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GC-MS Analysis of Pesticide Residues in Stored Grain Legumes and Cereals from Selected Markets in Rivers State Nigeria

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ABSTRACT

This study analyzed pesticide residues in stored grain legumes and cereals from selected major markets in Rivers State Nigeria. The samples obtained were kept in labeled Ziploc envelopes before the laboratory experiments. The samples were divided into sub-samples where some parts were tested for Maximum Residual Levels (MRLs) of pesticides before storage, while other composite samples were kept in the laboratory for 153 days to observe insect emergence. The research was carried out at Ignatius Ajuru University of Education research laboratory and Austino Research Laboratory, Rivers State, Nigeria. Pesticide residues in samples were determined and quantified using an Agilent 6890 gas chromatograph with a 5973 Mass Selective detector (GC-MS) 30m × 0.25mm, i.d. fused silica capillary column chemically bonded with SE-54 (DB-5),1 micron film thickness. A total of 23 pesticide residues were detected which included organochlorine > herbicides > fungicides > organophosphates. The severity of grain damage after four months of storage ranged from undamaged to severely damage. The results of this study show that there was a high incidence of pesticide residues in grain legumes and cereals sold in the major markets in Rivers State Nigeria. Organochlorine pesticides are much in use by grain merchants and farmers in Nigeria especially for crop protection as they were found in appreciable concentrations in all the samples across the markets. There is the need for National Agency for Food and Drug Administration and Control (NAFDAC), None Governmental Organizations (NGOs) and other relevant agencies to increase surveillance to check and control its illegal importation, sale and use.

Keywords: Toxicity, Maximum Residual Levels, Gas Chromatograph, Mass Selective Detector.

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INTRODUCTION

Pesticides are chemical agents belonging to a variety of different classes such as organochlorines, organophosphates, carbamates and pyrethroids used to manage pests or control their growth and reproduction. They are used both in agriculture and public health to boost food production and fight pests of public importance. (Ogah et al., 2015; Ali et al., 2015). However, the use of pesticides also comes with drawbacks such as contamination of the environment (Akinneye et al., 2006), toxic accumulation in the food chain and toxicity to human and animal health (Leong et al., 2007; El-Shahawia et al., 2010). Despite these shortcomings, pesticide use is still gaining widespread use in the agriculture and public health sector (Ogah et al., 2015). Since time immemorial mankind has had to contend with pests that attack both his cultivated or stored crops, domestic animals and their products such as hides and skin and even himself. To overcome these numerous challenges, more than 1100 pesticides are used in various combinations and at different stages of

crop growth and in-store to prevent, destroy, repel, or mitigate the effects of such pests' activities (Naylor, 2003). Akunyili and Ivbijaro (2012) traced the history of pesticide usage in Nigeria to British colonial government which was used to control pest of both public health and agriculture, where broad-spectrum pesticides were the commonest with tendencies of being toxic to both beneficial and non beneficial organisms and high rate of accumulation in water, food chain and ecosystem. Ivbijaro (1998) opined that there is evidence of poor pesticide education and usage in Nigeria citing the example of indiscriminate use for the purpose of effective rapid killing of crop pests even among the trained farmers. Also, the use of pesticides for purposes other than that which they were manufactured for (Akunyili and Ivijaro, 2012) such as the use of lindane in illegal fishing and not on cocoa pests and carbaryl in storing cowpea in lockup stalls instead of using it solely on field crops.

In order to regulate pesticide abuse either by manufacturers or end-users, governments regulate by preventing chemicals with unacceptable properties being introduced onto the market that may end up in the food chain and ecosystem. FAO (2016) opined that such a move is to protect the users of pesticides, the consumers of treated foodstuffs, domestic animals and at a later stage, the environment and to reduce food contamination with chemical pesticides and reduce threats it poses to farmers, grain merchants and public health worldwide (Holand et al., 2004; Ochii, 2010; Mada et al., 2014; Qasim et al., 2018). But with an increase in population and the absence of reliable and functional agrochemical industries in Nigeria (Anudu, 1998), pesticide usage and importation into the country are rather on the increase. This is because the pesticide is always considered as the first line of action in pests control in the tropics. Akunyili and Ivbijaro (2012) Manzoor et al. (2017) commended the effectiveness of organochlorine pesticides and caution its persistence and accumulation in the animal body which may have an effect on the liver such as stimulating the activity of microsomal enzymes in the liver and may further interfere with the metabolism of other compounds. Cereals and legumes are important parts of human diet being good and inexpensive sources of carbohydrates, deity fibers, protein and oil (Mada et al., 2014) and ensuring food security especially in developing countries (Chibbars, 2009). For either cereal or legumes to be considered good for consumption, it must be free from foreign materials such as insect exuvia and broken appendages, off-smell, unusual colour and mycotoxins and must also not contain concentration of active substances of pesticides above the maximum residue limits (MRLs) (Akinneye et al., 2018). The hazardous nature of pesticides and their inherent toxicity could be acute or chronic which ranges from minor discomfort to carcinogenic, endocrine, disruption and organic disorder, makes it important to check the permissible concentration of residues of these chemicals in food such as grain. The maximum permissible level concentration of pesticide from the point of application including the residues in storage, transport and preparation before consumption to when food is first offered for consumption (Akunyili and Ivbijaro, 2012) is so critical in determining the toxic levels man ingests in his food. FAO/WHO (2005) expressed pesticides as toxic in nature and do not differentiate between targeted and non-targeted species, therefore should be subjected to safe and judicious use. Its misuse has led to several accidents and the presence of such toxic elements in food, animal feeds and environment most be given top priority of concern.

These highly stable compounds can last for several decades in the environment before breaking down and has no global limitation. Pesticides released in one part of the world can be transported and deposited to other regions far away from the original source (Williams, 2000). Ogah et al. (2015) observed that these compounds are highly toxic and capable of causing adverse effects, notably death, diseases and birth defects among humans and animals others include congenital malformations, neurotoxic disorders, infertility and blood dyscrasias. Other side effects of pesticides may include cancer, allergies and hypersensitivity, damage to the nervous systems, reproductive disorders and disruption of the immune system (Strict, 1981; Maroni, 1990). In tropical Africa, it is a common practice for farmers and grain merchants to keep grain legumes and cereals for long term (1 to 36 months) which predispose them to severe pest infestation thereby incurring loss. To overcome these challenges, the grains are periodically treated with pesticides that tend to leave toxic residues and also alter their nutrient value, taste, palatability and food safety. Many studies have shown that pesticide residue penetrate the grain and accumulate over time especially in storage (Holland et al., 1994, Uygun et al., 2005; Mada et al., 2014) and grains treated with such chemicals shows presence of bound residue even after fairly long period of storage thus contributing to dietary intake of pesticide (Lahah and Wading, 2002). FAO/WHO (2013) set maximum residue limits (MRLs) for grain legumes and cereals and other feedstuffs in order to safeguard the consumers and vendors against such toxins. Therefore, the objective of this research was to determine the levels of pesticide residues in stored grain legumes and cereals from selected markets in Rivers State Nigeria to compare their residues content with FAO/WHO MRLs.

MATERIALS AND METHODS

Sample Collection

The research was carried out at Ignatius Ajuru University of Education research laboratory and Austino

Research Laboratory, Rivers State, Nigeria. Grain legume (groundnut and cowpea) and cereals (rice and maize) were used for the studies. The beans variety (iron bean) is a popular variety and much consumed in the state and the groundnut (kampala) variety, while the rice variety is a popular foreign rice and a yellow local a maize variety (Ogbia muno) were randomly sampled from traders in each of the major markets. Samples were collected from (Creek Road market, Mile 1 market and Mile III market) in Port-Harcourt Local Government Area (PHALGA) and (Rumuokwuta market, Choba market, Rumuokoro market and Rumuokoro slaughter market) in Obio-Akpor Local Government Area (OBALGA). In each market, each product was purchased from three different traders and put in an airtight Ziploc envelope containing information such as market place, produce, date of purchase and conveyed to the research laboratory. Some of the samples were kept in 250g plastic containers and replicated three times and kept on a laboratory bench for a period of 153 days to observe insect emergence. Grain samples were taken to Austino Research Laboratory for pesticide residue analysis before and after four months of storage in the laboratory to observe insect emergence.

Chemicals and Reagents

The chemicals, reagents and solvents used in the analysis included; Air-Zero grade, Nitrogen gas -UHP grade, ethylene chloride, anhydrous sodium sulfate, n-hexane and the standard of the pesticide used as internal standard.

Preparation of Samples

A 20g aliquot of sample was homogenized and a 10g aliquot was spiked. The sample was mixed with anhydrous sodium sulfate and was allowed to dry for about 30 min minimum. The samples were extracted within 18 to 24 h using methylene chloride in a soxhlet extractor. The extract was evaporated to dryness and the lipid content was determined. Duplicate portions of 10g of the samples were stored as whole grains in labeled glass bottles and stored in a refrigerator as backup samples.

Extraction and Clean-Up of Samples

Pesticide residues in the sample were extracted using established methods though with slight modifications. In brief, extracts for pesticide analysis were subjected to a sequential methylene chloride-n-hexane (1:1) clean-up specifically for the analyses. 40 microL of each sample was injected into a gas chromatograph, equipped with a wide-bore fused -silica capillary column in an Electron Capture Detector (ECD). The lipid content extracted using a 2.5 mL airtight syringe at a volume of 1 microL was injected through the injection port into the injector. The samples in the injector were held at a temperature ramp of 250°C and the detector at 280^{o}C. At the initial oven temperature of 200°C held for 1 min but subsequently increased to 230°C at 1.5°C min-1 and then held for 10 min.

Analysis of Pesticide Residue Content
GC-MS Conditions

All compounds were determined and quantified using an Agilent 6890 gas chromatograph with a 5973 Mass Selective detector (GC-MS) 30 m × 0.25mm, i.d. fused silica capillary column chemically bonded with SE-54 (DB-5), 1 micron film thickness. The carrier gas was nitrogen at a Dow rate of 1 mL min-1 using manual injection at an injection volume of 1 microL. The split ratio was 50:1 and the sample size was 1 microL. Oven temperatures were maintained initially at 200°C held for 1 min and heated to 230°C (1.5°C min-1) then held for 10 min.

Characterization and Identification

The characterization and identification of pesticides from the samples were completed in the m/z range varying from 35 to 450. The composition of the pesticides from the sample was determined using an Agilent 6820 gas chromatograph.

RESULTS

Grain legumes and cereals sampled from selected major markets in Rivers State infested by insect pest after 4 months of storage are shown in Table 1. Rice sampled from seven major markets in Port Harcourt stored for four months in the laboratory were found to be undamaged, while beans status was slightly damaged and only beans collected from Mile 1 market were severely damaged. Maize sampled from Rumuokoro and Rumuokoro slaughter was undamaged and maize sampled from creek road market was severely damaged. Groundnut sampled from the different markets ranged from slight to undamaged status after four months of storage. Table 2 shows the total pesticide detected from grain legume and cereal samples obtained from selected major markets in Rivers State, Nigeria. 23 pesticide residues were detected from the total samples. 57% of the compounds were organochlorine based, while fungicides and herbicides were 17% each and 9% was organophosphate based pesticide. Table 3 shows the Pesticide residues in grains sampled from Choba market. The result shows that Captan, Chlordane Alpha (cis) and Chrothalonil were above the MRL in rice and beans while DDT OP- and Hexazinone were above the MRL in all the grains sampled. Compounds like Hexachlorobenzene, Octachlorostyrene, Perthane, BHC1 Alpha, BHC1 beta, BHC1 delta, Simazine and Cyanazine were below the MRL. Table 4 shows the

Table 1. Categorization of damaged grain legumes and cereals sampled from selected major markets in Rivers State due to insect pest infestation after 4 months of storage.

	Creek Road	Mile iii	Mile i	Rumuokwuta	Rumuokoro	Rumuokoro Slaughter	Choba
Rice	Undamaged	Undamaged	Undamaged	Undamaged	Undamaged	Undamaged	Undamaged
Beans	Slight damage	Slight- damage	Severe damage	Slight- damage	Slight- damage	Undamaged	Slight damage
Maize	Severe damage	Slight- damage	Slight- damage	Slight damage	Undamaged	Undamaged	Slight damage
Groundnut	Undamaged	Slight damage	Slight- damage	Slight damage	Undamaged	Slight damage	Undamaged

Table 2. Pesticide residues detected from grain legume and cereal samples obtained from selected major markets in Rivers State, Nigeria.

Pesticides	Groups	Total	Abundance
Chlordane alpha (cis)	Organochlorines		
DDT 0P-			
Hexachlorobenzene			
Methoxychlor			
Endosulphan-alpha			
Endosulphan-sulfate			
DDE O P		13	57
DDT PP-			
BHC alpha			
BHC beta			
BHC delta			
Octachlorostyrene			
perthane			
Captan	Fungicides	4	17
Chlorothalonil			
Quintozene			
Tecnazene			
Atrazine	Herbicides	4	17
Hexazinone			
Simazine			
Cyanazine			
Diazinon	Organophosphates	2	9
Malathion			
	Total	23	100

results of pesticide residues from grains sampled from Rumuokoro market. From the table, DDT OP- and Hexazinone were above the MRL in all the grains, while Hexachlorobenzene, Octachlorostyrene, Tecnazene, BHC1 Alpha, BHC1 beta, BHC1 beta and Cyanazine were below

Table 3. Pesticide residues in grains sampled from Choba market in River State, Nigeria.

PRODUCTS		Captan	Chlordane Alpha (Cis)	Chrothalonil	DDT OP-	DDT PP-	Endosulphan-alpha	Endosulphan-Sulfate	Hexachlorobenzene	Methoxychor	Octachlorost-yrene	Perthane	Quintozene	Tecnazene	Diazinon	Atrazine	Hexazinone	Malathion	DDE O,P	BHC1 Alpha	BHC1 beta	BHC delta	Simazine	Cyanazine
RICE	Before	**0.14**	**0.23**	**0.10**	0.05	0.01	0.22	0.16	0.03	**0.14**	0.09	0.17	0.02	0.01	**0.13**	0.06	**0.16**	**0.29**	0.34	0.18	0.10	0.04	0.02	0.13
	After	**0.08**	**0.17**	**0.05**	0.01	0.03	0.14	0.07	0.02	**0.05**	0.04	0.09	-	-	0.04	0.01	**0.10**	**0.17**	0.19	0.10	0.04	0.06	-	0.09
	M.R.L	0.01	0.02	0.04	0.05		0.1	0.1	0.05	0.02			0.1		0.05		0.01	0.08						
BEANS	Before	0.10	**0.09**	0.07	**0.13**	0.04	0.05	0.23	0.16	**0.31**	0.16	0.17	**0.47**	0.18	**0.41**	**0.17**	**0.25**	0.01	**0.14**	0.05	0.06	0.10	0.12	0.10
	After	0.12	**0.03**	-	**0.08**	0.03	0.05	0.13	0.07	**0.19**	0.08	0.06	**0.28**	0.11	**0.33**	0.02	**0.15**	-	**0.07**	0.09	0.03	0.07	0.09	0.03
	M.R.L	5	0.02	0.2	0.05	0.05	1	1		0.01			0.1		0.05	0.02	0.01	0.5	0.05	1	1	1	0.01	
MAIZE	Before	**0.19**	0.10	0.04	**0.12**	0.06	0.11	**0.14**	0.02	**0.16**	0.03	0.05	0.21	0.33	**0.13**	0.07	**0.40**	0.12	0.16	0.11	0.17	0.04	0.01	0.05
	After	**0.11**	0.06	**0.09**	0.03	0.01	0.05	**0.08**	0.03	**0.21**	0.08	0.02	0.11	0.19	**0.10**	**0.12**	**0.23**	0.07	0.10	0.05	0.07	-	-	**0.06**
	M.R.L	0.01		0.04	0.05		0.5	0.5	0.05	0.02			0.1		0.05	0.1	0.01	2.0					0.2	0.05
GROUNDNUT	Before	0.03	**0.21**	0.05	0.14	0.09	0.11	0.04	0.20	**0.23**	0.03	0.16	0.15	0.11	**0.06**	0.21	0.01	0.20	0.06	0.12	0.15	0.06	0.11	0.16
	After	0.08	**0.05**	0.04	0.11	0.07	0.13	0.01	0.08	**0.14**	-	0.07	0.05	0.15	0.05	0.13	-	0.07	0.08	0.05	0.11	0.07	0.03	0.08
	M.R.L	5	0.02	0.1			0.2	0.2		0.05					0.05		0.01							

Table 4. Pesticide residues in grains sampled from Rumuokoro market in River State, Nigeria.

PRODUCTS		Captan	Chlordane Alpha (Cis)	Chrothalonil	DDT OP-	DDT PP-	Endosulphan-alpha	Endosulphan-Sulfate	Hexachlorob-enzene	Methoxychor	Octachlorost-yrene	Perthane	Quintozene	Tecnazene	Diazinon	Atrazine	Hexazinone	Malathion	D, DE, O, P	BHC Alpha	BHC beta	BHC delta	Simazine	Cyanazine
RICE	Before	**0.14**	**0.23**	**0.10**	0.05	0.05	0.22	0.16	0.03	**0.16**	0.09	0.17	0.02	0.05	**0.13**	**0.06**	**0.16**	**0.29**	0.32	0.18	0.12	0.04	0.02	0.13
	After	**0.08**	**0.17**	**0.05**	0.01	0.05	0.14	0.07	0.02	**0.05**	0.06	0.11	-	-	0.04	0.01	**0.10**	**0.19**	0.19	0.12	0.04	0.06	-	0.11
	M.R.L	0.01	0.02	0.04	0.05		0.1	0.1	0.05	0.02			0.1		0.05	0.02	0.01	0.08						
BEANS	Before	0.10	**0.10**	**0.07**	**0.13**	0.04	0.09	0.19	0.16	**0.31**	0.16	**0.14**	0.47	0.18	**0.41**	**0.17**	**0.23**	0.01	**0.14**	0.10	0.06	0.10	**0.12**	0.08
	After	0.14	0.01	-	**0.10**	0.03	0.15	0.13	0.07	**0.21**	0.08	0.06	0.28	0.11	**0.33**	**0.05**	**0.14**	-	**0.09**	0.09	0.03	0.07	**0.09**	0.05
	M.R.L	5	0.02	0.2	0.05	0.05	1	1		0.01		0.1			0.05	0.02	0.01	0.5	0.05	1	1	1	0.01	
MAIZE	Before	**0.17**	**0.10**	0.04	**0.12**	0.06	**0.11**	**0.15**	0.02	0**.16**	0.01	0.05	**0.19**	0.33	**0.13**	**0.07**	**0.36**	0.12	0.16	0.11	0.17	0.02	0.01	0.03
	After	**0.13**	**0.06**	**0.09**	0.05	0.016	0.05	**0.08**	0.03	**0.21**	0.08	0.04	**0.11**	0.21	**0.10**	**0.15**	**0.23**	0.07	0.10	0.07	0.09	-	-	**0.08**
	M.R.L	0.01	0.02	0.04	0.05		0.5	0.5	0.05	0.02			0.1		0.05	0.1	0.01	2.0					0.2	0.05
GROUNDNUT	Before	0.05	**0.19**	0.05	0.14	0.09	0.11	0.04	**0.20**	0.23	0.02	0.16	0.12	0.11	**0.06**	0.21	0.01	0.20	0.06	0.12	0.15	0.04	0.11	0.16
	After	0.08	**0.05**	0.02	0.11	0.07	0.13	0.01	**0.08**	0.14	-	0.09	0.05	0.15	0.01	0.15	-	0.07	0.01	0.05	0.11	0.07	0.03	0.10
	M.R.L	5	0.02	0.1			0.2	0.2	0.05						0.05		0.01							

Table 5. Pesticide residues in grains sampled from Rumuokwuta market in River State, Nigeria.

Products		Captan	Chlordane Alpha (Cis)	Chrothalonil	DDT, O P-	DDT, P P-	Endosulphan-alpha	Endosulphan-Sulfate	Hexachlorobenzene	Methoxychlor	Octachlorostyrene	Perthane	Quintozene	Tecnazene	Diazinon	Atrazine	Hexazinone	Malathion	D, DE O, P	BHC Alpha	BHC beta	BHC delta	Simazine	Cyanazine
Rice	Before	0.14	0.23	0.14	0.05	0.01	0.22	0.16	0.03	0.14	0.09	0.17	0.02	0.01	0.13	0.29	0.16	0.29	0.34	0.18	0.10	0.04	0.02	0.13
	After	0.08	0.19	0.03	0.01	0.03	0.14	0.07	0.02	0.07	0.04	0.11	ND	ND	0.06	0.01	0.10	0.17	0.20	0.12	0.04	0.06	ND	0.09
	M.R. L	0.01	0.02	0.04	0.05		0.1	0.1	0.05	0.02			0.1		0.05	0.02	0.01	0.08						
Beans	Before	0.14	0.10	0.07	0.13	0.04	0.09	0.19	0.16	0.31	0.16	0.14	0.47	0.18	0.41	0.17	0.23	0.05	0.14	0.05	0.06	0.10	0.16	0.08
	After	0.12	0.01	ND	0.08	0.03	0.05	0.13	0.09	0.19	0.08	0.06	0.30	0.11	0.33	0.02	0.14	ND	0.07	0.11	0.03	0.07	0.09	0.03
	M.R. L	5	0.02	0.2	0.05	0.05	1	1		0.01			0.1		0.05	0.02	0.01	0.5	0.05	1	1	1	0.01	
Maize	Before	0.17	0.10	0.04	0.12	0.06	0.11	0.18	0.02	0.16	0.01	0.08	0.19	0.33	0.13	0.10	0.36	0.12	0.16	0.11	0.12	0.02	0.01	0.03
	After	0.13	0.06	0.07	0.03	0.01	0.05	0.08	0.03	0.21	0.07	0.02	0.11	0.21	0.10	0.12	0.23	0.06	0.09	0.05	0.09	ND	ND	0.06
	M.R. L	0.01	0.02	0.04	0.05		0.5	0.5	0.05	0.02			0.1		0.05	0.1	0.01	2.0				0.02	0.05	
Groundnut	Before	0.03	0.19	0.05	0.14	0.09	0.11	0.05	0.17	0.23	0.02	0.16	0.10	0.11	0.05	0.21	0.01	0.18	0.06	0.11		0.04	0.11	0.16
	After	0.08	0.05	0.02	0.09	0.07	0.13	0.01	0.08	0.14	ND	0.06	0.05	0.15	0.01	0.11	ND	0.07	0.10	0.05		0.07	0.03	0.08
	M.R. L	5	0.02	0.1			0.2	0.2		0.05					0.05		0.01							

the MRL in the grains sampled.

Table 5 shows the results of pesticide residues from grains sampled from Rumuokwuta market. From the table, chlordane alpha (cis), methoxychlor and hexazinone were above MRL in all the grains while Octachlorostyrene, Perthane, BHC alpha, BHC beta and BHC delta were below the MRL in all the grains. Similar results were obtained in grains sampled from Mile 3 and Mile 1 markets (Table 6 and 7). Table 8 shows the pesticide residue level from grains sampled from Rumuokoro Slaughter market. From the table, none of the compounds exceeded the MRL in all the grains except for Chlordane alpha (cis) which exceeded the MRL in Rice, Beans and Groundnut, while Chlorothalonil, Octachlorostyrene, Perthane, Tecnazene, Malathion, BHC alpa, BHC beta, BHC delta and Cyanazine were below the MRL in all the grains. Table 9 shows the pesticide residue level from grains sampled from Creek Road market. From the table, Chlordane alpha (cis) and Methoxychlor exceeded the MRL in all the grains while Hexachlorobenzene, Octachlorostyrene, Perthane, Tecnazene, BHC alpha, BHC beta, BHC delta and Cyanazine were below the MRL in all the grains.

DISCUSSION

The result implicating grains contaminated with pesticide residues concur with an earlier report by Akinneye et al. (2018) and we presumed may be due to the absorption capacity of the grains. Also, the beans sampled from each market showing a high level of toxicity above the MRLs agree with the findings of Ogah et al. (2015) who reported beans samples contained residues of one or more organochlorine pesticides exceeding the MRLs with some exceeding with up to 8% above the MRL. This may also be due to the high susceptibility of beans to insect pest infestation both in-store and the field; as such, grain merchants tend to use heavy doses of chemicals to confer protection from insect pest attack so as to reduce both quantitative and qualitative loss which when left unchecked could result to huge economic and nutritional loss. However, the implication of these is as postulated by Akinneye et al. (2018) who indicated that when pesticide residue is found to exceed the MRL in any food, such commodity is said to be adulterated and unsafe for human consumption. Such commodities usually suffer set back at international markets for lacking to meet international standards or standards of the receiving country.

Although Ogah et al. (2015) on the other hand reported that residues that are below MRLs are not likely to cause significant health hazards even on a long-term basis, even with DDT, endosulfan and endrin once they are below their maximum

Table 6. Pesticide residues in grains sampled from Mile III market in River State, Nigeria.

Products		Captan	Chlordane Alpha (Cis)	Chrothalonil	DOT, O, P-	DOT, P, P-	Endosulphan-alpha	Endosulphan-Sulfate	Hexachlorob-enzene	Methoxychor	Octachlorost-yrene	Perthane	Quintozene	Tecnazene	Diazinon	Atrazine	Hexazinone	Malathion	D DE, O, P	BHC Alpha	BHC beta	BHCdelta	Simazine	Cyanazine
Rice	Before	0.05	0.19	0.05	0.14	0.09	0.11	0.14	0.17	0.23	0.04	0.16	0.10	0.11	0.05	0.21	0.03	0.18	0.06	0.12	0.15	0.04	0.11	0.15
	After	0.08	0.05	0.02	0.11	0.07	0.13	0.01	0.08	0.14	-	0.09	0.05	0.15	0.01	0.31	-	0.07	0.10	0.05	0.11	0.07	0.03	0.08
	M.R. L	0.01	0.02	0.04	0.05		0.1	0.1	0.05	0.02			0.1		0.05	0.02	0.01	0.08						
Beans	Before	0.10	0.06	0.09	0.13	0.04	0.09	0.19	0.16	0.31	0.18	0.14	0.47	0.20	0.41	0.17	0.23	0.01	0.14	0.07	0.06	0.10	0.12	0.08
	After	0.01	0.01	-	0.08	0.03	0.05	0.13	0.07	0.19	0.08	0.06	0.28	0.11	0.33	0.02	0.14	-	0.07	0.09	0.03	0.07	0.09	0.03
	M.R. L	5	0.02	0.2	0.05	0.05	1	1		0.01			0.1		0.05	0.02	0.01	0.5	0.05	1	1	1	0.01	
Maize	Before	0.19	0.10	0.04	0.12	0.02	0.11	0.15	0.02	0.16	0.01	0.05	0.19	0.33	0.13	0.07	0.36	0.12	0.16	0.13	0.17	0.02	0.01	0.05
	After	0.13	0.06	0.09	0.03	0.01	0.05	0.08	0.03	0.21	0.08	0.02	0.11	0.21	0.10	0.12	0.23	0.07	0.10	0.05	0.09	-	-	0.06
	M.R. L	0.01	0.02	0.04	0.05		0.5	0.5	0.05	0.02			0.1		0.05		0.01	2.0					0.2	0.05
Groundnut	Before	0.14	0.23	0.12	0.05	0.01	0.22	0.16	0.03	0.14	0.11	0.17	0.02	0.03	0.13	0.06	0.16	0.29	0.34	0.18	0.10	0.06	0.02	0.13
	After	0.08	0.17	0.03	0.01	0.03	0.14	0.07	0.02	0.05	0.04	0.11	-	-	0.04	0.01	0.10	0.17	0.19	0.12	0.04	0.060	-	0.09
	M.R. L	5	0.02	0.1			0.2	0.2		0.5					0.05		0.01							

Table 7. Pesticide residues in grains sampled from Mile I market in River State, Nigeria.

Products		Captan	Chlordane Alpha (Cis)	Chrothalonil	DOT, O, P-	DOT, P, P-	Endosulphan-alpha	Endosulphan-Sulfate	Hexachlorob-enzene	Methoxychor	Octachlorost-yrene	Perthane	Quintozene	Tecnazene	Diazinon	Atrazine	Hexazinone	Malathion	D1 DE1 O1P	BHC Alpha	BHC beta	BHC delta	Simazine	Cyanazine
Rice	Before	0.14	0.23	0.13	0.05	0.01	0.22	0.20	0.03	0.14	0.09	0.18	0.02	0.01	0.13	0.06	0.16	0.29	0.34	0.18	0.10	0.04	0.02	0.13
	After	0.08	0.17	0.03	0.01	0.03	0.14	0.07	0.02	0.05	0.04	0.11	-	-	0.04	0.01	0.10	0.17	0.19	0.12	0.04	0.06	-	0.09
	M.R. L	0.01	0.02	0.14	0.05		0.1	0.01	0.05	0.02			0.1		0.05	0.02	0.01	0.08						
Beans	Before	0.10	0.06	0.10	0.13	0.04	0.09	0.19	0.16	0.31	0.16	0.16	0.47	0.20	0.41	0.17	0.23	0.01	0.14	0.05	0.06	0.10	0.12	0.08
	After	0.12	0.01	-	0.08	0.03	0.05	0.13	0.07	0.19	0.08	0.06	0.28	0.11	0.33	0.02	0.14	-	0.07	0.09	0.03	0.07	0.09	0.03
	M.R. L	5	0.02		0.05	0.05	1	1		0.01			0.1		0.05	0.02	0.01	0.5	0.05	1	1	1	0.01	
Maize	Before	0.19	0.10	0.04	0.12	0.12	0.11	0.15	0.02	0.16	0.01	0.10	0.19	0.33	0.13	0.10	0.36	0.12	0.16	0.11	0.17	0.08	0.01	0.03
	After	0.13	0.06	0.09	0.03	0.03	0.05	0.08	0.03	0.21	0.08	0.02	0.11	0.21	0.10	0.12	0.23	0.07	0.10	0.05	0.11	-	-	0.06
	M.R. L	0.61	0.02	0.04	0.05	0.05	0.05	0.5	0.05	0.02			0.1		0.05	0.1	0.01	2.3					0.2	0.05
Groundnut	Before	0.05	0.19	0.05	0.14	0.14	0.11	0.04	0.20	0.23	0.02	0.16	0.10	0.12	0.06	0.21	0.01	0.20	0.06	0.12	0.15	0.04	0.11	0.16
	After	0.08	0.05	0.1	0.11	0.11	0.13	0.01	0.08	0.14	-	0.09	0.05	0.15	0.05	0.13	-	0.07	0.10	0.05	0.11	0.07	0.03	0.08
	M.R. L	5	0.02				0.2	0.2		0.05					0.05		0.01							

Table 8. Pesticide residues in grains sampled from Rumuokoro slaughter market in River State, Nigeria.

Products		Captan	Chlordane* Alpha (Cis)	Chrothalonil*	DDT, *O,	DDT, *P,	Endosulphan-* alpha	Endosulphan-* Sulfate	Hexachlorob-* enzene	Methoxychor*	Octachlorost-* yrene	Perthane	Quintozene	Tecnazene	Diazinon	Atrazine	Hexazinone	Malathion	DDE, O, P**	BHC* Alpha	BHC beta*	BHCdelta*	Simazine*	Cyanazine*
Rice	Before	0.03	0.04	0.02	0.16	0.12	0.05	0.10	0.08	0.06	0.09	0.03	0.11	0.10	0.02	0.07	0.07	0.03	0.05	0.06	0.17	0.08	0.21	0.03
	After	-	0.08	0.03	0.06	0.08	0.05	0.05	0.04	0.01	0.05	-	0.07	0.05	-	0.07	0.03	0.05	0.04	0.05	0.11	0.04	0.15	-
	M.R. L	0.01	0.02	0.04	0.05		0.1	0.1	0.05	0.02			0.1		0.05	0.02	0.01	0.08						
Beans	Before	0.10	0.06	0.05	0.13	0.04	0.09	0.19	0.16	0.29	0.16	0.14	0.47	0.18	0.39	0.17	0.23	0.01	0.12	0.05	0.06	0.10	0.11	0.18
	After	0.12	0.01	-	0.10	0.03	0.05	0.13	0.07	0.19	0.08	0.08	0.28	0.11	0.33	0.02	0.14	-	0.07	0.10	0.03	0.07	0.09	0.04
	M.R. L	5	0.02	0.2	0.05	0.05	1	1		0.01			0.1		0.05	0.02	0.01	0.5	0.05	1	1	1	0.01	
Groundnut	Before	0.03	0.17	0.05	0.14	0.12	0.11	0.04	0.15	0.23	0.02	0.16	0.10	0.11	0.05	0.17	0.01	0.18	0.06	0.12	0.13	0.04	0.11	0.14
	After	0.08	0.07	0.02	0.11	0.07	0.13	0.01	0.08	0.16	-	0.09	0.05	0.15	0.03	0.13	-	0.07	0.10	0.07	0.11	0.07	0.05	0.08
	M.R. L	5	0.02	0.1			0.2	0.2		0.05					0.05		0.01							

Table 9. Pesticide residues in grains sampled from Creek Road market in River State, Nigeria.

Products		Captan	Chlordane Alpha (Cis)	Chrothalonil	DDT O P-	DDT, P,	Endosulphan-alpha	Endosulphan-Sulfate	Hexachlorob-enzene	Methoxychor	Octachlorost-yrene	Perthane	Quintozene	Tecnazene	Diazinon	Atrazine	Hexazinone	Malathion	DDE O, P	BHC Alpha	BHC beta	BHC delta	Simazine	Cyanazine
Rice	Before	0.14	0.23	0.10	0.10	0.01	0.22	0.16	0.03	0.14	0.19	0.17	0.08	0.01	0.13	0.06	0.16	0.29	0.34	0.18	0.10	0.04	0.02	0.23
	After	0.08	0.15	0.03	0.01	0.03	0. 14	0.07	0.02	0.05	0.04	0.09	-	-	0.03	0.01	0.10	0.17	0.17	0.12	0.04	0.04	-	0.09
	M.R. L	0.1	0.02	0.04	0.05		0.1	0.1	0.05	0.02			0.1		0.05	0.02	0.01	0.08						
Beans	Before	0.10	0.10	0.07	0.13	0.04	0.09	0.19	0.20	0.31	0.16	0.14	0.57	0.18	0.41	0.17	0.23	0.01	0.14	0.10	0.06	0.10	0.12	0.08
	After	0.12	0.01	-	0.05	0.03	0.05	0.13	0.07	0.19	0.08	0.06	0.28	0.11	0.30	0.02	0.14	-	0.07	0.09	0.03	0.07	0.05	0.03
	M.R. L	5	0.02	0.2	0.05	0.05	1	1		0.01			0.1		0.05	0.02	0.01	0.5	0.05	1	1	1	0.01	
Maize	Before	0.03	0.06	0.02	0.16	0.12	0.07	0.10	0.08	0.06	0.09	0.03	0.13	0.10	0.02	0.09	0.07	0.03	0.08	0.06	0.17	0.08	0.21	0.03
	After	-	0.05	0.03	0.06	0.05	0.05	0.03	0.04	0.01	0.03	-	0.07	0.03	-	0.05	0.03	0.05	0.02	0.05	0.09	0.04	0.15	-
	M.R. L	0.01	0.02	0.04	0.05		0.5	0.5		0.02			0.1		0.05	0.1	0.01	2.0					0.2	
Groundnut	Before	0.03	0.19	0.05	0.14	0.09	0.11	0.05	0.17	0.23	0.02	0.20	0.20	0.11	0.05	0.22	0.01	0.18	0.06	0.12	0.15	0.04	0.11	0.16
	After	0.08	0.03	0.02	0.11	0.07	0.13	0.01	0.06	0.14	-	0.09	0.05	0.13	0.01	0.13	-	0.07	0.10	0.05	0.09	0.07	0.03	0.08
	M.R. L	5	0.02	0.1			0.2	0.2		0.02					0.05		0.01							

permissible intakes (MPIs).

The danger of such an assumption includes none consideration of other factors such as synergistic effects, bioaccumulation and bio-magnification theories. Health challenges of pesticide intake at whatever the dose include the ability to interact with other drugs and/ or food, carcinogenicity, neurotoxicity and teratogenic among others which cannot be traded for any reason (Strict, 1981; Maroni, 1990; Ogah et al., 2015; Manzoor et al., 2015; Atif et al., 2016). The presence of residual pesticide compounds in post-harvest grains agrees with Anzene et al. (2014) who reported about 10 organochlorine pesticide residues in stored grains with Lindane and Aldrin. Bakore et al. (2004) and Riaz et al. (2015) reported DDTs, and its metabolites, γ-HCH and its isomers, heptachlor, epoxide, aldrin, endosulfan and diazinon, Chlorpyrifos methyl and pirimiphos-methyl in stored grains being above MRLs. In a similar study, Akinneye et al. (2018) reported endrin to be absent in all grains sampled except in bean while Ogah et al. (2012) found the same compound 23% above its MRL in bean sampled. The presence of heavy organochlorine and other toxic pesticides in both cereal and legume crops stored and marketed in these major markets could be attributed to its persistent. This calls for urgent attention by the authorities such as NAFDAC as earlier reported by Ogah et al. (2015) although these pesticides have been banned in Nigeria and most countries of the world (Akunyili and Ivbijaro, 2012), its mere presence in foodstuff calls for monitoring to ensure that such banned pesticides are no longer manufactured or imported into the country. On the other hand, the presence of these toxic substances conferred various degrees of protection to the grain legumes and cereals in the store for up to four months. Although the various degree of damage which ranged from slightly damaged to moderately were recorded agrees with the works of earlier scientists that application of insecticide does not preclude total insect infestation (Ogunkoya and Ofuya, 2001; Aslam et al., 2002; Ogendo et al., 2004). Sources of these contamination or residues above MRLs could be traced to various sources among which could be attributed to the injudicious use of such banned pesticides in storage and/or uptake while on the field on heavily contaminated or treated soil with organochlorines (Ogah et al., 2012; Ali et al., 2015; Malik et al., 2017). Earlier, Taylor (1968) reported high residues levels of aldrin and dieldrin in yam peels in yam at harvest treated with aldrin dust at 2.5% during planting while Adesiyan (1981) detected phorate in both peels and pulp of water yam treated with thionazin and phorate used during planting to control nematodes. Adesiyan and Badra (1982) also reported tolerable residues of 0.02 to 0.3ppm of aldicarb and carbofuran in guinea yam treated at planting to control nematodes. Other reasons could be its availability as Akinneye et al. (2018) reported a high concentration of permethrin in stored grain and deduced as the most commonly used pesticide in the study area. To overcome these menaces, government needs to enforce the rule of prior informed consent (PIC) FAO of the UN that countries that wish to import banned or severely restricted pesticides shall give the pesticide manufacturer or exporting country their formal consent to import these compounds (Akunyili and Ivbijaro, 2012). They listed such pesticides to include carbon disulphide, hydrogen cyanide, ethylene dibromide, ethylene dichloride, ethylene oxide, methylbromide, trichloracetonitrile, chloropicrin, aluminium phosphide and aluminium sulphide. Others include Aldrin, dieldrin, endrin, lindane, HCH, DDT, Chlordane, mercury compounds and 2, 4,5T (2, 4, 5, trichloropheno-axyacetic acid).

CONCLUSION

The result of this study shows that there is a high incidence of pesticide residues in grain legumes and cereals sold in the major markets in Rivers State Nigeria. While some were below the MRLs majority of the chlorinated insecticides were above the MRLs. Organochlorine pesticides were much in use by grain merchants and farmers in Nigeria especially for crop protection purposes. There is a need for NAFDAC, NGOs and other relevant agencies to increase surveillance to check and control the illegal importation, sale and use of such compounds. When this is implemented, it will reduce morbidity and other health implications associated with pesticide toxicity annually ingested in stored foods treated with such hazardous compounds. Nigeria is a signatory to the Stockholm Convention 2001 that prohibits the use of organochlorides and organophosphates on foodstuff due to their low biodegradability, high bioaccumulation and persistent organic pollutants.

REFERENCES

Adesiyan SO (1981). In viro toxic effects of two organophosphates on the nematode *Scutellonema bradys.* African J. Agri. Sci. 8(2): 1-10.

Adesiyan SO and Badra T (1982). Granular nematicides for control of the yam nematode, Scutellonema bradys, and relevant residues in raw tubers. J. Nem.14(2): 213-216.

Akunyili D and Ivbijaro MFA (2012). Pesticide regulations and implementation in Nigeria. In Ivbijaro MFA and Akintola F (editors) (2012) Sustainable Environmental Management in Nigeria (2nd Edition) BookBuilders Pub. Ibadan, Nigeria. 445pp

Akinneye JO, Adedire CO, Arannilewa ST (2006). Potential of *Cleisthopholis patens* Elliot as a maize protectant against the stored product moth, *Plodia Interpunctella* (Hubner) (Lepidoptera; Pyralidae). African J. Biotech. 5(25): 2510-2515.

Akinneye JO, Alabadan AO, Adesina FP, Adeleye OA, Akinyemi MI (2018). Quantification of organochlorine residue on stored grains in Ondo State, Nigeria European J. Biomed and Pharm.l Sci. 6(1): 54-61.

Akinneye JO, Adedire CO, Arannilewa ST (2015). Potential of *Cleisthopholis patens* Elliot as a maize protectant against the stored product moth, *Plodia interpunctella* (Hubner) (Lepidoptera; Pyralidae). African J. Biotech. 5(25): 2510-2515.

Ali H, Qasim M, Saqib HAS, Arif M, Islam SU (2015). Synergetic effects of various plant extracts as bio-pesticide against Wheat Aphid (*Diurophous noxia* L.) (Hemiptera: Aphididae). African J. Agri.

Sci. and Tech.3(7): 310-315.
Ali H Youming H Baozhen T Zhanghong S Abrar M and Nafiu BS (2016). A way of reproductive manipulation and biology of *Wolbachia pipientis*. J. Exp. Bio. and Agric. Sci. 4(2) 156-168.
Anudu C (1998). Marketing of agrochemicals in Nigeria. Paper presented at the National Programme on Agricultural Technology, University of Agriculture, Makurdi, July 26-29, 16 pp.
Anzene JS, Tyohemba RL Ahile UJ and Emezi KSA (2014). Organochlorine pesticide residues analysis of postharvest cereal grains in Nasarawa State, Nigeria *International* J. Agron. Agric. Res. 5(5): 59-64.
Aslam M, Khan KA, Bajwa M (2002). Potency of some Spices against *Callosobruchus chinensis* Linnaeus, J. Biol. Sci. 2:449-52.
Atif I, Qasim M, Ali H, Qadir ZA, Idrees A, Bashir MH, Qinge J (2016). Acaricidal potential of some botanicals against the stored grain mites, *Rhizoglyphus tritici*. J. Ento. Zool Stud. 4(1): 611-617.
Bakore N, John PJ, Bhatnagar P (2004). Organochlorine pesticide residues in wheat and drinking water samples from Jaipur, Rajasthan, India. Environ Mon. Assess. 98: 381-389.
Chibbar R (2009). Grain legumes for ensuring nutritiontional security. International conference on grain legumes. Quality improvement value addition and trade Indian institute pulse research kampur India Tab 14-18.
El-Shahawia MS Hamza A Bashammakh AS and AlSaggaf WT (2010). An overview on the accumulation, distribution, transformations, toxicity and analytical methods for the monitoring of persistent organic pollutants. Talanta, 80: 1587-1597.
FAO/WHO (2013). Pesticide residues in food and feed: maximum residual limits; 2013. *Codex alimentarius.net/pesters/data/pesticides/details.*
FAO/WHO (2005). Food Safety Risk Analysis, Part II, Case Studies, Food and Agricultural Organization of the United Nations (FAO), World Health Organization (WHO).
Holand PT, Hamilton O Ohan B Skidmode MW (2004). Effect of storage and processing in plant products (IUPAC) report on pesticides (31). Pure and App. Chem. 60(2): 335-316.
Ivbijaro MFA (1998). National programme on agrochemical technology. A keynote address presented at the Centre for agrochemical technology, University of Agriculture, Makurdi, July 26-29.
Lahah JO, Wandiga SO (2002). The effect of boiling on the removal of persustant malallion resudure from stored grain, J. stored Prod. Res. 38:1-10.
Leong KH, Tan LB and Mustafa AM (2007). Contamination levels of selected organochlorine and organophosphate pesticides in the Selangor River, Malaysia between 2002 and 2003. *Chemosphere,* 66 (6): 1153-1159.
Mada DA Mahai S Adamu IG Girei MM (2014). Toxicity study of pesticide on storage of cereal, Legume and oil seed with regard to storage structures in Ganye, southern Adamawa State- *Nigeria.* International J. Engn Res. and Dev. 10(3):33-39.
Malik MA, Manzoor M, Ali H, Muhammad A, Islam S, Qasim M, Ahmad N, Idrees A, Muhammad A, Saqib HSA (2016). Evaluation of imidacloprid and entomopathogenic fungi, *Beauveria bassiana* against the red palm weevil *Rhynchophorus ferrugineus* (Coleoptera: Curculionidae). J. Ento. and Zoo Stud. 4(1): 262-268.
Manzoor M, Ali H, Hahzada S, Khalid H, Idrees A, Arif M (2015). Potential of Moringa (*Moringa oleifera*: Moringaceae) as plant growth regulator and bio-Pesticide against wheat aphids on wheat crop (*Triticum aestivum*; Poaceae). J. Biopesticides 8(2):120-127.
Manzoor M, Ahmad JN, Sharif MZ, Majeed D, Kiran H, Jafir M, Ali H (2017). Comparative effectiveness of entomopathogenic nematodes against red palm weevil (*Rhynchophorus ferrugineus*) in Pakistan. J. Ento and Zoo Stud**.** 5(5): 756-760.
Maroni HM (1990). Studying the effects of pesticides on humans (International Commission on Occupational Health). 1990. Proceedings of the 9th International workshop, 2-4 May 1990, International Centre for Pesticide Safety, Busto Garolfo, Milan, Italy. ICOH, Geneva, Switzerland.
Naylor REL (2003). Crop health – responding to weed, diseases, and pests. In: The Agricultural Notebook, 20 Edition; Richard J. Soffe (Ed.) Blackwell Science Ltd., Oxford, UK. Pp. 213-230.
Ochii P (2010). Sensitization workshop on safe and responsible use of agrochemicals, 8th February 2010, Yola Adamawa state Nigeria.
Ogah CO, Tettey J, Coker HB, Adepoju-Bello AA (2012). Analysis of Organochlorine pesticide residues in beans from markets in Lagos State, Nigeria. West African J. Pharm. (2012) 23(1): 60-68.
Ogah CO, Coker HB (2012). Quantification of Organophosphate and Carbamate Pesticide Residues in Maize. *J. Applied Pharm. Sci.*, 2(9): 093-097.
Ogendo JO, Deng AL, Belmain SR, Walker DJ, Musandu AAO (2004). Effect of insecticidal plant materials, *Lantana camara* L. and *Tephrosia vogelii* hook, on the quality parameters of stored maize grains. J. Food Techn Africa. 9:29–36.
Ogunkoya M, Ofuya TI (2001). Damage to Cowpea by *Callosobruchus maculatus* (F.) In a Humid Tropical Environment in Nigeria, J. App Trop.Agric. 2001; 6:45- 50.
Qasim M, Dilbar H, Saif Ul, Ali H, Islam W, Hussain M, Wang F, Wang L (2018). Effectiveness of Trichogramma chilonis Ishii against spiny bollworm in Okra and susceptibility to insecticides. J. Ento and Zoo. Stud. 6(1): 1576-1581.
Riaz U, Sajid I, Parwai AB, Abbas B, Akhlaq A (2015). Gas Chromatographic
Multi-Residue Pesticide Determination Method for Cereal Grains. American-Eurasian J. Agric. and Env. Sci. 2015; 15(8): 1617-1624.
Strict JC (1981). Pesticide and the immune system. In: RP Sharma (ed.), Immunologic Considerations in Toxicology Vol.1. CRC Press.
Taylor TA (1968). Insecticide residue in yams treated against yam beetle *Heteroligus sp.* infestation in Nigeria. J. West African Science Association 13(2): 139-145.
Williams M (2000). Nutrition and the Environment ACC SCN 21 Report, Geneva Switzerland, 2000**.**