Original Research Article

Health Risk Assessment of Organochlorine Pesticide Residues in Selected Herbal Medicines Sold in Lagos State, Nigeria

ABSTRACT

The use of herbal medicines has a very long history for therapeutic purposes. However, cases of toxicological effects have been reported. The present study aims to assess the safety level of herbal medicines by monitoring the organochlorine pesticide (OCP) residues content. This study assessed the presence of seventeen organochlorine pesticide residues in twenty-seven (27) herbal medicine samples (14 liquid and 13 solid) collected from seven Local Government Area of Lagos state, Nigeria. The residues were analyzed using Gas Chromatography-Mass Spectrometry (GC-MS) with solid phase extraction. Results showed the presence of banned OCP residues in all the selected samples at concentrations greater than the Maximum Residue limit, MRL. The Estimated Daily Intake, EDI measures the level of exposure to the pesticide residues for all the samples were found to be lower than the Acceptable Daily Intake, ADI. Health Risk Index (HRI) of all the selected samples was generally lesser than one (1) which indicates that long term exposure may not be of immediate concern to the consumers. The solid herbal medicines were found to have higher mean concentration, EDI and HRI when compared to the liquid herbal samples, suggesting that processing and preparation techniques for solid herbal medicines should be improved. The presence of the banned OCP residues in herbal medicine is, however, of public health interest and should be regularly monitored.

Keywords: Organochlorine pesticides, herbal medicines, Estimated daily intake, Health risk index.

1. INTRODUCTION

The use of herbs for medicinal purposes has a very long history and still constitutes a high proportion of the traditional therapeutic methods in use all over the world. The World Health Organization (WHO) estimated that approximately 80% of the world's population uses herbal products for therapeutic purposes, most frequently in the form of extracts from plants or of

the active components of plants [1,2]. Commercialization of herbal products is related to their extensive application in various production sectors, such as: food, pharmaceuticals, nutraceuticals, herbal agents, diet supplements, perfumes and fragrances, cosmetics or aromatizing products ; [3,4]. In recent years, the international market noted a doubled demand for medicinal plants. According to the WHO the current demand for plant-derived medical products amounts to 14 thousand million dollars a year, and by the year 2050 it will have increased to five billion dollars [4]. The observed growth of interest in the use of herbal products in developed countries is the result of the assumption that “natural” implies “harmless”. However, with the increasing popularity and global expansion of the market of herbal materials, the safety of herbal products is becoming a serious problem relating to public health [5,6].

Population growth has led to increased use of pesticides for crop cultivation. Research has shown that pesticides are used to cultivate more than one quarter of farm products [7]. A decrease in production of cereals (32%), vegetables (54%) and fruits (78%) has been reported without the use of pesticides [8,9].The adverse effects of persistent organic pollutants (POPs) in the ecosystem have been one of the major subjects of discussion all over the world. These chemicals are toxic and because of their ability to be transported long distance from the place of use and released either by water or wind, they tend to affect biota and humans in diverse ways [10,11]. Due to their ubiquitous nature, lipophilic properties, and persistence in the environment, they tend to accumulate in tissues of living organisms [12,13]. Many of these compounds have been classified as endocrine disruptors, because of their tendency to reduce the efficiency of thyroid hormones and to affect the neurobehavioral development and reproductive systems in animals and humans [2]. Carcinogenic cases of these compounds have been reported [14]. Initially, 12 POPs classified as “Dirty Dozen” were identified as endocrine disruptors [15]. Chemicals such as organochlorine pesticides (OCPs) in this group, are used for pest control because of their versatility [13]. These include insecticides such as aldrin, dieldrin, endrin, chlordane, dichlorodiphenyltrichloroethane (DDT), mirex, toxaphene, and heptachlor; fungicides - hexachlorobenzene (HCB) and industrial chemicals -polychlorinated biphenyls (PCBs). Other chemicals in this group that are unintentionally produced are polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) [15].

Organochlorines are compounds which contain a minimum of one covalently bonded chlorine atom. Organochlorines exhibit a large variety of structures with many diverse chemical properties. Due to high atomic weight of chlorine, these compounds are found to be denser than water. These compounds can be prepared from chlorine, hydrogen chloride and from other chlorinating agents. Organochlorines could enter an organisms’ body across the skin, from the lungs and could also be absorbed from the gut wall. Cyclodienes, hexachlorocyclohexane, endosulfan and lindane can easily pass through the skin, while the absorption is less in case of dicofol, toxaphene, DDT, mirex and methoxychlor [16]. It has been observed that absorption of organochlorines through skin and gut wall is greatly increased by fat and fat solvents. These compounds are volatile, and their significant part is stored in fat tissue and is excreted through biliary and urinary pathways, while storable lipophilic compounds could be excreted from maternal milk. They affect central nervous system causing hyper-excitable state in brain, convulsions, tremor, hyper-reflexia and ataxia. Cyclodienes, lindane and mirex can cause more severe effects as compared to DDT and methoxychlor. DDT has been extensively tested for its possible toxic effects on different animal models [17,18].

The extensively used and highly sensitive analytical techniques for determination and quantification of these pesticides at low concentrations in food samples are GC- MS, HPLC-MS, HPLC-DAD, and GC-ECD [19,20]. They can provide compound confirmation and

detailed information on the structure of the compound analyzed, such as separation and detection. The function of GC-MS is identification, quantification, and analysis of a compound [21]. The most widely used extraction techniques for pesticides in plants are microwave extraction (MAE) [22], ultrasound extraction (UAE) [23], Soxhlet [24], supercritical fluid extraction and accelerated solvent extraction [25].

The pesticides used in Africa from 1990 to 2016 were estimated to be 69,355.36 tons active ingredient (a.i), accounting for about 2.1% world total pesticide usage. Organochlorines may also interact with endocrine receptors like estrogen and androgens. Their poisoning may cause various symptoms including headache, nausea, dizziness, vomiting, tremor, lack of co-ordination and mental confusion. More than 17 million deaths have been reported to occur as a result of pesticide poisoning from 1960 till 2019 [26]. Despite the alarming statistics, this number is even assumed to be underestimated since majority of pesticide poisoning in the poor rural communities were not accounted for due to poor death registry [26]. Pesticides are used worldwide to prevent weeds, fungi and pests from attacking plants. Their wide usage has increased their enormous dispersal in soils, groundwater and drinking water [27]. This study aims to investigate OCPs residue and its levels in different herbal products both liquid and solid (capsule, tablet and tea) using GC-MS, estimate the daily intake of the herbal products, compare the obtained daily intake with Acceptable Daily Intake (ADI), and analyze human risk of OCPs exposure of the herbal products.

2. MATERIAL AND METHODS

2.1Chemicals

All chemicals used were of analytical grade. The chemicals used were Dichloromethane (HPLC grade), Hexane (HPLC grade), Methanol (HPLC grade), Accu Standards of 18 OCPs and Helium gas.

2.2 Sample Collection

A total of twenty-seven (27) samples (14 branded liquid herbal medicines and 13 branded solid herbal medicines) were purchased randomly from registered pharmacies in seven Local Government Area in Lagos State during the period of August 2021. Details of the number of samples are summarized in Table 1.

2.3 Sample Preparation

2.3.1 Solid Samples

5g of sample was weighed into a conical flask. 20mls of dichloromethane (DCM) was added and the mixture was agitated on a shaker for 45mins.

A cartridge was placed on solid phase manifold for sample treatment and to concentrate the sample with Nitrogen concentrator. The aliquot was then loaded on the cartridge placed on solid state manifold. 2ml of dichloromethane was used to elute the analyte and the DCM containing the analyte was run on GC-MS (CTX-ION ANALYTICS, AKURA ESTATE IKEJA, OFF ADENIYI JONES).

2.3.2 Liquid Sample:

10mls of liquid sample was measured into a conical flask and mixed with 20ml dichloromethane. The conical flask containing the sample was agitated on a shaker for 45minutes and then poured into a separating funnel and left to stand for 1 hour to allow the aqueous layer and organic phase separate. The aqueous layer was decanted, leaving the organic phase which was then loaded on solid phase manifold for treatment and concentration of the analyte.

2.3 Gas Chromatography-Mass Spectrometry Conditions

The sample extracted was loaded on a gas chromatography of 7890 (Agilent technologies GC System USA) coupled with an MS-Agilent technologies 5975 MSD. The principle behind the analysis is based on separation techniques. In this separation technique, the mobile phase used is Helium gas, while the stationary phase is the column of model Agilent technologies HP5MS of length 30m, internal diameter of 0.32mm and thickness 0.25microlitre. the volume of the sample injected into the GC is 1microlitre. GC is based on volatility which is temperature dependent. Initial temperature used is 60 degree Celsius for 0.5 minute to 140 degree Celsius at 20 degree per minute to 280 degree Celsius at 11 degree per minute held for 23 minutes. The mode is split less, injection temperature is 200 degree Celsius. The GC technique has been validated by the manufacturer as stated in the catalogue and it is accepted worldwide as far as Agilent technologies products are used.The sample extracted was placed in a vial bottle and the bottle was placed on an auto sampler tray. After the oven temperature has been programmed on the software, the samples were loaded sequentially, and the Command Run Sequence was initiated.

2.3.1 Extraction and Clean-up

The solid phase extraction cartridges were conditioned with 2ml methanol followed by distilled water and then ethyl acetate. The sample extract was loaded on the solid phase extraction column and eluted with 2ml dichloromethane. The eluate was concentrated under a gentle stream of nitrogen gas and reconstituted to 1 ml using n-hexane in an amber sample vial and taken for gas chromatograph-Mass spectrometry (GC-MS) analysis.

3.3.2 Method Validation

Standard reference material was obtained and analyzed for the eighteen [18,31] OCPs to check instrument recovery, consistency and efficiency.Precision was determined by analyzing the samples in duplicates. The sensitivity of the instrument was determined by calculating the limits of detection (LOD) and limits of quantification (LOQ). LOD is three times standard deviation of the blank signal, and this was calculated as the concentration at which baseline noise to signals is 3 at the expected retention time for the individual target pesticide LOQ was the concentration leading to a signal-to-noise ratio of 10.For measurement values below LOQ, a value equal to the LOQ was used for statistical analyses and computation of risk assessment. Duplicate determinations were done, and the results reported as mean ± standard deviation.

2.4 Risk Assessment

Risk was assessed by calculating the health risk index (HRI) using Equation 1.

Equation 1

HRI = EDI/ADI

This was done based on the levels of the OCP residues found in the herb samples. Estimated daily intakes (EDI) were determined and compared with the established acceptable daily intake (ADI).Estimated daily intake was found by multiplying the residual pesticide concentration (mg/kg-1) by the herbal product consumption rate (kg/ day-1) and dividing by body weight. Calculations were performed for adults. Adults were considered to have an average weight of 60 kg.

Equation 2

2.5 Risk Analysis

Risk analysis of the herbal products consumption on human health will be based on some guidelines provided by different international organizations as follows:

A. Acceptable Daily Intake (ADI)

Acceptable Daily Intake (ADI) is an amount of a specific substance which was originally applied for a food additive and later also for drug or pesticide in drinking water or food that can be orally ingested on daily basis over a lifetime without an appreciable health risk (WHO, 2019). ADI as an approach of toxicological evaluation was initiated by the Joint FAO/WHO Expert Committee on Food Additives in 1961 by collecting all relevant data, ascertaining the completeness of the available data, determining the no-effect level using the most sensitive indicator of the toxicity, and applying an appropriate safety factor to arrive at the ADI for man. ADI is usually defined as mg per kg body weight per day. The higher value of ADI means that the larger the amount of a compound that is safe for a regular ingestion. However, this formulation did not take consideration of consumption rates and different eating habits. To be compared with ADI, the individual exposure was calculated based on the Estimated Daily Intake (EDI) which is determined based on the

Equation 1 below:

EDI = (DC x CC)/mean body weight

Where DC = Daily consumption of herbal product, and *CC* is the concentration of the residue in the herb sample. If EDI is lower than ADI, it considers that the consumption is safe. On the other hand, if EDI is higher than ADI then it considers that the consumption has a potential problem.The second method is compared with Minimal Risk Level (MRL) formulated by EU pesticides databaseto evaluate the chronic effects. MRLs are generally based on the most sensitive substance-induced end point considered to be of relevance to humans. Serious health effects such as irreparable damage to the liver or kidneys, or birth defects are not

used as a basis for establishing MRLs, thus exposure to a level above the MRL does not mean that adverse health effects will occur.

3. RESULTS AND DISCUSSION

Table 1. Dosage as prescribed by manufacturers

			Adult Dosage/Daily		
Sample code	**Sample**	**Recommended dosage**	**ml**	**Mg**	**kg**
1	Manoll Herbal Health Tonic	15mls twice daily	30	30	0.00003
2	Oroki Herbal Mixture	4 tablespoonful twice daily	120	120	0.00012
3	Goko Cleanser	3 table spoonful 3 times daily	90	90	0.00009
4	Ruzu Herbal	2-4 tablespoon twice daily	40	40	0.00004
5	Marathon Extra Bitters	Half glass cup twice daily	120	120	0.00012
6	Yoyo Cleanser Bitters	3 tablespoonful once a day	45	45	0.000045
7	Asheitu Adams Bitter	1-3 tablespoon once a day	30	30	0.00003
8	Extrammune Herbal Syrup	10mls twice daily	20	20	0.00002
9	Ciklavit	2 tablespoon twice daily	40	40	0.00004
10	Ocigastro Herbal	2 tablespoonful twice daily	60	60	0.00006
11	Sakaku Herbal Cleanser	4 tablespoon once a day	40	40	0.00004
12	Supreme Blood Disease Herbal Mixture	3 tablespoonful three times daily	135	135	0.000135
13	Ozigar Herbal Mixture	2 tablespoonful twice daily	60	60	0.00006
14	Phd Herbal Pile Mixture	4 table spoonful 2 times daily	120	120	0.00012
	Solid				
15	Ginkgo	1 capsule daily		397.2	0.000397
16	M2-Tone Herbal Tablets	2 tablets x 2		629.7	0.002519
17	Jobelyn	1 capsule daily		353.3	0.000353
18	FIJK FLUSHER 10mg	2 capsules x 2		421.3	0.00168
19	Herbrise	2 capsules x 2		523	0.0020
20	Healthy Hour Super Herb Slimming Tea	1 teabag daily		2722	0.0027
21	Bee & Cee Capsule	3 capsules x 2		435.4	0.00087
22	Supa Flusher Herbal Capsule	2 capsules x 2		462.3	0.00092
23	Afritoxic Top-Up	2 capsules x 2		505.1	0.0020
24	Dakins Herb	5g (1 teabag) x 2		5000	0.01
25	Tradomed Green Tea	1 teabag x 2		5000	0.01
26	Unilag Pharmacognosy Herbal Products	1 tea bag x 2		3187	0.006374
27	Unilag Slimming Capsule	1 capsule daily		341	0.00341

Table 2. Mean concentration (ppm) of Selected OCPs residues (Liquid samples)

Compounds	1	2	3	4	5	6	7	8	9	10	11	Mean	MRL(mg/kg)
α-BHC	0.08 ±0.06	0.06 ±0.04	0.08 ±0.06	0.05 ±0.04	0.05 ±0.04	0.16 ±0.02	0.07 ±0.05	0.14 ±0.02	0.13 ±0.02	0.08 ±0.05	0.05 ±0.04	0.09 0.04	0.01
β-BHC	0.15 ±0.05	0.06 ±0.08	0.06 ±0.08	0 0	0.1 ±0.14	0.06 ±0.08	0.07 ±0.1	0.15 ±0.05	0.16 ±0.04	0.14 ±0.04	0.06 ±0.08	0.10 0.07	0.01
δ-BHC	0.09 ±0.12	0.09 ±0.13	0 0	0 0	0.09 ±0.13	0.09 ±0.13	0.2 ±0.03	0.19 ±0.03	0.09 ±0.13	0.09 ±0.12	0.2 ±0.02	0.10 0.09	0.01
HCB	0.19 ±0.13	0.15 ±0.21	0.06 ±0.08	0 0	0.09 ±0.13	0.15 ±0.21	0.21 ±0.16	0.14 ±0.2	0.16 ±0.22	0.14 ±0.2	0.15 ±0.21	0.14 0.17	0.01
p,p'-DDD	0.08 ±0.11	0.08 ±0.11	0.23 ±0.09	0 0	0 0	0.15 ±0.21	0.08 ±0.11	0.08 ±0.11	0.23 ±0.09	0.08 ±0.11	0 0	0.11 0.09	0.05
p,p'-DDE	0.06 ±0.08	0.17 ±0.08	0.17 ±0.08	0.16 ±0.08	0.16 ±0.08	0.05 ±0.07	0.17 ±0.08	0.16 ±0.08	0.05 ±0.07	0.05 ±0.07	0.16 ±0.08	0.12 0.08	0.05
p,p'-DDT	0.08 ±0.11	0.08 ±0.11	0 0	0.19 ±0.06	0.19 ±0.06	0.19 ±0.06	0.19 ±0.06	0.19 ±0.06	0.19 ±0.06	0.08 ±0.11	0.08 ±0.11	0.14 0.07	0.05
Aldrin	0.21 ±0.3	0.99 ±0.8	0.55 ±0.39	0.42 ±0.25	0.12 ±0.17	0.12 ±0.17	0.21 ±0.3	0.39 ±0.01	0.2 ±0.28	0.21 ±0.29	0.13 ±0.18	0.30 0.29	0.01
Endrin	0.35 ±0.49	0.36 ±0.51	0.2 ±0.28	0.12 ±0.17	0.21 ±0.3	0.27 ±0.38	0.6 ±0.2	0.34 ±0.48	0.59 ±0.17	0.35 ±0.49	0.27 ±0.38	0.37 0.34	0.01
Lindane	0.16 ±0.07	0.06 ±0.08	0.06 ±0.08	0.06 ±0.08	0.17 ±0.07	0.06 ±0.08	0.05 ±0.07	0.11 ±0.15	0.15 ±0.07	0.16 ±0.06	0.06 ±0.08	0.11 0.08	0.01
Methoxychlor	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0.1 ±0.14	0.02 0.03	0.01
Heptachlor	0 0	0.67 ±0.94	0 0	0 0	0 0	0.54 ±0.76	0.55 ±0.78	0.45 ±0.63	0.46 ±0.64	0.43 ±0.6	0 0	0.29 0.41	0.01
Heptachlor-epoxide (B)	0.11 ±0.15	0.27 ±0.08	0.27 ±0.08	0.28 ±0.09	0.28 ±0.09	0.27 ±0.08	0.11 ±0.15	0.26 ±0.06	0.28 ±0.09	0.11 ±0.15	0.11 ±0.15	0.20 0.11	0.01
Endosulfan I	0.98 ±0.37	0.37 ±0.52	1.04 ±0.46	1.05 ±0.49	0.99 ±0.39	0.09 ±0.12	0.36 ±0.51	0.96 ±0.37	1.07 ±0.45	0.4 ±0.57	0.05 ±0.07	0.69 0.40	0.500
Endosulfan II	0.45 ±0.64	0.66 ±0.93	0.54 ±0.76	0.54 ±0.76	0.49 ±0.69	0.46 ±0.65	0.45 ±0.63	0 0	0 0	0.43 ±0.61	0.33 ±0.47	0.41 0.57	0.500
Endosulfan sulfate	0.22 ±0.31	0.23 ±0.3	0.23 ±0.3	0 0	0.23 ±0.	0.22 ±0.31	0.15 ±0.2	0.15 ±0.	0.15 ±0.	0.37 ±0.1	0.37 ±0.1	0.21 0.21	0.500

Chlorothalonil	0.19 ±0.26	20 ±0.37	20 ±0.3	0.17 ±0.3	33 0.19 ±0.26	0 ±0.23	1 0.18 ±0.25	21 0.18 ±0.26	21 0 ±0.28	0.19 ±0.23	0.18 ±0.15	0.10 0.26	0.01

Values are represented as mean ± standard deviation (n=2)

Table1 shows the dosage of all the herbal samples as recommended by the manufacturers.
Table 2 presents the mean concentration of selected organochlorine pesticide residues present in liquid herbal medicines. The mean concentrations of hexachloro cyclohexane in the samples are shown. The α-BHC was detected in all the selected liquid samples with concentration ranging from 0.05-0.14mg/kg. The residue of hexachlorocyclohexane isomers revealed that β-BHC was present in all liquid samples except in sample 4, with concentration ranging from ND to 0.17mg/kg and the value is above the EU MRL of 0.01 mg/kg. δ-BHC was detected in all the liquid samples except in sample 3 and 4 with a concentration ranging from 0- 0.19 and value was found above its MRL of 0.01mg/kg. Lindane was also found to be present in all samples with ranged value of (0.05-0.17 mg/kg) and above MRL value of 0.01mg/kg. The presence of these pesticides is an indication sorghum farmer in Nigeria engaged in actively used in the cultivation of crops

Mean concentrations of cyclodiene isomers in liquid samples are also shown in Table 2. Two cyclodienes pesticides (Endrin, endosulfan I) were present in all liquid samples with ranged value of (0.12 – 0.6mg/kg) and (0.05 – 1.07mg/kg) respectively. These values are above their MRL of 0.01 and 0.05 respectively. Heptachlor-epoxide was also found to be present in all liquid samples with concentration values ranging from 0.11 – 0.28mg/kg and value was found above its MRL of 0.01mg/kg. Residue of cyclodiene derivatives revealed Heptachlor and Aldrin, were present in all liquid samples. Their ranged values are heptachlor (ND–0.67 mg/kg), and aldrin (0.12–0.99 mg/kg). The concentrations of heptachlor obtained in this present study were above the MRLs of 0.01 mg/kg.. Aldrin (1.272 mg/kg) had the highest concentration in sample 2. The aldrin residue levels recorded in this study were above the EU-MRls of 0.01 mg/kg. Endosulfan II was detected in all liquid samples except in sample 11 and 12 with concentration ranging from 0.00 – 0.66mg/kg and the value is above its MRL of 0.05mg/kg (Table 2).

Methoxychlor was not detected in the selected liquid samples except in sample 8 and 14. The concentration ranges from 0.1 – 0.16mg/kg and the value is above the EU MRL of 0.01mg/kg. The residue levels of three dichloro diphenyl ethane isomers revealed that p,p'-DDD ranged (0.00–023 mg/kg) and detected in all liquid samples except sample 4 while p, p'-DDE (0.05- 0.17) and p, p'-DDT (0.00-0.19mg/kg) were found present in all liquid samples except sample 3 and were also above the MLR standard limit. The concentrations of dichlorodiphenylethanes from this study were above the EU-MRL of 0.05 mg/kg.

Table 3. Mean Concentration Liquid vs Solid

	Liquid	Solid	Pvalue
a-BHC	0.05692 ± 0.01525	0.08536 ± 0.01301	0.1601
b-BHC	0.07808 ± 0.01887	0.09857 ± 0.01393	0.3816
d-BHC	0.6192 ± 0.4818	0.09857 ± 0.01779	0.2673
HCB	0.05154 ± 0.01561	0.1357 ± 0.02681	0.0104*
p,p'-DDD	0.01115 ± 0.01115	0.1089 ± 0.02134	0.0002***
p,p'-DDE	0.1688 ± 0.06709	0.1146 ± 0.01498	0.4184
p,p'-DDT	0.1369 ± 0.02508	0.1336 ± 0.01633	0.9100
Aldrin	0.2696 ± 0.2113	0.2961 ± 0.06248	0.9019
Endrin	0.08808 ± 0.03610	0.3718 ± 0.05804	0.0002**
Lindane	0.05846 ± 0.01975	0.1039 ± 0.01479	0.0686
Methoxychlor	0.1462 ± 0.01576	0.01643 ± 0.009487	< 0.0001***
Heptachlor	0.2300 ± 0.06620	0.1450 ± 0.04478	0.2863
Heptachlor-epoxide (B)	0.03731 ± 0.01363	0.2057 ± 0.01086	< 0.0001***
Endosulfan I	0.3600 ± 0.05427	0.6668 ± 0.05912	0.0004**
Endosulfan II	1.111 ± 0.2931	0.2029 ± 0.04613	0.0025***
Endosulfan sulfate	0.1108 ± 0.03916	0.1925 ± 0.02470	0.0789
Chlorothalonil	0.2600 ± 0.01557	0.05214 ± 0.01588	< 0.0001***

The results as displayed in table 3 show that 17 OCPs were present in varying concentrations in the twenty-seven herbal products (fourteen liquid and thirteen solid/capsule/tea) commonly sold in Lagos, Southwest Nigeria. Residues of organochlorine pesticides have the peculiar characteristics of relatively high chemical stability and persist in the environment for long periods [32]. The organochlorine pesticides detected include Aldrin, Alpha-BHC, Beta – BHC, Delta- BHC, Dieldrin, Endosulphan, p,p' DDT, Heptachlor, dichloro diphenyl ethane isomers, cyclodiene isomers (Endrin, Endosulfan I, Endosulfan II). In the selected herbal medicines Aldrin (0.99 mg/kg) had the highest concentration in liquid sample 2 and concentration of 2.84mg/kg in solid sample 27. The aldrin residue levels recorded in this study were above the EU-MRL of 0.01 mg/kg. A study by [28] also reported the EDI of Aldrin in fruits from Ghana to be above the ADI, which poses health risk to adult consumers. Previous work by [29] also reported that the estimated daily intakes for Aldrin and Dieldrin exceeded their acceptable daily intake in bean samples from Lagos markets, Nigeria. This poses a significant health risk to consumers.

Aldrin is highly toxic to humans, the target organs being the central nervous system and the liver. Severe cases of both accidental and occupational poisoning and a number of fatalities have been reported [5]. Its primary metabolic product, dieldrin, resists further transformation and is persistent in the environment. Even though the use of aldrin as a pesticide has been abolished, a primary breakdown product, dieldrin, can be persistent and can bioaccumulate. These compounds probably continue to represent a toxicological threat to humans. The

lethal dose of dieldrin is estimated to be approximately 10 mg/kg of body weight per day. The majority of those poisoned by aldrin or dieldrin recover, and irreversible effects have not been reported. Male volunteers exposed to dieldrin doses below 3 µg/kg of body weight per day for 18 months showed no effects on health. The concentration of dieldrin in blood and adipose tissue was found to be proportional to the daily intake [5,31].

Table 3 shows the comparison details between the mean concentrations of liquid samples and solid samples for each organochlorine analyzed in this study. Variety and residue of OCPs in both liquid and solid herbal samples were different. The results shows that about 64% of the organochlorines were higher in solid samples when compared with the liquid samples. These suggest the differences in production or processing method, characteristics and plant species used in formulation were most important in determining uptake. Plant lipid plays the major factor causing differences observed in plant uptake of lipophilic contaminant such as aldrin, dieldrin, heptachlor and heptachlor epoxide [30]. In addition, the soil-plant transfer of persistent organic chemical residues will depend on the physical and chemical characteristics of the soils. In this study, soil organic matter was not investigated. All the factors that might influence will combine in complex ways to control the uptake of chemicals from the soil into the medicinal plants. It cannot be explained in more detail due to the different number of plant combinations in each herbal product. Further studies should be conducted to ascertain the main factors which influence the OCP uptake by different kinds of crops.

Table 4.Estimated Daily Intake (EDI) in mg/kg/day Body weight of Liquid Samples

	1	2	3	4	5	6	7	ADI
a-BHC	4.00X10-08	1.10X10-07	1.20X10-07	3.33X10-08	1.00X10-07	4.13X10-08	6.75X10-08	0.008
b-BHC	7.25X10-08	1.20X10-07	9.00X10-08	0.00X10+00	2.00X10-07	5.25X10-08	7.75X10-08	0.008
d-BHC	4.25X10-08	1.80X10-07	0.00X10+00	0.00X10+00	1.80X10-07	6.38X10-08	4.50X10-08	0.008
HCB	9.50X10-08	3.00X10-07	9.00X10-08	0.00X10+00	1.80X10-07	1.16X10-07	7.75X10-08	0.008
p,p'-DDD	4.00X10-08	1.60X10-07	3.38X10-07	0.00X10+00	0.00X10+00	6.00X10-08	1.13X10-07	0.02
p,p'-DDE	2.75X10-08	3.30X10-07	2.48X10-07	1.07X10-07	3.20X10-07	1.24X10-07	2.50X10-08	0.02
p,p'-DDT	3.75X10-08	1.50X10-07	0.00X10+00	1.23X10-07	3.70X10-07	5.63X10-08	9.50X10-08	0.02
Aldrin	1.05X10-07	1.97X10-06	8.18X10-07	2.77X10-07	2.40X10-07	1.58X10-07	1.03X10-07	0.0001
Endrin	1.75X10-07	1.80X10-07	9.75X10-08	6.00X10-08	1.05X10-07	1.83X10-07	2.95X10-07	0.0002
Lindane	8.00X10-08	1.20X10-07	8.25X10-08	3.67X10-08	3.40X10-07	3.75X10-08	8.00X10-08	0.008
Methoxychlor	0.00X10+00	0.00X10+00	0.00X10+00	0.00X10+00	0.00X10+00	0.00X10+00	0.00X10+00	0.005
Heptachlor	0.00X10+00	1.33X10-06	0.00X10+00	0.00X10+00	0.00X10+00	0.00X10+00	2.23X10-07	0.0001
Heptachlor-epoxide (B)	5.25X10-08	5.40X10-07	4.05X10-07	1.83X10-07	5.50X10-07	1.84X10-07	5.25X10-08	0.0001
Endosulfan I	4.88X10-07	7.40X10-07	1.55X10-06	6.97X10-07	1.97X10-06	7.91X10-07	4.70X10-07	0.006
Endosulfan II	2.25X10-07	1.31X10-06	8.03X10-07	3.57X10-07	9.70X10-07	3.49X10-07	2.05X10-07	0.006

Endosulfan sulfate	1.10X10-07	4.50X10-07	3.38X10-07	0.00X10+00	4.60X10-07	1.13X10-07	1.83X10-07	0.006
Chlorothalonil	9.25X10-08	0.00X10+00	0.00X10+00	1.10X10-07	3.70X10-07	0.00X10+00	9.00X10-08	0.02

The estimated daily intake (EDI) was reported in table 4 for liquid products while table 5 shows the EDI for solid products. Due to higher concentration rate of the liquid base compounds in liquid samples and lesser quantity consumed, they were found to have lower EDI than solid samples. Health risk index was calculated and reported for liquid and solid samples respectively. These values were found to be lower than the acceptable daily intake for all the samples as set by European Union.

Table 5. Estimated Daily Intake (EDI) in mg/kg Body weight/Day of Solid Samples

	11	**12**	**13**	**14**	**15**	**16**	**17**	ADI
a-BHC	6.62X10-05	0.00X10+00	5.88X10-05	1.93X10-04	3.27X10-04	2.84X10-04	0.00X10+00	0.008
b-BHC	0.00X10+00	0.00X10+00	6.62X10-05	4.91X10-04	3.70X10-04	7.94X10-04	0.00X10+00	0.008
d-BHC	1.36X10-04	8.40X10-04	0.00X10+00	5.62X10-04	6.97X10-04	1.02X10-03	3.08X10-04	0.008
HCB	7.44X10-05	0.00X10+00	0.00X10+00	0.00X10+00	3.70X10-04	4.82X10-04	1.54X10-04	0.008
p,p'-DDD	0.00X10+00	3.04X10-04	0.00X10+00	0.00X10+00	0.00X10+00	0.00X10+00	0.00X10+00	0.02
p,p'-DDE	0.00X10+00	3.99X10-04	0.00X10+00	2.67X10-04	1.39X10-04	0.00X10+00	7.98X10-05	0.02
p,p'-DDT	1.82X10-06	1.05X10-05	4.85X10-06	2.39X10-05	8.72X10-06	3.97X10-05	1.27X10-05	0.02
Aldrin	4.96X10-03	0.00X10+00	0.00X10+00	2.11X10-02	2.44X10-02	0.00X10+00	1.09X10-02	0.0001
Endrin	0.00X10+00	0.00X10+00	5.75X10-04	0.00X10+00	5.63X10-04	5.75X10-04	0.00X10+00	0.0002
Lindane	0.00X10+00	0.00X10+00	7.35X10-05	3.51X10-04	4.36X10-04	5.67X10-04	0.00X10+00	0.008
Methoxychlor	2.71X10-04	1.72X10-03	2.41X10-04	1.18X10-03	1.05X10-03	1.91X10-03	5.52X10-04	0.005
Heptachlor	3.64X10-02	1.76X10-01	5.88X10-03	0.00X10+00	1.39X10-01	1.97X10-01	4.65X10-02	0.0001
Heptachlor-epoxide (B)	1.06X10-02	6.72X10-02	0.00X10+00	4.77X10-02	5.58X10-02	0.00X10+00	0.00X10+00	0.0001
Endosulfan I	8.16X10-04	7.35X10-04	1.03X10-04	4.91X10-04	4.13X10-03	5.48X10-03	1.72X10-03	0.006
Endosulfan II	4.41X10-04	5.35X10-03	7.40X10-04	2.95X10-03	2.27X10-03	4.05X10-03	8.71X10-04	0.006
Endosulfan sulfate	2.37X10-04	0.00X10+00	2.11X10-04	0.00X10+00	1.25X10-03	0.00X10+00	0.00X10+00	0.006
Chlorothalonil	9.93X10-07	6.30X10-06	8.83X10-07	4.21X10-06	1.15X10-05	1.52X10-05	4.86X10-06	0.02

HRI for non-carcinogenic effects measures the long-term exposure of the l contaminants present in the herbal preparations. If the HRI value is less than 1, then the exposed consumers are assumed to be safe, and if the HRI value is equal to or higher than 1, it is considered as a level of concern or poses a health risk. The results showed that the HRI values for seventeen (17) organochlorine pesticide residues were all less than 1, suggesting the consumption of these herbal preparations poses no health risk due to these pesticide residues. The non-carcinogenic risk of organochlorine pesticide residues in the herbal

preparations was calculated by the Health Risk Index (HRI), and the results are shown in Table 4 and 5 for liquid and solid herbal medicines respectively. HRI for non-carcinogenic effects measures the long-term exposure of the l contaminants present in the herbal preparations. If the HRI value is less than 1, then the exposed consumers are assumed to be safe, and if the HRI value is equal to or higher than 1, it is considered as a level of concern or poses a health risk.

4. CONCLUSION

Given the increasing significance of herbal plants across various aspects of human life, research on pesticide residue analysis is pivotal for assessing the quality of these raw materials and ensuring food safety for consumers. In this investigation, pesticide residues were detected in all samples analyzed, with a majority exceeding their respective Maximum Residue Limits (MRLs). The presence of organochlorine pesticides above the MRL indicates ongoing use of obsolete banned pesticides in crop cultivation and storage in Nigeria. Consequently, regulatory bodies in Nigeria, including NAFDAC, SON, and NESREA, should intensify efforts to enforce the prohibition of these substances. It is imperative to educate farmers and pesticide users about the hazards associated with using banned pesticides.Although the Estimated Daily Intake (EDI) levels, assessing exposure across all samples, fall below the Acceptable Daily Intake (ADI) for an adult weighing 60kg, the Health Risk Index (HRI) values generally remain below 1, suggesting that immediate long-term exposure concerns for consumers may be minimal. Nonetheless, the detection of banned pesticide residues in these samples remains a significant public health issue. Monitoring and enhancing the processing and preparation of solid herbal medicines is crucial, given their higher mean concentration, EDI, and HRI values. Evaluating the risk associated with pesticide exposure in herbal products is essential to safeguard consumer health. Furthermore, monitoring programs and risk assessment studies should extend to other pesticide residues like organophosphates and carbamates in the analyzed herbal samples.

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