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RISK ASSESSMENT OF HEAVY METALS AND POLYCYCLIC AROMATIC HYDROCARBONS IN GROUND WATER SAMPLES AROUND THE VICINITY OF AN ASPHALT PLANT IN NORTH CENTRAL, NIGERIA

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ABSTRACT. In this study, the concentration and risk of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in 9 composite samples around the vicinity of an Asphalt plant in North Central, Nigeria, was evaluated. Aqua-regia wet digestion was used for heavy metals extraction in the water samples while atomic absorption spectrometry was used quantification. For PAHs, liquid-liquid extraction was used for extraction while gas chromatography-mass spectrometry was used for quantification of PAHs in the extracts. The risk assessment was estimated using the hazard index (HI) and incremental lifetime cancer risk (ILCR) in all the samples studied. The results showed that Cd and Cr were present in concentrations higher than their permissible limits in water set by World Health Organization, while Pb was not detected. Total concentration of 14 PAHs ranged between 6.47–390 mg L^{-1} and were within the WHO permissible limits. High molecular weight PAHs were dominant (71.54%) relative to low molecular weight PAHs (28.46%). The risk assessment results revealed that 100% $ILCR_{total}$ values recorded for heavy metals were higher than the recommended limit. While 37.5% of $ILCR_{total}$ values recorded for PAHs were higher than the recommended values, implying that residents are exposed to health risks from both metals and PAHs.

KEY WORDS: Asphalt plant, Heavy metals, Polycyclic aromatic hydrocarbons, Water, Risk assessment

INTRODUCTION

Asphalt is a tiny solid stone mixed with sand and gravel in a paving machine for road construction [1]. Asphalt workers are exposed to different compounds and carcinogens such as polycyclic aromatic hydrocarbons during the production and paving of road constructions [2]. Water contamination by industrial activities has caused a serious societal hazard most especially in developing countries. Polycyclic aromatic hydrocarbons (PAHs) are organic compounds made up of two or more benzene rings, which are produced by incomplete combustion and pyrolysis of organic matters such as cigarette smoke, bush fire, automobile emissions and forest fire, among other [3, 4]. There are three major sources of PAHs which include pyrogenic (those produced when organic substances are exposed to higher temperatures and under low/no oxygen), petrogenic PAHs (are produced from crude oil maturation) and biological PAHs (those produced during degradation of vegetative matters [5].

Specifically, there are sixteen (16) priority PAHs focused by the United State Environmental Protection Agency (USEPA) noted to cause serious threats to human health depending on the level of exposure. They 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] [6, 7]. With rapid urbanization and industrial activities, the level of contaminants in water has a significant effect on human life needs urgent attention [8].

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Researchers have shown a well-developed method to assess the ecological threat of heavy metals that tends to accumulate in the soil, water and plants within the environment [9]. Heavy metals are a natural component of the earth's crust with high densities and atomic weights. Some trace heavy metals such as copper, zinc and selenium are essential to maintain the metabolism of the human body and at higher concentrations, can be poisonous [10]. Heavy metals may be chemically or physically combined with the natural compounds, which thus interfere with their methods of existence in the ambient. Diverse amounts of the aforementioned poisonous metals may be found in places such as industrial and consumer wastes, soils, plants, water among others [11, 12].

Water covers about 70% of Earth's crust which is essential to life. Thus, it is pertinent to ensure that sources of drinking water are free from various contaminants such as PAHs, heavy metals, microorganisms, and other hazardous compounds that can pose a serious threat to human health [13]. However, an increase in residential buildings in the vicinity of an Asphalt plant has drawn the attention of our Research group to quantify pollutants like PAHs and heavy metal in the groundwater samples used for domestic and industrial purposes. There are limited information on the general levels and risk of metals and PAHs in ground water in the vicinity of asphalt plants, Therefore, in this study, heavy metal concentrations, PAHs analysis and potential risk assessment of metals and PAHs in borehole and well-water samples within and around the vicinity of an Asphalt Plant in North Central, Nigeria, was carried out.

EXPERIMENTAL

Study area

The Asphalt Plant is located at industrial layout Gaa Imam, Offa Garage, at Ilorin South Local Government Area of Kwara State, North Central, Nigeria. The plant was established by the Kwara State Government in October 2016. It lies between latitude 8.47E and longitude 4.56N. It is surrounded by Club House, Kwara State Transport Management Agency office, industries and residential houses. A map of the study area is shown in Figure 1.

Reagents

Nitric acid (BDH analytical grade, Mumbai, India), anhydrous sodium sulfate (M&B laboratory chemicals, Guildford, United Kingdom), hydrochloric acid (BDH analytical grade, Mumbai, India), dichloromethane (Merck, Darmstadt, Germany), 60-120 mesh silica gel (Oxford laboratory reagent, India), Milli-Q water (Millipore, USA), PAHs standards (anthracene, fluorene and pyrene, Merck, Darmstadt, Germany) were used.

Sample collection and pre-treatment

Nine composite samples of borehole and well water samples were collected from within and around the Asphalt plant (labelled A – F) as shown in Table 1. Control samples of both borehole (G) and well water samples (H) were collected at a distance of 4 km from the sampling point. The well water was drawn using a fetcher and poured away severally before taken the samples and the borehole water was pumped for about 15 min before collecting the water samples into the pre-cleaned 1-liter plastic bottles. Three drops of 1 M HNO_3 were added to each water sample and put inside the ice chest at the sampling point and then transported to the laboratory before analysis. The same procedure was repeated for sample collection for PAHs in pre-cleaned glass bottle without the addition of 1 M HNO_3.

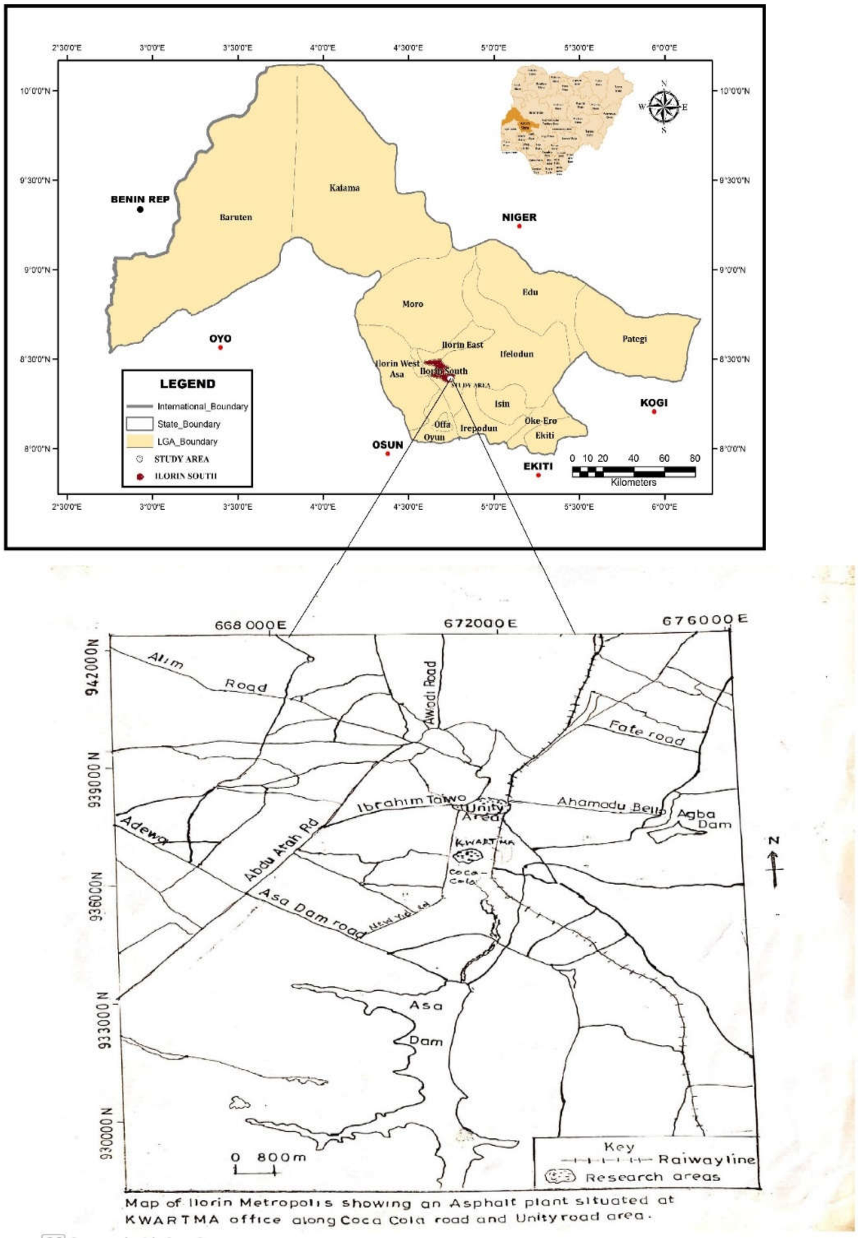

Figure 1. Showing the map of the study location.

Table 1. Location of sampling points indicating the sample codes.

Sample location	Sample code
Well water samples within the Asphalt plant	A
Borehole water samples within the Asphalt plant	B
Well water samples from Residential house 1 around the Asphalt plant	C
Borehole water samples from residential house 2 around the Asphalt plant	D
Well water samples from residential house 3 around the Asphalt plant	E
Borehole water samples from residential 4 around the Asphalt plant	F
Control well water samples	G
Control borehole water samples	H

Determination of heavy metals in the water samples

The water samples were digested using the aqua-regia method [14]. A 50 mL water sample was measured into a volumetric flask and digested with 12 mL HNO_3/HCl in ration 1:3 proportion in a water bath for 40 min till white fumes evolved from the mixture. The mixture was cooled, followed by the addition of 25 mL distilled water and filtered using Whatman No. 1 filter paper. The filtrate was poured into a 50 mL volumetric flask, distilled water added and made up to the mark. An atomic absorption spectrometer (205 Buck Scientific model, USA) was used to determine the concentration of metals (Zn, Pb, Ni, Mn, Cr and Cd) in the water samples.

A calibration curve was plotted for all elements (Zn, Cd, Mn, Ni and Cr) analyzed to measure the absorbance values for the blank and working standard solution prepared from the stock standard of each metal analyzed using Milli-Q water. The limits of detection of the instrument ranged from 0.004 – 0.007 mg L^{-1}.

Determination of PAHs in the water samples

Water samples were extracted by liquid-liquid extraction. A 100 mL of water sample was transferred into a 250 mL capacity separating funnel before extraction with 10 mL dichloromethane. The mixture was thoroughly shaken for about 30 minutes and the organic phase was collected for further successive re-extraction with 10 mL dichloromethane and the whole process of extraction was repeated once again. The organic layer was poured into a beaker containing 10 g of anhydrous sodium sulfate to remove residual water [15]. The sample clean-up was done for extracted water samples containing the organic layer by packing the column with silica gel and eluted with 5 mL dichloromethane. The first few drops of eluate were discarded and 10 mL of the eluate was collected in triplicates into a glass bottle cover with a rubber cap which was used to analyze PAHs of the water samples using gas chromatography-mass spectroscopy (Agilent 7890B GCMS, USA) [16].

Quality control measures

All laboratory glassware were washed with detergent, rinsed thoroughly with deionized water, soaked in 0.1 M nitric acid (HNO_3) overnight and oven-dried at 110 °C for 6 hours before use. Procedural blanks were carried out to check for impurities in reagents and reaction vessels. It was accomplished by carrying out the analytical procedure in the absence of the sample, and the value to the analytical result obtained was used as a correction.

A 10 mg L^{-1} of PAHs readily available standards (anthracene, fluorene, pyrene) was spiked to a known amount of water samples (X). The mixtures in X were taken for extraction and clean-up was done. A known amount of unspiked water samples (Y) was also taken for extraction and clean-up methods. The percentage recovery (% RC) of PAHs contents was calculated using equation 1 [17]:

$$(\%\ \mathrm{RC}) = \frac{\mathrm{X-Y}}{\text{Amount of spike added}} \times 100 \tag{1}$$

The % RC of PAHs was done to ascertain the quality assurance of the analytical procedure employed in the extraction and clean-up methods for the determination of PAHs contents in the water samples. The % RC of PAHs computed are 82.2, 91.4, and 95.6% for anthracene, fluorine and pyrene, respectively.

Statistical tool

The experimental data were subjected to Origin pro-2021 for the Pearson correlation in order to determine the linear relationship between the parameters under the study location.

Health risk assessment

The human health risk assessment models established by the United States Environmental Protection Agency (USEPA) [18–21] and United Nuclear Corporation (UNC) [22] give the relationship between the concentration of the toxic chemicals (heavy metals and the PAHs) and their apparent risk to human health. This procedure was carried out using the toxicological profiles of the potential toxic elements provided by the United State Environmental Protection Agency's Integrated Risk Information System (IRIS), the risk assessment information system (RAIS) and the United State Agency for Toxic Substances and Disease Registry – Toxicological profiles [19, 23–25]. In this study, the risk evaluation of the analyzed toxic elements (Zn, Pb, Ni, Mn, Cr, Cd and the PAHs) began with the evaluation of the chronic daily intake (CDI) of each of the metals through the ingestion exposure pathways and dermal absorption pathways.

The chronic daily intake (CDI) (mg $\mathrm{L^{-1}day^{-1}}$) for the oral and dermal pathways was evaluated using equations 2 and 3 [26]:

$$\mathrm{CDI_{oral\text{-}water}} = \frac{\mathrm{Cw\ x\ IngRw\ x\ EF\ x\ ED}}{\mathrm{BW\ x\ AT}} \tag{2}$$

For dermal pathway,

$$\mathrm{CDI_{derm\text{-}\ water}} = \frac{\mathrm{Cw\ x\ SA\ x\ KP\ x\ AF\ x\ \ ABS\ x\ ET\ x\ EF\ x\ ED}}{\mathrm{BW\ x\ AT}} \tag{3}$$

where BW is the bodyweight of the exposed person (60 kg), C_w is the concentration of the given heavy metal in the sampled drinking water (mg $\mathrm{L^{-1}}$), ED is the lifetime exposure period (30 years for the non-carcinogenic risks and average life expectancy of Nigerians of 55 years for the carcinogenic risks). EF is the exposure frequency (350 days/year^{-}), AT is the period through which the dose is averaged (ED x 365 days for non-carcinogenic risk and lifetime (55 years) x 365 days for the carcinogenic risk) and $\mathrm{IngR_w}$ is the ingestion rate of the drinking water (2 L $\mathrm{day^{-1}}$). KP is the dermal permeability constant (PAHs = 0.69, heavy metals = 0.0001), SA is the exposed skin surface area (18,000 $\mathrm{cm^2}$), AF is the Adherence factor (0.07), ET is the exposure time (0.58 hour /event) and ABS is the dermal absorption factor (0.001) [18, 20, 23, 27].

The carcinogenic and non-carcinogenic risk assessment

The ratio of the calculated chronic daily intake (CDI) to ingestion reference dose ($\mathrm{RfD_{oral}}$) of the selected heavy metals called target hazard quotient (HQ) is usually employed to highlight the level of the non-carcinogenic risks [24, 26]. The formula is given by USEPA as shown in equation 4:

$$\mathrm{HQ} = \frac{\mathrm{CDI}}{\mathrm{RfD}} \tag{4}$$

where CDI is the chronic daily intake of a given toxic constituent and RfD is the persistent reference dose for the element, i.e. for the Zn, Cd, Mn, Ni and Cr, we have 3.0E-1, 1.0E-3, 4.6E-2, 2.0E-2 and 3.0E-03 mg L^{-1} day^{-1} [26], and for Acy, Acp, Flr, Ant, Phe, Flt and Pyr, we have 6.0E-2, 6.0E-2, 4.0E-2, 3.0E-1, 3.0E-2, 4.0E-2 and 3.0E-1 mg L^{-1} day^{-1}. If HQ > 1, implies there is an increased probability of unfavourable health effects to the exposed populace. Conversely, if HQ < 1 then there is no possibility of negative health effects [28]. The hazard index (HI) is the sum of the HQ calculated using equation (5) [23, 26, 28]

$$\mathrm{HI} = \sum \mathrm{HQ} \tag{5}$$

From the toxicological profiles and risk system developed by International Agency for Research on Cancer (IARC), USEPA and WHO, the following heavy metals Cd, Ni and Cr are known human carcinogens with carcinogenic slope factors of 0.38, 0.84 and 0.5 (mg L^{-1} day^{-1}), respectively [24]. In addition, B(a)P, B(a)A, Chy, B(b)F, B(k)F , D(a,h)A and I(c,d)P are potential carcinogenic congeners and their carcinogenic slope factors are 7.3E-2, 7.3E-2, 7.3E-3, 7.3E-1, 7.3E-2, 7.3E-2 and 7.3E-2 (mg L^{-1} day^{-1}), respectively [27, 29, 30]. The carcinogenic risk estimation gives an index of risk or possibility of an aimed people to develop cancer of several types as a result of the ingestion of the carcinogens in the drinking water over a projected lifetime. Incremental Lifetime Cancer Risk (ILCR**)** that presents the carcinogenic risk was calculated using equation 6 [24, 31]:

$$\mathrm{ILCR} = \mathrm{CDI} \times \mathrm{CSF} \tag{6}$$

where CDI (mg L^{-1} day^{-1}) and CSF (mg L^{-1} day^{-1}) are the mean daily consumption of the heavy metals and the carcinogenic gradient factor. Cancer risk higher than 1E-4 is considered high as they pose a higher cancer threat while values below 1E-6 are assumed not to cause any cancer risk to the populace; the suitable range is flanked by 1E-4 and 1E-6. The carcinogenic slope factor for the dermal exposure pathway was obtained using a relevant modification factor referred to as the gastrointestinal absorption factor (ABS_{gi}), which utilizes the oral slope factor. The adjustment factor is based on the absorption of a chemical into the gastrointestinal tract. The values of ABS_{gi} for different toxic compounds are available in the USEPA report [18]. The carcinogenic slope factor for the dermal exposure pathway (equation 7) was calculated by USEPA [18] as:

$$\mathrm{CSF}_{\mathrm{dermal}} = \frac{\mathrm{CSF}_{\mathrm{oral}}}{\mathrm{ABS}_{\mathrm{gi}}} \tag{7}$$

where CSF_{oral} is the carcinogenic slope factor for the oral pathway (i.e. oral cancer slope factor) (mg kg^{-1} day^{-1}), CSF_{dermal} is the carcinogenic slope factor for dermal exposure pathway (mg kg^{-1} day^{-1}) and ABS_{gi} is the gastro intestinal absorption factor (PAHs = 0.31, Cr = 0.013, Ni = 0.002 and Cd = 0.001) [18, 20, 25].

RESULTS AND DISCUSSION

The mean concentration of Zn in water samples ranged from 0.03 - 0.25 mg L^{-1}, and followed the order: A > D > E > F > B > C > H > G (Figure 2). The concentration of zinc in all analyzed water samples was found below the permissible limit of 3.0 mg L^{-1} [32]. The control samples show lower Zn contents than other samples (A–F). Zn is an essential metal that helps to boost the body's immune system, but a higher amount of Zn in the body could result in nausea, vomiting, and stomach cramp [9].

The mean concentration of cadmium (Cd) in the water samples analyzed ranged between 0.01 - 0.04 mg L^{-1} and the trend follows: A > B > D > C > E > F and Cd was not detected in control samples (G and H). Samples A and B recorded relatively higher values of Cd in this study which is an indication of the industrial activities in this area (Asphalt production). The level of Cd in this study was found to be higher than the permissible limit of 0.003 mg L^{-1} [32]. Previous research revealed that acute or chronic exposure to Cd in the body could lead to liver or kidney damage [33].

Manganese (Mn) concentrations recorded in this study ranged from 0.01 - 0.44 mg L^{-1} in all the samples analyzed (Figure 2). Sample A and B recorded higher values of 0.43 and 0.44 mg L^{-1}, respectively because these samples were taken within the asphalt plant. Mn concentrations in this study were found to be lower than the permissible limit of 0.5 mg L^{-1}. Previous report revealed that high consumption of Mn can lead to hypertension in people above forty years old [34]. Nickel (Ni) values ranged between 0.01 - 0.05 mg L^{-1} in the water samples. Samples A, B and C were found to be higher than the permissible limit of 0.02 mg L^{-1} [32]. While sample D, E, F, G and H recorded lower values than the permissible limit. This is an indication that these samples were far away from the asphalt plant. Higher exposure to Ni in the body can result in various health threats like asthma, respiratory tract cancer, lung fibrosis and cardiovascular disease [35]. The concentration of chromium (Cr) was detected only in samples A, B and D, which were found to be higher than the permissible limit of 0.05 mg L^{-1}. Cr was not detected from samples C, E, F, G and H. The high amount of Cr in the body could lead to nerve tissue, liver, kidney and circulation damage [36].

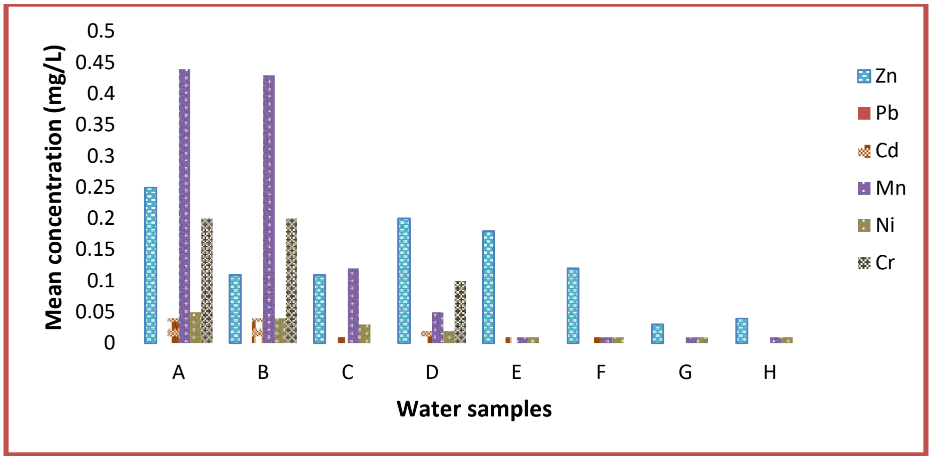

Figure 2. Mean concentration of heavy metals in the water samples analysed.

The result of the GCMS analysis revealed that fourteen (14) PAHs were detected from this study out of the sixteen (16) recognized PAHs by USEPA [37]. The low molecular weight (LMW) found in this study includes Acy, Acp, Flr, Ant and Phe. While the high molecular weight (HMW) includes; Flt, Pyr, B(b)F, Chy, B(a)A, B(a)P, I(cd)P, D(ah)A and B(ghi)P. Nap and B(k)F were not detected from this study (Table 2). This is similar to the report of PAHs in water samples from a Nigerian bitumen seepage [15].The mean concentrations of PAHs ranged between 0.05 - 0.45 mg L^{-1} (Figure 2). A total of 14 PAHs was detected from this study which accounted for 1140.00 mg L^{-1} (Table 2). The LMW PAHs accounted for 324.46 (28.46%) and HMW PAHs accounted for 815.54 (71.54%), respectively (Table 2). It was observed that a higher percentage of PAHs was recorded in HMW than LMW. This is contrary to the previous report by Itodo *et al.* [38] but similar to the report on the determination of polynuclear aromatic hydrocarbons in water and sediment of a creek in the Niger Delta region [39]. The summary of all the PAHs in each sample location (Figure 3) followed this trend A > B > C > D > E > F > G > H. Sample A recorded the highest values (390 mg L^{-1}) and sample H (control) recorded lowest values (6.74 mg L^{-1}). This could be attributed to the fact that the sample location is dominated by industrial activities which is confirmed from the Pearson correlation results (Tables 3 and 4).

Table 2. PAHs concentration from the vicinity of an Asphalt plant.

Name of PAHs	PAHs	Concentration (mg L^{-1})	% present	WHO limit
Acenaphthylene	Acy	26.30	2.31	0.02
Acenapthene	Acp	24.22	2.12	0.02
Fluorene	Flr	102.89	9.03	1.5
Anthracene	Ant	126.16	11.07	0.02
Phenanthrene	Phe	44.89	3.94	0.02
Fluoranthene	Flt	78.70	6.90	0.02
Pyrene	Pyr	64.71	5.68	0.02
Benzo(b) fluoranthene	B(b) F	37.15	3.26	0.02
Chrysene	Chy	25.56	2.42	0.02
Benzo(a) anthracene	B(a) A	21.79	1.91	0.02
Benzo(a) pyrene	B(a) P	197.61	17.33	0.7
Indeno(cd) pyrene	I(cd) P	266.45	23.37	0.02
Dibenzo(ah) anthracene	D(ah) A	48.96	4.29	0.02
Benzo(ghi) perylene	B(ghi) P	74.62	6.55	0.02
		Total PAHs = 1140.01	100.00	
		ΣLMW PAHs = 324.46		
		ΣHMW PAHs = 815.54		

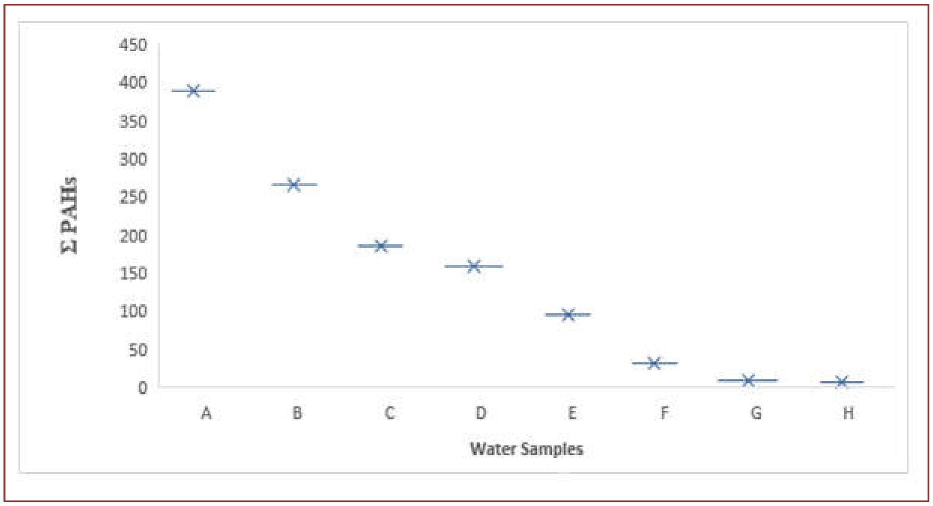

Figure 3. Summary of PAHs in each sampling point.

The inter relationship between the heavy metals (HMs), and polycyclic aromatic hydrocarbons (PAHs) were analyzed by Pearson correlation (Tables 3 and 4). There is a strong positive correlation (> 0.05) between Cd – Zn (r = 0.6554), Mn – Zn (r = 0.4368), Ni – Zn (r = 0.5325), Cr – Cd (r = 0.9636), Mn – Cd (r = 0.9254), Cr – Zn (r = 0.5514) as shown in Table 3. The result obtained in the correlation coefficient of HMs is similar to the previous reports [40, 41]. There is no positive correlation between lead and other metals because lead was not detected from this study. However, there is a positive correlation ($p > 0.05$) between Acp – Acy ($r = 0.7917$), Flr – Acp ($r = 0.8731$), Ant – Acp (0.9912), Phe – Acp ($r = 0.9882$), B(a)p – Ant ($r = 0.7656$), Pyr – Flr ($r = 0.9409$), B(c)F – Acy ($r = 0.7734$), B(a)A – Flr ($r = 0.9557$) Chy – Phe ($r = 0.5147$), D(ah) – Chy ($r = 0.6701$), and B(ghi) – Acp ($r = 0.9381$) as shown in Table 4. Therefore, the results from the Pearson correlation confirmed that the water samples from this location is polluted because of industrial and anthropogenic activities.

Table 3. Pearson correlation of Heavy metals of water samples from the Asphalt plant.

	Zn	Cd	Mn	Ni	Cr
Zn	1				
Cd	0.6554	1			
Mn	0.4368	0.9254	1		
Ni	0.5325	0.8905	0.9514	1	
Cr	0.5514	0.9636	0.9203	0.8629	1

Table 4. Pearson correlation of PAHs of water samples from the Asphalt plant.

	Acy	AcP	Flr	Ant	Phe	Flt	Pyr	B(c) F	Chy	B(a)A	B(a)P	I(c,d)P	D(ah)A	B(ghi)P
Acy	1													
AcP	0.7917	1												
Flr	0.9757	0.8731	1											
Ant	0.7661	0.9912	0.8597	1										
Phe	0.8278	0.9882	0.9164	0.9849	1									
Flt	0.8383	0.6615	0.8978	0.6453	0.7673	1								
Pyr	0.9797	0.8286	0.9409	0.8049	0.8372	0.7169	1							
B(c) F	0.7734	0.9659	0.8124	0.9601	0.9292	0.5077	0.8662	1						
Chy	0.8407	0.4163	0.7985	0.3894	0.5147	0.8773	0.7223	0.3335	1					
B(a)A	0.6684	0.7917	0.9557	0.7661	0.8278	0.8383	0.9779	0.7734	0.8407	1				
B(a)P	0.8861	0.7917	0.9757	0.7656	0.8778	0.8331	0.9057	0.7504	0.6407	0.5645	1			
I(c,d)P	0.9939	0.8511	0.9819	0.8014	0.8201	0.8345	0.9814	0.8176	0.7908	0.9393	0.7939	1		
D(ah)A	0.6507	0.2674	0.5302	0.2336	0.2712	0.3736	0.6631	0.3468	0.6701	0.6427	0.6109	0.6036	1	
B(ghi)P	0.7146	0.9381	0.7045	0.9638	0.9108	0.4347	0.6987	0.9623	0.1505	0.6172	0.5107	0.6958	0.1269	1

The results of the estimated carcinogenic (ILCR) and the non-carcinogenic (HI) risks for the HMs and the PAHs are presented in Table 5. The estimated $HI_{total\ (metals)}$ follows the order: A > B > D > C > E > F > H > G (Table 5). This implies that the highest HI is recorded in location A with a mean value of 3.2771 and the minimum was recorded at G with an average value of 0.0233. The values observed at C, E, F, G and H were within the recommended safe limit (<1) set by USEPA [25], while the values observed at A, B, and D exceeded the recommended limit. It follows that the risk of non-carcinogenic effects is high for members of the public living around locations A, B, and D. The Incremental Lifetime Cancer Risk was estimated for the heavy metals ($ILCR_{metal}$) that are human carcinogens and the mean values are 4.31E-3, 4.08E-3, 2.04E-3, 7.95E-4, 3.56E-4, 3.30E-4, 2.3E-4 and 2.3E-4 for A, B, D, C, F, E, G, and H, respectively. The cancer risks greater than 1.00E-4 are considered high and values below 1.00E-6 are considered not to pose any cancer risk to humans, it follows that the cancer risks are high for all the locations with location A leading the chart followed by B and D (Table 5).

The computed $HI_{total\ (PAHs)}$ and $ILCR_{total\ (PAHs)}$ associated with human exposure to PAHs in the water samples from all the locations are shown in Tables 6. The highest and lowest HI_{total} values are 409.51 and 0.00. The estimated $ILCR_{total\ (PAHs)}$ values ranged from 5.44E-1 and 0.00. The ILCRtotal($_{PAHs)}$ exceeds the acceptable range of 1.0E-4 and 1.0E-6 in some of the sampled locations except C, D, F, G and H whose values were 0.00 because no traces of the potential carcinogenic PAHs i.e. B(a)P, B(a)A, Chy, B(b)F, B[k]F, D(ah)A, I(cd)P and B(a)P were found in the water samples from these locations. The Cancer and the non-cancer risks for both heavy metals and PAHs revealed the ingestion pathway is the dominant route of exposure as compared with the dermal pathway. However, the result revealed that 100% of $\mathrm{ILCR}_{\text{total (metal)}}$ and 37.5% of $\mathrm{ILCR}_{\text{total (PAHs)}}$ are higher than the recommended limit in the samples, which implies that residents in this study area are in danger of both carcinogenic and non-carcinogenic health effects.

Table 5. Estimated hazard indices and incremental lifetime cancer risk of the heavy metals in the water samples for both ingestion and dermal absorption pathways.

Absorption path ways	Sample	HQ_Zn	HQ_Cd	HQ_Mn	HQ_Ni	HQ_Cr	HI_{ing}	$\mathrm{HI}_{\text{total (metal)}}$
	A	2.28E-02	1.10E+00	2.62E-01	6.85E-02	1.83E+00	3.2758	3.2771
Ingestion	B	1.00E-02	1.10E+00	2.56E-01	5.48E-02	1.83E+00	3.2433	3.2444
	C	1.00E-02	2.74E-01	7.15E-02	4.11E-02	0.00E+00	0.3966	0.3966
	D	1.83E-02	5.48E-01	2.98E-02	2.74E-02	9.13E-01	1.5366	1.5366
	E	1.64E-02	2.74E-01	5.96E-03	1.37E-02	0.00E+00	0.3101	0.3101
	F	1.10E-02	2.74E-01	5.96E-03	1.37E-02	0.00E+00	0.3046	0.3047
	G	2.74E-03	0.00E+00	5.96E-03	1.37E-02	0.00E+00	0.0224	0.0224
	H	3.65E-03	0.00E+00	5.96E-03	1.37E-02	0.00E+00	0.0233	0.0233
		HQ_Zn	HQ_Cd	HQ_Mn	HQ_Ni	HQ_Cr	$\mathrm{HI}_{\text{dermal}}$	$\mathrm{ILCR}_{\text{total (metal)}}$
	A	1.12E-05	1.79E-04	1.29E-04	3.36E-05	8.97E-04	1.25E-03	4.31E-03
Dermal	B	4.93E-06	1.79E-04	1.26E-06	2.69E-05	8.97E-04	1.11E-03	4.08E-03
	C	4.93E-06	4.48E-05	3.51E-06	2.02E-05	0.00E+00	7.34E-05	7.95E-04
	D	8.97E-06	8.97E-05	1.46E-05	1.34E-05	4.48E-04	5.75E-04	2.04E-03
	E	8.07E-06	4.48E-05	2.92E-06	6.72E-06	0.00E+00	6.25E-05	3.30E-04
	F	5.38E-06	4.48E-05	2.92E-06	6.72E-06	0.00E+00	5.98E-05	3.56E-04
	G	1.34E-06	0.00E+00	2.92E-06	6.72E-06	0.00E+00	1.10E-05	2.30E-04
	H	1.79E-06	0.00E+00	2.92E-06	6.72E-06	0.00E+00	1.14E-05	2.30E-04

Table 6. Estimated hazard index and incremental life cancer risk of the PAHs present in the water samples for both ingestion and dermal absorption path ways.

Absorption	Sample	HQ_Ac	HQ_Ac	HQ_Flr	HQ_Ant	HQ_Phe	HQ_Flt	HQ_Pyr	HI_{ing}	$\mathrm{HI}_{\text{total (PAHs)}}$
	A	4.12	7.08	276.79	7.70	24.01	15.02	2.32	337.04	371.52
Ingestion	B	4.55	3.27	294.38	3.35	15.16	34.57	1.77	357.05	409.51
	C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	D	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	E	3.34	0.71	133.58	0.48	1.83	4.32	1.81	146.07	162.94
	F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	G	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Sample	HQ_Ac	HQ_Ac	HQ_Flr	HQ_Ant	HQ_Phe	HQ_Flt	HQ_Pyr	$\mathrm{HI}_{\text{dermal}}$	$\mathrm{ILCR}_{\text{total (PAHs)}}$
	A	1.40	2.40	6.25	13.04	4.07	3.39	3.93	34.48	5.44E-01
Dermal	B	1.54	1.16	1.13	5.13	11.71	0.6	31.19	52.46	2.04E-01
	C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00E+00
	D	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00E+00
	E	1.13	0.24	4.52	0.16	1.46	0.61	8.75	16.87	1.94E-01
	F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00E+00
	G	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00E+00
	H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00E+00

CONCLUSION

The result of the PAHs showed a higher concentration of fourteen (14) PAHs in the water samples analyzed except for naphthalene and benzo(k)fluoranthene that were not detected. The results of both Cr and Cd were higher than the recommended limit and lead was not detected. The data obtained from this study showed a high level of contamination that rendered the water samples from this location to be unfit for domestic and industrial use. This high level of contamination was corroborated by the findings of the HI_{total} and $ILCR_{total}$ values recorded in some of the sample location are higher than the recommended limit, implying that the residents in these sampled locations are exposed to both carcinogenic and non-carcinogenic pollutants. Consequently, it is recommended that the citing of industry like Asphalt plant should be far away from residential buildings and adequate enlightenment programmes are recommended by various environmental agencies on the health risk associated with consuming polluted water.

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