Concentration of Polycyclic Aromatic Hydrocarbons in Water from Hand-Dug Wells in Some Communities in Ekpeyeland, Rivers State, Nigeria

Abstract

Well water sources from selected communities in Ekpeyeland were assessed for the concentrations of polycyclic aromatic hydrocarbons(PAHs). The assessment was conducted seasonally in six communities. The concentrations of the PAHs were determined using standard methods and procedures and finally quantified by the use of GC-MS chromatography. The result showed the presence of all the 16 USEPA priority PAHs in the examined water samples. Seasonal variations were not significant. The summed values of PAHs from stations and seasons were above the permissible limit required for by WHO. Classification of the different categories of PAHs identified higher molecular weight (HMW) PAHs more in concentration than lower molecular weight (LMW) PAHs in the wells. Source identification proved that both pyrogenic and petrogenic sources were responsible for the presence of PAHs in the well water. However, pyrogenic source was the more prominent source of PAHs in the water. There was high level of carcinogenic PAHs in the water and thus the water portends danger to the users. Therefore, the locals are advised not to consume the water to avoid its effect on the long run.

Introduction

The contamination of groundwater is a universal problem that has caused serious influence on human well-being (health)as well as ecological environment. Roughly one third of the worldinhabitantshinge on groundwater supply for consumption(Canadian and Solutions, 2010), and groundwater stands out as the major source of fresh water that is available for use athomes, agriculture and industries (Lezzaik et al., 2018).One of the major causes of water contamination is by industrial activities and has led to unfathomable andgrave hazard in most societies especially in countries withemerging industrial growth.

By definition, polycyclic aromatic hydrocarbons (PAHs) belong toa class of organic compounds which comprised of at least two or more fused benzene rings.They are products of incomplete combustion and pyrolysis of organic matters such as cigarette smoke, burning bush, emission from automobiles and forest fire, in the midst of others (Girelli et al., 2014). Notably, stands out are threemost important sources of PAHs which are pyrogenic (produced from organic substances under high temperatures in the presence of lowor absence of oxygen), petrogenic PAHs (arise from the process of crude oil maturation) and biological PAHs (those produced during degradation of vegetative matters (Hussein and Mona, 2016).

Currently, in water springs of several regions, a significant contamination risk of polycyclic aromatic hydrocarbons (PAHs)has been found in different resources, particularly in rural areas. These water sources contain groundwater and surface water. Over the course of modernera, 16 PAHs have been identified as main concern contaminants by the U.S Environmental Protection Agency (USEPA, 2012).

Precisely, there are sixteen (16) priority PAHs which has been identified by the United State Environmental Protection Agency (USEPA) well-known to cause severe threats to human health subject on the level of exposure. The notable PAHs include naphthalene [Nap], acenaphthylene [Acy], acenaphthene [Acp], fluorene [Flr], anthracene [Ant], phenanthrene [Phe], fluoranthene [Flt], chrysene [Chy], benzo (a) anthracene [B(a)A], pyrene [Pyr], benzo (a) pyrene [B(a)P], benzo (b) fluoranthene [B (b) F], indeno (1,2,3-cd) pyrene [I (cd)P], dibenzo (ah) anthracene [D(ah)], benzo (k) fluoranthene [B(k) F] and benzo (ghi) perylene [B (ghi) P](Yang et al., 2014;Hussain et al., 2015). Among these sixteen PAHs are seven notable ones which include benz[a]anthrance, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno [1,2,2-cd]pyrene, and dibenzo[a,h]anthracene, are potentially carcinogenic to humans according to the International Agency for Research on Cancer (An et al., 2016). These seven PAHs are the most used substances among polycyclic aromatic compounds to realize environmental monitoring and assess health risks (Larsson et al., 2018; Aslam et al., 2022). However, industrial expansion, urban progression, and universal climate change play an important role in groundwater contamination (Zhang et al., 2014).

PAHscongenersareformedthroughmultifacetedmechanismscomprisingcyclizationandaromatizationof carbon basedmaterialsinthepyrolyticphaseofignitionprocess,atvery high temperaturesthat are over 400˚C,withidealtemperatureinthe range of 700–900◦C(Lima et al., 2005).Thehigh temperature annihilationofPAHs necessitatesvery high temperatures and redoxcircumstances(Caneghem& Vandecasteele, 2014).Thus, the yield of PAHs is governed by the configuration of the fuel and adulteration andignition conditions such as temperature, available oxygen, time for the process and instability(Masto et al., 2015). Fuel contaminants, like creosote (a wood preservative), can be a vital sources of PAHs in incineration systems (Johansson& van Bavel, 2003). PAHs madefrom the combustion of biomass give the impression to be customarilyalliedtogasdischargesandsoot deposits,whereas LMW PAHs are favourably present in gas phase discharges. HMW PAHs are additionalrelated with residues (Bignal et al., 2008; Atkins et al., 2010).

Therefore this study was conducted to examine the concentrations of PAHs in selected communities in Ekpeyeland where intense oil refining activities is taken place and the likely sources and implications on the environment.

Materials and Methods

Description of the Study Area

The study area are some selected communities in Ekpeyeland in Ahoada East and Ahoada West Local Government Area of Rivers State. The geo-positions and coordinates of the LGAs are 5^{o}07' and 5^{o}41' North, 6^{o}38' 6^{o}64'East for Ahoada Eastand 5^{o}09' and 5^{o}59' North, 6^{o}28' and 6^{o}6'4 East for Ahoada West.Ekpeye shares is bounded by Engenni by the West, Ikwerre by the East, Abua by the south. Ekpeye is made up of six clans and the spoken language in the land is known as Ekpeye language.

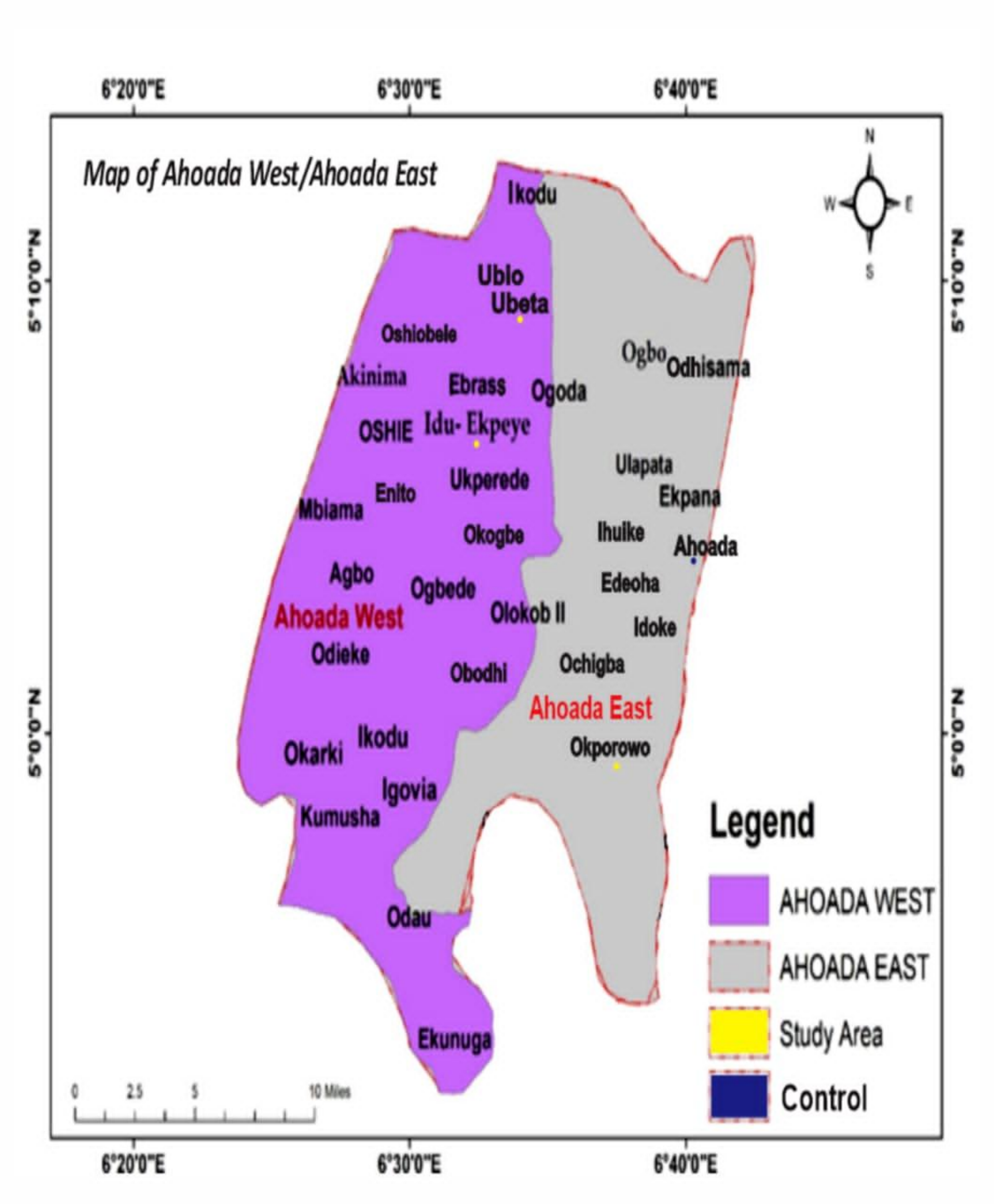

Fig 1.

Sampling and Sample Collection

Sampling was done between the months of January to July in 2023 in dry and wet season respectively. The water samples were collected from four separate wells within a sample community. Samples were collected from Ahoada (control), Idu-Ekpeye, Ubeta, Okporowo,Okoma I and Okoma II. The choice of these locations were chosen based on the presence of Illegal refining sites. The water samples were collected using pre-cleaned glass bottes supported by weight to sink it into the well and the water brought and corked.

Sample Preparation/ Extraction

The method described in Manousi and Zachariadis (2020)was used for sample preparation and extraction.This was achieved using the method of liquid–liquid extraction. A volume of 500ml of surface water was allowed to pass through a Whatman filter paper of 70mm pore space to remove suspended particles. The filtrate was poured into a 1litre separatory funnel.A surrogate (1mL of ortho-terphenyl was added to spike the sample.To accomplish an effective extraction, a mixed 100ml volume of 1:1 n-hexane and dichloromethane were added,and shaken briskly for 2 minutes with periodic emitting to dischargeextra pressure. Thereafter, the organic layer was permitted to isolate from the water segment for atleast 5 minutes.The water phase was allowed to drain into a 1000 mL beaker. The organic phase was cautiouslydecanted into a glass funnel which contained 20 g of anhydrous sodium sulphate**.** This step was repeated two times and the water phase transferred back into the separatory funnel to be re-extracted with 50 ml of the same solvent mixture.The combined extract was concentrated to 2 mL volume using a rotary evaporator.

The water sample extract was cleaned up by means of silica gel column chromatography. A pad of glass wool fabric was used to separate the requisiteanalytes segment from any compound that has potential interfering capacity.The extract so concentrated were transferred on to top of the column and 2 ml hexane rinse of the sample flask was equally transferred to the column.The straight chainconstituent (total petroleum hydrocarbon) of the column was first eluted with 30 ml of hexane and then thrown out. Afterwards, ultimate elution was done with 35 ml of dichloromethane and reserved for PAHs identification and quantification.

The aromatic portion was concentrated to 1 ml using rotary evaporator. An extra 20 ml hexane was added to the concentrated extracts and allowed to evaporate so that traces of dichloromethane will be totally removed. The ultimate extract was concentrated to 1 ml and thenanalyzed using a gas chromatography equipped with a flame ionization detector (GC/FID).

Instrumentation and Analysis of PAHs

Hawlett Packed Series 5890 GC was used to determine the 16 priority PAHs.The instrument set up for polycyclic aromatic hydrocarbons (PAHs) were as follows**:** The temperature was initially maintained at 100^{o}C, with an initial time of 1 minute at a rate increase of 1: 4^{o}C/mins and final temperature was pegged at 310^{o}C. The detector temperature was conventionalmaintained at 300^{o}C. A very efficientperformance capillary column HP-5 which was cross linked with PH ME Siloxane), with film thickness of 1 µm, length: 30 m, and phase ratio: 63 was used for analytes separation. Flame ionization detector (FID) type with air-hydrogen flame (Hydrogen: 35 mL/sec and air: 350 mL/min) as oxidant gas was used. The injector port (inlet) temperature was 280^{o}C in splitless mode. Injection volume was 1 µL. Helium was used as the carrier gas. Linear velocity was 30 cm/sec. Quantification was by external calibration techniques.

Quality control/assurance

All the chemicals/reagents used were of analytical grade.The sampling process was done with utmost care to avoid wrong method of sampling.Due procedures and carefulness were carried out to store and prepare thesamples in order to maintain the reliability of the samples**.** All apparatus used in the preparatory stages of the GC analysis were rinsed with a solvent mixture of dichloromethane and n-hexane. To avoid sample contamination from the previous extraction, the flask used for the sample concentration was rinsed again with the prepared mixture of n-hexane and dichloromethane after every round of concentration of the extract. The efficiency of extraction procedure was determined using asubstitute standard called orthoterphenyl.The replacement standards recovery rate ranged from 74 % to 105 %. All the spiky blanks had replacement standard recoveries which was in the range of 78–99%. The Quantification of the concentration of individual PAH was achieved by direct reading from a chromatogram.

Source Diagnosis of PAHs

Dissimilarapproaches were practicalcarried out to determine the sources of the PAHs in well water from the selected communities under study.The numerical values gottenremained used to assume a position withregard to the origin of PAHs whether it is petrogenic or pyrogenic. The five diverse parametric methods applied and their clarifications were;

LMW/HMW PAHs

For this ratio, the sum of all the values 2-3 rings (naphthalene, Acenaphthene, acenaphthylene, fluoranthene, phenanthrene and anthracene) PAHswere divided by the sum of values calculatedfrom all the other ring members of 4-6 (fluoranthene, chrysene, benzo (a) anthracene, pyrene, benzo (a) pyrene, benzo (b) fluoranthene,indeno (1,2,3-cd) pyrene, dibenzo (ah) anthracene, benzo (k) fluoranthene and benzo (ghi) perylene).When the ratio of LMW/HMW PAHs exceeds 1, then the inferredsource isreflectedas petrogenic origin, whereas values that are below 1 infers pyrogenic source(Vrana et al., 2001).

Ant/(Ant+Phe)

Here, the numerical value ofanthracene is divided by the sum of the value of anthracene and phenanthrene. In this grouping, if the values obtained from the ratio calculation ofAn/(An+Phe) decreases below 0.1, the origin of the PAHs suggests petrogenic, while higher than 0.1 ratio inferspyrogenic sources (Ilechukwu et al., 2016; Edori et al., 2020).

Flu/Flu + Py

For this ration, the determined values fluoranthene is divided by the fluoranthene +pyrene. If the calculated values is above 1, then pyrogenic origin is inferred, but when the value is less than 1, then petrogenic origin or sources is proposed(Qiu, 2009).

BaA/(BaA+Chr

The ratio of benzo(a)anthracene to that of the sum of benzo(a)Anthraceneand chrysene is used to diagnose the source of PAHs. If the calculated numerical value exceeds 0.2, the petrogenic source is suggested, when the calculated value ranged 0.2-0.35, then mixed petrogenic and pyrogenic source is the inferred option. However, if the ratio exceeds 0.35, then the origin is classed as pyrogenic (Guo et al., 2007).

IP/ (IP+ BgP

This diagnostic ratio [Indeno (1, 2, 3-cd) pyrene/(Indeno (1, 2, 3-cd) Pyrene + Benzo (ghi) Perylene)] is based on the classification that calculated values lower than 0.2 is proposedfor petrogenic origin, values which falls between between 0.2 - 0.5 is put forwardas mixed sources of origin (petrogenic or pyrogenic), and values greater than 0.5 are ruledout to be pyrogenic source (Tolosa et al., 2004;Nasher et al., 2013).

Results and Discussion

The results of the concentrations of polycyclic aromatic hydrocarbons in well water from selected communities of Ekpeyeland are given in Tables 1-3 and Figures 1-3.The results showed the presence of all the 16 priority PAHs in all the sampled stations in the different seasons. The results from human imposed exploration and exploitation of crude oil products were generally higher than the control station being Ahoada. The values of total PAHs in the well samples from all the stations were all lower than the WHO maximum limit of 0.002mg/L in assessable water. The highest PAHs total value was observed at OkomaI and Okoma II. The values of PAHs obtained from well water in the present research are lower than the values of Mohammed et al. (2023) in borehole water from central Parts of Nigeria where asphalt generation activities are predominant. The values were equally lower than those of Montuori et al. (2023) in groundwater from Camplania plain, Italy. The values were equally less than the values of Edori and Nyenke (2023) in groundwater samples from abattoirs in Port Harcourt, Nigeria.

The nature of the concentrations of PAHs observed in the wells from the examined stations is in consonance with the observation of Montuori et al. (2023) who detected all categories of PAHs in groundwater near an asphalt generation plant. When PAHs aregenerated from in industrial activities occasioned by massive incineration and burning, vehicular source releases, and burning of fuel such as wood, petroleumand grasses, it passes through the atmosphere and are deposited on land surface, surface runoff and then penetrate the water ecosystem by downward percolation andtransfer deep into the aquifer formation (Smail et al., 2012; Bichet et al., 2013).Numerousnumbers of current studies have displayed that PAHs formation and destruction are associatedoccurrencesthat is capable of leading to a net escalation of these unsafecombinations in the output of burningschemes (Ekpete et al., 2019; Younus, 2021; Mohammed et al., 2023; Montuori et al., 2023; Edori&Nyenke, 2023).

Within the vicinity and the near environment to illegal refining site, there is the presence of hydraulic cracking, which is accompanied by high temperatureand incomplete combustion that led to production of PAHs which finally settled on the soil surface of into unprotected open wells. The components settled on the top soil passed through cracks formed between the geologiclayers and carried by percolating water into the wells. Furthermore, exploration efforts, surface spills, underground leaching, and wastewater from the refining sites lead to groundwater damage, which explains the contamination of the nearby wells with differentlevels of PAHs in comparison to wells in the control position which are distant from the pollution source. The above observation is in consonance with the observation of Younus (2021) on the presence of PAHs in wells in Al-Zubair district near the Basra refinery, Iraq.

The likelihood of leakage and ensuingadulteration of the groundwater aquifers by outwardnoxious waste have been separatelyrecognizedin the work of other authors (Okoli et al., 2011; Edori and Nyenke, 2023). Several authors had recognized constituents of PAHs in groundwater in different Niger Delta and Nigerian communities (Adedosu et al., 2013; Ekpete et al., 2019; Edori&Nyenke, 2023;Mohammed et al., 2023) in areas of oil exploration and exploitation and incineration of organic based materials.However, WHO (2003) pegged the maximum allowable limit of PAHs to be present in drinking water to be 0.002 mg/L.

The values obtained in this study are higher than the stipulated standard for total PAHs in water, sounquestionably, these values are causes of health concern for the communities under investigation and the publicin general, particularlywith the known information that PAHs are carcinogenic in nature (ATSDR, 1995; Nwineewii& Marcus, 2015;Edori et al., 2020; Iyama et al., 2022).These PAHs now form part of the well water which is being used by the inhabitants for drinking, bathing, washing and preparation of foods, in that wayamassing the risk of raised concentrations in fleshy tissue of man and animals. Unavoidably man becomes the chief in receiving the pains of the greatest risk of bioaccumulation due to usageand his inclination to other path of entrance into his body (Nwineewii& Marcus, 2015).

The concentrations of PAHs are expected to differ depending on the season (Miura et al., 2019).This expectation is in agreement with the observed values of the present study where values of PAHs in the well were higher in the rainy season than the dry season. The differential values observed in the study could be alluded to the fact that the source of PAHs input into the well iscredited to the increased magnitude of incomplete incineration of petroleum products, raiseddomesticheating, decreased photo degradation, and reduced diffusion resulting from cloudy atmospheric conditions tranquil winds and low temperature (Miura et al., 2019), which all support less supply of oxygen during incineration.

In the advent of the presence of high level ofPAHs in a soil environment, it will enhance subsurface mobility andmay possiblycause danger to groundwater supplies. Improper waste management practices as observe in the area of study, such as the illegal discharge of toxic, industrial, and urban waste, contaminate the nearby soils with PAHs and steeply mobilize PAHs, endangering groundwater supplies. This is particularlycorrect for the very soluble LMW PAHs which accumulate on soil particles and could possibly contaminate groundwater by entering the shallow aquifer (Liu et al., 2012).

Table 1: Descriptive statistics of polycyclic aromatic hydrocarbons results in groundwater samples in Ahoada and IduEkpeye Communities

PAHs	Sampling locations											
	Ahoada (Control) town						Idu Ekpeye community					
	DS			WS			DS			WS		
	μ ± SD	Min	Max	μ ± SD	Min	Max	μ ± SD	Min	Max	μ ± SD	Min	Max
Nap	0.003 ±0.003	0.0002	0.005	0.003±0.0002	5.96	6.10	0.0004±0.0003	0.0001	0.0009	0.00065±0.00057	0.00021	0.0013
Ace	0.0003±0.0002	0.0001	0.0005	0.0003±0.0002	0.0001	0.0005	0.002±0.001	0.0003	0.0032	0.0036±0.0025	0.00048	0.005
Acy	0.0004±0.0002	0.0002	0.0005	0.0004±0.0002	0.0002	0.0005	0.0004±0.0004	0.0001	0.0009	0.00063±0.00068	0.00084	0.0014
Flu	0.0052±0.0030	0.0018	0.0055	0.0051±0.003	0.0018	0.0073	0.01±0.02	0.0002	0.030	0.017±0.027	0.00045	0.048
Phen	0.0314±0.046	0.028	0.085	0.029±0.05	0.0006	0.085	0.002±0.0007	0.0009	0.0023	0.0027±0.0028	0.00024	0.0058
Ant	0.0016±0.0013	0.0001	0.0024	0.002±0.001	7.9E-5	0.0024	0.0004±0.0004	0.0002	0.0009	0.0027±0.0015	0.0015	0.0039
Flt	0.00026±0.0003	0.0001	0.0006	0.0003±0.0003	9.5E-5	0.0006	0.0004±0.0005	0.00002	0.0009	0.0021±0.002	0.00045	0.0043
Pyr	0.0023±0.002	0.0005	0.0034	0.0023±0.0016	0.00045	0.0034	0.0002±2.8E-5	0.00009	0.0001	0.001±0.0.0014	0.00012	0.0027
BaA	0.0063±0.001	0.005	0.0076	0.0063±0.0013	0.005	0.0076	0.002±0.004	0.0002	0.0069	0.0087±0.014	0.00036	0.025
Chr	0.0009±0.008	0.0003	0.0020	0.0009±0.0009	0.00032	0.002	0.0001±0.0007	0.0002	0.0015	0.0027±0.0019	0.00058	0.0044
BbF	0.004±0.0007	0.0031	0.0044	0.0036±0.0007	0.0031	0.0044	0.02±0.016	0.005	0.034	0.037±0.030	0.017	0.072
BkF	0.0039±0.0006	0.0036	0.0046	0.0039±0.0006	0.0036	0.0046	0.01±0.015	0.0013	0.029	0.023±0.022	0.0032	0.046
BaP	0.0005±0.00007	0.0004	0.0006	0.0005±6.8E-5	0.0004	0.0006	0.003±0.0008	0.0016	0.0031	0.0041±0.0014	0.0029	0.0057
DBA	0.0022±0.0016	0.0003	0.0033	0.002±0.002	0.0027	0.0033	0.0023±0.001	0.0014	0.0036	0.0045±0.0022	0.0026	0.0070
Ind	0.0032±0.003	0.0003	0.0058	0.003±0.0027	0.0029	0.0058	0.019±0.016	0.0018	0.033	0.027±0.041	0.0028	0.0750
BghiP	0.002±0.003	0.0003	0.0059	0.00025±0.003	0.0025	0.0059	0.016±0.014	0.0006	0.029	0.030±0.026	0.0057	0.057

All units are expressed in mg/kg. DS = Dry sample, WS = Wet sample

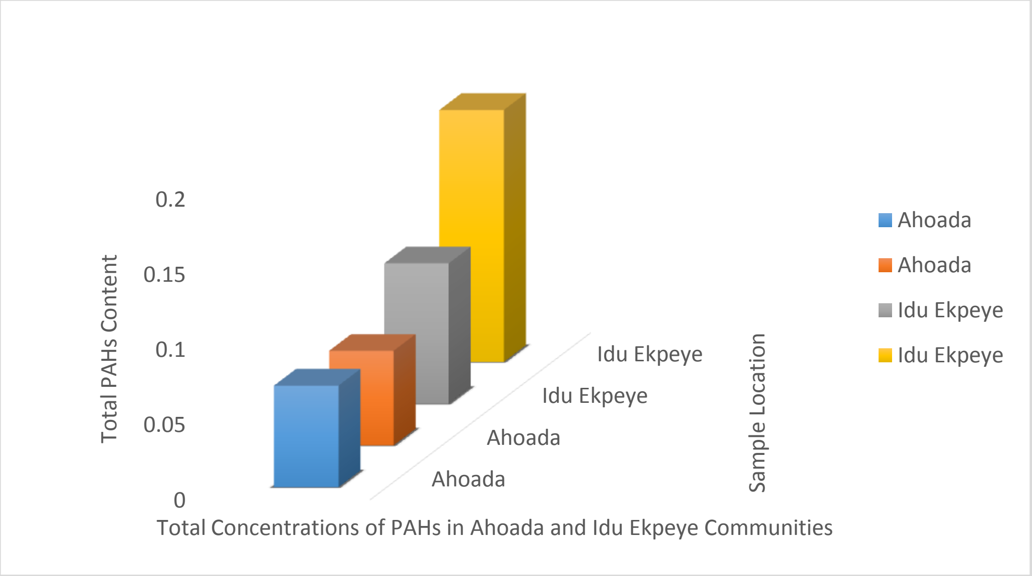

Fig 2.

Table 2: Descriptive statistics of polycyclic aromatic hydrocarbons results in groundwater samples in Okporowo and Ubeta Communities

PAHs	Sampling locations											
	Okporowo community						Ubeta community					
	DS			WS			DS			WS		
	μ ± SD	Min	Max	μ ± SD	Min	Max	μ ± SD	Min	Max	μ ± SD	Min	Max
Nap	0.00012±0.0001	0.00002	0.0002	0.00014±0.0002	1.4E-6	3.7E-4	0.0028±0.0033	0.00029	0.0065	0.0084±0.011	0.00036	0.021
Ace	0.0058±0.0003	0.00033	0.016	0.018±0.026	0.0005	0.047	0.0018±0.0012	0.00041	0.0028	0.0038±0.0030	0.00071	0.0068
Acy	0.0005±0.0073	0.00019	0.013	0.011±0.018	0.00039	0.032	0.0048±0.0045	0.0016	0.010	0.0051±0.0033	0.0030	0.0088
Flu	0.0052±0.008	0.00007	0.015	0.016±0.027	0.00032	0.047	0.0087±0.0097	0.0027	0.020	0.019±0.025	0.0055	0.049
Phen	0.008±0.0069	0.00018	0.013	0.018±0.016	0.00036	0.032	0.013±0.012	0.0013	0.026	0.0025±0.019	0.0025	0.037
Ant	0.0017±0.0003	0.0014	0.002	0.0045±0.0010	0.0034	0.0054	0.0039±0.0042	0,0013	0.0088	0.0035±0.0016	0.0022	0.0053
Flt	0.00017±0.0009	0.00017	0.0019	0.0018±0.0024	0.00036	0.0045	0.0008±0.0007	0.00005	0.0013	0.018±0.014	0.0029	0.030
Pyr	0.0018±0.0016	0.00018	0.0034	0.0026±0.0019	0.00033	0.0040	0.0007±0.0063	0.00053	0.013	0.019±0.0.018	0.0019	0.038
BaA	0.014±0.019	0.0014	0.036	0.028±0.039	0.0047	0.073	0.013±0.017	0.00006	0.032	0.099±0.14	0.00022	0.260
Chr	0.0009±0.008	0.0003	0.0020	0.027±0.026	0.00036	0.051	0.014±0.010	0.0072	0.026	0.029±0.014	0.016	0.043

BbF	0.004±0.0007	0.0031	0.0044	0.025±0.0035	0.022	0.029	0.024±0.011	0.011	0.031	0.046±0.027	0.018	0.071
BkF	0.0039±0.0006	0.0036	0.0046	0.017±0.002	0.015	0.019	0.0068±0.0054	0.00063	0.010	0.015±0.012	0.0026	0.026
BaP	0.0005±0.00007	0.0004	0.0006	0.019±0.018	0.00051	0.030	0.0079±0.0087	0.0027	0.018	0.017±0.022	0.0037	0.042
DBA	0.0022±0.0016	0.0003	0.0033	0.031±0.011	0.024	0.044	0.015±0.0055	0.011	0.021	0.027±0.0049	0.024	0.033
Ind	0.0032±0.003	0.0003	0.0058	0.029±0.024	0.0028	0.050	0.0085±0.0051	0.0085	0.018	0.028±0.0075	0.019	0.032
BghiP	0.002±0.003	0.0003	0.0059	0.041±0.036	0.020	0.082	0.019±0.013	0.0094	0.033	0.033±0.016	0.019	0.051

All units are expressed in mg/kg. DS = Dry season, WS = Wet season

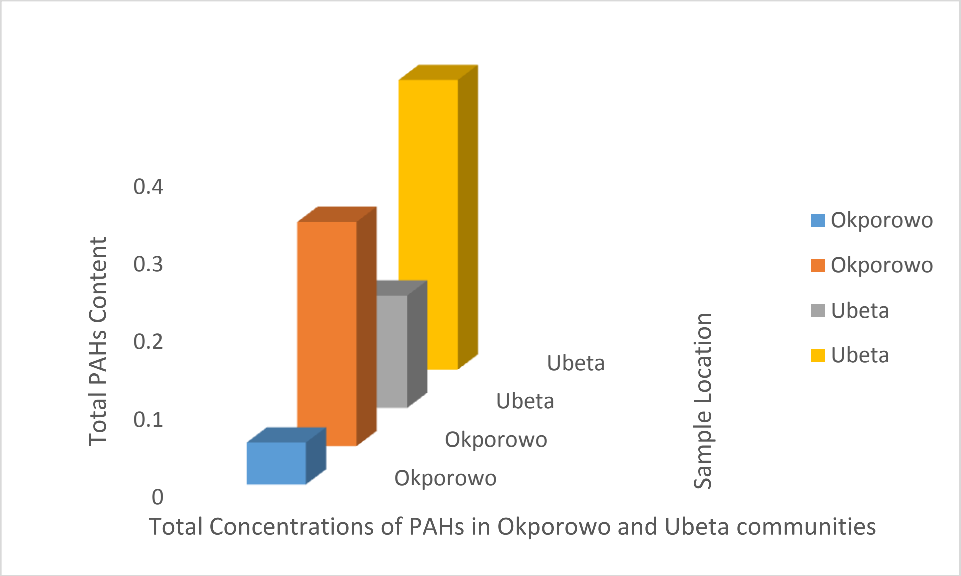

Fig 3.

Table 3: Descriptive statistics of polycyclic aromatic hydrocarbons results ingroundwater samples in Okoma I and II Communities

PAHs	Sampling locations											
	Okoma 1 community						Okoma 11 community					
	DS			WS			DS			WS		
	μ ± SD	Min	Max	μ ± SD	Min	Max	μ ± SD	Min	Max	μ ± SD	Min	Max
Nap	0.029 ±0.002	0.0270	0.0300	0.0465±0.0007	0.046	0.047	0.013±0.018	0.00023	0.027	0.017±0.022	0.0018	0.033
Ace	0.012±0.0014	0.0120	0.0122	0.027±0.0056	0.023	0.031	0.012±0.006	0.007	0.016	0.0096±0.0091	0.0031	0.016
Acy	0.020±0.014	0.010	0.030	0.033±0.007	0.028	0.038	0.014±0.004	0.011	0.017	0.030±0.014	0.029	0.031
Flu	0.0056±0.006	0.0012	0.010	0.0295±0.006	0.025	0.034	0.027±0.0007	0.027	0.0271	0.039±0.007	0.034	0.044

Phen	0.011±0.009	0.0046	0.018	0.0255±0.013	0.016	0.035	0.028±0.0035	0.025	0.030	0.023±0.028	0.029	0.043
Ant	0.025±0.004	0.022	0.028	0.029±0.004	0.026	0.032	0.008±0.009	0.001	0.015	0.015±0.018	0.0029	0.028
Flt	0.017±0.017	0.0046	0.030	0.038±0.018	0.025	0.051	0.012±0.004	0.0088	0.015	0.026±0.0014	0.026	0.028
Pyr	0.0097±0.00035	0.0095	0.01	0.024±0.002	0.022	0.025	0.019±0.016	0.0088	0.031	0.039±0.019	0.026	0.053
BaA	0.0065±0.0048	0.003	0.0099	0.032±0.0078	0.026	0.037	0.003±0.0033	0.001	0.0058	0.023±0.029	0.0029	0.044
Chr	0.0075±0.006	0.0029	0.012	0.029±0.011	0.021	0.037	0.016±0.02	0.0011	0.031	0.028±0.036	0.0025	0.054
BbF	0.012±0.015	0.0013	0.023	0.030±0.0057	0.026	0.034	0.017±0.007	0.012	0.022	0.029±0.0035	0.027	0.032
BkF	0.0029±0.002	0.0013	0.0044	0.013±0.013	0.0025	0.022	0.006±0.0058	0.0027	0.011	0.018±0.019	0.004	0.031
BaP	0.016±0.02	0.0015	0.03	0.021±0.0025	0.0031	0.039	0.0074±0.006	0.0028	0.012	0.017±0.017	0.0045	0.029
DBA	0.021±0.009	0.014	0.027	0.034±0.004	0.031	0.036	0.023±0.007	0.018	0.028	0.037±0.0049	0.033	0.040
Ind	0.0086±0.0.009	0.0021	0.015	0.016±0.016	0.0046	0.028	0.011±0.007	0.0058	0.016	0.019±0.014	0.0087	0.029
BghiP	0.01±0.01	0.0015	0.02	0.019±0.024	0.0025	0.037	0.015±0.02	0.00083	0.031	0.024±0.032	0.0017	0.047

All units are expressed in mg/kg. DS = Dry season, WS = Wet season

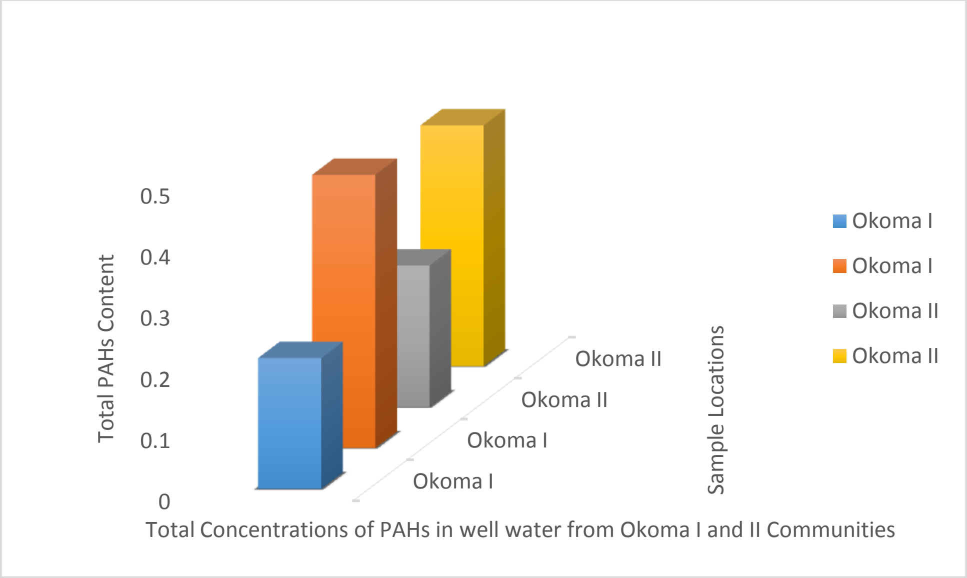

Fig 4.

Ring Size Analysis

The concentrations of the different ring categories of PAHs in well water from different stations in in Ekpeyeland is given in Table 4.The values of the individual compounds of the PAHs family showed that low molecular weight PAHs were more than high molecular weight PAHs in

Ahoada DS and WS samples. In all the other samples, high molecular weight PAHs were more concentrated than low molecular weight. However, the highest values of LMW was obtained at Okoma I(WS) sample station and HMW highest values were obtained at Ubeta WS station.

For the specific ring size analysis, 2-3 membered rings were higher than the other rings in Ahoada samples (DS and WS). Five (5) membered rings were the highest in IduEkpeye (DS and WS) samples. Six (6) membered rings was highest in Okporowo (DS) station and (5) membered rings was the highest in Okporowo (WS) station.In Ubeta sample station, the highest values were observed in the 5-membered rings for Ubeta DS and 4-membered rings for Ubeta (WS). In Okoma I and Okoma II stations (DS and WS), the 2-3-membered rings were higher than other ring members separately.

One vital property of theoutcome and harmfulness ofPAHs in any environment depends on the level of solubility in fats and their distribution amongst organic and other particulates matter(CCME, 2008).It has been established that HMW PAHs has more ability to remain sorbed to surfaces and are retained in tissues of living organisms when consumed (Nasher et al., 2013; Ekpete et al., 2019; Edori and Iyama, 2019; Patel et al., 2020). From the foregoing, it follows that those consuming this water are likely to accumulate PAHs in their systems or tissues. Looking at the present result, thehigher values of LMW PAHs in Ahoada station in both seasons implicated flared petroleum products from incomplete combustion that directly fall into the open wells after travelling a very long distance from illegal refining sites.

LMW PAHs (2-3 membered rings)are simplyconverted to other products through bacterial and fungal degradation (Edori, 2020).However, HMW PAHs (4-6 membered rings) strongly resists environmental situations and changes and therefore, not simply degraded or transformed to other products in the presence of either chemicals or microbes (Agbozu et al., 2017;Edori et al., 2020).

Generally, the domination of HMWring type in in this work is attributable to the sources, origin, fate, volatility, adsoptivity and absorptivity, transformation, solubility, degradation and mobility of the PAHs (Haritash& Kaushik, 2009; Agbozu et al., 2017; Jiao et al., 2017). The length of time between the deposition and sampling is also a factor which determines the dominance of either low or high molecular weight PAHs (Jiao et al., 2017). Thus, the large quantity of HMW PAHs (4-6 rings) observed in the present work is proposed on theintractablebehaviourof HMW PAHs to disintegration and affinity to water molecules and suspended particles on the well water surface(Obayori& Salam, 2010)

The contamination of HMW PAHs in a rural area is majorly from home and agronomic sources, while in ancity areas is due to industrialized, moveable, and internal sources (Montuori et al., 2023). However, in the present work, though in a local setting, the source of the HMW PAHs isis majorly from flared gases from artisanal oil stations.

Table 4: Concentrations of ring sizes of PAHs in well water from selected communities in Ekpeyeland

Location	Ring Type					
	LMW	HMW	2-3	4	5	6
Ahoada (DS)	0.0419	0.02556	0.0420	0.00976	0.0106	0.0052

Ahoada (WS)	0.0398	0.02305	0.0398	0.0098	0.002	0.00325
IduEkpeye (DS)	0.0152	0.073	0.0152	0.0027	0.0353	0.035
IduEkpeye (WS)	0.0273	0.1401	0.02728	0.0145	0.0686	0.057
Okporowo (DS)	0.02132	0.03267	0.02132	0.01687	0.0106	0.0052
Okporowo (WS)	0.06764	0.2214	0.06764	0.0594	0.092	0.07
Ubeta (DS)	0.035	0.1097	0.035	0.0285	0.0537	0.0275
Ubeta (WS)	0.0423	0.331	0.0423	0.165	0.105	0.061
Okoma I (DS)	0.1026	0.11129	0.1026	0.0407	0.0519	0.0186
Okoma I (WS)	0.1905	0.256	0.1905	0.123	0.098	0.035
Okoma II (DS)	0.102	0.1294	0.102	0.05	0.0534	0.026
Okoma II (WS)	0.1336	0.260	0.1336	0.116	0.101	0.043

Source Identification of PAHs in Well Water

The result of the sources and diagnostic ratios of PAHs categories are given in Table 5. For the diagnostic ratio of LMW/HMW, all station and seasonal values for Ahoada station (DS and WS) showed values greater than 1. All other stations and seasons values were less than 1. In the case of An/(An+Phe), all the diagnostic values showed > 0.1 except at Ahoada (DS) sample, which was 0.048. Fl/(Fl+Pyr) source identification values indicated diagnostic ratios of less than 1. The numerical values gotten from dividingBaA/(BaA+Chr) were all > 0.35 and the ratios of IP/ (IP+ BgP all were found to be between 0.309 to above 0.923.

The concept of source identification of PAHs is based on the numerical values of the ratio of the numerator to the denominator. The values obtained is then used to diagnose if the source is either natural of anthropogenic. From the academic standpoint, there exist majorly two sources of PAHs.To explain the specifics of PAHs sources in the well water samples, the applied diagnostic ratios, were able to distinguish the sources or basis of origin which were either petrogenic or pyrogenic sources of PAH in diversewell based on their physical, chemical properties and stability against effect heat, sunlight and temperature variations (Yunker et al., 2002; Edori, 2020;Sampaio et al., 2021). Various PAH congener proportions demonstrates the best probability to differentiate between the petrogenic and pyrogenic sources.

The values obtained from the present study indicated that for LMW/HMW ratios, Ahoada (DS and WS) indicated petrogenic sources of PAHs, while the rest stations indicated pyrogenic source values. The evaluation of An/(An+Phe) were all above 0.1 except at Ahoada (DS) station. All the values implicated pyrogenic sources except the Ahoada (DS) which showed petrogenic source. For the obtained values in Fl/Fl + Py ratio, the numerical relationship suggest petrogenic sources. The numerical values for BaA/(BaA+Chr ratio gave greater than 0.35 in all stations except at Okoma II (DS) station. The obtained values suggested the origin emanated from pyrolysis of petroleum products. For IP/ (IP+ BgP diagnostic values showed either pyrogenic or mixed sources of origin.The explanation of petrogenic source is that it resultedfrom direct contribution from petroleum and its products, whereas the pyrogenic sources resulted frompartialincineration of fossil fuels due to lack of oxygen, whichresulted from exhausts of vehicles) (Zeng & Vista, 1997; Boonyatumanond et al., 2007).

The different PAHsbases are also characterized based on their origin of production which include pyrogenic, petrogenic, and biogenic (Mojiri et al., 2019). Pyrogenic PAHs are shaped fromaccidental oxygen deficientburning of organic matter at elevated temperatures that may range from 350 to 1,200˚C (Abdel-Shafy and Mansour, 2016). However, there are cases of intentional pyrolytic developmentslike thermal cracking of complex petroleum molecules to smaller fraction hydrocarbonsor from thedistillation of coal into coal tar and coke also produce pyrogenic PAHs. The above explanation is the exact condition under which artisanal refining took place around the experimental area. The crude products were subjected to high temperature and uncontrolled cracking using woods from the forest.The expectation that pyrogenic PAHs should be generallyhigherinurbanareas(Abdel-ShafyandMansour,2016; Mojiri et al., 2019) due to high temperature equipment usage was also the case in the local refining process.

The cases of petrogenic PAHs present in this study is likely due to storage of petroleum anditsby-products. Other sources are seepages,transport, use, and leakage (Abdel-Shafy and Mansour, 2016) of the products from stored facilities in homes near to the examined wells, which was a common site in areas of illegal refining. The predominance of HMW PAHs over LMW PAHs in the present study is an indication of pyrogenic input sources. However, the dominance of LMW PAHs in any media suggest petrogenic sources (Marris et al., 2020). The possibility ofbiogenic PAHs due to microorganisms, phytoplankton, algae, and plants arising from slow biological conversion of organic materialscannot be altogether ruled (Mojirietal., 2019) considering the mixed sources of origin observed in IP/ (IP+ BgP) ratio. PAHs originating from gaseous phase discharge deposited inwater can also be a contributory factor considering the nature of flare and the distance travelled by the soot and other chemicals used in the process.

Table 5: Sources and diagnostic ratios of PAHs in well water from selected communities in Ekpeyeland

Stations	Diagnostic Ratios				
	LMW/HMW	An/(An+Phe)	Fl/(Fl+Pyr)	BaA/(BaA+Chr)	IP/ (IP+ BgP)
Ahoada (DS)	1.639	0.048	0.102	0.875	0.615
Ahoada (WS)	1.727	0.935	0.115	0.875	0.923
IduEkpeye (DS)	0.208	0.1667	0.667	0.922	0.543
IduEkpeye (WS)	0.195	0.500	0.636	0.763	0.474
Okporowo(DS)	0.653	0.175	0.086	0.940	0.615
Okporowo (WS)	0.306	0.200	0.409	0.509	0.414
Ubeta (DS)	0.319	0.231	0.533	0.481	0.309
Ubeta (WS)	0.128	0.583	0.486	0.773	0.459
Okoma I (DS)	0.923	0.694	0.637	0.464	0.462
Okoma I (WS)	0.744	0.532	0.613	0.525	0.457
Okoma II (DS)	0.788	0.222	0.387	0.158	0.423
Okoma II (WS)	0.514	0.395	0.400	0.451	0.442

Concentrations of Carcinogenic and Non-Carcinogenic PAHs

The result of concentrations of carcinogenic and non-carcinogenic PAHs is given in Table 6. The values of carcinogenic PAHs varied from 0.020 to 0.261 mg/L, while those of non-carcinogenic

PAHs varied from 0.025 to 0.2715 mg/L. The summed values of health risk PAHs were generally high even at the control station. The obtained value showed that the water if consistently consumed will likely be a potential source of health hazard to the consumers.The presence of both carcinogenic and non-carcinogenic PAHs at high concentration when compared to the permissible limit of PAHs in usable water is a pointer to these water sources as constituting serious health risk to the environment. Remarkably, these well are located in the heartbeat of the different community settlements and have been the major source of water for the locals.

Table 6: Concentrations(mg/L) of carcinogenic and non-carcinogenic PAHsin well water from selected communities in Ekpeyeland

PAHs Type	Location											
	Ahoada		IduEkpeye		Okporowo		Ubeta		Okoma I		Okoma II	
	DS	WS	DS	WS	DS	WS	DS	WS	DS	WS	DS	WS
Carcinogenic PAHs	0.021	0.020	0.056	0.107	0.029	0.176	0.089	0.261	0.075	0.175	0.083	0.171
Non-Carcinigenic PAHs	0.047	0.043	0.032	0.060	0.025	0.113	0.056	0.112	0.139	0.2715	0.148	0.223

Conclusion

The outcome of the data on PAHs in hand dug wells of Ekpeyeland revealedthe presence of all the 16 priority PAHs at moderate levels. The statistics valuesgotten from this work showed a moderate contamination of the wells with PAHsthat rendered the water samplesfrom this location to be unfit for domestic and industrial use. Residents and the locals who use the well water for domestic purposes are exposed to both carcinogenic and non-carcinogenic PAHs. However, this study largely proposes that the PAHs presence wereprincipallycredited to incinerationand little contribution from spilled or petrogenic sources. Source diagnosis revealedthe two input sources namely pyrogenic and petrogenic all contributed, although petrogenic contributed little**.** The level of HMW PAHs were generally more than the LMW PAHs in the examined well water.Accordingly, it is suggested that the illegal refining sites be completely removed from these areas and that for now, the locals should stop using water from the examined wells until the water has be declared fit for consumption**.**

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