International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2015): 78.96 | Impact Factor (2015): 6.391

Analysis of Pesticide Residues in Agricultural Soil Using High Performance Liquid Chromatography (HPLC)

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Abstract: ***This study investigated the level of pesticide residues in agricultural soil from three main location of south-western part of Nigeria namely: the cocoa plantations of idanre, Owena and Abata Ogun of shaki local government area of Oyo state. Quantitative analysis was performed using the high performance liquid chromatography method (HPLC).Identification of the pesticide residues was carried out by matching the retention times of the sample with that of the standard.The accuracy of the quantitative determination measured in terms of average percentage recovery of the seven pesticides in fifteen soil samples were 84.6% with a relative standard deviation of 11.6%.The concentration values of the pesticides in all the soil samples analysed ranged from 1.15x 10-3µg/kg to 8.36µg/kg.The results were compared with the FAO's maximum residue limit (MRL).All the pesticide residues detected in the soil samples analysed except paraquat, Propoxur and endosulfan were above the MRL at various percentage levels.The pesticides above this value are likely to pose significant risk to the human health and hence should therefore be monitored closely.***

Keywords: Pesticides Residue, Soil, Level

1. Introduction

The commercial use of pesticides to control weeds and pests in Agriculture development soon after world war (11).Pesticide use worldwide has increased dramatically since then and hundreds of different chemicals have been developed. Today the total agricultural use of pesticides in Europe is estimated to be about 350,000 tonnes of active ingredients per year which is about 28% of the total use throughout the world (Klassen,1995).Intensive agriculture practices often include the use of pesticides to enhance crop yield is sometimes concomitant with the occurrence and persistence of pesticide residues in soil and water.(Ware and Whitacre,2004).Pesticides may reach the soil through direct application to the surface of the soil, incorporation in top inches of the soil or probably during application to the crops (McEulen and Stephenson ,1979).

The fate of pesticides in the soil and water environment is influenced by the physico-chemical properties of the soil and water body presence of clay materials, organic matter, pH, climate, and other factors.(Singh,2001).The increased and persistent use of pesticides has caused pollution of soils and water worldwide. Pesticides are agents capable of destroying or inhibiting organism that are harmful to living organism. They include insecticides, fungicides, herbicides etc.(British Crop Protectiion Council,2003)

Insecticides are pesticides that are used for the eradication of insects, while herbicides are used for eradication of weeds.(Adeyeye, 1997). There are two major groups of pesticide namely natural and synthetic pesticides

Natural pesticides: A large number of different plant species contain natural insecticidal materials some of which have been used by main as insecticides and many cannot be profitably extracted. The most important example in ascending order of importance are nicotine, rotenone, and pyrethrum (melnikov,1971).Nicotine is extracted from a number of nicotinatobiccum instica glanca. It functions as a non-persistent contact pesticides against aphids and capsids. It is highly toxic to man and not effecting in cold weather nicotine is thus been displaced by organophosphorus compounds which on their part act on a wider circle of pest and are relatively cheaper and less toxic to man and animals

Rotenones occurs in the root of Derris elliptics and a species of and a species of lonchocarpus.It primary use is in hirticulture against aphids, caterpillars etc.

Related derivatives (Rotenoids) are toxic to fish and many insects, but are almost harmless to most warm-blooded animals. Prethrum is obtained from heads of Chrysanthernum cinarariae folium. It is a contact insecticide. Insects often recover from exposure to sublethal doses of pyrethrum meaning that the compound must be mixed with small amounts of other insecticides to ensure that the treated insects do not recover. The four main related compound of pyrethium are collectively term pyrethrins.(Cremlyn,1979) Synthetic pesticides are pesticides based on chemical nature of inorganic or organic origin. Inorganic Insecticides are those that do not contain carbon. They are usually white, stable chemiclas and do not evaporate and are frequently soluble in water, this include compound of boron, mercury, thallium, antimony and selenium. However arsenic is the only one being extensively used today. It exists in two forms: the arsenities (salt s of arsenious acid) (Idachefs and olayide,1985) Synthetic organic pesticides: The chemical era was opened by world war 11 and brings about the production of a totally new concept of pesticide chemical. Synthetic organic pesticides include organochlorine pesticides such as Paraxon, parathion, chlorthion, metasystec etc. Carbamate; They are derivatives of carbamic and amines. The mode of action is that of inhibiting the vital

enzymes, cholinesterase. They include carbaryl, propoxur, aldicarb, Zectran together with the natural plant toxin physostigmine. (Sharmal and Agarwal,1980)

2. Materials and Method

Materials Used: Acetone, conc H_2S0_4, Sodium Sulphate, Endosulfan, Lindane 2,4-dichlorophenoxylacetic acid, Paraquat, diazinon, propoxurs, glyphosphate.

Soxhlet extractor, HPLC chromatographic.

Study Area and Sampling
Study areas in Ondo Cocoa production regions and food crops production areas in Oyo State were selected. These sites included Idanre (an older cocoa producing areas) Owena (relatively intermediate cocoa producing area and saki (a food production area). A total of 15 soil samples were collected in the study areas from February to March 2016.Soil was collected from 5cm beneath the soil surface using a field soil auger.

Soil Code
Idr 001,Idr 002,Idr 003,Idr 004,Idr 005,Idr 006,Idr 007,Idr 008,Idr 009,Idr 010,Idr 011,Idr 012,Idr 013,Idr 014,Idr 015.

Sample Preparation and Extraction
The sample were dried at a temperature of 40^0c in the oven to a constant weight.20g of the soil sample were put in an extraction thimble. The soil sample inside the thimble was moistened with $2cm^3$ of distilled water and placed into the soxhlet extractor. The apparatus is fitted with $250cm^3$ round bottom flask containing $100cm^3$ of acetones solvent and reflux for 6hours using soxhlet extractor. The extract was dried and anhydrous sodium sulphate was added to remove water molecules and followed by filtration. The filtrate was concentrated prior to HPLC analysis. Apart from this normal analysis, spiking was performed to check the accuracy of the method. This is done by addition of standards whose concentrations were between 1.5ppm and 100ppm to 50g of each sample. The extraction is as described above. The percentage of the recovery studies conducted above was then calculated for each sample using the formula below.

$$\% \text{ recovery} = \frac{Cs_2 - Cs_1 * 100\%}{C_5}$$

Where Cs_1 is the concentration of pesticide in soil sapmle Cs_2 is the cone of pesticide in soil sample + Standard, C_5 is the concentration of pesticide present in the original standard. Where Cs_1 is the concentration of pesticide in soil sapmle Cs_2 is the cone of pesticide in soil sample + Standard, C_5 is the concentration of pesticide present in the original standard (FAO,1998).

High Performance Liquid Chromatography (HPLC)
100ppm stock standard were prepared. It was done by measurement of 0.01g powdered form of lindane, endosufan,glyphosate and $0.01cm^3$ liquid form of 2,4-dichlorophenoxy acetic acid and diazinon into $100cm^3$ volumetric flask. Small quantity of methanol was added to each flask to dissolve the standards. It was properly shaking to allow good mixture of the contents. The solution was then made up to $100cm^3$ mark of the flask. The following concentrations (80,60,40,20,and 10 ppm) were later prepared from 100ppm stock solution for lindane, endosulfam, diazinon, glyphosate and 2,4-dichlorophenoxy acetic acid.

3. Result and Discussion

Table 1: HPLC:Results of Pesticides Residues Detection in soil samples from Idanre

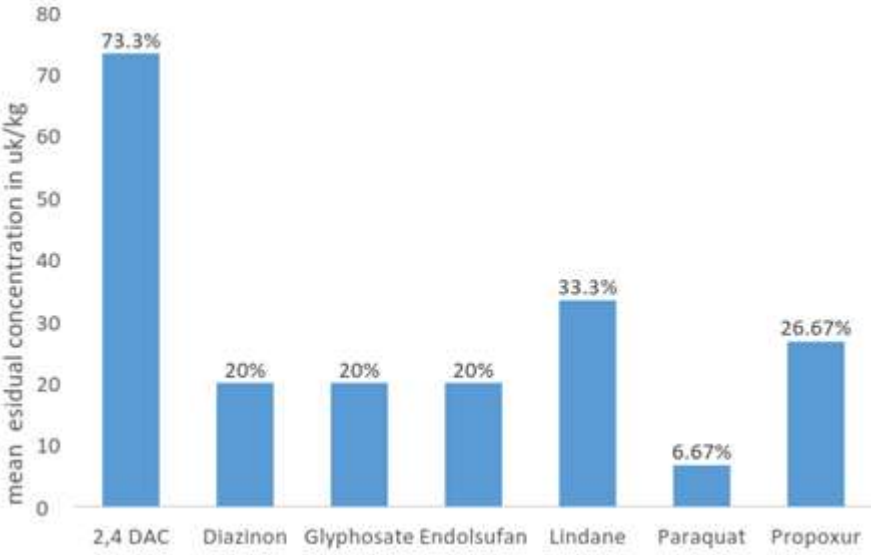
Sample code	Active ingredients	Std conc	Sample conc(ppm)
Idr 001	Diazonon	1.00	$3.56x10^{-4}$
002	Diazonon	1.00	$1.61 x10^{-4}$
003	Propaxur	1.00	$7.5 x10^{-4}$
004	Glyphosate	5.00	$5,24 x10^{-4}$
005	EndosulfaN	1.44	$7.5 x10^{-4}$

Table 2: HPLC:Results of Pesticides Residues Detection in soil samples from Owena

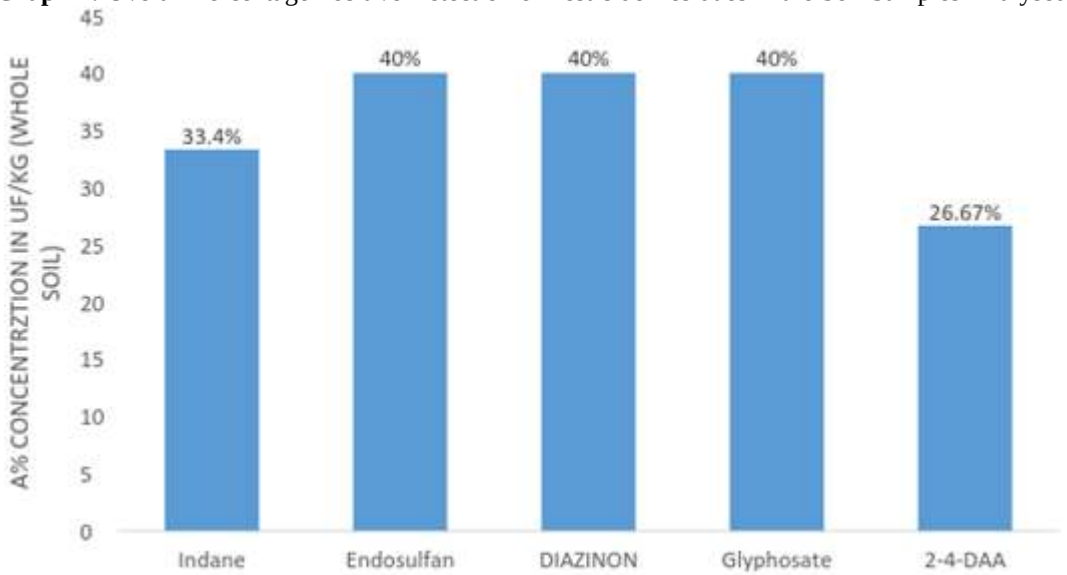
Sample code	Active ingredients	Std conc	Sample conc
Own006	2,4-DAA	1.44	$3.56x10^{-6}$
007	lindane	1.00	$1.61 x10^{-3}$
008	Diazonon	1.00	$7.5 x10^{-3}$
009	Glyphosate	5.00	$5.0 x10^{-3}$
010	Endosulfa	1.00	$8.36 x10^{-5}$

Table 3: HPLC:Results of Pesticides Residues Detection in soil samples from Saki

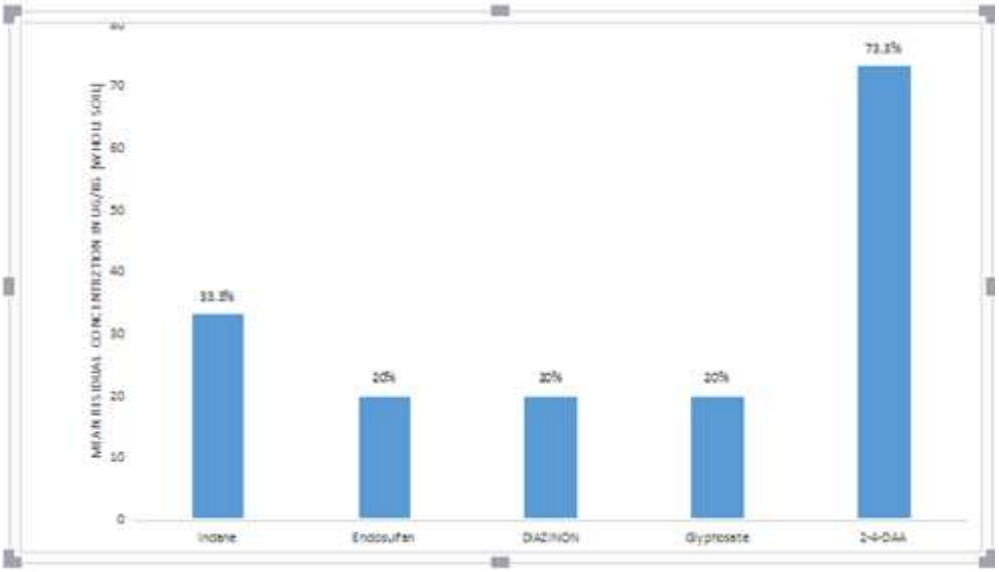
Sample code	Active ingredients	Std conc	Sample conc
OWN011	2,4-DAA	1.44	$2.34x10^{-6}$
012	lindane	1.44	$2.50 x10^{-3}$
013	Diazonon	1.00	$1.15 x10^{-3}$
014	Glyphosate	5.00	$1.22 x10^{-3}$
015	Endosulfan	1.00	$2.92 x10^{-5}$



Graph 1: Overall Percentage Positive Detection of Pesticide Residues in the Soil Samples Analysed.



Graph 2: Overall Percentage Below Detection of Pesticide Residues in the Soil Samples Analysed.



Graph 3: Overall Percentage above Detection of Pesticide Residues in the Soil Samples Analysed

The result of HPLC obtained in the course of this investigation are presented in Table 1-3.The concentration range of pesticides in all the soil samples analysed ranged from 1.15ug/kg to 8.36ug/kg. The average percentage recovery of the seven pesticides in fifteen soil samples was 84.6%, with a relative standard deviation of 11.6%.Figure 1 show the overall positive detection of the pesticide residue in the research carried out were as follows 2,4-DAA

73.33%,Diaxinon 20%, Paraquat 6.6% Glyphosphate 20%,endosulfan 20%,lindane 33.33% and Propoxur 26.67%The result showed that 2,4 DAA a phenoxy acetic acid pesticide, lindane an organochlorine persistent in the environment than other other classes of pesticides since they had the highest frequency of occurence as show by their overall percentage postion detection. Figure 1 show the overall positive detection of the pesticide residue in the research carried out were as follows 2,4-DAA 73.33%,Diaxinon 20%, Paraquat 6.6% Glyphosphate 20%,endosulfan 20%,lindane 33.33% and Propoxur 26.67%The result showed that 2,4 DAA a phenoxy acetic acid pesticide, lindane an organochlorine persistent in the environment than other classes of pesticides since they Fig.2-3 summarize the mean occurence of some pesticide residues relative to MRL. About 33.4% of lindane,40% endosulfan, 40% Diazinon,40% glyphosate and 26.67%DAA were below the MRL Consequently,73.3% 2,4 DAA,33.3% Lindane 20% endosulfan, 20% diazinon and 20% glyphosate were above the MRL. The findings of this study support evidence of high misuse of pesticides in areas like saki and Abata-ogun of Oyo state, particularly the use of organochlorine such as 2-4 DAA and Lindane because of high percentage of 73.3% ,33.3% respectively found above MRL and consequently related to the low percentage of organic matter in the soil samples of those areas. had the highest frequency of occurrence as show by their overall percentage positive detection.

4. Conclusion

Available data in this work suggest that a soil with low percentage of organic matter habour higher persistence of pesticides particularly organochlorine pesticides. It had been gather in this study through FAO/WHO.MRL that some degrees of contamination of soil by pesticides either in the cash crop regions (Idanre and Owena) or the food crops region (Saki and abata region) were seen. Although more prevalent in the food crop region as more herbicides were used.With higher percentage of organic matter experienced here the (2,4 DAA) will rapidly degrade, though with low percentage at the cash crop region of Idanre and Owena. Therefore, the need for pesticides in producing adequate food to meet satisfactory and acceptable quality for increasing populance is beyond dispute.It is right that monitoring of the residue levels in food and environment should continue. This would help to show any trend in the level of the contamination of the environment and generate data for future generation.

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