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Assessment of Selected Grains and Tuberous Crop Chips for Pesticide Residues in South Western Nigeria

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Abstract
Increasing awareness of the merits of pesticides' use engendered increase use and constitute a dangerous source of environmental contaminants particularly in food crops. This research aimed to assess the level of pesticide residues in some food items in southwestern Nigeria. Food product samples were collected from randomly selected open markets in Osun, Oyo and Ogun states. These food products included Glycine max (L.), Vigna unguiculata (L.), Colocasia esculenta (L.), Solanum tuberosum (L.), Sorghum spp., Zea mays L. ((White and Yellow maize), Oryza sativa L. (imported Rice, Local rice), Triticum aesticum L. and Dioscorea spp. (Yam chips). The samples were analysed for pesticide residues using Spectrophotometer 21D in 2016. Nineteen pesticides (herbicides, insecticides and fungicides) analysed were present in Glycine max, Colocasia esculenta and Solanum tuberosum. Paraquat (0.140 mgkg-1) and Nuvaluron (0.111 mgkg-1) had residues greater than their respective maximum residue limits (mrls) of 0.1 mgkg-1 and 0.01 mgkg-1. Vigna unguiculata had residues of Nuvaluron (0.119 mgkg-1), hydrogen phosphide (0.120 mgkg-1) and glufosunate ammonium (an herbicide)(0.113 mgkg-1) greater than their respective mrls 0.10, 0.10 and 0.05 mgkg-1. Residues of paraquat (0.032 mgkg-1), metalaxyl (0.06 mgkg-1), lindane (0.04 mgkg-1) and glufosunate ammonium (0.132 mgkg-1) in White maize were higher than their respective available mrls (0.03 mgkg-1, 0.05 mgkg-1, 0.01 mgkg-1 and 0.1 mgkg-1.) Most of the pesticides had their residues higher than their available mrls in most food items. This dangerous trend needs regular monitoring to ensure farmers' and wholesalers' comply with both the field and storage use of pesticides.

Keywords: Cocoyam, Glufosunate ammonium, Sorghum spp., Local rice, Spectrophotometer 21D

Introduction
Pesticide residue is any substance or mixture of substances in food for man or animals resulting from the use of a pesticide including any specified derivatives, such as degradation and conversion products, metabolites, reaction products and impurities considered to be of toxicological significance (IUPAC, 2014).Pesticide residue refers to the pesticides that may remain on or in food after they are applied to food crops. The presence of pesticide residues is a concern for consumers because pesticides are known to have potential harmful effects to other non-targeted organisms than pests and diseases. The major concerns are their toxic effects such as interfering with the reproductive systems and foetal development as well as their capacity to cause cancer, asthma etc. (Gilden et al, 2010).

The sensitization of populace to wash thoroughly before other forms of processing to reduce the pesticide residue content at the point of consumption would greatly reduce the health hazards associated with pesticide residue levels in such foodstuffs (e. g. dry fish), although, these insecticides were never completely eliminated by washing (Bhuiyah, et al., 2008).

Consumers expect a product to be free of pesticides (or low concentrations) and other contaminants (Thomas, 2011). The applied chemicals and/or their degradation products may remain as residues in the agricultural products, which becomes a concern for human exposure (Dasika et al., 2012).

According to Ogunfowokan et al. (2012), of all the various kinds of pesticides used by farmers in Nigeria, Lindane (Gammalin 20EC®) is the most popularly used as aqueous solutions for preventing insect pests of various kinds, and also for formulating other unauthorized pesticides that are locally applied to crops. Others in common use are dichlorodiphenyltrichloroethane(DDT), Dichlorvos, Chlorpyrifos, Endosulfan and Aldrin. Several food samples have been analysed for the presence of pesticides in Nigeria amongst which are the studies by Etonihu et al. (2011) on maize grains, white beans and sorghum purchased randomly from open markets in Nasarawa and Plateau States. It

was reported that 116 students of a school in Doma, Gombe State fell ill and were hospitalised after eating cowpea contaminated by pesticide. It was also reported that two children died and 112 people were hospitalised after eating cowpea treated with pesticide in Cross Rivers State (Shaibu, 2008). Again, in 2010 it was reported that 20 fast food outlets were closed in Nigeria because of fatalities traced to pesticide residue in their products (Chikwe, 2010). This research was designed to assess the level of pesticide residues in some food items sold in southwest Nigeria.

Materials and Methods

The food materials analysed were bought from five different randomly selected open markets Osun, Oyo and Ogun states. The food materials were Soybean (*Glycine max*), White cowpea (*Vigna unguiculata*), Cocoyam (*Colocasia esculenta*), Sweet potato (*Solanum tuberosum*), Guinea corn (red) (*Sorghum spp.*), Maize grain (white), Maize grain (yellow) (*Zea mays*), foreign Rice, Local rice (*Oryza sativa*), Wheat (*Triticum aesticum.*) and Yam flour chips (*Dioscorea spp.*)

Five grammes each of all the samples were washed in distilled water before milling using ethyl acetate as the solvents to do the extraction. After the extraction, the solutions were filtered using No 1 Whatman filter paper and the filtrate was evaporated to a watery residue (not dryness). Exactly 5 ml of ethyl acetate was added to the eluate. The residue was dissolved completely with 5 ml of ethyl acetate. Five (5) gram of mixture of sodium sulphate/sodium chloride (1:1) w/w was added and swirled. Then, 5 ml of cyclohexane was also added to obtain a total volume of 10.0 ml and swirled vigorously again. The solution was allowed to stand so the salt mixture could settle to the bottom of the flask. A solvent of ethyl acetate/cyclohexane (1:1), v/v) at 5 ml was used as blank to zero the machine (Spectrophotometer 21D). Each of the pesticides was read using their wavelengths (in parentheses).

Results

Table 1 shows the pesticide residues in soybean (dry), white cowpea and cocoyam. All the nineteen (19) pesticides analysed were present in soybean and cocoyam. White cowpea had 89.5% of the pesticide analysed. From the available Maximum Residue Limits (MRLs), paraquat (0.140 mgkg-1) and Nuvaluron (0.111 mgkg-1) had residues greater than their respective mrls of 0.1 and 0.01 mgkg-1. Seven of the detected pesticides had their residues less than their respective mrls. These were metalaxyl, glufosunate ammonium, glyphosphate, Dithiocarbamate, Cypermethrin, carbofuran and carbendazim (Table 1).

Table 1: Pesticide Residues (mgkg-1) in Soybean, Cocoyam and White Cowpea in South-Western Nigeria

Pesticides	Pesticide Wavelengths	Soybean		Cocoyam		White cowpea	
		Conc	MRL	Conc	MRL	Conc	M
Methoxylchlor	560	0.154	-	0.156	-	0.138	-
Paraquat	520	0.142	0.1	0.140	-	0.143	0.50
Novaluron	420	0.111	0.01	0.161	-	0.119	0.10
ylbromide	420	0.125	-	0.010	-	0.123	-
Metalaxyl	410	0.003	0.05	0.006	-	0.105	-
Lindane	540	0.110	-	0.036	-	0.116	-
Hydrogen phosphide	560	0.117	-	0.018	-	0.120	0.10
Glyfosunate ammonium	410	0.128	0.2	0.030	-	0.010	0.05
Glyphosphate	410	0.107	2.0	0.014	-	0.011	2.00
Dithiocarbamate	310	0.010	0.1	0.003	0.5	0.002	-
Dimethioate	320	0.100	-	0.001	-	0.010	0.10
Dichlorvos	420	0.002	-	0.002	-	0.003	0.10
Cypermethrin	550	0.004	0.05	0.005	-	0.005	0.05
Carbofuran	420	0.001	0.2	0.003	-	0.010	-
Carbendazim	520	0.002	0.5	0.003	-	ND	0.5
Mancozeb	310	0.014	-	0.015	-	ND	-
Pirimiphix	320	0.004	-	0.004	-	0.001	-
Endosulfan	560	0.001	-	0.010	-	0.002	-
Endrin	520	0.09	-	0.032	-	0.001	0.01

R= Residue, M= Maximum Residue Limit (According to FAO /WHO, 2013; and Thai Agricultural Standard, TAS9002 2013)

White cowpea had residues of Nuvaluron (0.119 mgkg-1), hydrogen phosphide (0.120 mgkg-1) and glufosunate ammonium (0.113 mgkg-1) greater than their respective mrls 0.10, 0.10 and 0.05 mgkg-1. Six pesticides with available mrls had residues less than their respective mrls. These

pesticides were Paraquat, Glyphosphate, Dimethoate, Dichlorvos, Cypermethrin and Endrin. Considering cocoyam, Dithiocarbamate with residue 0.003 mgkg-1 had its mrl as 0.5 mgkg-1. Mrls of the other pesticides were not available (Table 1).

Nuvaluron (0.133 mgkg-1), hydrogen phosphide (0.122 mgkg-1) and glufosunate ammonium (0.126 mgkg-1) had their concentration higher than their respective mrls of 0.01, 0.01 and 0.1 mgkg-1 in sweet potato. Other eight available mrls were higher than the residues of the pesticides contained in sweet potato (Table 2).

Table 2: Pesticide Residues (mgkg-1) in Sweet potato, Guinea Corn (red), Maize Grain (White) and Maize grain (White) in Southwest, Nigeria

Pesticides	Pesticide Wave lengths	Sweet potato		Guinea corn (red)		Maize grain (White)		Maize grain (yellow)	
		R	M	R	M	R	M	R	M
Methoxylchlor	560	0.148	-	0.012	-	0.148	-	0.141	-
Paraquat	520	0.152	0.2	0.05	0.03	0.032	0,03	0.026	0.03
Novaluron	420	0.133	0.01	0.037	40	0.041	-	0.048	-
Methylbromide	420	0.120	-	0.03	-	0.135	5.0	0.130	5.0
Metalaxyl	410	0.017	0.05	0.042	1	0.060	0.05	0.056	0.05
Lindane	540	0.124	-	0.126	0.01	0.040	0.01	0.030	0.01
Hydrogen phosphide	560	0.122	0.010	0.058	-	0.033	0.1	0.045	0.1
Glyfosunate ammonium	410	0.126	0.10	0.144	0.1	0.132	0.1	0.137	0.1
Glyphosphate	410	0.014	0.2	0.126	-	0.135	5.0	0.213	5.0
Dithiocarbamate	310	0.002	-	0.04	-	0.002	2.0	0.003	0.02
Dimethoate	320	0.002	0.05	0.002	0.01	0.004	-	0.002	-
Dichlorvos	420	0.010	0.10	0.001	0.2	0.001	0.2	0.001	0.2
Cypermethrin	550	0.004	0.2	0.003	0.5	0.003	0.3	0.002	0.0.3
Carbofuran	420	0.005	0.2	0.002	0.1	0.001	0.1	0.001	0.1
Carbendazim	520	0.003	20.0	0.001	0.1	0.001	-	0.001	-
Mancozeb	310	0.019	-	ND	-	0.002	-	0.001	-
Pirimiphix	320	0.009	-	ND	-	0.004	1.0	0.002	1.0
Endosulfan	560	0.021	-	0.001	-	0.001	-	ND	-
Endrin	520	0.006	-	0.001	-	0.001	-	0.002	-

R= Residue, M= Maximum Residue Limit (According to FAO /WHO, 2013; and Thai Agricultural Standard, TAS9002 2013)

From Table 2, guinea corn, white and yellow maize grains respectively contained 89.5%, 100% and 94.7% of the nineteen analysed pesticides. Paraquat (0.05 mgkg-1), lindane (0.126 mgkg-1) and glufosunate ammonium (0.144 mgkg-1) had their residues higher than available mrls of 0.03, 0.01 and 0.1 mgkg-1 respectively. The seven other available mrls were higher than the extracted pesticide residues in guinea corn.

Residues of paraquat (0.032mgkg-1), metalaxyl (0.06 mgkg-1), lindane (0.04 mgkg-1) and glufosunate ammonium (0.132 mgkg-1)in White maize were higher than their respective available mrls 0.03, 0.05, 0.01 and 0.1 mgkg-1. The remaining available mrls were higher than the pesticide residues extracted in white maize (Table 2). Metalaxyl (0.056 mgkg-1), Lindane (0.03 mgkg-1) and glufosunate ammonium (0.137 mgkg-1) had residues higher than mrls in yellow maize 0.05, 0.01 and0.1 mgkg-1 in the same order. The other nine pesticides with available mrls had their residues lower than mrls (Table 2).

Rice, local rice, wheat and yam flour chips respectively contained89.5%, 100%, 100% and 94.7% of the nineteen pesticide residues analysed (Table 3). All the available mrls were higher than the pesticide residues obtained in rice. Mancozeb and pirimiphix were not detected in rice while only mancozeb was not detected in yam flour chips (Table 3). Paraquat (0.127 mgkg-1) had residue greater than mrl (0.05 mgkg-1) in local rice. The other five available mrls were higher than the corresponding residues extracted in local rice (Table 3). The available mrls were higher than the residues extracted in wheat. Only glyphosphate had mrl (0.5 mgkg-1) which was greater than 0.032 mgkg-1 obtained in yam flour chips.

Table 3: Pesticide Residues (mgkg-1) in Foreign Rice, Local rice, Wheat and Yam flour chips in Southwest, Nigeria

Pesticides	Pesticide Wavelengths	Rice		Local rice		Wheat		Yam flour chips	
		R	M	M	R	M	R	M	R
Methoxylchlor	560	0.134	-	0.138	-	0.124	-	0.006	-
Paraquat	520	0.124	0.05	0.127	0.05	0.108	-	0.033	-
Novaluron	420	0.114	-	0.122	-	0.010	-	0.040	-
Methylbromide	420	0.006	5.00	0.011	-	0.050	-	0.145	-
Metalaxyl	410	0.002	0.005	0.004	-	0.014	-	0.040	-
Lindane	540	0.003	-	0.007	-	0.004	0.01	0.017	-
Hydrogen phosphide	560	0.010	0.10	0.016	-	0.002	-	0.028	-
Glyfosunate ammonium	410	0.010	0.90	0.010	-	0.003	-	0.033	-
Glyphosphate	410	0.012	30.0	0.025	-	0.011	20	-0.032	0.5
Dithiocarbamate	310	0.010	0.05	0.007	0.2	0.001	1.0	0.002	-
Dimethoate	320	0.007	-	0.005	0.5	0.003	0.05	0.010	-
Dichlorvos	420	0.004	0.15	0.003	7.0	0.010	7.0	0.002	-
Cypermethrin	550	0.005	2.00	0.001	2.00	0.001	2.0	0.001	-
Carbofuran	420	0.001	0.100	0.003	0.1	0.001	-	0.001	-
Carbendazim	520	0.002	2.00	0.003	2.0	0.001	0.05	0.004	-
Mancozeb	310	ND	-	0.003	-	0.013	-	ND	-
Pirimiphix	320	ND	-	0.001	-	0.010	-	0.001	-
Endosulfan	560	0.003	-	0.009	-	0.004	-	0.001	-
Endrin	520	0.001	-	0.020	-	-0.023	-	0.002	-

R= Residue, M= Maximum Residue Limit (According to FAO and WHO, 2013; and Thai Agricultural Standard, TAS9002 2013)

Discussion

A pesticide poisoning occurs when chemicals intended to control a pest affect non-target organisms such as humans, wildlife or bees (Gupta, 2011). There are three types of pesticide poisoning. The first is a single and short-term very high exposure which can be experienced by individuals who commit suicide, as well as pesticide formulators. The second type is long-term high level exposure, which can occur in pesticide formulators and manufacturers (Denis and Stephen, 2004). The third type is a long-term low level exposure, which individuals are exposed to from sources such as pesticide residue in food as well as contact with pesticide residues in air, water, soil, sediment, food materials, plants and animals (Hamilton and Crossley, 2004). The food items in this study are in the last category being found with large number of the analysed pesticide residues.

It was reported that 116 students of a school in Doma, Gombe State fell ill and were hospitalised after eating cowpea contaminated by pesticide. It was also reported that two children died and 112 people were hospitalised after eating cowpea treated with pesticide in Cross rivers state (Shaibu, 2008). Again, in 2010 it was reported that 20 fast food outlets were closed in Nigeria because of fatalities traced to pesticide residue in their products (Chikwe, 2010). The sensitization of populace to wash thoroughly before other forms of processing to reduce the pesticide residue content at the point of consumption would greatly reduce the health hazards associated with pesticide residue levels in such foodstuffs (e. g. dry fish), although, these insecticides were never completely eliminated by washing (Bhuiyah, et al., 2008).

In China, a number of incidents have occurred where state limits were exceeded by large amounts or where the wrong pesticide was used. Paraquat, lindane, glufosunate ammonium, hydrogen phosphide and Nuvaluron residues also exceeded the available maximum residue limits in most of the food items assessed. In August 1994, a serious incident of pesticide poisoning of sweet potato crops occurred in Shandong province, China. Because local farmers were not fully educated in the use of insecticides, they used the highly-toxic pesticide named parathion instead of Trichlorphon. It resulted in over 300 cases of poisoning and 3 deaths. Also, there was a case where a large number of students were poisoned and 23 of them were hospitalised because of vegetables that contained excessive pesticide residues (Bernard et al., 2004).

The Center for Disease Control and Prevention (CDC) estimates show an annual occurrence of 47.8 million, 2 million and 750,000 food-borne illnesses in the United States, United Kingdom and France respectively (Flora-Glad Ekezie, 2015). More than 100 million cases of diarrhoea in children aged less than five years in 2008 and the resulting 5 million deaths estimated to have occurred worldwide (Flora-Glad Ekezie, 2015). In 2008, Nigeria recorded annual nationwide estimates of 87 million cases of food-related illnesses, with 371,000 hospitalisations and 5,700 deaths, according to the centre for disease control and prevention (CDC) (Flora-Glad Ekezie, 2015).

In 2010, many people in Bekwarra local government of Cross River State, suffered from food poisoning due to consumption of 'moi-moi' and beans, as a result about 122 people were hospitalised, while death of two children was recorded. The 'moi-moi' and beans were said to have contained a large dose of highly toxic pesticides (Flora-Glad Ekezie, 2015).

In 2004, carbofuran pesticide residues (also detected in all the food items in this study) found on several batches of noodles manufactured in Nigeria may have resulted in 23 reported cases of vomiting and one death (Olurominiyi and Emily, 2011). In August 2011, six family members died in Gombi Local Government Area of Adamawa State, Nigeria after eating moinmoin prepared from suspected poisoned beans. Also, in June, 2012 people reportedly suffered from pesticides poisoning at Yassharu village in Kafur Local Government Area of Katsina State after eating maize preserved with pesticides. Maize in this study contained all the analysed pesticides except Endosulfan which is below detection limit white maize. More than 400 people reportedly died in Iraq in 1972 after eating bread that had been prepared from cereals treated with a fungicide (Olurominiyi and Emily, 2011). Also, at least 37 people reportedly died of Endosulfan (detected in all the food items except white maize in this study) in Republic of Benin during the 1999/2000 cotton growing season (Olurominiyi and Emily, 2011).

Conclusion and Recommendation

Majority of the farm produce contained higher number of pesticides analysed and most of the pesticides had their concentrations higher than their available mls. This is a dangerous trend and needs regular monitoring to ensure farmers' and wholesalers' comply with both the field and storage use of pesticides.

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