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Assessment of persistent organic pollutants in water samples from River Challawa in Kano, Nigeria

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Abstract

Almost every type of industrial process releases some amounts of toxic organic and inorganic compounds that ends up in water bodies and/or other environmental compartments. This study was aimed at assessing the levels Persistent Organic Pollutant in Challawa River Basin of Kano State, Nigeria. The investigation was particularly plan to assess the presence of PCBs and PAHs in River Challawa and compare the concentrations of the pollutants with the acceptable limit set by Nigerian Standard and other international regulatory agencies. Data were collected using reconnaissance survey; laboratory experiment as well as other secondary data sources. A total of 26 water samples were collected through stratified and systematic random sampling. Three sampling points were chosen and designated A, B and C along the stretch of the river (i.e. upstream, midstream, and downstream) from Yan Danko Bridge to Tamburawa bridge. The result shows that Polychlorinated biphenyls (PCBs) were not detected but polycyclic aromatic hydrocarbons (PAHs) were detected in all the samples analyzed using GCMS. The total concentrations of PAHs in the water samples range between 0.001 to 0.087mg/l. All the water samples were polluted with PAHs because most of the parameters analyzed exceed the threshold limits set by Nigerian standard. The analytical results revealed that most of the pollutants present in water were at significantly very high levels especially at Zamawa village situated very close to Challawa industrial estate - the major sources of effluent discharge point, making the drinking water around area is not fit for consumption. In conclusion, it can be said that industrial activities had impact on Challawa River basin and its environment. It is

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recommended among others that the industries should treat their effluents before releasing them into Challawa river basin.

Keywords: persistent, organic, pollutant, challawa river, Nigeria

1. Introduction

Environmental pollution is the presence of toxic substances naturally or due to man's activities in the environment at a level where acute effect can be recognized. These toxic substances do not only remain in the environment but are transferred directly or indirectly into the body of man in different ways. Direct transfer into the body of man as a result of ingestion of contaminated food and water may affect organs, such as liver (Duffus, 1990). Industries have been identified as the major source of these pollutants either as products or by- product. Almost every type of industrial process involves the release of trace quantity of toxic organic and inorganic compounds that can contaminate soil, water, air, aquatic organisms and crops thereby posing health hazard to human lives as well as natural functions of ecosystem.

The Persistent Organic Pollutants (POPs) are twelve toxicant, this are Dioxin, Mirex, Dichlorodiphenyl trichloroethane (DDT), Chlordane, Polyaromatic hydrocarbon (PAH), Polychlorinated biphenyls (PCBs), Furans, Aldrin, Dieldrin, Eldrin, Heptachlor and Toxaphene. POPs persist in the environment, bioaccumulate through food chain and possess risk to human (European Commission, 2009). POPs are grouped according to their use and origin. PCBs and PAHs originate industrial chemicals. Other 8 are pesticides introduced into environment from various activities or uses and the remaining two Furans and Dioxin from unintended industrial processes (Langer, 2005).

PCBs are a group of man-made chemicals. They are oily liquids or solids, clear to yellow in color, with no smell or taste. PCBs are very stable mixtures that are resistant to extreme temperature and pressure and therefore are group of synthetic organic chemicals that can cause a number of different harmful effects. There are no known natural sources of PCBs in the environment and are widely used in electrical equipment like capacitors, transformers, heat transfer fluids, lubricants, and plasticizers (Illinois, 2009).

PCBs enter air, water, soil and crops during their production and use. The pathways that lead to widespread distribution of PCBs in the environment are surface coatings, insulating materials, industrial activities, pesticides, dyes, paints, asphalt, condensates from pipelines, plasticizers, legend, chemical decontamination, carbonless copy paper, inks, plastics, lubricants, waxes, air conditioners, hydrogenation, electric motors, etc. (ATSDR, 2000). PCBs has some trade names for different mixtures (partial list) which include Aroclor, Pyranol, Pyroclor, Phenochlor, Pyralene, Clophen, Elaol, Kanechlor, Santotherm, Fenchlor, Apirolio, and Sovol (WHO, 2008).

Adults and children may come into contact with PCBs while swimming in contaminated water and by accidental swallowing of the water during swimming. However, both of these exposures are far less serious than exposures from ingesting PCB-contaminated food or inhalation of PCB-contaminated air.

The abbreviation PAHs denotes polycyclic aromatic hydrocarbons, which are a class of organic compounds, characterised by two or more fused aromatic rings. PAHs that occur in the environment are a cause for concern because of their mutagenic and carcinogenic effects (Kim & Vane, 2007). They are mostly anthropogenic in origin and commonly arises from run-off, industrial sewage discharges, spillage, shipping activities and many more. The natural sources could for instance be oil seepage from underground. Additionally, but to a lesser extent, petrogenic PAHs in sediments can originate from the digenesis of natural precursors like terpenes, pigments and steroids (Kim & Vane, 2007).

Most exposures to PAHs happen at very low levels through the air we breathe and the foods we eat. However, some PAHs are used to make dyes, plastics, and pesticides (Al-Rashdan, Murad, Helaleh, Nisar, Ibtisam & Al-Ballam, 2010).

Nigeria and International agencies such as EPA has a threshold limit of 0.0007 and 0.0005 milligrams of PAHs per litre of drinking water (Adeyemi, Grace, Chimezie & John, 2009).

Documented information on local status of Persistent Organic Pollutant (POPs) in Nigeria in respect of the extent of use; toxicology; residues, occupational accidents; persistence and bioaccumulation is very scanty (Soyombo, 2000). The analysis persistent POPs analysis is expensive, which deters the scientists in developing countries to participate in their investigation. This is clear from the relative lack of publications and information on POPs from countries in Africa, South Asia and South/Central America (Derek, 2003). Thus, there is dearth of information on the concentrations of POPs especially PAH and PCBs in the study area. There is therefore the need to carry out this investigation to determine the concentrations of the POPs and assess their possible threat on human health and other living organisms that interact directly and indirectly with the river ecosystem.

2. Methodology

2.1 Study Area

The study covered a distance of 10.7km along the Challawa River from Yan' Danko to Tamburawa bridges situated between latitudes of 11°52'55.2''N - 11°59'39.8''N and on longitudes 08°27'28.6''E - 08°31'45.6''E. This is an area where effluents flow from Challawa, Sharada industrial estate and municipal sewage from Kano city eventually end of in Challawa River through Salanta, Tatsawarki and Zamawa drainages.

Challawa River as shown in figure 2 is located on the southern part of Kano has a confluence with River Kano at Tamburawa and is about fifty kilometers (50km) in length. It flows from south to west and is about 500 meters above the sea level.

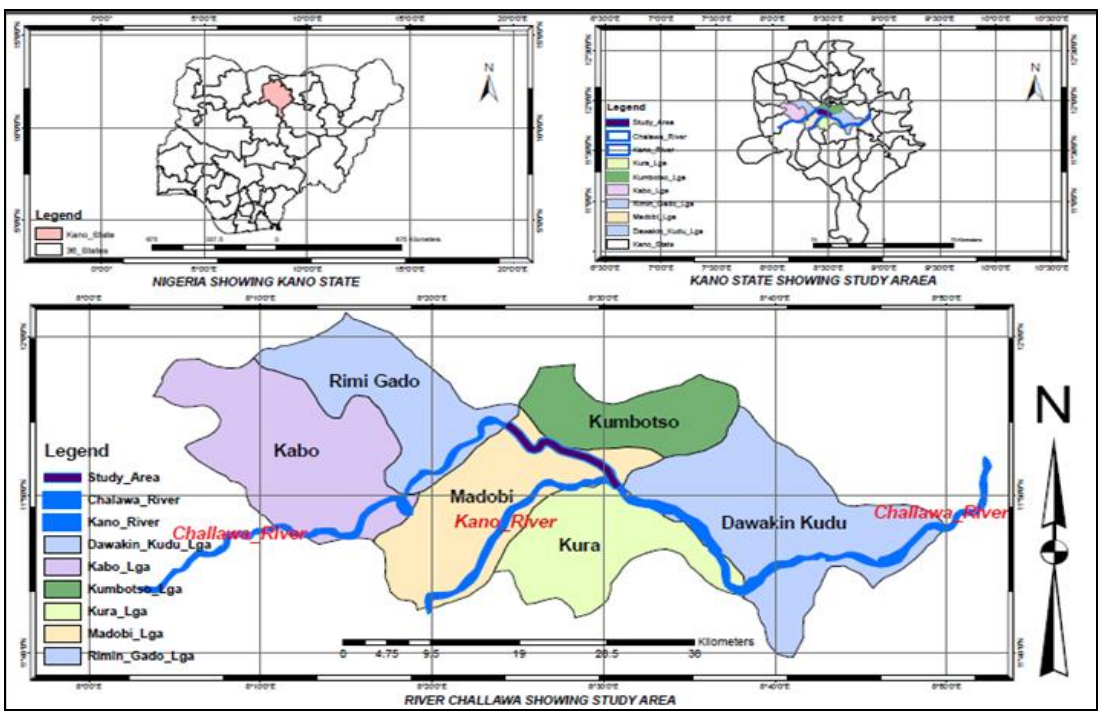

Figure 1: River Challawa showing the study area

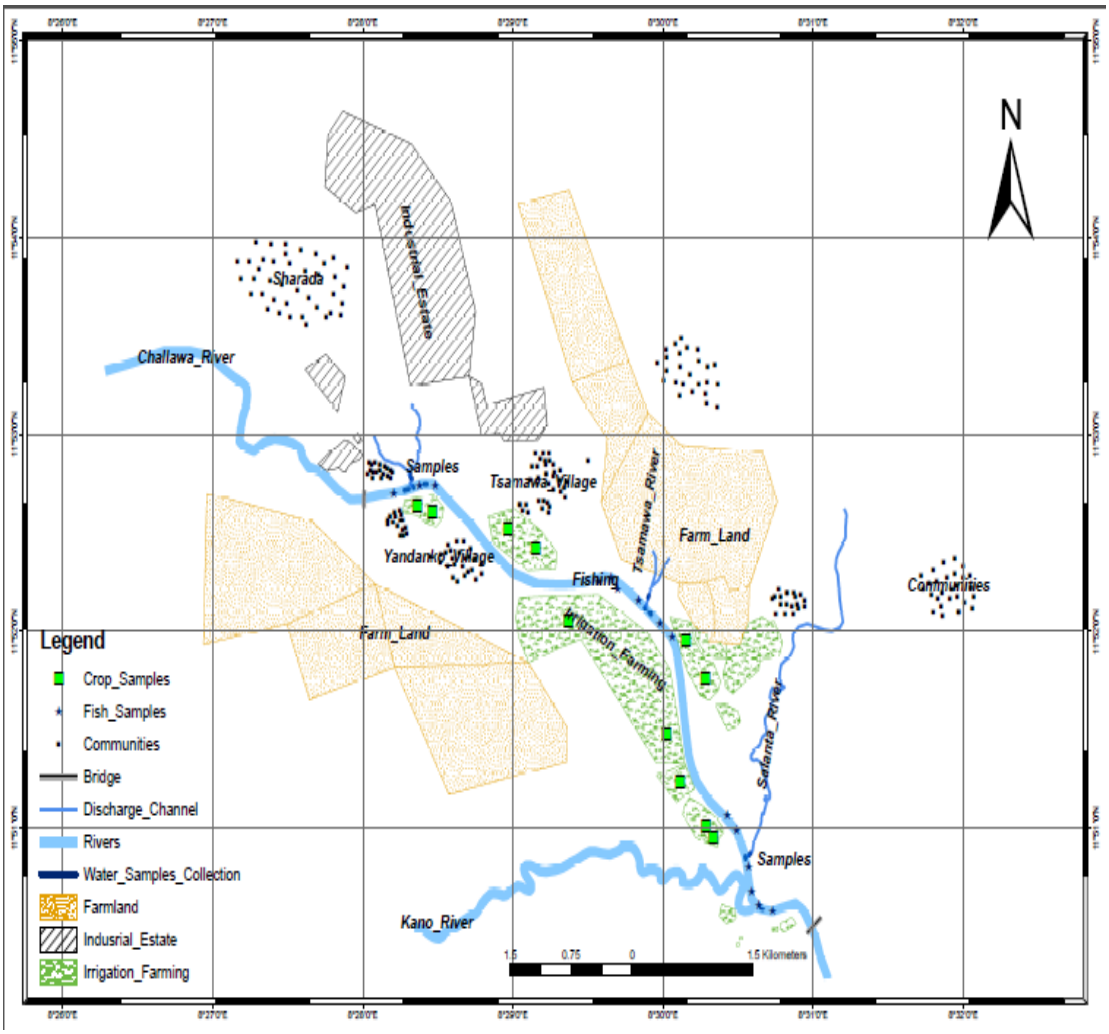

Figure 2: Study area showing effluent discharge and samples collection points

2.2 Sampling Procedures

2.2.1 Number of samples collected

A total of 26 water samples were collected according to the procedures. The required number of samples for a mobile matrix such as stream water, fish, etc. may be estimated as follows:

$$N \geq \sum (ts / U)^2$$

Where:

N = number of samples

t = Student- t statistic for a given confidence level of 95%

s = overall standard deviation, and

U = acceptable level of uncertainty,

Where: s = 0.5 mg/l

U = 0.2 mg/l

t = 95%

Using the curves, it was found that approximately 25 to 30 samples must be taken (APHA, 2005).

2.2.2. Water Sampling Techniques

Data were collected using reconnaissance survey, laboratory analysis and other secondary data. A total of 26 water samples were collected through stratified and systematic random sampling. Three sampling points were chosen at designated sites (A, B and C) along the stretch of the river (i.e. upstream, midstream, and downstream) respectively to the point of discharge from Yan Danko to Tamburawa bridges. Thus, 4 samples each were collected at the 3 designated sampling points and another sample at the control site making a total of 13 samples. The sampling procedure was performed for 2 seasons (wet and dry seasons) making a total of 26 water samples.

Water samples were collected by slowly lowering a tilted wide-mouth sample bottle into the water until the water began to run into it. The bottle was then turned slowly upright keeping the lip just under the surface of the water so that the whole sample was surface water and the bottle was carefully lifted with disposable wiping cloths and capped. Each water sample collected measured up to 4 litres. Samples were stored in a dark cool container and taken immediately to laboratory after placing the inscribed label, showing the name of the sample collector, location, time, date, sample number and sample name. All contaminated materials were then placed into a plastic bag for disposal or decontamination. Samples were transported to the laboratory in an ice chest (USEPA, 2004).

2.2.3 Laboratory Analysis

The whole sample reagents, apparatus and machine for this research were obtained from National Research Institute for Chemical Technology, Nigeria (NARICT), Environmental Pollution laboratory in Ahmadu Bello University Zaria. Digital Gas Chromatograph Mass Spectrophotometer (GCMS) was used in determining PCBs and PAHs.

2.2.4 PAHs and PCBs - GC/MS Analysis

PAHs were prepared by dissolving about 0.01 g of sample in hexane. From these solutions, mixed solution of PAHs ranging from 100–1000 pg/l were prepared in hexane. These solutions were stored in amber flasks at 21^{o}C. Three PAHs calibration points were prepared: 100, 500, and 1000 pg/l. d-PAHs (1000 pg/l) were added to stock calibration solutions as well as to the samples before extraction. The samples were corrected for a recovery by applying an internal standard method, since PAHs and d-PAHs follows the similar steps in extraction and analysis. Similar method adopted from (Al-Rashdan, et al., 2010).

All solvents were of HPLC-grade. Hexane and dichloromethane were supplied by (NARICT). The chromatographic column was used for clean up of the extract, filled with 2 g of silica gel and 1 g of Aluminium oxide. Nitrogen gas was used to concentrate the extract.

2.2.5 Extraction Procedure and Sample Preparation

5g water samples were spiked with d-PAHs, and extracted with mixed solvents of 150 ml hexane: dichloromethane (1 : 1), using a Soxhlet apparatus for 16 h. The solvents were reduced to 1 ml using a rotary evaporator and N2 gas. The extract was then passed through a cleanup column filled with 2 g of 100–200 mesh silica gel, followed by 1 g of aluminum oxide (considered to be the most efficient and selective for column chromatography separation) and anhydrous sodium sulfate. The column was washed with 10 ml of hexane and the PAHs were collected by eluting the column with 8 ml of hexane and 5 ml of dichloromethane. Finally, the extract was concentrated to 1 ml under a weak nitrogen flow at ambient temperature. This solution is then injected to GC/MS for PAHs analysis. Quantification of individual PAHs was based on internal calibration standard containing known concentrations of 26 PAHs and d-PAHs (Al-Rashdan et al., 2010)

2.2.6 Gas Chromatography—Mass Spectrometry Conditions

PAH Analyses were performed with the GCMS-QP2010 Plus Shimadzu, Japan interfaced to a mass selective detector. The separation of PAHs was performed using a 5% phenyl-methylsilicone (DB-5MS) bonded-phase fused-silica capillary column (Hewlett-Packard, 30 m 0.25 mm i.d., film thickness 0.25 m). The injector port was run in splitless mode. The oven temperature program was 20^{o}C for 2 min, raised to 32^{o}C and maintained at this temperature for 8 min. The transfer line was maintained at 31^{o}C. The mass spectra were collected by electronic impact at 70 eV. Stock solutions were used to establish the retention time of each analyte. Detection of PAHs was carried out using SIM mode, which is designed for preselected ion peaks, non-selected peaks are not identified and quantified (Al-Rashdan et al., 2010).

2.2.7 GC-MS Procedure Performance

The chromatograms of the 26 selected PAHs in the standards and water samples are shown in Figures 1.1 and 1.26, the PAHs shows a wide spectrum of volatility and all 16 PAHs behave the same in chromatographic area in the standard and the sample. The set of samples was analyzed along with a blank for PAH background correction. The results were corrected for recoveries using an internal standard method, assuming that PAHs and d-PAHs behave in a similar manner during extraction and analysis. Recoveries of d-PAHs were utilized to estimate recoveries of the native PAHs. The average recoveries of d-PAHs varied from 79.11% to 91.56% with relative standard deviation (RSDs) ranging from 7.02% to 8.86%. Chromatogram of polycyclic aromatic hydrocarbons (PAHs) obtained using the GC-MS method. Numbers on the chromatogram refer to the individual PAHs as indicated in different figures. The results obtained shows that the method is very accurate and precise. Similar method adopted from (Al-Rashdan et al., 2010).

2.2.8 GCMS Performance Tests

At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved. A 2 µL volume containing sample ng of perfluourotributylamine (PFTBA) is injected into the GC/MS for this purpose.

2.3 Calculations of PAH and PCBs Concentration

The concentration of each identified analyte in the sample can be calculated as follows Anonymous (1999):

$$\text{Concentration (ng / ml)} = 1000 \text{ X } \frac{(Ax)\,(Is)\,(Ve)}{(Ais)\,(RF)\,(Vi)}$$

Where:

Ax = area of characteristic ion(s) for analyte being measured

Is = amount of internal std injected, ng

Ve = volume of total sample, µL

Ais = area of characteristic ion(s) for internal standard

RF = response factor for analyte being measured

Vi = volume of analyte injected, µL

1000 = ` factor for converting 165icroliters to millilitres

3. Results and Discussion

The results of the assessment of the polycyclic aromatic hydrocarbons and polychlorinated biphenyls level of water samples analysed show that none of the PCBs congeners were detected while, PAH pollutant detected in the majority of the water samples analysed were Pyrene, Phenanthrene, Benzo(a) pyrene, Ethyl Pyrene, Chrysene, Benzo(a) pyrene, Fluorene etc. However, the total PAH concentrations detected in the water that ranges between 0.001 to 0.087mg/l were above the maximum permissible level of 0.0007 mg/L as stated by Nigerian standard organization for drinking water.

Analysis of Variance were obtained using Bartlett's test performance show that there is significant difference in the concentrations of PAHs in water samples at the various sampling points along the Challawa river.

Nigerian standard for drinking water set a threshold limit of 0.0007mg/L for PAH compound SON (2007).h while for U.S. Environmental Protection Agency Water 0.0001 mg/ L is the maximum

contaminant level (MCL) for benz(a)anthracene; 0.0002 mg/L for benzo (a) pyrene, benzo (b) fluoranthene, benzo (k) fluoranthene, chrysene; 0.0003 mg/L for dibenz (a,h) anthracene, 0.0004 mg/L for indenol (1,2,3-c,d) pyrene and 0.0002 mg/L for benzo (a) pyrene, benzo (b) fluoranthene, benzo (k) fluoranthene, chrysene (USEPA, 2000).

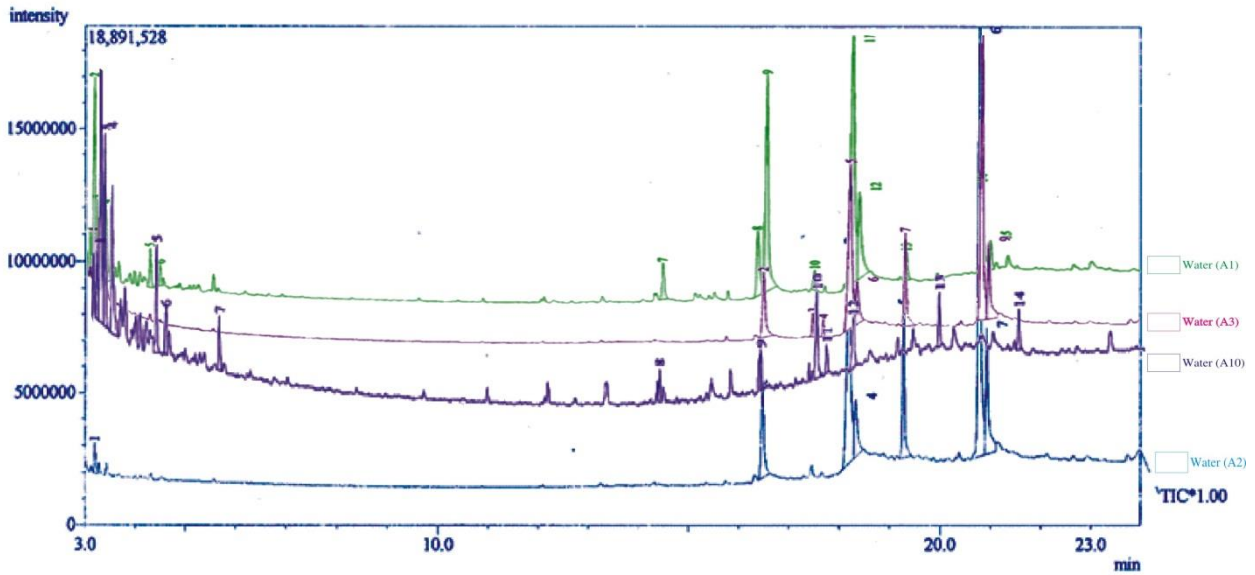

Figure 1.1 Chromatographic illustration of Water Samples A00, A1, A2 and A3 at the Upstream of Challawa River during Dry Season

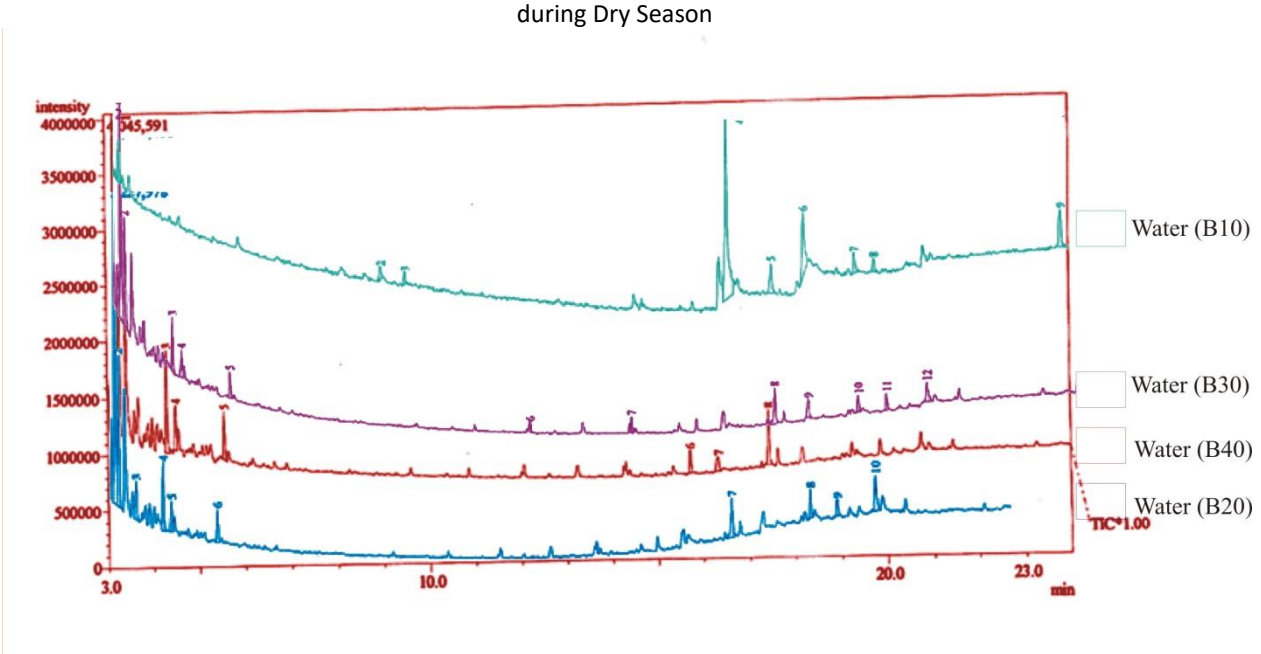

Figure 1.2 Chromatographic illustration of Water Samples B10, B20, B30 and B40 at the Middle stream of Challawa River during Dry Season

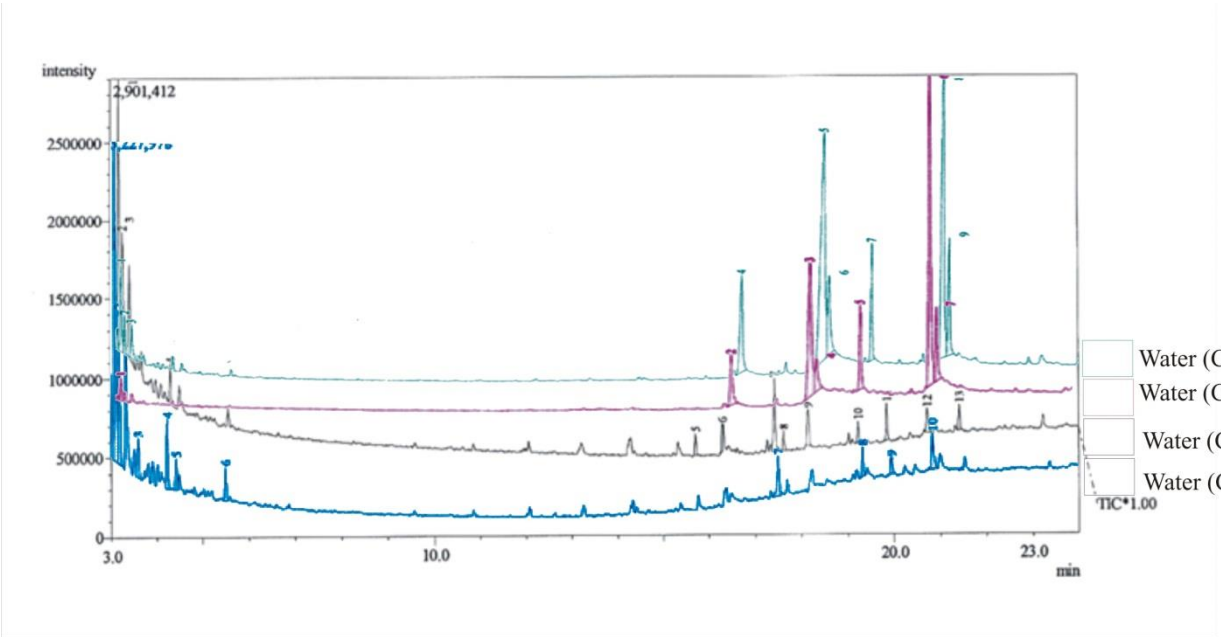

Figure 1.3 Chromatographic illustration of Water Samples C1, C2, C3 and C4 at the Down-stream of Challawa River during Dry Season

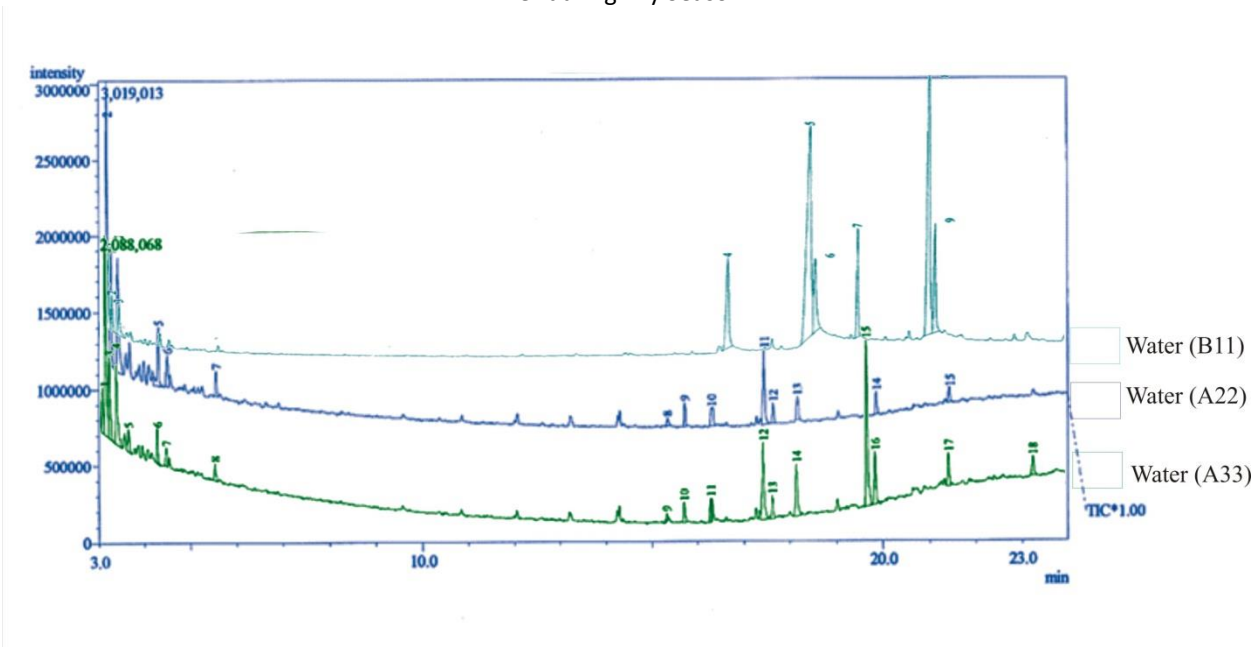

Figure 1.4 Chromatographic illustration of Water Samples A11, A22, A33 and A44 at the Upstream of Challawa River during Rainy Season

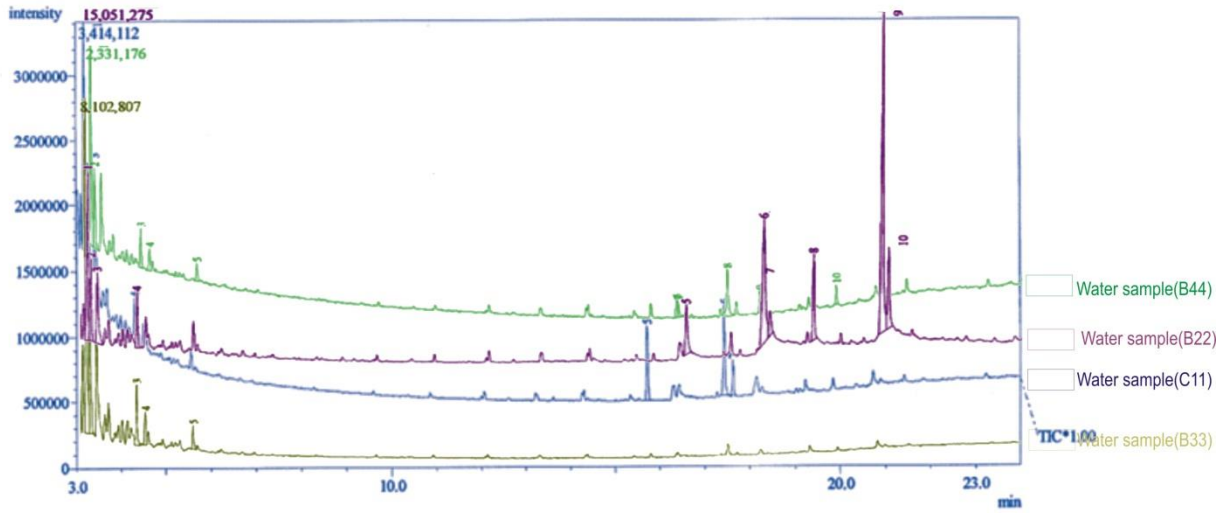

Figure 1.5 Chromatographic illustrations of Water Samples B11, B22, B33 and B44 at the Middle stream of Challawa River during Rainy Season

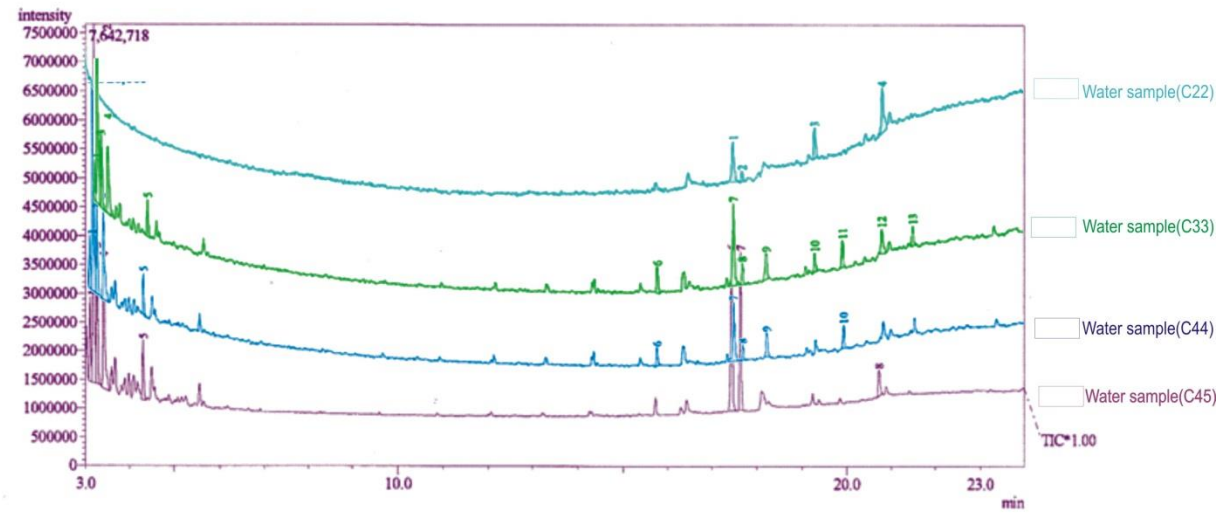

Figure 1.6 Chromatographic illustration of Water Samples C11, C22, C33 and C44 and C55 at the Down-stream of Challawa River during Rainy Season

Table 1. Concentration (mg/l) of PAH and PCBs detected in Water Samples Collected at Challawa River during Dry Season

Location	Sample Code	Pollutants Detected PCBs	PAH	RT (min)	% Area	Conc (mg/L)	Thresholds Nigeria (mg/L)
Control Point	A_{00}	ND	11-Octadecenoic acid,	17.431	34.19	0.001	0.0007mg/L
			methyl ester	17.638	6.35	0.001	0.0007mg/L
			Decanoic acid,	19.236	20.47	00.02	0.0007mg/L
			methyl ester	20.729	38.98	0.001	0.0007mg/L
Upstream	A_1	ND	EthylPyrene	3.268	16.39	0.002	0.0007mg/L
			Acenaphtylene	4.306	7.90	0.008	0.0007mg/L
			Phenanthrene	5.559	4.28	0.005	0.0007mg/L
			Chrysene	12.071	1.42	0.004	0.0007mg/L
			Pyrene	14.307	2.42	0.003	0.0007mg/L
			Benz (a)anthracene	17.435	8.67	0.003	0.0007mg/L
			Benzo (a) pyrene	18.163	4.36	0.001	0.0007mg/L
			Chrysene	9.243	2.76	0.005	0.0007mg/L
			Benz(a)anthracene	20.735	4.94	0.003	0.0007mg/L
			EthylPyrene	4.300	5.09	0.004	0.0007mg/L
			Phenylethane	15.716	2.76	0.003	0.0007mg/L
			Fluorene	17.629	2.33	0.001	0.0007mg/L
	A_2	ND	Benzo(a) pyrene,	3.193	1.52	0.002	0.0007mg/L
			Fluorene	16.480	7.83	0.003	0.0007mg/L
			EthylPyrene	18.201	26.61	0.006	0.0007mg/L
			Benzo(a) pyrene,	18.331	5.48	0.003	0.0007mg/L
			Chrysene	19.275	9.77	0.004	0.0007mg/L
			Pyrene	20.926	11.18	0.004	0.0007mg/L
	A_3	ND	Anthracene	3.191	3.10	0.005	0.0007mg/L
			EthylPyrene	16.479	8.52	0.003	0.0007mg/L
			Benzo(a) pyrene,	17.457	1.84	0.001	0.0007mg/L
			Fluorene	18.328	5.86	0.003	0.0007mg/ L
			Pyrene	19.274	9.10	0.004	0.0007mg/L
			Phenylethane	20.920	8.77	0.001	0.0007mg/L
			EthylPyrene	3.103	3.74	0.002	0.0007mg/L
	A_4	ND	Pyrene	3.103	4.45	0.020	0.0007mg/L
			EthylPyrene	3.176	26.32	0.008	0.0007mg/L
			Benzo(a) pyrene	3.262	12.11	0.003	0.0007mg/L
			Phenanthrene	3.410	13.34	0.003	0.0007mg/L
			Acenaphtylene	4.297	7.56	0.043	0.0007mg/L
			EthylPyrene	4.491	4.07	0.006	0.0007mg/L
			Phenylethane	5.550	3.65	0.007	0.0007mg/L
			Anthracene	14.301	2.27	0.087	0.0007mg/L
			Phenylethane	16.325	2.41	0.006	0.0007mg/L

ND - Indicates not detected
RT – Retention time of each of the compound in the samples
% Area – Percentage area the chromatogram of the compound

Location – The point where samples collected along the trench of the river Challawa
Conc (mg/l) – The concentration of organic pollutants obtained from the % Area of the chromatogram
Sample Code – The 2 -3 letters of the acronyms is the name given to the samples during laboratory analysis

Table 2: Concentration (mg/l) of PAH and PCBs detected in Water Samples Collected at Challawa River during Dry Season

Location	Sample Code	Pollutants Detected PCBs	PAH	RT (min)	% Area	Conc (mg/L)	Thresholds Nigeria (mg/L)
Middle Stream	B_{1O}	ND	Fluorene,	3.180	5.84	0.003	0.0007mg/L
			EthylPyrene	8.877	2.45	0.002	0.0007mg/L
			Benzo(a) pyrene	9.402	2.04	0.002	0.0007mg/L
			Pyrene,	19.238	3.93	0.001	0.0007mg/L
			Benzo (a) pyrene	19.658	2.10	0.004	0.0007mg/L
			Phenylethane	23.727	8.21	0.002	0.0007mg/L
			Anthracene	14.307	2.42	0.003	0.0007mg/L
	B_{2O}	ND	Benzo(a) pyrene	3.179	43.20	0.009	0.0007mg/L
			Pyrene	3.266	15.80	0.004	0.0007mg/L
			Phenanthrene	3.674	5.12	0.002	0.0007mg/L
			Anthracene	5.555	4.00	0.002	0.0007mg/L
			Benzo (a) pyrene	17.428	7.13	0.002	0.0007mg/L
			Phenylethane	19.234	3.65	0.005	0.0007mg/L
	B_{3O}	ND	Phenanthrene	3.183	38.33	0.001	0.0007mg/L
			EthylPyrene	3.268	16.39	0.004	0.0007mg/L
			Acenaphtylene	4.306	7.90	0.013	0.0007mg/L
			Phenylethane	12.071	1.42	0.002	0.0007mg/L
			Anthracene	14.307	2.42	0.003	0.0007mg/L
			Benz (a)anthracene	17.435	8.67	0.002	0.0007mg/L
			Chrysene	18.163	4.36	0.001	0.0007mg/L
			Fluorene	19.243	2.76	0.001	0.0007mg/L
			Phenylethane	19.857	3.42	0.002	0.0007mg/L
			Pyrene	20.735	4.94	0.002	0.0007mg/L
	B_{40}	ND	Pyrene	4.300	12.05	0.006	0.0007mg/L
			Phenanthrene	4.492	6.29	0.003	0.0007mg/L
			Benzo(a) pyrene	5.552	5.91	0.004	0.0007mg/L
			Phenylethane	15.719	2.95	0.032	0.0007mg/L
			Anthracene	16.328	3.31	0.004	0.0007mg/L
			Chrysene	17.433	8.32	0.002	0.0007mg/L
			EthylPyrene	16.466	7.00	0.001	0.0007mg/L

ND - Indicates not detected
RT – Retention time of each of the compound in the samples
% Area – Percentage area the chromatogram of the compound
Location – The point where samples collected along the trench of the river Challawa

Conc (mg/l) – The concentration of organic pollutants obtained from the % Area of the chromatogram
Sample Code – The 2 -3 letters of the acronyms is the name given to the samples during laboratory analysis

Table 3: Concentration (mg/l) of PAH and PCBs detected in Water Samples Collected at Challawa River during Dry Season

Location	Sample Code	Pollutants Detected PCBs	PAH	RT (min)	% Area (mg/L)	Conc Nigeria (mg/L)	Thresholds
Down Stream	C1	ND	EthylPyrene	3.191	2.12	0.002	0.0007mg/L
			Phenanthrene	16.468	7.24	0.007	0.0007mg/L
			Benzo(a) pyrene	18.186	26.79	0.004	0.0007mg/L
			Pyrene,	20.777	41.15	0.002	0.0007mg/L
			Chrysene	15.342	0.68	0.004	0.0007mg/L
	C_2	ND	Phenanthrene	3.191	2.82	0.003	0.0007mg/L
			EthylPyrene	16.466	7.00	0.001	0.0007mg/L
			Pyrene	18.144	6.97	0.004	0.0007mg/L
			Anthracene	19.267	8.38	0.003	0.0007mg/L
			Phenylethane	20.776	41.36	0.009	0.0007mg/L
			Chrysene	20.919	8.48	0.002	0.0007mg/L
			Benzo (a) pyrene	17.622	2.95	0.001	0.0007mg/L
	C_3	ND	EthylPyrene	3.190	4.62	0.013	0.0007mg/L
			Benzo(a) pyrene	3.275	1.65	0.005	0.0007mg/L
			Pyrene	20.722	10.84	0.002	0.0007mg/L
			Acenaphtylene	4.492	6.29	0.007	0.0007mg/L
			Phenanthrene	16.491	8.94	0.009	0.0007mg/L
			Benzo(a) pyrene	18.246	34.15	0.002	0.0007mg/L
			Chrysene	18.364	6.77	0.003	0.0007mg/L
			Phenylethane	19.269	6.44	0.005	0.0007mg/L
			Anthracene	20.790	28.05	0.003	0.0007mg/L
	C_4	ND	EthylPyrene	3.183	26.80	0.001	0.0007mg/L
			Fluorene	3.268	8.54	0.008	0.0007mg/L
			Anthracene	15.718	2.36	0.004	0.0007mg/L
			Benzo(a) pyrene	3.416	14.61	0.002	0.0007mg/L
			Pyrene	15.719	1.97	0.001	0.0007mg/L
			EthylPyrene	16.294	2.09	0.003	0.0007mg/L
			Phenanthrene	17.430	9.96	0.002	0.0007mg/L
			Phenylethane	17.421	12.73	0.001	0.0007mg/L
			Benzo (a) pyrene	17.622	2.95	0.002	0.0007mg/L
			Chrysene	18.144	6.97	0.002	0.0007mg/L
			Benz (a)anthracene	19.225	2.88	0.003	0.0007mg/L

ND - Indicates not detected
RT – Retention time of each of the compound in the samples
% Area – Percentage area the chromatogram of the compound
Location – The point where samples collected along the trench of the river Challawa

Conc (mg/l) – The concentration of organic pollutants obtained from the % Area of the chromatogram
Sample Code – The 2 -3 letters of the acronyms is the name given to the samples during laboratory analysis

Table 4: Concentration (mg/l) of PAH and PCBs detected in Water Samples Collected at Challawa River during Rainy Season

Location	Sample Code	Pollutants Detected PCBs	PAH	RT (min)	% Area	Conc (mg/L)	Thresholds Nigeria (mg/L)
Control Point	A_{O0}	ND	Acenaphtylene	3.178	40.02	0.003	0.0007mg/L
			Fluorene	3.264	15.07	0.001	0.0007mg/L
			EthylPyrene	3.411	19.02	0.004	0.0007mg/L
			Chrysene	4.299	7.14	0.003	0.0007mg/L
			Pyrene	14.307	2.42	0.001	0.0007mg/L
			Benz (a) anthracene	17.435	8.67	0.001	0.0007mg/L
			Benzo (a) pyrene	18.163	4.36	0.001	0.0007mg/L
Upstream	A_{11}	ND	EthylPyrene	3.107	5.30	0.005	0.0007mg/L
			Chrysene	19.85	3.42	0.001	0.0007mg/L
			Anthracene	20.73	4.94	0.003	0.0007mg/L
			EthylPyrene	4.300	5.09	0.008	0.0007mg/L
			Phenylethane	15.71	2.76	0.003	0.0007mg/L
			Pyrene	17.42	12.6	0.002	0.0007mg/L
			Fluorene	3.179	28.5	0.001	0.0007mg/L
			EthylPyrene	3.265	0.61	0.004	0.0007mg/L
			Benzo (a) pyrene	3.412	12.68	0.004	0.0007mg/L
			Chrysene	4.301	5.25	0.003	0.0007mg/L
			Acenaphtylene	4.495	3.05	0.001	0.0007mg/L
			Chrysene	5.555	2.33	0.001	0.0007mg/L
			Benz (a) anthracene	15.720	3.54	0.004	0.0007mg/L
	A_{22}	ND	Benzo (a) pyrene	4.300	4.54	0.001	0.0007mg/L
			Pyrene	15.715	3.71	0.003	0.0007mg/L
			Phenylethane	17.425	15.90	0.001	0.0007mg/L
			Benzo (a) pyrene	17.629	3.68	0.002	0.0007mg/L
			Benz (a) anthracene	18.151	5.43	0.001	0.0007mg/L
			Anthracene	19.233	2.77	0.001	0.0007mg/L
			Chrysene	19.845	4.63	0.001	0.0007mg/L
			EthylPyrene	3.261	0.84	0.001	0.0007mg/L
			Chrysene	4.490	3.53	0.003	0.0007mg/L
			Phenylethane	5.549	2.36	0.003	0.0007mg/L
			Benz (a) anthracene	15.342	1.09	0.014	0.0007mg/L
	A_{33}	ND	Acenaphtylene	3.103	3.74	0.014	0.0007mg/L
			Pyrene	4.300	12.05	0.005	0.0007mg/L
			Benz (a) anthracene	4.492	6.29	0.006	0.0007mg/L
			EthylPyrene	5.552	5.91	0.003	0.0007mg/L
			Fluorene	15.719	2.95	0.015	0.0007mg/L
			Phenylethane	16.328	3.31	0.004	0.0007mg/L
			Acenaphtylene	17.433	8.32	0.006	0.0007mg/L

			Phenanthrene	3.671	2.22	0.002	0.0007mg/L
			Phenylethane	4.296	2.88	0.002	0.0007mg/L
			Benzo (a) pyrene	4.492	1.77	0.001	0.0007mg/L
			Anthracene	5.549	1.61	0.002	0.0007mg/L
			Chrysene	15.342	0.68	0.004	0.0007mg/L
Middle Stream	B_{11}	ND	EthylPyrene	3.181	13.06	0.003	0.0007mg/L
			Benzo (a) pyrene	17.629	6.78	0.002	0.0007mg/L
			Anthracene	18.120	18.95	0.001	0.0007mg/L
			Phenanthrene	19.231	8.44	0.002	0.0007mg/L
			Pyrene	20.722	10.84	0.002	0.0007mg/L
			Fluorene	4.492	6.29	0.007	0.0007mg/L
			Benzo (a) pyrene	5.552	5.91	0.003	0.0007mg/L
			Benz (a) anthracene	15.719	2.95	0.002	0.0007mg/L
	B_{22}	ND	EthylPyrene	3.187	12.41	0.003	0.0007mg/L
			Phenylethane	18.306	2.55	0.001	0.0007mg/L
			Benzo (a) pyrene	19.261	6.86	0.001	0.0007mg/L
			Benz (a) anthracene	20.765	31.72	0.002	0.0007mg/L
			Chrysene	20.915	7.44	0.002	0.0007mg/L
			Benzo (a) pyrene	4.300	4.54	0.005	0.0007mg/L
			Pyrene	15.715	3.71	0.001	0.0007mg/L
			Fluorene	17.425	15.90	0.002	0.0007mg/L
			Anthracene	17.629	3.68	0.002	0.0007mg/L
	B_{33}	ND	Phenanthrene	3.183	38.33	0.002	0.0007mg/L
			EthylPyrene	3.268	16.39	0.01	0.0007mg/L
			Phenylethane	15.716	2.76	0.003	0.0007mg/L
			Pyrene	17.428	12.68	0.002	0.0007mg/L
			Benzo (a) pyrene	17.22	2.33	0.001	0.0007mg/L

ND - Indicates not detected
RT – Retention time of each of the compound in the samples
% Area – Percentage area the chromatogram of the compound
Location – The point where samples collected along the trench of the river Challawa
Conc (mg/l) – The concentration of organic pollutants obtained from the % Area of the chromatogram
Sample Code – The 2 -3 letters of the acronyms is the name given to the samples during laboratory analysis

Table 5: Concentration (mg/l) of PAH and PCBs detected in Water Samples Collected at Challawa River during Rainy Season

Location	Sample Code	Pollutants Detected PCBs	PAH	RT (min)	% Area	Conc (mg/L)	Thresholds Nigeria (mg/L
	B_{40}	ND	Phenanthrene	5.559	4.28	0.001	0.0007mg/L
			Chrysene	12.071	1.42	0.001	0.0007mg/L
			Pyrene	14.307	2.42	0.001	0.0007mg/L
			Benz (a anthracene	17.435	8.67	0.001	0.0007mg/L
			Benzo (a) pyrene	3.264	11.45	0.004	0.0007mg/L
			EthylPyrene	4.300	5.09	0.008	0.0007mg/L
			Phenylethane	16.328	3.31	0.004	0.0007mg/L
			Benzo (a) pyrene	17.433	8.32	0.006	0.0007mg/L
			Fluorene	3.264	9.47	0.002	0.0007mg/L
			Anthracene	3.413	10.94	0.001	0.0007mg/L
Down Stream	C_{11}	ND	EthylPyrene	3.184	32.72	0.003	0.0007mg/L
			Fluorene	3.269	10.96	0.001	0.0007mg/L
			Phenanthrenee	4.307	5.65	0.006	0.0007mg/L
			Anthracene	15.718	11.37	0.002	0.0007mg/L
			Benzo (a) pyrene	17.431	16.40	0.001	0.0007mg/L
			Pyrene	17.632	5.23	0.002	0.0007mg/L
			Chrysene	4.300	4.54	0.003	0.0007mg/L
	C_{22}	ND	Benz (a) anthracene	17.431	34.19	0.004	0.0007mg/L
			Chrysene	20.729	38.98	0.001	0.0007mg/L
			EthylPyrene	3.184	32.72	0.003	0.0007mg/L
			Benzo (a) pyrene	11.431	16.40	0.001	0.0007mg/L
	C_{33}	ND	Pyrene	15.719	1.97	0.001	0.0007mg/L
			EthylPyrene	16.294	2.09	0.003	0.0007mg/L
			Chrysene	3.264	9.47	0.002	0.0007mg/L
			Phenanthrene	3.413	10.94	0.001	0.0007mg/L
			Benzo(a) pyrene	4.300	4.54	0.001	0.0007mg/L
			Pyrene	15.715	3.71	0.003	0.0007mg/L
			Phenylethane	17.425	15.90	0.001	0.0007mg/L
			Fluorene	17.629	3.68	0.002	0.0007mg/L
			Benz (a) anthracene	18.151	5.43	0.001	0.0007mg/L
			Chrysene	19.845	4.63	0.001	0.0007mg/L
			Anthracene	20.727	4.89	0.002	0.0007mg/L
	C_{44}	ND	Chrysene	3.106	6.63	0.002	0.0007mg/L
			Phenanthrene	3.178	34.63	0.006	0.0007mg/L
			Benzo(a) pyrene	3.264	11.45	0.004	0.0007mg/L
			Phenanthrene	3.411	15.77	0.002	0.0007mg/L
			Benzo (a) pyrene	13.33	8.32	0.006	0.0007mg/L
			EthylPyrene	3.264	9.47	0.002	0.0007mg/L
			Anthracene	4.300	5.09	0.002	0.0007mg/L
			Phenylethane	15.716	2.76	0.001	0.0007mg/L
			Pyrene	17.428	12.68	0.001	0.0007mg/L
			Fluorene	17.629	2.33	0.002	0.0007mg/L

ND - Indicates not detected
RT – Retention time of each of the compound in the samples
% Area – Percentage area the chromatogram of the compound
Location – The point where samples collected along the trench of the river Challawa

Analysis of Variance was obtained by Bartlett's test performance. Means values PAHs recorded in water samples collected from the various sampling points were compared and tested at 95% confidence. The difference was found to be significant ($p < 0.05$).

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. oneway water f1
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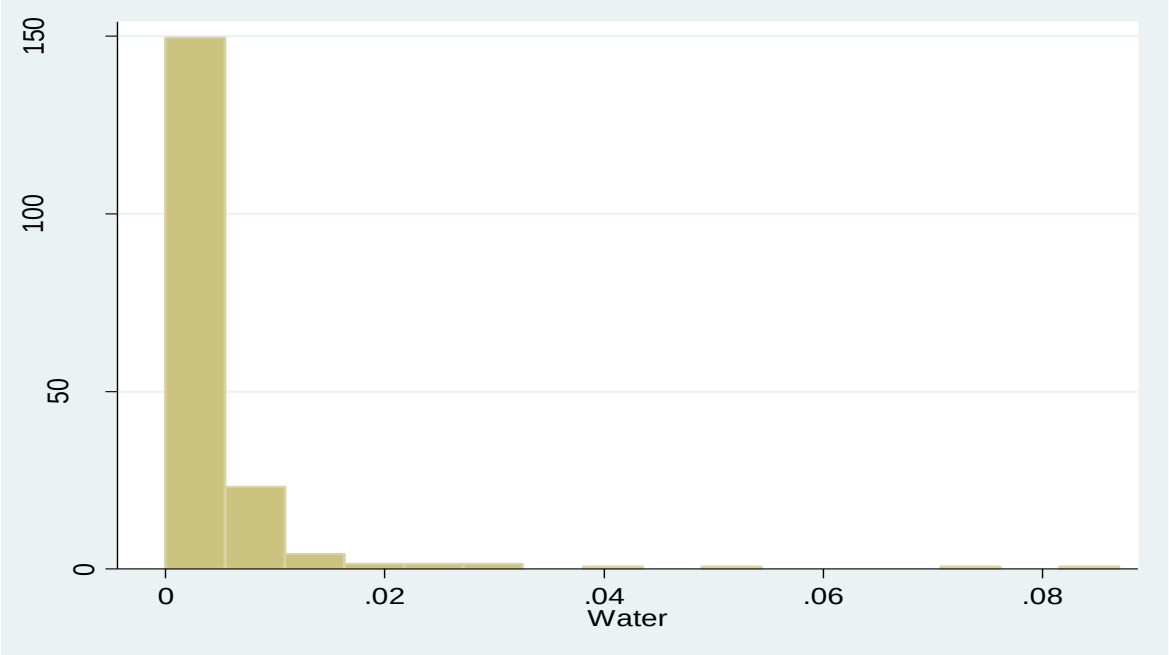
Source	SS	df	MS	F	Prob > F
Between groups	.005040882	25	.000201635	3.17	0.0000
Within groups	.015094654	237	.000063691		
Total	.020135536	262	.000076853		

Bartlett's test for equal variances: chi2(24) = 390.7767 Prob>chi2 = 0.000

note: Bartlett's test performed on cells with positive variance:
1 multiple-observation cells not used



4.3 Bar chart representation of water concentration against density

The result of water analysis revealed that the concentrations of PAHs exceeded the acceptable limit of 0.0007mg/L set by Nigeria drinking water quality standard.

Polychlorinated biphenyls (PCBs) were not detected in the whole samples analysed while, polycyclic aromatic hydrocarbons (PAHs) were detected at the Challawa River. The total concentrations of PAH detected ranges between 0.001 to 0.087mg/l.

Some selected PAHs compound notably Benz(a)anthracene, Benzo(b)fluoranthene, Benzo(a)pyrene, Dibenz(a,h)anthracene, and Indeno(1,2,3-c,d)pyrene Known animal carcinogens ATSDR (1995). While Benz(a)anthracene and Benzo(a)pyrene have been classified by Agency for Toxic Substances and Disease Registry (ATSDR) as Carcinogenic to humans

Pyrene causes skin, lungs, bladder, gastrointestinal cancer, Naphthalene its produce toxic reactions, especially newborns. Other PAHs compound also causes cataracts, liver and kidney damage. They also cause in nausea and vomiting. The levels of PAHs in most of the water samples analyzed exceeded the acceptable limit set by Nigeria and U.S standard.

Surprisingly the result also revealed the presence of synchronous PAH compound. This can be predominantly attributed to the discharge and emission of the industrial effluent of incomplete combustion processes of organic materials and indiscriminant discharge of untreated effluent in the river from Sharada and Challawa Industrial estate in the Kano city.

The analytical results revealed that some chemical are presents in water at significantly very high levels at Zamawa village which is very close to Challawa industrial estate and also the main effluent discharge point. This also means that pollutants could possibly affect the ground water quality of the villages that falls within the study area.

4. Conclusion and Recommendations

In conclusion, it can be said that industrial activities and effluent had impact on Challawa River basin and its environs especially those that are live in the immediate surroundings. The water resources in the study area are not properly managed. This is an indication that there is failure in the adoption of pollution abatement measures in the area.

Arising from the findings of this research, the following recommendations were made:-

There should be a regular monitoring and evaluation of water, fishes and crops quality in the study area and water development should go hand in hand with water quality consideration.

The industries should treat their liquid properly using modern equipment.

The industries should construct sanitary land fill to dispose their liquid and solid waste properly instead of dumping openly in their premises and water bodies

This research only checked the impact the industries has on environment with reference to surface water. It is also recommended that further work to be carried out in the future to check the impact on air quality

It is important to initiate campaign, to inform the people on the level of water, crops and fish contamination and the sanitation steps to be followed for ensuring safe drinking water.

The public at large should be educated on the possible impact associated with living around or nearby industrial site and its consequence.

People of the communities around the industrial estate should be employed in order to give them a sense of belonging and job opportunity.

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