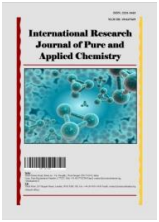

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Risk Assessment of Organochlorine Residues in Agricultural Crops Cultivated [2020] on/around Abandoned Tin Mine Areas in Jos South LGA, Plateau State, Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. Author VND designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript and managed literature searches. Authors MC and PMD managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Aims: To investigate the levels and the associated risks of 18 organochlorine residues in water, soil, sediment, and five vegetables cultivated on abandoned mine areas.
Study Design: Water, sediment, soil (at 0 -10cm, 11 – 20cn, 21 – 30cn) and vegetables samples were collected from the abandoned tin mine agricultural areas. These subsamples were separately combined and mixed so that a portion taken of the composite was representative of each subsample. The representative fractions were then treated for analysis
Place and Duration of Study: Samples were collected between February and May 2020 from the cultivated abandoned mine areas in Du, Jos - South Local Government Area, Plateau State, Nigeria,
Methodology Liquid–liquid extractions methods were used for the extraction of pesticide residues from water, sediment, soil and vegetables. The organochlorine residues were determined by GC/MS.
Results: The physico- chemical properties data obtained for the soils/sediment from abandoned

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mine sites in Jos South were very heterogeneous, hence, various behaviors of pesticide residues in different soil/sediment matrices. There were no significant differences (P= 0.05) in mean minerals among the various samples. The pesticides residues detected in water were b-endosulfan, p,p-DDD and methoxychlor. The residues recorded in water were above the WHO's MRL and Federal Food, Drug and Cosmetic Act (FFDCA,) for drinking water. Residues were also detected in sediment and soils samples. The 11 – 20cm subsoil accumulated the highest levels of the pesticide analyzed. The order of the accumulation of the OCP were; y-BHC>DDD>endrin>endrin ketone>a-endosulfan>b-endosulfan and of the sample type was water<surface soil<21-30cm subsoil<sediment<11-20cm subsoil. The results also showed the presence of OCPs in potato, tomato, cabbage, green beans, and green peppers. y-BHC in potato, tomato and green pepper, endrin in tomato, endrin ketone in potato, tomato and green beans and d-BHC in cabbage had EDI higher levels than ADI and so their HQ greater than 1. The health risks indices (HRI) less than 1 in all other OCP residues were obtained for adults and children that would consume the vegetables except for y-BHC and endrin ketone in potato and tomato, d-BHC in cabbage, d- BHC in green pepper and green beans where the HRI is above 1 that poses health risk**.** There is however no significant difference (P=0.05) among vegetable types. Positive correlation values (0.72, 0.83, 0.71, and 0.56) were observed between endrin and lindane, endrin and heptachlor, endrin and DDT respectively.
Conclusion: The consumption of vegetables that contained y-BHC, d-BHC, endrin and endrin ketone whose EDI and HQ were greater than 1 could pose non-carcinogenic health risks. Adults are likely to have less health risk from consuming these vegetables. The effective monitoring of pesticide residues in food items is required. There is also need to sensitize and educate the general public especially the end-users (farmers) on management practices of pesticides.

Keywords: Risk assessment; Organochlorine residue; Jos South; Abandoned mine; Vegetables.

1. INTRODUCTION

Pesticides are commonly used both in domestic and agricultural production to provide crop protection, boost up the yield in agricultural productivity, improve nutrition in food, its use is assumed an economic, labour-saving, and efficient tool for pest management, despite its adverse effects on ecological environment, human and animal's health [1,2]. Their widespread use combined with over-application, accidental spills, runoff from mixing-loading areas, and faulty waste disposal creates environmental concerns as well as toxic biological [3]. In 1990 when the use of pesticide was not as much in Jos - Plateau as in recent years, [4] 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 [5] Pesticides have been associated with a wide variety of human health hazards, ranging from acute impacts such as headache, vomiting, and diarrhoea to chronic impacts like cancer, reproductive harm, and endocrine disruption [6,7]. Pesticides are poisons produced because they have toxic effects on one pest or the other which are not target specific and may eventually cause diseases which may be chronic to non-target organisms [1, 8].

The dangers regarding the high level of pesticides in the environment have not been properly understood by the majority of farmers in Plateau State, Nigeria, therefore, the continuous indiscriminate use of pesticides especially, on potato, tomato, green beans and cabbage farms to curb the menace of blights and insects on the crops. In ignorance, farmers in the state prefer pesticides with long residual action not knowing that such persist in the environment for long periods without losing their toxicity [7] and the total amount absorbed by a single plant increases with time if the residue is persistent [9]. The use of pesticides can vary from one country to another according to the objectives and the national needs. It is also utmost worthwhile to consider the needs in pesticides of the harvest to be exported which will be subjected to the rules and regulations of the importer country. Thus, appropriate pesticides used correctly on due time can be of much importance to agriculture [10].

Organochlorine pesticides (OCPs) and persistent organic pollutants, are organic compounds that are hazardous and resistant to environmental degradation; hence, they are not easily eliminated from the environment, and they accumulate in environmental media and fatty tissue of living organism and long range transport [8, 11, 12, 13]. OCPs have been extensively used worldwide for several decades, because of their prolonged period of action, low cost and

toxicity against various pests. Although many are banned, several African countries still use OCPs especially for the prevention and control of malaria [13, 14]. The unlawful use of synthetic pesticides leads to sporadic presence of their residues in environment. Thus, it is necessary to re-assure the consumers that food products are free from undesired pesticide residues [1]. The aim of the work is to determine the levels and risks associated with 18 OCP residues in water, sediment, soils at 0 – 10, 11 – 20, 21 – 30 depths and in potato, tomato, green beans, green pepper and cabbage cultivated on or around abandoned mine sites of Jos South L.G.A of Plateau State, Nigeria.

2. MATERIAL AND METHODS

2.1 Study Area

The Jos Plateau lies in the North Central part of Nigeria. It is approximately 104km (65 miles) from North to South, and 80km (50 miles) from East to West covering an area of 8,600km^2. The Southern part of Jos Plateau is in the Benue Lowlands extending towards the River Benue flood plain. Jos Plateau is situated between latitudes 10°11′N and 8°55′N and longitude 8°21′E and 9°30′E.

2.2 Collection of Water, Sediment and Soil Samples

Soil samples from Du in Jos South Local Government Areas of Plateau State were collected from the abandoned tin mine agricultural areas. The agricultural soils were taken in triplicate at three depths (0-10cm, 11-20cm and 21-30cm) using spiral auger of 2.5cm diameter and mixed. The soil samples at each depth were then randomly selected and bulked together to form a composite sample before they were placed in clean labeled plastic bags and transported to the laboratory [15]. The samples were used for pesticide residues analysis. Sediments were collected from streams/ponds in the areas were water samples were collected.

2.2.1 Collection of plants samples

Approximately 1kg of Tomatoes (*Lycopersicon esculentum L*), potatoes (*Solamun tuberosum*), green beans (Phaseolus vulgaris) and green pepper (*Capsicum annuum L. cv. Lady Bell*) each were collected by sampling randomly in minimum of 10 locations on the abandoned sites. For cabbage (*Brassica oleracea* L. Var. Capatuta), a total composite sample of 10 kg were gathered by collecting 1 kg portions randomly from different location on the sites. These subsamples were separately combined and mixed so that a portion taken of the composite was representative of the each subsample.

2.3 Extraction of Pesticide Residues from Water Samples

Liquid–liquid extraction method was used for the extraction of pesticide residue according to the procedure described by [16]. A 50 ml volume of n-hexane was introduced into a 2 liter separating funnel containing 1 liter of filtered water and was shaken manually for 5 min and allowed to settle. After complete separation, the organic phase was drained into a 250 ml conical flask, while the aqueous phase was re-extracted twice with 50 ml of n-hexane. The three extracted organic phases were combined and dried by passing through a glass funnel containing anhydrous sodium sulfate. The organic fraction was concentrated using rotary evaporator [17].

2.3.1 Extraction of soil/sediment samples

Pesticide residues from dried soil/sediment samples were extracted according to [16]. A 10g portion of soil/sediment sample was transferred into an extraction thimble that had been previously washed with n-hexane and acetone and oven dried. The sample was extracted using 150 ml of n-hexane/acetone mixture 4:1 v/v for eight hours (8hrs) using soxhlet extractor. The extract was evaporated to dryness using a rotary evaporator at 40^{o}C. Each extract was dissolved in 10 ml n-hexane and subjected to clean-up procedure.

2.3.2 Extraction of pesticide residue from vegetable samples and analysis

The method used for the extraction of the vegetables was the USEPA method 3510 for extracting pesticide residues in non-fatty crops, using ethyl acetate as the solvent. Sodium hydrogen carbonate ($NaHCO_3$) was used to neutralize any acid that may be present and the vegetable samples were washed thoroughly with distilled water. Twenty grams (20g) of each of the samples was placed in a mortar and anhydrous sodium sulphate (Na_2SO_4) was used to remove water from the sample matrix. After weighing, the samples was washed thoroughly with distilled water and placed in a mortar and ground to a

paste using a pestle. The paste was transferred into a conical flask with the help of a spatula and 40ml of Ethyl acetate will be added and shaken thoroughly. A 5g portion of sodium hydrogen carbonate ($NaHCO_3$) was added to the mixture followed by 20g of anhydrous sodium sulphate (Na_2SO_4) and the entire mixture was shaken vigorously for one hour. This process is to ensure that enough of the pesticide residue dissolved in the ethyl acetate. The procedure was repeated for the samples from each area and the mixture was filtered into a labeled container before being centrifuged at a speed of 1800 rpm for 5mins. The organic layer was decanted into a container and a 1:1 mixture of 5 ml ethyl acetate and cyclohexane was added.

2.3.3 Sample clean-up

Silica gel was activated by heating at 1300C for 16hrs and stored in a desiccator. 5g of silica gel was packed in glass column. 1g of anhydrous Na_2SO_4 was added and the column was conditioned with 20ml n-hexane. Another portion of hexane was poured in the column to elute into a beaker labeled “waste”. The residue of the extraction step of each soil/sediment and vegetable samples were dissolved in 2ml of hexane from the top of the column. Sample vial was rinsed with additional hexane to complete quantitative transfer. Another 10ml of n-Hexane was added to the column and elute to waste. 10ml of (1+1) DCM and hexane were added before the column head dries out, and the eluent collected. The eluent concentrate to approximately 2ml for analysis [17]

2.3.4 GC-MS Determination of Organochlorine Pesticides (OCPs)

OCPs standard, 2000ppm (Catalog Number: M-8080) containing 18 OCPs components was purchased from AccuStandard by CTX- ION ANALYTICS Lagos. Five (5) point serial dilutions calibration standards (0.10, 1.00, 5.00, 10.00, 100.00ppm) were prepared from the stock and used to calibrate the GC-MS. Prior to calibration, the MS was auto-tuned to perfluorotributylamine (PFTBA) using already established criteria to check the abundance of m/z 69, 219, 502 and other instrument optimal & sensitivity conditions. Determination of the levels of OCPs in the sample was carried out using GC-MS by operating MSD in selective ion monitoring (SIM) and Scan mode to ensure low level detection of the target constituents. Agilent 6890A gas chromatograph coupled to 5973C inert mass spectrometer (with triple axis detector) with electron-impact source was used. The stationary phase of separation of the compounds was on HP-5 capillary column coated with 5% Phenyl methyl siloxane (30m length x 0.32mm diameter x 0.25µm film thickness). The carrier gas was helium used at constant flow of 1.2 mL/min at an initial nominal pressure of 026 psi and average velocity of 40.00 cm/sec. 1µL of the samples were injected in splitless mode at an injection temperature of 250 °C. Purge flow to spilt vent was 30.0 mL/min at 0.35 min with a total flow of 31.24 mL/min; gas saver mode was switched off. Oven was initially programmed at 50 °C (1 min) then ramped at 25 °C/min to 100 °C (3 min) and 5 °C/min to 300 °C (5 min). Run time was 51 min with a 3 min solvent delay. The mass spectrometer was operated in electron-impact ionization mode at 70eV with ion source temperature of 230 °C, quadrupole temperature of 150 °C and transfer line temperature of 300 °C. Acquisition of ion was via scan mode (scanning from m/z 50 to 500 amu at 2.0s/scan rate) and selective ion mode (SIM). After calibration, the samples were analyzed and corresponding OCPs concentrations obtained [16, 18, 19, 20].

2.4 Statistical Analysis

Each sample was analyzed in triplicate and the values were then averaged. Statistical analyses of experimental data were performed using the SPSS 23.0 package for Windows. All data were tested for goodness of fit to a normal distribution, using a Kolmogorov–Smirnow one-sample test. Data were log transformed where necessary to achieve homogeneity of variance. Evaluation of significant differences among means was performed using one-way ANOVA followed by Turkey’s post-hoc test, with $p = 0.05$ indicating statistical significance. Pearson product moment correlation coefficients (r) were used to express the associations of quantitative variables.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties of Sediment and Soil Samples

Table 1 presents the summary of the physicochemical properties of soil samples from the study. Sediment and soil pH values obtained in Jos South LGA ranged from 5.89 at JSD3 to 6.36 in JDS. The mean pH of the sediment, topsoil and subsoil were acidic. Soil pH is one of the factors which influences the bio-availability

and transport of pesticides in soils [7]. The EC values in the area were from 0.09dS/m in JSD1 and JSD2 to 0.2dS/m in JSD30. There was however no significant difference (P=0.05) in mean conductivity of soil among the various samples. The organic carbon is lowest (0.60%) in JSD1 and highest at (1.73%) in JSD3. The total carbon contents in the soils were low to medium. The organic matter was highest at JSD3 (2.97%) and lowest at JSD1(1.03%). The nutrient contents order was P>Ca>Mg>K>Na>N. There were no significant differences (P= 0.05) in mean minerals among the various samples. The percentage ranges of sand, clay and silk were 36.56 - 49.56, 28.44 – 37.4 and 22 – 26% respectively being mostly clayed loam. According to the data obtained, the soils are very heterogeneous, hence, various behaviors of pesticide residues in different soil matrices were noticed [21].

3.2 Concentrations OCP Residues in Water, Sediment and at Three Soil Depths

The results on pesticide residues determined in water, sediment and soil samples are summarized in Figure 1.

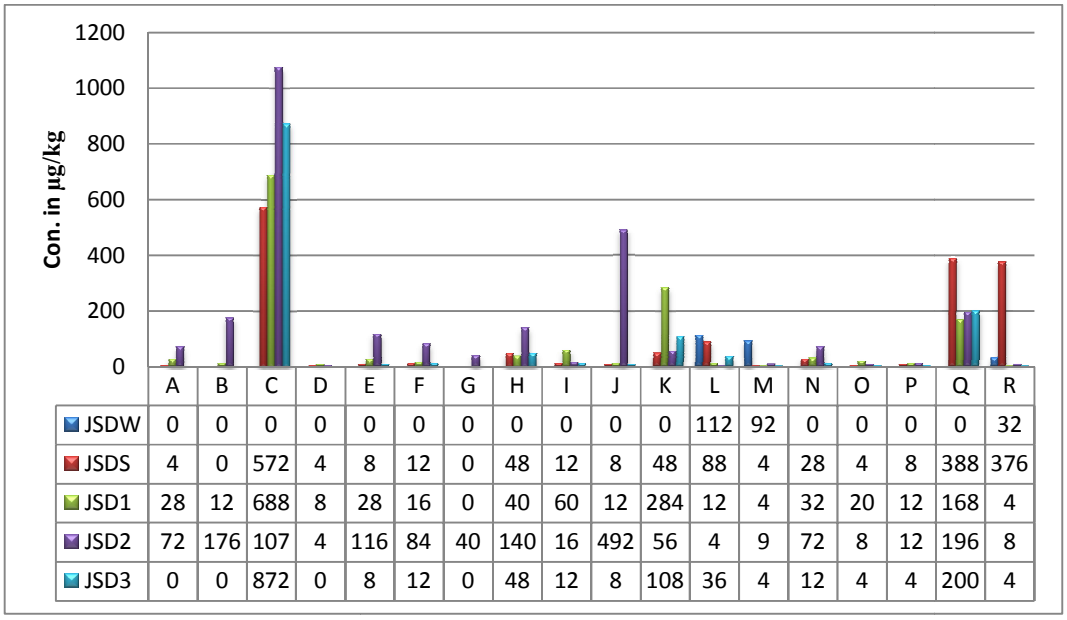
The pesticides residues detected in water were b- endosulfan, p,p-DDD and methoxychlor. The DDD recorded in this study was above the WHO MRL of 2.00µg/l for drinking water. The presence of p,p′-DDD in the water samples confirmed a likely current application by farmers of pesticides that might contain DDT in the study area (probably with different trade names). Also, DDT degrades slowly and persists for long time in the environment from previous contamination. Long-term exposure to low doses of DDT has been shown to affect the endocrine, reproductive systems, immune system and cause cancers. b-endosulfan was higher than the WHO MRL of 0.01µg/l for drinking water. The values of endosulfan detected in the water in this analysis were higher than in the work of [7]. The mean concentrations of a-BHC, b-BHC, y–BHC and d-BHC range between ND and 72µg/kg; ND and 176µg/kg; ND and 1076µg/kg and ND and 8µg/kg respectively with most of the highest values in the subsoil of 11 – 20cm. y – BHC was detected in almost all the locations with higher concentrations than with a– BHC and b- BHC. The presence of lindane in the soil samples may suggest the historical use or illegal use of BHC mixtures in the study area, since lindane has been officially discontinued as restricted chemical for use since 2002 [22]. The mean concentrations of heptachlor and hept- epoxide were from ND– 116µg/kg and ND – 40µg/kg respectively. Also, the highest concentrations were in 11 – 20cm soil. Aldrin and dieldrin presented the range of ND – 84µg/kg and ND - 60µg/kg respectively. The mean concentrations were above the WHO MRL of 0.03µg/g for drinking water and agricultural soils. The higher levels of dieldrin in the samples suggest the degradation of aldrin to dieldrin in the environment. The values obtained in this work were above levels obtained by [10] where aldrin (11.25µg/g) and dieldrin (13.37µg/g) were the most dominant compounds among the organochlorine pesticide in the sediment samples. Aldrin and dieldrin are chlorinated cyclodienes that were widely used in Nigeria. Due to the toxicity of this persistent pesticide which posed an imminent danger to human health, the National Agency for Food and Drug Administration and Control (NAFDAC) in 2008 banned the sale and supply of 30 different agrochemical products in the country which included dieldrin and aldrin but are still in use because of its low cost and affordability. The range for levels of endrin was ND - 284µg/kg, endrin aldehyde was ND – 72µg/kg and endrin ketone ND - 388µg/kg. The levels of a-endosulfan, b-endosulfan and endosulfan sulfate were at the range of ND – 140µg/kg, 4 – 112µg/kg and ND – 12µg/kg accordingly.

The concentrations of a-endosulfan were greater than those of b-endosulfan which suggests recent inputs of fresh technical endosulfan or lack of significant degradation [23]. Endosulfan pesticides are used to spray beans at the flowering stage to prevent insects' attack [24]. The concentrations of endosulfan in this study were higher than [23]. The DDD, DDE and DDT presented the values of 4– 942µg/kg, ND – 492µg/kg, ND – 20µg/kg in that order. The DDD was found to appear in all the samples while the DDE and DDT was found to appear in all but water sample. The concentrations of the degradation products, DDE and DDDs in all the samples points both sediments and soils were more than the parent compound DDT, which indicates past usage of the DDT pesticide. DDT normally degrades under aerobic condition to DDE and under anaerobic condition to DDD, thus a higher DDE + DDD/ DDT ratio is an indication of past usage. DDT, DDD, and DDE have all been classified by NAFDAC as probable human carcinogens [16]. Methoxychlor presented the values range of 4 - 396µg/kg.

The soil and the surface sediment (except b–BHC)t samples indicated all the pesticide residues analyzed. The order of accumulation of some few OCP residues was; y-BHC> DDE>endrin>endrin ketone>a- endosulfan>b-endosulfan and of the sample type was water<surface soil<21-30cm subsoil<sediment<11- 20cm subsoil. The values of the OCP residues in water were far lower than that in sediment. This could be as a result of the hydrophobic characteristic of organochlorine pesticides. It is expected that any organochlorine pesticide present in the study area preferably bind to the particle phase in aquatic system and then accumulated to the sediment through sedimentation process [9]. The 11 – 20cm subsoil accumulated the highest levels of pesticide. This differs with [9] where the highest values of pesticide residues was observed at the depth of 21 – 30cm but was in agreement with their work in that, the lowest concentration of residues was observed at depth of 0-10cm soil samples. All the detected OCP residues were above the WHO MRLs permissive limits[6, 25] (Table 2).

The levels of OCPs in five vegetables from abandoned mine sampling sites were also investigated in this study (Table 2). The ranges of the levels of BHC residues in the vegetables were from; a- BHC, ND 60µgkg; b– BHC, ND – 88µgkg and y- BHC, 4 – 1020µgkg with increasing levels from a–BHC <b – BHC <y–BHC for almost all the vegetables that were analyzed but the d- BHC had more frequency in detection with the exceptionally high concentration (756µgkg) in cabbage. a- BHC and b-BHC were more abundant in potato but y-BHC was more abundant in tomato whereas d-BHC was in cabbage. Heptachlor was detected in all the vegetables with concentrations ranging from 4 -44µg/kg but hept. epoxide was only detected in potato and cabbage with concentrations of 24µgkg and 16µgkg respectively. The levels of aldrin and dieldrin ranges were from 6 - 128µg/kg and 4 – 180µg/kg respectively with tomato accumulating the highest values. a– endosulfan, b–endosulfan, endosulfan sulfate levels ranged from ND – 272 µg/kg, 10 - 88µg/kg and 2–36µg/kg respectively with a– endosulfan, b– endosulfan having the highest values in tomato. Endrin, endrin aldehyde, endrin sulphate and endrin ketone had values ranging from ND–196µg/kg, ND – 300µg/kg, 2 -36µg/kg and ND – 733932µg/kg respectively.

The levels of OCP residues are shown on Table 2.



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
JSDW	0	0	0	0	0	0	0	0	0	0	0	112	92	0	0	0	0	32
JSDS	4	0	572	4	8	12	0	48	12	8	48	88	4	28	4	8	388	376
JSD1	28	12	688	8	28	16	0	40	60	12	284	12	4	32	20	12	168	4
JSD2	72	176	107	4	116	84	40	140	16	492	56	4	9	72	8	12	196	8
JSD3	0	0	872	0	8	12	0	48	12	8	108	36	4	12	4	4	200	4

Fig. 1. OCP residues levels I water, sediment and soil samples at three depths

Key: JSD= Jos South; W=water; S= sediment, Subscript 1 = 0 – 10; 2 = 11 – 20; 3 = 21 – 30, A-a-BHC, B=b-BHC, C=y-BHC, D=d-BHC, E=Heptachlor. F=Aldrin, G=Hept. epoxide, H=a-endosulfan, I=Dieldrin, J=p',p DDE, K=Endrin, L=b-endosulfan, M=p,p' DDD, N=endrin aldehyde, O=p,p'-DDT, P= endosulfan, Q=endrin ketone, R=Methoxychlor

Table 1. The physico – chemical properties of sediment and soils of the abandoned mine sites

Sample code	pH	EC dS/m	OC %	N %	OM %	P ppm	K cMol/kg	Ca cMol/kg	Mg cMol/kg	Na Mol/kg	EA cMol/kg	CEC cMol/kg	PBS %	Clay %	Silt %	Sand %	Textural Class
JSDS	6.36	0.11	0.98	0.049	1.68	14	0.16	1.74	0.54	0.023	1.61	4.07	60.44	28.44	22	49.56	S,C,L
JSD1	6.18	0.09	0.60	0.030	1.03	12	0.16	2.00	0.59	0.027	1.63	4.41	63.04	37.44	26	36.56	C
JSD2	6.15	0.29	1.02	0.051	1.76	18	0.15	1.81	0.57	0.027	1.62	4.18	61.24	36.44	24	38.56	C,L
JSD3	5.89	0.28	1.73	0.086	2.97	32	0.16	1.76	0.55	0.025	1.62	4.12	60.68	30.44	24	45.56	C,L
SD	0.43	0.04	0,10	0.02	0.11	03	0.03	0.55	0.06	0.001	0.34	1.22	12.43	6.60	05	12.04	

Key =JSD= Du, C=Clay, S= Sand. L=Loam Soil, 1=0 – 10, 2= 11 – 20 3 = 21 - 30 cm

Table 2. Mean concentrations in µg/kg (±SD) of pesticide residues in vegetable samples

Pesticide Residue	JSDP	JSDT	JSDCa	JSDGP	JSDGB	TOCPR	*MRL	**MRL	*ADI
a-BHC	60±12	ND	4±2	8±3	ND	72	10	0.02	3
b-BHC	88±13	4±1	4±1	10±	ND	106	10	0.02	3
y-BHC	708±57	1020±106	4±1	484±12	668±54	2884	10	0.02	3
d-BHC	12±3	4±2	756±22	2±0	4±1	778	10	0.02	3
Heptachlor	44±3	4±1	8±3	10±1	4±1	70	10	0.01	0.1
Aldrin	8±5	128±12	4±2	6±1	12±6	158	10	0.01	0.2
Hept. epoxide	24±11	ND	16±4	ND	ND	40	10	0.01	0.1
a -Endosulfan	40±5	272±12	N.D	18±5	36±2	366	10	0.02	6
Dieldrin	72±5	180±13	4±2	14±	12±2	282	10	0.01	0.2
p,p'-DDE	64±3	112±21	4±1	2±0	ND	182	50	0.02	20
Endrin	196±	196±43	ND	50±11	16±4	458	10	0.01	0.2
b Endosulfan	68±12	88±14	60±13	10±3	64±10	290	10	0.02	6
p,p'-DDD	12±3	8±2	68±34	2±0	ND	90	50	0.02	20
Endrin Aldehyde	96±7	300±45	ND	14±1	16±3	426	10	001	0.2
p,p'-DDT	4±0	4±1	20±6	4±2	ND	32	50	0.02	20
Endosulfan Sulfate	36±10	16±5	16±2	2±0	4±0	74	10	0.02	6
Endrin ketone	412±60	733932±134	12±3	158±	496±455	735010	10	0.01	0.2
Methoxychlor	60±13	116±65	328±34	4±1	4±1	512	10	0.02	5

*Sources: *Vincent et al.,(2018).** Federal Food, Drug and Cosmetic Act (FFDCA,2015). JSD = Jos South, P= iris potato, T= tomato, Ca = cabbage, GP=Green pepper, GB= Green Beans, TOCPR = Total OCP residues*

DDD, DDE and DDT level were from ND - 68µg/kg, ND -112µgkg and ND - 20µg/kg in that order indicating aerobic, anaerobic and the likelihood of fresh application of the banned pesticide on cabbage.

Methoxychlor residues were detected in all the vegetables ranging 4µg/kg in green pepper and green beans to 328µg/kg in cabbage. The use of pesticides is determined by the farmers who may tend to apply higher concentrations of pesticides and spray more frequently; therefore, the amount of pesticide residues left on the crop is higher. This in turn is dependent upon pest infestations, prevalence of diseases, and the type of crops grown. Reducing the application dose and the frequency of pesticide use can reduce the residue level [19]. The quantity of pesticides absorbed by a given plant generally depends upon the water solubility of the pesticide, the quantity of pesticide within the soil and the organic matter content of the soil. The total amount absorbed by a single plant increases with time if the residue is persistent. For non-polar pesticides, soil organic matter is the most important soil factor influencing the sorption of residues [19] Most of the OCP residues were above the MRL and the FFDCA limits. The observed levels of the OCP residue above the MRLs in this study might indicate that the farmers did not use the appropriate doses of pesticides and/or sprayed pesticides just before harvesting the crop or during transportation. In this work, 47% highest residue levels were found in tomato, 31% in potato and 17% in cabbage. Tomato tends to accumulate more of the pesticides. Tomato and potato blights in the area of recent forced farmers to use pesticide indiscriminately to try to curb the menace. The differences in the pesticides levels could be attributed to the selective use of the pesticides for the different vegetables. There was however no significant difference (P=0.05) with the levels of pesticides residue investigated among vegetable type.

3.3 Risk Assessment of Associated with OCP in Vegetable

y-BHC in potato, tomato and green pepper, endrin in tomato, endrin ketone in potato, tomato and green beans and d-BHC in cabbage with EDI higher than ADI had their HQ greater than 1 (>1) (Table 3) which indicates high potential health risk through consumption of the vegetables. Conclusively, all pesticides with EDI higher than ADI had their HQ greater than 1 (>1) which indicates high potential health risk through consumption [6]. Hence, the results obtained from this study indicated that, life time consumption of perishable foods like potatoes, tomatoes and green beans from abandoned mine of Jos South LGA of Plateau State, Nigeria could pose some health risk because it has been found that, the HQ greater than 1 (>1). However, the EDI were zero (because their values were negligible) and less than 1 for some OCPs at different sites indicating that no risk would be due to consumption of the vegetables grown on abandoned mine areas.

The health risks and the combined health risks estimated for adults and children for the consumption of vegetables are shown in Table 4 above. The health risks indices (HRI) less than 1 were obtained for adults and children for the consumption of potato, tomato in all other OCP residues except in y-BHC and endrin ketone in potato and tomato, d-BHC in cabbage, d- BHC in green pepper and green beans where the HRI is above 1 that poses less health risk. These results are similar to those obtained by [6] for the consumption of cabbage, lettuce, or onion from Kumasi. Presumably, all populations worldwide are exposed to pesticides. The ubiquitous dispersal of these substances is revealed by data on contamination of food as well as surface, ground, and drinking water [26]. Therefore, pesticide residues in plants may be unavoidable even when pesticides are used in accordance with good agriculture practices. Plant root uptake of persistent residues is a common form of plant contamination. The hazard posed by the pesticide residues in the plant depends on the toxicity of the residue, the ability of the plant to metabolize or eliminate the residue before it is harvested and the translocation of the residue to the harvested portions of the plant. It is therefore important that steps are taken to reduce the levels of pesticide residues on these vegetables [9]. The farmers need to use the appropriate doses of pesticides and restrict the spraying of pesticides just before harvesting the crop or during transportation in order to reduce the level of residues in vegetables [19].

3.3 Correlation Analysis among the OCPs

Positive correlation values (0.72, 0.83, 0.71, and 0.56) were observed between endrin and lindane, endrin and heptachlor, endrin and aldrin, endrin and DDT respectively. This shows active interaction of the pesticides within the samples. The time a pesticide remains in the sample depends on how strongly it is bound by soil components and how readily it is degraded [27].

Table 3. Estimated daily intake (EDI) values in mg/kg/day for adults and children in five vegetable from abandoned mine sites

OCP Residue	EDIPA	EDIPC	EDITA	EDITC	EDICaA	EDICaC	EDIGPA	EDIGPC	EDIGBA	EDIGBC
a-BHC	0.35	0.32	0	0	0.02	0.02	0.05	0.04	0.00	0.00
b-BHC	0.00	0.00	0.02	0.0212	0.02	0.02	0.06	0.05	0.00	0.00
y-BHC	3.84	3.54	5.87	5.406	0.02	0.02	2.78	2.57	3.84	3.54
d-BHC	0.02	0.02	0.02	0.0212	4.35	4.01	0.01	0.01	0.02	0.02
Heptachlor	0.02	0.02	0.02	0.0212	0.05	0.04	0.06	0.05	0.02	0.02
Aldrin	0.07	0.06	0.74	0.6784	0.02	0.02	0.03	0.03	0.07	0.06
Hept. epoxide	0.00	0.00	0	0	0.09	0.08	0.00	0.00	0.00	0.00
a -Endosulfan	0.21	0.19	1.56	1.4416	0	0.00	0.10	0.10	0.21	0.19
Dieldrin	0.07	0.06	1.04	0.954	0.02	0.02	0.08	0.07	0.07	0.06
p,p'-DDE	0.00	0.00	0.64	0.5936	0.02	0.02	0.01	0.01	0.00	0.00
Endrin	0.09	0.08	1.13	1.0388	0	0.00	0.29	0.27	0.09	0.08
b Endosulfan	0.37	0.34	0.51	0.4664	0.35	0.32	0.06	0.05	0.37	0.34
p,p'-DDD	0.00	0.00	0.05	0.0424	0.39	0.36	0.01	0.01	0.00	0.00
Endrin Aldehyde	0.09	0.08	1.73	1.59	0	0.00	0.08	0.07	0.09	0.08
p,p'-DDT	0.00	0.00	0.02	0.0212	0.12	0.11	0.02	0.02	0.00	0.00
Endosulfan Sulfate	0.02	0.02	0.09	0.0848	0.09	0.08	0.01	0.01	0.02	0.02
Endrin ketone	2.85	2.63	4220.11	3889.84	0.07	0.06	0.91	0.84	2.85	2.63
Methoxychlor	0.02	0.02	0.67	0	1.89	1.74	0.02	0.02	0.02	0.02

EDI=Estimated daily intake P= irish potato, T= tomato, Ca = cabbage, GP=Green pepper, GB= Green Beans; A= Adults; C= Children

Table 4. Health Index for OCP residues detected for Adult and Children in five vegetables around abandoned mine sites

OCP Residue	HIPA	HIPC	HITA	HITC	HICaA	HICaC	HIGPA	HIGPC	HIGBA	HIGBC	HICA	HICC
a-BHC	0.12	0.11	0	0	0.01	0.01	0.05	0.04	0.00	0.00	0.14	0.13
b-BHC	0	0.00	0.01	0.007	0.01	0.01	0.06	0.05	0.00	0.00	0.03	0.03
y-BHC	1.28	1.18	1.96	1.80	0.01	0.01	2.78	2.57	1.28	1.18	5.45	5.02
d-BHC	0.008	0.01	0.01	0.01	1.45	1.34	0.01	0.01	0.01	0.01	1.48	1.36
Heptachlor	0.23	0.21	0.01	0.01	0.02	0.01	0.06	0.05	0.01	0.01	0.28	0.26
Aldrin	0.35	0.32	0.25	0.23	0.01	0.01	0.03	0.03	0.02	0.02	0.63	0.58
Hept.epoxide	0	0.00	0.00	0.00	0.03	0.03	0.00	0.00	0.00	0.00	0.03	0.03
a-Endosulfan	0.035	0.03	0.52	0.48	0.00	0	0.10	0.10	0.07	0.06	0.66	0.61
Dieldrin	0.35	0.32	0.35	0.32	0.01	0.01	0.08	0.07	0.02	0.02	0.75	0.69
p,p'-DDE	0	0.00	0.21	0.20	0.01	0.01	0.01	0.01	0.00	0.00	0.23	0.21
Endrin	0.46	0.42	0.38	0.35	0.00	0.00	0.29	0.27	0.03	0.03	0.96	0.89

OCP Residue	HIPA	HIPC	HITA	HITC	HICaA	HICaC	HIGPA	HIGPC	HIGBA	HIGBC	HICA	HICC
b Endosulfan	0.06	0.06	0.17	0.16	0.12	0.11	0.06	0.05	0.12	0.11	0.49	0.45
p,p'-DDD	0	0.00	0.02	0.01	0.13	0.12	0.01	0.01	0.00	0.00	0.15	0.14
Endrin Aldehyde	0.46	0.42	0.58	0.53	0.00	0.00	0.08	0.07	0.03	0.03	1.09	1.01
p,p'-DDT	0	0.00	0.01	0.01	0.04	0.04	0.02	0.02	0.00	0.00	0.05	0.05
Endosulfan Sulfate	0.004	0.00	0.03	0.03	0.03	0.03	0.01	0.01	0.01	0.01	0.08	0.07
Endrin ketone	14.26	13.14	1406.70	1296.61	0.02	0.02	0.91	0.84	0.95	0.88	1422.24	1310.93
Methoxychlor	0.01	0.00	0.22	0.20	0.63	0.58	0.02	0.02	0.01	0.01	0.87	0.80

** HIPA = Health index potato in Adults HIPC = Health index, potato Children HITA = Health index tomato in Adults HITC= Health index tomato in children HIGBA = Health index green beans in Adults HIGBC = Health index green beans in children HIGPA = Health index green pepper in Adults HIGPC = Health index green pepper in children HICaA = Health index cabbage in Adults Health index cabbage in children HICA=combine health index in adults, HICC=combine health index in Children*

4. CONCLUSION

This study showed that the water, sediment, soil and vegetable samples had significant concentrations of the OCP pesticide residue and the pesticide residues were more in 11 – 20cm subsoil. Also, the research showed that the OCP pesticide residue values obtained were generally greater than MRLs. The results showed y-BHC in potato, tomato and green pepper, endrin in tomato, endrin ketone in potato, tomato and green beans and d-BHC in cabbage had estimated daily intake higher than ADI and so their HQ greater than 1. Consumption of these vegetables by adults and children could present non-carcinogenic health risks. Adults are less likely to have health risk from consuming these vegetables. Therefore, the monitoring of pesticide residues in food items is required. There should be proper surveillance and adequate health records of sales agent of these chemicals, farmers that engage in the use of pesticides, and victims of food poison. There is also need to sensitize and educate the general public especially the end-users (farmers) particularly on management practices of pesticides. The carcinogenic risks of the pesticides were not evaluated due to the unavailability of the cancer slope factors of the OCPs residues.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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