Heliyon 6 (2020) e05803

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Research article

Dietary risk assessment of organochlorine pesticide residues in maize-based complementary breakfast food products in Nigeria

Mosudi B. Sosan[a,*], Adeoluwa O. Adeleye[a], John Adekunle O. Oyekunle[b], Onehireba Udah[a], Philemon M. Oloruntunbi[a], Miracle O. Daramola[a], Waidi T. Saka[a]

[a] Department of Crop Production and Protection, Obafemi Awolowo University, Ile-Ife, 220005, Nigeria
[b] Department of Chemistry, Obafemi Awolowo University, Ile-Ife, 220005, Nigeria

ARTICLE INFO

Keywords:
Maize-based products
Organochlorine pesticide
Residues
Contamination
Health risk

ABSTRACT

The study assessed the levels of organochlorine pesticides (OCPs) in eight brands (A-H) of regularly consumed maize-based complementary/breakfast foods in Nigeria. We also evaluated the dietary exposure of infants and young children to the detected OCPs. The OCP residues were quantified using GC-ECD. A total of 10 OCPs residues (β-HCH, δ- HCH, heptachlor, endosulfan sulfate, aldrin, endrin, dieldrin, *p,p*'-DDE, *p,p*'-DDT and methoxychlor) were detected. Total OCPs burden was highest in brands F, D, and G with mean concentrations of 45.98 mg kg^{-1}, 28.54 mg kg^{-1} and 21.87 mg kg^{-1}, respectively and the lowest burdens in brands H (1.72 mg kg^{-1}) and A (6.61 mg kg^{-1}). Hazard index (HI) for all the age categories were >1 and all the 6 carcinogens (β-HCH, heptachlor, aldrin, dieldrin, *p,p*'-DDE, and *p,p*'-DDT) identified had cancer risk index range of 5.43×10^{-4} to 2.05×10^{-6} which were above acceptable risk. These results indicated the possibility of both systemic and cancer risks to infants and children consumers of the foods. Food brands manufacturers need to carry out regular pesticide residues analysis of raw materials especially maize prior to the production in order to ensure food safety and quality.

1. Introduction

Complementary foods are important constituents of the daily diet of infants and young children mostly as household's breakfast foods. Cereals and cereal-based foods are widely utilised complementary/breakfast foods and most notable and vital source (with respect to calories) of global food consumption with provision of carbohydrates, proteins, vitamins and minerals, which contribute more than 50% of energy supply for human beings around the globe (McKevith, 2004; Wrigley, 2010). In Africa, cereal-based foods accounted for about 77% of total energy supply or consumption (Adelakun and Oyelade, 2011) and these foods are typically made from a variety of cereal grains such as maize, rice, and millet (Day, 2013).

Maize is major component of complementary foods in most Nigerian households (Maziya-Dixon et al., 2004) and therefore a notable raw material in production of commercially available complementary food brands for infants and young children in Nigeria.

Effective utilization of maize has led to both national and global increase in its production. The global production of maize is 1,147,621,938 tonnes per annum and Nigeria production of maize was estimated to be 12.760 million tonnes per annum with only about 400,000 tonnes imported from other countries (Food and Agriculture Organisation Statistics (FAOSTAT), 2020). The surge in production and demand for maize in Nigeria has resulted in an increase in usage of pesticides for both production and storage to control myriad of field and storage pests. In 2018, a total of 147, 446 tonnes of pesticide (inclusive of 584 tonnes of hazardous pesticides) worth US$383, 628, 000 was imported into Nigeria as input for production of agricultural crops (FAOSTAT, 2020).

The pesticides used in agricultural production ranges from hazardous compounds such as organochlorine pesticides (OCPs) to others that are less harmful. Organochlorine compounds are known for their low aqueous solubility, low polarity, high lipid solubility, ability to bioaccumulate, long half-life and potential for long-range transport (Wang et al., 2009; Jayaraj et al., 2016). Many of the organochlorine pesticides are regarded as persistent organic pollutants (POPs) due to their capability to persist in the environment for a long period of times after its usage and this was responsible for the ban placed on the POPs usage by

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* Corresponding author.
E-mail address: msosan@oauife.edu.ng (M.B. Sosan).

https://doi.org/10.1016/j.heliyon.2020.e05803
Received 31 August 2020; Received in revised form 20 October 2020; Accepted 17 December 2020

United Nations Stockholm Convention (United Nations Environment Program (UNEP), 2011).

The human health effects linked with short period exposure to hazardous pesticides such as OCPs includes headache, dizziness, nausea, incoordination, vomiting and convulsion (Agency for Toxic Substances and Disease Registry (ATSDR) 2000; 2005), while the long-term exposure are associated with a broad spectrum of possible health effects in human that include neurotoxicity, reproductive toxicity, hepatotoxicity, Parkinson disease and cancer (Hong et al., 2014; Cohn et al., 2015; United States Environmental Protection Agency - Integrated Risk Information System (USEPA-IRIS), 2019).

The nutritional importance of cereal based products (such as maize-based) are well-known globally but, they could be a co-occurring potential hazards such as pesticides, mycotoxins, toxic elements and some food additives. The daily exposure of consumers to these multiclass pollutants, even at low concentrations, may pose a potential threat to human health (Yang et al., 2020). The misuse, abuse and continuous usage of banned pesticides such as OCPs have resulted in the presence of their residues in maize which serves as the raw materials for production of complementary food products. The OCPs residues were detected in maize that originated from Nigeria (Ogah et al., 2011; Anzene et al., 2014; Sosan et al., 2018) and other African countries such as Cote D'ivoire (Allé et al., 2009); Togo (Mawussi et al., 2009); Ghana (Akoto et al., 2013); Tanzania (Mahugija et al., 2017). The presence of pesticides residues have also been reported in cereal-based complementary foods for infants and children in Ghana (Akoto et al., 2015), Ethiopia (Mekonen et al., 2015), China (Yang et al., 2020) and in French manufactured baby and common foods (Nougadère et al., 2020).

Nigeria, like many developing countries is confronted with environmental health problems as a result of OCPs contamination. Dietary intake is regarded to be a major potential route of exposure to most pesticides (Nougadère et al., 2012; Zhou et al., 2012), and both infants and young children may be exposed to the OCP residues through consumption of contaminated foods at their early stages. The children are believed to be more vulnerable mainly as a result of such factors as high intake of food with respect to body weight (kg) when compared to adults, fairly restricted diet, not fully developed organs, rapid rate of metabolism and growth, and a lower detoxification capability (World Health Organisation (WHO), 2006; Liu and Schelar, 2012; Lombard, 2014; Nougadère et al., 2020). In spite of earlier reports of presence of OCP residues in maize, a raw material for complementary food products, the occurrence and levels of these pesticides in maize-based food product brands in Nigeria have neither been previously reported nor the health risks of the dietary exposure evaluated. This study, therefore was undertaken to assess the levels of OCPs in selected maize-based complementary foods products in Nigeria and the potential human health risks associated with their regular consumption.

2. Materials and methods

2.1. Reagents used and their sources

The reagents used in this study were of analytical grade. They included dichloromethane (GFS Chemicals, Columbus, USA), n–hexane (Ultrafine Limited, Marlborough House, London, UK), acetone (GFS Chemicals, Columbus, USA), silica gel 60–200 mesh (Labtech Chemicals, Lewes, UK), and anhydrous sodium sulphate (Merck, Darmstadt, Germany). The solvents, such as dichloromethane, n-hexane and acetone were further distilled to obtain higher purity, while silica gel and anhydrous sodium sulphate were heated in an oven at 100 °C for 12 h to remove any adsorbed water in the clean-up materials.

2.2. Sample collection, preparation and extraction

We collected random samples in three (3) batches for eight (8) most popular brands of maize-based complementary and breakfast food products (A-H) (Table 1). The brands were locally manufactured, ready to eat cereal food and majorly consumed as complementary foods for infants and breakfast food for older children. The 8 brands were widely available in Nigerian markets at the time of sample collection in the year 2019. Several samples of the brands with different production batches were randomly purchased from stores and markets. A uniform sample weight of 0.2 kg following World Health Organization (WHO)/Food and Agriculture Organisation (FAO) sampling recommendation (WHO/FAO, 1999) comprising 4–6 products with the same production batch number or production date were randomly selected to form the composite or laboratory samples ($n = 24$). Each maize-based food products sample was oven dried at 45 °C for 48 h until a constant weight was attained. To obtain a homogenous representative sample, each sample was pulverized to a homogenous powdered form using an electric powered blender (Japan). The blender was washed thoroughly with doubly distilled water, rinsed with acetone and dried in an aerated cupboard to avoid cross contamination. Each sample was then placed in ziploc bags and well labelled. All samples were stored in a refrigerator at 4 °C prior to further analysis.

Prior to extraction, Whatman thimble was pre-extracted to remove organic contaminants that might be adhering to the surface or pores of the thimble. Analysis of OCPs was conducted as described previously by Oyekunle et al. (2017). A 20 g of each homogenised complementary food sample was weighed into a pre-extracted Whatman thimble, and was Soxhlet extracted for an average period of 4 h using dichloromethane (DCM) as the extraction solvent. The extract was then concentrated by distilling-off the solvent (DCM) on a rotary evaporator at about 41 °C. The reduced extract was then preserved for clean-up.

2.3. Clean-up

A clean-up experiment was carried out to separate analytes from any interfering compounds. A column of about 15 cm (length) x 1 cm (internal diameter) was plugged at its lower end with glass wool and was then packed with 5 g activated silica gel prepared in a slurry form in DCM.

About 2 g of anhydrous sodium sulfate was placed on top of the column to absorb any water in the sample or the solvent. The pre-elution was done with 15 mL of DCM without exposing the sodium sulfate layer to air so as to prevent cracking of the packed silica gel adsorbent. The reduced extracts were run through the column and allowed to sink below the sodium sulfate layer. Elution was done with 3 × 10 mL portions of DCM. The eluents were collected and the accompanying solvent was then evaporated to dryness under a stream of pure nitrogen (99.99%).

2.4. Instrumental analysis

The instrumental analysis was carried out at the Nigerian Institute of Oceanography and Marine Research Central Laboratory, Lagos, Nigeria. Detection and determination of the pesticide residues were performed by reconstituting the dried sample eluents with 2 mL n-hexane before injecting 1 μL of the cleaned-up eluents into the injection port of an Agilent 7820A Gas Chromatograph system equipped with an Electron Capture Detector. The separation was performed on a fused silica capillary column (DB-17, 30 m × 0.250 mm internal diameter and film thickness of 0.25 μm). The temperatures of the injector and detector were 250 °C and 290 °C, respectively. Oven temperature started at 150 °C and increased to 280 °C at 6 °C per minute. The injection was through a splitless injector, using helium as a carrier gas at a flow rate of 2 mL/min. The run time was 21.67 min. The individual OCPs were identified by comparing the elution time of standard OCPs with those in the samples, while each OCP was quantified by comparing the peak areas of the OCPs in samples with those in standard.

Table 1. Product information on maize complementary food brands analysed.

Product brand	Batch No.	% composition (maize) (per 100 g)
A	237, 248, 249	75 g
B	4A, 4C, 4B	84 g
C	1905210A, 1907280A, 1905190B	85.62 g
D	91691478H, 91701478G, 91821478F	65.5 g
E	1181905H2, 2141905H2, 2041905H3	80 g
F	3A, 3B, 6B	79.4 g
G	190936 GA, 190520GA, 190624 GA	85.1 g
H	080819MI, 270319MI, 340819MI	87.7 g

2.5. Quality assurance and control

The blank determination, pesticide recovery experiment, limit of detection (LOD) and limit of quantification (LOQ) were carried out for quality control and assurance. Procedural blank determination was carried out to check for contamination from the solvents, pre-extracted thimble and glassware used with no organochlorine pesticide residue detected. In absence of certified pesticide reference materials, recovery experiment was carried out to determine the precision and accuracy of the analytical procedures using standard addition method as earlier described in Sosan et al. (2018) with little modification. Two samples weighing 20 g from each brand was used, with one sample spiked or fortified with 2 mg kg^{-1} standard mixture of pesticide of interest and another left un-spiked. The percentage recoveries of OCPs were determined which were within the 70–120 % range for acceptable recovery values as stated by the European Union's guidelines for evaluating the efficiency and precision of an analytical method (European Commission, 2017).

The calibration curve of each organochlorine pesticide was derived by running up to 8 serially diluted standard solutions that ranged between 0 to 10 mg kg^{-1} and linearity of calibration curve (R^2) was also estimated. The LOD and LOQ were estimated using the Eqs. (1) and (2)

$$\text{Limit of detection} = \frac{(3.3\ \ s)}{b} \tag{1}$$

$$\text{Limit of quantification} = \frac{(10\ \ s)}{b} \tag{2}$$

where b is calibration curve slope, and s is the residual standard deviation of calibration function (Stocka et al., 2016; Adeleye et al., 2019a).

2.6. Statistical analysis

The results obtained from the chromatographic analysis were summarized using descriptive statistics (mean, standard error and percentages). Welch's ANOVA was carried out on the concentrations of the OCPs detected and means separated by Games-Howell test while Kruskal Wallis test was used to examine whether differences exist between the hazard quotient of the 4 age groups using Statistical Analysis System (SAS) 9.0 version and SPSS version 20.

2.7. Health risk estimation

The concentration of OCP residues detected in the food products were compared with the European Commission MRLs (EC, 2016) and Food and Agriculture Organisation/World Health Organisation MRLs (FAO/WHO, 2020) for maize and its products in order to evaluate their levels of violation. The chronic or non-carcinogenic and carcinogenic health risk for each of the organochlorine pesticides residues detected in the maize based complementary/breakfast foods was also estimated. The chronic health risk was evaluated using the hazard quotient and hazard index, this was calculated by dividing estimated average daily dose (ADD) by their equivalent reference dose values as shown in Eqs. (3), (4), and (5) (USEPA, 2001; Fjeld et al., 2007; Adeleye et al., 2019b).

$$\text{Hazard Quotient} = \frac{\text{Average Daily Dose (mg kg}^{-1}\text{d}^{-1})}{\text{Reference Dose (mg kg}^{-1}\text{d}^{-1})} \tag{3}$$

$$\text{ADD} = \frac{\text{Mean concentration} \times \text{consumption rate} \times \text{Exposure frequency} \times \text{Exposure duration}}{\text{Body weight} \times \text{Average Time}} \tag{4}$$

$$\text{Hazard index} = \sum\nolimits_{i}^{n} HQi \tag{5}$$

The dietary intake of OCPs detected in this study were estimated for 4 age groups since the consumption of the products cut across many age groups. Consumption rate of complementary foods by children of age group <1–2 years was reported in a study in Nigeria to be 150 g/day (the lowest range) (Ojuri et al., 2018) which is equivalent to 3–4 servings per day (using the recommended serving on the product labels). The recommended serving on labels of the breakfast maize-based products were used to calculate consumption rate for the other 3 age groups (2 to <3 years, 3 to <6 years and 6 to <11 years old). It is assumed that at least one of the popular maize-based food brands are consumed as breakfast food daily and also followed recommended servings on the product label. The assumed average body weight of 11.4 kg, 13.8 kg, 18.6 kg, and 31.8 kg were used for children in age group <1–2 years, 2 to <3 years, 3 to <6 years and 6 to <11 years old respectively (United States Environmental Protection Agency (USEPA), 2008). It is assumed that absorption and bioavailability rates of pesticide residues in the children are 100%. The exposure frequency is 365 days per year, exposure duration is equal to the age of the exposed population and average time is exposure frequency multiplied by age of the exposed children. The reference dose (RfD) values were obtained from the United States Environmental Protection Agency - Integrated Risk Information System (USEPA-IRIS, 2019).

When the hazard quotient and hazard index are >1, the food products involved is considered unacceptable and could pose a health risk to the consumers. However, when the hazard index and quotient <1, the food involved is considered acceptable with no health risks to the consumers (USEPA, 2001; Fjeld et al., 2007; Akoto et al., 2015; Adeleye et al., 2019b).

For carcinogenic effects, the cancer risks were evaluated using the Eqs. (6) and (7)

$$\text{Cancer risk} = \text{Chronic Daily Intake x Cancer slope factor} \tag{6}$$

$$\text{Chronic Daily Intake (CDI)} = \frac{C \times CR \times EF \times ED}{BW \times LT} \tag{7}$$

where CDI is the life time average dose or chronic daily intake (mg kg^{-1} day^{-1}), C is the mean concentration of the pesticide residue in the food product (mg kg^{-1}), CR is the consumption rate of the food product (kg day^{-1}), EF is the frequency of exposure (days/year), ED is the duration of exposure (year), BW is the bodyweight (kg), LT is the life time or life expectancy (day) (Fjeld et al., 2007; USEPA, 2011; Gerba, 2019).

The EF is 365 days per year, ED is equal to the age of the exposed children and the LT = 25, 550 days (70 years). The oral cancer slope factor (mg kg^{-1} day^{-1}) $^{-1}$ for the OCPs were obtained from the United States Environmental Protection Agency (USEPA, 2007; USEPA-IRIS, 2019). The maximum acceptable risk level is 1×10^{-6} which implies risk of one in one million as a result of lifetime exposure.

3. Results

Table 2 shows the percentage recovery, linearity (R^2) of the calibration curve, limits of quantification and detection values of various pesticides residues in the maize-based food samples. Percentage recoveries for the pesticides were between 89.60% (endrin aldehyde) and 100.91% (endrin). The LOD of the detected organochlorine pesticides were in the range of 0.001–0.004 mg kg^{-1}.

The mean concentration of the OCPs in maize-based complementary food samples is presented in Table 3. The total OCPs detected in the complementary food samples were 8, 7 and 6 in brand E, G and A, respectively. In the three brands (E, G, and A), δ-HCH had the least mean concentration while endosulfan sulfate had the highest mean concentration, with the values ranging from 0.044 mg kg^{-1} to 4.814 mg kg^{-1} (Brand E), 0.043 mg kg^{-1} to 19.457 mg kg^{-1} (Brand G) and 0.028 mg kg^{-1} to 5.855 mg kg^{-1} (Brand A) for δ-HCH and endosulfan sulfate respectively. A total of 5 OCPs were detected in brands F and H with mean concentration ranging from 0.059 mg kg^{-1} (dieldrin) to 45.329 mg kg^{-1} (endosulfan sulfate) for brand F, and 0.071 mg kg^{-1} (*p,p'*-DDE) to 1.030 mg kg^{-1} (endosulfan sulfate) for brand H. Total of 4 OCPs were detected in brands B and C with a mean concentration of 0.157 mg kg^{-1} (*p,p'*-DDE) to 9.745 mg kg^{-1} (endosulfan sulfate) for brand B and 0.026 mg kg^{-1} (dieldrin) to 13.961 mg kg^{-1} (endosulfan sulfate) for brand C. Brand D was the least contaminated with only 3 OCPs with the highest and lowest mean concentration of 28.137 mg kg^{-1} (endosulfan sulfate) and 0.083 mg kg^{-1} (heptachlor), respectively.

Generally, endosulfan sulfate and aldrin were detected in all the food samples and the mean concentrations ranged from 1.030 mg kg^{-1} to 45.329 mg kg^{-1} (endosulfan sulfate) and 0.139 mg kg^{-1} to 3.219 mg kg^{-1} (aldrin). However, DDT and methoxychlor were only detected in one food sample each while γ-HCH, α-HCH, heptachlor epoxide, α-endosulfan, β-endosulfan, endrin aldehyde and *p,p'*-DDD were below detection limits in all of the samples. Brands F, D, and G recorded the highest OCP burden with mean concentrations of 45.98 mg kg^{-1}, 28.54 mg kg^{-1} and 21.87 mg kg^{-1}, respectively and the lowest OCP burden detected in brands H (1.72 mg kg^{-1}) and A (6.61 mg kg^{-1}).

The mean concentration of the OCPs in all the maize-based complementary foods is shown in Table 4. In total, endosulfan sulfate (16.04 ± 4.046 mg kg^{-1}) had the highest mean concentrations in the complementary food samples analysed and its mean concentration was statistically different from those of other OCPs ($p < 0.05$). Endosulfan sulfate was detected in all (100%) samples analysed while aldrin was detected in majority (95.8%) of the samples analysed at levels above EC Maximum Residue Limits (MRLs). Residues of *p,p'*-DDE occurred in 70.8% and 66.7% at levels above EC MRLs while dieldrin (8.3%), *p,p'*-DDT (8.3%) and methoxychlor (4.2%) had the lowest percentage occurrence and percentage at levels above MRLs. The percentage of food samples at levels above the FAO/WHO MRLs ranged from 95.8% (aldrin) to 8.3% (dieldrin and *p,p'*-DDT).

The estimation of non-carcinogenic risk of OCPs residues in complementary food products are presented in Table 5. The observed decreased in hazard quotient values associated with an increase in age of children was not significant ($p > 0.05$). In age <1–2 years category, all the detected OCPs except methoxychlor had HQ > 1 which ranges from 1.447 to 372.368. In children of age 2–3 years, the HQ of *p,p'*-DDT (1.686), endrin aldehyde (4.484), endosulfan sulfate (7.991), β-HCH (8.818), and aldrin (84.592) were >1. The HQ values of endrin aldehyde (3.326 and 1.946), endosulfan sulfate (5.929 and 3.468), β-HCH (6.542 and 3.827), and aldrin (62.762 and 36.710) were >1 for the 3–6 years

Table 2. Percentage recovery (R%), Linearity of the Calibration curve, Limit of Detection and Quantification of the Organochlorine pesticides.

Pesticides	% Recovery ± %RSD	Linearity (R^2)	LOD (mg kg^{-1})	LOQ (mg kg^{-1})
α-HCH	96.82 ± 4.071	0.9982	0.003	0.009
β-HCH	97.92 ± 2.530	0.9970	0.003	0.009
γ- HCH	99.52 ± 4.695	0.9989	0.003	0.009
δ- HCH	99.67 ± 0.760	0.9990	0.003	0.009
Heptachlor	98.84 ± 1.984	0.9985	0.001	0.003
Heptachlor epox.	98.95 ± 1.260	0.9941	0.003	0.009
Dieldrin	99.68 ± 4.214	0.9950	0.004	0.012
Aldrin	96.54 ± 5.052	0.9988	0.001	0.003
Endrin	100.91 ± 0.685	1.0000	0.004	0.012
Endrin aldehyde	89.60 ± 12.008	0.9984	0.001	0.003
α-Endosulfan	100.06 ± 0.763	0.9998	0.001	0.003
β-Endosulfan	97.51 ± 2.470	0.9951	0.002	0.004
Endosulfan sulfate	99.14 ± 6.901	0.9986	0.003	0.009
p,p'-DDE	98.83 ± 1.323	0.9988	0.003	0.009
p,p'-DDD	99.15 ± 6.901	0.9995	0.003	0.009
p,p'-DDT	96.61 ± 4.029	0.9997	0.003	0.009
Methoxychlor	97.53 ± 1.924	0.9979	0.001	0.009

Table 3. Mean concentration of the OCPs in maize-based complementary food brands in Nigeria.

Pesticide	Brand A	Brand B	Brand C	Brand D	Brand E	Brand F	Brand G	Brand H
α-HCH	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
β-HCH	BDL	BDL	BDL	BDL	0.103 ± 0.103	0.302 ± 0.302	0.073 ± 0.073	BDL
γ- HCH	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
δ- HCH	0.028 ± 0.028	BDL	BDL	BDL	0.044 ± 0.044	BDL	0.043 ± 0.043	0.146 ± 0.095
Heptachlor	0.083 ± 0.083	BDL	BDL	0.083 ± 0.083	0.108 ± 0.108	BDL	0.758 ± 0.758	BDL
Heptachlor Epo.	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
α-Endosulfan	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
β-Endosulfan	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Endosulfan Sulf.	5.855 ± 4.201	9.745 ± 8.456	13.961 ± 6.789	28.137 ± 13.414	4.814 ± 3.686	45.329 ± 8.397	19.457 ± 18.690	1.030 ± 0.173
Aldrin	0.448 ± 0.195	0.880 ± 0.815	0.139 ± 0.022	0.315 ± 0.031	3.219 ± 2.768	0.223 ± 0.056	1.280 ± 0.925	0.285 ± 0.092
Endrin	0.074 ± 0.074	BDL	BDL	BDL	0.118 ± 0.118	BDL	0.095 ± 0.095	0.192 ± 0.193
Endrin alde.	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Dieldrin	BDL	BDL	0.026 ± 0.026	BDL	BDL	0.059 ± 0.059	BDL	BDL
p,p'-DDE	0.124 ± 0.024	0.156 ± 0.050	0.097 ± 0.009	BDL	0.082 ± 0.046	0.063 ± 0.026	0.162 ± 0.025	0.071 ± 0.037
p,p'-DDD	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
p,p'-DDT	BDL	2.255 ± 1.128	BDL	BDL	BDL	BDL	BDL	BDL
Methoxychlor	BDL	BDL	BDL	BDL	0.098 ± 0.098	BDL	BDL	BDL
TOTAL OCP Burden	**6.612**	**13.037**	**14.223**	**28.535**	**8.586**	**45.976**	**21.870**	**1.724**

Means ± SE were in mg kg^{-1}.

n = 3.

BDL – Below detection limits of 0.001–0.004 mg kg^{-1}.

and 6–11 years age categories respectively which suggested potential health risks. In total, the hazard index was >1 for all the age groups.

Table 6 shows the carcinogenic risk of OCPs residues in the selected complementary/breakfast foods. For the children consumer of the complementary foods at age <1–2 years, the cancer risks ranged from 5.42 × 10^{-4} (aldrin) to 6.02 × 10^{-6} (dieldrin) with probability of 5 in 10, 000 people to 6 in 1,000,000 people developing cancer (such as hepatocellular carcinomas, liver carcinomas, hepatomas and liver tumors). For children of age 2–3 years, the OCPs assessed were above acceptable risk and ranged from 1.85 × 10^{-4} (aldrin) to 2.05 × 10^{-6} (Dieldrin) suggesting possibility of cancer risks between 2 in 10, 000 people to 2 in 1 million people.

For the 3–6 years and 6–11 years old categories, 6 OCPs namely β-HCH, heptachlor, aldrin, dieldrin, *p,p'*-DDE and *p,p'*-DDT had cancer risk above acceptable cancer risks with risks ranging from 2.74 × 10^{-4} to 3.04 × 10^{-6} (3–6 years categories) and 3.21 × 10^{-4} to 3.56 × 10^{-6} for the 6–11 years old categories with possibility of developing cancer such as hepatocellular carcinomas, liver carcinomas, hepatomas and liver tumours over a lifetime.

Table 4. The mean concentration of the OCPs in all the maize-based complementary food brands in Nigeria.

Pesticide	Means ± SE (mg kg^{-1})	Percentage Occurrence	EC MRLs	FAO/WHO MRLs	Percentage above EC MRLs	Percentage above FAO/WHO MRLs
α-HCH	BDL	0	0.01	NA	0	-
β-HCH	0.059 ± 0.040[b]	12.5	0.01	0.01[c]	12.5	12.5
γ- HCH	BDL	0	0.01	0.01	0	0
δ- HCH	0.033 ± 0.016[b]	20.8	0.01	0.01[c]	20.8	20.8
Heptachlor	0.129 ± 0.095[b]	16.7	0.01	0.02	16.7	16.7
Heptachlor Epoxide	BDL	0	0.01	NA	0	-
α-Endosulfan	BDL	0	0.05	NA	0	-
β-Endosulfan	BDL	0	0.05	NA	0	-
Endosulfan Sulfate	16.041 ± 4.046[a]	100	0.05	1.0[a]	100	70.8
Aldrin	0.849 ± 0.375[b]	95.8	0.01	0.02	95.8	95.8
Endrin	BDL	0	0.01	0.05[b]	0	0
Endrin aldehyde	0.060 ± 0.030[b]	16.7	0.01	0.05[b]	16.7	16.7
Dieldrin	0.010 ± 0.008[b]	8.3	0.01	0.02	8.3	8.3
p,p'-DDE	0.089 ± 0.014[b]	70.8	0.05	0.1	66.7	37.5
p,p'-DDD	BDL	0	0.05	0.1	0	0
p,p'-DDT	0.282 ± 0.195[b]	8.3	0.05	0.1	8.3	8.3
Methoxychlor	0.012 ± 0.012[b]	4.2	0.01	NA	4.2	-

BDL means below detection limits of 0.001–004 mg kg^{-1}, n = 24, Means with the same letters are not significantly different at $p < 0.05$.

NA- Not available.

[a] Used MRLs for most related crop (soya beans).

[b] Used MRLs for most related crop (vegetable).

[c] Used a surrogate value of related compound.

Table 5. Estimation of non-carcinogenic risk of OCPs residues in maize-based complementary food brands in Nigeria.

Pesticide	Means (mg kg^{-1})	Estimated Average Daily Intake (mg kg^{-1}day^{-1})				RfD (mg kg^{-1}day^{-1})	Hazard Quotient			
		<1–2 years	2–3 years	3–6 years	6–11years		<1–2 years	2–3 years	3–6 years	6–11 years
β-HCH	0.059	0.00078	0.00018	0.00013	0.00008	0.00002[a]	**38.816**	**8.818**	**6.542**	**3.827**
δ- HCH	0.033	0.00043	0.00010	0.00007	0.00004	0.00030*[b]	**1.447**	0.329	0.243	0.142
Heptachlor	0.129	0.00170	0.00039	0.00029	0.00017	0.00050[c]	**3.395**	0.771	0.572	0.335
Endosulfan Sulfate	16.041	0.21107	0.04795	0.03558	0.02081	0.00600[d]	**35.178**	**7.991**	**5.929**	**3.468**
Aldrin	0.849	0.01117	0.00253	0.00188	0.00110	0.00003[e]	**372.368**	**84.592**	**62.762**	**36.710**
Endrin aldehyde	0.060	0.00079	0.00018	0.00013	0.00008	0.00004*[f]	**19.737**	**4.484**	**3.326**	**1.946**
Dieldrin	0.010	0.00013	0.00003	0.00002	0.00001	0.00005[g]	**2.632**	0.598	0.444	0.259
p,p'-DDE	0.089	0.00117	0.00026	0.00020	0.00012	0.00050[g]	**2.342**	0.532	0.395	0.231
p,p'-DDT	0.282	0.00371	0.00084	0.00062	0.00037	0.00050[g]	**7.421**	**1.686**	**1.251**	0.731
Methoxychlor	0.012	0.00016	0.00004	0.00003	0.00002	0.00500[h]	0.032	0.007	0.005	0.003
Hazard Index							**483.367**	**109.808**	**81.471**	**47.653**
p-value (Kruskal Wallis Test)							**0.768 ns**			

* = surrogate values of related compounds were used for compounds without RfDs, ns = no significant difference at $p > 0.05$.

Endpoints of RfDs used (USEPA-IRIS, 2019).

Bold indicates hazard quotients that were above unity.

[a] Hyalinization of centrilobular cells in the liver/infertility.

[b] Liver and kidney toxicity (Hepatic, Urinary).

[c] Liver weight increases in males.

[d] Urinary, Cardiovascular effects.

[e] Hepatotoxic.

[f] Nervous and Hepatic toxicity.

[g] Liver lesions.

[h] Developmental system Effect.

4. Discussion

This study, to the best of our knowledge reports for the first time the occurrence and levels of organochlorine pesticides (OCPs) in maize-based complementary/breakfast foods in Nigeria, as well as the non-carcinogenic and carcinogenic health risks from contamination by some of the detected OCPs.

Maize is the main raw material for all the products analysed and the results obtained from the analysed samples were comparable with previous studies on maize in Nigeria and other African countries. Sosan et al.

Table 6. Carcinogenic risk of OCPs residues in complementary maize-based complementary food brands in Nigeria.

Pesticide	Means (mg kg^{-1})	Slope factor	Cancer Risk			
			<1–2 years	2–3 years	3–6 years	6–11 years
α-HCH	BDL	NA	-	-	-	-
β-HCH	0.059	1.8[a]	**3.99 x 10^{-5}**	**1.36 x 10^{-5}**	**2.02 x 10^{-5}**	**2.36 x 10^{-5}**
γ- HCH	BDL	NA	-	-	-	-
δ- HCH	0.033	NA	-	-	-	-
Heptachlor	0.129	4.5[b]	**2.18 x 10^{-4}**	**7.44 x 10^{-5}**	**1.10 x 10^{-4}**	**1.29 x 10^{-4}**
Heptachlor Epoxide	BDL	NA	-	-	-	-
α-Endosulfan	BDL	NA	-	-	-	-
β-Endosulfan	BDL	NA	-	-	-	-
Endosulfan Sulfate	16.041	NA	-	-	-	-
Aldrin	0.849	1.7[c]	**5.43 x 10^{-4}**	**1.85 x 10^{-4}**	**2.74 x 10^{-4}**	**3.21 x 10^{-4}**
Endrin	BDL	NA	-	-	-	-
Endrin aldehyde	0.060	NA	-	-	-	-
Dieldrin	0.010	1.6[c]	**6.02 x 10^{-6}**	**2.05 x 10^{-6}**	**3.04 x 10^{-6}**	**3.56 x 10^{-6}**
p,p'-DDE	0.089	0.34[d]	**1.14 x 10^{-5}**	**3.88 x 10^{-6}**	**5.75 x 10^{-6}**	**6.73 x 10^{-6}**
p,p'-DDD	BDL	NA	-	-	-	-
p,p'-DDT	0.282	0.34[e]	**3.60 x 10^{-5}**	**1.23 x 10^{-5}**	**1.82 x 10^{-5}**	**2.13 x 10^{-5}**
Methoxychlor	0.012	NA	-	-	-	-

BDL means below detection limits of 0.001–004 mg kg^{-1}, slope factor in ((mg kg^{-1}day^{-1}))$^{-1}$.

NA- Not available.

End point of cancer slope factor used (USEPA, 2007; USEPA-IRIS, 2019).

Bold indicates cancer risks that were above maximum acceptable risk of 1 x 10^{-6}.

[a] Hepatic nodules and hepatocellular carcinomas.

[b] Hepatocellular carcinomas.

[c] Liver carcinoma.

[d] Hepatocellular carcinomas, hepatomas.

[e] Liver tumours, benign and malignant.

(2018) reported 17 OCPs residues in maize samples in Southwestern Nigeria which were generally higher than the levels recorded from this study with the exception of endosulfan sulfate and aldrin. However, the percentage occurrence and the levels above their Maximum Residue Limits (MRLs) were within the range of 20% and 100% which are similar with those reported in this study. Food processing such as drying, cleaning, hulling, milling, thermal processing and storage have been reported to reduce pesticide residues in produce such as grains (Kaushik et al., 2009). The lower levels of residues in the maize based food products in comparison to residues earlier reported for raw maize could be due to effect of processing on contaminated maize produce that might have reduced the concentration of residues in the food products or could be that the raw maize utilised for production had lower levels of contamination.

Also, the results from this study are higher than those previously reported on maize and its products in other African countries such as Cote D'ivoire (Allé et al., 2009); Togo (Mawussi et al., 2009); Ghana (Akoto et al., 2013); Tanzania (Mahugija et al., 2017). This shows that the possible source of the contamination of the food products could be the raw materials most especially maize produced in Nigeria or imported from neighbouring countries that are often utilized for the production of these complementary foods. Furthermore, the high levels of the xenobiotics could have resulted from the contamination of maize from field and/or in storage (Anzene et al., 2014; Sosan et al., 2018). The field contamination could be due to application of the banned illegal pesticides for control of insect pest of maize by the farmers or contamination by irrigation waters or soils as the organochlorines are ubiquitous and could remain in soils contaminating agricultural produce for several years, and nonpoint sources through transportation (atmospheric deposition, runoff and leaching) from other agricultural farm land.

Endosulfan sulfate, the most predominantly detected OCP with higher concentrations was reported to be the most persistent and major metabolite of the endosulfans (Rosendahl et al., 2009). The persistence could have been one of the reasons for its high concentration in the maize-based food products. Its predominance and the high mean concentrations of endosulfan sulfate in all the food samples also showed that this compound is still in use despite its ban (Oyekunle et al., 2011). Endosulfan is still available in Nigeria markets either as a single formulation or in mixture or combination with other active ingredients. It is reported to be one of the most popular insecticides currently available in agrochemical shops and markets and are now been used as a replacement for Lindane (γ-HCH) (Sosan and Oyekunle, 2017). The levels of endosulfan sulfate detected in this study were higher than the concentrations earlier reported by Sosan et al. (2018) and Anzene et al. (2014) on maize from Nasarawa State, Nigeria. The higher concentrations of endosulfan sulfate could be due to volatilization and degradation of endosulfan (α- and β-isomers) present on the maize grains to a more persistence endosulfan sulfate leading to its increase in concentration, as the endosulfan (α- and β-isomers) are easily degraded with shorter half-life on plant and soils (Vaikosen et al., 2019).

Aldrin is another OCP often detected in the analysed samples. The occurrence and the high levels of the chemical could be a result of its recent usage on maize used in the production process of the complementary foods. Aldrin breaks down to dieldrin in foods such as vegetables, grains and other materials in the environment (ATSDR, 2002). The occurrence of DDE in almost all the samples indicates that DDT is still somehow being used, as DDE is the main metabolite of DDT. The acute effects of exposure to low doses of DDT on humans are limited. However, exposure to high doses of DDT leads to headache, sweating, dizziness, vomiting, tremors and seizures (ATSDR, 2002) while long-term exposures leads to chronic health effects such as tumor development and reproductive effects (Harada et al., 2016), and the food-borne DDT has been reported to be the greatest source of exposure for the general population (Kadawathagedara et al., 2018). Studies have reported that pre-natal exposure to DDT was negatively associated with infant birth weight (Lopez-Espinosa et al., 2011; Guo et al., 2014). However, pre-natal exposure to DDE was positively associated with growth of infants from birth to 24 months of age (Iszatt et al., 2015), and infant exposure to DDE was linked with decrease in initiation and duration of breast feeding (Karmaus et al., 2005).

The estimation of non-carcinogenic risk with HQ > 1 for 9 out of 10 for age-group <1–2 years and 5 out of 10 OCPs detected for 2–3 years and 3–6 years age categories suggested potential health risks such as hepatotoxicity, liver lesion, nervous toxicity, urinary/cardiovascular effects and infertility to consumers of these complementary foods. The results of this study showed that the most sensitive and vulnerable life stages or age group to the detected pesticides were infants, toddlers and young children up to 6 years of age. The sensitivity or vulnerability of the age groups to several pesticides or pollutants are due to their high food intake to body weight ratio, and immaturity of their defence systems against toxic chemicals (Nougadère et al., 2020). This findings are comparable with earlier study by Mekonen et al. (2015) that reported the deterministic and probabilistic exposure analyses carried out on maize-based complementary infant foods in southwest Ethiopia and found that consumer estimated daily intakes of total DDT for average and high consumers of the total population were above the health-based guidance value (provisional tolerable daily intake). Also, Akoto et al. (2013) reported that dieldrin, β-endosulfan, heptachlor, aldrin, and endrin detected in maize (the main raw materials for the complementary foods) from Ejura, Ghana had hazard risk >1 with great possibility for chronic toxicity to consumers of the maize from the region.

The high cancer risk values of the pesticide residues detected in the processed maize-based food brands show that there is possibility for adverse health effect on infants and young children consumer of the foods via dietary exposure to these detected pesticides. This corroborates earlier report by Akoto et al. (2015) that β-HCH, γ-HCH, dieldrin, and heptachlor detected in some of the ten (10) brands of cereal-based infant complementary food products had carcinogenic risk greater than acceptable risk levels of 1 in 1 million people with potentials for adverse effects on infants and young children consumers of the products.

The results from this exposure assessment indicated that estimated exposure levels affected the children irrespective of their age groups. The infants and children of younger age groups have higher exposure levels due to higher food consumption per body weight (kilogram) (European Food Safety Authority (EFSA), 2009) and the adverse health and developmental effects are the common problem for children due to their vulnerability to pesticides (United Nations Children's Fund (UNICEF), 2018). The dietary exposure of these notable OCPs such as endosulfan and aldrin appears to be consistent as they are frequently detected in food matrices in Nigeria, the reason for this may not be far-fetched because they are still available in Nigeria markets despite their ban. There is therefore a tendency for an increase in the adverse health risks for children who consume these products on regular basis if the ban on these chemicals are not strictly enforced by the regulatory agencies for food safety in Nigeria.

5. Conclusion

This study revealed that the 8 most popular maize-based complementary/breakfast food brands in Nigeria were contaminated with organochlorine pesticide residues above the European Commission and FAO/WHO Maximum Residue Limits (MRLs) with percentage of samples above the two limits ranging from 4.2% to 100% and 8.3%–95.8%, respectively. The dietary exposure estimation showed that the level of contamination could possibly pose both systemic and cancer risks to infants and children consumer of the complementary and breakfast foods in Nigeria. The brand manufacturers need to carry out routine analysis of raw materials prior to production of these maize-based complementary foods. A need for robust national legislation and more stringent monitoring of pesticide use for food storage is advocated. Also, there should be effort to harmonize all existing laws, standards and codes that regulate food safety practices by relevant agencies in Nigeria in order to ensure food safety, wellbeing and health of all ages.

Declarations

Author contribution statement

Mosudi B. Sosan: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Adeoluwa O. Adeleye: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

John Adekunle O. Oyekunle: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Onehireba Udah, Philemon M. Oloruntunbi, Miracle O. Daramola, Waidi T. Saka: Performed the experiments; Contributed reagents, materials, analysis tools or data.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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