

DIETARY RISK ASSESSMENT OF ORGANOPHOSPHATE AND ORGANOCHLORINE PESTICIDE RESIDUES IN GRAINS COMMONLY CONSUMED IN GOMBE STATE, NIGERIA

By

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Abstract

Pesticides are chemical substances that are applied, mainly for agricultural purposes to enhance yield, but form residues that results in health concerns. The pesticides residues (organophosphate, glyphosate and organochlorine) being non-target specific have been traced to humans and animals causing acute and chronic diseases and even death. Samples were taken from Akko, Gombe and Yamaltu-Deba Local Government Areas of Gombe State. Composite samples of the beans, maize, millet, rice and sorghum were collected, purified, homogenized and subjected to residues extractions using the QuEChERS method and gas chromatography/mass spectrophotometric (GC-MS) techniques for their quantification. The cleanup process had average recovery and standard error ranging between $82.53 \pm 0.32\%$ and $95.22 \pm 1.66\%$ respectively. The limit of detection (LOD) was 0.0006 mg/kg . The coefficient of determination (r^2) was 0.9854. The concentrations of the residues are in the order Gombe > Akko > Yamaltu-Deba. The organochlorine residues in the grains followed similar pattern. Organophosphate and glyphosate residues were in the order; Gombe > Yamaltu-Deba > Akko. Majority of the residues exceeded the WHO Maximum Residual Limits (MRLs) and the Acceptable Daily Intakes (ADIs). Conversely, the glyphosate residues were all below the respective international standards. The health indices determined revealed a variegated pattern with Gombe LGA ranking highest among the residues 6 out of 15 pesticides exhibiting Health Index (HI) values > 100% indicative of high health risk. However, the majority of the pesticides residues had HI values revealing that the exposed population were safe. Regular evaluation, and farmers and users' adherence to users' manual are recommended.

Keywords: Pesticide Residues, Organochlorine, Organophosphate, Health Index.

Introduction

The serenity of the environment is undoubtedly the most paramount endowment of human continual survival on planet earth. General life expectancy of the average human being is overtly or covertly anchored on the type of environment he/she lives. A pollution in the environment is capable of transmuting every atom of leverage on which life otherwise depends into colossus and adversity. Pollutants can drastically change the geography, physical, structural and chemical environment to become abhorrent to every human endeavor to achieve desired quality of livelihood. Man's actions or inactions at harnessing nature's endowment

through anthropogenic activities result in to a very large degree the incursion of undesired entities into the environment. The use of pesticides by man as a way of exploring nature's gift to further man's selfish desires is case in point.

Pesticides represent chemical formulations employed both at home and for farming against unwelcomed organisms for the purposes of providing serene environment for man, plant or animal of interest to thrive unfettered with resplendence. Mendel *et al.*, (2011) defined pesticides as chemical substances generally applied as weed-killers, or for the control of stored food crops against insects and fungi. The efficacy of pesticides

has been extolled by a number of experts to include enhancing farm yield via protection of crops and farm animals against disease-causing pathogens (bactericides and fungicides), kill weeds competing with crops and providing shelter for pathogens (herbicides), their application on storages to repel or eliminate storage insect pests such as weevils and termites (insecticides) and their domestic usage in protecting human against insect parasites such as flies, mosquitoes, ticks, bedbugs and other household creatures that are disease vectors. Dedeké *et al.*, (2018) reported that the use of pesticides in Nigeria has resulted in increase in agricultural production up to 55%.

Nevertheless, the pesticides leave in their trails residues which have been found to be persistent and hazardous to man and the environment due to their ability to bio-accumulate and be transported across living tissues. They are precursors of many metabolites, unreacted pesticides and by-products that have otherwise constituted contaminants to the environment and disease-causing agents to man. According to Parblu *et al.*, (2009) posited that most of the metabolites of the pesticides cause severe health conditions such as neurological damage, hypertension, cardiovascular diseases, skin disorder and cancer.

It is in view of the hazards associated with the use and applications of pesticides in spite of their efficacy and economic importance that the paper set out to profile the presence of some organochlorine, glyphosate and organophosphate pesticides detected in some of the common grains consumed as staple food across three Senatorial Districts of Gombe State. Samples of the grains were collected from strategic locations. The pesticides residues were extracted and separated standard Quick, easy, cheap, effective, rugged and safe (QuEChERS) procedures (Anastassiades, *et al.*, 2003) with some little modifications as adopted by (Jallow, *et al.*, 2017; Habib *et al.*, 2021 and Alsaikhan, *et al.*, 2021) in the determinations of pesticide residues and their concentrations

determined using Gas chromatography coupled with Mass Spectrophotometer (GC-MS). Measurement of pesticides level in foodstuffs is essential because high level of pesticides cause pathogenesis.

It is in connection with the above and the savagery being perpetuated by pesticides that the study poses to investigate the selected grains samples across the State with a view to enticing Government and Non-Governmental Agencies (NGOs), spirited public and private individuals, and environmentalist to take keen interest in the use/misuse of pesticides in our society in order to instigate and support the enactment of laws that will adequately regulate their usage. Furthermore, the grains under review have eluded researchers over the last decade or more for evaluation. The selected LGAs have not also been looked into in terms of the profiling of the pesticide residues in the post-harvest grains to ascertain their level of fitness for consumption, especially as staple food sources.

Pesticides Residues in our Environments

Pesticides help to enhance agricultural production, However, it significantly affects the quality of social and environmental lives of the people due to residues left in the trail of their applications. Pesticides are widely used in Nigeria and their traces have been found in air, water, soil and food samples (Mazlan, *et al.*, 2017). Pesticides according to Ahoudi *et al.*, (2018) are normally used in agricultural activities for protection against pest and diseases. Examples of pesticides includes, organochlorines, organophosphates, carbamate, pyrethroids, atrazines etc. Pesticide residue is any substance in food, water, air, soil or animal feeds resulting from the use of pesticides. The term may include the derivatives such as conversion products, metabolites, reaction products and impurities considered to be of toxicological significance. Pesticide residues in the increase in our environments due to pesticides over-use, misuse or unnecessarily used by the users who may not be oblivious of the implications of their actions. Poor disposal system and ineptitude may constitute the reasons that

have tremendously increased the concentrations of these residues in our environment (Godwin & Mary, 2019).

Residues of OCPs are due to be present in the environment for several reasons. Some of these pesticides may not be completely compatible with the soil conditions such as soil structure (clay, loam, sand), soil pH, soil water content and chemical characteristics of pesticide (water solubility, absorptivity, pesticide half-life). However, there are other human factors captured on record by researchers that have been sources of large presence of residues besides the inability of pesticide to completely succumb to degradation and production of environmentally friendly by-products. Konradsen, *et al* (2003) hinted pesticides misuse while Soares, *et al* (2003) added weak or total lack of legislation as reason for pesticides poisoning in developing countries like Nigeria. Osinbanjo (2002) submitted that Nigeria is one of the largest markets of pesticides with over 135 pesticides marketed under over 100 different brand names and with over a thousand metric tons applied on farms annually.

Pesticide residues are littered all over the environment due to their ubiquitous use. Akoto *et al* (2013) found substantial concentrations of the pesticides higher than the European Union MRLs in Maize from Ejura, Nasarawa State. Christiana (2019) found organochlorine pesticides residues in maize (2.295 mg/kg), guinea corn (1.885 mg/kg) and millet (1.558 mg/kg), all above FAO/WHO MRLs for cereals in samples from Benue State, Nigeria. Alexandra *et al* (2016) detected the residues in orange, mango and banana fruits sampled from Mubi, Adamawa State at varying proportions. Maigari *et al* (2021) found OCPs ranged from 0.00 to 0.098µg/kg between 60.99% to 63.89% of cabbage, lettuce calyces and tiger nut sampled from Gombe markets.

The ability for the pesticides to persist in soil, bio-accumulate and bio magnify within the food chain is a precursor for the proclivity to causing chronic diseases. Aful *et al* (2010)

asserted that DDT remains in soil from 4-30 years, while Christiana *et al.*, (2019) added that OCP residues have half-life between 15-30 years. Most of their active metabolites cause severe health conditions such as neurological damage, hypertension, cardiovascular diseases, disruption of deoxyribonucleic acid (DNA), hormonal impairment, sexual dysfunction etc: (Parbhu, *et al.*, 2009 Habib, *et al.*, 2021). Availability of data in Nigeria relating to pesticide use or poisoning from it has been very difficult to come by. FAO/WHO (2015) website information providing data on the estimated pesticide use did not capture figures from Nigeria due to unavailability of such data. This makes it impossible to establish an informed position in that regards and uneasy for proper monitoring.

However, Mazlan *et al* (2017) estimated between 125,000 - 130,000 metric tons of pesticide use annually in Nigeria. The World Bank-West Africa Production Programme (World Bank-WAAP, 2013), reported that 72% of farmers in Nigeria purchase/use one form of pesticides or the other from open markets in Nigeria, which heightens the chances of using adulterated products, thereby portending more danger for the environment. According to Bhanti, *et al* (2004) and FAO/WHO (2003), over 3million people world-wide are poisoned while 220,000 die annually from insecticide poisoning; especially in developing countries. Erhunmwunse *et al.*, (2012) hinted that pesticide use in Nigeria puts 2.2 million people at risk of exposure due to its residues. Godwin and May (2019) submitted that ingestion of contaminated food, inhalation and dermal exposure, with ingestion pathway having the highest indices than the other routes to pesticides residues.

In Cross River State, Nigeria, Shuaibu (2008) reported that 112 people were reportedly hospitalized and 2 died after eating pesticide poisoned cowpea. Chike (2010), in 2010 reported 20 fast food restaurants closed down due to fatalities traced to pesticide residues in their products. In another instance, Adegbola

et al. (2012) submitted that 116 students of Government Girls Secondary School, Doma, Gombe State, Nigeria were also hospitalized after consuming food poisoned from pesticide. The case of the killer noodles reported by the National Directorate of Food and Drugs Administration and Control (NAFDAC) pronounced to contain high concentration of pesticide residues in 2004 is a case in point (Zhao, *et al.*, 2016). In Adamawa State, Nigeria in 2018, 3 members of a family died of a meal of poisoned beans. In November, 2018 another 4 members of a family died in Ilorin, Kwara State, Nigeria after consuming a prepared meal from contaminated yam with another case, in 2019, a family of 7 at Mofoluku, Lagos died after eating food suspected to be contaminated with poisonous substance (Oguntade, *et al.*, 2020).

Analysis of pesticides in grains used as staple food in this part of Gombe State seems not have been give much attention in view of cases of pesticides poisoning captured by available records. This is gap that further informed this investigation. Pesticides and their potentials to destroy life and the environment ought to be a priority of all discerning Nigerians.

Method of Analysis

Description of the Study Area

Gombe State was created out of Bauchi State on 1st October, 1996 with a population of 2.4 million (2,365,040) by the 2006 census figure and a Land Area of 20265sqm (16,639km²) projected at a growth rate of 3.3%. Gombe State is located in the Centre of the north east of the country on latitude 9°30' and 12°30'N. Longitude 8°5' and 11°45'E. It is bordering the five other North-Eastern States. There are 11 Local Government Areas in Gombe State. The State capital is located in Gombe town (NHDR, 2018).

Preparation of Samples

Sample Collection and Treatment

Beans, maize, millet, rice and sorghum grains were collected from the different major markets in Akko, Gombe and Funakaye LGAs to form composite samples. The grain

crops being under-studied are widely cultivated and consumed in Gombe State, Nigeria and beyond as staple foods processed in different ways for commercial purpose and nourishment. Each collection was stored in air-tight polyethylene bags. The samples were separated from every form of impurities such as stones, sands and other unwanted particles or debris. They were oven dried at 35°C for 12 hours. The samples are thereafter being homogenized in a mortar into a fine powder sieved with a 2 mm sieve (Olga, 2019). Three equal replications were used for the extraction.

Extraction, Clean-up and Quantification Using the Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) Method

A 5 g finely ground sample was placed in centrifuge tube and 10 mL water were added. Later, 15 mL acetonitrile (NCCH₃) was added and the mixture shaken vigorously. Further, 0.5 g disodium hydrogen citrates hydrate (C₅H₄O₇Na₂. H₂O), 1 g trisodium citrate dihydrate (C₅H₃O₇Na₃.2H₂O), 4 g anhydrous magnesium sulphate (MgSO₄), and 1g sodium chloride (NaCl) were added, and the mixture was hand-shaken, then centrifuged. Afterwards, a 7.5 mL aliquot of the supernatant was transferred to a centrifuge tube (15 mL) containing 0.75 g anhydrous magnesium sulphate, and 0.125 g Primary-Secondary Amine, PSA for the removal of fat. Then, 0.5 g C18 (octadecyl silane or Graphitized Carbon Black, C₁₈HSi₃) was added for the removal of non-polar interferents.

The tube was vortexed and centrifuged. A 3 mL aliquot of the supernatant was transferred into a glass test tube, the extract was evaporated to nearly dryness under a stream of nitrogen and the residue was re-dissolved in 1.5 mL toluene (methylbenzene) prior to its injection into the GC-MS system (Alsaikhan, *et al* 2021, Habib, *et al* 2021 and Jun, *et al* 2021).

Health Risk Indices

Health risk is a measure of the tendency of harmful effects to human health as a result of

exposure to pollutants from the environment. The risk assessment is undertaken to predict the carcinogenic and non-carcinogenic risks that may arise as a consequence of exposure of both adults and children to organochlorine and organophosphate within the study area. Subsequently, the results will be transformed into Estimated Daily Intake (EDI) and the Health Index (HI) computed for both age brackets of adults and children to provide their health index status for eventual ranking using standard procedures. The above analysis availed the study the opportunity to adequately profile the pesticides. The data obtained were compared with World Health Organization (WHO) (2015) Minimum Residual Limits (MRLs) (Christiana, 2019). MRLs are the highest levels of residues probable to be in the food when the pesticide is used according to authorized agricultural practices (EFSA, 2010), they are however, not toxicological limits.

More importantly, the calculated EDIs will be measured against the Acceptable Daily Intake (ADI). The ADIs are toxicological limits which represent the estimate of the amount of the chemical in food or drinking water, expressed on a body-weight basis, that can be ingested daily over a lifetime without appreciable health risk to the consumer. Consequently, conclusion will be made and workable recommendations proffered to enable the community and government or its agencies take steps to address the alarming rate at which the pesticides degrade soil,

infiltrate food commodities and impair the environment at large. According to Suphya *et al.*, (2017), food substances can be characterized based on their Estimated Daily Intake (EDI), Chronic Dose Intake (CDI), Carcinogenic Risk Index (CRI) and Health Quotient (HQ) by the application of the following equations:

$$EDI = \frac{DC \times CC}{BW} \text{ (Vincent, et al., 2018) 1}$$

$$HI = \frac{EDI \times 100}{ADI} \text{ (Vincent et al., 2018) 2}$$

Where: EDI = Estimated Daily Intake (mg/kg), (DC = Daily Consumption rate of cereals = 0.4kg/person/day and 0.19kg/person/day for adults and children respectively based on the World Health Organization (WHO) (2004) as adopted by (Oluwatoyin, *et al* 2020) and; CC = Average Concentration of Pesticide and BW = Body weight (16.7kg for children and 60kg for adults), (WHO, 2004; Bwatanglang, *et al* 2019 & Oluwatoyin, *et al* 2020). ADI = Acceptable Daily Intake (Pesticide Database European Commission (PDEC), 2019 and Alsaikhan, *et al* 2021).

If EDI is lower than Acceptable Daily Intake (ADI), it is considered safe (Suphyia, *et al* 2017).

Results

The results of the analysis to characterize the grain samples based on their non-cancer risk factor:

Table 1: The Residue concentrations of Grains in Akko LGA with their Means±Standard Deviation

Pesticide	mg/kg	Beans	Maize	Millet	Rice	Sorghum	Mean ± SD
Organophosphate	Dichlorvos	0.454	0.677	0.656	0.5	0.359	0.529±0.00
	Pyroproxfen	0.433	0.531	0.455	0.285	0.198	0.380±0.00
	Disulfoton	0.645	0.774	0.443	0.65	0.583	0.619±0.01
	Chlorthiophos	0.872	1.008	0.562	0.444	1.044	0.786±0.02
	Chlorpyrifos	0.231	0.323	0.432	0.213	0.222	0.284±0.00
	Ethion	0.344	0.354	0.211	0.543	0.312	0.353±0.10
	Glyphosate	0.04	0.007	0.005	0.044	0.006	0.002±0.30

Organochlorine	α -lindane	0.285	0.154	0.774	0.145	0.06	0.284 \pm 0.27
	Aldrine	0.563	5.345	0.326	0.259	4.194	2.137 \pm 0.50
	Heptachlor Epoxide	0.006	0	0.007	0.007	0.007	0.005 \pm 0.00
	Endrine	0.638	5.743	1.132	1.006	0.484	1.801 \pm 0.00
	Endosufan I	0.296	1.187	0.357	0.102	0.74	0.536 \pm 0.00
	Endosulfan II	2.874	2.112	0.056	1.979	1.305	1.665 \pm 0.03
	Methoxychlor	0.049	0.008	0.024	0.011	0.043	0.027 \pm 0.00
	P'DDE	0.361	0.957	0.013	0.547	0.047	0.385 \pm 0.00

Table 2: The concentrations of Pesticide Residues in the various Grains in Gombe LGA with their Means and Standard Deviations

Pesticide	mg/kg	Beans	Maize	Millet	Rice	Sorghum	Mean \pm SD
Organophosphate	Dichlorvos	0.665	1.554	0.755	0.465	0.776	0.843 \pm 0.00
	Pyroproxfen	0.293	0.551	0.545	0.432	0.476	0.459 \pm 0.08
	Disulfoton	0.873	0.685	0.432	0.456	0.686	0.565 \pm 0.12
	Chlorthiophos	1.087	1.025	0.878	1.034	1.554	1.116 \pm 1.36
	Chlorpyrifos	0.411	0.344	0.556	0.456	0.233	0.400 \pm 1.05
	Ethion	0.567	0.532	0.476	0.466	0.543	0.517 \pm 0.01
	Glyphosate	0.055	0.025	0.064	0.026	0.013	0.036 \pm 0.02
Organochlorine	α -lindane	1.266	0.611	0.207	0.149	0.254	0.497 \pm 0.00
	Aldrine	0.377	0.315	0.231	1.214	0.328	0.439 \pm 0.00
	Heptachlor Epoxide	0.007	0.006	0.005	0.003	0.04	0.012 \pm 0.00
	Endrine	0.169	1.199	1.301	7.071	7.083	3.365 \pm 0.00
	Endosufan I	0.539	0.281	0.755	0.833	0.688	0.619 \pm 0.00
	Endosulfan II	0.558	3.489	1.383	1.229	2.954	1.923 \pm 0.11
	Methoxychlor	0.03	0.043	0.037	0.026	0.019	0.031 \pm 0.00
	P'DDE	0.471	0.356	0.023	0.069	0.327	0.249 \pm 0.00

Table 3: The concentrations of Pesticide Residues in the various Grains in Yamaltu-Deba LGA with their Means and Standard Deviations

Pesticide	mg/kg	Beans	Maize	Millet	Rice	Sorghum	Mean \pm SD
Organophosphate	Dichlorvos	0.515	0.674	0.643	0.465	0.556	0.571 \pm 0.00
	Pyroproxfen	0.453	0.321	0.247	0.432	0.44	0.379 \pm 0.00
	Disulfoton	0.684	0.776	0.681	0.323	0.676	0.682 \pm 0.00
	Chlorthiophos	0.324	0.432	1.333	0.765	1.556	0.882 \pm 0.09
	Chlorpyrifos	0.234	0.432	0.211	0.133	0.447	0.291 \pm 0.00
	Ethion	0.324	0.342	0.213	0.355	0.432	0.332 \pm 0.00
	Glyphosate	0.041	0.026	0.005	0.005	0.089	0.033 \pm 0.00

Organochlorine	α-lindane	0.508	0.137	0.529	0.431	0.883	0.498±0.01
	Aldrine	0.266	0.197	0.289	0.325	0.5	0.315±0.00
	Heptachlor						
	Epoxide	0.221	0.022	0.011	0.031	0.008	0.059±0.00
	Endrine	0.566	1.168	2.488	1.898	0.803	1.385±0.00
	Endosufan I	0.19	0.139	0.178	0.109	0.611	0.245±0.00
	Endosulfan II	0.862	0.51	2.882	0.491	0.391	1.027±0.00
	Methoxychlor	0.013	0.036	0.024	0.018	0.038	0.026±0.00
	P'DDE	0.116	0.019	0.02	0.031	0.024	0.042±0.00

Table 4: showing Minimum Residual Limits (MRLs) and Acceptable Daily Intakes (ADIs) of some of the pesticides.

Pesticide	mg/kg	MRLs (kg/day)	ADIs (Kg/Person/Day)
Organophosphate	Dichlorvos	0.02	0.004
	Pyroproxfen	0.004	0.1
	Disulfoton	0.2	0.03
	Chlorthiophos	0.01	0.043
	Chlorpyrifos	0.3	0.001
	Ethion	0.3	0.002
	Glyphosate	0.1	0.5
Organochlorine	α-lindane	0.01	0.015
	Aldrine	0.02	0.001
	Heptachlor Epoxide	0.0005	N.D
	Endrine	0.05	N.D
	Endosufan I	1	0.006
	Endosulfan II	1	0.0075
	Methoxychlor	0.01	N.D
	P'DDE	0.1	0.001

Note: N.D (Not Determined). MRLs and ADIs (Pesticides Database, European Commission, 2019; EFSA, 2015; WHO GEMS, 2015 & Adewole, *et al.*, 2021)

Table 5: Table of Dietary Risk Assessment of Organophosphate and organochlorine Pesticides Residues in Grains Commonly Consumed in Akko LGA, Gombe State.

S/N	Pesticide	mg/kg	Average Res.	EDI	HI (%)	EDI	HI (%)
1.	Organophosphate	Dichlorvos	0.529±0.00	3.50E-03	87.5	6.00E-03	145.5
2.		Pyroproxfen	0.380±0.00	2.50E-02	2.5	4.40E-03	4.18
3.		Disulfoton	0.619±0.01	4.10E-03	13.7	6.80E-03	22.7
4.		Chlorthiophos	0.786±0.02	5.00E-04	1.16	8.60E-03	20.1
5.		Chlorpyrifos	0.284±0.00	1.90E-03	190	3.00E-03	312.4
6.		Ethion	0.353±0.10	2.40E-03	120	3.90E-03	194.2
7.		Glyphosate	0.002±0.30	1.00E-05	0.002	2.20E-05	0.0044

8.	Organochlorine	α -lindane	0.284 \pm 0.27	1.90E-03	12.67	3.10E-03	20.8
9.		Aldrine	2.137 \pm 0.50	1.40E-02	14,300	2.4E-02	23,507
10.		Heptachlor E.	0.005 \pm 0.00	3.00E-05	N.D	5.50E-05	N.D
11.		Endrine	1.801 \pm 0.00	1.20E-02	N.D	2.00E-02	N.D
12.		Endosufan I	0.536 \pm 0.00	3.60E-03	60	5.90E-03	98.3
13.		Endosulfan II	1.665 \pm 0.03	1.10E-02	149.3	1.80E-02	224.2
14.		Methoxychlor	0.027 \pm 0.00	2.00E-04	N.D	3.00E-04	N.D
15.		P'DDE	0.385 \pm 0.00	2.60E-03	260	4.20E-03	423.5

Table 6: Table of Dietary Risk Assessment of Organophosphate and organochlorine Pesticides Residues in Grains Commonly Consumed in Gombe LGA., Gombe State.

Gombe LGA				Adults		Children	
S/N	Pesticide	mg/kg	Average Res.	EDI	HI (%)	EDI	HI (%)
1.	Organophosphate	Dichlorvos	0.843 \pm 0.00	5.60E-03	141.2	9.3E—3	231.8
2.		Pyroproxfen	0.459 \pm 0.08	3.10E-03	3.1	5.00E-04	0.5
3		Disulfoton	0.565 \pm 0.12	3.90E-03	12.6	6.00E-03	20.7
4		Chlorthiophos	1.116 \pm 1.36	7.50E-03	17.4	1.20E-02	28.5
5		Chlorpyrifos	0.400 \pm 1.05	2.70E-03	268	4.40E-03	440
6		Ethion	0.517 \pm 0.01	3.50E-03	173	5.70E-03	284.4
7		Glyphosate	0.036 \pm 0.02	2.40E-04	0.05	4.00E-04	0.08
8	Organochlorine	α -lindane	0.497 \pm 0.00	3.30E-03	22.2	4.80E-03	32.2
9		Aldrine	0.439 \pm 0.00	2.90E-03	2,940	4.80E-03	4,829
10		Heptachlor E.	0.012 \pm 0.00	8.00E-05	N.D	1.30E-04	N.D
11		Endrine	3.365 \pm 0.00	2.30E-02	N.D	3.70E-02	N.D
12		Endosufan I	0.619 \pm 0.00	4.20E-03	69.1	6.80E-03	113.5
13		Endosulfan II	1.923 \pm 0.11	1.30E-02	171.8	2.10E-02	28.2
14		Methoxychlor	0.031 \pm 0.00	2.10E-04	N.D	3.40E-04	N.D
15		P'DDE	0.249 \pm 0.00	1.70E-03	166.8	2.70E-03	273.9

Table 7: Table of Dietary Risk Assessment of Organophosphate and organochlorine Pesticides Residues in Grains Commonly Consumed in Yamaltu-Deba LGA, Gombe State.

	Pesticide	mg/kg	Average Res.	EDI	HI (%)	EDI	HI (%)
1.	Organophosphate	Dichlorvos	0.571 \pm 0.00	3.80E-03	95.6	6.30E-03	157
2.		Pyroproxfen	0.379 \pm 0.00	2.50E-03	2.5	4.20E-03	4.17
3		Disulfoton	0.682 \pm 0.00	2.50E-03	8.5	7.50E-03	24.9
4		Chlorthiophos	0.882 \pm 0.09	4.60E-03	10.6	9.70E-03	22.6
5		Chlorpyrifos	0.291 \pm 0.00	5.90E-03	590.9	3.20E-03	320
6		Ethion	0.332 \pm 0.00	2.00E-03	97.5	3.70E-03	182.6
7		Glyphosate	0.033 \pm 0.00	2.20E-04	0.04	3.60E-04	0.07

8	Organochlorine	α -lindane	0.498 \pm 0.01	3.30E-03	22.2	5.50E-03	36.5
9		Aldrine	0.315 \pm 0.00	2.10E-03	2,111	3.50E-03	3,465
10		Heptachlor E.	0.059 \pm 0.00	4.00E-04	N.D	6.50E-04	N.D
11		Endrine	1.385 \pm 0.00	9.30E-03	N.D	1.50E-02	N.D
12		Endosufan I	0.245 \pm 0.00	1.60E-03	27.4	2.70E-03	44.9
13		Endosulfan II	1.027 \pm 0.00	6.90E-03	91.7	1.10E-02	150
14		Methoxychlor	0.026 \pm 0.00	2.00E-04	N.D	2.90E-03	N.D
15		P'DDE	0.042 \pm 0.00	2.80E-04	28.1	4.60E-04	46.2

Source: (Field Study, 2022). NOTE: Not Determined. EDI (mg/kg/day)

Graph of Average Pesticides Residues in the Grains

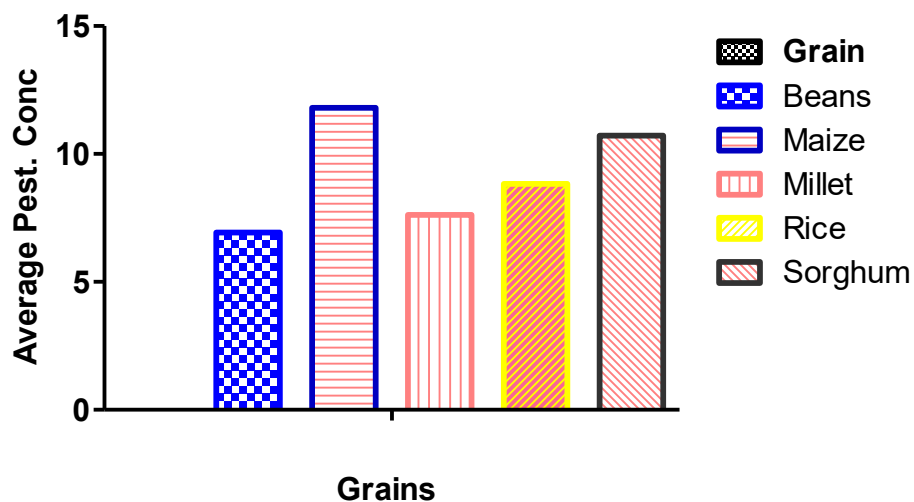


Fig. 1: Average Pesticides Residues Concentrations in the respective grains of the Study Areas.

Graph of Average Pesticides Residue Concentrations in the LGAs

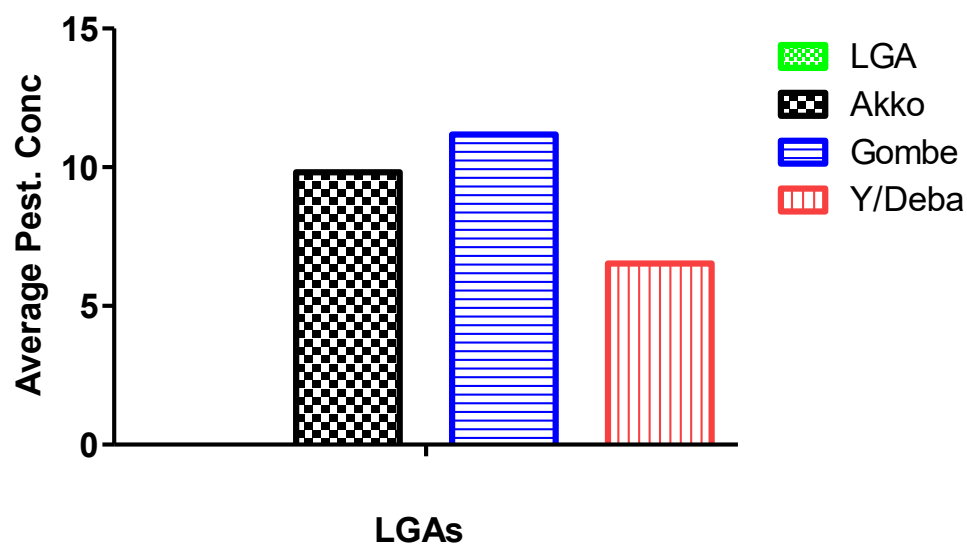


Fig. 2: Average Pesticides Residues Concentrations according to LGAs of the Study Areas

Discussion

The results displayed above speaks for themselves. Tables 1, 2, and 3 provide the average concentrations and the standard deviations of the various pesticides selected. The graphical representations in Figures 1 and 2 summarized the aforementioned Tables. The cumulative concentrations of the residues in the grains as shown in Fig. 1 reveals that the pesticides residues in the grains is in the ranking order of Maize > sorghum > beans > rice > millet. This is in agreement with Akoto *et al.* (2013) found maize to be highly contaminated with organophosphates and organochlorine among grains sampled in Egura town, Ghana. The pesticide loads may be due to the interest of the farmers and demand for the grains in the areas. The demand and consumption for maize is no doubt, the most sought for because of its position in the staple food pyramid for its multi-valued and multifarious applications in preparing the *tuwo*; semi-solid bolls usually eaten with soup, *kunu*-drink, a locally made refreshing drink and a number of other uses including feeding of livestock.

Fig. 2 shows the cumulative average concentrations of the residue according to the LGAs. Samples taken from Gombe LGA is the lead. This can be traced to a number of factors. Gombe LGA is the LGA of the State capital with a high population of some local farmers and civil servants that also engage in farming and depend heavily in the use of pesticides for virtually every aspect of the farming expedition also engage hired labors comprising of individuals that are stark illiterates or only possess little or no knowledge of the rudiments of applying the pesticides correctly. Korandsen *et al.* (2003) and Godwin & Mary (2019) asserted that the high concentrations of pesticides residue in our environment is due to misuse, abused and unnecessarily use of pesticide by businessmen and farmers that lack adequate knowledge. Table 4 displaces the MRLs and ADIs of the respective pesticides under review. Tables 5,6 and 7 above revealed that over 90% of the organochlorine residues in the study are higher than their respective MRLs provided

by FAO/WHO (2015) current Global Environment Monitoring System (GEMS/Food Diets). These results are in agreement with those of Anzene *et al.* (2014); Akinneye *et al.* (2018) and Christiana (2019) in their respective studies obtained organochlorine pesticides in grains higher than the MRLs. Nevertheless, in 2021, Kolakowski *et al.* (2020) reported glyphosate in soya beans, corn and barley in Canada below FAO/WHO MRLs.

The high concentration above the MRLs is not surprising in view of protracted and continuous use of the pesticides over a long period of time. The incessant use is not unconnected to the fact that the farmlands have may have lost fertility over long usage and the lands are generally bare; prone to erosion and as such require high reliance in soil supplements such as fertilizers and pesticides. Poor knowledge or flagrant disregard to manufacturer's directions on method of application of the pesticide cannot be ruled out also as allured to by some experts.

There are a number of other studies where pesticides concentrations exceeded their MRLs. Sheryl *et al.* (2021) discovered glyphosate residues in wheat sample in markets in South Africa higher than the MRLs. Isegbe *et al.* (2016) reported in the presence of pesticide residues in dried beans samples collected from Kano, Lagos and Abuja. In 2019, Christiana *et al.*, (2019) reported 2.295ppm in maize; 1.885ppm in Guinea corn and 1.558ppm in millet samples from some major markets in Lagos, Nigeria contained organochlorine residues; all above the MRLs. Habib *et al* (2021) and Alsaikhan *et al* (2021), both recorded similar results higher than MRLs in their studies on eggplant and cucumber respectively. These results can be adjudged to be unsafe on the basis of the MRLs.

However, since MRLs are not toxicological limits, their Average Daily Intake (ADI) which are recognized toxicological standards were also employed in the profiling. The calculated Estimated Daily Intake (EDI) in the table are generally within the brackets of

their ADIs. According to Nasreddine *et al.* (2016), as long as dietary exposure is lower or equal to the toxicological reference values (exposure \leq the ADI or ARfD), a consumer's health risk can be excluded with a degree of certainty.

Majority of the Health Index (HI) in Tables 5, 6 and 7 for both adults and children also demonstrate that the exposed population is safe. According to Vincent *et al.* (2018), HI value lower than 100% indicate safety net. Most of the HI are lower than 100%. However, dichlorvos, chlorpyrifos, ethion, aldrine, endosulfan II and Para para-dichloro diphenyldichloro ethylene (P'DDE), from Gombe samples; chlorpyrifos, aldrine, endosulfan II and P'DDE in samples from Akko and in Y/Deba where chlorpyrifos, ethion, aldrine and endosulfan II rose higher than 100%. It should be noted that aldrine, chlorpyrifos and endosulfan II are common among the LGAs with HI higher than 100%. This is due principally to their high concentrations in the grains.

Conclusion

The fact that some of the pesticides are still within safety limits today does not preclude the propensity for them to wreak havoc in future. It should be noted that pesticide residues are very persistent and possess the ability to accumulate in the environment due to their high resistance to environmental degradation; and bioaccumulation in human tissues that can exceed their thresholds when symptoms of their biochemical actions begin to manifest. The level of their distributions in the samples across the LGAs and their EDIs vis a-vis the HI, MRLs and ADIs are too close for comfort. It is therefore, pertinent to submit that the level of pesticides residues in the sample grains are high enough to elicit public concern to warrant urgent intervention by relevant institutions for actions to mitigate further deterioration.

Recommendations

1. National Food and Drugs Administration and Control (NAFDAC) and the Ministry of Agriculture and Rural Development

(FMARD) to ensure proper profiling and characterization of all pesticides before use in Nigeria.

2. It is recommended that efforts should be made in the line of shifting from chemical input-intensive agriculture to agro-ecological farming system.
3. Stoppage of use of agro-chemicals that have been classified as carcinogens and environmentally hazardous and ensure that they are not replaced by more toxic ones.
4. It recommends regular evaluation of grains and other food items to keep abreast with the development of happenings in the use of pesticides, as farmers and users' adherence to users' manual religiously while government or its agencies should regulate use and enlighten the users in the danger of not playing safe in order to mitigate the resultant effects of indiscriminate use.

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