Concentration and Estimated Human Health Risk of Polycyclic Aromatic Hydrocarbons in Water Samples around Automobile Repair Workshops in Eket Metropolis, Akwa Ibom State, Nigeria

ABSTRACT

Aims: Polycyclic aromatic hydrocarbons (PAHs) are very toxic and persistent environmental contaminants. The paper is aimed at investigating the cancer risk exposure of PAHs in borehole water collected around five (5) automobile repair workshops within Eket metropolis.
Place and Duration of Study: Samples were collected between June - August (2018) in wet season and November (2018) – January(2019) in dry season from boreholes around the vicinity of five (5) automobile repair workshops within Eket metropolis.
Methodology: The water sample was prepared in the laboratory following standard procedures and analysed for 16 United States Environmental Protection Agency (US EPA) priority PAHs using Gas Chromatography–Mass Spectrometer (GC–MS). A total of fifteen PAH congeners were detected in the samples.
Results: Total PAHs concentrations in borehole water from all sampling sites were in the range of 1.71–16.07 mg/L and 1.07–12.97 mg/L for both dry and wet seasons respectively. Low molecular weight PAHs were more dominant in all samples. The estimated cancer risks of exposure to PAHs by ingestion in the water samples ranged from 7.10×10^{-7} to 1.12×10^{-4} and 6.76×10^{-6} to 3.69×10^{-1} for adults and children respectively in both seasons. The estimated cancer risks due to dermal exposure to PAHs in the water samples ranged from to 7.18×10^{-3} to 1.07×10^{-1} and 5.67×10^{-3} to 1.08×10^{-1} for adults and children respectively in both seasons.
Conclusion: Carcinogenic risks due to dermal exposure calculated for both adults and children were higher than the US EPA acceptable cancer risk and much higher for children, which suggest that children could be prone to cancer and need to be monitored.

Comment [TV1]: Results of the cancer risks can be given in a single result statement

Keywords: *Toxicity; borehole water; cancer risk; ingestion; dermal; exposure.*

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are important and well known pollutants which have been identified in different environmental matrices worldwide. They are found at higher levels originating from different sources especially in areas associated with industrial and transportation activities. PAHs present in solid, liquid and gaseous phase could have an impact on human health through inhalation, dermal absorption and or ingestion [1]. PAHs enter the environment mostly as releases to air from volcanoes, forest fires, residential wood burning and exhaust from automobiles and trucks. They can also enter water through discharges from industrial plants, waste water treatment plants, dumpsites, automobile repair workshops etc if not properly disposed [2]. The movement of PAHs in the environment depends on properties such as how easily they dissolved in water. PAHs travel long distance away from the source of contamination. The solubility of PAHs decreases in water with increasing molecular weight, resulting in low concentrations in the water column [3,4]. Due to their hydrophobicity, the presence of PAHs in surface or ground water shows pollution.

Based on the cancer -causing ability and its occurrence, the United States Environmental Protection Agency (USEPA) has selected sixteen (16) PAHs as prevalent among others. These include: Chrysene(Chr), Benzo(a)pyrene(BaP), Benzo(a)anthracene(BaA),

Benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), Dibenzo(a,h) anthracene (DbA) and Indeno(1,2,3-cd)perylene (IcdP) considered as human carcinogens and others namely naphthalene (Nap), Anthracene (Ant), Acenaphthene (Ace), Benzo(ghi) perylene (BghiP), Fluoranthene (Fla), Fluorene (Flu), Phenanthrene (Phe), Acenaphthylene (Acy), and Pyrene (Pyr) noted as non-carcinogenic PAHs [5].

The types of PAHs present in water provides information on the derivative source of organic contaminants. The presence of Low Molecular Weight PAHs (LMW PAHs) such as naphthalene, fluorene and acenaphthene in environmental media is an indication of natural or petrogenic PAH contamination, while a prominent concentration of High Molecular Weight PAHs (HMW PAHs) such as fluoranthene, phenanthrene and pyrene and fewer LMW PAHs indicates combustion or pyrolytic origins. PAHs are of special interest because of their carcinogenicity, mutagenicity and teratogenicity [6]. Due to human health risk attached to the contamination of water by PAHs, it is imperative to monitor its presence in the environment. Water pollution has both short and long term effects. Organic pollutants such as PAHs have the ability to accumulate in living organism and undergo food chain magnification [7].

Akwa Ibom State being one of the most populated states in Nigeria has witnessed rise in number of vehicles for commercial and private purpose. Due to this increase in number of vehicles and their being prone to breakdown, there is also an increase in automobile repair workshops being sited in the state. It is presumed that there are environmental threats attached with this practice. PAHs which are possible by-products from automobile repair activities are usually carcinogenic even at very low concentration. This has posed serious effects on human health and therefore, there is a need to evaluate water quality to ensure its safety for consumption. The aim of this study was to investigate the concentration of 16 US EPA priority PAHs in water collected from boreholes around automobile repair workshops in Eket, Akwa Ibom State during both dry and wet seasons to assess and evaluate the human health risk associated with the water exposure via the dermal and ingestion pathways.

2. Materials and methods

2.1 Study Area

The study area, 'automobile repair workshops' located in Eket metropolis are sources of pollution. Eket is the second largest city in Akwa Ibom State, Nigeria with a land size covering an area of 176 km^2 situated between latitude 4°39°N 7°56°E and longitude 4.650°N 7.933°E. Figure 1 shows the location map of the study area. The area enjoys the influence of maritime which is all the year round. The stabilized ground surface in this area has greatly increased the rate of rainfall infiltration into the ground. In some locations boreholes are sited near mechanic workshop with little or no consideration to the possibility of the ground water contamination through seepage. Borehole water was collected around five (5) automobile repair workshops within Eket metropolis namely: (1) Automobile repair workshop at Edem Udo Street (W1) (2) Automobile repair workshop at Etebi Idung Iwak Street(W2) (3) Automobile repair workshop at Nkubia Street (W3) (4) Automobile repair workshop at Grace Bill road (W4) (5) Automobile repair workshop at RCC Road (W5) and a control sample from boreholes around serene environment (WS).

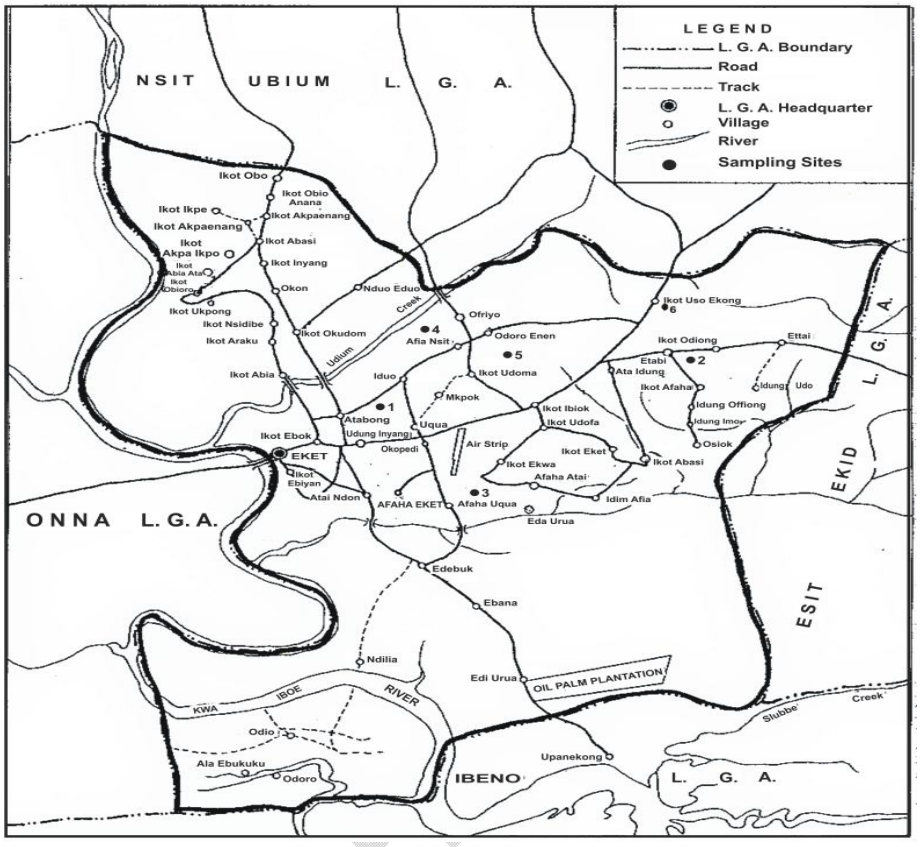

Fig. 1: Map of the study area (Eket) showing the sampling sites [8]

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2.2 Sampling

Samples were collected between June - August in wet season and November - January in dry season from boreholes around the vicinity of five (5) automobile repair workshops. Samples were collected in the morning using pre-washed amber bottles rinsed with the water sample and stored in ice chest. A control sample was also taken following the same procedure from a serene environment.

2.3 Reference Standards

A PAH standard mixture of 16 United States Environmental Protection Agency (US EPA) priority PAHs in 1000 mg/L dichloromethane was prepared as directed by the manufacturer (Sigma-Aldrich, St. Louis, MO, USA). The surrogate standard was a mixture containing naphthalene-d_8 (N-d_8), acenaphthalene-d_{10} (Ace-d_{10}), phenanthrene-d_{10} (P-d_{10}), chrysene-d_{12} (chr-d_{12}) and perylene-d_{12} (per-d_{12}) which was added to the samples before extraction and used as an internal standard. Serial dilutions of the standard solution were made from the stock solution for calibration and spiking experiments. All stock solutions were freshly prepared for each analysis in both seasons.

Comment [TV3]: Reference for preparation method followed

2.4 Extraction procedure for polycyclic aromatic hydrocarbons in water

Prior to the extraction, the sample bottles were properly washed with detergent, rinsed with water and finally rinsed with extraction solvent to remove the interferences. The reference method employed in the extraction of PAHs in water was US EPA 3510C (Liquid-liquid extraction) as adopted by [8].

Comment [TV4]: Author name can be mentioned followed by reference no.

Using a graduated cylinder, 50 mL of each sample was measured into a 1-liter separatory funnel. A drop of concentrated H_2SO_4 was added to the sample in the separatory funnel to release the hydrocarbon components and 5 mL of extraction solvent (n-Hexane) was also added. The sample was shaken vigorously for a few minutes with periodic venting to release excess pressure and allowed to stand for 10 minutes to separate the organic layer (top layer) from the water phase (lower layer). The extraction was repeated two (2) times using fresh portions of solvent. The three solvent extracts were combined and transferred into a glass vial with screw cap for further treatment [9].

2.5 Fractionation and Concentration

Following the procedure of [10], the soluble organic matters were fractionated into aliphatic and aromatic fractions using a glass column packed with neutral alumina. 10 g of the alumina was packed into the column and properly cleaned with redistilled hexane. The extract was poured onto the alumina and was allowed to elute using the redistilled hexane to remove the aliphatic fractions into a precleaned 25 mL glass container. The aromatic fraction was recovered by using the mixture of hexane and dichloromethane in ratio of 3:1. The aromatic fraction was concentrated to approximately 1.0ml using a rotary evaporator. The resulting extract was stored in an organic-free precleaned glass vial with screw cap for analysis. It was refrigerated at 4°C prior to gas chromatography-mass spectrometry (GC-MS) analysis.

2.6 Instrumental Analysis (US EPA 8270-C Method)

Analysis of PAHs were performed using gas chromatography-mass spectrometry (GC-MS) in selective ion mode (SIM) powered with HP chemstation software. The column used for the analysis was HP 5 with dimension 30 m × 0.25 mm × 0.25 µm for separating target analytes. Helium at 30.0 psi was used as the carrier gas at flow rate of 1.2 mL /min. The sample injection temperature was set at 270 °C and 320 °C and samples were injected at a volume of 1 µL in split mode. The oven was programmed at initial temperature of 65 °C for 3 mins and Ramp at 10.10 mins. The mass spectrometry acquisition parameters were set as follows: mass range at 128 – 202 am (Group 1-12), dwell time 25 seconds and resulting EM vat at 1694.1. Identification of individual PAHs was based on comparison of retention time between samples and standard solutions.

2.7 Quality Control

Spiked blank, reagent blank and appropriate PAH standard solutions were included with each set of samples to ensure the quality of the analytical method and corresponding analytical results. Samples were spiked with 1 µL of 1000 mg/L standard mixture consisting of 16 PAHs to 50 mL pre-extracted water samples. Distilled water (50 mL) was first pre-extracted in triplicate with 5 mL n-hexane as a blank sample. Spiked samples were then extracted and analyzed. There were no target compounds detected in the blank sample. The recoveries were 72% to 103% (average percentage recovery of 87%) with a relative standard deviation lower than 12%. Limit of detection for individual PAHs ranged from 0.10 to 14.00 mg/L with a signal to noise ratio of 3 and limit of quantization of signal to noise ratio of 10.

2.8 Exposure Assessment

Humans can be exposed to PAHs in water through ingestion and dermal adsorption. Health risk standards are not readily obtainable for the entire individual PAH congeners. Thus the risk of PAH congeners are determined with the toxicological factor approach and this is calculated by relating the potencies of different PAH mixtures to benzo(a)pyrene (BaP). BaP is said to possess the highest cancer-causing potency [11]. The concentrations of multi-component PAHs were converted into their BaP equivalents (BaPeq) for exposure assessment using the equation below

$$\text{Total BaPeq} = \sum_i C_i \times TEF_i \quad (1)$$

Where C_i is the concentration of individual PAHs and TEF_i is the toxic equivalent factor relative to benzo(a)pyrene [12]. The TEQ of individual PAHs was calculated based on the toxic equivalent factor (TEF) values proposed by [13] and adopted by [14]. International Agency for Research on Cancer (IARC) and United State Environmental Protection Agency (US EPA) identified Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene(BaP), Indeno(1,2,3-cd)pyrene (IcdP), Dibenzo(a,h)anthracene (DbA) and Benzo(ghi)perylene (BghiP) as possible human carcinogens.

Two possible paths of water exposure considered were ingestion and dermal absorption. Exposure doses of ingestion and dermal absorption were calculated using equations (2) and (3) respectively. These equations and values of some parameters were adopted from [4].

$$CD_i = \frac{C \times IR \times EF \times ED}{BW \times AT} \times CF \quad (2)$$

Where CD_i is the chronic daily intake through ingestion (mg/L/day), C is the BaPeq concentration in water (mg/L), IR is the ingestion rate of water for children (1 L/day) and adults (2 L/day); EF is the exposure frequency (365 days/year in this study), ED is the exposure duration (70 years); BW is the average body weight for adult (70 kg) and children (15 kg); AT is the average time for carcinogens (ED × 365 days), that is 70× 365 = 25,550 days; and CF is the conversion factor (1 L /1000 cm^3).

For dermal absorption:

$$CD_d = \frac{C \times SA \times K_p \times ET \times EF \times ED \times CF}{BW \times AT} \quad (3)$$

Where CD_d(mg/L/day) is the exposure dose via dermal absorption; C is the BaPeq concentration in water (mg/L), EF is the exposure frequency (350 days/year for dermal absorption was used in the calculation), ED is the exposure duration (70 years); BW is the average body weight for adult (70 kg) and children (15 kg); AT is the average time for carcinogens (ED × 365 days), that is 70× 365 = 25,550 days. SA is the exposed dermal surface area for adult (18,000 cm^2) and for children (6,600 cm^2); K_p is the dermal permeability coefficient (1.2 cm/h); ET is the exposure time for shower and bathing for adults (0.25 h/day) and for children (0.33 h/day) and CF is the conversion factor (1 L /1000 cm^3).

2.9 Toxicity and Risk Characterizations

Risk is a function of hazard multiplied by exposure. This cancer risk only accounts for direct oral or dermal water exposure. Cancer slope factor (SF) quantitatively defines the relationship between the exposure dosage of a carcinogen and its corresponding cancer risk. This SF value is the cancer slope factor which is expressed as the oral administrative dose derived from

rodent feeding studies whereas dermal exposure is presented as absorbed dose. According to the integrated Risk Information System of the US EPA [15], the geometric mean (GM) of the SF of BaP is 7.3 (mg/kg/day). Therefore, the SF value for dermal exposure was adjusted with the gastrointestinal absorption adjustment factor (AAF). The estimation of gastrointestinal absorption is 92% in the dose-response studies from which the cancer SF for BaP was derived [16] as adopted in [17]. As such the cancer slope factor (SF) for dermal BaP exposure is equal to 7.3 (mg/kg/day)/92% = 7.9 (mg/kg/day).

Carcinogenic risk (CRs) of ingestion and dermal exposure were calculated using equation (4) and (5) respectively as was adopted from the [4,18].

$$CR = CD_i \times SF \quad (4)$$

$$CR - CD_d \times SF \quad (5)$$

Where CR is the probability of developing cancer over a lifetime as a result of exposure to a contaminant. The CD_i and CD_d are the chronic exposures through ingestion and dermal absorption and SF is the corresponding slope factor. The total carcinogenic risk of BaP in water was calculated as the sum of the CR_s from ingestion and dermal exposure.

3. RESULTS AND DISCUSSION

3.1 Concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in Water

Generally, as seen in Table 1, the concentration of PAHs in water was usually low. This could be attributed to their weak solubility in water [19,20]. As such, the presence of trace levels of PAHs in water samples makes them difficult to be detected. Also, the concentration and number of PAHs detected in the dry season in all the studied samples were higher than in the wet season probably due to dissolution effect where the concentration is reduced. A total of 15 out of 16 priority PAHs by the US EPA were detected in water samples for both dry and wet seasons. Dibenzo(a,h)anthracene was not detected in any sampling point in both seasons. This was also the case in the research conducted by [21] were dibenzo(a,h)anthracene was not detected in any sample. The maximum BaP concentration found among the water samples were 0.17 mg/L in the dry season and 0.24 mg/L in the wet season. The maximum BaPeq concentration observed were 0.2438 mg/L in the dry season and 0.2746 mg/L in the wet season (Table 3). PAHs levels in the control site were in the range 0 – 0.07 mg/L in the dry season and wet season. As seen in table 1, the most abundant individual PAHs found in this study area was naphthalene in both dry (13.92 mg/L) and wet (10.05 mg/L) seasons, similar to the findings reported on the detection of PAHs in drinking water from a large mixed-use reservoir in China [21]. The individual PAH with the lowest mean concentration were BkF and BghiP with concentration of 0.01 mg/L in the dry season and Fla, Pyr, BkF and BghiP with concentration of 0.01 mg/L in the wet season (Table 1). Most individual PAHs were higher in concentration during the dry season than during the wet season due to dissolution effect. These results also suggest that precipitation might introduce PAHs to drinking water sources or the higher levels of dissolved organic carbon present during dry season. As seen in Table 2, Figures 2 and 3, 2- ring PAHs had the highest concentration in the entire water samples while 5-ring and 6-ring PAHs were the lowest in concentration during both seasons. This may be attributed to their lower water solubility and great tendency to adsorb onto solid phases [22]. The presence or occurrence of low molecular weight PAHs (LMW PAHs) in water samples is due to wet and dry deposition of particles from the atmosphere that contains absorbed PAHs such as naphthalene and phenanthrene. The presence of LMW PAHs in the water can also be

attributed to their high vapour pressure and water solubility, while the low concentration or absence of some high molecular weight PAHs (HMW PAHs) such as DbA can be attributed to their lower water solubility and great tendency to absorb onto solid phases [22]. The probable source of these compounds is organic matter combustion to low temperature [23]. As seen in table 2, total carcinogenic PAHs concentrations was of the range 0.08-0.98 mg/L in the dry season and 0.06-1.00 mg/L in the wet season.

TABLE 1. Mean concentrations of PAHs in mg/L of water samples at different sampling sites in the vicinity of automobile repair workshop and control site during both dry and wet seasons

Seasons	Sample Sites	PAHs Compounds (mg/l)																
		Nap	Acy	Ace	Flu	Ant	Phe	Fla	Pyr	Chr	BaA	BbF	BkF	BaP	IcdP	DbA	BghiP	Mean	S.D.
Dry Season	W1	12.29	0.12	-	0.10	0.27	0.09	0.18	0.22	-	-	0.52	0.01	0.17	0.20	-	0.08	1.19	3.50
	W2	-	-	0.18	-	0.13	0.06	0.21	0.29	0.33	-	0.07	0.10	0.15	-	-	0.19	0.171	0.09
	W3	0.75	-	-	0.20	-	-	0.45	0.27	-	-	0.09	-	0.13	0.07	-	0.15	0.26	0.23
	W4	13.05	0.38	-	0.18	0.10	0.03	-	-	0.20	0.12	0.19	-	0.09	0.04	-	0.14	1.32	3.89
	W5	13.92	0.67	-	-	0.43	0.28	-	0.03	0.15	0.26	0.06	-	-	0.17	-	0.10	1.61	4.33
	WS(control)	-	-	-	-	-	-	0.03	-	0.07	-	-	-	-	-	-	0.01	0.04	0.03
Wet Season	W1	8.35	-	-	2.23	0.18	0.20	0.01	0.09	-	-	0.13	0.21	0.10	0.27	-	0.16	1.08	2.49
	W2	0.09	-	-	0.17	0.20	0.05	0.01	0.09	0.03	0.11	-	-	0.13	0.19	-	-	0.11	0.07
	W3	0.95	-	0.08	-	0.13	0.27	-	0.01	0.38	0.20	-	0.08	0.24	0.10	-	-	0.24	0.27
	W4	7.97	0.11	-	0.34	0.21	0.16	-	0.42	0.29	0.12	0.01	-	0.03	0.19	-	0.05	0.83	2.25
	W5	10.05	-	1.27	0.39	-	-	0.43	0.03	0.14	0.22	0.02	-	0.10	0.20	-	0.12	1.18	2.96
	WS(control)	0.05	-	-	-	-	-	0.01	0.07	0.05	-	-	-	-	-	-	0.01	0.04	0.03

-: Below detectable limit (<0.001); W1: Edem Udo; W2: Etebi Idung Iwak; W3: Nkubia; W4: Grace Bill and W5: RCC automobile repair workshop and WS: Control sample

TABLE 2. PAH concentrations in associated water by number of rings and related parameters (dry and wet season)

SEASONS	SAMPLE SITES	ΣLMW PAHs	ΣHMW PAHs	Σ16EPA PAHs	ΣPAHcarc	2-ring	3-ring	4-ring	5-ring	6-ring
Dry Season	**W1**	12.87	1.38	14.25	0.98	12.29	0.58	0.40	0.70	0.28
	W2	0.37	1.34	1.71	0.84	-	0.37	0.83	0.32	0.19
	W3	0.95	1.16	2.11	0.44	0.75	0.20	0.72	0.22	0.22
	W4	13.74	0.78	14.52	0.78	13.05	0.69	0.32	0.28	0.18
	W5	15.30	0.77	16.07	0.74	13.92	1.38	0.44	0.06	0.27
	WS(control)	-	0.11	0.11	0.08	-	-	0.10	-	0.01
Wet Season	**W1**	10.96	0.97	11.93	0.87	8.35	2.61	0.10	0.44	0.43
	W2	0.51	0.56	1.07	0.46	0.09	0.42	0.24	0.13	0.19
	W3	1.43	1.01	2.44	1.00	0.95	0.48	0.59	0.32	0.10
	W4	8.79	1.11	9.90	0.69	7.97	0.82	0.83	0.04	0.24
	W5	11.71	1.26	12.97	0.80	10.05	1.66	0.82	0.12	0.32
	WS(control)	0.05	0.14	0.19	0.06	0.05	-	0.13	-	0.01

Σ*LMW PAHs:* Sum of low molecular weight PAHs; Σ*HMW PAHs*: sum of high molecular weight PAHs; Σ*16EPA PAHs:* sum of 16 EPA priority PAHs; Σ*PAHcarc*: sum of carcinogenic PAHs; *2-ring*: sum of 2-ring PAHs; *3-ring*: sum of 3-ring PAHs; *4-ring*: sum of 4-ring PAHs; *5-ring*: sum of 5-ring PAHs; *6-ring*: sum of 6-ring PAHs; -: Below detectable limit (<0.001); *W1:* Edem Udo; *W2:* Etebi Idung Iwak; *W3:* Nkubia; *W4:* Grace Bill and *W5:* RCC automobile repair workshop and *WS:* Control sample

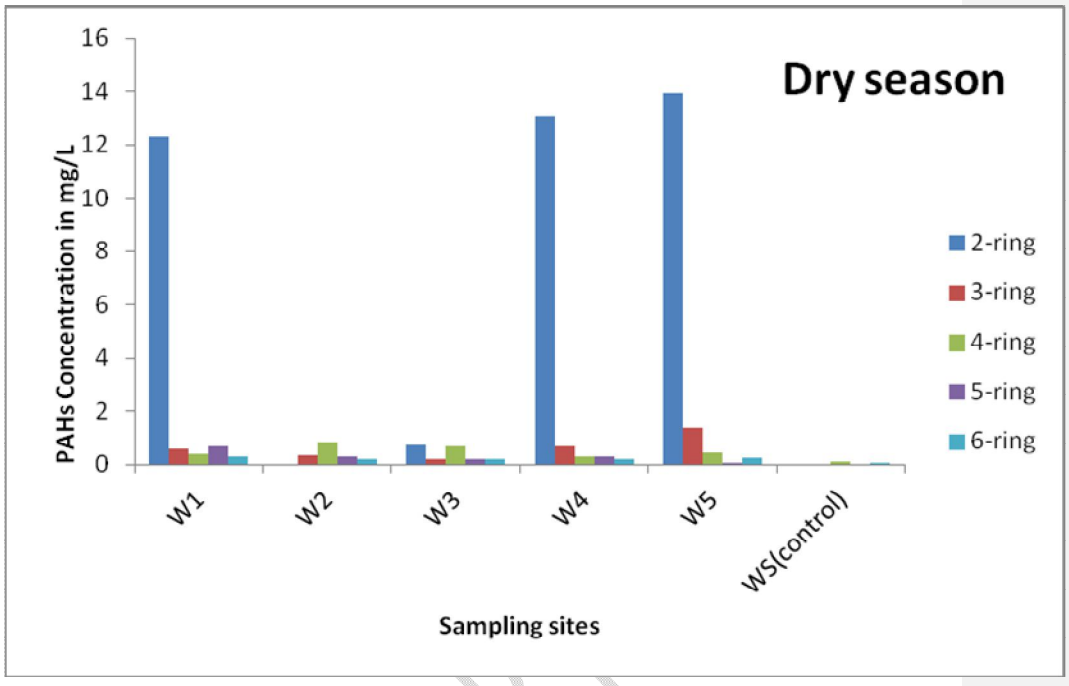

Fig. 2.: Analysis of the PAH concentration results based on number of rings for water around Edem Udo (W1), Etebi Idung Iwak (W2), Nkubia (W3), Grace Bill (W4) and RCC (W5) automobile repair workshop and Control sample (WS) during dry season

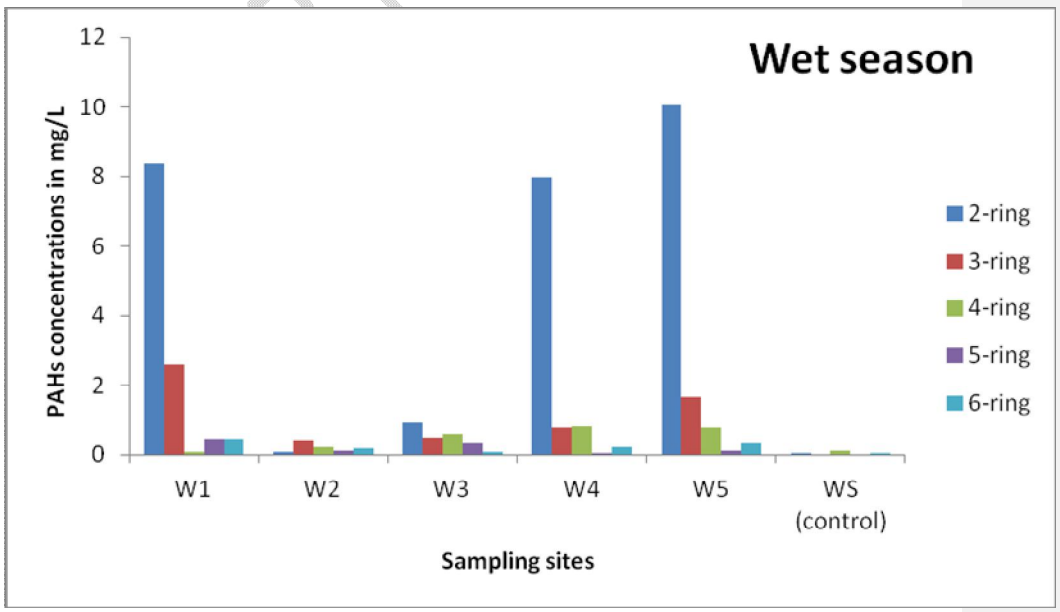

Fig. 3: Analysis of the PAH concentration results based on number of rings for water around Edem Udo (W1), Etebi Idung Iwak (W2), Nkubia (W3), Grace Bill (W4) and RCC (W5) automobile repair workshop and Control sample (WS) during wet season.

In drinking waters, the Environmental Protection Agency (EPA) considers benzo(a)pyrene to be the most toxic PAH in the list and its concentration alone is often used as a measure of risk. According to the EPA, its maximum contaminant level (MCL) should not exceed 0.002 mg/L [24]. The concentration range of BaP in this study was 0.03 mg/L to 0.24 mg/L as such the water samples are considered highly contaminated. This necessitated performance of risk assessment in this study.

3.2 Exposure Assessment

Table 4 shows the chronic daily intake and cancer risk of PAHs for adults and children present in water during both wet and dry season. Daily BaPeq exposure doses through ingestion and dermal absorption as well as their carcinogenic risk were calculated for both seasons. As seen in table 4, for ingestion (CD_i), the daily BaPeq intake in adults were within the US EPA acceptable cancer risk of $1 \times 10^{-6} – 10^{-4}$, except the intake of chrysene (2.14×10^{-7}) and BkF (3.14×10^{-7}) were below the acceptable limit during the dry season and Chr (2.55×10^{-7}), BbF (3.80×10^{-7}), BkF (6.23×10^{-7}) and BghiP(9.72×10^{-8}) during the wet season. For the daily BaPeq intake in children, they were mostly within the US EPA acceptable cancer risk except the intake of Chr (6.32×10^{-7}), BkF (9.27×10^{-7}) and BghiP (4.45×10^{-7}) in dry season were below the acceptable cancer risk. Intake of BaA (5.48×10^{-3}), BbF (1.13×10^{-3}), BkF (1.84×10^{-3}), BaP (5.06×10^{-2}) and IcdP (8.00×10^{-3}) were higher than US EPA acceptable cancer risk during the wet season. This indicates that in wet season, the children may be prone to cancer through ingestion. This was similar to the result obtained by [4], where the children were more prone to cancer through ingestion.

Comment [TV5]: Include more references which can support your results and previous literature data to be included related to the work.

For dermal absorption, daily BaPeq exposure(CD_d) in adults showed a risk greater than 1×10^{-4} for almost all the PAHs except BkF (8.14×10^{-4}) and BghiP (4.97×10^{-4}) during the dry season and Chr (6.59×10^{-4}), BbF (9.84×10^{-4}) and BghiP (2.51×10^{-4}) during the wet season which were within the US EPA acceptable limit of 1×10^{-4}. This indicates that the adults may be prone to cancer through dermal exposure in both seasons. In children, for dermal absorption, daily BaPeq exposure showed a risk greater than 1×10^{-4} except in BghiP (7.18×10^{-4}) during the wet season which was within the acceptable range.

3.3 Health Risk Assessment

As seen in table 4, the carcinogenic risk in adults during the dry season was of the range 7.96×10^{-6} to 1.12×10^{-4} for ingestion and 6.43×10^{-3} to 3.16×10^{-1} for dermal exposure. This shows that the probability of developing cancer over a life time is very negligible through ingestion and very high through dermal exposure. During the wet season, the carcinogenic risk in adults was of the range 7.10×10^{-7} to 1.19×10^{-4} for ingestion and 7.18×10^{-3} to 3.24×10^{-1} for dermal exposure. This is also confirming that the probability of developing cancer over a life time is greater through dermal exposure than through ingestion.

In children, the probability of developing cancer over a life time was high through ingestion and dermal exposure in both seasons. During the dry season, the carcinogenic risk was of the range 6.76×10^{-6} to 3.32×10^{-4} through ingestion and 6.43×10^{-3} to 1.07×10^{-1} through dermal exposure. This indicates that the probability of developing cancer over a life time was higher through dermal exposure than through ingestion. During the wet season, the carcinogenic risk was of the range 8.25×10^{-3} to 3.69×10^{-1} through ingestion and 5.67×10^{-3} to 1.08×10^{-1} through dermal exposure. This indicates that the probability of developing cancer over a life time was high through ingestion and exposure dose through dermal absorption. This was similar to the research carried out by [4].

Generally, cancer risk levels of ingestion in children were more than those of the adults which is attributed to the fact that most of their foods are prepared with much water such as taking tea, custards, cereals etc and drinking water. This was similar to the research carried out by [25]. In addition, the PAH intake by a child is pertinent because of their lower body weights relative to that of adults. Therefore, the risk assessment of PAH exposure to children may be considerably greater than those of adults [14, 26].

4. CONCLUSION

A thorough study was performed to monitor the concentration of PAHs in underground water samples collected from the boreholes around automobile repair workshops in Eket, Akwa Ibom State, Nigeria. It was possible to determine the concentrations of 15 PAHs out of 16 US EPA priority PAHs in the studied samples. The studied PAH compounds were found in almost all the samples. The total concentration (Σ16 EPA PAHs) of the studied PAHs were ranged 1.71 mg/L (W2) to 16.07 mg/L (W5) in the dry season and 1.07 mg/L (W2) to 12.97 mg/L (W5) in the wet season. The maximum BaPeq concentration observed were 0.2438 mg/L and 0.2746 mg/L in both dry and wet season respectively. This is considered as moderate contamination. Carcinogenic risks due to dermal exposure calculated for both adults and children were higher than the US EPA acceptable cancer risk and much higher for children, which suggest that children could be prone to cancer. Therefore, the risk assessment of PAH exposure to children may be considered greater than those of adults and need to be monitored. Finally, remediation measures should be put in place to reduce the adverse effects of dermal exposure in activities such as bathing in water polluted with PAHs.

Compliance with ethical standards

On behalf of all authors, the corresponding author states that there is no conflict of interest.

REFERENCES

1. Ma WL, Li YF, Qi H, Sun DZ, Liu LY, Wang DG.. Seasonal variations of sources of polycyclic aromatic hydrocarbons (PAHs) to a northeastern urban city. China. Chemosphere. 2010; 79, 441-447.

2. Agency for Toxic Substances and Disease Registry (ATSDR). 1990. *Public health statement, polycyclic aromatic hydrocarbons,* Atlanta, GA: U.S. Department of Health and Human Services.

3. Nasr IN, Arief MH, Abdel-Aleem AH, Malhat FM. Polycyclic aromatic hydrocarbons (PAHs) in aquatic environment at El menofiya Governorate, Egypt J. Appl Sci Res. 2010; 60(1), 13-21.

4. Olayinka OO, Adewusi AA, Olujimi OO, Aladesida AA,. Concentration of Polycyclic aromatic hydrocarbons and estimated human health risk of water samples around Atlas Cove, Lagos, Nigeria. Journal of health and pollution. 2018; 8(20), 1-12.

5. Paris A, Ledauphin J, Poinot P, Gaillard JL. Polycyclic aromatic hydrocarbons in fruits and vegetables: Origin, analysis, and occurrence. Environmental Pollution. 2018; 234, 96-106.

6. Kafilzadeh F, Shiva AH, Malekpour R. Determination of Polycyclic aromatic hydrocarbons (PAHs) in water and sediments of the Kor River, Iran. Middle East J. Sci. Res., 2011; 10(1), 1-7.

7. Vaikosen EN, Ebeshi BU, Airhihen B. Bioaccumulation of heavy metals and hydrocarbon in *Henichromis fasciatus* exposed to surface water in borrow pits located within on shore oil exploration and production area. Environmental pollution. 2014; 3(3), 38-55.

8. Ekanem AN, Udo GJ, & Okori BS. Determination of Polycyclic Aromatic Hydrocarbons in Soil and Water Around Automobile Repair Workshops within Eket Metropolis in Akwa Ibom State, Nigeria using GC-MS. Journal of Environmental Treatment Techniques, 2021; 9(4), 819-830. https://doi.org/10.47277/JETT/9(4)830

9. United State Environmental Protection Agency (US EPA)., 1996a. *Method 3510C, Separatory Funnel Liquid-Liquid Extraction.* United state environmental protection agency. Revision 3.

10. Bayowa AV. *Levels of polycyclic aromatic hydrocarbons (PAHs) in marshy soils and sediments within Warri and its environs, Nigeria* (Master's thesis, University of South Africa, Department of Environmental Science). 2014

11. Agency for Toxic Substances and Disease Registry (ATSDR). *Polycyclic aromatic hydrocarbons (PAHs).* Atlanta, G.A: U.S. Department of health and human services, public health service. 1996b.

12. Guo J, Liang Z, Liao H, Tang Z, Zhao X, Wu F. Sedimentary record of polycyclic aromatic hydrocarbons in Lake Erhai, Southwest China. Journal of Environmental Sciences. 2011; 23, 1308-1315.

13. Nisbet ICT, LaGoy PK.. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regulatory Toxicology and Pharmacology. 1992; 16, 290-300.

14. Wang L, Zhang S, Wang L, Zhang W, Shi X, Li X, Li X. Concentration and Risk Evaluation of Polycyclic Aromatic Hydrocarbons in Urban Soil in the Typical Semi-Arid City of Xi'an in Northwest China. International Journal of Environmental Research and Public Health. 2018; 15(4), 607-622. Doi:10.3390/ijerph15040607.

15. United State Environmental Protection Agency (US EPA). *Integrated Risk Information System for Benzo(a)pyrene (BaP)*. http://www.epa.gov/iris/subst/0136. htm. 2002.

16. Magee B, Anderson P, Burmaster D.. Absorption adjustment factor (AAF) distribution for polycyclic aromatic hydrocarbons (PAHs). Hum. Ecol. Risk. Assess. 1996; 2(4):841-73. Doi. org/10.1080/10807039609383653.

17. Pan EC, Sun H, Xu QJ, Zhang Q, Liu LF, Chen XD, Xu Y. Polycyclic Aromatic Hydrocarbons concentrations in drinking water in villages along the Huai River in China and their association with High cancer incidence in local population, BioMed Research International. 2015; 1-10.

18. United States Environmental Protection Agency (US EPA). Exposure factors handbook 2011 edition (final), office of Research and Development. National centre for Environmental Assessment, Washington, D.C.: P. 1436. https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=236252. 2011.

19. Henner P, Schiavon M, Morel JL, Lichtfouse E. Polycyclic aromatic hydrocarbon (PAH) occurence and remediation methods, Analysis Magazine. 1997; 25, 56-59.

20. Sibiya PN. *Modification, development and application of extraction methods for pahs in sediments and water* (Ph.D's thesis, University of the Witwatersrand, Johannesburg, Department of Chemistry) Johannesburg. 2012.

21. Sun C, Zhang J, Ma Q, Chen Y. Human health and ecological risk assessment of 16 polycyclic aromatic hydrocarbons in drinking source water from a large mixed-use reservoir. Int J Environ Res Public Health. 2015; 12(11), 13956- 69. Doi.org/10.3390/ijerph121113956.

22 Sun JH, Wang GL, Chai Y, Zhang G, Li J, Feng J. Distribution of polycyclic aromatic hydrocarbons (PAHs) in Henan Reach of the Yellow River, Middle China. Ecotoxicol Environ Saf. 2009; 72(5):1614-24. https://doi. org/10.1016/j.ecoenv.2008.05.010.

23. Nagy P, Fekete J, Sharma VK. Polycyclic aromatic hydrocarbons (PAHs) in surface waters of Rackevei-Soroksari Danube Branch, Hungary. *Journal of Environmental Science and Health, part A: Toxic/Hazardous Substances and Environmental Engineering.* 2007;*42(3),* 231-240.

24. Maliszewska-Kordybach B. Polycyclic aromatic hydrocarbons in agricultural soils in Poland: Preliminary proposals for criteria to evaluate the level of soil contamination. Appl. Geochem. 1996; 11, 121–127.

25. Onyedikachi UB, Belonwu CD, Wegwu MO, Emmanuel E, Matthew AF. Sources and Cancer Risk Exposure of Polycyclic Aromatic Hydrocarbons in Soils from Industrial Areas in Southeastern, Nigeria. Journal of Chemical health risks. 2019; 9(3), 203-216.

26. United State Environmental Protection Agency (US EPA). Risk Assessment Guidance for Super Fund, Volume1, Human Health Evaluation Manual (PartB, Development of Risk Based Preliminary Remediation Goals); OSWER, 9285.7- 01B.EPA/540/R-92/003; U.S. Environmental Protection Agency: Washington, DC, USA. 1991.