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Determination of Organochlorine Pesticides of Soil in Arable Farmland of Joseph Sarwuan Tarka University, Makurdi, Benue State

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ABSTRACT

Six sub-soil samples from portions (A and B) were collected from designated sites in Joseph Sarwuan Tarka University commercial rice plot, analysed for pesticide residues and metabolites using gas chromatography-mass spectrometry. It was found that all detected organochlorine pesticides were lower than the US maximum residue limit of 0.03 mg/kg for agricultural soils. Higher concentrations were found in soil samples A, with Heptachlor, Aldrin, O-terphenyl and Dieldrin being present. O-terphenyl showed the highest concentration (mg/kg) of 0.01 in soil sample A and 0.0099 in soil sample B. Mean concentration (mg/kg) of pesticides detected in soil sample A shows that Heptachlor was 0.006±0.002, Aldrin (0.005±0.001), O-terphenyl (0.01±0.001) and Dieldrin (0.005±0.002). Heptachlor epoxide, Mirex, Endrin and Endosuulfan II were not detected. Physicochemical properties of soil samples A and B were similar. Presence of pesticides residues in samples A and B, suggests possibility of their continued use by farmers in the area despite restrictions in Nigeria. Sustainable remediation options to improve agricultural produce and reduce health threats remain a priority.

KEYWORDS: Pesticide residue, Organochlorine, Physicochemical, Soil, Extraction.

1. INTRODUCTION

Pesticide residues in food, crops are classified as organochlorines, organophosphates, carboxylic acids and their derivatives. Organochlorines (OCs) are synthetic, persistent chemicals with high molecular mass, moderate polarity and stability, used in agriculture and industry for pesticidal qualities. They have field half-life of 15-9 days.[1,2] Organochlorine pesticides (OCPs) are lipophilic, bioaccumulate in adipose tissues, alter nerve membranes of enzymes and pose environmental health risks.[3] Most OCPs have acute toxicity at concentrations higher than environmental limits. Daily cosmetic use with estrogenic activity exposes the skin, accumulates and harms internal organs.[4] OCP levels vary with age and consumption rates of contaminated products.[5] This is a follow-up study to that of Onuwa et al.[6] to check dessipation trends and its aim is to identify and quantify pesticide residues in soil within farmland in comparison with maximum residue limits (MRLs).

2. MATERIALS AND METHODS

2.1. Study Area
Soil samples were collected at Joseph Sarwuan Tarka (J.S. Tarka) University rice plot designated as sites 'A' further divided into two portions coded A and B for the two samples. The site was within latitude 7° 47' 0''N, longitude 8° 44' 40''E as shown in Figure 1.
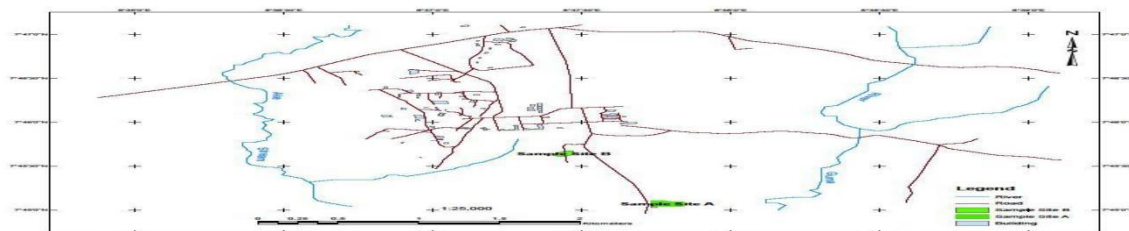

Figure 1: Map of South-Core, Joseph Sarwuan Tarka University Makurdi showing sampling Sites (Onuwa et al., 2017).

2.2. Materials

Materials used were washed, rinsed with distilled water and dried. All reagents were of analytical grades. This includes H_2O, $Ca(OH)_2(aq)$, CH_3CN, NH_4OACl, $Na_2SO_4(s)$ and C_6H_{12} obtained from Thermo Fisher Scientific USA. Instrument/equipment were GC-MS (Agilent 6890N), Agilent 5975B mass selective detector, atomic absorption spectrophotometer (210VGP), centrifuge, flame photometer (FP-64), hydrometer-pulse splitless mode with an injection volume of µL, mechanical shaker and roller.

2.3. Sample Collection and preparation

Soil Samples (A and B) were collected from J.S Tarka University Makurdi rice plot according to standard method used by Ize-Iyamu *et al.*[7] . Two portions of soil samples were collected 132 m apart, using soil auger of 90 cm (claw of 20 cm). Six soil sub-samples were obtained, homogenized and bulked to form a composite, taken to laboratory in plastic bags. They were dried at room temperature for 6 days, then mechanically treated followed by soil analysis. They were ground, separated with 2 mm sieve, extracted using a soil-packed bulb column, 25 g of each sample was weighed into a glass jar, fortified, 25 g of pre-cleaned sand and 50 g of granular sodium sulphate were added. Mixture was manually shaken for 30 s, placed on a roller for 30 s, allowed to stand for 20 mins for absorption of residual moisture from the soil by Na_2SO_4. Mixture was transferred to a 250 mL bulb column; sample jar was rinsed three times with 5 mL hexane and transferred to the bulb column. Soil was extracted with 250 mL acetone-hexane mixture (1:1 v/v), the eluate collected, concentrated to 100 mL using rotary evaporator. Soil extract was cleaned-up to remove interference. Concentrated soil eluate was washed.

2.4. Soil Texture

This was carried out according to standard hydrometer method of mechanical analysis described APHA [8] and adopted with by Juo [9] using glass cylinder, hydrometers, thermometer and (5 %) sodium hexametaphosphate as dispersing agent. Soil pH was determined by a calibrated gas electrode pH meter to pH 7.0, 4.0 buffer before used. CEC was measured using centrifuge based on standard method by FAO.[10]

2.5. Extraction of Soil Samples

It was based on standard method described by Fosu-Mensah[11] and applied by Awe *et al.*[12] Soil sample (10 g) was weighed into 250 mL flask, 10 mL acetonitrile was added and ultra-sonicated for 5 mins. Flasks were closed with additional 10 mL acetonitrile, placed on a mechanical shaker for 30 mins at 300 M/Min and contents separated into layers after standing for 10 mins. Supernatant (10 mL) was taken, dried over 2 g $Na_2SO_{4(s)}$ through filter paper into 50 mL flask. Extract was reduced to 2 mL using rotary film evaporator,cleaned-up and passed to GC vials for analysis. Extracts were kept frozen.

2.6. Pesticide Residues Analysis and Recovery

OCPs in sample extracts were determined by 6890N gas chromatograph interfaced with 5975B mass selective detector (Agilent Technologies, Santa Clara, USA). ADB-5 capillary column (30 m length × 0.25 µm film thickness × 0.25 mm) was used for separation and helium gas (flow rate 1mL/min) used as carrier gas. The column had initial temperature of 70 °C, held for 20 mins, increased at 25 °C min^{-1} to 150 °C, 200 °C at 3 °C min^{-1}, then to 300 °C at 2 °C min^{-1}. Temperature of injection port, ion source, quadrupole and transfer lines were 250, 230,150 and 280 °C each. Sample was injected into the GC via a pulsed split less mode with an injection volume of 4µL. Quantification of pesticides was done using Mass Spectrometry Detector. Retention time, peak area and peak height of samples were compared with standards for detection of analytes. Method was optimized, validated using spiked and internal standards of required pesticide samples obtained from NIST to evaluate recoveries of OCPs which ranged 80-120 %. Procedure blanks and triplicate samples were analysed. Limit of detection was 0.001ppm.

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3. RESULTS AND DISCUSSION

3.1. Physicochemical and organochlorine analysis of Soil

The results from the physicochemical and organochlorine analysis in the soil samples are given in Tables 1-3 and Figures 1 and 2.

Table 1: Mean concentration in (mg/kg) of Organochlorine pesticides in Soil Samples

Heptachlor	0.006 ± 0.002
Aldrin	0.005 ± 0.001
Heptchlor epoxide	ND
Mirex	ND
O-Terphenyl	0.01 ±0.001
Dieldrin	0.005 ± 0.002
Endrin	ND
Endosulfan 11	ND

ND: Not detected.

Table 2: Mean Physicochemical Properties of Soil Samples

Physicochemical Properties	Soil Samples	
	Sample A	**Sample B**
pH	5.65 ± 200.	6.19 ± 0.20
CEC (mol/kg)	6.88 ± 0.21	7.28 ± 0.18
Ca (mg/kg)	2.82 ± 0.08	2.92 ± 0.03
Mg (mg/kg)	2.60 ± 0.10	2.77 ± 0.08
K (mg/kg)	0.25 ± 0.03	0.28 ± 0.01
Na (mg/kg)	0.21 ± 0.01	0.25 ± 0.02
TEB (mol/kg)	5.88 ± 0.21	6.23 ± 0.12
Exchangeable Acid	1.00 ± 0.00	1.10 ± 0.00
Sand (%)	68.18 ± 0.07	69.78 ± 0.08
Silt (%)	12.17 ± 0.29	12.47 ± 0.50
Clay (%)	19.65 ± 0.27	17.75 ± 0.55
Texture Class	Sandy loam	Sandy loam

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Table 3: Coefficient of Variation for Physicochemical Properties of Soil samples

Physicochemical Properties	Soil Samples	
	Sample A (%)	Sample B (%)
pH	4	3
CEC (mol/kg)	3	3
Ca (mg/kg)	3	1
Mg (mg/kg)	4	3
K (mg/kg)	12	3
Na (mg/kg)	5	8
TEB (mol/kg)	4	2
Exchangeable Acid	0.0	0.0
Sand (%)	0.1	0.1
Silt (%)	2	4
Clay (%)	1	3

TEB: total exchangeable base, **CEC:** Cations exchangeable capacity.

3.2. Organochlorine Pesticide Residues in Soil Samples.

Table 1 shows mean concentration in (mg/kg) of OCPs in soil samples. O-Terphenyl has the highest value of 0.01 ± 0.001 followed by heptachlor (0.006 ± 0.002) then closely by dieldrin, aldrin with values of 0.005±0.002, 0.005±0.001, respectively. Endrin and Endosulfan II were not detected. Aldrin was reported in surface water in South Africa to range in value (µg/L) from 0.03-0.253, heptachlor (0.031-0.127), Dieldrin (<LOD-0.086). Dieldrin was detected in Ghanian soil to be within 0.02-0.03 mg/kg. All these values were higher than values obtained from this work for same pesticides but slightly above US MRL of 0.02 mg/kg for agricultural soils.[11,13] Other peaks shown were due to presence of untargeted pesticides. Four out of the eight OCPs; heptachlor, aldrin, O-Terpheny, dieldrin and were detected in soil samples A and B while heptachlor epoxide, mirex, endrin and endosulfan II were not detected in both samples. Concentration of all detected OCPs were lower than the United States maximum residue limit for agricultural soils.[14] Table 2 shows mean physicochemical properties of soil samples. pH, CEC, Ca, Mg, K, TEB, exchangeable acid and particle size distribution were all higher in soil sample B except clay particle (19.65 ± 0.27 %) that was more distributed in A. The pH of soil samples A (5.65±0.20) and B (6.19±0.20) were acidic. Low pH values were due to constant use of fertilizers on the site which conditions its acidity. pH values of samples A and B were low compared to that reported by Onuwa *et al*.[6] in analysis organophosphorus and OCPs in crops and soil on same site which ranged 7.2-7.3. Mean CEC (mol/kg), TEB (mol/kg), Ca, Mg, K, Na (mg/kg) for samples A and were (6.88±0.21, 5.88 ± 0.21, 2.82 ± 0.08, 2.60 ± 0.10, 0.25 ± 0.03, 0.21 ± 0.01) and (7.28±0.18, 6.23 ± 0.12, 2.92 ± 0.03, 2.77 ± 0.08, 0.28 ± 0.01, 0.25 ± 0.02), respectively (Table 2). CEC for samples A and B were all below 12 showing that the soil needs help through soil enrichment using a variety of amendments. The values were low compared to that of Onuwa *et al*.[6] whose CEC values ranged 7.8-8.1 mol/kg, indicating high content of sand. Soil CEC (below 12) indicates lack of significant nutrients. Soils with higher CEC values tend to hold more cations. Particle size shows that both soil samples were sandy-loam textural class which is the best for growing root crops. Table 3 shows coefficient of variation; a measure of precision for replicate data. Good precision is observed in all parameters except K for sample A (12 %).
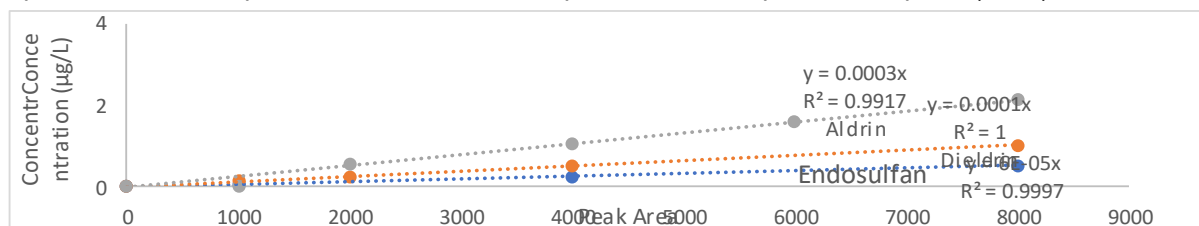

Figure 1: Calibration Curve for Aldrin, Dieldrin and Endosulfan Standards

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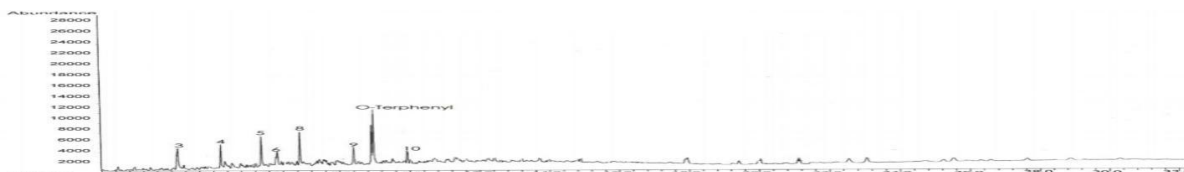(Available at: http://acsnigeria.org/publications/proceedings)

Figure 2: Representative Chromatograph of Organochlorine Pesticides for Sample B

Figure 1 shows the calibration curves for dieldrin, aldrin, endosulfan standards. Figures 2 shows representative chromatograph of OCPs residues for samples B.

4. CONCLUSION

This study detected four OCP residues in soil sample A and B while other four were not detected. This suggests their use by rice farmers in the area, which is tolerable for now but may accumulate to posts potential health risk of intended consumers of the produce and calls for proactive pesticide residue analysis of attendant crops.

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