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QUANTIFICATION OF ORGANOCHLORINE RESIDUE ON STORED GRAINS IN ONDO STATE, NIGERIA.

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ABSTRACT
The objective of this research is to quantify the residue of chlorinated pesticide content of the four grain samples and compare their residues content with FAO/WHO MRLs. Permethrin in bean samples from location 2 (5.04 ppm) and 3 (4.44 ppm) were significantly different ($p < 0.05$) from the samples from location 4 (0.00 pm) and also different from sample from location 1 (2.0 ppm). There were a few exceptions in some markets such as Heptachlor (B) which was not detected in the beans sample from Location 1. There was a conspicuously high quantity (8.49 ppm) of Permethrin in the rice samples from Location 4 but Endrin was found to be absent in all rice samples. Likewise Endrin was found to be absent in all wheat samples while only the sample from Location 2 contained Lambda Cyalothrin but did not contain p,p-DDD. The Permethrin levels in wheat samples were also considerably high. The maize samples had the highest concentration in many of the organochlorine pesticide. The concentration of alpha-BHC in maize was 0.03 ppm, beta-BHC had a concentration of 0.14 ppm, 0.073 ppm for Lindane, 0.09 ppm for Chlorothalonil and 0.14 ppm in Aldrin. Almost 80% of the pesticide monitored exceeded their MRL; while some pesticide concentration slightly exceeded their maximum residue limit some concentrations were significantly higher than their MRL.

KEYWORDS: Cereal grains, Organochlorine, Permethrin, Endrin, Maximum Residue Limit (MRL).

INTRODUCTION
Agriculture has always been a very important activity in the Nigerian economy, providing gainful employment and livelihood for about 70% of the populace.[1] Challenges of agriculture in Nigeria can be grouped into biotic and abiotic factors. One of the biotic factors is insect pests or diseases which attack crops either on the field or in storage and therefore affect crop production, contributing to low productivity. Solving this challenge has attracted the increase use of pesticides since 1940s.[2]

Pesticides are substances used to kill, repel, or control certain forms of plant or animal life that are considered to be pest.[3] Nowadays, more than 1100 pesticides are used in various combinations and at different stages of cultivation and during postharvest storage to protect crops against a range of pests and fungi and/or to provide quality preservation and its use in agriculture constitute 75% world usage.[4] Pesticides belong to different chemical classes but the major ones are organochlorines, organophosphates, carbamates and pyrethroids.[5] Apart from benefits derive from using pesticide, there are also drawbacks to it usage has it poses a serious havoc to the environment.[6] Being persistence in the environment, their accumulations in the food chain, their sub acute and chronic toxicity are detrimental to human and animal health.[7, 8]

Organochlorines (OCs) are the most persistent class of pesticides and have been banned in most countries due to their adverse effects on human health and environment.[9] OCs are characterized with their high chemical stability and lipid solubility (not water soluble). OC levels in soil generally decline very slowly. The rate of decline varies depending on ph, climate, and soil type.[10] Hence, such compounds may remain in soil and in the tissues of various organisms long after their use.[11]

Some researchers have reported the contaminations of chlorinated pesticides in stored grains. Aldrin, BHC, chlordane, DDT, dieldrin, HCB and heptachlor have all been found as residues in grains and livestock.[10, 12] Cereal grain is considered to be good for consumption not only if it is free from foreign materials, smell, unusual colour, mycotoxins, contaminations with live pests, but also when the concentration of active substances of pesticides does not exceed the maximum residue limits (MRLs). European Union[13] and

FAO/WHO[14] set a maximum residue limits (MRLs) in cereals and feeding stuff, among other compounds. Hence, the objective of this research is to quantify the residue of chlorinated pesticide content of the four grain samples and compare their residues content with FAO/WHO MRLs.

MATERIALS AND METHODS

Study Area

Akure is located in South – Western of Nigeria, a largest city and capital of Ondo State. It is located between latitudes 07^0 16^1 and 07^0 18^1 N and longitudes 05^0 09^1 and 05^0 11^I E.

Collection of Samples

Grain Samples were maize (*Zea mays* L), brown beans (*Vigna unguiculata*),wheat (*Triticum aestivum*) and Rice (*Oryza sativa*). Grains were purchased from four markets across Akure, Ondo State. The markets are represented as follows: Location 1 – Oba market, Location 2 – Isikan market, Location 3 – Nepa market and Location 4 – Shasha market. To obtain random sampling, about 200g were purchased from five different sales outlets. The samples were code-named and stored in glass bottles with tight covers to protect them from moisture and contamination. They were then stored in the refrigerator 4^0C until when ready for use.

Chemicals

All chemicals were of analytical grade and 99% purity. Reagents used include Anhydrous Sodium Sulphate, Ethyl Acetate, n-Hexane and all pesticides tested (Fisher Scientific, Allentown UK). The solvents were re-distilled in all-glass apparatus before use.

Preparation of Samples

The samples were cleaned by picking out stones and other extraneous materials. Each market sample from different outlets was thoroughly mixed and a 200.0g portion was taken and milled to 20 mesh particle size to produce a good homogenate. The milled samples were then stored in glass bottles with appropriate labels in a refrigerator at 4^0C. Duplicate portions (200.0g) of the samples were stored as whole grains in labelled glass bottles in the refrigerator as backup samples.

Extraction and Clean-up of Samples

Extraction of samples for the analysis was according to the methods of Sharif et *al.* and Wei-Guo *et al.*[15] with slight modifications. The milled sample was properly mixed and 2.0g was weighed into a sample vial. 1.0g of sodium sulphate that has been previously heated at 650^0C for one hour in a furnace and stored in a desiccator was added to absorb any moisture present. Ethyl acetate (10.0ml) was added to the vial. The mixture was mixed for 5min by shaking and then allowed to stand for 45min. It was mixed again and centrifuged for 5min. at 2500rpm. The supernatant was carefully transferred into a flask. The residue was further extracted twice as described above, using 10.0ml ethyl acetate each time. The supernatants were combined and reduced to about 5ml using a rotary evaporator at 35^oC. The solution was then transferred into a sample tube. This was then taken for cleanup to remove other unwanted co-extractives.

Silica gel column chromatography (Clean up)

The chromatographic column (20cm x 8mm I.D.) was packed with cotton wool to 10ml point on the syringe; 1g of anhydrous sodium sulphate was placed at the top of the column followed by 2g of Activated Silica gel and another layer of 1.0g anhydrous Sodium Sulphate to absorb any moisture present in the sample or the solvent. The column was conditioned with 5ml of the eluting solvent mixture made up of Ethyl acetate and Hexane (50:50). The sample extract (1ml) was loaded on the cartridge. The sample tube was rinsed three times with 1.0ml eluting solvent, and the rinses added to the column. The sample was then eluted with 5.0ml of the same solvent mixture into a receiving glass tube. The column was rinsed with another 3.0ml of the eluting solvent mixture into the same receiving glass tube. The eluant was then evaporated to dryness and the residue reconstituted in 1.0ml ethyl acetate for GC-MS analysis.

Organochlorines: Alpha-BHC, beta-BHC, Lindane, chlorothalonil, Delta_BHC, Heptachlor, Aldrin, dieldrin, dichlorodiphenyltrichloroethane (DDT), endosulfan I, endosulfan sulphate, Endrin, Heptachlor epocide, Endosulfan II, dichlorodiphenyldichloroethane (DDD), Permethrin and Lambda cyalothrin.

Preparation of Calibration Curves

Stock solutions of pure standards of organochlorine were prepared and then serially diluted to produce different concentrations of the pesticides. Stock standard solutions were stored in amber coloured bottles at 4^0C while working standard solutions were prepared fresh before use. Standard solutions of the pesticides were run on GC/MS under the set chromatographic conditions and mean peak areas were plotted against concentrations to obtain calibration curves of individual pesticides.

Data Analysis

All data were subjected to statistical analysis of New Duncan Multiple Range Test (NDMRT) at 0.05 level of significance using Statistical Package for Social Science version 21.

RESULT

Concentration of organochlorine pesticides in beans samples

The concentration of organochlorine pesticide in beans samples is presented in Table 1. The four markets surveyed in this research are represented as follows: Location 1 represents Oja-Oba, Location 2 represents Isikan market, Location 3 represents Nepa Market and Location 4 represents Shasha market. There were a few exceptions in some markets such as Heptachlor (B) was not detected in the beans sample from Location 1, Endrin

and Dieldrin were also found to be absent in the samples from Location 3. Only Lambda Cyalothrin was found to be absent in the sample from Location 2 while Endrin, Permethrin and Lambda Cyalothrin were not found in the sample from Location 4. Beans samples from location 3 and 4 showed significant level of difference ($p < 0.05$) from location 1 and 2 in the concentration of Endrin in the samples. There was also a significant level of difference ($p < 0.05$) in the concentration of Endosulfan Sulfate in location 3 and 4, while there was no difference between location 1 and 2. The results for Permethrin showed that samples from location 2 and 3 were significantly different ($p < 0.05$) from the sample from location 4 and also different from sample from location 1.

Organochlorine pesticides in rice samples

Table 2 below shows the results of analysis of organochlorine pesticides in rice samples. Endrin was found to be absent in all samples, Dieldrin was absent in rice samples from Location 3 while only the rice from Location 1 contained Lambda Cyalothrin. There was a conspicuously high quantity (8.49ppm) of Permethrin in the rice samples from Location 4 and was significantly different ($p<0.05$) from other locations.

Organochlorine pesticides in the wheat samples

The results obtained from the analysis of organochlorine pesticides in the wheat samples across all the markets are presented in Table 3. Endrin was found to be absent in all samples while only the sample from Location 2 contained lambda Cyalothrin but did not contain p,p-DDD. The Permethrin levels in these wheat samples were also considerably high.

Organochlorine pesticides in the maize samples

Table 4 shows the results of analysis of maize samples collected from the four markets. Endrin was found to be absent, a trend that has occurred in the other samples except Beans. p,p-DDD was also not detected in samples from Location 1 and Location 3. In some pesticide, there were significant differences ($p<0.05$) from one location to another.

Concentration of organochlorine pesticides in grain samples

Table 5 shows the mean concentrations of organochlorine pesticides in each grain across the four markets in Akure metropolis. Of all the four grains sample analysed, the maize samples had the highest concentration in many of the organochlorine pesticide. The concentration of alpha-BHC in maize was 0.03ppm, beta-BHC had a concentration of 0.14ppm, 0.073ppm for Lindane, 0.085ppm for Chlorothalonil and 0.14ppm in Aldrin.

Alpha_BHC had the highest concentration in maize and the lowest concentration in wheat but there was no significant difference between alpha-BHC concentrations in the grains. Concentrations of Beta-BHC ranged from 0.05ppm – 0.14ppm, with maize been the highest and wheat having the lowest concentration. Maize sample had the highest concentration of Delta-BHC with a value of 0.08ppm while Wheat had the lowest concentration of 0.019ppm. The highest concentration of Heptachlor (B) was detected in wheat with the value of 0.05ppm while the lowest concentration of 0.035ppm was detected in Rice.

The results also showed that Endrin was only detected in the Beans samples with a concentration of 0.07ppm. Endosulfan and its other derivatives had remarkably high concentrations in Rice and generally high concentrations in the other grains compared to other pesticides except in Lambda Cyalothrin and Permethrin. DDD had the highest concentration in wheat and the lowest concentration of 0.087ppm in Beans. The concentration of DDT was also conspicuously high in all the grains with a range between 0.24ppm- 0.49ppm.

Permethrin and Lambda Cyalothrin had the highest concentration compared to all the other pesticides across all the markets and grains. Concentration of Permethrin in Rice was as high as 5.99 and it showed significant difference from other grains with 3.86ppm in wheat, 2.87 ppm in beans and 1.45ppm in maize. Concentration of Lambda Cyalothrin in beans was 3.87ppm, in Rice the concentration of Lambda Cyalothrin was 1.0ppm, 1.03ppm in wheat and 3.91ppm in maize. The mean concentration of Lambda Cyalothrin in beans was significantly different from the concentration in other grains.

Maximum Residue Limit (MRL) of Organochlorine Pesticides for each grain in ppm

Figures 1 – 4 are charts showing the comparison between the FAO maximum residue limit and the concentrations of the organochlorine pesticide residues tested in this experiment. Almost 80% of the pesticide monitored exceeded their MRL; while some pesticide concentration slightly exceeded their maximum residue limit some concentrations were significantly higher than their MRL. Pesticides such as Endosulfan I, Endosulfan II and p,p-DDT had concentrations that were conspicuously higher than the standard set by WHO. Pesticides such as α-BHC, Heptachlor (B) and p,p-DDD slightly exceeded the MRL while pesticides such as Endosulfan II, Endosulfan Sulfate, p,p-DDT, β-BHC and Aldrin had concentrations that were more than double the maximum residue limit. Chlorothalonil was the only organochlorine pesticide found to be below the maximum residue limit for all the grains.

Table 1: Concentration of Organochlorine Pesticides in Beans samples.

Pesticides	Concentration (ppm)			
	Location1	Location 2	Location 3	Location 4
α-BHC	0.01±0.006 [a]	0.02±0.005 [a]	0.02±0.005 [a]	0.03±0.004 [a]
β-BHC	0.05±0.006 [a]	0.06±0.03 [a]	0.06±0.01 [a]	0.13±0.011 [b]
Lindane	0.04±0.006 [a]	0.03±0.01 [a]	0.03±0.006 [a]	0.027±0.001 [a]
Chlorothalonil	0.05±0.006 [a]	0.07±0.01 [ab]	0.05±0.006 [a]	0.079±0.011 [b]
δ-BHC	0.08±0.006 [a]	0.1±0.03 [a]	0.08±0.02 [a]	0.21±0.004 [a]
Heptachlor (B)	0.0±0.0 [a]	0.05±0.009 [a]	0.055±0.005 [a]	0.094±0.0017 [b]
Aldrin	0.08±0.011 [a]	0.1±0.01 [a]	0.083±0.01 [a]	0.17±0.02 [b]
Heptachlor Epocide	0.02±0.006 [a]	0.045±0.02 [a]	0.032±0.006 [a]	0.076±0.001 [b]
Endosulfan I	0.24±0.05 [b]	0.13±0.011 [ab]	0.22±0.05 [a]	0.41±0.08 [c]
Dieldrin	0.057±0.03 [a]	0.06±0.005 [a]	0.00±0.00 [a]	0.15±0.005 [b]
Endrin	0.11±0.006 [b]	0.17±0.0 [c]	0.0±0.0 [a]	0.0±0.0 [a]
Endosulfan II	0.42± 0.1 [a]	0.5±0.006 [b]	0.6 3±0.11 [ab]	1.24±0.14 [c]
DDD	0.06±0.006 [a]	0.07±0.004 [a]	0.078±0.001 [a]	0.14±0.001 [b]
Endosulfan Sulfate	0.26±0.005 [b]	0.28±0.05 [b]	0.2±0.08 [a]	0.73±0.06 [c]
DDT	0.2±0.1 [a]	0.27±0.05 [b]	0.28±0.06 [b]	0.65±0.05 [c]
Lambda Cyalothrin	7.75±0.2 [c]	0.0±0.0 [a]	3.74±0.5 [b]	0.0±0.0 [a]
Permethrin	2.0±0.6 [b]	5.04±0.57 [c]	4.44±1.3 [c]	0.0±0.0 [a]

Means ±Standard Error not followed by the same letter(s) in the same row are significantly different ($p<0.05$) from one another.

Table 2: Concentration of Organochlorine Pesticides in Rice samples.

Pesticides	Concentration (ppm)			
	Location1	Location 2	Location 3	Location 4
α-BHC	0.02±0.004 [a]	0.03±0.005 [a]	0.02±0.006 [ab]	0.05±0.006 [b]
β-BHC	0.03±0.006 [a]	0.17±0.017 [a]	0.06±0.011 [a]	0.17±0.011 [a]
Lindane	0.02±0.002 [a]	0.04±0.006 [ab]	0.02±0.002 [a]	0.07±0.02 [b]
Chlorothalonil	0.06±0.007 [a]	0.1±0.01 [ab]	0.06±0.0011 [ab]	0.12±0.01 [b]
δ-BHC	0.1±0.03 [a]	0.18±0.04 [b]	0.1±0.003 [a]	0.22±0.011 [c]
Heptachlor (B)	0.018±0.001 [a]	0.04±0.008 [a]	0.065±0.002 [b]	0.039±0.007 [bc]
Aldrin	0.1±0.006 [a]	0.14±0.0 [c]	0.06±0.006 [a]	0.09±0.006 [b]
Heptachlor Epocide	0.02±0.005 [a]	0.09±0.001 [b]	0.034±0.001 [c]	0.13±0.006 [d]
Endosulfan I	0.3±0.001 [a]	0.39±0.05 [ab]	0.25±0.003 [a]	0.5±0.06 [b]
Dieldrin	0.11±0.006 [b]	0.14±0.003 [bc]	0.0±0.0 [a]	0.17±0.01 [c]
Endrin	0.0±0.0 [a]	0.0±0.0 [a]	0.0±0.0 [a]	0.0±0.0 [a]
Endosulfan II	0.61± 0.005 [a]	1.02±0.1 [bc]	0.84 ±0.23 [ab]	1.3±0.11 [c]
DDD	0.1±0.02 [ab]	0.23±0.07 [bc]	0.0±0.0 [a]	0.35±0.06 [c]
Endosulfan Sulfate	0.26±0.02 [a]	0.45±0.028 [b]	0.55±0.028 [bc]	0.61±0.006 [c]
DDT	0.37±0.02 [a]	0.52±0.011 [b]	0.3±0.006 [a]	0.54±0.023 [b]
Lambda Cyalothrin	4.5±0.25 [b]	0.0±0.0 [a]	0.00±0.00 [a]	0.0±0.0 [a]
Permethrin	7.06 ±1.2 [b]	4.4±0.11 [a]	6.79±0.011 [b]	8.49±0.28 [c]

Means ±Standard Error not followed by the same letter(s) in the same row are significantly different ($p<0.05$) from one another.

Table 3: Concentration of Organochlorine Pesticides in Wheat samples.

Pesticides	Concentration (ppm)			
	Location1	Location 2	Location 3	Location 4
α-BHC	0.02±0.004 [ab]	0.008±0.005 [a]	0.02±0.001 [b]	0.02±0.004 [b]
β-BHC	0.07±0.001 [d]	0.034±0.002 [a]	0.07±0.0011 [c]	0.05±0.004 [b]
Lindane	0.017±0.0006 [a]	0.014±0.001 [a]	0.024±0.001 [b]	0.02±0.002 [b]
Chlorothalonil	0.05±0.005 [b]	0.032±0.0005 [a]	0.057±0.006 [c]	0.06±0.01 [b]
δ-BHC	0.13±0.03 [c]	0.06±0.003 [a]	0.09±0.01 [b]	0.08±0.005 [b]
Heptachlor (B)	0.06±0.002 [b]	0.03±0.0005 [a]	0.06±0.003 [b]	0.06±0.017 [b]
Aldrin	0.088±0.002 [bc]	0.05±0.003 [a]	0.11±0.02 [c]	0.06±0.02 [ab]
Heptachlor Epocide	0.04±0.001 [d]	0.003±0.0012 [a]	0.04±0.001 [c]	0.031±0.0006 [b]

Endosulfan I	0.19±0.06 [b]	0.09±0.006 [a]	0.22±0.03 [b]	0.25±0.011 [b]
Dieldrin	0.07±0.002 [bc]	0.018±0.0003 [a]	0.08±0.001 [c]	0.06±0.006 [b]
Endrin	0.00±0.0 [a]	0.00±0.0 [a]	0.00±0.0 [a]	0.00±0.0 [a]
Endosulfan II	0.45± 0.06 [ab]	0.35±0.1 [a]	0.88 ±0.1 [c]	0.53±0.13 [b]
DDD	0.12±0.01 [c]	0.00±0.0 [a]	0.06±0.04 [b]	0.09±0.005 [bc]
Endosulfan Sulfate	0.39±0.28 [b]	0.24±0.04 [a]	0.58±0.09 [c]	0.21±0.08 [a]
DDT	0.27±0.05 [ab]	0.16±0.005 [a]	0.29±0.07 [b]	0.28±0.005 [ab]
Lambda Cyalothrin	0.00±0.0 [a]	4.13±0.25 [b]	0.00±0.00 [a]	0.00±0.0 [a]
Permethrin	4.28±0.2 [c]	1.24±0.58 [a]	2.65±0.8 [b]	7.30±0.9 [d]

Means ±Standard Error not followed by the same letter(s) in the same row are significantly different ($p<0.05$) from one another.

Table 4: Concentration of Organochlorine Pesticides in Maize samples.

Pesticides	**Concentration (ppm)**			
	Location1	**Location 2**	**Location 3**	**Location 4**
α-BHC	0.03±0.006[a]	0.03±0.005[a]	0.04±0.0012[a]	0.03±0.004[a]
β-BHC	0.14±0.029[a]	0.14±0.006 [a]	0.17±0.009[a]	0.11±0.011 [a]
Lindane	0.08±0.002 [a]	0.07±0.006 [a]	0.12±0.005 [b]	0.03±0.04 [a]
Chlorothalonil	0.08±0.0012 [ab]	0.07±0.005 [a]	0.12±0.05[b]	0.07±0.0005[a]
δ-BHC	0.11±0.05 [a]	0.1±0.03 [a]	0.12±0.01 [a]	0.12±0.01 [a]
Heptachlor (B)	0.03±0.006 [b]	0.02±0.002 [ab]	0.00±0.00 [a]	0.08±0.011 [c]
Aldrin	0.13±0.01 [a]	0.12±0.01 [a]	0.2±0.03 [b]	0.11±0.02 [a]
Heptachlor Epocide	0.11±0.04 [b]	0.1±0.02 [b]	0.09±0.06 [ab]	0.06±0.04 [a]
Endosulfan I	0.15±0.08 [a]	0.11±0.05 [b]	0.5±0.001 [c]	0.3±0.04 [b]
Dieldrin	0.11±0.03 [a]	0.12±0.04 [a]	0.13±0.04 [a]	0.11±0.005 [a]
Endrin	0.0±0.0 [a]	0.0±0.0 [a]	0.0±0.0 [a]	0.0±0.0 [a]
Endosulfan II	0.63± 0.2 [a]	0.57±0.06 [a]	1.2 ±0.14 [c]	0.74±0.1 [b]
DDD	0.0±0.0 [a]	0.0±0.0 [a]	0.24±0.01 [c]	0.15±0.05 [b]
Endosulfan Sulfate	0.6±0.15 [ab]	0.62±0.4 [b]	0.56±0.07 [a]	0.71±0.2 [c]
DDT	0.6±0.2 [c]	0.55±0.06 [c]	0.5±0.08 [b]	0.35±0.4 [a]
Lambda Cyalothrin	15.66 ±4.5 [b]	0.0±0.0 [a]	0.0±0.0 [a]	0.0±0.0 [a]
Permethrin	5.8±1.2 [b]	0.0±0.0 [a]	0.0±0.0 [a]	0.0±0.0 [a]

Means ±Standard Error not followed by the same letter(s) in the same row are significantly different ($p<0.05$) from one another.

Table 5: Concentration of Organochlorine Pesticides in Grain samples

Pesticides	**Grains (ppm)**			
	Beans	**Rice**	**Wheat**	**Maize**
α-BHC	0.02±0.004 [a]	0.03±0.005 [a]	0.02±0.003 [a]	0.03±0.004 [a]
β-BHC	0.08±0.02 [a]	0.09±0.03 [a]	0.06±0.009 [a]	0.14±0.011 [a]
Lindane	0.03±0.002 [a]	0.03±0.01 [a]	0.019±0.002 [a]	0.07±0.02 [a]
Chlorothalonil	0.06±0.007 [a]	0.07±0.01 [a]	0.049±0.006 [a]	0.09±0.01 [a]
δ-BHC	0.12±0.03 [a]	0.14±0.03 [a]	0.087±0.01 [a]	0.11±0.004 [a]
Heptachlor (B)	0.05±0.02 [a]	0.04±0.009 [a]	0.05±0.007 [a]	0.03±0.017 [a]
Aldrin	0.11±0.02 [a]	0.09±0.01 [a]	0.08±0.01 [a]	0.14±0.02 [a]
Heptachlor Epocide	0.04±0.01 [a]	0.06±0.02 [a]	0.02±0.011 [a]	0.09±0.01 [a]
Endosulfan I	0.25±0.06 [a]	0.32±0.05 [a]	0.19±0.03 [a]	0.25±0.08 [a]
Dieldrin	0.07±0.03 [a]	0.09±0.03 [a]	0.06±0.01 [a]	0.11±0.005 [a]
Endrin	0.07±0.04 [a]	0.0±0.0 [a]	0.0±0.0 [a]	0.0±0.0 [a]
Endosulfan II	0.7± 0.2 [a]	0.85±0.1 [a]	0.55 ±0.11 [a]	0.78±0.14 [a]
DDD	0.09±0.02 [a]	0.15±0.07 [a]	0.25±0.02 [a]	0.09±0.05 [a]
Endosulfan Sulfate	0.36±0.12 [a]	0.41±0.07 [a]	0.35±0.08 [a]	0.62±0.03 [a]
DDT	0.35±0.1 [a]	0.39±0.05 [a]	0.25±0.03 [a]	0.49±0.05 [a]
Lambda Cyalothrin	3.87±2.2 [a]	1.0±0.25 [a]	1.03±0.5 [a]	3.91±1.2 [a]
Permethrin	2.87±1.2 [b]	5.99±0.76 [b]	3.86±1.3 [b]	1.45±0.7 [a]

Mean ±S.E represents three (3) replicates. Means not followed by the same letter(s) in the same row are significantly different ($p<0.05$) from one another.

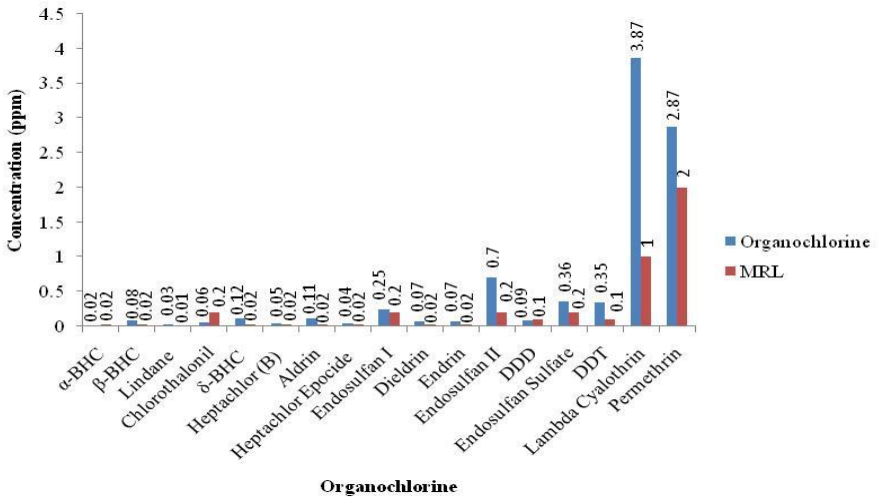

Figure 1: Chart showing comparison between MRL and Concentration of organochlorine pesticides in Beans.

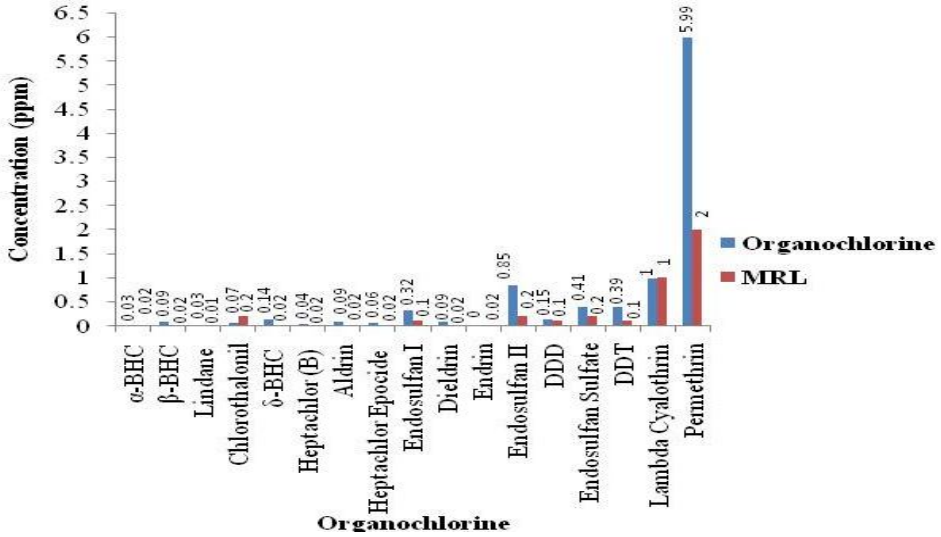

Figure 2: Chart showing comparison between MRL and Concentration of organochlorine pesticides in Rice.

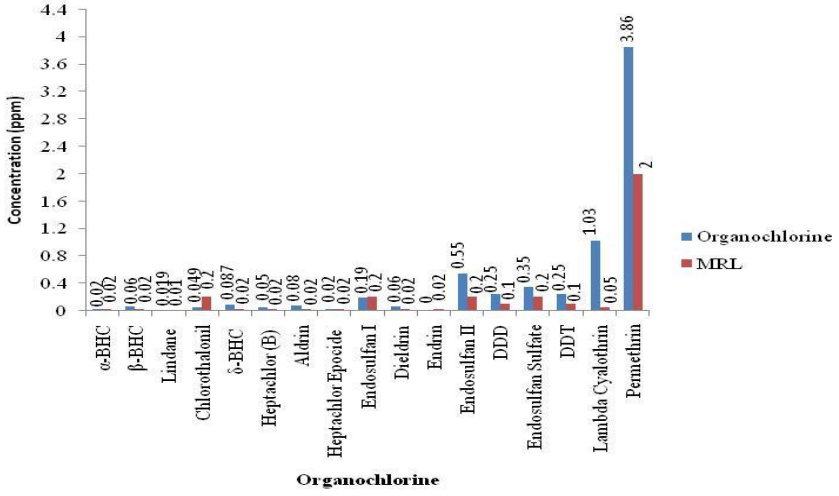

Figure 3: Chart showing comparison between MRL and Concentration of organochlorine pesticides in wheat.

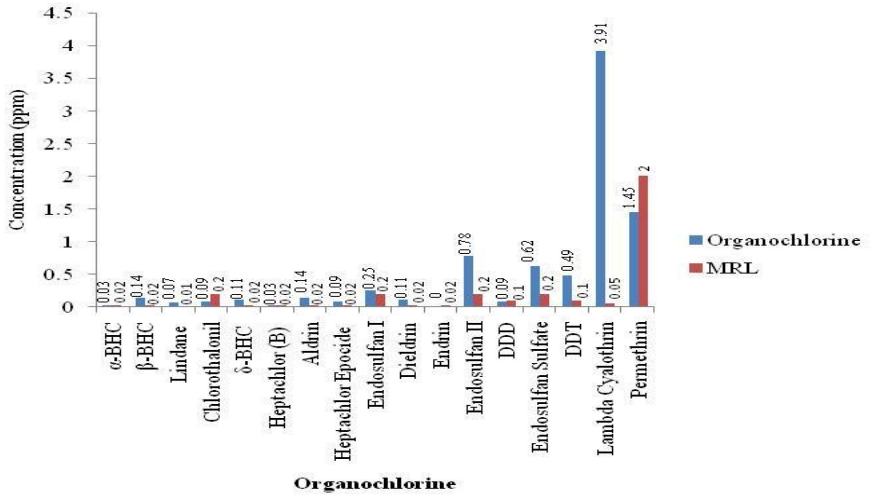

Figure 4: Chart showing comparison between MRL and Concentration of Organochlorine pesticides in Maize.

DISCUSSION

The concentrations of organochlorine pesticides across the grain samples were lower in the wheat samples while the maize, rice and beans samples had higher mean concentration of the individual pesticides, although for each of the pesticides there was no significant difference in the quantity of pesticides with respect to the grains except for permethrin that had significantly different concentrations in the maize sample compared with the other three grains. The type of grain affected the concentration of the pesticides found in them which may be due to the absorption capacity of the grains. Permethrin was also the pesticide found to be at the highest concentration in all the grain samples. This high concentration of Permethrin in all the grain samples tested may be due to the fact that it is the most commonly used pesticide in the area under study. For many of the pesticides monitored there was significant difference between the concentrations of residues that were found across the various markets from which the grains were bought.

The concentrations obtained from the study were compared with the FAO/WHO maximum residue limit for each of the grains. The results obtained showed concentration level of about 80% of the organochlorine to have exceeded the maximum residue limit set by FAO/WHO in cereals. The maximum residue limit (MRL) of a pesticide is the maximum concentration of its residue that is legally permitted to remain in any food after it has been treated with the pesticide. According to FAO/WHO[14], MRL is not expected to be exceeded in any foodstuff if the pesticide was applied in accordance with directions for its safe use. If a pesticide residue is found to exceed the MRL in any food, the food commodity is said to be adulterated because it contains an unsafe or illegal amount of the residue. Noncompliance with MRLs can impact negatively on international trade in agricultural produce as each commodity must meet international standards or standards of the receiving country.

The levels of organochlorine pesticides in the beans samples tested in this study exceeded their MRL. Ogah *et al.*[9] suggested that this probably be because beans are highly susceptible to infestation by weevils and are consequently often subjected to postharvest treatment with pesticides to maintain good quality during storage and avoid economic losses. Endrin was found to be absent in all grains sampled except in bean and this was in line with Ogah *et al.*,[9] reporting Endrin to had the lowest violating concentration of 23% above its MRL in bean sampled. The result of this study is in contrast with the study of Obida *et al* who also found varying ranges of Organochlorine pesticides in bean samples in Northeastern Nigeria. In which Endosulfan, DDT and Endrin were detected in the grain samples but their levels were below their MRL.

Several researchers have reported chlorinated pesticide residue in the studied grains. Anzene *et al*[16] also reported levels of organochlorine pesticide (OCPs) residues in post harvest grains which include Millet, guinea corn and maize grains. The result indicated the presence of varying amounts of ten (10) organochlorine pesticide residues in all the samples where Lindane and Aldrin residues were reported to be above the maximum residue limits (MRLs) set by WHO/FAO for cereals as reported in this current study. Bakore *et al.*[17] reported that all of the wheat samples from India were contaminated with various organochlorine pesticide residues of DDTs and its metabolites, γ-HCH and its isomers, heptachlor, epoxide and aldrin. Riaz *et al.*[12] detected Endosulfan in rice samples. However, all the residual quantities were found to be much lower than maximum residual limits (MRLs).

Consumption of grains with pesticide residue above the stipulated maximum residue limit may result in accumulation of the chemicals in the body, which could eventually lead to adverse health effect. According to Ogah *et al.*[9], the accumulation of different pesticide into

the body may resulted into additive or synergistic effects which can make pesticides that were detected at 'safe levels' to eventually pose health hazards.

CONCLUSION

The amount of pesticide residues detected in grains from Akure, Ondo State, Nigeria showed that the grains samples monitored in the present study contain various levels of the pesticides residue. Many of the already banned organochlorine pesticides were found in most of the grain samples which could be a direct consequence of previously treated or contaminated soil. There is also a possibility of misuse/abuse of the various pesticides or ignorant about the banned pesticides. This further attests to the persistence of organochlorine pesticides and efforts should still be made towards completely eradicating its use by appropriate authorities.

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