International Journal of Physical Sciences Vol. 2 (9), pp. 237-241, September, 2007
Available online at http://www.academicjournals.org/IJPS
ISSN 1992 - 1950 © 2007 Academic Journals

Full Length Research Paper

Concentrations of residues from organochlorine pesticide in water and fish from some rivers in Edo State Nigeria

Ize-Iyamu, O.K., Asia, I. O.* and Egwakhide, P. A.[2]

[1]Department of Chemistry, Ambrose Alli University, Ekpoma, Nigeria.
[2]Department of Chemistry, University of Benin, Benin-City, Nigeria.

Accepted 3 July, 2007

The levels of organochlorine pesticide residues in water and fish from some rivers in Edo State were determined. The water samples were extracted with 15% diethyl ether in hexane, the extracts were treated with copper tunings for the elimination of sulphur interference and analyzed using a gas chromatograph fitted with an electron capture detector. In all the water samples analyzed, the organochlorine pesticide residues determined (Lindane, Aldrin, pp-DDE, op-DDD, pp-DDD, op-DDT, and pp-DDT) were present, except in Ikoro River, where the water samples exhibited non-detectable levels of pp-DDE and pp-DDT. The level of pp-DDT, (0.7442 ppb) was highest in Ogba River, followed by Lindane (0.7130 ppb), Aldrin (0.5985ppb). Lindane (0.7928 and 0.5912ppb) was found to be highest in river Ovia and Ikoro respectively followed by Aldrin (0.7731 and 0.4867 ppb). The other organochlorine pesticides were present in varied levels from 0.3097 - 0.4860 ppb in Ogba River; ND-0.3100 ppb in Ikoro River and 0.3019 - 0.5557 ppb in Ovia River. The pesticides residues in fish samples were extracted by Soxhlet extraction process using a mixture of hexane and acetone, the extracts cleaned and analyzed using a gas chromatograph fitted with an electron capture detector. The organochlorine pesticide residues detected in water were also present in the fishes but at higher concentrations. This can be due to OCPs being lipophilic. The concentrations of these OCP residues were more in the bottom to middle feeders (Cts) than in the top to middle feeders (Tzs). Lindane levels (0.063 µg/g); 0.054 and 0.039 µg/g were detected in fish from Ovia, Ogba and Ikoro rivers respectively. While Aldrin was found present in 0.059 and 0.027 µg/g in the bottom and top feeders from Ovia river. However these levels were quite high when compared with the allowable Federal Environmental Protection Agency (FEPA) now Federal Ministry of Environment limits and can be harmful if the trend is not checked.

Key words: organochlorine, pesticide residues, rivers, fishes, safety, water, seafood.

INTRODUCTION

Pesticide is a general classification that includes insecticides, rodenticides, fungicides, herbicides and fumigants. Although pesticides may be selectively toxic to these forms of life, they may still be toxic to man if food contaminated by them is ingested. Pesticides are known to be toxic to man (Ademoroti, 1996). Some of the symptoms of pesticides poisoning include irritation, dizziness, tremor, tonic and chronic convulsion (Winter, 1992). DDT in particular can block potassium influx across the membranes of nerve fibres and causes increase negative after-potentials. DDT also induces the mixed function oxidize system thereby altering the metabolism of xenobiotics and steroid hormones (Ademoroti, 1996).

Organochlorine pesticides are among the first set of pesticides in use and still in use in Nigeria despite their ban in developed countries due to the associated problems of indiscriminate potency and persistency. The chemical stability of these compounds, their high lipid solubility and toxicity to human and animals (Bouwman et al., 1990; Caldas et al., 1999), has led government and researchers to be concerned with their presence in the environment.

Many ignorant farmers, fishermen and some other

*Corresponding author. E-mail: imoasia2000@yahoo.com.

users have abused their use for agricultural and fishing purposes. Being persistent and toxic, they pose serious environmental and health hazards, not only in the areas of applications, but up the food chain as the receiving water body contains other edible zooplanktons apart from fish that ingest these toxic chemicals which reside mostly in the fatty parts of their bodies. Consequently, bioaccumulation and biomagnifications takes place up the food chain; hence the need for proper monitoring. However not much is done in this regard here in Nigeria, as limited data are available (Atuma, 1985; Atuma and Okor 1985; Osibanjo and Adeyeye, 1995). Moreover, there has been no report on OCPs residues in fish from these rivers in Edo State. Fish constitutes a major component of most aquatic habitats; they are important source of food and are also a key unit in many natural food webs. They also share many physiological properties with mammals and are often the primary indicator of the toxification of streams and lakes, hence the need for this research which is focused on ascertaining the levels of OCPs in some common specie of fish in the selected rivers in Edo state where fishing is the predominant occupation of the people and the potential health risk posed to consumers from the exposure to these compounds through the ingestion of fish grown in these rivers. Fishes sold in the major markets especially the popular “Yanga” market are caught from these rivers under study.

MATERIALS AND METHODS

Fishes of different species [Tilapia Zilli, (Tz) and Clarias lazera, (Ct)] and water samples were collected from Ikoro, Ovia and Ogba rivers in the southern part of Edo State.

The samples were refrigerated and extraction done within few days of collection. Composite sampling was carried out for the water samples. The reagents used were n-hexane, acetone, methylene chloride and anhydrous sodium tetraoxosulphate (VI) (analytical grade). The n-hexane and acetone were double distilled in all glass apparatus.

The extraction was carried out following methods from literature; Osibanjo and Adeyeye (1995) and Osibanjo and Tongo (1985) as described by Saleh and Lee (1978) with slight modification. Soxhlet extraction was used for the fish samples, though time consuming, it has the advantages of ease of handling and completeness of solvent recovery.

10 g of each sample and 30 g of anhydrous sodium tetraoxosulphate (VI) was ground into dry powder. The ground sample was put in the thimble of the Soxhlet extractor. Extraction was carried out for 8 h with 135 ml of acetone: hexane mixture (2:1). At the end of the extraction process, the extract was transferred into a round bottom flask connected to a pre-weighed receiver through a Liebig condenser, and concentrated to about 10 ml on a water bath maintained at 90^{o}C. The remaining solvent in the concentrated extract was evaporated using a rotary evaporator. The receiver contained the fat extract, to which 15 ml acetone/hexane mixture was added and the content transferred into a separating funnel, the receiver was rinsed with about 30 ml solvent mixture and poured into the separating funnel. The aqueous and organic layer separated. The aqueous layer in the clean bottle was transferred into the separating funnel for further extraction with 45 ml mixed solvent, this was done twice before discarding the aqueous layer while the organic layer was transferred into 250 ml volumetric flask in each case. The organic layer taken up in the volumetric flask was filtered through anhydrous sodium tetraoxosulphate (VI) layer on glass wool into a rotary flask and then concentrated to 5 ml at 45^{o}C.

The fish extract was cleaned up using 1gm of deactivated silica gel, this was packed in a micro column (7mm id) (ASTM, 1979) and washed with 10 ml hexane. 20 ml of hexane and another 20 ml of 15% methylene chloride in hexane were used to elute solvents. Each fraction/eluent was concentrated to 1 ml in a stream of nitrogen before they were analyzed using the gas chromatograph.

Water samples

The solvents used were n-hexane and diethyl ether. 60 ml of 15% diethyl ether in hexane was introduced into a 2l separating flask containing 1l of the water sample and shaken vigorously for about 2 min and then allowed to stand for about 10 min for complete separation. After separation, the bottom aqueous layer was drained into the original sample bottle while the organic layer filtered into a 250 ml conical flask through an anhydrous sodium tetraoxosulphate (VI) layer that has been prewashed with 15% diethyl ether in hexane. A second extraction was carried out on the aqueous layer (separated from the original/initial sample) with another 60 ml, 15% diethyl ether in hexane and the process repeated. A third extraction was carried out using 60 ml of hexane only and the process repeated. The separating funnel rinsed with 50 ml hexane. The extracts were concentrated to 10 ml with a rotary evaporator at 45^{o}C and low pressure. The 10 ml extracts were further reduced to 1 ml under Nitrogen gas at 50^{o}C, before analysis with the Gas chromatograph (Osibanjo and Adeyeye 1995, 1997). No clean up was done for the water sample. However the extract was treated with copper tunings for the elimination of sulphur interference by adding 10 g of copper tunings that have been previously extracted in hexane for 3 h, until no black copper sulphide was formed. The level of the pesticide residues were determined using the Varian Gas Chromatograph, model 3700 using Electron Capture Detector. The following conditions were maintained. Gas pressure was 60 psi and injector temperature was 220^{o}C, column temperature was 190^{o}C, detector temperature was 270^{o}C, the carrier gas was nitrogen (at 30 ml/min), column length 200 cm, id 2 mm, the glass spiral column packed with 1.5% 0V - 17 and 1.95% 0V-210 on chromosorb WHP 80/100 mesh. There were no peaks when solvents and blanks were chromatographed, before the samples were analyzed under the same condition. Known standards, were also chromatographed, the retention time were used to identify the compounds present in the samples.

RESULTS AND DISCUSSION

Table 1 shows the results obtained from the analyses of the water samples indicating the levels of contamination of the water bodies by organochlorine pesticide (OCPs) while Tables 2 - 4 shows the concentration of organochlorine pesticides residues in fish samples obtained from the three rivers under study.

The samples analyzed contained relatively low concentrations of OCPs residues. The most commonly occurring OCP residues were Lindane, Aldrin, op-DDD, pp-DDD, pp-DDE, op-DDT and pp-DDT in Ogba and Ovia rivers, while pp-DDE, op-DDT and pp-DDT were not detected in Ikoro River. Lindane and Aldrin occurred most frequently in all the samples analyzed, with Lindane and Aldrin having a range of 0.5712 - 0.8143 and 0.5031 - 0.7037 ppb respectively. In Ogba River, pp DDE, op-DDT and

Table 1. Concentration (ppb) of the organochlorine pesticide residues in the water samples analyzed.

River	Sample code	pH	Temp^{0}C	Lindane	Aldrin	pp-DDE	OpDDD	ppDDD	op-DDT	ppDDT
Ogba	R(og)1	6.05	27.0	0.6812	0.5823	0.4634	0.2983	0.3510	0.6739	0.7313
	R(og)2	6.32	26.5	0.7143	0.6113	0.5044	0.3089	0.3281	0.6892	0.7461
	R(og)3	6.15	26.7	0.7436	0.6018	0.4901	0.3218	0.3417	0.7142	0.7553
Mean residues concentration				**0.7130**	**0.5985**	**0.4860**	**0.097**	**0.3403**	**0.6924**	**0.7442**
Ikoro	R(ik)1	7.05	27.0	0.5712	0.4629	ND	0.3005	0.3089	ND	ND
	R(ik)2	7.15	26.5	0.6002	0.5123	ND	0.2883	0.3107	ND	ND
	R(ik)3	6.91	27.0	0.6018	0.4849	ND	0.2910	0.3103	ND	ND
Means residues concentration				**0.5912**	**0.4867**	**ND**	**0.2933**	**0.3100**	**ND**	**ND**
Ovia	R(ov)1	6.09	26.8	0.7648	0.7512	0.3567	0.3110	0.3391	0.4266	0.5417
	R(ov)2	5.98	26.0	0.7992	0.7983	0.3812	0.3067	0.3249	0.4516	0.5652
	R(ov)3	6.36	27.3	0.8143	0.7698	0.3601	0.2879	0.3027	0.4692	0.5602
Means residues concentration				**0.7928**	**0.7731**	**0.3660**	**0.3019**	**0.3222**	**0.4491**	**0.5557**

Table 2. Concentration (µg/g) of the organochlorine pesticide residues in fish samples from Ogba River (mean values).

Pesticides	Tz_1	Tz_2	M	Ct_1	Ct_2	M'
Lindane	0.025	0.022	0.024	0.052	0.056	0.054
Aldrin	0.018	0.020	0.019	0.042	0.045	0.044
pp-DDE	0.014	0.009	0.012	0.023	0.025	0.024
op-DDD	0.006	0.003	0.005	0.010	0.012	0.011
pp-DDD	0.012	0.010	0.011	0.027	0.029	0.028
op-DDT	0.023	0.026	0.024	0.048	0.052	0.050
pp-DDT	0.031	0.035	0.033	0.051	0.056	0.054

Top to middle feeders: Tz = Tilapia zilli; M = mean.
Middle to Bottom feeder-: Ct = Catfish; M' = mean.

Table 3. Concentration (µg/g) of the organochlorine pesticide residues in fish samples from Ovia River (mean values).

Pesticides	Tz_1	Tz_2	M	Ct_1	Ct_2	M'
Lindane	0.030	0.034	0.032	0.063	0.064	0.063
Aldrin	0.023	0.027	0.025	0.057	0.060	0.059
pp-DDE	0.015	0.012	0.014	0.028	0.027	0.027
pp-DDE	0.015	0.012	0.014	0.028	0.027	0.027
op-DDD	0.009	0.007	0.008	0.013	0.018	0.016
pp-DDD	0.011	0.014	0.013	0.030	0.028	0.029
op-DDT	0.028	0.030	0.029	0.051	0.057	0.054
pp-DDT	0.032	0.036	0.034	0.056	0.062	0.059

pp-DDT have ranges of 0.4634 - 0.5044, 0.6739 – 0.7142 and 0.7313 - 0.7553 ppb respectively. While in Ovia River, pp-DDE, op-DDT and pp-DDE have ranges of 0.3567- 0.3918, 0.4266 - 0.4692 and 0.5417-0.5652 ppb respectively.

The highest lindane level of 0.8143 ppb was obtained for sample from river Ovia labeled R(OV). The high contamination might not be unconnected with the extensive use of lindane, which is marketed as Gammalin 20 and used by farmers for agricultural purposes for crop protection and the use by some fishermen in that locality. R(OV) also contained the highest concentration of Aldrin (0.7937 ppb). This could be due to run-offs from farms (agricultural practices) in the locality, as the farmers use

Table 4. Concentration (µg/g) of the organochlorine pesticide residues in fish samples from Ikoro River (mean values).

Pesticides	Tz_1	Tz_2	M	Ct_1	Ct_2	M'
Lindane	0.019	0.013	0.016	0.036	0.041	0.039
Aldrin	0.009	0.014	0.012	0.018	0.022	0.020
pp-DDE	0.002	0.004	0.003	0.005	0.008	0.007
op-DDD	0.008	0.008	0.008	0.014	0.018	0.016
pp-DDD	0.010	0.016	0.013	0.016	0.021	0.019
op-DDT	0.004	0.003	0.004	0.006	0.008	0.007
pp-DDT	0.005	0.002	0.004	0.006	0.009	0.008

Aldrex 40, (where Aldrin is the major component) for crop protection, as there are quite a number of privately owned farms, amongst others under the supervision of the state ministry of agriculture not too far from the river. There is also a wood processing factory few metres away from the river.

Farming is relatively low in Ikoro and nearby villages; the inhabitants are mainly Ijaws, Urhobos (from Delta State of Nigeria), who are predominantly fishermen. The relatively low levels and non-detectable levels of OCPs in Ikoro river might be due to the strict enforcement of the legislation on the ban on indiscriminate use of pesticides for fishing by the council health workers through the village head in that locality.

The OCPs level in Ogba River may be due to the discharge of the municipal water into the river as one of the major underground drainage systems in that part of the State empties into the river few meters from the river source and flows downstream to the village. Fishing and farming activities are relatively low compared with the other two villages.

There are no apparent effect of pH and temperature of the water samples analyzed on the concentration of these residues in the water bodies.

The mean pesticides residue levels obtained for all the samples were higher than those obtained by Osibanjo and Tongo (1985) from the studies carried out for some rivers in Nigeria. In all cases, though, the levels were very low when compared to FEPA allowable limit of <0.01 ppm (FEPA, 1991), there is need to monitor the levels of residues as it may increase with time.

The levels of OPCs residues exhibited in samples collected from the same point at different times were different. For example, the residue levels exhibited by all the pesticide in sample R $(Og)_1$ were different from the levels in $R(Og)_2$ collected from the same point on a different day. This can be observed in all the three rivers studied. These differences in concentration could be due to the fact that when the water is turbulent, there might be mixing tendency compared with when it has low tide. $R(Og)_1$ was collected at low tide, while $R(Og)_2$ was collected of high tide. This difference in concentration of residues exhibited at different times is comparable with studies by some researchers as cited by Osibanjo and Tongo (1985).

The levels of OCPs residues were higher than that obtained in the water samples from the same rivers. This could be attributed to the pesticide being lipophilic; they reside and accumulate in fatty tissues. Pesticides enter fishes not only by ingestion but also through dermal absorption and respiration. When these chemicals are taken in by the fish, they bioaccumulate, biomagnify, and remain in the fish till they are caught and consumed by man or eaten by bigger fishes which are eventually eaten by humans.

It can be seen from the results that samples Tz_1 and Tz_2, are middle to top feeders, they exhibit lower residue levels compared with samples Ct_1 and Ct_2, which are mainly bottom feeders. This could be due to the settlement of the sediments at the bottom of the rivers with time (Kidwell et al., 1995; Gold-Bouchot et al., 1995). The pesticides finally settle in the sediments at the bottom of the river, which is subsequently taken up by the middle to bottom feeders. This agrees with the study reported by Osibanjo and Tongo (1985).

Conclusion

This study shows some degree of contamination of fish in some rivers in Edo State by the OCPs residues. The levels of most of the OCPs in water and fish is on the increase, the continuous use of the contaminated water for drinking and other domestic purposes over a long period of time, and the use of pesticides for fishing by farmers in these areas will definitely lead to a dangerous high concentration of the not easily metabolized chemical in the body. There is serious need for the monitoring of these pesticide residues in water, food and the environment, as this will go a long way towards preventing various environmental and public health hazards, as most of the sea foods in the markets in the southern part of Edo state come from these rivers.

REFERENCES

Ademoroti CMA (1996). Environmental chemistry and Toxicology. Foludex press ltd Ibadan pp. 79–209.

ASTM (1979). The American Society for Testing and Materials, Method D 3086-79. Standard text method for Organochlorine Pesticides in water. Additional clean-up procedure using silica gel.
Atuma S (1985). Residues of Organochlorine Pesticides in some Nigerian food materials. Bull. Environ. Contam. Toxicol. 35: 735–738.
Atuma S, Okor D (1985). Gas chromatographic determination of pentachlorophenol in human blood and urine. Bull. Environ. Contam. Toxicol. 35: 406.
Bouwman H, Coetzee A, Schutte CHJ (1990). Environmental and health implications of DDT-contaminated fish from the Pongolo Flood Plain. J. Afr. Zool. 104: 275-286.
Caldas ED, Coelho RLC, Souza KR, Siba SC (1999). Organochlorine Pesticides in Water, Sediment, and Fish of Paranoá Lake of Brasilia, Brazil Bull. Environ. Contam. Toxicol. 62: 199-206.
FEPA (1991). Guidelines and Standards for Environmental Pollution Control in Nigeria. Lagos p. 35.
Gold-Bouchot G, Silva-Herrera T, Zapata-Peréz O (1995). Organochlorine pesticide residue concentrations in biota and sediments from Rio Palizada, Mexico. Bull. Environ. Contam. Toxicol. 54: 554-561.
Kidwell JM, Phillips LJ, Birchard GF (1995). Comparative analysis of contaminant levels in bottom feeding and predatory fish using the National Contaminant Biomonitoring Program Data. Bull. Environ. Contam. Toxicol. 54: 919-923.
Osibanjo O, Adeyeye A (1997). OCPs residues in foodstuffs of Animal origin in Nigeria. Bull. Environ. Contam. Toxicol. 58: 206–212.
Osibanjo O, Tongo A (1985). Baseline study of levels of OCPs in Nigeria rivers and their sediments.
Osibanjo O.and Adeyeye A. (1995). OCPs residues increase Toxicol. 54(3): 460–465.
Saleh FY, Lee GF (1978). Analytical methodology for kepone in Water and Sediment. Anal. Chem. 49: 316.
Winter C (1992). Dietary pesticide risk assessment. Rev. Environ. Contam. Toxicol. 127: 23-67.