Qatar University

Graduate Studies

College of Art and Science

Determination of Pesticide Residues of Organochlorine in Some Local and Imported Foods in Qatar

A project in

The Department of Biological and Environmental Sciences

By

Noora Mahmoud Al-Shamary

Submitted in Partial Fulfillment

Of the Requirements

For the Degree of

Master of Science

May 2015

COMMITTEE PAGE

The Project of Noora Mahmoud Al-Shamary was reviewed and approved by the following:

We, the committee members listed below accept and approve the project of the student named above. To the best of this committee's knowledge, the project conforms the requirements of Qatar University, and we endorse this project for examination.

Name: Dr. Mohammad Ahmad Al-Ghouti

Signature: ……..... Date: ……

Name: Dr. Saeed Hashim Al-Meer

Signature: ……..... Date: ……

Name: Dr. Talaat Abdel-Fattah Ahmad

Signature: ……..... Date: ……

ABSTRACT

The study was aimed to examine the residues of pesticide in vegetables and fruits in Qatar. The total numbers of samples that were collected were 127 samples of seven most consumed fresh vegetables and fruits from local and import production. The samples were then extracted using Acceleration Solvent Extractor (ASE) and cleaned up using two solid phase extraction (SPE): florisil and silica gel. Gas chromatography with an electron capture detector (GC/ECD) was used to analyze the ten organochlorine pesticides (OCPs). In addition, scan mode of gas chromatography with mass spectrometry (GC/MS) was used in to screen the pesticides residues in these vegetables and fruits. Ninety percent of the imported samples recorded residues above the MRL with at least one of the selected OCPs and about 30% of the local samples (mostly leafy vegetables) contained residues above the MRL. The most frequently detected OCPs in the samples were heptachlor (found in 75 samples) and was detected mostly in imported samples, g-chlordane (found in 22 samples) and a-chlordane (found in 19 samples). Two statistical analysis tests were used to determine significance (pair-difference t-test and analysis of variance (ANOVA)). In most of the comparisons between the washed and unwashed samples, no-significant differences were observed ($P > 0.05$). Though, it seems that the effects of washing the samples with tap water differ in organochlorine residues based on the type of vegetables and fruits. The interaction between the washing treatment and countries for heptachlor on parsley showed significant difference. Accordingly, there

is a dire require for controlling program for residues of pesticides in food products, especially in imported food products.

ملخص البحث

كان الهدف من هذه الدراسة هو التعرف على بقايا المبيدات الحشرية في الأغذية في دولة قطر. تم تحليل 127 عينة لسبعة أنواع من الخضروات والفواكه الأكثر إستهلاكا في قطر من مصدرين: محلي ومستورد. تم استخلاص العينات بإستخدام جهاز (ASE) وبعدها تمت عملية التنظيف باستخدام نوعين من مستخلصات التنظيف الصلبة: الفروليسيل(florisil) و السيليكا (Silica gel) . تم تحليل عشرة مركبات من المبيدات الكلورية العضوية باستخدام جهاز الفصل الطيفي للغازات (GC / MS), وكانت 90٪ من العينات المستوردة تفوق مستوى الحد الأعلى المسموح به في احدى من المبيدات الكلورية العضوية ، وحوالي 30٪ من العينات المحلية (ومعظمهم من الخضروات الورقية) تحتوي على بقايا تفوق مستوى الحد الأعلى المسموح به. وبشكل عام, سباعي الكلور (heptachlor) وجد في (75 عينة) من العينات المستوردة في معظمها، الكلوريدان الفا (a-chlordane) (وجد في 22 عينة) وعلى الكلوريدان بيتا (وجد في 19 عينة).تم استخدام نوعين من اختبارات التحليل الاحصائي هما (t-test) و (ANOVA) لتحديد مدى تباين العينات بإختلاف العوامل المؤثرة. وفي معظم المقارنات بين العينات المغسوله بالماء والغير مغسوله, لم يلاحظ أي اختلافات تذكر ($P>0.05$). ومع هذا, يبدو أن تأثير غسل العينات بالماء يأتر على بقايا المواد الكلورية العضوية في بعض أنواع الخضروات والفواكه. وأظهرت نتائج المقارنات بأن التفاعل بين تأثير الغسيل بالماء والدول المنتجة ينتج فرق كبير في بقايا سباعي الكلور (heptachlor). وفقا لذلك، هناك حاجة ماسة لوضع برنامج لرصد بقايا المبيدات في المحاصيل الغذائية، وخاصة في المحاصيل الغذائية المستوردة.

LIST OF ABBREVIATIONS

ASE: Accelerated solvent extraction

DDT: dichlorodiphenyltrichloroethane

ECD: Electron-capture detector

EPA: Environmental Protection Agency

GC/ECD: Gas chromatography/ Electron-capture detector

GC/MS: Gas chromatography/ Mass spectrometry

GC: Gas chromatography

LC: Liquid Chromatography

MRL: Maximum Residue Level

MS: Mass spectrometry

OCPs: Organochlorine Pesticides

PCBs: Polychlorinated biphenyls

Table of Contents

LIST OF TABELS

LIST OF FIGURES

ACKNOWLEDGMENTS

First, my success was only by Allah. I give deep thanks to Mr. Ismail Al-Shaikh from the Environmental Studies Center at Qatar University for his guidance and support since starting my master study. My special and heartily thanks to my supervisor Dr. Mohammad Al-Ghouti. It is with his supervision that this work came into existence. I am also deeply thankful to my committee members Dr. Talaat Ahmad and Dr. Saeed Al-Meer for their help and advices. I would like to thank my colleagues in Environmental Science master program who became my second family; Mohammad Shehadi, Rabab Ahmad, Feda Al-Hadad, Rukaya Ammar, Maryam Al-Kaabi and Salma Al-Hajri. They are good friends and were always willing to help and give their best suggestions. I also thank my family who encouraged me and prayed for me throughout the time of my research. This thesis is heartily dedicated to my parents who without their prayers and help I could not achieve this stage.

1 INTRODUCTION

Fresh fruit and vegetables are significant sources of vitamins and minerals, thus they are an essential element of a healthy diet .On the other hand, fresh fruit and vegetables may contain toxic substances such as pesticides. Pesticides are several and diverse group of chemical compounds, which are applied to crops at various stages of cultivation and production and post-harvest treatment of agricultural products (Bakirci *et al*., 2014). With their environmental stability, ability to bioaccumulate and toxicity, environment contamination and human health effects have resulted duo to the increase use of pesticides (IARC, 2015; NTP, 2015 & Bolognesi & Merlo, 2011).

Due to the pesticides vulnerability to insect and disease attacks various types of pesticides are broadly used in vegetables and fruits. In general, pesticides are indiscriminately used and in huge amounts (Bempah *et al*., 2012). There are many types of pesticides which can be categorized into many classification based on the pest that they control, chemical composition, mode of action, etc. Based on chemical composition, they are classified into: organochlorine compounds, organophosphorus compounds, carbamates, pyrethroids and neonicotinoids (Mao, 2012).

Since the 1940s, organochlorine pesticides (OCPs) have broadly been used because of their effectiveness in the control of pests and diseases. OCPs were used to control pest on agricultural crops like cotton (Safiatou *et al*.2007). OCPs are known by their lipophilic properties and low water solubility (Bulut *et al*., 2011).

Consequently, they can pose environment problems to human health as they easily accumulate in human adipose tissue. Based on their toxicity, many OCPs are already banned from use or trade in many countries. Though most of OCPs are no longer in use in many countries, they are still being found as residues in food products as means of environmental contamination (Ahmad *et al*., 2010 & Feink *et al*., 2011).

To protect consumer health and to guarantee that food is safe, the controlling of residues of pesticide in food products must be pursued (Yang *et al*., 2013). Therefore, the allowed levels of pesticide residues in foodstuffs are legislatively controlled through setting maximum residue levels (MRLs). These MRLs limit the types and amount of pesticides that can be legally present in foods, as determined by various regulatory bodies which minimize consumer exposure to harmful or unnecessary intake of pesticides worldwide (Kmellara *et al*.,2010). Codex Alimentarius Commission (FAO/WHO, 2013) put values for MRL of OCPs in food items.

Recently, the government of Qatar has attempted to encourage agricultural production. Qatar's agricultural products (such as: vegetables and fruits) are consumed locally. Despite a noticeable increase in agricultural production in Qatar, however, this increase does not fulfill the need of residents in Qatar, and Qatar need to import large amounts of food products from other countries.

According to the Ministry of Environment, regulations and policies on pesticides have already been established and implemented. One of these policies is the ban of the use of extremely toxic pesticides and persistent pesticides that affect

animals and human (Qatar National Implementation Plan (NIP) for Stockholm Convention on Persistent Organic Pollutants (POPs), 2011). OCPs are considered to be one of the POPs that can persist, bio-accumulate, and cause serious effects on human health. However, the lack of information on these pesticide residues in the imported food products has encouraged us to perform this research on determining the concentrations of OCPs in imported food and to compare the results with our local products.

The study was aimed to examine the occurrence of organochlorine pesticides residues in some local and imported vegetables and fruits in Qatar, as a prelude to assess the risks related to their consumption. In order to achieve this aim, the following specific objectives were carried out:

1. Determine the amount of 10 organochlorine pesticides (Heptachlor, aldrin, dieldrin, Endrin, a-chlordane, g-chlordane, endosulfane I, methoxychlor, α-BHC and β –BHC) in seven mostly consumed vegetables and fruits in Qatar using Gas chromatography-electron capture detector (GC-ECD).
2. Screen the residues of pesticides in these vegetables and fruits using scan mode of Gas chromatography- mass spectrometry (GC-MS).
3. Perform statistical analyses to data obtained.

2 LITERATURE REVIEW

At various stages of cultivation and during the post-harvest storage of crops pesticides are applied (Bakirci *et al*., 2014). The use of pesticides is intended to prevent the destruction of food crops by controlling agricultural pests or unwanted plants and to improve plant quality (Bakirci & Hisil, 2012). To guarantee the worldwide food supply, pesticides use in agriculture is still necessary (Jardim *et al*., 2014).

2.1 Classification of Pesticides

2.1.1 Pesticides Classification Based on Type of Pest They Control

Pesticides are often classified according to the type of target organism they control. Table 1 shows different types of pesticides and their target organism (Singh, 2012).

Table 1: Different pesticides and their target organism (Singh, 2012).

Pesticide	Target Pest / Function	Pesticide	Target Pest / Function
Acaricide	Mites, ticks	Growth regulator	Regulates insect and plant growth
Algaecide	Algae	Herbicide	Weeds
Anticoagulant	Rodents	Insecticide	Insects
Attractant	Attracts insects or birds	Miticide	Mites
Avicide	Birds	Molluscicide	Snails, slugs
Bactericide	Bacteria	Nematicide	Nematodes
Defoliant	Plant leaves	Piscicide	Fish
Desiccant	Disrupts water balance in arthropods	Predacide	Vertebrate predators
Fungicide	Fungi	Repellent	Repels vertebrates or arthropods
Silvicide	Woody vegetation	Rodenticide	Rodents

2.1.2 Pesticides Classification Based on Chemical Composition

Another way to classify pesticides is to consider the chemical composition of pesticides products. The commonly utilized pesticides can be categorized into five classes, namely (Mao, 2012):

1. *Organochlorine compounds:* DDT, BHC/HCH, Aldrin, Endosulfan, Heptachlor, Methoxychlor,Chlordane, Dicofol.
2. *Organophosphorus compounds:* Parathion, Monocrotophos, Chlorpyrifos, Quinalphos, Phorate, Diazinon, Fenitrothion,Acephate, Dimethoate, Fenthion, Isofenfos, Phosphamidon, Temephos, Triazophos.
3. *Carbamates:* Aldicarb, Oxamyl, Carbaryl, Carbofuran, Carbosulfan, Methomyl, Methiocarb, Propoxur, Pirimicarb.
4. *Pyrethroids:* Allethrins, Deltametrin, Resmethrin, Cypermethrin, Permethrin, Fenvalerate, Pyrethrum.
5. *Neonicotinoids:* Acetamiprid, Imidacloprid, Nitenpyram, Thiamethoxam.

These types of pesticides played an major role in the increase of agricultural productivity and quality owing to their effectiveness in preventing, repelling or mitigating the effects of pests and diseases (Miao, 2013).

An organophosphate is an organic ester of phosphoric or thiophosphoric acid which is the basis of many insecticides, herbicides and nerve gases. Since these pesticides are very persistent compounds, they consider to be highly toxic to bees,

wildlife, and humans according to the Environmental Protection Agency (EPA) (Bernal, 2012).

Carbamate compounds are compounds that are generally used as insecticides and they are esters of carbamic acid. These compounds are referred to as *N*-methylcarbamates. There are many important benefits of using carbamate pesticides. Carbamate pesticides can protect and increase agricultural production and protect human and animal health from insect-vector-mediated diseases. Though, poisoning from these compounds may occur to humans and animals when they are overexposed (Gupta, 2014).

Pyrethroids are synthetic insecticides derived from the natural pyrethrins. Structurally they have 2 or 3 chiral centers. This means that they have 2 or 4 diastereomers and 4 or 8 enantiomers. The use of pyrethroids is extensive around the world (Corcellas *et al*., 2015). They are common in agronomics both on crops and directly over grain before storage, in veterinary on cattle and pets, as domestic insecticides and even for health purposes against scabies, lice or vectors of some diseases such as malaria or typhus (Barr *et al*., 2010).

A new class of insecticides known as Neonicotinoids share a general mode of action which is affecting the central nervous system of insects, resulting in paralysis and death. Sass 2014 stated that EPA mentioned that the neonicotinoid pesticides have uncertainties in identification, since their initial registration regarding the potential environmental fate and effects can relate to pollinators.

2.1.3 Pesticides Classification Based on Other Chemical Composition

Singh 2012 classified pesticides into seven groups as follows (Singh, 2012):

1. *Organotin compounds:* Triphenyltin acetate, Trivenyltin chloride, Tricyclohexyltin, hydroxide, Azocyclotin.
2. *Organomercurial compound:* Ethyl mercuric chloride, Phenyl mercuric bromide.
3. *Dithiocarbamate fungicides:* Zineb, Maneb, Mancozeb, Ziram.
4. *Benzimidizole compounds:* Benomyl, Carbendazim, Thiophanate methyl.
5. *Chlorphenoxy compounds:* 2,4-D, TCDD, DCPA, 2,4,5-T, 2,4-DB, MCPA, MCPP.
6. *Dipyridiliums:* Paraquat, Diquat.
7. *Miscellaneous:* DNOC, Bromoxyl, Simazine, Triazamate.

2.1.4 Pesticides Classification Based on Organic Structure

According to the organic structure of pesticides compounds, they can be classified in to three groups (Singh, 2012):

1. *Aliphatic compounds:* Methyl bromide, Malathion, Glyphosate, Aldicarb, EPTC, Maneb.
2. *Aromatic compounds:* 2,4-D, Diuron, Carbaryl, Permethrin.
3. *Heterocyclic ring compounds:* Nicotine, Captan, Benomyl, Atrazine.

2.1.5 Pesticide Classification based on mode of Action

Pesticides can affect different part in living organisms. They can be classified according to their mode of action they cause (Brown, 2013):

1. *Nerve poisons:* Organochlorine and Organophosphorus pesticides and Carbamates.
2. *Anticoagulants:* Warfarin.
3. *Juvenile hormones:* Azadirachtin, Fenoxycarb, Methoprrne, Hydroprene. Antifeedents: Neem, Citrus derived limonoids and their synthetic derivatives.
4. *Repellents:* Permethrin, Neem oil, Citronella oil.

2.1.6 Pesticides Classification Based on Pesticidal Action

Based on pesticidal action, pesticides can be classified in to two main groups (Singh, 2012):

1. *Stomach insecticide:* DDT, BHC/HCH, Methoxychlor, Lead arsenate, Paris green, NaF.
2. *Contact insecticide:* Chlordane, Aldrin, Nicotine, Parathion.

2.2 Positive and negative impacts of using pesticides

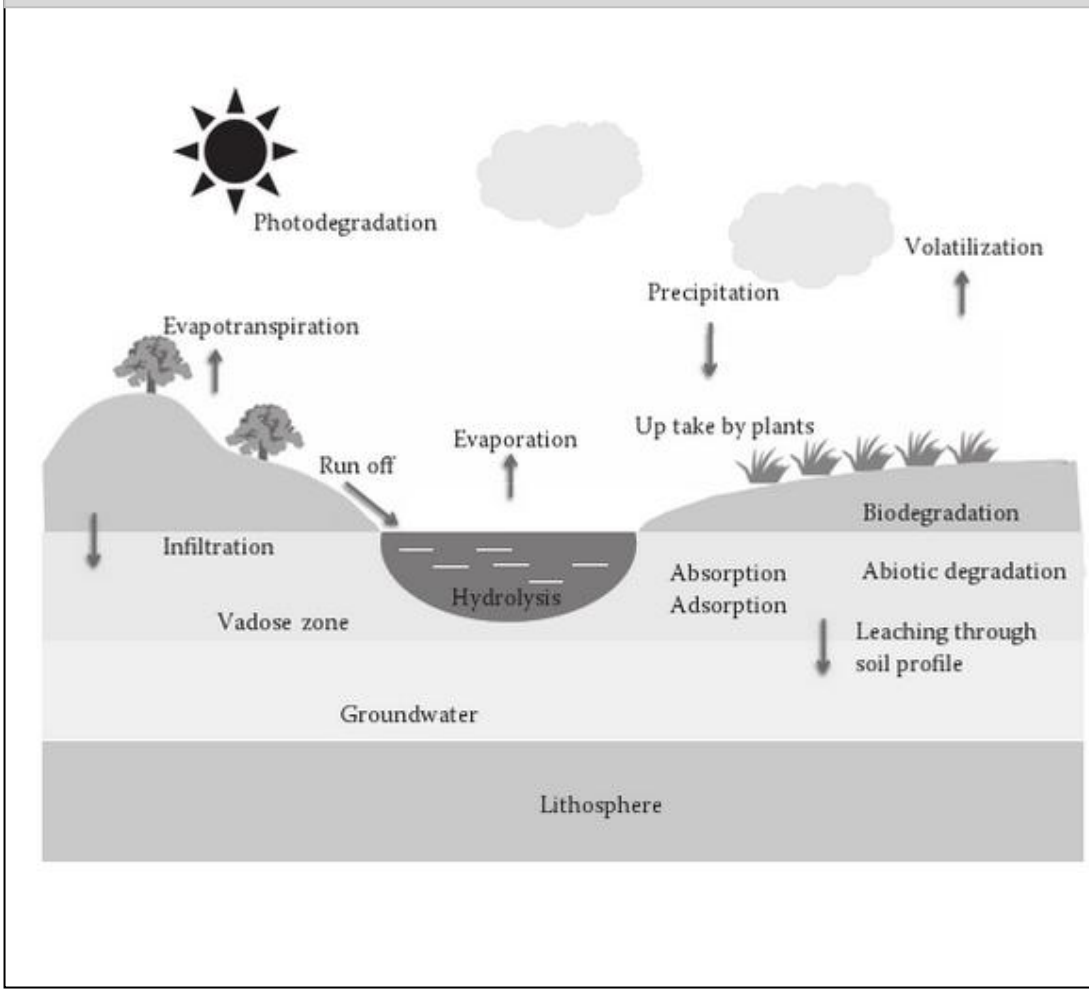
Using of pesticides in agriculture have many profits. These benefits include: production improvement, crop losses protection and vector disease control (Aktar *et al*., 2009). The yield of crops such as vegetables, corn, maize and cotton improved and the losses of crops decreased as the application of pesticides including insecticides, fungicides, herbicides, rodenticides are introduced to protect crops from pests (Carvalho, 2006). The most effective treatment for vector-borne diseases is to kill the vectors. Insecticides are the efficient compounds that can kill and control the insects that can cause serious disease such as malaria, which daily cause death to about 5000 people (Ross, 2005).

However, the use of pesticides can cause many harm to the environment and human. Pesticides can be carried by wind or leached by torrential rains causing contaminations of water bodies and soils (Fenik *et al*., 2011). Although pesticides help in controlling insects and weeds, they can be toxic to a many other organisms such as non-target organisms (Bakırcı *et al*., 2014 & Aktar *et al*., 2009). Bioaccumulation and biomagnifications of these compounds consider as major problems associated with using them (Rowe, 2015). Many pesticides are stored in the body tissue since they are not able to be broken down.. Pesticides can cause direct threat to human health and life. Accumulation of pesticides in the body may be carcinogenic, neruotoxic and can disrupt hormonal and enzymatic regulation (Fenik *et al*., 2011).

2.3 Pathways and routs of exposure of pesticides in nature

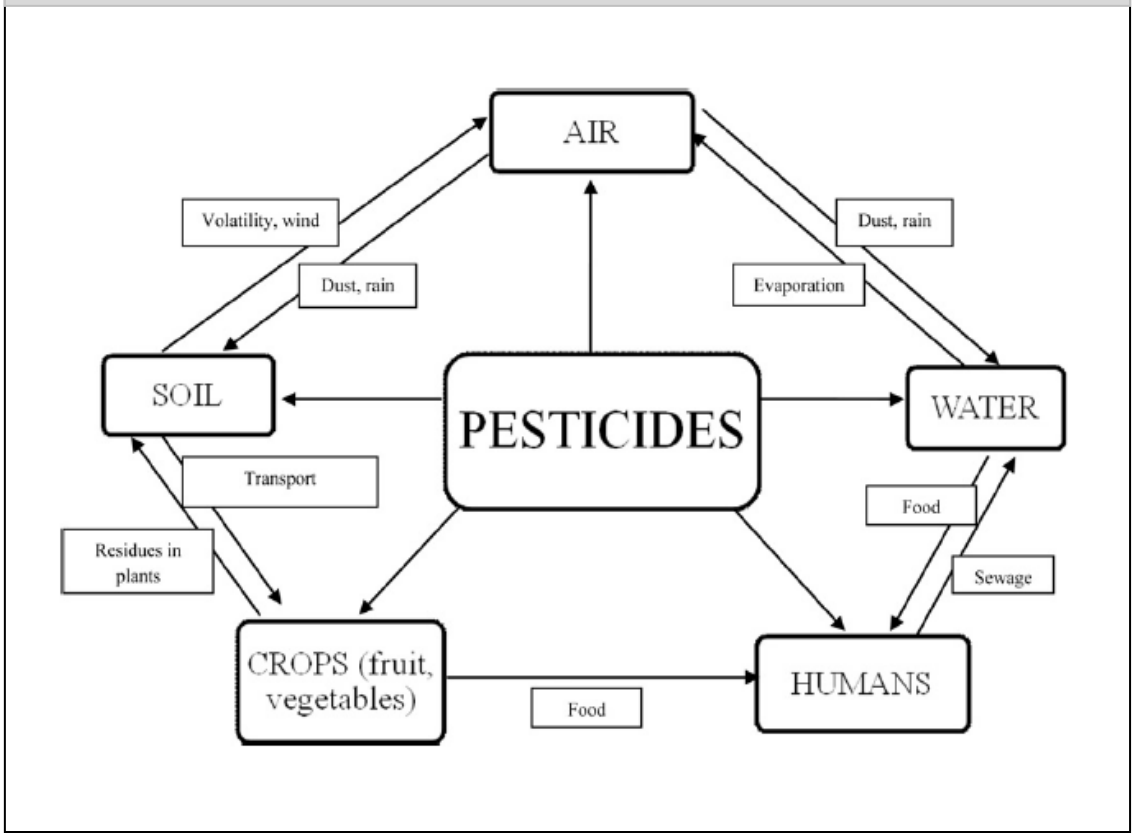
Pesticides can enter the environment via different pathways (Figure 1), such as transformation and degradation, volatilization, absorption and desorption, runoff to surface waters, uptake by plants, and transport to groundwater (Rathore & Nollet, 2012).

Figure 1: Transport of pesticides in the environment (Rathore & Nollet, 2012).



Therefore, pesticides have many routs of exposure Figure 2); they can circulate in to the air, water, soil, crops and human (Fenik *et al*., 2011). However, the major concerns are from consumption of pesticide laden food crops (Boobis *et al*., 2008). Pesticides are mainly transported from their source of application to neighboring crops and land by rain and wind. This transportation may be undesirable or harmful (Moreno *et al*., 2006).

Figure 2: The route of exposure of pesticides (including crops) (Fenik *et al*., 2011).



2.3.1 Pesticides in crops (Vegetables and Fruits)

Occurrence of residues of pesticide in food is the main consequence of application of pesticide on crops. More than a thousand compounds may be applied to agricultural crops to control unwanted pest such as insects and weeds (Ortelli, Edder, & Corvi, 2006). Many Fruits and vegetables are marketed all over the world and no information is known about the compounds of pesticides that applied on the production process (Stan, 2000). Comparing to other food groups, vegetables and fruits often contain higher levels of residue of pesticide (Chen *et al*., 2011).

Recently, many researchers from various areas and different residue levels have reported the presence of different pesticides residues in fruits and vegetables (Bai, Zhou, &Wang, 2006; Chen *et al*., 2011; Hjorth *et al*., 2011; Knezˇevic´ & Serdar, 2009; Osman, Al-Humaid, Al-Rehiayani, & Al-Redha, 2010; Pico, la Farre, Soler, & Barcelo, 2007).

Table 2 summarizes the concentration of selected organochlorine pesticides in selected vegetables from various regions of the world. For the fruits, strawberries and lemon, no data were reported for the selected organochlorine pesticides. Not all the selected OCPs were studied in the selected vegetables and fruits. There is a lack of information for the selected OCPs residues especially for lemon and strawberries. Only one study reported OCPs residues for parsley and watercress.

Table 2: Summary of reviewed articles reporting some of the selected organochlorine pesticides within the selected vegetables and fruit.

OCPs	Cucumbers			Tomatoes		
	Concentration (mg/kg)	Country	Reference	Concentration (mg/kg)	Country	Reference
a-BHC	<0.1	Indonesia	(Shoiful et al., 2013)			
b-BHC	<0.1	Indonesia	(Shoiful et al., 2013)			
Heptachlor	<0.08	Indonesia	(Shoiful et al., 2013)	0.045* ± 0.018	Ghana	(Bempah et al., 2011)
Aldrin	<0.03	Indonesia	(Shoiful et al., 2013)			
Dieldrin	<0.04	Indonesia	(Shoiful et al., 2013)	0.004±0.008	Ghana	(Bempah etal., 2012)
	0.010±0.004	Ghana	(Bempah et al., 2012)	0.008±0.004	Ghana	(Bempah et al., 2011)
	0.022±0.009	KSA	(Osman et al., 2010)			
Endrin				0.009±0.002	Ghana	(Bempah et al., 2011)
a-Chlordane	<0.06	Indonesia	(Shoiful et al., 2013)			
g-Chlordane	<0.03	Indonesia	(Shoiful et al., 2013)			
Endosulfane I	0.04-0.11	Turkey	(Bakirci et al., 2014)			
	0.15	KSA	(Salim et al., 2011)			
Methoxychlor	0.020*±0.002	Ghana	(Bempah et al., 2012)	0.004±0.002	Ghana	(Bempah etal., 2012)

[1] Concentration ± standard deviation

[2] Concentration Rang

Conti. Table 2

Potatoes			Parsley			Watercress		
Concentration (mg/kg)	Country	Reference	Concentration (mg/kg)	Country	Reference	Concentration (mg/kg)	Country	Reference
<0.100	Indonesia	(Shoiful et al., 2013)	--	--	--	--	--	--
0.0140±0.006	Egypt	(Soliman, 2001)	--	--	--	--	--	--
<0.100	Indonesia	(Shoiful et al., 2013)	--	--	--	--	--	--
<0.080	Indonesia	(Shoiful et al., 2013)	--	--	--	--	--	--
<0.030	Indonesia	(Shoiful et al., 2013)	--	--	--	--	--	--
<0.040	Indonesia	(Shoiful et al., 2013)	--	--	--	--	--	--
--	--	--	--	--	--	--	--	--
--	--	--	--	--	--	--	--	--
--	--	--	--	--	--	--	--	--
<0.060	Indonesia	(Shoiful et al., 2013)	--	--	--	--	--	--
<0.030	Indonesia	(Shoiful et al., 2013)	--	--	--	--	--	--
--	--	--	0.020	KSA	(Salim et al., 2011)	0.014	KSA	(Salim et al., 2011)
--	--	--	--	--	--	--	--	--
--	--	--	--	--	--	--	--	--

2.3.1.1 Maximum Residue Level (MRL)

Maximum Residue Level (MRL) for residues of pesticide is defined as the maximum concentration of residue (mg/kg) that is permitted by law in specific foodstuff (Al-Saeid & Selim, 2013). To protect consumer health and to guarantee that food is safe, the monitoring of residues of pesticide in foodstuffs must be pursued. Therefore, the allowed levels of pesticide residues in foodstuffs are legislatively controlled through setting maximum residue levels (MRLs). These MRLs limit the types and amount of pesticides that can be legally present in foods, as determined by various regulatory bodies which aim at minimizing consumer exposure to harmful or unnecessary consumption of pesticides in the world.

In addition, MRLs help ensure adequate use of pesticides through authorization and registration and allow free movement of the products treated with pesticides (Kmellara *et al*.,2010; Knez˘evic´ & Serdar, 2009). Table 3 shows the MRLs of the selected pesticides in the selected vegetables and fruits (FAO/WHO, 2013).

Table 3: Maximum Residue Level (MRL) of the selected vegetables and fruit, According to Codex Alimentarius Commission (FAO/WHO, 2013).

Selected vegetables and fruit	Maximum Residue Level/ µg/kg									
	a-BHC	b-BHC	Heptachlor	Aldrin	Dieldrin	Endrin	a-Chlordane	g-Chlordane	Endosulfane I	Methoxychlor
Cucumbers	10	10	10	20	20	10	10	10	50	10
Tomatoes	10	10	10	10	10	10	10	10	500	10
Potatoes	10	10	10	10	10	10	10	10	50	10
Parsley	10	10	10	50	50	10	10	10	50	10
Watercress	10	10	10	50	50	10	10	10	50	10
Strawberries	10	10	10	10	10	10	10	10	50	10
lemon	10	10	10	50	50	10	10	10	500	10

2.4 Organochlorine Pesticides (OCPs)

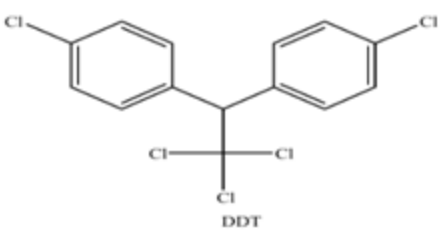
Organochlorine pesticides (also known as chlorinated hydrocarbons where one or many hydrogen atoms replaced by the chlorine) are primarily insecticides with relatively low mammalian toxicity, fat soluble and normally persistent in the environment. Many chlorinated hydrocarbons have the ability to accumulate inside the body due to their lipophilic nature (Singh, 2012). Their main characteristics are:

1. Occurrence of carbon atoms, chlorine atoms, hydrogen atoms and oxygen atoms sometimes exist. Number and position of Cl in molecule decides the toxicity.
2. Presence of cyclic carbon chains including benzene ring.
3. Lack of any particular active intra-molecular sites.
4. They are nonpolar and lipophilic in nature and have a affinity to concentrate in the lipid rich tissues, thereby causing its bio-concentration, and biomagnifications at different trophic level in the food chain.
5. Chemically unreative, therefore highly persistent in the environment, resistant to microbial degradation.

Organochlorine group chemicals were first used as pesticides in the 1940s. Organochlorine compounds were used widely from 1945 to 1965 in different application including agriculture and in protection of the buildings timber and humans from a wide range of insect pests. After awareness that these compounds are highly persistent, legal action has been taken to phase out this class of insecticides

(Singh, 2012). It includes DDT, Lindane, Endosulfan, Aldrin, Dieldrin, Chlordane, Heptachlor and Endrin (Figure 3).

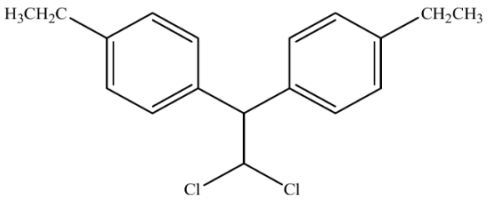
Figure 3: Structure of different organochlorine pesticides (Singh, 2012).



DDT

IUPAC : 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane

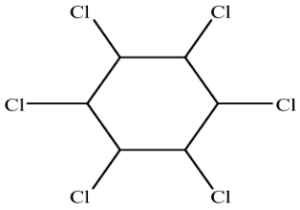
FORMULA: $C_{14}H_9Cl_5$



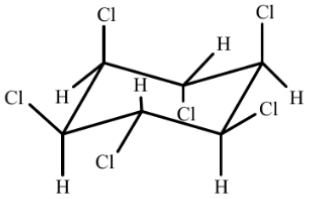
Ethyl- DDD

IUPAC: 1,1-dichloro-2,2-bis(4-ethylphenyl)ethane

FORMULA : $C_{18}H_{20}Cl_2$



HCH



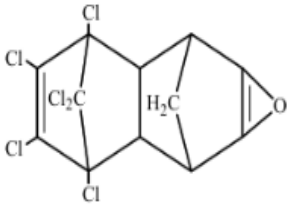
γ-HCH

IUPAC: 1,2,3,4,5,6-hexachlorocyclohexane

FORMULA: $C_6H_6Cl_6$

IUPAC: 1α,2α,3β,4α,5α,6β-hexachlorocyclohexane

FORMULA: $C_6H_6Cl_6$

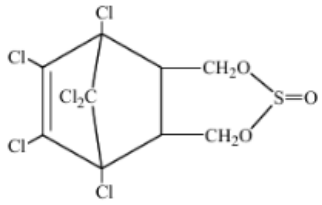


Endrin

IUPAC: (1R,4S,4AS,5S,6S,7R,8R,8a*R*)-1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-6,7-epoxy-1,4:5,8-dimethanonaphthalene OR 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4A,5,6,7,8,8a-octahydro-EXO-1,4-exo-5,8-dimethanonaphthalene

FORMULA: $C_{12}H_8CL_6O$

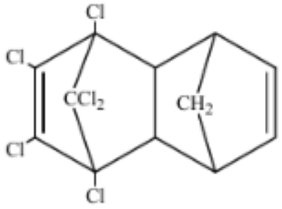
Cont. Figure 3



Endosulfan

IUPAC: 1,4,5,6,7,7-hexachloro-8,9,10-trinorborn-5-en-2,3-ylenebismethylene sulphite or 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine 3-oxide

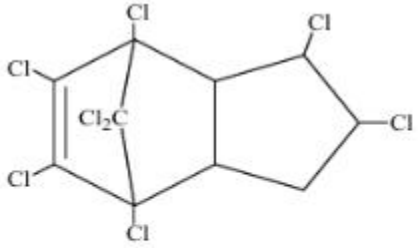
FORMULA: $C_9H_6Cl_6O_3S$



Aldrin

IUPAC: (1R,4S,4AS,5S,8R,8a*R*)-1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene

FORMULA: $C_{12}H_8CL_6$

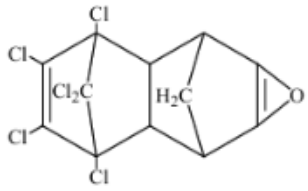


Chlordane

IUPAC: 1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene

FORMULA: $C_{10}H_6CL_8$

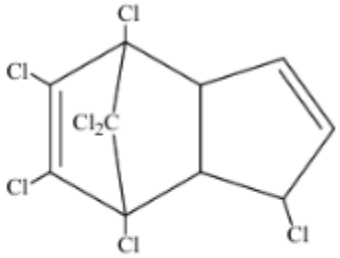
Cont. Figure 3



Dieldrin

IUPAC: (1R,4S,4AS,5R,6R,7S,8S,8a*R*)-1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-6,7-epoxy-1,4:5,8-dimethanonaphthalene OR 1,2,3,4,10,10-hexachloro-6,7-EPOXY-1,4,4a,5,6,7,8,8a-octahydro-ENDO-1,4-exo-5,8-dimethanonaphthalene

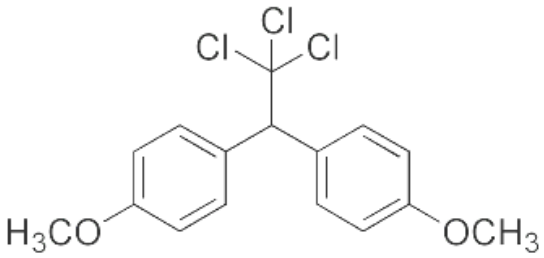
FORMULA: $C_{12}H_8CL_6O$



Heptachlor

IUPAC: 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene

FORMULA: $C_{10}H_5CL_7$



Methoxychlor

IUPAC: 1, 1, 1-Trichlori-2,2-bis(4-methoxyphenyl) ethane

FORMULA: C16H15Cl3O2

2.5 Toxicity of Pesticides

Pesticides are characterized by various degrees of toxicity to non-target species, including human beings, thus they are a diverse category of biologically active compounds. The majority of the currently used pesticides are acutely toxic to humans. Neurological effects, reproductive or development problems, and cancer may be consequences of pesticide exposure also can cause chronic health effects such as (Bolognesi & Merlo, 2011).

Table 4 shows the most currently applied classes of synthetic pesticides. Pesticides on target species have many primary effects which are: sodium channel interference or neurotransmitter receptors interaction which lead to neurotoxicity, disruption of energy metabolism leading to paralysis, or blocking chitin synthesis causing growth inhibition (Bolognesi & Merlo, 2011). Since the mechanism of action for organophosphates and carbamates is same, serious additive toxicity can be created (Bolognesi & Merlo, 2011).

2.5.1 Acute toxicity

The serious and the less perilous manifestations of every pesticide are recognized by the WHO. The lethality of the specialized substance and its details are taken into account in the pesticides framework. Since the acute oral and dermal toxicity are typical procedures in toxicology, the acute oral and dermal toxicity to the rat are taken into account in the classification (WHO, 2006).

Table 4: Mode of action of some pesticides (Bolognesi & Merlo, 2011).

Chemical group	Active ingredients	Mode of action
Organochlorines	DDT	Opening sodium channels within the axons of the neuron: continual nerve impulse transmission
	Chlordane, mirex, heptachlor, aldrin, dieldrin, endosulfan	Interaction with the γ-aminobutyric acid (GABA)-receptor chloride channel
Organophosphates	Malathion, trichlorfon, monocrotophos, dimethoate, oxydemetonmethyl, dicrotophos, disulfoton, dichlorvos, mevinphos, methamidophos, acephate	Irreversible inhibition of cholinesterase enzyme (ChE) by phosphorylation
Carbamates	Carbaryl, methomyl, carbofuran, aldicarb, oxamyl, thiodicarb, methiocarb, propoxur, bendiocarb, carbosulfan aldoxycarb, promecarb, fenoxycarb, primicarb, indoxacarb alanycarb furathiocarb	Reversible inhibition ChE by carbamylation
Pyrethroids	Allethrin, tetramethrin, resmethrin bioresmethrin phonothrin, fenvalerate permethrin, bifenthrin, lambda-cyhalothrin, cypermethrin cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, flucythrinate, fluvalinate, prallethrin tefluthrin tralomethrin zeta-cypermethrin	Disruptors of voltage-sensitive sodium channels (VSSCs)
Nicotinoids	Imidacloprid, acetamiprid, thiamethoxam, nitenpyram, clothianidin, dinotefuran, thiacloprid	Irreversible blockage of postsynaptic nicotinergic acetylcholine receptors

Most of the classifications are derived from the acute oral lethal dose (LD_{50}) (Table 5). Since handling pesticides has the highest dermal exposure, dermal toxicity must always be considered.

Table 5: Classification of pesticides by hazard (WHO, 2006).

Class		LD50 for the rat (mg/kg bw)			
		Oral		Dermal	
		Solid	Liquid	Solid	Liquid
Ia	Extremely hazardous	5 or less	20 or less	10 or less	400 or less
Ib	Highly hazardous	5–50	20-200	10–100	40-400
II	Moderately hazardous	50–500	200-2000	100–1000	400-4000
III	Slightly hazardous	Over 500	Over 2000	Over 1000	Over 4000

Studies in developing countries have shown rates of annual frequency of severe pesticide poisoning in rural workers to be up 18.2 per 100 thousands full-time workers and 7.4 per million school children (Bolognesi & Merlo, 2011). The occurrences found to be higher because of the utilization of banned pesticides in developed countries, the inadequate regulation, the absence of preparing and observation frameworks, and poor individual defensive gear in developing countries. The majority of cases regarding pesticide poison caused from carbamate or organophosphate. Inhibition of nervous system enzyme (acetyl cholinesterase) may occur from these two compounds. (Ecobichon, 2001).

The principle target of OCPs is the nervous system, in which a hyperexcitable state developed. Serious inebriation by these mixes causes myoclonic jolting

developments, and after that summed up tonic-clonic shakings took after by trance state and respiratory depression (Bolognesi & Merlo, 2011).

2.5.2 Chronic Toxicity:

Neurological effects

Discoveries from numerous epidemiological studies come with agreement with the theory that pesticide introduction may predispose the Parkinson's malady (Ritz *et al*, 2009). The Parkinson disease is the main common neurodegenerative movement disorders, which affects one percent of the population over 65 years. The main symptoms of this disease are akinesia, tremor, rigidity, and postural instability. Experimental studies point out the possibility that toxic environmental compounds, such as pesticides, may cause pathogenesis of Parkinson's disease through the inhibition of the mitochondrial function (Ritz *et al*, 2009).

Pesticide presentation worsen Parkinson's malady hazard demonstrated by the epidemiological studies which examin the danger of Parkinson. A deliberate audit of the accessible confirmation from studies directed in the United States shows that the danger of Parkinson's disease in subjects ever presented to pesticides is more than twofold contrasted with control subjects. (Bolognesi & Merlo, 2011). Organochlorines, organophosphorus, chlorophenoxy esters, and botanicals have been recognized as particular classes of pesticides representing that may possibly cause the Parkinson disease development. Notwithstanding the epidemiological studies and

experimental proofs, Parkinson's disease caused from pesticide still hard to presume (Benjamin *et al*, 2001).

Carcinogenicity

Pesticides are presently ordered by universal organizations and boards (for example: International Agency for Research on Cancer (IARC)) according to their possible properties for cancer-causing on the premise of the accessible proof from human and examining studies (IARC, 2015). Human studies are very complicated and hard to discovered, even though there is agreement that the strongest proof for making a causal connection between exposure to an operator and disease event in people originates from epidemiological studies. An operator can be sensibly recognized as a potential human cancer-causing agent by method for creature bioassays (Bolognesi & Merlo, 2011).

The US NTP has grouped various dynamic fixings in pesticides as 'sensibly expected to be a human cancer-causing agent' and the IARC and the US EPA, taking after deliberate and thorough audits of the human and exploratory studies, have inferred that some compound mixes utilized as a part of pesticides (insect poisons, fungicides, herbicides, and other comparative mixes) are known, likely or conceivable cancer-causing agents (NTP, 2015).

Genotoxicity

Genotoxic potential is an essential danger component for long term exposure impacts, for example, cancer-causing and conceptive toxicology (Padula *et al*, 2012). Genotoxic mixes are compounds that demonstrate by immediate or roundabout DNA harm or by a clastogenic occasion. The lion's share of pesticides have been tried in a wide assortment of mutagenicity examines that cover quality changes, chromosomal adjustments, and DNA harm. Test information uncovered that different agrochemical dynamic substances have mutagenic properties prompting diverse hereditary endpoints (Bolognesi & Merlo, 2011). Notwithstanding some harshness in the consequences of fleeting tests, comparative profiles of genotoxic movement produced from pesticides with comparable synthetic structure. The genotoxic capability of agrochemical fixings give a frail reaction in a couple genotoxicity tests (Bolognesi & Morasso, 2000).

Word related presentation to pesticides mixtures has been connected with an increment in genotoxic harm in various studies. The effect of dose increment of cytogenetic harm was likewise uncovered in some biomonitoring studies identified with the degree of introduction as amount of pesticides utilized the expansion of territory of pesticide application and lacking working conditions. The confirmation of a hereditary peril identified with presentation coming about because of the serious utilization of pesticides anxieties the requirements for instructive projects for ranchers to decrease the utilization of chemicals in agribusiness and to actualize insurance measure (Benjamin *et al*, 2001).

The current exploratory proof recommends an irrelevant danger for the overall public presented to low levels of pesticide buildups. Notwithstanding, various open inquiries stay at present on genotoxic danger of pesticides for purchasers, for example, the wellbeing risk for rehashed ingestions of pesticide deposits and the potential genotoxic harm from concurrent introduction of a few dynamic mixes (Bolognesi & Merlo, 2011).

Reproductive Toxicity

Introduction to pesticides may represent a danger to human propagation (Padula *et al*, 2012). Working with or applying pesticides fitting in with diverse synthetic classes, for example, organochlorines and organophosphates, which are utilized essentially as a part of rural settings, seems to reliably diminish richness and fecundability. Epidemiological proof proposes that abnormal state of introduction to DDT or DDE is connected with unfriendly fetal development and preterm conveyance. Word related presentation to dibromochloropropane influences male conceptive capacity delivering azospermia and oligospermia, germinal epithelium harm, hereditary adjustment in sperm, (for example, twofold Y-bodies), expanded rates of unconstrained premature births in wives of uncovered laborers, hormonal lopsided characteristics, and adjusted sex proportion in posterity (Padula *et al*, 2012). The constraint of the absence of a standard accepted measure of presentation are applied to all these studies have. The trial confirmation from creature studies is

restricted and can't help in affirming the human information (Bolognesi & Merlo, 2011).

Although a few pesticides cause conceptive or formative poisonous quality at high dosages in creature models, unfriendly wellbeing impacts in people presented to natural levels are hard to survey. Just a couple of pesticides such as DDT, herbicides, pentachlorophenol, dibromochloropropane, parathion, chlorophenoxyacetic, atrazine, parathion, and oxydemeton-methil, are referred to actuate formative deserts, for example, orofacial clefts, hypospadias, complete odd venous return, spina bifida, and appendage decrease in occupationally uncovered populaces. Studies concentrating on particular conception imperfections reported relationship between rural work and innate contortions including a marginally expanded danger for focal sensory system deformities. Watchful evaluation of introduction to particular pesticides in the further studies is expected to connection this impact to particular mixes or classes of pesticides (Bolognesi & Merlo, 2011).

2.5.3 Toxicity of the selected Organochlorine Pesticides

Heptachlor firmly associated just with dimyristoylphosphatidylcholine DMPC, which is a kind of phospholipid situated in the outside moiety of the human erythrocyte layer (Suwalsky *et al*, 1997). Extra examinations performed on frog thoughtful neural connections demonstrated a huge abatement in the potential contrast and short out current reactions after use of heptachlor. These outcomes have been deciphered as a hindrance of the dynamic transport of particles affected by the pesticide (Quevedo *et al*, 1997). It can be concluded, therefore, that toxic effects of heptachlor are related to its perturbation of the structure of phospholipid bilayer, which is important for cell membrane functions. Endosulfan, aldrin and dieldrin showed to act as antagonists of androgen receptors based on in vitro assay (Andersen *et al*., 2002; Li *et al*., 2008 & Nativelle-Serpentini *et al*., 2003). They were examined to repress the aromatase protein (CYP19) and also repress the rate-restricting chemical of estrogen and rostenedione. Like different organochlorines, endosulfan and dieldrin adjust the estradiol digestion system by impelling CYP1 compounds (Badawi *et al*., 2000; Bradlow *et al*., 1995). Concentration of (5M) dieldrin and (1 M) endosulfan showed significant enhancement on the cell proliferation and ER transactivation gene response in MCF-7 cells as examined by vitro assay (Andersen *et al*., 2002). Endosulfan brought on adjustments in testicular capacities at high measurements.

Methoxychlor has been indicated to prompt testicular apoptosis in rats taking after oral presentation to single measurements of 50 mg/kg b.wt (Vaithinathan *et al*., 2010). However, if the dosages contrasted with those commonplaces of word related and ecological exposures, the dosages tried are unrealistically high.

The α-isomer of BHC among 8 isomers, has been ordered as a non-genotoxic cancer-causing agent on the grounds that it impels hepatocellular carcinomas in rodents with high measurement long haul organization yet needs mutagenicity in the Ames test (Nagasaki, 1975). Worry about the conceivable antagonistic wellbeing impacts of long haul introduction to this compound in people has prompted it being banned or confined in industrialized nations. Despite the fact that it has been named a non-genotoxic cancer-causing agent, a few examinations showed that high amassing of α-BHC displayed restraining impact on liver tumor development impelled by some known cancer-causing agents in rat (Angsubhakorn *et al*, 1981) and (Thamavit *et al*, 1975). These results are raise concerns as to how α -BHC plays a role in hepatocarcinogenesis (Puatanachokchai, 2006).

Shi *et al*. (2011) demonstrated that more than 30 µM fixations of β-BHC prompted the apoptotic cell in Sertoli cells of rodent connected with FasL levels expanded articulation which could prompt the Fas initiation. Impel of apoptosis may occur duo to these two qualities. β-BHC has been demonstrated to incite actuation of caspase-3, which cause initiation of cell apoptosis (Khan *et al*., 2000) and caspase-8, which believed to be part in transduction of death signal (Said *et al*., 2004).

Effects on the central nervous system which cause muscle contractions and hyperexcitability, and in severe cases death may be consequences of endrin ingestion (Curley *et al*. 1970 & Runhaar *et al*. 1985). Exposure of animals to endrin causes central nervous system effects, particularly convulsions (Deichmann *et al*. 1970 & Quick *et al*. 1989). In animals exposed to lethal doses of endrin, unspecific degeneration of the liver, kidney, and brain has been observed (Treon *et al*. 1955).

Massive doses of chlordane (350 mg/kg) administered intraperif (intraperit to laboratory rats produced progressive behavioral manifestations of poisoning: early perceptual intolerance with increased respiratory involvement; reflex muscular activity leading to ataxia; and, finally tonic paralysis and death (Hyde & Falkenbegr, 1976). Chlordane probably causes cancer and can cause liver cancer, behavioral disorders in children, problems in the endocrine system, nervous system, digestive system, and liver (EPA, 2011).

2.6 Pesticides use in the Arab countries

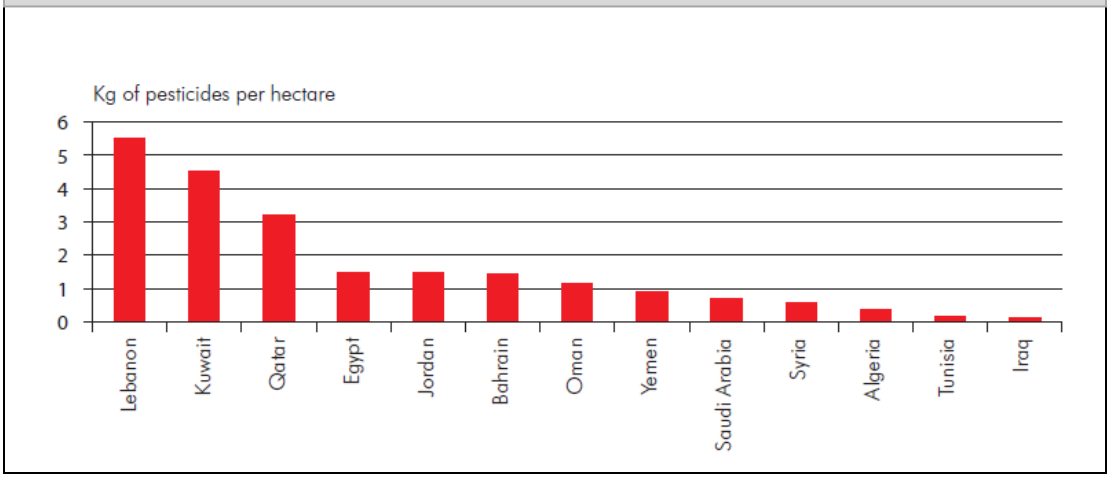
There is a lack of and a gap in the provision of recent data on the use of pesticides in Arab countries. Fewer than half the Economic and Social Commission for Western Asia member countries provided data for year 2000, and only two countries provided such data for year 2001 (Table 6). Syria and Yemen were the countries that showed the highest consumption of insecticides in year 2000.

Table 6: Total insecticides consumption in tons per year (Bashour, 2009).

Country	2000	2001
Bahrain	7	6
Iraq	190	...
Jordan	61	...
Oman	91	...
Qatar	60	...
Syria	1,219	994
Yemen	933	...

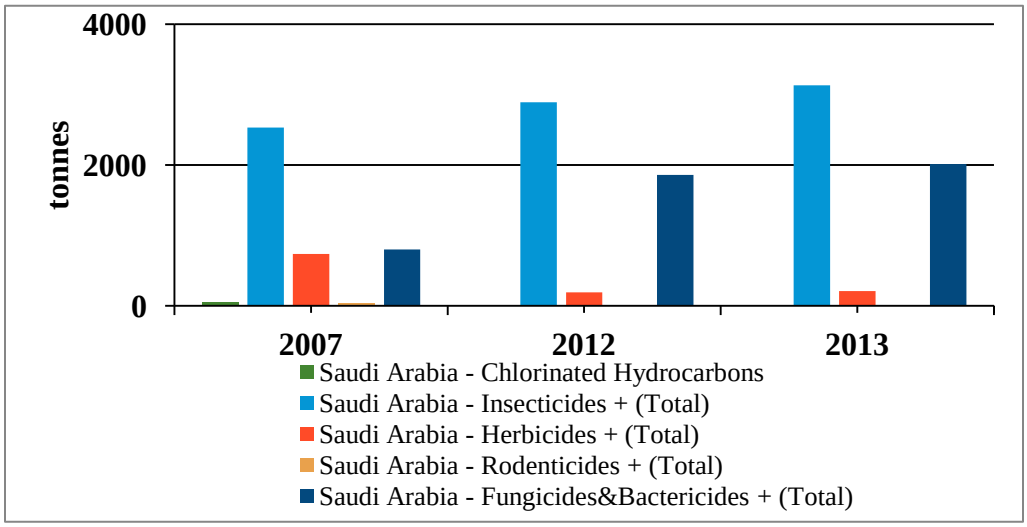
The data in Figure 4 shows that the rates of pesticides usage per hectare in 13 Arab countries in 2002. Lebanon, Kuwait and Qatar showed the highest consumption per hectare of pesticides among these countries. They are 2 to 3 times the rates used in Egypt, Jordan and Oman (Bashour, 2009).

Figure 4: Amount of pesticides used in kg/ha in selected Arab countries (Bashour, 2009).



The Knoema Resource Statistics for Saudi Arabia (Figure 5) showed the annual pesticides consumption in tones in the years 2007, 2012 and 2013 according to the Food and Agriculture Organization. The rate of consumption of insecticides, fungicides and bactericides has been increased. No recent data is available for the use b consumption of pesticides in Qatar.

Figure 5: Pesticides consumption in Saudi Arabia (Knoema Resource Statistics, FAO, 2013)



2.7 Techniques used to analyze the residues of pesticides in food products

Since pesticides have wide ranging chemistries within the contaminants, the analysis poses a number of challenges for laboratories and operators. Many techniques including: Gas chromatography-mass spectrometry (GC-MS), Gas chromatography-electron capture detector (GC-ECD), Gas chromatography/ flame photometric detector (GC/FPD), Liquid chromatography–mass spectrometry (LC-MS) and High-performance liquid chromatography (HPLC) were used to analyze the residues of pesticides in many products such as: water, milk, fish, chicken, egg, meat, fruit and vegetables (Essumang *et al*., 2009; Ahmad, 2010; Jardim, 2014; Hjorth *et al*., 2011; Ortelli, Edder, & Corvi, 2006; Knezˇevic´ & Serdar, 2009).

Chromatography is a set of laboratory techniques for the separation of mixtures (USDA, 2012). Gas chromatography (GC) is definitely one of the main techniques used for detection, identification and quantification of many groups of non-polar or semi-polar substances. GC has high separation power in combination with a wide range of detectors, thus it is a unique tool in the analysis of ultra trace levels of toxic compounds that may occur in foods and feeds since (Hajšlová, 2007).

GC with electron capture detector (ECD) is used to analyze halogenated compounds and is primarily used in the environmental, forensic and pharmaceutical markets. Within an ECD, when certain molecules pass by the detector, they capture some of the electrons in the sample and this reduces the current measured. The compensation for this reduction is recorded as a positive peak. The

flame photometric detector (FPD) enables accurate and sensitive detections of volatile sulfur and phosphorus compounds. The principle of detection is done in a reducing flame by formation of excited sulfur and excited hydrogen phosphorous oxide species. The characteristic chemiluminescent emission from these species measured by a photomultiplier tube. Identification and quantification of a wide range of organic compounds are done by GC/MS. GC/MS separates the complex sample matrices into their component parts by utilizing a compound's intrinsic affinity for a stationary phase. Identification of compounds by their mass spectra is carried out by using mass Spectrometry Detection. The identification is done by comparing the obtained mass spectra (each compound has a single mass spectrum) with a mass spectral database.

Unlike gas chromatography, Liquid chromatography (LC) can be removed securely a very wide range of organic compounds from small drug metabolites molecules to peptides and proteins. An LC/MS is an HPLC system with a Mass Spectrometry Detector. The Mass Spectrometry Detector (MS) coupled with an LC scans the molecules and produces a full spectrum of high resolution, separating all ions having different masses.

Multi-residue methods based on LC/MS are increasing by being used in this field, however, GS/MS methods still play a significant role in analyzing residues and in some cases it becomes the only method of choice. Table 7 summarizes the techniques that were used to find out the pesticides residues in fruits and vegetables.

Table 7: Techniques for determination of pesticides residues in fruit and vegetables

Sample	Technique	Reference
Apples, Arugula, Apricot, Aubergine, Banana, Bean, Carrot, Cabbage, Cherry, Cauliflower, Grape, Cucumber, Kiwifruits, Leek, Lemon, Lettuce, Orange, Mushroom, Peaches, Onion, Pear, Pepper, Plum, Potato, Pomegranate, Purslane, Strawberry, Tomato, Tangerine	GC-ECD and GC-MS	Bakirci *et al*., 2014
Apple, Grape, Broccoli, Leaf mustard, Cabbage, Lettuce, Capsicum, Orange, Cauliflower, Pakchoi cabbage, Peach, Chinese cabbage, Pear, Cucumber, Radish, Eggplant, Spinach, Legumes, Tomato	GC-ECD	Chen et al., 2011
Fruits and vegetables	GC-MS	Knez˘evic´ & Serdar, 2009
Cherry, Apricot Peach Grape Pepper Tomato Spinach Courgette Cucumber	UPLC/MS/MS	Bakirci& Hisil, 2011
Cashew apple, guava, kaki and peach	GC-ECD, GC-FPD and LC-MS/MS[1]	Jardim, 2014
Fat vegetable matrices like avocado	LP-GC–MS–MS[2]	Moreno *et al*, 2006

[1]Liquid Chromatography- Tandem Mass Spectrometry
[2]Low-Pressure Gas Chromatography–Tandem Mass Spectrometry

3 METHODOLOGY

3.1 Materials

3.1.1 Chemicals and reagents

Organic solvents to dissolve and extract samples were acetone and hexane purchased from Sigma-Aldrich (USA). Standard solutions were prepared from the stock solution (100ppm) that were prepared from Pesticide Mix Standard (Z-014C-R, 1mL, 2mg/mL in Toluene: Hexane 1:1, 20 compounds) diluted in Hexane. Decachlorobiphenyl (M-8082-ISC-WL-10mL, 5µg/mL in Hexane) was used as surrogate standard. The Pesticide Mix Standard and Decachlorobiphenyl were purchased from AccuStandard (USA). All standard solutions were stored in refrigerator at 4^{o}C. Anhydrous sodium sulfate was obtained from Fluka (Sigma-Aldrich (USA)). Dionex ASE Prep DE (Diatomacceous earth) was used in the extraction procedure.

3.1.2 Glassware and general instruments

An Accelerated Solvent Extractor (Dionex ASE 200 and ASE 350), solvent evaporator (Dionex SE 500), AS 220.R2 analytical balance, and Stuart- orbital shaker were used. Additionally, a mortar, pestle, extraction cells, cellulose filter disks, collection vials (60ml), caps, test tubes, pipettes and spatulas were used in the extraction protocol. Moreover, gloves, funnels, volumetric flasks, beakers, and GC

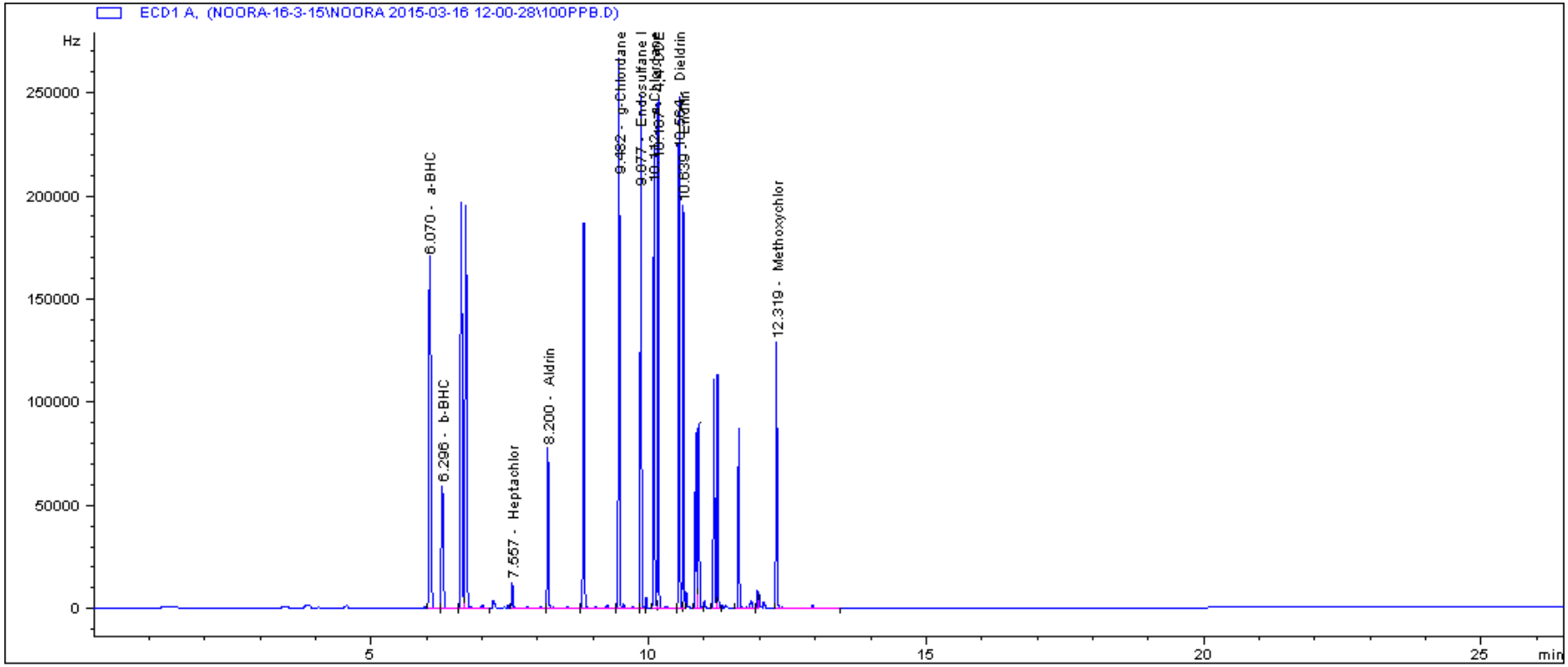
vials were used. GC7890A/MS 5973 and GC6890N/ECD (Agilent, Santa Clara, USA) were used for the quantification analyses.

3.2 Preparation of standard solutions

100ppm stock standard solution was prepared by adding 1mL of Pesticide Mix Standard (Z-014C-R, 1mL, 2mg/mL in Toluene: Hexane 1:1, 20 compounds) in to 20mL volumetric flask and add Hexane up to the mark. Calibration standard solutions were prepared from the 100ppm stock solution with a range between 5ppb to 1000 ppb. Figure 6 shows the preparation of standards in the ESC lab at Qatar University. The chromatogram of the prepared standard solution for 10 selected OCPs (Heptachlor, aldrin, dieldrin, Endrin, a-chlordane, g-chlordane, endosulfane I, methoxychlor, α -BHC and β –BHC) is shown in (Figure 7).

Figure 6: Preparation of standard solutions

Figure 7: Chromatograph of 100ppb of the 10 selected OCPs by GC/ECD.



3.3 Samples collection

Various samples of vegetables and fruit from local and imported sources were sourced from different locations in Qatar. The local samples were collected from Al-Mazrouah hall located in Umm Salal Ali where they sell fresh domestic vegetables and fruits from the 34 of the most prominent local farms (Figure 8). Meanwhile, the imported samples had been collected from the local markets: Market1, Market2 and Market3. The samples of leafy vegetables (parsley and watercress), vegetables (cucumber, tomatoes and potatoes), and fruits (lemons and strawberries) of each crop had two samples (domestic and imported).

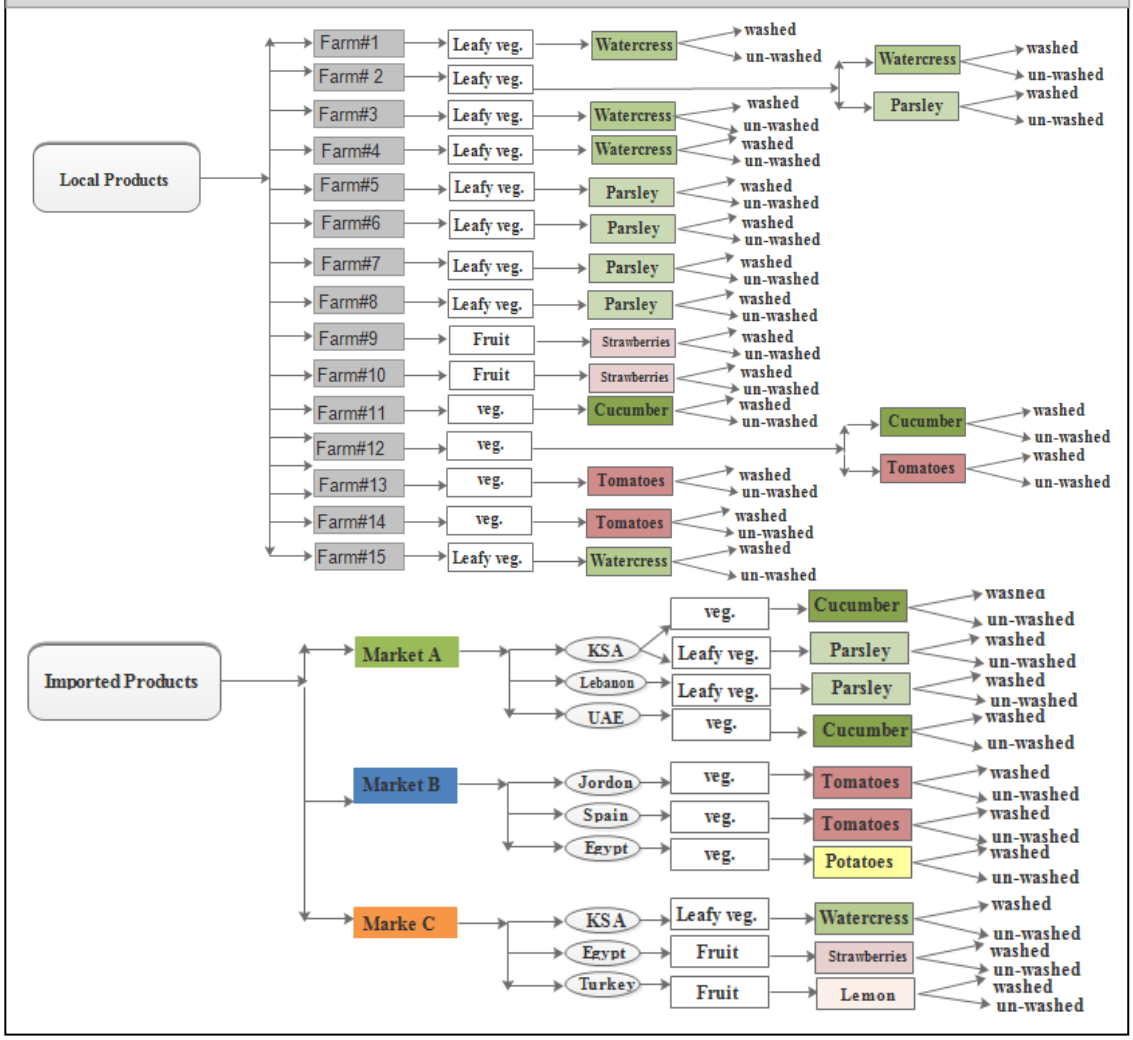
Figure 8: Al-Mazrouah Hall, Umm Salal Ali area.

A total samples consist of 127 samples of seven vegetables and fruits were examined including two groups: local and imported, and two sub groups: washed and unwashed samples. The samples taken included: 26 samples of fruits and 101 samples

of vegetables. Samples were extracted within 24 hours and stored at 4^{o}C until the analysis.

The simple random sampling and stratified random sampling were used as sampling procedures for collecting the vegetables and fruits. For all vegetables and fruits except strawberries, simple random sampling was used. For strawberries sampling, the stratified random sampling procedure was used. The overall of sampling collection is shown in Figure 9 .

Figure 9: Overall of sampling collection.



3.4 Samples preparation and extraction

Over the past 30 years, various methods have been published that are linked to particular analytical techniques for determining OCPs in food and environmental matrices. On the other hand, many books that summarize methods are available. For example, EPA methods for determination of OCPs in sediment and biological samples are outlined by Keith (Keith, 1996). Methods for separating, isolating and recovering of OCPs from sediment, soils and biological samples were reviewed and recommended by Wells and Hess (Wells & Hess, 2000). Overview of modern analytical methodology for OCP and PCBs were provided by De Boer and Law (Boer & Law, 2003).

The EPA Method 8081A (Appendix 2) was chosen as a reference method for the preparation and extraction method with some modification. Additionally, the Dionex Application Note 332 "Accelerated solvent extraction of pesticide residues in food products", 2012, was used as extraction method for vegetables and fruits (Appendix 3). The fresh fruits and vegetables samples were collected from farms and market a day before extraction. Each sample was divided in to two groups: washed sample with water and unwashed sample. No sample digestion is needed prior to extraction.

Samples were extracted using Dionex - Accelerated Solvent Extractor (ASE 200 and ASE 350). The extraction conditions are shown in Table 8.

Table 8: Extraction Conditions (Dionex Application Note 332, 2012).

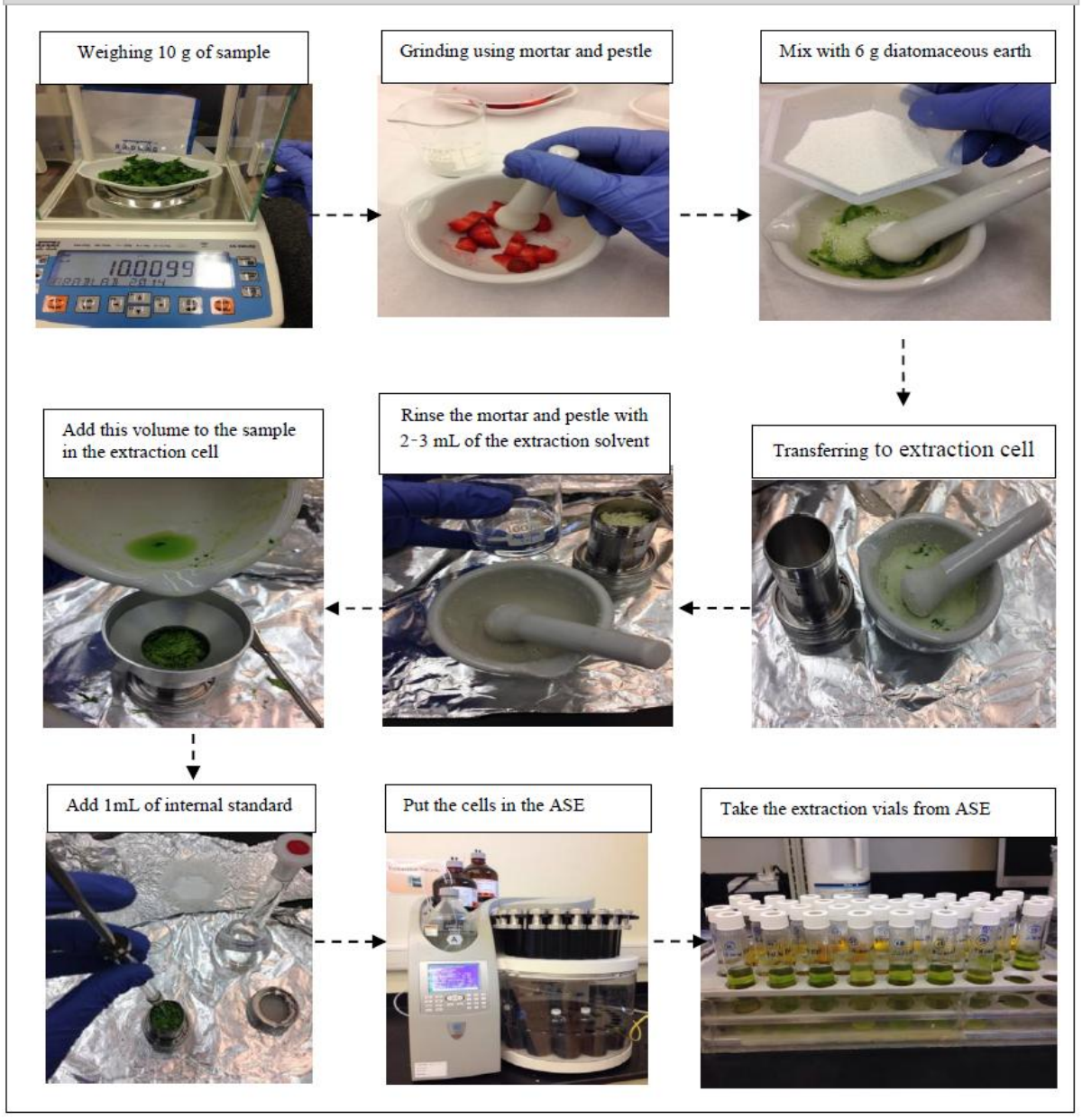
Temperature:	100 °C
Pressure:	1500 psi*
Heatup Time:	5 min
Static Time:	5 min
Flush Volume:	60%
Purge Time:	100 s
Static Cycles:	1–2
Total Extraction Time:	14–18 min per sample
Total Solvent Used:	15–45 mL per sample

*Pressure studies show that 1500 psi is the optimum extraction pressure for all accelerated solvent extraction applications.

3.4.1 Extraction procedure

The washed samples were washed under tap water for 2 min and dried by tissue before weighing. Figure 10 shows the extraction procedure that was carried out.

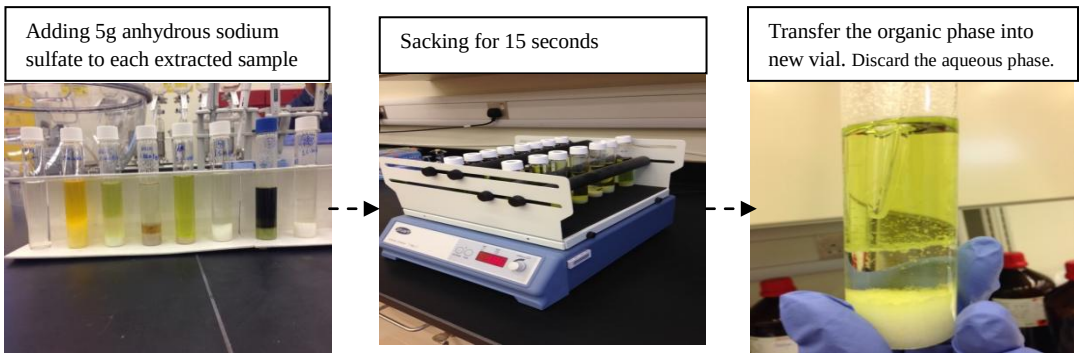
Figure 10: Extraction Procedure



3.5 Samples Clean-up

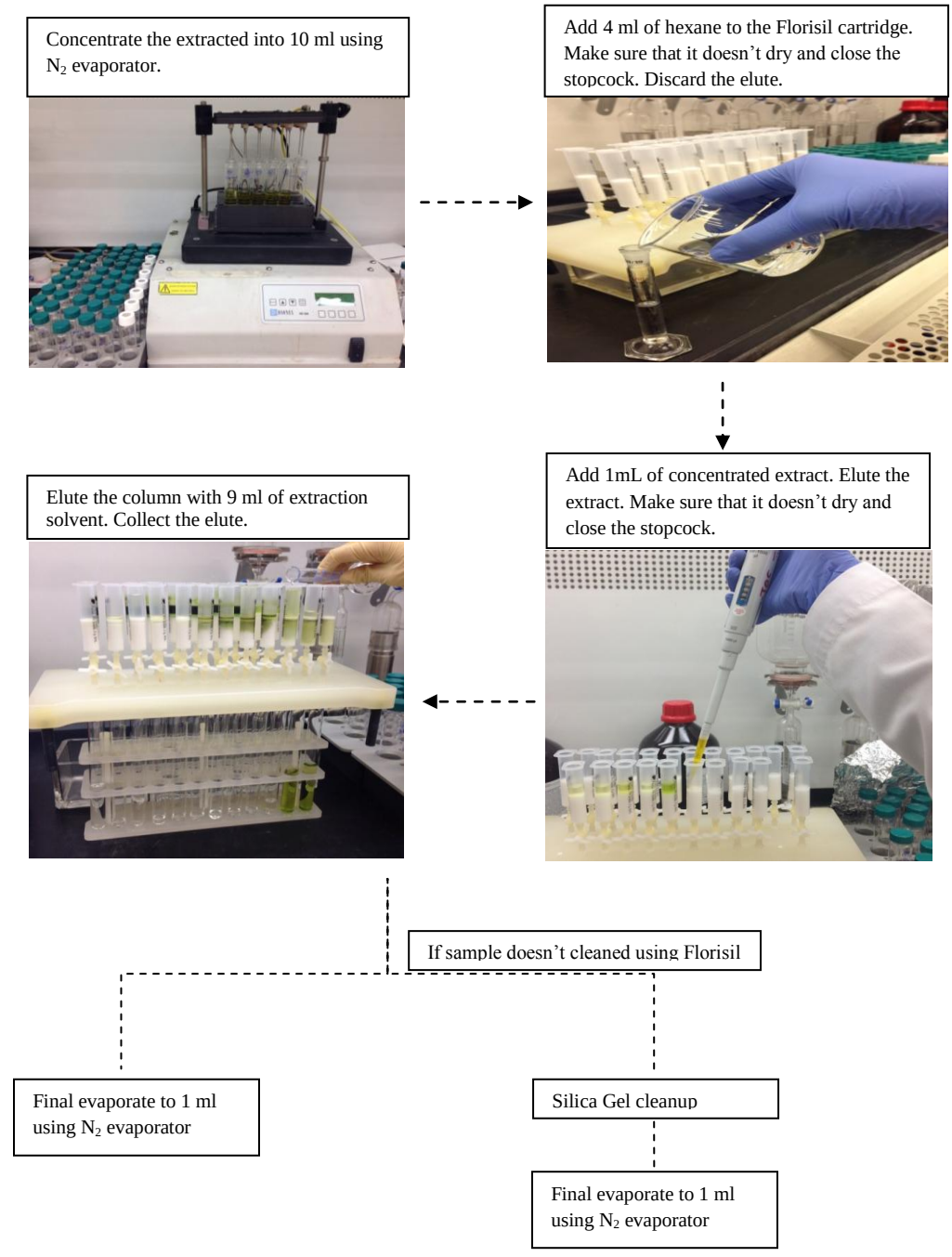
A clean-up procedure is usually carried out to remove co-extracted compounds that may cause interference in the chromatographic determination or be detrimental to the analytical instrumentation. Following extraction, 5 g of anhydrous sodium sulfate were added to the collection vial to adsorb co-extracted water. The vial was shaken for 15 s and the water-free extract was decanted into a clean vial (Figure 11) (Appendix 3).

Figure 11: Post extraction step



Two solid phase extraction techniques were used (Florisil and Silica Gel). The EPA method 3620C- Florisil Cleanup and Method 3630C- Silica Gel Cleanup were used as reference methods for cleaning the samples (Appendix 4 & Appendix 5). All samples were cleaned up using 2g Florisil Clean-Prep Cartridge. However, some interferants that are not removed by Florisil Cartridge would be removed by a second cleanup technique which was Silica Gel cleanup. Figure 12 shows the Florisil Cleanup procedure.

Figure 12: Cleanup procedure



3.6 Quality Control and Quality Assurance Measures (QC/QA)

The Limit of detection and limit of quantitation were calculated for all analytes as mentioned in (Appendix 6). In general, "the Limit of detection (LOD) is defined as the lowest concentration of an analyte in a sample that can be detected under the stated conditions of the test. The Limit of quantitation (LOQ) is the lowest concentration of an analyte in a sample that can be determined with acceptable precision and accuracy under the stated conditions of test" (Analytical Procedures and Methods Validation, 2000). The LOD and LOQ were calculated using 10 samples of the lowest concentration of spike (10ppb) (Shrivastava & Gupta, 2011). Refer to Appendix 6 for calculation data.

Table 9: Limit of Detection (LOD) and Limit of Quantitation (LOQ) calculated from the calibration line at low concentration.

Analyte	LOD /ppb	LOQ /ppb
a-BHC	1.999	6.663
b-BHC	1.538	5.125
Heptachlor	2.293	7.641
Aldrin	1.601	5.338
g-Chlordane	2.061	6.870
Endosulfane I	2.287	7.624
a-Chlordane	2.577	8.593
Dieldrin	1.923	6.408
Endrin	1.923	6.408
Methoxychlor	1.712	5.707

The evaluation of the recoveries of studied pesticides were done by adding known concentration of an internal standard (Decachlorobiphenyl) to about 10% of total number of samples. The Range from 93.6% to 106.6% was the percent recoveries in spiked samples. Table 10 shows the recoveries of the Decachlorobiphenyl.

Table 10: Recoveries of Decachlorobiphenyl.

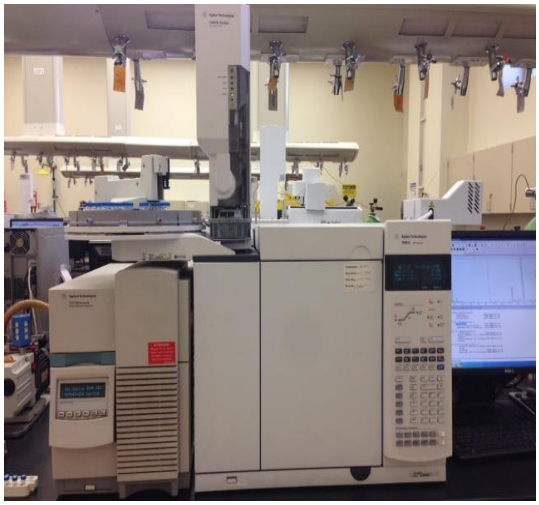
Sample #	Spiked concentration /ppb	Recovered concentration/ppb	Recovery/%
1	50.00	47.34	94.68
2	50.00	46.80	93.60
3	50.00	53.30	106.60
4	50.00	53.00	106.00
5	50.00	52.30	104.60
6	50.00	48.40	96.80
7	50.00	48.30	96.60
8	50.00	50.90	101.80
9	50.00	48.80	97.60
10	50.00	50.18	100.36

3.7 Samples Analysis

The samples analysis was conducted using a GC–electron capture detector (ECD), and by GC–MS scan mode (Figure 13). The GC/ECD analyses were performed on an Agilent 6890 N equipped with a splitless injector and a 7683 autoinjector (Agilent, Santa Clara, USA). The analysis by GC/MS was carried out on an Agilent 7890A MSD 5973 equipped with a split/splitless Inlet and a 7683B

autoinjector (Agilent, Santa Clara, USA). Separations were conducted using an HP-1 30 m 0.25 mm 0.25 µm column for GC/ECD and Rxi-5SILMS 30 m 0.25 mm 0.25 µm column (Agilent, Santa Clara, USA) for the GC/MS.

Figure 13: GC/ECD and GC/MS instruments at Environmental Studies Center-Qatar University.



GC7890A/MS 5973

GC6890N/ECD

For the GC/ECD, samples were analyzed as follows: the program initial temperature was set at 110^{o}C (held for 0.5 min), increased to 320^{o}C at 10^{o}C /min (held for 5 min). Helium was used as carrier gas at a flow rate of 3.5 ml/min, pressure at 20.90 psi and average velocity at 85 cm/sec. Nitrogen gas was used as makeup gas at pressure 50 psi. The injection volume was 1µl, and the injector temperature was held at 250^{o}C.

Analyses by GC/MS were carried out as follows: the program initial temperature was set at 70^{o}C (held for 0.5 min), increased to 250^{o}C at 25^{o}C /min,

raised to 290^{o}C at 5^{o}C /min (held for 3.5 min). Helium was used as carrier gas at a flow rate of 1.4 ml/min, pressure 11.747 psi, and average velocity 1.595 min. The injection volume was 1µl, and the injector temperature was held at 300^{o}C. The GC/MS data were acquired and processed with a wiley7n.1 and NIST98 Libraries.

3.8 Statistical Data Analysis

In this project two statistical analysis tests were used, pair-difference t-test and analysis of variance (ANOVA). The pair-difference t-test is simply used to test two independent populations have different mean values on some measure (Statistical Consultant, 2015). By using the t-test statistic we check the significant difference by determining the p-value between washed and unwashed samples. The analysis of variance (ANOVA) was used to compare between two factors.

To compare all possible pairs of means for heptachlor in parsley, using of the least significant difference (LSD) was necessary. The LSD formula is shown below:

$$LSD = t_{\alpha}\sqrt{MS_E(\frac{1}{n_i}+\frac{1}{n_j})}$$

Where:

t = critical value from the t-distribution table
MS_E = mean square error, obtained from the results of ANOVA test
n = number of samples used to calculate the means

If the difference between means is greater than or equal LSD value, then the difference is significant. Otherwise, the difference is not significant.

4 RESULTS AND DISSCUSION

A total 127 samples were analyzed, 101 samples of vegetables (cucumbers, tomatoes, potatoes, parsley, watercress) and 26 samples of fruits (strawberries, lemon). About 58 samples were local, and 69 were imported. The origin of analyzed samples is shown in Figure 14.

Figure 14: Origin of analyzed samples

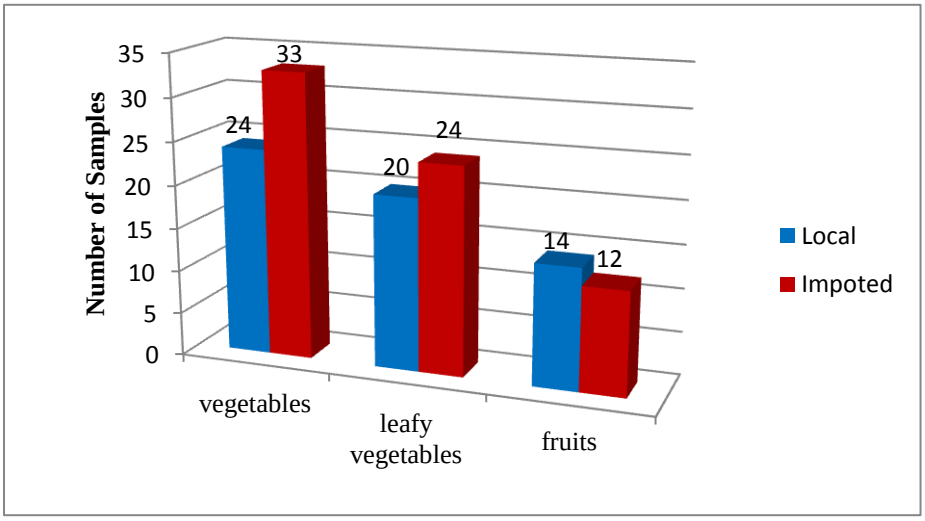
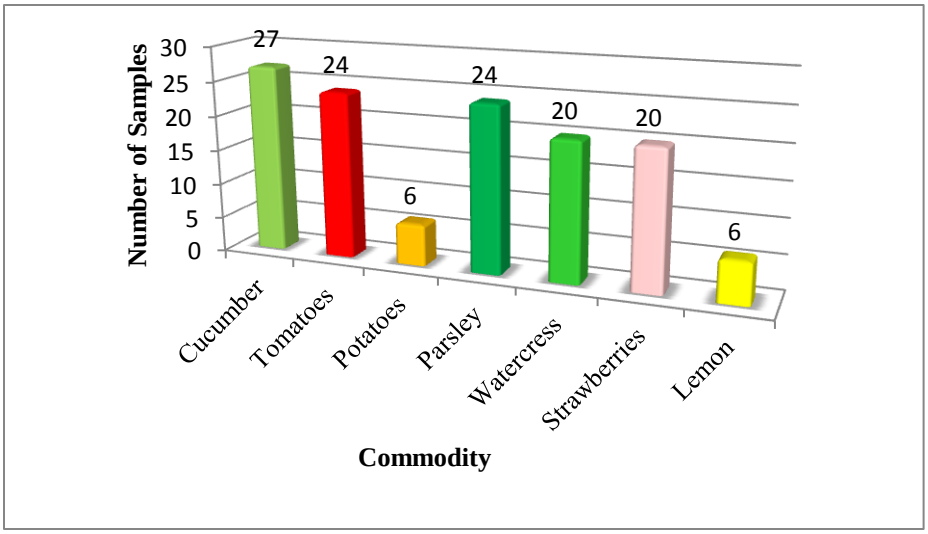


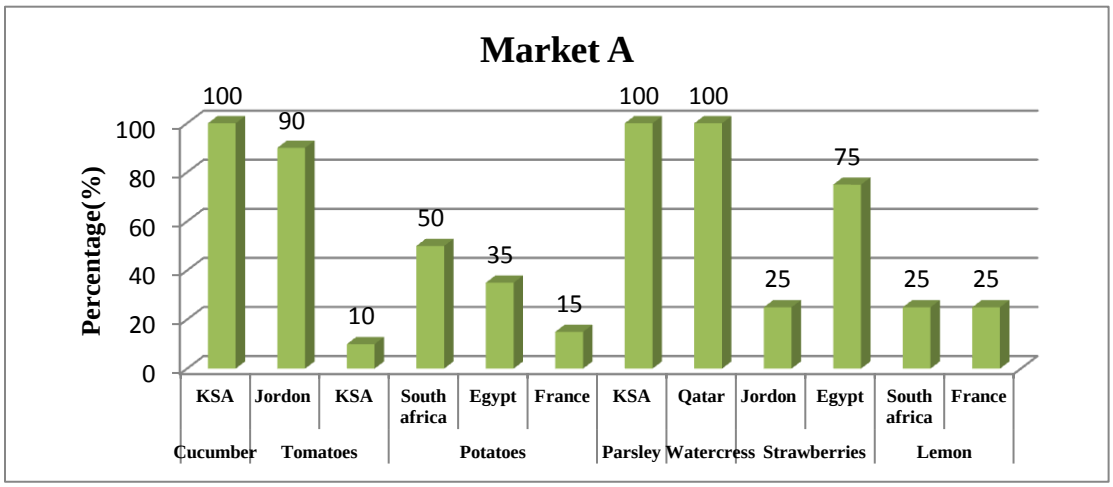
Figure 15 presents the number of samples according to its commodity. Since the season of production of local lemon and potatoes was inconsistent with the project time (the season production in May), only imported lemon and potatoes samples were analyzed.

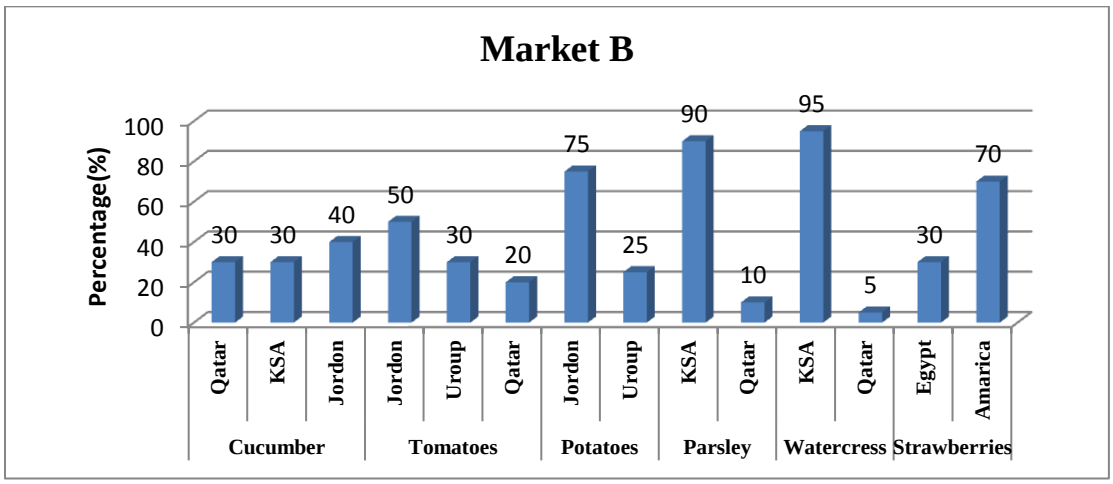
Figure 15: Distribution of samples by commodity

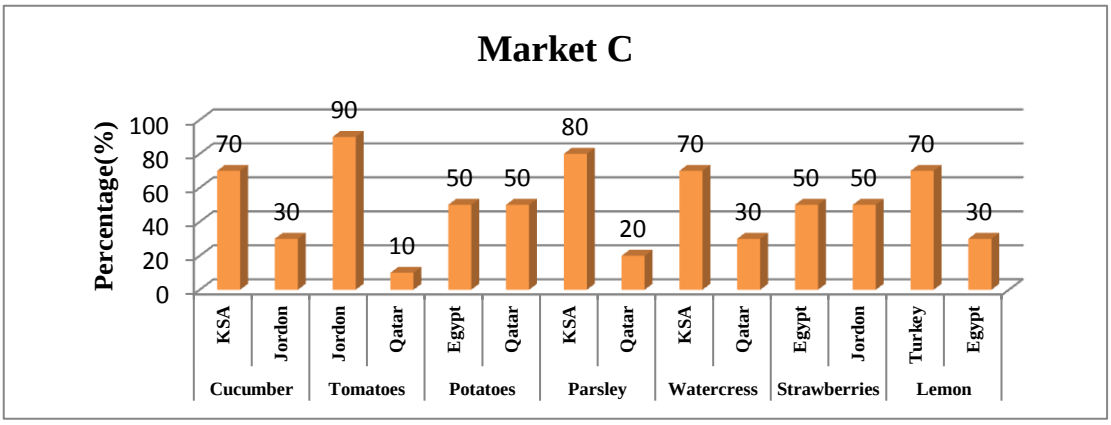


The imported vegetables and fruit samples were collected from three Markets in Qatar: Market A, Market B, and Market C as mentioned in Figure 9. These markets are the most popular places as most Qatar residents buy from them. Thus, in our collection of the imported samples from these markets, for each crop the high percentages of offering countries were considered. Figure 16 shows the percentages of selected vegetables and fruit in the three Markets (A, B & C).

Figure 16: Percentages of selected vegetables and fruit in the three Markets (A, B & C).





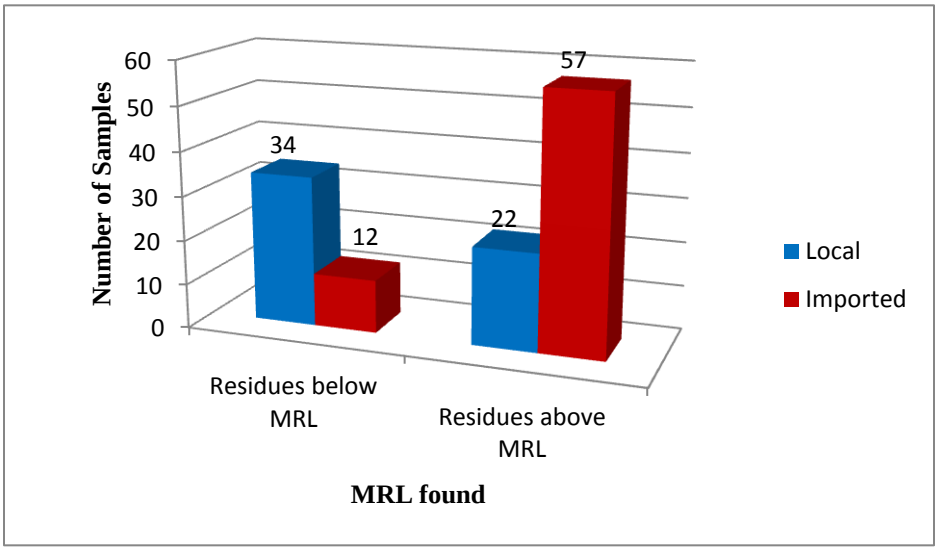


4.1 Organochlorine Residues in vegetables and fruit samples

This study is the first extensive study to determine the levels of pesticide residues on various vegetables and fruit commonly consumed in Qatar. Residues of 10 OCPs (Heptachlor, aldrin, dieldrin, Endrin, a-chlordane, g-chlordane, endosulfane I, methoxychlor, α -BHC and β –BHC) were identified for local and imported vegetables and fruit using GC/ECD.

According to the origin of samples, the number of samples containing residues above MRL is shown in Figure 17. The imported samples were higher than local samples in exceeding the MRL. About 57 samples (90%) of the imported samples were above the MRL in containing at least 1 of the selected organochlorine pesticides, whereas about 22 samples (30%) of local samples showed residues above the MRL in containing at least 1 of the selected organochlorine pesticides.

Figure 17: Occurrence of residues of pesticide in fruit and vegetables samples.



All local samples of cucumbers and tomatoes were residue-free or below the MRLs. In addition, all local strawberries samples were free of OCPs residue except two samples showed concentration of heptachlor higher than the MRL. However, only 12 samples of the total imported samples were free or below MRLs of OCPs residue. The rest of the imported samples contained at least one residue of OCPs that were above the MRLs.

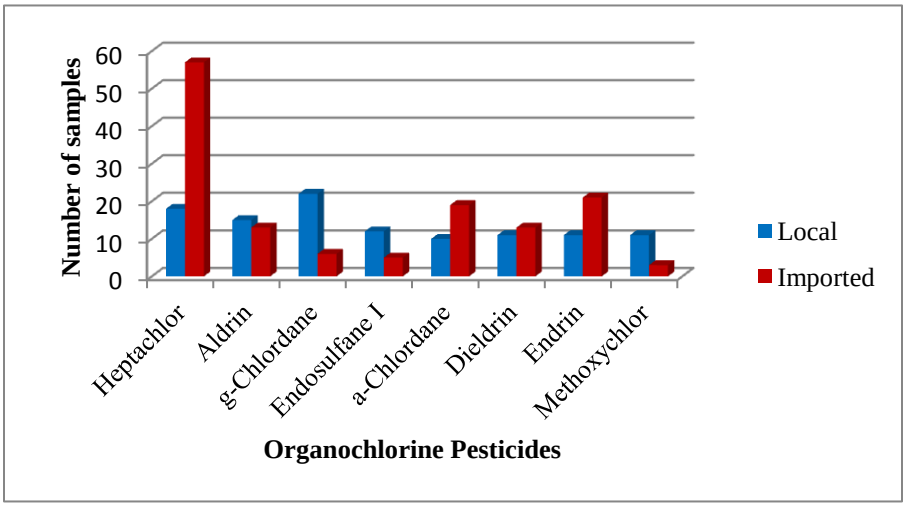
Almost 63% of the 127 samples analyzed had at least one OCPs residue. In terms of co-occurrence of pesticide residues, 8 local samples and 24 imported samples were shown to contain one residue of the 10 selected OCPs residues. While 20 local samples and 41 imported samples contained two or more of the selected OCPs pesticide residues.

The MRL values of the samples were exceeded most often for heptachlor. In all types of imported vegetables (cucumbers, tomatoes, potatoes, parsley, watercress) and fruits (strawberries, lemon), heptachlor concentration was higher than the MRL (>10µg/kg). The highest concentration of heptachlor pesticide residue was 144 µg/kg found in imported strawberries from Egypt.

Residues of OCPs in the imported samples were found most frequently are Heptachlor (57 samples), followed by endrin (21 samples), a-chlordane (19 samples), aldrin (13 samples) and dieldrin (13 samples). Whereas in local samples, the OCPs residue that were found most frequently were g-chlordane (22 samples), followed by heptachlor (18 samples), aldrin (15 samples), and endosulfane I (12 samples) as

shown in Figure 18. Six imported samples contained g-chlordane, five samples contained endosulfane I, and only three samples contained methoxychlor. For local samples, 11 samples contained dieldrin, endrin and methoxychlor, and about 10 samples contained a-chlordane. The OCPs that are not found in any sample were α-BHC and β –BHC.

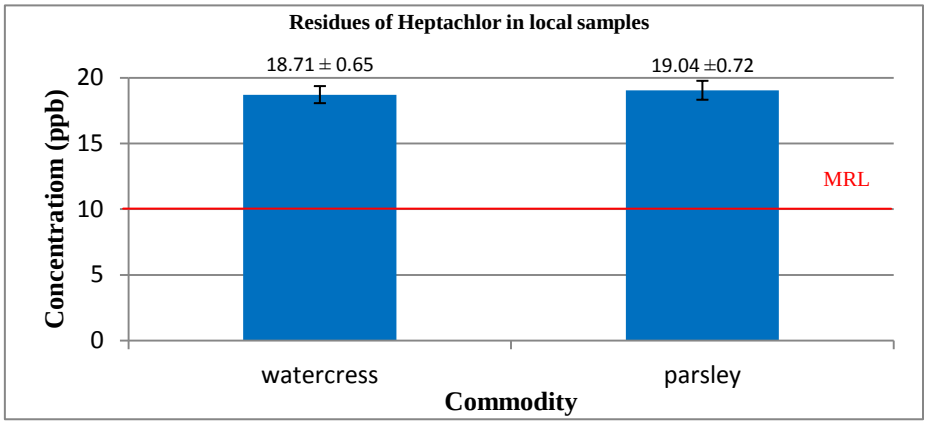
Figure 18: Residues of OCPs found in local and imported samples

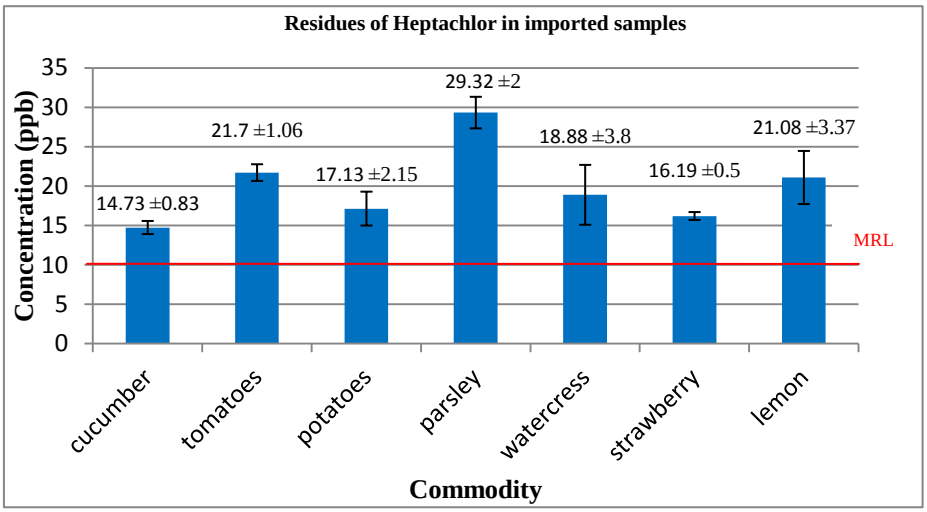


Over all, the most often found OCPs were heptachlor (found in 75 samples), g-chlordane (found in 22 samples) and a-chlordane (found in 19 samples).The influence of incubation temperatures on heptachlor degradation was studied at 20°C and 30°C (Pokethitiyook & Poolpak, 2012). At 30°C, smaller amount of heptachlor residue was presented than that of 20°C. This explained why the imported samples which were collected from markets showed high pesticides residues, since the temperature is low at market and it can influence pesticides accumulation.

The concentration of heptachlor compound that were found in collected local and imported samples is shown in Figure 19. The MRL of heptachlor is 10ppb. Heptachlor was found in two commodity (watercress and parsley) with average concentration 18.71 ± 0.65 (SE) and 19.04 ± 0.72 (SE) respectively. While in imported samples, heptachlor was detected in all commodities. The highest concentration was detected in collected parsley samples with average concentration 29.32 ±2, which means that they exceeded the MRL by about 20 ppb. The collected imported cucumber samples showed the least concentration of heptachlor with average concentration 14.73 ±0.83; they just exceeded the MRL by 4 ppb.

Figure 19: Residues of heptachlor in the local and imported samples





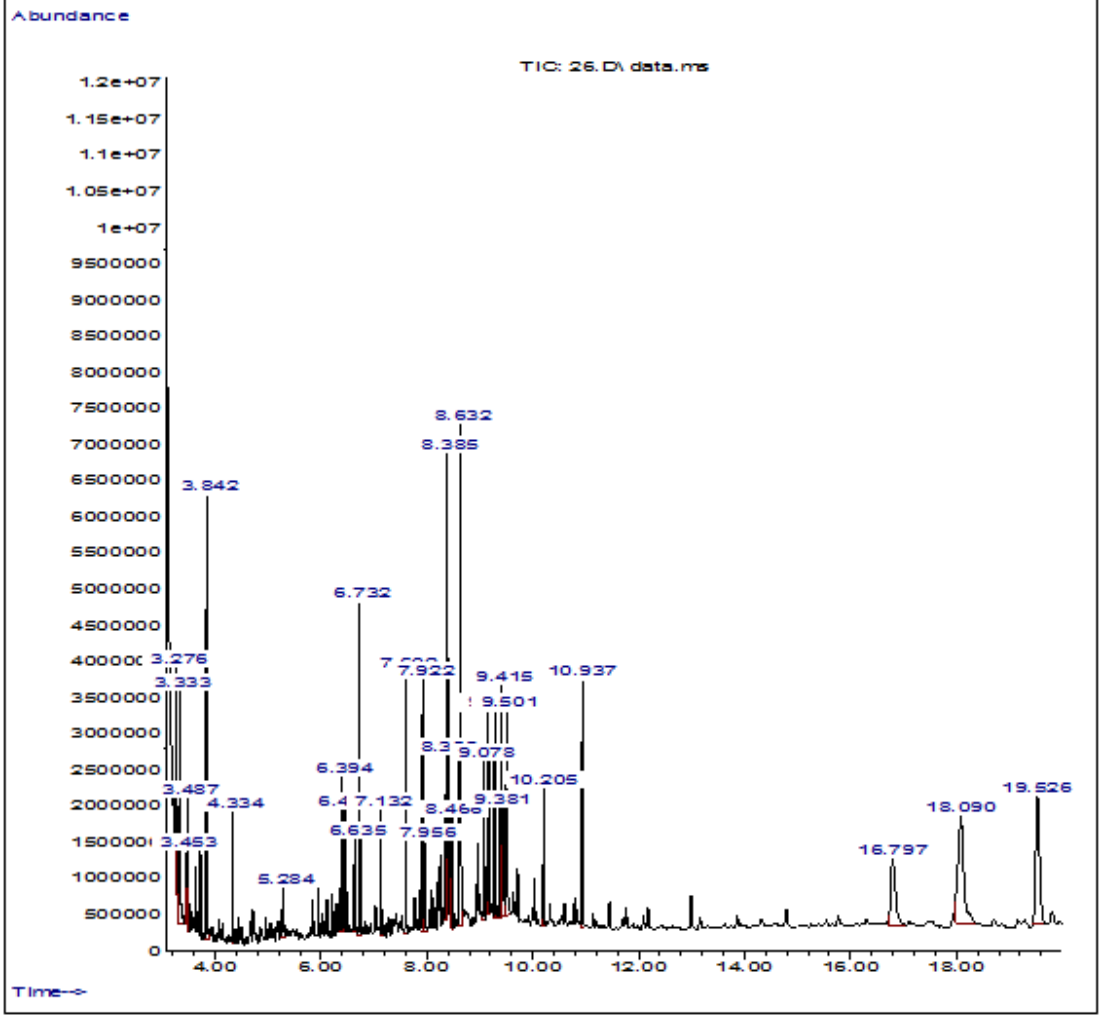
4.2 Scanning of vegetables and fruit samples by GC/MS

An Agilent 7890A mass spectrometric detector (MS 5973) was used to scan the samples under scan mode. The GC/MS data were acquired and processed with a wiley7n.1 and NIST98 Libraries.

Due to the complexity of the matrix, cleaning sample is necessary before GC/ MS. Thus, in this experiment the solid-phase extraction (SPE) such as florisil and silica were used. Nevertheless, recent advances in the clean-up techniques concentrate on the use of a combination of two or more SPE adsorbents commercially available. Weak anion-exchange sorbents such as aminopropyl (NH_2), primary–secondary amine (PSA), or diethylaminopropyl (DEA) modified silica together with strong anion-exchange sorbents are most often used adsorbents for clean-up of food samples (Yamazaki & Ninomiya, 1999).

The total ion chromatograms obtained after injecting 1µl of sample in the first instance gave the total profile of the volatiles and semi-volatiles characterizing that specific product. As an example, Figure 20 shows the recorded total ion chromatogram of the HP-1-capillary GC–MS analysis of imported cucumber sample. Many fatty acids in all the samples were detected by matching with wiley7n.1 and NIST98 Libraries.

Figure 20: Total ion chromatogram of imported cucumber by GC/MS.



The NH_2 and primary-secondary amine (PSA) sorbents provided the most effective clean-up among bonded-silica phases sine they can remove high amount of sample matrix interferences (Schenck & Lehotay, 2000 & Schenck *et al*, 2002). And because of its higher capacity, PSA was significantly better than NH_2 for removal of fatty acids (Anastassiades *et al*, 2003 & Saito *et al*, 2004).

Since florisil and silica were used for cleanup, heavy matrix interferences were observed in most of the samples, consisting primarily of fatty acids. Anastassiades *et al*, 2003 & Saito *et al*, 2004 showed that fatty acid matrix interferences can alter ionization efficiency when using MS detection. Thus the detection and identification of trace levels of pesticides in this complex profile can be very time-consuming and laborious.

4.3 Statistical data analysis

Two statistical analysis tests were used to determine significant differences between means. To compare between washed and unwashed, paired t-test was used. Analysis of variance (Factorial analysis) was used for determination of the significant differences among the countries where vegetables and fruits were imported from as well as washed and unwashed. In addition, the interaction between country and washing treatments were tested using LSD (Least Significant Differences) test.

Paired t-test analyses were performed to compare between residuals in washed and unwashed vegetables and fruits. Paired t-test revealed that in most of the comparisons between the washed and unwashed samples, no-significant differences were observed ($P > 0.05$). It means that most of the pesticides remain on the skin of vegetables after washing with water such as cucumber, tomatoes, and potatoes (Gutierrez & Londoño, 2009). The results are comparable with those were obtained by washing; this only removes loose surface residues and major portions of polar

compounds. Non-polar pesticides are tenaciously held in the waxy layers of the peel of fruits and vegetables. Rialch 2012 reported that the pesticide residues that are on the surface of vegetables require two to three times washings. Soliman 2001, noted that reduction of organochlorine pesticides residues were more efficient by washing the vegetables with acetic acid or sodium chloride solutions compared to washing with tap water. This could explain why there were no differences in the presence of organochlorine substances between washed samples by tap water and unwashed samples.

Though, it seems that the effects of washing samples with tap water differ in organochlorine residues based on the type of vegetables and fruits. Statistically significant differences ($P \leq 0.05$) in presence of some organochlorine compounds between washed and unwashed imported samples were noted in three commodities (parsley, watercress and strawberries). Heptachlor compound in imported parsley showed difference in significant between the washed and unwashed samples ($P = 0.0018$) as shown on Table 11. Meanwhile, heptachlor in imported strawberries showed difference in significant between the washed and unwashed samples ($P = 0.027$). In imported watercress samples, the compound a-chlordane showed also significant difference between the washed and unwashed ($p=0.017$). Refer to (Appendix 10) for the t-test analysis data.

The pesticide residues from green leafy vegetables (such as: Parsley and watercress) are removed satisfactorily by normal processing such as washing (Rialch,

2012). Kin & Huat (2010), reported that washing strawberries with tap water, acetic acid, sodium chloride or sodium carbonate can be an effective method to reduce the intake of pesticide residues. Other researchers stated that tap water reduced the pesticides residues in strawberries samples, though acidic solution was more effective in the elimination of the OCs pesticides (Kin & Huat 2010).

Analysis of variance (ANOVA) was performed using Minitab software to determine significant differences between two factors (washed/unwashed treatment and country source). The analysis was done for the compounds that showed residues in most of the samples for particular crop. Table 11 shows the analysis of variance for Heptachlor in parsley samples.

Table 11: Pair-difference t-test for the imported parsley for the presence of heptachlor residue

Parsley	
Heptachlor	
washed	unwashed
15.342	43.534
12.525	25.657
14.744	36.250
16.784	37.367
13.597	39.105
13.090	20.379

t-Test: Paired Two Sample for Means

	Variable 1	*Variable 2*
Mean	14.34723501	33.715319
Variance	2.509094233	77.60202923
Observations	6	6
Pearson Correlation	0.674717695	
Hypothesized Mean Difference	0	
df	5	
t Stat	-6.060360156	
P(T<=t) one-tail	0.000882592	
t Critical one-tail	2.015048372	
P(T<=t) two-tail	**0.001765183**	
t Critical two-tail	2.570581835	

Table 12: Analysis of variance data for Heptachlor in parsley samples.

Analysis of Variance for Heptachlor in parsley samples, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Treat	1	565.57	559.33	559.33	15.00	**0.002**
Country	2	80.58	80.71	40.35	1.08	**0.364**
Treat*Country	2	660.15	660.15	330.08	8.85	**0.003**
Error	**15**	559.26	559.26	**37.28**		
Total	20	1865.56				

The ANOVA analysis for heptachlor in parsley samples showed that there were significant difference in the treatment washed/unwashed (P =0.002), where no significant difference between counties (P= 0.364), and significant difference in the interaction between washing treatment and countries showed highly significant differences (P= 0.003) (Table 12). This means that washing decreased the heptachlor residues in parsley. Heptachlor concentration in the three different countries (KSA, Lebanon, and Qatar) showed no significant difference, i.e. the concentration in all countries was approximately the same.

Table 13 shows the calculated LSD for all possible pairs of mean. Table 14 shows the overall means of all possible interaction between the washing treatment and the countries (KSA, Lebanon and Qatar) for heptachlor in parsley.

As shown in Table 13 the calculated LSD value between washed Qatari parsley and washed KSA parsley was (6.59), and the difference of mean between these two groups as shown in (Table 14) was (13.62) was higher than the LSD, which indicates significant difference. The mean of the washed KSA parsley samples were higher than the mean of the washed local parsley samples, this means that the washed local parsley is better than the washed KSA parsley. Meanwhile, the difference of mean between unwashed Qatari parsley and unwashed KSA parsley was greater than LSD value (6.59), which means that the difference was significant. The mean of the unwashed KSA parsley samples were higher than the mean of the unwashed local parsley samples, this means that the unwashed local parsley is better than the unwashed KSA parsley. For the comparison between the washed Qatari parsley and washed Lebanon parsley the LSD value was (6.68) and the mean difference was greater than the LSD, which means that the difference was significant. The mean of the washed Qatari parsley samples were higher than the mean of the washed Lebanon parsley samples, this means that the washed Lebanon's parsley is better than the washed local parsley. Whereas no significant difference was observed between the unwashed Qatari parsley and unwashed Lebanon parsley.

Table 13: The calculated LSD for all possible pairs of means of heptachlor in parsley.

	Lebanon (washed)	KSA (washed)	Qatar (unwashed)	Qatar (washed)	Lebanon (unwashed)	KSA (unwashed)
KSA (unwashed)	6.68	6.58	6.59	5.92	6.01	0.00
Lebanon (unwashed)	9.32	6.68	6.68	6.68	0.00	6.01
Qatar (washed)	6.68	6.59	6.59	0.00	6.68	5.92
Qatar (unwashed)	6.68	6.59	0.00	6.59	6.68	6.59
KSA (washed)	6.68	0.00	6.59	6.59	6.68	6.58
Lebanon (washed)	0.00	6.68	6.68	6.68	9.32	6.68

For the comparison between the imported parsley samples, no significant differences between the washed KSA samples and washed Lebanon samples and between the unwashed KSA samples and the unwashed Lebanon samples were observed. However, there was a difference in significant between the washed KSA samples and the unwashed Lebanon samples. The mean of washed KSA samples was greater than the mean of unwashed Lebanon samples. This indicated that the unwashed Lebanon's parsley is better than the washed KSA's parsley. Meanwhile, the comparison between the unwashed KSA samples and washed Lebanon samples showed significant difference. The mean value of unwashed KSA samples was greater than the mean of washed Lebanon samples. This means that the washed Lebanon' parsley is better than the unwashed KSA' parsley.

Table 14: The overall means of all possible comparisons for heptachlor in parsley.

A: *Overall mean of washed and unwashed parsley samples*

	Washed	Unwashed
Mean	19.89	30.29

B: *Overall mean of KSA, Lebanon, and Qatar parsley samples*

	KSA	Lebanon	Qatar
Mean	24.37	21.54	27.03

C: *All possible pairs of means*

	Washed	Unwashed
KSA	15.30	35.70
Lebanon	13.34	29.74
Qatar	25.14	28.92

D: *Mean differences between all possible groups*

	Lebanon (washed)	KSA (washed)	Qatar (unwashed)	Qatar (washed)	Lebanon (unwashed)	KSA (unwashed)
KSA (unwashed)	22.36*	20.40*	10.56*	6.79	5.96	0.00
Lebanon (unwashed)	16.40*	14.44*	4.60	0.83	0.00	5.96*
Qatar (washed)	15.57*	13.62*	3.77	0.00	0.83	6.79*
Qatar (unwashed)	11.80*	9.84*	0.00	3.77*	4.60*	10.56*
KSA (washed)	1.95	0.00	9.84*	13.62*	14.44*	20.40*
Lebanon (washed)	0.00	1.95	11.80	15.57*	16.40*	22.36*

*The difference is significant.

The ANOVA analysis of a-chlordane in watercress is shown in Table 15. Significant difference was observed between counties (P= 0.002), i.e. a-chlordane residue was different depending on the country. The washing treatment and the interaction between the washing treatment and countries were not significant.

Table 15: Analysis of variance data for a-chlordane in watercress samples.

Analysis of Variance for a-Chlordane, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Treat	1	119.03	56.11	56.11	0.59	**0.459**
Country	1	1507.15	1474.54	1474.54	15.40	**0.002**
Treat*Country	1	155.36	155.36	155.36	1.62	**0.227**
Error	12	1148.73	1148.73	95.73		
Total	15	2930.27				

For the methoxychlor in cucumber samples, the ANOVA analysis shown in Table 16 showed that no significant differences were shown between the washed/unwashed samples (P > 0.05), countries and interaction between the washing treatment and countries.

Table 3: Analysis of variance data for methoxychlor in cucumber samples.

Analysis of Variance for Methoxyc, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Treat	1	2.578	1.779	1.779	1.35	**0.284**
Country	1	0.505	0.580	0.580	0.44	**0.529**
Treat*Country	1	0.969	0.969	0.969	0.73	**0.420**
Error	7	9.254	9.254	1.322		
Total	10	13.306				

Similarly, heptachlor in tomatoes showed also no significant differences in all the comparisons between the washing treatment, countries or interaction between the both as shown in Table 17.

Table 4: Analysis of variance data for heptachlor in tomatoes samples.

Analysis of Variance for Heptachl, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Treat	1	186.1	186.1	186.1	1.62	**0.271**
Country	1	195.3	195.3	195.3	1.70	**0.262**
Treat*Country	1	73.3	73.3	73.3	0.64	**0.469**
Error	4	458.4	458.4	114.6		
Total	7	913.1				

5 CONCLUSION

This study is the first study that provided important information regarding pesticide residues in vegetables and fruit in Qatar. 127 samples, which included 26 fruits and 101 vegetables, from local and imported sources were investigated for organochlorine pesticide residues. According to the results, the imported samples were much higher than local samples in exceeding the MRL. MRL values were exceeded most often for heptachlor OCPs. Most, if not all, of the pesticides residues found in local samples were detected on the leafy vegetables (parsley and watercress).

The statistical analysis of data was essential to identify and compare the results. The significant difference between the washed and unwashed samples was examined using t-test. And the significant differences between the two factors (washing treatment and countries) were studied using analysis of variance (ANOVA). The lowest significant differences (LSD) provided the significance between the interaction of washing treatment and countries.

The level of pesticide residues contamination may be considered a potential public health problem. The results also underscore the need for regular monitoring of large samples to determine the pesticide residues, especially for the imported samples.

6 RECOMMENDATION

The findings of this study suggest the need for a monitoring program to investigate the occurrence of residues of pesticide in foodstuffs, especially imported food products. All government sectors like (Qatar University, Ministry of Environment and Supreme Council of Health) should work together in this field, perform many scientific researches and share their results to the concerned parties in order to investigate the pesticides issues in products sold in Qatar.

Future studies should consider the processing factors other than washing with tap water in order to account for the reduction or removal of pesticides such as: washing (with acetic acid, sodium chloride and soap) and peeling. Also as a recommendation, we need to look to other types of food that are sold in Qatar and may contain pesticides residues, such as grains and dates. Future studies also should look to the presence of other type of pesticides such as organophosphorous and carbamates compounds.

7 REFERENCES

A. Anastassiades, S.J. Lehotay, D. Štajnbaher, F.J. Schenck. (2003). J. AOAC Int., 86, 412.

Alan R. Boobis, Bernadette C. Ossendorp, Ursula Banasiak, Paul Y. Hamey,Istvan Sebestyen, Angelo Moretto. (2008). Cumulative risk assessment of pesticide residues in food. *Toxicology Letters*,180, 137-150.

Alankar Shrivastava, Vipin B Gupta. (2011). Methods for the determination of limit of detection and limit of quantitation of the analytical methods. *Chronicles of Young Scientists*, 2(1), 21-25.

Amy E. Brown. (2013). Mode of Action of Insecticides and Related Pest Control Chemicals for Production Agriculture, Ornamentals, and Turf. Retrieved From the University of Maryland website: http://pesticide.umd.edu

Analytical Procedures and Methods Validation.(2000). *Food and Drug Administration*. Retrieved From the Environmental Protection Agency website: http://www.fda.gov

Andersen, H.R., Vinggaard, A.M., Rasmussen, T.H., Gjermandsen, I.M., Bonefeld-Jørgensen, E.C. (2002). Effects of currently used pesticides in assays for estrogenicity, androgenicity, and aromatase activity in vitro. *Toxicol. Appl. Pharmacol*., 179, 1–12.

Andréia Nunes Oliveira Jardim, Denise Carvalho Mello, Fernanda Caroline Silva Goes, Elcio Ferreira Frota Junior, Eloisa Dutra Caldas. (2014). Pesticide residues in cashew apple, guava, kaki and peach: GC–lECD, GC–FPD and

LC–MS/MS multiresidue method validation, analysis and cumulative acute risk assessment. *Food Chemistry*, 164, 195-204.

Badawi, A.F., Cavalieri, E.L., Rogan, E.G. (2000). Effect of chlorinated hydrocarbons on expression of cytochrome P450 1A1, 1A2 and 1B1 and 2- and 4 hydroxylation of 17beta-estradiol in female Sprague-Dawley rats. *Carcinogenesis*, 21, 1593–1599.

Bai, Y., Zhou, L., & Wang, J. (2006). Organophosphorus pesticide residues in market foods in Shaanxi area, China. Food Chemistry, 98, 240–242.

Benjamin C.L. Lai, MD, MSc , Joseph K.C. Tsui, MD, FRCP(UK), FRCPC. (2001). *Epidemiology of Parkinson's disease*. BCMJ, 43 (3), 133- 137.

Bradlow, H.L., Davis, D.L., Lin, G., Sepkovic, D., Tiwari, R., 1995. Effects of pesticides on the ratio of 16 alpha/2-hydroxyestrone: a biologic marker of breast cancer risk. *Environ. Health Perspect*. 103, 147–150.

C. Bolognesi & F.D. Merlo (2011). Pesticides: Human Health Effects. *Reference Module in Earth Systems and Environmental Sciences*. 438–453.

C. Bolognesi, F.D. Merlo. (2011). Pesticides: Human Health Effects. *Reference Module in Earth Systems and Environmental Sciences*. 438–453.

C.J. Wang & Z.Q. Liu. (2007). Foliar uptake of pesticides—Present status and future challenge. *Pesticide Biochemistry and Physiology*, 87(1), 1-8.

Cayo Corcellas, Ethel Eljarrat, Damià Barceló. (2015). First report of pyrethroid bioaccumulation in wild river fish: A case study in Iberian river basins (Spain). *Environment International*, 75, 110-116.

Chai Mee Kin & Tan Guan Huat. (2010). Headspace solid-phase microextraction for the evaluation of pesticide residue contents in cucumber and strawberry after washing treatment. *Food Chemistry*, 123(3), 760-764.

Chen, C., Qian, Y., Chen, Q., Tao, C., Li, C., & Li, Y. (2011). Evaluation of pesticide residues in fruits and vegetables from Xiamen, China. Food Control, 22, 1114–1120.

Claudia Bolognesi & Gabriella Morasso. (2000). *Genotoxicity of pesticides: potential risk for consumers*. Trends in Food Science & Technology, 11, (4–5), 182–187.

Crentsil Kofi Bempah, Jacob Asomaning, Daniel Ayirebi Ansong, Juliana Boateng and Stephen Boahen Asabere. (2012). Contamination levels of selected organochlorine and organophosphorous pesticides in Ghanaian fruits and vegetables. Nutrition and food science. *Emir. J. Food Agric*, 24 (4): 293-301.

Curley A, Jennings RW, Mann HT, et al. 1970. Measurement of endrin following epidemics of poisoning. *Bull Environ Contam Toxicol*, 5, 24-29.

D.K. Essumang1, G.K. Togoh and L. Chokky.(2009). Pesticide residues in the water and fish (lagoon tilapia) samples from lagoons in Ghana. *Chemical Society of Ethiopia*, 23(1), 19-27.

Dana Boyd Barr, Anders O. Olsson, Lee-Yang Wong, Simeon Udunka, Samuel E. Baker, Ralph D. Whitehead Jr., Melina S. Magsumbol, Bryan L. Williams, Larry L. Needham. (2010). Urinary Concentrations of Metabolites of Pyrethroid Insecticides in the General U.S. Population: National Health and Nutrition Examination Survey 1999–2002. *Environ Health Perspect*ives, 118, 742-748.

de Boer J, Law RJ (2003). Developments in the use of chromatographic techniques in marine laboratories for the determination of halogenated contaminants and polycyclic aromatic hydrocarbons. PubMed. Retrieved From the NCBI website: http://www.ncbi.nlm.nih.gov

Deichmann WB, MacDonald WE, Blum E, et al. 1970. Tumorigenicity of aldrin, dieldrin and endrin in the albino rat. *Industrial Medicine*, (39), 37-45.

Donald J. Ecobichon. (2001). Pesticide use in developing countries. *Toxicology*. 160 (1–3), 27–33.

Environmental Protaction Agency. (2014). *What is a pesticides?*. Retrieved From the Environmental Protection Agency website: http://www.epa.gov/pesticides/

F.J. Schenck, S.J. Lehotay, V. Vega. (2002). Comparison of solid-phase extraction sorbents for cleanup in pesticide residue analysis of fresh fruits and vegetables. *Journal of Separation Science*, 25, 883-890.

F.J. Schenck, S.J. Lehotay. (2000).Does further clean-up reduce the matrix enhancement effect in gas chromatographic analysis of pesticide residues in food?. *J. Chromatogr. A.*, 868, 51-61.

FAO/WHO, 2004. Food and Agriculture Organization/World Health Organization, Food standards program. *Codex Alimentarius Commission*. Twenty-seventh Session, Geneva, Switzerland.

Fei Yang, Zhaoyang Bian , Xiaoshui Chen, Sansan Liu, Yang Liu and Gangling Tang. (2013). Analysis of 118 Pesticides in Tobacco after Extraction With the Modified QuEChRS Method by LC–MS-MS. *Journal of Chromatographic Science*, 1-5.

Food and Agriculture Organization. (2013). Resource Statistics - Pesticides Consumption, 2013. Retrieved From Knoema website: http://knoema.com/FAORSPestConsum2013

Food and Agriculture Organization/World Health Organization.(2013). Pesticide Residues in Food and Feed. Retrieved From the CODEX alimentarius website: http://www.codexalimentarius.net/pestres/data/pesticides

Gilbert Ross. (2005). Risks and benefits of DDT. American Council on Science and Health, 1771-1772.

Gozde Turkoz Bakırcı, Dilek Bengu Yaman Acay, Fatih Bakırcı, Semih Otles. (2014). Pesticide residues in fruits and vegetables from the Aegean region,Turkey. *Food Chemistry*, 160, 379-392.

Gozde Turkoz Bakırcı, Yas_ar Hısıl. (2011). Fast and simple extraction of pesticide residues in selected fruits and vegetables using tetrafluoroethane and toluene followed by ultrahigh-performance liquid chromatography/tandem mass spectrometry. *Food Chemistry*, 135, 1901-1913.

Hjorth, K., Johansen, K., Holen, B., Andersson, A., Christensen, H. B., Siivinen, K., et al. (2011). Pesticide residues in fruits and vegetables from South America e A Nordic project. *Food Control*, 22, 1701–1706.

IARC. (2015). *IARC Monographs Volume 112: evaluation of five organophosphate insecticides and herbicides*. Retrieved From the International Agency for Research on Cancer website: http://www.iarc.fr

Isam Bashour. (2009). Pesticides, Fertilizers and Food Safety. *Arab Environment: Future Challenges*. Chapter 10, 137-144.

J.A. Gutierrez, A. Londoño. (2009). Determinación de plaguicidas organoclorados y organofosforados en tomates de cadena en las ciudades de Pereira y Armania, Colombia. *Boletín Latinoamericano y del Caribe de Plantas Medicinales y Aromáticas*, 8 (3), 165–171.

J.L. Fern´andez Moreno, F.J. Arrebola Li´ebanas, A. Garrido Frenich, J.L. Mart´ınez Vidal. (2006). Evaluation of different sample treatments for determining pesticide residues in fat vegetable matrices like avocado by low-pressure gas chromatography–tandem mass spectrometry. *Journal of Chromatography*, 1111, 97-105.

Jana Hajšlová, Tomáš Cajka. (2007). Gas chromatography–mass spectrometry (GC–MS). Food *Toxicants Analysis*. 12, 419-473.

Jennifer Sass. (2014). Neonicotinoid pesticides - bad for bees, and may be bad for people too. Retrieved From the SWITCHBOARD website: http://switchboard.nrdc.org

Jolanta Fenik, Maciej Tankiewicz, Marek Biziuk.(2011). Properties and determination of pesticides in fruits and vegetables. Trends in Analytical Chemistry, 30(6), 814- 826.

K.M. Soliman. (2001). Changes in concentrations of pesticide residues in potatoes during washing and home preparation. *Food and Chemical Toxicology*, 39, 887–891.

Keith LH .(1996). *Compilation of EPA's sampling and analysis methods*. Boca Raton.

Kmellara, B., Abrankoa, L., Fodora, P., & Lehotay, S. J. (2010). Routine approach to qualitatively screening 300 pesticides and quantification of those frequently detected in fruit and vegetables using liquid chromatography tandem mass spectrometry (LC–MS/MS). *Food Additives and Contaminants*, 27(10), 1415–1430.

Knezˇevic´ , Z., & Serdar, M. (2009). Screening of fresh fruit and vegetables for pesticide residues on Croatian market. Food Control, 20, 419–422.

Li, J., Li, N., Ma, M., Giesy, J.P., Wang, Z. (2008). In vitro profiling of the endocrine disrupting potency of organochlorine pesticides. *Toxicol. Lett*, 183, 65–71.

M. H. EL-Saeid and M. T. Selim. (2013). Multiresidue Analysis of 86 Pesticides Using Gas Chromatography Mass Spectrometry: II-Nonleafy Vegetables. *Journal of Chemistry*. Retrieved From the Hindawi Publishing Corporation website: http://www.hindawi.com

M. Isabel Pinto, Gerhard Sontag, R.J. Bernardino, J.P. Noronha. (2010). Pesticides in water and the performance of the liquid-phase microextraction based techniques. A review. Microchemical Journal, 96, 225-237.

Margaret Cunningham. (2015).Use of Pesticides: Benefits and Problems Associated with Pesticides. Retrieved From the Study website: www.study.com/academy

Mariana Gonzalez, Karina S.B. Miglioranza, Julia E. Aizpún de Moreno & Víctor J. Moreno. (2005). Evaluation of conventionally and organically produced

vegetables for high lipophilic organochlorine pesticide (OCP) residues. Food and Chemical Toxicology, 43(2), 261-269.

Mario Suwalsky , Maritza Benites, Fernando Villena, Felipe Aguilar, Carlos P Sotomayor .(1997). The organochlorine pesticide heptachlor disrupts the structure of model and cell membranes. *Biochimica et Biophysica Acta (BBA) – Biomembranes*, 1326 (1), 115–123.

Md. Wasim Aktar,Dwaipayan Sengupta, and Ashim Chowdhury. (2009). Impact of pesticides use in agriculture: their benefits and hazards. Interdiscip Toxicology, 2(1), 1-12.

N. Ito, H. Nagasaki, H. Aoe, S. Sugihara, Y. Miyata. (1975). Development of hepatocellular carcinomas in rats treated with benzene hexachloride. J. Natl Cancer Inst., 54, 801–805.

National Implementation Plan (NIP) for Stockholm Convention on Persistent Organic Pollutants (POPs). (2011). Ministry of Environment. Retrieved From: http://chm.pops.int/Implementation/NIPs/NIPSubmissions

National Pesticides Information Center. (2011). *Types of Pesticides*. Retrieved From the National Pesticides Information Center website: http://www.npic.orst.edu

Nativelle-Serpentini, C., Richard, S., Seralini, G.E., Sourdaine, P. (2003). Aromatase activity modulation by lindane and bisphenol-A in human placental JEG-3 and transfected kidney E293 cells. *Toxicol. In Vitro,* 17, 413–422.

Ortelli, D., Edder, P., & Corvi, C. (2006). Multiresidue analysis of 74 pesticides in fruit and vegetables by liquid chromatography-electrospray-tandem mass spectrometry, 520, 33–45.

Osman, K. A., Al-Humaid, A. M., Al-Rehiayani, S. M., & Al-Redha, K. N. (2010). Monitoring of pesticide residues in vegetables marketed in Al-Qassim region, Saudi Arabia. *Ecotoxicology and Environmental Safety*, 73, 1433‑1439.

Padula G, Ponzinibbio MV, Picco S, Seoane A. (2012). *Assessment of the adverse effects of the acaricide amitraz: in vitro evaluation of genotoxicity*.PuLMed, 22(9), 657-616.

Pico, Y., la Farre, M., Soler, C., & Barcelo, D. (2007). Identification of unknown pesticides in fruits using ultra-performance liquid chromatography-quadrupole time of-flight mass spectrometry. Imazalil as a case study of quantification. Journal of Chromatography A, *Anayitica Chimica Acta* 1176(1–2), 123–134.

Pratibha Rialch . (2012). Removing Pesticides from Fruits and Vegetables. Retrieved From the Center for Science and Environment website: http://www.cseindia.org

Prayad Pokethitiyook & Toemthip Poolpak. (2012). *Heptachlor and Its Metabolite: Accumulation and Degradation in Sediment*. InTech, Bangkok, Thailand.

Qing Miao, MSHongmei Liu, Weijun Kong, Bao Gong, Yun Qi, Meihua Yang. (2013). Rapid analysis of multi-pesticides in Morinda officinalis by GC–

ECDwith accelerated solvent extraction assisted matrix solid phasedispersion and positive confirmation by GC–MS. Journal of Chromatography B, 974, 65-74.

Quevedo, L., Norris, B., Benites, M. and Suwalsky, M. (1997). Interaction of the Organochlorine Pesticide Dieldrin with Phospholipid Bilayers. *Verlag der Zeitschrift für Naturforschung*, 450-458.

Quick MP, Shaw IC, Manser PA. 1989. A surprising case of endrin poisoning in dogs. *Journal of the Forensic Science Society*, 29(5):331-338.

R.C. Gupta. (2014). Carbamate Pesticides. *Encyclopedia of Toxicology (Third Edition)*, 661-664.

Rafael Vargas-Bernal, Gabriel Herrera-Pérez and Esmeralda Rodríguez-Miranda. (2012). Evolution and Expectations ofja Enzymatic Biosensors for Pesticides. Soundararajan, 978-953.

Rafat Ahmad, Nida' M. Salem', Hussein Estaitieh. (2010). Occurrence of organochlorine pesticide residues in eggs, chicken and meat in Jordan. *Chemosphere*,78 (6), 667–671.

Rathore, Hamir S., and Nollet, Leo M. L., eds. (2012). *Pesticides : Evaluation of Environmental Pollution.* USA: CRC.

Rawiwan Puatanachokchai, Keiichirou Morimura, Hideki Wanibuchi, Mayuko Oka, Anna Kinoshita, Fukui Mitsuru, Shuji Yamaguchi, Yoshihiko Funae, Shoji Fukushima (2006). Alpha-benzene hexachloride exerts hormesis in preneoplastic

lesion formation of rat hepatocarcinogenesis with the possible role for hepatic detoxifying enzymes. Cancer Letters, 240(1), 102-113.

Ritz B, A Manthripragada, S Costello, S Lincoln, M Farrer, M Cockburn, J Bronstein. (2009). Dopamine transporter genetic variants and pesticides in Parkinson's disease. *Environmental Health Perspectives.* doi:10.1289/ehp.0800277.

Runhaar EA, Sangster B, Greve PA, et al. 1985. A case of fatal endrin poisoning. Hum Toxicol 4:241-247.

S. Angsubhakorn, N. Bhamarapravati, K. Romruen, S. Sahaphong, W. Thamavit, M. Miyamoto. (1981). Further study of α-benzene hexachloride inhibition of aflatoxin B1 hepatocarcinogenesis. *Br. J. Cancer*, 43, 881–883.

S. Vaithinathan, B. Saradha, P.P. (2010). Mathur Methoxychlor induces apoptosis via mitochondria- and FasL-mediated pathways in adult rat testis. *Chem. Biol. Interact*., 185, 110–118.

S.M. Khan, L.M. Dauffenbach, J. Yeh. (2000). Mitochondria and caspases in induced apoptosis in human luteinized granulosa cells *Biochem. Biophys. Res. Commun*., 269, 542–545.

SafiatouBerthe Dem, 2007. pesticide residues in soil and water from four cotton growing area of Mali, West Africa. *Journal of Agriculture, Food and Environment Sciences*, 1, 1-9.

Sait Bulut, Levent Akkaya, Veli Gök, Muhsin Konuk. (2011). Organochlorine pesticide (OCP) residues in cow's, buffalo's, and sheep's milk from Afyonkarahisar region, Turkey. *Springer Science, Business Media*, 181, 555–562.

Singh, Dileep K. (2012). *Toxicology: Agriculture and Environment: Pesticide Chemistry and Toxicology.* UAE: Bentham Science Publishers.

Sinha, N., Narayan, R., Shanker, R., Saxena, D.K.. (1995). Endosulfan induced biochemical changes in the testis of rats. *Vet. Hum. Toxicol*. 37, 547–549.

Stan, H. J. (2000). Pesticide residue analysis in foodstuffs applying capillary gas chromatography with mass spectrometric detection State-of-the-art use of modified DFG-multimethod S19 and automated data evaluation. *Journal of Chromatography A*, 892, 347–377.

T.M. Said, U. Paasch, H.J. Glander, A. Agarwal. (2004). Role of caspases in male infertility. *Hum. Reprod*, 10, 39–51.

Treon JF, Cleveland FP, Cappel J. 1955. Toxicity of endrin for laboratory animals. *Agricultural and Food Chemistry*, 3:842-848.

United State National Toxicology Program. (2015). *Regulatory Actions for Years 2010 to 2015*. NTP, US. Retrieved From the National Toxicology Program website: http://ntp.niehs.nih.gov \

United States Department of Agriculture. (2012). Electron Capture Detectors (ECD). Retrieved From the United States Department of Agriculture website: http://www.dm.usda.gov

W. Thamavit, T. Hiasa, N. Ito, N. Bhamarapravati.(1974).The inhibitory effect of α-benzene hexachloride on 3′-methyl-4-dimethyl-aminoazobenzene and DL-ethionine carcinogenesis in rats. Cancer Res., 34, 337–340.

Wells DE, Hess P. (2000). *Separation, clean-up and recoveries of persistant trace organic contaminants from soils, sediment and biological matrices.* Amsterdam.

World Health Organization (2010). The WHO recommended classification of pesticides by hazard and guidelines to classification: 2009.

World Health Organization. (2006).*The WHO recommended Classification of Pesticides by Hazard and Guidelines to Classification*. Retrieved From the World Health Organization website: http://www.who.int

Xuejin Mao, YiqunWan, AipingYan , MingyueShen , YuanlongWei. (2012). Simultaneousdeterminationoforganophosphorus,organochlorine, pyrethriod andcarbamatepesticidesin Radix astragali by microwave-assistedextraction/dispersive-solidphase extraction coupledwithGC–MS. Talanta, 97,131-141.

Y. Saito, S. Kodama, A. Matsunaga, A. Yamamoto. (2004). J. AOAC Int., 87 (6), 1356.

Y. Shi, Y. Song, Y. Wang, Y. Wang, X. Liang, Y. Hu, H. Yu, X. Guan, J. Cheng, K. Yan. (2011). β-Benzene hexachloride induces apoptosis of rat Sertoli cells through generation of reactive oxygen species and activation of JNKs and FasL. Environ. *Toxicol.*, 26, 124–135.

Y. Yamazaki, T. Ninomiya. (1999). *Journal of AOAC Int.*, 82, 1474.

Statistical Consultant. (2015). *T-Test*. Retrieved From the Statistically Significant Consulting website: http://www.statisticallysignificantconsulting.com/Ttest.htm

8 A PPENDIX

8.1 Appendix 1: Samples Collection

Figure 1: Collection of local vegetables samples from Al-Mazrouah hall

Figure 2: Collection of imported vegetables samples from markets.

Figure 3: Collection of local leafy vegetables samples from Al-Mazrouah hall.

Figure 4: Collection of imported leafy vegetables samples from markets.

Figure 5: Collection of local fruit samples from Al-Mazrouah hall.

Figure 6: Collection of local fruit samples from Markets A, B & C.

8.2 Appendix 2: The Scope and Application of EPA Method 8081A

METHOD 8081A

ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8081 is used to determine the concentrations of various organochlorine pesticides in extracts from solid and liquid matrices, using fused-silica, open-tubular, capillary columns with electron capture detectors (ECD). When compared to the packed columns, these columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis. The compounds listed below may be determined by either a single- or dual-column analysis system.

Compound	CAS Registry No.
Aldrin	309-00-2
α-BHC	319-84-6
β-BHC	319-85-7
γ-BHC (Lindane)	58-89-9
δ-BHC	319-86-8
Chlorobenzilate	510-15-6
α-Chlordane	5103-71-9
γ-Chlordane	5103-74-2
Chlordane - not otherwise specified	57-74-9
DBCP	96-12-8
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Diallate	2303-16-4
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorocyclopentadiene	77-47-4
Isodrin	465-73-6
Methoxychlor	72-43-5
Toxaphene	8001-35-2

1.2 This revision of Method 8081 no longer includes the PCBs as Aroclors in the list of target analytes. The analysis of PCBs should be undertaken using Method 8082, which includes specific cleanup and quantitation procedures designed for PCB analysis. This change was made to obtain PCB data of better quality and to eliminate the complications inherent in a combined organochlorine pesticide and PCB method. Therefore, if the presence of PCBs is expected, use Method 8082 for

8.3 Appendix 3: Accelerated Solvent Extraction of Pesticide Residues in Food Products. Dionex Application Note 332, 2012.

Application Note 332

Accelerated Solvent Extraction of Pesticide Residues in Food Products

Introduction

Residue analysis in crops and food products is routinely performed in regulatory and industrial laboratories around the world. Many of the traditional procedures used to perform these extractions are time-consuming and solvent-intensive. Accelerated solvent extraction is an extraction technique that speeds the extraction process and reduces the total amount of solvent used. The system uses conventional liquid solvents at elevated temperatures and pressures, which results in increased extraction kinetics. Extraction of samples ranging from 1 to 30 g typically requires 12–17 min and 15–50 mL of solvent.

In the environmental industry, accelerated solvent extraction has been compared extensively to traditional preparation techniques, and has been found to generate similar extracts in a more efficient manner. Accelerated solvent extraction is now widely used in environmental applications to replace time- and solvent-intensive techniques such as Soxhlet and sonication. The principles of accelerated solvent extraction technology are based on conventional liquid extraction theory, so the transfer of existing solvent-based extraction processes to accelerated solvent extraction is simple. In addition, the ability to extract up to 24 samples unattended can result in a dramatic increase in laboratory efficiency.

Equipment

Thermo Scientific Dionex ASE 200 accelerated solvent extraction system* equipped with 11, 22, or 33 mL cells
Thermo Scientific Dionex vials for collection of extracts (40 mL, P/N 049465; 60 mL, P/N 049466)
Cellulose filter disks (P/N 049458)

*Thermo Scientific Dionex ASE 150 and 350 accelerated solvent extraction systems can be used for equivalent results.

Reagents

Fisher Scientific Acetone, Optima grade
Fisher Scientific Acetonitrile, Optima grade
Fisher Scientific Hexane, Optima grade
Thermo Scientific Dionex ASE Prep DE (P/N 062819)
Fisher Scientific sodium sulfate, anhydrous added after extraction

Extraction Conditions

Temperature:	100 °C
Pressure:	1500 psi*
Heatup Time:	5 min
Static Time:	5 min
Flush Volume:	60%
Purge Time:	100 s
Static Cycles:	1–2
Total Extraction Time:	14–18 min per sample
Total Solvent Used:	15–45 mL per sample

*Pressure studies show that 1500 psi is the optimum extraction pressure for all accelerated solvent extraction applications.

Sample Preparation

Weigh dry samples (1–20 g) and add directly to extraction cells containing a cellulose extraction filter. Grind wet samples (1–10 g) and mix with 6 g of Dionex ASE™ Prep DE (diatomaceous earth) using a mortar and pestle. Rinse the mortar and pestle with 2–3 mL of the extraction solvent. Add this volume to the sample in the extraction cell.

Extraction

Perform the sample extractions according to the outlined conditions. Following extraction, add 5 g of anhydrous sodium sulfate to the collection vial to absorb coextracted water. Shake the vial for 15 s and decant the water-free extract into a clean 60-mL vial. Rinse the original vial with 5 mL of the extraction solvent and decant this volume into a second vial. Concentrate the combined volume to approximately 10 mL under nitrogen.

Analytical

Analyze organochlorine pesticides using a gas chromatograph with a 30 m × 0.25 mm i.d. RTX-5 capillary column (Restek Corporation, Belefonte, USA). Set up a 1-µL splitless injection volume with the injector at 275 °C and the electron capture detector (ECD) maintained at 300 °C with a nitrogen atmosphere. Program the run from 140 °C (3 min) to 265 °C at 10 °C/min. Quantify results using endosulfan I or endrin aldehyde as the internal standard. Pass pesticide extracts through carbon or C18 cleanup cartridges prior to analysis. Quantify results by GC analysis with ECD detection (U.S. EPA Method 8151) or GC with MS detection (U.S. EPA Method 8270).

Results and Discussion

Samples (10 g) of raw potato and banana were spiked with 100 µL of a standard solution in hexane containing 12 organochlorine pesticides. Hexane with 10% acetone was chosen as the extraction solvent because it delivered good recoveries of the analytes with fewer interferences (co-extractables) than a 1:1 mixture. Resulting extracts were clear (after sodium sulfate treatment) upon concentration and suitable for GC/ECD analysis. The necessity of the drying step limits the amount of raw sample that can be extracted to 10 g. Results are presented in Tables 1 and 2. These results represent three extractions with duplicate GC injections of each extract.

Table 1. Recovery of Organochlorine Pesticides Spiked onto Raw Banana at the 100 ppm Level*

Compound	Av. Recovery (%)	SD (µg/kg)	RSD (%)
α-BHC	100.3	2.3	2.3
β-BHC	102.2	2.3	2.3
ϒ-BHC	98.9	3.2	3.2
Heptachlor	89.2	7.6	8.5
Aldrin	89.4	2.2	2.5
Heptachlor Epoxide	93.5	2.1	2.2
Dieldrin	93.7	1.6	1.7
4,4'-DDE	92.1	1.8	1.9
2,4'-DDD	95.4	2.5	2.6
Endrin	94.4	2.7	3.0
4,4'-DDD	88.0	2.7	3.0
4,4'-DDT	89.6	5.8	6.4

*n = 3.

Table 2. Recovery of Organochlorine Pesticides Spiked onto Raw Potato at the 100 ppm Level*

Compound	Av. Recovery (%)	SD (µg/kg)	RSD (%)
α-BHC	96.3	6.3	6.6
β-BHC	108.6	2.3	2.1
ϒ-BHC	97.4	6.6	6.8
Heptachlor	93.9	3.5	3.7
Aldrin	95.9	3.3	3.4
Heptachlor Epoxide	95.2	2.4	2.6
Dieldrin	97.1	0.55	0.57
4,4'-DDE	95.4	0.67	0.70
2,4'-DDD	95.7	0.85	0.89
Endrin	97.8	1.8	1.9
4,4'-DDD	93.7	1.8	1.9
4,4'-DDT	93.0	4.5	4.8

*n = 3.

Table 3. Recovery of Spiked Pesticides from Wheat by Accelerated Solvent Extraction

Compound	Spike Level (µg/kg)	Spike Level (µg/kg)
o-Methoate	74	85.4
Trifluralin	44	99.6
Dichlorvos	18	60.5
Phorate	18	92.8
Demeton	38	96.7
Dimethoate	58	87.8
Carbofuran	22	96.6
Atrazine	14	92.8
Diazinon	26	96.9
Disulfoton	22	87.9
Triallate	68	87.8
Parathion-methyl	40	115.7
Chlorpyrifos-methyl	8	115.4
Carbaryl	92	54.1
Linuron	102	83.6
Malathion	22	104.5
Phorate-sulfone	32	105.7
Parathion	84	101.2
Endosulfan-alpha	56	94.1
Disulfoton-sulfone	98	77.1
Imazalil	40	108.8
Endosulfan-beta	68	93.3
Endosulfan sulfate	20	77.0
Methoxychlor-*o,p*	48	89.9
Diclofop-methyl	36	81.8
Methoxychlor-*p,p'*	50	114.9
Azinphos-methyl	56	94.2

A 5-g sample of ground wheat grain was spiked with 100 µL of a standard solution containing 29 pesticides and herbicides at levels ranging from 8–102 ppb (see Table 3) and extracted at 100 °C with acetonitrile. Spike levels and recovery results are shown in Table 3. Recoveries ranged from 54.1–115.7%. The average recovery was 95.3% if the two outliers, dichlorvos and carbaryl, are excluded. Following the spike studies, 12 naturally incurred grain samples were extracted by the traditional wrist shaker extraction with acetonitrile, using post-extraction solid phase extraction (SPE) cleanup, and by accelerated solvent extraction using either acetone or acetonitrile as the extraction solvent. The accelerated solvent extraction took 12 min per sample and required 12–15 mL of solvent, while the shaker extraction took approximately 1 h per sample (including post-extraction SPE cleanup on carbon or C18) and used 130 mL of acetonitrile per sample. The accelerated solvent extraction extracts did not require post-extraction processing.

Extraction results for two compounds identified in these extracts, methyl chlorpyrifos and malathion, are shown in Table 4. The detected amounts compared well between the two techniques, with the accelerated solvent extraction values generally 10–20% higher. In all cases, samples with nondetectable levels (ND) were identified as such by both techniques. Acetonitrile and acetone appear to be good solvent choices for this application.

Table 4. Extraction of Incurred Pesticides in Wheat by accelerated solvent extraction and Conventional Wrist Shaker Extraction

Sample No.	Solvent	Sample Weight (g)	Methyl Chlorpyrifos (µg/kg)		Malathion (µg/kg)	
			Shaker	Accelerated Solvent Extraction	Wrist Shaker	Accelerated Solvent Extraction
1	Acetone	20.31	70	90	40	50
2	Acetone	19.78	80	100	40	50
3	Acetone	20.91	50	60	60	70
4	Acetone	10.13	ND	ND	ND	ND
5	Acetone	10.24	30	70	40	100
6	Acetone	9.93	ND	ND	ND	ND
7	Acetone	5.32	ND	ND	ND	ND
8	Acetone	5.39	ND	ND	ND	ND
9	Acetonitrile	19.85	60	80	60	80
10	Acetonitrile	20.4	70	90	60	70
11	Acetonitrile	5.30	ND	ND	ND	ND

ND = not detected.

Conclusion

Using accelerated solvent extraction, pesticide residue analysis laboratories can increase sample throughput while reducing overall solvent usage. The simplicity of the accelerated solvent extraction technique, combined with results showing excellent correlation to existing methods, have resulted in the rapid acceptance of accelerated solvent extraction for environmental analysis. The promulgation of U.S. EPA Method 3545 now provides a means for environmental test laboratories to take full advantage of accelerated solvent extraction technology. In addition to the wide range of target analytes covered under Method 3545 for organic pollutants in solid waste, accelerated solvent extraction has been applied successfully to the extraction of total petroleum hydrocarbons (TPH), dioxins, and furans from a variety of matrices. accelerated solvent extraction has also been applied to the extraction of explosives from soil, PCBs from fish and other marine tissues, and polyurethane foam (PUF) air sampling cartridges.

Suppliers

Fisher Scientific, 2000 Park Lane, Pittsburgh, PA 15275-1126 USA, Tel: 800-766-7000, www.fishersci.com.

Restek Corporation, 110 Benner Cir., Bellefonte, Pennsylvania, 16823 USA, Tel.: 814-353-1300, www.restekcorp.com.

"Extraction of TCL/PPL (Target Compound List/Priority Pollutant List) BNAs and Pesticides Using Accelerated Solvent Extraction with Analytical Validation by GC/MS and GC/ECD" Document 116064.A, Dionex Corporation (now part of Thermo Fisher Scientific), June 16, 1994.

8.4 Appendix 4: The Scope and Application of EPA Method 3620C- Florisil Cleanup

METHOD 3620C

FLORISIL CLEANUP

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 Florisil®, a registered trade name of U. S. Silica Co., is a magnesium silicate with basic properties. It is used to separate analytes from interfering compounds prior to sample analysis by a chromatographic method.

1.2 Florisil® has been used for the cleanup of pesticide residues and other chlorinated hydrocarbons; the separation of nitrogen compounds from hydrocarbons; the separation of aromatic compounds from aliphatic-aromatic mixtures; and similar applications for use with fats, oils, and waxes. Additionally, Florisil® is considered good for separations with steroids, esters, ketones, glycerides, alkaloids, and some carbohydrates.

1.3 Florisil® cleanup may be accomplished by either using a glass chromatographic column packed with Florisil® or using solid-phase extraction cartridges containing Florisil®.

1.4 This method includes procedures for cleanup of sample extracts containing the following analyte groups:

Phthalate esters	Chlorinated hydrocarbons
Nitrosamines	Organochlorine pesticides
Nitroaromatics	Organophosphates
Haloethers	Organophosphorus pesticides
Aniline and aniline derivatives	PCBs

Other analytes may potentially be cleaned up using this method provided that adequate performance is demonstrated.

1.5 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and

8.5 Appendix 5: EPA Method 3630- Silica Gel Cleanup

METHOD 3630C

SILICA GEL CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Silica gel (silicic acid) is a regenerative adsorbent of silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used in column chromatography for the separation of analytes from interfering compounds of a different chemical polarity. It may be used activated, after heating to 150 - 160°C, or deactivated with up to 10% water.

1.2 This method includes guidance for standard column cleanup of sample extracts containing polynuclear aromatic hydrocarbons, derivatized phenolic compounds, organochlorine pesticides, and PCBs as Aroclors.

1.3 This method also provides cleanup procedures using solid-phase extraction cartridges for pentafluorobenzyl bromide-derivatized phenols, organochlorine pesticides, and PCBs. This technique also provides the best separation of PCBs from most single component organochlorine pesticides. When only PCBs are to be measured, this method can be used in conjunction with sulfuric acid/permanganate cleanup (Method 3665).

1.4 Other analytes may be cleaned up using this method if the analyte recovery meets the criteria specified in Sec. 8.0.

1.5 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 This method provides the option of using either standard column chromatography techniques or solid-phase extraction cartridges. Generally, the standard column chromatography techniques use larger amounts of adsorbent and, therefore, have a greater cleanup capacity.

2.2 In the standard column cleanup protocol, the column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is accomplished with a suitable solvent(s) that leaves the interfering compounds on the column. The eluate is then concentrated (if necessary).

2.3 The cartridge cleanup protocol uses solid-phase extraction cartridges packed with 1 g or 2 g of silica gel (silicic acid) adsorbent. Each cartridge is solvent washed immediately prior to use. Aliquots of sample extracts are loaded onto the cartridges, which are then eluted with suitable solvent(s). A vacuum manifold is required to obtain reproducible results. The collected fractions may be further concentrated prior to gas chromatographic analysis.

2.4 The appropriate gas chromatographic method is listed at the end of each technique. Analysis may also be performed by gas chromatography/mass spectrometry (Method 8270).

8.6 Appendix 6: Data on Detection Limit (LOD) and Quantitation Limit (LOQ)

Table1: Calculation of LOD and LOQ for a-BHC

Column A	Column B	
Analyte	a-BHC	Pesticides
Spike Conc.		10
Units		ppb
Replicate	1	10.0560
Replicate	2	10.5930
Replicate	3	9.5870
Replicate	4	8.6650
Replicate	5	9.7530
Replicate	6	10.8390
Replicate	7	9.7580
Replicate	8	9.6380
Mean	Average(B7..B14)	9.8611
Std. Dev.	STDEV(B7..B14)	0.6663
LOD	(t-value)*(B16)	1.9989
LOQ	10*B16	6.6631

Table2: Calculation of LOD and LOQ for b-BHC

Column A	Column B	
Analyte	b-BHC	Pesticides
Spike Conc.		10
Units		ppb
Replicate	1	10.5000
Replicate	2	10.1000
Replicate	3	9.9000
Replicate	4	9.8000
Replicate	5	10.4000
Replicate	6	10.0100
Replicate	7	10.6000
Replicate	8	8.9900
Mean	Average(B7..B14)	10.0375
Std. Dev.	STDEV(B7..B14)	0.5125
LOD	(t-value)*(B16)	1.5376
LOQ	10*B16	5.1255

Table3: Calculation of LOD and LOQ for Heptachlor

Column A	Column B	
Analyte	Heptachlor	Pesticides
Spike Conc.		10
Units		ppb
Replicate	1	10.9850
Replicate	2	10.5960
Replicate	3	9.6570
Replicate	4	9.6320
Replicate	5	10.9520
Replicate	6	9.7530
Replicate	7	8.7620
Replicate	8	9.8670
Mean	Average(B7..B14)	10.0255
Std. Dev.	STDEV(B7..B14)	0.7645
LOD	(t-value)*(B16)	2.2934
LOQ	10*B16	7.6448

Table4: Calculation of LOD and LOQ for Aldrin

Column A	Column B	
Analyte	Aldrin	Pesticides
Spike Conc.		10
Units		ppb
Replicate	1	12.1020
Replicate	2	11.3560
Replicate	3	12.0350
Replicate	4	10.8960
Replicate	5	10.9980
Replicate	6	11.8560
Replicate	7	11.9210
Replicate	8	10.8640
Mean	Average(B7..B14)	11.5035
Std. Dev.	STDEV(B7..B14)	0.5338
LOD	(t-value)*(B16)	1.6014
LOQ	10*B16	5.3380

Table5: Calculation of LOD and LOQ for g-Chlordane

Column A	Column B	
Analyte	g-Chlordane	Pesticides
Spike Conc.		10
Units		ppb
Replicate	1	10.7590
Replicate	2	9.8540
Replicate	3	10.8350
Replicate	4	10.3280
Replicate	5	8.9560
Replicate	6	9.7680
Replicate	7	10.0230
Replicate	8	11.0290
Mean	Average(B7..B14)	10.1940
Std. Dev.	STDEV(B7..B14)	0.6870
LOD	(t-value)*(B16)	2.0611
LOQ	10*B16	6.8705

Table6: Calculation of LOD and LOQ for Endosulfane I

Column A	Column B	
Analyte	Endosulfane I	Pesticides
Spike Conc.		10
Units		ppb
Replicate	1	10.6500
Replicate	2	10.2560
Replicate	3	9.6570
Replicate	4	9.6310
Replicate	5	10.9450
Replicate	6	8.9700
Replicate	7	9.7810
Replicate	8	8.7530
Mean	Average(B7..B14)	9.8304
Std. Dev.	STDEV(B7..B14)	0.7624
LOD	(t-value)*(B16)	2.2871
LOQ	10*B16	7.6238

Table7: Calculation of LOD and LOQ for a-Chloordane

Column A	Column B	
Analyte	a-Chloordane	Pesticides
Spike Conc.		10
Units		ppb
Replicate	1	10.9840
Replicate	2	9.5610
Replicate	3	8.7520
Replicate	4	9.7260
Replicate	5	10.8630
Replicate	6	11.0510
Replicate	7	10.8860
Replicate	8	9.7640
Mean	Average(B7..B14)	10.1984
Std. Dev.	STDEV(B7..B14)	0.8593
LOD	(t-value)*(B16)	2.5779
LOQ	10*B16	8.5930

Table8: Calculation of LOD and LOQ for Dieldrin

Column A	Column B	
Analyte	Dieldrin	Pesticides
Spike Conc.		10
Units		ppb
Replicate	1	11.0150
Replicate	2	10.9870
Replicate	3	11.2050
Replicate	4	9.8520
Replicate	5	10.8610
Replicate	6	9.6480
Replicate	7	9.2870
Replicate	8	10.9350
Mean	Average(B7..B14)	10.4738
Std. Dev.	STDEV(B7..B14)	0.7493
LOD	(t-value)*(B16)	2.2480
LOQ	10*B16	7.4935

Table9: Calculation of LOD and LOQ for Endrin

Column A	Column B	
Analyte	Endrin	Pesticides
Spike Conc.		10
Units		ppb
Replicate	1	10.5240
Replicate	2	10.2680
Replicate	3	9.8460
Replicate	4	10.8320
Replicate	5	9.8870
Replicate	6	9.7630
Replicate	7	10.8710
Replicate	8	8.9530
Mean	Average(B7..B14)	10.1180
Std. Dev.	STDEV(B7..B14)	0.6408
LOD	(t-value)*(B16)	1.9225
LOQ	10*B16	6.4084

Table10: Calculation of LOD and LOQ for Methoxychlor

Column A	Column B	
Analyte	Methoxychlor	Pesticides
Spike Conc.		10
Units		ppb
Replicate	1	12.0640
Replicate	2	11.7830
Replicate	3	11.3520
Replicate	4	10.9860
Replicate	5	10.6830
Replicate	6	12.1530
Replicate	7	11.8710
Replicate	8	10.8920
Mean	Average(B7..B14)	11.4730
Std. Dev.	STDEV(B7..B14)	0.5707
LOD	(t-value)*(B16)	1.7120
LOQ	10*B16	5.7067

8.7 Appendix 7: Results for OCPs concentration in local vegetables and fruit

Table 1: OCPs concentration in local cucumber

	cucumber											
	washed						unwashed					
OCPs	Farm#649				Farm#953		Farm#649				Farm#953	
a-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
b-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Heptachlor	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Aldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	10.92	<LOQ	<LOQ	<LOQ	<LOQ	17.64	<LOQ
g-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endosulfane I	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
a-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Dieldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Methoxychlor	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Table 2: OCPs concentration in local tomatoes

	Tomatoes											
	washed						unwashed					
OCPs	Farm#197		Farm#953		Farm#241		Farm#197		Farm#953		Farm#241	
a-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
b-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Heptachlor	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Aldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	7.06	11.99	<LOQ
g-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endosulfane I	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
a-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Dieldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Methoxychlor	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Table 3: OCPs concentration in local parsley

	Parsley									
	washed					unwashed				
OCPs	Farm#224	Farm#963	Farm#696	Farm#1224	Farm#260	Farm#224	Farm#963	Farm#696	Farm#1224	Farm#260
a-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
b-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Heptachlor	17.11	<LOQ	33.56	31.84	33.14	22.75	24.20	28.52	25.10	<LOQ
Aldrin	<LOQ	11.21	13.99	5.81	<LOQ	8.89	14.01	5.84	<LOQ	<LOQ
g-Chlordane	22.03	15.37	10.59	18.16	14.65	18.06	15.17	8.44	12.00	19.45
Endosulfane I	13.54	10.83	56.45	32.24	76.72	14.84	17.77	18.58	12.08	17.55
a-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Dieldrin	<LOQ	<LOQ	<LOQ	6.54	<LOQ	<LOQ	<LOQ	23.04	<LOQ	<LOQ
Endrin	7.25	8.74	7.23	7.07	7.72	8.17	6.76	7.74	6.92	<LOQ
Methoxychlor	10.95	11.32	18.27	14.31	<LOQ	12.82	18.76	9.61	17.97	18.59

Table 4: OCPs concentration in local watercress

	Watercress									
	washed					unwashed				
OCPs	MoE farm	Farm# 576	Farm#963	Farm#183	Farm#701	MoE farm	Farm# 576	Farm#963	Farm#183	Farm#701
a-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
b-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Heptachlor	18.86	53.43	30.52	20.11	37.86	17.11	22.51	33.75	16.43	24.21
Aldrin	9.22	10.17	<LOQ	19.57	18.76	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
g-Chlordane	9.92	8.92	4.81	13.59	43.15	16.24	16.67	4.78	4.32	50.51
Endosulfane I	<LOQ	<LOQ	<LOQ	9.23	<LOQ	<LOQ	<LOQ	<LOQ	10.10	<LOQ
a-Chlordane	16.61	11.35	25.29	17.20	20.97	12.57	20.63	32.14	45.88	24.56
Dieldrin	14.02	10.61	6.45	14.45	6.45	10.93	16.17	4.90	7.78	<LOQ
Endrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	6.67	<LOQ	7.55
Methoxychlor	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	15.16	7.16

Table 5: OCPs concentration in local strawberries

	Strawberries														
	washed							unwashed							
OCPs	Farm#301					Farm#1223		Farm#301					Farm#1223		
a-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
b-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Heptachlor	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Aldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	10.85	17.54
g-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endosulfane I	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
a-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Dieldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Methoxychlor	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

8.8 Appendix 8: Results for OCPs concentration in imported vegetables and fruit

Table 1: OCPs concentration in imported cucumber

	cucumber															
	washed								**unwashed**							
OCPs	**KSA**					**UAE**			**KSA**					**UAE**		
a-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
b-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Heptachlor	<LOQ	<LOQ	<LOQ	17.30	<LOQ	31.99	<LOQ	43.49	31.83	31.60	16.02	<LOQ	12.37	16.28	19.65
Aldrin	<LOQ	7.60	11.79	10.30	7.43	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	18.44
g-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endosulfane I	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
a-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Dieldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	8.18	7.31	8.87	7.09	<LOQ	<LOQ	<LOQ	6.82	<LOQ	<LOQ
Methoxychlor	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Table 2: OCPs concentration in imported tomatoes

	Tomatoes											
	washed						unwashed					
OCPs	Jordon			Spain			Jordon			Spain		
a-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
b-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Heptachlor	<LOQ	34.35	24.97	26.54	16.25	25.12	38.65	17.79	52.07	42.14	16.71	37.16
Aldrin	<LOQ	11.70	9.02	<LOQ	<LOQ	0.97	<LOQ	17.39	<LOQ	0.48	24.54	4.08
g-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	8.10	<LOQ	<LOQ	<LOQ	<LOQ
Endosulfane I	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
a-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Dieldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	13.29	<LOQ	<LOQ	<LOQ	<LOQ
Endrin	<LOQ	<LOQ	<LOQ	6.80	6.58	<LOQ	<LOQ	6.40	7.42	<LOQ	<LOQ	<LOQ
Methoxychlor	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Table 3: OCPs concentration in imported potatoes

	Potatoes					
	washed			unwashed		
OCPs	**Egypt**					
a-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
b-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Heptachlor	19.09	11.52	17.89	14.80	42.31	24.17
Aldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
g-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endosulfane I	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
a-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Dieldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endrin	6.91	6.45	6.86	7.36	6.55	7.39
Methoxychlor	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Table 4: OCPs concentration in imported parsley

	Parsley													
	washed							unwashed						
OCPs	KSA					Lebanon		KSA					Lebanon	
a-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
b-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Heptachlor	55.34	42.53	27.10	34.74	36.78	63.60	23.09	43.53	25.66	<LOQ	36.25	37.37	39.10	20.38
Aldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	27.61	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
g-Chlordane	7.10	27.59	<LOQ	10.42	6.99	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endosulfane I	25.94	22.31	<LOQ	59.70	16.69	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
a-Chlordane	43.05	25.31	<LOQ	11.51	14.40	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Dieldrin	<LOQ	10.24	<LOQ	24.49	19.53	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endrin	7.72	9.08	<LOQ	6.68	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Methoxychlor	22.06	26.60	<LOQ	<LOQ	17.99	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Table 5: OCPs concentration in imported watercress

	watercress									
	washed					unwashed				
OCPs	KSA									
a-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
b-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Heptachlor	37.05	12.66	<LOQ	15.91	12.52	<LOQ	<LOQ	15.23	96.07	19.92
Aldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
g-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endosulfane I	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
a-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	13.89	13.41	17.76
Dieldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	14.07	14.11	18.14
Endrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	9.19	7.38	6.41
Methoxychlor	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Table 6: OCPs concentration in imported strawberries

	Strawberries					
	washed			unwashed		
OCPs	Egypt					
a-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
b-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Heptachlor	88.09	17.64	15.68	16.08	144.35	15.38
Aldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
g-Chlordane	<LOQ	<LOQ	7.71	<LOQ	<LOQ	<LOQ
Endosulfane I	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
a-Chlordane	20.34	8.94	21.13	13.65	11.29	15.56
Dieldrin	16.87	9.87	21.41	15.27	9.86	16.69
Endrin	<LOQ	6.55	<LOQ	<LOQ	<LOQ	7.83
Methoxychlor	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Table 7: OCPs concentration in imported lemon

	Lemon					
	washed			unwashed		
OCPs	Turkey					
a-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
b-BHC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Heptachlor	37.83	39.67	12.30	<LOQ	15.71	19.90
Aldrin	<LOQ	<LOQ	<LOQ	<LOQ	8.25	<LOQ
g-Chlordane	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	9.58
Endosulfane I	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	8.31
a-Chlordane	10.68	8.54	6.72	6.65	6.00	6.14
Dieldrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Endrin	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Methoxychlor	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

8.9 Appendix 9: MRLs Results for OCPs concentration in local vegetables and fruit.

	cucumber											
	washed						unwashed					
OCPs	Farm#649				Farm#953		Farm#649				Farm#953	
a-BHC	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
b-BHC	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Heptachlor	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	19.63	33.98	<MRL	<MRL	<MRL
Aldrin	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
g-Chlordane	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Endosulfane I	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
a-Chlordane	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Dieldrin	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Endrin	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Methoxychlor	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL

	Tomatoes											
	washed								unwashed			
OCPs	Farm#197		Farm#953		Farm#241		Farm#197		Farm#953		Farm#241	
a-BHC	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
b-BHC	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Heptachlor	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Aldrin	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
g-Chlordane	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Endosulfane I	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
a-Chlordane	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Dieldrin	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Endrin	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Methoxychlor	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL

	Parsley									
	washed					unwashed				
OCPs	Farm#224	Farm#963	Farm#696	Farm#1224	Farm#260	Farm#224	Farm#963	Farm#696	Farm#1224	Farm#260
a-BHC	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
b-BHC	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	10.90	<MRL
Heptachlor	17.11	<MRL	33.56	31.84	33.14	22.75	24.20	28.52	25.10	<MRL
Aldrin	<MRL	<MRL	13.99	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
g-Chlordane	22.03	<MRL	10.59	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Endosulfane I	132.54	109.83	56.45	32.24	76.72	146.84	175.77	98.58	52.08	71.55
a-Chlordane	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Dieldrin	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	23.04	<MRL	<MRL
Endrin	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Methoxychlor	10.95	11.32	48.27	14.31	<MRL	12.82	18.76	<MRL	97.97	78.59

	Watercress									
	washed					unwashed				
OCPs	MoE farm	Farm# 576	Farm#963	Farm#183	Farm#701	MoE farm	Farm# 576	Farm#963	Farm#183	Farm#701
a-BHC	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
b-BHC	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Heptachlor	18.86	53.43	304.52	202.11	370.86	176.11	220.51	330.75	1631.43	241.21
Aldrin	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
g-Chlordane	<MRL	<MRL	<MRL	<MRL	43.15	<MRL	<MRL	<MRL	<MRL	50.51
Endosulfane I	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	10.10	<MRL
a-Chlordane	12.61	11.35	25.29	17.20	20.97	16.57	20.63	32.14	45.88	24.56
Dieldrin	14.02	10.61	<MRL	14.45	<MRL	10.93	16.17	<MRL	<MRL	<MRL
Endrin	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Methoxychlor	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL

	Strawberries													
	washed							unwashed						
OCPs	Farm#301					Farm#1223		Farm#301					Farm#1223	
a-BHC	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
b-BHC	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Heptachlor	<MRL	24.75	<MRL	26.13	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Aldrin	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
g-Chlordane	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Endosulfane I	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
a-Chlordane	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Dieldrin	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Endrin	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Methoxychlor	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL

8.10 Appendix 10: T-test analysis results.

Table1: Pair-difference t-test for the imported cucumber in the presence of methoxychlor residue.

Cucumber	
Methoxychlor	
washed	unwashed
0.609	3.570
0.554	2.996
1.219	1.682
1.756	0.912
0.051	2.349
2.298	0.443

not significant

t-Test: Paired Two Sample for Means

	Variable 1	*Variable 2*
Mean	1.081163219	1.992164781
Variance	0.703026976	1.458152148
Observations	6	6
Pearson Correlation	-0.849037029	
Hypothesized Mean Difference	0	
df	5	
t Stat	-1.132801353	
P(T<=t) one-tail	0.15433884	
t Critical one-tail	2.015048372	
P(T<=t) two-tail	**0.308677679**	
t Critical two-tail	2.570581835	

Table2: Pair-difference t-test for the imported tomatoes in the presence of heptachlor residue.

Tomatoes	
Heptachlor	
washed	unwashed
34.349	17.792
24.972	52.065
26.535	42.137
16.254	16.713
25.118	37.158

not significant

t-Test: Paired Two Sample for Means

	Variable 1	*Variable 2*
Mean	25.44545364	33.17301575
Variance	41.31912733	240.1573809
Observations	5	5
Pearson Correlation	0.034783793	
Hypothesized Mean Difference	0	
df	4	
t Stat	-1.04284439	
P(T<=t) one-tail	0.177949245	
t Critical one-tail	2.131846782	
P(T<=t) two-tail	**0.355898491**	
t Critical two-tail	2.776445105	

Table3: Pair-difference t-test for the imported potatoes in the presence of heptachlor residue.

Potatoes	
Heptachlor	
washed	unwashed
19.095	14.799
11.522	42.306
17.893	24.166

not significant

t-Test: Paired Two Sample for Means

	Variable 1	*Variable 2*
Mean	16.16991928	27.09017314
Variance	16.5627588	195.5703389
Observations	3	3
Pearson Correlation	-0.981380043	
Hypothesized Mean Difference	0	
df	2	
t Stat	-1.051059367	
P(T<=t) one-tail	0.201746447	
t Critical one-tail	2.91998558	
P(T<=t) two-tail	0.403492893	
t Critical two-tail	4.30265273	

Table4: Pair-difference t-test for the imported potatoes in the presence of methoxychlor residue.

Potatoes	
g-Chlordane	
washed	unwashed
6.279	6.165
4.938	4.907
5.176	5.113

not significant

t-Test: Paired Two Sample for Means

	Variable 1	*Variable 2*
Mean	5.464341653	5.395115635
Variance	0.511678985	0.455607976
Observations	3	3
Pearson Correlation	0.999889869	
Hypothesized Mean Difference	0	
df	2	
t Stat	2.880370745	
P(T<=t) one-tail	0.051179348	
t Critical one-tail	2.91998558	
P(T<=t) two-tail	**0.102358696**	
t Critical two-tail	4.30265273	

Table5: Pair-difference t-test for the imported potatoes in the presence of endrin residue.

Potatoes	
Endrin	
washed	unwashed
6.912	7.360
6.445	6.549
6.859	7.385

not significant

t-Test: Paired Two Sample for Means

	Variable 1	*Variable 2*
Mean	6.738782609	7.098076142
Variance	0.065278775	0.226654097
Observations	3	3
Pearson Correlation	0.991580476	
Hypothesized Mean Difference	0	
df	2	
t Stat	-2.76363383	
P(T<=t) one-tail	0.054892989	
t Critical one-tail	2.91998558	
P(T<=t) two-tail	**0.109785978**	
t Critical two-tail	4.30265273	

Table6: Pair-difference t-test for the imported cucumber in the presence of a-chlordane residue.

Watercress	
a-Chlordane	
washed	unwashed
4.885	13.890
4.786	13.412
4.857	17.760

significant

t-Test: Paired Two Sample for Means

	Variable 1	*Variable 2*
Mean	4.842234663	15.0206741
Variance	0.002601217	5.68446544
Observations	3	3
Pearson Correlation	0.340016408	
Hypothesized Mean Difference	0	
df	2	
t Stat	-7.446946606	
P(T<=t) one-tail	0.008779233	
t Critical one-tail	2.91998558	
P(T<=t) two-tail	**0.017558465**	
t Critical two-tail	4.30265273	

Table7: Pair-difference t-test for the imported Strawberries in the presence dieldrin residue.

Strawberries	
Dieldrin	
washed	unwashed
16.868	15.269
9.866	9.864
21.413	16.691

not significant

t-Test: Paired Two Sample for Means

	Variable 1	*Variable 2*
Mean	16.04906622	13.94140543
Variance	33.83864853	12.97586416
Observations	3	3
Pearson Correlation	0.979538107	
Hypothesized Mean Difference	0	
df	2	
t Stat	1.5206375	
P(T<=t) one-tail	0.133866655	
t Critical one-tail	2.91998558	
P(T<=t) two-tail	0.26773331	
t Critical two-tail	4.30265273	

Table8: Pair-difference t-test for the imported Strawberries in the presence g-chlordane residue.

Lemon	
g-Chlordane	
washed	unwashed
4.288	5.987
6.751	5.037
6.472	9.585

not significant

t-Test: Paired Two Sample for Means

	Variable 1	*Variable 2*
Mean	5.837025806	6.86947779
Variance	1.820023672	5.755089471
Observations	3	3
Pearson Correlation	0.21864691	
Hypothesized Mean Difference	0	
df	2	
t Stat	-0.720519108	
P(T<=t) one-tail	0.273019429	
t Critical one-tail	2.91998558	
P(T<=t) two-tail	0.546038858	
t Critical two-tail	4.30265273	

Table9: Pair-difference t-test for the imported lemon in the presence of a-chlordane residue.

Lemon	
a-Chlordane	
washed	unwashed
10.682	6.651
8.536	6.000
6.716	6.138

not significant

t-Test: Paired Two Sample for Means

	Variable 1	*Variable 2*
Mean	8.644634438	6.262766518
Variance	3.942144711	0.117534556
Observations	3	3
Pearson Correlation	0.778676385	
Hypothesized Mean Difference	0	
df	2	
t Stat	2.382024522	
P(T<=t) one-tail	0.070063635	
t Critical one-tail	2.91998558	
P(T<=t) two-tail	**0.140127271**	
t Critical two-tail	4.30265273	

Table10: Pair-difference t-test for the imported lemon in the presence of methoxychlor residue.

Lemon	
Methoxychlor	
washed	unwashed
0.580	0.096
1.440	0.314
1.616	0.033

not significant

t-Test: Paired Two Sample for Means

	Variable 1	*Variable 2*
Mean	1.211913693	0.14789415
Variance	0.306812804	0.021756221
Observations	3	3
Pearson Correlation	0.147620081	
Hypothesized Mean Difference	0	
df	2	
t Stat	3.340057874	
P(T<=t) one-tail	0.039571408	
t Critical one-tail	2.91998558	
P(T<=t) two-tail	**0.079142816**	
t Critical two-tail	4.30265273	