ASSESSMENT OF THE LEVELS OF PERSISTENT ORGANIC POLLUTANTS (*POLYCHLORINATED BIPHENYLS*) IN EFFLUENTS FROM PETROLEUM PRODUCTS TANK FARM IN CALABAR JETTY, CROSS RIVER STATE, NIGERIA

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ABSTRACT: This study has its objectives of assessing the levels of polychlorinated biphenyls in five soil samples collected from the effluent channel of petroleum product tank farm in Calabar Jetty, Cross River State. The five soil samples were subjected to analytical procedure by extracting with n-hexane/acetone mixture volume (1:1). The extracts were distilled at 56^{o}C to remove acetone and the residue from each extract was mixed with 20ml of distilled water and separated with a separatory funnel. The hexane phase was collected from each sample and the clean-up process was carried out using florisil column prepared according to slurry packing technique (1cm x 25cm glass column containing 5.0g florisil, 60-100mesh, conditioning for 4hrs at 250^{o}C) then deactivated with 5% water by weight, with a layer of anhydrous sodium sulphate on top to remove interferences before they were analyzed and quantified using GC-ECD/MS instrumentation. The results revealed presence of PCBs in all the samples except the control sample. The chromatograms identified some PCB congener numbers present in the samples and they are: PCB 18, PCB 33, PCB 44, PCB 48, PCB 122, PCB 145, PCB 150, and PCB 167. The results indicated the various concentrations of PCBs present and levels of PCBs were at toxic limits which could be detrimental to the environment and human health. Thus suggestions were made on the best way to dispose these effluents.

Keywords - Polychlorinated biphenyl, Congener, Effluents, Tank farm, Jetty.

1.0 INTRODUCTION

Polychlorinated biphenyls (PCBs) are compounds containing some chlorine atoms attached at different positions of the biphenyls molecule. Biphenyls molecule is a molecule made of two benzene compounds joined together by carbon to carbon single bond. These Polychlorinated biphenyls do not occur in nature, they are introduced into the environment by anthropogenic activities. PCBs have been sold out to different countries with many trade names such as: Aroclor, Chlorextol,Clophen,Phenoclor, Fenclor, Kanechlor, Pyranol, Sovol etc.[1]

PCBs are introduced into the environment through leakages from most electrical equipment containing capacitors, hydraulic oil, petroleum product effluents, transformers and liquid heat exchangers or coolants. The PCBs when given off goes into the air, water, sediment and soil. It was eventually banned in 1979 by United States Stockholm convention and was classified among the persistent organic pollutants in 2001.[2] Some electrical equipment at elevated temperature emits PCBs into the atmosphere which goes into the food chain thereby affecting the fishes and other aquatic organisms in the river. These fishes when consumed by man causes ailments such as birth defects.[3]They affect the hormone system in man especially the sperm count and causes cancer in animals.[4]

In the phase of all these, it is pertinent that these effluents from the petroleum tank farm in Calabar Jetty identified to be toxic should be properly treated using the most effective method of destruction to reduced its toxicity level before been discharged to the environment.

2.0 MATERIALS AND METHODS

2.1 Sample Collection

The soil samples were collected from the effluent channel of the company. The sampling was done using shovel, auger, and spade. The soil samples were collected at different depth ranging from (0.05 – 0.20m) depth. Five (5) samples were collected from company Hamdza(^{H}). The samples were poured into polythene sack bag and taken to the laboratory where pH, conductivity and temperature were taken before storage.

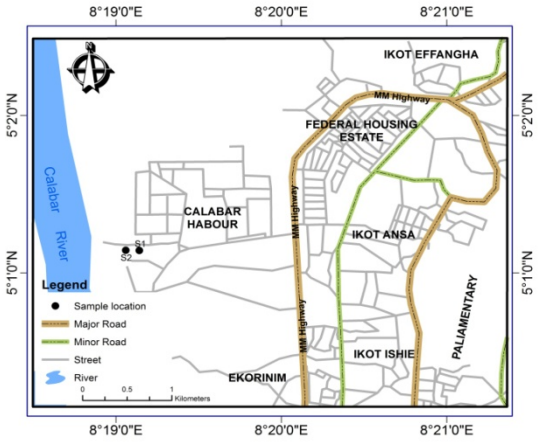


FIGURE 1: Sample site

2.2 Sample preparation

The samples were air dried for a period of two months and all foreign materials such as leaves, sticks and stones were removed in the process. The samples were then crushed with pestle and mortar, sieved to a fine powder using a sieve with aperture 100micron.

2.3 Extraction process

100g of each sample was weighed into a sample bottle and 100ml mixture of n-hexane: acetone, 1:1 (v/v) was added for batch extraction. The mixture was allowed to stay for 24hrs after which decantation was carried out. The liquid was filtered into a round bottom flask and was distilled to a temperature of 56^{o}C to remove all acetone present. The residue was collected and poured into a separating funnel. 20ml of distilled water was poured into the separating funnel. The mixture was shaken thoroughly and allowed to settle in phases (Hexane/ Water phase). The hexane phase was collected in vial bottles for gas chromatography and mass spectrometry analyses. The procedure was repeated four times for the five samples.

2.4 Gas chromatography clean-up process

The samples were allowed to evaporate to dryness in air then dissolved in 1-2ml of hexane. The elution was done with 50ml n-hexane through florisil column prepared according to slurry packing technique (1cm x 25cm glass containing 5.0g florisil, 60-100mesh, conditioning for 4hrs at 250^{o}C) then deactivated with 5% water by weight, with a layer of anhydrous sodium sulphate on top, and rinsed with 50ml n-hexane before use. The fraction obtained was then used for G-C analysis.[5]

2.5 GC – ECD/ MASS SPECTROMETRY (Hewlett Packard 6890).

The GC equipment with Ni electron capture detector (ECD) having DB – XLB fused silica capillary column(60m x 0.25m, 0.25um thickness) at 50KPa pressure was used. Helium gas of very high purity was used as the carrier gas at 54.4ml/min. Following the injection, the GC temperature was initially set at 60^{o}C for 1min,then temperature was programmed to 140^{o}C at 10^{o}C/min, at 0.9^{o}C/min to 220^{o}C/min and at 5^{o}C/min to 290^{o}C (hold for 15mins). Identification of the PCB ion peaks were based on the retention time relative to the Internal Standard and their relative abundances of the ions monitored. The mass spectrometry connected to the GC gives the qualification by comparing the integrated ions current response of the target ions to those of the internal standard and their relative abundances of the ions monitored.

3.0 RESULTS

The five samples show variation in temperature, pH, conductivity and appearance as seen in Table 1, the samples except the control sample 5^{H} have the presence of polychlorinated biphenyl compounds with various retention time and concentration as shown in Figures 1-5 and Tables 2-6.

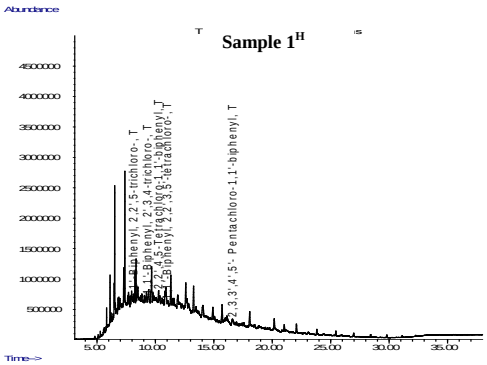


Figure 1: GC/MS chromatogram of sample 1^{H}

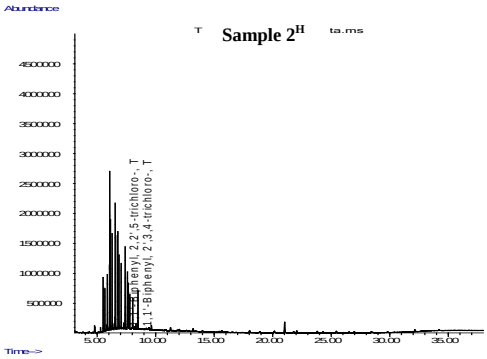


Figure 2: GC/MS Chromatogram of sample 2^{H}

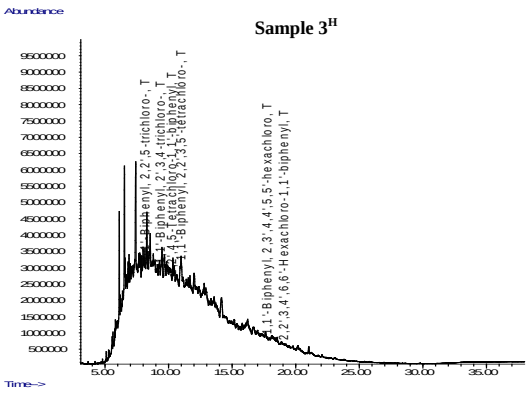


Figure 3: GC/MS chromatogram of sample 3^{H}

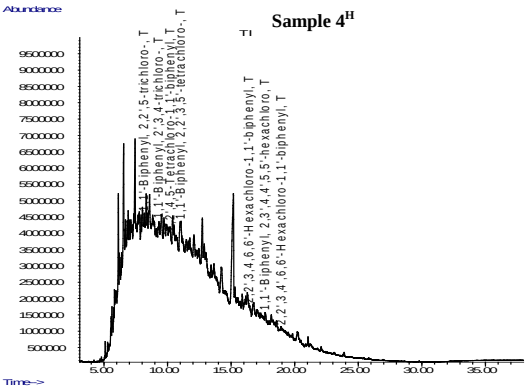


Figure 4: GC/MS chromatogram of sample 4^{H}

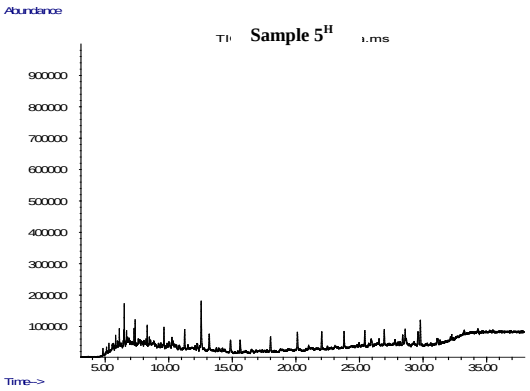


Figure 5: GC/MS \Chromatogram of control sample 5^{H}

Table 1: Physical properties of soil samples from company Hamdza(^{H})

S/No	Sample Name	Temperature (^{o}C)	pH	Conductivity(µScm^{-1})	Appearance
1	Sample 1^{H}	27.9± 0.10	7.79± 0.05	1.10± 0.06	Black
2	Sample 2^{H}	27.2± 0.10	7.79± 0.03	0.25± 0.01	Black
3	Sample 3^{H}	27.7± 0.20	7.53± 0.03	1.46± 0.10	Black
4	Sample 4^{H}	27.3± 0.10	7.72± 0.01	0.92± 0.07	Black
5	Sample 5^{H}	27.9± 0.10	7.69± 0.02	2.26± 0.10	Brown

Table 2**:** GC-MS identified compounds in sample 2^{H}

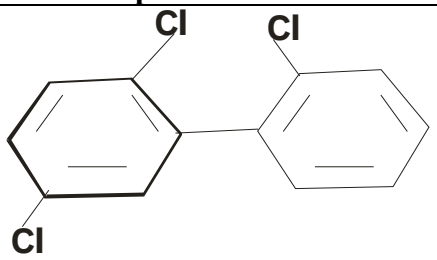
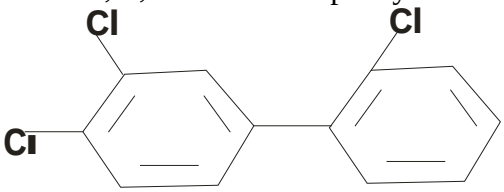
PCB congener No.	Retention time (mins)	Concentration (ppm)	IUPAC name and structure of compound Identified
18	8.196	0.090± 0.002	 2,2’,5 – trichlorobiphenyl
33	9.347	0.010± 0.001	 2’,3,4 – trichlorobiphenyl

Table 3:GC-MS identified compounds in sample1[H]

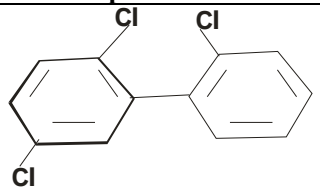
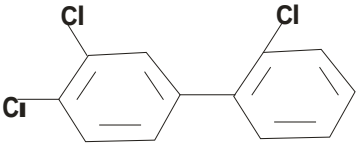
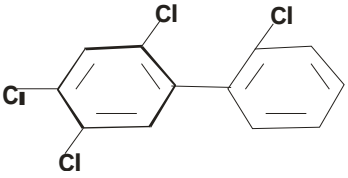
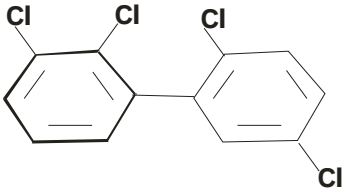
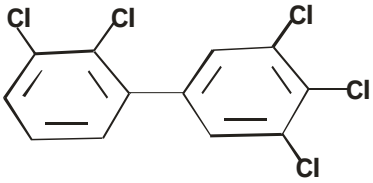
PCB congener No.	Retention time (mins)	Concentration (ppm)	IUPAC name and structure of compound Identified
18	8.156	0.06	 2,2',5 – trichlorobiphenyl
33	9.352	0.05	 2',3,4 – trichlorobiphenyl
48	10.291	0.13	 2,2',4,5 – tetrachlorobiphenyl
44	11.035	0.03	 2,2',3,5' – tetrachlorobiphenyl
122	16.625	0.02	 2,3,3',4',5' – pentachlorobiphenyl

Table 4**:** GC-MS **r**esults in sample 5[H]

PCB congener No.	Retention time (mins)	Concentration (ppm)	IUPAC name and structure of compound identified
ND	ND	ND	ND

ND: Not Detected.

Table 5:GC-MS identified compounds in Sample 3[H]

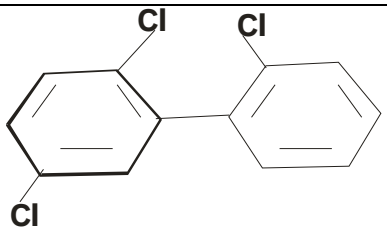
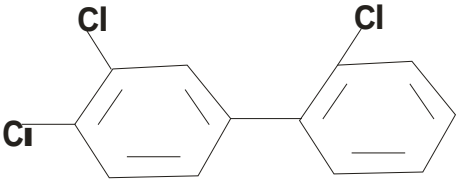
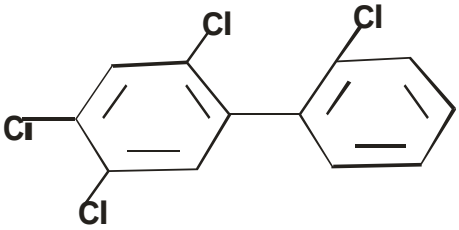
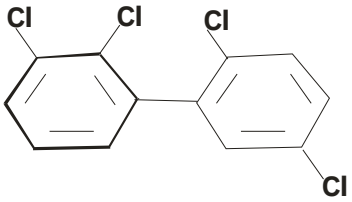
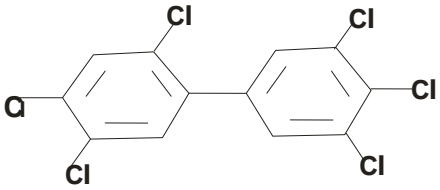
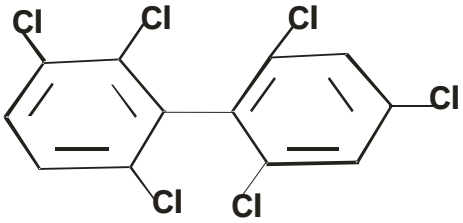
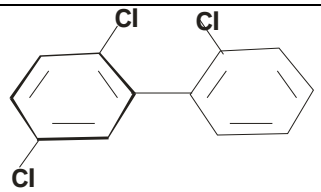
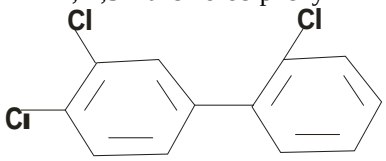
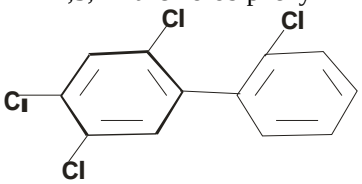
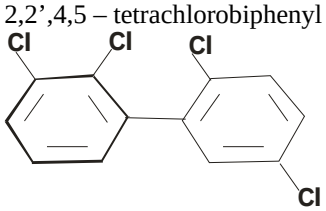
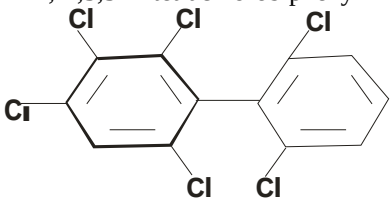
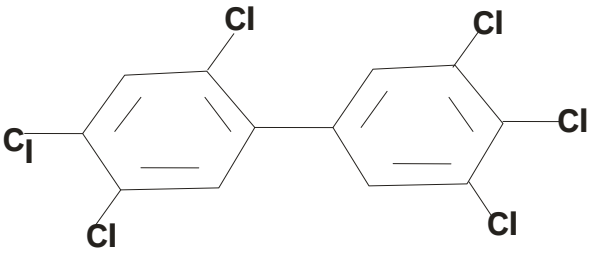
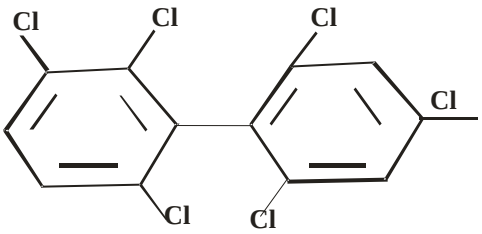
PCB congener No.	Retention time (mins)	Concentration (ppm)	IUPAC name and structure of compound identified
18	8.180	0.610±0.002	 2,2',5 – trichlorobiphenyl
33	9.393	0.120± 0.006	 2',3,4 – trichlorobiphenyl
48	10.268	0.100± 0.004	 2,2',4,5 – tetrachlorobiphenyl
44	11.018	0.300± 0.004	 2,2'3,5' – tetrachlorobiphenyl
167	17.758	0.020± 0.001	 2,3',4,4',5,5' – hexachlorobiphenyl
150	19.063	0.020± 0.001	 2,2',3,4',6,6' – hexachlorobiphenyl

Table 6:GC-MS identified compounds in sample 4^{H}

PCB Congener No.	Retention time (mins)	Concentration (ppm)	IUPAC name and structure of compound identified

18	8.179	0.32	 2,2',5 – trichlorobiphenyl
33	9.318	0.21	 2',3,4 – trichlorobiphenyl
48	10.251	0.12	 2,2',4,5 – tetrachlorobiphenyl
44	11.046	0.23	 2,2',3,5' – tetrachlorobiphenyl
145	16.425	0.02	 2,2',3,4,6,6' – hexachlorobiphenyl
167	17.695	0.03	 2,3',4,4',5,5' – hexachlorobiphenyl
150	18.977	0.03	 2,2',3,4',6,6' hexachlorobiphenyl

4.0 DISCUSSION

The parameters in Table 1 show that the temperature of the five samples were between the range 27.2± 0.10°C to 27.9 ± 0.10°C with a mean temperature of 27.55 ± 0.10°C. These temperature values were relatively the same as the room temperature on the day of sampling. The pH values tend slightly to alkalinity and were between the range 7.53 ± 0.03 to 7.79 ± 0.05,this same range was reported by Moret[6] in sediments from Porto Marghera area. The electrical conductivity of four samples were very low except for control sample 5 which has a high value of 2.96 ± 0.10µScm^{-1}. These

low values in electrical conductivity validate one of the physical properties of PCBs having low electrical conductivity in nature. The dark colour observed may be as a result of the types of effluent discharge and also the presence of PCB, since the control sample was lighter in colour. GC-MS chromatogram in figure1-figure4 and table 2,3,5,and 6 results indicated the presence of PCB 18, PCB33, PCB 44, PCB 48, PCB 122, PCB 145, PCB 150 and PCB 167. In all the samples there were PCBs present except for sample 5^{H}.The chromatogram for the control sample in figure 5 and result in table 4 has no identified PCB peak present in the sample .The identified PCBs have ortho-substituted congeners which had been reported by Simon to cause neurotoxic and immunotoxic diseases while the di-ortho substituted congeners, PCB 145 and PCB 150 interfere with intracellular signal transduction, and also leads to neurotoxicity.[7]It is also reported by Chauhau that ortho-substituted PCBs can disrupt the thyroid hormone movement by binding to transthyretin.[8]Other symptoms of PCBs include skin and ocular lesions, reduction in the levels of immune system, women affected with high concentration of PCBs also experience problem during their menstrual period.[9][10][11]Pregnant women exposed to PCBs before delivery gave birth to children with low cognitive ability, and motor sensory problems.[12][13][14]The International Agency for Research on Cancer (IARC) has grouped some PCBs such as the 3,3',4,4',5- pentachlorinated biphenyls as being carcinogenic to man[15] and this can be compared with the PCB 122 identified in this study. When people are exposed to these toxic PCB compounds, they cause a great retardation and damage in steroid and other reproductive hormone development.[16][17][18]

5.0 CONCLUSION

The congener numbers present in the effluent samples; PCB 18, PCB33, PCB 44, PCB 48, PCB 122, PCB 145, PCB 150 and PCB 167 are toxic to man since the concentration identified is higher compared with 0.0005ppm EPA concentration of PCB limit for water. Proper treatment has to be taken in the disposal of the effluents from Calabar tank farm in Nigeria. Some of these treatment processes include; Incineration at very elevated temperature, proper mixing and extended residence time.[19]PCBs are chemically reduced or degraded toxically by addition of glycols and also organometallic compounds of sodium.[20]Microbial enzymes can also biodegrade soil contaminated with PCBs.[21]It is obvious that these effluents released into the environment in Calabar can be treated by degradation through various means so as to eliminate some of these ailments associated with PCBs, such as birth defect in man and hormonal imbalance and cancer in animals.[3][4]

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