



Pesticide Residues Detected in Selected Crops, Fish and Soil from Irrigation Sites in the Upper East Region of Ghana



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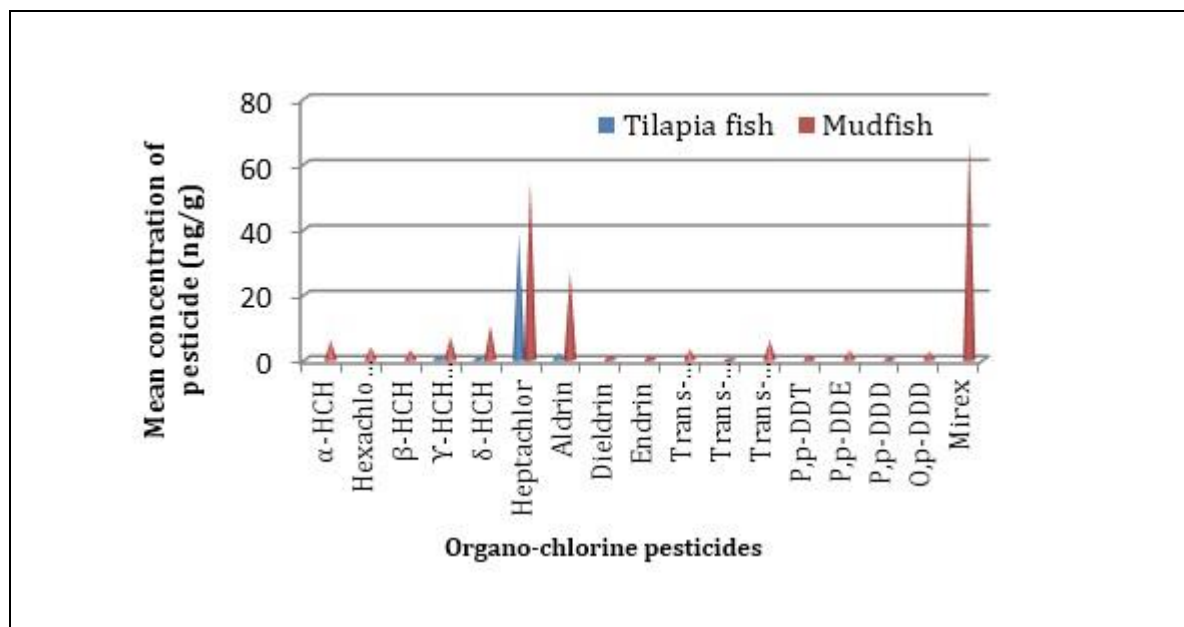
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ABSTRACT

Crops, soil and fish from irrigation farms were investigated in the Upper East Region of Ghana. Questionnaire was administered to collect pesticide use information from farmers, and tomatoes, okro, pepper and garden eggs as well as fish and soil samples were collected and analysed using Gas Chromatography-Electron Capture Detector (GC-ECD). The results were compared with standard acceptable Maximum Residue Limits (MRLs). The results indicated that up to 35.9% of 50 respondent farmers frequently cultivated tomatoes. 50% of the farmers have been using agrochemicals for the past 5 years, with glyphosphate as the most commonly used (42%). 65 % of the farmers indicated that information on proper use or handling of agrochemicals was obtained from colleague farmers. High levels of organochlorine residues (2.232-5.112 ng/g) were found in okro and garden eggs from the Tono site, and also pepper and tomatoes from Pungu site. 6 pesticides residues were found in 5 varieties of tomatoes samples analysed with Lindane and Aldrin having the highest concentration of 0.00069 and 0.027 µg/g respectively. 4 soil samples contained detectable levels of β -HCH and α -Endosulfan (organochlorines), while all 6 samples had one or more traces of 10 organophosphate pesticides. Chlorpyrifos was widely available and in quite high levels. 21 organochlorine residues were detected in tilapia and mud fishes, 17 in fishes from the Precast yard water. Residual concentration of Aldrin and Cis-heptachlor (1069.7 ng/g and 780.7 ng/g respectively) in tilapia from the Tono dam was noted to be above the acceptable limits.

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GRAPHICAL ABSTRACT



Introduction

Agriculture can undoubtedly be seen as the most important source of pesticide discharge into the ecosystem [1]. Pesticide use is expected to protect food crops especially vegetables management [2,3]. Close to half of the world's crops are destroyed by pests and diseases [4,5]. Control of pests is therefore vital in order to achieve projected productivity and to improve crop yields, and contribute to achieving the Millennium Development Goal (MDG) to eradicate extreme poverty and hunger.

There are thousands of pesticides used in the agricultural sector worldwide [6] and Ghana currently consumes about 25% of these pesticides [7]. Notwithstanding the beneficial effects of pesticides, their adverse effects on vegetable quality and health give cause for concerns [8-12]. When a crop is treated with a pesticide some amount of the pesticide or its metabolites remain in the crop even after it is harvested [13]. Post-harvest practices and food processing leave pesticide residues [14]. Also, the World Health Organization (WHO) and Food and Agriculture Organization (FAO) are also

concerned about chemical use in the field of vector control especially in tropical countries [15].

Pesticides can broadly be classified as insecticides, fungicides and herbicides. Insecticides are mainly organochlorines, organophosphorus, carbamates and pyrethroids. Chemical modification of pesticides has led to production of compounds that are more toxic to crops and less rapidly degraded [16]. Farmers even mix cocktails of various chemicals to increase the potency [2]. The organochlorine pesticides (OCPs) are among the major types of pesticides, notorious for their high non-specific toxicity, bio accumulate, high persistence in the physical environment and ability to enter the food chain [17-22]. Pesticide residue in the food chain pose a great threat all over the world and in all organisms [23] and to human health and the environment [24,25]. Organochlorine pesticides are extensively used by most Ghanaian farmers due to their low cost, high efficacy and wide range suitability to plants [26]. Thus there is increasing concern about the adverse effect of pesticides on vegetables and the health of Ghana's human resources [27]. The

environmental persistency of organochlorine insecticides has led to the ban of most of them [28] and replaced by the more friendly organophosphates and Carbarmates [29]. However, some of these compounds have still been detected in the environment and subsequently in crops [30].

Humans are also greatly exposed to the effect of micro pollutants by eating foods either from contaminated earth or water [31,32]. Organochlorines have been implicated in a broad range of adverse human health effects [33-38, and 22]. Significant atmospheric transport of pesticides to aquatic ecosystems can also result from aerial drift of pesticides, volatilization from applications in terrestrial environments, and wind erosion of treated soil in. Organochlorine pesticides in surface water may go into aquatic organisms such as fishes and also remain in sediments. Fish are an integral link in the aquatic food chain and have been reported to also accumulate organochlorines [39].

The WHO has indicated that the total worldwide pesticide poisoning could be as high as 2 million cases a year with twenty thousand poisoning resulting in death [40]. Furthermore, pesticides contribute to biodiversity losses and deterioration of natural habitat [41].

Research work on crop science has reported that pesticide residues are probably in virtually everything consumed from farms [42]. The United Nations (U.N) has warned that about 30% of pesticides marketed in developing nations contain toxic substances which pose a serious threat to both human health and the environment [40]. Some studies conducted in Ghana revealed levels of organochlorine pesticides in water, sediments, food and vegetable [26,27-43]. Some farmers are of the view that the more or as often as they apply pesticides the greater the chances of higher yield and also destroying crop pest [44]. Twelve farmers were once reported dead a result of

misapplication of pesticides in the Upper East Region of Ghana [45].

Therefore, this work was set up to determine the levels of agro based organochlorines in tomatoes, okro, pepper, and garden eggs from Tono, Ve, Wuru, and Pungu in the Upper East region. Residues and their levels were also determined in Tilapia and mudfish from Tono irrigation site and compared with standard acceptable levels [46].

Experimental

Samples

Questionnaire was administered to vegetable farmers at Tono, Wuru, Pungu and Ve irrigation sites all in the Upper East region of Ghana. Petomech (Semillas), "Nameless species", Petomech (Technisem), One I Old and 5 PK tomato varieties, okro, pepper, garden eggs, *Tilapia zilli* (tilapia), *Clarias gariepinus* (mud fish) and soil samples were collected for analyses.

Glassware/Equipment

Cutting knife, catching net, zip-lock bag, aluminium foil, Ice-chest, chopping board, conical flask, measuring cylinder, spatula, electronic balance, shovel, tray, spoon, plastic plates, deep freezer, glass blender, rotary evaporator, GC-EC machine, sonicator and Gas chromatograph.

Reagents/Chemicals

The reagents used in this study included anhydrous sodium sulphate (Na_2SO_4), sodium bicarbonate, ethyl acetate of spectra purity, *n*-Hexane (Pesticide residue) and acetone (HPLC Grade) purchased at Scientificals Ltd. at Circle Accra and MES Equipment at Achimota, Accra.

Methods

Fifty farmers were interviewed; 10 each were randomly selected from Tono and Wuru, and 15 each from Ve a and Pungu for questionnaire administration. The questions sought information about the frequency of pesticides use, and farmers' source of information on pesticide use among others.

Sample collection

In 2010, Petomech (Semillas), Petomech (Technisem) and "Nameless" tomato species from Tono irrigation project site, and One I old and 5 PK from Ve a irrigation site were collected from the farms. In 2013, soil samples were collected from a farmland at the Tono irrigation site 2 weeks after the crops have been harvested. One sample was collected from the main farmland and two others from downstream lowlands all in duplicates. In each case the collected composite samples were wrapped in aluminium foil, put into a black plastic bag and stored in the deep freezer until it was taken for extraction.

Then in 2014, samples of tomatoes, okro, pepper and garden eggs were collected from irrigated farms and gardens at Tono, Ve a, Wuru and Pungu communities. Also, 9 tilapia and mud fishes each were collected from Tono Dam (Bay 1, 3 and 6), Tono Dam (Bay 2, 4 and 5) and another dam at the Precast yard area of the irrigation project. Fishes of similar sizes were selected randomly from the sample for analyses. In all cases the samples were wrapped separately in aluminium foil in the farm, labelled with unique sample identities and placed in zip lock bags. They were then put in an ice chest box containing ice blocks and transported to the Organic Laboratory of Ghana Atomic Energy Commission, Accra for storage in a freezer until they were taken for preparation and analysis were carried out.

Sample preparation

In the laboratory 160g each of the vegetable samples was blended to

homogenise into paste, and 50g of the soil was also sieved using 2 mm mesh sieve. The fish samples were gutted and skin-off muscle tissues. Muscle tissue taken from three (3) similarly sized fishes was pooled together to form composite samples. The tissues were chopped into pieces using separate chopping boards and knives. They were then homogenized separately in a blender and transferred into plates lined with aluminium foil in order to prevent cross contamination. Triplicate samples of each fish were prepared. About 10 g of fish sample was taken and 30 g of anhydrous sodium sulphate (Na_2SO_4) was added to the sample and thoroughly mixed using a spatula in order to absorb moisture in the sample.

Extraction of pesticides

About 20.0 g of each of the homogenized vegetable samples were measured and macerated with 40 mL of ethyl acetate in a conical flask and swirled for a while. To that mixture, about 5.0 g of Sodium bicarbonate was added to neutralize the acid content. This was followed by the addition of about 20.0 g of Sodium sulphate to absorb moisture. The mixtures were then sonicated for 10 minutes to obtain uniform mixtures. The organic phase was decanted three times after adding 40, 40 and 20 ml of ethylacetate separately into round bottom flask [47].

To 10 g of the sieved soil in 100 mL conical flask, 20 mL 1:1 hexane-acetone mixture was added to extract. The conical flask was covered with aluminium foil, swirled for a while and then sonicated for 20 minutes before it was decanted and filtered. The process was repeated three consecutive times and the filtrate concentrated in the rotary evaporator [48].

About 50 mL of 1:3 (v/v) acetone/*n*-hexane already prepared mixture was measured and added to the fishes sample for extraction. Samples were thoroughly mixed using a spatula, then covered tightly and

placed in a sonicator which contained distilled water and sonicated for about 30 minutes to warm and shake the content. The sonicated content was filtered using filter paper in a funnel into a 250 mL round bottom flask. To the sample in the extraction jar, 50 mL of the extraction solvent mixture was added and sonicated for another 30 minutes. The organic layer was decanted into the earlier round bottom flask and concentrated at a temperature of 60 °C using a rotary evaporator to a volume of 1 mL for clean-up.

Clean-up process

A silica gel clean-up [47] of the vegetable samples was carried out by measuring 3.0 g portion of deactivated silica gel into the column, followed by addition of 1.0 g of anhydrous Sodium sulfate. 1.0 g of activated charcoal was introduced to absorb colour in the tomatoes and pepper samples. The extracts then in 40 mL ethyl acetate were transferred into the column and the extract vial rinsed three times with 10 mL ethyl acetate. The columns were eluted three times with 5 mL portion of ethyl acetate into a conical flask before it was concentrated to dryness using a rotary evaporator at 40 °C.

The soil was cleaned by adding 15 mL of 1:1 hexane-acetone mixture to the soil extract concentrate, and filtered through a column of 4 g silica and 0.5 g sodium sulphate conditioned with hexane in a column. This extract was filtered through activated charcoal and concentrated to dryness.

Clean-up of the fishes was done by packing the clean-up columns with 6.0 g alumina as an adsorbent and 1.0 g sodium sulphate to remove excess water. 0.5 g activated charcoal was used to remove colour. Eluent of the fishes were concentrated at 55 °C to near dryness. The column was then conditioned with 10 mL of hexane (eluting solvent) and eluted with 30 mL of the extraction solvent. This was done by adding 15 mL of the eluting solvent to dissolve the analyte in the round

bottom flask and then dropped into the column gently via the walls using a Pasteur pipette. Another 15 mL of the eluting solvent was used to wash the round bottom flask and then dropped on the column. The eluent was collected in a round bottom flask to be concentrated for picking.

Picking process for the analysis

Each residue of the vegetables was dissolved and collected in 2 mL ethyl acetate for gas chromatography. To the soil concentrate 2.0 mL of ethylacetate was added and the analyte mixture was then picked into a GC for gas chromatography. To each concentrated fish eluent 2.00 mL of ethylacetate was added and the analyte mixture was then picked into a GC vial for gas chromatography.

GC-ECD analysis

Seven (7) residues were analysed in each of the vegetables samples, nine (9) organochlorine and 10 organophosphate pesticides analysed in each soil sample, and 21 residues assessed in each of tilapia and mud fishes' samples.

Gas chromatograph GC-2010 equipped with ⁶³Ni electron capture detector (ECD) with split/splitless injector that allowed the detection of contaminants even at trace level concentrations (in the lower ng/g range) from the matrix was employed. The injector and detector temperature were set at 280 °C and 300 °C respectively.

A fused silica ZB-5 column (30 mix 0.25 mm, 0.25 µm film thickness) was used in combination with initial temperature of 60 °C, held for 1 min, ramp at 30°C per min to 180 °C, held for 3 min, ramp at 3°C per min to 220 °C, held for 3 min, ramp at 10°C per min to 300 °C. Nitrogen was used as carrier gas at a flow rate of 1.0 mL per min and make up gas of 29 mL. The injection volume of the GC was 1.0 µL. The residues detected by the GC analysis were

confirmed by the analysis of the extract on two other columns of different polarities. The first column was coated with ZB-1 (methyl polysiloxane) connected to ECD and the second column was coated with ZB-17 (50% phenyl, methyl polysiloxane) and ECD was also used as detector for investigating fifteen different organochlorines pesticides. The conditions used for these columns were the same.

Result

Vegetable cultivation, pesticide usage and farmers source of pesticide information

Results of the administered questionnaire indicated that most farmers cultivated tomatoes (Figure 1a), used glyphosphate (Figure 1b) and got pesticide information from their colleagues (Figure 1c). Further preliminary analyses of five tomato samples

indicated that the tomatoes do not contain detectable levels of most of the analysed pesticides. However, six of the residues analysed, including DDE, Lindane and Aldrin (Figures 2a-2c) in all the samples. Sample identification in Figures 2a-2c: A=One I old; B=5 P K; D=Petomech from Semillas; E="Nameless species"; F=Petomech from Technisem. From Figures 3a and 3b it is indicated that pesticides residues were not detected in most of the soil samples. Less than 0.01 $\mu\text{g/g}$ mean amount of Beta-HCH was found in soil samples 5 and 6, while 0.01 $\mu\text{g/g}$ and 0.01 $\mu\text{g/g}$ of Alpha-Endosulfan were found in sample 2. On the other hand, Chlorpyrifos was present in all the samples, and the pesticide of highest concentration detected in the soil, a mean of 0.56 $\mu\text{g/g}$, was profenofos in sample 2. Sample 2 was also found to contain the highest number of pesticide residues.

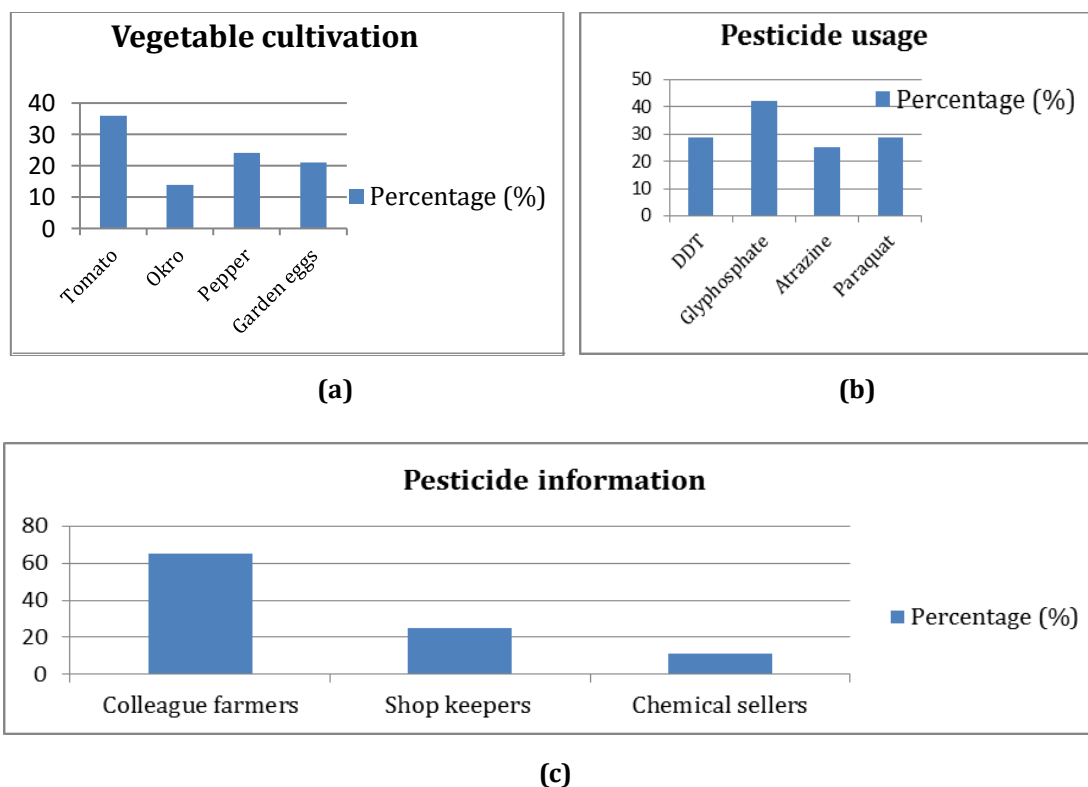


Figure 1. (a) Vegetables cultivated by farmers, (b) Farmers' use of pesticides; (c) Farmers' sources of pesticide information

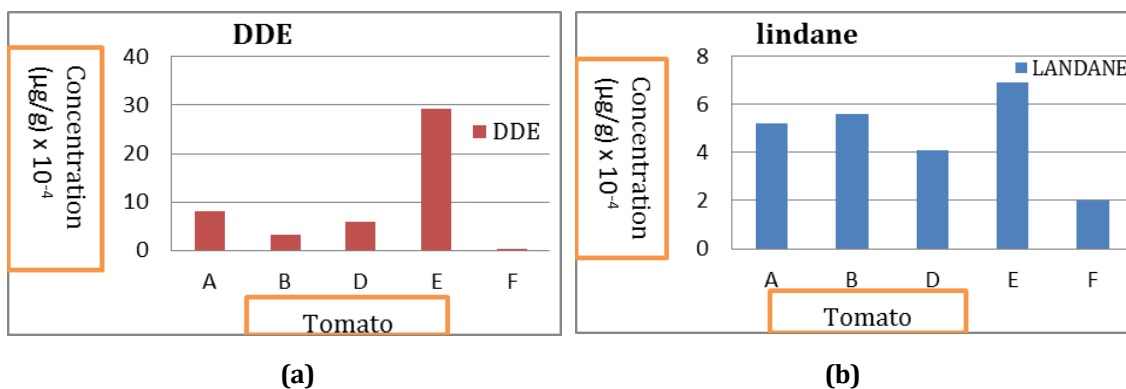
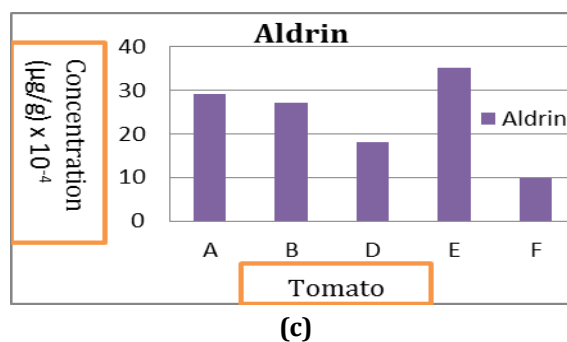


Figure 2. (a) Levels of DDE in the tomatoes; (b) Levels of Lindane in the tomatoes; (c) Levels of Aldrin in the tomatoes



Lindane, aldrin, dieldrin, p, p'-DDE, p, p'-DDT, α -HCH, β -HCH, δ -HCH were all present in the samples. From Figure 4a, four residues were detected in tomatoes and three in pepper from Pungu. All the other tomato samples did not have the residues analysed (Figures 4b-4d). Six residues were detected in okro samples from Vea (Figure 4b), one in

okro from Pungu and two each in that from Wuru and Tono (Figures 4b, 4c and 4d respectively). Also, two and one residues respectively were found in pepper from Wuru and Tono. Four residues were also found in garden eggs from Tono (Figure 4d), compared to two in those from Pungu and no detection in the Wuru samples.

Organochlorine (Figure 3a) and organophosphate (Figure 3b) pesticide residue in the soil samples

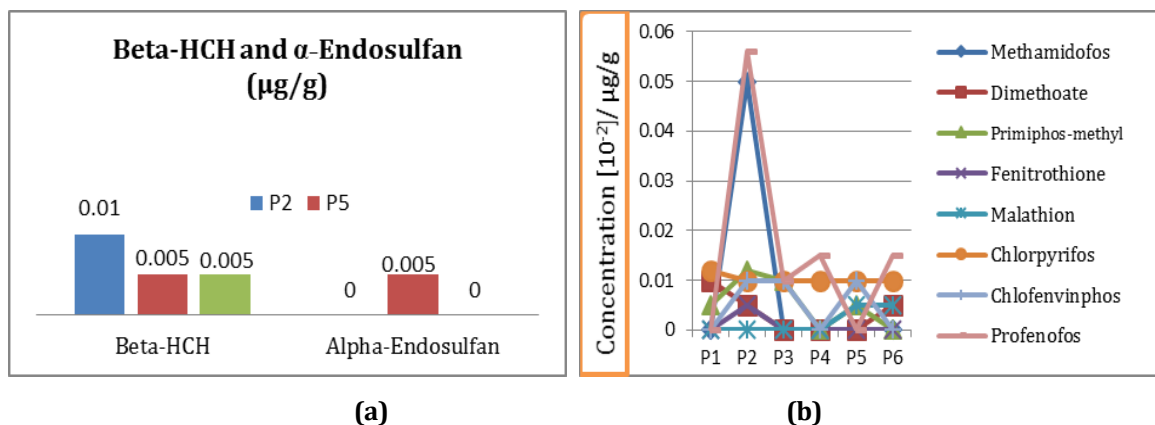


Figure 3. (a) Organ chlorine pesticide residues, (b) Organophosphate pesticide residues

Levels of organ chlorines in tomato, okro, pepper and garden eggs are presented in Figures 4a-4d

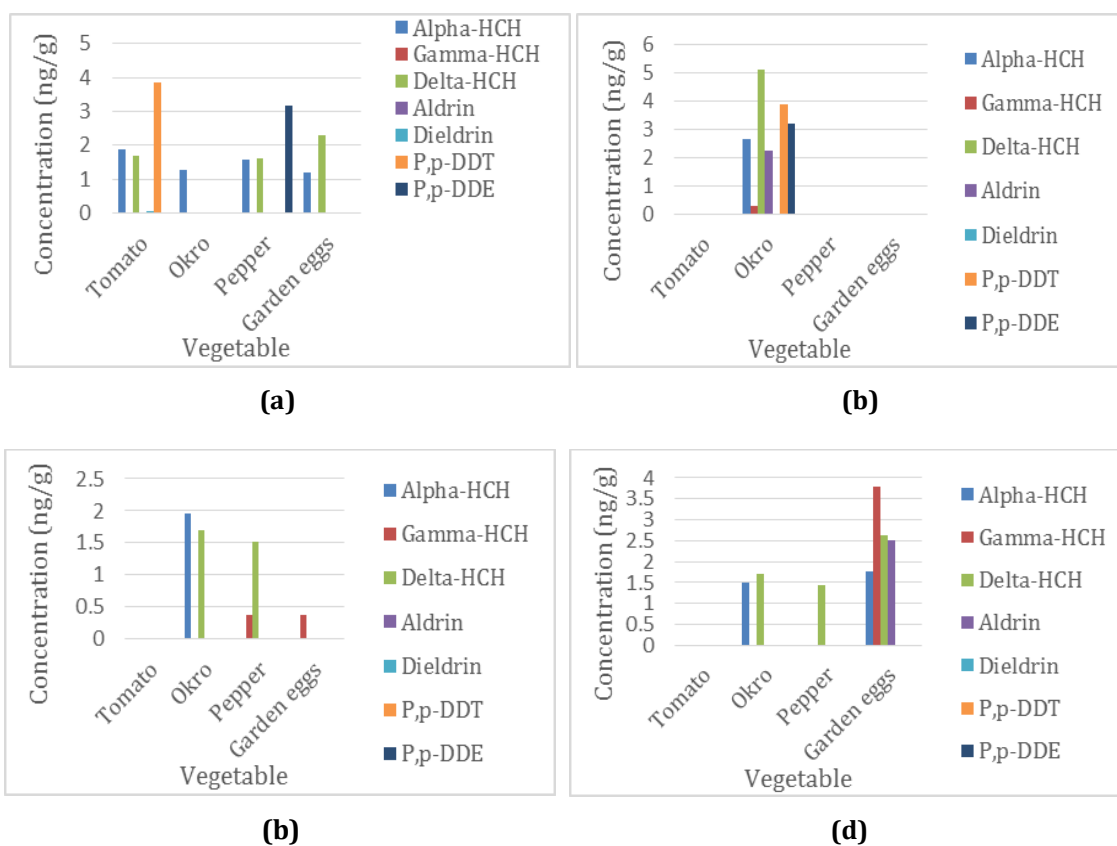


Figure 4. (a) Organ chlorines in vegetables-Pungu, (b) Organ chlorines in vegetables-Vea, (c) Organ chlorines in vegetables-Wuru, (d) Organ chlorines in vegetables-Tono

The probe for organochlorine pesticides in tilapia fish and mud fish found nineteen (19) residues in all. *O, p*-DDE and *cis*-Chlordane were absent in all the samples analysed. From figure 5a, the mean concentration of aldrin was highest in both of tilapia and mud fish, 10.6 ng/g and 9.7 ng/g respectively. At Tono dam water (Bay 1, 3 and 6) δ -HCH (lindane) was detected only in mud fish with a mean concentration of 0.1 ng/g. Also, *o, p*-DDT was found only in tilapia fish at an average concentration of 0.1 ng/g.

Cis-heptachlor, 1069.7 ng/g, was the highest organochlorine pesticide residue found in tilapia from Tono Dam water (Bay 2, 4 and 5) followed by aldrin at a concentration of 780.6 ng/g also found in tilapia (Figure 5b). Aldrin, *Trans*-Nonachlor, *p,p*-DDT and α -HCH were found in minute concentrations only in the mud fish while 102.7 ng/g of *trans*-

heptachlor was detected in the tilapia (Figure 5b). From the ANOVA (Table 1a), the difference in test values is statistically significant ($p < 0.05$). The 5% LSD showed that there is no significant difference in organochlorine pesticides concentration in tilapia fish from Tono Dam water (Bay 1, 3 and 6) and Precast water. There is however significant difference between the levels in tilapia fish from Tono Dam water (Bay 2, 4 and 5) and Precast water, and also between that in Tono Dam water (Bay 2, 4, 5 and Bay 1, 3 and 6).

Analyses of variance (ANOVA) of the residue levels in the fishes from Precast water, Tono Dam water (Bay 2, 4 and 5) and Tono Dam water (Bay 1, 3 and 6) are presented in Tables 5.1 a-5.5 b. The ANOVA (Table 2a) found that the test is statistically significant. The 5% LSD showed that there is significant difference in

organochlorine pesticides concentration in mud fish from Tono Dam water (Bay 1, 3, 6 and Bay 2, 4 and 5); Tono Dam water (Bay 1, 3 and 6) and

Precast water, and also between Tono Dam water (Bay 2, 4 and 5) and Precast water.

Comparison of mean Organ chlorine pesticide residue concentration in tilapia and mud fish from Tono dam

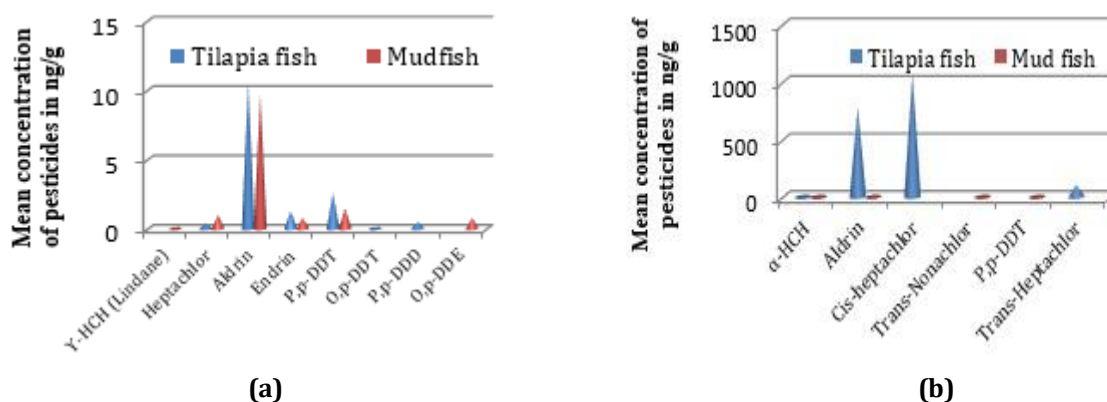


Figure 5. (a) Pesticides in fishes-(Bay 1, 3 and 6), (b) Pesticides in fishes-(Bay 2, 4 and 5), (c) Organ chlorine pesticides in Tilapia fish and mudfish from precast water

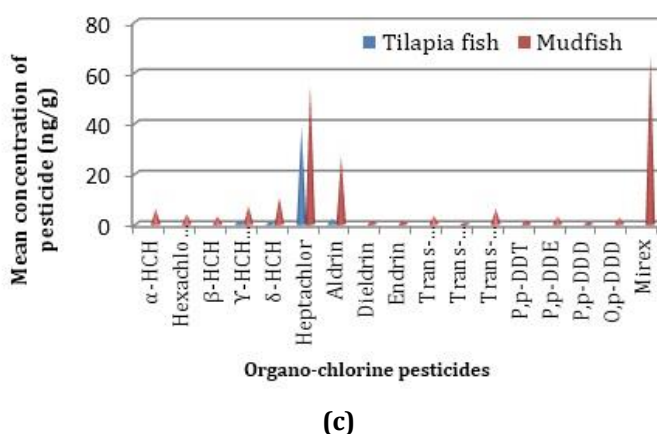


Table 1a. Comparison of differences in organochlorine concentrations in tilapia fish from the three sampling sites

Source	DF	Sum of Square	Mean Square	F-value	Pr > F
Model	2	1235333.230	617666.615	1704.93	<.0001
Error	3	1086.845	362.282		
Corrected Total	5	1236420.075			

Least Significant Difference (LSD) = 60.574

Table 1b. Grouping of dams according to levels of significance

T Grouping	Mean	N	BLK
A	977.10	2	Tono Dam water (Bay 2, 4 and 5)
B	21.50	2	Precast water
B	7.75	2	Tono Dam water (Bay 1, 3 and 6)

Table 2a. Comparison of the differences in organochlorine concentration in mudfish from the three sampling sites

Source	DF	Sum of Square	Mean Square	F-value	Pr > F
Model	2	12202.96333	6101.48167	10029.8	<.0001
Error	3	1.82500	0.60833		
Corrected Total	5	12204.78833			

Least Significant Difference (LSD) = 2.4822

Table 2b. Grouping of dams according to levels of significance

T Grouping	Mean	N	BLK
A	100.10	2	Precast water
B	6.95	2	Tono Dam water (Bay 1, 3 and 6)
C	2.10	2	Tono Dam water (Bay 2, 4 and 5)

The ANOVA (Table 3a) shows that the difference in the test values is not statistically significant. The LSD at 5% revealed no significant difference ($p > 0.05$) in the mean pesticides concentration in the two species of fish from Tono Dam water (Bay 1, 3 and 6).

From the ANOVA (Table 4a), the test is statistically significant. The LSD at 5% revealed a significant difference ($p < 0.05$) in organochlorine pesticide mean concentration between tilapia fish and mud fish from Tono Dam.

The ANOVA (Table 5a) shows that the difference in the test values is statistically significant. The LSD at 5% revealed that there is significant difference ($p < 0.05$) in organochlorine pesticides mean concentration between tilapia fish and mud fish from Precast water.

Seventeen (17) organochlorine pesticides were detected in the fishes from Precast water, all of which were found in mud fish. Only γ -HCH (lindane), δ -HCH and aldrin were found in the tilapia fish. The pesticide with highest concentration, 66.9 ng/g, was Mirex while several isomers of DDT were found in the mud fish (Figure 5c).

Discussion

Organ chlorines are fairly complex, stable compounds and therefore persist for a long time in the environment, either in their original form or as stable metabolites. They are capable of bio-accumulating in tissues of human beings such as breast milk and blood via the food chain [20]. It has been estimated that persistence of these compounds range from 4-30 years in the environment, due to their high resistance to biological and chemical degradation [12].

Table 3a. Comparison of the mean pesticide concentrations between tilapia fish and mudfish from Tono Dam water (Bay 1, 3 & 6)

Source	DF	Sum of Square	Mean Square	F-value	Pr > F
Model	1	0.64	0.640	0.08	0.8091
Error	2	16.93	8.465		
Corrected Total	3	17.57			

Least Significant Difference (LSD) = 12.518

Table 3b. Grouping of fishes according to levels of significance

T Grouping	Mean	N	BLK
A	7.750	2	TILAPIA
A	6.950	2	MUDFISH

Table 4a. Comparison of the mean pesticide concentrations between tilapia fish and mudfish from Tono Dam water (Bay 2, 4 & 5)

Source	DF	Sum of Square	Mean Square	F-value	Pr > F
Model	1	950625.00	950625.00	1781.50	0.0006
Error	2	1067.22	533.61		
Corrected Total	3	951692.22			

Least Significant Difference (LSD) = 99.391

Table 4b. Grouping of dams according to levels of significance

T Grouping	Mean	N	BLK
A	977.10	2	TILAPIA
B	2.10	2	MUDFISH

Table 5a. Comparison of the mean pesticide concentrations between tilapia fish and mudfish from precast water

Source	DF	Sum of Square	Mean Square	F-value	Pr > F
Model	1	6177.96	6177.96	2733.61	0.0004
Error	2	4.52	2.26		
Corrected Total	3	6182.48			

Least Significant Difference (LSD) = 6.4683

Table 5b. Grouping of fishes according to levels of significance

T Grouping	Mean	N	BLK
A	100.10	2	MUDFISH
B	21.50	2	TILAPIA

From the preliminary work the most frequently cultivated vegetables in the selected communities are tomatoes (35.9%), while others were pepper (24.1%), garden eggs (21%) and okro (14%). Agrochemicals frequently used for vegetable cultivation were glyphosphate (42%), dichlorodiphenyltrichloroethane (29%), atrazine (25%) and paraquat (19%). The largest portion (65%) of vegetable farmers got their information on agrochemicals use from colleague farmers; 24% from shop

keepers and 11% from chemical sellers. Up to 50% of farmers have handled agrochemicals in the past 5 years. Thus, the main source of information to farmers is informal and this could be determined.

Metabolites of DDT such as O, *p'*-DDT, *p*, *p'*-DDT, *p*, *p'*-DDE were found in some of the samples analysed. Over 3.8 ng/g of P, *p*-DDT was detected in tomatoes from Pungu and also in okro from Ve'a, while over 3.2 ng/g of *p*, *p*-DDE was found in okro from Ve'a and also in pepper from the Pungu irrigation site.

Adverse effects of organochlorines especially DDT demonstrated in experimental animals include infertility, a decrease in the number of implanted ova, intrauterine growth retardation, cancer, neurological developmental disorders and mortality [49]. Eating food with large amounts of DDT would most likely affect the nervous system. People who ingested large amounts of DDT became excitable and had tremors, reduction in the duration of lactation and seizures [50] and other challenges [51]. Long-term exposure to moderate amounts (20-50 mg/kg of body weight every day) of DDT may cause liver problems [51]. Results from the current study suggest that there is possibility of sporadic use of DDT or past extensive use of the pesticide in the area as it has been banned in Ghana for over a decade. It is known that DDT application is accompanied with environmental hazards due to its high persistence, toxicity and bio-accumulation and this resulted in restriction or ban of its uses [52].

The concentration of lindane in okro from Veia (0.274 ng/g), garden eggs from Wuru (0.374 ng/g) and garden eggs from Tono (3.792 ng/g) was higher than the WHO accepted limits. This has however been the case in several reports from other places. Research into fruits and vegetables in Eastern Romania [53] and the findings of Nakata et al. [54] in Shanghai and Yixing, China, also found elevated levels of pesticides above acceptable limits of the WHO.

α -HCH was widely found in tomatoes, pepper, garden eggs and okro from Pungu and in okro from Veia and Wuru irrigation sites. It was also the most occurring residue in okro and garden eggs from Tono. Generally, hexachlorocyclohexanes have high ability to accumulate in fat tissues [55].

Results of preliminary analyses of tomatoes collected from Tono and Veia project site (Figures 4a-4c) found generally low concentrations of the analysed pesticides but

higher concentration of DDE, Lindane and Aldrin in the samples. Maximum residue limit of pesticides in tomatoes established by European Union (EU) are 0.01 $\mu\text{g/g}$ of Lindane, 0.01 $\mu\text{g/g}$ of Aldrin and 0.05 $\mu\text{g/g}$ of DDE. In the current study, the highest amounts of Lindane, Aldrin and DDE in various tomatoes were 0.00056 $\mu\text{g/g}$, 0.027 $\mu\text{g/g}$ and 0.00003243 $\mu\text{g/g}$ respectively. The concentrations of the three pesticides in the samples were all below the maximum residue limits of the EU. Aldrin, Lindane and DDE were found in Petomech (Semillas), 0.018 $\mu\text{g/g}$ of Aldrin being the highest. They were also found in "Nameless species" of which 0.035 $\mu\text{g/g}$ level of Aldrin was the highest. Lindane and Aldrin were 0.00012 $\mu\text{g/g}$ and 0.0097 $\mu\text{g/g}$ respectively in Petomech (Technisem).

In the soil samples, more organophosphate pesticides were detected compared to organochlorides (Figure 3a and 3b). Water solubility of organophosphates is variable but generally higher than the organochlorines. Residues generally break down quite quickly in water and are not generally detected except where the contamination is quite recent. Residues in soil are short-lived and are probably only of interest for 5–15 days after spraying unless in shaded areas or where the concentrations applied are high due to their short half-life [56]. Solubility of organochlorine pesticides and insecticides tend to connect in suspended matters, precipitate in sediments, accumulate and concentrate in biota of aquatic systems [25]. These compounds are not readily metabolized or excreted from the body and are readily stored in fatty tissues. They can bioaccumulate through food chains to secondary consumers such as fish, piscivorous birds, and mammals including humans [57].

More pesticides were found in fish from the precast dam water compared to Tono Dam water (Bay 1, 3 and 6) and Tono Dam water (Bay 2, 4 and 5). This may be because many

different types of crops are observably cultivated around the precast area resulting in the use of many different types of pesticides. Generally, the ability of fish to metabolize organochlorines is moderate; therefore loading of contaminants in fish is well reflective of the state of the pollution in surrounding environments [58].

Uptake of a chemical may be by dietary and/or dermal absorption, transportation through respiratory surfaces and the process of bioaccumulation [59]. However, different species of fish vary in their ability to store residues in their tissues [49]. Determination of organochlorine concentrations in fish may therefore indicate the extent of aquatic contamination and the accumulation characteristics of these compounds in tropical aquatic biota [60]. From the current study, Tilapia from Tono dam contained more pesticide contaminants compared to mud fish, while more contaminants were found mud fish from the Precast water than in the Tilapia. Generally, there was more DDT residue in mud fish than in Tilapia.

The levels of DDT residue were lower compared to findings from earlier work done [61] which reported a concentration of 980 ng/g DDTs in mud fish.

Also, previous studies [55] reported a mean concentration of 11.8 ng/g α -HCH in tilapia fish from Lake Naivasha in Nairobi, compared to the far lower amount (1.2 ng/g) detected in tilapia fish from Tono Dam water (Bay 2, 4 and 5) in the current study. The concentration of aldrin in tilapia fish from Tono Dam water (Bay 2, 4 and 5), 780.6 ng/g, was however far in excess of that (0.7 ng/g and 1.4 ng/g) reported [21] in tilapia fish from Weija Dam and Nsawam Dam respectively in Ghana. It was also higher than the FAO/WHO Maximum Residue Limit of 200 ng/g [46]. Aldrin has been a popular pesticide used in crops such as corn which is widely cultivated in the current study area. The residue may have been washed into the dam when it was

used on the farms. Aldrin is rapidly metabolized by organisms but its metabolite, dieldrin is more toxic and persistent [62].

Very high levels (1069.7 and 102.7 ng/g) of Cis-heptachlor and trans-heptachlor respectively, found in tilapia from Tono Dam water (Bay 2, 4 and 5) must have resulted from recent chemical applications. Heptachlor does not persist in the environment for long but is metabolised to heptachlor epoxide which is toxic, persists and accumulate in the environment [55]. Except Cis-heptachlor, all the pesticides residues were below the stipulated Australian Maximum Residue Limit (AMRL) of 50 - 1000 ng/g.

Cyclodiene are neurotoxins and also affect the reproductive system, liver and kidney [55]. Carbamates pesticide residue is, probably only of interest for 10–20 days after spraying, thus in certain soils and in water, extended monitoring may be required due to their short half-life [56].

Modern ways of managing pesticide application such as the use of nanotechnology [24] must be applied in order to minimise pesticide pollution in the manner detected.

Conclusion

The study found that most farmers do not receive pesticide use education from the right personnel. Also, most of the analysed pesticides were not present in tomatoes which were identified as the most cultivated vegetable in area. DDT which is banned in the country was also found to be absent in most of the samples. Therefore, consumption of the tomatoes will not cause any health effect to humans resulting from pesticidal effects. The tomato is safe for consumption notwithstanding that Aldrin, Lindane, DDE, Propanal, Chlorpyrifos and β -Endosulfan that were detected may have cumulative effect on consumers.

More organophosphates than organochlorines were found in the soil samples. This may have resulted from the use

of more organophosphate pesticides by the farmers compared to organochlorine based inputs.

Organochlorine residues were found in all the vegetable samples. All organochlorines in tomatoes and garden eggs samples analyzed were below detection limits. High levels organochlorine pesticide residues were found in okro and garden eggs from Tono, pepper from Pungu, and tomatoes from Pungu ranging from 2.232-5.112 ng/g, 2.620-3.792 ng/g, and 3.177 ng/g-3.845 ng/g respectively. Okro from Vea and Tono, garden eggs from Tono, and also pepper and tomatoes from Pungu had organochlorines pesticide residues above their maximum accepted residue limits.

Pesticide residues were detected in various degrees both in tilapia and mudfish from Tono Dam water and precast irrigation water. Generally, more of the residues occurred in from the precast dam. The mudfish had more DDT residue than the Tilapia fish.

Aldrin and cis-heptachlor which were present at very high levels are among the organochlorine pesticides banned by Environmental Protection Agency (EPA) of Ghana. The residual concentration of aldrin and cis-heptachlor, in tilapia fish from Tono dam water (Bay 2, 4 and 5) were above the FAO/WHO Maximum Residue Limits (MRLs). They were however within the Australian Maximum Residue Limits (AMRLs).

Recommendations

Alternative measures to pest control should be practiced by farmers. MoFA should deploy more Agricultural Extension Officers to educate and monitor farmers on the proper use of pesticides.

List of Abbreviations

FAO	Food and Agricultural Organisation
TDWT	Tono Dam water tilapia fish

TDWM	Tono Dam water mudfish
PRWT	Precast water tilapia fish
PRWM	Precast water mudfish
R1	Replicate 1
R2	Replicate 2
R3	Replicate 3
MRLs	Maximum Residue Limits
GC-ECD	Gas Chromatography-Electron Capture Detector
FAO	Food and Agriculture Organisation
WHO	World Health Organisation
MDG	Millennium Development Goal
OCPs	Organochlorine pesticides
USEPA	United States Environmental Protection Agency
UNDP	United Nations Development Programme
DDT	Dichlorodiphenyltrichloroethane
HCH	Hexa Chloro Heptaclor
ANOVA	Analyses of variance
DDE	Dichlorodiphenyltrichloroethane
ATSDR	Agency for Toxic Substances and Disease Registry
AMRL	Australian Maximum Residue Limit

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No potential conflict of interest was reported by the authors.

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