A Study of the Content of Pesticide Residue in Agricultural Soils Around Federal University Gusau, Zamfara State Nigeria

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Abstract
In this study, the assessment of levels of pesticide residue in agricultural soil in farmlands around Federal University Gusau was carried out. The objectives of this study are to determine soil parameters such as pH, moisture content, electrical conductivity, soil organic matter content, water holding capacity, identify the pesticide residues within the study area and assess the level of pesticide residue in the soil within the area. The sampling area covered arable farmland to the north, south, west and eastern boarders of the university campus. Analyses of cleaned sample extracts were performed using Gas Chromatography equipped with Flame Ionization Detector (GC-FID). A total of twelve agricultural soil samples were taken from the location at a depth of 20cm from the topsoil. The result obtained showed the presence of organochlorine and organophosphorous pesticides. Seventeen pesticide residues and derivatives were detected. These include; 2,4 dichloro, Hexachlorobenzene (HCB), Endosulfan, Aldrin, *p,p'*-DDD, g- chlordane, Profenofos, Carbofuran (a carbamate), DDVP, Dichlorvos, Heptachlor, t-nonachlor, Isopropylamine, Glyphosate, Biphenyl, Dichlorobiphenyl and Lindane. Physicochemical studies of the samples gave a pH that ranges from slightly acidic to slightly basic. The results when compared with IAEA/FAO/CODEX Alimentarius guideline are observed to be within the maximum residue limit.
Keywords: Pesticides, Agricultural soil, Gusau , Gas chromatography, FAO
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1.0 Introduction

Environmental pollution has become one of the greatest threats to human existence. Pollution can occur in soil, water, air etc. One of the practices likely to cause pollution is the application of pesticides on agricultural soils.

Pesticides belong to a group of xenobiotics considered to be harmful to humans and wildlife, whose fate and activity depends on their propensity to degradation. Pesticides are extensively used in modern agriculture and are an effective and economical way to enhance the yield quality and quantity, thus ensuring food security for the ever-growing population around the globe [1]. Pesticides are being used today to control a variety of insects, weeds and plant diseases. Chemical fertilizers and insecticides have greatly improved agricultural yields, raising food grain production from 9.7 million metric tons in 1961 to almost 20 million metric tons in 1993[2, 3]. These agrochemicals are widely used to boost crop output and prevent postharvest losses, thus they are found in a variety of environmental matrices (soil, water, and air), leaving residues in food and causing deleterious consequences when concentrations surpass the maximum residue limit (MRL) [2] .

Pesticides became an important tool for plant protection and crop yield enhancement as agricultural development progressed. Pest infestations result in the loss of roughly 45 percent of yearly food output; therefore, effective pest management using a wide array of pesticides is required to combat pests and boost crop production [4] .

Over the past decades, the usage of pesticides has accelerated over 40% and presently over 4.2 million tons are used worldwide yearly [5]. When discovered in high enough amounts as residues, several of these pesticides can be toxic to plants, animals, and people. Human health risks vary by pesticide and exposure level. Moderate human health hazards from improper use of pesticides include mild headaches, flu, skin rashes, blurred vision and other neurological disorders, while rare but serious human health hazards include paralysis, blindness and even death [6] .

Farmers' practices in most African nations regarding the use of pesticides seems to be unpredictable thanks to lack of information or proper training. Consequently, the non-observance of fine agricultural practices, especially the abusive use of agricultural inputs like pesticides is often observed on farms [7] . Processes of pesticide abuse include; the mix of various classes of pesticides before spraying, improper use of nozzle for spraying, which makes it difficult to achieve the specified dose of pesticide and ignorance of when pesticides are to be used [8] .

The soil is not only imperative for food production; but plays a key role within the functioning of the ecosystem [9] . Agricultural purpose can have significant positive and negative impacts on the soil. Some pesticides can persist in the soil, where they affect organisms that plays a part in the functioning of the ecosystem.

Farmers tend to use any pesticides whether or not they are banned or not recommended for a particular usage provided they are available for other applications and that they function well controlling pests or if they can be fond cheaply[10].

In Nigeria today, about 30 pesticides are banned by the National Agency for Food and Drug Administration and Control (NAFDAC). Among the banned pesticides are aldrin, binapacryl, captafol, chlordane, chlordimeform, DDT, dieldrin, dinoseb, ethylene dichloride, heptaclor, lindane, parathion, phosphamidon, monocroptophos, methamidophos, chlorobenzilate, toxaphene, endrin, merix endosulfan, delta HCH, and ethylene oxide [11]. However, these chemicals still find their way into the market and get used by farmers.

Available literature suggests that information relating to pesticide residues in agricultural soil is very little in Gusau and no information is available on levels of pesticide residues in soils around the study area whose population is made up of mostly local farmers. An attempt to assess the types of pesticide residues (i.e. organophosphorous, carbamate and organochlorine) used and their concentration levels in some selected agricultural soils was undertaken.

The monitoring of their residue level in agricultural soils is very important because it provides valuable information on the possibility of soil contamination and environmental risk resulting from their application.

It is therefore the aim of this study to investigate the types and levels of pesticide residues in soil samples collected from arable lands in the study area

2.0 Materials and Methods

2.1 Description of the study area

Zamfara state is an agrarian state located in northwestern region of the country. Her people are known for the production of cereals and grains as well as animal husbandry. The study was carried out on arable farm lands surrounding the Federal University Gusau located along Zaria road on the eastern part of the state. Gusau is situated on latitude 12.16^o N, 6.66^o E longitude and 450m elevation above sea level.

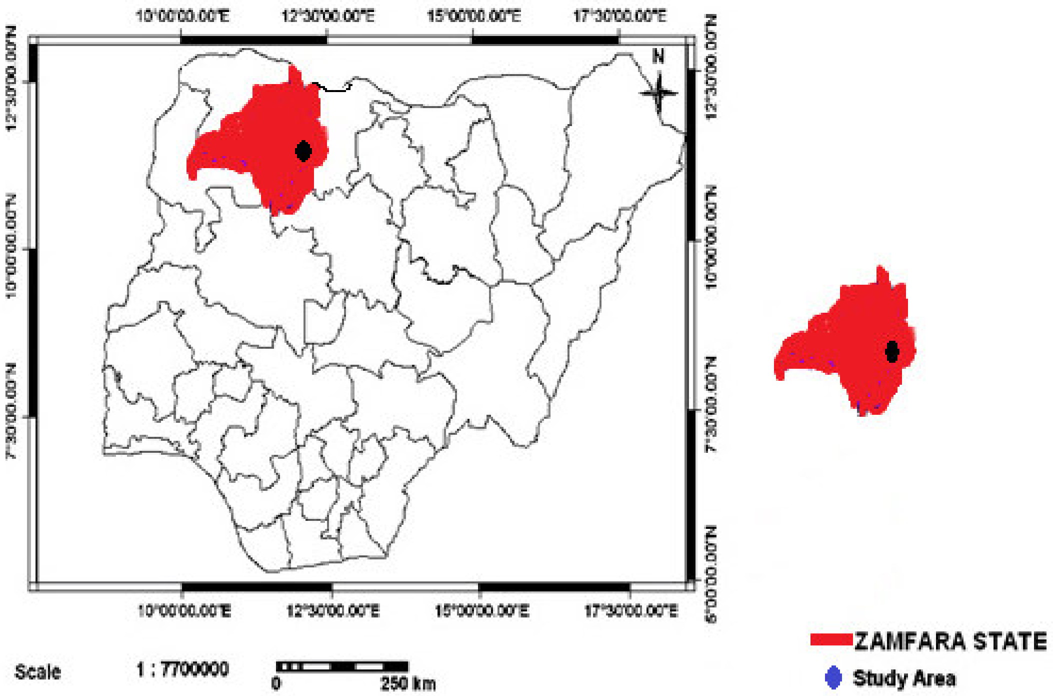

Fig 1: Location map of the study area.

2.2 sampling

Soil samples were collected from agricultural plots of land in the North, South, East and Western end of the university campus. A total of twelve (12) samples were collected from the study area comprising of three samples from each location. Soil samples collected were labelled $N_1 - N_3$, $S_1 - S_3$, $E_1 - E_3$, and $W_1 - W_3$, for those from the north, south, east and western end respectively. Soil samples were taking from a depth 0-20cm and 500m apart using auger as well as stainless steel hand trowel and transferred to the laboratory in a sterile polyethene bag. The samples were dried for 24 hours at a temperature of 25ºC, homogenized, sieved (2mm sieve mesh) and stored in the dark for characterization.

3.0 Extraction procedure

The homogenized samples were analyzed according to AOAC method [12] where 10g sieved sample was weighed and quantitatively transferred into a 500 mL beaker. 6g sodium sulphate was added and extracted using 300ml n-hexane. The filtrate was concentrated. A 10 mL of acetonitrile was added to the sample and place in a shaker for 2 minutes. An additional 10 mL portion of acetonitrile was added, and the separating funnel closed tightly and placed on a horizontal shaker. It was then set to shake continuously for 30 minutes at 300 rpm/min and finally allowed to stand for 5 minutes to sufficiently separate the phases. A 10 mL of the supernatant was carefully taken and dried over 2g anhydrous $MgSO_4$ through filter paper into 50 mL round bottom flask. This was then concentrated to about 1mL using the rotary evaporator, and made ready for clean up.

3.1 Clean-Up of extract (purification using Silica SPE cartridge)

1ml of filtered residue was dissolved in 50ml of chloroform and transferred to a 100ml volumetric flask and diluted to the mark at room temperature. Next, 1 ml of 20 vol% benzene and 55 vol% methanol was added. The flask was corked and heated in a water bath at 40^0c for 10 minutes. The organic sample was extracted with hexane and water, so that the final mixture of the reagent, hexane and water, is in proportion of 1:1:1. The mixture was vigorously shaken mannually for 2minutes and emulsion broken by centrifugation. Half of the top hexane phase were transferred to a small test tube for injection.

3.2 Gas chromatography

The final extracts were analyzed using Gas Chromatograph-Buck M910 scientific gas chromatography equipped with Flame ionization detector that allowed the detection of contaminants even at trace level concentrations (µg/g) from the matrix to which other detectors do not respond. The GC conditions used for the analysis were capillary column coated with VF-5 (30 m + 10 m EZ guard column x 0.25 mm internal diameter, 0.25 µm film thickness). The injector and detector temperature were set at 250 ºC and 280ºC respectively. The oven temperature was programmed as follows: 120 ºC held for 4 min, ramp at 10 ºC/ min to 180 ºC, held for 2 min, and finally ramp at 5 ºC/ min to 300 ºC. Helium was used as carrier gas at a flow rate of 1.0 mL/ min and detector make-up gas of 29 Ml min-1. The injection volume of the GC was 10.0 µL. The total run time for a sample was 43 min. The residue levels were quantitatively determined by the external standard method using peak area. Measurement was carried out within the linear range of the detector. The peak areas whose retention times coincided with the standards were extrapolated on their corresponding calibration curves to obtain the concentration.

4.0 Results and discussions

The physicochemical properties of the soil shows a pH range of 6.90 – 7.05 with N_1 having the least pH and W_1 the highest. Conductivity measurements shows a range of 2.8 – 556.3 µc/cm. Percentage organic carbon ranges from 0.624 – 0.459. The soil water content ranges from 1.207 – 9.773 while the water holding capacity of the samples ranges from 5.583 – 37.380 with W_2 and E_2 having the least and the highest holding capacity respectively. This can be attributed to the nature of the soil which for W_2 is more of loamy while E_2 is more of a clayey soil. (Table 1). The soil pH and organic content determines the absorption and leaching capacity of the soil. [8] reports that degradation of organic matter is greater under acidic conditions. Organic matter are strongly bonded to organochlorine pesticides thus samples with low organic matter tend to have lower organochlorine pesticides [8,13] . The results of the pesticide concentrations and distribution are presented in fig 2- 6. The pesticide residues detected in the soil samples were 2,4 dichloro, HCB, Endosulfan, Aldrin, P^1P^1-DDD, G-chlordane, Profenofos, Carbofuran, DDVP, Dichlorvos, Heptachlor, t-nonachlor, Isopropylamine, Glyphosphate, Biphenyl, Dichlorobiphnyl and Lindane. The most dorminant residues were those of 2,4 dichloro, which were detected in all the samples studied followed by HCB and Dichlorvos found in all soil samples except in W_3 and E_2.

Lindane was the least detected residue occurring in three soil samples W_1, W_2 and W_3 only. Similar concentrations of carbofuran were detected in samples N_1 and N_2, an indication of a common source since the portions were just 500m away. Lindane was also observed in the study of on organochlorine pesticide residues in vegetable farmlands soil in Zamfara state [8]. Similarly, the pH of the soil studied which ranges from 6.29 – 6.45 was obsserved to be closely related to that of the present study. Lindane residue was also found to be present in the study on the soils of cocoa plantation in ondo state Nigeria [14].

Endosulfan II, BHC, heptachlor, P.P^1-DDT were found to be present in the soil and water samples analysed from Fadama farrming communities in Minna, North central Nigeria suggesting a common use of these pesticides by farmers in Nigeria [15].

Presence of Profenofos, DDVP, Glyphosate in the study area is an indication of a recent application since organophorus pesticides are unstable and degrades easily in the environment.

Most of the pesticides found in the study by other researchers were also found in the current study. This suggests that these pesticides are still readily available despite the ban placed on some of them by NAFDAC in Nigeria.

Table 1 Soil physicochemical properties

Samples	Grid reference	pH(H_2O)	EC(us/cm)	% OC	WC	% WHC
N_1	N12^0 07.35^1 E006^0 47.049^1	6.90	37.6	0.400	8.776	29.736
N_2	N12^0 07.34^1 E006^0 47^1	7.01	39.5	0.342	7.846	27.964
N_3	N12^0 07.38^1 E006^0 46.85^1	6.96	42.4	0.151	5.753	22.166
S_1	N12^0 08.1^1 E006^0 46.899^1	6.90	69.2	0.120	8.426	29.257
S_2	N12^0 08.11^1 E006^0 46.77^1	6.98	2.8	0.024	8.706	35.898
S_3	N12^0 08.02^1 E006^0 47.05^1	6.97	36.6	0.155	9,219	31.427
E_1	N12^0 07.94^1 E006^0 47.5^1	6.99	7.4	0.329	9.312	31.187
E_2	N12^0 07.61^1 E006^0 47.535^1	6.95	8.9	0.388	9.116	37.380
E_3	N12^0 07.35^1 E006^0 47.458^1	6.98	11.9	0.217	9.773	32.527
W_1	N12^0 07.62^1 E006^0 46.74^1	7.05	56.3	0.241	7.892	27.832
W_2	N12^0 07.7^1 E006^0 46.7^1	6.99	48.3	0.459	1.207	5.583
W_3	N12^0 08.087^1 E006^0 46.764^1	7.01	52.6	0.003	9.407	31.708

Key: OC= organic content, EC= electrical conductivity, WC = water content, WHC = water holding capacity

Table 2: List of banned Chemicals in Nigeria

S/N	Pesticide	Category
1	Aldrin	Insecticide
2	Binapacryl	Fungicide
3.	Captafol	Fungicide
4.	Chlordane	Insecticide
5.	Chlordimeform	Insecticide
6.	DDT	Insecticide
7.	Dieldrin	Insecticide
8.	Dinoseb and Dinoseb salts	Herbicide
9.	Heptachlor	Herbicide
10.	Lindane	Insecticide
11.	Ethylene dichloride	Fumigant
12.	Parathion	Insecticide
13.	Methyl parathion	Insecticide
14.	Phosphamidon	Insecticide
15.	Monocropthophos	Insecticide
16.	Methamidophos	Insecticide
17.	Chlorobenzilate	Insecticide
18.	Toxaphene	Insecticide
19.	Pentachlorophenol	Herbicide, Insecticide
20.	Ethylene oxide	Fumigant, Disinfectant
21.	HCF (mixed isomer)/BHC	Insecticide
22.	EDB (1,2 dibromoethene)	Fumigant
23.	2,4,5 trichlorophenoxy acetic acid	Herbicide
24.	Endrin	Insecticide
25.	Mirex	Insecticide
26.	Ethylene dibromide	Fumigant
27.	Hexachlorobenzene	Fungicide
28.	Endosulfan	Insecticide/acaricide
29.	Delta HCH	Agricultural insecticide
30.	Flouracetamide	Rodenticide

Source: [16]

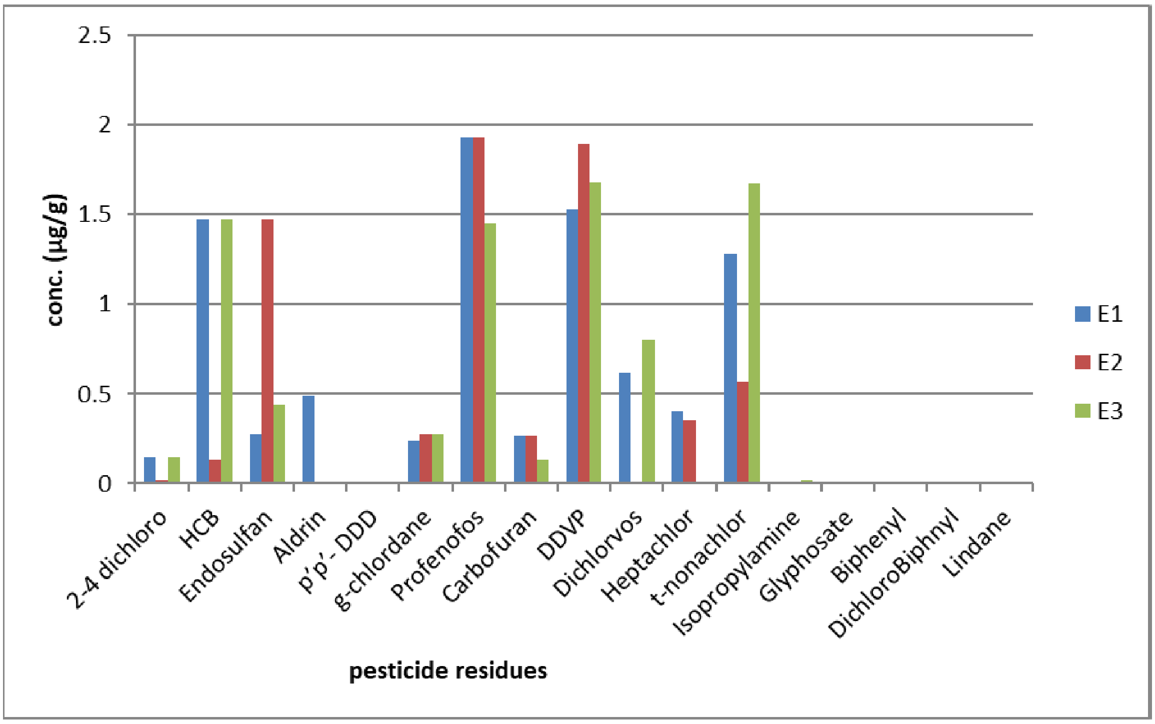

Fig 2: Distribution of residues in samples E_1, E_2 and E_3

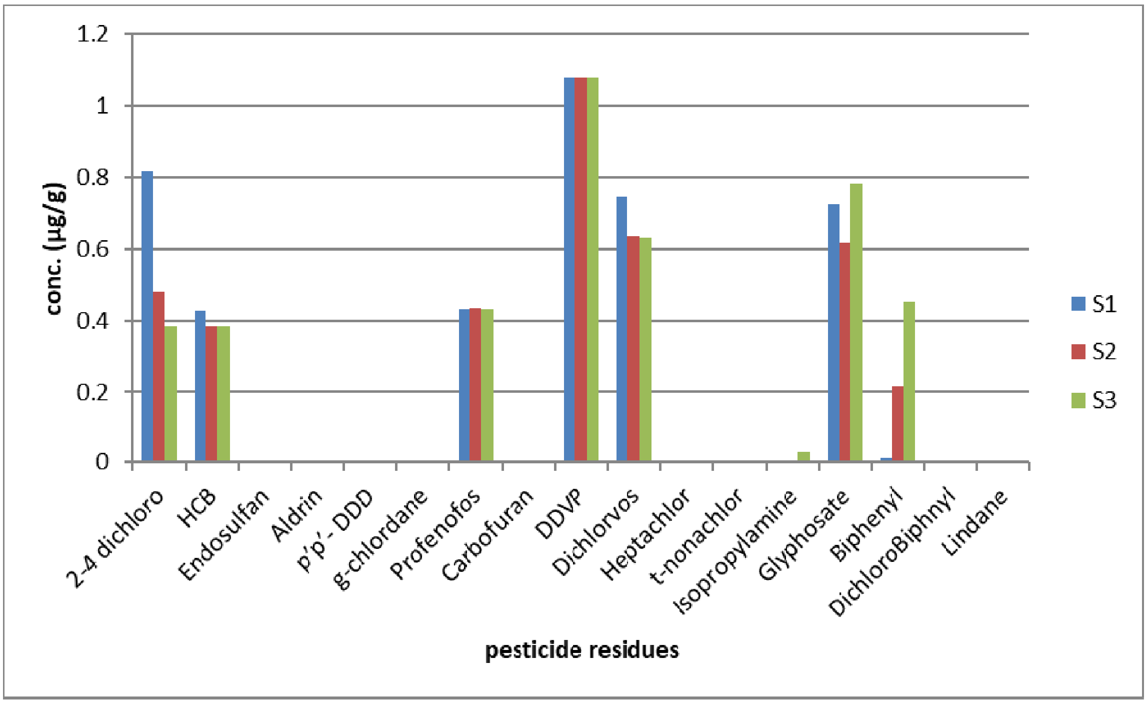

Fig 3: Distribution of residues in samples S_1, S_2 and S_3

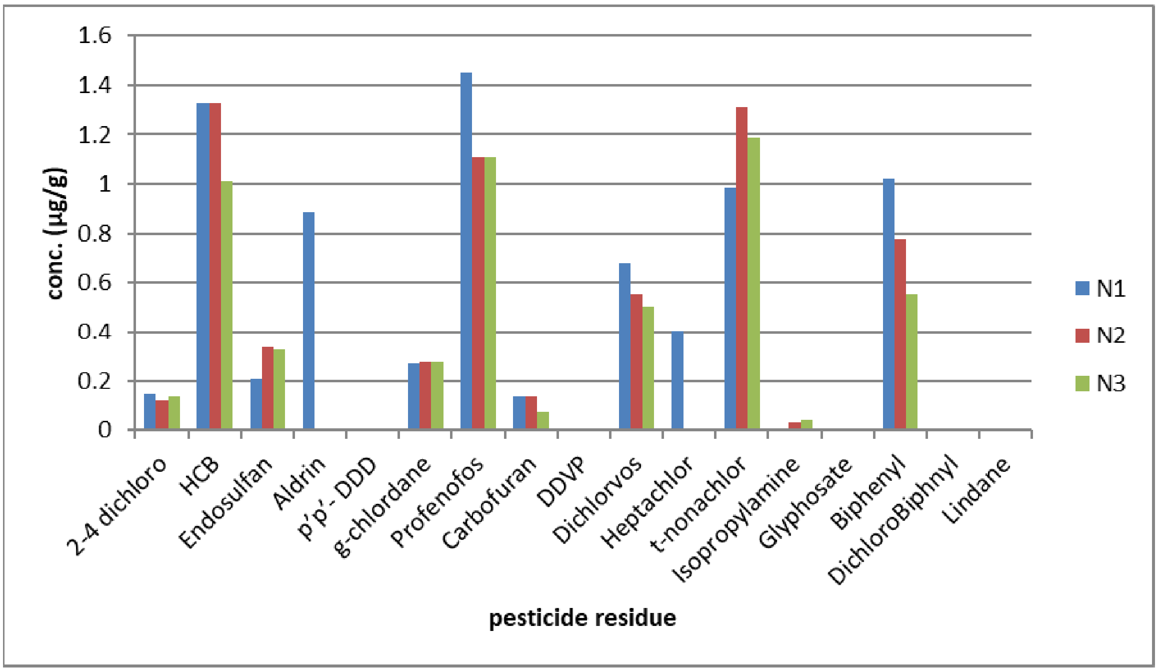

Fig 4: Distribution of residues in samples N_1, N_2 and N_3

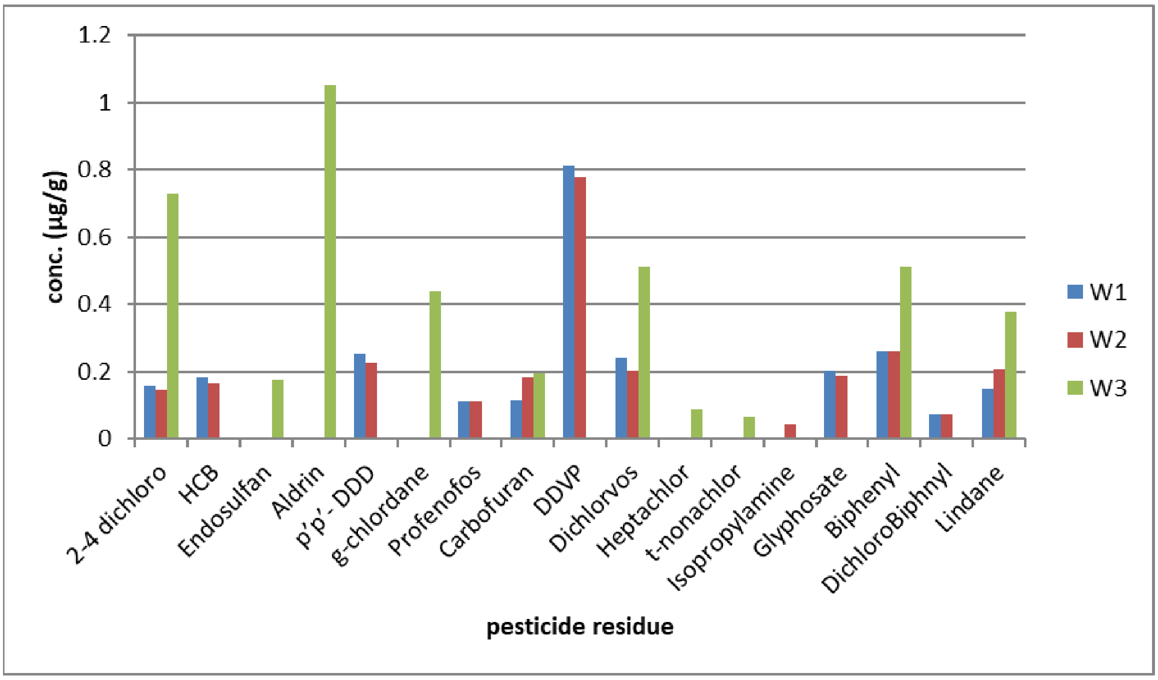

Fig 5: Distribution of residues in samples W_1, W_2 and W_3

5.0 Conclusion

Although residue of pesticides found in the study area are within the limit set by IAEA/FAO/CODEX Alimentarius, the use of prohibited pesticides are still very much in use in Nigeria. The result from the present study shows the presence of banned organochlorine and organophosphorous pesticides as well as their derivatives. This suggests an absence of enforcement and feed back mechanism on the part of regulatory bodies. These pesticides in the soil are taken up by plants and are in turn consumed by livestocks and man. As a result of the continous cropping farming system practiced in this area, there are chances of bioaccumulation and transport into water bodies as well as dispersal by wind current which will poses a great risk to human health. Environmental protection agencies in local communities should intensify efforts aimed at enlightening rural farmers on the indiscriminate use of agrochemicals. Environmental risk assessment procedures should be adopted accordingly to minimize related risks to soil life thereby maintaining a sustainable ecosystem.

6.0 Recommendation and suggestion.

The authors would like to recommend periodic assessment of pesticide residues on the soil, water and plant produce from the study area. This will help educate farmers on the use of agro chemicals as well as help policy makers and government agencies monitor the use of these chemicals. We would also like to suggest further assessment of pesticide residue to cover, crops, house dust and water sources in the area.

7.0 Acknowledgment

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