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MARKET BASKET SURVEY FOR SOME PESTICIDES RESIDUES IN FRUITS AND VEGETABLES FROM GHANA

Crentsil Kofi Bempah[1,2], Jacob Asomaning1, Juliana Boateng[3]*

Address: Crentsil Kofi Bempah,

[1]Nuclear Chemistry and Environmental Research Center, National Nuclear Research Institute, Ghana Atomic Energy Commission, P.O. Box LG 80, Legon, Accra-Ghana.

[2]Faculty of Environmental Sciences and Process Engineering, Chair of Environmental Geology Erich-Weinert-Straße 1, 03046 Brandenburgische Technische Universität, Cottbus, Germany.

[3]Environmental Protection Agency, P.O Box M 326, Ministries, Accra-Ghana.

*Corresponding author: crentbempah@fastmail.fm

ABSTRACT

A study was conducted to investigate the organochlorine, organophosphorus and synthetic pyrethroid pesticide residues in fruits and vegetables from markets in Ghana. For this purpose, a total of 309 fruits and vegetable samples, were collected and analyzed by gas chromatography with electron capture detector. The obtained results showed that the predominance of organochlorine followed by organophosphorus and synthetic pyrethroid pesticides in most of the analyzed samples. The detected concentrations of them were most significant in vegetable samples. The results obtained showed that 39.2 % of the fruits and vegetable samples analyzed contained no detectable level of the monitored pesticides, 51.0 % of the samples gave results with trace levels of pesticide residues below the maximum residue limit (MRL), while 9.8 % of the samples were above the MRL. The findings point to the urgent need to establish reliable monitoring programs for pesticides, so that any exceedance in concentration over environmental quality standards can be detected and appropriate actions taken.

Keywords: Pesticide residues, fruits, vegetables, maximum residue limit, Ghana

INTRODUCTION

Pesticides are widely used in fruit and vegetables because of their susceptibility to insect and diseases. They have been widely used throughout the world since the middle of the last century for their various benefits. Pesticides have been applied in agriculture and animal production to eliminate pests. In this way, to increase both animals and crops outputs, improve quality of products, and decrease the incidence of illnesses propagated by insects **(Bempah, 2008)**.

In fruits and vegetables production, insecticides are used to control pests and fungicides to control diseases. They are directly applied to the crops and some may still be present as residues in the fruits and vegetables after their harvest. It is true that that most insecticides and fungicides are toxic substances, but when used properly they constitute an important input in fruits and vegetable production in order to produce economically marketable products **(Choy and Seeneevassen, 1998)**. However such improper usage has occasionally been accompanied by hazards to man and the environment **(Bempah *et al*., 2011)**.

Residues of most pesticides are present in all compartments of agro-ecosystems, but perhaps the most real risk of human is through consumption of residues in food as vegetables and fruits **(Price, 2008)**. Some of these pesticides in particular are persistent and very resistant to microbial degradation. The high toxicity of most pesticides has made their use very restrictive and currently forbidden in most developed countries since 1970s **(FAO, 1985; Mansour, 2004; Barriada-Pereira *et al*., 2005)** and some of them are included in Global Stockholm Convention on POPs **(UNEP, 2004)**.

The organophosphate, organochlorine and related pesticides act by binding to the enzyme acetyl cholinesterase, disrupting nerve function, resulting in paralysis and may cause death. They may produce acute effects manifesting as meiosis, urination, diarrhea, diaphoreses, lacrimation, excitation of central nervous system and salivation. The chronic exposure involves neurotic and behavioral effects. Specific effects of pesticides can include cancer, allergies and hypersensitivities, damage to the central and peripheral nervous systems, reproductive disorders and disruption of the immune system **(Tahir *et al*., 2009)**.

Whereas many of the banned pesticides are no longer in use in the developed world, they are still used in many developing countries including Ghana. Other legitimate pesticides are also used in variety of applications. Additionally, there are indications of widespread contamination of various components of the environment with dichlorodiphenyltrichloroethane, and their hexachlorocyclohexane (BHC) residues in several Third World nations **(Bempah, 2008; Baird and Cann, 2005)**.

The problems of environmental pollution in these countries are not well documented **(Edwards, 1973; Saeed *et al*., 2001)**. Consequently, because of potential toxic and persistent nature of some pesticides, developed nations like United States, Japan, and European Union have put in place measures for pesticides control and monitoring in the environment. Consequently, regular survey studies and monitoring programs of pesticides residues have been carried out **(Ministry of Agriculture, Fisheries and Food, 1989; Luke *et al*., 1988; Yamaguchi *et al*., 2003)**.

Fruits and vegetables are vey important group of crops and they constitute major part of human diet contributing nutrients and vitamins. Many farmers in the villages have taken up vegetable and fruits production on commercial basis. However, in the urban areas people depend on the market for their vegetable and fruits requirement. These market vegetables and fruits mostly contain pesticide residues because of their overuse in the field, which cause harmful effect for the human health **(Chowdhury *et al.,* 2011)**.

The publicity regarding the high level of pesticides in the environment has created a certain apprehension and fear in the public as to the presence of pesticide residues in their daily food. The public is confused and alarmed about their food safety. This has therefore led government and researches to be concerned with their presence in food.

Keeping in view of the potential toxicity, persistent nature and cumulative behavior as well as the consumption of vegetables and fruits, many developed countries have established legal directives to control levels of pesticides in food, through maximum residue levels **(FAO/WHO, 2004; European Council, 2006),** based on the acceptable daily intake (ADI) and potential daily intake (PDI) which should not be exceeded in food items.

Regular survey and monitoring programs of pesticides residues in foodstuffs have been carried out for decades in most developed countries **(Youshida *et al*., 1992; Dejonckheere *et al*., 1996 a; Neidert and Saschenbrecker 1996; Roy *et al*., 1995, 1997; Tadeo *et al.,* 2000; Fontcuberta *et al*., 2008; Barriada-Pereira *et al*., 2005)**. But, in developing countries such as Ghana, limited data are available on pesticide residues, in fruits **(Bempah and Donkor, 2011)**, in fruits and vegetables **(Bempah *et al*., 2011; Ninsin, 1997;**

Mawuenyegah, 1994), in quality cocoa beans **(Botchwey, 2000)**, water and fish **(Osafo and Frempong, 1998)**, meat **(Darko and Acquaah, 2006)**.

At present, pesticide residues in food materials are not controlled in Ghana and there is little information available on the levels of pesticides residues in food. Consequently, there is little information available on the dietary intake of pesticides by the Ghanaian population. Therefore the only way to assess dietary pesticide intake of the public is to carry out analysis of the food that constitutes the diet of an average consumer **(Bempah and Donkor, 2011)**.

Total diet surveys sometimes called "market basket survey" have been the method of choice for monitoring of pesticides residues in foods and the assessment of the daily intake by the population. The selection of foods to be analyzed is always based on food consumption surveys that form the basis for the selection of the diets, and reflects the current food supply and food consumption patterns of the population **(Saeed *et al.*, 2001)**.

This study therefore presents data on the level of pesticide residues in selected fruits and vegetables sold in the local markets of Ghana. The study is also dealing with the daily intake of these pesticides through consumption of fruits and vegetables.

MATERIAL AND METHODS

Sample collection

A total of 309 samples of fruits and vegetables were purchased from the main urban and rural markets of the country throughout the year 2009. The fruit samples used in this study included papaya, water melon, banana, mango, pear and pineapple, whilst the vegetable samples included tomato, lettuce, cabbage, carrot, onion and cucumber. The sample size was at least one kg for small and medium sized of fresh product. The minimum weight for large sample sizes was 2 kg (for example pineapple, cabbage, and water melon), where the unit was generally more than 250 g **(Codex Alimentarius Commission, 2000)**.

The samples were sealed and labeled with a unique sample identity and placed in an iced chest box. All samples were transported to Pesticide Residues Laboratory of Ghana Atomic Energy Commission, and were refrigerated (at 5 ^{o}C). These samples were then extracted and analyzed (within 24 hrs from the time of their collection) for the presence of pesticide residues. For the analysis, only the edible portions were included, whereas bruised and/or rotten parts were removed.

Chemicals and materials

Pesticide grade ethyl acetate and analytical grade acetone were supplied by Labscan (Dublin, Ireland), sodium hydrogen carbonate and sodium sulphate were purchased from E. Merck (Germany). Solid-phase florisil cartridges column size (500 mg/8 mL) was obtained from Honeywell Burdick & Jackson (Muskegon, USA). Pesticide reference standards (98.0 % purity) were obtained from Dr. Ehrenstofer GmbH (Germany), and stored in the freezer at -20 ^{o}C to minimize degradation. Homogenizer - FOSS 2096 based on Tecator Technology. Centrifuge - CRi multifunction was from Thermo Electron Industries SAS, (France), Macerator - Ultra-turax macerator, Type T 25 generator was purchased from IKKA® Werke. Rotary vacuum evaporator - Büchi RE-200 was from Büchi Labortechnic AG, Postfach, Switzerland) and a 20-port vacuum manifold (water, USA) were employed for the cleanup of the extracts.

Sample preparation

Fresh fruit and vegetable samples were thoroughly shredded and homogenized. Approximately 20.0 g of the sample was macerated with 40 mL of ethyl acetate. Sodium hydrogen carbonate 5.0 g and anhydrous sodium sulphate 20.0 g were added to remove moisture and further macerated for 3 minutes using the ultra-turax macerator. The samples were then centrifuged for 5 minutes at 3,000 rpm to obtain the two phases. The supernatant was transferred to a clean graduated cylinder (25 mL) to measure its volume.

Solid-Phase extraction

A solid phase extraction was carried out using SPE column according to Netherlands analytical methods of pesticide residues and foodstuffs with modification **(Ministry of Public Health, Welfare and Sports, Netherlands, 2007)**. The florisil column (500 mg/8 mL) cartridge was conditioned with 5 mL of a mixture solution of acetone:n-hexane (3:7, v/v) through the column. The sorbent was never allowed to dry during the conditioning and sample loading steps. The extract column was fitted with 20-port vacuum manifold with a receiving flask placed under the column to collect the eluate. Sample loading was performed under vacuum at flow rates of 5 mL min^{-1}. After the passage of the extract, the column was dried by vacuum aspiration under increased vacuum for 30 min. The pesticides were eluted with 10

mL (3, 3, 4 mL) of ethyl acetate, concentrated to 1 mL using a rotary evaporator and then dried by a gentle nitrogen stream. This was dissolved in 1 mL of ethyl acetate; pesticides were then quantified by gas chromatograph equipped with electron capture detector (GC-ECD).

Gas chromatography- electron capture detector (GC-ECD) analysis

Gas chromatograph GC-2010 equipped with ^{63}Ni electron capture detector (ECD) equipped with split/splitless injector that allowed the detection of contaminants even at trace level concentrations (in the lower µg/g range) from the matrix was employed. The injector and detector temperature were set at 280 ^{o}C and 300 ^{o}C respectively. A fussed silica ZB-5 (30 m x 0.25 mm, 0.25 µm film thickness) was used in combination with the following oven temperature program: initial temperature 60 ^{o}C, held for 1 min, ramp at 30 ^{o}C min^{-1} to 180 ^{o}C, held for 3 min, ramp at 3 ^{o}C min^{-1} to 220 ^{o}C, held for 3 min, ramp at 10 ^{o}C min^{-1} to 300 ^{o}C. Nitrogen was used as carrier gas at a flow rate of 1.0 mL min^{-1} and make up gas of 29 mL min^{-1}. The injection volume of the GC was 1.0 µl. The residues detected by the GC analysis were confirmed by the analysis of the extract on two other columns of different polarities. The first column was coated with ZB-1 (methyl polysiloxane) connected to ECD and the second column was coated with ZB-17 (50 % phenyl, methyl polysiloxane) and ECD was also used as detector. The conditions used for these columns were the same.

Quantitation

An external method was employed in the determination of the quantities of residues in the sample extracts. A standard mixture of known concentration of pesticide was run and the response of the detector for each compound ascertained. The area of the corresponding peak in the sample was compared with that of the standard. All analyses were carried out in triplicates and the mean concentrations computed accordingly.

Quality control and quality assurance

Quality control and quality assurance were included in the analytical scheme. The recovery, precision and linearity of studied pesticides were evaluated by adding a working mixture to 20 g of chopped untreated samples; the spiked samples were made to stand for at least 1 hour before the extraction. Ten replicate samples were extracted and analyzed

according to the proposed procedure as described previously. Precision was calculated based on daily repeatability of 10 samples, whereas reproducibility was carried out on 5 different days. Recoveries were calculated for three replicate samples. Percent recoveries in spiked samples ranged 87 % - 120 %. Accordingly, the sample analysis data were corrected for these recoveries. Detection limit(s) of the method were also assessed based on the lowest concentrations of the residues in each of the matrices that could be reproducibly measured at the operating conditions of the GC; which were 0.001 mg/kg. Blank analyses were also carried in order to check any interfering species in the reagents.

RESULTS AND DISCUSSION

A total of 309 samples of fruits and vegetables were analyzed for organochlorine, organophosphorus and pyrethroid pesticides. Table 1 gives names and the incidence of pesticide residues in the fruits and vegetable samples analyzed. Residues occurred in 41.4 and 58.9 % of all fruits and vegetable samples, respectively. The reason for this might be that, vegetables are highly sensitive to pest and need for successive applications of pesticides treatments, leaving in consequence higher level of residues that tolerated and protected from pest infestation.

Table 1 Number of fruit and vegetables samples analyzed and number of samples with pesticide residue detected

English name	Scientific name	No. of samples	No. of samples with residues
Fruits			
Papaya	*Carica papaya*	20	13
watermelon	*Citrullus lanatus*	15	8
banana	*Musa sapientum*	34	8
Mango	*Mangifera indica*	25	11
pear	*Pyrus communis*	20	7
pineapple	*Ananas sativus*	25	15
Total		139	62
Vegetables			
Tomato	*Lycopersicon esculentus*	30	15
Lettuce	*Lactuca sativa*	30	14
Cabbage	*Brassica oleracea*	25	17
Carrot	*Daucus carota*	25	13
Onion	*Allium cepa*	30	13
Cucumber	*Cucumis sativus*	30	13
Total		170	85

Levels of pesticide residues found in fruits collected from the various market centers

The identities of all the three groups of pesticide (organochlorine, organophosphorus and pyrethroid) residues found in fruits are given in Table 2.

Table 2 The detected levels (mg/kg) of pesticide residues in Ghanaian fruits samples.

Pesticide types	Papaya	Watermelon	Banana	Mango	Pear	Pineapple
Organochlorines						
Lindane	0.100*±0.004 (0.092-0.105)[a]	0.004±0.002 (0.004-0.006)	<LOD[b] -	0.010±0.010 (0.006-0.022)	0.009±0.003 (0.006-0.012)	0.133*±0.014 (0.121-0.153)
Methoxychlor	0.006±0.002 (0.004-0.012)	<LOD -	0.008±0.004 (0.004-0.012)	0.004±0.001 (0.004-0.006)	<LOD -	0.031*±0.023 (0.007-0.052)
Aldrin	0.013*±0.007 (0.009-0.019)	<LOD -	<LOD -	<LOD -	0.012*±0.009 (0.010-0.016)	0.006±0.002 (0.004-0.008)
Dieldrin	0.017*±0.020 (0.002-0.040)	<LOD -	0.090*±0.103 (0.013-0.203)	<LOD -	<LOD -	0.012*±0.008 (0.007-0.018)
Endrin	<LOD -	<LOD -	0.006±0.002 (0.004-0.012)	<LOD -	<LOD -	0.004±0.002 (0.004-0.008)
p,p'-DDE	<LOD -	0.004±0.001 (0.004-0.008)	<LOD -	0.010±0.004 (0.005-0.011)	<LOD -	<LOD -
p,p'-DDT	0.012±0.006 (0.008-0.014)	0.008±0.004 (0.006-0.010)	0.038±0.032 (0.005-0.062)	0.020±0.002 (0.018-0.021)	<LOD -	<LOD -
Organophosphorus						
Diazinon	<LOD -	<LOD -	<LOD -	<LOD -	<LOD -	0.007±0.003 (0.001-0.009)
Dimethoate	0.008±0.002 (0.002-0.012)	0.004±0.001 (0.004-0.006)	<LOD -	0.010±0.014 (0.004-0.018)	<LOD -	0.006±0.002 (0.002-0.008)
Pirimiphos-methyl	<LOD -	<LOD -	<LOD -	0.004±0.001 (0.002-0.006)	<LOD -	0.014±0.012 (0.008-0.018)
Chlorpyrifos	0.008±0.002 (0.004-0.010)	0.003±0.002 0.002-0.005	0.006±0.002 (0.004-0.012)	0.005±0.003 (0.003-0.007)	0.017±0.007 (0.012-0.025)	0.055*±0.011 (0.041-0.062)
Profenofos	0.003±0.002 (0.001-0.005)	<LOD -	<LOD -	<LOD -	<LOD -	<LOD -
Malathion	0.003±0.002	<LOD	<LOD	<LOD	<LOD	0.006±0.002

	(0.002-0.006)	-	-	-	-	(0.002-0.008)
Pyrethroids						
Permethrin	0.015±0.015 (0.005-0.032)	<LOD -	<LOD -	0.010±0.008 (0.002-0.012)	0.006±0.003 (0.004-0.008)	0.041±0.022 (0.025-0.066)
Cyfluthrin	<LOD -	0.035*±0.005 (0.030-0.040)	0.010±0.010 (0.006-0.022)	<LOD -	0.004±0.002 (0.004-0.008)	0.020±0.002 (0.018-0.021)
Cypermethrin	0.035±0.005 (0.030-0.040)	<LOD -	0.012±0.006 (0.007-0.012)	0.008±0.002 (0.004-0.012)	<LOD -	0.022*±0.003 (0.019-0.025)
Fenvalerate	0.020±0.002 (0.018-0.021)	0.019±0.003 (0.013-0.021)	<LOD -	0.008±0.004 (0.006-0.014)	<LOD -	<LOD -
Deltamethrin	<LOD -	<LOD -	0.016±0.021 (0.008-0.040)	<LOD -	0.008±0.002 (0.007-0.010)	0.044±0.018 (0.026-0.062)

Legend: Each value is the mean of five samples with four determinations, [a] Range in bracket, [b] LOD= 0.001 mg/kg sample. Values designated by asterisks are higher than the EC-MRLs for the respective pesticide (see MRLs in Table 5-7)

Among the various organochlorine pesticides in the present study, lindane is the predominant compound in the fruit samples. The detected levels of it varied greatly. For instance, the minimum value for it was detected in watermelon (0.004 mg/kg) and the maximum of 0.133 mg/kg was found in pineapple. Minimum values for methoxychlor were detected in mango (0.004 mg/kg) and the maximum of 0.031 mg/kg was found in pineapple. 0.006 mg/kg of aldrin was detected in pineapple and the maximum of 0.013 mg/kg was found in papaya. Minimum value of 0.017 mg/kg of endrin was found in papaya and maximum value of 0.090 mg/kg was detected in banana whilst 0.004 mg/kg of p,p'-DDE was found in watermelon and maximum of 0.010 mg/kg was found in mango. Moreover, minimum value of p,p'-DDT (0.008 mg/kg) in watermelon and maximum value of 0.038 mg/kg was found in banana.

With respect to the organophosphorus pesticides, Table 2 shows that diazinon and malathion were the least predominant pesticide with residues of 0.007 mg/kg and 0.006 mg/kg in pineapple samples. However, chlorpyrifos was the most dominant pesticide residues. The minimum value of 0.003 mg/kg of it was found in watermelon and the maximum value of 0.055 mg/kg in pineapple. Following chlorpyrifos is dimethoate, where the minimum value

was 0.004 mg/kg in watermelon and maximum value of 0.010 mg/kg in mango. Minimum value of pirimifos-methyl (0.004 mg/kg) was detected in mango and maximum value of 0.014 mg/kg was found in pineapple. Malathion was found to contain a minimum value of 0.003 mg/kg in papaya and maximum value of 0.006mg/kg in pineapple.

Among various pyrethroid pesticides, permethrin, cyfluthrin and cypermethrin were the most predominant pesticides found in fruits, followed by fenvalerate and deltamethrin. Maximum value of permethrin (0.041 mg/kg) was found in pineapple and the minimum value of 0.006 mg/kg was present in pear. Cyfluthrin recorded maximum value (0.035 mg/kg) in watermelon and minimum value (0.004 mg/kg) in pear. Moreover, 0.035 mg/kg of cypermethrin was recorded in papaya samples whilest minimum value of 0.008 mg/kg was recoded in mango samples. Maximum values of fenvalerate (0.021 mg/kg) and deltamethrin (0.044 mg/kg) were present in banana and pineapple samples whilst minimum value of 0.008 mg/kg was recorded in mango and pear samples, respectively.

Levels of pesticide residues found in vegetables collected from the various market centers

In regard to the organochlorine pesticides found in vegetable samples, Table 3 indicates that methoxychlor and *p,p'*-DDT were the most predominant pesticides with maximum residual concentrations of 0.041 mg/kg and 0.035 mg/kg present in onion samples whilst minimum residual concentrations of 0.008 mg/kg and 0.004 mg/kg were also present in carrot samples. Following this trend, maximum value of 0.100 mg/kg (cucumber), and 0.041 mg/kg (lettuce) and a minimum of 0.006 mg/kg (lettuce) and 0.008 mg/kg (cabbage) were recorded for lindane and *p,p'*-DDE, respectively. Maximum residual concentrations of aldrin, dieldrin and endrin were detected in carrot, cabbage and lettuce to be 0.010, 0.035 and 0.040 mg/kg, respectively whilst minimum concentration values were detected in onion (0.006 mg/kg), tomato (0.004 mg/kg) and cabbage (0.007 mg/kg), respectively.

In the case of organophosphorus pesticides found in vegetable samples, diazinon is the most predominant pesticide residues found in the analyzed vegetable samples followed by profenofos, chlorpyrifos, malathion, dimethoate and the least being pirimifos-methyl. Maximum value (0.016 mg/kg) of diazinon was recorded in cabbage and minimum (0.004 mg/kg) in lettuce. Corresponding values for profenofos were 0.012 mg/kg in carrot and 0.003 mg/kg in cucumber, respectively. Furthermore, chlorpyrifos achieved a maximum value of 0.055 mg/kg in onion and a minimum value of 0.007 mg/kg in tomato. The maximum

detected residue of malathion was detected in tomato (0.038 mg/kg), and the minimum value was found in lettuce (0.003 mg/kg). Maximum concentration values of dimethoate and pirimifos-methyl were detected in lettuce and tomato to be 0.021 mg/kg and 0.017 mg/kg, respectively whilst minimum concentration values were also detected in onion (0.006 mg/kg) and cabbage (0.003 mg/kg) samples, respectively.

Table 3 The detected levels (mg/kg) of pesticide residues in Ghanaian vegetables samples.

Pesticide types	Tomato	Lettuce	Cabbage	Carrot	Cucumber	Onion
Organochlorines						
Lindane	0.008±0.002 (0.004-0.010)[a]	0.006±0.002 (0.004-0.006)	0.100*±0.004 (0.095-0.102)	<LOD[b] -	<LOD -	0.019*±0.002 (0.016-0.020)
Methoxychlor	0.004±0.002 (0.002-0.008)	0.023*±0.008 (0.031-0.022)	0.023*±0.008 (0.031-0.022)	0.008±0.004 (0.006-0.012)	0.020*±0.002 (0.018-0.021)	0.041*±0.022 (0.025-0.066)
Aldrin	<LOD -	0.008±0.004 (0.006-0.012)	<LOD -	0.010±0.021 (0.008-0.040)	<LOD -	0.006±0.002 (0.004-0.008)
Dieldrin	0.004±0.008 (0.002-0.040)	<LOD -	0.035*±0.013 (0.030-0.052)	<LOD -	0.010±0.004 (0.005-0.013)	<LOD -
Endrin	<LOD -	0.040*±0.035 (0.080-0.015)	0.007±0.003 (0.005-0.009)	0.016*±0.008 (0.006-0.032)	<LOD -	<LOD -
p,p'-DDE	0.013±0.009 (0.007-0.015)	0.041±0.022 (0.025-0.066)	0.008±0.004 (0.006-0.010)	<LOD -	<LOD -	0.023±0.008 (0.016-0.031)
p,p'-DDT	0.012±0.006 (0.008-0.014)	0.020±0.002 (0.018-0.021)	0.032±0.010 (0.030-0.040)	0.004±0.002 (0.004-0.008)	0.009±0.003 (0.005-0.013)	0.035±0.005 (0.030-0.040)
Organophosphorus						
Diazinon	0.009±0.003 (0.003-0.013)	0.004±0.001 (0.002-0.006)	0.016±0.005 (0.010-0.019)	0.005±0.002 (0.003-0.011)	0.009±0.006 (0.003-0.011)	0.008±0.004 (0.004-0.010)
Dimethoate	0.013±0.009 (0.007-0.019)	0.021±0.013 (0.018-0.024)	<LOD -	0.020±0.014 (0.018-0.024)	<LOD -	0.006±0.002 (0.002-0.008)
Pirimiphos-methyl	0.017±0.007 (0.012-0.025)	<LOD -	0.003±0.001 (0.001-0.006)	<LOD -	0.010±0.007 (0.006-0.021)	<LOD -

Chlorpyrifos	0.026±0008 (0.018-0.025)	0.011±0.010 (0.001-0.021)	0.007±0.003 (0.003-0.009)	0.040±0.026 (0.038-0.044)	<LOD -	0.055±0.011 (0.041-0.062)
Profenofos	0.010±0.004 (0.005-0.011)	<LOD -	0.008±0.004 (0.002-0.010)	0.012±0.009 (0.010-0.016)	0.003±0.001 (0.001-0.009)	0.040±0.002 (0.008-0.044)
Malathion	0.038±0.032 (0.005-0.062)	0.003±0.003 (0.001-0.006)	0.004±0.001 (0.004-0.008)	0.007±0.003 (0.005-0.011)	0.010±0.008 (0.008-0.012)	<LOD -
Pyrethroids						
Permethrin	0.015±0.015 (0.005-0.032)	0.040±0.033 (0.080-0.025)	0.049±0.026 (0.022-0.078)	0.037±0.013 (0.030-0.052)	0.005±0.003 (0.003-0.009)	<LOD -
Cyfluthrin	<LOD -	0.008±0.002 (0.004-0.010)	0.016±0.014 (0.010-0.018)	<LOD -	0.004±0.002 (0.004-0.008)	0.009±0.003 (0.005-0.013)
Cypermethrin	0.035±0.005 (0.030-0.040)	<LOD -	0.012±0.006 (0.007-0.012)	0.014±0.002 (0.010-0.018)	0.009±0.003 (0.006-0.013)	<LOD -
Fenvalerate	0.014±0.008 (0.010-0.016)	<LOD -	0.011±0.010 (0.003-0.017)	0.006±0.002 (0.004-0.008)	0.010±0.006 (0.007-0.013)	0.020±0.018 (0.014-0.022)
Deltamethrin	<LOD -	0.015±0.011 (0.007-0.023)	0.010±0.010 (0.009-0.020)	0.004±0.008 (0.015-0.063)	<LOD -	0.038±0.030 (0.012-0.045)

Each value is the mean of five samples with four determinations, [a] Range in bracket, [b] = 0.001 mg/kg sample. Values designated by asterisks are higher than the EC-MRLs for the respective pesticide (see MRLs in Table 5-7)

Considering pyrethroid pesticide residues in vegetable samples (Table 3), it was noticed that, permethrin and fenvalerate was the most predominant pesticides, followed by cyfluthrin, cypermethrin and deltamethrin having the same frequency of occurrence.

Interestingly, the pyrethroid pesticides detected in vegetable samples followed a certain pattern. Maximum values of 0.049 mg/kg and 0.016 mg/kg in cabbage samples and a minimum of 0.005 mg/kg and 0.004 mg/kg in cucumber were recorded for permethrin and cyfluthrin, respectively. Similarly, maximum residual concentration of fenvalerate and deltamethrin were recorded in onion samples with concentrations of 0.020 and 0.038 mg/kg whilst their minimum concentration values were also recorded in carrot samples with residual values of 0.006 and 0.004 mg/kg, respectively. Despite this trend, cypermethrin recorded a

maximum of 0.035 mg/kg and minimum value of 0.009 mg/kg in tomato and cucumber samples, respectively.

The data further showed occurrence of some pesticide residues in fruits and vegetables at levels exceeding maximum residue limits (MRLs) (see Table 5-7). Compared with the MRLs established by **European Council (2006)**, methoxychlor is most often exceeded MRL values (41.6 %), followed by lindane and dieldrin (33.3 %), aldrin and endrin (16.6 %), chlorpyrifos, cyfluthrin and cypermethrin (8.3 %).

Overall residues were found in 41.4 % of fruit and 58.9 % of vegetable samples, respectively. The pesticide residues above the MRL were found in 5.4 % and 4.4 % of all the samples of fruit and vegetables, respectively. Similar work was conducted by **Anderson (2001)** in a Danish market where residues were found in 54 % of the samples of fruit and 13 % of vegetables, respectively. In addition to this, residues above the MRL were found in 4 % and 1 % of fruits and vegetable samples, respectively.

In general, the highest contamination frequencies occurred in organochlorine pesticides. This may indicate its illegal use and/or its persistent and lipophilicity nature of the organochlorine pesticides. This study therefore suggest the possibility of sporadic use of these pesticides for agriculture or mainly due to the past extensive use of these pesticides for agriculture in Ghana as it has been banned for over a decade ago. These findings corroborate the findings of **Nakata *et al*., (2002)** who found elevated levels of organochlorine pesticides residues in fruits and vegetables collected from Shanghai and Yixing, China. Similarly, in an investigation carried out by **Hura *et al*., (1999)**, by monitoring organochlorine residues in fruits and vegetables at Eastern Romania, it was concluded that organochlorine pesticides were found in all analyzed samples. In India, further results were obtained by **Kannan *et al*., (1992)** who found DDT, aldrin, dieldrin at mean levels of 62.0, 0.22, and 2.1 ng/g, respectively.

Pyrethroid pesticides were the next in prevalence, but in most cases, its level was below the maximum permissible level of the various fruits and vegetable samples with the exception of cyfluthrin and cypermethrin which exceeded MRLs in watermelon and pineapple samples, respectively. Similar results were obtained by **Zawiyah *et al*., (2007)** who detected cypermethrin between the range of 0.16-1.48 mg/kg in fruits and vegetables collected from local markets at Sungai Buloh and Selayang, Malaysia. Results by **Kumari *et al.*, (2006)** found residues of cypermethrin and fenvalerate ranging from 0.045-0.064 µg/g, 0.046-0.067 µg/g, respectively in grapes. In India, **Seyed and Somashekar (2010)** reported levels of

cypermethrin and fenvalerate ranging from 0.003-0.051 mg/kg and 0.001-0.231 mg/kg in grape samples, respectively.

In a related development, **Choy and Seeneevassen, (1998)** monitored pyrethroid insecticides in vegetable and fruits at the market level in Mauritius and found that 36.2 % of the vegetable and fruit samples analyzed gave results with levels of insecticides residues below the MRL, whilst 2.3 % of the samples showed results above the MRL. In Brazil, **Rodrigues *et al*., (2010)** found malathion and chlorpyrifos with concentration ranging from 0.4 to 9.2 µg/kg in different vegetal fruits. The presence of pyrethroid residues in fruits and vegetable is also an indication of change in usage pattern of insecticides in Ghana where shift has taken place from organochlorine pesticides to the easily degradable, greater photostability and relatively low toxicity compound as compared to organochlorine and organophosphorus pesticides **(Bempah and Donkor, 2011)**.

The data therefore show the decreased concentrations of the residues of organophosphorus pesticides, which were detected in some of the analyzed samples of fruits and vegetables under investigation except chlorpyrifos which exceeded MRL in pineapple samples. This might due to its ability to degrade rapidly in the environment than organochlorine pesticides. Similar results were obtained by **Abou-Arab and Abou Donia (2001)** who found that samples collected from Egypt contained organophosphorus pesticides particularly, malathion, dimethoate and profenofos at levels ranging from 0.061 to 1.756mg/kg. In **2006, Bai *et al.*,** concluded that the organophosphorus pesticide residues were present in fruits and vegetables in Shaanxi area of China.

The general means of total pesticides residues in fruits and vegetable samples were 1.585 mg/kg and 1.097 mg/kg, respectively. In general, contamination of fruits with organochlorine pesticide residues was higher than those of organophosphorus and synthetic pyrethroid pesticides. The same trend was observed in vegetables; where contamination levels with organochlorine pesticides were higher than those of organophosphorus and synthetic pyrethroid pesticides (Table 4).

Table 4 The levels of pesticide residue concentration in fruit and vegetable samples analyzed

Commodity type	Residues (mg/kg)			
	OCPs	OPPs	SPPs	∑OCPs+OPPs+SPPs
Fruits	0.655	0.506	0.424	1.585
Vegetables	0.556	0.207	0.334	1.097

Each value is a general mean, calculated from the data of Table 2 and 3.

OCPs: Organochlorine pesticides

OPPs: Organophosphorus pesticides

SPPs: Synthetic pyrethroid pesticides

Table 5 Maximum residue levels for organochlorine pesticides

Commodity	Maximum residue levels, MRLs (mg/kg)						
	Gamma-HCH	methoxychlor	aldrin	dieldrin	endrin	*p,p'*-DDE	*p,p'*-DDT
Fruits							
Papaya	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Water melon	0.01	0.01	0.03	0.03	0.01	0.05	0.05
Banana	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Mango	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Pear	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Pineapple	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Vegetables							
Tomato	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Lettuce	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Cabbage	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Carrot	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Onion	0.01	0.01	0.01	0.01	0.01	0.05	0.05
Cucumber	0.01	0.01	0.02	0.02	0.01	0.05	0.05

Table 6 Maximum residue limit for Organophosphorus pesticides

Commodity	Maximum residue levels, MRLs (mg/kg)					
	Diazinon	Dimethoate	Pirimiphos-methyl	Chlorpyrifos	Profenfos	Malathion
Fruits						
Papaya	0.02	0.02	0.05	0.50	0.05	-[a]
Water melon	0.02	0.02	0.05	0.05	0.05	-
Banana	0.02	0.02	0.05	3.00	0.05	0.50
Mango	0.02	0.02	0.05	0.05	0.05	-
Pear	0.30	0.02	0.10	0.50	0.05	0.50
Pineapple	0.02	0.02	0.05	0.05	0.05	-
Vegetables						
Tomato	0.50	0.02	0.20	0.50	0.05	3.00
Lettuce	0.02	0.50	0.50	0.05	0.05	3.00
Cabbage	0.02	0.02	0.50	0.50	0.05	-
Carrot	0.20	0.02	0.05	0.10	0.05	0.50
Onion	0.50	0.02	0.10	0.20	0.05	3.00
Cucumber	0.02	0.02	0.10	0.05	0.05	3.00

[a]- No EC MRL

Table 7 Maximum residue levels for pyrethroid pesticides

Commodity	Maximum residue levels, MRLs (mg/kg)				
	Permethrin	Cyfluthrin	Cypermethrin	Fenvalerate	Deltamethrin
Fruits					
Papaya	0.05	0.02	0.05	0.02	0.05
Water melon	0.05	0.02	0.20	0.02	0.05
Banana	0.05	0.02	0.05	0.02	0.05
Mango	0.05	0.02	0.05	0.02	0.05
Pear	0.05	0.20	1.00	0.05	0.10
Pineapple	0.05	0.02	0.05	0.02	0.05
Vegetables					
Tomato	0.05	0.05	0.50	0.05	0.20
Lettuce	0.05	0.50	2.00	0.02	0.50
Cabbage	0.05	0.20	0.50	0.05	0.10
Carrot	0.05	0.02	0.05	0.02	0.05
Onion	0.05	0.02	0.10	0.02	0.10
Cucumber	0.05	0.10	0.20	0.02	0.10

CONCLUSION

From the results obtained, it can be concluded that most of the fruit and vegetable samples analyzed did not contain residues of the monitored pesticides above the European Council Directive for maximum residues limit (MRL), Although some pesticide residues were detected in higher concentration. This study discloses that even low exposure to these pesticide residues puts consumer on risk in a cumulative manner. So an analysis showing the residues in undetectable or safe range does not essentially mean that it is absolutely safe and free of any untoward effects. The most disturbing findings was that residue of some pesticides which is banned and not approved for use on fruits and vegetables such as the organochlorines were found in some fruits and vegetable samples. On the basis of the above findings, the results recommend the need for stringent standards to govern the application of pesticides in the field to ensure that pesticides are applied only when necessary and in a safer manner.

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