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Health risk assessment of pesticides residue in maize and cowpea from Ejura, Ghana

O. Akoto [a,*], H. Andoh [a], G. Darko [a], K. Eshun [b], P. Osei-Fosu [b]

[a] Department of Chemistry, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana
[b] Ghana Standards Authority, P.O. Box MB 245, Accra, Ghana

HIGHLIGHTS

- Pesticides applications leave residues on food which can have chronic health effect.
- The study is to measure pesticides residues in maize and cowpea.
- 15 organochlorines, 13 organophosphorus and 9 pyrethroids pesticides were investigated in maize and cowpea samples.
- Health risk estimation revealed that some residues in maize exceeded the ADI.
- There is potential for chronic toxicity to consumers of these food items.

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ABSTRACT

Low productivity in agriculture due to damage cause by pests has led to the application of pesticides to control pest infestation. Residues of pesticides applied on crops are often found in the food which can cause chronic effect on the health of humans who consume such products. The aim of this study is to measure pesticides residues in maize and cowpea and compare the values with stablished safety limits. A total of 37 pesticides comprising 15 organochlorines, 13 organophosphorus and 9 pyrethroids pesticides were identified in maize and cowpea samples obtained from farms in Ejura. Analytical methods included solvent extraction of the pesticide residues and their subsequent quantification using gas chromatograph equipped with Electron Capture Detector and Pulse Flame Photometric Detector after clean-up on alumina/activated charcoal column. The results showed that the mean concentration of pesticides in maize ranged from 0.001 to 0.103 mg kg^{-1} for organochlorine pesticides, 0.002–0.019 mg kg^{-1} for organophosphorus pesticides and 0.002–0.028 mg kg^{-1} for pyrethroids pesticides. In cowpea the mean concentration ranged from 0.001 to 0.108 mg kg^{-1} for organochlorine pesticides, 0.002–0.015 mg kg^{-1} for organophosphorus pesticides and 0.001–0.039 mg kg^{-1} for pyrethroids pesticides. Maximum Residue Limits for β-HCH, β-endosulfan, *p,p′*-DDE and *p,p′*-DDD were exceeded in both maize and cowpea samples. Health risk estimation revealed that residues of heptachlor, dieldrin, endrin, β-endosulfna, γ-chlordane and chlorfenvinphos found in maize exceeded the Acceptable Daily Intake. Similarly the levels of heptachlor and *p,p′*-DDD found in cowpea also exceeded the Acceptable Daily Intake. This suggests a great potential for chronic toxicity to consumers of these food items.

1. Introduction

Agriculture in Ghana is associated with low yields due to damage caused by pests, and diseases (Horna et al., 2008). This has led many farmers to use large quantities of pesticides to control pests and diseases. The use of pesticides in Ghana's agriculture continues to increase as more food is needed to meet the demands of the growing population and also for export (MoFA, 2010). In 2003, it was estimated that, about 87% farmers in Ghana use pesticides to control pests and disease (Dinham, 2003). Because of their ability to persist in the environment, accumulate in food chain and their subsequent toxic effect on humans, the uses of organochlorine pesticides have been banned in Ghana and replaced with organophosphorus, and synthetic pyrethroids which are less persistent but have higher acute toxicity (Darko and Acquah, 2008; USEPA, 1998; Wang et al., 2007). Although the use of pesticides has led to the enhancement of quality and quantity of food worldwide, however, their use in crop production often contaminate food crops (Darko and Akoto, 2008; Bempah et al., 2011a,b; Ogah et al., 2011). Human exposure to low doses of pesticides through

* Corresponding author. Tel.: +233 208216685.
E-mail address: wofakmann@yahoo.com (O. Akoto).

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contaminated food may lead to chronic toxicity. Some of the chronic effects associated with chronic exposure of humans to certain pesticides include birth defects, cancers, genetic change, blood disorders, nerve disorders, endocrine disruption and reproductive effects (Mansour, 2004).

Food, which is required for growth and maintenance of our body, has been the major route of human exposure to pesticides (Juraske et al., 2009; Bempah et al., 2011a,b). Maize and cowpea are some of the important staple food crops grown in Ghana. Maize is also the main component of poultry and livestock feed. Cowpea is an important source of dietary protein for many people in Ghana, especially in areas where access to animal protein is limiting (Yakubu et al., 2012). Unfortunately, maize and cowpea are highly susceptible to pest infestation, both in the field and in storage. So some farmers have resorted to indiscriminate use of pesticides to reduce the damage caused to these crops. Pesticides used in this way often contaminate food crops. Several studies in Ghanaian have reported high levels of pesticide residues in fruits and vegetables (Darko and Akoto, 2008; Armah, 2011; Bempah et al., 2011a,b), fish (Afful et al., 2010; Fianko et al., 2011), meat daily products (Darko and Acquaah, 2007; 2008) and fruits-based soft drinks (Bempah et al., 2011a,b). At the international levels, many studies have also showed contamination levels of pesticides in fruits and vegetables (Pang et al., 1995; Anwar 2008), maize, cowpea, common beans and wheat (Khan et al., 2007; Gwary et al., 2011; Ogah et al., 2011; Riazuddin et al., 2011).

Analysis of pesticide residues in food is a key tool for monitoring the levels of human exposure to pesticide residues. Pesticide residues in food are usually monitored with reference to Maximum Residue Limits (MRLs) and Average Daily Intakes (ADIs). The MRL is an index that represents the highest concentration (expressed in mg kg^{-1}) of pesticide residue that is legally permitted or accepted in a food or animal feed after the use of pesticides (FAO, 2002). A consumer exposure is of concern if the Estimated Dietary Exposure to a pesticide exceeds the ADI. The ADI is the estimate amount of a chemical in food (mg kg^{-1} body weight d^{-1}) that can be ingested daily over a life time without appreciable health risk to the consumer (FAO, 2002).

Exposure of the population to pesticides could be high in Ghana where staple foods like maize and cowpea are assumed to be potentially contaminated by pesticides. The proof of significant contamination of maize and cowpea has been reported in Togo. Similar works conducted in Nigeria by Gwary et al. (2011) and Ogah et al. (2011) have also reported some levels of pesticides in common beans. However, in Ghana, there is no information on the health risk based on the exposure of the population to pesticides through maize and cowpea consumption. This work provides baseline information on contamination levels of pesticides in maize and cowpea from Ejura, the largest maize production district in Ghana and to assess the human health risk through Estimated average daily intakes (EADIs) as compared with ADIs set by FAO/WHO (2010).

2. Materials and methods

2.1. Sample collection and preparation

Cowpea and maize samples not treated with pesticides after harvesting were taken directly from 10 maize and 10 cowpea farms during harvest from Ejura in the Ashanti Region of Ghana in December 2012. The samples were packed in black polyethylene bags and labeled accordingly and transported to the laboratory. In the laboratory, the samples were ground into flour to obtain a homogenous composite. They were then packed in freezer bags and stored in a refrigerator at 4 °C until further analysis.

2.2. Extraction and clean-up of pesticide residues

All reagents and chemicals were of analytical grade and were used as received. Extraction of pesticide residues in maize and cowpea samples was done according to the methods developed by Khan et al. (2007) and Riazuddin et al. (2011) with slight modifications. Each sample of 5.0 g was placed into a flask and 30 mL of acetone: methanol (1:1 v/v) extraction solvent was added. The content of the flask was shaken continuously on mechanical flash shaker at 200 rpm for 3 h. The extract was filtered through a Buchner funnel fitted with Whatman filter paper under suction. The filtrate was transferred into a 500 mL separating funnel and 150 mL sodium sulphate solution was added. The mixture was partitioned with 30 mL of dichloromethane and vigorously shaken for 2 min releasing pressure intermittently. The phases were allowed to separate and the lower dichloromethane phase was collected into a flask. The aqueous layer was partitioned twice using 10 mL portions of dichloromethane each time. The dichloromethane extracts were combined and dried on 20 g anhydrous sodium sulphate in mini-glass column. The dried extract was concentrated to approximately 2 mL in a rotary evaporator at 37 °C and stored in a 2 mL sample vial. This was then taken for clean-up.

For the clean-up, 15 g mixture of alumina and activated charcoal (12:1) slurry was packed with dichloromethane in a mini-glass column and topped up with 2 cm layer of anhydrous sodium sulphate. The column was conditioned with 5 mL of dichloromethane and the sample extract was loaded on the column. Sample vial was rinsed two times with 2 mL aliquots of dichloromethane and the rinsed added to the column. Sample was eluted with 30 mL dichloromethane and elutes concentrated to approximately 2 mL using a rotary evaporator at 37 °C. The final extracts were refrigerated at 4 °C until GC analysis.

2.3. Analysis of pesticide residue contents

Before the analysis recovery experiments were run for the maize and cowpea samples. Two samples for the various sample types were spiked at 0.5 mg kg^{-1} levels. The spiked samples were extracted and analysed under the same conditions as the samples.

Gas chromatograph equipped with Electron Capture Detector (ECD) and Pulsed Flame Photometric Detector (PFPD) was checked for limit of detection. Instrumental limit of detection for organochlorines (OCs) pesticides was 0.005 mg kg^{-1}, pyrethroids pesticides was 0.001 mg kg^{-1} and organophosphorus (OP) pesticides was 0.001 mg kg^{-1}.

Separation and Quantification of OC and synthetic pyrethroid were carried out using Varian CP-3800 gas chromatograph with a CombiPAL Autosampler equipped with an Electron Capture Detector (ECD, ^{63}Ni), on 30 m + 10 EZ Guard × 0.25 mm internal diameter fused silica capillary.

Column coated with VF-5 ms (0.25 μm film). The column oven temperature was programmed from 70 °C, held for 2 min to 180 °C at a rate of 25 °C per min, then from 180 °C to ECD temperature set at 300 °C at a rate of 5 °C per min. Purified nitrogen gas was used as carrier at the flow rate of 1.0 mL per min and make up gas of 29 mL per min. The injector and detector temperature were maintained at 300 °C, respectively. The injector volume of the gas chromatograph was 1.0 μL.

OP pesticides were separated and quantified by Varian CP-3800 gas chromatograph with a CombiPAL Autosampler equipped with pulsed flame photometric detector (PFPD) on 30 mm × 0.25 mm internal diameter fused silica capillary column coated with VF-1701 ms (0.25 μm film). The column oven temperature was performed as: initial temperature was 70 °C, and increased to 200 °C at the rate of 25 °C min^{-1} then ramped to 250 °C at the rate of 20 °C min^{-1}, keeping the final temperature for 2 min. The carrier

gas was nitrogen gas at the flow rate 2 mL min^{-1}. The injector and detector temperature were maintained at 250 °C and 280 °C, respectively. The injector volume of the gas chromatograph was 2.0 μL.

Pesticide residues were identified when the retention times matched those of the standards. Identified pesticides were quantified using the external standard method of comparing sample peak areas with those of the pesticide standards under the same conditions. Each sample was analysed three times and the mean values obtained.

2.4. Statistical analysis

The results obtained from the three matrices were statistically analysed through MS-Excel and SPSS version 16. Elements of descriptive statistics of samples generated included mean, range, minimum, maximum and standard deviations.

The concentration of OC, OP and synthetic pyrethroid pesticide residues in maize and cowpea samples were compared with the MRLs recommended by European Union (2011). MRL of a pesticide is the maximum concentration of its residue that is legally permitted to remain in food after it has been treated with the pesticide (FAO, 2002). Estimated average daily intakes (EADIs) of a pesticide residue and food consumption assumption were used to determine long term health risks to consumers. The food consumption rates for maize and cowpea in Ghana is quoted to be 0.122 kg d^{-1} and 0.014 kg d^{-1}, respectively (MoFA, 2010). For each type of exposure, the EADI was obtained by multiplying the mean residual pesticide concentration (mg kg^{-1}) in the food of interest and the food consumption rate (kg d^{-1}) (Darko and Akoto, 2008). The health risk indices were obtained by dividing the EADI by their corresponding values of ADI (FAO/WHO, 2010), assuming average adult's body weight of 60 kg.

When the health risk index >1; the food involved is considered a risk to the consumers. When the index <1, the food involved is considered acceptable (Hamilton and Crossley, 2004; Darko and Akoto, 2008).

3. Results and discussion

In recovery experiments, the samples of maize and cowpea were spiked with a solution containing a mixture of the pesticide standards. OC pesticides were recovered in the range of 74–106% for maize and 72–92% for cowpea. OP pesticides were recovered in the range of 64–95% for maize and 70–93% for cowpea. Pyrethroids were recovered in the range of 74–90% for maize and 76–97% for cowpea. These results show that the methods used in this study have suitable range with good reproducibility. The limits of detection (LOD) determined as 3δ varied for the different pesticides. They were generally in the range of 0.001–0.005 mg kg^{-1} (dry weight).

Maize and cowpea samples were analysed for residues of 37 pesticides comprising of 15 OC (β-HCH, γ-HCH, δ-HCH, heptachlor, methoxychlor, aldrin, dieldrin, endrin, γ-chlordane, α-endosulfan, β-endosulfan, endosulfan sulphate, *p,p*-DDT, *p,p*-DDE and *p,p*-DDD), 13 OP (dimethoate, methamidophos, ethoprophos, phorate, diazinon, fonofos, pirimiphos-methyl, chlorfenvinphos and profenofos) and 9 synthetic pyrethroids (bifenthrin, fenopropathrin, λ-cyhalothrin, permethrin, cyfluthrin, cypermethrin, fenvalerate, allethrin and deltamethrin). The results showed that all samples analysed for pesticide residues were contaminated by the various pesticides investigated to some extent.

Mean residual concentration of the various OC pesticides in the maize and cowpea samples are presented in Table 1. The results showed that residual concentration in the maize ranged between 0.001 and 0.103 mg kg^{-1} while that of the cowpea range from 0.001 to 0.118 mg kg^{-1}.

The mean levels of β-HCH, γ-HCH and δ-HCH isomers of HCH detected in maize samples were 0.045 ± 0.018 mg kg^{-1}, 0.001 ± 0.000 mg kg^{-1} and 0.002 ± 0.001 mg kg^{-1}. But 0.025 ± 0.014 mg kg^{-1}, 0.002 ± 0.000 mg kg^{-1} and 0.003 ± 0.001 mg kg^{-1} were detected in cowpea. Heptachlor was detected at mean levels of 0.005 ± 0.005 mg kg^{-1} in maize and 0.010 ± 0.002 mg kg^{-1} on cowpea. Methoxychlor concentrations in maize and cowpea were 0.002 ± 0.001 mg kg^{-1} and 0.003 ± 0.001 mg kg^{-1} respectively. Endrin was recorded in 0.002 ± 0.00 mg kg^{-1} in maize and 0.002 ± 0.001 mg kg^{-1} in cowpea. Mean levels of γ-chlordane detected were 0.005 ± 0.001 mg kg^{-1} in maize and 0.002 ± 0.001 mg kg^{-1} in cowpea. Aldrin was detected at mean levels of 0.003 ± 0.000 mg kg^{-1} in maize and 0.003 ± 0.001 mg kg^{-1} in cowpea while its epoxide, dieldrin was detected at levels between 0.002 ± 0.000 mg kg^{-1} and 0.003 ± 0.002 mg kg^{-1} in maize and cowpea respectively. Endosulfan, a mixture of α and β isomers, is among the banned OC pesticides in Ghana. The residual levels of α-endosulfan were 0.001 ± 0.001 mg kg^{-1} in maize and 0.001 ± 0.001 mg kg^{-1} in cowpea while β-endosulfan was detected at mean levels of 0.103 ± 0.101 mg kg^{-1} and 0.081 ± 0.045 mg kg^{-1}

Table 1
Concentration of organochlorine pesticide residues detected in maize and cowpea and EU MRL.

Pesticide	Maize			Cowpea		
	Range (mg kg^{-1})	Mean ± SD (mg kg^{-1})	EU MRL (mg kg^{-1})	Range (mg kg^{-1})	Mean ± SD (mg kg^{-1})	EU MRL (mg kg^{-1})
β-HCH	0.016–0.062	0.045 ± 0.018	0.020	0.003–0.040	0.025 ± 0.014	0.010
γ-HCH	0.001–0.001	0.001 ± 0.000	0.010	0.001–0.002	0.002 ± 0.001	0.010
δ-HCH	0.002–0.002	0.002 ± 0.001	0.020	0.003–0.004	0.003 ± 0.001	0.010
Heptachlor	0.001–0.011	0.005 ± 0.005	0.010	0.008–0.012	0.010 ± 0.002	0.010
Aldrin	0.002–0.003	0.003 ± 0.000	0.010	0.001–0.004	0.003 ± 0.001	0.010
γ-Chlordane	0.003–0.007	0.005 ± 0.001	NA	0.002–0.003	0.002 ± 0.001	0.010
α-Endosulfan	0.001–0.001	0.001 ± 0.001	0.050	0.001–0.001	0.001 ± 0.001	0.050
β-Endosulfan	0.028–0.274	0.103 ± 0.101	0.050	0.006–0.123	0.081 ± 0.045	0.050
Endosulfan sulphate	0.007–0.010	0.009 ± 0.002	0.050	0.002–0.009	0.006 ± 0.003	0.050
p,p′-DDE	0.010–0.091	0.064 ± 0.033	0.050	0.034–0.077	0.053 ± 0.018	0.050
p,p′-DDD	0.052–0.121	0.102 ± 0.029	0.050	0.108–0.118	0.118 ± 0.006	0.050
p,p′-DDT	0.002–0.003	0.002 ± 0.001	0.050	0.002–0.003	0.003 ± 0.001	0.050
Methoxychlor	0.002–0.003	0.002 ± 0.002	0.010	0.002–0.004	0.003 ± 0.001	0.010
Endrin	0.002–0.003	0.002 ± 0.001	0.010	0.001–0.002	0.002 ± 0.001	0.010
Dieldrin	0.001–0.002	0.002 ± 0.000	0.010	0.001–0.005	0.003 ± 0.002	0.010
Total (mg kg^{-1})		0.354 ± 0.169			0.314 ± 0.077	

SD = standard deviation.
NA = MRL not available for commodity analysed.

in maize and cowpea respectively. Endosulfan sulphate, a metabolite of endosulfan was detected at mean levels of 0.009 ± 0.002 mg kg^{-1} in maize and 0.006 ± 0.003 mg kg^{-1} in cowpea. Dichlordiphenyltrichloroethane (DDT) is a potent nonsystemic insecticide. Use of DDT is banned in Ghana as agricultural pesticide. In the environment *p,p′*-DDT degrades slowly into *p,p′*-DDE under aerobic condition and to *p,p′*-DDD under anaerobic condition by microbial activities. From Table 1, residual concentrations of *p,p′*-DDT were 0.002 ± 0.001 mg kg^{-1} in maize and 0.003 ± 0.001 mg kg^{-1} in cowpea. its metabolites, *p,p′*-DDE was detected at mean levels of 0.064 ± 0.033 mg kg^{-1} in maize and 0.053 ± 0.018 mg kg^{-1} in cowpea, while *p,p′*-DDD concentration were 0.102 ± 0.029 mg kg^{-1} and 0.118 ± 0.006 mg kg^{-1} in maize and cowpea respectively.

β-endosulfan with a mean concentration of 0.103 ± 0.101 was the most common contaminant in the maize while *p,p′*-DDD was the most contaminant in the cowpea at a mean concentration of 0.118 ± 0.006 mg kg^{-1}. The mean residual concentration of β-HCH, β-endosulfan, *p,p′*-DDE and *p,p′*-DDD were found exceeding the EU MRLs in both maize and cowpea (EU, 2012). OC pesticide residues have been reported in different food commodities in Ghana (Darko and Acquaah, 2007; Darko and Akoto, 2008; Anwar 2008; Bempah et al., 2011a,b; Riazuddin et al., 2011). Also, a study carried out in Nigeria showed contamination levels of DDT, endrin, dieldrin and lindane in beans (*P. vulgaris*) collected from both field and storage facilities (Gwary et al., 2011).

Table 2, represents a summary of the mean concentrations of OP pesticide residues found in maize and cowpea grains. The total residual concentration of the various OP ranged from 0.001 to 0.019 mg kg^{-1} in maize while those detected in cowpea had their concentration ranged between 0.002 and 0.015 mg kg^{-1}.

The mean concentration value of dimethoate recorded was 0.005 ± 0.001 mg kg^{-1} and 0.008 ± mg kg^{-1} in maize and cowpea, respectively. Methamidophos mean concentrations value were 0.003 ± 0.000 mg kg^{-1} and 0.005 ± 0.003 mg kg^{-1} in maize and cowpea respectively. Chlorpyrifos was detected at levels of 0.013 ± 0.004 mg kg^{-1} and 0.015 mg kg^{-1} in maize and cowpea respectively. Mean residual concentrations of malathion were 0.019 ± 0.021 mg kg^{-1} and 0.014 mg kg^{-1} in maize and cowpea, respectively. Residual concentration of fenitrothion was 0.006 ± 0.004 mg kg^{-1} in maize and 0.003 mg kg^{-1} in cowpea. Parathion-methyl residual concentration was 0.002 ± 0.001 mg kg^{-1} in maize and 0.002 ± 0.000 mg kg^{-1} in cowpea, respectively. Mean residual concentration of chlorfenvinphos was 0.019 ± 0.011 mg kg^{-1} and 0.009 ± 0.008 mg kg^{-1} in maize and cowpea respectively. Profenofos mean concentration value was 0.005 ± 0.000 mg kg^{-1} and 0.005 mg kg^{-1} in maize and cowpea, respectively. Fonofos, diazinon and pirimiphos-methyl were detected in only maize with residual concentration of 0.001 ± 0.000 mg kg^{-1}, 0.002 ± 0.000 mg kg^{-1} and 0.002 ± 0.001 mg kg^{-1} respectively.

In the maize, malathion with a mean concentration of 0.019 ± 0.021 mg kg^{-1} was the highest whereas the fonofos concentration of 0.001 mg kg^{-1} was the lowest. In the cowpea, the minimum concentration was recorded by parathion-ethyl with 0.002 mg kg^{-1} while the maximum concentration was recorded by chlorpyrifos with 0.015 ± 0.007 mg kg^{-1}. Among the OP pesticides investigated, ethoprophos and phorate were not detected in both samples whereas diazinon, pirimiphos-methyl and fonofos were detected only in the cowpea samples. All the OP pesticide residues detected in both samples were below the prescribed MRL by EU. A similar work conducted in Nigeria by Ogah et al. (2011) reported significant concentration of diazinon (0.0278 mg kg^{-1}), pirimiphos-methyl (0.0925 mg kg^{-1}) and chlorpyrifos (0.0982 mg kg^{-1}) which were above their MRLs in beans (*P. vulgaris*). OP pesticide residues such as ethoprophos (1.13544 mg kg^{-1}), phorate (0.67820 mg kg^{-1}) and fenitrothion (0.16500 mg kg^{-1}) were found in cabbage with their levels exceeding the EU-MRL by Armah (Armah, 2011). Another studies conducted by Darko and Akoto (2008) on vegetables obtained from markets in Kumasi also show relatively high levels of dimethoate and malathion in tomatoes, egg plant and paper.

The concentrations of pyrethroids residues analysed in maize and cowpea are presented in Table 3. Pyrethroids were detected in all maize and cowpea samples. The mean concentration of pesticides observed in maize ranged from 0.002 to 0.028 mg kg^{-1} while that in cowpea was from 0.001 to 0.039 mg kg^{-1}. Bifenthrin had mean concentration of 0.003 ± 0.001 mg kg^{-1} in maize and 0.002 ± 0.001 mg kg^{-1} in cowpea. Concentration of fenpropathrin residue was of 0.017 ± 0.025 mg kg^{-1} in maize and 0.003 ± 0.003 mg kg^{-1} in cowpea. The mean concentration of permethrin in maize was 0.004 ± 0.002 mg kg^{-1} in maize and 0.001 ± 0.001 mg kg^{-1} in cowpea. Mean residual levels of λ cyhalothrin detected in the samples are 0.028 ± 0.018 mg kg^{-1} in maize and 0.039 ± 0.032 mg kg^{-1} in cowpea while the levels of cyfluthrin was 0.005 ± 0.001 mg g^{-1} in maize and 0.010 ± 0.007 mg kg^{-1} in cowpea. Cypermethrin was detected at mean concentration of 0.005 ± 0.001 mg kg^{-1} and 0.006 ± 0.004 mg kg^{-1} in maize and cowpea, respectively. Mean fenvalerate levels were 0.014 ± 0.002 mg kg^{-1} in maize and 0.008 ± 0.004 mg kg^{-1} in cowpea. The level

Table 2
Concentration of organophosphorus pesticide residues detected in maize and cowpea compared with EU MRL.

Pesticide	Maize			Cowpea		
	Range (mg kg^{-1})	Mean ± SD	MRL (mg kg^{-1})	Range (mg kg^{-1})	Mean ± SD (mg kg^{-1})	MRL (mg kg^{-1})
Dimethoate	0.004–.005	0.004 ± 0.001	0.020	0.004–.011	0.008 ± .003	0.020
Methamidophos	0.003–.003	0.003 ± 0.000	0.010	0.003–.008	0.005 ± 003	0.010
Ethoprophos	ND	ND	0.020	ND	ND	0.020
Phorate	ND	ND	0.050	ND	ND	0.050
Diazinon	0.002–.002	0.002 ± .001	0.010	ND	ND	0.010
Pirimiphos-methyl	0.002–.003	0.002 ± 0.001	5.000	ND	ND	0.050
Chlorpyrifos	0.008–.019	0.013 ± 0.004	0.050	0.009–0.021	0.015 ± 0.007	0.050
Malathion	0.007–.056	0.019 ± 0.021	8.000	0.001–0.027	0.014 ± 0.011	0.020
Fenitrothion	0.002–.010	0.006 ± 0.004	0.050	0.0002–005	0.003 ± 0.004	0.010
Parathion-methyl	0.001–0.003	0.002 ± 0.001	0.020	0.002–0.002	0.002 ± 0.000	0.020
Chlorfenvinphos	0.011–0.039	0.019 ± 0.011	0.020	0.002–0.020	0.009 ± 0.008	0.020
Profenofos	0.005–0.005	0.005 ± 0.000	0.050	0.005–0.012	0.011 ± 0.006	0.050
Fonofos	0.001–0.001	0.001 ± 0.001	NA	ND	ND	NA
Total (mg kg^{-1})		0.075 ± 0.035			0.067 ± 0.042	

SD = standard deviation.
NA = MRL not available for commodity analysed.
ND = not detected.

Table 3
Concentration of pyrethroids pesticide residues detected in maize and cowpea compared with EU MRL.

	Maize			Cowpea		
	Range (mg kg^{-1})	Mean ± SD (mg kg^{-1})	MRL (mg kg^{-1})	Range (mg kg^{-1})	Mean ± SD (mg kg^{-1})	MRL (mg kg^{-1})
Bifenthrin	0.002–0.005	0.003 ± 0.001	0.050	0.002–0.003	0.002 ± 0.001	0.050
Fenpropathrin	0.002–0.060	0.017 ± 0.025	0.010	0.001–0.008	0.003 ± 0.003	0.010
λ-Cyhalothrin	0.007–0.056	0.028 ± 0.018	0.020	0.001–0.083	0.039 ± 0.032	0.050
Permethrin	0.002–0.007	0.004 ± 0.002	0.050	0.001–0.003	0.001 ± 0.001	0.050
Cyfluthrin	0.004–0.007	0.005 ± 0.001	0.050	0.002–0.018	0.010 ± 0.008	0.020
Allethrin	0.002–0.021	0.009 ± 0.007	NA	0.001–0.008	0.003 ± 0.003	NA
Cypermethrin	0.004–0.006	0.005 ± 0.001	0.300	0.002–0.011	0.006 ± 0.004	0.050
Fenvalerate	0.010–0.016	0.014 ± 0.002	0.020	0.005–0.015	0.009 ± 0.004	0.020
Deltamethrin	0.002–0.003	0.002 ± 0.001	2.000	0.003–0.013	0.007 ± 0.005	1.000
Total (mg kg^{-1})		0.087 ± 0.058			0.080 ± 0.061	

SD = standard deviation.
NA = MRL not available for commodity analysed.

Table 4
Health risk estimation for organochlorine pesticide residues in maize and cowpea.

Pesticide	Maize				Cowpea			
	ADI (mg kg^{-1} d^{-1})	EADI (mg kg^{-1} d^{-1})	Hazard index	Health risk	ADI (mg kg^{-1} d^{-1})	EADI (mg kg^{-1} d^{-1})	Hazard index	Health risk
β-HCH	NA	5.49×10^{-3}	–	–	NA	3.50×10^{-4}	–	–
γ-HCH	0.0003	1.22×10^{-4}	0.48	No	0.0003	2.80×10^{-5}	0.09	No
δ-HCH	0.0030	2.44×10^{-4}	0.08	No	0.0030	4.20×10^{-5}	0.01	No
Heptachlor	0.0001	6.10×10^{-4}	6.10	Yes	0.0001	1.40×10^{-4}	1.40	Yes
Aldrin	0.0001	3.66×10^{-4}	3.66	Yes	0.0001	4.20×10^{-5}	0.42	No
γ-Chlordane	0.0005	6.10×10^{-4}	1.22	Yes	0.0005	2.80×10^{-5}	0.06	No
α-Endosulfan	0.0060	1.22×10^{-4}	0.02	No	0.0060	1.40×10^{-5}	0.002	No
β-Endosulfan	0.0060	1.26 × 10–2	2.10	Yes	0.0060	1.13×10^{-3}	0.19	No
Endosulfan sulphate	NA	1.10×10^{-3}	–	–	NA	8.40×10^{-5}	–	–
p,p′-DDE	0.0200	7.81×10^{-3}	0.39	No	0.0200	7.42×10^{-4}	0.04	No
p,p′-DDD	0.0200	1.24×10^{-2}	0.62	No	0.0200	1.32 × 10–1	6.60	Yes
p,p′-DDT	0.0200	2.44×10^{-4}	0.01	No	0.0200	4.20×10^{-5}	0.002	No
Methoxychlor	0.0050	2.44×10^{-4}	0.05	No	0.0050	4.20×10^{-5}	0.01	No
Endrin	0.0002	2.44×10^{-4}	1.22	Yes	0.0002	2.80×10^{-5}	0.14	No
Dieldrin	0.0001	2.44×10^{-4}	2.44	Yes	0.0001	4.20×10^{-5}	0.42	No

NA = ADI not available for the endosulfan sulphate and β-HCH.

Table 5
Health risk estimation for organophosphorus pesticide residues in maize and cowpea.

Pesticide	Maize				Cowpea			
	ADI (mg kg^{-1} d^{-1})	EADI (mg kg^{-1} d^{-1})	Hazard index	Health risk	ADI (mg kg^{-1} d^{-1})	EADI (mg kg^{-1} d^{-1})	Hazard index	Health risk
Dimethoate	0.0020	4.88×10^{-4}	0.244	No	0.0020	1.12×10^{-4}	0.056	No
Methamidophos	0.0010	3.66×10^{-4}	0.366	No	0.0010	7.00×10^{-5}	0.070	No
Diazinon	0.0050	2.44×10^{-4}	0.049	No	0.0050	–	–	–
Ethoprophos	0.0004	–	–	–	0.0004	–	–	–
Phorate	0.0005	–	–	–	0.0005	–	–	–
Fonofos	NA	3.66×10^{-4}	–	–	NA	–	–	–
Pirimiphos-methyl	0.0300	2.44×10^{-4}	0.008	No	0.0300	–	–	–
Chlorpyrifos	0.0100	1.57×10^{-3}	0.159	No	0.0100	2.10×10^{-4}	0.021	No
Malathion	0.0300	2.32×10^{-3}	0.077	No	0.0300	1.96×10^{-4}	0.007	No
Fenitrothion	0.0060	7.32×10^{-4}	0.122	No	0.0060	4.20×10^{-5}	0.007	No
Parathion-ethyl	0.0050	2.44×10^{-4}	0.049	No	0.0050	2.80×10^{-5}	0.006	No
Chlorfenvinphos	0.0005	2.32×10^{-3}	4.640	Yes	0.0005	1.26×10^{-4}	0.252	No
Profenofos	0.0300	6.10×10^{-4}	0.020	No	0.0300	1.54×10^{-4}	0.005	No

NA = ADI not available for fonofos.

of deltamethrin detected in maize was 0.002 ± 0.001 mg kg^{-1} and 0.007 ± 0.005 mg kg^{-1} in cowpea. Residual levels of allethrin detected in the samples are 0.009 ± 0.007 mg kg^{-1} in maize and 0.003 ± 0.003 mg kg^{-1} in cowpea.

Mean residual concentration of λ-cyhalothrin (0.028 mg kg^{-1}) was highest in maize while lower levels of deltamethrin (0.002 mg kg^{-1}) was observed. In the cowpea, the highest residual concentration was detected for λ-cyhalothrin (0.039 mg kg^{-1}) and the lowest concentration was recorded for permethrin (0.001 mg kg^{-1}). Among the pyrethroids, pesticides investigated, only λ-cyhalothrin (0.039 mg kg^{-1}) and fenpropathrin (0.017 mg kg^{-1}) residues were found slightly exceeding the EU-MRL of 0.020 mg kg^{-1} and 0.010 mg kg^{-1} respectively, in maize. All the detected pyrethroids residues in the cowpea were found to be lower than their respective EU-MRL.

A similar study carried by Armah (2011) reported high residues levels of allethrin (1.5241 mg kg^{-1}), deltamethrin (4.74690 mg kg^{-1}), cypermethrin (0.31180 mg kg^{-1}), fenvalerate 2 (0.20590 mg kg^{-1}), permethrin (0.14700 mg kg^{-1}), ethoprophos (1.13544 mg kg^{-1}), phorate (0.67820 mg kg^{-1}), chlorfenvinp

Table 6
Health risk estimation for pyrethroid pesticide residues in maize and cowpea.

Pesticide	Maize				Cowpea			
	ADI (mg kg^{-1} d^{-1})	EADI (mg kg^{-1} d^{-1})	Hazard index	Health risk	ADI (mg kg^{-1} d^{-1})	EADI (mg kg^{-1} d^{-1})	Hazard index	Health risk
Bifenthrin	0.01	3.66×10^{-4}	0.037	No	0.01	2.80×10^{-5}	0.003	No
Fenpropathrin	0.03	2.07×10^{-3}	0.069	No	0.03	4.20×10^{-5}	0.001	No
λ-cyhalothrin	0.02	3.42×10^{-3}	0.171	No	0.02	5.46×10^{-4}	0.027	No
Permethrin	0.05	4.88×10^{-4}	0.010	No	0.05	1.40×10^{-5}	0.003	No
Cyfluthrin	0.04	6.10×10^{-4}	0.015	No	0.04	1.40×10^{-4}	0.004	No
Cypermethrin	0.05	6.10×10^{-4}	0.012	No	0.05	8.40×10^{-5}	0.002	No
Fenvalerate	0.02	1.71×10^{-3}	0.086	No	0.02	1.26×10^{-4}	0.006	No
Deltamethrin	0.01	2.44×10^{-4}	0.024	No	0.01	9.80×10^{-5}	0.010	No
Allethrin	NA	1.10×10^{-3}	–	–	NA	4.200×10^{-5}	–	–

NA = ADI not available for allethrin.

(0.31520 mg kg^{-1}) and fenitrothion (0.16500 mg kg^{-1}) in cabbage cultivated in Ghana. Bempah et al. (2011a,b) have also reported similar residue levels of permethrin, cyfluthrin, cypermethrin, fenvalerate and deltamethrin in pear, lettuce, watermelon, pineapple, carrot and onion. Study conducted in South Africa also showed the presence of cyfluthrin (0.014 mg kg^{-1}), fenitrothion (0.117 mg kg^{-1}), fenvalerate (0.007 mg kg^{-1}), permethrin (0.076 mg kg^{-1}) and cypermethrin (0.017 mg kg^{-1}) in wheat samples (Dalvie and London, 2009).

Prethroids pesticides are known to break down quickly in direct sunlight, therefore their concentrations in the environment are expected to be low. The residual concentrations of pyrethroids pesticides reported in this study were not in agreement with studies carried out in fruits and vegetables in Ghana (Armah, 2011; Bempah et al., 2011a,b). The values reported by Armah (2011) and Bempah et al. (2011a,b) were exceedingly high compared to that of this study. This may be attributed to early harvest of fruits and vegetables which do not allow most of the applied pyrethroids to degrade as compared to maize and cowpea cultivation in which the crops are allowed on the field to dry and therefore stay on the field for a longer time before harvest.

ADIs, EADIs and corresponding Hazard Indices as well as the Health Risk Assessment for systemic effects associated with pesticide residues encountered in maize and cowpea are summarised in Table 4. The hazard indices values as presented in Table 4 showed that heptachlor, aldrin, γ chlordane, β-endosulfan, endrin and dieldrin in maize and heptachlor and *p,p′*-DDD in cowpea were >1. This shows that there is health risk associated with maize and cowpea consumption, indicating that lifetime consumption of maize and cowpea from Ejura could pose some health risks due to the levels of organochlorine residues present in them.

Health hazard indices of the OP pesticide residues in maize and cowpea are shown in Table 5. The results showed that the hazard indices of all the pesticides analysed were less than 1 except that of chlorfenvinphos, indicating no direct hazard to human health, in spite of their presence in the maize. However, hazard index of chlorfenvinphos in the maize samples >1, indicating a great potential for systemic toxicity with the consumption of maize. The hazard indices of all the OP pesticides in the cowpea were less than 1, suggesting that, there is no health hazard associated with the consumption of cowpea contaminated by investigated OP pesticides.

Table 6, presents the health risk analysis of pyrethroids pesticides encountered in maize and cowpea. As shown in the table, all the hazard indices values were less than 1, representing no health risks to consumers of the maize and cowpea from Ejura.

4. Conclusion

This study has shown that there were some degree of pesticides contamination in maize and cowpea sampled from Ejura. Comparing residual concentration of various pesticide with the European Union MRLs, the residual levels of β-HCH, β-endosulfan, *p,p′*-DDE, *p,p′*-DDD, fenpropathrin and λ-cyhalothrin in maize and β-HCH, β-endosulfan, *p,p′*-DDE and *p,p′*-DDD in cowpea were found exceeding their respective MRL. The findings show that maize was highly contaminated with the investigated pesticides recording a total of 0.345 mg kg^{-1}, 0.087 mg kg^{-1}, and 0.075 mg kg^{-1} for organochlorine, organophosphorus and pyrethroid pesticides respectively. Analysis of health risk assessment revealed that heptachlor, aldrin, dieldrin, endrin, γ-chlordane and chlorfenvinphos in maize and, heptachlor and *p,p′*-DDD in cowpea had great potential for systemic toxicity to the consumers. The research has provided important information on pesticide residue contamination in maize and cowpea from Ejura for the first.

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