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Assessment of Pesticide Residues in Vegetables at the Farm Gate: Cabbage (*Brassica oleracea*) Cultivation in Cape Coast, Ghana

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ABSTRACT

Pesticide residue analysis carried out at the farm gate, market level and other spatial scales may be of immense significance as an indicator of the potential risks that pesticide exposure has on human health. Cabbage samples at the farm-gate were analysed to determine the types of pesticides used by vegetable farmers in Cape Coast and ascertain whether levels of pesticide residues are below permissible Maximum Residue Limits. Twenty-one pesticide residues were detected in the cabbage samples of which 9 are *pyrethroids* and 12 are *organophosphates*. Pesticide residues at levels exceeding the Maximum Residue Limits were found in more than two-thirds of the total number of samples. The results are as follows: Allethrin (1.52411 ± 3.024054 mg kg^{-1}), deltamethrin (4.74690 ± 1.694768 mg kg^{-1}), cypermethrin (0.31180 ± 0.367967 mg kg^{-1}), fenvalerate 2 (0.20590 ± 0.150179 mg kg^{-1}), permethrin (0.14700 ± 0.066119 mg kg^{-1}), ethoprophos (1.13544 ± 0.442078 µg g^{-1}), phorate (0.67820 ± 0.809661 µg g^{-1}), chlorfenvinp (0.31520 ± 0.155821 µg g^{-1}) and fenitrothion (0.16500 ± 0.189241 µg g^{-1}). High levels of pesticide residue were observed for allenthrin (9.566 mg kg^{-1}) and phorate (2.077 µg g^{-1}). Three of the pesticide residues (cypermethrin, permethrin and parathion) are considered to be potentially carcinogenic. Methamidophos and fenvalerate are the only pesticide residues that were not detected in any of the samples whereas fonofos, profenofos, clorfenvinp and pirimiphos-methyl were restricted to cabbage samples from only one location. Strong correlations exist among a number of pesticide residues suggesting a common origin. Principal component analysis indicates that the data is a two-component system explaining 63% of total variance. Component 1 shows strong positive factor loadings on cypermethrin, deltamethrin and cyfluthrin 3 whereas component 2 shows strong negative factor loadings on phorate and fenvalerate 2. Cluster analysis grouped the pesticide residues into two spatially dissimilar categories of 6 and 4 members. The high levels and wide assortment of pesticide residues found in this study suggest the need to put into effect regulations regarding the proper use of pesticides on vegetables.

Key words: Pyrethroids, organophosphates, cabbage, human health, cluster analysis, principal component analysis

INTRODUCTION

Since 1950, the use of pesticides has increased 50 folds and 2.5 million tons of industrial pesticides are now used annually (Farag *et al.*, 2011). This is to be expected as food security issues particularly in developing countries are very high on the international agenda. Pests contribute significantly to food losses and the control of pests is very central to the attainment of food security at all spatial scales (Iya and Kwaghe, 2007; Al-Eed *et al.*, 2006). Pesticides are extensively used in agricultural production to check or control pests, diseases weeds and other plant pathogens in an effort to reduce or eliminate yield losses and preserve high product quality (Eskenazi *et al.*, 2008;

Sanborn *et al.*, 2004). Although pesticides are manufactured under very strict regulation processes to function with logical certainty and minimal impact on human health and the environment, serious concerns have been raised about health risks resulting from residues in food (Damalas and Eleftherohorinos, 2011; Eskenazi *et al.*, 2008). By their very nature, most pesticides show a high degree of toxicity because they are intended to kill certain organisms and thus create some risk of harm (Abdelgadirand and Adam, 2011; Zidan, 2009). Within this framework, pesticide use has evoked grave concerns not only of potential effects on human health but also about impacts on wildlife and sensitive ecosystems (Power, 2010; Damalas and Eleftherohorinos, 2011).

In developing countries such as Ghana, farmers face immense risks of exposure owing to the use of toxic chemicals that are banned or restricted in other countries (Nasr *et al.*, 2007; Al-Eed *et al.*, 2006; Adhikari, 2010). Wrong application techniques, badly maintained or totally unsuitable spraying equipment and inadequate storage practices exacerbate these risks (Al-Wabel *et al.*, 2011). Often the reuse of old pesticide containers for food and water storage also contributes to the risk of exposure (Ecobichon, 2001; Damalas and Eleftherohorinos, 2011). Pesticide residues in/on plants may be unavoidable even when pesticides are used in accordance with good agriculture practices (Uysal-Paha and Bilisli, 2006). Research conducted for the past decade in Ghana and internationally point to the presence of pesticide residues in a number of food items including strawberries, onions, cucumber, lettuce, cabbage, okra, pepper, tomatoes, beans, oranges and lemons (Hanson *et al.* 2007; Hussain *et al.*, 2002; El-Nahhal, 2004). Pesticide residues do not only constitute a possible danger to soil microfauna and microflora (Pal *et al.*, 2006). In fact, their toxic effects on humans are manifest when bioaccumulation occurs along the food chain after initial plant uptake (Hanson *et al.*, 2007; Pal *et al.*, 2006; Al-Wabel *et al.*, 2011).

Vegetable production is a key component of Ghana's food security strategy (Parker *et al.*, 2010). One such vegetable is cabbage and a wide array of pests attacks it. Consequently, pesticides such as Attak, Desbin, PAWA-karate, Dursban 4 E, Fura 3G, Bossmate 2.5 E and Pyrinex among others, is used in Ghana to deal with these pests. Most vegetable farmers in Ghana (87%) use synthetic chemical pesticides to control pests on vegetables including a number of highly persistent organochlorine pesticides (Essumang *et al.*, 2008). Lax regulations have allowed inappropriate application practices to develop, such as mixing of two or more pesticides (Farag *et al.*, 2011). Lack of knowledge of the types, use and the effects (additive, synergistic, independent and antagonistic) of these pesticides among small and large scale farmers has resulted in their misuse and consequently their accumulation in various foods and feed items (Essumang *et al.*, 2008; Farag *et al.*, 2011). According to Farag *et al.* (2011) reliable pesticide residue analysis may be of immense significance as indicators of the potential risks of pesticide exposure on human health.

Pesticides residues on crops are monitored with reference to maximum residue limits and are based on analysis of quantity of a given residue remaining on food product samples. The Maximum Residue Limit (MRL) is not a health-based exposure limit and thus exposure to residue in excess of an MRL does not necessarily imply a risk to health (Boobis *et al.*, 2008). This is because the use of a pesticide would not be allowed if the proposed MRL resulted in long-term and short-term exposure of pesticide residue and the human diet above safety limit. The units of the pyrethroid and organophosphate residues are given in $mg\,kg^{-1}$ and $\mu g\,g^{-1}$, respectively. The aim of the study was to assess whether pesticide residues in cabbage grown under pesticide application comply with the allowed MRLs set by the European Union. Specifically, this study therefore set out to:

- Determine the types of pesticides used by vegetable farmers in Cape Coast
- Assess and compare the levels of pesticide residues in cabbage from two main vegetable-growing hubs in Cape Coast

- Compare the levels of pesticide residues to the EU allowed Maximum Residue Limit (MRL) values for each active ingredient identified

MATERIALS AND METHODS

Study area: Forty cabbage samples was collected from a cabbage farm close to the industrial area (Fig. 1) and the University of Cape Coast Technology farm in the Cape Coast Metropolis (5° 14" 0' N to 5° 5" 30' N and 1° 14" 30' W to 1° 22" 30 W) (Parker *et al.*, 2010). Sampling was carried out from December 2010 to April 2011.The original samples were then condensed into 10 composite samples. The metropolis covers about 122 km². The vegetation is mainly coastal savanna grassland. The area has a bi-modal rainy season from May to June and August to October with an annual rainfall ranging between 750 and 1000 mm (Parker *et al.*, 2010). The soils at the research site are Acrisols (Parker *et al.*, 2010).

Experimental procedure

Extraction process: The method of extraction used was the USEPA method 3510 for extracting multi-residue pesticides in non fatty crops. The extraction was done with ethyl acetate as the solvent. Sodium hydrogen carbonate ($NaHCO_3$) was used to neutralise any acid that may be present. The sample was washed thoroughly with distilled water. The sample was placed in mortor and anhydrous sodium sulphate (Na_2SO_4) was used to remove water from the sample matrix. Twenty grams of the fresh cabbage was weighed using the Libror-3200 series weighing balance. After weighing, the sample was washed thoroughly with distilled water. The sample was placed in a mortar and with the help of a pestle it was ground into a paste. The paste was transferred into a conical flask with the help of a spatula. Ethyl acetate (40 mL) was added and the mixture was shaken thoroughly. A 5 g portion of sodium hydrogen carbonate ($NaHCO_3$) was added
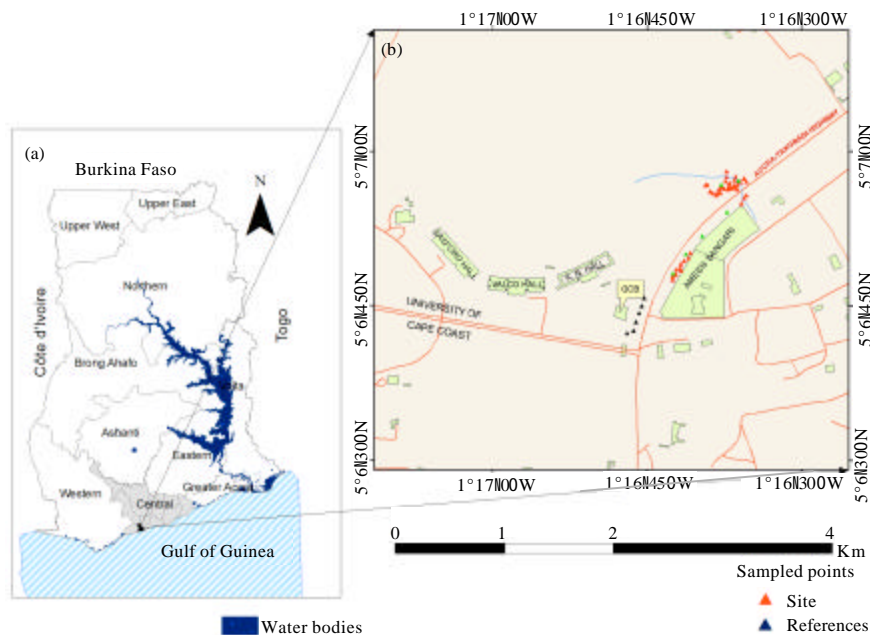

Fig. 1: Map of study area showing sampling points; (a) Ghana-central region and (b) Research area (Cape coast)

to the mixture followed by 20 g of anhydrous sodium sulphate (Na_2SO_4) and the entire mixture was shaken vigorously for four to five hours. This was to ensure that enough of the pesticide residue dissolved in the ethyl acetate. The procedure was repeated for the samples from each location. The mixture was then filtered into a labeled container. The mixture was centrifuged at a speed of 1800 rpm for 5 min and the organic layer was decanted into a container. A 1:1 mixture of 5 mL ethyl acetate and cyclohexane was then added.

Procedure for clean-up: A 10 mm chromatographic column was filled with 3 g activated silica gel and topped up with 2 to 3 g of anhydrous sodium sulphate. Next, 5 mL of n-hexane was added to the column by allowing the tap to run. The residue in 2 mL n-hexane was then transferred onto the column and the extract rinsed thrice with 2 mL hexane. The procedure was repeated for all the samples. The samples from the UCC Technology village (School farm) were labeled S.F 1-S.F 5 and the samples from the farm behind Ameen Sangari industries were labeled A.M 1-A.M 5. The samples were sealed and placed in the refrigerator at the laboratory below room temperature to prevent evaporation of the ethyl acetate. The crude extract was filtered and taken to the Ghana Standards Board Analytical Chemistry Laboratory for Gas Chromatography analysis. Spectroscopic data on pesticide residues detected in the samples is shown in appendix 1.

Gas chromatography: The instrument used in the GC analysis was Varian CP-3800 GC. It is easily configured to perform online analysis for monitoring critical gas and liquid process streams. A 25 μL glass Hamilton syringe was used to inject the GC samples. Only 2-4 μL of the sample was injected onto the column. The syringe was examined carefully before it was filled. A small amount of the liquid was slowly drawn by raising the plunger and then pressed to expel the liquid back into the liquid. This served to "rinse" the syringe with the sample, ensuring that what was measured in the GC run was the composition of the mixture. The rinsing process was repeated twice. Then the plunger was slowly drawn up again while the needle was in the liquid and the syringe was carefully filled with the liquid. Small air bubbles in the syringe did not affect the GC run. The sample was injected into the injector port. Two things were done sequentially and quickly. The needle of the syringe was pushed through the injector pot and immediately the plunger was pressed to inject the sample. Then immediately the start button on the recorder was pressed. A bit of resistance was felt from the rubber septum in the injector port. The recorder was observed for some time. Within several minutes, it recorded several peaks and the GC run was ended. The recorder printed out the peaks, the retention times and the areas under the peaks.

Calculation of pesticide residue concentration: The pesticide residue concentration was deduced from the following equation:

$$C = a/b \times d \times f$$

Where:
C = Concentration of pesticide residue (ppm)
a = The concentration of the identified analyte in the sample solution from GC determination step (ppm)
b = The sample equivalent in the extraction step (ppm)
d = The dilution factor of GPC cleanup step
f = The dilution factor of Silica gel column cleanup step

Multivariate statistics: Descriptive statistics of pesticide residues were performed using MS-Excel and SPSS version 16. Elements of descriptive statistics of samples (distribution, dispersion, central tendency) generated included mean, range, minimum, maximum, skewness, kurtosis, variance, median, mode, standard deviation and percentiles. Cluster analysis and Principal Component Analysis (PCA) were also performed using SPSS version 16. PCA produces several important outputs of which two namely Eigen values: the variances accounted for by the component; and eigenvectors: that specify the directions of the PCA axes were considered in the analysis.

RESULTS

Concentrations of pesticide residues: Twenty-one pesticide residues were detected in the cabbage samples of which 9 (allenthrin, bifenthrin, lambda-cyhalothrin, fenvalerate 2, cyfluthrin 3, cypermethrin, cypermethrin 2, permethrin and deltamethrin) are pyrethroids and 12 (diazinon, fenitrothion, ethoprophos, chlorpyrifos, phorate, fonofos, pirimidophos-m, profenofos, malathion, dimethoate, chlorfenvinp and parathion-et) are organophosphates. The level of Allethrin detected in A.M.1 was higher than the Maximum Residual Limit (MRL) by a factor of 20. The level detected in A.M.1 is not legally permitted or acceptable in food under the laws of the EU. Levels of allethrin residues detected in all other samples fall below the MRL for cabbage. Eu maximum residual limits of permitted in cabbage are shown in Table 1 and levels of pesticide residues in samples from Ameen Sangari is shown in Table 2.

The levels of allethrin residues detected in cabbage from four S.F. locations were slightly above the allowed MRLs (Table 3). There was no detected residue of allethrin in S.F3. The average allethrin residue in cabbage from A.M locations was relatively higher than in the S.F samples.

The average value for phorate residue in the cabbages from A.M samples was 1.475 µg g^{-1} (Table 4). This value is 30 times above the MRL. This is quite high and may be due to over application of pesticides on the cabbage from this location i.e. (vegetable farm behind Ameen Sangari industries). The average peak value for phorate residues in the cabbage from S.F. samples was 0.024 µg g^{-1}. This value is below the MRL. The levels of ethoprophos detected in the cabbage from the vegetable farm behind Ameen Sangari industries were above the maximum residue limit (Table 5).

Table 1: EU Maximum Residue Limits (MRLs) of Permitted in Cabbage

Peak name	MRLs	Year of adoption
Allethrin	0.5 mg kg^{-1}	2008
Bifenthrin	0.5 mg kg^{-1}	1995
Cyfluthrin3	0.1 mg kg^{-1}	2008
Fenvalerate	3.0 mg kg^{-1}	---
Permethrin	5.0 mg kg^{-1}	---
Lambda-cyhalothrin	0.3 mg kg^{-1}	2009
Deltamethrin	2 mg kg^{-1}	---
Cypermethrin	0.7 mg kg^{-1}	2009
Methamidophos	1.0 µg g^{-1}	---
Ethoprophos	0.02 µg g^{-1}	2005
Phorate	0.05 µg g^{-1}	2006
Diazinon	0.5 µg g^{-1}	2005
Chlorpyrifos	1.0 µg g^{-1}	2003
Malathion	0.5 µg g^{-1}	2006
Parathion-et	0.05 µg g^{-1}	2004
Dimethoate	0.05 µg g^{-1}	2003
Fenitrothion	0.5 µg g^{-1}	---

Table 2: Types and levels of pesticide residues in samples from Ameen Sangari area

Peak name	AM1-AM5 (mg kg^{-1})				
	AM1	AM2	AM3	AM4	AM5
Allethrin	9.566	0.339	0.355	0.297	0.270
Bifenthrin	0.036	0.013	0.009	0.019	0.008
Lambda-cyhalothrin	0.077	0.104	0.095	0.036	0.068
Permethrin	0.161	0.104	0.077	0.070	0.228
Cyfluthrin3	0.134	0.130	0.138	0.103	0.106
Cypermethrin	1.168	0.420	0.257	0.370	0.657
Cypermethrin 2	0.041	0.050	0.053	0.028	0.077
Fenvalerate	ND	ND	ND	ND	ND
Fenvalerate2	0.126	0.482	0.288	0.365	0.333
Deltamethrin	7.052	6.815	6.799	3.377	5.833

ND: Not detected; AM1-AM5 represents the five sites at the farm near Ameen Sangari industries

Table 3: Types and levels of pesticide residues in samples from UCC technology farm

Peak name	SF1-SF5 (mg kg^{-1})				
	SF1	SF2	SF3	SF4	SF5
Allethrin	0.915	0.550	ND	0.714	0.711
Bifenthrin	0.009	0.009	0.004	0.007	0.011
Lambda-cyhalothrin	0.048	0.064	0.048	0.068	0.097
Permethrin	0.068	0.208	0.159	0.149	0.246
Cyfluthrin3	0.033	0.032	0.018	0.028	0.033
Cypermethrin	0.046	0.099	0.042	0.038	0.021
Cypermethrin 2	0.011	ND	0.011	ND	ND
Fenvalerate	ND	ND	ND	ND	ND
Fenvalerate2	0.064	0.074	0.169	0.102	0.056
Deltamethrin	2.751	4.243	3.344	3.253	4.002

ND: Not detected; SF1-SF5 represents the five sites at the University of Cape Coast Technology village

Table 4: Types and levels of pesticide residues in samples from Ameen Sangari area

Peak name	AM1-AM5 (μg g^{-1})				
	AM1	AM2	AM3	AM4	AM5
Methamidophos	ND	ND	ND	ND	ND
Ethoprophos	1.166	1.661	1.592	1.358	1.601
Phorate	0.933	0.863	0.811	2.077	1.977
Diazinon	0.075	0.004	0.004	0.062	0.052
Fonofos	0.255	0.026	0.018	0.010	0.047
Pirimiphos-m	0.055	0.010	0.011	0.073	0.023
Chlorpyrifos	0.078	0.042	0.006	0.039	0.089
Malathion	0.242	0.047	0.024	0.036	0.110
Parathion-et	0.018	0.015	0.019	0.021	0.051
Chlorfenvinp	0.423	0.396	0.311	0.047	0.399
Dimethoate	ND	0.059	ND	ND	ND
Fenitrothion	ND	ND	ND	ND	0.010
Profenofos	ND	ND	ND	ND	0.024

ND: Not detected; AM1-AM5 represents the five sites at the farm near Ameen Sangari industries

Table 5: Types and levels of pesticide residues in samples from UCC Technology Farm

| | SF1-SF5 (µg g^{-1}) | | | | |
Peak name	SF1	SF2	SF3	SF4	SF5
Methamidophos	ND	ND	ND	ND	ND
Ethoprophos	0.655	0.714	0.531	ND	0.941
Phorate	0.053	0.024	0.010	0.019	0.015
Diazinon	0.006	ND	0.001	ND	ND
Fonofos	ND	ND	ND	ND	ND
Pirimiphos-m	ND	ND	ND	ND	ND
Chlorpyrifos	0.062	0.009	0.063	0.006	0.013
Malathion	0.008	0.023	0.032	0.023	0.064
Parathion-et	0.017	0.013	0.01	0.018	0.006
Chlorfenvinp	ND	ND	ND	ND	ND
Dimethoate	ND	0.038	0.027	0.037	0.054
Fenitrothion	0.018	0.226	0.406	ND	ND
Profenofos	ND	ND	ND	ND	ND

ND: Not detected; SF1-SF5 represents the five sites at the Unuversity of Cape Coast Technology Village

Table 6: Summary statistics of pesticide residue concentrations

Pesticide residue	Mean	Standard deviation	Minimum	Maximum
Allethrin	1.52411	±3.024054	0.270 mg kg^{-1}	9.566 mg kg^{-1}
Bifenthrin	0.01250	±0.009168	0.004 mg kg^{-1}	0.036 mg kg^{-1}
Lambda-cyhalothrin	0.07050	±0.022912	0.036 mg kg^{-1}	0.104 mg kg^{-1}
Permethrin	0.14700	±0.066119	0.068 mg kg^{-1}	0.246 mg kg^{-1}
Cyfluthrin3	0.07550	±0.050610	0.018 mg kg^{-1}	0.138 mg kg^{-1}
Cypermethrin	0.31180	±0.367967	0.021 mg kg^{-1}	1.168 mg kg^{-1}
Cypermethrin 2	0.03871	±0.023991	0.011 mg kg^{-1}	0.077 mg kg^{-1}
Fenvalerate2	0.20590	±0.150179	0.056 mg kg^{-1}	0.482 mg kg^{-1}
Deltamethrin	4.74690	±1.694768	2.751 mg kg^{-1}	7.052 mg kg^{-1}
Ethoprophos	1.13544	±0.442078	0.531 µg g^{-1}	1.661 µg g^{-1}
Phorate	0.67820	±0.809661	0.010 µg g^{-1}	2.077 µg g^{-1}
Diazinon	0.02914	±0.032396	0.001 µg g^{-1}	0.075 µg g^{-1}
Fonofos	0.07120	±0.103666	0.010 µg g^{-1}	0.255 µg g^{-1}
Pirimiphos-m	0.03440	±0.028228	0.010 µg g^{-1}	0.073 µg g^{-1}
Chlorpyrifos	0.04070	±0.031376	0.006 µg g^{-1}	0.089 µg g^{-1}
Malathion	0.06090	±0.069840	0.008 µg g^{-1}	0.242 µg g^{-1}
Parathion-et	0.01880	±0.012182	0.006 µg g^{-1}	0.051 µg g^{-1}
Chlorfenvinp	0.31520	±0.155821	0.047 µg g^{-1}	0.423 µg g^{-1}
Dimethoate	0.04300	±0.013172	0.027 µg g^{-1}	0.059 µg g^{-1}
Fenitrothion	0.16500	±0.189241	0.010 µg g^{-1}	0.406 µg g^{-1}

Summary statistics of pesticide residue concentrations: Pesticide residue concentrations show a high degree of variability as shown in Table 6. The highest pesticide residue concentration (9.566 mg kg^{-1}) is attributed to allethrin while the lowest (0.001 µg g^{-1}) is attributed to diazinon. The highest mean concentration of pesticide residue (4.7469 mg kg^{-1}) is attributed to deltamethrin.

Correlation of pesticide residues: Strong associations exist among pesticide residues at different levels of confidence (Table 7). Bifenthrin has strong positive correlations with cypermethrin and malathion at the 0.01 level suggesting a common origin. Lambda-cyhalothrin is strongly correlated

Table 7: Correlation matrix of pesticide residues

	Bifenthrin	Lambdacyhalothrin	Permethrin	Cyfluthrin3	Cypermethrin	Fenvalerate2	Deltamethrin	Phorate	Chlorpyrifos	Malathion	Parathion-et
Bifenthrin	1										
Lambdacyhalothrin	0.073	1									
Permethrin	-0.094	0.229	1								
Cyfluthrin3	0.560	0.406	-0.327	1							
Cypermethrin	0.827**	0.150	0.046	0.752*	1						
Fenvalerate2	0.041	0.197	-0.369	0.716*	0.317	1					
Deltamethrin	0.459	0.695*	0.026	0.857***	0.717*	0.499	1				
Phorate	0.354	-0.138	-0.170	0.717*	0.604	0.728*	0.383	1			
Chlorpyrifos	0.328	-0.317	0.042	0.247	0.608	0.200	0.182	0.434	1		
Malathion	0.826**	0.195	0.322	0.489	0.910**	-0.021	0.582	0.330	0.562	1	
Parathionet	-0.027	-0.137	0.137	0.400	0.450	0.414	0.281	0.719*	0.535	0.259	1

**Correlation is significant at the 0.01 level (2-tailed). *Correlation is significant at the 0.05 level (2-tailed)

with deltamethrin at the 0.05 level. Cyfluthrin 3 shows strong positive correlation with cypermethrin, fenvalerate 2 and phorate at the 0.05 level and with deltamethrin at the 0.01 level. Cypermethrin is strongly correlated with deltamethrin, phorate, chlorpyrifos and malathion at different levels of confidence. Fenvalerate 2 shows strong positive with phorate at the 0.05 level whereas parathion-et shows strong positive correlation with phorate at the 0.05 level.

Principal component and cluster analyses: Principal component analysis indicates that the data on pesticide residues is a two-component system explaining 63% of the variability in the data (Table 8). The First component alone explains almost half of the variability in the data whereas first three components extracted explain approximately 80% of the variability in the data. The screen plot (Fig. 2) confirms that the data is a two-component system. From the component matrix (Table 9), component 1 shows strong positive factor loadings on cypermethrin, deltamethrin and cyfluthrin 3 suggesting a common origin whereas component 2 shows strong negative factor loadings on phorate and fenvalerate 2. Component 3 exhibits strong positive factor loadings on

Table 8: Variance of data explained by each component

Component	Initial eigenvalues			Extraction sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	5.013	45.573	45.573	5.013	45.573	45.573
2	1.993	18.117	63.690	1.993	18.117	63.690
3	1.869	16.988	80.678	1.869	16.988	80.678
4	1.241	11.279	91.958	1.241	11.279	91.958
5	0.455	4.134	96.092	0.455	4.134	96.092
6	0.285	2.594	98.686	0.285	2.594	98.686
7	0.088	0.804	99.490	0.088	0.804	99.490
8	0.041	0.369	99.858	0.041	0.369	99.858
9	0.016	0.142	100.000	0.016	0.142	100.000
10	-3.287E-17	-2.988E-16	100.000	3.287E-17	2.988E-16	100.000
11	-2.743E-16	-2.493E-15	100.000	2.743E-16	2.493E-15	100.000

Extraction method: Principal component analysis

Table 9: Component matrix of extracted components

Component matrix[a]	Component										
	1	2	3	4	5	6	7	8	9	10	11
Bifenthrin	0.690	0.419	-0.153	-0.522	0.199	0.051	0.065	0.031	0.067	8.938E-11	6.014E-9
Lambdacyhalothrin	0.250	0.454	0.763	0.312	-0.121	0.000	0.193	0.010	0.005	-6.753E-10	-2.471E-9
Permethrin	-0.058	0.563	-0.266	0.723	0.197	0.208	-0.055	-0.023	0.025	1.380E-9	-6.061E-11
Cyfluthrin3	0.898	-0.145	0.381	-0.116	0.036	-0.083	-0.012	-0.080	-0.008	4.239E-9	-7.828E-10
Cypermethrin	0.944	0.227	-0.191	-0.100	0.008	-0.041	-0.062	0.070	0.009	-2.854E-10	-1.273E-8
Fenvalerate2	0.579	-0.618	0.399	0.087	-0.052	0.319	-0.034	0.098	-0.006	5.296E-10	2.766E-9
Deltamethrin	0.802	0.233	0.470	0.145	-0.145	-0.096	-0.167	-0.042	0.020	-2.387E-9	4.428E-9
Phorate	0.762	-0.523	-0.117	0.079	0.321	0.097	0.068	-0.090	-0.012	-2.509E-9	-2.313E-9
Chlorpyrifos	0.564	-0.113	-0.644	0.051	-0.480	0.124	0.060	-0.054	0.023	1.140E-10	1.337E-10
Malathion	0.764	0.554	-0.311	-0.040	0.007	0.014	0.018	0.026	-0.095	-1.375E-10	4.665E-9
Parathion-et	0.557	-0.439	-0.325	0.535	0.055	-0.308	0.048	0.067	0.017	3.862E-10	3.865E-9

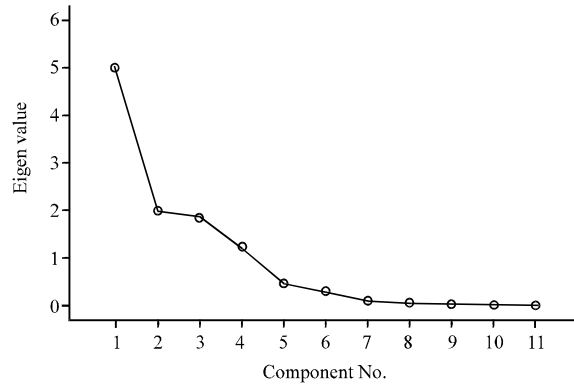Extraction method: Principal component analysis, [a]11 components extracted

Fig. 2: Scree plot showing eigenvalues and number of components extracted
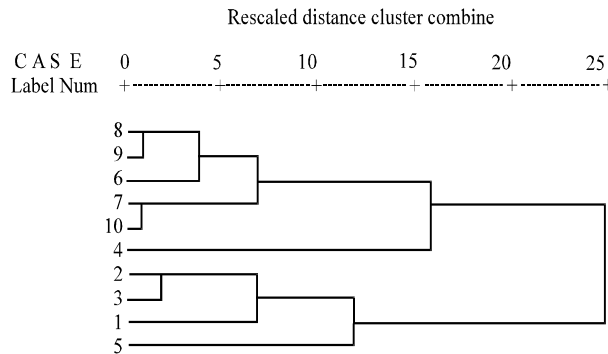

Fig. 3: Dendrogram showing each cluster and respective members

lambda-cyhalothrin and strong negative factor loadings on chlorpyrifos. Cluster analysis grouped the sample locations into two spatially dissimilar categories based on the levels of pesticide residues. Cluster one consists of 6 members whereas cluster two consists of 4 members (Fig. 3).

DISCUSSION

The levels of allethrin detected in samples from both locations were above the MRL for cabbage. This may either be due to early harvest of the cabbage which does not allow most of the allethrin to decompose or be degraded by the cabbage plant or due to differences in soil composition in these sites. Fenvalerate was not detected in any of the samples analysed from the two locations. This may be attributed to the fact that they do not use pesticides that contain fenvalerate as an active ingredient. It may also be due to decomposition or degradation of fenvalerate before the analysis was carried out. Some of the pesticides used on cabbage in the farm behind Ameen Sangari industries include Attak, Desbin, PAWA-karate whereas on the UCC Technology farm Dursban 4 E, Fura 3G, Bossmate 2.5 E, Pyrinex are used. It has been established that the levels of Lambda-cyhalothrin, Chlorpyrifos, Fenitrothion and Cypermethrin residue in tomatoes were above their respective MRL values (Essumang *et al.*, 2008). Consequently, this study confirms the work of Essumang *et al.* (2008) regarding the observation that some pesticide residues in vegetables are above the allowed MRLs. However, unlike in this study which focused on cabbage, Essumang *et al.* (2008) experimented on tomatoes. They collected tomato fruits from different

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market places in Kumasi in the Ashanti region and Cape Coast in the central region of Ghana for analysis. The levels of ethoprophos detected in the cabbage from the vegetable farm behind Ameen Sangari industries were above the maximum residue limit by factors ranging from 58.3 and 80.1. The application of pesticides on tomatoes will be different from the application of pesticides on the cabbage used in this research in terms of dosage and the frequency of pesticide application. There were no detected peaks of fenvalerate and methamidophos in the samples used in this research. Significant levels of fenvalerate and methamidophos have been detected in the analysis of pesticide residues in fruits and vegetables in Sweden (Pihlstrom *et al.*, 2007). This work appears to contradict the work of Pihlstrom *et al.* (2007) given that neither fenvalerate nor methamidophos were detected in the study. It is important however; to distinguish that Pihlstrom *et al.* (2007) based their work on market-level sampling whereas this study focused on cabbage obtained at the farm gate. Again, Ripley *et al.* (2000) reported pesticide residues in vegetables (cabbage) and fruits in Canada; however, the levels were far below the MRLs. EL-Saeid (2003) used Supercritical Fluid Extraction (SFE) in the analysis of pesticide residues unlike in this study where Gas Chromatography was used. Also, EL-Saeid (2003) sampled canned foods, fruits and vegetables whereas this study sampled fresh cabbage. Ahn *et al.* (2011) has shown that diazinon and chlopyrifos residues were stable up to 30 months and this needs public attention. An integrated approach to pesticide use should be encouraged and this should fit broadly in a framework in which certain criteria are used for pesticides selection, specific instructions are followed for their application on crops and residue analysis is used as one of the tools for enforcement (Damalas and Eleftherohorinos, 2011). Pesticides that are selected for use on vegetables should be:

- Biologically effective (high selectivity, fast impact, optimal residual effect, good plant tolerance, low risk of resistance)
- User friendly (low acute toxicity and low chronic toxicity, optimum formulation, safe packaging, easy application method, long store stability)
- Environmentally friendly/compatible (low toxicity to non-target organisms, fast degradation in the environment, low mobility in the soil, no residues in food and fodder above the MRLs, low application rate)

Presence of pesticide residues in vegetables and fruits is an indicative change in use pattern of pesticides in Ghana where shift has taken place from organochlorines to the easily degradable groups of pesticides over the last few years. Monitoring studies are imperative to know actual status of contamination due to toxic pesticide residues for future policies as well as to strengthen the confidence of consumer in quality of food. It is therefore, suggested that such studies may be extended to other fruits grown in different agro-climatic regions of Ghana. These issues are central to minimising the risk posed to human health on exposure to pesticides in food.

CONCLUSION

Pesticides are extensively used in agricultural production to check or control pests, diseases weeds and other plant pathogens in an effort to reduce or eliminate yield losses and preserve high product quality. This study assessed the types of pesticides used by cabbage farmers and the levels of pesticide residues in detected in the cabbage samples of which 9 are *pyrethroids* and 12 are *organophosphates*. The cabbage samples from two vegetable growing hubs in Cape Coast, Ghana. Twenty-one pesticide residues were results are as follows: Allethrin (1.52411 ± 3.024054 mg kg^{-1}),

deltamethrin (4.74690±1.694768 mg kg^{-1}), cypermethrin (0.31180±0.367967 mg kg^{-1}), fenvalerate 2 (.20590±0.150179 mg kg^{-1}), permethrin (0.14700±0.066119 mg kg^{-})^1, ethoprophos (1.13544 µg g^{-1}±0.442078), phorate (0.67820 µg g^{-1}±0.809661), chlorfenvinp (0.31520±0.155821 µg g^{-1}) and fenitrothion (0.16500±0.189241 µg g^{-1}). High levels of pesticide residue were observed for allenthrin (9.566 mg kg^{-1}) and phorate (2.077 µg g^{-1}). Methamidophos and fenvalerate were not detected in any of the samples. The level of Allethrin detected in some cabbage samples was higher than the Maximum Residual Limit (MRL) by a factor of 20. At least one pesticide residue was detected in more than half the samples analyzed. Broadly, this could be attributed to wrong application techniques, badly maintained or totally unsuitable spraying equipment, inadequate storage practices and often the reuse of old pesticide containers for food and water storage. Certainly, this suggests the need to enforce regulations and educate vegetable farmers regarding the proper use and management of pesticides.

ACKNOWLEDGMENTS
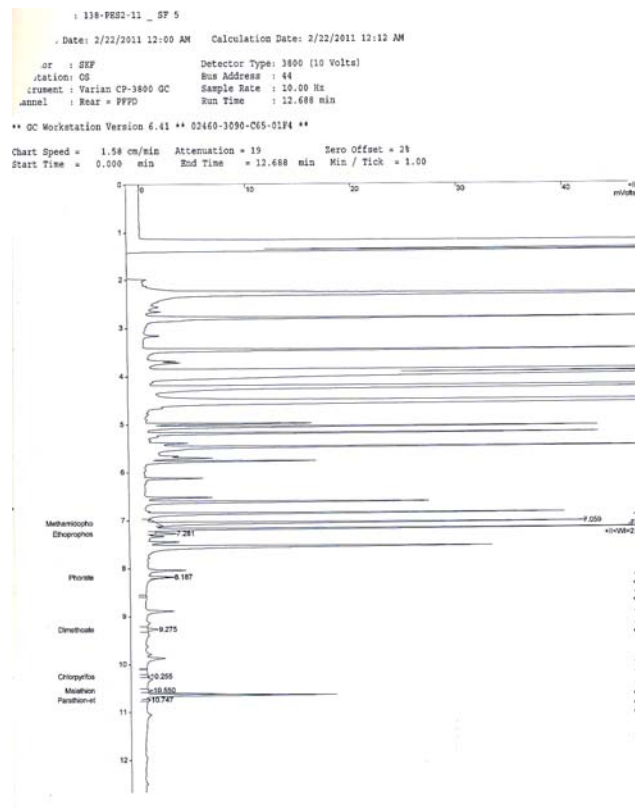
APPENDIX

Appendix continued:

Appendix continued:

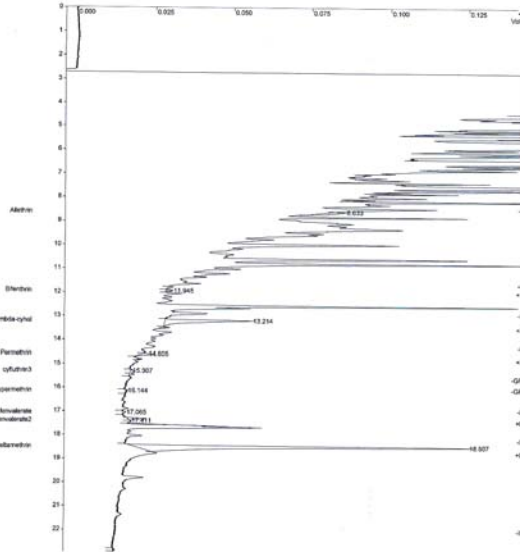Sample ID   : 134-PES2-11 _ SF 5

Injection Date: 2/21/2011 7:29 PM   Calculation Date: 2/21/2011 7:52 PM

Operator   : SKF   Detector Type: 3800 (10 Volts)
Workstation: OS   Bus Address : 44
Instrument : Varian CP-3800 GC   Sample Rate : 10.00 Hz
Channel   : Middle = ECD   Run Time   : 22.978 min

** GC Workstation Version 6.41 ** 02460-3090-C65-01F4 **

Chart Speed =   0.87 cm/min   Attenuation = 68   Zero Offset = 2%
Start Time =   0.000 min   End Time = 22.978 min   Min / Tick = 1.00
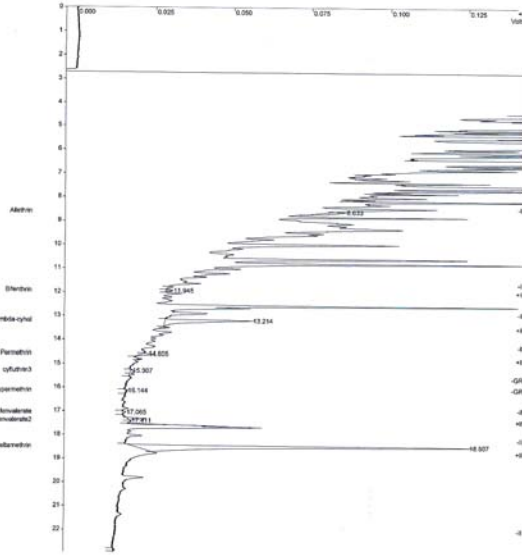
: 137-PES2-11 _ SF 4

Date: 2/21/2011 11:43 PM   Calculation Date: 2/21/2011 11:56 PM

.or : SKF   Detector Type: 3800 (10 Volts)
station: Od   Bus Address : 44
.rument : Varian CP-3800 GC   Sample Rate : 10.00 Hz
.annel : Rear = PFPD   Run Time   : 12.688 min

** GC Workstation Version 6.41 ** 02460-3090-C65-01F4 **

Chart Speed =   1.58 cm/min   Attenuation = 66   Zero Offset = 2%
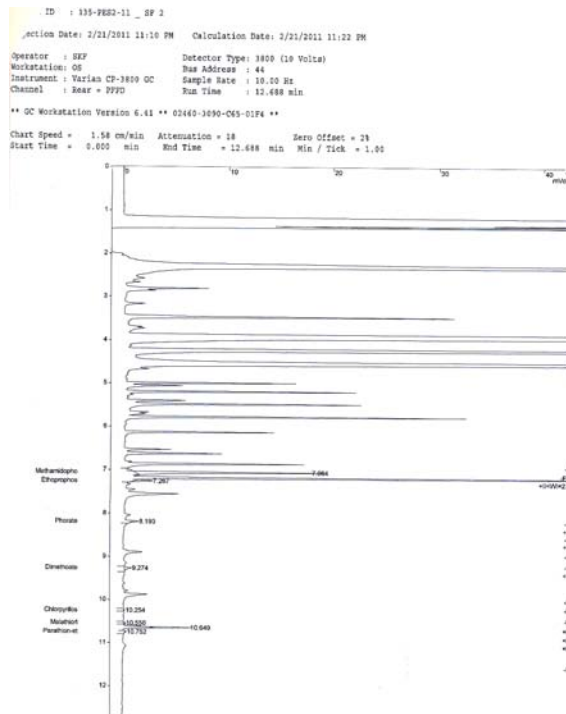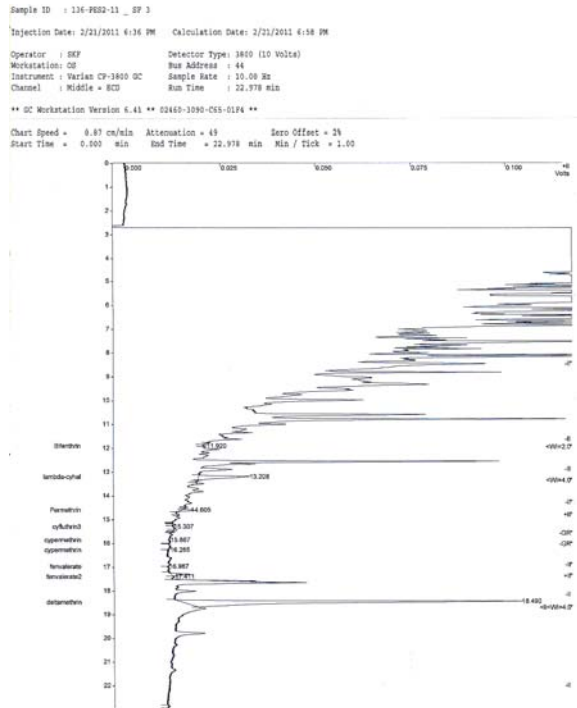Start Time =   0.000 min   End Time = 12.688 min   Min / Tick = 1.00

Appendix continued:

Sample ID : 136-PES2-11 _ SF 3

Injection Date: 2/21/2011 6:36 PM   Calculation Date: 2/21/2011 6:58 PM

Operator   : SKF   Detector Type: 3800 (10 Volts)
Workstation: OS   Bus Address : 44
Instrument : Varian CP-3800 GC   Sample Rate : 10.00 Hz
Channel   : Middle = ECD   Run Time   : 22.978 min

** GC Workstation Version 6.41 ** 02460-3090-C65-01F4 **

Chart Speed =   0.87 cm/min   Attenuation = 49   Zero Offset = 2%
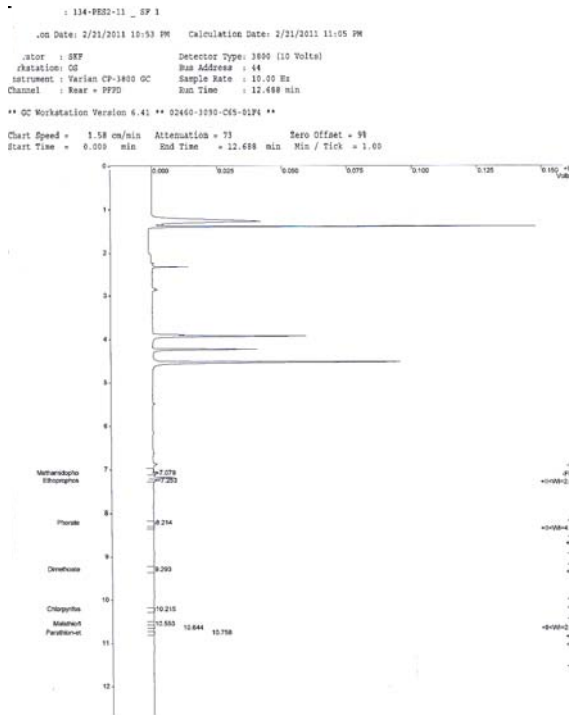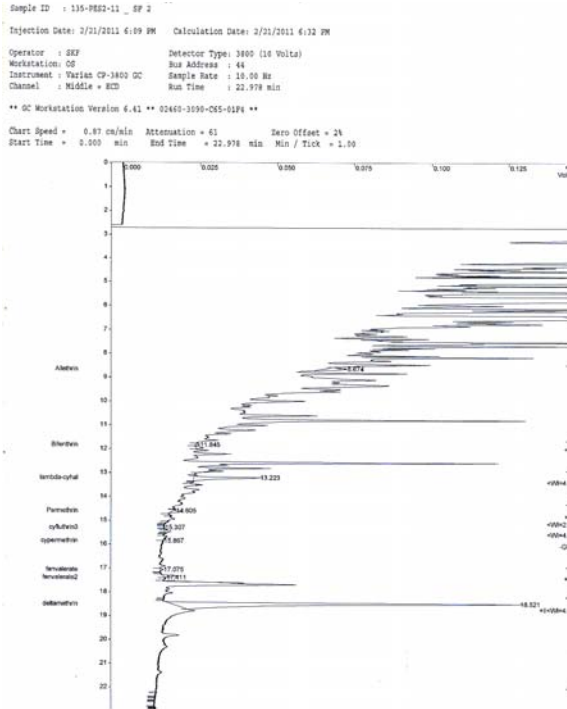Start Time =   0.000 min   End Time = 22.978 min   Min / Tick = 1.00

. ID : 135-PES2-11 _ SF 2

,ection Date: 2/21/2011 11:10 PM   Calculation Date: 2/21/2011 11:22 PM

Operator   : SKF   Detector Type: 3800 (10 Volts)
Workstation: OS   Bus Address : 44
Instrument : Varian CP-3800 GC   Sample Rate : 10.00 Hz
Channel   : Rear = PFPD   Run Time   : 12.688 min

** GC Workstation Version 6.41 ** 02460-3090-C65-01F4 **

Chart Speed =   1.58 cm/min   Attenuation = 18   Zero Offset = 2%
Start Time =   0.000 min   End Time = 12.688 min Min / Tick = 1.00

Appendix continued:

Sample ID : 135-PES2-11 _ SF 2

Injection Date: 2/21/2011 6:09 PM   Calculation Date: 2/21/2011 6:32 PM

Operator : SKF   Detector Type: 3800 (10 Volts)
Workstation: OS   Bus Address : 44
Instrument : Varian CP-3800 GC   Sample Rate : 10.00 Hz
Channel   : Middle = ECD   Run Time   : 22.978 min

** GC Workstation Version 6.41 ** 02460-3090-C65-01F4 **

Chart Speed = 0.87 cm/min Attenuation = 61   Zero Offset = 2%
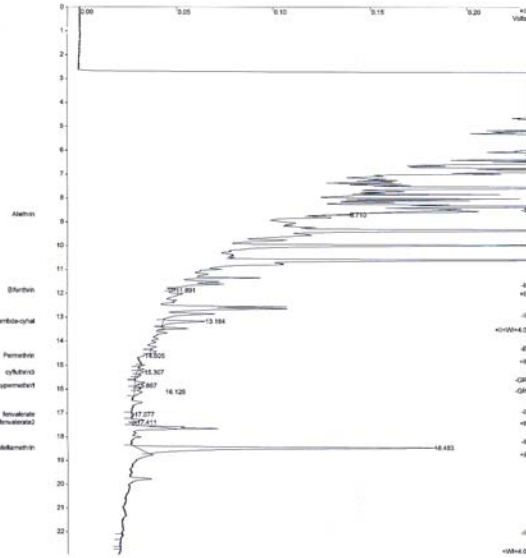Start Time = 0.000 min   End Time   = 22.978 min Min / Tick = 1.00

: 134-PES2-11 _ SF 1

.on Date: 2/21/2011 10:53 PM   Calculation Date: 2/21/2011 11:05 PM

.ator : SKF   Detector Type: 3800 (10 Volts)
rkstation: OS   Bus Address : 44
strument : Varian CP-3800 GC   Sample Rate : 10.00 Hz
Channel   : Rear = PFPD   Run Time   : 12.688 min

** GC Workstation Version 6.41 ** 02460-3090-C65-01F4 **

Chart Speed = 1.58 cm/min Attenuation = 73   Zero Offset = 9%
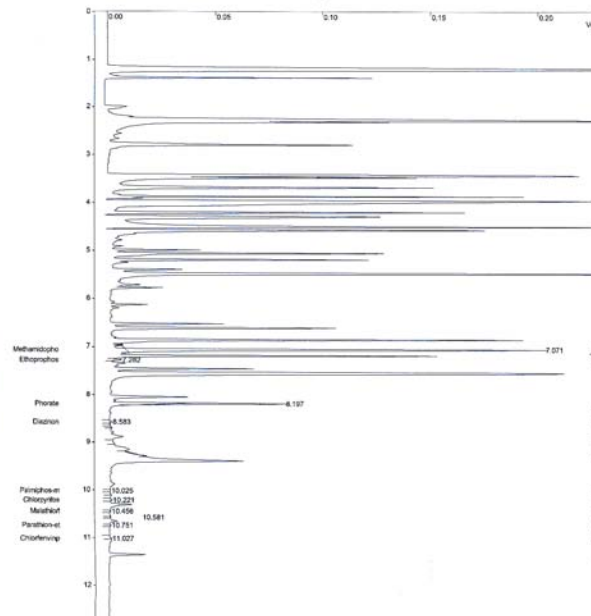Start Time = 0.000 min   End Time   = 12.688 min Min / Tick = 1.00

Appendix continued:

Sample ID : 134-PES2-11 _ SF 1

Injection Date: 2/21/2011 5:42 PM   Calculation Date: 2/21/2011 6:05 PM

Operator   : SKF   Detector Type: 3800 (10 Volts)
Workstation: OS   Bus Address : 44
Instrument : Varian CP-3800 GC   Sample Rate : 10.00 Hz
Channel   : Middle = ECD   Run Time   : 22.978 min

** GC Workstation Version 6.41 ** 02460-3090-C65-01F4 **

Chart Speed =   0.87 cm/min   Attenuation = 40   Zero Offset = 2%
Start Time =   0.000 min   End Time   = 22.978 min   Min / Tick = 1.00

: 143-PES2-11 _ AM 5
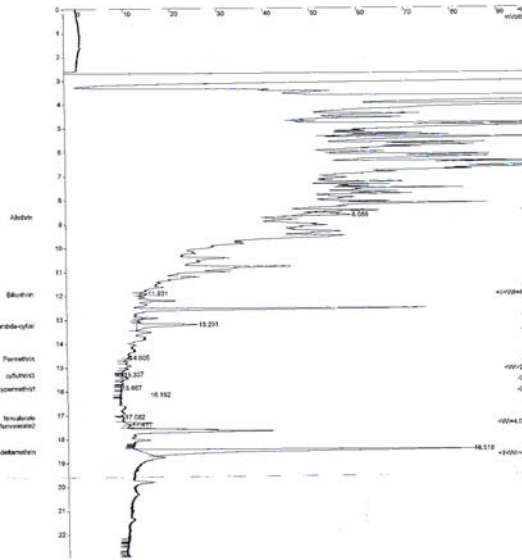
d Date: 2/22/2011 1:24 AM   Calculation Date: 2/22/2011 1:36 AM

.cor   : SKF   Detector Type: 3800 (10 Volts)
.station: OS   Bus Address : 44
.strument : Varian CP-3800 GC   Sample Rate : 10.00 Hz
.hannel   : Rear = PFPD   Run Time   : 12.688 min

** GC Workstation Version 6.41 ** 02460-3090-C65-01F4 **

Chart Speed =   1.58 cm/min   Attenuation = 89   Zero Offset = 2%
Start Time =   0.000 min   End Time   = 12.688 min   Min / Tick = 1.00

Appendix continued:

Appendix continued:

Sample ID : 142-PES2-11 _ AM 4

Injection Date: 2/21/2011 9:15 PM   Calculation Date: 2/21/2011 9:38 PM
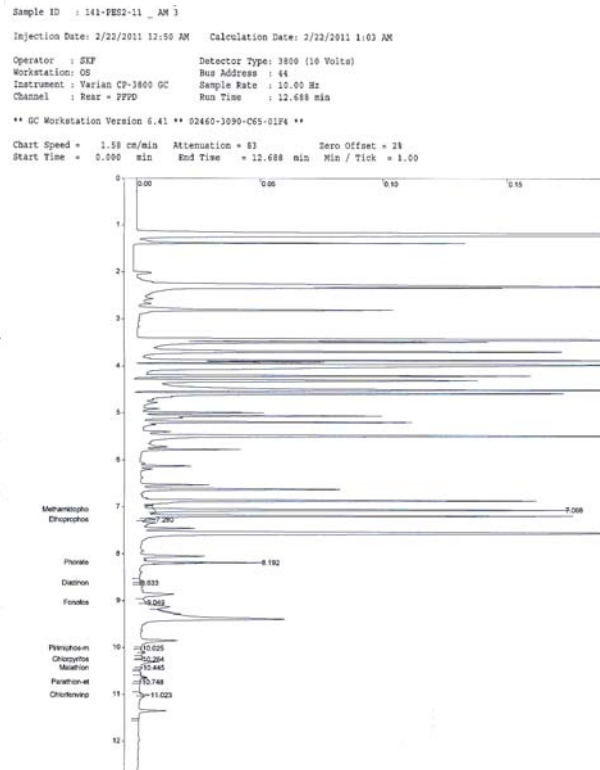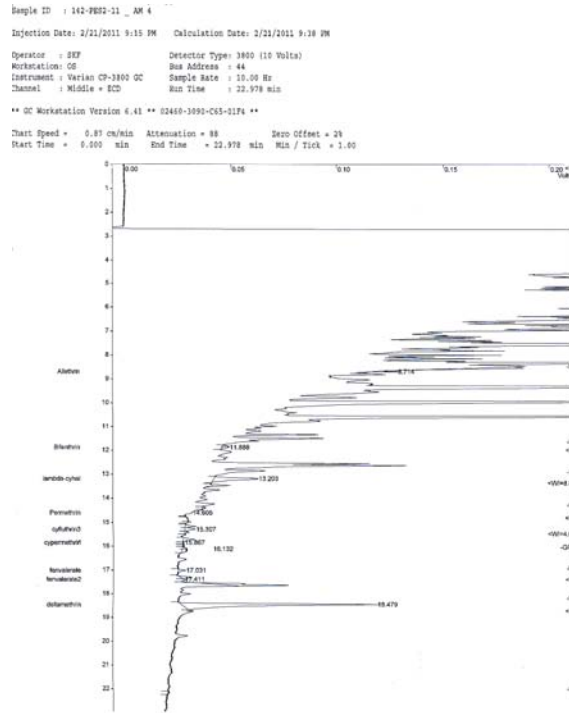
Operator   : SKF   Detector Type: 3800 (10 Volts)
Workstation: OS   Bus Address : 44
Instrument : Varian CP-3800 GC   Sample Rate : 10.00 Hz
Channel   : Middle = ECD   Run Time   : 22.978 min

** GC Workstation Version 6.41 ** 02460-3090-C65-01F4 **

Chart Speed =   0.87 cm/min   Attenuation = 88   Zero Offset = 2%
Start Time =   0.000 min   End Time   = 22.978 min Min / Tick = 1.00

Sample ID : 141-PES2-11 _ AM 3

Injection Date: 2/22/2011 12:50 AM   Calculation Date: 2/22/2011 1:03 AM

Operator   : SKF   Detector Type: 3800 (10 Volts)
Workstation: OS   Bus Address : 44
Instrument : Varian CP-3800 GC   Sample Rate : 10.00 Hz
Channel   : Rear = PFPD   Run Time   : 12.688 min

** GC Workstation Version 6.41 ** 02460-3090-C65-01F4 **

Chart Speed =   1.58 cm/min   Attenuation = 83   Zero Offset = 2%
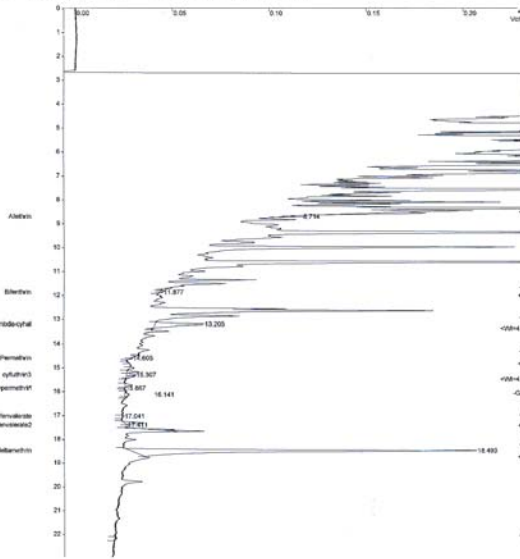Start Time =   0.000 min   End Time   = 12.688 min Min / Tick = 1.00

Appendix continued:

Appendix continued:

Sample ID   : 140-PES2-11 _ AM 2

Injection Date: 2/21/2011 8:32 PM   Calculation Date: 2/21/2011 8:45 PM

Operator   : SKF   Detector Type: 3800 (10 Volts)
Workstation: OS   Bus Address   : 44
Instrument : Varian CP-3800 GC   Sample Rate : 10.00 Hz
Channel   : Middle = ECD   Run Time   : 22.978 min

'* GC Workstation Version 6.41 ** 02460-3090-C65-01P4 **

Chart Speed =   0.87 cm/min Attenuation = 101   Zero Offset = 2%
Start Time =   0.000 min   End Time = 22.978 min   Min / Tick = 1.00

ID   : 139-PES2-11 _ AM 1

Injection Date: 2/22/2011 12:17 AM   Calculation Date: 2/22/2011 12:29 AM

Operator   : SKF   Detector Type: 3800 (10 Volts)
Workstation: OS   Bus Address   : 44
Instrument : Varian CP-3800 GC   Sample Rate : 10.00 Hz
Channel   : Rear = PFPD   Run Time   : 12.688 min

'* GC Workstation Version 6.41 ** 02460-3090-C65-01P4 **

Chart Speed =   1.58 cm/min Attenuation = 81   Zero Offset = 2%
Start Time =   0.000 min   End Time = 12.688 min   Min / Tick = 1.00
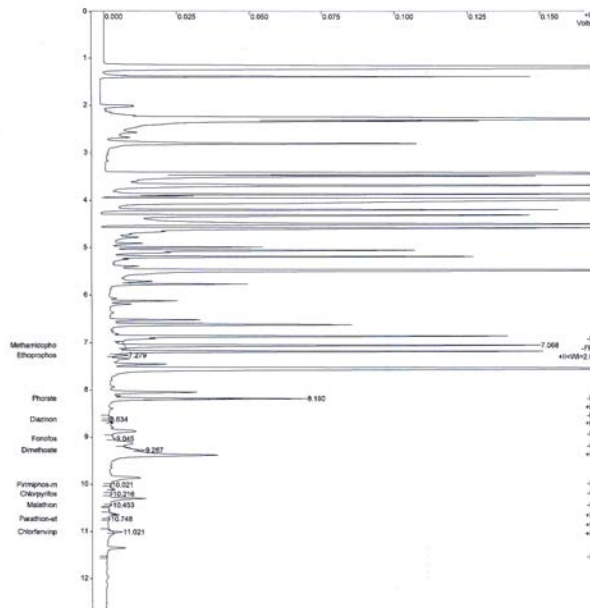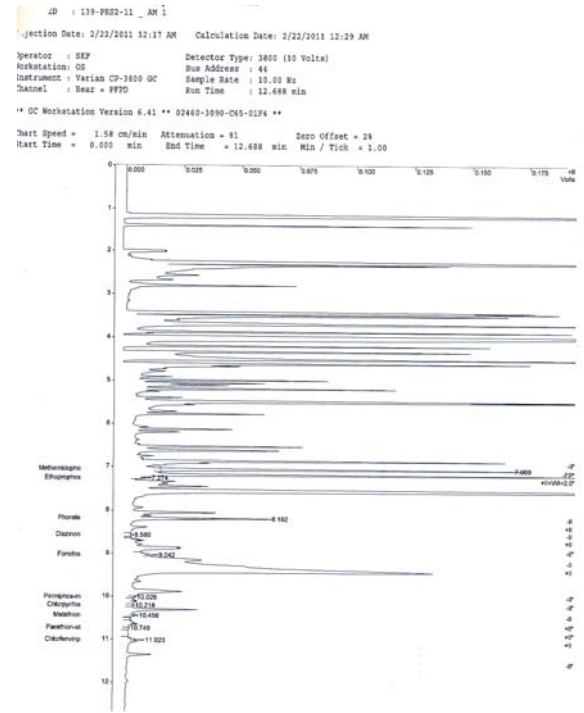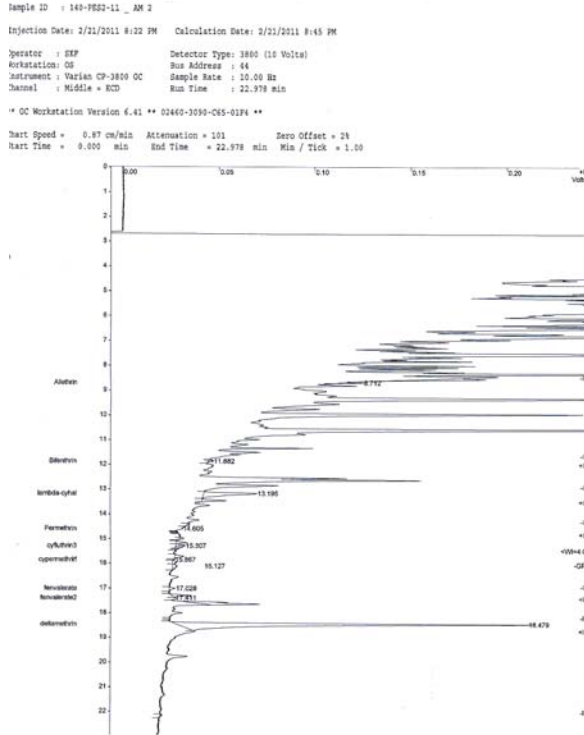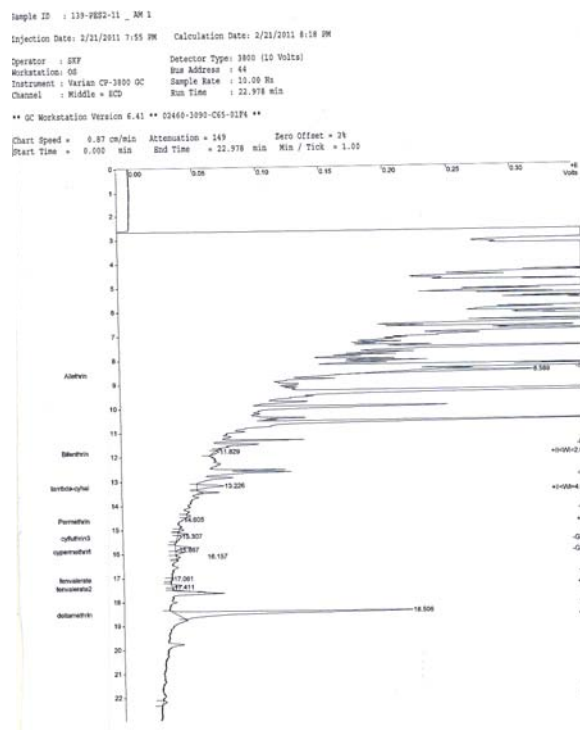

Appendix continued:

Appendix 1: Spectroscopic data on pesticide residues

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