

Determination of Organochlorine Pesticide Residues and Trace Metal Concentration in Well and Stream waters from Agricultural Farm Settlement in Ile-Oluji, Ondo State

ABSTRACT

Pollutants are constantly introduced into the aquatic environment primarily due to amplified industrial activity, technical development, growing human population and mistreatment of natural resources, agriculture and domestic wastes run-off. Among these pollutants, Organochlorine Pesticides and some trace metals are found as one of the most hazardous because of their toxicity to organisms. This study investigated the levels of organochlorine pesticide (OCP) residues and Trace Metal concentration in Well and Stream waters from Agricultural Farm Settlement in Ile-Oluji Ondo State. Composite samples of Well and Stream waters were collected randomly within the Farm Settlement and its vicinity. Quantitative determination of the OCPs was determined using Gas Chromatography-Mass Spectrometer after liquid-liquid extraction with (v/v) ethyl acetate/dichloromethane mixture and the Trace Metal was determined using Atomic Absorption Spectrophotometer. The results show that organochlorine pesticide residues were not detected in all the well water samples except for AKN where Heptachlor was detected in the concentration of 0.11 mg/L while all samples from the stream were contaminated with the Organochlorine pesticides at appreciably higher concentration. The results also show that all the trace metals analyzed for are present except for some well samples where Lead are below the detection limit. The mean concentration of some of the sampling sites were below the permissible limit for WHO while some are higher than the permissible limit.

Keywords: Organochlorine, water, Trace Metal, Atomic Absorption Spectrophotometer, Gas Chromatography

INTRODUCTION

The need for the development of agriculture in Nigeria had led to various forms of activities such as pesticide application that may tend to perturb the fragile ecology and pose some environmental risk to Ile-Oluji as a point of concern. Pesticides belongs to some group of few and most important toxic substances released into the environment to kill unwanted organism. Though many has misunderstood the term pesticide as it is often referred to as insecticides, But it is also applicable to herbicides, fungicides, and various other substances used to control unwanted pests. Organochlorine pesticides (OCPs) belongs to the class of hydrocarbons characterize by its cyclic structure, most of the organochlorine pesticides (e.g., aldrin, chlordane, dichlorodiphenyltrichloroethane (DDT), dieldrin, endrin, heptachlor, and hex-chlorobenzene) contain persistent organic pollutants (POPs) that resist degradation and thus remain in the environment for many years [1,2] 2015. Trace metal refers to any metallic chemicals elements that has a relatively high density and is toxic or poisonous at low concentration. Examples of trace metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr) and lead (Pd). Trace metal are natural components of the earth's crust. They enter our bodies via food, drinking water and air. As trace elements, some Trace metal like copper, selenium, zinc are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning [3].

In Nigeria,,Ondo state is a major producer of Cocoa with an estimated output of 45,004.5 metric ton. in 2007, this represents about 40% of the total annual cocoa production in Nigeria [4]. As result of this, the use of organochlorine pesticides is high in this region, particularly in the extensive cocoa plantations found in the Central and the Southern Senatorial District of the State of which Ile Oluji form a major part. Unfortunately, the few available work on the level of

Organochlorine pesticides and Trace Metal contamination of water of Ondo State in Nigeria provide no data on Agricultural Farm Settlement in Ile-Oluji, Ondo State [5,6]. With a long history of pesticide usage on their Cocoa Plantation. Hence, this study is designed to provide information on the concentration of Organochlorine Pesticide Residues and trace elements concentration present in (Well and Stream water) in this farm settlement environment.

MATERIALS AND METHOD

Map 1 : The study Area

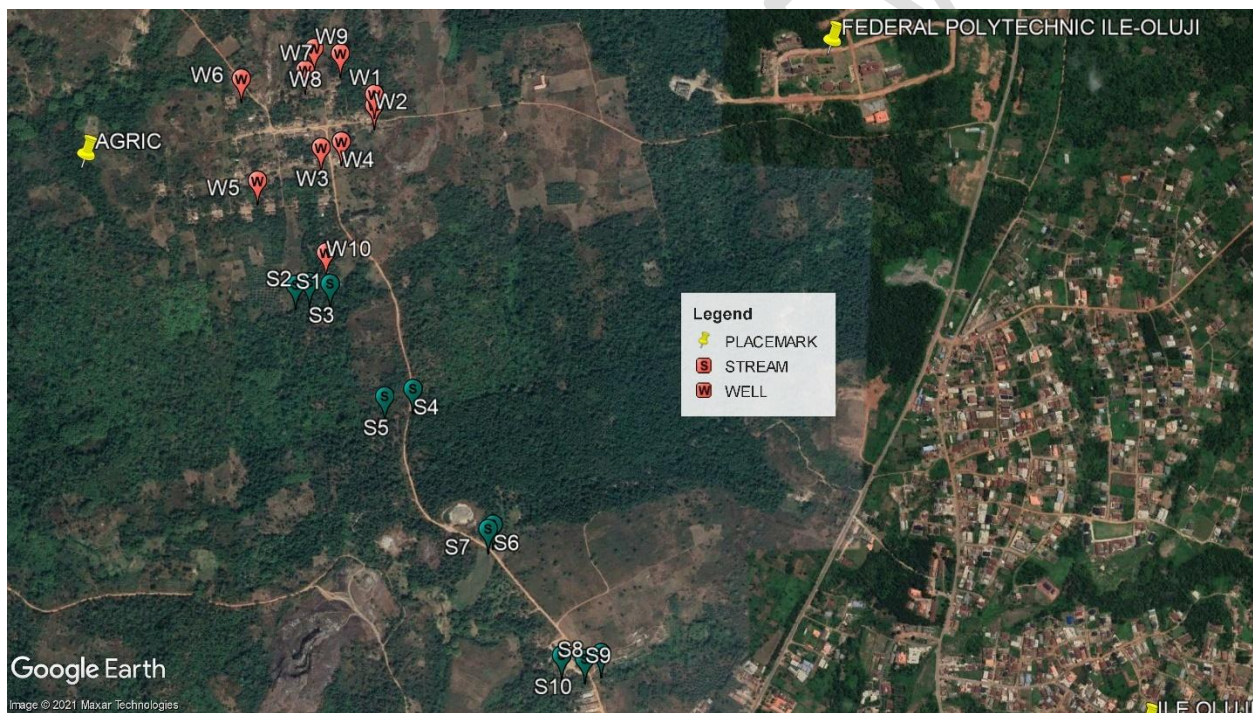


Table 1: Sampling sites and their geographical position

WELL	EASTINGS	NORTHINGS	NAMES
WELL 1	704637.000mE	800289.000mN	BAL
WELL 2	704637.000mE	800256.000mN	ORO
WELL 3	704477.000mE	800129.000mN	AKN
WELL 4	704538.000mE	800147.000mN	KAY
WELL 5	704286.000mE	800029.000mN	AKW
WELL 6	704236.000mE	800334.000mN	AFL
WELL 7	704428.000mE	800361.000mN	AGB
WELL 8	704455.000mE	800426.000mN	FAS
WELL 9	704534.000mE	800411.000mN	OLA
WELL 10	704493.000mE	799815.000mN	ADJ
STREAM	EASTINGS	NORTHINGS	NAMES
STREAM 1 PT1	704402.000mE	799717.000mN	CH ¹
STREAM 1 PT2	704444.000mE	799725.000mN	CH ²
STREAM 1 PT3	704506.000mE	799721.000mN	CH ³
STREAM 2 PT1	704757.000mE	799408.000mN	OY ¹
STREAM 2 PT 2	704672.000mE	799385.000mN	OY ²
STREAM 3 PT1	705000.000mE	799003.000mN	OY ³
STREAM 3 PT2	704985.000mE	798990.000mN	ADE ¹
STREAM 4 PT1	705327.000mE	798620.000mN	ADE ²
STREAM 4 PT2	705278.000mE	798602.000mN	AKD ¹
STREAM 4 PT3	705208.000mE	798613.000mN	AKD ²

Sample Collection, Preservation, Preparation, and Storage

Geographic Processing System (GPS) was used for this study to get the geographical location of each sampling point. The arbitrary selection of sampling points was done independently based on the locations of all the points. Samples of Well and Stream waters was collected in an undisturbed area in the vicinity of site. After collection the water samples was randomly homogenized to form a composite sample of (2.5 L). Concentrated Sulphuric acid (5.0 mL) was added to each of the Organochlorine Pesticide test samples[7] and HNO_3 (15ml) to Trace Metal sample immediately after the collection to prevent microbial degradation of samples. The samples was kept cool at a temperature of 4°C and this temperature was maintained while in the refrigerator before analysis[8].

Extraction of Organochlorine Pesticide Residues

500 cm^3 of the water sample was measured and transferred into a 1000 cm^3 separatory funnel. The aqueous sample was be extracted three times with 100 cm^3 portion of 1:1 (v/v) ethyl acetate/dichloromethane mixture. The separatory funnel was shaken for 3minutes, letting out the pressure intermittently and clamped for 30 min to allow phase separation. The combined organic phases was collected into a 500 cm^3 beaker with the aqueous phase discarded. 20 g of anhydrous sodium sulfate was added to the combined organic layer to dry any water molecule in it and allowed to settle. The organic content was then decanted into a 250 cm^3 round bottom flask and the content evaporated to dryness using Buchi Rotavapor R-215 rotary evaporator at 40°C . The pesticide in the rotary flask will then dissolved and collected with 2 cm^3 of ethyl acetate and transferred into a 2 cm^3 vial ready for a clean-up [7].

Clean-up of Samples Extracts

Ten grams (10g) portion of deactivated silica gel was weighed and transferred into a 10 mm internal diameter glass chromatographic column followed by the addition of 3g of anhydrous sodium sulfate. 10cm³ of the 1:1 (v/v) ethyl acetate/dichloromethane mixture was used to wet and rinse the column. The extract in 2 cm³ ethyl acetate was transferred into the column and the extract vial rinsed (three times) with 2 cm³ ethyl acetate and added to the column. The column was eluted with 80 cm³ portion of ethyl acetate/dichloromethane at a rate of 5 cm³/min into a conical flask as fraction one. The column was eluted again with 50 cm³ portion of ethyl acetate/dichloromethane for the second elution and added to the first extract. All the fractions of each sample was concentrated to dryness using Buchi Rotavapor R-215 rotary evaporator at 40°C. Each residue will be dissolved and collected in 2 cm³ ethyl acetate for GC-MS analysis [7].

Gas Chromatographic –Mass spectrometer Analysis of Extracts from Water Samples

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 8860A gas chromatograph coupled to 5977C inert mass spectrometer (with triple axis detector) with electron-impact source (Agilent Technologies) was used. The stationary phase of separation of the compounds was HP-5 capillary column coated with 5% Phenyl Methyl Siloxane (30m length x 0.32mm diameter x 0.25µm film thickness) (Agilent Technologies). 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. 1 μ L of the samples were injected in splitless mode at an injection temperature of 250 °C. Purge flow to split 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 concentration obtained [9,10]

Trace Metal Analysis Using Atomic Absorption Spectroscopy (AAS)

AAS was used for the determination of trace metals in the Water Samples. After digestion, the sample was analyzed using AAS Buck Scientific 211VGP [8].

Statistical analysis:

Statistical analysis was carried out using the statistical package for social sciences (IBM SPSS 23.0).

RESULTS AND DISCUSSION

Table 2: Concentration (mg/L) of organochlorine pesticide residue in samples of Well waters sampling site

[illegible]

Endosulfan sulfate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p'-DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 3: Concentration (mg/L) of organochlorine pesticide residue in samples of Stream waters sampling site

TARGET COMPOUNDS	ADE ¹	ADE ²	CH ¹	CH ²	CH ³	AKD ¹	AKD ²	OY ¹	OY ²	OY ³
alpha.- Lindane	0.04	0.02	0.07	0.03	0.01	0.04	0.04	0.03	0.02	0.04
.beta.- Lindane	0.03	0.04	0.14	0.04	0.02	0.04	0.03	0.05	0.01	0.04
Gamma – Lindane	0.01	0.02	0.19	0.03	0.05	0.02	0.02	0.03	0.02	0.03
Delta – Lindane	0.02	0.04	0.04	0.02	0.01	0.02	ND	0.05	0.01	0.02
Heptachlor	0.01	0.05	0.03	0.02	0.06	0.04	0.02	0.04	ND	0.03
Chlordane	0.01	ND	ND	ND	ND	ND	0/03	0.01	ND	ND
Aldrin	ND	ND	ND	ND	ND	ND	0.03	ND	ND	ND
Heptachlor epoxide	0.02	0.02	0.17	0.02	0.07	0.02	0.02	0.02	ND	0.02
Endrin	0.01	N.D	N.D	0.05	0.05	0.04	ND	0.05	0.03	0.05
alpha-Endosulfan	0.04	0.03	0.01	0.03	0.11	0.05	0.01	0.04	ND	0.03
p,p'-DDE	N.D	ND	N.D	ND	ND	ND	ND	ND	ND	ND

beta.- Endosulfan	0.01	0.04	0.01	0.03	0.15	0.04	ND	0.01	ND	0.03
m,p'-DDD	0.02	ND	N.D	0.02	0.19	0.02	0.01	0.02	0.04	0.02
Nonachlor	ND	0.04	N.D	ND	0.41	0.04	ND	ND	ND	ND
Endosulfan sulfate	ND	ND	N.D	ND	0.43	0.04	ND	ND	0.02	ND
p,p'-DDT	0.02	ND	N.D	0.01	0.58	0.05	ND	ND	ND	0.02
Methoxychlor	0.02	0.04	N.D	ND	0.46	0.05	ND	ND	ND	ND
Endrin ketone	ND	ND	N.D	ND	0.08	0.03	ND	ND	ND	ND

Table 4: Concentration (mg/L) of Trace Metals in samples of Stream waters sampling site

SAMPLES	Cr	Cu	Fe	Mn	Ni	Pb	Zn
ADE ¹	0.110	0.160	0.250	0.052	0.010	0.028	0.231
ADE ²	0.147	0.097	0.184	0.093	0.030	0.053	0.104
CH ¹	0.088	0.060	0.144	0.122	0.034	0.035	0.386
CH ²	0.045	0.068	0.171	0.080	0.015	0.016	0.032
CH ³	0.244	0.319	1.807	0.255	0.106	0.178	0.340
AKD ¹	0.371	0.461	5.919	0.388	0.188	0.213	0.376
AKD ²	0.315	0.412	4.712	0.409	0.145	0.195	0.215
OY ¹	0.188	0.104	0.409	0.106	0.064	0.088	0.432

OY ²	0.031	0.110	0.449	0.150	0.008	0.012	0.517
OY ³	0.018	0.078	0.547	0.193	0.017	0.020	0.271
WHO(2011) standard	0.03	2.00	0.3	0.40	0.02	0.01	3.00

Table 5: Concentration (mg/L) of Trace Metals in samples of Well waters sampling site

SAMPLE CODES	Cr	Cu	Fe	Mn	Ni	Pb	Zn
BAL	0.213	0.197	0.135	0.115	0.022	0.073	0.170
ORO	0.157	0.126	0.087	0.034	0.008	BDL	0.120
AKN	0.325	0.392	0.600	0.293	0.105	0.146	0.250
KAY	0.195	0.211	0.178	0.084	0.068	0.090	0.123
AKW	0.075	0.114	0.160	0.041	0.004	0.018	0.340
AFL	0.058	0.088	0.185	0.068	0.016	0.034	0.210
AGB	0.068	0.053	0.157	0.025	0.009	BDL	0.110
ADJ	0.501	0.421	2.436	0.322	0.218	0.209	0.310

OLA	0.043	0.083	0.625	0.214	0.011	0.015	0.306
FAS	0.024	0.120	0.312	0.132	0.002	0.010	0.216
WHO(2011) Standard	0.03	2.00	0.3	0.40	0.02	0.01	3.00

BDL= Below Detection Limit

Organochlorine pesticide residues

The results of the organochlorine pesticide residues analyzed in Streams and Well water samples from farm settlement Ile Oluji is shown in Tables 2 and 3 . It was observed in Table 2 that organochlorine pesticide residues were not detected in all the well water samples except for AKN where Heptachlor was detected in the concentration of 0.11 mg/L, this shows that the well water may be free from organochlorine pesticide contamination. Table 3 shows that all samples from the stream were contaminated with the Organochlorine pesticides at appreciably higher concentration with the following ranges in (mg/L): alpha.- Lindane (0.01—0.07); beta.- Lindane (0.01—0.14); Gamma - Lindane (0.01—0.19); delta - Lindane (0.01—0.04);aldrin (ND— 0.03); Chlordane (ND—0.03); α -endosulphan (ND—0.04); β -endosulphan (ND— 0.15); p,p'-DDE (ND); m,p'-DDD (ND— 0.19); p,p'-DDT (ND—0.58); Heptachlor (ND—0.06) ; endrin (ND— 0.05) ; Heptachlor epoxide (ND— 0.17); Noncolor (ND— 0.41); Methoxychlor (ND— 0.46); Endrin ketone (ND— 0.08) and Endosulfan sulfate (ND—0.43). CH¹ and CH³ account for the presence of the highest concentration of these organo chlorine pesticides. The high concentration of this pesticides suggests an indication of recent usage of some of these pesticides in the study area. Some of the pesticides such as chlordane, heptachlor, DDT, DDE, and

endosulfan detected at this study area are known to have endocrine and estrogenic disrupting properties which may have biodiversity impact on the of the aquatic habitats.[11] The presence of DDT and some of its degradation metabolite such as DDE and DDD in the sample area can be attributed to their wide usage before their banning since various DDT metabolites can persist for a long time in the environment [12] or it could be as a result of contamination by organochlorine pesticide residues due to water runoff or leaching of organochlorine pesticide residue in the sediment of some of the sampling sites. [5] The concentration of Organochlorine pesticide residues in the stream water sample was higher when compared to some previous studies on surface water of ondo state [5,13] This is because Organochlorine pesticides are generally nonbiodegradable, toxic and persists in the environment for a long period of time. The nature of persistence makes Organochlorine pesticides accumulate in the food chain and in lower organisms like planktons. Organochlorine Pesticides become concentrated due to several chemical processes and are adsorbed from water to sediments and bottom substrates. Organochlorine pesticides are known to be carcinogenic especially through nasal inhalation and dermal contact. Ingestion of pesticides is known to cause dizziness, convulsions, skin irritation and nasal congestion [14]

Statistical analysis using ANOVA ($P < 0.05$) shows that Concentration of Organochlorine Pesticide Residues is significantly different across the sample of stream water and well water and the interaction between Organochlorine Pesticide Residues and water sample is significantly different

Trace Metal Analysis

The mean concentrations (mg/L) of selected heavy metals assessed from the stream and well water samples collected from farm settlement Ile-Oluji Ondo State is show in Tables 4 and 5.

Iron (Fe)

The mean concentration of Fe in the stream water sample ranged from 0.144 to 5.919mg/L. The highest value was recorded at AKD¹ whilst the minimum value was recorded at ADE¹. The mean concentration of Fe in the well water sampling sites ranged from 0.087 to 2.436 mg/L. The highest value was recorded at ORO while the minimum value was recorded at ADJ. The mean concentration of Fe from some of the sampling site were below the permissible limit of 0.3 mg/L for WHO (WHO 2011) while some are higher than the permissible limit of 0.3 mg/L for WHO [15]. High Concentration of Iron in water can damage fabrics[8].

Lead (Pb)

The mean concentration of Pb in the stream water sample ranged from 0.012 to 0.213mg/L; the highest value was recorded at OY² whilst the lowest value was recorded at AKD¹. All the mean concentration of Pb obtained at the stream sites were above the permissible limits of 0.01 mg/L respectively for WHO, Guideline/ standard values [15]. The mean concentration of Pb in the well water sample range from 0.010 to 0.209 mg/L; the highest value was recorded at ADJ whilst the lowest value was recorded at FAS. Though the Pb concentration in the sample collected at ORO and AGB is below the Detection Limit the mean Pb concentration obtained at the other site were above the permissible limits of 0.01 mg/L respectively for WHO, Guideline/ standard values except for FAS that is equal to the permissible limits of 0.01 mg/L. Lead are known to bio-accumulate sometimes and even undergo bio-magnification in organisms such as fishes and even plants with serious health implications to the aquatic ecosystem [16].

Manganese (Mn)

The mean Concentration of Mn in the stream water sampling sites ranged from 0.052 to 0.193mg/L. The highest value was recorded at OY³ while the minimum value was recorded at ADE¹. The mean concentration of Mn in the well water sampling sites ranged from 0.025 to 0.322 mg/L. The highest value was recorded at ADJ while the minimum was recorded at AGB. The mean concentration of Mn from all the sampling site were below the permissible limit of 0.40 mg/L for WHO [15].

Copper (Cu)

The mean Concentration of Cu in the stream water sample ranged from 0.060 to 0.461 mg/L, the highest value was recorded at AKD¹ whilst the lowest value was recorded at CH¹. The mean Cu concentration in the well water sample ranged from 0.053 to 0.421 mg/L; the highest value was recorded at ADJ whilst the lowest value was recorded at AGB. All the mean Cu concentration obtained at the stream sites were below the permissible limits of 2.00 mg/L respectively for WHO, Guideline/ standard values. [15]. Though the concentration of Cu in all the sample were below the permissible limits , the presence of Cu in the sample may be as a result of long time usage of Copper Sulphate as fungicide to dress cocoa pod.

Zinc (Zn)

The concentration of Zn in the stream water sample ranged from 0.032 mg/L – 0.517 mg/L. The highest value was recorded at OY² while the lowest was recorded at CH² sites.

The concentration of Zn in the well water sample ranged from 0.110 mg/L – 0.340 mg/L. The highest value was recorded at AKW while the lowest was recorded at AGB sites. The Zn concentration of the water samples were below the permissible limit of 3.0 mg/L respectively for WHO, Guideline/ standard values. [15]. Excess zinc concentration in the body accumulates in

the body. Although zinc is not a human carcinogen, but excessive intake of zinc through contaminated food chain could lead to vomiting, dehydration, abdominal pain, lethargy and dizziness [8]

Nickel (Ni)

The concentration of Ni in the stream water sample ranged from 0.008 mg/L – 0.188 mg/L. The highest value was recorded at AKD¹ while the lowest was recorded at OY¹ sites. The Concentration of Ni in the well water sample ranged from 0.002 mg/L – 0.218 mg/L. The highest value was recorded at ADJ while the lowest was recorded at FAS sites. The mean concentration of Ni from some of the sampling sites were below the permissible limit of 0.01 mg/L for WHO [15] while some are higher than the permissible limit of 0.01 mg/L for WHO [15]. The consumption of nickel is dependent on its physicochemical procedure and the major target organs for nickel-induced toxicity are the lungs the higher respiratory tract for inhalation and the kidney[16].

Chromium (Cr)

The concentration of Cr in the stream water sample ranged from 0.018 mg/L – 0.371mg/L. The highest value was recorded at ADJ while the lowest was recorded at OY³ sites. The concentration of Cr in the well water sample ranged from 0.024 mg/L – 0.501 mg/L. The highest value was recorded at AKW while the lowest was observed at FAS sites. The mean concentration of Ni from some of the sampling sites were below the permissible limit of 0.01 mg/L for WHO (WHO 2011) while some are higher than the permissible limit of 0.01 mg/L for WHO (WHO 2011).

Statistical analysis using ANOVA ($P < 0.05$) shows that The distribution of trace metal is significantly different In the sample of stream and well water and the interaction between trace metal and water sample is significantly different.

CONCLUSION

The result indicates pollution due to high concentration of Organo chlorine and Trace metals in the samples of stream and well water. The values obtained from the results were below the permissible limit for WHO while some are higher than the permissible limit.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

REFERENCES

1. Sharma T, Banerjee BD, Mazumdar D, et al (2015) Association of organochlorine pesticides and risk of epithelial ovarian cancer: A case control study. *J Reprod Heal Med* **1**:76–82.
2. Yadav IC, Devi NL, Syed JH, Cheng Z, Li J, Zhang G, Jones KC (2015) Current status of persistent organic pesticides residues in air, water, and soil, and their possible effect on neighboring countries: A comprehensive review of India. *Sci Total Environ* **511**:123–137.
3. Kishore K.K. Xianguang M, Christodoulatos C and Veera M.B. (2008) ‘biosorption mechanism of nine different heavy metal onto biomatrix from rice husk’ *journals of hazardous materials*,**53**: 1222-1234.

4. Ajayi J.R, Afolabi M.O, Ogunbodede E.F, Sunday A.G (2010). Modelling rainfall as a constraining factor for cocoa yield in Ondo State. *Am. J. Sci. Ind. Res* **1**: 127-134.
- 5 Akinlawo S (2016) Determination of Organochlorine Pesticide Residues in Water and Sediment Samples from Selected Areas of River Ilaje, Nigeria. *American Chemical Science Journal* **11(2)**: 1-6.
- 6.Idowu G. A., Aiyesanmi A. F. and Owolabi B. J. (2013) Organochlorine pesticide residue levels in river water and sediment from cocoa-producing areas of Ondo State central senatorial district, *Nigeria Journal of Environmental Chemistry and Ecotoxicology* Vol. **5(9)** :242-249.
- 7.Osesua, B. A, Omogbehin, S.A and Anyekema, M (2019) Determination of Pesticide Residues in Fish and Water from Dukku River, Birnin Kebbi, Kebbi State, Nigeria. *International Research Journal of Applied Sciences, Engineering and Technology*.**5(10)**: 1-15.
- 8 .Ogbunike C .C and Ezeibeonu A. P (2020) Comparative Assessment of Trace and Heavy Metals in Available Drinking Water From Different Sources in the Centre of Lagos and off Town (Ikorodu LGA) of Lagos State, Nigeria , *Advance Journal of Chemistry section A*, **3(1)** :94-104.
9. Singh RP. (2001) Comparison of organochlorine pesticide levels in soil and groundwater of Agra, India. *Bull Environmental Contaminant Toxicology*; **67**:126–32.
10. Turgut C, Atatanir L, Mazmanci B, Mazmanci MA, Henkelmann B, Schramm KW (2011). *The occurrence and environmental effect of persistent organic pollutants (POPs) in Taurus Mountains soils. Environment Science Pollution Research*.

11. Soto, A. M., Chung, K. L. and Sonnenschein C., (1994) "The pesticides endosulfan, toxaphene, and dieldrin have estrogenic effects on human estrogen-sensitive cells," *Environmental Health Perspectives*, **102(4)** : 380–383
12. Van Dyk, L. P Wiese, I. H. and. Mullen, J. E (1982) "Management and determination of pesticide residues in South Africa," *Residue Reviews*, . **82** : 37–124,
13. Aderonke A.O, Aderemi O.O, Olabode I.A and Nelson, T (2013) Organochlorine Pesticide Residues in Sediments and Waters from Cocoa Producing Areas of Ondo State, Southwestern Nigeria. *ISRN Soil Science* ,2013, D1 31647: 1-12
14. Oladunni B. O, Temitope M. S and Adelaja O. O (2016) Determination of the Level of Pesticides in Sediment and Water from the Lagos Lagoon , *Journal of Advanced Agricultural Technologies* Vol. **3(3)**: 222 -225
15. W.H.O.(2011). *Guidelines for drinking water quality*, 4th edn. World Health Organization, Geneva
16. Aliyu J A, Saleh Y and Kabiru S (2015) Heavy Metals Pollution on Surface Water Sources in Kaduna Metropolis, Nigerias, *Science World Journal* **10 (2)** : 1-5
16. Mahipal, S .S and Rajeev, K. (2019). Contaminant of Heavy Metals in Groundwater & its Toxic Effects on Human Health & Environment, *International Journal of Environmental Sciences & Natural Resources* **18 (5)** : 149-153

APPENDIX

Univariate Analysis of Variance

Tests of Between-Subjects Effects

List 1 : Dependent Variable: Concentration of trace metal in the samples of Stream water

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	111.081 ^a	69	1.610	7043.617	.000
Intercept	16.925	1	16.925	74052.993	.000
Water_sample	17.826	9	1.981	8665.769	.000
Trace_metal	29.547	6	4.925	21546.142	.000
Water_sample * Trace_metal	63.708	54	1.180	5161.867	.000
Error	.016	70	.000		
Total	128.022	140			
Corrected Total	111.097	139			

a. R Squared = 1.000 (Adjusted R Squared = 1.000)

Note: The distribution of trace metal is significantly different

Note: The distributions of the sample of stream water is significantly different

Note: The interaction between trace metal and water sample is significantly different.

Tests of Between-Subjects Effects

List 2 : Dependent Variable: Concentration of trace metal in the samples of well water

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	12.920 ^a	69	.187	16053.331	.000
Intercept	4.746	1	4.746	406891.445	.000
Trace_metal	2.611	6	.435	37312.135	.000
Water_sample	3.692	9	.410	35167.715	.000

Trace_metal *	6.617	54	.123	10505.512	.000
Water_sample					
Error	.001	70	1.166E-5		
Total	17.667	140			
Corrected Total	12.921	139			

a. R Squared = 1.000 (Adjusted R Squared = 1.000)

Note: The distribution of trace metal is significantly different

Note: The distributions of the sample of well water is significantly different

Note: The interaction between trace metal and well water sample is significantly different

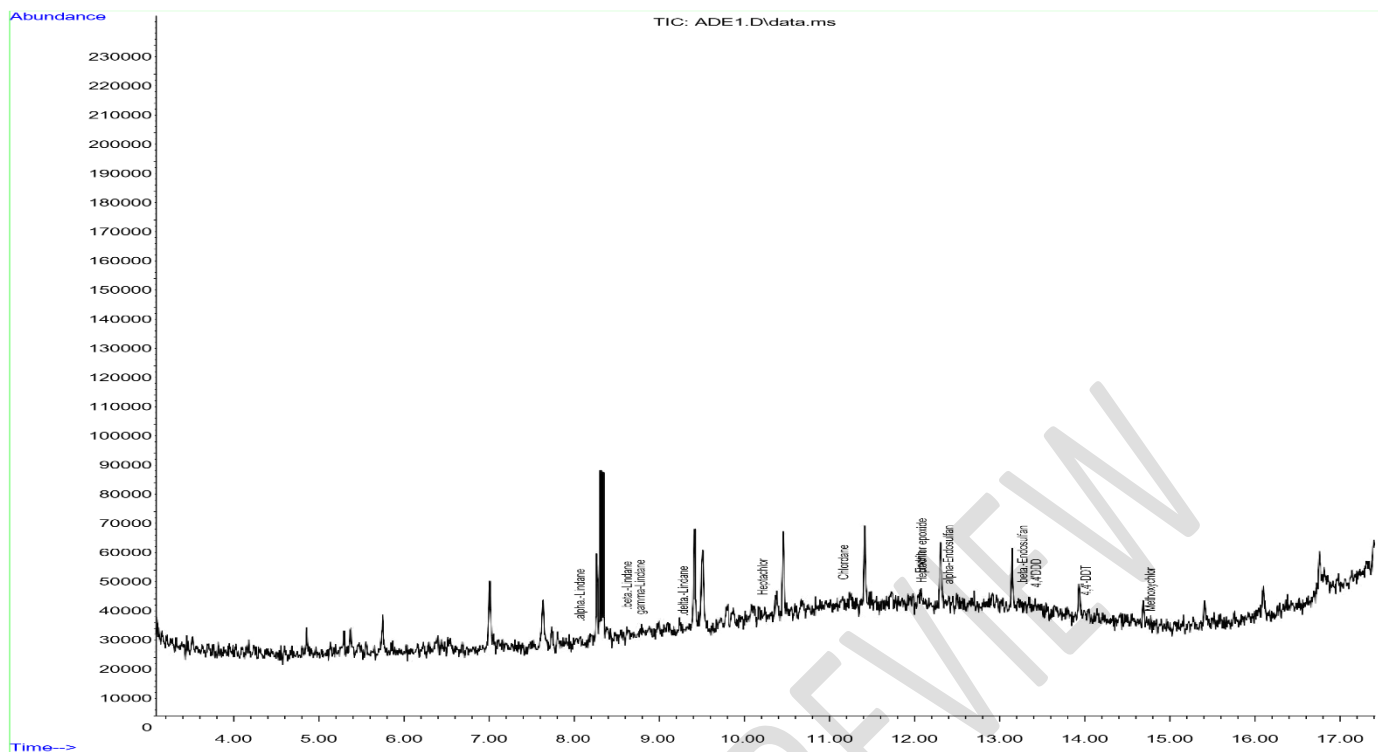
Tests of Between-Subjects Effects

List 3 :Dependent Variable: Concentration of Organochlorine Pesticide Residues in Sample of Stream Water

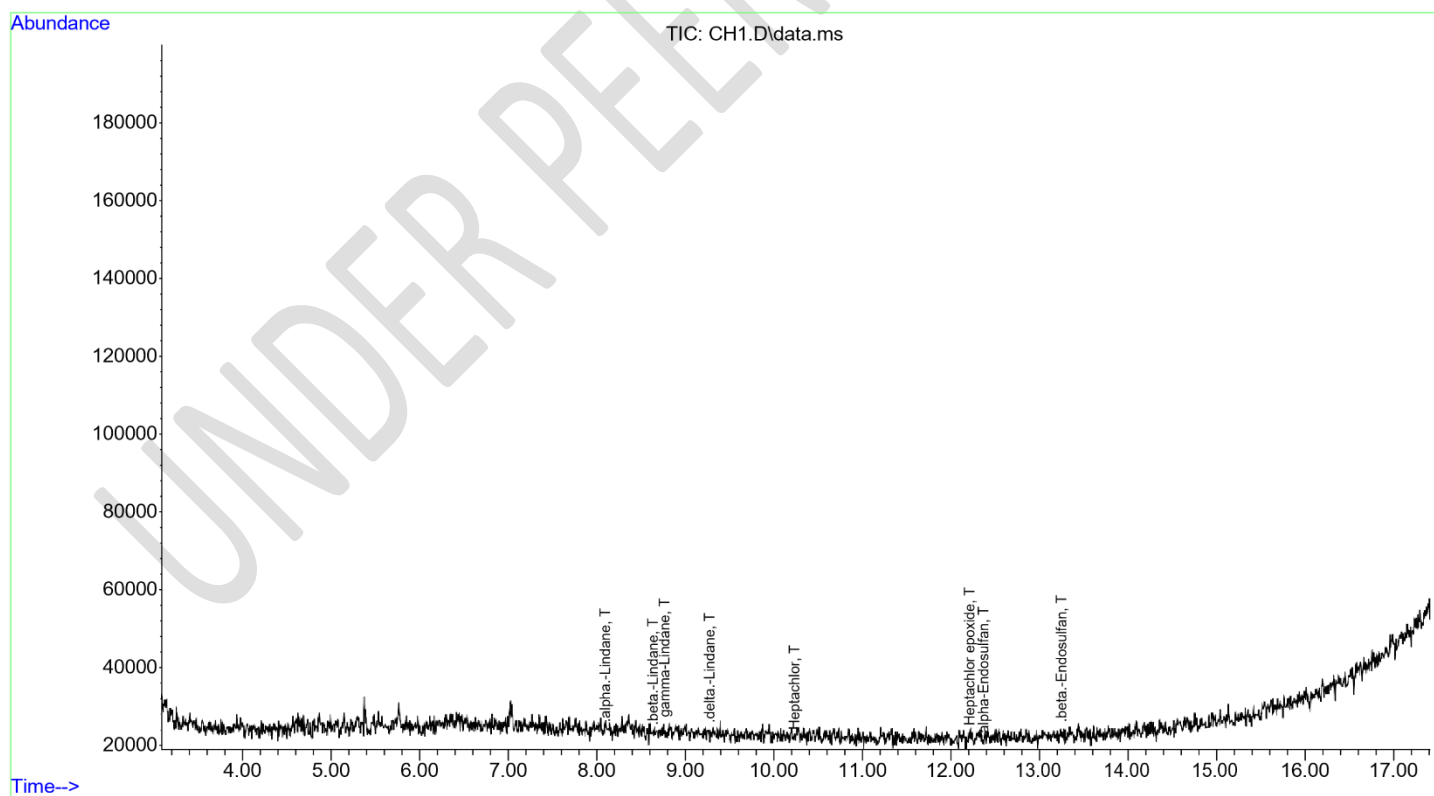
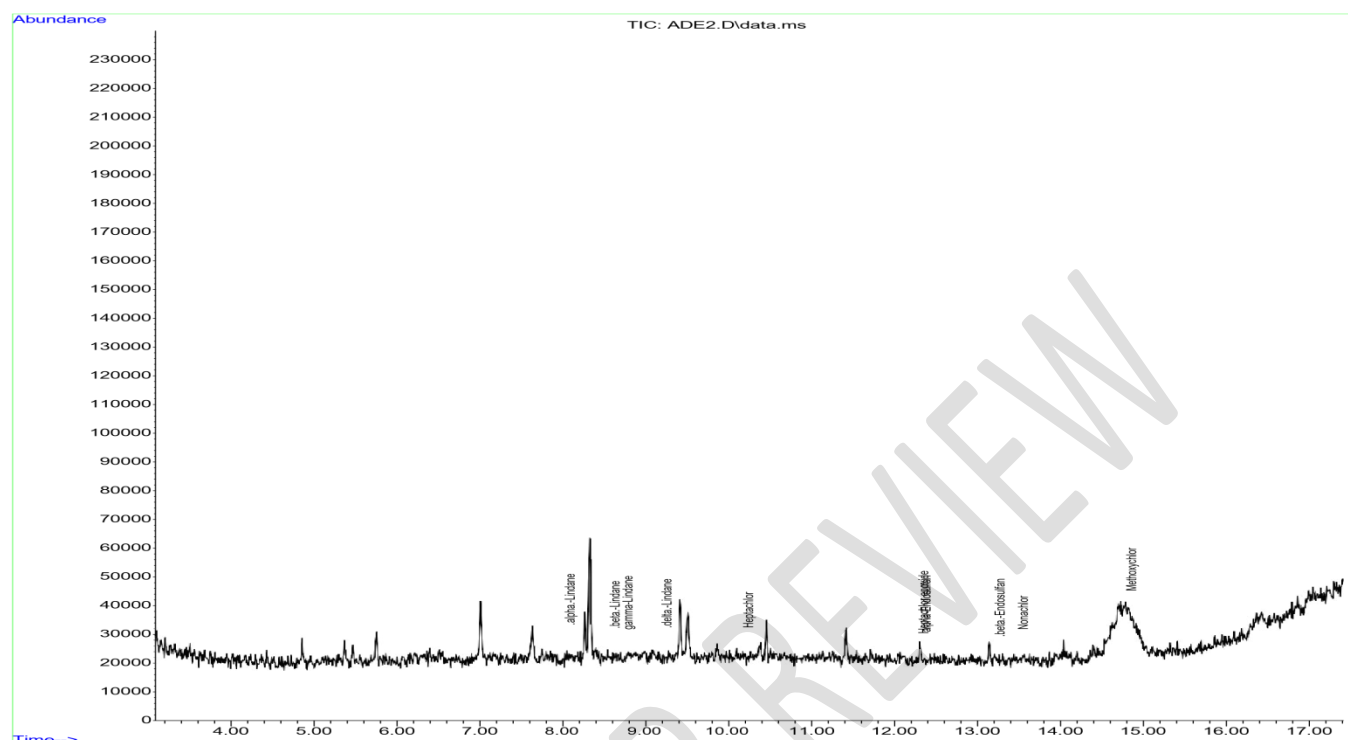
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	2.518 ^a	174	.014	10.474	.000
Intercept	.399	1	.399	288.726	.000
organochlorine	.120	17	.007	5.102	.000
Stream_water	.799	9	.089	64.235	.000
organochlorine * Stream_water	1.461	148	.010	7.147	.000
Error	.332	240	.001		
Total	3.537	415			
Corrected Total	2.849	414			

a. R Squared = .884 (Adjusted R Squared = .799)

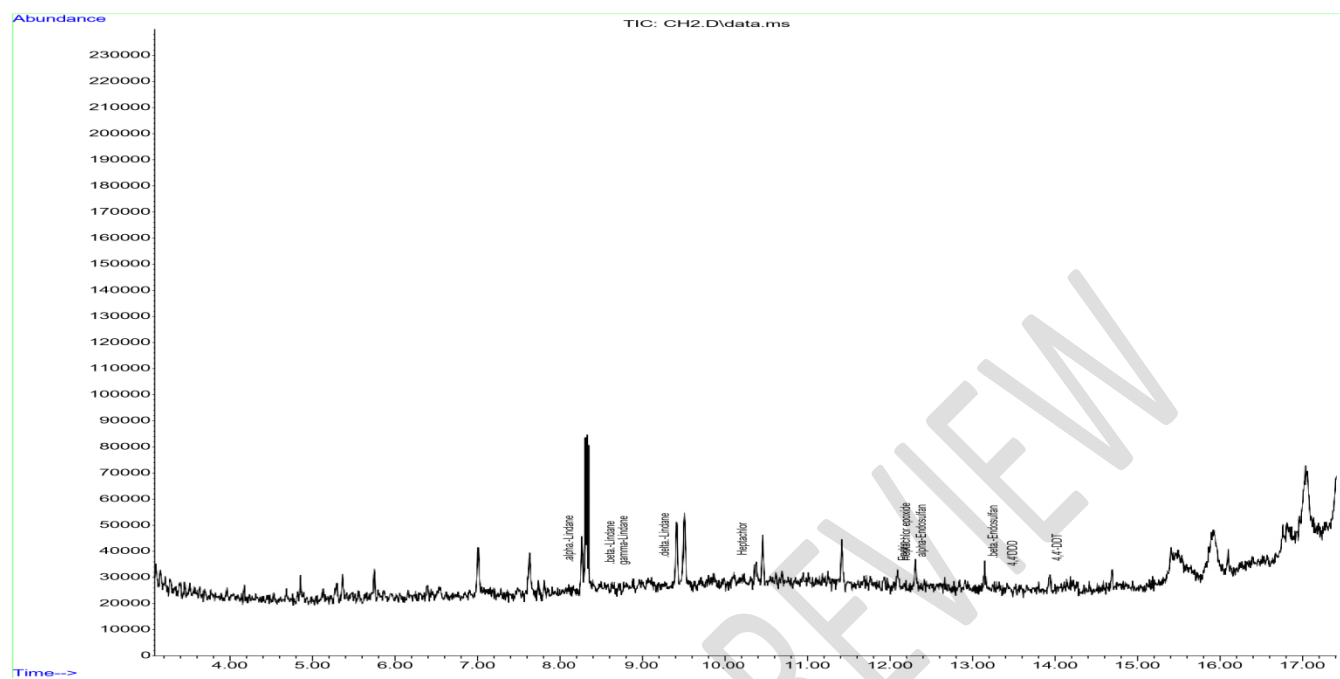
**** Interaction between organochlorine and Stream water is significant.



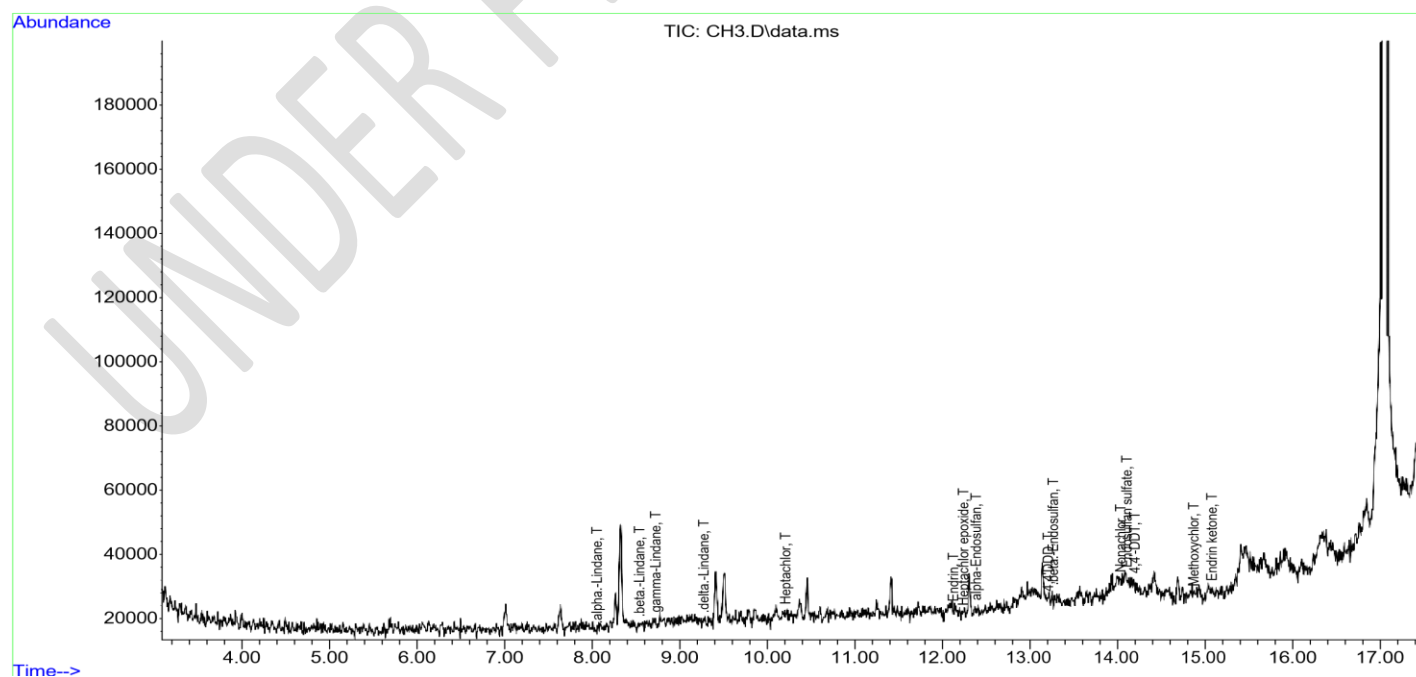
GC-MS CHROMAMATOGRAM FOR THE STREAM SAMPLE OF ADE¹



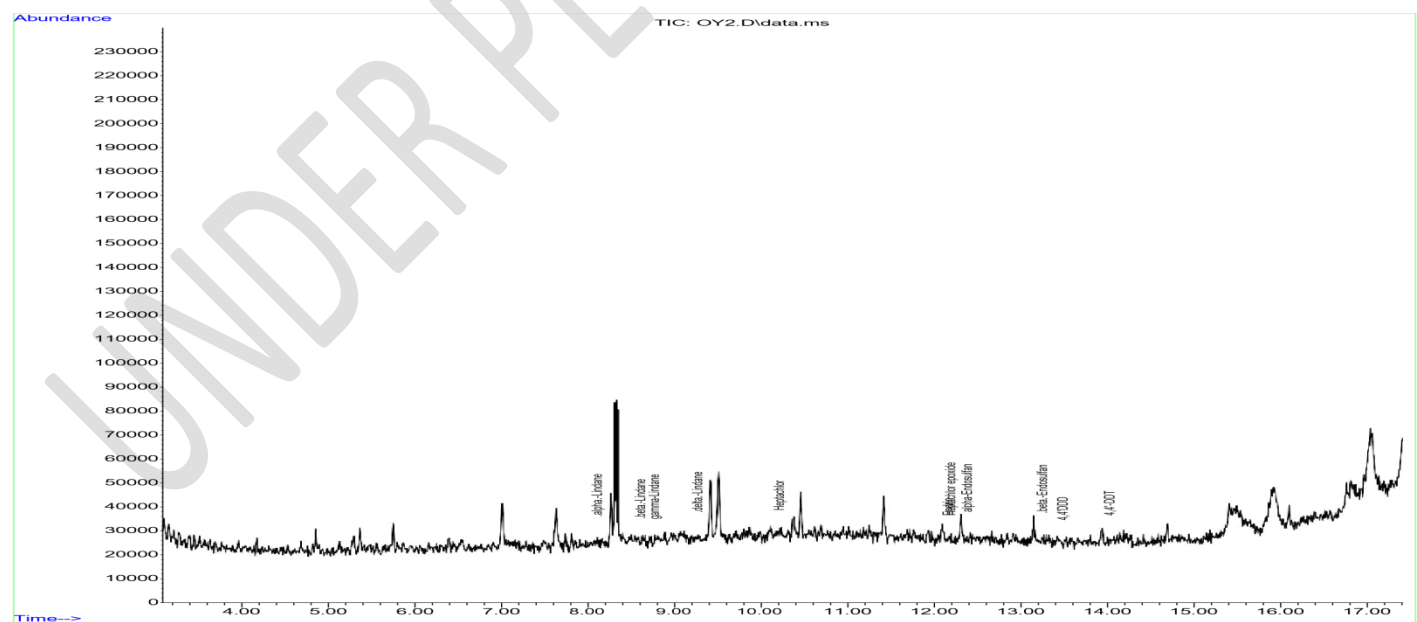
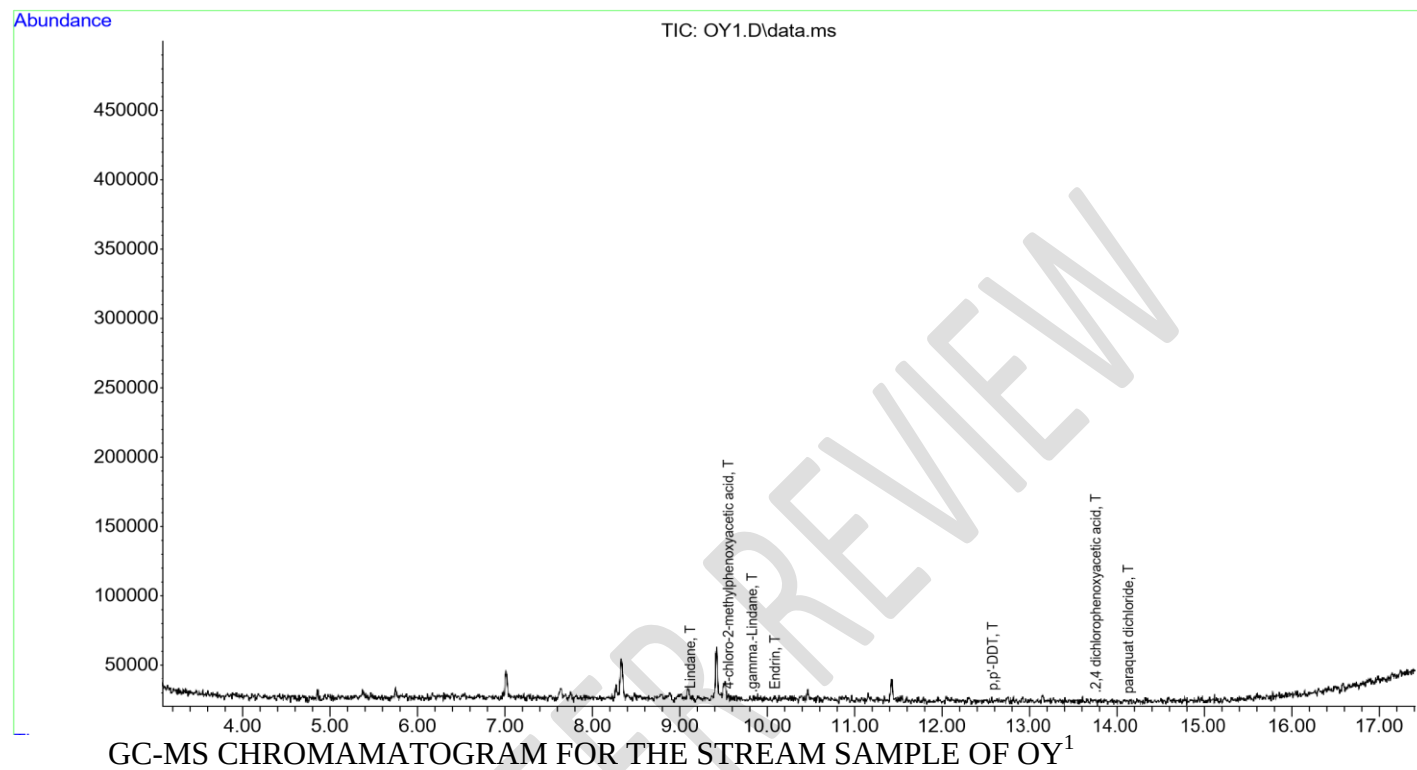
GC-MS CHROMAMATOGRAM FOR THE STREAM SAMPLE OF AD²
GC-MS CHROMAMATOGRAM FOR THE STREAM SAMPLE OF CH¹

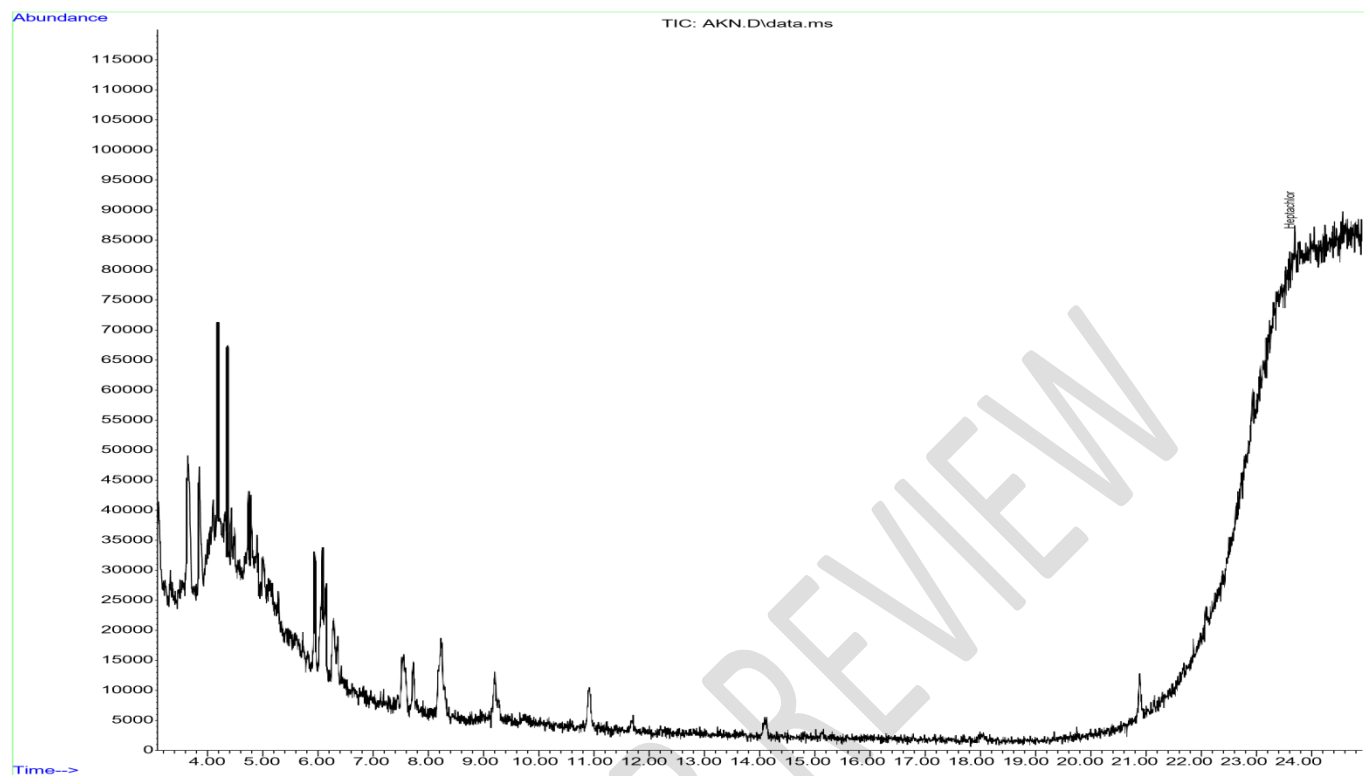


GC-MS CHROMAMATOGRAM FOR THE STREAM SAMPLE OF CH²

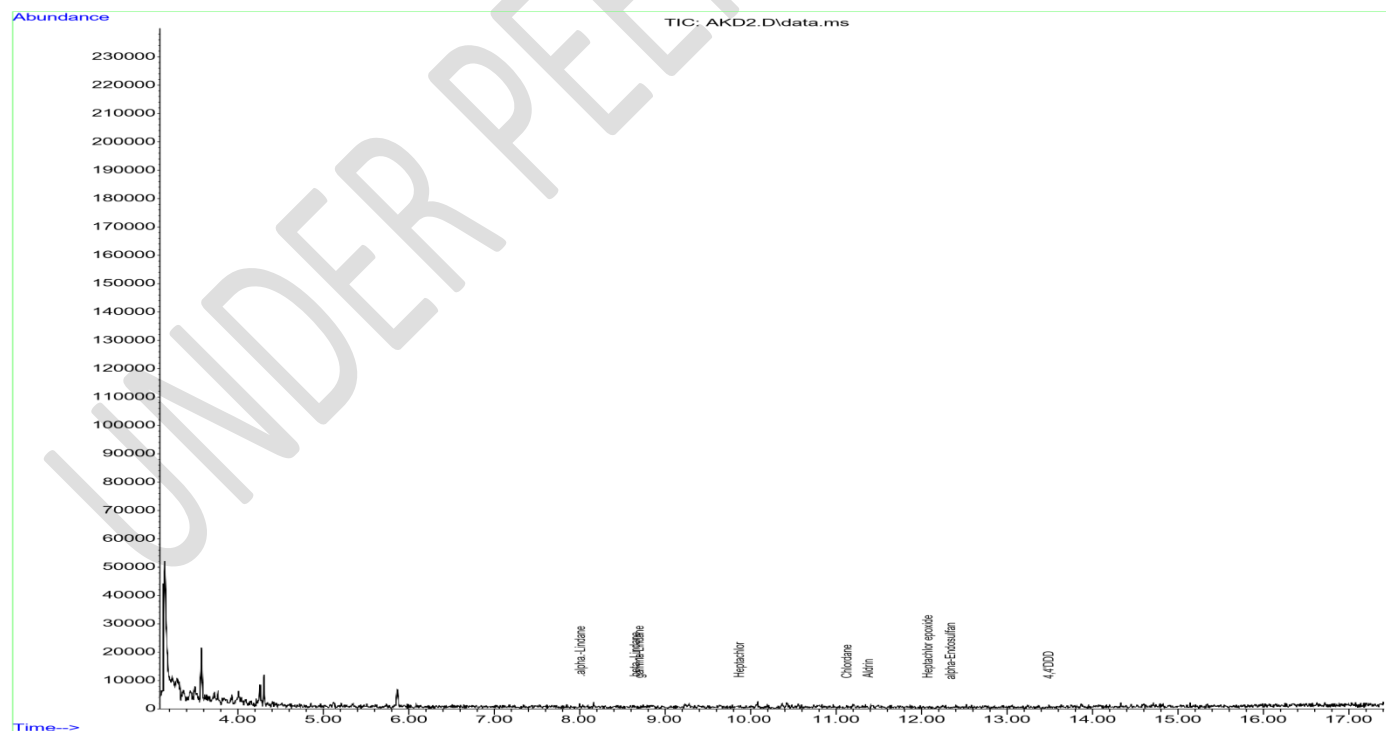


GC-MS CHROMAMATOGRAM FOR THE STREAM SAMPLE OF CH³





GC-MS CHROMAMATOGRAM FOR THE STREAM SAMPLE OF AKD ¹



GC-MS CHROMAMATOGRAM FOR THE STREAM SAMPLE OF AKD ²

