



Residues of organochlorine pesticides in vegetables marketed in Greater Accra Region of Ghana

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ABSTRACT

Residual levels of organochlorine pesticides (OCPs) were determined in 240 samples of vegetables collected from selected markets from Greater Accra region of Ghana in July 2010 to February 2011. The determination was done using gas chromatography with electron capture detector (GC–ECD). The compounds targeted were lindane, heptachlor + its epoxide, endrin, dieldrin, o,p'-DDE, p,p'-DDE, o,p'-DDD, o,p'-DDT and p,p'-DDT. The results indicated that all the vegetables sampled had some levels of one or more OCPs in them. Residues of pesticides were found in 71.9% of all the vegetable samples analyzed indicating high incidence of these xenobiotics in the vegetables from the markets and 31.48% samples were above the maximum residue levels (MRLs). The most frequently found and abundant pesticides were the metabolites of DDT (o,p'-DDE, p,p'-DDE and o,p'-DDD), followed by lindane and then o,p'-DDT. The residue levels and the detection rate of the OCPs indicate that, vegetables from supermarket had higher OCPs levels, followed by roadside grocery stores and open markets. The results recommend the need for regular monitoring of a greater number of samples for long periods for pesticide residues especially in fruits and vegetables to protect consumers' health.

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1. Introduction

Agriculture is Ghana's most important economic sector, employing more than half the population on a formal and informal basis and accounting for almost half of GDP and export earnings. More than two-thirds of Ghana's population live in rural areas and their livelihood continue to revolve around agriculture (Clark, 1994). In the process of development of agriculture, pesticides have become an important tool as a plant protection agent for boosting food production. Further pesticides play a significant role by keeping many dreadful diseases.

Vegetables are important group of crops and they constitute major part of the human diet contributing to humans required nutrients and vitamins. Many farmers in the villages have taken up vegetable production on commercial basis and some grow them in home gardens. But in the urban areas people depend on the market for their vegetable requirements (Chowdhury, Razzaque, & Khan,

2011). For better production and esthetic value, farmers are using a large amount of insecticides during the entire period of growth of vegetables, even at fruiting stage and sometimes farmers also ignored the recommended waiting period between the harvest and last spray (Baig, Akhtera, Ashfaq, & Asi, 2009).

As an agriculture-based nation, use of pesticides contributes much to the national development and prevents people from suffering diseases. The use of pesticides has been increasing very rapidly because of the expansion of area cultivated under food crops and vegetables. Pesticides are widely used in vegetables because of their susceptibility to insect and disease attacks. Farmers in general use many types of pesticides to control harmful insects to minimize crop loses, however, most of them are illiterate and use pesticides indiscriminately. It is reported that huge pesticides are used on crops and vegetables and their irrational use are common with applications being carried out on periodic basis throughout the growing season.

For example in Ghana, it is estimated that 87% of farmers use pesticides in vegetables production (Bempah & Donkor, 2010). Among these pesticides, major concern has been directed to organochlorines (OCs) because of their persistency, low cost, versatility against various pests, bioaccumulative nature and

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potential toxic effects to wildlife and humans. The irrational and continuous use of these pesticides results in frighteningly accumulation of high residual levels in primary agriculture products (Sudaryanto et al., 2007).

The problem of residues accumulation needs more attention in vegetables because most of time these are consumed either raw or without much storage time (Kumar, Gupta, Garg, & Kumar, 2006). Consequently, interest on pesticide toxicity has particularly increased over the past years owing to increasing evidence of carcinogenic, mutagenic and teratogenic effects in experimental animals and exposed humans (Tahir, Naik, Rehman, & Shahzad, 2009). Furthermore, the usage of these chemicals has occasionally been accompanied by risk to human health and the environment because of their toxic potential, high persistence, bioaccumulation (Bempah, Donkor, Yeboah, Dubey, & Osei-Fosu, 2011).

Consequently, concerns about environmental contamination by persistent organochlorine pesticides (OCPs) used in agriculture and in vector control are certainly justified. These fears of environmental pollution have motivated many countries to investigate the magnitude of human and animal health implication (Manirakiza, Akinbamijo, Covaci, Pitonzo, & Schepens, 2003). For this reason, it is important to develop a program that seek to monitor pesticide residues in food for an extensive evaluation of food quality which is a priority objective of pesticide research to avoid possible risks to human health.

These programs could determine the amount of the contamination problem and recognize a way to solve the situation. Pesticide residue monitoring studies have been reported in many developed countries on fruits and vegetables (Baig et al., 2009; Fontcuberta et al., 2008; Luke, Matsumoto, Cairns, & Hundley, 1988; Rosa, González-Rodríguez, Rial-Otero, Cancho-Grande, & Simal-Gándara, 2008). In contrast, there is very little information on the levels of pesticide residues in fruits, vegetables and other food crops in developing countries, like Ghana. Few studies conducted so far in Ghana reveal levels of pesticides in water, sediments, food, fruits and vegetables (Bempah & Donkor, 2010; Bempah et al., 2011; Darko & Acquah, 2006; Ntow, 2001, 2005; Osafo & Frempong, 1998) which are emanating from current and past use of these chemicals.

No data are available on the levels of pesticide residues in vegetables sold in local markets of Ghana. Therefore, the present study was undertaken to monitor pesticide residues in vegetables grown in Ghana to provide background information on the levels and distribution of these residues. It will also look for the safety of vegetables in terms of pesticide residues.

2. Materials and methods

2.1. Sample collection

A total of 240 vegetable samples were purchased from different market centers (supermarkets, roadside grocery stores and open markets) within Greater Accra region of Ghana during the period of July 2010 to February 2011. Composite samples consisting of 1–2 kg of each vegetable samples (tomato, carrot, cabbage and lettuce samples) was collected on a monthly basis and each was put and sealed in sterile polyethylene bags and labeled with a unique sample identity and placed in an iced chest box and transported to pesticide residues laboratory of Ghana Atomic Energy Commission. During the transportation of the samples, it was assured that these were protected against any alterations in the residue-situation. In the laboratory, samples were frozen in the refrigerator and analyzed within a week after collection.

2.2. Chemicals and reagents

Pesticide reference standards, with certified purity of at least 98% were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Pesticide grade ethyl acetate and acetone were supplied by Labscan (Dublin, Ireland) and anhydrous sodium hydrogen carbonate and sodium sulfate analytical grade were purchased from Merck (Darmstadt, F.R. Germany). Solid-phase florasil cartridges column size (500 mg/8 mL) was obtained from Honeywell Burdick & Jackson (Muskegon, USA).

2.3. Analysis of pesticide residues

2.3.1. Extraction and clean up

Netherlands analytical methods for pesticide residues in foodstuffs (2007) with modifications were followed. A 50 g amount of fresh vegetable samples were chopped 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 3000 rpm to obtain the two phases. The extraction process was followed by a clean-up step using solid-phase extraction with florasil. The florasil column (500 mg/8 mL) cartridge was conditioned with 10 mL of ethyl acetate. Pesticides in sample extract (5 mL) were eluted with 10 mL (3, 3, and 4 mL) of ethyl acetate, concentrated to 1 mL using a rotary evaporator and then dried by a gentle nitrogen stream. This was dissolved in 1 mL of ethyl acetate; pesticides were then quantified by gas chromatograph with electron capture detector (GC–ECD).

2.3.2. Gas chromatographic determination

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

The residues detected by the GC analysis were confirmed by the analysis of the extract on two other columns of different polarities. The columns were ZB-1 (methyl polysiloxane) and ZB-17 (50% phenyl, methyl polysiloxane). The conditions used for these columns were the same, as stated in Netherlands analytical methods.

2.3.3. Quantitation

An external standard method was used to determine the quantities of residues in the sample extracts. A standard mixture containing known amounts of pesticides was run and the response of the detector for each compound was determined. The area of the corresponding peak in the sample was compared with that of the known standard.

2.3.4. Quality control and quality assurance

Quality control and quality assurance were incorporated in the analytical scheme. First the GC method was validated using

Table 1
Incidence (%) of organochlorine pesticides in vegetables from markets in Greater Accra region.

Scientific name	English name	No. of sample	% with one or more residues
<i>Daucus carota</i>	carrot	60	26.4
<i>Brassica oleracea</i>	cabbage	60	39.5
<i>Lactuca sativa</i>	lettuce	60	16.7
<i>Solanum lycopersicum</i>	tomato	60	29.6

chromatographic parameters including recoveries, reproducibility and limits of detection (LOD) as proposed by Netherlands analytical methods of pesticide residues in foodstuffs with modifications (Ministry of Public Health, Welfare and Sports, 2007). For recovery experiments, untreated samples of vegetables were spiked with organochlorine mixture of standards at levels close to the limit of permissible levels. For each fortification level, three replicated samples were analyzed by GC/ECD. The efficiency of the method was validated statistically with recoveries studies, fortification samples were analyzed in triplicate. The reproducibility of all pesticides was within the range of 80.0% – 103.5% for all the organochlorine pesticides spiked.

3. Results and discussion

Carrot, cabbage, lettuce and tomatoes are mostly used uncooked. Pesticides are the part of majority of chemicals applied on them. The present study determined the pesticide residues in carrot, cabbage, lettuce and tomato samples collected from different markets in Greater Accra region of Ghana and compared with MRLs set in EC directives that have been implemented into UK legislation for vegetables (2006) and concentration falling above the levels are identified and discussed.

3.1. Incidence of pesticide residues in vegetables from markets in Greater Accra region of Ghana

Incidence of pesticide residues in the vegetables samples analyzed are presented in Table 1. In all, 240 samples of vegetables were analyzed for pesticide residues from July 2010 to February 2011. The monitored OCPs are lindane, heptachlor + its epoxide, endrin, dieldrin, o,p-DDE, p,p-DDE, o,p-DDD, o,p-DDT and p,p-DDT. Table 1 shows the number of samples surveyed and those containing one or more pesticide residues in each kind of vegetable samples.

Overall, 26.4% of carrot, 39.5% of cabbage, 16.7% of lettuce and 29.6% of tomato samples contained one or more detectable residues and are discussed accordingly (Table 1).

3.1.1. Occurrence and levels of OCPs in vegetables from supermarkets

Table 2 illustrates vegetable samples collected from supermarkets that were analyzed for 9 different organochlorine pesticides. Among the monitored OCs in vegetables, the o,p-DDT was found with the highest concentration of 0.239 µg/g, followed by o,p-DDE with the concentration of 0.236 µg/g all in the same tomato samples analyzed. o,p-DDE, p,p-DDE and o,p-DDD were the most predominant OCPs found in all the four vegetable samples analyzed, followed by lindane, o,p-DDT, p,p-DDT and heptachlor + its epoxide which were present in three vegetable samples.

The results showed that lindane was found in three vegetable samples (carrot, cabbage and tomato) and exceeded MRL in all the three vegetable samples. Heptachlor + its epoxide were detected in cabbage, lettuce and tomato samples and exceeded MRL value in tomato samples. However, endrin and dieldrin was below the MRL value in cabbage, and tomato samples analyzed. The results also showed that o,p-DDE, p,p-DDE, and o,p-DDE were tested and found in all the four vegetable samples, however, the aforementioned pesticides violated MRL in cabbage and tomato samples. o,p-DDT and p,p-DDT was detected in three vegetable samples (carrot, cabbage and tomato), o,p-DDT exceeded MRL level in cabbage and tomato samples where as p,p-DDT violated MRL in tomato samples respectively.

The sum of mean levels of the nine pesticides illustrate that, tomato followed by cabbage, carrot and lettuce contained the highest concentrations with residual values of 0.110, 0.09, 0.040 and 0.020 µg/g, respectively.

3.1.2. Occurrence and levels of OCPs in vegetables from roadside grocery stores

Table 3 shows data for levels of detected pesticide residues found in vegetables samples from roadside grocery stores. The data revealed that, o,p-DDE was found with the highest concentration of 0.239 µg/g in cabbage, followed by o,p-DDT with the concentration of 0.204 µg/g in tomato samples. Organochlorine pesticides including, o,p'-DDE, p,p-DDE and o,p-DDD were found in all the four vegetable samples as in the case of vegetables collected from supermarkets. This is followed by lindane, and o,p-DDT in three vegetable samples through endrin, p,p-DDT and heptachlor + its epoxide in two vegetable samples, then to dieldrin which was present in only tomato samples.

Data in Table 3 shows that lindane was detected in three vegetable samples (cabbage, lettuce and tomato) and violated MRL in cabbage and tomato samples. Out of the three prevalent OCPs (o,p'-DDE, p,p-DDE and o,p-DDD), o,p'-DDE violated MRL in all the vegetable samples analyzed, followed by o,p'-DDD which exceeded

Table 2
The levels of organochlorine pesticide residues detected in vegetable samples collected from supermarkets in Greater Accra region.

Pesticides	Pesticide level, µg/g			
	Carrot	Cabbage	Lettuce	Tomato
Lindane	0.040* ± 0.035	0.141* ± 0.032	–	0.045* ± 0.018
Heptachlor + its epoxide	–	0.002 ± 0.001	0.009 ± 0.002	0.072* ± 0.035
Endrin	–	0.007 ± 0.003	–	0.009 ± 0.002
Dieldrin	–	–	–	0.008 ± 0.004
o,p-DDE	0.040 ± 0.035	0.127* ± 0.158	0.053 ± 0.011	0.236* ± 0.136
p,p-DDE	0.008 ± 0.004	0.117* ± 0.009	0.042 ± 0.411	0.068* ± 0.032
o,p-DDD	0.072* ± 0.019	0.141* ± 0.032	0.009 ± 0.002	0.148* ± 0.012
o,p-DDT	0.050 ± 0.005	0.178* ± 0.049	–	0.239* ± 0.180
p,p-DDT	0.032 ± 0.010	0.009 ± 0.010	–	0.174* ± 0.044
Σ Mean level	0.040	0.090	0.020	0.110

Limit of detection for all the pesticides, 0.01 µg/g.

*Values designated by asterisks are higher than the EC MRLs for the respective pesticides (see MRLs in Table 5). Each value is the mean of 20 samples with three determinations.

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