LEVELS OF ORGANOCHLORINE INSECTICIDE RESIDUES IN COWPEA GRAINS AND DRIED YAM CHIPS FROM MARKETS IN ILE-IFE, SOUTHWESTERN NIGERIA: A PRELIMINARY SURVEY

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ABSTRACT

Cowpea grains and dried yam chips obtained from two wholesale markets in Ile-Ife, Nigeria were analysed for their organochlorine insecticides (Aldrin, Dieldrin, Heptachlor, Endrin, Chlordane and Endosulfan) content. The aim of the study was to evaluate the consumption safety status of these food items. Qualitative and quantitative analysis of the insecticides after clean-up on silica gel adsorbent were carried out using Gas Chromatography equipped with Electron Capture Detector (GC-ECD). Organochlorine insecticide residues were detected in all the samples of cowpea and dried yam chips analysed with highest mean concentration of Aldrin (0.580 ± 0.456 mg kg^{-1}) and Heptachlor (0.402 mg kg^{-1} $\pm$ 0.073) measured in dried yam chips and cowpea respectively. The levels of the residues detected in the cowpea grains and dried yam chips were generally above the EU-MRLs, suggesting that the foodstuffs were not safe for human consumption as bioaccumulation of these residues was likely to pose health risks to the consumers.

Keywords: Cowpea, Yam Chips, Organochlorine, Insecticides, Residues

INTRODUCTION

Cowpea (*Vigna unguiculata* L. Walp) and Yam (*Dioscorea* spp) are important major staple food crops in sub-Sahara Africa (Adetiloye *et al*., 2006). The two crops are known to constitute very important food items among the over 250 ethnic groups of Nigeria. Insect pests are major constraints to the production of these crops. Cowpea is severely attacked at every stage of its growth by a myriad of insects that make the use of tolerant varieties and insecticide sprays imperative (Dugje *et al*., 2009). In storage, the crop is attacked by weevils (*Callosobruchus maculatus* Fab.) regarded as the major insect pest on the crop (Singh *et al*., 1990).

In Nigeria and other West African countries, yam is sold either as fresh tuber or as dried chips. To overcome the high perishability due to their high moisture content and the seasonal nature of their production, yams are processed into dried chips and flour, particularly in Benin Republic and Nigeria (Hounhouigan *et al.,* 2003). The thick paste prepared from dried yam chip flour, "Amala", is popular and consumed in the urban areas of Nigeria and Benin (Mestres *et al*., 2004). Insect proliferation in yam chips in storage has been reported to be a major problem by producers, wholesalers and retailers of the product (Mestres *et al.,* 2004) and thus insecticides are used regularly on the chips during storage to prevent infestation of boring insects and weevils which cause considerable damage on the stored produce (Adisa, 1985; Vernier, 1998).

In an attempt to reduce the incidence of insect pests of cowpea in the field and storage and those of dried yam chips, the use of insecticides is usually relied upon. These insecticides are misused, overused or unnecessarily used by farmers and retailers who have very limited or no information about how to apply them or their health implications when present in foodstuffs. Hence, harmful levels of pesticide residues or metabolites are left adsorbed unto the foodstuffs to which they are applied. For example, in Northern Nigeria, about 95 percent of stored cowpea is treated with insecticides and farmers use these insecticides even when they are not required (Lowenberg-DeBoer and Ibro, 2008) while at the wholesale level, traders add pesticides after buying beans before transporting them to market locations (Integrated Regional Information Networks, IRIN, 2008). Yam chips are commonly stored in jute sacks with the application of some insecticides such as actellic, phostoxin or a mixture of lindane and/or kerosene with water (Orkwor *et al.*, 1997).

According to Ogunfowokan *et al.* (2012), of all the various kinds of pesticides used by farmers in Nigeria, Lindane (Gammalin 20EC®) is the most popularly used as aqueous solutions for preventing insect pests of various kinds, and also for formulating other unauthorized pesticides that are locally applied to crops. Others in common use are dichlorodiphenyltrichloroethane (DDT), Dichlorvos, Chlorpyrifos, Endosufan and Aldrin. FAO/WHO (1990) stated that an approximately three million people are poisoned and 220,000 die each year around the world from insecticide poisoning, the majority of which occur in developing countries, although far greater quantities are used in developed countries (Bhanti *et al.*, 2004). The publicity regarding the high level of pesticides in the environment has created a certain apprehension and fear in the public as to the presence of pesticide residues in their daily food (Damalas and Eleftherohorinos, 2001; Armah, 2011; Bempah *et al.*, 2012).

The consumption of contaminated food is an important route of exposure to insecticide residues, and may pose a public health risk (Macintosh *et al.,* 1996). Exposure to pesticide residues through diet is assumed to be five orders of magnitude higher than other exposure routes, such as air and drinking water (Juraske *et al.,* 2009). The indiscriminate use of insecticides in Nigeria has resulted in the occurrence of the residues in biotic and other abiotic compartments (Osibanjo and Bamgbose, 1990; Adeyemi *et al.,* 2008). Several cases of food poisoning after the consumption of meals prepared from cowpea grains and yam flour produced from dried yam chips which are suspected to contain appreciable amount of organochlorine insecticide residues have been reported (Adedoyin *et al.*, 2008; Pesticide News, 2008; Adeleke, 2009).

Limited number of pesticide residues monitoring efforts in the country have revealed the presence of pesticide residues in kolanut (Ivbijaro, 1977); fish (Osibanjo and Bamgbose, 1990; Ogunfowokan *et al.*, 2012); cereals (Osibanjo and Adeyeye, 1995), meat (Osibanjo and Adeyeye, 1997), fruits, vegetables and fresh yam tubers (Adeyeye and Osibanjo, 1999), blood of cocoa farmers and drinking water of farming communities (Sosan *et al.*, 2008), smoked fish (Musa *et al.,* 2010), agricultural soils (Oyekunle *et al.*, 2011); maize samples (Ogar *et al.*, 2011) and beans (*Phaseolus vulgaris* L.) (Ogah *et al.*, 2012). Insecticide residues in food products are not properly monitored in Nigeria with virtually no data available on the levels of insecticide residues in cowpea grains and dried yam chips which constitute an important part of meal of people of Nigeria. There is evidence that this group of chemicals is still being used in agriculture clandestinely under unknown trade names in developing countries such as Nigeria (Fatoki and Awofolu, 2003; Sosan *et al.*, 2008).

This study was designed, as a preliminary survey, to investigate the occurrence and levels of organochlorine insecticide residues in cowpea grains and dried yam chips in selected wholesale markets in Ile-Ife, Osun State, Nigeria. The reliance of a large proportion of the inhabitants of the study area with an estimated population of over 500,000 people (Oyedeji *et al.*, 2011) makes this study important. Thus the aim of the present study was to evaluate the consumption safety status of these food items obtained from the two wholesale massively patronized markets of the study area with respect to their organochlorine insecticide residue levels.

MATERIALS AND METHODS

Sample Collection and Preparation

Ten samples of cowpea grains and ten samples of dried yam chips consisting of five samples each of cowpea grains and dried yam chips were collected from randomly selected wholesale traders in each of the Odo Ogbe Market (Ife Central Local Government Area) and Better Life Market (Ife East Local Government Area) in Osun State, Nigeria. These two markets were chosen because they are the biggest and most patronized markets within the study area. Foreign matters such as grains, pebbles and pod remnants were manually removed from the cowpeas, and both cowpea and yam chip samples were further dried to a constant weight. Each of the samples was thoroughly ground to powdered form using an agate pestle and mortar.

Extraction Procedure

Accurately weighed 20 g portion of each powdered sample selected by coning and quartering method was weighed into a pre-extracted Whatman extraction thimble. Following the method described by Oyekunle *et al.* (2011), the sample extraction was carried out in a Soxhlet extractor for 4 hours using dichloromethane (DCM) as the extracting solvent. The extract was concentrated by distilling-off the solvent (DCM) to about 3 mL using a distillation kit operated at 39-41°C. The concentrated extract was cooled down to room temperature and then concentrated further to about 2 mL under a stream of high purity (99.99%) nitrogen. The reduced extract was then preserved for chromatographic clean up prior to Gas Chromatographic analysis.

Clean-up Experiment

For the clean-up experiment, a column of about 15 cm x 1 cm i.d. was packed with about 5 g activated silica gel prepared in a slurry form in n-hexane. About 0.5 cm^3 of anhydrous sodium sulfate was placed at the top of the column to absorb any water in the sample or the solvent. The column was pre-eluted with 15 mL of n-hexane without the exposure of the sodium sulfate layer to air in order to prevent drying up and breaking of the adsorbent. The reduced extract was turned into the column and allowed to migrate below the sodium sulfate layer. Elution was done with 2 x 10 mL portions of the extracting solvent (DCM). The eluate was then collected, dried with anhydrous sodium sulfate and evaporated to dryness under a stream of analytical grade nitrogen (99.99%).

Gas Chromatographic Analysis

The detection and determination of the insecticide residues were performed by dissolving the sample eluate in 1 mL n-hexane before injecting 1 µL of the 1.0 mL purified extract into the injection port of a Hewlett Packard 5890 Series II Gas Chromatograph equipped with a ^{63}Ni Electron Capture Detector (GC-ECD) and ChemStation software which was used for the identification and integration of peaks of the analytes. The column consisted of a DB-5 fused silica capillary column (30 m length × 0.32 mm i.d. × 0.25 µm film thickness). The column temperature was programmed from 60°C at a rate of 20°C/min to 140°C, held for 1 min, and then continued at a rate of 11°C/min to 280°C, held for 4 min so as to enhance good resolution at different boiling points. The temperatures of the injector and detector were 250°C and 280°C, respectively. The injection was carried out on a splitless injector at 250°C and the purge activation time was 30 s. The carrier gas was Nitrogen at 29.2 cm^3/sec., measured at 150°C. The run time was 23 minutes. Identification of insecticide residues was accomplished using reference standards and relative retention time techniques, while the concentration of the residues was determined by comparing the peak areas of the samples with the corresponding peak areas of the reference standards of known concentrations (Williams, 2011).

Analyte Residues Analyzed

All the samples were analysed for their Aldrin, Dieldrin, Endrin, Heptachlor, Chlordane and Endosulfan content. The average concentration of each insecticide was compared to the European Union (EU) Maximum residue limits (MRLs) database regulation (EU) No. 600/2010. No MRL is yet established for dried yam chips but that of yams was used instead.

Statistical Analysis

Descriptive statistics (mean, range and standard error) were used to analyze the results obtained using SAS version 9.2 software (SAS Institute, 2003).

QUALITY CONTROL MEASURES

Quality control measures adopted to ensure that the analytical procedures used comply strictly with appropriate standards and specifications and also to further ensure that the results obtained are reliable, valid and of high quality include the determinations of percentage recovery and detection limit.

Percent Recovery (%R) Determination

Two samples of pulverized cowpea grains and dried yam chips, each weighing 20 g were chosen. For each foodstuff, one sample was spiked with 10 mg kg^{-1} standard mixture consisting of some of the available organochlorine insecticides of interest. The mixture was thoroughly mixed together to ensure maximum homogenization. The other sample was left unspiked. The two samples were extracted and clean up following the procedures of Oyekunle *et al.* (2011). Using an injection needle, 1.0 μL of the mixture was injected into the GC column for GC-ECD analysis. The recoveries of OCs were determined by comparing the peak areas of the OCs after spiking with those of the unspiked and the percentage recovery (%R) was evaluated based on the expression:

$$\%R = \frac{\text{Peak area of A} - \text{Peak area of A}'}{\text{Peak area of OC in standard}} \times 100$$

where A = OC in spiked sample and A' = OC in unspiked sample.

Determination of Limit of Detection (LOD)
The limits of detection (LOD) were evaluated by the determination of concentrations that gave signals equal to the blank signal plus three standard deviations of the blank based on the empirical and more specific definition described by Miller and Miller (2000) using the relationship:

$$y_C = y_B + 3S_B$$

where y_C= analyte signal equivalent to detection limit; y_B= blank signal; and S_B= standard deviation of the blank. From the value of y_C, the analyte concentration corresponding to the detection limit was evaluated for GC-ECD determination of OCs.

RESULTS AND DISCUSSION

In Table 1, percentage recovery for the insecticides ranged from 89.65% (Dieldrin) to 98.23% (Endrin) in the food sample used while the LOD values were between 0.283 and 1.971 μg/kg for Endosulfan and Aldrin, respectively. Coupled with the LOD values of 0.283, 0.563, 0.925, 0.970, 1.003 and 1.971 μg/kg for Endosulfan, Endrin, Chlordane, Heptachlor, Dieldrin and Aldrin, respectively, the procedures outlined for OCs assessment in this study are adjudged reliable and efficient. A representative chromatogram of the analyzed samples is shown in Figure 1.

Table 1: Percentage Recovery (%R) and Calculated Limits of Detection (LOD) for Some of the Insecticides

Insecticide residue	% R	Calculated LOD (μg/kg)
Heptachlor	93.42±6.43	0.970
Aldrin	94.57±3.95	1.971
Dieldrin	89.65±2.51	1.003
Chlordane	95.75±4.55	0.925
Endosulfan	91.26±5.42	0.283
Endrin	98.23±1.59	0.563

The mean concentration of organochlorine insecticide residues in cowpea grains and dried yam chips from Better Life and Odo-Ogbe markets is presented in Table 2. The mean concentration of residues in cowpea grain samples from Odo Ogbe market ranged from 0.045 mg kg^{-1} ± 0.004 (Dieldrin) to 0.258 mg kg^{-1} ± 0.070 (Heptachlor), while those in samples from Better Life market ranged from 0.068 mg kg^{-1} ± 0.016 (Dieldrin) to 0.546 mg kg^{-1} ± 0.106 (Heptachlor). The most predominant residue in cowpea grains from the two markets was Heptachlor while the least concentration was dieldrin. The relatively high concentration of Heptachlor in cowpea grains sampled from the two markets implied that Heptachlor was an active ingredient in one of the common insecticides applied for cowpea insect control. The high concentration of its residues measured in the food stuff was either a reflection of the past usage which resulted in bioaccumulation or probably arising from the cultivation of the crop on contaminated soils where application of the insecticides were intense. According to ATSDR (2007), the primary exposure of human beings to Heptachlor is through contaminated foods as

Heptachlor is used primarily by farmers to kill termites, ants and soil insects in seed grains and on crops, as well as by exterminators and home owners to kill termites. However, in dry yam chips, the mean concentration of residues detected in samples from Odo-Ogbe market ranged from 0.027 ± 0.004 mg kg^{-1} (Dieldrin) to 0.264 mg kg^{-1} ± 0.038 (Heptachlor) while in Better Life market, the mean concentration ranged from 0.045 ± 0.014 mg kg^{-1} (Dieldrin) to 1.050 ± 0.908 mg kg^{-1} (Aldrin). Thus, the most predominant residues detected in dried yam chips sampled from Odo-Ogbe market was Heptachlor and Aldrin from Better life market. This result further indicated that insecticides containing these two OC compounds are active ingredients of common insecticides likely to have been used in the control of insect pests of yam and dried yam chips.

Table 2: Mean Concentration (mg kg^{-1}) of OC Residues in Cowpea Grains and Dried Yam Chips from Odo- Ogbe and Better Life Markets in Ile-Ife, Nigeria

	Cowpea grains		Dried yam chips	
	Better Life Market (Mean ± SE)	Odo-Ogbe Market (Mean ± SE)	Better Life Market (Mean ± SE)	Odo-Ogbe Market (Mean ± SE)
Aldrin	0.277 ± 0.073 (0.168-0.509)	0.076 ± 0.023 (0.043-0.164)	1.050 ± 0.908 (0.067-4.682)	0.110 ± 0.020 (0.068-0.182)
Dieldrin	0.068 ± 0.016 (0.007-0.098)	0.045 ± 0.004 (0.042-0.059)	0.045 ± 0.014 (ND-0.085)	0.027 ± 0.004 (0.013-0.036)
Heptachlors	0.546 ± 0.106 (0.296-0.759)	0.258 ± 0.070 (0.147-0.446)	0.488 ± 0.107 (0.204-0.57)	0.264 ± 0.038 (0.152-0.348)
Endrins	0.199 ± 0.037 (0.141-0.243)	0.105 ± 0.031 (0.042-0.197)	0.198 ± 0.081 (0.085-0.501)	0.118 ± 0.015 (0.091-0.163)
Chlordanes	0.185 ± 0.064 (0.047-0.364)	0.125 ± 0.060 (0.051-0.309)	0.107 ± 0.017 (0.07-0.122)	0.053 ± 0.008 (0.035-0.057)
Endosulfans	0.264 ± 0.050 (0.105-0.398)	0.191 ± 0.051 (0.09-0.259)	0.427 ± 0.114 (0.27-0.525)	0.263 ± 0.058 (0.175-0.349)

n = 5 for each market
ND = Not detected
SE = Standard error of mean
MRL = Maximum residue level

Table 3 shows mean concentration of insecticide residues detected in cowpea and dried yam chips across the two markets. All the OC insecticide residues measured were detected in most of the samples. Heptachlor was the most predominant residue in all the cowpea samples. It occurred at a mean concentration of 0.402 ± 0.073 mg kg^{-1} and accounted for 34% of the total cyclodiene compounds measured in the cowpea samples. This was followed by Endosulfan with a mean concentration of 0.227 ± 0.029 mg kg^{-1} (20%). In dry yam chips, Aldrin was the most predominant with a mean concentration of 0.580 ± 0.456 mg kg^{-1} (38%) while Heptachlor and Endosulfan were also recorded in the food item with a mean concentration of 0.354 ± 0.049 mg kg^{-1} (23%) and 0.345 ± 0.043 mg kg^{-1} (22%), respectively. The least frequently detected insecticide from the food stuff was Dieldrin with a mean concentration of 0.056 ± 0.073 mg kg^{-1} in cowpea and 0.036 ± 0.007 mg kg^{-1} in yam chips. These accounted for 5% and 2%, respectively of the insecticides measured. The lowest levels of Dieldrin measured in the food stuffs indicated that the Dieldrin residues present could be due to decomposition of Aldrin (ATSDR, 2002).

Table 3: Mean Concentration (mg kg^{-1}) of OC Residues Detected in Cowpea and Dried Yam Chips from Ile-Ife Markets, Nigeria

Pesticide	Cowpea grains (n=10)			Dried yam chips (n=10)		
	Mean ± SE (mg kg^{-1})	Range (mg kg^{-1})	(%)	Mean ± SE (mg kg^{-1})	Range (mg kg^{-1})	(%)
Aldrin	0.177 ± 0.049	0.043 – 0.509	15	0.580 ± 0.456	0.067 – 4.682	38
Dieldrin	0.056 ± 0.009	0.007 – 0.098	05	0.036 ± 0.007	ND – 0.084	02
Heptachlors	0.402 ± 0.073	0.147 – 0.760	34	0.354 ± 0.049	0.151 – 0.606	23
Endrins	0.152 ± 0.022	0.042 – 0.243	13	0.158 ±0.039	0.085 – 0.501	10
Chlordanes	0.154 ± 0.038	0.047 – 0.364	13	0.080 ± 0.012	0.035 – 0.158	05
Endosulfans	0.227 ± 0.029	0.09 – 0.398	20	0.345 ± 0.043	0.175 – 0.572	22

ND = Not detected
SE = Standard error of mean

In Nigeria, Heptachlor is among the insecticides that have been banned and is supposed to have been phased out of agrochemical stores. It is, however, suspected that it is still being sold under different names or labels or added as one of the active ingredients to other insecticides currently in use by Nigerian farmers. Farmers and consumers face immense risks of exposure due to the use of toxic chemicals that are banned or restricted in other countries (Nasr *et al.*, 2007; Adhikari, 2010). For example, Bhuiyan *et al.* (2009) in Bangladesh reported that all Persistent Organic Pollutants (POPs) like DDT and heptachlor import and production had been banned, yet at least five POPs insecticides including DDT and heptachlor are still in use under different names or labels.

Aldrin, being marketed as Aldrin dust and Aldrex 40EC®, is an emulsifiable concentrate which has been used for a long time to control cocoa mirids , termites, locusts, ants and other insect pests. As dust, aldrin is used as soil insecticide for yam beetles, termites and crickets. Yam sets for planting are rolled completely in aldrin dust just before planting. Aldrin rapidly breaks down to Dieldrin in food and other materials in the environment (ATSDR, 2002). The predominance of Aldrin in dried yam chips from Better Life market therefore suggests non-observance of the waiting period or abuse of the insecticide because ordinarily, Dieldrin (a metabolite of Aldrin) was expected to be found as residues. This corroborates the report of Dinham (1993) that the short interval between harvests to market and the likelihood of no testing for pesticide residues in developing countries contributed to frighteningly high residual levels in urban markets. In addition, Better Life market has been known to be a major wholesale market for the dried yam chips from Saki (a town in southwestern Nigeria known for production of yam chips) and other towns within the region. Earlier, Adeyeye and Osibanjo (1999) reported that about 98% of fresh tubers samples from Nigeria market contained aldrin and dieldrin while Adeleke (2009) reported that aldrin was the insecticide commonly used by farmers to preserve dried yam chips in areas where yam flour were produced. Endosulfan which is marketed under various trade names such as Thionex 35EC®, Endocel 35EC®, is a broad spectrum insecticide acting as a contact and stomach poison used for the control of bean aphids and thrips is now commonly used by subsistence farmers in Nigeria as a replacement for lindane, another OC marketed as Gammalin 20 EC®, which has been for a long time a popular household trade name in most agricultural communities of Nigeria.

Table 4 presents the highest Insecticide residues found in the foodstuffs compared with the EU's Maximum Residue Limits (MRLs). The mean concentrations of the residues in both cowpea and dried yam chips were found to be above the MRL for the food stuffs. The level of Heptachlor detected in cowpea was higher than the MRL by a factor of 40 while in yam chips it was higher by a factor of 35. The concentrations of Aldrin in yam chips and cowpea were higher than the EU's MRL by a factor of 29 and 9, respectively. The comparison of the insecticide residues concentration observed from this study with EU-MRLs indicated that all OC residues in all the samples were far above MRL.

Table 4: Highest Insecticide Residues Found in Cowpea Grains and Dried Yam Chips from Ile-Ife Markets compared with EU's Maximum Residue Limits (mg kg^{-1})

Insecticide	**Highest amount found**		**Maximum Residue Limit**	
	Cowpea	Yam chips	Cowpea	Yam chips
Aldrin	0.509	4.682	0.02	0.02
Dieldrin	0.098	0.085	0.02	0.02
Heptachlors	0.760	0.606	0.01	0.01
Endrins	0.243	0.501	0.01	0.01
Chlordanes	0.364	0.158	0.01	0.01
Endosulfans	0.398	0.572	0.05	0.05

The results obtained in this study generally agreed with those reported in Togo by Mawussi *et al.* (2009) and Sonchieu *et al.* (2010) in Northern Cameroun while the Estimated Total Diet Intakes (ETDIs) for Aldrin and Dieldrin in *P. vulgaris* in Lagos, Nigeria have been reported to exceed their maximum permissible intakes (MPIs) by 100% and 17%, respectively (Ogar *et al.*, 2012). In Ghana metropolis, Heptachlor concentrations in tomato fruits were reported to be above the MRL values (Bempah and Donkor, 2011). With the mean levels of OCs in the foodstuffs higher, in most cases, than the recommended EU's MRLs, this study has established the presence of insecticide residues in the food items at levels that should give cause for concern. This is because the foodstuffs might not be safe for human consumption all the time as the continued exposure to sub-lethal quantities of the insecticides for a prolonged period of time may result in chronic illness in humans of which the symptoms are not immediately apparent but manifest later. Hence, there is the need for the stakeholders to educate the marketers of foodstuffs generally on the implications of pesticide residues in food items and the safe methods of insecticide applications to ward off insect pests.

CONCLUSION

This study has provided the preliminary information on the concentration of some OC insecticides in cowpea and dried yam chips in southwestern Nigeria. The study not only confirmed the presence of insecticide residues in the food items but that the levels of the residues from the markets were generally above the EU-MRLs suggesting that the foodstuffs were not safe for human consumption. Thus, there is need for regular and continuous monitoring of pesticide residues especially in food items that form the bulk of daily diet of many Nigerians. As also advocated by Sosan and Akingbohungbe (2009), the effective regulation of pesticides being imported into the country and the strict enforcement of the laws by the regulatory agencies will help in reducing the risks associated with the use of pesticides among the farmers and other users.

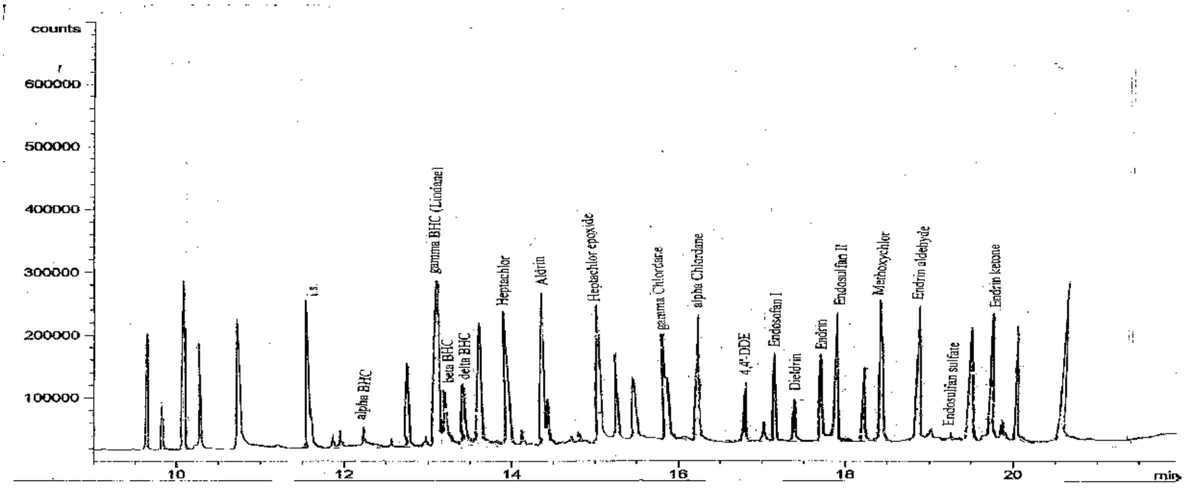

Fig. 1: A Representative Chromatogram of the Analyzed Samples

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