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Levels of organochlorine and synthetic pyrethroid pesticide residues in selected fruits in the yilo and lower manya krobo districts of the eastern region of Ghana

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ABSTRACT

Locally produced fruits (mango, pineapple and banana) were sampled and purchased from farms and markets within the Yilo and Lower Manya Krobo districts and analyzed for pesticide residues by gas chromatography equipped with an Electron Capture Detector (GC-ECD). In all, 80 samples made up of 40 mango samples and 20 samples each of pineapples and bananas were extracted and analyzed for mainly organochlorine residues (γ-HCH, δ-HCH, aldrin, dieldrin, heptachlor, γ-chlordane, endosulfan s, *p, p'*-DDE etc.) and synthetic pyrethroid residues (allethrin, bifenthrin, fenpropathrin, permethrin, cyfluthrin etc.). Analysis indicates that about 88% of the mangoes sampled from the farms contained one or more of these pesticide residues. 75% and 65% of the pineapples and bananas respectively from farms and markets had one or more of the analyzed pesticide residues. The data revealed that about 6.2% of the fruit samples analyzed contained organochlorine pesticide residues of γ-HCH (0.013mg/kg and 0.038mg/kg respectively in mangoes and pineapples); δ-HCH [0.014mg/kg (mango) and 0.024mg/kg (pineapple)]; methoxychlor [0.027mg/kg (mango) and 0.048mg/kg (pineapple)]. Synthetic pyrethroid residues of cyfluthrin [0.078mg/kg (mango) and 0.059mg/kg (pineapple)] and fenvalerate [0.025mg/kg and 0.028mg/kg respectively for mango and pineapple] were also found above their respective maximum residue limits whereas 78.2% of detected pesticide residues were below the MRLs. Nonetheless, the continuous consumption of these fruits with even the modest pesticide levels can result in accumulation that could result in deadly chronic effects. In assessing the consumers' perception of pesticide residues in fruits, about 69% of the respondents were aware of pesticide residues in fruits and the corresponding adverse effect on human health. Some have experienced pesticide poisoning after fruit consumption. Thus many wish pesticide usage in fruit and crop cultivation in general is curbed or minimized to only those who can ensure reduced levels.

Introduction

Over the past 40-50 years, no single subject in the area of food quality and food safety has attracted more attention than the issue of pesticide residues in food. There is however the worldwide demand for adequate supplies for pest–free good quality commodities and foodstuffs and this necessitates the continued use of conventional pesticides for some time to come and hence the continued associated problems of pesticide residues. To minimize the economic losses caused by insects, fungi and weeds, various insecticides, fungicides, rodenticides and herbicides are used on food and cash crops on a massive scale (Delaplane, 1996).

Pesticides have a long history against insects and other pests. These pesticides were either inorganic chemicals or compounds extracted from plant and animal sources. Around World War II, the production of synthetic organic pesticides increased tremendously. Initially, the more persistent class of organochlorine pesticides were favoured, but it did not take long to realise the side effects of pesticides including losses of wildlife and beneficial insects, residues in crops and food chain, health hazards to humans and animals, etc. Moreover, many of the pests for whom these were designed to kill developed resistance and pest resurgence became a common phenomenon (Brown and Pol, 1971). All along this time, pesticide manufacture and consumption showed an exponential increase.

The business of pesticide companies flourished through the introduction of other classes of pesticides and targeting different pests. The pesticide import in Ghana started in 1954 through the Government of the then Gold Coast (now Ghana). In a policy change, the pesticide business was handed over to the private sector in the early 1980s. Since then, pesticide consumption has been on the rise. The pesticide consumption figures for 2010 stood at 615,000 metric tonnes for solid pesticides and 16,000 ('000 Litres) for the liquids (Ghana EPA, 2011). Insecticides comprise 85% of the total pesticides; and food crop is the major recipient of these chemicals.

A variety of pesticides are being imported into Ghana. It has been found that more than 80% of the total intake of pesticide residues in human beings is through the food chain (Martinez *et al.*, 1997; Trotter and Dickerson, 1993). There is a vital need for the continuous monitoring of pesticide residues in food especially fruits and other environmental media.

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Pesticides constitute a vital group of compounds and their use has to be controlled due to their high toxicity and widespread use in agricultural practices. For field and post-harvest protection of crops, the use of pesticides could lead to extensive environmental pollution. To ensure the safety of food for consumers, numerous legislations such as Codex directives (CODEX Committee on Pesticide Residues, 2003) have established maximum residue limits (MRLs) for pesticides in foodstuffs.

Ordinary people think they can choose either to smoke or drink alcohol. But they have little or no control over the water they drink, which makes any health risk within it that much scarier (Economist, 1986).

Although the production and use of many types of organochlorine pesticides and some synthetic pyrethroids have been severely restricted (or completely banned in most cases) in many countries including Ghana, some such as hexachlorocyclohexane (mixed isomers) are nevertheless still being used in large quantities in many parts of Ghana (Now *et al*., 2005), and in other developing countries because of their effectiveness as pesticides and their relatively low cost (Racke *et al*., 1997) as well as inadequate regulation and management on the production, trade and use of these chemicals (Darko and Acquaah, 2007).

Mangoes, pineapples and to some extent bananas have, over the past years, become some of the major export commodities for the people of coastal areas of south-eastern Ghana in the absence of cocoa which does not do well in the coastal areas. The national best farmer for 2009 is the single major exporter of the mango produce and for which his award was largely based. A lot of small scale associations are into commercial cultivation and export of these commodities.

Materials and methods

Sampling

The Yilo and Lower Manya Krobo districts (0.0° N, 0.0°, 0.20°W and 6.20°N) are located in the south eastern part of Ghana, between the Akwapim range and the Volta Lake.

Figure 1 shows the farms and markets within the study districts in relation to the whole country, Ghana (inserted).

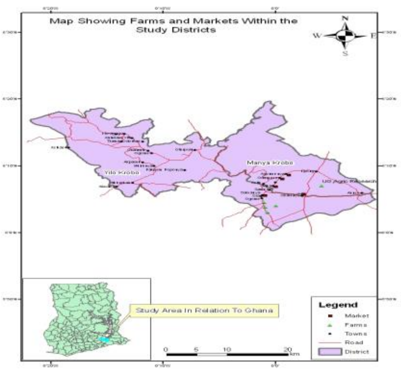

Figure1

Sampling from farms

Twenty (20) samples of mangoes (Keith and Kent varieties) and ten (10) local variety pineapples (Each sample weight = 1Kg) were sampled from 10 commercial farms within the two districts of the study, using the *Codex* sampling plan (FAO/WHO, 2000). The samples were sealed and labelled with a unique sample identification number and transported to the Ghana Standards Board pesticide residue laboratory.

These samples were then extracted and analysed (within 48 hours from the time of sampling) for the presence of pesticide residues.

Sampling from the local markets and other locations

Twenty (20) samples of mangoes (Keith and Kent varieties), 10 samples of local variety pineapples and 10 samples of bananas (sample weight = 1 kilogramme) was bought from local markets and dealers dotted within the study area. As much as possible, the sources of the fruits were verified to ensure that though being bought from different dealers, their origins are also different. All samples were packaged in transparent plastic bags and refrigerated at 5 °C. These samples were then extracted and analysed (within 48 hours from the time of sampling) for the presence of pesticide residues.

All the sampling was not done on the same day; time was allowed in between samples to ensure diversity and consistency with Codex sampling requirements. (FAO/WHO, 2000)

Materials and Methods

Reagents and Certified reference standards

Pesticide grade ethyl acetate, analytical grade acetone, sodium hydrogen carbonate and sodium sulphate were supplied by BDH Laboratory Supplies, England. Solid-phase florisil cartridges column size (1000 mg/6mL) was packed and used. The individual certified reference standards, lindane, beta-HCH, delta-HCH, aldrin, heptachlor, gamma-chlordane, alpha-endosulfan, p,p'-DDE, dieldrin, endrin, beta-endosulfan, p,p'-DDT, p,p'-DDD, endosulfan sulfate, methoxychlor, allethrin, fenpropathrin, bifenthrin, lambda-cyhalothrin, permethrin, cyfluthrin, cypermethrin, fenvalerate and deltamethrin used for the identification and quantification were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). All standards were stored in the freezer at -20 °C to minimize degradation.

Preparation of Florisil

About 100g of 60 to 100 mesh florisil was transferred into a beaker, and placed in an oven at 130^0C overnight. The florisil was then cooled in a desiccator and 3g of the activated florisil was weighed and poured into a column which has been plugged with glass wool followed by 1.5g layer of anhydrous sodium sulphate. Each day a new pack of florisil column was prepared.

Instrumentation and Apparatus

Information pertaining to the identity of instruments and apparatus typically used for pesticide analysis is listed below.

- Gas Chromatograph- Varian CP-3800 Gas Chromatograph equipped with a CombiPAL Autosampler and Electron Capture Detector. Analytical column - 30m + 10m EZ Guard x 0.25mm internal diameter fused silica capillary coated with VF-5ms (0.25μm film) from Varian Inc.
- Centrifuge - Hermle Z 300, Jouan CR3i multifunction
- Macerator - IKA Ultra Turrax homogenizer
- General laboratory glassware - Round bottomed flasks, volumetric flasks, centrifuge tubes
- Water Bath - Bibby, RE 200B and Buchi, B-491
- Rotary film evaporator (RFE) - Bibby RE 200 and Buchi Ratovapor R-210
- Ultrasonic bath - Decon FS400b
- Vortex mixer - Thermolyne (Maxi Mix-Plus)

Sample preparation

Stalks, stones and peels (where applicable) were removed from each fruit sample and homogenized to maintain homogeneity using the laboratory blender. Appropriate representative sub-samples were taken for analysis, in accordance with *GSB-WI-T*. *Sampling of commodities for* *analysis, including labeling, preparing and storage (an SOP in the GSB Laboratory)*

Extraction Procedure

A sub sample of prepared matrix (about 20g) from the homogenized fruit samples (Chapter 3.6 above) was weighed into a sample bottle. Pesticide grade ethyl acetate (about 40mL) was added and macerated for 30 seconds. Analar anhydrous sodium sulphate (about 20g) and sodium hydrogen carbonate (about 5g) were added and macerated for a further 90 seconds. The macerate was then centrifuged at 3000rpm for 5 minutes.

An aliquot (4mL≡ 2.0g) was pipetted into a round-bottomed flask (50mL) and evaporated to approximately 2ml (Rotary Film Evaporator temperature of 35^0C), not to dryness for extract purification.

Sample Cleanup

The already packed 'Florisil' (1000mg/6mL) cartridge was conditioned with about 10 ml of ethyl acetate and the extract was loaded from a 2mL pipette onto the cartridge and the elute collected into 100 ml round bottom flask.

The cartridge was eluted again with 10mL of ethyl acetate and the filtrate concentrated below 40ºC to approximately 1mL on the rotary evaporator just to dryness. The extract was re-dissolved in ethyl acetate (2ml, standard opening vial) prior to quantization by GC-ECD.

Chromatographic conditions for the determination of the pesticide standards

A summary of the typical GC-ECD conditions used for the quantization of the pesticide standards are stated below:

ECD detector: Varian Factor four VF- 5ms, 30 m + 10 m column guard x 0.25 mm I.D. and 0.25 µm film thickness. Detector temperature of 300^oC, injector 270^oC, oven for organochlorines: 70^oC for 2 min, 70^oC –180^oC at 25^oCmin^{-1} maintained for 1 min, 180^oC – 300^oC at 5^oCmin^{-1}; oven for synthetic pyrethroids: 90^oC for 1 min, 90^oC – 240^oC at 30^oCmin^{-1}, 240^oC – 300^oC at 5^oCmin^{-1} maintained for 5 min, carrier gas (N_2) 1.0 ml min^{-1}, with an injection volume 1 uL.

Quality Control

All reagents used during the analysis were exposed to same extraction procedures and solvents used were run to verify for any interfering substances within the runtime. In all batches of pesticide residues analysis, reagent blanks, procedural matrix blanks and triplicate samples were included. For the reagent blanks in each extraction procedure, no pesticides were detected. All extracts were kept frozen until quantification was completed.

Recalibration curves were run with each batch of samples to check that the correlation coefficient was kept above r^2=0.99 The method used was an international method, optimized and validated using various agricultural products (Chung *et al*, 2010. Fortified samples were determined with good recoveries.

$$\text{Recovery (\%)} = \frac{\text{Concentration of Pesticide recovered from fortified sample}}{\text{Concentration of Pesticide added to sample}} \times 100$$

Concentration of Pesticide added to sample

The recoveries of pesticide residues ranged between 90% and 110% for most of the pesticides analyzed in this study.

Chromatographic Calibration

Mixed instrument calibration standards were prepared from the individual stock standards by serial dilution to obtain four concentration levels. The mixed standards, using the pesticide mixtures with concentrations of 0.005, 0.01, 0.02, and 0.05, were plotted against the peak area to obtain a calibration curve. The area of the curve had R^2= 0.996. Recalibration curves were run with each batch of samples to check that the correlation coefficient was kept above 0.99.

Limit of detection (LOD)

The limit of detection of the pesticides determined was based on the extract of the fortified samples that were serially diluted by factor of two to give different concentrations. One out of each concentration that gave a response three times the standard deviation of the least fortified sample was noted. And this was used to estimate the statistical significance of differences between low level analyte responses and the combined uncertainties in both the analyte and the background measurement (G. Wells *et al,* 2011).

Survey on the general public's perceptions of pesticide residues on fruits and any related adverse health effects.

Formal interview and structured questionnaires were used to gather information about fruit consumers' perception on pesticide use, pesticide residues and any health effects in fruit consumption as reported by Ntow *et al*., (2006). Four groups of data were queried from randomly selected respondents:

1. Personal
2. Lifestyle, i.e. hygiene and eating, and
3. Pesticide perception and
4. Pesticide effects on health

Table 1. Overview of questions from questionnaire on pesticides used to gather the views of the public in the districts.

Data group	Description
Personal data	Sex, marital status; age; level of education etc
Fruit consumption	How many times in a day do you eat fruits (one, two, three); what time of the day do you take your fruits; do you wash your fruits before eating (yes/no); if you wash; then with what? (only water, water and soap, other)?
Pesticide perception and health	Knowledge of application of pesticides in fruit production; knowledge of pesticide residues in fruits; any reaction or symptoms on intake of fruits

The questionnaires were administered at various locations within the study districts. The study objectives were explained to the public and their consent to participate in the study were sought. The interviews and questionnaires were conducted in English but translated into local languages for those who needed that assistance.

In all, 52 people were interviewed. Pesticide perceptions and health risks were assessed by asking the public the possible reaction and symptoms experienced upon consumption of fruits. The data was analysed by the statistical software SPSS.

Table 2. Summary demographic characteristics of 52 people surveyed

Variable	Mean (range) or %
Age (years)	33 (18-55)
Sex (male)	65.4%
(Female)	34.6%
Marital status (married)	56%

Table 3 above summarizes the demographic characteristics of the respondents captured in the survey. The average age of the respondents was 33 years, 34 of the respondents (65.4%) were male, 18 (34.6%) and 28 (56%) were married and living with their family. On the average, each person takes in fruits once a day. All the respondents captured in this survey are patrons of one or more of the fruits studied.

Table 3. Responses from the 52 fruit consumers sampled

Variable	Total respondents Number	%
A. Peoples' knowledge of pesticide residues in fruits		
Yes	36	69.2
No	12	23.1
Total	48	92.3
B. Number of times fruits are taken		
Once	22	42.3
Twice	10	19.2
Thrice	8	15.4
Other	10	19.2
Total	50	96.1
C. Washing of fruits before eating		
Yes	35	67.3
No	14	26.9
Total	49	94.2
D. Pesticide poisoning cases among public after intake of fruits*		
Headache	1	1.9
Dizziness	2	3.9
Vomiting	3	5.8
Itching	2	3.9
Stomach ache	7	13.5
General weakness	12	23.1
Unconsciousness	0	0.0
Others	6	11.5
None	7	13.5
Total	40	76.9
E. Peoples' recommendations to discontinue use of pesticides in fruit production		
Yes	27	51.9
No	21	40.4
Total	48	92.3

*Multiple responses: total responses per item over total respondents.

All respondents had knowledge about pesticides use on vegetable and fruit farms and about 69% were aware of pesticide residues in fruits and the corresponding adverse effect on human health.

On the whole, about 38% of the respondents complained of one or more of the following conditions after eating fruits: headache, dizziness, vomiting, itching, weakness or stomach ache. Thus over 40% of the respondents advocated the curtailment of pesticide use on fruits or farmers being educated on proper application to reduce the incidence of residues.

Results and discussions

Percentage pesticides in fruits sampled

Occurrence of pesticides in the fruits sampled and analyzed is presented in Table 4 and Figure 2.

Table 4. Overall percentage pesticide residues in one or more fruits from the farms and markets in the districts

Scientific name	Common name	No. of samples	No. with residues	% with residues
Magnifera indica	Mango	40	35	88
Ananas comosus	Pineapple	20	15	75
Musa sapientum	Banana	20	13	65

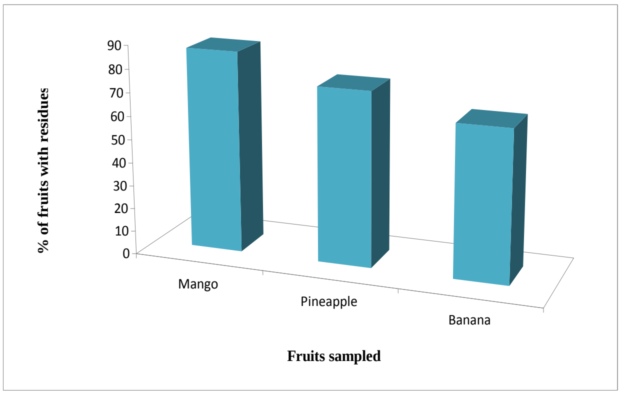

Figure 2. A graph showing the overall percentage total fruits with residues sampled from the various farms and markets.

Figure 2 indicates about 35 of 40 samples (about 88%) of mangoes had one or more residues, 75% of pineapples samples (15 out of 20) had residues whilst banana samples had the lowest percentage of 65% (13 out of 20) of residues. The lower residue levels found in banana could be as a result of the fact that most of this produce is grown in the wild and pesticide use is greatly reduced, except for pesticide drifts from use on nearby farms i.e. unintended uses.

Mean concentration levels of pesticide residues in Mango (*Magnifera indica)* from farms

Table 5. Concentrations of organochlorine pesticide residues (mg/kg) detected in mangoes from the farms in the study area.

Pesticides	Yilo Farms (mg/kg)		Manya Farms (mg/kg)	
	MF1 (Mean±SD)	MF2 (Mean±SD)	MF3 (Mean±SD)	MF4 (Mean ± SD)
β-HCH	<LOD	<LOD	<LOD	0.005±1.00
γ-HCH	0.001±2.03	0.002±1.22	0.002±0.36	0.003±1.21
Heptachlor	<LOD	0.002±0.22	<LOD	0.002±0.22
δ-HCH	0.006±1.72	<LOD	0.002±1.00	0.006±0.30
α-endosulfan	<LOD	0.010±8.23	0.004±0.01	0.010±8.23
p,p'-DDE	0.005±3.02	0.012±2.44	0.008±2.60	0.012±4.10
β-endosulfan	0.003±1.23	<LOD	0.001±1.01	<LOD
p,p'-DDT	0.001±0.12	<LOD	0.001±1.10	<LOD
Endosulfan sulf.	0.009±1.43	0.003±1.12	0.001±1.00	0.004±2.10
Methoxychlor	0.002±1.17	0.003±1.00	0.002±1.54	0.001±1.20

Each value is a mean of ten farm samples with three determinations

LOD= Limit of Detection. MF1, MF2, MF3, MF4 = Mango Farms at sites within the study area

SD = Standard Deviation

Table 5 gives the residual concentrations of organochlorine pesticides in mangoes from farms within the study area. The results showed that endosulfan sulfate recorded the highest mean concentration (0.009mg/kg) followed by γ-HCH (0.006mg/kg), p,p'- DDE (0.005mg/kg), β-endosulfan (0.003mg/kg), methoxychlor and δ-HCH (0.002mg/kg each) and p,p'-DDT (0.001mg/kg) in farm MF1.

p,p'-DDE recorded the highest mean levels of 0.008mg/kg and 0.012mg/kg respectively in farms MF3 and MF4. α-endosulfan recorded a level of 0.010mg/kg in farm MF4.

Considering farm MF2, p,p'-DDE recorded the highest concentration level (0.012mg/kg), followed by α-endosulfan (0.010mg/kg), endosulfan sulfate and methoxychlor (0.003mg/kg each) and both γ-HCH and heptachlor recorded (0.002mg/kg each) in mango samples.

γ-HCH was detected in mango samples from all farms while δ-HCH was not detected in farm MF2 but at relatively higher concentrations in MF1 and MF4.

Technical endosulfan consists of α- and β- isomers. It is one of the few cyclodiene pesticides that are still used extensively to control a number of insects on crops. In the environment, the cyclic sulphite group of endosulfan can be oxidized to the corresponding sulphate (endosulfan sulphate) (Chandler *et al*., 1991; Guerin *et al*., 1992; Kathpal *et al*., 1997), which is more persistent than its parent compound (Guerin, 2001).

Although many organochlorine pesticides such as DDT and heptachlor had been banned from use on food crops since 1985, they have remained in the environment where they continue to be incorporated into plant biomass. The mean residue levels of *p,p'*-DDE was 0.005mg/g and 0.008mg/kg in farms MF1 and

MF3 respectively. Levels of 0.012mg/kg of *p,p'*-DDE were detected in samples from farms MF2 and MF4. *p,p'*-DDT was detected only in samples from farms MF1 and MF3 with mean concentrations of 0.001mg/kg.

The presence and high concentrations of *p,p'*-DDE may be due to metabolic conversion and dehydrochlorination of *p,p'*-DDT. DDT can be biodegraded into DDE under aerobic conditions and DDD under anaerobic conditions, and a value of DDT/(DDD+DDE) > 1 can be used as an indicator of possible new sources of DDT. From this study, all the DDT / (DDD+DDE) values obtained were < 1 in 100% of mango samples. This suggests that DDT concentrations in mangoes from the farms in the study districts were mainly due to historic use, even though the existence of point and non-point sources cannot be totally ruled-out.

Comparison of organochlorine pesticide residues from the different farms

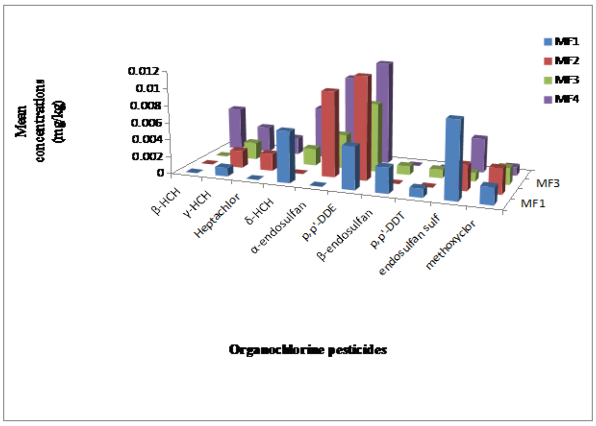

Figure 3. Comparative representations of the levels of organochlorie pesticide residues in mango samples from the different farms.

From Figure 3, it is observed that p,p'-DDE presented the highest levels of organochloride residues throughout the farms. Though γ-HCH was detected is samples from all the farms, levels are not as high as compared to metabolites such as *p,p'*-DDE. Endosulfan sulphate was also detected in 100% of mango samples; perhaps as metabolites of used parent compounds. α- and β-isomers were not detected in all samples from the farms, even though a high levels of 0.010mg/kg each was detected in farms MF2 and MF4. Lower results in other samples confirm its restricted use in Ghana which does not include fruits (It is registered for use on cotton) (Ntow, 2001).

Methoxychlor was detected in 100% of mangoes sampled from the farms in the study districts (Figure 3). However, mean concentrations were low, perhaps in agreement with its characteristics of higher concentrations in fatty samples like fish than in fruits.

Comparison of synthetic pyrethroid residues from the different farms

Mango samples were also screened for the less persistent synthetic pyrethroids. Frequency and mean concentrations detected are tabulated and discussed below:

Table 6 summarizes the mean concentrations of detected synthetic pyrethroids in mangoes sampled from the farms within the study districts. Cyfluthrin recorded the highest mean concentrations with levels of 0.015mg/kg each in farms MF2 and MF4. The other two farms i.e. MF1 and MF3 also had relatively high levels of 0.012mg/kg and 0.010mg/kg respectively. Permethrin results in three farms were also significant, with values of 0.010mg/kg, 0.006mg/kg and 0.009mg/kg respectively in farms MF1, MF2 and MF4 respectively. Bifenthrin and fenvalerate recorded 0.005mg/kg and 0.001mg/kg each in farms MF1 and MF2 respectively.

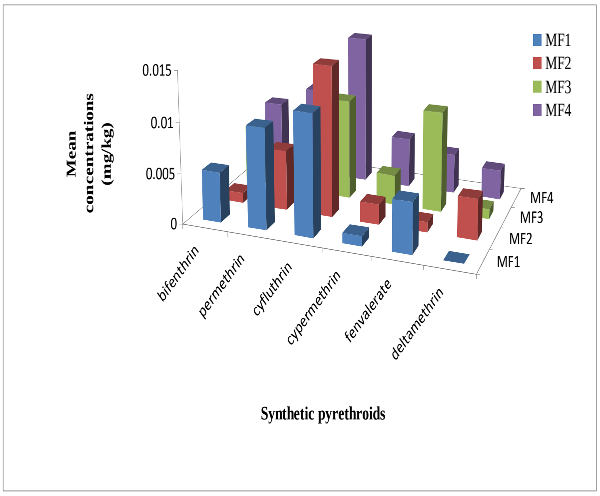

Figure 4. Comparison of synthetic pyrethroid residues in mangoes from the various farms

Figure 4 presents a comparative plot of the various levels of synthetic pyrethroid residues in mangoes from the farms. Prominent bars of cyfluthrin from the various farm mangoes are an indication of its levels of detection. Apart from deltamethrin which was not detected in farm MF1 in Yilo farms, all other five were detected in all samples from the farms.

The present results are in accordance with the findings of Pang *et al.* (1995) and Pylypiw (1993) who also found synthetic pyrethriod residues in fruits and other farm commodities. Karol *et al*. (2000) found bifenthrin and permethrin in substantial quantities (0.128mg/kg) in fruits and vegetable in Pakistan but no such levels were recorded in the present study.

Mean concentration levels of pesticide residues in pineapple (*Ananas comosus)*from farms.

The residue levels of organochlorine in pineapple (*Ananas comosus)* from farms in the districts are summarized below in Table 4.4. Although 13 organochlorine pesticides were being sought in this study, a number of them were not detected in some samples.

Lindane (γ- and δ-HCH) was detected in 100% of pineapple samples from the farms within the study districts with mean concentrations ranging from 0.002mg/kg in farm samples PN4 to as high as 0.011mg/kg in farms PN2. Heptachlor was detected only in samples from one of the farms in the Yilo farms, PN1. Comparing this study with a similar one carried out in Nigeria where HCH total mean concentration in pineapples was 0.002mg/kg (Adeyeye and Osibanjo, 1999), pineapples in farms in the study area were more contaminated with lindane [being the sum of δ-HCH and γ-HCH].

These results also corroborate the findings of Awumbila and Bokuma (1994) who found 20 different pesticides being used in Ghana on farms with the organochlorine lindane being the most widely used and distributed pesticide, accounting for 35% of those used on farms.

Endosulfan was widely detected in pineapples from almost all farms, except from farms within the PN1 farms where the sulfate was not detected. However, unlike in the mango samples, the α-isomer was most predominant with mean concentrations as high as 0.012mg/kg recorded from farms PN1 and PN3. These relatively higher levels of the isomer compared to the sulfate could be an indication of use of the parent compound, endosulfan on pineapples in the farms.

Table65. Mean concentrations of synthetic pyrethroid residues (mg/kg) in mangoes from farms

Pesticides	Yilo Farms (mg/kg)			Manya farms (mg/kg)
	MF1 (Mean±SD)	MF2 (Mean±SD)	MF3(Mean±SD)	MF4 (Mean±SD)
Bifenthrin	0.005±1.54	0.001±1.10	0.006±1.88	0.007±1.10
Permethrin	0.010±2.23	0.006±2.30	0.001±3.11	0.009±1.00
Cyfluthrin	0.012±5.11	0.015±1.91	0.010±2.72	0.015±4.20
Cypermethrin	0.001±1.00	0.002±1.10	0.003±2.00	0.005±2.15
Fenvalerate	0.005±1.11	0.001±0.86	0.010±1.90	0.004±0.86
Deltamethrin	<LOD	0.004±1.20	0.001±2.01	0.003±2.01

Each value is a mean of ten farm samples with three determinations
LOD= Limit of Detection. MF1, MF2, MF3, MF4 = Mango Farms at sites within the study area
SD = Standard Deviation

Table 7. Concentrations of Organochlorine pesticide residues (mg/kg) detected in pineapples from the farms

Pesticides	**Yilo Farms (mg/kg)**		**Manya Farms (mg/kg)**	
	PN1 (Mean±SD)	**PN2 (Mean±SD)**	**PN3 (Mean±SD)**	**PN4 (Mean ± SD)**
γ-HCH	0.004±1.00	0.004±3.11	0.006±1.99	0.009±2.00
Heptachlor	0.001±0.09	<LOD	<LOD	<LOD
δ-HCH	0.006±1.72	0.011±1.70	0.005±1.72	0.002±0.80
α-endosulfan	0.012±3.20	0.008±0.90	0.012±1.20	0.005±1.11
p,p'-DDE	0.006±2.10	0.012±1.23	<LOD	0.002±1.23
β-endosulfan	0.004±1.50	0.004±1.90	0.002±1.00	0.005±2.33
p,p'-DDT	0.001±1.00	<LOD	<LOD	0.002±1.02
Endosulfan sulf.	<LOD	0.003±2.10	0.003±2.10	0.003±0.94
Methoxychlor	0.006±1.87	0.003±1.00	0.008±1.11	0.012±2.65

Each value is a mean of five farm samples with four determinations
LOD= Limit of Detection. PN1, PN2, PN3, PN4 = Pineapple Farms at sites within the study area
SD = Standard Deviation

Table 8. Concentrations of organochlorine pesticide residues (mg/kg) fruits from the markets in the districts

Pesticides	**Yilo markets (mg/kg)**			**Manya markets (mg/kg)**		
	Mango (Mean±SD)	**Pineapple (Mean±SD)**	**Banana (Mean±SD)**	**Mango (Mean±SD)**	**Pineapple (Mean±SD)**	**Banana (Mean±SD)**
β-HCH	0.002±1.23	<LOD	<LOD	<LOD	<LOD	<LOD
γ-HCH	0.001±0.06	0.006±1.43	<LOD	0.004±1.43	0.009±0.93	0.004±1.22
Heptachlor	0.002±0.91	0.003±1.01	<LOD	<LOD	<LOD	<LOD
δ-HCH	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
α-endosulfan	0.004±2.44	0.005±1.59	0.004±1.39	0.002±1.59	0.004±1.22	0.004±2.00
p,p'-DDE	0.005±1.01	0.004±1.91	0.002±0.09	0.001±0.0	0.002±0.70	<LOD
β-endosulfan	<LOD	0.010±2.11	0.003±1.10	0.002±1.15	0.002±1.23	0.007±2.05
p,p'-DDT	0.002±2.00	<LOD	0.007±2.13	<LOD	0.002±0.50	0.007±3.20
endosulfan s	0.004±1.24	<LOD	0.002±1.22	0.003±0.89	0.004±1.00	0.004±1.22
Methoxychlor	0.015±3.12	0.011±4.00	<LOD	0.004±1.00	0.008±2.01	<LOD

LOD= Limit of Detection. SD = Standard Deviation

Table 9. Concentrations of synthetic pyrethroid residues (mg/kg) in the various fruits in the markets of the study districts

Pesticide	**Yilo markets (mg/kg)**			**Manya markets (mg/kg)**		
	Mango (Mean±SD)	**Pineapple (Mean±SD)**	**Banana (Mean±SD)**	**Mango (Mean±SD)**	**Pineapple (Mean±SD)**	**Banana (Mean±SD)**
Bifenthrin	0.001±1.00	<LOD	<LOD	<LOD	<LOD	<LOD
Permethrin	0.006±0.71	0.006±0.90	0.006±2.56	0.004±1.02	0.001±0.03	0.012±2.55
Cyfluthrin	0.015±0.91	0.012±1.01	0.002±1.02	0.011±1.58	0.010±2.45	0.003±1.00
Cypermethrin	0.002±1.23	0.005±1.23	0.008±1.60	0.004±2.51	0.006±1.32	0.004±2.01
Fenvalerate	0.001±2.44	0.005±1.11	<LOD	0.004±1.59	0.005±0.77	<LOD
Deltamethrin	0.004±1.01	0.004±1.40	<LOD	0.007±1.10	0.007±1.70	0.006±2.78

LOD= Limit of Detection. SD = Standard Deviation

Table 10. Highest concentration of pesticide residues (mg/kg) found in fruits from farms and markets within the study area compared with FAO/WHOs MRLs.

Pesticides	Highest amounts found			Maximum residue limits (mg/kg)		
	Mango	Pineapple	Banana	Mango	Pineapple	Banana
Organochlorines						
β-HCH	0.007	-	-	0.01	0.01	0.01
γ-HCH	0.013	0.038	0.004	0.01	0.01	0.01
δ-HCH	0.014	0.024	-	0.01	0.01	0.01
Heptachlor	0.006	0.004	-	0.01	0.01	0.01
α-endosulfan	0.030	0.046	0.008	0.05	0.05	0.05
p,p'-DDE	0.043	0.026	0.002	0.05	0.05	0.05
β-endosulfan	0.006	0.027	0.010	0.05	0.05	0.05
p,p'-DDT	0.004	0.005	0.014	0.05	0.05	0.05
Endosulfan sulfa.	0.024	0.013	0.006	0.05	0.05	0.05
Methoxychlor	0.027	0.048	-	0.01	0.01	0.01
Pyrethroids						
Bifenthrin	0.020	0.033	-	0.03	0.05	0.1
Permethrin	0.036	0.035	0.018	0.05	0.05	0.05
Cyfluthrin	0.078	0.059	0.005	0.02	0.02	0.02
Cypermethrin	0.018	0.037	0.012	0.7	0.05	0.05
Fenvalerate	0.025	0.028	-	0.02	0.02	0.02
Deltamethrin	0.018	0.040	0.006	0.05	0.05	0.05

(-) Not detected

p,p'-DDE and *p,p'*-DDT were detected in samples from most farms; except in PN3 where neither DDT nor its metabolites were detected. DDT/DDE ratios as can be calculated from Table 7 are indicative of historic uses of DDT rather than fresh inputs. Methoxychlor was detected in relatively high concentrations in 100% of samples of pineapples, mean concentrations ranging from 0.003mg/kg in farms PN2 to as high as 0.012mg/kg in farms PN4.

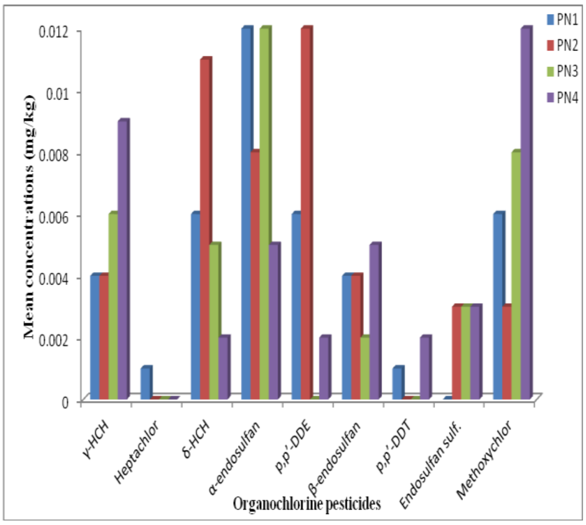

Figure 5. Mean levels of organochlorine pesticide residues in pineapples from the farms.

For clearer comparisons of frequency and levels of occurrence, Figure 5 indicates high levels of α-endosulfan, methoxychlor and γ-HCH (lindane). These are active compounds and their detection at levels recorded should be worrying to the consumer, unlike in mangoes where *p,p'*-DDE and endosulfan sulfate were detected in significant mean concentrations. These levels could be an indication of recent uses of these more persistent compounds on pineapple instead of the approved less persistent pyrethroids.

Table 11. Mean concentrations of synthetic pyrethroid residues in pineapples from farms.

Pesticides	Yilo Farms (mg/kg)		Manya farms (mg/kg)	
	PN1 (Mean±SD)	PN2 (Mean±SD)	PN3(Mean±SD)	PN4 (Mean±SD)
Bifenthrin	0.006±1.88	0.007±1.10	0.007±2.50	0.013±3.21
Permethrin	0.001±3.11	0.009±1.00	0.009±3.11	0.009±0.99
Cyfluthrin	0.010±2.72	0.015±4.20	0.006±1.22	0.006±2.00
Cypermethrin	0.008±5.00	0.005±2.15	0.008±5.00	0.005±2.15
Fenvalerate	0.010±1.90	0.004±0.86	<LOD	0.004±1.94
Deltamethrin	0.001±2.01	0.007±2.01	0.011±2.10	0.010±1.23

Each value is a mean of five farm samples with four determinations

LOD= Limit of Detection. PN1, PN2, PN3, PN4 = Pineapple farms at sites within the study area

SD = Standard Deviation

Table 8 summarizes the mean concentrations of detected synthetic pyrethroids residues in samples of pineapple from the farms within the study districts. Bifenthrin was detected in all samples from the districts with mean concentrations ranging from 0.006mg/kg – 0.013mg/kg. Permethrin had levels of 0.001mg/kg in farms PN1 and 0.009mg/kg was recorded in samples from all other three farms, PN2-PN4. Cyfluthrin, Cypermethrin and Deltamethrin were all detected in 100% of farm pineapple samples with mean values ranging from 0.001mg/kg-0.010mg/kg of deltamethrin residues and 0.006mg/kg-0.015mg/kg of cyfluthrin residues. Fenvalerate was not detected in any sample from farms PN3.

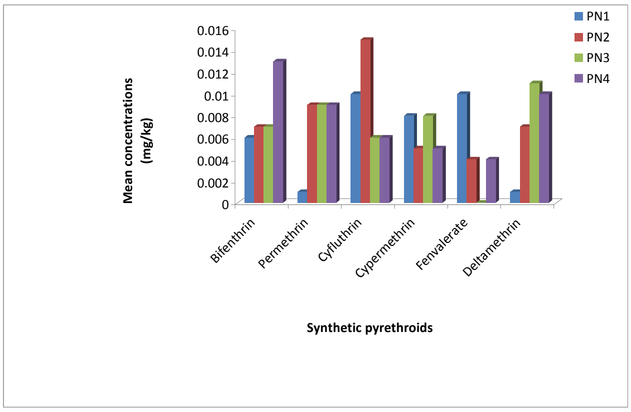

Figure 6. Comparison of synthetic pyrethroid residues in pineapples from the various farms

Figure 6 corroborates the widespread detection of the synthetic pyrethroids in pineapple samples from farms within the districts. In an exception of fenvalerate that was not detected in farms PN3, all the other farms had significant levels of these synthetic pyrethroid residues.

Mean concentration of organochlorine and synthetic pyrethroid residues detected in fruits from the markets

Table 9 below summarizes the organochlorine pesticide residual concentrations detected in fruit samples from the markets within the study districts. The β-isomer of HCH was detected with a mean value of 0.002mg/kg in mangoes from Yilo markets but not in any other fruit from the other markets sampled in the two districts. δ-HCH was not detected in any sample from any of the markets sampled while the γ-isomer was detected in all but banana from the markets. Mean concentrations of 0.001mg/kg and 0.004mg/kg were recorded in mango whilst pineapples were 0.006mg/kg and 0.009mg/kg respectively from Yilo and Manya farms.

Endosulfan was detected in all fruits from the markets with mean values of between 0.002mg/kg to 0.010mg/kg; and there was a 100% occurrence of the α-isomer in all fruits sampled. Endosulfan sulfate was not detected in pineapples from the Yilo markets; the β-isomer being absent from mangoes from the Yilo markets as well. Significantly high levels of *p,p'*-DDT (0.007mg/kg each) were detected in banana sampled from the markets as compared to the farms in the districts. This result could suggest fresh use and/or the past widespread use of DDT in agriculture (Nakata *et al.*, 2002). Since bananas are not cultivated on commercial scale within the study districts, the levels could be attributed to contaminated soil as a result of DDTs stability and persistency. Most of this fruit is grown in the backyard gardens and on old rubbish dumps which might contain metal-based pesticides. Due to DDTs persistence, some of this could be found in the soil and taken up into fruits that are cultivated on these soils. Initial survey did not indicate any fresh inputs and so such alarming levels could be as a result of recent uses.

Table 10 summarizes synthetic pyrethroids detected in mango, pineapple and banana in the study areas. Allethrin, Fenpropathrin and Lambda-cyhalothrin were all omitted from the table because levels in all samples were below the LOD, perhaps confirming pyrethroids break down quickly after application and are extremely less persistent compared to the organochlorines.

Bifenthrin, though registered in Ghana as an insecticide and permitted to be used on fruits, was only detected in mango in Yilo Krobo markets with mean concentration of 0.001mg/kg.

Permethrin, Cyfluthrin and Cypermethrin were detected in all fruits sampled from the markets in the area. With concentrations ranging from 0.001mg/kg to 0.015mg/kg, the synthetic pyrethroids are perhaps the most widely distributed residues (among ones detected) in fruits from the markets within the study area.

Fenvalerate was not detected in any banana samples from the two market areas, perhaps confirming their temporary nature or the fact that banana is not exposed to much pesticides as the other two fruits. Similarly, deltamethrin was not detected in banana from Yilo markets but a mean concentration of 0.006mg/kg was detected in Manya market samples (Table 10). The widespread detection and distribution of synthetic pyrethroids in fruits is a positive indication compliance of farmers moving away from the more persistent organochlorines to the less persistent synthetic pyrethroids.

Tolerance Limits

The concentration of organochlorine pesticides in various fruits samples from farms and markets within the study districts were compared with maximum residue limits (MRLs) set forth by the FAO/WHO Codex Alimentarius Commission (Table 10).

From table 4.8, the highest concentration of γ-HCH (lindane) was found in pineapple samples from the farms and markets (0.038mg/kg) and this value is relatively higher than the MRLs of this pesticide in the survey fruits (0.01mg/kg). The corresponding lindane value in mango was also above MRL, 0.013mg/kg as compared to 0.010 mg/kg. Level in banana (0.004mg/kg) was however below MRL.

δ-HCH was also found to be above the MRL values of 0.01mg/kg in all three fruits sampled. Levels of 0.014mg/kg and 0.024mg/kg were respectively found in mangoes and pineapples from the study area. Banana from the study area, however, do not record residues of this pesticide.

Concentrations of α- and β- endosulfan were quite high (0.030mg/kg and 0.046mg/kg) but are not above MRL values of 0.05mg/kg set for these fruits (Table 11). This therefore makes the rather high levels of endosulfan "favourable".

Methoxychlor recorded the highest amount of residues of 0.027mg/kg and 0.048mg/kg respectively in mangoes and pineapples. These levels are almost thrice and five times respectively their MRL values of 0.01mg/kg.

Levels of DDT in banana were significantly high (0.014mg/kg) but very much below the MRL value of 0.05mg/kg. All other organochlorine pesticides detected had values lower than their corresponding MRL values in all three fruits and therefore do not present any significant health risks to consumers.

For the pyrethroids, cyfluthrin recorded the highest levels of 0.078mg/kg and 0.059mg/kg respectively in mangoes and pineapples. These levels are three to four times above the MRL value set for this pesticide in the sampled fruits (0.02mg/kg). Fenvalerate is the only other pyrethroid which presented mean values above the MRLs set forth for these pesticides by the European Union (EU) (Table 11). High values of 0.025 mg/kg and 0.028mg/kg were detected in mangoes and pineapples respectively as against the MRL values of 0.02mg/kg.

Generally, Table 4.8 reveals that most of the fruit samples analyzed contain residues of the monitored pesticides below the MRLs adopted by the FAO/WHO Codex Alimentarius Commission, except for methoxychlor, cyfluthrin and fenvalerate (in mangoes and pineapples).

Conclusions

The data revealed that most mango and pineapple samples and all banana samples analyzed contain residues of the monitored organochlorine residues (γ-HCH, δ-HCH, aldrin, dieldrin, heptachlor, γ-chlordane, endosulfan s, *p, p'*-DDE etc.) and synthetic pyrethroid residues (allethrin, bifenthrin, fenpropathrin, permethrin, cyfluthrin etc.) below the European Union maximum residue limits (MRLs). Some pesticide residues (heptachlor, γ-chlordane, endrin, dieldrin, allethrin, labda-cyhalothrin and fenpropathrin) were largely undetected in the fruits sampled.

The analyzed fruit matrices however showed the presence of a few pesticide residues (δ-HCH, γ-HCH, methoxychlor, cyfluthrin and fenvalerate) at concentrations above EU MRLs.

The widespread detection and distribution of synthetic pyrethroids in fruits is a positive indication of compliance of farmers moving away from the more persistent organochlorines to the less persistent synthetic pyrethroids.

Significantly high levels of *p,p'*-DDT (0.007mg/kg each) were detected in banana sampled from the two markets as compared to the farms in the districts and this could be attributed to contaminated soil as a result of DDTs stability and persistencysince initial survey did not indicate any fresh inputs .

The results also show that 15.6% of the fruit samples analyzed contained no detectable levels of monitored pesticides, 78.2% of the samples gave results with trace levels of pesticide residues below the MRLs, whilst only 6.2% of the samples were above the MRL.

About 69% of the respondents in the survey on the general public's perceptions of pesticide residues on fruits and any related adverse health effects were aware of pesticide residues in fruits and the corresponding adverse effect on human health. Some have experienced pesticide poisoning after fruit consumption. Thus many wish pesticide usage in fruit and crop cultivation in general is curbed or minimized to only those who can ensure reduced levels.

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