ASSESSMENT OF RIVER KATSINA-ALA FOR CONTAMINATION BY POLYCYCLIC AROMATIC HYDROCARBONS FROM ACTIVITIES OF ANIMAL ROASTING ALONG THE BANKS

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Abstract: Polycyclic Aromatic Hydrocarbons (PAHs) were assessed in River Katsina-Ala water due to its suspected contamination by activities of animal roasting with used tires on the river bank. The samples collected were analyzed with gas chromatography and detected with flame ionization detector (FID). The results show contamination of the water with the 16 listed PAHs. Mean concentrations of the study showed naphthalene, acenaphthene, fluorene, fluoranthene, chrysene, and benzo[g, h, i] perylene to be within acceptable limits of the Canadian water quality guidelines and Netherlands maximum permissible concentration for PAH. Anthracene, pyrene, benz[a]anthracene and benzo[a] pyrene however exceeded the acceptable limits. The total PAH concentration over the period of study ranged from 2.4259 µg/L-3.7421 µg/L. Monitoring of the river water at the spot of roasting activity should be carried out frequently toassess the level of contamination for possible health risks.
Keywords: Animal roasting, benzo[a]pyrene, contamination, polycyclic aromatic hydrocarbons.

Introduction

Nigeria experiences a lot of environmental challenges at the moment. Contamination of soil, water and air has been reported due to agricultural and savannah fires (Lammel *et al*., 2013) and metals like cadmium, lead, iron (Adewoyin *et al*., 2013) cobalt, copper, manganese, nickel and zinc (Okoye & Ibeto, 2008; Odoh *et al*.,2011; Pam *et al*., 2013) in soils of mechanic workshops among others.

Water bodies have reportedlybeen contaminated by effluents from abattoirs (Makwe & Chup, 2013). This has caused ground water around the regions of the effluents to be affected. River water has been reportedly affected by these discharges such that the qualities of parameters of river water like dissolved oxygen, biological oxygen demand, total suspended solids and total solids have been impacted upon (Omole & Longe, 2008). Water bodies too are also contaminated with metals like chromium and lead which have been reported to contaminate wells in the vicinity of metal workshops in Gboko, Benue state (Okoye & Nyiaghthagher, 2009).

One prominent contaminant in the environment nowadays is the polycyclic aromatic hydrocarbons. These are a group of organic compounds that consist of fused aromatic rings though not having heteroatoms or substituents (Fetzer, 2007; Sojinu *et al*., 2011). They emanate from incomplete combustion of materials in the environment. Such materials include garbage, petroleum products, coal, meat and tobacco (Lau *et al*., 2010). They are grouped into low molecular weights (2-3 rings) and high molecular weights (4-6 rings). Polycyclic aromatic hydrocarbons have been associated with carcinogenic and mutagenic effects (Liu & Korenga, 2001). WHO reports have in fact indicated an increasing prevalence of cancer around the world including Nigeria (Elima *et al*., 2014). Cancer is a medical condition whereby uncontrolled division of abnormal cells occurs in a part of the body giving rise to malignant tissues (www.en.wikipedia.org/wiki/cancer). More so, no study on PAH contamination of water associated with tire assisted animal roasting had earlier been documented in this environment. It is against this background that a preliminary assessment is being conducted on the river Katsina-Ala water to ascertain the polycyclic aromatic hydrocarbons levels due to activities of butchers that roast animals along the river bank.

Materials and Methods

Study area

Katsina-Ala Local Government of Benue state has its headquarters in Katsina-ala town. The Local government area has an area of 2402 km^2 with a population of 224,718 as reported in the 2006 census (www.en.wikipedia.org/wiki/Katsina-Ala). Katsina-Ala township lies between latitude 7^o 03' N and longitude 9^o 25'E (Dam, 2012).

There are communities on the banks of River Katsina-Ala which is a tributary of River Benue, in fact it is its most important tributary (Ityavyar *et al*., 2011). The river takes its source from the Bamenda highlands in northwestern Cameroon (www.en.wikipedia.org/wiki/Katsina_Ala_River). Another important waterbody is the lake Akata which is a tourist site due to an annual fishing festival which is hosted in it (Ityavyar *et al*., 2011).

Collection of water sample

Water samples were collected from the river at the spot of roasting activityin the months of March, June and September; 2014. These choice of months was informed by the need to assess the effect of the pollutant washed from the banks into the river due to rainfall. The samples were collected in pre-cleaned and sterilized dark colored plastic bottles to prevent action of ultraviolet light which could cause degradation of analyte (Anyakora & Coker, 2006) at a depth of 1-2 m. The samples were then acidified at point of collection with concentrated hydrochloric acid. This is necessary to render any micro-organism that may cause biodegradation of samples inactive. The samples were transported to the laboratory at a temperature below 10^{o}C by putting them in ice packed coolers and stored in a refrigerator until ready for analysis.

PAH extraction from water samples

The procedure adopted from Adedosu *et al*. (2013) was employed. 200 ml of water sample was transferred into a 1 L separating funnel and 60 ml of redistilled dichloromethane was then added. The separating funnel was shaken vigorously for about 2 min with periodic venting to release vapor pressure. The organic layer was allowed to separate for 10 min and was recovered into the 250 ml flask. The aqueous layer was re-extracted twice with 60 ml of the extractant. The combined extract was dried by passing through a funnel containing anhydrous sodium sulphate. The dried extract was concentrated with a stream of nitrogen gas.

Clean up of sample extract

The extract in each case was separated into the aliphatic profiles and polycyclic aromatic hydrocarbons by packing the glass columns with activated alumina. 10 ml of the treated alumina was packed into the column and cleaned properly with redistilled hexane. The extract was poured onto the alumina and was allowed to run down with the aid of the redistilled hexane to remove the aliphatic profiles into a pre-cleaned 20 ml capacity glass container. The aromatic fraction was recovered by introducing a mixture of hexane and dichloromethane in the ratio of 3:1 (75:25 ml). The most polar PAH was finally removed with the dichloromethane into a pre-cleaned borosilicate beaker. The mixture was concentrated to 1ml by a stream of the nitrogen gas before employing gas chromatographic analysis coupled with flame ionization detector.

Instrumentation

The gas chromatographic analysis was carried out using the gas chromatograph (Model HP6890 powered with HP chemstation Rev.A.09.01 [1206] software) coupled with flame ionization detector. The separation of PAH constituents in the sample was made possible on column HP-1 with length 30 m using nitrogen as carrier gas. Injection and detector temperatures were 250^oC and 320^oC, respectively. Initial temperature was 60^oC for 5 min and was increased by 15^oC/min for 14 min and maintained for 3 min then 10^oC/min for 5 min maintained for 4 min.

Results and Discussion

The result of polycyclic aromatic hydrocarbon concentrations in Katsina-Ala river is presented in Table 1. River Katsina-Ala was contaminated with PAH at the spot that tire roasting activities were carried out. The result further indicated that all the 16 priority listed PAH were detected in the river water. The mean concentration of PAH for the three months that studies were undertaken showed phenanthrene(0.431±0.281) to have presented the highest concentration while Benzo[g,h,i]perylene (0.014±0.003) had the least concentration in the river water at that spot. The reason for this is not clear but phenanthrene being a 3 membered ring PAH with low molecular weight may have been deposited in the water from the air after roasting activities. Since phenanthrene has a lower weight it may have acquired kinetic energy as the burning was taking place and as they lose the energy they are eventually deposited in the river water. Benzo[g,h,i]perylene which has a higher molecular weight may not have acquired kinetic energy enough hence may have been washed into the river during rainfall or washing of the animals in the river water after the roasting.

Other PAHs whose concentration where found to be present in the order of their magnitutude include acenaphthene (0.375±0.229)> benzo[k]fluoranthene (0.307±0.069) >fluorene (0.292±0.168) and Benzo[b]Fluoranthene (0.259±0.042). Naphtalene, acenaphthylene, anthracene, pyrene, benzo[a]anthracene, chrysene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and dibenzo[a,h]anthracene were present in varying concentrations as shown in the table.

The results were lower when compared with that of a study carried out by Falahundin (2012) on sea water where average concentration of benzo[b]fluoranthene was 9.323 μg/L, benzo[a]anthracene (11.039 μg/L), dibenzo[a,h] anthracene (13.105 μg/L), benzo[a]pyrene (14.122 μg/L), indeno[1,2,3-cd]pyrene (17.426 μg/L) and chrysene (18.293 μg/L). The PAHs when compared with the Canadian water quality guidelines and Netherlands maximum permissible concentrations for PAH (Table 4 and 5) indicated that naphthalene (0.144±0.004), acenaphthene (0.375±0.229), fluorene (0.292±0.168), fluoranthene (0.109±0.033), chrysene (0.126±0.033), and benzo[g,h,i]perylene (0.014±0.003) were below the acceptable limits. However, anthracene (0.155±0.065), pyrene (0.187±0.063), benzo[a]anthracene (0.126±0.029) and benzo[a]pyrene (0.153±0.039) exceeded the acceptable limits.

Table 1: Results of polycyclic aromatic hydrocarbon concentrations in river Katsina-Ala

			Concentration of PAH (μg/L)			
S/N	**No of rings**	**PAH**	**S_1**	**S_2**	**S_3**	**Mean ± SD**
1.	2	Naphthalene	0.1479	0.1397	0.1458	0.144 ± 0.004
2.	3	Acenaphthylene	0.0695	0.1095	0.241	0.140 ± 0.090
3.	3	Acenaphthene	0.1647	0.6180	0.3408	0.375 ± 0.229
4.	3	Fluorene	0.1377	0.4716	0.2658	0.292 ± 0.168
5.	3	Phenanthrene	0.1993	0.7447	0.3489	0.431 ± 0.281
6.	3	Anthracene	0.0817	0.1810	0.2029	0.155 ± 0.065
7.	4	Fluoranthene	0.0739	0.1157	0.1399	0.109 ± 0.033
8.	4	Pyrene	0.1707	0.1329	0.2564	0.187 ± 0.063
9.	4	Benzo(a)anthracene	0.1201	0.1004	0.1577	0.126 ± 0.029
10.	4	Chrysene	0.0928	0.1594	0.1252	0.126 ± 0.033
11.	5	Benzo(b)fluoranthene	0.2595	0.2162	0.3010	0.259 ± 0.042
12	5	Benzo(k)fluoranthene	0.2951	0.2444	0.3802	0.307 ± 0.069
13	5	Benzo(a)pyrene	0.2534	0.2106	0.2884	0.153 ± 0.039
14	6	Indeno[1,2,3-cd]pyrene	0.1677	0.1354	0.1544	0.153 ± 0.016
15	6	Dibenz(a,h)anthracene	0.1753	0.1482	0.1034	0.142 ± 0.036
16	6	Benzo(g,h,i)perylene	0.0166	0.0144	0.0099	0.014 ± 0.003
		Total	**2.4259**	**3.7421**	**3.5769**	

The average sum of PAH concentrations based on the number of cyclic rings is presented in Table 2. The result showed that PAH with 5 rings have the highest average concentration (0.719 µg/L) over the period studied followed by PAH with 4 rings (0.548 µg/L). It had been reported that PAHs linked to carcinogenic and tetragenic activities include benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and dibenzo[a,h]anthracene (Ravindra *et al*, 2008). The listed PAHs belong to the PAHs with 4 and 5 rings which indicate that the presence of this PAH collectively in higher concentrations in the river water may pose health risks in the future.

Table 2: Average sum of PAH concentration based on number of rings

Number of Rings	2	3	4	5	6
∑PAH(µg/L)	0.144	1.393	0.548	0.719	0.309

Table 3: Indices for prediction of PAH source

Sample	Phe/Ant	Flu/Pyr	Chr/B(a)A
S1	2.44	0.43	0.77
S2	4.11	0.87	1.59
S3	1.72	0.54	0.79

The result of diagnostic ratio to determine the sources of the PAH is presented in Table 3. It has been reported that the ratio of phenanthrene to anthracene and fluoranthene to pyrene in a sample has helped to identify petrogenic and pyrolytic sources of PAH (Kalilzadeh *et al*, 2011). Phenanthrene to anthracene ratio values greater than 10 indicates that the PAH emerged from petrogenic sources while for Phenanthrene to Anthracene ratio values less than 10 is an indication that the PAH is from pyrolytic sources while Fluoranthene to Pyrene ratios greater than 1 also indicate pyrolytic sources. On the other hand, if the ratio is less than 1, the PAH source is petrogenic. Furthermore, the ratio of chrysene to benzo[a]anthracene can be used to indicate if the source of contamination is petrogenic or pyrolytic. If chrysene to benzo[a]anthracene value is less than 1, the PAH is from pyrolytic source while if the values are greater than 1 it indicates a petrogenic origin. For the samples collected in march (S_1), the ratio of phenanthrene to anthracene was less than 10 and that of chrysene to benzo(a)anthracene was less than 1 indicating contributions from pyrolytic sources while the ratio of fluoranthene to pyrene is less than 1 which points to petrogenic sources.

Table 4: Netherlands maximum permissible concentrations (MPCs) for PAHs

PAH	MPC water (µg/L)	MPC soil (mg/kg)	MPC sediments (mg/kg)
Naphtalene	1.2	0.14	0.14
Anthracene	0.07	0.12	0.12
Phenanthrene	0.3	0.51	0.51
Fluoranthene	0.3	2.6	2.6
Benz[a]anthracene	0.01	0.25	0.36
Chrysene	0.34	10.7	10.7
Benzo[a]pyrene	0.05	0.26	2.7
Benzo[g,h,i]perylene	0.033	7.5	7.5
Benzo[k] Fluoranthene	0.04	2.4	2.4

Source: (Kalf *et al.*, 1997)

Table 5: CCME environmental quality guidelines for PAH

Substance	Drinking water (µg/L)	Fresh water life (µg/L)
Naphthalene		1.1
2-methylnaphthalene		-
Acenaphtylene		-
Acenaphthene		5.8
Fluorene		3.0
Anthracene		0.012
Phenanthrene		0.4
Pyrene		0.025
Fluoranthene		0.04
Benz(a)anthracene		0.018
Chrysene		-
Benzo(a)pyrene	0.01	0.015
Dibenz(a,h)anthracene		-

Source: Canadian Council of Ministers of Environment (2008)

From the study, there are indications that the samples collected in June (S_2) were contaminated with PAH from pyrolytic sources since phenanthrene to anthracene ratio was less than 10 while the ratio of fluoranthene to pyrene is less than 1 and chrysene to benzo[a]anthracene, greater than 1. This indicates that petrogenic sources also contributed PAH to the contamination of the sample at that point. Similarly, phenanthrene to anthracene ratio was determined to be less than 10 and chrysene to benzo[a]anthracene ratio was also less than 1 in the sample collected in September (S_3). ThesePAHswere contributed from pyrolytic origin while fluoranthene to pyrene ratio less than 1 is an indication that petrogenic sources also contributed to the water contamination. The rubber tires used for roasting may have been responsible for the contributions due to petrogenic sources since PAHs are obtained from pyrolysed rubber tires (Juma *et al*., 2006) which are products of the petrochemical industries.

Conclusion

The study carried out to ascertain possible PAH contamination of water due to activities of butchers that roast animals along the river banks with used car tires revealed that the water samples collected from river Katsina-Ala in Benue state from the spots where roasting takes place were actually contaminated with all the 16 priority PAHs though the concentrations were within acceptable limits except for anthracene, pyrene, benzo(a)anthracene and benzo(a)pyrene which exceeded the Canadian and Netherlands recommended limits. The results also showed that the total concentration of PAH in the River water as analysed in March, June and September, 2014 was 2.4258 µg/L, 3.7421 µg/L, and 3.5769 µg/L respectively. The presence of total amounts of 4 and 5 ringed PAH in high concentration could pose health risks in the future. Caution must therefore be employed by the community that relies on the water for one domestic activity or the other to avoid possible health hazards in the future. The study also showed that the PAH in the river water were contributed from pyrolytic and pyrogenic sources.

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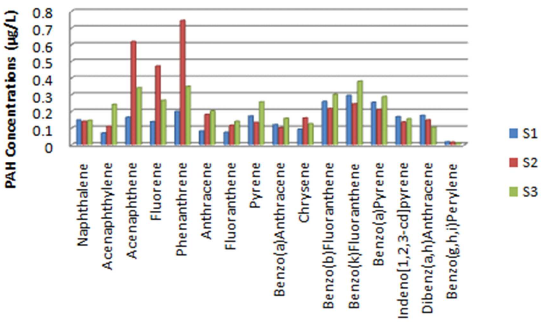

Fig 1: Individual PAH concentrations at different sample collections

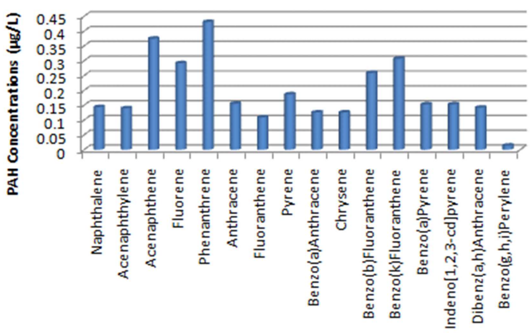

Fig 2: Mean concentration of individual PAHs over the period