico-chemical properties of the soils sample from the lettuce farms and organophosphate pesticides were investigated and reported (Table 16). Correlations between soil moisture, sand, clay contents, soil texture and Diazinon, Dimethoate, Pirimiphos, Chlorpyrifos, Parathion, Profenofos and Malathion levels in the lettuce were not significant at $P<0.05$. These observations suggest that soil moisture, sand and clay contents and soil texture had no effect on Diazinon, Dimethoate, Pirimiphos, Chlorpyrifos, Parathion, Profenofos and Malathion levels of the lettuce. pH of the soils however correlated negatively and significantly with Chlorpyrifos ($r = -0.372$; $P<0.05$) levels of the lettuce. This suggests that increasing soil pH, would lead to reduction of Chlorpyrifos levels in the lettuce. The observation agreed favourably with that of Akoto *et al.* (2015) where pesticides residues in some vegetable were reported to decrease with increase in soil pH. Thus, pesticides molecules adhered firmly onto soil particles and persisted in the soils. Hence low levels of the pesticides molecules were freely available in the soil to be taken by the lettuce crops as indicated by Fosu-Mensah *et al.* (2016). Again, soil pH exhibited a significant positive correlations with Pirimiphos ($r = 0.551$; $P<0.05$) and Profenofos ($r = 0.387$; $P<0.05$) levels of the lettuce. These correlations suggest that pH of the soil had direct positive correlation with Pirimiphos and Profenofos levels of the lettuce. These findings however were at variance with that reported by Akoto *et al.* (2015) and Fosu-Mensah *et al.* (2016) where increased pH contents of soils led to less pesticides uptake by crops due to increased pesticides adsorption onto soil particles.

Organic carbon contents of the soils correlated positively and significantly with Diazinon ($r = 0.281$; $P<0.05$) and Dimethoate ($r = 0.413$; $P<0.05$) levels of lettuce. Thus Diazinon and Dimethoate appear to be freely available for uptake by the lettuce crop due to the apparent inability of the pesticides molecules to be absorbed onto the organic carbon contents of the soils due to apparent suficient active absorption sites on the organic carbon compounds as reported by Akoto *et al.* (2013).

Total nitrogen contents of the soils correlated positively and significantly with Parathion ($r = 0.301$; $P<0.05$) levels of the lettuce whilst available phosphorous correlated positively and significantly with Malathion ($r = 0.413$; $P<0.05$) levels of the lettuce. The correlations indicate that organic matter, total nitrogen and available phosphorus contents of the soils directly contributed positively to Diazinon, Dimethoate, Parathion and Malathion levls of the lettuce. These observations were at variance with that of Akoto *et al.* (2013) where high nitrogen contents of the soils correlated negatively with organophosphate pesticides in some leafy vegetables. Cation exchange capacity, K^+ and H^+ correlated positively and significantly with Diazinon ($r = 0.524$, $r = 0.163$ and $r = 0.204$; $P<0.05$) levels in the lettuce respectively (Table 16). These observations indicate that increasing CEC, K^+ and H^+ ions contents of the soils would lead to increased Diazinon levels of the lettuce. The positive correlation between H^+ ion and Diazinon levels of the lettuce agreed with that of Fosu-Mensah *et al.* (2016) where H^+ ion contents of soils made pesticides molecules available in soils for uptake by some leafy vegetables.

Calcium ions contents of the soils correlated negatively and significantly with Malathion ($r = - 0.271$; $P<0.05$) levels of the lettuce and correlated positively and significantly with Diazinon ($r = 0.317$; $P<0.05$) and Profenofos ($r = 0.374$; $P<0.05$) levels of the lettuce

(Table 16). Mg^{2+} ions contents of the soils also correlated negatively and significantly with Malathion ($r = -0.341$; $P<0.05$) and positively with Diazinon ($r = 0.126$; $P<0.05$) and Profenofos ($r = 0.272$; $P<0.05$) levels of the lettuce.

Positive correlations observed between soil calcium ion contents and Diazinon and Profenofos levels of the lettuce, Mg^{2+} ion contents and Diazinon and Profenofos levels show that as cations contents increase in the soils, levels of respective pesticides in the lettuce also increase. These observations were at variance with that of Fosu-Mensah *et al.* (2016). However, negative correlations indicate that as Mg^{2+} increase, concentrations of Malathion in the lettuce from the lettuce farms also decrease.

Na^{+} ions contents of the soils correlated positively and significantly with Chlorpyrifos ($r = 0.145$; $P<0.05$) levels of the the lettuce whilst Al^{3+} ions contents correlated positively and significantly with Chlorpyrifos ($r = 0.023$; $P<0.05$) and Malathion ($r = 0.172$; $P<0.05$) levels of the lettuce (Table 16). The observed correlations indicate that increased in Na^{+} and Al^{3+} contents could result in increased in the levels of the respective pesticides in the lettuce from the lettuce farms and this agreed favourably with that of Asare (2011) who reported positive correlation ($r = 0.509$; $P<0.05$) between CEC and Methamedophos levels.

Silt contents of the soils correlated positively and significantly with Diazinon ($r = 0.461$; $P<0.05$) and Dimethoate ($r = 0.548$; $P<0.05$) levels in the lettuce. Bulk density of the soils correlated negatively and significantly with Diazinon ($r = -0.541$; $P<0.05$) levels in the lettuce and positively with Pirimiphos ($r = 0.307$; $P<0.05$), Chlorpyrifos ($r = 0.313$; $P<0.05$), Parathion ($r = 0.362$; $P<0.05$), Profenofos ($r = 0.386$; $P<0.05$) and Malathion (r

= 0.371; P<0.05) levels in the lettuce (Table 16). The positive correlation observed between silt and bulk density of soils and the respective pesticides indicate that increasing silt contents and bulk density of soils would lead to an increase in the levels of the respective pesticides in the lettuce leaves. These observations agreed favourably with of Fosu-Mensah *et al.* (2016) where strong positive correlation between silt contents of soil and Dieldrin and HCH was observed. However, these findings were in contrary to that of Aiye- sanmi and Shoewu and Idowu (2012) which reported no significant (p > 0.05) correlations between silt and total organochlorine pesticides measured in soil samples from selected cocoa farms in Nigeria.

In cases where significant negative correlations were observed between exchangeable cations and respective pesticides, increasing exchangeable cations contents of the soils would lead to reduction in levels of the respective pesticides in the lettuce. These observations corresponded well with that of Fosu-Mensah *et al.* (2016) where significant negative correlation (r = -0.492; P<0.05) was observed between exchangeable cation and Lindane.

Table 16: Correlations of soil properties with organophosphate pesticides in lettuce

Soil chemical properties	Diaz	Dime	Piri	Chlo	Para	Prof	Mala
Soil pH (1:1)	-0.500*	-0.723*	0.521	-0.331	0.617	0.417*	0.524
Organic carbon (%)	0.281*	0.413*	0.353	0.320	0.206	0.352	0.413
Total N (%)	0.417	0.313	0.236	0.467	0.301*	0.301	0.745
Available P (mg/kg soil)	-0.308	0.207	-0.304	-0.328	-0.205	0.282	0.318**
Exchangeable cations							
CEC	0.524*	0.412	0.301	0.302	-0.457	0.501	-0.341
Ca^{2+}	0.317*	0.285	0.331	0.217	-0.216	0.374*	-0.271*
Mg^{2+}	0.126*	0.182	0.127	0.297	0.341	0.272*	-0.341*
K^{+}	0.163*	0.177	0.182	0.193	-0.415	0.208	0.301
Na^{+}	0.073	0.062	0.061	0.145*	0.062	0.051	0.060
Al^{3+}	0.066	0.109	0.071	0.023*	0.069	0.056	0.172*
H^{+}	0.204*	0.319	0.217	0.211	0.189	0.139	0.168
Physical properties							
Soil moisture (%)	0.486	0.323	0.344	0.457	0.324	0.374	0.361
Sand (%)	-0.427	-0.453	-0.420	-0.506	-0.342	0.510	-0.397
Silt (%)	0.461*	0.548*	0.322	0.371	0.348	0.241	0.520
Clay (%)	-0.261	0.374	0.815	3.018	3.209	5.312	3.118
Bulk density (Mg/m^3)	-0.541*	0.377	0.307*	0.313*	0.362*	0.386*	0.371*
Soil texture	-0.362	-0.324	0.516	0.427	0.433	0.429	0.428

*Correlation is significant at 0.05 level and **Correlation is significant at 0.01 level; Diaz = Diazinon; Dime = Dimethoate; Piri = Pirimiphos; Chlo = Chlorpyrifos; Para = Parathion; Prof = Profenofos; Mala = Malathion.

4.5.11 Correlations of soil properties with organochlorines pesticides in lettuce samples

Correlations between physico-chemical properties of the soils from the lettuce farms and the organochlorine pesticides were assessed and reported (Table 17). Results obtained showed that correlations between CEC, Mg^{2+}, soil moisture, sand and silt content of the soils and Lindane, Heptachlor, Aldrin, Dieldrin, Beta Endosulfan, Beta HCH, Methoxychlor and Endrin in the lettuce were not significant ($P<0.05$). Thus, CEC, Mg^{2+}, soil moisture, sand and silt contents of the soils from the lettuce farms had no effect on Lindane, Heptachlor, Aldrin, Dieldrin, Beta Endosulfan, Beta HCH, Methoxychlor and

Endrin levels of the lettuce. These obsevations were at variance with that of Sheng *et al*. (2001) where levels of organochlorine pesticides in some leafy vegetables depended on organic matter, amounts and types of of clay, ion exchange capacity and pH of the soil. The results reported (Table 16) also showed that pH of the soil also correlated positively and significantly with Heptachlor ($r = 0.241; P<0.05$) levels of the lettuce.

Organic carbon contents of the soils correlated positively and significantly with Heptachlor ($r = 0.570; P<0.05$) and Aldrin ($r = 0.371; P<0.05$) levels of the lettuce whilst total nitrogen correlated positively and significantly with Dieldrin ($r = 0.562; P<0.05$) levels o the lettuce. Available phosphorous contents of the soils also correlated positively and significantly with Heptachlor ($r = 0.149; P<0.05$) levels of the lettuce.

Ca^{2+} ions contents of soils correlated positively and significantly with Beta HCH ($r = 0.244; P<0.05$) and Methoxychlor ($r = 0.563; P<0.05$) levels of the lettuce whilst K^+ ions contents of the soils correlated positively and significantly with Endrin ($r = 0.533; P<0.05$) levels of the lettuce. Na^+ ions contents correlated positively and significantly with Heptachlor ($r = 0.157; P<0.05$), Dieldrin ($r = 0.142; P<0.05$) and Beta Endosulfan ($r = 0.123; P<0.05$) levels of the lettuce.

Table 17: Correlations of soil properties with organochlorine pesticides in lettuce samples

Soil chemical properties	Lin	Hepta	Ald	Diel	Beta E	Beta H	Meth	End
Soil pH (1:1)	-0.431	0.241*	0.327	0.372	-0.318	-0.411	0.413	-0.236
Organic carbon (%)	-0.331	0.570*	0.371*	0.331	0.217	0.145	0.222	-0.140
Total N (%)	-0.224	0.271	-0.263	0.562*	0.311	0.372	-0.472	0.218
Available P (mg/kg soil)	-0.246	0.149*	-0.344	0.236	-0.553	0.258	-0.381	0.167
Exchangeable cations								
CEC	0.326	0.429	0.255	-0.411	-0.366	-0.561	0.411	0.184
Ca^{2+}	0.370	-0.318	0.121	-0.101	-0.422	0.244*	0.563*	0.301
Mg^{2+}	0.108	-0.279	-0.141	-0.126	0.227	-0.231	0.221	-0.109
K^{+}	-0.187	0.438	-0.221	0.135	0.153	-0.222	0.177	0.533*
Na^{+}	-0.124	0.157*	-0.133	0.142*	0.123*	0.071	0.048	-0.374
Al^{3+}	0.189	0.244	0.127	0.023*	0.067	0.168	-0.114	0.122
H^{+}	0.133	0.428	-0.364	0.341	-0.112	0.243	-0.133	0.241*
Physical properties								
Soil moisture (%)	0.247	-0.277	0.381	0.233	0.261	0.371	0.232	-0.231
Sand (%)	0.262	-0.218	0.348	-0.207	-0.138	0.281	0.317	0.255
Silt (%)	-0.349	-0.282	-0.211	-0.307	-0.141	0.055	-0.217	-0.441
Clay (%)	-0.217	0.321	-1.211	3.420	1.281	1.272*	-1.211	0.223
Bulk density (Mg/m^3)	0.228	0.237	0.501*	0.197*	0.242*	0.283*	0.406	0.323
Soil texture	0.466	0.416*	0.126	-0.114	-0.218	-0.251	0.271	-0.213

*Correlation is significant at 0.05 level and **Correlation is significant at 0.01 level; Lin = Lindane; Hepta = Heptachlor; Ald = Aldrin; Diel = Dieldrin; Beta E = Beta Endosulfan; Beta H = Beta HCH; Meth = Methoxychlor; End = Endrin.

Al^{3+} ions contents of the soils correlated positively and significantly with Dieldrin ($r = 0.023$; $P<0.05$) levels of the lettuce whilst H^{+} ions contents correlated positively and significantly with Endrin ($r = 0.241$; $P<0.05$) levels of the lettuce. Positive correlations between pH, total nitrogen, available phosphorus, Ca^{2+}, Na^{+}, K^{+} and organic carbon contents of the soils and organochlorines pesticides levels in the lettuce indicate that physico-chemical properties of the soil contributed to the organochlorines levels of the lettuce. These observations agreed favourably with that of Sheng *et al.* (2001) where pesticides levels depended on organic matter, amounts and type of clay, ion exchange capacity and pH. As contents of these physico-chemical properties of the soil increase, organochlorine pesticides levels of soils increase and pesticides and pesticides molecules become available for plants to absorb from soils. This according to Sheng *et al.* (2001) resulted in elevated pesticides levels in some vegetables.

Bulk densities of the soils correlated positively and significantly with Aldrin ($r = 0.501$; $P<0.05$), Dieldrin ($r = 0.197$; $P<0.05$), Beta Endosulfan ($r = 0.242$; $P<0.05$) and Beta HCH ($r = 0.283$; $P<0.05$) levels of the lettuce (Table 17). Soil texture also correlated positively and significantly with Heptachlor ($r = 0.416$; $P<0.05$) levels of the lettuce. Thus, the observed positive correlations obtained for the soil bulk densities and soil texture positively affected the organochlorine pesticides levels of the lettuce. Hence as bulk densities of the soils increased, Aldrin, Dieldrin, Beta Endosulfan and Beta HCH contents of the lettuce also increased whilst increased in texture of the soils also contributed positively to Heptachlor levels of the lettuce. The correlation between soil texture and Heptachlor levels of the lettuce could be due to reduced absorption of pesticides molecules onto organic matter of the soils. This could have caused pesticides molecules to be weakly absorbed onto limited adsorption sites on the organic matter components of the soil. Hence high Heptachlor levels were freely available for lettuce plants to absorb them as indicated by Chaudhari, *et al.* (2013) and Ahmad *et al.* (2013).

4.5.12 Correlations of soil properties with synthetic pyrethroids in lettuce samples

The correlations between physico-chemical properties of the soils from lettuce farms and synthetic pyrethroid pesticides in the lettuce were investigated and reported (Table 18). Nonsignificant correlations existed between soil organic carbon, total nitrogen, available phosphorous, exchangeable cations, soil bulk density and soil texture and Allethrin, Permethrin, Cyfluthrin, Cypermethrin, Fenvalerate and Deltamethrin levels of the lettuce ($P>0.05$). These indicate that properties of the soil did not have effect on Allethrin, Permethrin, Cyfluthrin, Cypermethrin, Fenvalerate and Deltamethrin in the lettuce. These findings were at variance with that reported by Oros *et al*. (2005) where synthetic pyrethroids were found to persist for longer periods in soils due to their affinity for organic carbon and clay contents of soils. Hence pesticides molecules become available for plants to absorb from soils thereby increasing levels of pesticides in the plants.

pH of the soil correlated positively and significantly with Cyfluthrin ($r = 0.588$; $P<0.05$) and Deltamethrin ($r = 0.544$; $P<0.05$) levels of the lettuce. Soil moisture correlated positively with Cypermethrin ($r = 0.213$; $P<0.05$) levels of the lettuce whilst sand contents of the soils correlated positively and significantly with Allethrin ($r = 0.583$; $P<0.05$) and Cypermethrin ($r = 0.651$; $P<0.05$) levels of the lettuce. Silt contents correlated more positively and significantly with Cyfluthrin ($r = 0.574$; $P<0.05$) and moderately positively and significantly with Deltamethrin ($r = 0.129$; $P<0.05$) levels of the lettuce. Clay content of the soils correlated positively and significantly with Permethrin ($r = 0.301$; $P<0.05$) levels of the lettuce. These observations indicate that as pH, moisture, silt and clay contents of the soils increase, Deltamethrin, Cypermethrin, Cyfluthrin and Permethrin levels of the lettuce from the lettuce farms also increase. Thus high quantities of Deltamethrin, Cypermethrin, Cyfluthrin and Permethrin were available in the soils to be absorbed by the lettuce plants.

The observed correlations between pH, Cyfluthrin and Deltamethrin levels of the lettuce, soil moisture contents and Cypermethrin levels, silt contents and Cyfluthrin, sand contents, Allethrin and Cypermethrin levels in the lettuce were at variance with that reported by Fosu-Mensah *et al*. (2013) and Asare (2011) where pH, soil moisture, silt and sand contents of soils correlated negatively and significantly with Cyfluthrin Deltamethrin, Allethrin and Cypermethrin levels in some vegetables. The observed correlation between clay contents of the soil and Permethrin levels in the lettuce however agreed favourably with that made by Copaja and Gatica-Jeria (2021) and Barriuso, (2021) where increased in clay content of soils resulted in an increased adsorption of synthetic pyrethroids onto soils. Thus, increased quantities of Permethrin were available for the lettuce plants to absorb. The correlation between clay contents of the soil and Permethrin levels in the lettuce was at variance with a report by Yang *et al.* (2019) in which highly significant correlations existed between synthetic pyrethroids levels in some vegetable crops and clay contents of soils.

Table 18: Correlations of soil properties with synthetic pyrethroids in lettuce samples

Soil chemical properties	Alle	Perm	Cyfl	Cyper	Fen	Delta
Soil pH	0.371	0.313	0.588*	-0.321	-0.413	0.544*
Organic carbon (%)	0.307	0.312	-0.382	-0.317	0.451	0.312
Total N (%)	S-0.317	0.351	0.342	0.318	0.327	0.313
Available P (mg/kg soil)	0.219	-0.314	0.323	0.371	0.318	0.319
Exchangeable cations						
CEC	0.107	0.033	0.092	0.071	0.052	0.055
Ca^{2+}	0.066	-0.048	0.081	-0.092	-0.073	0.069
Mg^{2+}	-0.271	0.316	0.319	0.127	-0.312	-0.310
K^{+}	0.225	0.380	0.342	0.320	-0.337	-0.361
Na^{+}	0.421	-0.271	0.179	0.281	0.224	0.415
Al^{3+}	0.278	-0.327	-0.322	-0.327	0.241	0.366
H^{+}	-0.381	-0.347	-0.359	0.327	0.348	0.219
Physical properties						
Soil moisture (%)	-0.327	0.223	0.219	0.213*	0.203	0.377
Sand (%)	0.583*	0.460	0.651*	0.211	0.433	0.492
Silt (%)	0.264	-0.108	0.574**	0.418	0.2216	0.129*
Clay (%)	-0.328	0.301*	0.372	-0.334	-0.271	0.239
Bulk density (Mg/m^3)	-0.233	-0.249	0.238	-0.233	-0.221	0.549
Soil texture	0.222	0.290	0.230	0.374	0.315	0.301

*Correlation is significant at 0.05 level and **Correlation is significant at 0.01 level; Alle = Allethrins; Perm= Permethrin; Cyfl = Cyfluthrin; Cyper = Cypermethrin; Fen = Fenvalerate; Delta = Deltamethrin.

4.6 Occurrence of Unapproved Pesticides in the Investigated Vegetables

It is expected that pesticides apply on vegetables and other food commodities should be those which have been registered by Ghana EPA or other international bodies such as USEPA, EU among others. However, there are number of pesticides detected herein which are not registered.

4.6.1 Occurrence of unapproved organophosphate pesticides in the investigated vegetables

Among the organophosphate pesticides (Diazinon, Dimethoate, Pirimiphos, Chlorpyrifos, Parathion, Profenofos and Malathion) detected in the investigated vegetables, Parathion was not registered by Ghana EPA for use in Ghana.

Mean concentrations of Parathion in cabbage heads ranged from 0.032 mg/kg (farms) to 0.018 mg/kg (markets) whilst that of the carrot roots ranged from 0.023 mg/kg (farms) to 0.016 mg/kg (markets). Parathion levels of green pepper 0.025 mg/kg (farms) and 0.020 mg/kg (markets) whilst those of the lettuce were 0.027 mg/kg (farms) and 0.018 mg/kg (markets). Though Parathion is unregistered for use in Ghana, its levels in the cabbage heads, carrot roots, green pepper fruits and lettuce leaves were below 0.05 mg/kg permitted by USEPA/EU (USEPA, 2013; EU, 2009). However, continuous consumption of these vegetables could lead to bioaccumulation in the blood and tissues of consumers. Thus consumers are likely to brain and spinal cord problems and liver and kidney damages as indicated by Sharma *et al.* (2017). In order to prevent the influx of unregistered pesticides into our system, EPA, Ghana Standard Authority and other bodies responsible for safe use of pesticides in Ghana should ensure that all pesticides used for agricultural purposes are dully investigated and registered.

The European Union (EU, 2015) has not approved Diazinon, Dimethoate, Chlorpyrifos, Parathion and Profenofos to be used as agrochemicals. Levels of Daizinon ranged from 0.021 mg/kg in green pepper from the markets to 0.041 mg/kg in cabbage from the cabbage farms, Dimethoate ranged from 0.030 mg/kg in green pepper from the green pepper markets to 0.040 mg/kg in cabbage from the cabbage farms, Chlorpyrifos ranged from 0.002 mg/kg in green pepper from farms to 0.017 mg/kg in lettuce from farms, Parathion ranged from 0.016 mg/kg in carrot from markets to 0.027 mg/kg in cabbage from markets whilst that of Profenofos ranged from 0.003 mg/kg in carrot from markets to 0.022 mg/kg in green pepper from the markets. Diazinon and Dimethoate levels of cabbage, carrot, green pepper and lettuce were above 0.01 mg/kg set by USEPA and European Union (US, 2013; EU, 2009) whilst Chlorpyrifos levels of carrot and green pepper were below 0.01 mg/kg USEPA/EU recommended limit. Parathion and Profenofos levels of cabbage, carrot and lettuce were below 0.05 mg/kg (allowed by USEPA/EU) and 0.01 mg/kg (allowed by USEPA/EU) for Parathion and Profenofos (USEPA, 2013; EU, 2009).

Malathion and Pirimiphos are registered by Eupean Union (EU, 2015) to be used for agricultural purposes. Pirimiphos levels of the carrot roots were 0.042 mg/kg (farms) and 0.039 mg/kg (markets). Pirimiphos contents of the cabbage heads were 0.041 mg/kg (farms) and 0.038 mg/kg (markets). Pirimiphos levels of the green pepper were 0.020 mg/kg (farms) and 0.018 mg/kg (markets) whilst those of lettuce were 0.032 mg/kg (farms) and 0.031 mg/kg (markets). Pirimiphos levels observed were above the 0.010 mg/kg USEPA/EU allowed for all vegetables investigated.

Malathion levels of the cabbage, carrot, green pepper and lettuce were 0.013, 0.010, 0.014 and 0.029 mg/kg (farms) whilst those of the cabbage, carrot, green pepper and lettuce from markets were 0.015, 0.008, 0.014 and 0.022 mg/kg respectively. Aside Malathion levels of the lettuce from the farms, Malathion levels in remaining investigated vegetables were above 0.020 mg/kg permitted by USEPA/EU (USEPA, 2013; EU, 2009).

The occurrences of these unregistered pesticides in the investigated vegetables are likely to affect health status of consumers especially when consumed over an extended period. For instance Profenofos and Chlorpyrifos are extremely toxic to aquatic organisms, birds, bees and could also affect brain development in children as indicated in a reported by Werner *et al.* (2021). Long term exposure to the identified unregistered organophosphate could lead anxiety, loss of memory, loss of appetite, disorientation, depression, weakness, headache, diarrhoea, nausea and vomiting as reported by Kedia, and Palis (2008).

4.6.2 Occurrence of unapproved organochlorines pesticides in investigated vegetables

Organochlorine pesticides (Aldrin, Dieldrin, Endrin, Heptachlor, Beta Endosulfan, Beta HCH, P'P' DDE and Methoxychlor) contents of the vegetables investigated are unregistered in Ghana for use as active chemical ingredients in pesticides due to its high toxicity in humans, other organisms, slower rate of degradation in the environment and the ease of bioaccumulation as indicated by Zaynab *et al*. (2021) and (Jepson *et al.*, 2014). This situation in Ghana is a dangerous as these highly toxic are continuously being used on vegetable farms. The occurred banned pesticides (Aldrin, Dieldrin, Endrin, Heptachlor, Beta Endosulfan, Beta HCH, P'P' DDE and Methoxychlor) in the investigated vegetables could be due to inadequate monitoring and regulatory systems to check their importation and application in the agricultural settings of Ghana. The presence of these banned pesticides on the Ghanaian agrochemical markets may have emerged due to readily available and their easy access from unlicensed or unregistered agrochemical dealers.

Lindane levels of the cabbage heads, carrot roots, green pepper fruits and lettuce were 0.023, 0.007, 0.007 and 0.005 mg/kg respectively (farms) whilst the levels were 0.020, 0.006, 0.004 and 0.007 mg/kg respectively in vegetables bought from the markets. Heptachlor levels of cabbage heads, carrot roots, green pepper fruits and lettuce farms were 0.019, 0.007, 0.023 and 0.006 mg/kg respectively (vegetables from farms) whilst Heptachlor levels from the markets were 0.018, 0.003, 0.021 and 0.006 mg/kg respectively. P’P’- DDE levels of the cabbage heads, carrot roots, green pepper fruits were 0.026, 0.032, 0.033 and 0.036 mg/kg respectively (farms) whilst those vegetables from the markets had Heptachlor levels of 0.020, 0.029, 0.031 mg/kg 0.027 mg/kg in cabbage heads, carrot roots, green pepper fruits and lettuce respectively.

Aldrin levels in cabbage heads, carrot roots, green pepper fruits and lettuce from the farms were 0.033, 0.027, 0.022 and 0.026 mg/kg respectively whilst those from the markets were 0.019, 0.021, 0.012 and 0.022 mg/kg. Mean levels of Dieldrin in the cabbage heads, carrot roots, green pepper fruits and lettuce from the farms were 0.034, 0.025, 0.022 and 0.026 mg/kg respectively whilst levels in those from the markets were 0.032, 0.013, 0.017 and 0.025 mg/kg. Mean levels of Beta Endosulfan in the cabbage heads, carrot roots, green pepper fruits and lettuce from the farms were 0.040, 0.055, 0.059 and 0.057 mg/kg respectively whilst those from the markets were 0.028, 0.054, 0.030 and 0.052 mg/kg.

Mean levels of Beta HCH in cabbage heads, carrot roots, green pepper fruits and lettuce detected from the farms were 0.003, 0.005, 0.016 and 0.006 mg/kg respectively whilst those from the markets were 0.002 mg/kg, 0.003 mg/kg, 0.010 mg/kg and 0.008 mg/kg respectively. Mean levels of Methoxychlor in cabbage heads, carrot roots, green pepper fruits and lettuce from the farms were 0.007, 0.006, 0.002 and 0.004 mg/kg respectively whilst levels in those from the markets were 0.006, 0.005, 0.005 and 0.004 mg/kg respectively. Mean levels of Endrin also in cabbage heads, carrot roots, green pepper fruits and lettuce from the farms were 0.025, 0.029, 0.006 and 0.004 mg/kg respectively whilst levels in those from the markets were 0.015, 0.023, 0.005 and 0.006 mg/kg.

Mean levels of Lindane in cabbage heads from the farms and the markets were above of 0.010 mg/kg USEPA/EU recommended limit. However, mean levels of Lindane in carrot, green pepper and lettuce were below 0.010 mg/kg USEPA/EU recommended limit. Mean levels of Heptachlor in cabbage heads and green pepper fruits from the farms and markets were above 0.010 mg/kg USEPA/EU recommmended level whilst the levels in carrot and lettuce from the farms and markets were below 0.010 mg/kg allowed by USEPA/EU (USEPA, 2013; EU, 2009). Mean levels of Aldrin and Dieldrin were above 0.010 mg/kg USEPA/EU acceptable levels in vegetables.

Mean levels of Beta Endosulfan in cabbage heads and green pepper fruits from the farms and markets were above 0.050 mg/kg USEPA/EU allowed levels whilst Beta Endosulfan levels of carrot roots and lettuce from the farms and markets were below 0.050 mg/k limit set by USEPA/EU (USEPA, 2013; EU, 2009). Aside the green pepper fruits from the farms, Beta HCH levels of the vegetables were below 0.010 mg/kg limit set by the USEPA/EU (USEPA, 2013; EU, 2009). P'P' DDE and Methoxychlor levels of the vegetables were above 0.05 mg/kg and 0.010 mg/kg allowed by USEPA/EU for P'P' DDE and Methoxychlor respectively. Endrin levels in cabbage heads and carrot roots from the farms and the markets were above 0.010 mg/kg acceptable level set by USEPA/EU (USEPA, 2013; EU, 2009) whilst that of green pepper fruits and lettuce from the farms and markets were below 0.010 mg/kg acceptable level set by USEPA/EU (USEPA, 2013; EU, 2009). These findings reaffirm that reported by Asare (2011) where high levels of Aldrin and Endrin were detected watermelon fruits and low levels of P’P’ DDT, P’P’ DDE, Heptachlor, Methoxychlor and Lindane were detected in the watermelon fruits.

Consumption of high levels of Aldrin and Dieldrin could pose carcinogenic health risks to adult whilst high levels of Aldrin, Dieldrin and Heptachlor could also pose carcinogenic health risks to children as reported by Adeleye *et al*. (2019). High Aldrin, Dieldrin, Heptachlor and Endosulfan levels in some of the vegetables could lead to acute and chronic health effects among individuals who consume the vegetables over an extended period of their lives. The acute effects may include headache, dizziness, irritability, vomiting nervousness, confusion, nausea, and convulsion as indicated by ATSDR (2002), whilst the chronic health effects may include reproductive defects, neurotoxicity, tremor and cancers as reported by Adeleye *et al*. (2019) and ATSDR, (2015).

4.6.3 Occurrence of unapproved synthetic pyrethroid in investigated vegetables

Out of the six synthetic pyrethroids (Allethrin, Permethrin, Cyfluthrin, Cypermethrin, Fenvalerate and Deltamethrin) that occurred in the vegetables, Cypermethrin and Deltamethrin have been approved by the European Union (EU, 2015) for use on crops in the European countries. However, except Allethrin, Permethrin. Cyfluthrin, Cypermethrin, Fenvalerate and Deltamethrin have been registered and approved by Ghana EPA (EPA, 2019) to be used as active chemical constituents of one or more synthetic pyrethroid pesticides for agricultural purposes.

Cypermethrin levels ranged from 0.034 to 0.044 mg/kg (lettuce), 0.031 to 0.039 mg/kg (cabbage), 0.021 to 0.022 mg/kg (carrot roots) and 0.017 to 0.019 mg/k (green pepper fruits). These mean levels were below acceptable MRL 1.0 mg/kg (cabbage), 0.05 mg/kg (carrot), 0.05 mg/kg (green peppe) and 2.00 mg/kg (lettuce) set by USEPA/EU (EU, 2013; US, 2009). Levels of Deltamethrin ranged from 0.026 mg/kg to 0.040 mg/kg (lettuce), 0.051 to 0.061 mg/kg (cabbage), 0.013 to 0.017 mg/kg (carrot) and 0.050 to 0.062 mg/kg was (green pepper). These mean levels except that of green pepper, were below acceptable MRLs 1.0 mg/kg (cabbage), 0.05 mg/kg (carrot) and 0.02 mg/kg (lettuce) set by the USEPA/EU (EU, 2013; US, 2009). Green pepper had high Deltamethrin levels and ranged from 0.051 to 0.061 mg/kg and was level above 0.02 mg/kg acceptable levels set by SEPA/EU (EU, 2013; USEPA, 2009). The high levels of Deltamethrin in the green pepper fruits could induce inflammation, nephro-and hepatotoxicity and also influence the activity of antioxidant enzymes in tissues as reported by Chrustek *et al.* (2018) when the green pepper fruits are consumed by patrons over extended period. Thus, consumption of green pepper fruits with such levels of Deltemethrin could be detrimental to the human health.

Mean levels of Allethrin ranged from 0.004 to 0.005 mg/kg (lettuce), 0.006 to 0.004 mg/kg (cabbage), 0.008 to 0.009 mg/kg (carrot) and 0.005 to 0.006 mg/kg (green pepper). Mean levels of Allthrin in all vegetables were below 0.010 mg/kg allowed by USEPA/EU (EU, 2013; USEPA, 2009).

4.7 Health Quotient of Organophosphate, Organochlorine and Synthetic Pyrethroid Pesticides in Investigated Vegetables

Ideally, pesticides levels in the vegetables and other food crops should not exceed acceptable levels set by local (Ghana EPA) and international organizations such as the World Health Organization, USEPA and European Union. The acceptable levels of a pesticide residues recommended by Codex Alimentarius Commission (2000), USEPA and EU are those legally and toxicological accepted on or in food commodities and animal feeds (WHO, 2013). If good agricultural practices (GAP) are observed by farmers, pesticides residues in food crops are likely to be below the maximum recommended level for human consumption (Leong *et al.*, 2020). According to Mebdoua (2019), presence of pesticides residues above MRLs in food crops indicate that the GAP was violated by farmers. According to Njoku *et al.* (2017) infants, children and adults are commonly exposed to pesticides via ingestion of pesticides contaminated foods and water. Consumption of food crops containing pesticides residues have associated health impacts ranging from headaches and nausea to chronic impacts such as cancer, reproductive issue and endocrine disruption and others on consumers as reported by Recio-vega *et al.* (2008), Berrada *et al.* (2010) and Gilden *et al.* (2010).

4.7.1 Estimation of health quotient of organophosphate in investigated cabbage heads

Health quotient (HQ) of organophosphate pesticides in cabbage heads obtained from the farms and the markets were estimated and reported (Table 19). Diazinon and Pirimiphos in cabbage heads from the farms had the highest health quotient (1.44E-03) whilst Malathion (2.28E-04), Chlorpyrifos (3.68E-04), Profenofos (1.40E-04) Dimethoate (1.40E-03) and Parathion (2.80E-04) were the health quotients reported for the corresponding pesticides. Cabbage heads from the markets had health quotient of 1.58E-04 (Parathion), 1.35E-03 (Dimethoate) and 1.40E-03 (Diazinon), 1.35E-03 (Pirimiphos), 1.25E-04 (Chlorpyrifos), 1.40E-04 (Profenofos) and 6.25E-04 (Malathion).

Table 19: Health quotient of organophosphate pesticides in cabbage heads

Pesticide	Source	Mean level (mg/kg)	**ADI** (mg/kg)	EDI (mg/kg/day)	HQ
Diazinon	Farm	0.041	0.01	1.44E-05	1.44E-03
Dimethoate		0.040	0.01	1.40E-05	1.40E-03
Pirimiphos		0.041	0.01	1.44E-05	1.44E-03
Chlorpyrifos		0.021	0.02	7.35E-06	3.68E-04
Parathion		0.032	0.04	1.12E-05	2.80E-04
Profenofos		0.004	0.01	1.40E-06	1.40E-04
Malathion		0.013	0.02	4.55E-06	2.28E-04
Diazinon	Market	0.040	0.01	1.40E-05	1.40E-03
Dimethoate		0.038	0.01	1.35E-05	1.35E-03
Pirimiphos		0.038	0.01	1.35E-05	1.35E-03
Chlorpyrifos		0.015	0.01	1.25E-06	1.25E-04
Parathion		0.018	0.04	6.30E-06	1.58E-04
Profenofos		0.004	0.01	1.40E-06	1.40E-04
Malathion		0.015	0.02	1.25E-06	6.25E-04

The estimated HQ values indicate that health quotients were directly related to the levels of pesticides in vegetables. These HQ data were below 1 indicating that acceptable health risks were associated with the consumption of the cabbage heads for the farms and markets as reported by EU (2013), US (2009), Akoto *et al.* (2015) and Hossain *et al.* (2015). Although the HQs indicated acceptable risks, continuous intake of the vegetables could lead to a build up of the pesticides in the fatty tissues of consumers. Thus, ingestion of the cabbage heads constantly over an extent period could induce chronic health effects such as Parkinson’s disease as reported by Gill and Garg (2014) and cancers as indicated by Barnhoorn *et al.* (2015).

Diazinon (0.040 mg/kg), Dimethoate (0.038 mg/kg), Pirimiphos (0.038 mg/kg) and Chlorpyrifos (0.015 mg/kg) found to cause health issues in consumers of the cabbage heads from the markets during the time of study as their levels were above acceptable levels sunctioned by USEPA/EU although their HQs (Table 19) predicted otherwise.

The HQ for Diazinon (1.40E-03) in cabbage heads from the markets was the highest and corresponded favourably with HQ (1.38E-03) reported by Akomea-Frempong *et al.* (2017) in a study which investigated organophosphate pesticides in vegetables in Kumasi, Ghana. The lowest HQ (1.40E-04) estimated for Profenofos also corresponded favourably with the HQ (1.38E-04) computed by Akoto *et al.* (2015) in a study conducted on tomato fruits. The HQ for the organophosphate pesticides in the cabbage heads from various sampling locations ranged from 1.40E-04 (Profenofos) to 1.44E-03 (Diazinon). These were below unity indicating that risks associated with organophosphate pesticides in the cabbage heads were acceptable (Table 19).

4.7.2 Health quotient of organochlorine pesticides in investigated cabbage heads

Health quotient estimated for organochlorine pesticides in the cabbage heads from cabbage farms and the markets were presented (Table 20). The HQs were Beta HCH (6.85E-04), Lindan (5.25E-04), Beta Endosulfan (9.13E-03), Heptachlor (4.34E-03), Aldrin (7.72E-03), Methoxychlor (1.60E-03), Dieldrin (7.72E-03) and P’P’-DDE (1.80E-03). These HQs were also below unity. The HQs indicate that acceptable risks were associated with the organochlorine pesticides detected in the cabbage. Hence consumers were not at risk for consumption of the cabbage heads.

Table 20: Health quotient of organochlorine pesticides in cabbage heads

Pesticides	Source	Mean (kg/kg)	**ADI (mg/kg/day)**	EDI (mg/kg/day)	HQ
sLindane	Farm	0.023	0.01	5.25E-05	5.25E-04
Heptachlor		0.019	0.01	4.34E-05	4.34E-03
Aldrin		0.033	0.01	7.72E-05	7.72E-03
Dieldrin		0.034	0.01	7.76E-05	7.72E-03
Beta Endosulfan		0.040	0.04	9.13-05	9.13E-03
Beta HCH		0.003	0.01	6.85E-06	6.85E-04
Methoxychlor		0.007	0.01	1.60E-05	1.60E-03
Endrin		0.025	0.01	5.71E-05	5.17E-03
Lindane	Market	0.020	0.01	4.57E-05	4.57E-03
Heptachlor		0.018	0.01	4.11E-05	4.11E-03
Aldrin		0.019	0.01	4.34E-05	4.34E-03
Dieldrin		0.032	0.01	7.31E-05	7.31E-03
Beta Endosulfan		0.028	0.04	6.40E-05	1.60E-03
Beta HCH		0.002	0.01	3.43E-05	3.43E-03
Methoxychlor		0.007	0.01	1.60E-05	1.60E-03
Endrin		0.015	0.01	3.43E-05	3.43E-03

Although HQ data (Table 20) indicated acceptable risk of Lindane, Heptachlor, Aldrin and Dieldrin, their levels were above their respective acceptable levels recommended by USEPA/EU (USEPA, 2013; EU, 2009). Thus they appear to pose unacceptable health problems when the cabbage heads are ingested continuously overtime. These issues could emerge due to possible accumulation of Lindane, Heptachlor, Aldrin and Dieldrin in fatty tissues of consumers. These data agreed favourably with that of Munawar *et al.* (2021) where HQs below 1 were recorded for P'P' DDE, Beta HCH, DDT and Beta Endosulfan in vegetables.

4.7.3 Health quotient of synthetic pyrethroid pesticides in investigated cabbage heads

Health quotient of synthetic pyrethroid pesticides in cabbage heads from vegetable farms and markets were also estimated and the data presented (Table 21). The estimated HQ for synthetic pyrethroid pesticides in cabbage heads from farms were Allethrin (2.10E-04), Permethrin (2.59E-04), Cyfluthrin (1.75E-04), Cypermethrin (2.73E-05), Fenvalerate (4.73E-04) and Deltamethrin (1.79E-03) whilst that of markets were Allethrin (1.40E-04), Permethrin (1.82E-04), Cyfluthrin (4.05E-04), Cypermethrin (2.17E-05), Fenvalerate (4.20E-03) and Deltamethrin (2.14E-03). Estimated HQ for synthetic pyrethroid pesticides in cabbage heads from the farms and markets were below 1 (Table 21) indicating that synthetic pyrethroid pesticides in the cabbage heads appeared not to pose health risk to consumers as interpreted by EU (2013), USEPA (2009), Akoto *et al.* (2015) and Hossain *et al.* (2015). However, Fenvalerate levels in cabbage heads from farms and markets were above levels permitted by USEPA (2009) and EU (2013). Thus it appears to pose unacceptable health problems suh as reproductive dysfunction, developmental impairment, among others when the cabbage heads are ingested continuously overtime as reported by Garey and Wolff (1998).

Table 21: Health quotients of pyrethroids pesticides in cabbage heads

Pesticide	Source	Mean (mg/kg)	ADI (mg/kg)	EDI (mg/kg/day)	HQ
Allethrin	Farm	0.006	0.01	2.10E-06	2.10E-04
Permethrin		0.037	0.05	1.30E-05	2.59E-04
Cyfluthrin		0.010	0.02	3.50E-06	1.75E-04
Cypermethrin		0.039	0.5	1.37E-05	2.73E-05
Fenvalerate		0.027	0.02	9.45E-06	4.73E-04
Deltamethrin		0.051	0.01	1.79E-05	1.79E-03
Allethrins	Market	0.004	0.01	1.40E-06	1.40E-04
Permethrin		0.026	0.05	9.10E-06	1.82E-04
Cyfluthrin		0.023	0.02	8.05E-06	4.05E-04
Cypermethrin		0.031	0.5	1.09E-05	2.17E-05
Fenvalerate		0.024	0.02	8.40E-05	4.20E-03
Deltamethrin		0.061	0.01	2.14E-05	2.14E-03

4.7.4 Health quotients of organophosphate pesticides in carrot root samples

Health quotient (HQ) of organophosphate pesticides in carrot roots from the carrot farms and markets were estimated and data presented (Table 22). Health quotient of organophosphate pesticides (OPPs) present in carrot root samples (from farms and markets)were estimated in order to predict human health risk which could emerged from the levels of OPPs in the carrot roots. The estimated HQ for OPPs in carrot roots from the carrot farms were Diazinon (1.26E-03), Dimethoate (1.37E-03), Pirimiphos (1.47E-03), Chlorpyrifos (2.45E-04), Parathion (1.61E-04), Profenofos (2.80E-04) and Malathion (3.50E-04).

Table 22: Health quotient of organophosphate pesticides in carrot

Pesticides	Source	Mean (mg/kg)	ADI (mg/kg)	EDI (mg/kg/day)	HQ
Diazinon	Farm	0.036	0.01	1.26E-05	1.26E-03
Dimethoate		0.039	0.01	1.37E-05	1.37E-03
Pirimiphos		0.042	0.01	1.47E-05	1.47E-03
Chlorpyrifos		0.007	0.01	2.45E-06	2.45E-04
Parathion		0.023	0.04	8.05E-05	1.61E-04
Profenofos		0.008	0.01	2.80E-06	2.80E-04
Malathion		0.010	0.01	3.50E-06	3.50E-04
Diazinon	Market	0.035	0.01	1.23E-05	1.23E-03
Dimethoate		0.032	0.01	1.12E-05	1.12E-03
Pirimiphos		0.039	0.01	1.37E-05	1.37E-03
Chlorpyrifos		0.005	0.01	1.75E-06	1.57E-04
Parathion		0.010	0.04	1.05E-06	8.75E-05
Profenofos		0.003	0.01	1.05E-06	1.05E-04
Malathion		0.008	0.01	2.80E-06	2,80E-04

The estimated HQs for the OPPs levels of carrot roots from the farms were below 1. These indicate that acceptable risks were associated with OPPs of carrot roots from the farms. Thus, individuals consuming these carrot roots are mostly likely free from unwanted health issues linked to human exposure to OPPs.

The estimated HQ-values (Table 22) could have resulted from the fact that these pesticides might have been applied to the carrot plants at their early stage of cultivation. The low HQ-values could have also resulted due to the fact that carrot plants are morphologically effective in metabolizing OPPs to lower levels upon maturity. These observations corresponded to that of Bonmatin *et al*. (2015).

Estimated HQ-data for HQs levels of carrot roots from the markets were Diazinon (1.23E-03), Dimethoate (1.2E-03), Pirimiphos (1.37E-03), Chlorpyrifos (1.57E-04), Parathion (8.75E-05), Profenofos (1.05E-04) and Malathion (2.80E-04). These values were also below 1 indicating that individuals who bought and consumed carrot roots from markets within the study area appeared to be free from unwanted health issues associated with human exposure to OPPs.

Generally, estimated HQs were relatively high for carrot roots sampled from the farms than those from the markets. These observations were accepted as pesticides degradation continued during transport of carrots to the markets.

Though the estimated HQs predicted no health risks, continuous ingestion of the carrot roots might expose consumers to health risk associated with Diazinon, Dimethoate and Pirimiphos since their levels in the carrot roots were above 0.01 mg/kg allowed by USEPA (2009) and EU (2013).

4.7.5 Estimate HQs for organochlorine pesticides in carrot roots

Health quotient for organochlorine pesticides in carrot roots from the carrot farms and the markets were also estimated and data reported (Table 23). The estimated HQs for the organochlorine pesticides were below 1 (Table 23). These indicate that consumers of the carrot roots appeared not be at risk from organochlorine pesticides levels of the carrot roots. These findings agreed favourably with that of Akoto *et al.* (2016) who reported that HQ below 1, the food concerned is considered acceptable whilst above 1, the food concerned is considered to be a risk to the consumer.

Table 23: Health quotient of organochlorines pesticides in carrot

Pesticides	Source	Mean (mg/kg)	ADI**(mg/kg/day)**	EDI (mg/kg/day)	HQ
Lindane	Farm	0.007	0.01	1.60E-05	1.60E-03
Heptachlor		0.007	0.01	1.60E-05	1.60E-03
Aldrin		0.032	0.01	7.31E-05	7.31E-03
P’P’- DDE		0.027	0.04	1.54E-05	1.54E-03
Dieldrin		0.025	0.01	5.71E-05	5.71E-03
Beta Endosulfan		0.055	0.04	1.26E-04	3.14E-03
Beta HCH		0.005	0.01	1.14E-05	1.89E-02
Methoxychlor		0.006	0.01	1.37E-05	1.37E-03
Endrin		0.029	0.01	6.62E-05	6.62E-03
Lindane	Market	0.006	0.01	1.37E-05	1.37E-03
Heptachlor		0.003	0.01	6.85E-06	6.85E-04
Aldrin		0.029	0.01	6.62E-05	6.62E-03
P’P’- DDE		0.021	0.04	4.80E-05	1.20E-03
Dieldrin		0.012	0.01	2.74E-05	2.74E-03
Beta Endosulfan		0.054	0.04	1.23E-04	3.08E-03
Beta HCH		0.003	0.01	6.85E-06	6.85E-04
Methoxychlor		0.005	0.01	1.14E-05	1.14E-03
Endrin		0.023	0.01	5.25E-05	5.25E-03

The estimated HQ-values (Table 23) could have resulted from the rapid breakdown of the pesticides by active soil enzymes which might have been released from dying organisms, soil micro-organisms, roots of plant or in excreta of soil animals as reported by Sherene (2017).

However, continuous ingestion of the carrot roots could pose risk to consumers since Aldrin 0.032 mg/kg), Dieldrin (0.025 mg/kg), Beta Endosulfan (0.055 mg/kg) and Endrin (0.029) levels of carrot roots from the farms were above 0.01 mg/kg permitted for each of the pesticides by USEPA and EU (EU, 2013; USEPA, 2009). These observations also corroborated well with that of Ekevwe *et al.* (2021) who reported HQs below 1 for Endosulfan 1 (3.0E-02), Lindane (1.0E-02) and Methoxychlor (7.5E-01) but mean levels were above 0.01 mg/kg set by EU.

4.7.6 Estimated HQs for synthetic pyrethroids in carrot roots

Health quotient (HQ) of synthetic pyrethroids in carrot roots were also estimated and presented (Table 24). Estimated HQ values were below 1. This indicates that consumers of the carrot roots at the time of this study appeared to be safer from the effects of the synthetic pyrethroids (Table 24). The estimated HQ-values (Table 24) could have resulted from an increased rate of leaching due to low soil organic matter and low clay contents as reported by Asare (2011).

However continuous consumption of these carrot roots over extended period could instigate some unwanted health issues associated with Permethrin and Cypermethrin. This is due to the fact that Permethrin (0.023 mg/kg) and Cypermethrin (0.021 mg/kg) contents of the carrot roots exceeded 0.02 mg/kg permitted by USEPA (2009) and European Union (2013). This finding agreed favourably with that of Akomea-Frimpong *et al*. (2016) where health quotient of some synthetic pyrethroids in ready- to-eat vegetables were found to below 1. Though the estimated HQs herein suggested no pending danger from the synthetic pyrethroids, they could accumulate in fatty tissues of consumers and exert chronic health effect when exposed to them over an extended period as reported by Kumar *et al.* (2013).

Table 24: Health quotient of synthetic pyrethroids pesticides in carrot roots

Pesticides	Source	Mean (mg/kg)	USEPA/EU (mg/kg)	EDI (mg/kg/day)	HQ
Allethrin	Farm	0.009	0.01	3.15E-06	3.15E-04
Permethrin		0.023	0.05	8.05E-06	1.61E-04
Cyfluthrin		0.014	0.02	4.90E-06	2.45E-04
Cypermethrin		0.021	0.01	7.35E-06	7.35E-04
Fenvalerate		0.018	0.02	6.30E-06	3.15E-04
Deltamethrin		0.013	0.01	4.55E-6	4.55E-04
Allethrin	Market	0.008	0.01	2.80E-06	2.80E-04
Permethrin		0.011	0.05	3.85E-06	7.70E-05
Cyfluthrin		0.010	0.02	3.50E-06	1.75E-04
Cypermethrin		0.021	0.01	7.35E-06	7.35E-04
Fenvalerate		0.019	0.02	6.65E-6	3.33E-04
Deltamethrin		0.017	0.01	5.95E-6	5.95E-04

4.7.7 Health quotient of organophosphate pesticides in green pepper fruits investigated

Health quotient (HQ) of organophosphate pesticides (OPPs) in green pepper fruits from the farms and the markets were estimated to assess the risk associated with OPPs levels of the investigated green pepper fruits (Table 25). The HQ-values were below 1 indicating that consumers of the green pepper at the time of this work appeared not to be affected by OPPs levels of the green pepper fruits.

Estimated HQ-values for green pepper fruits from the farms had the order, Profenofos (7.35E-03) > Pirimiphos (7.00E-04) > Malathion (4.90E-04) > Diazinon (3.33E-04) > Parathion (1.75E-04) > Dimethoate (1.40E-04) > Chlorpyrifos > (7.00E-05). Although the estimated HQs suggested no apparent health risk, possible bioaccumulation of organophosphate pesticides in fatty tissues of humans could cause consumers to suffer unwanted health issues associated with organophosphate pesticides as by Akomea-Frempong *et al*. (2017). For example, concentration of Pirimiphos (0.020 mg/kg) and Profenofos (0.021 mg/kg) levels of green pepper fruits from the farms were above 0.01 mg/kg set by the USEPA and EU for each of the pesticides. Thus, though HQs predicted no apparent health risk of Pirimiphos and Profenofos, they could initiate some health issues in consumers when the green pepper fruits ingested over an extended period.

The estimated HQs for green pepper fruits from the markets were Dimethoate (1.05E-03) > Profenofos (7.70E-04) > Pirimiphos (6.30E-04) > Malathion (4.90E-04) > Chlorpyrifos (2.10E-04) > Diazinon (1.84E-04) > Parathion (1.75E-04) > Dimethoate (1.05E-03). The HQs were below 1 indicating that acceptable health risks were associated with OPPs levels of the investigated green pepper fruits from the markets. Thus, individuals who consumed these green pepper fruits at the time of this appeared to be free from the unwanted health issues associated with OPPs.

Though the estimated HQs for Dimethoate (1.05E-03), Pirimiphos (6.30E-04) and Profenofos (7.70E-04) were below 1, Dimethoate (0.030 mg/kg), Pirimiphos (0.018) and Profenofos (0.022) levels of the green pepper fruits from the markets are of health concern since they were above 0.01 mg/kg acceptable by USEPA (2009) and EU (2013) as levels protective of human health (Table 25).

Table 25: Health quotient of organophosphate pesticides in green pepper

Pesticides	Source	Mean (mg/kg)	**ADI(mg/kg/day)**	EDI (mg/kg/day)	HQ
Diazinon	Farm	0.038	0.04	1.33E-05	3.33E-04
Dimethoate		0.040	0.01	1.40E-06	1.40E-04
Pirimiphos		0.020	0.01	7.00E-06	7.00E-04
Chlorpyrifos		0.002	0.01	7.00E-07	7.00E-05
Parathion		0.025	0.04	8.75E-06	1.75E-04
Profenofos		0.021	0.01	7.35E-05	7.35E-03
Malathion		0.014	0.01	4.90E-06	4.90E-04
Diazinon	Market	0.021	0.04	7.35E-06	1.84E-04
Dimethoate		0.030	0.01	1.05E-05	1.05E-03
Pirimiphos		0.018	0.01	6.30E-06	6.30E-04
Chlorpyrifos		0.006	0.01	2.10E-06	2.10E-04
Parathion		0.020	0.04	7.00E-06	1.75E-04
Profenofos		0.022	0.01	7.70E-06	7.70E-04
Malathion		0.014	0.01	4.90E-06	4.90E-04

4.7.8 Health quotient of organochlorine pesticides in green pepper fruits investigated

Health quotient (HQ) of organochlorine pesticides in the green pepper fruits from the studied farms and markets were also estimated and data reported (Table 26). Health quotients for organochlorine pesticides in green pepper fruits from the study farms were Aldrin (7.54E-03) > Heptachlor (5.25E-03) > Dieldrin (5.02E-03) > Beta HCH (3.65E-03) > Lindane (1.60E-03) > Endrin (1.37E-03) > Beta Endosulfan (1.35E-03) P’P’- DDE (1.26E-03) > Methoxychlor (4.57E-04). Health quotients for organochlorine pesticides in green pepper fruits bought from the study markets were Aldrin (7.54E-03) > P’P’- DDE (6.85E-03) > Heptachlor (4.80E-03) > Dieldrin (3.88E-03) > Beta Endosulfan (2.72E-03) > Beta HCH (2.28E-03) > Methoxychlor (1.14E-03) > Lindane (9.13E-04).

Table 26: Health quotient of organochlorines pesticides in green pepper

Pesticides	Source	Mean (mg/kg)	ADI(mg/kg/ day)	EDI (mg/kg/day)	HQ
Lindane	Farm	0.007	0.01	1.60E-05	1.60E-03
Heptachlor		0.023	0.01	5.25E-05	5.25E-03
Aldrin		0.033	0.01	7.54E-05	7.54E-03
P'P'- DDE		0.022	0.04	5.02E-05	1.26E-03
Dieldrin		0.022	0.01	5.02E-05	5.02E-03
Beta Endosulfan		0.059	0.04	1.35E-04	1.35E-03
Beta HCH		0.016	0.01	3.65E-05	3.65E-03
Methoxychlor		0.002	0.01	4.57E-06	4.57E-04
Endrin		0.006	0.01	1.37E-05	1.37E-03
Lindane	Market	0.004	0.01	9.13E-06	9.13E-04
Heptachlor		0.021	0.01	4.80E-05	4.80E-03
Aldrin		0.031	0.01	7.08E-05	7.08E-03
P'P'- DDE		0.012	0.04	2.74E-05	6.85E-03
Dieldrin		0.017	0.01	3.88E-05	3.88E-03
Beta Endosulfan		0.030	0.04	6.85E-05	2.72E-03
Beta HCH		0.010	0.01	2.28E-05	2.28E-03
Methoxychlor		0.005	0.01	1.14E-05	1.14E-03
Endrin		0.005	0.01	1.14E-05	1.14E-03

These estimated HQs were below 1 indicating that at the time of this study, organochlorine pesticides contents of green pepper fruits harvested by farmers and those bought from the markets appeared to be safe for consumption as predicted by the HQ data. These observations corroborated well with that of Njoku *et al.* (2017) where HQs below 1 were recorded for pesticides in vegetables sold in some markets in Lagos State, Nigeria and Munawar*et al.* (2021) who reported HQs below 1 for organochlorine pesticides in vegetables from Cameron Highlands and Malaysia. However, Heptachlor, Aldrin, Dieldrin, Beta HCH and Beta Endosulfan contents of green pepper fruits from the study farms 0.023, 0.033, 0.022, 0.016 mg/kg and Beta Endosulfan respectively could pose serious public health issue since they were above USEPA (2009) and EU (2013) 0.01 mg/kg protective of human health. This observation is due to the fact that organochlorine pesticides have high affinity for fat contents of human tissues. Thus, they could accumulate in fatty tissue to levels that could induce unwanted health outcomes in consumers as reported by Chiu *et al*. (2015).

4.7.9 Health quotients of synthetic pyrethroid pesticides in green pepper fruits samples

Health quotient (HQ) of synthetic pyrethroids in the green pepper fruits sampled from the farms and markets were also estimated and data presented (Table 27). Estimated HQs ranged from Cymethrin (1.19E-04) to Deltamethrin (2.17E-03) (Table 27).

HQs for synthetic pyrethroids contents of green pepper fruits from the study farms and markets were below 1. This implies that at the time of this study, acceptable risks were associated with synthetic pyrethroids contents of the green pepper fruits. Hence, consumers were not likely to suffer health issues of synthetic pyrethroids upon ingestion of the green pepper fruits.

Though estimated HQs predicted no apparent unwarranted health issues of synthetic pyrethroids, Deltamethrin contents of green pepper fruits from farms (0.062 mg/kg) and markets concentrations of the Deltamethrin (0.050 mg/kg) were above 0.02 mg/kg allowed by USEPA (2009) and EU (2013) to be protective of human health (Table 27). Thus, consumers of green pepper fruits within the study area overtime could suffer some unwanted health issues of Deltamethrin as indicated in a report by Asare (2011).

Table 27: Health quotients of pyrethroid pesticides in green pepper

Pesticides	Source	Mean (mg/kg)	ADI (mg/kg)	EDI (mg/kg/day)	HQ
Allethrin	Farm	0.005	0.01	1.75E-06	1.75E-04
Permethrin		0.022	0.05	7.70E0-6	1.54E-04
Cyfluthrin		0.029	0.04	1.02E0-5	2.54E-04
Cypermethrin		0.019	0.05	6.65E-06	1.39E-04
Fenvalerate		0.020	0.04	7.00E-06	1.75E-04
Deltamethrin		0.062	0.01	2.17E-05	2.17E-03
Allethrin	Market	0.006	0.01	2.10E-06	2.10E-04
Permethrin		0.026	0.05	9.10E-06	2.82E-04
Cyfluthrin		0.026	0.04	9.10E-06	2.28E-04
Cypermethrin		0.017	0.05	5.95E-06	1.19E-04
Fenvalerate		0.018	0.04	6.30E-06	1.58E-04
Deltamethrin		0.050	0.01	1.75E0-5	1.75E-03

4.7.10 HQs of organophosphate pesticides in investigated lettuce

Health quotients (HQs) of organophosphate, organochlorine and synthetic pyrethroid pesticides in lettuce from the vegetable farms and markets were assessed and data presented (Table 28). HQs for Diazinon, Dimethoate, Pirimiphos, Chlorpyrifos, Parathion, Profenofos and Malathion were 1.19E-03, 1.02E-03, 1.12E-03, 5.95E-04, 2.36E-04, 2.45E-04 and 2.03E-04 respectively for lettuce from farms within the study area whilst those bought from markets had HQs of 1.09E-03, 8.75E-04, 1.09E-03, 4.90E-04, 1.58E-02, 1.400E-04 and 1.54E-04 respectively.

Table 28: Health quotient of organophosphate pesticides in lettuce investigated

Pesticides	Source	Mean (mg/kg)	**ADI(g/kg g/day)**	EDI (mg/kg/day)	HQ
Diazinon	Farm	0.034	0.01	1.19E-05	1.19E-03
Dimethoate		0.029	0.01	1.02E-05	1.02E-03
Pirimiphos		0.032	0.01	1.12E-05	1.12E-03
Chlorpyrifos		0.017	0.01	5.95E-06	5.95E-04
Parathion		0.027	0.04	9.45E-06	2.36E-04
Profenofos		0.007	0.01	2.45E-06	2.45E-04
Malathion		0.029	0.05	1.02E-05	2.03E-04
Diazinon	Market	0.031	0.01	1.09E-05	1.09E-03
Dimethoate		0.025	0.01	8.75E0-6	8.75E-04
Pirimiphos		0.031	0.01	1.09E-05	1.09E-03
Chlorpyrifos		0.014	0.01	4.90E-06	4.90E-04
Parathion		0.018	0.04	6.30E-06	1.58E-02
Profenofos		0.004	0.01	1.40E-06	1.400E-04
Malathion		0.022	0.05	7.70E-06	1.54E-04

Health quorients for organophosphate pesticides contents of the lettuce were below 1. This indicates health risks associated with contents of the lettuce were acceptable. Although estimated HQs for Diazinon (1.19E-03), Dimethoate (1.02E-03) and Pirimiphos (1.12E-03) predicted acceptable risk, their contents in the lettuce were above 0.02 mg/kg permitted by USEPA (2009) and EU (2013) for Diazinon, Dimethoate and Pirimiphos. Hence, continuous consumption of the lettuce could lead to bioaccumulation of Diazinon, Dimethoate and Pirimiphos in the tissues of consumers and cause consumers to endure negative effects of the pesticides. Observations made herein are at variance with that of Elgueta *et al.* (2020) where the estimated HQs for Methamidophos (15.00), Difenoconazole (13.48), Boscalid (1334) and Cyprodinil (1435) for their contents in lettuce from farms of Metropolitan Region Chile were above 1.

4.7.11 HQs of organochlorine pesticides in investigated lettuce

Health quotient (HQ) of the organochlorine pesticides in lettuce from the farms and markets within the study areas of the Asante-Mampong Municipality were assessed and reported (Table 29). Health quotient (HQ) estimated for organochlorine contents of lettuce from the farms were Aldrin (8.22E-03) > Beta Endosulfan (3.25E-03) > P'P' DDE (1.49E-03) > Dieldrin (1.48E-03) > Beta HCH (1.37E-03) > Lindane (1.14E-03) > Endrin (9.13E-04) = Methoxychlor (9.13E-04) whist those purchased from thr markets were Aldrin (5.71E-03) > Beta Endosulfan (2.97E-03) > Beta HCH > (1.82E-03) > Lindane (1.60E-03) > Heptachlor (1.37E-03) > (1.26E-03). HQ-values were below 1 indicating that at the time of this study, individuals who ingested lettuce from the investigated farms and merkets appeared to be free from negative effects of organochlorine pesticides on humans and these corroborated well with that of Elgueta (2020) *et al*. who reported HQ-values of organochlorine pesticides in lettuce from farms of Metropolitan Region of Chile below 1. Thus, risks associated with organochlorine pesticides contents of the lettuce were acceptable. Though estimated HQs for the pesticides predicted acceptable risk levels, Aldrin (0.036 mg/kg), Dieldrin (0.026 mg/kg) and Beta Endosulfan (0.057 mg/kg) contents of the lettuce were above 0.01 mg/kg allowed by USEPA (2009) and EU (2013) for Aldrin and Dieldrin and 0.05 mg/kg allowed by USEPA (2009) and EU (2013) for Beta Endosulfan. Hence patrons of lettuce might endure some unwanted effects of Aldrin and Dieldrin and Beta Endosulfan as reported by Asare (2011), Bempah *et al*. (2021) and Darko *et al*. (2007).

Table 29: Health quotient of organochlorine pesticides in lettuce from study sites

Pesticides	Source	Mean (mg/kg)	**ADI(mg/kg/day)**	EDI (mg/kg/day)	HQ
Lindane	Farm	0.005	0.01	1.14E-05	1.14E-03
Heptachlor		0.006	0.01	1.37E-05	1.37E-03
Aldrin		0.036	0.01	8.22E-05	8.22E-03
P'P'- DDE		0.026	0.04	5.94E-05	1.49E-03
Dieldrin		0.026	0.01	5.94E-05	1.48E-03
Beta Endosulfan		0.057	0.04	1.30E-04	3.25E-03
Beta HCH		0.006	0.01	1.37E-05	1.37E-03
Methoxychlor		0.004	0.01	9.13E-06	9.13E-04
Endrin		0.004	0.01	9.13E-06	9.13E-04
Lindane	Market	0.007	0.01	1.60E-05	1.60E-03
Heptachlor		0.006	0.01	1.37E-05	1.37E-03
Aldrin		0.025	0.01	5.71E-05	5.71E-03
P'P'- DDE		0.022	0.04	5.02E-05	1.26E-03
Dieldrin		0.025	0.01	5.71E-05	5.71E-03
Beta Endosulfan		0.052	0.04	1.12E-04	2.97E-03
Beta HCH		0.008	0.01	1.82E-05	1.82E-03
Methoxychlor		0.004	0.01	9.13E-06	9.13E-04
Endrin		0.006	0.01	1.37E-05	1.37E-03

4.7.12 Estimated HQs for synthetic pyrethroids in investigated lettuce

The health quotients for synthetic pyrethroids in lettuce investigated were estimated and reported (Table 30). Health quotient (HQ) estimated for synthetic pyrethroids contents of lettuce from the farms were Fenvalerate (6.65E-04) > Permethrin (2.28E-04) > Allethrin (1.75E-04) > Cyfluthrin (2.67E-05) Cypermethrin (1.54E-05) whilst that of markets were Fenvalerate (5.60E-04) > Deltamethrin (3.50E-04) > Allethrin (1.40E-04) > Permethrin (1.05E-04) > Cyfluthrin (1.50E-05) > Cypermethrin (1.19E-05).

Table 30: Health quotient of pyrethroids pesticides in lettuce

Pesticides	Source	Mean (mg/kg)	**ADI (mg/kg/day)**	EDI (mg/kg/day)	HQ
Allethrin	Farm	0.005	0.01	1.75E-06	1.75E-04
Permethrin		0.026	0.04	9.10E-06	2.28E-04
Cyfluthrin		0.064	0.84	2.24E-05	2.67E-05
Cypermethrin		0.044	1.00	1.54E-05	1.54E-05
Fenvalerate		0.019	0.01	6.65E-06	6.65E-04
Deltamethrin		0.026	0.04	2.10E-06	2.28E-04
Allethrin	Market	0.004	0.01	1.40E-06	1.40E-04
Permethrin		0.013	0.04	4.20E-06	1.05E-04
Cyfluthrin		0.036	0.84	1.26E-05	1.50E-05
Cypermethrin		0.034	1.00	1.19E-05	1.19E-05
Fenvalerate		0.016	0.01	5.60E-06	5.60E-04
Deltamethrin		0.040	0.04	1.40E-05	3.50E-04

HQs-values were below 1 indicating that risks posed by their occurrence in the lettuce were acceptable. Hence, consumers might not be at risk from synthetic pyrethroids contents of the lettuce. This finding agreed favourably with that of Nisha *et al.* (2021) where estimated HQs for Acetamiprid (0.731) and Cypermethrin (0.890) were below 1. These HQs were considered to be acceptable risks and health status of consumers of those lettuce were suggested not to be affected by Acetamiprid and Cypermethrin contents of the lettuce (Riyazuddin *et al*, 2021).

4.6.13 Combined health quotients and health risk indices of pesticides in investigated vegetables

The combined health quotients (CHQs) and health indices (CHIs) for the organophosphate, organochlorine, and synthetic pyrethroid pesticides of cabbage heads, carrot roots, green pepper fruits and the lettuce leaves from the study sites were computed and presented (Table 31). The combined health hazard quotients (CHQs) of the investigated pesticides to consumers were determined to investigate possibility of unwanted health issues associated with pesticides upon consumption of the investigated vegetables. Combined hazard quotient (CHQs) above 1 implies consumers of the vegetables might have unwanted health issues whilst CHQ below 1 indicates that consumers of the vegetables might not endure adverse health issues linked to the pesticide. Even though, combined health quotients for organophosphates, organochlorines and synthetic pyrethroid pesticides contents of the investigated vegetables where below 1, continuous consumption could lead to their accumulation in tissues of consumers.

Combined health quotients (CHQs) for organophosphate, organochlorine and synthetic pyrethroid pesticides in cabbage heads from the farms were 5.30E-03, 3.87E-02 and 2.93E-03 respectively with associated CHI of 4.69E-02 whilst that of the markets were 5.15E-03, 3.15E-02 and 7.09E-03 respectively with CHI 4.37E-02. Estimated CHQs of pesticides in carrots roots from the farms were organochlorine (4.78E-02) > organophosphate (5.13E-03) > synthetic pyrethroid (2.23E-03) pesticides. The CHI linked to the combined HQs of the organophosphate, organochlorine and synthetic pyrethroid pesticides contents of the carrot roots from the carrot farms was 5.52E-02. CHQs for organophosphate, organochlorine and synthetic pyrethroid pesticides contents of carrot roots from the carrot markets were 4.37E-03, 2.28E-02 and 2.19E-03 respectively.

CHQs associated with organophosphate, organochlorine and synthetic pyrethroid pesticides contents of green pepper from the farms were 4.90E-03, 2.75E-02 and 3.07E-

03 respectively with CHI of 3.55E-02. Conversely, CHQs of organophosphate, organochlorine and synthetic pyrethroid pesticides contents of green pepper from the markets were 3.02E-03, 3.08E-02 and 2.65E-03 respectively with associated CHI of 3.65E-02. Organophosphate, organochlorine and synthetic pyrethroid pesticides contents of lettuce from the farms had estimated CHQs of 4.61E-03 (organophosphate), 2.01E-02 (organochlorine) and 1.34E-03 (synthetic pyrethroids) and the CHQs (HI) associated with each class of pesticides in the lettuce from the farms was 2.61E-02. At the market level, the estimated CHQs were 2.27E-02 (organochlorine) > 4.00E-03 (organophosphate) > 1.18E-03 (synthetic pyrethroids) with corresponding CHI of 2.79E-02 for individual class of the investigated pesticides contents of lettuce from the markets.

Estimated CHQs and CHIs were below 1 indicating that consumers of cabbage heads, carrot roots, green pepper fruits and lettuce leaves in the Asante-Mampong Municipality at the time of this study were not expected to suffer adverse health issues linked to the investigated class of pesticides as predicted by their CHQs and CHIs estimated data (Table 30). These findings corroborated favourably with that of Akomea-Frempong *et al*. (2017) where HIs were estimated to be organophosphates (2.45×10^{-3}) and synthetic pyrethroids (2.57×10^{-3}). Hence the need for Ghana EPA (GEPA) to put measures in place to ensure that farmers would not apply pesticides above recommended levels to vegetables.

Table 31: Combined HQ and HI of pesticides in investigated cabbage, carrot, green pepper and lettuce samples

Vegetables	Pesticide	Sample sites	CHQ(HI)	CHI
Cabbage	Organophosphate	Farm	5.30E-03	
	Organochlorines		3.87E-02	4.69E-02
	Synthetic Pyrethroids		2.93E-03	
Cabbage	Organophosphate	Market	5.15E-03	
	Organochlorines		3.15E-02	4.37E-02
	Synthetic P yrethroids		7.09E-03	
Carrot	Organophosphate	Farm	5.13E-03	
	Organochlorines		4.78E-02	5.52E-02
	Synthetic Pyrethroids		2.23E-03	
Carrot	Organophosphate	Market	4.37E-03	
	Organochlorines		2.28E-02	2.94E-02
	Synthetic Pyrethroids		2.19E-03	
Green pepper	Organophosphate	Farm	4.90E-03	
	Organochlorines		2.75E-02	3.55E-02
	Synthetic Pyrethroids		3.07E-03	
Green pepper	Organophosphate	Market	3.02E-03	
	Organochlorines		3.08E-02	3.65E-02
	Synthetic Pyrethroids		2.65E-03	
Lettuce	Organophosphate	Farm	4.61E-03	
	Organochlorines		2.01E-02	2.61E-02
	Synthetic Pyrethroids		1.34E-03	
Lettuce	Organophosphate	Market	4.00E-03	
	Organochlorines		2.27E-02	2.79E-02
	Synthetic Pyrethroids		1.18E-03	

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary

This chapter presents summary, conclusion from the study as well as recommendations made.

Vegetables provide vital nutrients for good maintenance of human body and health as indicated by Hanif *et al.* (2006). These nutrients include minerals and vitamins which help to improve normal functioning of the immune system, promote healthy living among humans, among others as reported by Yahia *et al.* (2019). Vegetables also contain active compounds which reduce effects of cardiovascular diseases in humans (Alissa and Ferns, 2012). However, vegetables contamination with high levels of pesticides occur as farmers frequently apply pesticides to crops in an attempt to reduce loses and maximum profits (Asare, 2011). Although vegetables play vital roles in health status of individuals, their accumulation by pesticides could detrimentally affect population who via ingestion become exposed to pesticides.

Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method for multi-pesticides extraction and clean-up for vegatables and soils was used. The levels of pesticides in the vegetables and soils were analysed using Gas Chromatography-Mass Spectrometry (Varian C-P GC-ECD).

This study investigated levels of organophosphate, organochlorine and synthetic pyrethroid pesticides in cabbage, carrot, green pepper and lettuce grown in the Asante-

Mampong Municipality of the Ashanti Region of Ghana. The study also investigated correlation between pesticides levels in the investigated vegetables of selected farmlands and their associated physico-chemical parameters. Again, HQ and HI were investigated.

Complete Randomized Design method of sampling was used in collecting soil and vegetable samples. In all, twelve (12) vegetable farms were randomly selected from twenty (20) identified farms between January 15, 2021 and June 15, 2021. The twelve (12) farms were selected due to their large sizes compared to the eight (8) farms that were not included in this study. The average size of the farms where soils and vegetables were collected from were about two acres. Soil samples from the twelve (12) experimental farms were collected on the March 20, 2021 on the day vegetables were collected.

Chemical properties and physical compositions of the soil samples as well as organophosphate, organochlorine and synthetic pyrethroid pesticides contents of the soil samples were determined. Fresh and healthy cabbage, carrot, green pepper and lettuce obtained from the farms and the markets within the Asante-Mampong Municipality were analysed for their pesticides levels.

Laboratory data collected were statistically treated using one-way ANOVA to determine difference in properties of the soils. Pesticides contents of the soils and vegetables were reported in the form mean ± standard deviation of the mean levels using GenStat (Version 11.10) and the data obtained reported.

Soil samples used for chemical analysis, exchangeable cations and physical properties determination were taken at depth 0 to 20 cm from the twelve (12) different cabbage, carrot, green pepper and lettuce farms. pH of soils of the experimental farms ranged from 5.78 to 6.27. Organic carbon contents ranged from 0.76 to 0.87 %, total nitrogen contents ranged from 0.08 to 0.10 % whilst phosphorus contents were from 10.51 to 11.06 mg/kg. Cation exchange capacity (CEC) of the soil ranged from 2.86 ± 1.47 to 3.94 ± 1.01 cmol/kg, exchangeable Ca^{2+} ions ranged from 4.40 to 5.14 cmol/kg, Mg^{2+} (1.05 to 1.28 cmol/kg), K^{+} (0.45 to 0.56 cmol/kg), Na^{+} (0.23 to 0.49 cmol/kg), Al^{3+} (0.12 to 0.17 cmol/kg) and H^{+} (0.16 to 0.19 cmol/kg).

Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, Al^{3+} and H^{+} ions contents of the soils were low. These indicate that soils had reduced number of active sites. Thus, pesticides adsorption onto the soil particles was limited and weak. Hence, pesticides persisted for longer period in the soils. This was expected as pesticides molecules could easily leached into soil solution as reported by Asare (2011). Moisture contents of the soils ranged from 4.24 ± 1.23 to 6.41 ± 2.31 %, sand contents ranged from 79.11 to 81.78 %, silt 18.22 to 20.89 %, clay 9.56 to 10.67 % whilst soil bulk densities from 1.23 to 1.27 Mg/m^3. The soils were Bediase series (Orthi-Ferric Acrisol) in nature, with deep yellowish-red sandy-loam character and were free from concretion and stones.

Mean levels of organophosphate pesticides contents of soil from the vegetable farms ranged from 0.016 ± 0.05 to 0.059 ± 0.004 mg/kg. Dimethoate contents of soils were from 0.032 ± 0.003 to 0.043 ± 0.003 mg/kg, Pirimiphos 0.032 ± 0.006 to 0.040 ± 0.012 mg/kg, Parathion 0.033 ± 0.004 to 0.053 ± 0.003 mg/kg and Profenofos levels ranged from 0.051 ± 0.004 to 0.059 ± 0.004 mg/kg. The mean levels were above that recommended by USEPA/EU to be acceptable for soils. Organochlorine pesticides contents of the soils ranged from 0.013 ± 0.002 to 0.052 ± 0.003 mg/kg. Lindane ranged from 0.042 ± 0.002 to 0.050 ± 0.004 mg/kg, P'P'- DDE 0.041 ± 0.002 to 0.054 ± 0.002 mg/kg, Beta Endosulfan 0.044 ± 0.005 to 0.052 ± 0.003 mg/kg and Beta HCH ranged from 0.039 ± 0.006 to 0.048 ± 0.007 mg/kg. These mean levels were above recommended levels for organochlorine levels in the soils set by USEPA/EU as the permissible limit. These elevated organochlorine pesticides levels could be attributed to continuous use of the pesticides on the same soil and agreed favourably with that of Asare, (2011). Mean levels of synthetic pyrethriods contents of the soils ranged from 0.022 ± 0.006 to 0.074± 0.040 mg/kg. Mean levels of Allethrin ranged from 0.052 ± 0.004 to 0.060 ± 0.006 mg/kg whilst those of Cypermethrin were from 0.052 ± 0.002 to 0.072 ± 0.010 mg/kg. These were also above recommended levels in the soils allowed by USEPA/EU. These agreed favourably with that of Akomeah-Frimpong *et al.*, (2017) who recorded higher levels of Deltamethrin (0.021 mg/kg), Permethrin (0.46) and Fenvalerate (0.050) in ready-to-eat vegetables in Kumasi.

Parathion, Profenofos and Malathion contents of cabbage heads from the vegetable farms were 0.032 ± 0.011, 0.004 ± 0.002 and 0.013 ± 0.007 mg/kg whilst that of cabbage heads bought from the markets were Parathion (0.018 ± 0.008 mg/kg), Profenofos (0.004 ± 0.001 mg/kg) and Malathion (0.015 ± 0.001 mg/kg) and were below acceptable limits permitted by USEPA and EU. However, Parathion, Profenofos and Malathion levels were at variance with that of Asare (2011) where high levels of Diazinon (0.05 mg/kg), Dimethoate (0.022 mg/kg) and Chlorpyrifos (3.05 mg/kg) were reported for watermelon fruits grown at Nsadwir.

Beta Endosulfan, Beta HCH and Methoxychlor contents of cabbage heads from the farms were 0.040 ± 0.007, 0.003 ± 0.001 and 0.007 ± 0.002 mg/kg respectively whilst contents of those purchased from the markets were 0.028 ± 0.008 mg/kg (Beta Endosulfan), 0.002 ± 0.001 mg/kg (Beta HCH) and 0.006 ± 0.002 mg/kg (Methoxychlor) and below 0.010 mg/kg recommended by USEPA (2009) and EU (2013).

Mean contents of Lindane, Heptachlor, Aldrin, Dieldrin and Endrin of cabbage heads from the vegetable farms were 0.023 ± 0.008, 0.019 ± 0.008, 0.033 ± 0.005, 0.034 ± 0.007 and 0.025 ± 0.007 mg/kg respectively whilst that of cabbage heads bought from the vegetable markets were 0.020 ± 0.004 mg/kg (Lindane), 0.018 ± 0.001 mg/kg (Heptachlor), 0.019 ± 0.006 mg/kg (Aldrin), 0.032 ± 0.005 mg/kg (Dieldrin) and 0.015 ± 0.002 mg/kg (Endrin).

Allethrin (0.006 ± 0.002 mg/kg), Permethrin (0.037 ± 0.003 mg/kg), Cyfluthrin (0.010 ± 0.003 mg/kg), Cypermethrin (0.039 ± 0.001 mg/kg and Deltamethrin (0.051 ± 0.009 mg/kg) occurred in cabbage heads from the vegetable farms whilst that of cabbage heads bought from the markets Allethrin (0.004 ± 0.003 mg/kg), Permethrin (0.026 ± 0.008 mg/kg), Cyfluthrin (0.023 ± 0.007 mg/kg), Cypermethrin (0.031 ± 0.006 mg/kg) and Deltamethrin (0.061 ± 0.005 mg/kg). These mean levels were below USEPA (2009) and European Union (2013) acceptable levels of 0.01, 0.05, 0.03, 1 and 0.10 mg/kg respectively.

Diazinon (0.036 ± 0.007 mg/g), Dimethoate (0.039 ± 0.006 mg/kg), Pirimiphos (0.042 ± 0.004 mg/kg), Aldrin (0.032 ± 0.004 mg/kg), Dieldrin (0.025 ± 0.007 mg/kg) and Endrin (0.029 ± 0.007 mg/kg) occurred in carrot roots from the carrot farms whilst 0.035 ±

0.006 mg/kg (Diazinon), 0.032 ± 0.010 mg/kg (Dimethoate), 0.039 ± 0.005 mg/kg (Pirimiphos), 0.047 ± 0.008 mg/kg (Aldrin), 0.026 ± 0.003 mg/kg) (Dieldrin) and 0.023 ± 0.004 mg/kg (Endrin) occurred in carrot roots bought from the markets within the study area.

Diazinon, Dimethoate and Pirimiphos levels were above 0.010 mg/kg recommended by USEPA (2009) and European Union (2013). High levels of Diazinon, Dimethoate and Pirimiphos occurred in the carrot roots corroborated favourably with that of Asare (2011) where high levels of Diazinon (0.057 mg/kg), Dimethoate (0.022 mg/kg) and Chlorpyrifos (3.05 mg/kg) in watermelon fruits grown at Nsadwir. Aldrin, Dieldrin and Endrin contents of carrot roots were also above their respective allowable levels USEPA (2009) and European Union (2013).

Green pepper from the farms had Dimethoate (0.040 ± 0.005 mg/kg,), Pirimiphos (0.020 ± 0.0001 mg/kg), Profenofos (0.021 ± 0.002 mg/kg), Aldrin, (0.033 ± 0.005 mg/kg) and Dieldrin (0.022 ± 0.002 mg/kg) whilst that of green pepper fruits from markets were Dimethoate (0.030 ± 0.008 mg/kg), Pirimiphos (0.018 ± 0.002 mg/kg), Profenofos (0.022 ± 0.004 mg/kg), Aldrin (0.031 ± 0.005 mg/kg) and Dieldrin (0.017 ± 0.002 mg/kg). In all cases, mean concentrations of individual peaticides were above acceptable levels set by USEPA (2009) and the European Union (2013).

Mean concentrations of Diazinon, Dimethoate, Pirimiphos and Chlorpyrifos in lettuce from the lettuce farms were 0.034 ± 0.003 mg/kg, 0.029 ± 0.004 mg/kg and 0.032 ± 0.004 mg/kg respectively occurred whilst that of lettuce purchased from vegetable markets were Diazinon (0.031 ± 0.002 mg/kg), Dimethoate (0.025 ± 0.006 mg/kg), Pirimiphos (0.031 ± 0.008 mg/kg) and Chlorpyrifos (0.014 ± 0.005 mg/kg). These levels were above 0.01 mg/kg acceptable by USAEPA (2009) and European Union (2013). However, mean levels of Parathion, Profenofos and Malathion in lettuce from the farms and the markets were 0.05, 0.010 and 0.010 mg/kg respectively suctioned by USAEPA (2009) and the European Union (2013) to be protective of human health. Parathion, Profenofos and Malathion levels of lettuce from the markets agreed favourably with that reported by Kocourek *et al.* (2017) and Wongnaa *et al.* (2017).

Mean concentrations of Lindane (0.005 ± 0.001 mg/kg), Heptachlor (0.006 ± 0.002 mg/kg), P’P’- DDE (0.026 ± 0.001 mg/kg), Beta HCH (0.006 ± 0.004 mg/kg), Methoxychlor (0.004 ± 0.002 mg/kg) and Endrin (0.004 ± 0.001 mg/kg) occurred in lettuce from the farms whilst those from the markets had mean concentrations of Lindane (0.007 ± 0.003 mg/kg), Heptachlor (0.006 ± 0.002 mg/kg), P’P’- DDE (0.022 ± 0.004 mg/kg), Beta HCH (0.006 ± 0.004 mg/kg), Methoxychlor (0.005 ± 0.003 mg/kg) and Endrin (0.006 ± 0.002). These mean levels were below recommended maximum residue limits allowed by USEPA (2009) and the European Union (2013). Similarly, mean concentrations of Aldrin, Dieldrin, Beta Endosulfan in lettuce from the farms were 0.036 ± 0.003 mg/kg, 0.026 ± 0.005 mg/kg and 0.057 ± 0.005 mg/kg respectively whilst those in lettuce purchased from the markets were 0.027 ± 0.003 mg/kg (Aldrin), 0.025 ± 0.002 mg/kg (Dieldrin) and 0.052 ± 0.004 mg/kg (Beta Endosulfan). The mean levels were above maximum allowable residue limits suctioned by USEPA and the European Union. Levels of organochlorines above MRL in the lettuce could be detrimental to the health status of consumers due to their high affinity for fats and their sunsequent accumulations in the fatty tissues of humans. Hence, EPA should put measures in place to ensure that levels of pesticides in vegetable and other food crops would not exceed the recommended MRLs for human consumption.

Mean levels of Allethrin, Permethrin, Cyfluthrin, Cypermethrin, Fenvalerate and Deltamethrin in lettuce from the lettuce farms and markets were below maximum acceptable levels suctioned by USEPA (2009) and the European Union (2013). These observations agreed favourably witth that of Kocourek *et al.* (2019) and Wongnaa *et al.* (2019). These observations indicate that consumers of lettuce at the time of this study were likely to be free from adverse effects of synthetic pyrethroids.

Cabbage heads, carrot roots, green pepper fruits and lettuce leaves cultivated in the Asante-Mampong Municipality at the time of this study appeared not to pose health risk issues linked to organophosphate, organochlorine and synthetic pyrethroid pesticides upon consumption. This observation was affirmed by the estimated HQs and HIs which were below 1 for each member of each class of the pesticides investigated herein. Of the twenty-two (22) pesticides found in this study, only four (4) are currently approved for used by the European Union (EU pesticides approval list 2015). These were Malathion, Pirimiphos, Cypermethrin and Deltamethrin. However, in Ghana, eleven (11) have been approved for used by the Ghana EPA. They were Diazinon, Dimethoate, Chlorpyrifos, Malathion, Pirimiphos, Profenofos, Cypermethrin, Deltamethrin, Permethrin, Cyfluthrin and Fenvalerate. None of the organochlorine pesticides found herein has received approval for used by European Union and Ghana EPA. Hence, consumers of vegetables contaminated with organochlorine pesticides at the time of this study were likely to endure some health isuues associated with organochlorines.

5.2 Conclusion

The results of this study indicate that cabbage, carrot, green pepper and lettuce growers in the Asante-Mampong Municipality of the Ashanti Region of Ghana apply pesticides which are not recommended for use on crops. Desire to control pests, diseases, and maximize crop yield have led to application of large quantities of pesticides on cabbage, carrot, green pepper and lettuce grown in the municipality.

This study identified organophosphate, organochlorine and synthetic pyrethroid pesticides to be the most commonly used for cabbage, carrot, green pepper and lettuce cultivation. These pesticides occurred in the soils sampled in soils samples taken at depth 0 to 20 cm below the soil surface. Organophosphate, organochlorines and synthetic pyrethroid pesticides levels in the soils ranged from 0.016 ± 0.01 to 0.059 ± 0.007 mg/kg, 0.013 ± 0.006 to 0.054 ± 0.002 mg/kg and 0.022 ± 0.017 to (0.074 ± 0.039 mg/kg respectively. Mean levels of Dimethoate, Pirimiphos and Profenofos (organophosphate pesticides) in soil samples from all vegetable farms were above USEPA and EU recommended levels. Similarly, Lindane, P’P’-DDE, Beta Endosulfan and Beta HCH (organochlorine pesticides) mean levels of the soils were above recommended levels by USEPA and EU. Aside, Allethrin and Cypermethrin (synthetic pyrethroids) mean levels were above USEPA and EU recommended levels for soils. These indicate that vegetables which absorb nutrients from 0 to 20 cm below soil surfaces are likely to be contaminated with the pesticides.

Mean soil moisture contents ranged from 4.24 ± 1.23 to 6.41 ± 2.31%, sand contents ranged from 79.11 ± 4.59 to 81.78 ± 2.53%, clay ranged between 9.56 ± 2.71 to 10.67 ± 4.47% and silt contents ranged from 18.22 ± 4.54 to 20.89 ± 4.60%). Soil bulk densities ranged from 1.23 ± 0.08 to 1.27 ± 0.06 Mg/m^3, pH was 5.78 ± 0.12 to 6.27 ± 0.32, organic carbon contents ranged from 0.76 ± 0.09 to (0.87 ± 0.09%, available phosphorus components were between 10.51 ± 1.00 to 11.03 ± 0.69 mg/kg and cation exchange capacity ranged between 2.86 ± 1.47 to 3.94 ± 1.01. These soil properties were found to have contributed significantly to Diazinon, and Profenofos, Dimethoate, Pirimiphos, Heptachlor, Aldrin, Beta HCH, Methoxychlor, Dieldrin, Beta Endosulfan, Allethrin, Cyfluthrin and Deltamethrin levels of the vegetables.

The results obtained from the experimental farms and the markets indicated that cabbage, carrot, green pepper, lettuce farmers in the Asante-Mampong Municipality apply almost same pesticides on their vegetables. For instance, Diazinon was present in all vegetables at concentrations which ranged 0.040± 0.007 to 0.041± 0.004 mg/kg in the cabbage heads, Diazinon levels ranged from 0.035 ± 0.006 to 0.036 ± 0.007 mg/kg in carrot roots, Diazinon ranged from 0.021 ± 0.004 to 0.038 ± 0.004 mg/kg in the green pepper and Diazinon ranged between 0.031 ± 0.002 to 0.034 ± 0.003 mg/kg in the lettuce. When pesticides levels in all vegetables were compared with maximum limits set by USEPA and European Union, it was realized that mean levels of the Diazinon, Dimethoate, Pirimiphos, Chlorpyrifos (organophosphate pesticides), Lindane, Heptchlor, Dieldrin, Beta HCH and Endrin (organochlorine pesticides) and Fenvalerate and Deltamethrin (synthetic pyrethroids) were above recommended levels by USEPA and European Union (USEPA, 2009; EU, 2013).

The findings herein confirm that cabbage, carrot, green pepper and lettuce cultivated in the Asante-Mampong Municipality of the Ashanti Region of Ghana are contaminated with organophosphate, organochlorine and synthetic pyrethroids pesticides. The findings further indicated that water bodies and other food crops in the Asante-Mampong Municipality and its surrounding communities where cabbage, carrot, green pepper and lettuce are produce on large scale may be contaminated with high levels of pesticides. Cabbage, carrot, green pepper and lettuce farmers as well as consumers are likely to have elevated levels of pesticides in their tissues, blood and other bodly fluids. Thus, it is important that the vegetable farmers in the Asante-Mampong are educated on handling and application of pesticides. If farmers continuously applying pesticides at such high levels, it is likely that consumers would experience negative effects of the pesticides.

Health quotient and health risk indices for organophosphate, organochlorine and synthetic pyrethroid pesticides in the carrot, cabbage, green pepper and lettuce from the study sites were all below 1. This indicates that acceptable risks were associated with their consumption. Health quotients and health risk indices had direct relation to pesticides levels in the vegetables. However, consumers could be at risk from exposure to multiple pesticides when the vegetables are ingested regularly. The health risk indices of the pesticides in vegetable from the farms were 4.69E-02 (cabbage), 5.52E-02 (carrot), 3.55E-02 (green pepper) and 2.61E-02 (lettuce) whilst those in the vegetables from the markets were 4.37E-02 (cabbage), 2.94E-02 (carrot), 3.65E-02 (green pepper) and 2.79E-02 (lettuce). These HIs were similar to 1.21E-04 and 1.38E-04 reported by Hossain *et al.* (2015) and Akoto *et al.* (2015) respectively in similar works conducted on tomato fruits.

5.3 Recommendations

Based on the findings of this study, it is recommended that Ghana Environmental Agency, Food and Drug Authority and Ghana Standard Authority should:

1 Educate on handling and use of approved pesticides and at recommended levels to vegetables farms and vegetable croops.

2 Educate on negative health issues linked to pesticides applications.

3 Educated to allow ample time between pesticides application and harvesting period.

4 Finally, further studies should be done to determine pesticides levels in cucumber, garden eggs, tomatoes, onion among other vegetables which are also consumed by majority of people living in the Asante-Mampong municipality of the Ashanti Region of Ghana.

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APPENDICES

Appendix 1: The combined health risk of various pesticides in the investigated vegetables

Pesticide	Combined health index
Organophosphorus	4.82E-02
Organochlorine	3.09E-02
Synthetic pyrethroids	1.84E-02
Total	9.75E-02

Appendix 2: Acceptable maximum daily intake of organochlorine pesticides residues in in the various vegetables

Pesticides	Cabbage		Carrot		Green pepper		Lettuce	
	US/EUMLs	ADI(mg/ kg/daily)	US/EU MRLs	ADI(mg/ kg/daily)	US/EU MRLs	ADI(mg/ kg/daily)	US/EU MRLs	ADI(mg/ kg/daily)
Lindane	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Heptachlor	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Aldrin	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Dieldrin	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Beta Endosulfan	0.05	0.04	0.05	0.04	0.05	0.04	0.01	0.01
Beta HCH	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
P’P’ DDE	0.05	0.05	0.05	0.04	0.05	0.04	0.05	0.04
Methoxychlor	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Endrin	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

EU (2013); US EPA (2009), Akoto *et al.* (2015); Hossain *et al.* (2015).

Appendix 3: Acceptable maximum daily intake of organophosphate pesticides residues in in the various vegetables

Pesticides	**Cabbage**		**Carrot**		**Green pepper**		**Lettuce**	
	US/EU MRLs	ADI(mg/ kg/daily)	US/EU MRLs	ADI(mg/ kg/daily)	US/EU MRLs	ADI(mg/ kg/daily)	US/EU MRLs	ADI(mg/ kg/daily)
Diazinon	0.01	0.01	0.01	0.01	0.05	0.04	0.01	0.01
Dimethoate	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Pirimiphos	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Chlorpyrifos	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Parathion	0.05	0.04	0.05	0.04	0.05	0.04	0.05	0.04
Profenofos	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Malathion	0.02	0.01	0.02	0.01	0.02	0.01	0.05	0.05

Source: EU (2013); US EPA (2009), Akoto *et al*. (2015); Hossain *et al*. (2015).

Appendix 4: Acceptable maximum daily intake of synthetic pyrethroids pesticides residues in the various vegetables

Pesticides	**Cabbage**		**Carrot**		**Green pepper**		**Lettuce**	
	US/EU MRLs	ADI(mg/ kg/daily)	US/EU MRLs	ADI(mg/ kg/daily)	US/EU MRLs	ADI(mg/ kg/daily)	US/EU MRLs	ADI(mg/ kg/daily)
Allethrins	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Permethrin	0.05	0.05	0.05	0.05	0.05	0.05	1.00	0.84
Cyfluthrin	0.03	0.02	0.02	0.02	0.05	0.04	1.00	0.84
Cypermethrin	1.0	0.50	0.02	0.01	0.05	0.04	2.00	1.00
Fenvalerate	0.02	0.02	0.02	0.02	0.05	0.04	0.02	0.01
Deltamethrin	0.10	0.01	0.02	0.01	0.02	0.01	0.05	0.04

EU (2013); US EPA (2009), Akoto *et al.* (2015); Hossain *et al.* (2015)