

Monitoring of Pesticide Residues in Fruits and Vegetables and Related Health Risk Assessment in Kumasi Metropolis, Ghana

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Abstract: The objective of present research study was to assess the concentration of pesticide residues in fruits and vegetables from markets in Kumasi and to generate awareness about the lethal effects of these pesticides on human beings as well as to estimate the potential health risks associated with the pesticide residue with regard to consumers. A total of 350 locally produced fruits and vegetables were purchased from six main markets in Kumasi and analyzed by gas chromatography equipped with electron capture detector for organochlorine (gamma-HCH, methoxychlor, aldrin, dieldrin, endrin, p,p'-DDE, p,p'-DDT) and pyrethroid (permethrin, cyfluthrin, cypermethrin, fenvalerate, deltamethrin) residues. The residual concentrations of selected pesticides in the various fruit and vegetable samples and the potential health risks associated with the exposure to these pesticides were also assessed. The results obtained showed that 37.5% of the fruit and vegetable samples analyzed contained no detectable level of the monitored pesticides, 19.0% of the samples gave results with levels of insecticides residues above the MRL, while 43.5% of the samples showed results below the MRL. The analysis of health risk estimates revealed that none of the pesticides exceeded the reference dose in both fruit and vegetables except endrin which exceeded reference dose in vegetables, suggesting a great potential for systemic toxicity in children considered the most vulnerable population subgroup. Based on observations made in these studies, it is proposed that more extensive monitoring investigation covering all fruits and vegetables in all the ten regions of Ghana be carried out to find the exact position of pesticide residues.

Key words: Ghana, health risk assessment, Kumasi, organochlorine, pesticide residues, pyrethroid

INTRODUCTION

Farmers around the world including Ghana use pesticides as a preventive policy against the possibility of a devastating crop loss from pests and diseases. Accordingly in Ghana, for several decades now, pesticides have been employed in agriculture not only to control and eradicate crop pests but also in the public health sector for disease vector control. Nevertheless, there has been a rapid increase in the quantity and use of pesticides in agriculture over the past ten years (Hodgson, 2003).

Moreover, this growth trend is expected to heighten for the next decades. Agricultural pesticides are used in the cocoa, coffee and cotton farming, in vegetable and fruit production, and for other mixed crop farming systems involving cereals (mostly maize), tuber crops (e.g., yam, cassava), legumes (e.g., cowpeas, beans), sugarcane, rice, etc. The majority of these pesticides are employed in the forest areas or farming regions noted for the production of these crops located in Ashanti, Brong

Ahafo, Eastern and Western regions of Ghana (Ntow, 2005; Amoah *et al.*, 2006).

Dinham (2003b) estimates that 87 % of farmers in Ghana use chemical pesticides to control pests and diseases on vegetables and fruits. Whereas Ntow (2001) gave the proportions of pesticides used extensively on vegetable farms, whether small or large by farmers. Insecticides are widely used in vegetable production in Ghana probably due to the farmers' perception of insect's control. They reason as long as it is profitable, and no better alternatives are available, the spraying of pesticide is a good investment (Hardy, 1995).

More so, chemical control method is very effective, rapid in curative action, adaptable in most situations, flexible in meeting changing agronomic, ecological and economical conditions (Metcalf, 1975; Newsom *et al.*, 1976). Among the different types pesticides known, organochlorine pesticides are extensively used by farmers, because of their cost effectiveness and their broad spectrum activity. However, because of their highly toxic and persistent nature, their residues still appear as

pollutants in food as well as in the environment (Bempah *et al.*, 2011). Pyrethroid insecticides have greater photostability, enhanced insecticidal activity, and relatively low toxicity as compared with organochlorine and organophosphorus insecticides (Pang *et al.*, 1994a, 1994b).

Pesticides are widely used in fruit and vegetables because of their susceptibility to insect and diseases attack. Consequently, food safety is a major public concern worldwide. During the last decades, the increasing demand of food safety has stimulated research regarding the risk associated with consumption of fruit and vegetables as they constitute major part of human diet contributing nutrients and vitamins. Therefore, residues of pesticides could affect the ultimate consumers especially when these commodities are freshly consumed. The total dietary intake of pesticides residues that remain on agricultural commodities are known as carcinogens/or toxins and therefore it is desirable to reduce these residues (Zawiyah *et al.*, 2007).

In general, food is the main exposure route. Exposure to pesticide residues through the diet is assumed to be five orders of magnitude higher than other exposure routes, such as air and drinking water (Juraske *et al.*, 2009). According to the World Health Organization (WHO, 2003), food consumption consists on averaged for 30% (Based on mass) of fruit and vegetables, and fruit and vegetables are the most frequently consumed food group (WHO, 2003). Furthermore, because fruit and vegetables are mainly consumed raw or semi-processed, it is expected that they contain higher pesticides residue levels compared to other food groups of plant origin, such as bread and other foodstuffs bases on cereal processing (Claeys *et al.*, 2011).

Given the potential risk of pesticides for public health, the use of pesticides in fruit and vegetable production is subjected to constant monitoring. Although pesticide residues in foodstuffs have been carried out for decades in most developed countries (Claeys *et al.*, 2011; Tadeoa *et al.*, 2000; Fontcuberta *et al.*, 2008; Barriada-Pereira *et al.*, 2005), but, fruits and vegetables of Ghana is not much investigated from pesticide contamination point of view. Everyday people are being encouraged to consume more vegetables and fruits. Thus there has been escalation in the growth of vegetables and fruits in the urban and rural areas of Ghana to meet the domestic consumption as well as international markets, hence, a large population at the risk (Bempah *et al.*, 2011).

Therefore, the objective of present research work was to assess the concentration of pesticide residues in fruits and vegetables from markets in Kumasi and to generate awareness about the lethal effects of these pesticides on human beings as well as to estimate the potential health risks associated with the pesticide residue with regard to consumers.

MATERIALS AND METHODS

Materials and reagents: Standards of gamma-HCH, methoxychlor, aldrin, dieldrin, endrin, p,p'-DDE, and p,p'-DDT were obtained from Supelco (Bellefonte, PA, USA). Permethrin, cyfluthrin, cypermethrin, fenvalerate and deltamethrin were purchased from Chem. Service, Inc. (West Chester, PA). Acetone, n-hexane, dichloromethane and methanol were Super Purity Solvents from Romil (Cambridge, UK). Ethyl acetate (PAR) for instrumental analysis was from Pancreac (Barcelona, Spain). Alumina for column chromatography was from Sigma (St. Louis, USA). Solid-phase florisil cartridges column size (500 mg/8mL) was obtained from Honeywell Burdick & Jackson (Muskegon, USA).

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 Labortechnik AG, (Postfach, Switzerland) and a 20-port vacuum manifold (Water, USA) was employed for the clean up of the extracts.

A Shimadzu gas chromatograph, GC-2010 (Shimadzu Corporation, Analytical and measuring instruments Division, Tokyo, Japan) equipped with ⁶³Ni Electron Capture Detector (ECD), CTC AOC-20s autosampler, AOC-20i split-splitless auto injector, Programmed Pneumatic Control (PPC) and a computer running star workstation data processor. For separation, a 5 % diphenyl 95 % dimethyl siloxane capillary column (30 m × 0.25 mm, 0.25 µm film thicknesses) was employed.

Sampling: A total of 350 samples of various fruits and vegetables were purchased from several local markets around Kumasi metropolis, during August 2009 and June 2010. Kumasi is a big commercial and industrial city known to have developed rapidly and have attracted large population in recent years. The centrality of Kumasi as nodal city with major arterial routes linking it to other parts of the country, and the fact that it is the largest recipient of agricultural produce consumed locally makes it important in controlling pesticide residues in fruits and vegetables which seems to be a substantial contemporary public health problem to guarantee food quality and to evaluate alimentary risk. Fruits and vegetables sold in Kumasi are mainly grown in villages around the city and are harvested and sold fresh. The markets where these foodstuffs were purchased include Kejetia, Tafo, Bantama, Asafo and Kumasi central markets (which is considered to be one of the biggest markets in West Africa sub-region). The sample size was at least one kg for small and medium sized of fresh product. The

Table 1: Names of samples and incidence of pesticide residues in fruits and vegetables from Kumasi markets

English name	Scientific name	No. of samples	% With one or more residues
Fruits			
Papaya	Carica papaya	20	83
Watermelon	Citrullus lanatus	15	50
Banana	Musa sapientum	25	67
Mango	Mangifera indica	25	58
Pear	Pyrus communis	20	42
Pineapple	Ananas sativus	15	75
Vegetables			
Tomato	Lycopersicon esculentus	30	67
Lettuce	Lactuca sativa	30	75
Cabbage	Brassica oleracea	25	83
Carrot	Daucus carota	25	67
Okra	Hibiscus esculentus	30	50
Green pepper	Piper nigrum	30	50
Onion	Allium cepa	30	58
Cucumber	Cucumis sativus	30	58

Table 2: Analytical recoveries (%)±SD of seven organochlorine and five pyrethroid pesticides in carrot samples at 0.01, 0.02 and 0.1 mg/kg fortification levels (n = 3)

Pesticides	Analytical recoveries (%) ± SD at different fortification levels (mg/kg)		
	0.01	0.02	0.1
Gamma-HCH	98.2±6.2	97.5±4.7	93.4±9.6
Methoxychlor	87.3±9.4	87.0±8.5	92.5±10.1
Aldrin	92.4±10.5	96.4±5.3	94.0±4.5
Dieldrin	97.8±5.1	88.9±10.5	91.5±7.2
Endrin	97.0±5.6	93.1±5.3	97.2±4.3
p,p'-DDE	92.3±9.8	91.6±10.4	92.8±10.6
p,p'-DDT	95.1±7.1	95.4±7.3	94.1±3.9
Permethrin	88.0±10.2	88.6±10.2	92.1±9.7
Cyfluthrin	98.3±7.1	96.4±5.5	97.4±5.4
Cypermethrin	102.3±10.3	98.1±7.3	101.3±8.7
Fenvalerate	104.0±5.5	103.8±3.8	98.7±6.4
Deltamethrin	96.7±4.8	95.9±5.6	101.0±8.5

SD: Standard deviation

minimum weight for large sample sizes was 2 kg, where the unit was generally more than 250 g (Codex Alimentarius, 2000). The various collected samples (item, scientific name, number) are presented in Table 1.

The collected 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, Ghana Atomic Energy Commission, and were refrigerated (at 5°C). These samples were then extracted and analyzed (within 24 h from the time of their collection) for the presence of pesticide residues. For the analysis, only the edible portions were included, whereas bruised or rotten parts were removed.

Extraction procedure and cleanup: Fresh fruits 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 sulfate 20.0 g were added to remove moisture and further macerated for 3 min using the ultra-turax macerator. The samples were then centrifuged for 5 min at 3,000 rpm to obtain the two phases. The extraction process was followed by a clean-up step using solid-phase extraction with florisil (5 g) and

alumina (2 g) deactivated with Milli-Q water (5 %) as adsorbents. Pesticides in sample extract were eluted with 35 mL of hexane:ethyl acetate (80+20, V+V), concentrated to 1 mL using a rotary evaporator and then dried by a gentle nitrogen stream. This was dissolved in 5 mL of hexane; pesticides were then quantified by gas chromatograph equipped with electron capture detector (GC-ECD).

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.

Recovery rate and limit of detection: Carrot samples were fortified at 0.01, 0.02 and 0.1 mg/kg by adding 5.0 mL of a mixed standard solution. Recovery and precision (expressed as relative standard deviation) were calculated for three replicate samples and the data are presented in Table 2. The table shows that the recovery rate for twelve

pesticides were within acceptable range. The method is applicable for the determination of eleven pesticides in fruit and vegetable samples (Zawiyah *et al.*, 2007). Percent recoveries in spiked samples ranged 87.3% - 104.0 %, Table 2. 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.

Gas chromatographic determination: The residues were analyzed by Shimadzu gas chromatograph GC-2010 equipped with ⁶³Ni electron capture detector that allowed the detection of contaminants even at trace level concentrations from the matrix to which other detector do not respond. The GC conditions and the detector response were adjusted so as to match the relative retention times and response. The conditions used for the analysis were: capillary column coated with ZB-5 (30 m × 0.25 mm, 0.25 μm film thickness). Carrier gas and make-up gas was nitrogen at a flow rate of 1.0 and 29 mL/min, respectively. The injector and detector temperature were set at 280 and 300°C, respectively. The oven temperature was programmed as follows: 60°C held for 1 min, ramp at 30°C/min to 180°C, held for 3 min, ramp at 3°C/min to 220°C, held for 3 min, ramp at 10°C/min to 300°C. The injection volume of the GC was 1.0 μL. The residues detected by the GC analysis were further 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.

Health risk estimation: Health risk estimations were done based on an integration of pesticide analysis data, and exposure assumptions. The following assumptions were made based on the U.S Environmental Protection Agency's guidelines (EPA, 1996): a) hypothetical body weights of 10 kg for children and b) maximum absorption rate of 100% and bioavailability rate of 100%. Food consumption rates were based on the International Food Policy Research Institute data, (2004).

Food consumption rate for fruits and vegetables in Ghana is found to be 0.064 kg/person/day and 0.137 kg/person/day, respectively. Hence, for each type of exposure, the estimated lifetime exposure dose (mg/kg/day) was obtained by multiplying the residual pesticide concentration (mg/kg) in the food of interest times the food consumption rate (kg/day), and dividing the product by the body weight (kg). The hazard indices

to children was estimated as ratios between estimated pesticide exposure doses, and the reference doses which are considered to be safe levels of exposure over the lifetime.

RESULTS AND DISCUSSION

The fruits and vegetables under study are mostly used uncooked. Pesticides are the part of majority of chemicals applied on them. The present investigation determined the pesticide residues in various fruits and vegetables samples collected from different markets of Kumasi city and compared them with the limits set by the European Commission (2006).

Table 1 gives the scientific, English and the incidence of pesticide residues in fruits and vegetables samples analyzed. Residues occurred in 58 and 49% of all fruits and vegetables samples, respectively.

The method used was validated under optimized conditions by determining the limits of detection (LOD) and quantitation (LOQ), the recovery and precision at different fortification levels. The recovery values ranged from 87.3-104.0%, and precision ranged from 3.8-10.6% (Table 2). For the analysis of pesticide residues at ng/g or μg/g levels, accuracy and recovery of 70-120% considered acceptable (Herdman *et al.*, 1988; Pose-Juan *et al.*, 2006; Gonzalez-Rodriguez *et al.*, 2008a, 2008b; Berrada *et al.*, 2010; Gilbert-Lopez *et al.*, 2010; Osman *et al.*, 2010) and fulfill the criteria for quantitative methods (SANCO, 2003). The limits of detection (LODs) were determined at a signal to noise ratio (S/N) ratio of 3 for the individual pesticides where as the limits of quantitation (LOQs) obtained at a signal to noise ratio (S/N) of 10 for each pesticides by GC-ECD, respectively. The LODs (0.001-0.005 mg/kg) and LOQs (0.004-0.010 mg/kg) for the tested pesticides were much lower than the maximum residue levels (MRLs), allowed for fruits and vegetables in European Union countries. Residue samples that were considered non-detections were assigned a value of zero. The LODs achieved with the method are similar to those previously obtained by other authors in fruits and vegetables (Gelsomino *et al.*, 1997; Osman *et al.*, 2010).

Chlorinated pesticide residues in fresh fruits and vegetables: Fresh fruits and vegetables studied in this research are produced and consumed locally with no or minimal preparation which may constitute an important potential source of pesticide residues. Washing under running water is most commonly the only treatment given to many fruits and vegetables prior to consumption in Ghanaian setting. The pesticide residues will not only affect the nutritional values of the fruits and vegetables but also have deleterious effect on human beings using

Table 3: Organochlorine pesticide residues (mg/kg; fresh wt) in fruits and vegetables

Concentration and range of pesticides								
Commodity	Gamma-HCH		Methoxychlor		Aldrin		Dieldrin	
	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range
Fruits								
Papaya	0.100±0.004	0.092-0.105	0.006±0.002	0.004-0.012	0.013±0.007	0.009-0.019	0.017±0.020	0.002-0.04
Water Melon	0.004±0.002	0.004-0.006	-	-	-	-	-	-
Banana	-	-	0.008±0.004	0.004-0.012	-	-	0.090±0.103	0.013-0.203
Mango	0.010±0.010	0.006-0.022	0.004±0.001	0.004-0.006	-	-	-	-
Pear	0.009±0.003	0.006-0.012	-	-	0.012±0.009	0.010-0.016	-	-
Pineapple	0.133±0.014	0.121-0.153	0.031±0.023	0.007-0.052	0.006±0.002	0.004-0.008	0.012±0.0080	.007-0.018
Vegetables								
Tomato	0.129±0.013	0.104-0.155	0.016±0.005	0.010-0.017	0.040±0.033	0.080-0.015	-	-
Lettuce	0.040±0.035	0.080-0.015	0.006±0.003	0.005-0.007	0.011±0.010	0.009-0.021	-	-
Cabbage	0.100±0.004	0.095-0.102	0.023±0.008	0.031-0.022	-	-	0.035±0.013	0.030-0.052
Carrot	-	-	0.008±0.004	0.006-0.012	0.010±0.021	0.008-0.040	-	-
Okra	0.008±0.010	0.006-0.012	-	-	-	-	-	-
Green Pepper	-	-	0.016±0.014	0.006-0.032	0.020±0.002	0.018-0.021	0.058±0.005	0.052-0.062
Onion	0.019±0.002	0.016-0.020	0.041±0.022	0.025-0.066	-	-	-	-
Cucumber	-	-	0.020±0.002	0.018-0.021	-	-	0.010 ±0.004	0.005-0.013
∑ Mean Level	0.055		0.016		0.016		0.037	
Concentration and range of pesticides								
Commodity	Endrin		p,p'-DDE		p,p'-DDT			
	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range		
Fruits								
Papaya	-	-	-	-	0.012±0.006	0.008-0.014		
Water Melon	-	-	0.004±0.001	0.004-0.008	0.008±0.004	0.006-0.010		
Banana	0.006±0.002	0.004-0.012	-	-	0.038±0.032	0.005-0.062		
Mango	-	-	0.010±0.004	0.005-0.011	0.020±0.002	0.018-0.021		
Pear	-	-	-	-	-	-		
Pineapple	0.004±0.002	0.004-0.008	-	-	-	-		
Vegetables								
Tomato	-	-	-	0.190-0.051	0.016±0.020	0.006-0.002		
Lettuce	-	-	-	0.173-0.193	0.050±0.400	0.050-0.005		
Cabbage	0.007±0.003	0.0050.009	0.008±0.004	0.006-0.010	0.032±0.010	0.030-0.040		
Carrot	0.040±0.035	0.016-0.031	-	-	0.009±0.003	0.005-0.013		
Okra	0.023±0.008	0.016-0.031	0.011±0.010	0.008-0.021	0.037±0.013	0.030-0.052		
Green Pepper	-	-	-	-	-	-		
Onion	-	-	0.023±0.008	0.016-0.031	0.035±0.005	0.030-0.040		
Cucumber	-	-	0.07±0.015	0.053-0.082	0.004±0.001	0.004-0.008		
∑ Mean level	0.016		0.039		0.023			

SD: Standard deviation

these food items. National and international regulations on food quality have lowered the maximum permissible levels of pesticide residues in human food; hence, an increasing important aspect of food quality should control the concentration of pesticide residues in food.

The mean concentrations and range of pesticide residues (organochlorine and pyrethroid) found in fruits and vegetables sampled from the local markets of Kumasi metropolis in Ghana are summarized in Table 3 and 4.

Among the detected organochlorine pesticide residues, the results showed that gamma-HCH in some commodities were between 0.008 mg/kg in okra and 0.133 mg/kg in pineapple with range of 0.006-0.012 and 0.121-0.153, respectively (Table 3). The presence of an average mean sum of 0.055 mg/kg was recorded during

the entire study. Gamma-HCH is a reasonably stable compound and only under alkaline condition decomposes to yield trichlorobenzene. It is considered as one of the less persistent organochlorine pesticides. The high level of gamma-HCH 0.055 mg/kg obtained from the analysis might not be connected with the extensive use of technical lindane (gamma-HCH) which is marketed as Gammalin 20 and used by some farmers for agricultural purposes for crop protection in Ghana. This result is comparable with mean concentration level of 0.002 and 0.004 mg/kg reported in Nigeria and India markets respectively (Bhanti and Taneja, 2007; Adeyeye and Osibanjo, 1999). This further suggested that lindane is extensively used in Ghanaian agricultural sector on fruit and vegetable cultivation. However, lindane level from Kumasi is

Table 4: Synthetic pyrethroid pesticide residues (mg/kg fresh wt) in fruits and vegetables

Commodity	Concentration and range of pesticides					
	Permethrin		Cyfluthrin		Cypermethrin	
	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range
Fruits						
Papaya	0.015±0.015	0.005-0.032	-	-	0.035±0.005	0.030-0.040
Water Melon	0.040±0.033	0.080-0.025	0.008±0.002	0.004-0.010	-	-
Banana	-	-	0.010±0.010	0.006-0.022	0.012±0.006	0.007-0.012
Mango	0.016±0.021	0.002-0.031	-	-	0.008±0.002	0.004-0.012
Pear	0.006±0.003	0.004-0.008	-	-	0.004±0.002	0.004-0.008
Pineapple	0.041±0.022	0.025-0.066	0.020±0.002	0.018-0.021	0.022±0.003	0.019-0.025
Vegetables						
Tomato	0.020±0.002	0.018-0.021	-	-	0.016±0.005	0.006-0.020
Lettuce	0.090±0.102	0.011-0.051	-	-	0.060±0.026	0.030-0.080
Cabbage	0.049±0.026	0.022-0.078	0.016±0.014	0.010-0.018	-	-
Carrot	0.037±0.013	0.030-0.052	-	-	0.014±0.002	0.010-0.018
Okra	-	-	0.011±0.010	0.007-0.021	0.008±0.006	0.006-0.014
Green Pepper	0.007±0.003	0.005-0.013	-	-	-	-
Onion	-	-	0.009±0.003	0.005-0.013	-	-
Cucumber	0.012±0.008	0.008-0.016	-	-	0.009±0.003	0.006-0.013
∑ Mean Level	0.030		0.012		0.019	
Commodity	Concentration and range of pesticides					
	Fenvalerate		Deltamethrin			
	Mean±SD	Range	Mean±SD	Range		
Fruits						
Papaya	0.020±0.020	0.018-0.021	-	-		
Water Melon	-	-	0.015±0.011	0.007-0.023		
Banana	-	-	0.016±0.021	0.008-0.040		
Mango	0.008±0.004	0.006-0.004	-	-		
Pear	-	-	0.008±0.002	0.007-0.010		
Pineapple	-	-	0.044±0.018	0.026-0.062		
Vegetables						
Tomato	-	-	0.013±0.005	0.011-0.017		
Lettuce	0.023±0.008	0.013-0.016	0.016±0.021	0.006-0.024		
Cabbage	0.011±0.010	0.003-0.017	0.010±0.010	0.009-0.020		
Carrot	0.006±0.002	0.004-0.008	0.010±0.033	0.009-0.063		
Okra	0.030±0.005	0.019-0.041	-	-		
Green Pepper	0.007±0.003	0.007-0.015	0.023±0.008	0.022-0.034		
Onion	0.037±0.003	0.013-0.042	0.038±0.030	0.021-0.045		
Cucumber	0.012±0.008	0.008-0.016	-	-		
∑ Mean level	0.017		0.022			

SD: Standard deviation

extremely low, compared to elevated levels of lindane reported for fruits and vegetable from Shanghai, China (Nakata *et al.*, 2002).

Methoxychlor concentration in fruit and vegetable samples was a little high, perhaps being as a result of historical use of DDT of which technical methoxychlor contains about 88 % of the p,p'-isomer together with more than 50 structurally related contamination, which might have been added to the actual amount of methoxychlor present (Bempah and Donkor, 2010). A mean value of 0.004 and 0.041 mg/kg was achieved in mango and onion samples, with range of 0.004-0.006 and 0.025-0.066, respectively. A mean sum value of was 0.016 mg/kg achieved for all the testes commodities.

Aldrin is an alicyclic chlorinated hydrocarbon and is rapidly converted to the epoxide form; dieldrin (GESAMP, 1993). The presence of an average of 0.006 mg/kg in pineapple and 0.040 mg/kg in tomato with range values of 0.004-0.008 and 0.080-0.015, respectively recorded in the analyzed samples declare that, there may be conversion of aldrin to dieldrin by an epoxidation in biological systems (Rumsey and Bond, 1974) and, therefore dieldrin is expected to be found in relatively higher levels than aldrin. Hence, concentration levels of dieldrin varied from 0.010 mg/kg in cucumber and 0.090 mg/kg in banana with a range of 0.005-0.013 and 0.013-0.203, respectively. A mean sum value of 0.016 mg/kg and 0.037 mg/kg was recorded for aldrin and dieldrin, respectively.

Endrin was recorded in 0.004 mg/kg in pineapple with a range of 0.004-0.008 and 0.040 in carrot with a range of 0.080-0.015. Endrin recorded low mean sum value of 0.016 mg/kg in all the tested commodities. The low level of endrin was as result of its susceptibility to volatilization, photodegradation, and heat to form metabolites of endrin (Fan and Alexeeff, 1999). Moreover, it could also result from biodegradation of endrin aided by fungi and bacteria, and the major transformation product δ -ketoendrin indicated elsewhere (IPCS, 1992).

p,p'-DDE were between 0.004 mg/kg in watermelon and 0.173 mg/kg in lettuce with range of 0.004-0.008 and 0.050-0.400, respectively while p,p'-DDT contents varied from 0.006 mg/kg and 0.050 mg/kg in tomato and lettuce samples with a range of 0.004-0.008 and 0.022-0.078 in tomato and lettuce samples, respectively. The presence of mean sum values of 0.039 and 0.023 mg/kg for p,p'-DDE and p,p'-DDT was recorded in all the tested fruit and vegetable samples, respectively. DDT is generally used against a wide variety of agricultural and forest pests and against insect pests including vectors such as mosquito and tse-tse flies.

In the environment, DDT can be degraded by solar radiation or metabolized in organisms, could also play a role since most of the fruits and vegetables harvested and brought to the open markets are always left under the heat of the sun (Bempah and Donkor, 2010). Dehydrochlorination of DDT gives its metabolite DDE. This proves the high concentrations levels of DDE. The results corroborate the findings of Abou-Arab and Abou Donia (2001) who detected levels of DDT and its derivatives at levels ranging from 0.009 to 0.116 mg/kg and mean value of 0.05 mg/kg in West African city farms (Manirakiza *et al.*, 2003).

Among the different organochlorine pesticide residues found in fruit and vegetable samples, p,p'-DDE was found with the highest concentration of 0.173 mg/kg in lettuce, followed by gamma-HCH (0.133 mg/kg) in pineapple, dieldrin (0.090 mg/kg) in banana, p,p'-DDT (0.050 mg/kg) in lettuce, methoxychlor (0.041 mg/kg) in onion, aldrin (0.040 mg/kg) and endrin (0.040 mg/kg) in tomato and carrot samples, respectively.

Synthetic pyrethroid pesticide residues in fresh fruits and vegetables: The levels of five pyrethroid residues in fruits and vegetables collected from local markets in Kumasi are illustrated in Table 4. The results showed that, the levels of permethrin in all the commodities were between 0.006 mg/kg in pear and 0.090 mg/kg in lettuce with range of 0.004-0.008 and 0.011-0.051, respectively. Cyfluthrin contents varied from 0.008 mg/kg in watermelon and 0.020 mg/kg in pineapple with a range of 0.004-0.010 and 0.018-0.021, respectively. Residual levels of cypermethrin detected in the samples are 0.004

mg/kg in pear and 0.060 mg/kg in lettuce with a range of 0.004-0.008 and 0.030-0.080, respectively. The levels of fenvalerate detected in the commodities varied between 0.006 mg/kg in carrot and 0.037 mg/kg in onion with range of 0.004-0.008 and 0.031-0.042, respectively while the levels of deltamethrin varied between 0.008 mg/kg in pear and 0.044 mg/kg in pineapple with range of 0.007-0.010 and 0.026-0.062, respectively.

The data in Table 4 also shows different pyrethroid residues in fruit and vegetable samples, where permethrin was found with the highest concentration of 0.090 mg/kg in lettuce, followed by cypermethrin with concentration of 0.060 mg/kg in pineapple, deltamethrin with concentration of 0.044 mg/kg in pineapple, fenvalerate with concentration of 0.037 mg/kg in onion and cyfluthrin with a concentration of 0.020 mg/kg in pineapple.

The results of the present investigation further support the findings of the study carried out in India by Kumar *et al.* (2006) with residues of cypermethrin and fenvalerate ranging 0.045-0.064 mg/kg, 0.046-0.067 mg/kg respectively in grapes. A similar study was also carried out in Danish market which indicated residues of pyrethroid insecticides in 54% of the samples of fruit and 13 % of vegetables (Andersen and Paulsen, 2001). A simple and rapid liquid chromatography (LC) method also proved the occurrence of 9 pyrethroid insecticides (biphenthrin, cypermethrin, fenpropathrin, fenvalerate, flucythrinate, methothrin, permethrin, py-115, and tetramethrin) in fruits and vegetables (Pang *et al.*, 1995).

Tolerance limits: The concentration of organochlorine and synthetic pyrethroid pesticide residues in the various fruit and vegetable samples in Kumasi metropolitan city markets were compared with maximum residue limits set forth by European Commission (2006). Generally, the residual levels were either the same, below, or above the MRL guidelines (Table 5 and 6). The low lipid content may explain the low residual contents in these kinds of commodities despite the high amount of water (Bempah and Donkor, 2010).

The residual concentration level of gamma-HCH in papaya, pineapple, tomato, lettuce, cabbage and onion samples were above the MRL values similar to methoxychlor which exceeded MRL values in pineapple, tomato, cabbage, green pepper, onion and cucumber. Dieldrin level was above MRLs in papaya, banana, cabbage and green pepper while aldrin exceeded MRLs in papaya, pear, tomato and green pepper. Moreover, endrin exceeded MRL in carrot and okra while p,p'-DDE exceeded MRLs in tomato, lettuce and cucumber. The residual level of p,p'-DDT was relatively lower than the permitted levels in all the tested commodities (Table 5).

In the case of synthetic pyrethroid pesticide residues, cypermethrin exceeded MRL in lettuce while fenvalerate

Table 5: Highest organochlorine pesticide residue found in the various fruit and vegetables samples from Kumasi metropolitan city markets compared with EC MRL (mg/kg)

Commodity	Concentration and MRL of pesticides					
	Gamma-HCH		Methoxychlor		Aldrin	
	Concentration	MRL	Concentration	MRL	Concentration	MRL
Fruits						
Papaya	0.100	0.01	0.006	0.01	0.013	0.01
Water Melon	0.004	0.01	-	-	-	-
Banana	-	-	0.008	0.01	-	-
Mango	0.010	0.01	0.004	0.01	-	-
Pear	0.009	0.01	-	-	0.012	0.01
Pineapple	0.133	0.01	0.031	0.01	0.006	0.01
Vegetables						
Tomato	0.129	0.01	0.016	0.01	0.040	0.01
Lettuce	0.040	0.01	0.006	0.01	0.011	0.01
Cabbage	0.100	0.01	0.023	0.01	-	-
Carrot	0.008	0.01	0.010	0.01	-	-
Okra	0.008	0.01	-	-	-	-
Green Pepper	-	-	0.016	0.01	0.020	0.01
Onion	0.019	0.01	0.041	0.01	-	-
Cucumber	-	-	0.020	0.01	-	-

Commodity	Concentration and MRL of pesticides							
	Dieldrin		Endrin		p,p'-DDE		p,p'-DDT	
	Concentration	MRL	Concentration	MRL	Concentration	MRL	Concentration	MRL
Fruits								
Papaya	0.017	0.01	-	-	-	-	0.012	0.05
Water Melon	-	-	-	-	0.004	0.05	0.008	0.05
Banana	0.090	0.01	0.006	0.01	-	-	0.038	0.05
Mango	-	-	-	-	0.010	0.05	0.020	0.05
Pear	-	-	-	-	-	-	-	-
Pineapple	0.012	0.01	0.004	0.01	-	-	-	-
Vegetables								
Tomato	-	-	-	-	0.190	0.05	0.006	0.05
Lettuce	-	-	-	-	0.173	0.05	0.050	0.05
Cabbage	0.035	0.01	0.007	0.01	0.008	0.05	0.032	0.05
Carrot	-	-	0.040	0.01	-	-	0.009	0.05
Okra	-	-	0.023	0.01	0.011	0.05	0.037	0.05
Green Pepper	0.058	0.01	-	-	-	-	-	-
Onion	-	-	-	-	0.023	0.05	0.035	0.05
Cucumber	0.010	0.02	-	-	0.070	0.05	0.004	0.05

Table 6: Highest synthetic pyrethroid pesticide residues found in the various fruit and vegetables samples from Kumasi metropolitan city markets compared with EC MRL (mg/kg)

Commodity	Concentration and MRL of pesticides									
	Permethrin		Cyfluthrin		Cypermethrin		Fenvalerate		Deltamethrin	
	Concentration	MRL	Concentration	MRL	Concentration	MRL	Concentration	MRL	Concentration	MRL
Fruits										
Papaya	0.015	0.05	-	-	0.035	0.05	0.020	0.02	-	-
Water Melon	0.040	0.05	0.008	0.02	-	-	-	-	0.015	0.05
Banana	-	-	0.010	0.02	0.012	0.05	-	-	0.016	0.05
Mango	0.016	0.05	-	-	0.008	0.05	0.008	0.02	-	-
Pear	0.006	0.05	-	-	0.004	1.00	-	-	0.008	0.10
Pineapple	0.041	0.05	0.020	0.02	0.022	0.05	-	-	0.044	0.05
Vegetables										
Tomato	0.020	0.05	-	-	0.016	0.50	-	-	0.013	0.20
Lettuce	0.090	0.05	-	-	0.060	2.00	0.023	0.02	0.016	0.50
Cabbage	0.049	0.05	0.016	0.20	-	-	0.011	0.05	0.010	0.10
Carrot	0.037	0.05	-	-	0.014	0.05	0.006	0.02	0.040	0.05
Okra	-	-	0.011	0.02	0.008	0.50	0.030	0.02	-	-
Green Pepper	0.007	0.05	-	-	-	-	0.010	0.02	0.023	0.20
Onion	-	-	0.009	0.02	-	-	0.037	0.02	0.038	0.10
Cucumber	0.012	0.05	-	-	0.009	0.20	0.010	0.02	-	-

Table 7: Health risk estimation for systemic effects associated with pesticide residues in fruits

Pesticide	Reference dose (mg/kg/day)	Estimated dose (mg/kg/day)	Hazard index	Health risk
Gamma-HCH	0.005	1.63×10^{-3}	0.326	No
Methoxychlor	0.005	7.0×10^{-5}	0.014	No
Aldrin	-	-	-	-
Dieldrin	-	-	-	-
Endrin	0.0003	3.0×10^{-5}	0.100	No
p,p'-DDE	0.020	4.0×10^{-5}	0.006	No
p,p'-DDT	0.020	3.0×10^{-4}	0.015	No
Permethrin	0.250	1.5×10^{-4}	0.001	No
Cyfluthrin	0.025	8.0×10^{-5}	0.003	No
Cypermethrin	0.050	7.0×10^{-5}	0.007	No
Fenvalerate	-	-	-	-
Deltamethrin	0.010	1.3×10^{-4}	0.013	No

Table 8: Health risk estimation for systemic effects associated with pesticide residues in vegetables

Pesticide	Reference dose(mg/kg/day)	Estimated dose (mg/kg/day)	Hazard index	Health risk
Gamma-HCH	0.005	8.0×10^{-4}	0.160	No
Methoxychlor	0.005	6.5×10^{-4}	0.130	No
Aldrin	-	-	-	-
Dieldrin	-	-	-	-
Endrin	0.0003	3.1×10^{-4}	1.030	Yes
p,p'-DDE	0.020	1.1×10^{-3}	0.054	No
p,p'-DDT	0.020	3.4×10^{-4}	0.017	No
Permethrin	0.250	4.9×10^{-4}	-	No
Cyfluthrin	0.025	1.6×10^{-4}	0.006	No
Cypermethrin	0.050	2.8×10^{-4}	0.028	No
Fenvalerate	-	-	-	-
Deltamethrin	0.010	3.1×10^{-4}	0.031	No

Reference dose for aldrin, dieldrin and fenvalerate were not available

exceeded MRLs in lettuce, okra and onion. Deltamethrin exceeded MRL in green pepper. However, the levels of cyfluthrin, and cypermethrin detected in some of the commodities were all below their respective MRLs (Table 6). Furthermore, permethrin had the highest mean sum value, followed by deltamethrin, cypermethrin, fenvalerate and cyfluthrin with concentrations of 0.030, 0.022, 0.019, 0.017 and 0.012 mg/kg, respectively.

The results of the study indicated that despite majority of growers using agrochemicals in a responsible way residue levels in fruits and vegetables are higher than the MRL and could pose health problems as this popular fruit and vegetables are consumed regularly by the population.

Overall the data revealed that, organochlorine pesticide residues was present in 59.2% whiles synthetic pyrethroid residues were present in 67.2% fruits and vegetables. The high presence of pyrethroid insecticides residues in fruits and vegetables 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 groups of these insecticides in the last decade. It is also as a result of the photostability and relatively low toxicity as compared with organochlorine insecticides. The present findings are in good agreement with these of survey conducted in India, Pakistan and Egypt (Masud, 1992; Seyed and Somashekar, 2010; Dogehim *et al.*, 2001; Gyana *et al.*, 2007; Mukeherjee *et al.*, 2007).

Health risk estimates: The health risk estimates for systemic effects associated with pesticide residues in

fruits and vegetables are summarized in Table 7 and 8. The table comprises of reference daily dose and computed average maximum daily intake values and corresponding hazard indices during the study period for children who are considered to be the most vulnerable population subgroup.

The hazard indices values showed that, only the endrin is showing the health risk associated with vegetables indicating a great potential for systemic toxicity in children. Thus endrin appears to have some health risk associated with it while rests of the pesticides were found to be under safe limit (Table 8).

CONCLUSION

In conclusion, pesticide residues were found in all the monitored fruits and vegetable samples from all the selected markets from Kumasi metropolis. In all, 37.5% of fruit and vegetable samples analyzed contained no detectable level of the monitored pesticides, 19.0% of the samples gave results with levels of pesticide residues above the MRL, while 43.5% of the samples showed results below the MRL. The above results suggest that the consumers of the Kumasi metropolitan city are exposed to concentration of pesticides that may cause chronic diseases. On the basis of the above findings, the results recommend the need for continues survey and monitoring programs for pesticide in all food commodities in order to protect the end user for the indiscriminate exposure of pesticides. A future study in a longer period of time would allow obtaining a deeper knowledge about the fulfillment of vegetables produced in Ghana with respect to the use

of pesticides and their presence in these fruits and vegetables.

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