DETERMINATION OF THE AMOUNT OF RESIDUES OF ORGANOCHLORINE PESTICIDES (OCPs) IN SELECTED FRUITS, VEGETABLES AND TUBERS FROM NIGERIAN MARKETS (CASE STUDY OF DELTA NORTH DISTRICT)

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Abstract

Residue levels of organochlorine pesticides have been investigated in selected raw fruits, vegetables and tubers from markets within the Delta North Senatorial District of Delta state, Nigeria, using Varian 3700 Gas Chromatograph equipment with a Nickel-63 electron capture detector. In fruits, mean total – DDT was highest in guava (psidium guajava) while mean aldrin value was highest in banana (Musa sapientum). Total HCH was found to be in highest amount in kola nut (cola nitida). In vegetables, mean total-DDT was highest on green leaf (Amaranthus specie) followed by tomato (Solanum lycopersicum). Aldrin, pp-DDE and total-DDT were all below the detection limit in onion (Allium cepa). In tubers, mean and maximum concentration of total DDT were highest in cassava (minihot esculentus) 40.7 and 120 ug/kg respectively. The average levels were generally low and none were above the FAOs maximum Residue Limits (MRL).

Nigeria witnessed the influx of synthetic pesticides in the 1950s when agricultural activities were at its peak (Northern groundnut pyramid, cocoa in the west and palm production in the Midwest. The term pesticides is an umbrella word which denotes a large variety of compounds of diverse chemical nature and biological activity. They are grouped together on the basis that they are used to kill or eliminate pest. Pesticides are therefore regarded as "killers of pests". Pesticides include: Inseciticides, Herbicides, fungicides, nematicides, rodenticides, mollusicicides, defoliants and Desiccants, Avicides etc. other substances like attractants and repellants are also classed as pesticides. (Adesina 2005). Organochlorine pesticides are insecticides such as DDT, cyclodienes (Aldrin, Dieldrin etc), Hexachlorocylohexane etc. Residues of these organochlorine pesticides are always left in the environment after usage in agricultural production. Their non-biodegradability and persistent nature in the environment makes its availability for plant uptake very possible; giving rise to deposition in man through bioaccumulation and biomagnification (Adesina, 1986). Persistent organochlorine pesticide residues have been found to be carcinogenic, teratogenic and even mutagenic in animals and man (Osibanjo and Adeyeye, 1995).

Today, over 300 different brands are imported as efforts are continuously geared towards boosting agriculture to meet with the demands for food; although no local production of synthetic pesticides have so far been reported. The number of pesticides is likely to increase tremendously in the future because of the high demand for good quality agricultural products and the urgent need for self-sufficiency in food production. Although, it is difficult to obtain data on the exact annual consumption levels of organochlorine pesticides (OCPs), the persistent organochlorine pesticides (OCPs) notably: hexachlorocydorexane (HCH), aldrin, dieldrin and DDT among others are still very much in use for the control of pests of cocoa, cotton, tubers, cereals, fruits and vegetables and in vector control programmes to guarantee food security. (Atuma and Okor, 1985).

The control and monitoring of these OCPs residues in the environment is inevitable and the need is pressing because of their potential toxic and persistent nature. Regular surveys or surveillance studies and monitoring programmes of OCPs residues have been carried out for decades in developed countries such as UK, and Canada (MAFF, 1989), the US (Luke etal, 1988) and in some developing countries such as India (Handa, 1988; Kaphalia etal, 1990) and Tunisia (Driss and Bouguerra, 1987).

In Nigeria, series of research have been carried out on OCPs residues in high (Atuma etal, 1985; Osibanjo and Bamgbose, 1990), in cereals (Osibanyo and Adeyeye, 1995) in meat (Osibanjo and Adeyeye 1997) and few researches in fruits, vegetables and tubers from selected Nigerian markets in South-West Nigeria (Adeyeye and Osibanjo 1999). However, there is paucity of data about amount of OCPs residues in most other foodstuffs such as vegetables, fruits, tubers in Nigerian markets from other parts of Nigeria as research is just being focused into these areas. This paper therefore presents data on the level of OCPs in the commonly consumed fruits, vegetables and tubers from

Nigerian markets in Delta North Senatorial District in continuation of the surveillance programme on OCPs residues in food stuffs in Nigeria. This surveillance study is also important based on the toxicologists assertion that there is need to increase the predictive capability with respect to the assessment of the possible hazards of potentially dangerous chemicals; organochlorine pesticides inclusive. Recent reports have warned on the use of certain agro-chemicals that have been proved to be deleterious to health. For instance, recently, American scientists claim to have discovered a link between the killer Virus HIV and the insecticide/ nematicide Temik (aldicarb). The active ingredient of the insecticide aldicarb can breakdown the immuene system of animals and humans leaving them vulnerable to the AIDs as well as other diseases they may come in contact with. Whereas, temik has been adjudged to be an effective nematicide in addition to possessing growth promoting characteristics (Brown, 1983).

Experimental (Materials and Methods)

Sampling and Sample Preparation

Samples of various fruits, vegetables and tubers were purchased from local markets within the Northern part of Delta State; referred to as Delta North Senatorial district to ensure that they originated from with the area of purchase. Sampling took place twice between October 2012 and April 2013. For fruits and vegetables, each sample was chopped and 500g portion was homogenized, kept in a glass bottle and stored frozen until extraction. Orange juice were squeezed into glass bottles, and stored frozen until analysed. Portions of two units of tubers samples from each location were cut, peeled and homogenized together, 500g portions of such were stored in glass containers for further analysis.

Extraction Procedure

All solvents (hexane, acetone, benzene) were redistilled from analytical grade supplies while sodium sulphate was soxhlet- extracted before use. Solvent and reagent blanks did not show any peak when chromatographed. Fruits and vegetables were extracted in duplicate using the procedure of Sissons etal (1968) as described for hexane soluble insecticides in vegetables (Sissons and Tellings, (1970). A twenty-five (25) gram sample was macerated with 25cm^3 of acetone and 100cm^3 of hexane for three (3) minutes. The upper layer was washed in a separating funnel successively with 1 x 200cm^3 and 2 x 100cm^3 portions of 2% sodium tetraoxosuphate solutions, 75cm^3 of hexane layer was dried (with analydroum sodium tetraoxosulphate (vi)) and concentrated to 5cm^3, ready for clean-up. Clean up was by the tetraoxosulphate (vi) acid method according to UNEP /FAO/IAEA (1986).

The method of Lee (1968) was adopted for tuber extraction five (5) grams of the prepared samples was macerated with 30cm^3 of a- cetone and 56g of anhydrous sodium tetraoxosulphate (vi) for 3 minutes, followed by maceration with (2 x 30cm^3) hexane for 3 minutes. The organic phase was decanted together into a separating funnel, washed

with (2 x 100cm^3) 2% sodium tetraoxosuphate (vi) and concentrated to 5cm^3 in a rotary evaporator, 1.0cm^3 of an aliquot of the extract was cleaned using 1.0g of 5% deactivated silica gel (previously activated over night at 300^{0}C) packed in a 7-mm i.d microcolumn (ASTM, 1979) and washed with 10cm^3 of hexane. Eluting solvents were 20cm^3 of hexane (fraction A) followed by 20cm^3 of benzene/ hexane (15:85) (fraction B).
Each fraction was concentrated to 0.5cm^3 in a stream of nitrogen before being chromatographed.

Quantification

Analysis was carried out on a varian 3700 gas chromatograph equipped with a Nickel -63 electron capture detector, using a glass column (200 x 2mm i.d) packed with 1.5% OV -17/ 1.95% OV-210 on chromosorb WHP (80/100mesh). Column, injector and detector temperatures were 190,220 and 270^{0}C, respectively, with nitrogen as carrier gas flowing at 30cm^3 per minute.

Identification of compounds was by comparing their retention times to those of known standards from sulpelco, U.S.A. Peak identities were confirmed by running the samples and standards on a second column of 3% QF-1/3% SE-30, under the same conditions as the first. Organochlorine residues reported were those detected on the two columns. Fractionation separated DDE (in fraction A) from dieldrin (in fraction B) both otherwise difficult to separates on OV – 17/ OV -210 column. Recoveries from fortified samples were greater than 95% for all pesticides under study, except aldrin with 30%. Detection limits (μg/kg) were 1.0 for all pesticides except heptachlor epoxide (2.0) and dieldrin (4.0)

Results and Discussion

Table 1 gives the scientific (botanical), English and Nigeria (Ibo) names and the incidence of OCPs residues in the fruits, vegetables and tuber samples analysed.

Table 1 Names of samples and incidence of organochlorine residues in fruits, vegetables and tubers from Nigerian markets.

Fruits

Scientific Name	English Name	Nigerian Name (Ibo)	No of Samples	% with one or more residue
Ananas Sativus	Pineapple	Aku-olu	10	100
Psidium guajava	Guava	Gova	10	100
Citrus sinensis	Sweet orange	Oloma	10	82

Musa sapientum	Bananna	Ogede	10	73
Musa Paradisiaca	Plantain	Ogedejioko	10	91
Cola nitida	Kola nut	Oji	10	100
Garania kola	Bitter kola	Adu	10	100

Vegetables

Scientific Name	**English Name**	**Nigerian Name (Ibo)**	**No of Samples**	**% with one or more residue**
Capsicum frutescens	Redpepper	Osenpkiri	10	86
Allium cepa	Onion	Yabasi	10	70
Talinum triangulare	Water leaf	Gbologi	10	100
Capsicum frutescens	Red pepper	Ose Oyibo	10	89
Solannum lypersicum	Tomato	Tomanto Nkpulu	10	100
Hibiscus esculentus	Okro	Okuru	10	100
Cucurbita maxima	Pumpkinleaf	Ugu	10	87
Amaranthus specie	Green	Grini	10	92

Tubers

Scientific Name	**English Name**	**Nigerian Name (Ibo)**	**No of Samples**	**% with one or more residue**
Diascorea rotundata	White yam	Jiocha	10	55
Colocasia esculentus	Cocoyam	Ede, akasi	10	54
Impomea batatas	Sweetpotato	Nduku	10	60

Mamhot esculentus	Cassava	Mba Akpu	10	72

Table 2 Mean and Range of organochorine residues in fruits from Nigerian markets (µg/kg fresh weight)

Species	**HCB**	**Lindane**	**Total HCH**	**Aldrin**	**pp-DDE**	**Total DDT**
Ananas satirus	BDL	1.8 (1.3-2.7)[a]	2.4 (1.4-4.5)	1.6 (1.2-4.0)	2.1 (1.0-3.2)	2.0 (2.0-4.6)
Psidium guajava	BDL -	3.5 (1.4-5.6)	4.2 (1.6-8.9)	1.5 (1.5-2.0)	2.9 (2.0-4.5)	20.1 (5.0-40.5)
Citrus sinensis	1.3 (1.2-1.7)[a]	1.4 (1.2-2.2)	1.7 (1.3-3.5)	1.5 (1.4-1.9)	1.2 (1.0-1.4)	5.4 (1.0-8.5)
Musa sapientum	BDL -	2.5 (1.2-17.0)	6.3 (1.5-20.1)	2.4 (1.4-10.5)	1.8 (1.0-2.9)	3.4 (2.0-5.6)
Musa paradisiaca	1.2 (1.2-1.5)	1.4 (1.2-2.3)	2.2 (1.3-3.4)	1.6 (1.5-4.5)	2.1 (1.0-3.0)	2.0 (1.0-4.0)
Cola nitida	1.4 (1.1-6.0)	110.4 (10.2-126)	125.5 (25-130)	BDL -	2.9 (1.5-3.9)	14.2 (2.5-17.5)
Garcinia kola	1.5 (1.2-1.7)	5.0 (2.0-9.8)	5.0 2.1-10.5)	BDL -	BDL -	BDL -
Overall mean	1.35	18.00	21.04	1.72	2.17	7.85

Note; a Range in bracket; BDL = below detection limit, total HCH = addition of all HCH isomers; Total DDT= addition of all DDT isomers)

Mean total – DDT was highest in guava (*Psidium guajava*) while mean aldrin value was highest in banana. Also, total – HCH was found to be in highest concentration in kola nut (cola nitida) followed by Lindane. The DDTs were below the detection limit in bitter kola (*Garcinia kola*) and aldrin in kolanut (*cola nitida*) while endosulphan was below the detection limit in all fruit samples.

Table 3 Shows the mean and range of organochlorine residues in vegetables from Nigerian markets.

Table 3: mean and range of organochlorine residues in selected vegetables from Nigerian markets (µg/kg fresh weight).

Species	HCB	Lundane	Total HCH	Aldrin	pp-DDE	Total DDT
Capsicium frutescens	1.4 (1.2-1.6)[a]	1.6 (1.2-5.0)	3.5 (1.5-6.5)	1.6 (1.5-2.5)	7.5 (1.5-20.0)	20.5 (4.5-30.0)
Allium cepa	BDL -	1.3 (1.0-2.5)	7.0 (1.5-18.0)	BDL -	BDL -	BDL -
Talinus triangulare	1.3 (1.2-1.5)[a]	2.0 (1.5-4.0)	3.0 (1.5-7.5)	1.6 (1.5-2.0)	1.3 (1.0-1.8)	13.5 (1.5-32.0)
Capasicum frutescens	1.5 (1.0-1.5)[a]	1.4 (1.5-5.0)	3.0 (1.0-4.5)	1.5 (1.2-2.5)	7.0 1.5-18.0)	18.5 4.0-19.5)
Solannum lycopersicum	3.0 (1.5-10.0)[a]	1.5 1.0-4.5)	3.0 (1.0- 6.5)	1.5 (1.0-3.0)	5.0 (2.0-12.1)	70.1 (10-100)
Hibiscus esculentus	1.6 (1.2-2.5)[a]	2.5 1.5-3.0)	4.5 (1.5-9.5)	1.6 (1.5-1.8)	1.2 (1.0-1.5)	6.0 2.0-8.0)
Cucurbita maxima	BDL -	2.0 (1.6-4.5)	2.5 (1.5-10.5)	1.5 (1.5-2.0)	1.5 (1.0-1.9)	18.0 (2.0-25.0)
Amaranthus specie	1.5 (1.0-2.5)[a]	2.5 1.5-3.9)	2.2 (1.0-8.0)	5.5 (1.5-8.5)	3.5 (1.5-12.5)	72.2 (5.0-120)
Over means	1.72	1.85	3.59	2.11	3.89	31.26

Note: 'a' Range in brackets; BDL = below detection limit; Total HCH= addition of all HCH Isomers;
Total – DDT = addition of all DDT Isomers.

In the vegetables (Table 3.0), the mean total-DDT was highest in green leaf (*Amaranthus specie*) followed by tomato (*Solanum lycopersicum)*, Aldrin, pp-DDE and total-DDT were all below the detection limit in Onion (*Allium cepa*). On the whole, the overall mean for total-DDT level was higher than the other parameters analysed in all the vegetables, but the overall mean value for total-HCH was lower in vegetables than in the fruits.

The results of the analysis for OCPs in tubers are presented in table 4

Table 4: mean and range of organochlorine residues in selected tubers from Nigerian markets (µg/kg fresh weight).

Species	Total-HCH	Aldrin	Dieldrin	pp-DDE	Total DDT
Dioscorea rotundata	15.0 (10-40)[a]	4.0 (2.0-9.0)	23.0 (12-62)	11.5 (4-30)	26.1 (5-15)
Colocasia esculentus	18.1 (5.0 -58)[a]	9.5 (3.1-105)	50.2 (0.5-60)	16.2 (105-22)	19.5 (10-25)
Impomea batatas	12.1 (5.0 -25)[a]	4.0 (3.0-7.5)	15 (10.5-35)	BDL -	BDL -
Manihot esculentus	10.5 (5.5-25)[a]	4.5 (3.0-15)	31 (6.5-70)	20.5 (5.5-25)	40.7 (15-120)
Overall average mean	13.93	5.50	29.80	16.06	28.77

Note: a= Range in bracket; BDL = below detection limits; total-HCH = addition of all HCH isomers, Total-DDT = addition of all DDT isomers.

Mean and maximum concentrations of total-DDT were highest in cassava *manihot esculentus*) (40.7 and 120 µg/kg, respectively), total –HCH was highest in cocoyam (*colocasia esculentus*) and lowest in cassava, and dieldrin was highest in cocoyam and lowest in sweet potato.-Dieldrin had the highest mean value (29.80µg/kg) followed by total-DDT and aldrin the least (5.50µg/kg). Analytes below the detection limits in all the samples were HCB, heptachlor eposide, pp-DDE, DDTs and endosulphan. Most aldrin in the tubers analysed were found to had been metabolished to dieldrin, as was DDT to DDE, the more stable metabolite in each case. This is an indication of less recent exposure of cultivatable lands to new sources of the pesticides. Accumulation may be traceable to indirect sources or from historical use.

Samples collected from Asaba metropolis had high lindane, DDT, aldrin/ dieldrin and total HCH values than others in white yam. This may be attributed to the source of the yam (Benue state) where inorganic fertilizers, herbicides/pesticides are used to boost agricultural production. Samples from Agbor and environs had similarly high values of Lindane, DDT, aldrin, total-HCH due also to their dependence in fertilizer, herbicides etc to boost agricultural production in the area hence are commonly referred to as food basket of Delta State. The high values found in samples collected from Kwale and environs indicates the availability of persistent organic pollutants in the soil due to crude oil exploration, land and water pollution that is common in the area.

Table 5.0 compares the highest residue levels in the samples under investigation with the FAOs maximum residue limits (MRL) FAO/WHO, 1986).

Table 5 Highest pesticide residue found in fruits, vegetables and tubers from Nigerian markets compared with FAOs maximum residue limits (µg/kg).

Pesticide	**Highest amount found**			**Maximum residue Limit**		
	Fruits	**Vegetables**	**Tubers**	**Fruits**	**Vegetables**	**Tubers**
Lindane	120.0	5.00	BDL	500	2000	200
Total DDT	40.5	120.0	120.0	1000	1000	500
Aldrin	10.5	8.50	15.0	50	100	100

Note: a = FAO/WHO, 1986.

The levels were generally low and below the Maximum Residue Limits (MRL) in all the samples analysed. The sample's results reflected also the observable amounts reported by Adeyeye and Osibanjo (1999). The high water and low lipid contents of the samples and the lipophilic nature of the pesticides contribute to their low residue contents. The samples also had less OCPs than cereals, pulses and meat as observed from results obtained from studies on such other food items (Osibanjo and Adeyeye, 1995, 1997). The later foodstuff have less water and greater lipid content than the samples under study, and therefore greater potential to accumulate more OCPs. Nigerian fruits showed mean levels of HCB, total-HCH and aldrin higher than those from the USA (Luke, etal 1988) but much lower or in the same order with those from India Kaphalia, etal; 1990). Similarly in the vegetables, HCB, total HCH and total-DDT were higher than those from the U.S.A, but were about the range of values from several countries reported by GEMS/Food (1988).

Conclusion

In the developed countries, emphasis is on herbicide usage of weed control in agriculture. Furthermore, the use of most of the OCPs have been banned or highly restricted in such countries as Canada, USA, most European countries and Russia since the 1970s (Edwards, 1975), thereby replacing them with the less persistent organophosphates and carbamates. Contrary to these, OCPs are still in use in developing countries such as India and Nigeria for increased food production and disease and pest control in plants and animals for the growing population.

In 1990 for instance, Nigeria, imported 1.65 million tons of insecticides made up mainly of the OCPs (Federal office of Statistics, 1990). Currently, the volume might have increase beyond the level as at 1990 owing to the aggressive governmental approach to food security etc in the transformation agenda of the present administration. Hence, the level of OCPs in food were higher in Nigeria and India than in the U.S.A. The residue levels were higher in Indian foods (Kannan, etal, 1992) compared with most other developing countries.

Recommendation

If the use of OCPs in agriculture and food production cannot be discontinued, then it must be regulated with emphasis on good agricultural practices as any careless mishandling or wrong application could lead to serious deleterious health effects on man and the environment. Efforts must therefore be continued in their future monitoring/surveillance in food and the environment to forestall any serious problem and also to build up a database for future regulatory legislation in the country and vigorous enforcement of available legislations by relevant federal and state agricultural, environmental and food ministries, Departments and Agencies.

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