IJAAR PUBLISHING®

International Journal of Advanced Academic Research | ISSN: **2488-9849**
Vol. 9, Issue 6 (June, 2023) | www.ijaar.org

# ANALYSIS OF ORGANOCHLORINE AND ORGANOPHOSPHATE PESTICIDE RESIDUES CONCENTRATION IN OWE RIVER, ILE-OLUJI, ONDO STATE, NIGERIA.

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***ABSRTACT***

*Pollution of Water caused by synthetic pesticides in water bodies have been a great concern globally and in developing countries such as Nigeria in particular as most of these pesticide compounds are persistent and bio-accumulative with high toxicity effects on ecosystems and humans. Among these pollutants, Organochlorine and Organophosphate Pesticides are found as one of the most hazardous because of their toxicity to organisms. This study investigate the levels of Organochlorine and Organophosphate pesticide residues in samples of water collected from Owe river, Ile-Oluji, Ondo State. Composite samples of the waters were collected randomly from four sampling point and analyzed for Organochlorine and Organophosphate pesticide residues using Gas Chromatography-Mass Spectrometer The results shows the presence of the Organochlorine pesticide residues in the following range: beta.- Lindane (0.01—0.06); Gamma - Lindane (0.03—0.25); delta - Lindane (0.16—2.26); Endosulfan ether (0.86-4.96); aldrin (BDL— 0.03); Chlordane (ND—0.36); alpha-endosulphan (BDL –0.09); Dicofol (ND— 0.05); Mirex (0.02 - 0.03); beta-endosulphan (0.06— 1.11); p,p,, DDT (0.05—0.07); Heptachlor (0.03—0.05); endrin (0.01—0.03); Methoxychlor (0.06— 0.07) and Organophosphate pesticide residues in the following range: azinphos methyl (0.32); Coumaphos (0.35-0.38); Dimethoate (4.13 -28.57); Merphos (0.13-3.93). The results revealed higher level of Organochlorine in the water and the Organophosphate residues. The mean concentrations of some of the sampling sites were below the permissible limit for WHO while some are higher than the permissible limit. This therefore necessitates a continuous monitoring.*

***Keywords:*** *Organochlorine, Organophosphate Gas Chromatography, Pollution, Water*



Published *30/06/2023*
Adehuga, O.S., Sheriff, U.I and Olalekan, O. (2023). Analysis of Organochlorine and Organophosphate Pesticide Residues Concentration in Owe River, Ile-Oluji, Ondo State, Nigeria. *International Journal of Advanced Academic Research*, 9(6), 436-447.

## INTRODUCTION

Pollution of Water is caused by the contamination of water bodies such as rivers, streams, lakes, oceans and groundwater by human activities such as the application of pesticides. This affects organisms and plants that live in these aquatic environments and in almost all cases the effect is damaging not only to the individual species and populations but also to the natural biological communities. Water pollution occurs when pollutants are discharged either directly or indirectly into water bodies without adequate control or treatment. It is a major cause of global concern as it leads to onset of numerous fatal diseases such as cancer which can lead to death (Erickson, 2013). Synthetic pesticides are man-made substance use in the modern agriculture for the control of several groups of pests. But these pesticides are harmful to man and the environment in general as non target organisms. The most commonly used pesticides include insecticides, herbicides, fungicides and rodenticides (Yadav et al., 2015). Modern agricultural pesticides rely on the usage of synthetic pesticides (mainly herbicides, insecticides and fungicides) in order to prevent losses by pests. The application of pesticides may lead to contamination of aquatic environments through several ways such as spray drift, surface runoff and leaching. Besides habitat loss, overexploitation of species, introduced species, aquatic organisms are affected by the pollution of surface waters with pesticides from agriculture in particular (IUCN, 2009).

The application of pesticides give rise to a range of benefits, including increased the quality and quantity of food and reduced insect-borne disease but raised the issues on the potential detrimental effects to the environment, including water resources. The associated environmental impacts are mainly due to the persistent and ubiquitous characteristics of various pesticides that posed havoc to the biodiversity (Sharma *et al;* 2019). The dissolution of pesticides depends on the nature of the compound, pesticide application techniques and climatic factors. The pesticides that are not readily degrading will either get accumulated in soils or mobilized from one site to another in the form of degraded products, with unknown toxicity to human health (Sharma *et al;* 2019). The occurrence of pesticides in the water body is derived by the runoff from the agricultural field and industrial wastewater. Despite the soil matrix that serves as a storage compartment of pesticide due to the high affinity of agrochemicals with soil, surface water resources like streams, estuaries and lakes, as well as the groundwater are susceptible to pesticide contamination because of the close interconnection of soil with water bodies. The low concentration of pesticides built up in water can get magnified through the food chain and enter aquatic organisms that are hazardous for human consumption (Sharma *et al;* 2019). Importantly, chronic exposure to pesticides through water ingestion can mimic the human body's hormones that reduce body immunity, interrupt hormone balance, trigger reproductive-related issues, posing carcinogenic effects and reduce intelligence particularly towards the children under the body development stage (Yadav et al., 2015). Organochlorines (OC) are a group of chlorinated compounds widely used as pesticides. These chemicals belong to the class of persistent organic pollutants (POPs) with high persistence in the environment. OC insecticides were earlier successfully used in control of malaria and typhus, yet they are banned in most of the advanced countries (Aktar *et al.*, 2009). The review statistics on the use of different pesticides shows that 40% of all pesticides used belong to the organochlorine class of chemicals (Gupta, 2004; FAO, 2005). Due to their low cost and the need against various pests, organochlorine insecticides such as DDT, hexachlorocyclohexane (HCH), aldrin and dieldrin are among the most widely used pesticides in developing countries of Asia (FAO, 2005; Gupta 2004). Organophosphates (OPs) are a class of insecticides, several of which are highly toxic.. Organophosphates are used in agriculture, homes, gardens and veterinary practices; however, in the past decade, several organophosphate has been banned, including parathion, which is no longer registered for any use, and chlorpyrifos, which is no longer registered for home use (Salameh et al., 2014).

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. As a result of this, the use of pesticides that contain organochlorine and organophosphate 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 form a major part. Unfortunately the few available works on the level of organochlorine and organophosphate pesticide contamination of water of Ondo state in Nigeria provide no data on some rivers in Ile-oluji, Ondo state. With a long history of pesticides usage on their cocoa plantation. Hence, this study is designed to provide information on the concentration of organochlorine and organophosphate pesticide residues present in owe river water in this settlement.

## MATERIALS AND METHOD

### Sample Collection, Preservation, Preparation and Storage

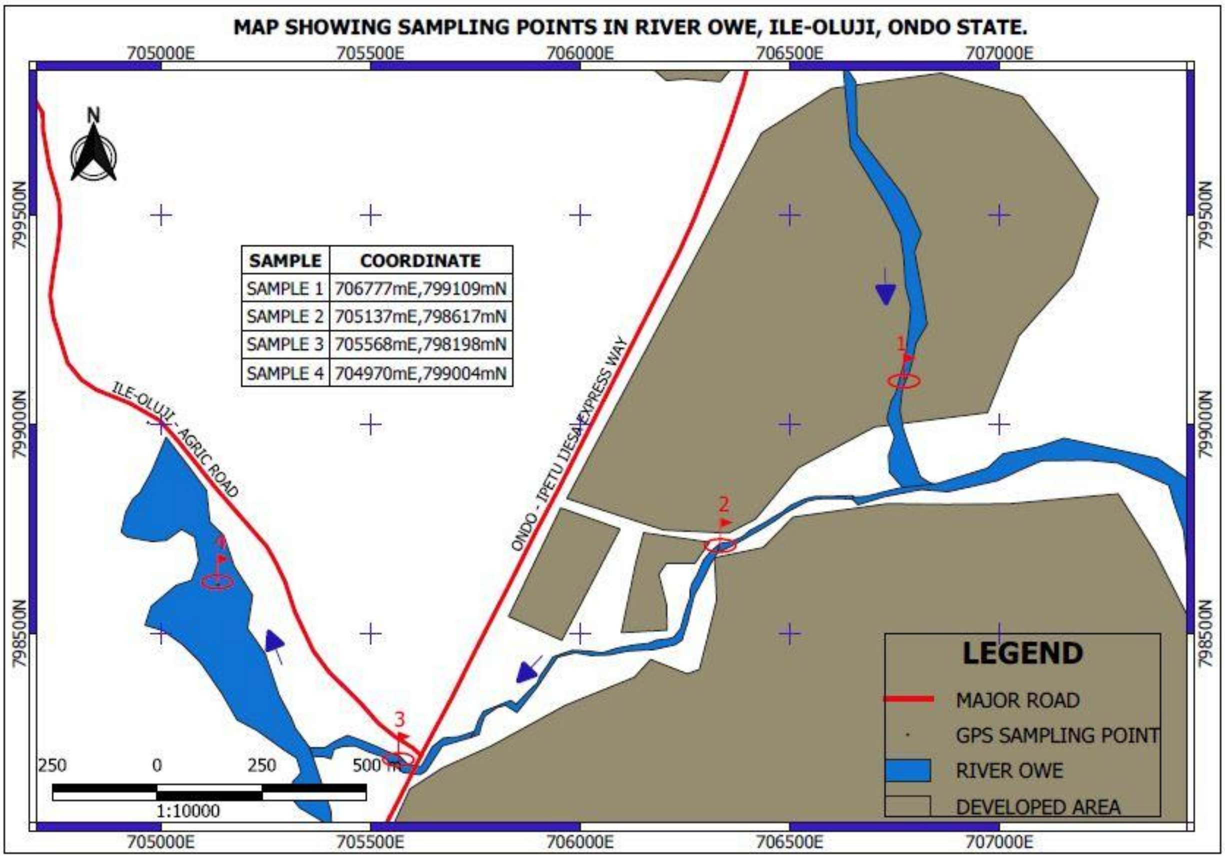



**Fig 1: Map showing the sampling points in owe river, ile-oluji, ondo state.**

Geographic positioning 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 location of all the points. Four sampling points (olorungbohunmi, tipper garage, ministry of agric, akintiyemi) were located and 2.5 litre sample was collected from the four sampling points for organochlorine and organophosphate analysis, after collection, the water samples was randomly homogenized to form a composite sample. Concentrated sulphuric acid (5.0 ml) was added to each of the organochlorine and organophosphate test samples. The samples was kept in a refrigerator before analysis (Osesua *et al.,* 2019)

**Extraction of organochlorine residues in water samples**

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 were 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 (Osesua *et al.,* 2019)

**Extraction of organophosphate residues in water samples**

The water samples were adjusted to $p^H4$ with 2 ml $H_2SO_4$, while 10g of Nacl was added to all water samples to increase extraction efficiencies. N-hexane (50ml) was introduced into a two litre separating funnel containing 1 litre of filtered water and was shaken vigorously for5minutes and allowed to settle. After complete separation, the organic phase was drained into a 200ml conical flask. The aqueous phase was re-extracted with 50ml of nhexane. The samples were then centrifuged for 6 minutes to separate the extract from the pellet **(**Mustapha, 2020).

**Clean-up of Samples Extracts**

Granular silica gel (Mesh Size 60-200A) was activated by heating at $130^0$ C for 16hrs and stored in a desiccator. A glass column was packed with 5g of silica gel and 1g of Anhydrous $Na_2$ $S0_4$ was added. 20ml n-Hexane was added to the column and eluted into a beaker. The 2ml sample extract was added to the top of the column quantitatively. Another 10ml of n-Hexane was added to the column and eluted to waste. Before the column head dried out, 10ml (1+1) Dichloromethane + Hexane was added and the eluent was collected. The eluent was then concentrated to 2ml using a rotary evaporator and analyzed using Agilent 8860A gas chromatograph coupled to 5977C inert mass spectrometer (with triple axis detector) with electron-impact source (Turgut *et al.,* 2011).

## RESULTS AND DISCUSSION

**Table 1: Concentration (mg/L) of organochlorine pesticide residue in Owe River, Ile-Oluji, Ondo State, Nigeria**

| S/N | Target compounds | MOA | AKY | OGB | TPG |
|---|---|---|---|---|---|
| 1. | alpha-lindane | BDL | BDL | BDL | BDL |
| 2. | beta-lindane | 0.01 mg/ | 0.03 mg/L | 0.06 mg/L | 0.02mg/L |
| 3. | gamma-lindane | 0.03 mg/L | 0.25 mg/L | 0.07 mg/L | 0.03mg/L |
| 4. | delta-lindane | 0.17 mg/L | 2.26 mg/L | 1.42 mg/L | 0.16mg/L |
| 5. | Endosulfan ether | 0.48 mg/L | 4.96 mg/L | 1.47 mg/L | 0.86mg/L |
| 6. | Heptachlor | 0.03 mg/L | 0.03 mg/L | 0.05 mg/L | 0.03mgL |
| 7. | Aldrin | BDL | BDL | 0.03 mg/L | BDL |
| 8. | Heptachlor Epoxide | BDL | BDL | BDL | BDL |
| 9. | Chlordane | BDL | 0.36 mg/L | BDL | BDL |
| 10. | alpha- Endosulfan | BDL | BDL | 0.09 mg/L | BDL |
| 11. | Dieldrin | BDL | BDL | BDL | BDL |
| 12. | Dicofol | BDL | 0.01 mg/L | 0.05 mg/L | BDL |
| 13. | Endrin | 0.01 mg/L | 0.03 mg/L | 0.02 mg/L | 0.02mg/L |
| 14. | beta-Endosulfan | 0.09 mg/L | 0.08 mg/L | 1.11 mg/L | 0.06mg/L |
| 15 | Mirex | 0.02 mg/L | 0.03 mg/L | 0.02 mg/L | 0.02mg/L |
| 16. | p,p’-DDT | 0.05 mg/L | 0.06 mg/L | 0.07 mg/L | 0.06mg/L |
| 17 | Methoxychlor | 0.06 mg/L | 0.07 mg/L | 0.07 mg/L | 0.06 mg/L |

**Table 2: Concentration (mg/L) of organophospate pesticide residue in Owe River, Ile-Oluji, Ondo State, Nigeria**

| Target | Compound | MOA | AKY | OGB | TPG |
|---|---|---|---|---|---|
| 1 | azinphos methyl | 0.32mg/L | 0.32 mg/L | BDL | 0.32 mg/L |
| 2 | Coumaphos | BDL. | 0.35 mg/L | BDL | 0.38 mg/L |
| 3 | Diazinone | BDL | BDL | BDL | BDL |
| 4 | Dichlorvos | BDL | BDL | BDL | BDL |
| 5 | Dimethoate | 28.57 mg/L | 15.79 mg/L | 4.13 mg/L | 5.16 mg/L |
| 6 | Ethyl para thion | BDL | BDL | BDL | BDL |
| 7 | Ethoprop | BDL | BDL | BDL | BDL |
| 8 | Ethyl azinphos | BDL | BDL | BDL | BDL |
| 9 | Fensulfoth ion | BDL | BDL | BDL | BDL |
| 10 | Merphos | 3.93 mg/L | BDL | 0.13 mg/L | 0.15 mg/L |
| 11 | Methyl par athion | BDL | BDL | BDL | BDL |
| 12 | Malathion | BDL | BDL | BDL | BDL |
| 13 | Phorate | BDL | BDL | BDL | BDL |
| 14 | Ronnel | BDL | BDL | BDL | BDL |
| 15 | Sulprofos | BDL | BDL | BDL | BDL |
| 16 | Terbufos | BDL | BDL | BDL | BDL |
| 17 | Tetrachlorvinphos | BDL | BDL | BDL | BDL |
| 18 | Trichlorfon | BDL | BDL | BDL | BDL |

(M.O.A – Ministry of agriculture, O.G.B – Olorungbohunmi, AkY – Akintiyemi, and TPG - Tipper garage)

## Organochlorine pesticide residues

The results of the organochlorine pesticide residues analyzed in Owe River is shown in Table 1. Table 1 shows that some samples from the river were contaminated with the Organochlorine pesticides at appreciably higher concentration with the following ranges in (mg/L): beta - Lindane (0.01—0.06); Gamma - Lindane (0.03—0.25); delta - Lindane (0.16—2.26); Endosulfan ether (0.86-4.96); aldrin (BDL— 0.03); Chlordane (ND—0.36); alpha-endosulphan (BDL–0.09); Dicofol (ND— 0.05); Mirex (0.02 - 0.03); beta-endosulphan(0.06— 1.11); p,p"DDT (0.05—0.07); Heptachlor (0.03—0.05) ; endrin (0.01—0.03); Methoxychlor (0.06— 0.07).$CH^1$ and $CH^3$account for the presence of the highest concentration of these organo chlorine pesticides. The high concentration of this pesticides suggests an indication of usage of some of these pesticides in the study area. Some of the pesticides such as chlordane, heptachlor, DDT, 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(Soto*et al*.,1994 )" The presence of DDT 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(Van Dyk*et al.*,1982) 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. (Akinnawo, 2016) 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 (Akinnawo ,2016; Aderonke*et al*.,2013)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(Oladunni *et al*.,2016)Many studies has shown that organochlorines act as endocrine disrupting chemicals (EDCs) by interfering with molecular circuitry and function of the endocrine system.Many of the organochlorine molecules are carcinogens and neurotoxic (Kaiser, 2000). The hazardous nature of organochlorines was explained by citing different examples. The menace caused by endosulfan is of great concern. Endosulfan remains in the environment for longer periods and bio-accumulates in plants and animals which leads to contamination of food consumed by humans. It affects mainly the central nervous system and was found to have higher acute inhalation toxicity than dermal toxicity. Gastrointestinal absorption of endosulfan is very high (USEPA, 2010).

## Organophosphatepesticide residues

The results of the Organophosphate pesticide residues analyzed in Owe River are shown in Table 2. Table 2 shows the presence of the concentration of pesticides in (mg/L):azinphos methyl(0.32); Coumaphos(0.35-0.38); Dimethoate(4.13 -28.57.); Merphos(0.13-3.93).while some are below detection limit. The results show that some samples from the waters were contaminated with the Organophosphate pesticides but at appreciably lower in concentration than the Organochlorine pesticide. The presence of these pesticides could be caused by the longer duration of pesticide application in this area. Organophosphate pesticides are known to be stable, highly toxic and more or less persistent and are found in all compartments of the environment such as soil , water and air.(Wu *et al.,* 1999,).The resistance of these compounds to environmental degradation has raised concerns regarding their ability for bioaccumulation and potential public health impact (Pajoumand *et al.*, 2002).

## CONCLUSION

The result indicates pollution due to the presence of organophosphate pesticides and high concentration of Organo chlorine in the river. The results of the laboratory analysis of this study provide threshold values of pesticide residues of organophosphates and Organo chlorine pesticides that were present in river. The values obtained from the results were below the permissible limit for WHO while some are higher than the permissible limit This study indicates that organophosphate residues showed concentrations values that may have potential risk to the ecological balance of the River.

## REFERENCES

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

Akinnawo 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.

Aktar MW, Sengupta D, Chowdhury A. (2009). Impact of pesticides use in agriculture: their benefi ts and hazards. *Interdisciplinary Toxicology* **2**(1): 1–12

Erickson, B. E. (2013).Bee Study Prompts Action. Journal of Chemical Engineering, 91(6): 9-21.

International Union of Conservation of Nature, [IUCN], (2011). Annual report. https://www.iucn.org/content/2011

FAO. (2005). *Proceedings of the Asia Regional Workshop*, Regional Offi ce for Asia and the Pacifi c, Bangkok.

Gupta PK. (2004). Pesticide exposure—Indian scene. *Toxicology* **198**: 83– 90.

Kaiser J. (2000). Endocrine disrupters: Panel cautiously confi rms low-dose effects. *Science* **290**: 695–697.

Mustapha D (2020)Quantitative Analysis of Organophosphate Pesticides Residues in Water and Sediment Samples of River Benue, Jimeta Adamawa State ,International Journal of Research and Review Vol.7; Issue: 4; 279-286

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

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 Technolog*y.**5(10)**: 1-15

Pajoumand A, Jalali N, Abdollahi N, Shadnia S (2002): Survival following severe aluminium phosphide poisoning. Journal of Pharmacy Practice and Research ; 32: 297-299.

Salameh RP, Daldi I, Brochard P, Saleh BA (2014). Pesticides in Lebanon: a knowledge, attitude and practice study. Environ. Res.94:1-6.

Sharma, A.; Kumar, V.; Shahzad, B.; Tanveer, M.; Sidhu, G.P.S.; Handa, N.; Kohli, S.K.; Yadav, P.; Bali, A.S.; Parihar, R.D.Worldwide pesticide usage and its impacts on ecosystem. *SN Appl. Sci.* **2019**, *1*, 1446, doi:10.1007/s42452-019-1485-1

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

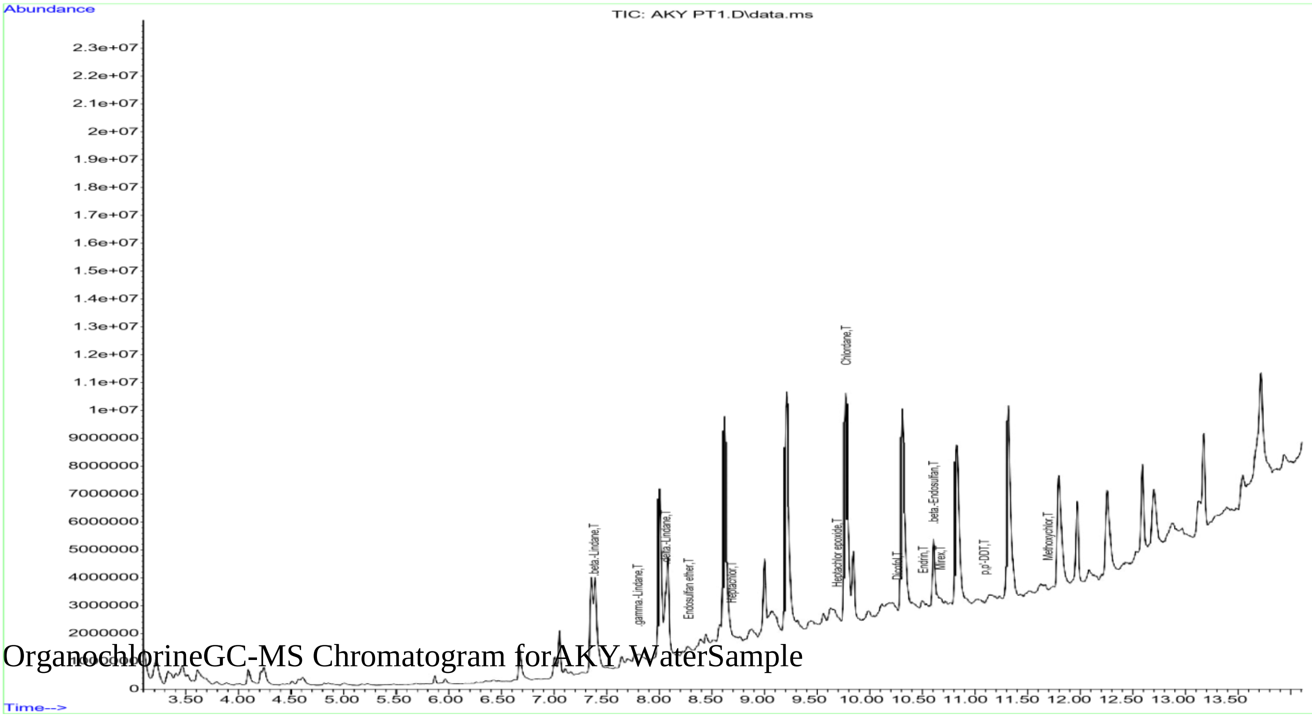
Turgut C, Atatanir L, Mazmanci B, Mazmanci MA, Henkelmann B, Schramm KW ( 2011). *The occurrence and environmental effect of persistent organic pollutants (POPs) in Taurus Mountains soils. Environment Science Pollution Research*

USEPA. (2010). Endosulfan. The Health Effects Divion's Human Health Risk Assessment. EPA DP Barcode: D372569. June 2010. Docket No.: EPA-HQOPP-2002-0262-0178; http: //www.regulations.gov

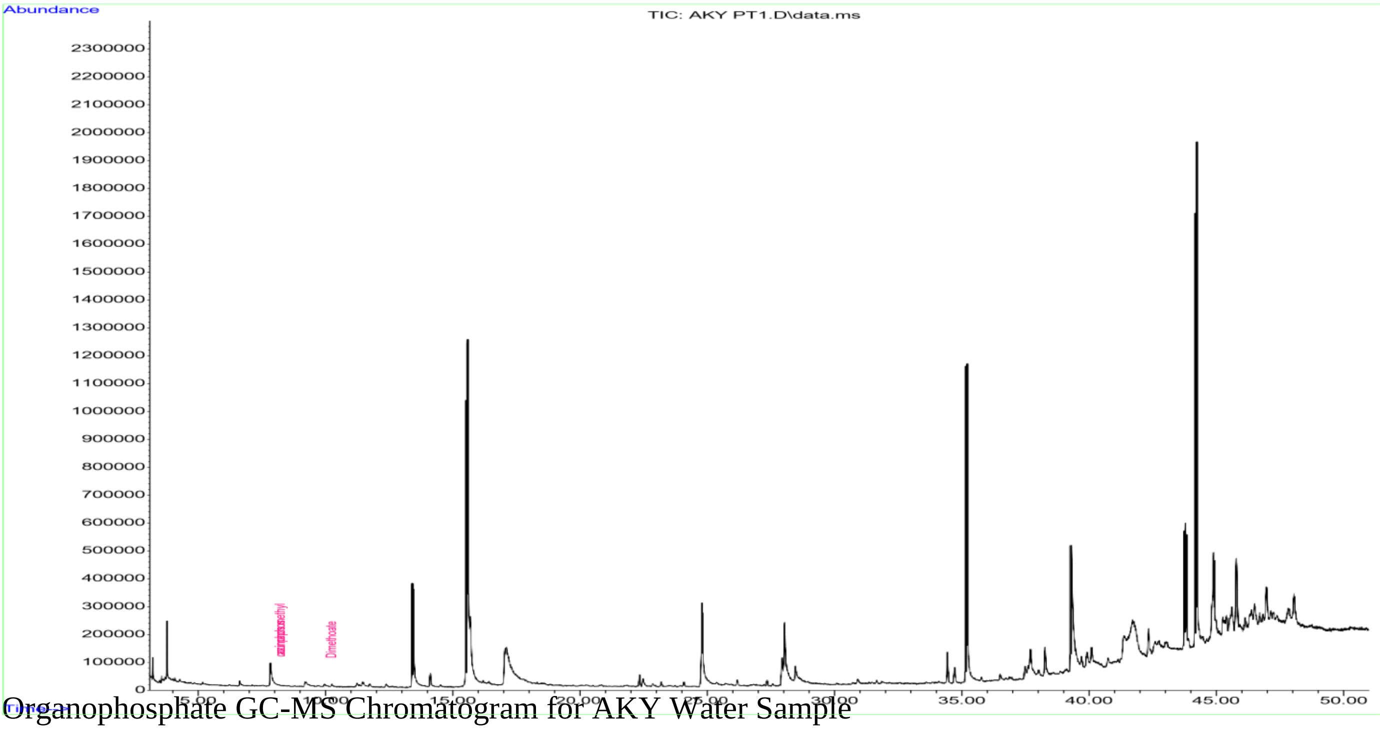
Van Dyk, L. P Wiese, I. H. and. Mullen, J. E (1982) "Management and determination of pesticide residues in South Africa," *Residue Reviews*, . **82** : 37–124,

Wu, Y, Zhang, J, Zhou, Q, (1999). Persistent Organochlorine residues in sediments from Chinese river/estuary systems. EnvironmentalPollution 105: 143 - 150

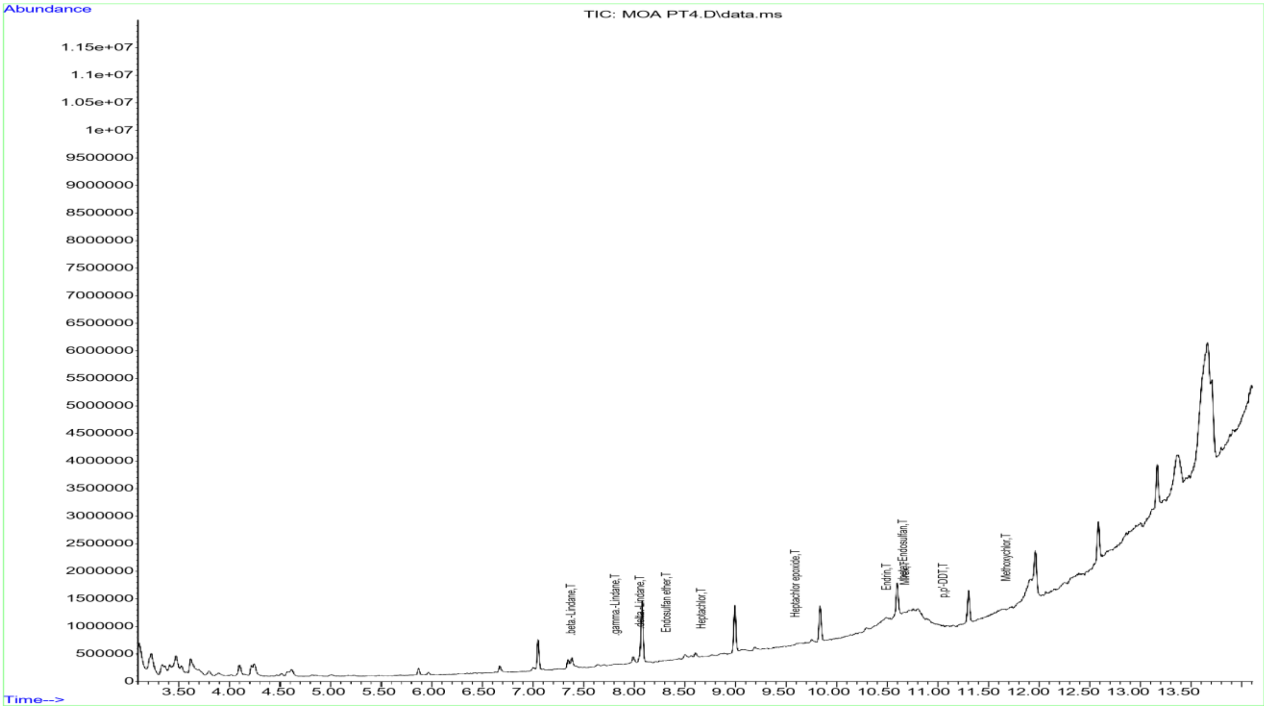
Yadav, I.C., Devi, N.L., Syed, J.H., Cheng, Z., Li, J., Zhang, G. et al. (2015).Current status of persistent organic pesticides residues in air, water, and soil, and their possible effect on neighboring countries: A comprehensive review of India. Science of the Total Environment, 511 (10):123–137



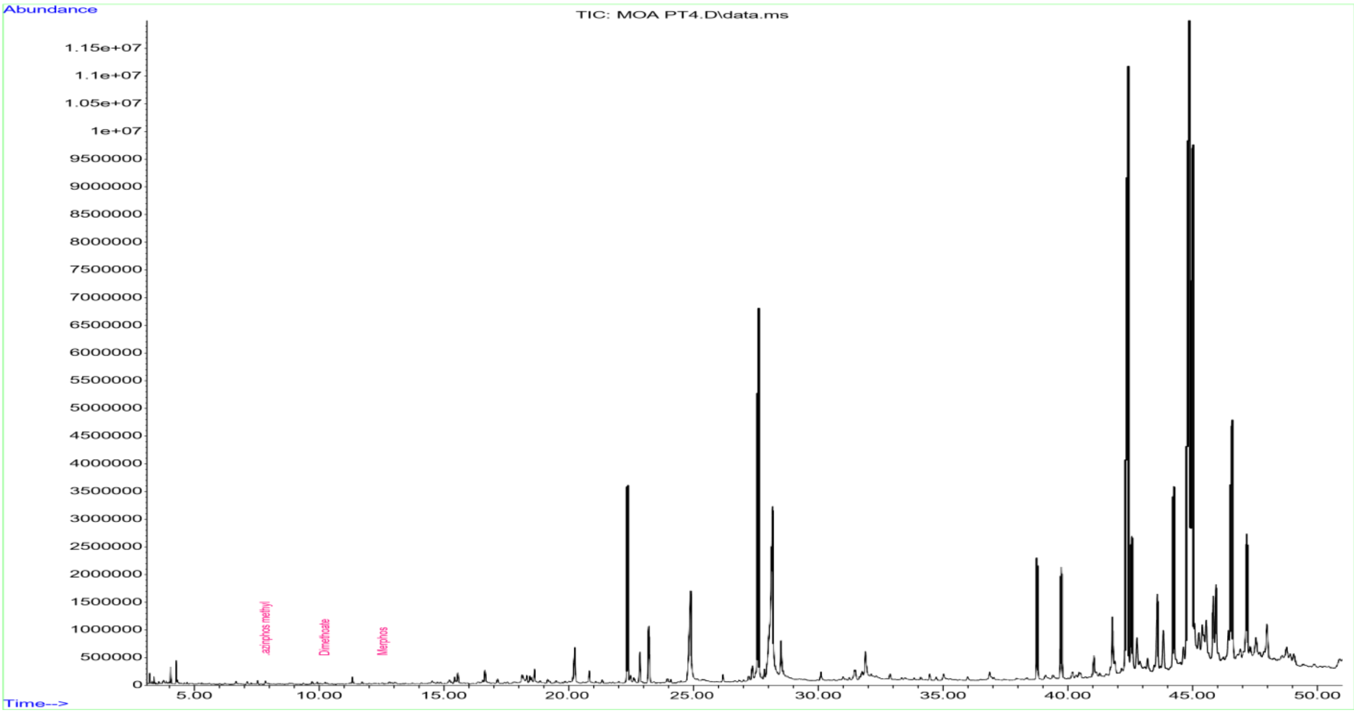

OrganochlorineGC-MS Chromatogram forAKY WaterSample



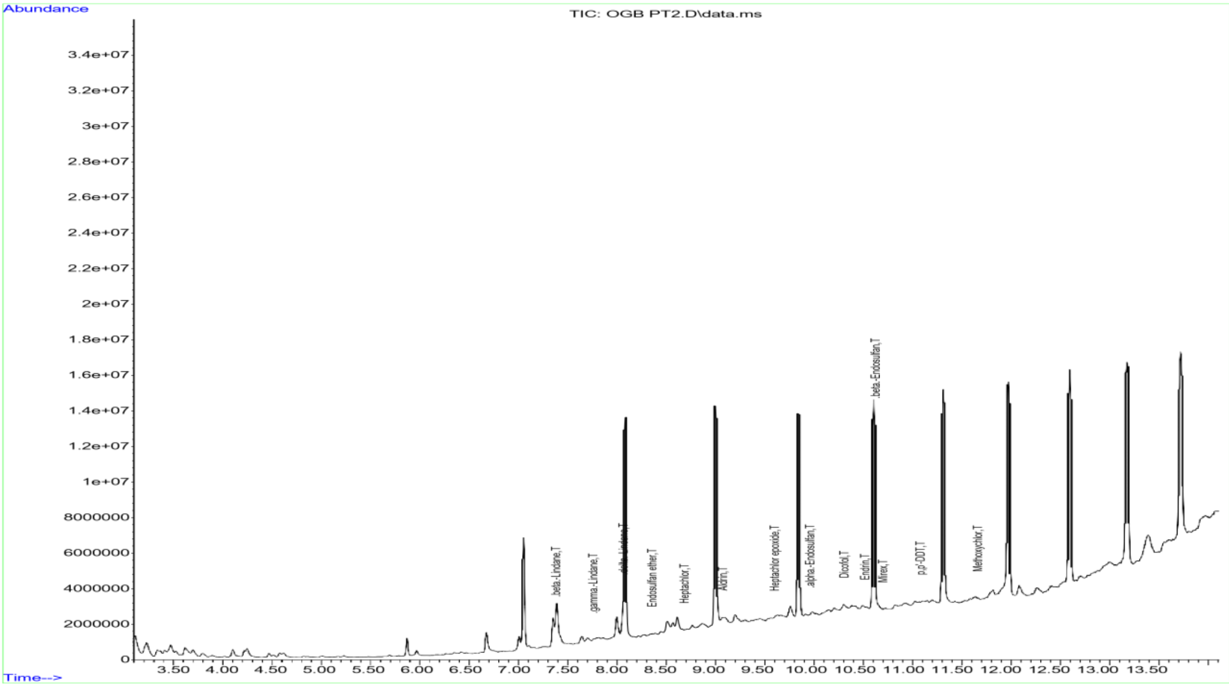

Organophosphate GC-MS Chromatogram for AKY Water Sample



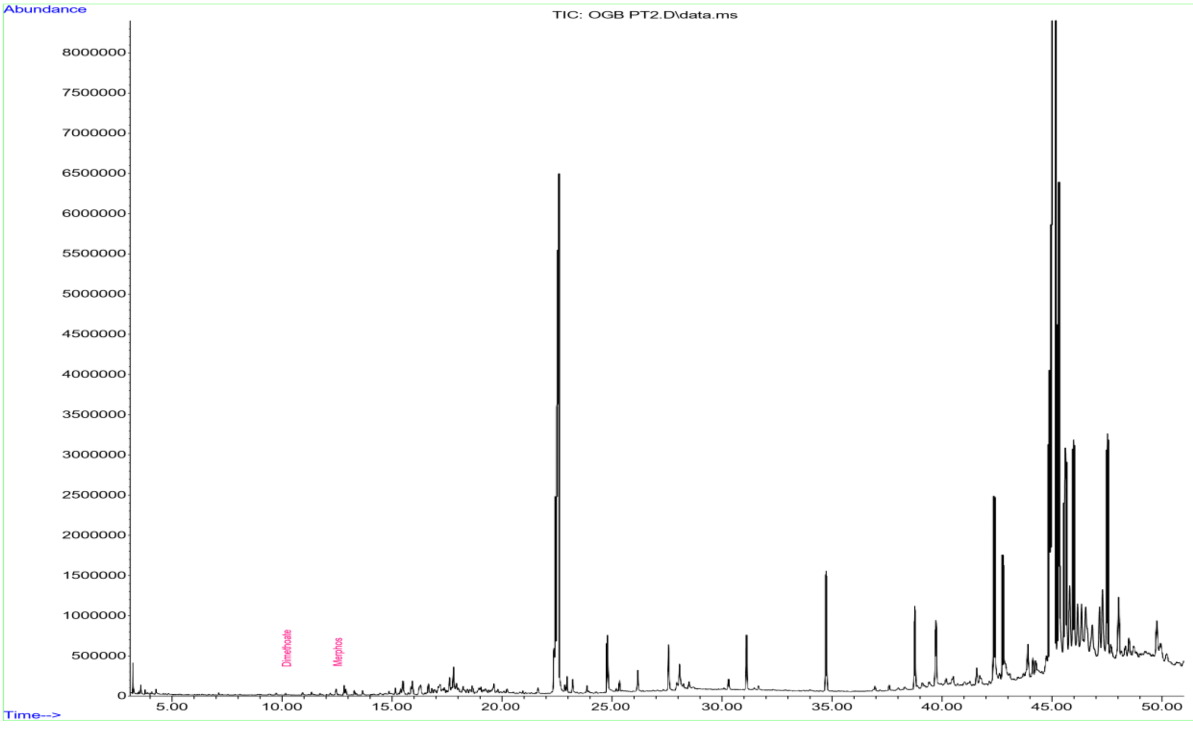

Organochlorine GC-MS Chromamatogram for MOA water sample



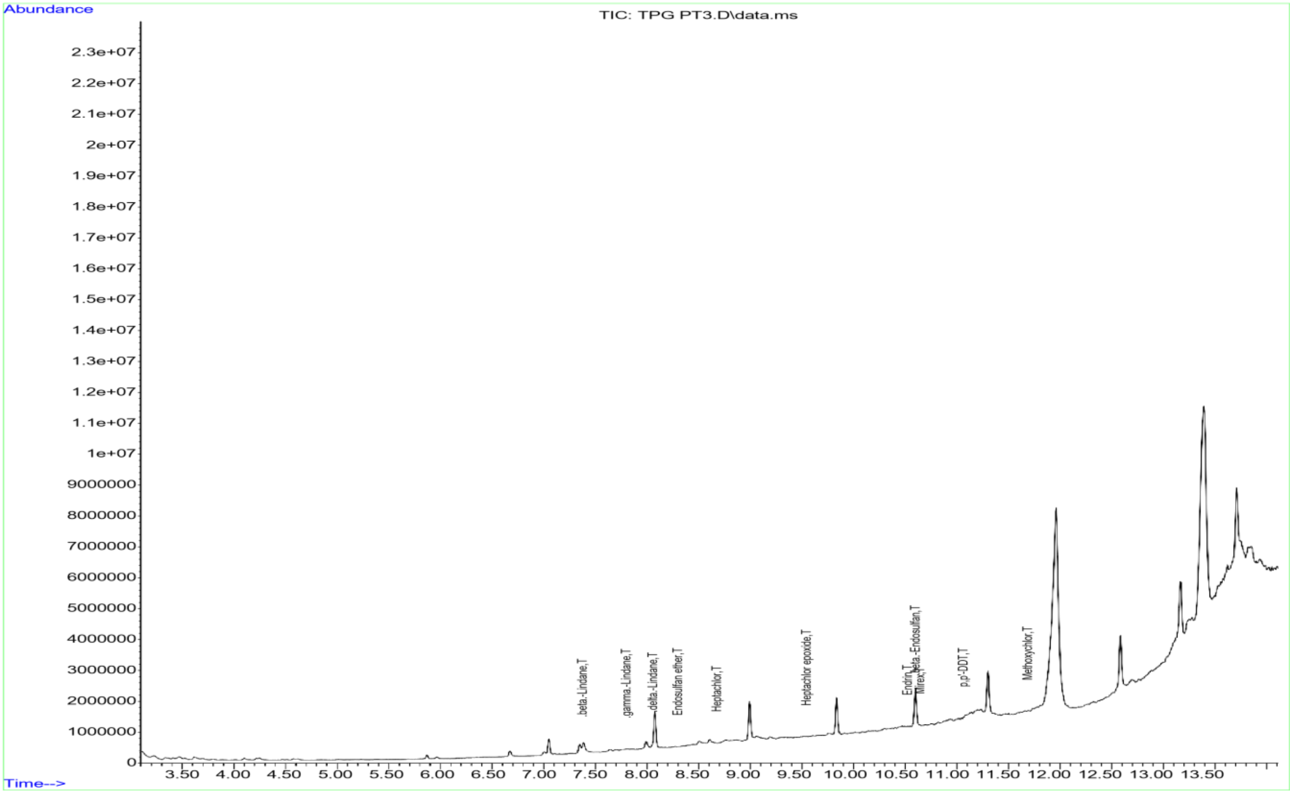

Organophosphate GC-MS Chromatogram for MOA Water Sample



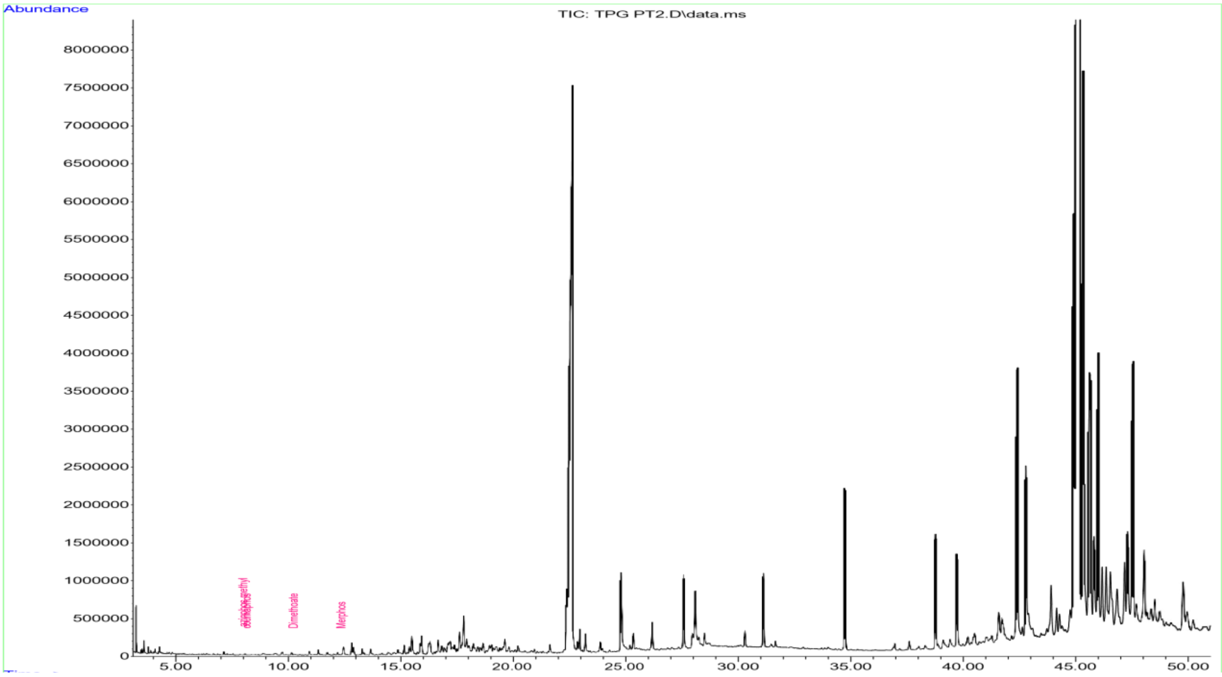

Organochlorine GC-MS Chromatogram for OGB water sample




Organophosphate GC-MS Chromatogram for MOA Water Sample




Organochlorine GC-MS Chromatogram for TPG water sample




Organophosphate GC-MS Chromatogram for TPG Water Sample