

International Journal of Advances in Scientific Research and Engineering (ijasre)

DOI: 10.31695/IJASRE.2023.9.7.6

Volume 9, Issue 7 July - 2023

## Detection and Screening of Some Persistant Organic Pollutants (Pops) in Dogon Ruwa Community of Kaltungo Local Government area of Gombe State, Nigeria

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## ABSTRACT

"Persistent Organic Pollutants" (POPs) are chemical contaminants identified by scientist at World War (II). These contaminants found their way into the environment as result of human activities such as agriculture, industrialization and transportation. They are persistent and can travel long range in the atmosphere to regions where they have never been used or produced, posing serious health effects on humans, wildlife and aquatic environments. This research has identified some of these pollutants in soil and water samples obtained from four different locations from a community within Kaltungo known as Dogon Ruwa. The samples were analyzed for the presence of these pesticides pollutants. QuECHERS method was adopted for the extraction and cleans up, and Gas Chromatography coupled with mass selective detector known as Mass Spectrometer was used for detection. Pesticides of interest are Organochlorine (OC) and Organophosphate (OP). Thirteen Organochlorines pesticides (OCP) with their mean concentration in PPM were determined and the value for water given as; Aldrin 63.9ppm, Endrin 27.3025ppm, Endosulfan I 14.31ppm, Endosulfan II, 2.1ppm, Methoxychlor 9.5325ppm, Heptachlor 25.605ppm, Heptachlor epoxide 273.965ppm, Deltalindane 13.7725ppm, Alpha lindane1446.8625ppm, Gmma-lindane 12.265ppm, P,P-DDE 22.475ppm, P,P-DDD13.2045ppm and P,P-DDT 5.4775ppm. The mean concentrations for soil are; Aldrin 40.1675ppm, EndosulfanI 188.384ppm, Endosulfan II 2.1125ppm, Methoxychlor 1.0125ppm, (Heptachlor 6.795ppm, Heptachlor epoxide 0.14ppm, Delta lindane1.614ppm, Alphalindane8.315ppm, Gmma-lindane 12.125ppm, P,P-DDE 3.4525ppm, P,P-DDD 0.485ppm, P,P-DDT 0.485ppm and Endrin 0.645ppm. Five Organophosphates (OP) with their mean concentrations for Water samples includes, Ethoprophos 0.8075ppm, Disulfan 0.02ppm, Ronnel 3.485ppm, Chlorpyrofos 2030.55ppm and Phosphorodithioic acid 1.8425ppm, and for Soil sample; Ethoprophos 0.2675ppm, Disulfoton 0.0075ppm, Ronnel 3.6575ppm, Chloropyrofos 3,154.9475ppm and Phosphorodithioic 0.7825ppm were detected from each of the samples analyzed.

Keywords: Bioaccumulation. Persistant Organic Pollutants, Pollutants, Organ chlorines, Organophosphates.

## I.0 NTRODUCTION

Progress in agriculture, industrialization, Transport and Technology are usually important components of economy development of a nation, however these man activities has adversely affects all living organisms in the biosphere resulting in many environmental issue including contamination of the environment by substances that are lethal to all living organism plants and animals inclusive, and one of these environmental contaminants is pesticides Pollutants known as "Persistent Organic Pollutants" (POPs) [1]. POPs are organic compounds which when release into the environment resist degradation by biological, chemical and photolytic processes [2]. They are pesticides and literature shows there are over five hundred (500) compounds known as pesticides and its metabolites worldwide [2]. POPs are also characterized by low water solubility, low vapor pressure, and low rates of degradation, leading them to bioaccumulate and exert toxicity to organisms and humans [3]. these pesticides were originally produced to enhance food production and feed a hungry world by increasing crop yield but their impact on health require a prompt and accurate analysis [4].

Pesticides are mixtures of chemicals, or of biological origin intended for repelling, controlling or destroying pest while regulating the growth of plants [5]. pesticides pollutants are mostly man-made chemicals produced for agricultural and industrial

uses and these chemicals end up contaminating all region of the world [6]. Pesticides used for agricultural purposes are of three major classes; insecticides, fungicides and herbicides with other minor ones including rodenticides, nematicides, garden chemicals, household disinfectants molluscicides and acaricides. and generally they show a wide spectrum of the beneficial effects by improving plants health, maintaining agro-ecosystem and food supply [7], but due to constant application of these Pesticides, their pollutants has become one of the main drivers of the negative impact of modern industrial agriculture on the environment resulting in environmental issues [8]. However, contamination of the environment and food by pesticides has become a topical issue of considerations in many parts of the world, as a result many researchers are investigating the occurrence, distribution and concentrations of these pesticides pollutants in commercially sold farm produce, animal products, soil, water and sediments [9]. According to literature only 15% of pesticides applied directly get to tis target species and the remaining 85% is distributed in soil and water which is why some researcher on POPs in the environment are focusing on determining their uncertainties due to their ambient sources, atmospheric transport and fate which controls their concentration [10][11] In addition to their the negative effects through applications of runoff and pesticide drift can carry pesticides into distant aquatic environments or other fields including human settlements [12]. Other source of pesticides pollution is non-point source by fertilizers, pathogen and pesticides [13] also as result of the increasing case of pesticides pollution and the need to boost crop production. The need to identify and screen these pesticides arise to cope their lethal effects on non-target species [4], because even at low concentration, exposure to these pollutants can harm humans and other organisms [14]. As such there is need to screen these pesticide pollutants to test the chemical's potential of being a pollutants and to ascertain that they are threat to human health and can cause environmental and ecological damages [15].

This study will be limited to identifying Organchlorines and Organphophates. Organochlorines are group of chlorinated compounds widely used in chemical industries and for agriculture as pesticides they are affordable readily available making their usage very high, statistics show that 40% pesticides used are Organochlorine pesticides [16]. Some examples of organochlorine pesticides include; DDT, Chlordane, Dicofol, BHC/HCH, Aldrin, Endosulfan, Heptachlor, Chlordane, Methoxychlor [17]. Organophosphate are esters of phosphoric acids and these forms of esters. Examples include; Parathion, Malathion, Monocrotophos, Chloropyrifos, Quinalphos, Phorate, Triazophos, Temepos, Diazinon,Fenitrothion, Acephate, Dimethoate, Fenthion, Isofenfos, Phosphamidon [18]

However due to increasing use of these pesticides by farmers and lack of knowledge on its usage and maintenance [19]. the need to know their environmental effect is paramount as such this research aim is to screen and identify these pesticides to confirm their presence within the community and provide information on the fate of the POPs in the environment and the information obtained from this research will be made available in templates to the community to help farmers know the toxic and non-degradable nature of the pesticides they use in their farms and might help minimize or avoid its usage by going for safer alternatives like organic fertilizer (including organic waste, animal and green manure, biological pest control) and also minimizing the risk of human exposure which The Stockholm Convention and other POPs regulatory bodies are working so hard to protect human health and the environment from POPs[20]. The application of GC-MS aid in identification of these pesticides. The GCMS is a material analysis method that employs gas chromatography fitted with mass selection detector called mass spectrometer [21].

The pesticide pollutants identified were found to have same characteristics of POPs stated in the Stockholm Convection which includes their long range transport, bio accumulation factor, persistent, and their adverse effect on humans [22].

## 2.0 METHODOLOGY

The study area is a small village known as Dogon Ruwa located under Awak township of Kaltungo local government area of Gombe state. According to Mindat. org this village is situated at latitude  $9^{\circ}$  52<sup>'</sup> 0<sup>°</sup> North and Longitude 11<sup>°</sup> 24<sup>'</sup> 0<sup>°</sup> East and has a tropical savanna wet climate. The distance from kaltungo to Dogon Ruwa village is 2.7 km (1.6 miles) The Dogon Ruwa people are known for their agricultural activities and they principally grow crops such as millets, groundnuts, fruits as well as vegetables. Other small trade activities also take place in this locality such as welding, and car repair and maintenance [23].

#### 2.1 Sampling

The sample collections were done using compass bearing (East South, North West, North East and South) and a total of four different samples each of soil and water were obtained for this purpose. The soil sample collection was done in three categories; first the top soil, followed by soil from 15 meters depth and then 30 meters depth respectively from each location. The soil samples were homogenized in the laboratory and weighed 15g before extraction. Water samples were collected from their irrigation water source in a water can, appropriately labelled for each location. The samples were transported to the laboratory for analysis.

#### 2.2 Materials and reagents

All materials and reagents were of standard analytical grade and these includes: dichloromethane (DCM), Acetonitrile, anhydrous sodium sulfate, sodium acetate, sodium chloride, vortex mixer, magnesium sulfate, a weighing balance, fume chamber, centrifuge machine, micro syringe, the obtained soil and water samples.

#### 2.3 Extraction method

The method adopted for the extraction of pesticides was the QuEChERS method. QuEChERS is an acronym for quick, easy, cheap, effective rugged and safe. This method was first used in 2003 where it was used for the analysis of pesticides residue in fruits and vegetables and its procedures involve an initial extraction of target analyte using acetonitrile for soil sample and dichloromethane for water sample, just as in the extraction procedures below [7].

#### 2.4 QuEChERS Method for Water Extraction

During water extraction 10mL of water sample was placed in a 15mL centrifuge tube and 2.5mL dichloromethane was added and the tube was capped and vortex for 3mins before adding 4g of anhydrous magnesium sulfate (MgSO4). 1.5g Sodium acetate and 1g NaOAC was added. The tubes were vortex vigorously for 1min and centrifuged for 10mins at 7000RPM. One milliliter of the supernatant was transferred into a 2mL vial containing 500mg MgSO4. The vials were shaken and subsequently centrifuged. The extract was transferred into a PTFE capped vial (obtained from Agilent GC-MS) for further analysis using GC-MS.

#### 2.5 QuEChERS Method for Soil Extraction

During sample extraction of soil, 5g of soil sample was placed in centrifuge tube and 10mL acetonitrile were added and the mixture shaken vigorously. Further, 1.5g Sodium acetate anhydrous (NaOAC) was added to the tube, 4g anhydrous magnesium sulfate (MgSO4) and 1g sodium chloride (NaCl) were added and the mixture were shaken vigorously using a vortex mixer and then centrifuged for 10mins at 7000RPM. Afterwards, 7.5mL aliquot of the supernatant was transferred to a centrifuged the aliquot of the supernatant was transferred into a glass test tube and allowed to evaporated to nearly dryness under a stream of nitrogen and the residue was re-dissolved in 1.5mL dichloromethane before its injection into the GC-MS.

Note: Sample extraction in this case was done three times to obtained the required amount of sample for the extraction and making the sample to be 15g in total and the aliquot were added together before analysis. This method was Adopted from [24]

#### 2.6 Statistical data analysis

The data obtained during this research work will be presented as mean and relative standard deviation in tables of results adopted from [25]

## **3.0 RESULT AND DISCUSSION**

The tables below show the identified organ chlorine and Organophosphate pesticides, with their mean concentration and standard deviation from soil and water samples obtained from the study area.

Table 1: The mean concentration and standard deviation levels of HCHs and Aldrins Determined in Soil Samples of the						
Four Locations (East, West, North and South)						

		α-НСН	ΔНСН	ү-НСН	Aldrin	Endrin
Soil Samples	Mean	8.315	1.615	12.125	40.1675	0.645
-	SD	6.943	2.846	73.730	6.768	5.095
Water Mean	Mean	65.07	13.7725	12.265	63.96	27.3025
	SD	1595	13.011	11.355	71,427	0.95

 Table 2: The mean concentration and standard deviation levels of Heptachlor and DDTs Determined in Soil Samples of the Four Locations (East, West, North and South)

		Heptachlor	Heptaclor expoxide	P,P-DDT	P,P-DDE	P,P-DDD
Soil Samples	Mean	25.602	273.965	5.4775	22.475	13.2025
	SD	6.768	0.082	0.711	5.095	0.242
Water Samples	Mean	6.795	0.14	0.485	3.4525	0.2575
	SD	19.439	258.082	9.013	30.917	24.364

# Table 3: The mean concentration and standard deviation levels of Endosulfans and Methoxychlor Determined in Soil Samples of the Four Locations (East, West, North and South)

		Endosulfan 1	Endosulfan 11	Methoxychlor
Soil Samples	Mean	188.384	2.1125	1.0125
	SD	140.124	0.846	1.136
Water Samples	Mean	14.31	2.1	9.5325
	SD	23.887	0.95	7.390

Table 4: The mean concentration and standard deviation levels of Organophosphate (Ethopropos, Disulfan, Ronnel, Chloropyrofos and phophorodithioic acid, Determined in Soil Samples of the Four Locations (East, West, North and South).

		Ethopropos	Disulfoton	Ronnel	Chloropyrofos	Phosphorodithioic acid
Soil Samples	Mean	0.1625	0.005	3.1	759	0.356
	SD	0.085	0.550	05.409	389.08	0.17
Water Samples	Mean	0.9125	0.0225	4.0425	2141.415	2.46
	SD	0.969	0.244	2.82	66883.65	4.034

## 3.5 DISCUSSION

The levels of organochlorine and organophosphates pesticide residues in the soil and water samples obtained from the four different locations from Dogon Ruwa within the Awak community in Kaltungo were determined using GC-MS. This results of organophosphate from the analysis shows high concentration of chlorpyrifos from one research location to another determining its highest concentration in water sample. According to table 4, which could be linked to this particular organophosphate pesticides been used on several crops including corn, soybean, wheat, and varieties of vegetables and fruits making it one of the most widely

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DOI: 10.31695/IJASRE.2023.9.7.6

used pesticides applied to farm for it multipurpose function on various crops, and even local resident can get exposed to it toxic effect when its drifts in the air and come in contact with their drinking water. Furthermore, the mean concentrations for all samples of OCP determined in water from the four different locations ranging from the highest to the lowest mean concentrations which are; concentration of organophophates in water sample- Chloropyrofos 2,141.415ppm > Ronnel 4.0425ppm > Phosphorodithioic acid 2.46ppm > Ethopropos 0.9125ppm > Disulfoton 0.0225ppm and that of organophosphates in soil ranging from the highest to the lowest: Chloropyrofos 389.9275ppm > Ronnel 3.1ppm  $\geq$  Phosphorodithioic acid 0.17ppm > Ethopropos 0.1625ppm > 0.005ppm as seen in the table 4 of results.

From the result, the mean concentration of each Organochlorine pesticides determined are; Dalta-lindane  $\Delta 1446.8625$ ppm > Heptachlor 273.965ppm > Aldrin 63.96ppm > Endrin 27.3025ppm > Heptachlor 25.605ppm > P,P-DDE22.475ppm > Endosulfan 1.14.31ppm > Delta-Lindane 13.7725ppm > P,P-DDD 13.2045ppm > Gamma-lindane 12.265ppm > Methoxychlor 9.5325ppm > P,P-DDT 5.4775ppm > Endosulfan II, 2.1ppm.

In Soil sample the same OCP were determined but at different mean concentration in ppm as can be seen below from the high mean concentration to the loweset mean concentration; Endosulfan 1, 188.384ppm > Aldrin 40.1675ppm >Gamma-lindane 12.125ppm > Apha-lindane8.315ppm >Heptachlor 6.795ppm >P,P-DDE 3.4525ppm > Endosulfan 11, 2.1125ppm > Dalta-lindane 1.615ppm > Methoxychlor 1.0125ppm > Endrin 0.645ppm > PPDDT

## **4.0 CONCLUSION**

Conclusively, from the results obtained, 13 organochlorines were identified from all of the samples analysed and these organochlorines are known to volatized into air, runoff and may also reach into surface and ground water and can accumulate by plants or other organisms in the soil and human exposure can occur through taking farm produce already polluted by these pesticides, drinking water or taking sea food that the pollutants have bioaccumulated in. other possible mean of human exposure includes inhalation, direct ingestion and pesticides drift that can directly affect closed vicinity of the sprayed pesticides area. The detected Organochlorines includes, three isomers of hexachlorocyclohexane ( $\alpha$ -HCH,  $\Delta$ -HCH, $\gamma$ -HCH), Aldrin, Endrin, Heptachor, Heptaclor epoxides,Endosulfal 1&11, DDTS (P,P-DDT, P.P-DDD and P,P DDE) and lastly methoxychlor. which according to literatures the existence of all of these Organochlorine pesticides in the environment was as a results of their continuous usage in agriculture without environment health consideration even though, they have played an important role in increasing crops yield but however their environment and human health effects is a matter of great concern even though according to other literatures, this pesticides have been banned because of their persistent nature and environmental health effects. But however they can still be detected and at a risky concentration just as can be seen in the result.

Furthermore, 5 organophosphates were also detected during the analysis. Human exposure to organophosphate had been through ingestion, inhalation, and dermal contacts and the toxicology of organophosphate usually occurs in farmers and agricultural industrial workers and some common symptoms of exposure includes anxiety, confusion, drowsiness seizure, insomnia, memory loss and respiratory depression. The followings are the identified organophosphate Ethopropos, Disulfan, Ronnel Chloropyrofos and Ethathioic acid, with chloropyrofos having the highest mean concentration of 389.9 PPM in water and 2141. 4 in soil. And according to literatures, this particular Organophophate is used in almost all crops as such acts as multipurpose pesticdes which was why it is found at this concentration. From the results obtained, This proves that, there are pesticides pollution in Dogon Ruwa community as a result of agricultural activities taking place in the community.

## 4.1 Recommendations

From the result obtained, it is recommend that Governmental and non-governmental organizations tackling the issues of environmental pollution should put more effort especially in communities where agricultural activities is the major occupation of the habitat, to enlighten the farmers and guide them on the right ways to use agro-allied chemicals and also guide them on the right choice of the pesticides and proper method of applications and lastly recommendation on priority consideration to capacity building and the regulation of toxic chemicals use should be given utmost consideration especially in African countries

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#### ACKNOWLEDGMENT

Authors appreciate and thank Tertiary Education Trust Fund (TETFund) for funding this research through Institutional Based Research (IBR) Scheme.