Organochlorine Residues in the Nigeria Environment: A Study on Residues in Adoka Rice Farm, Benue State

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Abstract: ***The use of pesticides containing organochlorine on farmlands is a means of improving agricultural yield, but analysis of pesticide residues is a way to determine the level of human exposure to these chemicals and hence their potential human health hazards. Increased use of pesticides results in contamination of the environment and the excess accumulation of pesticide residues in food products, which has always been a matter of serious concern. Soil samples were collected on the farm land to determine the concentration of organochlorine pesticides. Control samples were collected 5 km away where there was little or no application of organochlorine pesticides. Standard analytical methods were employed for the determination of some physicochemical parameters. Collected samples were analyzed for residues of organochlorine pesticides using GC - MS after careful extraction and cleanup. The results of the physicochemical analysis showed that the mean pH value of soil samples ranged from is 6.2 indicating slight acidity that were within WHO accepted limits. The mean total organic carbon (TOC) value is 14.57%, to while the mean cation exchange capacity (CEC) is 7.85 cmol/kg in soil. The mean Electrical conductivity carbonates content and moisture content also exhibit minimal significance in the soil. DDT was the only OCP detected in this analysis with average concentration of 10.5 mg/kg which is above the EU/WHO MRL of 0.05 mg/kg. Potential source analysis traced the occurrence of high residual levels of DDTs to historical applications. TOC was pointed as a significant variable controlling OCP distribution, and artificial influences possibly contributed to the fate of OCPs in the soils. The OCP contamination levels in the agricultural soils based on national standards are generally considered safe for crop production, but however, pose significant carcinogenic risks to exposed populations based on the calculated results of the ILCR parameters.***

Keywords: Organochlorine, Risk Assessments, Environment, Rice Farm

1. Introduction

Pesticides are chemical agents capable of destroying pests or controlling their growth and reproduction while the term pesticide residues covers a broad variety of compounds formed from chemical degradation or metabolic transformation of pesticides (Aktar*et al*., 2009). Pesticide contamination of waters body can affect aquatic animals and plants, as well as human health when water is used for public consumption (Cerejeira*et al.*, 2003). The increased use of pesticides has resulted in contamination of the environment and also caused many associated long - term effects on human health (Bankar*et al*., 2012). Pesticides have been associated with a wide spectrum of human health hazards, ranging from short - term impacts such as headaches and nausea to chronic impacts like cancer, reproductive harm and endocrine disruption (Bankar *et al.*, 2012).

Pesticide residues in food and crops are a direct result of the application of pesticides to crops growing in the field, and to a lesser extent from pesticide residues remaining in the soil (Puri, 2014). Depending on the chemical structure pesticides residues can be classified as organochlorines organophosphates and, carboxylic acids and their derivatives (Maksymiv, 2015).

This study is aimed at identification and risk assessment of Organochlorine Chlorine pesticide (OCPs) residues and shows the extent of absorption of applied Organochlorine Chlorine pesticide (OCPs) from soil to crop grown, in selected farmlands in Adoka, Otukpo L. G. A, Benue State.

1.1 Significance of the Study

Pesticide residues can cause and have caused damage to health and even death. Therefore the study will help to identify the importance of proper monitoring of applying chemicals used in enhancing agricultural produce and the need for sustainable remediation options and to evaluate the risks associated with the farmlands under study.

2. Materials and Methods

2.1 Study area

The location of sample collection will be Adoka in Otukpo Local Government area in Benue state. Its geographical coordinates are 7° 27' 0"North, 7° 58' 0"East. It is occupied by the Tiv, Idoma and Igede peoples, who speak Tiv, Idoma, and Igede languages respectively.

The occupation of most inhabitants of Adoka and Benue as a whole is mostly farming, so almost all ages engage themselves in farming activities to source for livelihood. Nearby states like Kogi visit the area to purchase food commodity especially on their market day due to cheap and affordable price of food items.

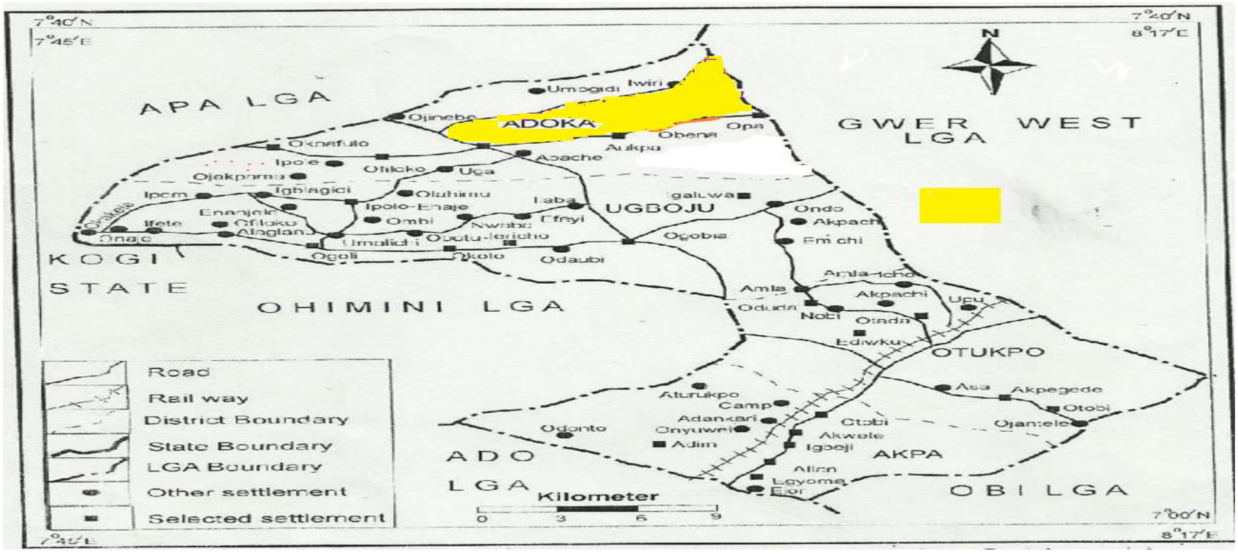

Figure 1: Map showing Adoka in Otukpo local government area of Benue State

2.2 Sample collection and treatment

Soil profile of depth 0 - 20cm was collected because nutrients uptake by plants is usually within this horizon, which is also most prone to surface run - off into water bodies. Five (5) soil samples was collected from different soil profiles, then package in a sterile amber sample collection bottle and transported to Academic Research Laboratory for analysis. The soil samples was air - dried in the laboratory for 2 weeks, picked for obvious non - soil and extraneous materials, ground in agate mortar and sieved through a 2mm mesh. These were stored in black polythene bags prior to analysis.

2.3 Physicochemical Analysis of Sample

The pH of the soil samples was determined by the method of APHA, 2017. The soil cation exchange capacity was determined by AOAC 2016, while the wet oxidation method of Walkley and Black described by Schulte (1934) was used to determine the total organic carbon contents from which organic matter content was calculated. The moisture content was determined by thermo - gravimetric method.

2.4 Extraction of Organochlorine Residues from Soil Sample

All the reagents used were of analytical grade and glass wares used for the study were cleansed as prescribed by Method 1699 of USEPA (2007). Extraction of the soil samples was carried out by the method described by Parveen *et al., (*2007). Ten grams of each sample and 20 g of anhydrous sodium sulphate was grounded into dry powder. The grinded sample was extracted with 150 ml of a mixture of Acetone and n - Hexane (2: 1). After extraction, the extract was transferred into a round bottomed - flask connected to a pre - weighed receiver through a Liebig condenser and concentrated to about 20ml on a water bath maintained between 50^{o}C and 55^{o}C. The remaining solvent in the concentrated extract was evaporated using a rotary evaporator. The almost - dry extracts were cleaned up in a micro - columns.

Two grams of activated silica gel was packed into a chromatographic micro - column of 10 mm internal diameter and approximately 10 cm long. The silica gel was conditioned with 10ml n - Hexane, while the sample extracts were dissolved in 5ml n - Hexane before they were loaded onto the separate micro - column. Elution of each of the sample was done with 50 ml of ethyl - acetate: hexane mixture (9: 1). The eluents were then concentrated on a rotary evaporator at about 45^{o}C and under a gentle stream of nitrogen gas. The almost - dry concentrates were then dissolved in 2ml acetone and were transferred into vials for subsequent injection into the Gas Chromatograph.

2.4 Statistical Analysis

Data obtained were expressed as mean ± standard deviation (SD) and One Way Analysis of Variance (ANOVA) was used to compare obtained means and to test for the significant differences for the physicochemical properties. Values with $P \leq 0.05$ were considered statistically significant.

2.5 Human Health Risk Assessment Model

Human health risk assessment was carried out to estimate the nature and probability of adverse health effects in humans as a result of exposure to OCPs through soil and rice around the vicinity of the study areas. Assessment was carried out for adults, adolescence and children for carcinogenic health risk. The incremental lifetime cancer risk (ILCR) represents the incremental probability that an individual will develop cancer during his lifetime as a result of exposure to a potential chemical carcinogen (Chiang *et al.*, 2009).

Therefore, the ILCR of the three pathways within the scope of the study was calculated using the following equations adapted from the USEPA standard models.

$$ILCR - ingestion = \left(\frac{CS \times CSF \times \sqrt[3]{\frac{\Box\Box}{70}} \times IRsoil \times EF \times ED}{CF \times BW \times AT}\right)$$

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$$\text{ILCR}-\text{dermal} = \left(\frac{CS \times CSF \times \sqrt[3]{\frac{\square\square}{70}} \times SA \times FE \times AF \times ABS \times EF \times ED}{BW \times AT \times CF}\right)$$

$$\text{ILCR}-\text{inhalation} = \left(\frac{CS \times CSF \times \sqrt[3]{\frac{\square\square}{70}} \times IRair \times EF \times ED}{BW \times AT \times PET}\right)$$

where CS is the concentration of the contamination in soil and rice (mg/kg); CSF is the carcinogenic slope factor (1/(mg/kg/d)); BW is the average body weight (kg); IR_{soil} is the ingestion rate of soil (mg/d); EF is the exposure frequency (d/yr); ED is the exposure duration (yr); AT is the average life span (d), SA is the surface area of the skin that contacts the soil (cm^2/d); FE is the fraction of dermal exposure ratio to soil; CF is the conversion factor (106 mg/kg); AF is the skin adherence factor for soil (mg/cm^2); ABS is the dermal absorption factor (chemical specific); IR_{air} is the inhalation rate (m^3/d); and PET is the particle emission factor (m^3/kg). The total risks in different age groups were estimated as the sum of individual risk for the three exposure pathways.

Table 1: Values of the parameters for the estimation of the incremental lifetime cancer risk. (USEPA 2000)

Exposure parameters	Childhood	Adolescence	Adulthood
BW	10	47	60
(IRsoil)	200	100	100
EF*	350	350	350
ED	6	14	30
AT	LT×365	LT×365	LT×365
LT	72	72	72
SA	2800	2800	5700
FE	0.61	0.61	0.61
AF	0.2	0.2	0.07
ABS	0.13	0.13	0.13
IRair	10.9	17.7	17.5
PET	1.36×10^9	1.36×10^9	1.36×10^9

Table 2: The carcinogenic slope factor (1/ (mg/kg/d)) of OCPs through ingestion, dermal contact and inhalation.

OCPs	$CSF_{ingestion}$	CSF_{dermal}	$CSF_{inhalation}$
DDT	3.40E−01	4.86E−01	3.40E−01
Dieldrin	1.60E+01	1.60E+01	1.61E+01
α - HCH	6.30E+00	4.49E+00	6.30E+00
Heptachlor	4.50E+00	6.25E+00	NA

NA= Not Available

3. Results and Discussion

3.1 Physicochemical properties

The results obtained showed that PH values analysed were slightly acidic and slightly basic for different samples being analysed ranging from 5.0± 2.0 to 7.0± 1.0. The moderate acidic soil may tend to have an increased micronutrient solubility and mobility as well as increased heavy metal concentration in the soil (Odu*et al.*, 1985). At low PH, metals are more bioavailable to plants, and hence could pose severe toxicity problems compared to strongly acidic soils (Oluyemi*et al.*, 2008). The PH of the rice samples was relatively neutral, thus recommended for human consumption.

Total organic carbon in the soils under the present study was low to moderate ranging from 6.90±0.31% to 23.80±0.18% in soil samples s shown in Table 4.1. There was no significant variation in the values of percentage T. O. C obtained for all the soil samples analysed. OCPs have the tendency to be absorbed by soil organic matter (SOM) due to their hydrophobicity, and high soil organic matter content provides adequate carbon for soil microbes to facilitate the degradation of OCPs. Consequently, TOC is a clearly significant variable that influences OCP behavior in soil.

Results of CEC shows that soils from the farmland has moderate values of CEC ranging from 5.60±0.13 to 12.0 ± 0.33 cmol/kg. The CEC of the soils greater than 10cmol/kg regarded as being suitable for crop production (FAO, 1976). For soil with lower CEC, it is advisable to increase the clay content of the soil.

Table 3: Physicochemical parameters of soil samples

Soil samples	PH	TOC (%)	CEC (cmol/kg)
Sample A	5.0±2.0	23.80±0.18	8.30±0.62
Sample B	7.0±1.0	19.40±0.19	9.80±0.43
Sample C	6.0±1.0	22.80±0.10	6.10±0.55
Sample D	8.0±1.0	21.30±0.06	7.40±0.23
Sample E	6.0±1.0	10.60±0.55	9.50±0.41

Results presented as mean ± standard deviation of three replicates. No significant difference at p<0.05.

3.2 Concentrations of OCPs in soil and rice samples

Table 4 reveals the total and mean concentration of OCPs analyzed from the soil The concentration of DDT was found to be high in some samples, low in some samples and were not detected at all in some samples. These results were above the EC MRLs (0.05 mg/kg) and FAO/WHO MRLs (0.1 mg/kg)

Table 4: Concentration of OCP residues in soil in mg/kg

Soil Samples	DDT	Endrin
Sample A	1.9	ND
Sample B	ND	ND
Sample C	32.4	ND
Sample D	41.3	ND
Sample E	29.35	ND
Mean	10.5	

3.3 Risk Assessment of OCPs in soils

The ILCR in this study was calculated as a means for interpreting the integrated lifetime risks of exposure to soil - borne OCPs through the pathways of ingesting, dermal contact and inhalation.

The total risk is the sum of all the risk associated with the three exposure pathway.

The risk of concern is associated with the present of DDT in the analyzed sample. The total risk in children is estimated to be 9.114×10^{-3}, in adolescence it is estimated to be 1.700×10^{-2}, while in adults, it is estimated to be 2.760×10^{-2}.

Table 5: Risk values at for different exposure pathways

OCPs	Exposure pathway	Dermal	Inhalation	Ingestion	Total risk
DDT	Child	6.300×10^{-3}	1.197×10^{-11}	2.814×10^{-3}	9.114×10^{-3}
	Adolescence	5.250×10^{-3}	1.617×10^{-10}	1.170×10^{-2}	1.700×10^{-2}
	Adults	6.300×10^{-3}	2.900×10^{-10}	2.130×10^{-2}	2.760×10^{-2}
Endrin	Child	-	-	-	-
	Adolescence	-	-	-	-
	Adults	-	-	-	-

4. Conclusion

The present study has provided the first systemic data on the contamination status of OCPs in agricultural soils in Adoka, Otukpo L. G. A, Benue state. The high detection frequencies of OCPs in soil samples indicated their wide spread in agricultural soil of the study area, with DDTs, being the most dominant OCPs. The residual level of OCPs in the farmland is generally higher than those of corresponding counterparts in the control site. The close relationship between TOC and a part of OCPs indicates that the former is an important factor influencing the persistence of these OCPs in soils. However, there is still a high potential of carcinogenic risk for exposed populations, especially agricultural producers/farmers.

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