Analysis and quantification of the levels of insecticide residues in maize sold in South Eastern Nigeria

J. C. Asogwa[1*], E. N. Nwankwo[1], J. O. Ezekwesili-Ofili[2], K. K. Asogwa[2] and C. R. Okwor[3]

[1] Department of Parasitology and Entomology, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria

[2] Department of Biochemistry, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria

[3] Department of Microbiology, Federal University of Technology, Minna, Niger State, Nigeria

Correspondence Author: J. C. Asogwa

Received 2 Sep 2023; Accepted 10 Oct 2023; Published 17 Oct 2023

Abstract

Pesticides are important in reducing losses caused due to insect pest both in the field and storage but the dangers associated with its use including problem of residues is of serious public health concern. Maize grains treated with insecticide in order to prevent insect pest attack are healthy and safe for consumption if the active ingredients of such insecticides are within the maximum residue level (MRLs) set by regulatory bodies. Assessing the contamination of cereals and their manufactured products with pesticide residues is a topic of global importance, and monitoring studies are needed to analyse residues at trace levels. This study investigated the levels of insecticide residues in maize sold in South East Nigeria. Maize grains presumed to be treated with insecticides were collected from four different maize sellers each from five major markets across the South East to analyse and quantify the level of presence or absence of residues on the samples. The maize samples were sorted out by removing stones and other unwanted material from the samples. 30.0g of each sample was grinded into smaller particles to produce a uniform sample maize powder. Extraction was performed according to the methods of Sharif *et al*. (2006). The milled samples of maize were properly mixed and 2.0g was weighed into a 20.0ml sample vial. Anhydrous sodium sulphate (1.0g) was added and mixed with the sample to absorb any moisture present. The sodium sulphate was previously heated at 650^0C for one hour and stored in a desiccator. Ethyl acetate (10.0ml) was added to the vial. The mixture was vortex mixed for 5 minutes and then allowed to stand for 45 minutes. It was mixed again and centrifuged for 5 minutes at 2500rpm. The supernatant was carefully transferred into a flask. The residue was further extracted twice as described above, using 10.0 ml ethyl acetate each time. The supernatants were combined and reduced to about 1ml under a gentle stream of nitrogen gas at 36^0C. For the clean-up, solid phase extraction cartridges (florisil, 500mg/6ml) were used. The analysis of maize samples for pesticide compounds was performed on a Gas Chromatography –Mass Spectrometry (GC-MS), an auto sampler and a split-splitless injector. Among the pesticide compounds analysed for residue in maize grains in Enugu, Abia, Imo, Anambra and Ebonyi State respectively, lindane (0.06,0.13,0.05,0.05,0.05mg/kg) (organochlorine), dichlorvos (0.36, 1.09,0.51,0.51 and 0.53mg/kg) (organophosphate) and carbofuran (0.23mg/kg) (carbamate) absent in Enugu, exceeded their maximum residue levels (MRL) of 0.02, 0.1and 0.05mg/kg respectively set by pesticide regulatory bodies. The result shows that occurrence of pesticide residues (dichlorvos, lindane and carbofuran) in the maize samples which exceeded its MRLs could be considered serious threats to human health. An investigation into continuous monitoring and stringent regulation of pesticide residues not only limited to maize grains but also on other food and products are recommended.

Keywords: pesticide, residues, maize grains, maximum residue level, analysis

Introduction

In agriculture, pesticides are extensively used for their economic benefits in fighting crop pests and reducing competition from weeds, thus improving yields and protecting crop quality, reliability, and the price of production. The widespread use of these compounds has resulted in contamination of environmental compartment (Tariq *et al*., 2004, Fernandez-Alvarez *et al*., 2008, Xue *et al*., 2005, Harner *et al*., 2005) [33, 10, 37, 13]. Misuse of highly toxic pesticides, coupled with a weak or totally absent legislative framework in the use of pesticides, is one of the major reasons for high incidence of pesticide poisoning in developing countries (Konradsen *et al*., 2003) [20]. In addition, agricultural plants used for feeding livestock may be contaminated and, consequently, pesticides may become exposed to human consumption via animal feed. In recent years, increasing attention has been paid to the risks posed to consumers by chemical contaminants or residues in foodstuffs (Leeman *et al*., 2007) [22].

Pesticides are any substance which may be administered for the control of insects, arachnids or other pests (FAO, 2006) [9]. Since pesticides are essentially poisons meant to kill or ward off unwanted living organisms, it is not surprising that they could produce adverse health impacts on people. Most affected are the people who directly apply the pesticides (such as farmers and applicators), followed by members of their immediate family, and ultimately, the general public who consume food products with high residues of pesticides. Children are the most vulnerable, partly due to biological factors as well as enhanced exposure factors (Zahm and Ward 1998, UNEP 2004) [38, 36]. It has been reported that globally an estimated 1 million to 5 million cases of pesticide poisoning occur every year, resulting in 20,000 fatalities among agricultural workers. It is a sobering fact that although developing countries use only 25% of the world's production of pesticides, they experience 99% of deaths due to pesticides

(Jeyaratnam, 2009) [18].

Pesticide residues are deposits of pesticide active ingredients, its metabolites or breakdown products present in some component of the environment after its application, spillage or dumping (Chen *et al*., 2009) [4]. Residue levels and risk monitoring are important aspect of agricultural product quality in many countries. The consumption of pesticide contaminated food product may become potential health risk for human body. Some investigations illustrate that pesticide via polluted agricultural crops may cause toxicity (Chen *et al*., 2009) [4]. Moreover, it may be associated with chronic illness such as genetic mutation, cancers, blood and reproductive disorder (Damalas and Eleftherohorinos, 2011) [5]. These negative effects indicate that extensive studies on agricultural products are necessary, and the World Health Organization (WHO) considers them as a severe public health problem (Leong *et al*., 2020) [23].

Different types of pesticides are used in different countries for different types of crops to prevent pests, insects and weeds. Because of the expansion of worldwide trade, more foods which are treated by pesticides are being imported into different countries. These worldwide trades increase the expansion of pesticide residues in different areas of the world and it's the issue of public health concern. There are a number of strategies which can be used to minimize pest and disease problems and reduce pesticide residues in food grains, vegetables and fruits (Gale and Buzby, 2009) [12].

Residues of organophosphate and organochlorine insecticides, especially DDT and hexachlorocyclohexane (HCH) have been detected in man and his environment of the world due to injudicious and indiscriminate use (Hayes and Laws, 1991) [14]. Seventy- five percent of all pesticides in the world are used in developed countries, but use in developing countries is increasing (Lee, 2006) [21].

In Lagos state, Ogah *et al*. (2011a) [27] determined the incidence and quantity of organochlorine pesticide residues in maize samples collected from various markets and compared values obtained with established safety values in order to highlight possible health hazards. The results showed that 96% of the maize samples contained residues of one or more organochlorine pesticides. Mean concentrations ranged from 7.9-52.0µg/kg and maximum residue limits (MRLs) of some pesticides were exceeded in up to 7% of samples. The estimated total diet intakes (ETDIs) for aldrin and dieldrin exceeded their maximum permissible intakes.

Perusal of the residue data on pesticides in samples of fruits, vegetables, cereals, pulses, grains, wheat flour, oils, eggs, meat, fish, poultry, cow milk, butter and cheese in India indicates their presence in sizeable amounts. For example, the fungicide hexachlorobenzene (HCB) was identified in water, human milk and human fat samples collected from Faridabad and Delhi. HCB residues were also found in various raw food commodities from some markets in India. DDT and Hexachlorocyclohexane (HCH) residues were detected in groundnut and sesame oil samples collected from Tamil Nadu (ICMR Bulletin, 2001) [15].

High levels of insecticide residues arising from improper application and multiple sprays of sub-lethal doses of persistent OP are reported to be responsible for several cases of food poisoning and health threat to humans in both rural and urban areas of developing countries (WHO, 2018). However, in spite of the ban of some OP, their use is still high in most developing countries, particularly because of their low cost compared to newer insecticides.

Regrettably, even though organochlorines are banned from importation, sales and use, third world nations continue to use them. For example, in Nigeria, there are evidence of their continued application to crops, vegetables and fruits. Few studies conducted so far in Nigeria revealed levels of organochlorine pesticides in water, segements, food and vegetable (Osafo and Frempong, 1998; Ntow 2001; Darko and Aquaah, 2006) [28, 25, 6] which are emanating from current and past use of these chemicals. Moreover, pesticide residues in food materials are not properly monitored nor controlled in Nigeria and limited information is available for the level of pesticide residues in food.

A survey of literature shows that there is dearth of information on the estimated levels of insecticide residues in foodstuff particularly in maize grains which is among important staple, highly strategic and priority food crops consumed in Nigeria. This calls for concern as the toxicological effects of the chemicals which humans and animals are exposed to daily are ever-increasing. It is therefore necessary to determine the levels of pesticide residues in this food crop sold in South East of Nigerian markets and this observation prompted the inception of this research study.

Materials and methods

Study area

Analysis of maize samples from major markets of South East for insecticide residues was performed at the Spring Board Laboratory Ltd, Awka, Anambra State.

Design of the study

One major market each was selected in each State for the collection of maize (*Zeamais*) samples that are presumed to have been treated with insecticides before sale. Four maize sellers were randomly selected from each of the markets in 5 South Eastern major markets namely; Ogbete Main market (Enugu State), Eke Awka market (Anambra State), Okigwe market (Imo State), Ariaria market (Abia State) and Abakiliki market (Ebonyi State).

Collection of maize samples from the market for quantification of insecticide levels

Samples of maize, *Z. mays* were randomly obtained from 4 maize sellers' shop in the 5 major markets across South East of Nigeria. The samples were properly labelled and stored in glass bottles with tight covers to protect them from moisture and contamination. They were placed in the refrigerator at a temperature of 4ºC until ready for use.

Preparation of maize samples

The maize samples were cleaned by picking out stones and other extraneous materials. Each sample was thoroughly mixed and a 30.0g portion was taken and milled to 20 mesh particle size to produce a good homogenate. The milled samples were then stored in glass bottles with appropriate labels in a refrigerator at 4^0C. Duplicate portions (30.0g) of the samples was stored as whole grains in labelled glass bottles in the refrigerator as backup samples.

Analytical quality assurance

All solvents and reagents were of analytical grade and above 99% purity (to be purchased at International Institute of Tropical Agriculture (IITA). The solvents were distilled in all-glass apparatus before use.

Extraction and clean-up of samples

Extraction of maize samples for the analysis of organophosphate pesticide residue was conducted according to the methods of Sharif *et al*. (2006) [31]. The milled samples of maize were properly mixed and 2.0g was weighed into a 20.0ml sample vial. Anhydrous sodium sulphate (1.0g) was added and mixed with the sample to absorb any moisture present. The sodium sulphate was previously heated at 650^{0}C for one hour and stored in a desiccator. Ethyl acetate (10.0ml) was added to the vial. The mixture was vortex mixed for 5 minutes and then allowed to stand for 45 minutes. It was mixed again and centrifuged for 5 minutes at 2500rpm. The supernatant was carefully transferred into a flask. The residue was further extracted twice as described above, using 10.0 ml ethyl acetate each time. The supernatants were combined and reduced to about 1ml under a gentle stream of nitrogen gas at 36^{0}C. This was then taken for florisil clean-up.

For the clean-up, solid phase extraction cartridges (florisil, 500mg/6ml) were used. Each cartridge was conditioned with 5.0ml of the eluting solvent mixture (hexane/ ethyl acetate 50:50) and the sample extract (1ml) was loaded on the florisil. The sample tube was rinsed three times with 1.0ml eluting solvent, and the rinses were added to the florisil column. The sample was then eluted with 5.0ml of the same solvent mixture into a receiving glass tube. The florisil columns were rinsed with another 3.0ml of the eluting solvent mixture into the same receiving glass tube. The eluent was evaporated to dryness under a gentle stream of nitrogen gas and the residues were reconstituted in 1.0ml ethyl acetate for GC-MS analysis.

Analysis of pesticide residue in maize samples

The analysis of maize samples for pesticide compounds was performed as was described by Botwe *et al*. (2011) [3] on a GC-MS, an auto sampler and a split-splitless injector. The DB-5 fused silica capillary column of 30m × 0.25µm i.d. × 0.25µm film thickness was coated with cross-linked 5% phenyl dimethyl polysiloxane. The carrier gas was helium (99.999% purity) at a flow rate of 1.0ml/min. Oven temperature was maintained initially at 70^{0}C for 1minute, increased at 15^{o}C/ minutes to 175^{o}C, then at 2^{0}C/ minutes to 215^{o}C, at 10^{o}C/minutes to 26^{o}C and finally at 20^{o}C/minutes to 290^{o}C and held for 8minutes. Injection volume was 1µL, injected in splitless mode at injection temperature of 250^{o}C. The mass spectrometer was operated in electron impact (EI) ionization mode with a detector voltage of 700V, ion source temperature of 200^{o}C, GC interface temperature of 320^{o}C and emission current of 150µV.

Identification and quantification of pesticide residues

A pesticide residue was identified if the retention times matched those of the standards and the relative abundances are within 10% of those of the standards. An identified pesticide was quantified using the external standard method of comparing sample peak areas with those of the pesticide standards under same conditions. Each sample was analysed three times and the mean values obtained. The pesticide content of each will be calculated as:

$$\text{Pesticide content}= \frac{As\times Vf}{Wt_s \times CF}$$

Where As= peak area of sample

Vf = final volume of clean extract

$Wt_{s=}$ weight of sample extracted

CF= calibration factor.

The CF of each pesticide will be calculated as:

<u>Peak area of standard</u>

Total Amount of Standard injected

Statistical analysis

Statistical differences among the different pesticide in the maize grains from different market across the South East were done using turkey post-hoc test at <0.05.

Results

Pesticide residues in maize grains

Pesticide residue detected in maize grains collected from Enugu State

Table 1 shows the class of pesticide residues with their corresponding retention time, area, height and the levels of pesticides detected from maize samples from Enugu State. There are seven groups of pesticide residues detected in maize samples from Enugu State. Out of the seven pesticide residues detected from the maize samples, four belongs to organochlorine groups (lindane, g-chlordane, t-nonachlor and dicofol) and the three remaining three belongs to organophosphate groups (lsopropylamine, dichlorvos and glyphosphate).

Table 1: Class of pesticide, area, height and level of pesticide residues detected from Enugu State

Pesticide types	Retention time(min)	Area	Height	Level of residues (mg/kg)
Organochlorines				
Lindane	5..370	6234.7000	156.744	0.06
g-chlordane	14.436	3737.3100	93.856	0.02
t-nonachlor	42.100	5021.1522	126.045	0.01
Dicofol	35..203	8346..3186	209.389	0.009
Organophosphates				
Isopropylamine	0.446	4747.7259	134.888	0.01
Dichlorvos	9.490	5534.1676	138.961	0..36
Glyphosate	25.033	4510.1688	113.169	0.003

Pesticide residues detected in maize grains collected from Abia state

Table 2 shows the pesticide residues detected in maize sample screened for residues in Abia State. Eight pesticide residues including lindane, g-chlordane, dichlorobiphenyl, tetradifon, isopropylamine, dichlorvos, glyphosphate, carbofuran and were detected from the sample of maize analysed. Out of the eight pesticides detected, dichlorobiphenyl, lindane, g-chlordane and tetradifon belongs to organochlorine, isopropylamine, dichlorvos, glyphosphate belongs to organophosphate group and carbofuran belonging to carbamate group.

Table 2: Class of pesticide, area, height and level of pesticide residues detected from Abia state

Pesticide type	Retention time	Area	Height	Level of residue
Organochlorines				
Lindane	5.823	5491.5868	311.948	0.13
g-chlordane	12.380	3772.7770	214.331	0.01
Dichlorobiphenyl	4.686	11715.6365	661.563	0.04
Tetradifon	27.230	4894.1058	278.122	0.001
Organophosphate				
Isopropylamine	0.270	12931.7240	480.725	0.02
Dichlorvos	7.570	8130.0383	461.112	1.09
Glyphosphate	17.316	9975.9888	564.840	0.012
Carbamate				
Carbofuran	21.500	11343.2784	638.182	0.23

Table 3: Class of pesticide, area, height and level of pesticide residues detected from Imo state

Pesticide type	Retention time (min)	Area	Height	Level of residues
Organochlorines				
Lindane	5.823	5491.5868	311.948	0.05
g-chlordane	12..380	3772.7770	214.331	0.02
Dichlorobiphenyl	4.686	11715.6365	661.563	0.04
Tetradifon	27..230	4894.1058	278.122	0.001
Organophosphates				
Isopropylamine	0.270	12931.7240	480.725	0.02
Dichlorvos	7..570	7112..3047	461.112	0.51
Glyphosphate	17..316	9975.9888	564.840	0.01
Carbamate				
Carbofuran	21.500	11343.2784	638.182	0.23

Pesticide residues detected in maize grains collected from Imo State

Table 3 below shows pesticide residues detected in maize samples from Imo state after analysis for presence or absence of residues in them. Lindane, g-chlordane Dichlorobiphenyl, and tetradifon belonging to organochlorine group were detected in the maize samples. In addition, isopropylamine, dichlorvos and glyphosphate belonging to organophosphate and carbofuran belonging to carbamate were also present in the samples.

Pesticide residues detected in maize grains collected from Anambra state

Table 4 below shows the pesticide residues detected in maize collected from Anambra State. From the table below, lindane, g-chlordane, dichlorobiphenyl, and tetradifon belonging to organochlorine was detected. Also, isopropylamine, dichlorvos and glyphosphate belonging to organophosphate pesticide and carbofuran belonging to carbamate were detected.

Table 4: Class of pesticide, area, height and level of pesticide residues detected from Anambra state

Pesticide type	Retention time (min)	Area	Height	Level of residues
Organochlorines				
Lindane	5.816	5310.9935	112.267	0.05
g-chlordane	12.380	3762.5781	76.270	0.02
Dichlorobiphenyl	4.690	12007.1692	237.826	0.03
Tetradifon	27.230	4895.4780	99.104	0.001
Organophosphate				
Isopropylamine	0.356	9700.8933	137.876	0.01
Dichlorvos	7.570	8187.5140	164.928	0.51
Glyphosphate	17.316	9974.6486	201.873	0.008
Carbamate				
Carbofuran	21.500	11334.9679	229.241	0.23

Pesticide residues detected in maize grains collected from Ebonyi State

Lindane, g-chlordane, dichlorobiphenyl, Isopropylamine, dichlorvos, glyphosphate, carbofuran and tetradifon are pesticide residues detected in maize samples from Ebonyi State. These residues belong to different class of pesticide groups. Lindane, g-chlordane, dichlorobiphenyl and tetradifon belong to organochlorine groups; isopropylamine, dichlorvos and glyphposphate belong to organophosphate group and carbofuran belonging to carbamate group of pesticide is the only residue detected from the chemical group. (Table 5).

Table 5: Class of pesticide, area, height and level of pesticide residues detected from Ebonyi state

Pesticide type	Retention time (min)	Area	Height	Level of residues
Organochlorines				
Lindane	5.816	5310.9935	112.267	0.05
g-chlordane	12.380	3762.5781	76.270	0.02
Dichlorobiphenyl	4.690	12007.1692	237.826	0.03
Tetradifon	27.230	4895.4780	99.104	0.001
Organophosphate				
Isopropylamine	0.356	9700.8933	137.876	0.01
Dichlorvos	7.570	8187.5140	164.928	0.51
Glyphosphate	17.316	9974.6486	201.873	0.008
Carbamate				
Carbofuran	21.500	11334.9679	229.241	0.23

The level of organochlorines, organophosphates and carbamate in maize samples from South East is presented in Table 6. The detected pesticides in maize samples across the South East in the present study were in the following ranges; lindane (0.05-0.13mg/kg), g-chlordane (0.01-0.02mg/kg), t-nonachlor (0.00-0.01mg/kg), dicofol (0.00-0.097), Isopropylamine (0.01-0.02mg/kg), dichlorobiphenyl (0.00-0.04mg/kg), tetradifon (0.00-0.0016), dichlorvos (0.36-1.09mg/kg), glyphosate (0.003-0.008) and carbofuran (0.00-0.23mg/kg). However, t-nonachlor and dicofol were absent in samples from Abia, Imo, Anambra and Ebonyi State but its presence in Enugu maize samples do not exceed maximum its permissible limit. DichloroBiphenyl, Carbofuran and tetradifon was not detected in samples from Enugu State. Across the state, there is significant difference ($p<0.05$) in the level of dichlorvos detected from Enugu, Abia and Imo. Also, there is significant difference ($p<0.05$) in the level of lindane detected from Enugu and Abia State. There is significant difference ($p<0.05$) in the level of glyphoshate detected in maize samples from Enugu and Abia, Enugu and Imo State. No significant ($p>0.05$) difference in the level of tetradifon detected from Abia, Imo, Anambra and Ebonyi maize samples.

Comparison between the FAO/WHO maximum residue limit and the level of the organophosphates, organochlorine and carbamate pesticide residues in maize collected across the south east tested in this experiment shows that dichlorvos, lindane and carbofuran detected in maize samples exceeded its maximum residue limit of 0.1mg/kg, 0.02mg/kg and 0.05mg/kg respectively set by FAO/WHO. (Table 6). Isopropylamine, g-chlordane, t-nonachlor, glyphosphate, dicofol, tetradifon and dichloroBiphenyl detected in the samples analysed are in trace amount and do not exceed its safe limit set by FAO/WHO (Table 6).

Table 6: Level of pesticide residue (mg/kg) detected from maize across South East of Nigeria and their maximum permissible level already established by reputable international regulators

Pesticide residue	Enugu	Abia	Imo	Anambra	Ebonyi	Maximum permissible limits with references
Organoclorines						
Lindane*	0.06 ± 0.01^a	0.13 ± 0.01^b	0.05 ± 0.01^a	0.05 ± 0.01^a	0.05 ± 0.01^a	0.02 (FAO/WHO, 2021)
g-chlordane	0.02 ± 0.01^a	0.01 ± 0.01^a	0.02 ± 0.01^a	0.02 ± 0.01^a	0.02 ± 0.01^a	0.1 (ICPS, 2021)
t-nonachlor	0.01 ± 0.01^a	ND	ND	ND	ND	0.04 (Singh, 2018)
Dicofol	0.009±0.01	ND	ND	ND	ND	0.05(EFSA.2018)
DichloroBiphenyl	ND	0.04 ± 0.01^a	0.04 ± 0.01^a	0.03 ± 0.01^a	0.03 ± 0.01^a	0.2 (EC, 2006)
Tetradifon	ND	0.001 ± 0.01^a	0.001 ± 0.01^a	0.001 ± 0.01^a	0.001 ± 0.01^a	0.05(EFSA,2018)
Organophosphates						
Isopropylamine	0.01 ± 0.01^a	0.02 ± 0.01^a	0.02 ± 0.01^a	0.01 ± 0.01^a	0.01 ± 0.01^a	0.1 (USEPA, 2021)
Dichlorvos*	0.36 ± 0.01^a	1.09 ± 0.01^c	0.51 ± 0.01^b	0.51 ± 0.01^b	0.53 ± 0.01^b	0.1 (IFS/FAO/WHO, 2021)
Glyphosphate	0.003 ± 0.01^a	0.012 ± 0.01^b	0.012 ± 0.01^b	0.008 ± 0.01^a	0.008 ± 0.01^a	0.05 (EFSA,2018)
Carbamate						
Carbofuran*	ND	0.23 ± 0.01^a	0.23 ± 0.01^a	0.23 ± 0.01^a	0.23 ± 0.01^a	0.05 (TAS, 2008)

[1]All values expressed as mean ± standard error (±SE).

[2]Different superscript letters indicate significant difference ($p< 0.05$) in pesticides mean values across studied states using Turkey-*bpost hoc* test.

[3]ND: Not detected.

[4]Pesticides concentrations above permissible limits*.

Discussion

The high level of organochlorine (lindane), organophosphate (dichlorvos) and carbamate (carbofuran) found in this present study could possibly be due to poor storage practices and bad pesticide application to prevent insect infestation. Majority of grains are often stored for a long time at ambient temperatures and with this, if proper management is not carried out, there are usually insect infestation. Grains are highly susceptible to infestation by pests, so they are consequently often subjected to post-harvest treatment with pesticides to maintain good quality during storage and to avoid economic losses due to insect pest attack. This is usually practiced without considering the health implication and adhering strictly on the pesticide use. Good storage practices such as use of plant-based insecticides, sanitation, constant monitoring have been reported as alternative way of reducing the quantity of pesticide treatment on grains (Akinneye *et al*., 2018) [1] On the other hand, low level of organophosphate (isopropylamine and glyphosphate) and organochlorine (dichlorobiphenyl, dicofol, tetradifol, t-nonachlor, g-chlordane) in the present study is an indication of good storage practices and a good pesticide application to prevent pest attack. It is also an indication that pesticide was applied in accordance to the direction of its use.

This study has revealed that some organochlorines and carbamate pesticides were absent in some maize grains across the South East. For example, t-nonachlor and dicofol was not found on grains from Abia, Imo, Anambra and Ebonyi State. Also, dichlorobiphenyl, tetradifol and carbofuran were not found in maize from Enugu State. This reveals the possibility that these pesticides were not used at all or that they were used in accordance with standard specifications on the maize grains. Dichlorvos, lindane and carbofuran are the most occurring pesticide in the present study even though carbofuran was not detected in maize samples from Enugu State. This is in disagreement with the findings of Ogah and Coker who recorded pirimiphosmethyl as the most frequent occurring pesticide in their study. Also, the current findings are in disagreement with findings of Fleurat-Lessard *et al*. (2007) [11] that reported pirimiphosmethyl as the most widely used pesticide in the major grain-producing countries to protect against insect attack. Greater number of researchers have studied grain and reported the presence of pesticide residues.

Rice, wheat, cereal and pulses were analysed for pesticide residue by Jagadish *et al*. (2015) [17] and they detected chloropyrifos as the most occurring residue. This is not in accordance with present findings that detected dichlorvos, lindane and carbofuran (only absent in Enugu sample), as the most occurring pesticide in their study site.

The concentrations of pesticides obtained from the present study were compared with the FAO/WHO maximum residue limit for the maize grains across the states. The result showed that organophosphate (dichlorvos), organochlorines (lindane) and carbamate (carbofuran (in Abia, Imo, Anambra and Ebonyi samples) were above the maximum residue limits. Sawaya *et al*. (2000) [30] determined the residues level of organophosphate and carbamate in food items of the Kuwait population and found that the residues found were below permissible limit set. The present study is in disagreement with the findings of Sawaya *et al*. (2000) [30] as all the organophosphate (with the exception of isopropylamine and glyphosphate) and carbamate reported in the present above safe limit already set by FAO/WHO. If pesticide residues are found to exceed the MRL in any food, such a food commodity is said to be unsafe or unhealthy for consumption and therefore, be rejected from international trade for not meeting international standards or standards of the receiving country (NAFDAC, 2022) [24].

Consumption of grains with pesticide residue above the set maximum residue limit may result in accumulation of such chemicals in the body, which could eventually lead to adverse health effect. Organophosphate, organochlorine and carbamate have been found to cause neurodevelopmental toxicity in human (Bjðrling-Poulsen *et al*., 2008) [2]. Additive or synergistic effects of accumulated chemicals in the body can make pesticides that were detected to be safe for consumption before, to eventually pose health hazards (Oga *et al*., 2012) [26]. Quantity of such food consumed, length of time for consumption and toxicity of such residue also determines their effect on human or animal body (Petersen, 2000) [29].

Conclusion

Residues of organophosphates, organochlorines and carbamate were detected from the samples of maize sourced and analysed across South East of Nigeria. These residues have originated from improper application on food samples in the South East zone because of their persistent nature. Although most of the pesticide residues are below the FAO/ WHO MRLs, some exceeded the recommended MRLS. Among the pesticide residues detected, dichlorvos, lindane and carbofuran exceeded its MRL values set by international regulatory bodies. These residues might reach the top of the food chain by bioaccumulation. It is expected that an appreciable build-up of residues with time will occur because of the continuous use of these pesticides. This may pose serious public health problems. To avert a health disaster, it is essential that a system of monitoring of residues in the key component of food chain is encouraged so as to generate data for policy making and curtailment of the use of some pesticide.

Acknowledgement

The Authors thank in a special way the management and staffs of Spring Board Nigeria LTD, Awka for carrying out chemical analysis on the samples of the maize grains for the presence or absence of residues. We equally thank Dr. Godwin Nwosu for the statistical analysis conducted.

Conflict of interest

We declare no conflict of interest.

References

1. Akinneye JO, Adedolao AO, Adesina P. Quantification of organophosphate and carbamates residue on stored grains in Ondo State, Nigeria. Journal of Biological Medical. 2018;2(1):1-6.
2. Bjðrling-Poulsen M, Anderson HR, Grandjean P. Potential developmental neurotoxicity of pesticides used in Europe. Environmental Health. 2008;7:50.
3. Botwe BO, Ntow WJ, Kelderman P, Drechsel P, Carboo D, Nartey VK, *et al*. Pesticide Residues Contamination of Vegetables and their Public health Implications in Ghana. Journal of Environmental Issues in Agricultural Developing Countries. 2011;3(2):1-18.
4. Chen C, Chen M, Chen Z, Qian Y. Organophosphate pesticide residues in milled rice (*Oryzae sativa*) on the Chinese market and dietary risk assessment addition contamination. 2009;26:340-347.
5. Damalas CA, Elefterohorins IG. Pesticide exposure, safety issues, and risk assessment indicator. International Journal of Environmental Resources. 2011;8:1402-1419.
6. Darko G, Aquaah SO. Levels of organochlorine pesticides residues in meat. International Journal of Environmental Science and Technology, 2006, 4521-4524.
7. European Commission. Reproduction is authorized, except for commercial purposes, provided the source is acknowledged. Directorate General for Health and consumers European Commission-B-1049. Brussels. 2008;10(2772):13509.
8. European Food Safety Authority. Evaluation of impact of glyphosphate and other pesticides and its residues in food and feed on animal health. Journal of European Food Safety Authority. 2018;16(5):5283, 25p.
9. FAO. Food and agricultural organization of the United Nation. International code of conduct on the distribution of pesticide, Rome, 2006.
10. Fernandez-Alvarez M, Llompart M, Lamas JP, Lores M, Garcia-Jares C, Cela R, *et al*. Simultaneous determination of traces of pyrethroids, organochlorines, and other main plant protection agents in agricultural soils by headspace solid-phase microextraction-gas chromatography. Journal of Chromatography. 2008;1188(2):154.
11. Fleurat-Lessard F, Chaurand M, Marchegay G, Abecassis J. Effects of processing on the distribution of pirimiphos-methyl residues in milling fractions of durum wheat. Journal of Stored Product Research. 2007;4(43):384-395.
12. Gale F, Buzby JC. Imports from China and food safety issues. Ecology Information Bulletin. 2009;52:1-37.
13. Harner T, Shoeib M, Kozma M, Gobas FA, Li SM. Hexachlorocyclohexanes and Endosulfans in Urban, Rural and High Altitude Air Samples in the Fraser Valley, British Columbia: Evidence for Trans-Pacific Transport. Environmental Science Technology. 2005;39(3):724.

14. Hayes WJ, Laws ER. Classes of pesticides. In: *Handbook of pesticides toxicology*, vol. 2, Academic Press Inc. San Diego, 1991, 771p.
15. ICMR Bulletin. Pesticide Pollution: Trends and Perspective. 2001;31(9):2-6.
16. International Programmeon Chemical Safety (IPCS). Available online: https://apps.who.int/iris/bitstream/handle/10665/37286/924154094X-eng.pdf (accessed on 19 November 2021).
17. Jagadish GK, Jaylakshmi SK, Sreeramulu K. Evaluation of pesticide in rice, wheat, cereal and pulses of Bidar district Karnataka, India. Biological Sciences and Pharmaceutical Research. 2015;3:100-106.
18. Jeyaratnam J. Acute pesticide poisoning: A major global health problem. World Health Statistic. 2009;43(3):139-144.
19. Joint FAO/WHO. Meetingon Pesticide Residues (JMPR). Available online: https://ec.europaa.eu/food/system/files/202012/scicom_scf_out03_en.pdf (accessed on 19 November 2021).
20. Konradsen F, Van der Hoek W, Cole DC, Hutchison G, Daisley H, Singh S, *et al*. Reducing acute poisoning in developing countries-options for restricting the availability of pesticides. Toxicology. 2003;192:249-261.
21. Lee P. Registering Skeptism: Does the EPA's pesticide review protect children? Environmental Health Perspectives. 2006;114(10):592-595.
22. Leeman WR, Van Den Berg JK, Houben GF. Transfer of chemicals from feed to animal products: The use of transfer factors in risk assessment. Food Additional Contamination. 2007;24(1):1.
23. Leong WH, Teh SY, Hossain MM, Nadarajaw T, Zabidi-Hussin Z, Chin SY, *et al*. Application, monitoring and adverse effects in pesticide use: The importance of reinforcement of Good Agricultural Practices (GAPs). Journal of Environmental Management. 2020;260:109987.
24. NAFDAC. https://www.nafdac.gov.ngrevised/-press-release-by-dg-on- the- ban-phase-out-and-reclassification-of-pesticides/(2022).
25. Ntow WJ. Organochlorine pesticides in water, sediments crops and human fluids in a farming community. Ghana Archives of Environmental Contamination and Toxicology. 2001;40:557-563.
26. Ogah CO, Coker HB, Adepoju-Bello AA. Organophosphate and carbamate pesticide residues in beans from markets in Lagos State, Nigeria. Journal of International Resources Engineering Sciences. 2012;2(1):50-59.
27. Ogah CO, Coker HA, Adepoju-Bello AA. Pesticide residue levels in maize samples from markets in Lagos State, Nigeria. Nigerian Quarterly Journal of Hospital Medicine. 2011a;21(2):169-174.
28. Osafo AS, Frempong E. Lindane and endosulfan residues in water and fish in Ashanti region of Ghana. Journal of the Ghana Science Association, 1998, 135-140.
29. Petersen BJ. Pesticide residues in food: Problems and data needs. Regulatory Toxicology and Pharmacology. 2000;31:297-299.
30. Sawaya W, Al-Awadh FA, Saeed T, Al-Omair A, Hussain AH. Dietary intake of organophosphate pesticides in Kuwait. Food Chemistry, Food Chemistry. 2000;89:331-338.
31. Sharif Z, Man YB, Hamid NS, Keat CC. Determination of organochlorine and pyrethroid pesticides in fruits and vegetables using solid phase extraction clean-up cartridges. Journal of Chromatography. 2006;1127:254-261.
32. Singh K. Human Health Risks of Persistent Organic Pollutant Exposures in the Canadian Arctic. Ph.D. Thesis, Department of Biology, University of Ottawa, Ottawa, ON, Canada, 2018, 236.
33. Tariq MI, Afzal S, Hussain I. Pesticides in shallow ground water of Bahawalnagar, Muzafargh, D.G Khan and Rajan Pur districts of Punjab, Pakistan Environmental International. 2004;30(4):471.
34. Thai Agricultural Standard. Pesticide residues: maximum residue limits. National Bureau of Agricultural Commodity and Food Standards Ministry of Agriculture and Cooperatives 50 Phaholyothin Road, Ladyao, Chatuchak, Bangkok 10900. www.acfs.go.th Published in the Royal Gazette, 2008;125:Special Section 139D.
35. US Environmental Protection Agency (USEPA). Available online: https://archive.epa.gov/pesticides/chemicalsearch/chemical/foia/web/pdf/103601-247.pdf (Accessed on 19 November, 2021).
36. UNEP. Childhood pesticide poisoning, information for Advocacy and Action. Prepared for the United Nations Environment Programme (UNEP). United Nations Environment Programme (UNEP Chemicals) with the assistance of UNEP's Information Unit for Conventions, 2004.
37. Xue N, Xu X, Jin Z. Screening 31 endocrine- disrupting pesticides in water and surface sediments samples from Beijing Guanting reservoir. Chemosphere. 2005;61(11):1594.
38. Zahm SH, Ward MH. Pesticides and childhood cancer. Journal of Environmental Health Perspective. 1998;106(3):893-903.