Chemistry Africa (2021) 4:349–366
https://doi.org/10.1007/s42250-020-00224-6

ORIGINAL ARTICLE

Determination of Organochlorine Pesticide Residues in Some Evaporated Milk Samples in Nigeria Using Gas Chromatography-Mass Spectrometry

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Received: 28 November 2020 / Accepted: 29 December 2020 / Published online: 8 February 2021

Abstract
Concentrations of organochlorine pesticides (OCPs) residues in six different popularly consumed evaporated milk samples available in Nigeria (coded A, B, C, D, E and F) were analysed. This was done in order to determine the extent of exposure of consumers to OCPs through regular consumption of the milk samples. The OCPs content of the milk samples, obtained using liquid–liquid extraction (LLE) technique, were qualitatively and quantitatively analyzed using Gas Chromatography-Mass Spectrometry (GC–MS). Eighteen OCPs congeners detected included α-HCH, β-HCH, γ-HCH, δ-HCH, Heptachlor, Heptachlor epoxide, Aldrin, Dieldrin, Endosulfan I, Endosulfan II, Endosulfan sulphate, p,p′-DDD, p,p′-DDE, p,p′-DDT, Endrin, Endrin aldehyde, Endrin ketone and Methoxychlor at levels ranging from total OCPs concentrations of 21.632 µg/mL in B to 39.010 µg/mL in C. Most of the milk samples had various OCPs contents above the stipulated WHO/FAO average daily intake (ADI) threshold. The highest cumulative HRI and HR value for non-carcinogenic and carcinogenic health risks for both adults and children were found in sample C suggesting that long-term non-carcinogenic health problems could emanate from the unguarded consumption of this particular milk product over a long period of time.

Keywords Consumption · Daily intake · Evaporated milk · Health risks · Pesticides · Nigeria

1 Introduction

Consumable milk is one of the main forms of animal protein often obtained from animals such as buffalo, cow and goat. Milk production is a distinctive feature of the female animals and human being because they possess the udder and the breast, respectively which contains the mammary gland [1]. Milk is highly consumed by human beings at all stages of life because it serves as a reliable source of energy, fat, minerals, vitamins and proteins [2].

A good number of evaporated milk products are available in Nigeria markets with the raw milk coming from the dairy farm. The primary source of such milk products (the cows) are often allowed to graze over a wide expanse of land such as the farm lands and the forest since open grazing is more economical. More often than not, these cows have direct contact with agricultural products and sometimes feed on farm produce during such open grazing. Beyond this, the cows are fed from streams and rivers which are sometimes not too distant from the grazing region.

Between 1948 and 1949, synthesized chemicals were of great relevance starting with the use of dichlorodiphenyltrichloroethane (DDT) for malaria control and hexachlorocyclohexane (HCH) for locust control. Dichlorodiphenyltrichloroethane was effective for malaria control in the 1940s. It showed a decisive role in the eradication of malaria from Europe and the United States. Within a short time, DDT got a unique position by saving millions of lives and by preventing disease outbreaks much more than any other man-made chemicals in history [3]. A huge success

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was recorded in the use of these organochlorine pesticides (OCPs) up to 1980 when suggestions were made for controlled usage of OCPs because of the serious health risks such as cancers, endocrine disruption, immune system disorder, reproductive problems among other chronic diseases that could emanate from their persistence or high resistance under ambient environmental conditions [4]. Increase in agricultural productivity and the affordable price of these pesticides were the major considerations of farmers. Hence, the drastic increase in the application of these substances to agricultural produce all over the developing world despite the public health risks and outcries that have led to their being banned in developed countries [5]. Unfortunately, less than one percent of the applied pesticides in agriculture usually reach the target pest while the remainder is stored in the various compartments of the environment [6]. For example, upon application, most part of the pesticides volatilize from the soil are transported to non-target components [7], penetrate into the soil through percolation-related phenomena, get to aquatic bodies through run-off [8, 9], and aerial fallout especially as a result of wet precipitation [7, 8].

The main entry points of pesticides into biotic factors include contaminated feed, water and udder. Quite a number of studies have confirmed the presence of these OCPs in water bodies in various countries of the world such as Nigeria [10–13], Ghana [14], South Africa [15] and China [16]. Pesticides find their way into meat and milk as a result of open grazing of animals on contaminated feedstock prior to milking and thus may enter the upper echelon of the food chain where they bioaccumulate as a result of their lipophilicity [17]. Contamination of milk with organochlorines such as Hexachlorocyclohexane (HCH) isomers, Dichlorodiphenyltrichloroethane (DDT) and isomers, Heptachlor, Chlordane, Aldrin, Dieldrin and so on (Fig. 1) may cause neurodevelopment delay [18], reproductive defects, preterm and immune toxicity [19, 20].

Evidently, awareness about the levels, health impacts and reduction or total removal of xenobiotics such as OCPs from human consumables is both a matter of necessity and urgency. A number of methods have been employed for the quantitative detection of OCPs in water and other consumables [9, 21]. The bulk of these methods are chromatographic techniques coupled to suitable detectors such as the electron capture, thermal conductivity and mass spectrometry [21–23]. Selectivity and specificity for analytes [24], ability to characterize such analytes [25], availability and cost of instrumentation are the major factors considered for selecting a suitable chromatographic technique for the quantification and identification of OCPs in various matrices. These factors, coupled with the high vapour pressure of OCPs have made the use of Gas Chromatography (GC) coupled to Mass Spectrometry (GC–MS) a highly preferred technique for OCPs determination [26]. Although, the more expensive GC coupled to a tandem Mass Spectrophotometer (GC–MS-MS) is considered more sensitive [23], meticulous sample preparation processes involving LLE technique followed by clean-up that reduces matrix effect prior to quantification helps to mitigate the lower sensitivity of the GC–MS [27, 28] and bridge the gap in effectiveness between the liquid–liquid extraction and microextraction.

The present study was aimed at investigating the content of OCPs in six popularly consumed evaporated milk products in Nigeria. This was done to provide reliable scientific data bothering on the possible carcinogenic and non-carcinogenic health risks associated with their long-term consumption. The novelty of this work is that most of the previous studies were based on evaluation of OCPs in randomly selected milk brands. However, a preliminary survey based on respondents randomly interviewed prior to sample collection to determine the consumers' choice as regards commonly consumed evaporated milk were used for the choice of the samples used for this study.

2 Methodology

2.1 Sample Collection

The response of 210 respondents randomly interviewed prior to sample collection to determine the consumers' choice as regards commonly consumed evaporated milk samples in Nigeria informed the selection of the six types of evaporated milk samples eventually used for this study. The milk samples (coded A–F) were purchased from sales outlets within Ile-Ife environment and kept in a refrigerator prior to the extraction to achieve a storage temperature of about 4ºC.

2.2 Reagents Used and Their Sources

Reagents such as ethanol, acetone, dichloromethane (DCM) and sodium chloride used for this procedure were supplied by GFS Chemicals, Columbus. Silica gel was supplied by Labtech chemicals while the anhydrous sodium sulphate was supplied by Merc, Germany. They were all of analytical grade.

2.3 Extraction of OCP Residues from Samples

Five millilitres (5 mL) of each sample was transferred into 500 mL volumetric flask and thoroughly mixed with about 100 mL distilled water. One spatula of sodium chloride was then added to make OCPs less soluble in the aqueous layer

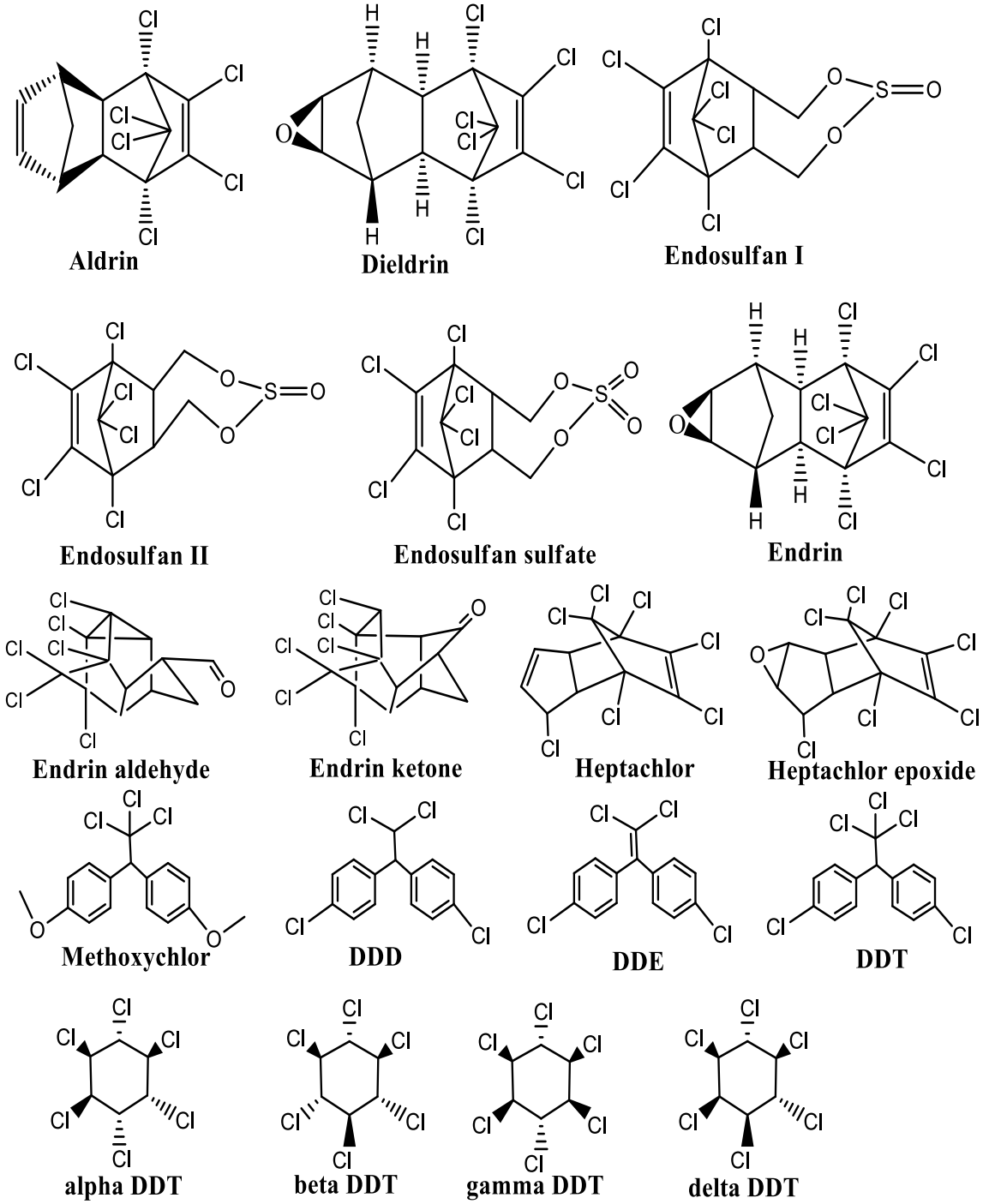

Fig. 1 Structure of common organochlorine pesticides

and more readily available for DCM extraction. The mixture was diluted up to 500 mL in the flask and subjected to thorough mixing. Each component of the solvent extraction setup was washed and rinsed properly with the solvent mixture (1:2:2 of Acetone-Dichloromethane-Ethanol). A 500 mL separating funnel was used to carry out the LLE of the diluted milk sample in which case half of the separating funnel was filled with the diluted sample and extracted with about 20 mL DCM in triplicates. This process was carried out for the other half of the diluted milk sample. The extracts were transferred into an amber coloured vial and stored at 4 °C in readiness for clean-up.

Table 1 Percentage recovery of OCPs

OCPs	Amount used for spiking (µg/mL)	Amount recovered from spiking (µg/mL)	Percentage recovery (%R)
Heptachlor	25.62	23.04	89.92
Endrin	19.72	18.23	92.45
Endosulfan	21.57	20.78	96.34
4,4′-DDT	21.81	20.78	95.28

2.4 Clean-Up Procedure

The clean-up stage is essential to remove or reduce all forms of impurities which might be associated with the eluate. A column was packed with glass wool followed by the addition of activated silica gel earlier prepared in a slurry form. Anhydrous sodium sulphate was then added to the top of the silica gel in order to absorb the water in the sample and the solvent. Dichloromethane was first introduced into the packed column to prevent any interference by organic contaminants. The recovered eluate was left to dry completely under ambient air and then reconstituted with 1 mL of n-hexane in the amber coloured vials prior to GC–MS determination.

2.5 Instrumental Analysis, Quality Assurance and Quality Control

The qualitative identification and quantification of the OCPs was carried out using the GC–MS at CTX-ION Analytical Limited, Ikeja, Lagos, Nigeria. The efficiency of this analytical procedure was validated by recovery analysis since

Table 2 Concentrations (µg/mL) of OCPs in analysed evaporated milk samples

OCPs	EU MRL	ADI (µg/g/day)	Samples					
			A	B	C	D	E	F
Aldrin	0.05	0.0001	0.414	1.102	2.468	0.520	0.832	1.026
Dieldrin	0.02	0.0001	1.882	4.584	2.860	3.812	5.742	8.330
Endosulfan I	0.10	0.006	0.758	0.620	1.486	4.230	4.028	1.920
Endosulfan II	0.10	0.006	1.536	1.100	1.420	1.084	0.432	1.786
Endosulfan sulphate		0.006	1.054	BDL	BDL	0.028	0.042	0.302
Endrin	0.01	0.0002	0.176	0.170	0.164	0.000	0.174	0.000
Endrin aldehyde	0.01	0.0002	5.188	4.120	4.486	10.412	3.114	5.150
Endrin ketone		0.0002	1.358	0.842	10.020	7.604	1.766	2.240
Heptachlor	0.02	0.0001	7.832	5.228	7.100	2.750	5.064	3.626
Heptachlor epoxide	0.02	0.00013	BDL	BDL	BDL	0.346	BDL	0.374
Methoxychlor	0.01	0.1	2.100	0.950	2.836	1.082	3.414	1.506
p,p′- DDD	0.05	0.01	4.718	1.326	0.632	0.220	0.532	0.444
p,p′- DDE	0.05	0.01	0.278	0.170	0.732	0.382	0.106	0.196
p,p′- DDT	0.05	0.01	0.306	0.066	0.434	0.336	0.220	0.214
α- HCH	0.05	0.005	0.750	0.344	1.970	0.854	1.142	0.944
β- HCH	0.05	0.005	0.358	0.282	0.774	0.342	0.860	1.044
γ- HCH	0.05	0.005	0.312	0.292	0.884	0.346	0.192	0.464
δ- HCH	0.05	0.005	1.270	0.436	0.744	0.664	1.134	0.732
Total			30.290	21.632	39.010	35.012	28.794	30.298
Mean ± SD			1.683 ± 2.057	1.272 ± 1.618	2.295 ± 2.600	1.945 ± 2.814	1.600 ± 1.793	1.683 ± 2.062
Variance			4.231	2.618	6.760	7.920	3.215	4.251
Coefficient of Variation			1.22222	1.27201	1.1329	1.44679	1.12063	1.22519

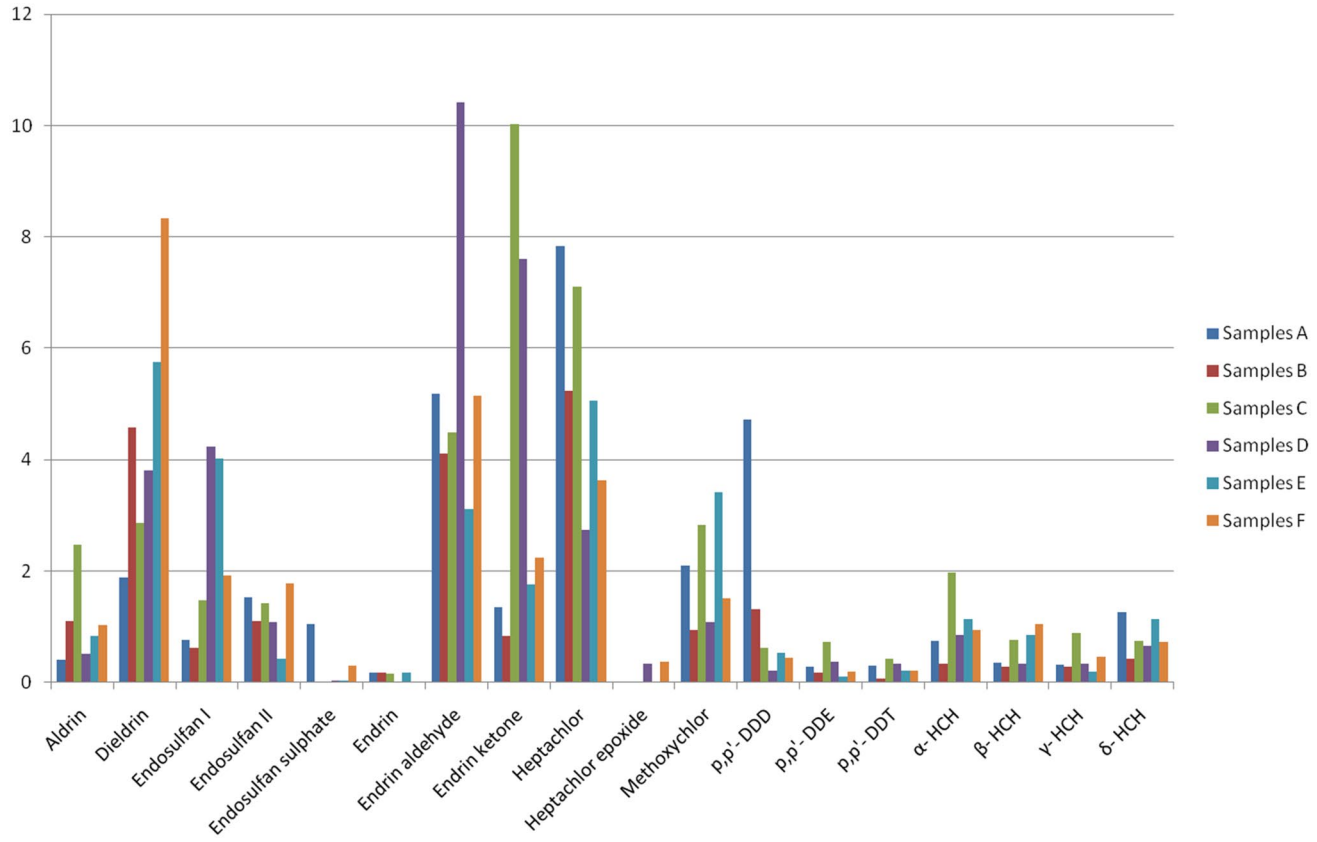

Fig. 2 OCP contents of evaporated milk sample

a certified reference material was unavailable. A standard solution of mixture of Heptachlor, Endrin, Endosulfan and p,p′-DDT was prepared and 10 mL of this solution was used to spike the measured value of milk sample (5 mL) while the equivalent milk volume (5 mL) was kept unspiked. These two milk samples were taken through the extraction, clean-up and reconstitution procedures as enumerated earlier. The samples were subjected to GC–MS analysis and percentage recovery (% R) was evaluated using Eq. 1.

$$\% \, R = \frac{(A - B)}{C} \times 100 \tag{1}$$

where A and B are the amounts of OCPs recovered from spiked and unspiked samples respectively; and C represents the amount of OCPs used for spiking. In order to achieve reliable results, the quality assurance of the analytical procedures was given special attention. All materials for sample preparation were thoroughly washed and rinsed with acetone. Blank determination was equally carried out. All reagents used were of analytical grade.

2.6 Health Risk Assessment

Carrying out the health risk assessment is important to assess the health risks associated with dietary exposure of consumers to pesticides content of the milk samples. This was done by investigating the carcinogenic and non-carcinogenic health risks through the Estimated Average Daily Intake (EADI), Cancer Benchmark Concentrations (CBC) and the Health Risk Index (HRI). Estimated Average Daily Intake of the pesticides was used to obtain the long term health risk associated with contaminated food consumption, HRI was used for the assessment of the carcinogenic and non-carcinogenic health risk with an assumption of body weights of 60 kg and 16.7 kg for adults and children, respectively [21]. The carcinogenic effect of each of the OCPs was obtained from the Hazard Ratio (HR) calculated using CBC.

Estimated Average Daily Intake was determined by multiplying the Residual pesticide concentrations of each OCP (µg/g) by the food consumption rate (kg/day) and dividing by body

weight. Calculations were performed for adults and children who were considered to have average weight of 60 kg and 16.7 kg, respectively at a consumption rate of 0.00983 kg/day of milk [29].

$$\text{EADI} = \frac{F \times \text{Cr}}{\text{Mean body weight}} \quad (2)$$

where F = food consumption data and Cr is the concentration of the residue in the food sample. Samples with HRI > 1 are classified toxic and unsafe for consumption [29].

$$\text{HRI} = \frac{\text{EADI}}{\text{ADI}} \quad (3)$$

where ADI is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime [30].

The Cancer Benchmark Concentration (CBC) was calculated using the formula of [31] stated as:

$$\text{CBC} = \frac{(\text{RL}/\text{OSF}) \times \text{Bw}}{\text{CR}} \quad (4)$$

where RL is the maximum acceptable risk level (1×10^{-6}), OSF is the Oral Slope Factor (mg/kg/day), Bw is the body weight (kg) and CR is the consumption rate (kg/day). The CBC for carcinogenic effect is derived by setting the risk to one in one million due to lifetime exposure. The OSFs for the pesticides were obtained from [32]. The Hazard Ratio (HR) was determined to evaluate the carcinogenic potency of each sample with respect to each OCP using Eq. 5.

$$\text{HR} = \frac{\text{EADI}}{\text{CBC}} \quad (5)$$

3 Results and Discussion

The reliability of the analytical procedures adopted was tested in terms of percentage recovery (%R) and the values obtained are as shown in Table 1 With percentage recovery values of 89.92% of Hepachlor to 96.34% of Endosulfan, the analytical procedure was believed to be efficient to produce reliable results since the %R values of the OCPs fell within the [33] acceptable range of 70–110%.

The concentrations of organochlorine pesticides (OCPs) in the six (6) different milk samples obtained using Gas Chromatography–Mass Spectrometry (GC–MS) are summarized in Table 2.

The results obtained from the study indicated that three major classes of OCPs (Hexachlorocyclohexane, HCH; Dichlorodiphenylethanes; and Cyclodienes) were detected. The highest total concentrations of OCPs (39.010 µg/mL) were recorded in sample C in which OCPs levels fell within the range of below detection limit (BDL) of Endosulfan sulphate and Heptachlor epoxide to 10.020 µg/mL of Endrin ketone, while the lowest total concentrations of OCPs (21.632 µg/mL) were found in Sample B with individual OCPs concentrations also ranging from BDL of Endosulfan sulphate and Heptachlor epoxide to 5.228 µg/mL of Heptachlor. The level of OCPs in the milk samples have been pictorially demonstrated in Fig. 2.

Aldrin levels in the samples ranged from 0.414 µg/mL in sample A to 2.468 µg/mL in sample C. The International Agency for Research and Cancer (IARC) classified Aldrin as a Class 2B Carcinogen [34]. All the milk samples contained levels of Aldrin exceeding the designated ADI value (0.0001 µg/g/day) for Aldrin in food [35]. Dieldrin occured at levels that ranged between 1.882 µg/mL in sample A to 8.330 µg/mL in Sample F. Aldrin is readily converted to Dieldrin under ambient environmental conditions and in the body system [9]. Thus, the levels of Dieldrin detected in the samples might be as a result degradation of Aldrin to Dieldrin. Also, all the milk samples contained amounts of Dieldrin exceeding the designated ADI value (0.0001 µg/g/day) for Dieldrin in food [35]. Hence, consumption of these milk samples should not be too regular. The maximum amount of Dieldrin and Aldrin reported in this study are much lower than the values of 10.4 mg/kg and 59.9 mg/kg, respectively, reported by [36] for the leaf samples of cabbage from selected agricultural area in northern Nigeria but higher than the values reported by Adeleye et al. [21] for Amaranths (0.205 and 0.509 mg/kg, respectively) and Fluted pumpkin (1.465 and 0.391 mg/kg, respectively) leaf samples obtained from south-western Nigeria.

Endosulfan is a mixture of two stereoisomers, α-Endosulfan (Endosulfan I) and β-Endosulfan (Endosulfan II) in ratio 70:30, respectively with the former being the most toxic [37]. Endosulfan I showed levels ranging from 0.620 µg/mL in sample B to 4.230 µg/mL in sample D. The recommended ADI value for Endosulfan I in foods is 0.006 µg/g/day [38]. In some studies in animals, Endosulfan induced alterations in the testes and reduced the amount and quality of sperm [39]. It is equally implicated in the reduction of the level of testosterone in the blood [40]. Animal studies have shown that swallowing Endosulfan in contaminated food over long periods affects mainly the kidneys [41]. The milk samples investigated contained levels of Endosulfan I exceeding the designated ADI value (0.006 µg/g/day) for Endosulfan in food [38]. Compared to the level of Endosulfan I in cocoa bean samples (ND—12.11 µg/g) collected

Table 3 Potential non-carcinogenic health risk for adults

OCPs	ADI (µg/g/day)	A			B			C		
		EDI (µg/g)	HRI		EDI (µg/g)	HRI		EDI (µg/g)	HRI	
Aldrin	0.0001	0.00068	6.8	Yes	0.00181	18.1	Yes	0.00404	40.4	Yes
Dieldrin	0.0001	0.00308	30.8	Yes	0.00751	75.1	Yes	0.00469	46.9	Yes
Endosulfan I	0.006	0.00124	0.20667	No	0.00102	0.17	No	0.00243	0.405	No
Endosulfan II	0.006	0.00252	0.42	No	0.0018	0.3	No	0.00233	0.38833	No
Endosulfan sulphate	0.006	0.00173	0.28833	No	–	–	–	–	–	–
Endrin	0.0002	0.00029	1.45	Yes	0.00028	1.4	Yes	0.00027	1.35	Yes
Endrin aldehyde	0.0002	0.0085	42.5	Yes	0.00675	33.75	Yes	0.00735	36.75	Yes
Endrin ketone	0.0002	0.00222	11.1	Yes	0.00138	6.9	Yes	0.01642	82.1	Yes
Heptachlor	0.0001	0.01283	128.3	Yes	0.00857	85.7	Yes	0.01163	116.3	Yes
Heptachlor epoxide	0.0001	–	–	–	–	–	–	–	–	–
Methoxychlor	0.1	0.00344	0.0344	No	0.00156	0.0156	No	0.00465	0.0465	No
p,p′- DDD	0.01	0.00773	0.773	No	0.00217	0.217	No	0.00104	0.104	No
p,p′- DDE	0.01	0.00046	0.046	No	0.00028	0.028	No	0.0012	0.12	No
p,p′- DDT	0.01	0.0005	0.05	No	0.00011	0.011	No	0.00071	0.071	No
α- HCH	0.005	0.00123	0.246	Yes	0.00056	0.112	Yes	0.00323	0.646	Yes
β- HCH	0.005	0.00059	0.118	Yes	0.00046	0.092	No	0.00127	0.254	Yes
γ- HCH	0.005	0.00051	0.102	Yes	0.00048	0.096	No	0.00145	0.29	Yes
δ- HCH	0.005	0.00208	0.416	Yes	0.00071	0.142	Yes	0.00122	0.244	Yes
OCPs	ADI (µg/g/day)	D			E			F		
		EDI (µg/g)	HRI		EDI (µg/g)	HRI		EDI (µg/g)	HRI	
Aldrin	0.0001	0.00085	8.5	Yes	0.00136	13.6	Yes	0.00168	16.8	Yes
Dieldrin	0.0001	0.00625	62.5	Yes	0.00941	94.1	Yes	0.01365	136.5	Yes
Endosulfan I	0.006	0.00693	1.155	Yes	0.0066	1.1	Yes	0.00315	0.525	No
Endosulfan II	0.006	0.00178	0.29667	No	0.00071	0.11833	No	0.00293	0.488333	No
Endosulfan sulphate	0.006	4.60E-05	0.00767	No	6.90E-05	0.0115	No	0.00049	0.081667	No
Endrin	0.0002	0	0	No	0.00029	1.45	Yes	0	0	No
Endrin aldehyde	0.0002	0.01706	85.3	Yes	0.0051	25.5	Yes	0.00844	42.2	Yes
Endrin ketone	0.0002	0.01246	62.3	Yes	0.00289	14.45	Yes	0.00367	18.35	Yes
Heptachlor	0.0001	0.00451	45.1	Yes	0.0083	83	Yes	0.00594	59.4	Yes

Table 3 (continued)

OCPs	ADI (µg/g/day)	D			E			F		
		EDI (µg/g)	HRI		EDI (µg/g)	HRI		EDI (µg/g)	HRI	
Heptachlor epoxide	0.0001	0.00057	5.7	Yes	–	–	–	0.00061	6.1	Yes
Methoxychlor	0.1	0.00177	0.0177	No	0.00559	0.0559	No	0.00247	0.0247	No
p,p′- DDD	0.01	0.00036	0.036	No	0.00087	0.087	No	0.00073	0.073	No
p,p′- DDE	0.01	0.00063	0.063	No	0.00017	0.017	No	0.00032	0.032	No
p,p′- DDT	0.01	0.00055	0.055	No	0.00036	0.036	No	0.00035	0.035	No
α- HCH	0.005	0.0014	0.28	Yes	0.00187	0.374	Yes	0.00155	0.31	Yes
β- HCH	0.005	0.00056	0.112	Yes	0.00141	0.282	Yes	0.00171	0.342	Yes
γ- HCH	0.005	0.00057	0.114	Yes	0.00031	0.062	Yes	0.00076	0.152	Yes
δ- HCH	0.005	0.00109	0.218	Yes	0.00186	0.372	Yes	0.0012	0.24	Yes

by Oyekunle et al. [9] from south-western Nigeria, the Endosulfan I content in sample D can be considered much lower. Similarly, Endosulfan II showed levels with a range of 0.432 µg/mL in sample E to 1.786 µg/mL in sample F. These values were equally beyond the recommended ADI value for Endosulfan in food but much lower than the values obtained by Oyekunle et al. [9] from cocoa beans (ND—49.29 µg/g) collected from Ondo State in South-western Nigeria. People exposed to high levels of Endosulfan in contaminated food or exposed during field spraying suffered tremors and seizures while some died [41]. Endosulfan sulfate is a product of oxidation and the major metabolite of Endosulfan. Compared to the stereoisomers of endosulfan, endosulfan sulphate is the most persistent. Endosulfan sulphate showed levels with a range of BDL in sample B and C to 1.056 µg/mL in sample A. This Endosulfan sulfate level is much higher than the ADI value (0.006 µg/g/day) for Endosulfan sulphate in foods but much lower than the values reported by Oyekunle et al. [9] for cocoa beans (0.48–48.04 µg/g) collected from Osun State, Nigeria. Tremors and seizures, including systemic effects which may be secondary to the seizures have been reported for acute Endosulfan exposure [41].

It has been established that exposure to Endrin can cause various harmful effects including headache, dizziness, nervousness, nausea, vomiting, convulsions, severe CNS injury or damage and death [42]. In the milk samples, levels of Endrin ranged from BDL in samples D and F to 0.176 µg/mL in sample A. The assigned threshold value for daily intake for Endrin (ADI value) is 0.0002 µg/g/day [35]. Levels beyond the designated ADI values were observed for samples A, B, C and E. The level of Endrin in sample A was very close to that obtained from green algae (0.18 µg/mL) of a riverine ecosystem of South-South part of Nigeria in a study carried out by [43]. Levels of Endrin aldehyde ranged between 3.114 µg/mL in sample E to 10.412 µg/mL in sample D. The stipulated ADI value for Endrin aldehyde residues in food is 0.0002 µg/g/day [44]. This ADI value is much lower than the Endrin aldehyde content of the milk samples. Also, the Endrin aldehyde content of the milk samples is much higher than the values reported by [43] for sediment (0.0005 µg/g), green algae (0.6 µg/mL), daphnid (0.74 µg/mL) and fresh water fish (1.06 µg/mL) of a riverine area of Edo state, South-south, Nigeria. Furthermore, Endrin and Endrin aldehyde were found to be 0.045 and 0.208 mg/kg, respectively in kolanuts obtained from Osun state, Nigeria [45]. The values reported in this study were much higher than the maximum values obtained for these two OCPs in the kolanut sample. Adeleye et al. [21] reported values of 0.351 and 3.491 mg/kg for Endrin and Endrin aldehyde, respectively in fluted pumpkin leaves sourced from South-western Nigeria. Endrin ketone showed levels ranging from 0.842 µg/mL in sample B to 10.020 µg/mL in sample C (the

Table 4 Potential non-carcinogenic health risk index for children

OCP	ADI	A EDI	HRI		B EDI	HRI		C EDI	HRI	
Aldrin	0.0001	0.002437	24.36898	Yes	0.006487	64.86623	Yes	0.014527	145.2721	Yes
Dieldrin	0.0001	0.011078	110.7788	Yes	0.026982	269.8247	Yes	0.016835	168.3461	Yes
Endosulfan I	0.006	0.004462	0.743627	No	0.003649	0.608244	No	0.008747	1.457822	Yes
Endosulfan II	0.006	0.009041	1.506874	Yes	0.006475	1.079142	Yes	0.008358	1.393074	Yes
Endosulfan sulphate	0.006	0.006204	1.034014	Yes	–	–	–	–	–	–
Endrin	0.0002	0.001036	5.17988	Yes	0.001001	5.003293	Yes	0.000965	4.826707	Yes
Endrin aldehyde	0.0002	0.030538	152.6887	Yes	0.024251	121.2563	Yes	0.026406	132.0281	Yes
Endrin ketone	0.0002	0.007993	39.96749	Yes	0.004956	24.78102	Yes	0.05898	294.9	Yes
Heptachlor	0.0001	0.046101	461.0093	Yes	0.030773	307.732	Yes	0.041792	417.9222	Yes
Heptachlor epoxide	0.0001	–	–	–	–	–	–	–	–	–
Methoxychlor	0.1	0.012361	0.123611	No	0.005592	0.055919	No	0.016693	0.166933	No
p,p′-DDD	0.01	0.027771	2.777122	Yes	0.007805	0.780514	No	0.00372	0.37201	No
p,p′-DDE	0.01	0.001636	0.163637	No	0.001001	0.100066	No	0.004309	0.430872	No
p,p′-DDT	0.01	0.001801	0.180119	No	0.000388	0.038849	No	0.002555	0.255462	No
α- HCH	0.005	0.004415	0.882934	No	0.002025	0.404972	No	0.011596	2.319174	Yes
β- HCH	0.005	0.002107	0.421454	No	0.00166	0.331983	No	0.004556	0.911188	No
γ- HCH	0.005	0.001837	0.367301	No	0.001719	0.343756	No	0.005203	1.040685	Yes
δ- HCH	0.005	0.007476	1.495102	Yes	0.002566	0.513279	No	0.004379	0.875871	No
OCP	ADI	D EDI	HRI		E EDI	HRI		F EDI	HRI	
Aldrin	0.0001	0.003061	30.60838	Yes	0.004897	48.97341	Yes	0.006039	60.39269	Yes
Dieldrin	0.0001	0.022438	224.383	Yes	0.033799	337.9872	Yes	0.049032	490.3228	Yes
Endosulfan I	0.006	0.024899	4.14979	Yes	0.02371	3.951621	Yes	0.011302	1.883593	Yes
Endosulfan II	0.006	0.006381	1.063445	Yes	0.002543	0.423808	No	0.010513	1.752134	Yes
Endosulfan sulphate	0.006	0.000165	0.027469	No	0.000247	0.041204	No	0.001778	0.296273	No
Endrin	0.0002	0	0	No	0.001024	5.121018	No	0	0	No
Endrin aldehyde	0.0002	0.061287	306.437	Yes	0.01833	91.64856	Yes	0.030314	151.5704	Yes
Endrin ketone	0.0002	0.044759	223.7944	Yes	0.010395	51.97539	Yes	0.013185	65.92575	Yes
Heptachlor	0.0001	0.016187	161.8713	Yes	0.029808	298.0786	Yes	0.021343	213.4346	Yes
Heptachlor epoxide	0.0001	0.002037	20.36635	Yes	–	–	–	0.002201	22.01449	Yes

Table 4 (continued)

OCP	ADI	D			E			F		
		EDI	HRI		EDI	HRI		EDI	HRI	
Methoxychlor	0.1	0.006369	0.063689	No	0.020096	0.200956	No	0.008865	0.088647	No
p,p′-DDD	0.01	0.001295	0.129497	No	0.003131	0.313147	No	0.002613	0.261349	No
p,p′-DDE	0.01	0.002249	0.224854	No	0.000624	0.062394	No	0.001154	0.11537	No
p,p′-DDT	0.01	0.001978	0.197777	No	0.001295	0.129497	No	0.00126	0.125965	No
α- HCH	0.005	0.005027	1.005368	Yes	0.006722	1.344414	Yes	0.005557	1.11132	Yes
β- HCH	0.005	0.002013	0.402618	No	0.005062	1.012431	Yes	0.006145	1.229044	Yes
γ- HCH	0.005	0.002037	0.407327	No	0.00113	0.226031	No	0.002731	0.546242	No
δ- HCH	0.005	0.003908	0.781691	No	0.006675	1.334996	Yes	0.004309	0.861744	No

highest OCP concentration observed). It is observed to have a proportional relationship to Endrin and Endrin aldehyde. The stipulated ADI value for Endrin ketone residues in food is 0.0002 µg/g/day [44]. A study on rodents suggests that exposure to Endrin aldehyde or Endrin ketone may cause liver disease [46]. All the milk samples (A, B, C, D, E and F) contained levels of Endrin ketone exceeding the designated ADI value in food as well as the level of Endrin ketone in the gill (78.8 ng/g) and muscle (11.2 ng/g) of fish (*Pomadasys commersonnil*) sourced by Olisah et al. [47] from the Swartkops estuary in South Africa.

Heptachlor levels in the samples ranged between 2.750 µg/mL in Sample D and 7.832 µg/mL in sample A. Acute inhalation exposure of Heptachlor by humans has been associated with nervous system effects in a few case studies [48]. Also, gastrointestinal effects such as nausea and vomiting have been reported to occur following accidental ingestion of Heptachlor [49]. All the samples showed elevated levels of Heptachlor much higher than the ADI value (0.0001 µg/g/day) for Heptachlor in food [35] and also higher than the heptachlor residue level in maize (0.005 mg/kg) and cowpea (0.01 mg/kg) obtained from Ghana in a study carried out by Akoto et al. [50]. Heptachlor epoxide showed levels ranging from BDL in Sample A, B, C and E to 0.374 µg/mL in sample F. The ADI value for heptachlor epoxide in food is 0.000013 µg/g/day [35]. Some studies in animals suggest that young animals exposed during gestation and infancy may be very sensitive to Heptachlor and Heptachlor epoxide. Changes in nervous system and immune function were found in these animals [51]. Levels below the designated ADI values were observed for four of the samples while samples D and F had values higher than the stipulated ADI value.

Methoxychlor levels in the samples ranged between 0.950 µg/mL in Sample B to 3.414 µg/mL in Sample E. The ADI value for Methoxychlor is 0.1 µg/g/day [35]. Studies in animals show that exposure to Methoxychlor adversely affects the ovaries, uterus, and mating cycle in females, and the testes and prostate in males. Fertility is decreased in both female and male animals [52]. All the samples showed elevated levels of Methoxychlor which are much higher than the expected designated ADI value. DDD levels in the samples ranged from 0.220 µg/mL in Sample D to 4.718 µg/mL in Sample E. These concentrations are much higher than the ADI value (0.01 µg/g/day) for DDD [53]. Tests in animals also suggest that short-term exposure to DDT and metabolites in food may have a harmful effect on reproduction. In addition, products of DDT metabolism such as DDD and DDE can cause harmful effects on the adrenal gland [52]. DDE level in the samples ranged between 0.170 µg/mL in Sample B to 0.732 µg/mL in Sample C. The ADI value for DDE is 0.01 µg/g/day [53]. A study in humans showed that

Table 5 Potential carcinogenic health risk for adults

OCPs	SF	CBC	A			B			C		
			EDI	HR		EDI	HR		EDI	HR	
Aldrin	17	3.59045E-05	0.00068	18.9391	Yes	0.00181	50.4115	Yes	0.00404	112.521	Yes
Dieldrin	16	3.81485E-05	0.00308	80.7371	Yes	0.00751	196.862	Yes	0.00469	122.941	Yes
Endosulfan I			0.00124			0.00102			0.00243		
Endosulfan II			0.00252			0.0018			0.00233		
Endosulfan sulphate			0.00173								
Endrin			0.00029			0.00028			0.00027		
Endrin aldehyde			0.0085			0.00675			0.00735		
Endrin ketone			0.00222			0.00138			0.01642		
Heptachlor	4.5	0.000135639	0.01283	94.5892	Yes	0.00857	63.1823	Yes	0.01163	85.7422	Yes
Heptachlor epoxide	9.1	6.70743E−05									
Methoxychlor			0.00344			0.00156			0.00465		No
p,p′- DDD	0.24	0.002543235	0.00773	3.03944	Yes	0.00217	0.85324	No	0.00104	0.40893	No
p,p′- DDE	0.34	0.001795225	0.00046	0.25624	No	0.00028	0.15597	No	0.0012	0.66844	No
p,p′- DDT	0.34	0.001795225	0.0005	0.27852	No	0.00011	0.06127	No	0.00071	0.39549	No
α- HCH	6.3	9.68851E-05	0.00123	12.6954	Yes	0.00056	5.78004	Yes	0.00323	33.3384	Yes
β- HCH	1.8	0.000339098	0.00059	1.73991	Yes	0.00046	1.35654	Yes	0.00127	3.74523	Yes
γ- HCH	1.3	0.00046952	0.00051	1.08622	Yes	0.00048	1.02232	Yes	0.00145	3.08826	Yes
δ- HCH	1.8	0.000339098	0.00208	6.13392	Yes	0.00071	2.09379	Yes	0.00122	3.59778	Yes
Total		0.007655052	0.04963	6.4833	Yes	0.03545	4.63093	Yes	0.06393	8.35135	Yes
OCPs	SF	CBC	D			E			F		
			EDI	HR		EDI	HR		EDI	HR	
Aldrin	17	3.59045E−05	0.00085	23.6739	Yes	0.00136	37.8783	Yes	0.00168	46.7908	Yes
Dieldrin	16	3.81485E−05	0.00625	163.833	Yes	0.00941	246.667	Yes	0.01365	357.812	Yes
Endosulfan I			0.00693			0.0066			0.00315		
Endosulfan II			0.00178			0.00071			0.00293		
Endosulfan sulphate			4.60E-05			6.90E-05			0.00049		
Endrin			0			0.00029			0		
Endrin aldehyde			0.01706			0.0051			0.00844		
Endrin ketone			0.01246			0.00289			0.00367		
Heptachlor	4.5	0.000135639	0.00451	33.25	Yes	0.0083	61.1918	Yes	0.00594	43.79265	Yes

Table 5 (continued)

OCPs	SF	CBC	D			E			F		
			EDI	HR		EDI	HR		EDI	HR	
Heptachlor epoxide	9.1	6.70743E-05	0.00057	8.49804	Yes				0.00061	9.094388	Yes
Methoxychlor			0.00177			0.00559			0.00247		
p,p′- DDD	0.24	0.002543235	0.00036	0.14155	No	0.00087	0.34208	No	0.00073	0.287036	No
p,p′- DDE	0.34	0.001795225	0.00063	0.35093	No	0.00017	0.0947	No	0.00032	0.178251	No
p,p′- DDT	0.34	0.001795225	0.00055	0.30637	No	0.00036	0.20053	No	0.00035	0.194962	No
α- HCH	6.3	9.68851E-05	0.0014	14.4501	Yes	0.00187	19.3012	Yes	0.00155	15.99833	Yes
β- HCH	1.8	0.000339098	0.00056	1.65144	Yes	0.00141	4.15809	Yes	0.00171	5.04279	Yes
γ- HCH	1.3	0.00046952	0.00057	1.21401	Yes	0.00031	0.66025	No	0.00076	1.618673	Yes
δ- HCH	1.8	0.000339098	0.00109	3.21441	Yes	0.00186	5.48514	Yes	0.0012	3.5388	Yes
Total		0.007655052	0.057386	7.49649	Yes	0.047169	6.16181	Yes	0.04965	6.485912	Yes

increasing concentrations of p,p′-DDE in human breast milk were associated with reductions in the duration of lactation. An additional study in humans found that as the DDE levels in the blood of pregnant women increased, the chances of having a pre-term baby also increased [52]. DDT levels in the samples ranged between 0.214 µg/mL in Sample F to 0.434 µg/mL in Sample C. International Agency for Research on Cancer (IARC) classified DDT as a Class 2B (possibly carcinogenic to humans) residue [34]. The ADI value for DDT is 0.01 µg/g/day [53]. People who swallowed large amounts of DDT became excitable and had tremors and seizures; they also experienced sweating, headache, nausea, vomiting, and dizziness [52]. All the samples showed elevated levels of DDD, DDE and DDT which were much higher than the expected designated ADI value. These results are comparable with the levels of DDD (0.128 mg/kg), DDE (0.053 mg/kg) and DDT (0.247 mg/kg) obtained by Olutona and Livingstone [54] in a study carried out on the OCPs content of some selected malt drinks in Nigeria where the concentration of the DDE exceeded the ADI value.

α- HCH levels in the samples ranged between 0.344 µg/mL in Sample B to 1.970 µg/mL in Sample C. The ADI value for α- HCH is 0.005 µg/g/day [55]. Long-term oral administration of α-HCH, β-HCH, γ-HCH, or technical-grade HCH to laboratory rodents has been reported to result in liver cancer [56]. β-HCH levels in the samples ranged between 0.282 µg/mL in Sample B to 1.044 µg/mL in Sample E. The ADI value for β- HCH is 0.005 µg/g/day [55]. All the samples had levels exceeding the stipulated ADI value for α-HCH andβ-HCH. **γ**- HCH levels in the samples ranged between 0.192 µg/mL in Sample E to 0.884 µg/mL in Sample C. The ADI value for γ-HCH is 0.005 µg/g/day [55]. In humans, breathing toxic amounts of γ-HCH and/or α-, β-, and δ-HCH can result in dizziness, headaches, and possible changes in the levels of sex hormones in the blood [56]. All the samples (except sample F) had levels exceeding the stipulated ADI value for **γ**- HCH.δ- HCH levels in the samples ranged between 0.436 µg/mL in sample B to 1.270 µg/mL in sample A. The ADI value for δ- HCH is 0.005 µg/g/day [55]. All the samples had levels exceeding the stipulated ADI value. These results are similar to the concentrations of α-HCH (0.10–3.10 µg/g), β-HCH (0.32–1.87 µg/g), γ-HCH(0.30–1.3 µg/g) and δ- HCH (0.06–3.37 µg/g) detected by Oyekunle et al. [9] in cocoa beans obtained from Ondo State, South-western Nigeria, based on the fact that they are all greater than their respective ADI values. The concentrations of the OCPs were above the respective European Union set maximum residue limits (EU MRLs) for different classes of OCPs. The presence of these pesticides in these evaporated milk samples is an indication that farmers in Nigeria still use these pesticides for crop production despite their prohibition. These crops

Table 6 Potential carcinogenic health risk for children

OCP	OSF	CBC	A			B			C		
			EDI	HR		EDI	HR		EDI	HR	
Aldrin	17	3.59045E-05	0.002437	67.87451	Yes	0.006487	180.6738	Yes	0.014527	404.6012	Yes
Dieldrin	16	1.0618E-05	0.011078	1043.322	Yes	0.026982	2541.155	Yes	0.016835	1585.514	Yes
Endosulfan I			0.004462			0.003649			0.008747		
Endosulfan II			0.009041			0.006475			0.008358		
Endosulfan Sulphate			0.006204								
Endrin			0.001036			0.001001			0.000965		
Endrin aldehyde			0.030538			0.024251			0.026406		
Endrin ketone			0.007993			0.004956			0.05898		
Heptachlor	4.5	3.77529E-05	0.046101	1221.124	Yes	0.030773	815.116	Yes	0.041792	1106.987	Yes
Heptachlor epoxide	9.1	1.8669E-05									
Methoxychlor			0.012361			0.005592			0.016693		
p,p′-DDD	0.24	0.000707867	0.027771	39.23194	Yes	0.007805	11.02608	Yes	0.00372	5.255224	Yes
p,p′-DDE	0.34	0.000499671	0.001636	3.274155	Yes	0.001001	2.003319	Yes	0.004309	8.623677	Yes
p,p′-DDT	0.34	0.000499671	0.001801	3.604373	Yes	0.000388	0.776511	No	0.002555	5.113366	Yes
α-HCH	6.3	2.69664E-05	0.004415	163.7225	Yes	0.002025	75.09355	Yes	0.011596	430.0172	Yes
β-HCH	1.8	9.43823E-05	0.002107	22.32411	Yes	0.00166	17.58805	Yes	0.004556	48.27177	Yes
γ-HCH	1.3	0.000130683	0.001837	14.0569	Yes	0.001719	13.15395	Yes	0.005203	39.81385	Yes
δ-HCH	1.8	9.43823E-05	0.007476	79.20979	Yes	0.002566	27.18731	Yes	0.004379	46.39642	Yes
OCP	OSF	CBC	D			E			F		
			EDI	HR		EDI	HR		EDI	HR	
Aldrin	17	3.59045E−05	0.003061	85.25395	Yes	0.004897	136.3896	Yes	0.006039	168.1962	Yes
Dieldrin	16	1.0618E−05	0.022438	2113.203	Yes	0.033799	3183.178	Yes	0.049032	4617.816	Yes
Endosulfan I			0.024899			0.02371			0.011302		
Endosulfan II			0.006381			0.002543			0.010513		
Endosulfan Sulphate			0.000165			0.000247			0.001778		
Endrin			0			0.001024			0		
Endrin aldehyde			0.061287			0.01833			0.030314		
Endrin ketone			0.044759			0.010395			0.013185		
Heptachlor	4.5	3.77529E−05	0.016187	428.7616	Yes	0.029808	789.555	Yes	0.021343	565.3339	Yes

Table 6 (continued)

OCP	OSF	CBC	D			E			F		
			EDI	HR		EDI	HR		EDI	HR	
Heptachlor epoxide	9.1	1.8669E−05	0.002037	109.1112	Yes				0.002201	117.8958	Yes
Methoxychlor			0.006369			0.020096			0.008865		
p,p′-DDD	0.24	0.000707867	0.001295	1.82944	Yes	0.003131	4.423147	Yes	0.002613	3.691371	Yes
p,p′-DDE	0.34	0.000499671	0.002249	4.500963	Yes	0.000624	1.248822	Yes	0.001154	2.30952	Yes
p,p′-DDT	0.34	0.000499671	0.001978	3.958606	Yes	0.001295	2.591706	Yes	0.00126	2.52166	Yes
α-HCH	6.3	2.69664E-05	0.005027	186.4174	Yes	0.006722	249.2735	Yes	0.005557	206.0715	Yes
β-HCH	1.8	9.43823E-05	0.002013	21.32816	Yes	0.005062	53.63295	Yes	0.006145	65.10756	Yes
γ-HCH	1.3	0.000130683	0.002037	15.58732	Yes	0.00113	8.646868	Yes	0.002731	20.89787	Yes
δ-HCH	1.8	9.43823E-05	0.003908	41.40608	Yes	0.006675	70.72302	Yes	0.004309	45.65476	Yes

are capable of contaminating the udder of cows as well as their water and feed during open grazing. Coupled with this, unsafe and careless farming practice could as well lead to direct contamination of the milk samples with the OCPs while milking. The results obtained in this study are consistent with the values earlier reported for OCPs in various samples where the OCP contents are greater than the EU/MRLs standards. For instance, Adeleye et al. [21] reported that the OCPs in amaranths and fluted pumpkin obtained in South-western Nigeria exceeded the EU MRLs. In the same vein, Olutona and Livingstone [54] reported that the OCPs (except **γ**- HCH) content of five different malt drinks are greater than the EU MRLs. Similar trend was observed by Akan et al. [36] when the OCPs contents of spinach, lettuce, cabbage, onions and tomatoes were compared to that of EU MRLs.

The non-carcinogenic health risks of the OCPs in the evaporated milk samples for adults, as seen in Table 3, revealed that Aldrin, Dieldrin, Endrin, Endrin aldehyde, Endrin ketone, Heptachlor and all the HCHs have HRI > 1 in sample A. Similar trend was observed in sample B (except for β-HCH and **γ**-HCH having HRI < 1) and C. In sample D, Aldrin, Dieldrin, Endosulfan I, Endrin aldehyde, Endrin ketone, Heptachlor, Heptachlor epoxide and all the HCH have HRI > 1. Except for Endrin and Heptachlor epoxide, sample E showed a similar trend to D. Aldrin, Dieldrin, Endrin aldehyde, Endrin ketone, Heptachlor, Heptachlor epoxide and the HCH OCPs had HRI > 1 in sample F. Consequently, it can be inferred that in all the milk samples, Aldrin, Dieldrin, Endrin aldehyde, Endrin ketone and Heptachlor had HRI > 1 which implies that the adult consumers of these evaporated milk samples might be prone to long-term potential non-carcinogenic health risk from these OCPs. However, all the milk samples showed no potential non-carcinogenic health risk in adults with respect to Endosulfan sulphate, Methoxychlor, p,p′-DDD, p,p′-DDE and p,p′-DDT.

In children, the milk samples showed potential non-carcinogenic health risk with respect to Aldin, Dieldrin, Endrin aldehyde, Endrin ketone and Heptachlor. No potential non-carcinogenic health risk was obtained for children with respect to Methoxychlor, p,p′-DDE and p,p′-DDT. This results (as seen on Table 4) is similar to the values reported by Adeleye et al. [21] for fluted pumpkin where Aldrin, Dieldrin, Endrin aldehyde and Heptachlor were found to equally have HRI values > 1 in the children category. The highest non-carcinogenic health risk index for children (490.32) was obtained from Dieldrin found in sample F while the lowest (0.03885) was found in p,p′-DDT obtained from sample B.

As seen in Table 5, all the samples showed carcinogenic potencies in adult consumers with respect to Aldrin, Dieldrin, Heptachlor, α-HCH, β-HCH and δ-HCH. Also, they all showed no carcinogenic potency with respect to DDE and DDT. The highest carcinogenic potency value was

Table 7 Correlation coefficients of the OCPs in the milk samples

OCPs	Aldrin	Dieldrin	Endosulfan I	Endosulfan II	Endosulfan sulphate	Endrin	Endrin aldehyde	Endrin ketone	Heptachlor	Heptachlor epoxide	Methoxychlor	p,p′-DDD	p,p′-DDE	p,p′-DDT	α- HCH	β- HCH	γ- HCH	δ- HCH
Aldrin	1.00																	
Dieldrin	− 0.08	1.00																
Endosulfan I	− 0.28	0.25	1.00															
Endosulfan II	0.18	0.02	− 0.61	1.00														
Endosulfan sulphate	− 0.46	− 0.34	− 0.43	0.47	1.00													
Endrin	0.26	− 0.52	− 0.43	− 0.35	0.16	1.00												
Endrin aldehyde	− 0.36	− 0.18	0.44	0.15	− 0.05	**− 0.71**	1.00											
Endrin ketone	0.61	− 0.34	0.27	0.11	− 0.41	− 0.23	0.46	1.00										
Heptachlor	0.33	− 0.65	− 0.64	0.16	0.52	**0.82**	− 0.56	− 0.04	1.00									
Heptachlor epoxide	− 0.29	0.55	0.42	0.36	− 0.13	− 1.00	0.68	0.17	**− 0.82**	1.00								
Methoxychlor	0.34	− 0.11	0.23	− 0.40	0.01	0.54	− 0.56	0.13	0.48	− 0.53	1.00							
p,p′-DDD	− 0.37	− 0.58	− 0.58	0.30	**0.92**	0.47	− 0.16	− 0.42	**0.71**	− 0.44	0.01	1.00						
p,p′-DDE	**0.74**	− 0.52	− 0.13	0.33	− 0.16	0.04	0.22	**0.91**	0.34	− 0.09	0.18	− 0.11	1.00					
p,p′-DDT	0.38	− 0.49	0.21	0.23	0.12	− 0.09	0.35	**0.82**	0.27	0.06	0.40	0.02	**0.82**	1.00				
α-HCH	**0.77**	− 0.15	0.16	0.05	− 0.25	0.12	− 0.15	**0.75**	0.30	− 0.14	0.68	− 0.31	**0.77**	**0.79**	1.00			
β-HCH	0.38	0.68	0.22	0.10	− 0.20	− 0.21	− 0.41	0.06	− 0.13	0.23	0.53	− 0.45	0.01	0.15	0.56	1.00		
γ-HCH	**0.89**	− 0.20	− 0.28	0.50	− 0.21	− 0.01	− 0.03	**0.77**	0.31	− 0.02	0.19	− 0.22	**0.91**	0.66	**0.80**	0.32	1.00	
δ-HCH	− 0.34	− 0.26	0.12	− 0.14	0.68	0.36	− 0.25	− 0.26	0.49	− 0.32	0.66	0.59	− 0.16	0.31	0.16	0.16	− 0.26	1.00

Bold represents strong correlation

observed for sample E as 246.667 (Dieldrin) while the lowest was obtained in sample D as 0.142 (DDD). In children, the milk samples showed potential carcinogenic health risk in terms of Aldrin, Dieldrin, Heptachlor, p,p′-DDD, p,p′-DDE and the HCHs while none of the samples showed no carcinogenic potency in terms of any of the OCPs as seen in Table 6. Just like what obtains in the non-carcinogenic health risk assessment, the highest carcinogenic potency in children (4617.816) was obtained from Dieldrin in sample F while the lowest (0.776) was detected in p,p′-DDT from sample B. This result implies that children are at greater risk of carcinogenic exposure from the consumption of these milk samples compared to adults. Hence, need to control the rate of consumption by children. Furthermore, samples F and B having very high and low cumulative health risk indices, respectively confirmed the respective high cumulative OCPs load in both samples (as seen in Table 1) and this further suggests that the continuous consumption of these milk samples could put consumers at greater risk of both carcinogenic and non-carcinogenic health risks compared to other milk samples. Precisely, the risk of exposure to cancer from the consumption of these products is about four times higher than the set benchmark HRI (HRI = 1) by the European Commission Regulation (EC) in 1999 [33].

The correlation coefficients of the OCPs in Table 7 indicated that out of 153 possible pairs of different congeners, 17 pairs (11.1%) were very strongly positively correlated, 18 pairs (11.8%) were moderately positively correlated while 60 (39.2%) were weakly positively correlated. Also, 2 pairs (1.3%) were strongly negatively correlated, 9 pairs (5.9%) were moderately negatively correlated while 47 (30.7) were weakly negatively correlated. It could therefore be inferred that OCPs in the evaporated milk drinks were contributed by different factors. The r value of 0.80 obtained from α-HCH and γ-HCH pair suggests that both OCP residues are basically from the same source. The same deductions can also be made for the γ-HCH & p,p′-DDE (r = 0.91) and endrin ketone and p,p′-DDE (r = 0.91) pairs.

4 Conclusion

In this study, varying concentrations of OCPs were observed in the evaporated milk samples with the highest OCP load was detected in sample E. The study concluded that the highest estimated cumulative carcinogenic and non-carcinogenic potencies of the OCPs in children were found in samples F and C, respectively, and this could lead to serious health issues with constant consumption of these milk samples. In adults, the highest cumulative non-carcinogenic and carcinogenic health risks were found to come from sample C. Considering the consumption rate of these products in Nigeria, the regular consumption of these products (especially sample C) could possibly pose a long term non-carcinogenic and carcinogenic health risks to regular consumers due to the possible accumulation of the studied OCPs in the body.

Compliance with Ethical Standards

Conflict of interest On behalf of all authors, the corresponding author states that no conflict of interest.

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