LEVELS OF ORGANOCHLORINE INSECTICIDE RESIDUES IN FRESH TOMATOES FROM SOME SELECTED FARMING COMMUNITIES IN NAVRONGO, GHANA

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DEPARTMENT OF THEORETICAL AND APPLIED BIOLOGY

BY

NUNIFANT KONLAN TIMOTHY (BSc. CHEMISTRY)

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DECLARATION

I hereby declare that this submission is my own work towards the MSc and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.

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NUNIFANT KONLAN TIMOTHY Mr J. L. TERLABIE

(STUDENT) (SUPERVISOR)

DATE.................... DATE....................................

....

Dr P.K. BAIDOO

(HEAD OF DEPARTMENT)

DATE..................................

DEDICATION

I dedicate this thesis to my parents Mr and Mrs Nunifant for their love and support towards my education.

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First and foremost, I thank the Lord Almighty for the protection and direction that made it possible that I get this far.

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ABSTRACT

The concentrations of organochlorine insecticides residues in five tomato varieties from three farming communities in Navrongo (Bonia, Korania and Nangalkenia) were determined using gas chromatography in January and February 2011. A total of nineteen different organochlorine insecticides were detected, with at least five different residues in each sample. The residues were detected in the range of 0.0038 to 15.9007µg/kg. Beta HCH recorded the highest mean concentration (15.9007 µg/kg) at Korania and Cis-chlordane recorded the lowest mean concentration of 0.0038 µg/kg at Nangalkenia.

The mean concentrations of heptachlor, delta HCH, gamma HCH (Lindane), beta HCH and p, p-DDT were relatively higher than the other organochlorine pesticides detected.

Cis-heptachlor epoxide, oxychlordane, Cis-chlordane, hexachlorobenzene, and Cis-Nonachlor were not detected in most of the samples.

Two of the organochlorine insecticide residues detected (beta HCH and delta HCH) exceeded the UK/EC Maximum Residue Limits (MRLs). Although, almost all the organochlorine residues detected were below the UK/ EC MRLs, bioconcentration in the fatty tissues of consumers could result in chronic health effects.

A pair-wise comparison among concentrations of the organochlorine insecticides in the varieties indicated no statistically significant differences in concentrations.

Questionnaire survey indicated that most tomato farmers do not experience any health problems that can be associated with pesticide use.

In view of the damaging effects on human health and the environment, regular monitoring and analysis of organochlorine residues in the study area is recommended.

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ABBREVIATIONS

ADHD attention deficit hyperactivity disorder

ATSDR Agency for Toxic Substances and Disease Registry in the United States

CAC Codex Alimentarius Commission

CCPR Codex Committee on Pesticide Residues

DDA 2,2-bis(4-chlorophernyl)-acetic acid.

DDD Dichlorodiphenyldichloroethane

DDE Dichlorodiphenyldichloroethylene

DDT Dichlorodiphenyltrichloroethane

DNA Deoxyribonucleic acid

ECD electron capture detector

EDs endocrine disrupting chemicals

FAO Food and Agricultural Organization of the United Nations

GAEC Ghana Atomic Energy Commission

GAP Good Agricultural Practice(s) in the use of pesticides

GC Gas chromatography/ Chromatograph

HCB Hexachlorocyclobenzene

HCH Hexachlorocyclohexane

HPTLC High Performance Tin Layer Chromatography

IARC	International Agency for Research on Cancer
IUPAC	International Union of Pure and applied chemistry
JMPR	Joint FAO/WHO Meeting on Pesticide Residues
K_{ow}	octanol-water partition coefficient
LSD	Least significant difference
MCPA	4-chloro-2-methylphenoxy acetic acid
mg/L	Milligram per liter
MRL	Maximum residue limit/level
ND	Not Detected
ng/ml	nanogram per millimeters
o, p-isomer	ortho, para-isomer
OCPs	Organochlorine pesticides
OCs	Organochlorines
ORs	Odd ratios
p, p-isomer	para, para-isomer
PCB	Polychlorinated biphenyls
PD	Parkinson’s disease
POPs	Persistent organic pollutants
ppb	parts per billion
UN	United Nations
WHO	World Health Organization
γ- isomer	gamma isomer
µg/Kg	Microgram per kilogram

µg/L	Microgram per liter
µL	microliters

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

Pesticides are a group of chemicals made for the purpose of killing or otherwise deterring pest species. Pesticides are made in different forms: powders for mixing with water and spraying, granules and dusts for dusting, liquids for spraying, coatings on seeds, pellets to kill rodents, and others. They are sold in different packages: cans, bottles, buckets, bags and others.

Pesticides can be classified by target organism as insecticides (for controlling insects), herbicides (for controlling weeds), fungicides (for controlling fungi or moulds), or other pest control formulations. Many pesticides can also be grouped into chemical families. Prominent pesticide families include organochlorines, organophosphates, and carbamates. Organochlorine hydrocarbons (e.g. DDT) could be separated into dichlorodiphenylethanes, cyclodiene compounds, and other related compounds.

Pesticides are released into the environment during manufacturing, transport, handling and application to crops. They are inherently toxic and often associated with environmental contamination and adverse health effects in non-target organisms including humans.

Organochlorine (OC) pesticides are a large class of multipurpose chlorinated hydrocarbon chemicals. Many organochlorine pesticides are persistent organic pollutants (POPs), a class of chemicals known to break down very slowly and bioaccumulates in lipid rich tissue such as body fat. Organochlorine pesticides break down slowly in the environment and accumulate in the fatty tissues of animals. Thus, they stay in the environment and food web long after being applied (Swackhamer and Hites, 1988). DDT, now banned in Ghana because of its harm to the health of wildlife and people, is a notable example of an organochlorine pesticide.

There are many ways people can be exposed to these chemicals. Wind and rain may move pesticides away from where they were used, causing contamination of surface waters, groundwater and/or soil (Bouman et al., 2002, Shomar, et al., 2005)

Exposure may also occur through consumption of contaminated foods. Pesticides are carried long distances via atmospheric and oceanic currents from where they are manufactured and used, and build up in the fatty tissues of animals (Bentzen et al., 2008). Many studies have linked organochlorine pesticide exposure with consumption of contaminated animal products, mostly meat, dairy, fish, and marine mammals (Hagmar et al., 2001). Fetuses and children may be exposed to pesticides in utero as well as through breast milk (Jurewicz and Hanke, 2008).

In vegetable and fruit production, insecticides are used to control pests and fungicides to control diseases. They are applied directly to the crops and some may still be present as residues in or on the vegetables and fruits after their harvests, especially where there is abuse, misuse and overuse of the pesticides. As a result, consumers of food crops are exposed to pesticides which raise some health concerns. Residues from fruits and vegetables pose a greater threat to public health because they are usually taken raw or partially cooked.

Studies have shown an association between pesticide residues and health problems such as cancer, attention-deficit (hyperactivity) disorder, nervous system disorders and weakened immune systems (Wolff et al., 1993, Zahm et al., 1997, Sagiv et al., 2010). Many organochlorine pesticides are also endocrine disrupting chemicals (EDs) (Soto et al., 1995, Andersen et al., 1999). This means they have subtle toxic effects on the body's hormonal systems. Endocrine disrupting chemicals often mimic the body's natural hormones, disrupting normal functions and contributing to adverse health effects.

Due to the damaging effects on human health and the environment, concerns about pesticide residues in food have been growing. Many countries have introduced legislation to protect consumers from the hazards of pesticides. Most national governments today pay considerable attention to the data requirements for pesticide registration. In addition, even registered pesticides should follow a re-registration process which meets today's guidelines, regulatory triggers and safety profiles. The Pesticides Control and Management Act of 1996 (Act 528) makes the Environmental Protection Agency (EPA) of Ghana the lead Agency responsible for a comprehensive pesticide regulatory program. In that capacity, the EPA has the sole authority and responsibility to register all pesticides imported, exported, manufactured, distributed, advertised, sold or used within Ghana.

More recently, global conservation programs have arisen to protect all countries from environmental contaminants. For example, the Stockholm Convention on Persistent Organic Pollutants (POPs) is a global treaty entered in force in May 2004. The aim is to eliminate the production and use of twelve priority POPs including organochlorine pesticides such as aldrin, dieldrin, DDT and metabolites, endrin, heptachlor, chlordane, mirex and toxaphene. In August 2010, α and β- hexachlorocyclohexanes, lindane, chlordecone and pentachlorobenzene were added.

In Ghana, the organochlorines have been banned from use (EPA Ghana, 2008). However, they have been detected in food, meat sediments, water, human blood and breast milk (Ntow, 2001; Darko and Acquaah, 2007; Afful et al., 2010; Osei Tutu, 2011). This is partly because they have long environmental half-lives and so can persist in the environment years after they have been applied. The second reason is that they are still being used illegally.

In order to ensure that consumers are not exposed to unacceptable pesticide residue levels and also to preserve the environment, the amounts of residues found in food must be as low as possible. Pesticide residues in food crops can be reduced by following Good Agricultural Practices (GAP). A maximum residue level (MRL) is the highest level (concentration) of a pesticide residue that is legally tolerated in or on food or feed. It is the maximum residue levels likely to be left in food after it has been properly treated with a pesticide.

The idea to regulate pesticide residues to safe levels was originally introduced by the Joint FAO/WHO Expert Committee on Food additives in 1955. In order to implement the Joint FAO/WHO Food Standards Programme, Codex Alimentarius Commission (CAC), comprising 120 member nations, was established in 1964. The Codex Committee on Pesticide Residues (CCPR) is a subsidiary body of the Codex Alimentarius Commission that advises on all matters relating to pesticide residues. Its primary objective is to develop Maximum Residue Limits (MRLs) in order to protect the health of the consumer while facilitating international trade.

MRLs are determined by taking into account the food intake, the average body weight of human beings, and pesticide residue levels under good agricultural practices. A problem in establishing international MRLs is that daily intake of particular food commodities is quite different from one country to another depending on dietary customs. For this reason, MRLs set by the Codex Alimentarius Commission are a reference, not a directive, for individual countries.

The European Commission (EC) fixes MRLs for all food and animal feed marketed within the European Union. These are called EC/UK MRLs. The Regulation covers pesticides currently or formerly used in agriculture in or outside the European Union (EU). Where a pesticide is not specifically mentioned, a general default MRL of 0.01 mg/kg applies (https://secure. pesticides.gov.uk/MRLs).

Codex MRLs are used as guidance on acceptable levels but are only relevant within the European Union where they apply to a commodity for which EC statutory MRLs are not set.

1. 1. 2 USAGE OF PESTICIDES IN GHANA

Pesticides are widely used in many areas of modern agriculture as they are considered economically important for high yield production. In Ghana, there has been a rapid rise in the quantity of pesticides used in agriculture over the past ten years (Hogson, 2003). It is estimated that 87% of farmers in Ghana use chemical pesticides to control pests and diseases on vegetables (Dinham, 2003). The situation with pesticide use in Ghana is similar to those in many other African countries: the overall level of pesticide use is low but in the areas where they are used, the picture is similar to those countries where pesticides are heavily used. Pesticide use in Ghana is concentrated on cocoa, vegetables and fruits. More often than not, in these crops pesticides are over- and misused with the known negative effects on productivity, human health and environment (Gerken et al., 2001).

Organochlorine pesticides are widely used by farmers in Ghana because of their effectiveness and their broad-spectrum activity. Lindane is widely used on cocoa plantations, on vegetable farms, and for the control of stem borers in maize. Endosulfan, marketed as thiodan, is widely used in cotton growing areas on vegetable farms, and on coffee plantations (Gerken et al., 2001). Organochlorine pesticides such as DDT, Lindane and endosulfan are also employed to control ectoparasites of farm animals and pets in Ghana (Ntow et al., 2006).

The use of pesticides is not peculiar to agriculture alone. Pesticides have also been used in the public health sector. For example, temephos have been used by the Onchoccerciasis Programme in the Volta Basin for control of black flies (*Simulium spp*.) which transmit Onchocerciasis (African river blindness) to human beings and for control of domestic pests, e.g. cockroaches, flies, mosquitoes, ectoparasites including ticks, and other insects. Pesticides have also been used to control black flies along the banks of the Tano and Pra Rivers (Ntow, 2005).

1.2 OBJECTIVES

1.2.1 MAIN OBJECTIVE

To determine the levels of organochlorine insecticide residues in fresh tomatoes and assess if they pose any health risk to consumers.

1.2.2 SPECIFIC OBJECTIVES

1. To determine the levels of organochlorine insecticide residues in fresh tomatoes from selected farming communities in Navrongo

2. To compare the levels with UK/EC MRLs.
3. To determine if the farmers experience any health problems
4. To compare the insecticide residue levels in five tomato varieties.

1.3 JUSTIFICATION

The modern man is constantly exposed to a variety of toxic chemicals through the food we eat, the water we drink, the air we breathe, and the environment we live in. What is most worrying is that humans are exposed to such chemicals while still in the womb of the mother. The organochlorine pesticides are of greater concern because they are non-biodegradable and persistent. They accumulate in the environment and biomagnify through the human food chain (Simonich and Hites, 1995; Tanabe et al., 1998; Fisher, 1999; Muir et al., 1999). Pesticide residues above the recommended maximum residue levels (MRLs) make food commodities hazardous for human consumption. For example, pesticide residues have been associated with a wide range of health problems including endocrine disruption, reproductive and immune dysfunction, neurobehavioral and developmental disorders and cancer (Sanborn, 2004; Snedeker, 2001; Cocco et al., 2000; Andersen et al., 1999; Porta et al., 1999; Hoyer et al., 1998; Soto et al., 1995).

About 759 chemical and biological pesticides are used worldwide in the agriculture and health sectors. Of this, 33 pesticides have been classified by World Health Organization (WHO, 1998) as extremely hazardous to human health (class Ia), 48 as highly hazardous (class Ib), 118 as moderately hazardous (class II) and 239 as slightly hazardous (class III) and 149 pesticides have been considered as unlikely to cause acute hazard in normal use (class IV).

The Third World uses 80% of the world's pesticide and the World Health Organization (WHO, 1998) estimates that all of the 220,000 annual pesticide related deaths occur in the Third World.

Children are particularly vulnerable to the effects of exposure to pesticides. Reduced immunity in infants and children, and the concomitant increase in infection, also with developmental abnormalities, neurobehavioural impairment and cancer and tumour induction or promotion have been attributed to pesticides (Landrigan et al., 1993).

Residues in fruits and vegetables pose a greater risk because they are usually taken raw or partially cooked and also, they are usually harvested shortly after application (Amoah et al., 2006).

Due to the wide range of health problems caused by pesticides, their use has been a major concern. Many organochlorines have been banned or restricted.

Since the early 1960s, tomato farming has been taking place in the Upper East Region, especially in Navrongo on commercial basis for local consumption and for sale in other parts of Ghana, such as Tamale, Bolgatanga, Kumasi and Accra (Third World Network (TWN), 2007). Despite this long time cultivation of tomatoes with the massive pesticide use, there is no information about the likelihood of exposure of pesticides by the consumers and about the environmental contamination. This study seeks to address this concern.

CHAPTER TWO

LITERATURE REVIEW

2.1 Occurrence and levels of organochlorine pesticides in the environment and in humans

Organochlorine pesticides have been used in Ghana for more than 40 years, for agriculture and public health purposes. Various studies have been conducted on the agricultural and mining communities and on human fluids to evaluate the environmental contamination status and the level of accumulation in human body (Asante and Ntow, 2009).

A study conducted by Osei Tutu (2011) determined the types and levels of Organochlorine pesticide residues in the breast milk of 21 primiparae mothers in La, a suburb of Accra in the Greater Accra region of Ghana. Liquid-liquid extraction procedure was employed and extract clean-up was done using silica gel solid phase extraction. Fourteen different organochlorine pesticides residues namely p,p'-DDT, p,p'-DDE, gamma-HCH, delta-HCH, heptachlor, aldrin, Endrin, endrin-aldehyde, endrin-ketone, alpha-endosulphan, endosulphan-sulphate, gamma-chlordane, dieldrin, and methoxychlor were identified and quantified in the individual breast milk samples using a Gas Chromatograph (GC) with an Electron Capture detector. The GC recoveries of spiked samples were between 89 to 97%. p,p'- DDE recorded 100% incidence ratio. Also p,p'-DDT, delta-HCH, gamma-HCH, and endosulfan sulfate recorded incidence ratios of 76.79, 95.25, 80.95 and 85.71%, respectively for the breast milk samples. The concentrations of organochlorine pesticide residues in the human breast milk samples ranged from 1.839 to 99.05 µg/kg fats. With the exception of Endosulphan Sulphate whose mean concentration (99.052 µg/kg) was above the Australian Maximum Residue Limit (MRL) of 20 µg/kg for milk, the mean concentrations for all the other organochlorines detected were below their respective limits.

Afful et al. (2010) investigated the levels of organochlorine pesticide residues in the Densu basin using fish samples as a case study. Six fish species were collected from the sampling towns, Weija and Nsawam along the Densu river basin in the Greater Accra Region of Ghana. The extracts were cleaned-up using florisil adsorbent and characterized for organochlorine content using Gas Chromatograph (GC) equipped with Electron Capture Detector (ECD). Fourteen organochlorines (OCs) namely gamma-HCH, delta-HCH, heptachlor, aldrin, gammachlordane, p,p'-DDE, alpha-endosulfan, dieldrin, endrin, endrin-aldehyde, endosulfan-sufate, p,p'-DDT, endrinketone and methoxychlor were identified and quantified. A 100% incidence was recorded for gamma-HCH, delta-HCH, heptachlor, aldrin, gamma-chlordane, alpha-endosulfan, dieldrin and p, p'-DDT, while 75% incidence was recorded for the metabolites, p,p'-DDE and endosulfan-sulfate. The concentrations of OCs ranged from 0.3 to 71.3 µg/kg and were however, below the Australian Maximum Residue Limits (MRL) of 50 to 1000 µg/kg for fresh water fish.

Ntow et al. (2008), assessed the accumulation of persistent organochlorine contaminants in milk and serum of farmers in Ghana. Concentrations of persistent organochlorine (OC) pesticides such as dichlorodiphenyltrichloroethane and its metabolites (DDTs), hexachlorocyclohexane isomers (HCHs), hexachlorobenzene (HCB) and dieldrin in samples of human breast milk and serum collected from vegetable farmers in Ghana during 2005 were determined. The levels of DDTs, HCHs and dieldrin in the breast milk samples were found to correlate positively with age of the milk sample donors. DDTs and dieldrin residues were significantly higher ($p < 0.005$) in males than females and there was association between breast milk and serum residues. When the daily intakes of DDTs and HCHs to infants through human breast milk were estimated, some individual farmers (in the case of DDTs) and all farmers (in the case of HCHs) accumulated OCs in breast milk above the threshold (tolerable daily intake guidelines proposed by Health Canada) for adverse effects, which may raise concern on children health.

Studies by Darko and Acquaah (2007) reported that beef samples from the Kumasi and Buoho abattoirs in Ghana contain organochlorine pesticides (Lindane, Aldrin, Dieldrin, Endosulfan, DDT and DDE) residues. Organochlorine residues were found in all the samples. The average concentration of lindane in beef fat samples from Kumasi was 4.03 µg/kg and 1.79 µg/kg in beef fat from Buoho. The average levels of lindane were 2.07 µg/kg for lean meat samples from Kumasi abattoir and 0.60 µg/kg in lean meat samples from Buoho. Endosulfan concentration in meat samples from Buoho was 2.28 µg/kg in the fat and 0.59 µg/kg in the lean beef. 1,1-dichloro-2,2-bis(pdichlorodiphenyl) ethylene (DDE) recorded mean concentrations of 118.45 µg/kg in beef fat and 42.93 µg/kg in lean beef samples from Kumasi abattoir. Beef samples from Buoho had DDE concentration of 31.89 µg/kg in the fat and 5.86 µg/kg in the lean beef. 1, 1, 1-trichloro-2, 2-bis-(4'-chlorophenyl) ethane (DDT) recorded an average concentration of 545.22 µg/kg in beef fat and 18.85 µg/kg in lean beef samples from Kumasi abattoir. The average concentration of DDT in beef fat from Buoho was 403.82 µg/kg but lean meat samples from the same sampling site recorded mean concentration of 10.82 µg/kg for DDT. Most of the organochlorine residues detected were below the maximum limits set by the FAO/WHO (5000 µg/kg for DDT and DDE, 100 µg/kg for lindane, 200 µg/kg for aldrin and diedrin and 200 µg/kg for endosulfan).

Amoah et al. (2006) analysed pesticide contamination of vegetables in Ghana's urban markets. A total of 180 vegetable samples were randomly purchased from nine major markets and twelve specialized selling points in three major Ghanaian cities: Accra, Kumasi and Tamale. Chlopyrifos (Dursban) was detected on 78% of the lettuce, lindane on 31%, endosulfan on 36%, lambdacyhalothrin (Karate) on 11%, and DDT on 36%. Most of the residues measured exceeded the maximum residue limit for consumption (10 to 100 μg/kg for lettuce).

Pesticide residues in the Volta Lake, were also analysed by Ntow (2005). Lindane and endosulfan were identified in concentrations ≤ 0.008 ppb and 0.036 ppb, respectively in water and ≤ 2.3 ppb and 0.36 ppb, respectively in sediment. DDT and DDE were also found in sediment samples (in concentrations ≤ 9.0 ppb and 52.3 ppb, respectively). No significant contamination was noted in the lake, however. The pesticide levels found in the study were comparable to a study by Osafo and Frempong (1998). Although DDT is banned for agricultural use in Ghana, it was detected in sediment samples, along with its metabolite, DDE and the study demonstrated the well-known environmental persistence of this substance, even in tropical environments (Kidd et al., 2001), justifying its prohibition from agricultural use in Ghana. The DDT concentration in the sediment, however, was lower than the DDE level indicating a high degradation rate under hot, dry climatic conditions (Jiries et al., 2002), typically of a tropical lake. Because most OC pesticides, including those detected in the study have the ability to accumulate in biological tissues, and are very toxic to fish and many aquatic invertebrate species, they pose a potential threat to sediment-dwelling organisms.

Ntow (2001) determined organochlorine pesticide levels in water, sediment, tomato, and mothers' breast milk collected from the environs of Akomadan, a prominent vegetable-farming community in Ghana. Endosulfan sulfate was the most frequently occurring (78%) OC in water with a mean of 30.8 μg/L. Lindane was detected in 38 samples (76% of analysed samples). Sediment samples showed the most number of OC compounds. The concentration was highest in sediment for lindane (mean 3.2 µg/kg) and least for β-endosulfan (mean 0.13 µg/kg). Heptachlor epoxide was present at a quantifiable level in tomato (mean 1.65 µg/kg fresh weight) and in sediment (mean 0.63 µg/kg dry weight). HCB was detected in 55% and DDE in 85% of all blood samples analyzed. For milk samples, 95% indicated quantifiable amounts of HCB, whereas 80% showed DDE. The mean values of HCB and *p,p′*-DDE in blood were 30 µg/kg and 380 µg/kg, respectively. The mean values of HCB and *p,p′*-DDE in milk were 40µg/kg fat (1.75 µg/kg whole milk) and 490 µg/kg fat (17.15 µg/kg whole milk), respectively. The study showed that residues of OC pesticides are present in environmental samples at Akomadan and in human fluids of its inhabitants. The residues were attributed to agricultural activities in the area.

In Nigeria, Adeyeye and Osibanjo (1999) determined residue levels of organochlorine pesticides in raw fruits, vegetables and tubers from markets in Nigeria. In the fruits, total HCH, aldrin and total DDT were detected in 77, 38 and 30% of all samples, respectively. In the vegetables, total HCH, HCB, total DDT and aldrin were detected from 95, 53, 50 and 30%, respectively, of all samples. Aldrin + dieldrin, total HCH, and total DDT were detected from 98, 79 and 49%, respectively, of all tuber samples. Other pesticides were below their detection limits. The average levels were generally low and none were above the FAOs maximum residue limits.

In China, a study by Odhiambo et al. (2007) determined residual levels of organochlorine pesticides (OCPs) in 34 samples of 19 varieties of vegetables collected from selected sites around Deyang city and Yanting County, Southwest China. The determinations were done using a gas chromatograph with electron capture detector (GC-ECD). The results indicated that all the vegetable samples had some levels of one or more OCPs in them. Residues of DDTs were found in 94.12% while HCHs were in 91.18% of all the samples analyzed indicating high incidence of these xenobiotics in the vegetables from the areas investigated. Among the HCH isomers, γ-HCH was the most prevalent but β-HCH was the most abundant indicating both old and fresh inputs of HCHs. DDT metabolites p,p-DDE and p,p'-DDD were more prevalent than the parent material, p,p-DDT suggesting minimal fresh inputs of DDT. The OCPs residue levels in the vegetables were generally low (≤ 1.3 ng/ g wet weight) except in one sample of green pepper (*Capsicum annum L*) in which the concentrations (ng/g wet weight) of o,p'-DDT (82.59), p,p'-DDE (61.41) and total DDT (148.44), all exceeded the Chinese Extraneous Maximum Residue Limit of 50 ng/ g for DDTs in vegetables according to the guidelines of the Chinese quality standard for food (GB 2763-2005).

In Albania, a preliminary study by Marku and Nuro (2005) determined the concentrations of chlorinated pesticides in the sediments and some fish species of Shkodra Lake. Seven sediment stations were chosen to represent different conditions of the lake. Biota samples were taken from the fat tissue of nine fish species. The concentrations of the chlorinated pesticides (except DDTs and Lindane) were found to be generally low. The total concentration of chlorinated pesticides in sediments was lower than the average values reported for the sediments in the Adriatic Sea.

A study conducted by Barkat (2005) in Parkistan determined residue levels of insecticides in fresh fruit and vegetable samples. Six hundred and eight samples of vegetables and fruits were analysed using high performance thin layer chromatography (HPTLC) methods. The most commonly detected residues were those of methamidophos (9.8% of 608 samples), cypermethrin (8.5%), endosulfan (4.9%), chlorpyrifos (4.4%), trichlorfon (3.3%), methidathion and methomyl (2.8%), dimethoate (2.6%) and λ-cyhalothrin(1.8%) depending on the type of insecticide being used by the grower. Of all analysed fruit and vegetable samples (608), 250 samples (41%) contained detectable residues. Of these, 13.8% had residues that exceeded Codex maximum residue limits (MRLs). For individual crops, contaminated samples ranged from 10 to 100% of the number of samples analysed.

In Mauritius, Lee and Seeneevassena (1997) monitored the amount of some insecticide residues in seasonal vegetables and fruits at the market level throughout the year. Locally produced vegetables and fruits were purchased from main urban and rural markets and analysed by gas liquid chromatography for pesticide residues. A total of 126 samples of vegetables and 2 samples of fruits were extracted and analysed for insecticide residues. 115 samples of the vegetable and fruit extracts were analysed for the presence of the pyrethroid insecticides cyfluthrin, cypermethrin and deltamethrin. Fifty-two samples of the vegetable and fruit extracts were analysed for the presence of organophosphorus insecticide dichlorvos, diazinon, fenitrothion, methamidophos, profenofos, phosphamidon, malathion and parathion. The data showed that most of the vegetable and fruit samples analysed did not contain residues of the monitored insecticides above the accepted maximum residue limit (MRL) as adopted by the FAO/WHO Codex Alimentarius Commission (CAC), although some insecticide residues have been detected in certain samples only. The following insecticides have been detected in some of the samples of vegetables and fruits analysed, but they have been mostly detected below the MRL: cypermethrin, deltamethrin, methamidophos, profenofos and malathion. The results obtained showed that 61.5% of the vegetable and fruit samples analysed contained no detectable level of the monitored insecticides, 36.2% of the samples gave results with levels of insecticide residues below the MRL, while 2.3% of the samples showed results above the MRL. Only three samples contained levels of insecticide residues above the MRL.

2.2 Effects of organochlorine pesticides on human health

Over 300 foreign chemicals, including several known carcinogens have been identified in the adipose tissue and other organs including brain cells and nervous system. The brain and the endocrine (hormonal) glands are the target site for the fat-soluble toxins to accumulate. Continued exposure to these chemicals for a long period may result in symptoms of mild cognitive dysfunction (including problems in identifying words, colours or numbers and unable to speak fluently) and hormonal imbalances leading to infertility, breast pain, menstrual disturbances, adrenal gland exhaustions and early menopause. Eventually these toxins are stored in the fatty body tissues and in cells of the brain. These stored toxins may be slowly released and recirculated in the blood, contributing to many chronic illnesses. Whenever the body is under stress, the stored fat is released along with the toxins and circulates freely through out the body. The resulting exposure can target various organs and body systems, contributing to many chronic illnesses. The nature of health effects depend on the type of pesticide, dose, timing, duration of exposure and the susceptibility of the exposed individual (Xavier et al., 2004).

2.2.1 Cancer

Case–control studies have linked pesticide exposure to childhood cancer (Zahm et al., 1997). A number of studies have demonstrated that maternal employment in agriculture has a link with leukemia. The most convincing evidence that herbicides are human carcinogens comes from epidemiological studies (Hoar and Blair, 1986). It is reported that the population living around the active agricultural regions are highly prone to cancer. Thyroid and bone cancers are prevalent in agricultural regions where fungicides are extensively used (Schreinemachers et al., 1999). Recent studies have shown that the incidence of hormone related organ cancers or hormonal cancers have increased among farmers. Exposure to endocrine disrupting pesticides, particularly to DDT and phenoxy herbicides, is the suspected cause in some of these hormonal cancers (Burananatrevedh and Roy, 2001). The association between different types of pesticides and prostate cancer shows moderate risk among farmers exposed to organochlorine insecticides and acaricides specifically DDT and Dicofol (Settimi et al., 2003). Over the last 10 years, breast cancer in women has increased worldwide by 33%. Various studies have linked our environment and the substances we are exposed to as prime suspects. There is growing evidence that the breast cancer epidemic is related to exposure to a wide range of environmental contaminants including DDT, other carcinogenic pesticides and oestrogenic stimulants. Organochlorine pesticides such as DDT and its metabolites DDD and DDE, dieldrin, heptachlor, HCH and its isomers were detected in the blood of breast cancer patients, irrespective of age, diet and geographic locations when compared to normal women (Mathur et al., 2002).

A study was conducted in New York by Wolff et al. (1993) to determine whether exposure to PCBs and to DDE [1,1-dichloro-2,2-bis(p-chlorophenyl) ethylene], the major metabolite of DDT, is associated with breast cancer risk in women. The study analyzed sera from the stored blood specimens of 14290 participants enrolled between 1985 and 1991 in the New York University Women's Health Study, a prospective cohort study of hormones, diet, and cancer. Cohort members who developed breast cancer were included as case patients in a nested case control study.

DDE and PCBs were measured by gas chromatography in the sera of 58 women with a diagnosis of breast cancer 1–6 months after they entered the cohort and in 171 matched control subjects from the same study population who did not develop cancer. The results showed that mean levels of DDE and PCBs were higher for breast cancer case patients than for control subjects, but paired differences were statistically significant only for DDE (P = 0.031). After adjustment for first-degree family history of breast cancer, lifetime lactation, and age at first full-term pregnancy, conditional logistic regression analysis showed a fourfold increase in relative risk of breast cancer for an elevation of serum DDE concentrations from 2.0 ng/mL (10th percentile) to 19.1 ng/mL (90th percentile). For PCBs, the relative risk for a change in serum levels from 3.9 ng/mL (10th percentile) to 10.6 ng/mL (90th percentile) was less than twofold, a nonsignificant association that was further reduced after adjustment for DDE. Therefore, breast cancer was strongly associated with DDE in serum but not with PCBs.

2. 2. 2 Effect on reproductive system

There is a growing concern that pesticides, having estrogenic property may cause a variety of reproductive disorders in wild life and human populations. Recent in vitro data suggest that the interaction between some weak estrogenic organochlorines, dieldrin, endosulfan, toxaphene and chlordane cause a synergistic increase in their estrogenic potency, an effect due to joint action on estrogenic receptors (Wade et al., 1997).

Exposure to pesticides may play a role in adverse pregnancy outcomes (Fowler, 2001). It has been shown that there is detectable levels of 2, 4-D and MCPA ([4 chloro-2 methylphenoxy] acetic acid in the semen of farmers who recently used the pesticides. As these pesticides can be excreted in the semen, they could be toxic to sperm cells and be transported to the woman and developing embryo/fetus (Tye et al., 1994). Farm workers attending the plant protection operations and persons working in the pesticide manufacturing units are more prone to pesticide toxicity. In brief, exposure to pesticides with endocrine disrupting potential raises a particular concern for male fertility because of the possible occurrence of effects at low concentrations and additive interactions with other environmental risk factors. Epidemiological studies have confirmed an increased risk of delayed conception associated with exposure to pesticides. Moreover, an increased risk of spontaneous abortion has been noted among wives of exposed workers (Petrelli and Mantovani, 2002). Birth abnormalities were reported in the offspring of registered users of pesticide as well as the general population living around agricultural areas (Garry, 1996). Studies show a stronger association between fetal death due to congenital abnormalities and residential proximity to applications of pyrethroid and observed elevated risk when the exposure occurred during the third – eighth week of pregnancy (Bell et al., 2001). In a study, umbilical cord blood was analyzed in a new-born, whose parents had been exposed to pesticides. The results indicated the presence of detectable DDE, the main metabolite of DDT. There was a positive correlation between maternal DDE and the consumption of fish (Sarcinelli et al., 2003). A cohort study of serum shortly after delivery indicated that DDE and other organochlorine pesticides may pose a risk to preterm birth in countries that continue to use such insecticides for malaria control (Torres- Arreola et al., 2003).

2.2.3 Endocrine disruption

Endocrine disruptors are exogenous chemical substances that cause adverse effects in the endocrine system. These chemicals mimic the action of hormones and can damage or disrupt the normal functioning of an organism. In humans, endocrine glands which include adrenal, thyroid, pancreas, ovary and testis produce hormones which are distributed to receptors through the blood stream. Many pesticides acts as endocrine disruptors and affect sperm quality and reproductive development. There is now considerable evidence that male reproductive function is declining in human and wild life populations (Petrelli and Mantovani, 2002), that the mechanism of action may be disturbed testicular apoptosis and altered hepatic biotransformation of steroids. Sexual differentiation is regulated by reproductive hormones. Diethylstilbestrol is the best known endocrine disrupter and has caused abnormalities of sexual differentiation in both exposed female and male human fetuses (Toppari, 2002). Organochlorine contaminants in the human diets relate to the potential ability of many of these chemicals at low doses to act as endocrine disruptors (Smith and Gangolli, 2002). Such chemicals are capable of disrupting the normal functioning of endocrine system and may pose a growing threat to human and wild life health. These compounds can modulate both the endocrine and immune systems resulting in alteration of homeostasis, reproduction, development and behavior. The chemicals in the environment cause endocrine disruption and result in pathological effects on the male and female reproductive system, thyroid function and the central nervous system (Amaral-Mendes, 2002).

2.2.4 Immune system dysfunction

Experimental and epidemiological studies show that many pesticides in widespread use around the world are immunosuppressive. Organochlorine pesticides that are known to alter the immune system are DDT, chlordane, aldrin, lindane, hexachlorobenzene, mirex, and arochlor (a PCB)

Frequent exposure of multiple toxins causes the detoxification system to be overloaded and inefficient, leading to the accumulation of toxins, dead cells and microorganism build up in the blood. To combat these foreign bodies, the immune system will produce excessive inflammatory chemicals. Under a hyper excited state, the immune system will produce auto antibodies. This may lead to symptoms of immune dysfunction such as allergies, inflammatory states, swollen glands, recurrent infections, chronic fatigue syndrome and auto immune diseases (Freidman, 1967; Glick, 1974; Street and Sharma, 1975; Loose et al., 1977; Desi et al., 1978; Giurgea et al., 1978).

2.2.5 Parkinson's disease

Parkinson's disease (PD) is the most common neurodegenerative disorder. It is now proposed that environmental factors in conjunction with genetic susceptibility may form the underlying molecular basis for idiopathic PD (Uversky et al., 2002). Epidemiological and experimental data suggest the potential involvement of specific agents as neurotoxicants such as pesticides (organochlorine and organophosphorus) in the pathogenesis of nigrostriatal degeneration, supporting a relationship between the environment and Parkinson's disease (Di Monte et al., 2002). Recent studies show clearly that genetic factors play a minor role in determining whether an individual develops this disease, rekindling an interest in the etiological significance of environmental factors (Lockwood, 2000). *In vitro* studies have provided proof that several pesticides including rotenone stimulate the formation of alpha-synuclein fibrils (one of the principal constituents of Lewy bodies). Moreover, a meta analysis of all case control studies so far showed a positive, statistically significant association between pesticide exposure and Parkinson's disease (Vanacore et al., 2002).

2.2.6 Cytotoxic defects

The potential genetic hazard of pesticides to human beings is of great concern. Results from the biological monitoring or cytogenetic methods for the detection of health risks to pesticides have showed DNA damage in peripheral lymphocytes among workers employed in municipality. The observed DNA damage was found to be significantly lower in workers taking some of the necessary safety precautions during their work (Undeger and Basaran, 2002). Malaoxon is the first and main metabolite that is more toxic than the parental compound, Malathion. Malaoxon can damage DNA in human lymphocyte, by various mechanisms including oxidative damage. Hydrogen peroxide and reactive oxygen species may be involved in the formation of DNA lesions induced by Malaoxon. Malaoxon can also methylate DNA bases (Janusz and Dorota, 2001).

Increased chromatid breaks and chromosomal aberrations in human lymphocytes were observed in workers occupationally exposed to pesticides. Bolognesi et al. (2002) observed micronuclei frequency in peripheral blood lymphocytes among the farm workers, which was more evident among workers who avoided protective measures.

2.2.7 Childhood developmental disorders

A study in India (Kuruganti, 2005) assessed the effect of pesticide exposure on the abilities of children to perform developmental tasks. In all, 1,648 children were individually tested using a rapid assessment tool that measured children's memory, stamina, analytical, motor, and tactile perception abilities through various games and activities. The study controlled for major confounding factors such as socio-economic background, maternal education, schooling, media exposure, and the like. In more than 80 percent of the tasks tested, children heavily exposed to pesticides performed significantly worse than the less-exposed children.

Sagiv et al. (2010) found higher risk for attention deficit hyperactivity disorder (ADHD) at higher levels of PCBs and p,p'-DDE in a longitudinal cohort study including 788 mother–infant pairs. The PCB and p,p'-DDE levels in cord serum were moderately associated with attention deficit hyperactivity disorder (ADHD) in children aged 7–11 years born in 1993–1998 in a PCB-contaminated area (ORs = 1.76). These results support the view that low-level prenatal organochlorine exposure is associated with attention deficit hyperactivity disorder (ADHD)-like behaviors in childhood.

A study in Mexico (Guillette et al., 1998) compared Yaqui children who were exposed to large amounts of pesticides with children who lived in the foothills, where pesticide use is avoided, found that functionally, the exposed children demonstrated decreases in stamina, gross and fine eye-hand coordination, 30-minute memory and the ability to draw a human figure.

2.2.8 Diabetes

The prevalence of diabetes has been increasing globally over the past few decades (King et al., 1998). Recent epidemiologic studies have shown that background exposure to persistent organic pollutants, especially organochlorine pesticides, is strongly associated with type 2 diabetes. Lee et al. (2006) demonstrated a very strong relationship between the levels of persistent organic pollutants in serum, particularly oxychlordane and transnonachlor, and the risk of type 2 diabetes in the general American population by extensive analysis of the National Health and Nutrition Examination Survey 1999–2002 data (Lee et al., 2006). This association was higher in obese people than among the non-obese.

The associations between the serum concentrations of organochlorine pesticides and the prevalence of diabetes were examined in the Mexican-American population (Cox et al., 2007) and Korean population (Son et al., 2010). Exposure of *p*, *p*'-DDE was related to the incidence of diabetes in a cohort of Great Lakes sport fish consumers from 1994 to 2005 (Turyk et al., 2009). Lee et al. (2010) also investigated whether several persistent organic pollutants predict the risk of type 2 diabetes within the Coronary Artery Risk Development in Young Adults (CARDIA) cohort (Lee et al., 2010). Some persistent organic pollutants, such as trans-nonachlor and highly chlorinated PCBs, were associated with the incidence of type 2 diabetes over an 18-year period, especially in obese people. Persistent organic pollutants showed strong associations at relatively low exposures, resulting in inverted U-shaped dose–response curves instead of the traditional dose– response relationship with diabetes.

2.3 Cultivation of tomato in Navrongo

Tomato cultivation has been a significant economic activity in the Upper East region, especially in Navrongo. Tomatoes have long been the most lucrative crop in the Upper East region and it is perceived to be more profitable than rice, maize, groundnuts, yam, pepper and dairy. Close to 90% of the two million people living in the area cultivates them (Third world network (TWN), 2007). The most common tomato varieties grown in Navrongo include pectomech and 'No Name' (plate 2.1 and 2.2). Others are tropimech, chico and Cal J (from Kenya).

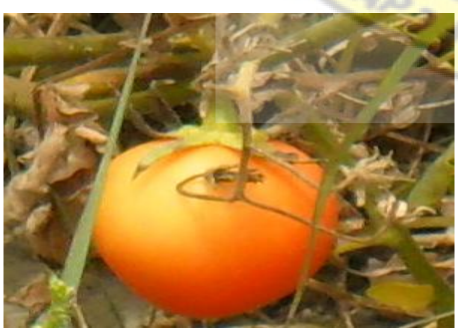


Plate 2.1: picture showing the pectomech variety

Plate 2.2: picture showing the 'No Name' variety

The tomatoes are cultivated in the dry season under irrigation from the Navrongo-Tono Dam, one of the largest agricultural dams in West Africa. The dam covers a total catchment area of 3600 hectares. There are nine villages living and farming around the project's area and each area has a population of 3-5,000 people. The dam was built between 1975 and 1985 by Taysec, a British engineering company.

Tomatoes from Navrongo are sold in many other parts of the country including Tamale, Kumasi, and Accra.

CHAPTER THREE

MATERIALS AND METHODS

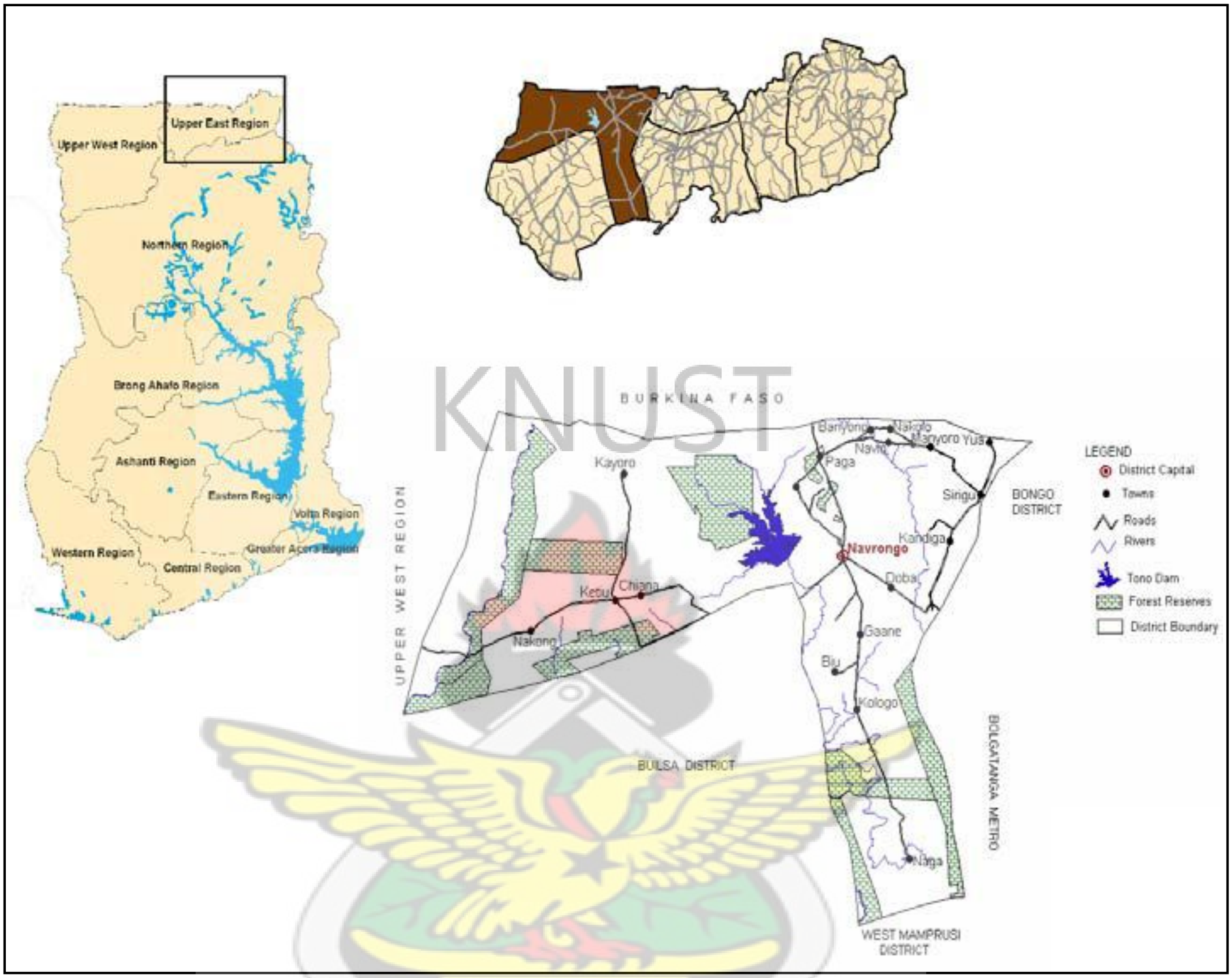
3.1 Description of study area

Navrongo is the district capital of the Kasena/Nankana East district, one of the nine districts in the Upper East Region in the northern part of Ghana. It is bordered by the Republic of Burkina Faso, and the Bolgatanga, Bongo, Builsa, Sissala and Mamprusi West Districts. It stretches for

55 kilometres from north to south and 53 kilometres from east to west. Its geographical coordinates are 10° 53' 42" North, 1° 5' 38" West (Google satellite map). The population of the town in 2005 was estimated to be 25,470 (2005 population estimates for cities in Ghana). The terrain is flat and the ecology is of the sahel (hot and dry), with the vegetation consisting mostly of semi-arid grassland interspersed with short trees.

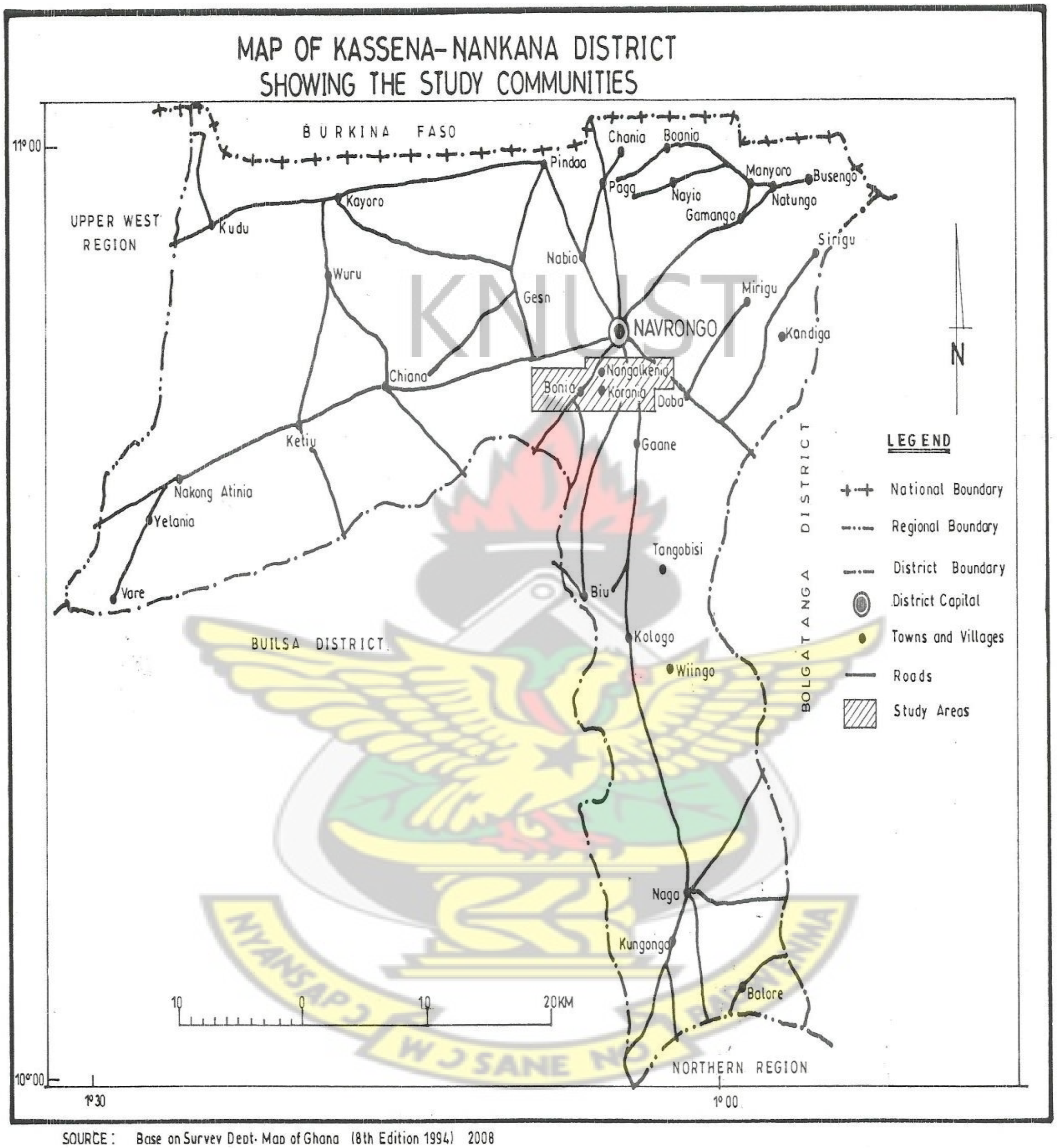
Bonia, Korania and Nangalkenia are farming communities located South-West of Navrongo, along the Navrongo-Sandema road.

The study area is shown in figures 3.1 and 3.2 below.



Source: Glowa Volta Project (SEF), 2007

Figure 3.1: A map showing the Kasena /Nankana District of the Upper East Region, Ghana.



SOURCE : Base on Survey Dept· Map of Ghana (8th Edition 1994) 2008

Figure 3.2: A map showing the study areas in Navrongo, Upper East Region, Ghana.

3.2 Materials and reagents

Tomato fruits were bought from three farming communities in Navrongo (Bonia, Korania, and Nangalkenia) within the months of January and February, 2011. The fruits were bought directly from the farmers during harvest.

Samples were immediately wrapped in aluminium foil that had already been cleaned with acetone. They were then placed in zip lock bags and appropriately labeled. The labeled samples were then placed in ice chest containing ice and transported to the Department of Chemistry, Ghana Atomic Energy Commission (GAEC) within 17 hours after sampling. They were then kept in freezer at a temperature of about -20 ºC prior to analysis.

A total of 30 samples of tomato fruits were sampled for analysis of the organochlorine pesticide residue levels using gas chromatography.

Analytical grade acetone, sodium sulphate, ethyl acetate and sodium hydrogencarbonate were bought from a local chemical shop (Fregeosco Co. Ltd) in Accra who also obtained their supplies from CDH group in India.

3.3 Experimental procedure

The method used for the extraction and clean-up procedures was the EPA-method 3540C (US EPA, 1994)

3.3.1 Extraction

Each fruit sample was chopped with a sharp knife on a chopping board. This was then blended in a Salton elite glass blender to obtain a homogenous representative sample. The knife, chopping board and blender were washed thoroughly to avoid cross contamination.

20g of sodium sulphate (Na_2SO_4) and 5g of sodium hydrogencarbonate ($NaHCO_3$) were weighed and added to a separation funnel. 20g of blended sample was added followed by 40ml of ethyl acetate ($CH_3COOCH_2CH_3$).

The mixture was shaken for ten minutes and allowed to settle. The supernatant (extract) was decanted into a round bottomed flask. This was evaporated in a BÜCHI Rotavapor R-200 rotary evaporator.

3.3.2. Clean-up

In order to remove any interfering substances co-extracted with the insecticide residues the extract was cleaned up. 1.5 g of activated florisil was packed into a column that had been pluged with glass wool. The column was further packed with 0.5g and 1.0 g of activated charcoal and sodium sulphate (Na_2SO_4) respectively. 10ml of ethyl acetate was used to condition the column prior to the clean- up.

Extract was transferred onto the florisil column using a Pasteur pipette and waited until it was eluted. The sample tube (round bottomed flask) was rinsed with 2 ml ethyl acetate and this was repeated twice to get all the extract from the tube. The 9 ml of ethyl acetate was put on the column after the last rinse. The solvent (extract) was concentrated (evaporated) to dryness in a BÜCHI Rotavapor R-200 rotary evaporator. The dried residue for each sample was dissolved in 1.5ml of isooctane and picked into GC vials for analysis.

3.3.3 Analysis

A gas chromatograph, 2010 SHIMADZU C113245, equipped with an Electron Capture Detector (ECD) was employed. The chromatographic separation was done on an SGE BPX-5 of 60 m capillary column with 0.25 mm internal diameter and 0.25 µm film thicknesses and equipped with 1 m retention gap (0.53 mm, deactivated). The GC conditions were as follows: The oven temperature programme was as follows: Initial temperature was set at 90^oC for 3 min and ramped at 30^oC/min to 200^oC for 15min and then to 265^oC at a rate of 5^oC/min for 5min then to 275^oC at the rate of 3^oC/min and allowed to stay for 15 min giving a total run time of 58min. The injector setting is a pulsed spitless mode with a temperature of 250^oC at a pressure of 1.441 bar. Pulsed pressure was 4.5 bar, pulsed time 1.5min, pruge flow of 55.4ml/min with a purge time of 1.4 min. The injection volume was 1.5mL. The detector temperature was 300°C. Nitrogen gas (N_2) was used as the carrier gas, maintained at a constant flow rate of 30mL/min.

3.4 Analytical quality assurance

The efficiency of the analytical method (the extraction and clean-up methods) was determined by recoveries of an internal standard. In doing this, one blended tomatoes sample in each batch of analysis was spiked with a 50µL of 100ng/ml internal standard (isodrin) and extracted under the same conditions as the analytes. To check for cross contamination and interferences, a blank sample was analysed in each batch of analysis.

All glassware used for the analysis were always washed with a detergent with hot water, rinsed with tap water and then with distilled water. They were further rinsed with acetone and then placed over night in an oven at about 40 ºC.

3.5 Statistical analysis

The mean concentrations of residues were determined statistically using STATA 11.2 and compared to the UK/EC MRLs as a measure of safety to consumers. Pairwise comparisons of the mean concentrations were used to determine whether the detected organochlorine residues at different sampling locations or in different varieties of tomato samples varied significantly or not. All analyses were performed using the statistical software package STATA 11.2. Data are presented as means with a level of significance of 5% (P = 0.05). A p value > 0.05 was interpreted as no significant difference.

3.6 Questionnaire

Questionnaire were administered to the tomato farmers from all the three communities. Farmers were questioned on the type of insecticide used, their level of education, time of insecticide application and subsequent harvest, the contacts they make with pesticide dealers, extension officers, etc., if they experienced any health problems, the size of their farms, the number of years they have been farming, types of pesticides used, etc (Appendix 1).

CHAPTER FOUR

RESULTS

4.1 Occurrence and levels of OCs in the tomato samples from Navrongo.

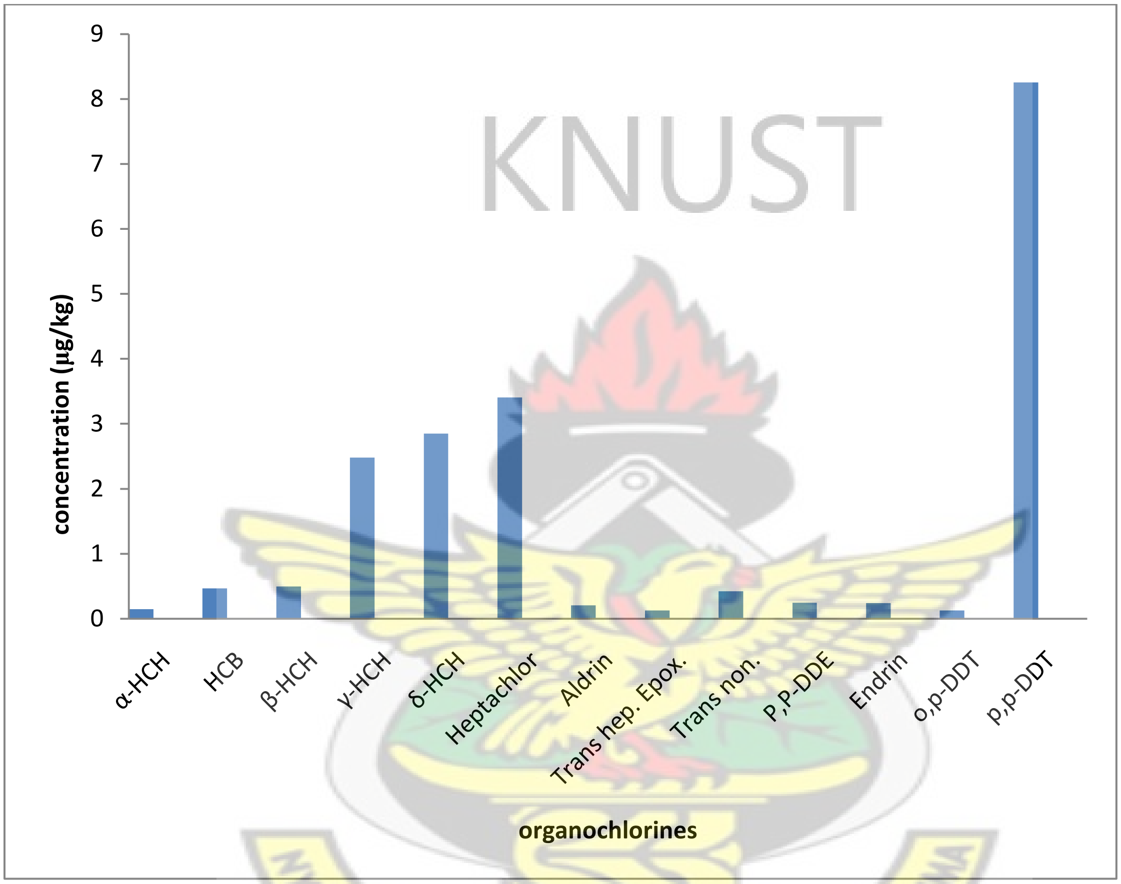


Figure 4.1: Average concentrations of OCs (µg/kg) in tomatoes from Bonia, Navrongo.

Figure 4.1 shows that a total of thirteen organochlorines pesticides were detected at Bonia. The level of p,p –DDT was the highest (8.2535µg/kg), followed by heptachlor (3.4079µg/kg), delta HCH (2.8518µg/kg) and then gamma-HCH (2.4797µg/kg). The rest were very low. The lowest value was recorded for trans-heptachlor epoxide (0.1269µg/kg).

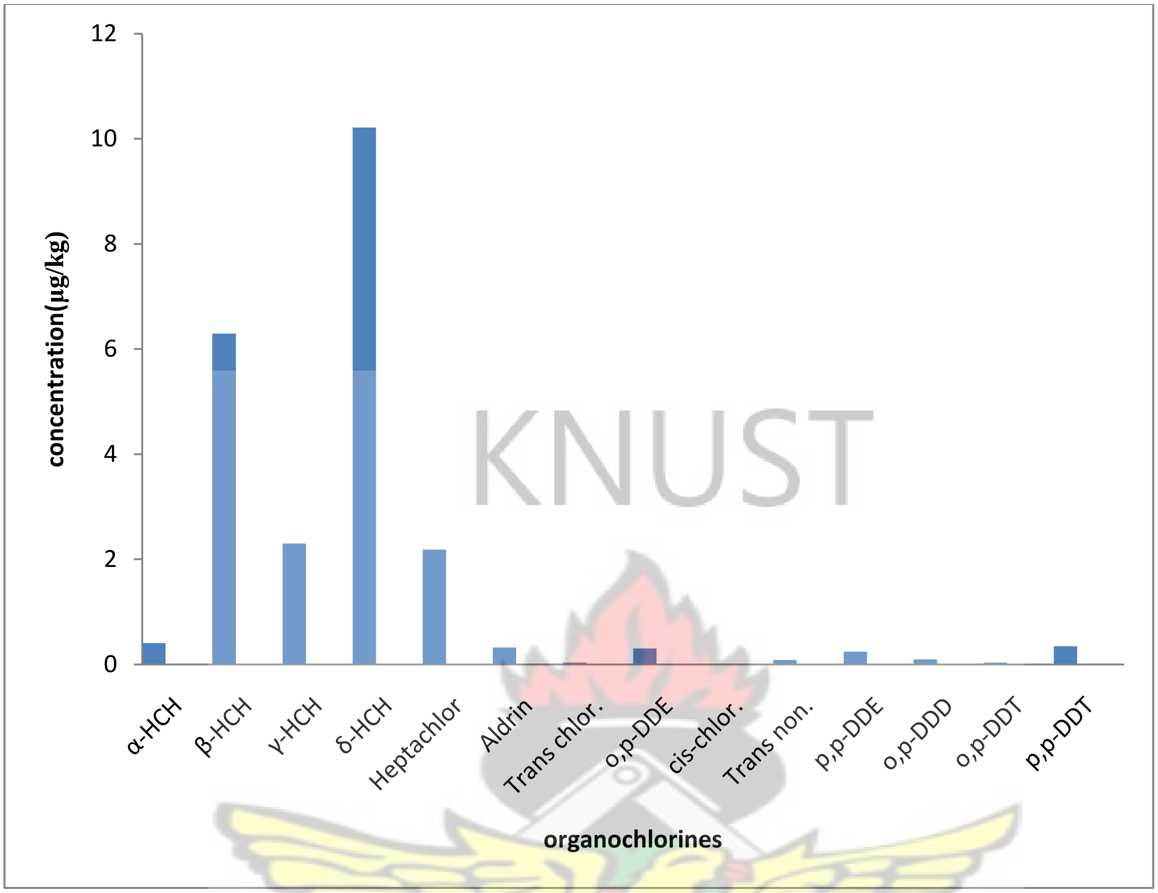


Figure 4.2: Average concentrations of OCs (µg/kg) in tomatoes from Nangalkenia, Navrongo.

Fourteen organochlorine pesticides were detected at Nangalkenia as shown in figure 4.2. Delta HCH recorded the highest (10.2133µg/kg) and the cis-chlordane the lowest (0.0038µg/kg). The concentrations of the HCH isomers (delta HCH, beta HCH and gamma HCH) were generally higher compared to the other insecticides that were detected.

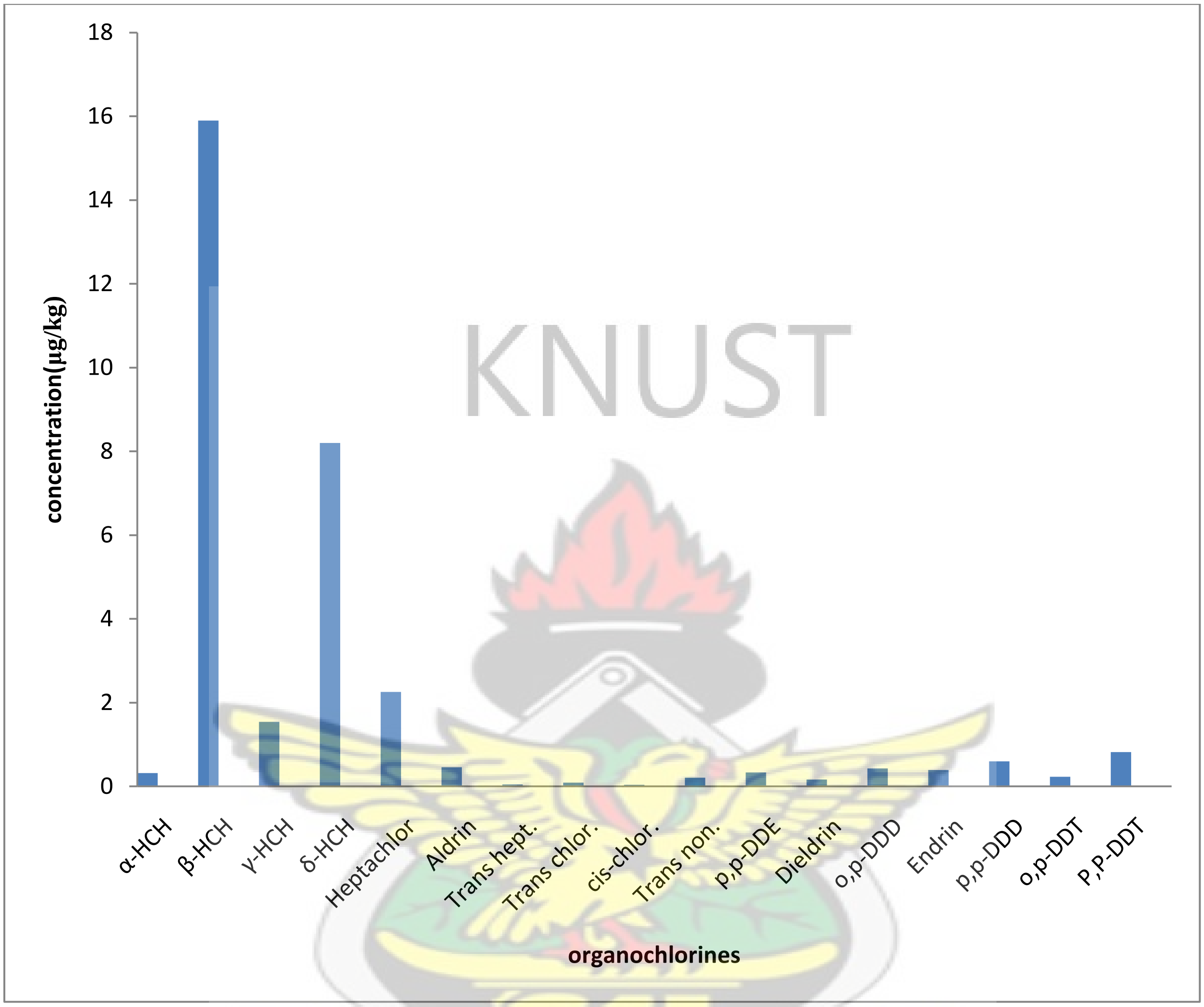


Figure 4.3: Average concentrations of OCs (µg/kg) in tomatoes from Korania , Navrongo.

Of all the seventeen organochlorine pesticides that were detected, beta-HCH was the highest (15.9007µg/kg) followed by delta-HCH (8.2022µg/kg). Cis-chlordane was the lowest (0.0374µg/kg).

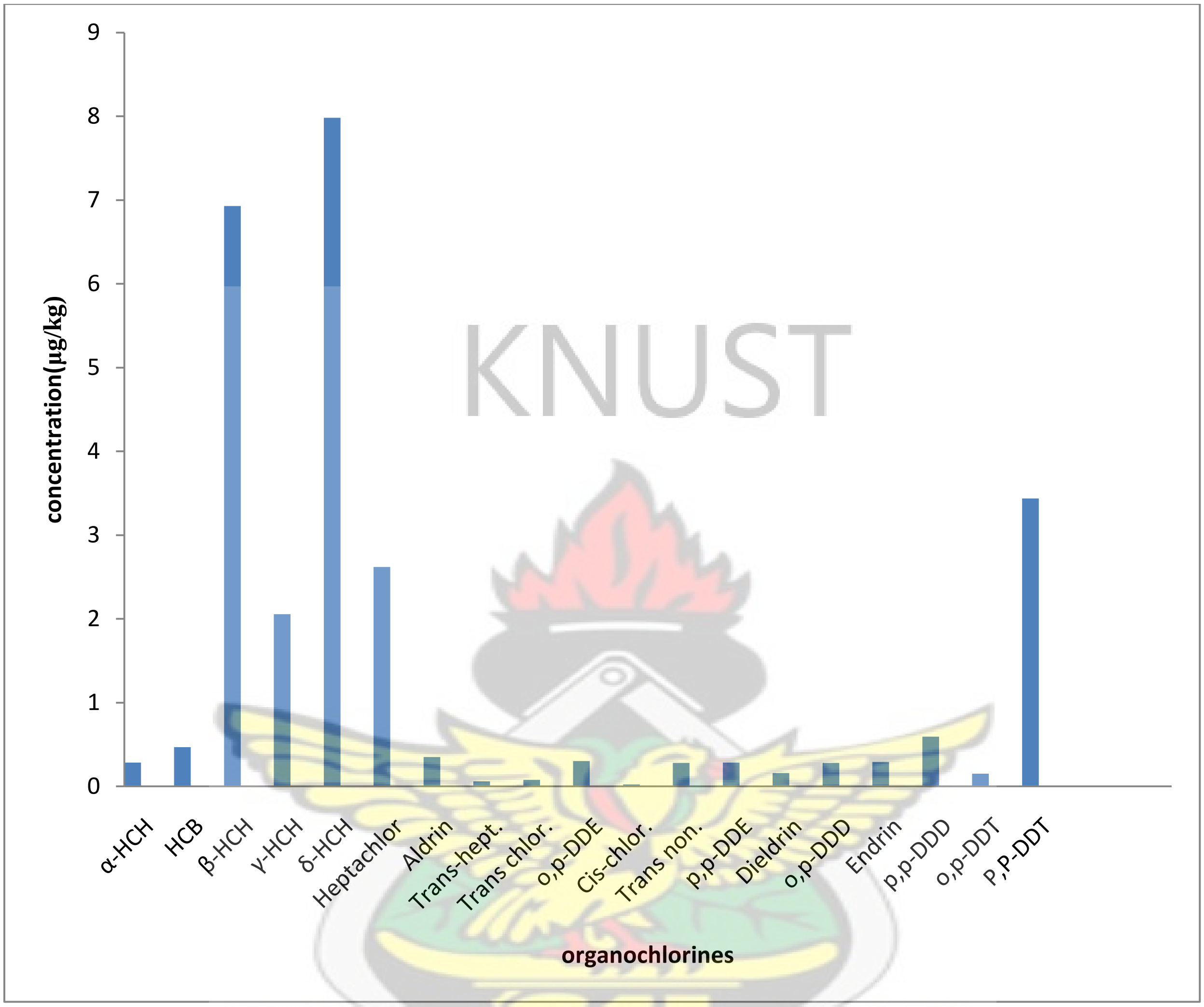


Figure 4.4: Overall average concentrations of OCs (µg/kg) from all the three study areas in Navrongo.

Overall, a total of 19 different organochlorine insecticide residues were detected in fresh tomato fruits sampled from the three farming communities (Bonia, Korania and Nangalkenia) in Navrongo. Delta HCH had the overall highest concentration (7.9808µg/kg) and cis-chlordane recorded the overall lowest concentration (0.0206µg/kg). Of all the 30 samples analysed, at least 5 different organochlorine residues were detected in each sample.

Cis-heptachlor epoxide, oxychlordane, and cis-Nonachlor were not detected in all three communities.

4.2 Comparison of organochlorine residues with the UK/EC MRLs

Table 4.1: Comparison of mean concentrations of OCs from the three study areas in Navrongo, upper East region of Ghana with the UK/EC MRLs

Name of Pesticide	**Sample Location (sample mean levels of pesticide)**			**Grand sample mean levels**	**UK/EC MRLs (µg/kg)**
	Bonia	Korania	Nangalkenia		
Alpha-HCH	0.1468	0 .3204	0.4062	0.2854	10
Hexachlorobenzene	0.4690	ND	ND	0.4690	10
Beta-HCH	0.4971	15.9007	6.2936	6.9287	10
Gamma-HCH	2.4797	1.5419	2.3009	2.0569	10
Delta-HCH	2.8518	8.2022	10.2133	7.9808	10
Heptachlor	3.4079	2.2528	2.1839	2.6194	10
Aldrin	0.2073	0.4594	0.3253	0.3490	10
cis-Heptachlor epoxide	ND	ND	ND	ND	10
Oxychlordane	ND	ND	ND	ND	10
Trans-Heptachlor epoxide	0.1269	0.0423	ND	0.0592	10
Trans-Chlordane	ND	0.0867	0.0353	0.0764	10
Op-DDE	ND	ND	0.3021	0.3021	50
Cis-Chlordane	ND	0.0374	0.0038	0.0206	10
Trans-Nonachlor	0.4215	0.2076	0.0853	0.2818	10
pp-DDE	0.2468	0.3356	0.2443	0.2830	50
Dieldrin	ND	0.1593	ND	0.1593	10
Op-DDD	ND	0.4271	0.0982	0.2809	50
Endrin	0.2413	0.3875	ND	0.2900	10
pp-DDD	ND	0.5938	ND	0.5938	50
Op-DDT	0.1272	0.2279	0.0367	0.1518	50
Cis-Nonachlor	ND	ND	ND	ND	10
pp-DDT	8.2535	0.8213	0.3439	3.4371	50

ND= Not detected

Source of UK/EC MRL values: https://secure.pesticides.gov.uk/MRLs

Table 4.1 shows that, the average concentration of beta HCH at Korania (15.9007 μk/kg) was higher than the UK/EC MRL value of 10 μk/kg and that of delta HCH at Nangalkenia (10.2133 μk/kg) was also marginally higher than the UK/EC MRLs value of 10 μk/kg. The average concentrations of the rest were found to be far below the UK/MRLs.

4.3 Comparison of mean concentrations of organochlorine insecticide residues among the varieties of tomatoes

The mean concentrations of the organochlorines in the various tomato varieties are shown in table 4.2 below.

Pairwise comparison shows that no significant differences of concentrations of the organochlorine residues exist among the varieties ($p>0.05$). For example, pairwise comparison of heptachlor concentration between Pectomech and 'No Name' showed no significant differences ($p=0.6760$) as shown in Appendix 3.

Table 4.2: Comparison of mean concentrations of OCs among tomato varieties from the three study areas in Navrongo, Upper East Region of Ghana

Name of Pesticide	Variety (sample mean levels of pesticide)		
	pectomech	no-name	other
Alpha-HCH	0.2727	0.3024	0.2939
Hexachlorobenzene	ND	0.4690	ND
Beta-HCH	4.4552	10.2401	7.7266
Gamma-HCH	2.0229	1.9241	2.5254
Delta-HCH	6.9150	9.0804	8.8774
Heptachlor	2.0318	3.1256	3.7044
Aldrin	0.3738	0.3226	0.32845
cis-Heptachlor epoxide	ND	ND	ND
Oxychlordane	ND	ND	ND
Trans-Heptachlor epoxide	0.0432	0.0699	ND
Trans-Chlordane	0.0428	0.1307	0.0353
Op-DDE	ND	0.3021	ND
Cis-Chlordane	0.0206	ND	ND
Trans-Nonachlor	0.5786	0.2039	0.0000
pp-DDE	0.2623	0.2925	0.3109
Dieldrin	0.0156	0.303	ND
Op-DDD	0.2221	0.3922	0.0716
Endrin	0.2149	0.3875	0.2677
pp-DDD	0.3785	0.8090	ND
Op-DDT	0.1858	0.1281	0.0907
Cis-Nonachlor	ND	ND	ND
pp-DDT	0.8498	8.1025	0.2990

ND= Not detected

4.4 Comparison of mean concentrations of organochlorine insecticide residues among the sampling locations.

Table 4.1 shows the average concentrations of the organochlorines at Bonia, Korania and Nangalkenia. Pairwise comparison of concentrations of the organochlorine insecticide residues among the sampling locations using statistical software of STATA 11.2 shows that most of the organochlorine residues had statistically significant differences in concentrations at different sampling locations ($p<0.05$). For example, a pairwise comparison of alpha HCH between Bonia and Nangalkenia showed significant differences in the concentrations of alpha HCH between the two locations ($p= 0.0140$). Concentrations of beta HCH between Bonia and Korania differed significantly ($p=0.038$).

Some few however, showed no significant differences. For example, comparison between Bonia and Korania for heptachlor gave no significant differences ($p = 0.7250$).

4.5 Questionnaire survey

4.5.1 Age of tomato farmers

Table 4.3 shows that most tomato farmers in Navrongo are aged between thirty to sixty years. Most of these farmers have been growing tomatoes and using pesticides for over ten years.

Table 4.3: Age of tomato farmers in Navrongo, Upper East Region

Age of farmers	Number of respondents
10-20	0
21-30	2
31-40	7
41-50	16
51-60	5
61-70	0
Total	30

4.5.2 Educational levels of tomato farmers

Figure 4.5 shows that 36% of the farmers were illiterates, 7% were primary school leavers, 30% were middle school leavers, 17% were SSS/SHS leavers, 7% had Certificate A and 3% were HND graduates.

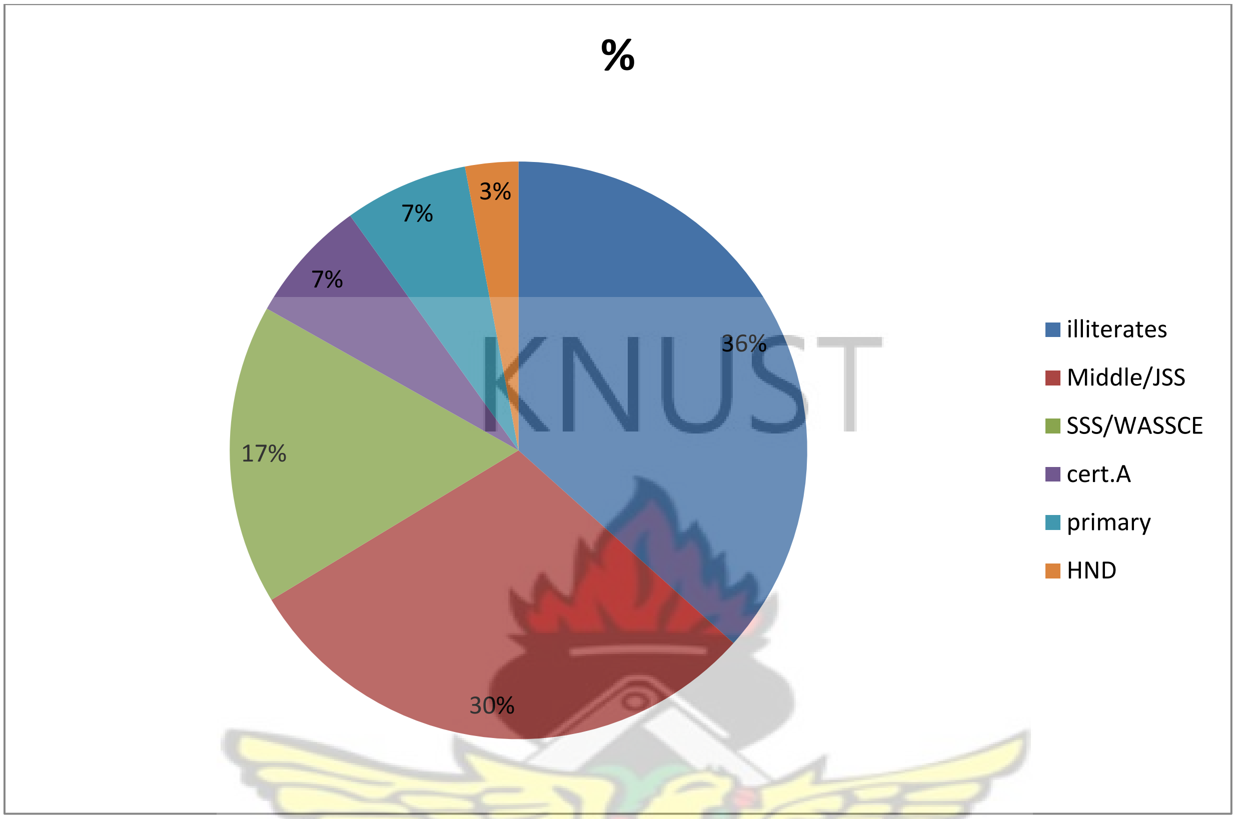


Figure 4.5: Educational levels of tomato farmers in Navrongo, Upper East Region

4.5.3 Pesticides commonly used in Navrongo

Questionnaire administered to the tomato farmers and field visits indicated that pesticides have been used in the cultivation of tomatoes in Navrongo. Pesticides commonly used are: karate (lambda cyhalothrin), lambda, carbofuran (carbamate), mancozeb (carbamate), ridomil (metalaxyll), sunpyrifos (chlorpyrifos-ethyl), kocide (cupric hydroxide- a fungicide), cypermethrin (pyrethroid), dimethoate (organophosphate), methylthiophanate and Top cop (50% Sulphur, 8.4 % tribasic copper sulphate-a fungicide).

4.5.4 Protective measures employed

Field visits to farms indicated that most of the farmers take protective measures such as wearing of gloves and nose masks during spraying as shown in the table 4.3 below.

Table 4.4: Protective measures employed by tomato farmers in Navrongo, upper East Region

Protective measures employed	Number of respondents
Goggles, gloves, coat, boot and nose mask	8
Gloves, coat, boot and nose mask	5
Goggles, gloves, coat and boot	2
Gloves, boot and nose mask	7
Goggles and nose mask	2
Boot and nose mask	2
Gloves and boot	2
None	2
Total	30

4.5.5 Time allowed between application and subsequent harvest

Table 4.5 shows that most farmers harvest tomato fruits at least two weeks after application.

Table 4.5: Time elapsed between application of pesticides and harvest in Navrongo, Upper East Region

Time elapsed between application and harvest	Number of respondents
less than one week	0
one week	2
two weeks	12
more than two weeks	16
Total	30

4.5.6 Health effects on tomato farmers

Although many of them have been growing tomatoes and applying the insecticides for over ten years, many of the respondents did not seem to experience any health problems. A few however, said they feel transient headaches and nausea soon after application. This is shown in table 4.4 below.

Table 4.6: Health effects of tomato farmers in Navrongo, Upper East region

Health effect	Number of respondents
Yes	2
No	28
Total	30

4.6 Calculation of recovery

The percentage recovery of the internal standard (isodrin) which had been added to one sample in each batch of analysis was calculated from the relationship:

$$\text{Percentage Recovery (\%R)} = \frac{\text{isodrin concentration determined from analysis}}{\text{initial isodrin concentration}} \times 100$$

1^{st} run- The percentage recovery was 78.30%

2^{nd} run- The percentage recovery was 79.45%

Therefore average: (78.3 + 79.45)/2 =78.88%

The average percentage recovery was 78.88%

There were no significant peaks in the chromatograms of the blanks.

CHAPTER FIVE

DISCUSSION

5.1 Occurrence and levels of OCs in the tomato samples

Figures 4.1, 4.2 and 4.3 show the mean concentrations of the nineteen organochlorine pesticides that were detected. The detected levels ranged from 0.0038 to 15.9007µg/kg. The highest concentration of 15.9007µg/kg was recorded for beta-HCH at Korania.

The concentrations measured in this work were lower compared to those of similar works done elsewhere in Ghana. For example, Essumang et al. (2008) reported that the concentrations of insecticides in tomatoes from Ghana ranged between 0.03 to 10.76 mg/kg (or 30 to 10760 µg/kg). Afful et al. (2010) also reported levels of organochlorine residues in the Densu basin as ranging from 0.3 to 71.3 µk/kg.

The low levels of the organochlorines in this work could be due to minimal misuse of these pesticides in the study area as a result of their ban from agricultural use.

Although the levels were generally lower than those of similar works, the results show that organochlorine insecticides are still found in the environment, despite the fact that they have been banned from use in Ghana (EPA, 2008).

The presence of these pesticides in the environment years after their ban could be due to their ability to persist in the environment. Persistency is defined as a half-life greater than two months in water or six months in soil and sediment. These chemicals are difficult to degrade into less hazardous substances in the environment. They are lipophilic compounds that tend to bioaccumulate in fatty tissues through the food chain. Bioaccumulation of organochlorine pesticides is defined as a log K_{ow} value greater than five or bioaccumulation factor in aquatic species greater than 5000. These pesticides are water insoluble and semi-volatile, enabling their entry in the atmosphere and transport over long distances globally, mainly by air mass movements. They can reach polar or high mountainous regions and are effectively deposited in cold regions by snow through the phenomenon of cold condensation and global distillation (Wania and Mackay, 1995).

Their detection also indicates that some Ghanaian farmers still use these agrochemicals illegally. Farmers prefer the organochlorine pesticides because they are relatively cheap and very effective (Essumang et al., 2008).

The concentrations of the parent p, p-DDT was higher in all the three communities than its main break-down product (p, p-DDE). From table 4.1, the average concentrations of p,p-DDT at Bonia, Korania and Nangalkenia were 8.2535µg/kg, 0.8213 µg/kg and 0.3439 µg/kg respectively, while those of p,p-DDE were 0.2468 µg/kg,0.3356 µg/kg and 0.2443 µg/kg respectively. This suggests a recent use of DDT in these areas, since p,p-DDT is the major component of technical-grade DDT(65-80%).

Table 4.1 also shows that in all three communities the concentrations of gamma HCH were higher than alpha HCH. This suggests a fresh input of the gamma HCH (lindane), since photochemical transformation of the gamma isomer yields the alpha isomer.

The detection of the breakdown products of DDT (DDE and DDD) is an indication of photochemical degradation of the DDT (Wandiga, 1995).

In all the three communities the average concentration of heptachlor was higher than that of heptachlor epoxide. For example, the average concentration of heptachlor in Bonia was 3.4079µg/kg while that of trans-heptachlor epoxide was 0.1269 µg/kg and cis-heptachlor epoxide was not detected at all. Heptachlor undergoes both biological and chemical transformation to heptachlor epoxide and other degradation products in the environment. Heptachlor epoxide degrades more slowly and, as a result, is more persistent than heptachlor (ATSDR 2005a). Therefore, the higher concentrations of heptachlor than heptachlor epoxide indicate that this insecticide has been used recently.

The detection of the HCHs and DDTs at appreciable levels is worrisome, since they are among organochlorines listed by the Stockholm Convention as persistent organic pollutants. The International Agency for Research on Cancer (IARC) has classified HCH (all isomers) as possible human carcinogens. Long-term exposure to α-HCH, β-HCH, γ-HCH, or technical-grade HCH has been reported to result in liver cancer. It can also result in blood disorders, dizziness, headaches, and possible changes in the levels of sex hormones in the blood (IARC, 2001; ATSDR, 2005b).

5.2 Comparison of mean concentrations (µg/kg) of organochlorine insecticides residues in tomato samples with UK/MRLs

Table 4.2 shows that with the exception of beta HCH at Korania and delta-HCH at Nangalkenia, all the nineteen organochlorine insecticides detected were below the UK/EC MRLs. This means that tomatoes from Navrongo poses minimal risk to consumers and therefore safe for consumption. However, it is important to note that, the effect of a pesticide on human health does not depend only on the quantity of the pesticide accumulated. It also depends on the length and frequency of exposure and the health of the person at the time of the exposure (Karalliedde et al., 2003). Therefore, even though the levels are lower than the UK/EC MRLs, there is still a cause for concern. This is because consumers who frequently consume these tomatoes may have these organochlorines accumulated in their bodies. Besides, consumers who already have other sources of exposure such as drinking water, meat, etc will suffer the cumulative effect of these ubiquitous pesticides.

The results of the present study are comparable with those of other studies. For example, Darko and Acquaah (2007) found that the levels of organochlorines in meat from the Kumasi and Buoho abattoirs were lower than the maximum limits set by FAO/WHO. Adeyeye and Osibanjo (1999) found that residue levels of organochlorine pesticides in raw fruits, vegetables and tubers from markets in Nigeria were generally low and none were above the FAOs maximum residue limits. In a similar study, Usman et al. (2009) found that all the marketed fruits and vegetables sampled from Lahore, Parksitan had residue levels below the maximum residue limit (MRL) set by WHO.

The results of the study are lower than those found in vegetables from three major markets in Ghana (Amoah et al., 2006) which exceeded the MRLs for consumption. In a similar study by Odhiambo et al. (2007), the organochlorine residues detected in vegetables exceeded the Chinese Extraneous Maximum Residue Limit of 50ng/g (50μg/kg) for DDTs in vegetables.

These lower levels compared to UK/EC MRLs suggests minimal misuse of organochlorine insecticides in Navrongo compared to those places where the levels exceeded the Maximum Residue limits.

5.3 Comparison of mean concentrations of organochlorine residues among the varieties of tomatoes.

Statistical analysis shows no significant differences in the mean concentrations among the varieties ($p>0.05$) as shown in Appendix 3.

The crops were grown under the same soil conditions and the same pesticides were applied on them in the same way. Therefore, the lack of significant differences between them suggests that they have similar absorption or accumulation abilities.

The cuticle or cuticular membrane (CM) of fruits limits the loss of substances from the fruits internal tissues, protects the fruits against physical, chemical, and biological attacks and protects the fruits against the external environment both while the fruit is on the plant and after harvest (Antonio et al., 2005). Therefore, the lack of significant differences in pesticide residues could be attributed to similar cuticle thickness.

5.4 Comparison of mean concentrations of organochlorine residues among locations

Statistical analysis shows that there were significant differences in the mean concentrations of most of the organochlorine residues among the sampling locations (Bonia, Korania and Nangalkenia) as shown in Appendix 2. This variation may be due to differences in the agricultural practices in applying the pesticides. For example, it could be as a result of differences in time elapsed between application and harvest.

5.5 General information about tomato farmers

Information gathered from the questionnaire and field visits, indicates that most of the farmers take precautionary measures seriously. For example they use gloves and nose masks when spraying. Most also allow the normal waiting period of two weeks after application before harvesting. This suggests that the farmers are aware of the toxic effects of pesticides.

5.6 Health Effects

The responses from questionnaires administered to the tomato farmers shows that the farmers do not experience any significant health problems after spraying. This could mean that they follow the correct ways of handling and spraying of pesticides. For example, the field visits and questionnaires show that the farmers take precautionary measures seriously during spraying. However, this does not mean that pesticides have no effect on the farmers. Low levels of exposure to pesticides over long period of time can result in chronic effects. Major health impacts from chronic exposure include cancers, reproductive and endocrine disruption, neurological damage, and immune system dysfunction (Sanborn, 2004; Moses, 1999). Long-term regular exposure to pesticides causes approximately 772,000 new cases of diseases every year (WHO and UNEP, 1990). The pesticides may be accumulating in their bodies and could pose health problems in the future (Ejobi et al., 1996).

5.7 Recovery

The mean recovery in this study (78.88%) was within the normal acceptable range of 70 - 120 % (Hill, 2000). This indicates good performance of extraction and clean-up. Therefore, the results were not corrected for recoveries.

5.8 Educational background of tomato farmers

The study found that a significant proportion of the tomato farmers are illiterates (36%). 30% of them were middle school/JSS leavers and 2 % were primary school leavers. This means that majority of the farmers cannot read instructions and warnings on pesticide containers.

However, the questionnaire and field visits show that both the literates and illiterates generally obey good agricultural practices. For example, most seemed to be aware that it is not safe to harvest tomato fruits shortly after application. They both take precautionary measures during spraying.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The average levels of organochlorine residues in tomatoes sampled in this study were generally quite low when compared to UK/EC MRLs. Only two of the nineteen organochlorine residues detected in the study were above the UK/EC MRLs. Although the concentrations are generally low, the study shows that the organochlorine insecticides are still being used despite the fact that they have been banned from use in Ghana.

The two most common varieties of tomatoes in Navrongo, Pectomech and 'No Name' had no significant differences in mean concentrations of organochlorine insecticides suggesting similar pesticide accumulation abilities.

Most of the organochlorine residues detected were below the maximum limits set by the UK/EC. Therefore, tomatoes from Navrongo are safe for consumption. However, because of their lipid solubility and resistance to metabolism, they can bioaccumulate in human tissues of consumers. So, chronic exposure could pose health problems. Therefore, constant monitoring of organochlorine residues in the study area is essential.

6.2 RECOMMENDATIONS

In view of the serious health risk associated with the organochlorine insecticides, there is the need for the tomato farmers to be sensitized against illegal use of banned pesticides. The farmers should be educated through the mass media in local languages and through workshops about the damaging effects of these pesticides on human health and the environment. In addition, the following recommendations are made:

1. Similar research should be conducted to determine the organochlorine levels in the drinking water as well as the water of the irrigation dam. This will enable us know if these are other ways through which residents are exposed to pesticides.
2. Because organochlorines can be stored in the mother's body and transferred prenatally to the developing fetus or postnatally from breast milk to the nursing infant, further research should be conducted to determine the concentrations of organochlorines in the blood or milk of nursing mothers in the area. This will enable us know the level of exposure of developing fetus and infants to organochlorines.
3. Laws banning the use of pesticides must be strictly enforced to ensure that these banned pesticides are not smuggled into the country.

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APPENDICES

Appendix 1: Questionnaire for tomato growers in Navrongo

SECTION A: Personal information

1. Name of farmer ……………………………………………………………..

2. Age-------- 3. Sex ------ 4. What is your level of education? Tick where appropriate. A. degree B. HND C. Cert. A D. SSSCE/WASSCE E Tech/vocational. F. middle school/JSS G. Primary H. Illiterate

SECTION B: General information on farms

- Do you grow any crop apart from tomatoes? [ ] Yes [ ] No.
- If yes what other crops do you grow? …………………………………
- How many growing seasons do you have in a year? …………………………..
- What is the size of your farm? ……………………………………
- Do you use any soil improvement method?

  [ ] Yes [ ] No
- If yes, what do you use?

  [ ] fertilizer [ ] manure [ ] crop rotation [ ] mulching

  Others…………………………………………..

SECTION C: Chemicals used

1. Which type of chemicals do you apply? Tick if you apply.

agrochemical	Tick	Agrochemical	Tick
1. Thiodan/endosulphan		8. methylthiophanate	
2. Dursban/Lorsban/chlorpyrifos		9. metalaxyll	
3. carbofuran(furadan)		10. Karate	
4. Lambda		11. Warrior	
5. Kocide		12. Demand	
6. mancozeb		13. DDT	
7. dimethoate			

Any other. Specify--

----

2. For how long have you handled the pesticides stated in (1)?

   A. 1 year **B**. 1-5 years **C**. 6-10 years **D**. above 10 years

3. Are you able to read and understand the instructions of pesticides labels?

   [ ] Yes [ ] No

4. If no, who provides you with the information?

   A. Other farmers **B**. Chemical sellers **C**. Friends **D**. Extension Officers

5. Do you normally mix two or more pesticides in other to enhance its effectiveness?

   [ ] Yes [ ] No

6. If yes, which chemicals do you normally mix?

……………………………………………...

SECTION D: Protective measures employed.

1. Which of the following protective apparatus do you use during application? Tick if yes

A. Goggles B. Gloves C. Coat D. boot E. nose mask

2. How long after application do you harvest your crops?

one week [ ] less than a week [ ] two weeks [ ]

more than two weeks [ ] Others. Specify---

3. Do you experience any health problems? YES [ ] NO [ ]

4. If yes, describe briefly --

Thank you very much.

Appendix 2: Analysis of variance of mean concentrations of pesticides among locations

Table 1a: ANOVA of alpha-HCH and sample location

Source	df	SS	MS	F	Prob>F
Between groups	2	0.161711	0.080856	6.47	0.0124
Within groups	12	0.14991	0.012493		
Total	14	0.311622	0.022259		

Bartlett's test for equal variance: $\chi^2(2) = 5.1658\ Prob > \chi^2 = 0.076$

Table 1b: Comparison of alpha-HCH by sample location

Paired Sample location	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Bonia Vs Korania	0.1736	0.0740	0.0730	0.0730
Bonia vs Nangalkenia	0.2593	0.0140	0.0160	0.0140
Korania vs Nangalkenia	0.0858	0.7720	0.5130	0.5900

Table 2a: ANOVA of beta-HCH and sample location

Source	df	SS	MS	F	Prob>F
Between groups	2	123.4755	61.7378	14.85	0.0278
Within groups	3	12.4709	4.15670		
Total	5	135.9465	27.1893		

Table 2b: Comparison of beta-HCH by sample location

Paired Sample location	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Bonia Vs Korania	15.4036	0.038	0.029	0.038
Bonia vs Nangalkenia	5.79653	0.253	0.178	0.233
Korania vs Nangalkenia	-9.6071	0.073	0.055	0.071

Table 3a: ANOVA of gamma-HCH and sample location

Source	df	SS	MS	F	Prob>F
Between groups	2	2.723154	1.361577	2.79	0.101
Within groups	12	5.85209	0.487674		
Total	14	8.575244	0.612517		

Bartlett's test for equal variance: $\chi^2(2) = 0.0501\ Prob > \chi^2 = 0.975$

Table 3b: Comparison of gamma-HCH by sample location

Paired Sample location	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Bonia Vs Korania	-0.93779	0.1400	0.1270	0.1330
Bonia vs Nangalkenia	-0.17884	1.0000	0.9300	0.9750
Korania vs Nangalkenia	0.75895	0.3540	0.2800	0.3140

Table 4a: ANOVA of delta-HCH and sample location

Source	df	SS	MS	F	Prob>F
Between groups	2	72.84504	36.42252	9.44	0.0062
Within groups	9	34.72356	3.858174		
Total	11	107.5686	9.778964		

Bartlett's test for equal variance: $\chi^2(2) = 3.6955\ Prob > \chi^2 = 0.158$

Table 4b: Comparison of delta-HCH by sample location

Paired Sample location	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Bonia Vs Korania	5.35043	0.0260	0.0270	0.0260
Bonia vs Nangalkenia	7.36157	0.0060	0.0060	0.0060
Korania vs Nangalkenia	2.01114	0.4410	0.3300	0.3800

Table 5a: ANOVA of heptachlor and sample location

Source	df	SS	MS	F	Prob>F
Between groups	2	4.673581	2.336790	0.97	0.4053
Within groups	12	28.76958	2.397465		
Total	14	33.44316	2.388797		

Bartlett's test for equal variance: $\chi^2(2) = 3.1209\ Prob > \chi^2 = 0.210$

Table 5b: Comparison of heptachlor by sample location

Paired Sample location	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Bonia Vs Korania	-1.15511	0.7250	0.4890	0.5640
Bonia vs Nangalkenia	-1.22396	0.7840	0.5180	0.5970
Korania vs Nangalkenia	-0.06885	1.0000	0.9980	1.0000

Table 6a: ANOVA of Aldrin and sample location

Source	df	SS	MS	F	Prob>F
Between groups	2	0.155653	0.077827	4.19	0.0444
Within groups	11	0.204379	0.01858		
Total	13	0.360032	0.027695		

Bartlett's test for equal variance: $\chi^2(2) = 1.7096\ Prob > \chi^2 = 0.425$

Table 6b: Comparison of Aldrin by sample location

Paired Sample location	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Bonia Vs Korania	0.252075	0.0460	0.0470	0.0450
Bonia vs Nangalkenia	0.118025	0.7390	0.4950	0.5720
Korania vs Nangalkenia	-0.13405	0.4680	0.3490	0.3980

Table 7a: ANOVA of trans-Heptachlor epoxide and sample location

Source	df	SS	MS	F	Prob>F
Between groups	1	0.005726	0.005726	66.25	0.0039
Within groups	3	0.000259	0.0000864		
Total	4	0.005985	0.001496		

Table 7b: Comparison of trans-Heptachlor epoxide by sample location

Paired Sample location	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Bonia Vs Korania	-0.0846	0.0040	0.0040	0.0040
Bonia vs Nangalkenia	-	-	-	-
Korania vs Nangalkenia	-	-	-	-

Table 8a: ANOVA of trans-Chlordane and sample location

Source	df	SS	MS	F	Prob>F
Between groups	1	0.002114	0.002114	0.17	0.7063
Within groups	3	0.036888	0.012296		
Total	4	0.039002	0.00975		

Table 8b: Comparison of trans-Chlordane by sample location

Paired Sample location	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Bonia Vs Korania	-	-	-	-
Bonia vs Nangalkenia	-	-	-	-
Korania vs Nangalkenia	-0.0514	0.7060	0.7060	0.7060

Table 9a: ANOVA of trans-Nonachlor and sample location

Source	df	SS	MS	F	Prob>F
Between groups	2	0.113677	0.056839	0.43	0.6749
Within groups	4	0.523221	0.130805		
Total	6	0.636898	0.106150		

Bartlett's test for equal variance: $\chi^2(1) = 5.9547 Prob > \chi^2 = 0.015$

Table 9b: Comparison of trans-Nonachlor by sample location

Paired Sample location	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Bonia Vs Korania	-0.2139	1.0000	0.7820	0.8820
Bonia vs Nangalkenia	-0.3362	1.0000	0.7410	0.8480
Korania vs Nangalkenia	-0.1223	1.0000	0.9580	0.9900

Table 10a: ANOVA of pp-DDE and sample location

Source	df	SS	MS	F	Prob>F
Between groups	2	0.023781	0.011891	0.53	0.6072
Within groups	4	0.202824	0.022536		
Total	6	0.226605	0.020600		

Bartlett's test for equal variance: $\chi^2(2) = 6.9590\ Prob > \chi^2 = 0.031$

Table 10b: Comparison of pp-DDE by sample location

Paired Sample location	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Bonia Vs Korania	0.088853	1.0000	0.7280	0.8230
Bonia vs Nangalkenia	-0.00249	1.0000	1.000	1.0000
Korania vs Nangalkenia	-0.09135	1.0000	0.675	0.771

Table 11a: ANOVA of op-DDD and sample location

Source	df	SS	MS	F	Prob>F
Between groups	1	0.240419	0.240419	2.46	0.1606
Within groups	7	0.683619	0.09766		
Total	8	0.924037	0.115505		

Bartlett's test for equal variance: $\chi^2(1) = 7.5786\ Prob > \chi^2 = 0.006$

Table 11b: Comparison of op-DDD by sample location

Paired Sample location	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Bonia Vs Korania	-	-	-	-
Bonia vs Nangalkenia	-	-	-	-
Korania vs Nangalkenia	-0.32892	0.1610	0.1610	0.1610

Table 12a: ANOVA of Endrin and sample location

Source	df	SS	MS	F	Prob>F
Between groups	2	0.01425	0.01425	10.22	0.193
Within groups	4	0.001394	0.001394		
Total	6	0.015644	0.007822		

Table 12b: Comparison of Endrin by sample location

Paired Sample location	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Bonia Vs Korania	0.14620	0.1930	0.1930	0.1930
Bonia vs Nangalkenia	-	-	-	-
Korania vs Nangalkenia	-	-	-	-

Table 13a: ANOVA of op-DDT and sample location

Source	df	SS	MS	F	Prob>F
Between groups	2	0.051481	0.025741	2.52	0.1605
Within groups	6	0.061293	0.010215		
Total	8	0.112774	0.014097		

Bartlett's test for equal variance: $\chi^2(2) = \ 2.1820\ Prob > \chi^2 = \ 0.336$

Table 13b: Comparison of op-DDT by sample location

Paired Sample location	Mean difference $\bar{\mathbf{x}}_\mathbf{a} - \bar{\mathbf{x}}_\mathbf{b}$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Bonia Vs Korania	0.100733	0.7190	0.4730	0.5610
Bonia vs Nangalkenia	-0.09047	1.0000	0.6400	0.7440
Korania vs Nangalkenia	-0.1912	0.2150	0.1730	0.2000

Table 14a: ANOVA of pp-DDT and sample location

Source	df	SS	MS	F	Prob>F
Between groups	2	146.1362	73.0681	0.98	0.4166
Within groups	4	597.0878	74.63598		
Total	6	743.224	74.3224		

Bartlett's test for equal variance: $\chi^2(2) = \ 20.6791\ \ Prob > \chi^2 = \ 0.0000$

Table 14b: Comparison of pp-DDT by sample location

Paired Sample location	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Bonia Vs Korania	-7.43213	0.7070	0.4730	0.5530
Bonia vs Nangalkenia	-7.90955	0.9640	0.5930	0.6870
Korania vs Nangalkenia	-0.47742	1.0000	0.9980	1.0000

Appendix three: Analysis of variance of mean concentrations of pesticides among varieties of tomatoes

Table 1a: ANOVA of alpha-HCH and variety

Source	df	SS	MS	F	Prob>F
Between groups	2	0.002895	0.001448	0.06	0.9455
Within groups	12	0.308727	0.025727		
Total	14	0.311622	0.022259		

Bartlett's test for equal variance: $\chi^2(2) = 0.0357$ $Prob > \chi^2 = 0.982$

Table 1b: Comparison of alpha-HCH by variety

Paired variety	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Pectomech vs Noname	0.02979	1.0000	0.9490	0.0730
Pectomech vs Others	0.0212	1.0000	0.9860	0.0140
Noname vs Others	-0.00859	1.0000	0.9980	0.5900

Table 2a: ANOVA of beta-HCH and variety

Source	df	SS	MS	F	Prob>F
Between groups	2	40.92249	20.46124	0.65	0.5844
Within groups	3	95.02398	31.67466		
Total	5	135.9465	27.18929		

Bartlett's test for equal variance: $\chi^2(1) = 0.5246$ $Prob > \chi^2 = 0.469$

Table 2b: Comparison of beta-HCH by variety

Paired Sample location	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Pectomech vs Noname	5.78493	1.0000	0.589	0.715
Pectomech vs Others	3.27143	1.0000	0.885	0.957
Noname vs Others	-2.5135	1.0000	0.937	0.982

Table 3a: ANOVA of gamma-HCH and variety

Source	df	SS	MS	F	Prob>F
Between groups	2	0.536466	0.268233	0.4	0.6787
Within groups	12	8.038778	0.669898		
Total	14	8.575244	0.612517		

Bartlett's test for equal variance: $\chi^2(2) = 0.0578$ $Prob > \chi^2 = 0.972$

Table 3b: Comparison of gamma-HCH by variety

Paired variety	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Pectomech vs Noname	-0.09877	1.0000	0.9780	0.9960
Pectomech vs Others	0.50255	1.0000	0.7450	0.8360
Noname vs Others	0.60132	1.0000	0.6880	0.7810

Table 4a: ANOVA of delta-HCH and variety

Source	df	SS	MS	F	Prob>F
Between groups	2	13.66487	6.832436	0.65	0.5426
Within groups	9	93.90373	10.43375		
Total	11	107.5686	9.778964		

Bartlett's test for equal variance: $\chi^2(1) = 0.7444$ $Prob > \chi^2 = 0.388$

Table 4b: Comparison of delta-HCH by variety

Paired variety	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Pectomech vs Noname	2.16539	0.8910	0.5630	0.6530
Pectomech vs Others	1.96235	1.0000	0.8560	0.9300
Noname vs Others	-0.20304	1.0000	0.9980	1.0000

Table 5a: ANOVA of heptachlor and variety

Source	df	SS	MS	F	Prob>F
Between groups	2	6.397597	3.198799	1.42	0.2797
Within groups	12	27.04556	2.253797		
Total	14	33.44316	2.388797		

Bartlett's test for equal variance: $\chi^2(2) = 0.9309$ $Prob > \chi^2 = 0.628$

Table 5b: Comparison of heptachlor by variety

Paired variety	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Pectomech vs Noname	1.09377	0.6760	0.4650	0.5350
Pectomech vs Others	1.67258	0.5520	0.3990	0.4570
Noname vs Others	0.57880	1.0000	0.9000	0.958

Table 6a: ANOVA of Aldrin and variety

Source	df	SS	MS	F	Prob>F
Between groups	2	0.00865	0.004325	0.14	0.8748
Within groups	11	0.351382	0.031944		
Total	13	0.360032	0.027695		

Bartlett's test for equal variance: $\chi^2(2) = 1.4151\ Prob > \chi^2 = 0.493$

Table 6b: Comparison of Aldrin by variety

Paired variety	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Pectomech vs Noname	-0.051254	1.0000	0.8880	0.9510
Pectomech vs Others	-0.045364	1.0000	0.9510	0.9860
Noname vs Others	0.00589	1.0000	0.9990	1.0000

Table 7a: ANOVA of trans-Heptachlor epoxide and variety

Source	df	SS	MS	F	Prob>F
Between groups	1	0.00085547	0.000855	0.5	0.5304
Within groups	3	0.00512954	0.001710		
Total	4	0.00598501	0.001496		

Bartlett's test for equal variance: $\chi^2(1) = 1.3361\ Prob > \chi^2 = 0.248$

Table 7b: Comparison of trans-Heptachlor epoxide by variety

Paired variety	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Pectomech vs Noname	0.02670	0.5300	0.5300	0.5300
Pectomech vs Others	-	-	-	-
Noname vs Others	-	-	-	-

Table 8a: ANOVA of trans-Chlordane and variety

Source	df	SS	MS	F	Prob>F
Between groups	2	0.00983998	0.00492	0.34	0.7477
Within groups	2	0.02916185	0.014581		
Total	4	0.03900183	0.009750		

Bartlett's test for equal variance: $\chi^2(1) = 3.3361\ Prob > \chi^2 = 0.068$

Table 8b: Comparison of trans-Chlordane by variety

Paired variety	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Pectomech vs Noname	0.08790	1.0000	0.7910	0.9040
Pectomech vs Others	-0.00745	1.0000	0.9990	1.0000
Noname vs Others	-0.09535	1.0000	0.8280	0.9290

Table 9a: ANOVA of trans-Nonachlor and variety

Source	df	SS	MS	F	Prob>F
Between groups	2	0.27989654	0.139948	1.57	0.3142
Within groups	4	0.35700149	0.08925		
Total	6	0.63689804	0.10615		

Bartlett's test for equal variance: $\chi^2(1) = 4.6067\ Prob > \chi^2 = 0.032$

Table 9b: Comparison of trans-Nonachlor by variety

Paired variety	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Pectomech vs Noname	-0.37475	0.6630	0.4300	0.5270
Pectomech vs Others	-0.5786	0.5670	0.3790	0.4670
Noname vs Others	-0.20385	1.0000	0.8370	0.9230

Table 10a: ANOVA of pp-DDE and variety

Source	df	SS	MS	F	Prob>F
Between groups	2	0.00415085	0.002075	0.08	0.9202
Within groups	9	0.2224544	0.024717		
Total	11	0.22660525	0.0206		

Bartlett's test for equal variance: $\chi^2(2) = 1.8760\ Prob > \chi^2 = 0.391$

Table 10b: Comparison of pp-DDE by variety

Paired variety	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Pectomech vs Noname	0.03018	1.0000	0.9550	0.9880
Pectomech vs Others	0.04862	1.0000	0.9340	0.9780
Noname vs Others	0.01844	1.0000	0.9900	0.9990

Table 11a: ANOVA of op-DDD and variety

Source	df	SS	MS	F	Prob>F
Between groups	2	0.10716602	0.053583	0.39	0.6909
Within groups	6	0.81687142	0.136145		
Total	8	0.92403744	0.115505		

Bartlett's test for equal variance: $\chi^2(1) = 3.9767\ Prob > \chi^2 = 0.046$

Table 11b: Comparison of op-DDD by variety

Paired variety	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Pectomech vs Noname	0.1701	1.0000	0.8140	0.9020
Pectomech vs Others	-0.15045	1.0000	0.9360	0.9800
Noname vs Others	-0.32055	1.0000	0.7500	0.8480

Table 13a: ANOVA of op-DDT and variety

Source	df	SS	MS	F	Prob>F
Between groups	2	0.01437454	0.007187	0.44	0.6643
Within groups	6	0.09839928	0.0164		
Total	8	0.11277382	0.014097		

Bartlett's test for equal variance: $\chi^2(2) = 0.5338\ Prob > \chi^2 = 0.766$

Table 13b: Comparison of op-DDT by variety

Paired Sample variety	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Pectomech vs Noname	-0.05775	1.0000	0.8680	0.9400
Pectomech vs Others	-0.09510	1.0000	0.6910	0.7940
Noname vs Others	-0.03735	1.0000	0.9590	0.9890

Table 14a: ANOVA of pp-DDT and variety

Source	df	SS	MS	F	Prob>F
Between groups	2	137.077055	68.53853	0.9	0.4424
Within groups	8	606.146953	75.76837		
Total	10	743.224009	74.32240		

Bartlett's test for equal variance: $\chi^2(1) = \ 24.2042\ Prob > \chi^2 = \ 0.0000$

Table 14b: Comparison of pp-DDT by variety

Paired Sample location	Mean difference $\bar{x}_a - \bar{x}_b$	Bonferroni (P-value)	Scheffe (P-value)	Sidak (P-value)
Pectomech vs Noname	7.25272	0.698	0.4690	0.5480
Pectomech vs Others	-0.55083	1.0000	0.9980	1.000
Noname vs Others	-7.80355	1.0000	0.7340	1.0000

Appendix four: Raw data of pesticides residues in tomatoes

Ghana Atomic Energy Commission
Department of Chemistry
Pesticide Residue Laboratory

Analysis of organochlorine pesticide residue in Tomatoes

Concentrations (ug/kg) of organochlorine pesticide residue in Tomatoes

	NANGALKENIA			Sample Location			KORANIA			
Name of Pesticide	FF1A	FF1B	FF1C	FF2	FF3	FF4	FF5	FF6	FF7	FF8
alpha-HCH	0.3439	0.4062	0.4176	0.4570	0.5367	0.1207	0.3325	0.3458	0.1589	0.4277
Hexachlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
beta-HCH	4.5795	4.5055	7.7266	8.3629	15.9007	ND	ND	ND	ND	ND
gamma-HCH	2.5942	1.6560	1.8418	3.0116	1.0370	1.1304	2.6459	2.1413	1.3137	0.9834
delta-HCH	14.6775	9.4035	8.8774	7.8949	9.1643	8.6143	7.1697	9.3307	6.6618	8.2723
Heptachlor	3.0741	1.1982	2.2623	2.2010	1.6004	2.2905	4.1957	2.4726 /	0.3452	2.6121
Aldrin	0.3829	0.2466	0.2793	0.3924	0.3391	0.3916	0.5960	0.4267	0.3273	0.6754
Trans-Heptachlor Epoxide	.ND	ND	ND	ND	ND	0.0333	0.0353	0.0495	ND	0.0511
Trans Chlordane	ND	ND	0.0353	ND	ND	0.2513	0.0378	0.0100	ND	0.0477
O'P-DDE	0.3021	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cis-Chlordane	ND	ND	ND	0.0038	ND	ND	0.0374	ND	ND	ND
Trans- Nanochlor	0.0853	ND	ND	#VALUE!	0.2486	0.2053	#VALUE!	ND	ND	0.1689
P'P DDE	0.2173	0.2083	0.2874	0.2641	0.2476	0.6101	0.1211	0.1801	ND	0.5192
Dieldrin	ND	ND	ND	ND	ND	0.3030	0.0156	ND	ND	ND
O'P-DDD	0.0618	0.0863	0.0716	0.1731	0.1788	1.1479	0.3785	0.1801	ND	0.2503
Endrin	ND	ND	ND	ND	ND	0.3875	ND	ND		ND
P'P DDD	ND	ND	ND	ND	ND	0.8090	0.3785	ND		ND
O'P-DDT	ND	ND	0.0073	0.0697	0.0829		0.2552	0.1732	ND	0.4003
PP-DDT	ND	ND	0.2990	0.3888	0.3748	2.2873	0.5222	0.3819	ND	0.5404

ND – Not Detected

Ghana Atomic Energy Commission
Department of Chemistry
Pesticide Residue Laboratory

Analysis of organochlorine pesticide residue in Tomatoes

Concentrations (ug/kg) of organochlorine pesticide residue in tomatoes

Sample Location	BONIA				
Name of Pesticide	F1A	F1B	F2	F3	F4
alpha-HCH	0.1651	0.1701	0.0505	0.1167	0.2317
hexachlorobenzene	0.4690	ND	ND	ND	ND
beta-HCH	ND	ND	ND	ND	0.4971
gamma-HCH (lindane)	2.6175	3.2090	1.5718	1.8586	3.1418
delta-HCH	3.6154	ND	2.0881	ND	ND
Heptachlor	6.1904	5.1465	0.9456	2.5071	2.2497
Aldrin	0.0725	0.3776	ND	0.3265	0.0525
cis-Heptachlor epoxide	ND	ND	ND	ND	ND
oxychlordane	ND	ND	ND	ND	ND
trans-Heptachlor epoxide	0.1269	ND	ND	ND	ND
trans-Chlordane	ND	ND	ND	ND	ND
o,p-DDE	ND	ND	ND	ND	ND
cis-Chlordane	ND	ND	ND	ND	ND
trans-Nonachlor	0.2762	0.0000	0.9883	ND	ND
p,p-DDE	0.2072	0.3344	ND	0.1987	ND
Dieldrin	ND	ND	ND	ND	ND
o,p-DDD	ND	ND	ND	ND	ND
Endrin	ND	0.2677	ND	0.2149	ND
p,p-DDD	ND	ND	ND	ND	ND
o,p-DDT	ND	0.1777	ND	0.0819	0.1219
cis-Nonachlor	ND	ND	ND	ND	ND
p,p-DDT	29.3662	ND	1.1072	1.1580	1.3824

ND – Not Detected