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SOURCE IDENTIFICATION AND ECOTOXICOLOGICAL RISK ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBONSIN SEDIMENT FROM KOMADUGU RIVER BASIN, YOBE STATE, NIGERIA

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) were determined in sediments from five sampling points designated as S1 to S5 from Komadugu River basin, Yobe State, Nigeria. The concentrations of PAHs in sediment samples ranged from 1.42E-04 to 1.65E-01 mg/kg. Dry season were observed to show the highest concentrations of all the studied PAHs with a total value of 2.72E+00 mg/kg, while the rainy season shows the lowest concentrations with a total value of 1.88E+00 mg/kg. The concentrations of the studied PAHs in the sediment samples were below the maximum allowable concentrations (MACs) of 0.15 to 3.0 mg/kg. Results of the study shows that the ratio of BaA/BaA + Chr were between 0.40 and 0.50 with mean of 0.57, which indicate pyrogenic sources, the Ant/Ant + Phe ratios were between 0.21 and 0.63 indicating fuel combustion sources, while Flua/Flua+Pyr of 0.44 confirmed the combustion of fuel as the main PAH source in the study area. The diagnostic ratios show both fuel combustion and pyrogenic sources of PAH in the study area. The m-ERM-q in the sediments were below 0.1 indicating an 11 percent probability of toxicity and are therefore classified as low priority sites.

Keywords: PAHs, sediments, diagnostic ratios, ERM, MACs, Komadugu River.

INTRODUCTION

Polycyclic aromatic hydrocarbons are lipophilic, which means that there are more soluble in oil than in water. The higher molecular weight PAHs are less soluble in water and easily evaporated (Glenn, 1995). Due to the nature of PAHs, there are easily found in soil, sediment and oily substances compared to water and air (Glenn, 1995). The sources of PAHs into the environment includes crude oil, fossil fuel, coal tar, smoke, smokes from cigarette, smokes form wood burning and coal deposits (Wania and Mackay, 1996). Combustion processes produces various types of PAHs in both relative amount of individual PAHs and in which isomers are produced (Glenn, 1995). The burning of coal yield a different mixture of PAHs than motor fuel combustion and the natural source of PAHs includes release from forest fire and from volcanic eruptions. PAHs that are found in the environment comes from incomplete combustion of fossil fuels and those PAHs that are found in the marine sediment comes from atmospheric deposition, dumping of sewage from residential homes and also from long range transport as a result of industrial activities (Santodonato, 1981).

PAHs are produced in all processes of incomplete combustion of organic substance (Sims and Overcash, 1983; Menzie *et al*., 1992; Wild and Jones, 1995). Their production is favoured by an oxygen deficient flame, temperature in the range of 650^0C – 900^0C and fuel which are not highly oxidized. Natural sources of pyrogenic PAHs such as volcanic activity and forest fire do not significantly contribute – for the present to overall PAHs emissions (Sims and Overcash, 1983; Ellenhorn and Barceloux, 1988; Wild and Jones,1995).

Komadugu - Yobe Systemin Yobe State covers an estimated area of about 47, I 53 square kilometers and supports a human and livestock population of over 1.4 million and I million respectively (NPC, 199I; RIM, 1992). The State shares border with the Niger Republic to the North, Jigawa and Bauchi States to the West, Borno State to the East and Gombe and Borno States to the South. The area of study, which is in the Northern part of the State is Sahelian in nature and is being threatened by desertification. The Komadugu - Yobe basin from which the State derived its name, supplies up a source of over 1.12 billion cubic meters of surface water per year.

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It is located between latitude 10°N and 13°N and longitude 9.45°E and 12.30°E° (GIS, 2015). The Komadugu - Yobe River originates from the Jos Pleateau and Kano ends up in the Lake Chad, the river was formed by the confluence of the Hadejia and Jam'are rivers. The distance between the confluence upstream of Gashua near Karage and the outlet at Yau is about 280 km but the length along the Yobe River is about 660 km due to the extensive river meanders (GIS, 2015). The curvature is of advantage because it provides a large increase in river, frontage and easier abstraction of irrigation water for a large area. The geological formation of the upstream part of the basin consists largely of impermeable basement complex rocks, which dips away to the east where it is covered by the permeable lakes sediments of the Chad formation. In some areas, the sediments are covered with oriented longitudinal dunes (Schultz, 1976). The three main rivers in the Hadejia- Jamaare - Yobe River System are the rivers Hadejia, Jarnaare and Komadugu - Yobe. The Hadejia River is formed by the confluence of the river Kano and Challawa at Tamburawa. It has a poorly defined channel and characterized by numerous oxbow lakes. The rivers pass through Hadejia and Madachi towns and enter a number of lakes and swamps.

MATERIALS AND METHODS

Sampling Points

Samples were collected within the Komadugu river basin from Nguru (12^0 50'N; 10^0 24'E) to Gashua (12^0 51'N; 11^0 06'E) (Fig. 1). Water and Sediment samples were collected at Nguru town designated $S_{1.}$ Point S_2 to S_3 was located 14 Km away from point S_1, Point S_4 to S_5 were also located 14 Km away from each other, making a total of 70 Km for this study. Water and Sediment samples were collected approximately 10 meters away from the bank of the river. The water and sediment samples were collected on seasonal basis (dry, rainy seasons and hamattan period).

Sediment Samples

Sediment samples were collected in accordance with method described by (Boyd and Tucker, 1992). Sediment samples were collected within the Komadugu river basin from Nguru to Gashua points S_1 to S_5 (Fig. 1) using a plastic hand trowel sampler by scooping 1-5cm of the top layer sediment. One kilogram (1kg) of sediment samples were collected at each point and were placed in an amber glass bottles, the labeled.

Extraction of PAHs in Sediment Samples

Analysis for PAH in sediment samples was carried out in accordance with USEPA (2000) 8270 analytical method. 10g of the sample was dried using anhydrous sodium sulphate and 1mls of 60 µg/mls o-Terphenyl surrogate standard added and mixed thoroughly with the sample. 30mls of methylene chloride was then added and the sample extracted. The sample extract was subsequently filtered through glass wool containing anhydrous sodium sulphate in a glass funnel. About 2gm of silica gel was added and allowed to stand for a while. The extract was then decanted and allowed to concentrate at room temperature to 1mls volume.

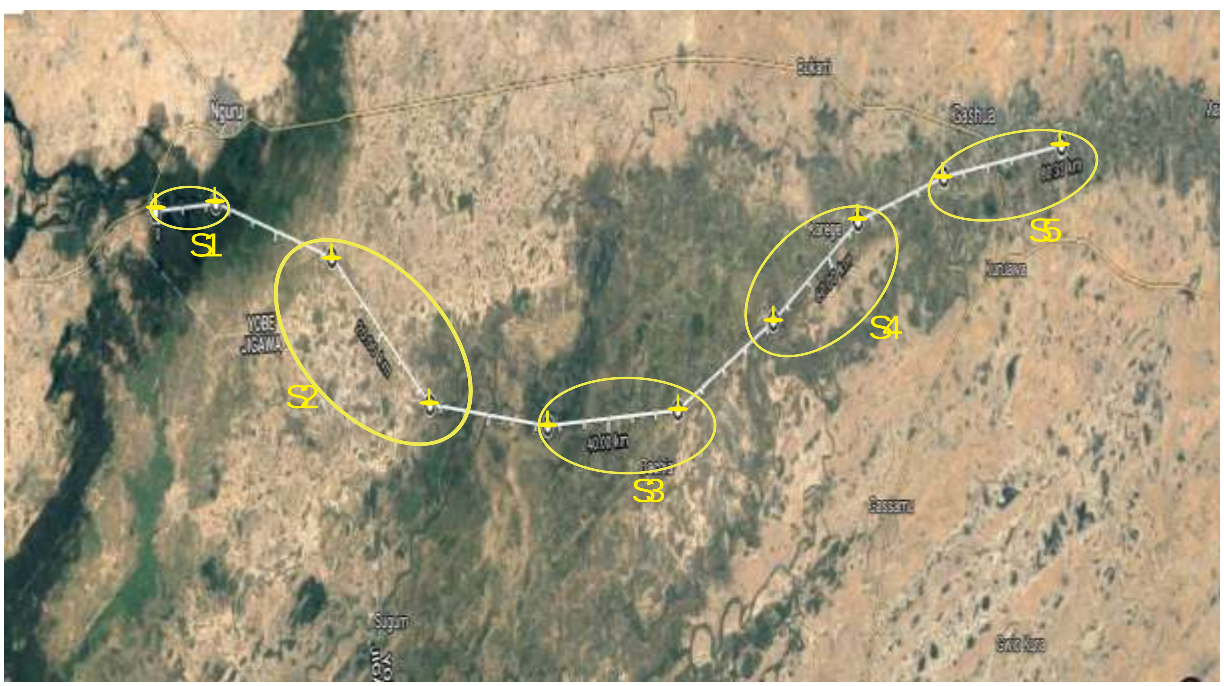

Fig. 1. Map Showing 5 Sampling Points. Source: GIS, 2015

Instrumental Analysis of PAHs Using GSMS for Sediment and Fish Samples

The extract was thereafter analyzed using Agilent 7890A GC/MS previously calibrated with PAHs standards. The equipment turned out the concentration of the PAHs as the sample details were supplied for sediment samples. The extract was thereafter analyzed using Agilent 7890A GC/MS previously calibrated with PAHs standards. The equipment turned out the concentration of the PCBs as the sample details were supplied for sediment samples.

Identification of PAH Sources in Sediment Samples

Diagnostic ratios were used to distinguish the possible sources of PAH in the sediment. The following ratios were used as source indicators: Ant/Ant+Phe, BaA/BaA+Chr and LMW-PAH to HMW-PAH.

Carcinogenic Risk Assessment of PAHs in Sediment Samples

Health risk associated with the PAHs in sediments was evaluated using the toxicity equivalency factor (TEF) method described by Nisbet and LaGoy (1992) (TEF for each PAH will be an estimate of the relative toxicity of the PAH compounds compared to BaP). The total equivalent concentration will be expressed as BaP equivalent (BaPeq).

BaPeq for individual PAH were estimated using the equation $BaPeq = \sum Cn \times TEFn$

Ecological Risk Assessment of PAHs in Sediment Samples

The mean ERM quotient approach was used to evaluate the possible ecotoxicity of PAHs in the sediment. The mean ERM quotient values were calculated according to the method formular suggested by Long and Macdonald (1998): $m - ERM - q = \sum(\frac{Ci}{ERMi})/n$

Benzo(a)pyrene Equivalent

Toxic equivalent factors (TEF) was developed for a number of individual PAHs to express its potency relative to benzo(a)pyrene, which has a TEF of unity. The concentration of each of the individual PAHs compounds were multiplied by its TEF proposed by (Nisbet and LaGoy, 1992). $BaPeq = \sum Cn \times TEFn$

RESULTS

Concentrations of Some PAHs in Sediment Samples from Different Sampling Points

Tables 1 to 3 shows the mean concentrations of some polycyclic aromatic hydrocarbon in sediment samples for rainy, dry seasons and harmattan period from points S1 to S5 of Komadugu river basin, Yobe State Nigeria. The concentration of naphthalene ranged from 2.00E-02 to 5.00E-02 mg/kg; 1.42E-04 to 4.00E-02 mg/kg 2-methylnaphthalene; 8.70E-05 to 3.10E-02 mg/kg acenaphthylene; 1.90E-02 to 3.00E-02 mg/kg acenaphthene; 2.11E-04 to 3.30E-02 mg/kg Fluorene; 2.00E-02 to 3.20E-02 mg/kg phenanthrene; 2.00E-02 to 2.90E-02 mg/kg anthracene; 1.42E-02 to 3.70E-02 mg/kg fluoranthene; 1.29E-03 to 6.00E-02 mg/kg pyrene; 2.00E-02 to 3.00E-02 mg/kg benzo(a)anthracene; 3.00E-02 to 4.00E-02 kg benzo(b)fluoranthene; 2.06E-02 to 1.98E-02 mg/kg benzo(k)fluoranthene; 2.64E-02to 7.00E-02mg/kg chrysene; 2.00E-02 to 5.00E-02 mg/kg benzo(a)pyrene; 2.80E-02 to 5.20E-02mg/kg dibenz(a.h)anthracene; 2.00E-02 to 4.00E-02 mg/kg benzo(g,h,i)perylene and 5.64E-04 to 6.00E-02 mg/kg indinol(1,2,3-cd)pyrene. The highest total concentration of 1.98E-01 mg/kg was observed at point S3 during the rainy season, while point S4 shows the lowest total value of 2.47E-01 mg/kg during the same period.

Total Concentrations of Some Polycyclic Aromatic Hydrocarbon (PAHs) in Water, Sediment and Fish Samples During the Rainy, Dry Seasons and Harmattan Period

For the sediment samples, the total concentrations of the studied PAHs during the rainy, dry seasons and harmattan period ranged from 1.88E+00 to 2.72E+00 mg/kg Figure 1. The highest total concentration was observed during the dry season, while the lowest total concentration was observed during the rainy season.

Table 1. Mean Concentrations of Some Polycyclic Aromatic Hydrocarbon in Sediment Samples from Different Sampling Points of Komadugu River Basin, Yobe State, Nigeria During the Rainy Season.

			Concentrations (mg/kg)				
PAHs	**No. of Rings**	**MACs S1**	**S2**	**S3**	**S4**	**S5**	
Naphthalene	2	1	5.00E-02	5.00E-02	5.00E-02	5.00E-02	5.00E-02
2-methyl Napthalene	2	1	4.00E-02	4.00E-02	1.42E-04	2.67E-02	2.67E-02
Acenapthylene	3	3	2.00E-02	2.00E-02	8.70E-05	1.33E-02	1.33E-02
Acenaphthene	3	3	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02
Fluorene	3	3	3.00E-02	3.00E-02	2.14E-04	2.11E-04	1.50E-02
Phenanthrene	3	3	3.00E-02	3.00E-02	3.00E-02	3.00E-02	3.00E-02
Anthracene	3	3	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02
Fluoranthene	4	3	1.00E-02	1.00E-02	1.00E-02	1.01E-03	1.42E-04

Pyrene	4	3	5.00E-02	2.00E-02	2.80E-02	1.29E-03	2.80E-02
Benz(a)anthracene	4	0.15	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02
Chrysene	4	-	3.00E-02	3.00E-02	3.00E-02	3.00E-02	3.00E-02
Benz(b)fluoranthene	5	0.3	1.00E-02	1.00E-02	9.78E-04	1.10E-03	1.18E-03
Benz(k)fluoranthene	5	-	3.00E-02	3.00E-02	1.98E-01	2.93E-03	2.06E-02
Benz(a)pyrene	5	0.3	3.00E-02	3.00E-02	4.58E-03	9.13E-03	2.64E-03
Dibenz(a,h)anthracene	5	0.3	2.00E-02	2.00E-02	2.80E-04	8.21E-04	9.12E-04
Benzo(g,h,i)perylene	6	3	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02
Indinol(1,2,3-cd)pyrene	6	-	2.00E-02	2.00E-02	2.00E-02	5.64E-04	1.51E-02
∑ of 17 PAHs			**4.50E-01**	**4.20E-01**	**4.52E-01**	**2.47E-01**	**3.14E-01**

MACs = Maximum Allowable Concentrations(ATSDR, 2006)

Table 2. Mean Concentrations of Some Polycyclic Aromatic Hydrocarbon in Sediment Samples from Different Sampling Points of Komadugu River Basin, Yobe State, Nigeria During the Harmattan Period.

			Concentrations (mg/kg)				
PAHsNo. of RingsMACs			**S1**	**S2**	**S3**	**S4**	**S5**
Naphthalene	2	1	3.00E-02	2.00E-02	3.00E-02	2.00E-02	2.00E-02
2-methyl Napthalene	2	1	3.00E-02	3.00E-02	2.00E-02	2.50E-02	2.70E-02
Acenapthylene	3	3	3.00E-02	2.00E-02	3.10E-02	1.20E-02	1.40E-02
Acenaphthene	3	3	3.00E-02	2.00E-02	2.00E-02	1.90E-02	2.00E-02
Fluorene	3	3	3.30E-02	2.40E-02	3.00E-02	3.00E-03	2.00E-02
Phenanthrene	3	3	3.20E-02	2.00E-02	3.00E-02	3.00E-02	2.80E-02
Anthracene	3	3	2.10E-02	2.00E-02	2.00E-02	2.00E-02	2.30E-02
Fluoranthene	4	3	1.30E-02	3.00E-02	3.00E-02	1.20E-02	2.00E-02
Pyrene	4	3	6.00E-02	3.00E-02	3.10E-02	2.90E-02	2.80E-02
Benz(a)anthracene	4	0.15	3.00E-02	3.00E-02	3.00E-02	2.50E-02	2.80E-02
Chrysene	4		3.50E-02	3.00E-02	3.00E-02	3.10E-02	4.00E-02
Benz(b)fluoranthene	5	0.3	4.00E-02	5.00E-02	4.00E-02	4.00E-02	3.90E-02
Benz(k)fluoranthene	5		4.50E-02	4.00E-02	5.00E-02	3.00E-02	5.00E-02
Benz(a)pyrene	5	0.3	3.60E-02	3.70E-02	3.80E-02	7.00E-02	6.10E-02
Dibenz(a,h)anthracene	5	0.3	4.00E-02	4.00E-02	4.50E-02	5.00E-02	4.80E-02
Benzo(g,h,i)perylene	6	3	3.00E-02	3.00E-02	3.20E-02	3.00E-02	2.00E-02
Indinol(1,2,3-cd)pyrene	6	-	2.00E-02	4.00E-02	2.50E-02	6.00E-02	3.30E-02
∑ of 17 PAHs			**5.55E-01**	**5.11E-01**	**5.32E-01**	**5.06E-01**	**5.19E-01**

MAC = Maximum Allowable Concentrations(ATSDR, 2006)

Table 3. Mean Concentrations of Some Polycyclic Aromatic Hydrocarbon in Sediment Samples from Different Sampling Points of Komadugu River Basin, Yobe State, Nigeria During the Dry Season.

			Concentrations (mg/kg)				
PAHsNo. of Rings		**MACs**	**S1**	**S2**	**S3**	**S4**	**S5**
Naphthalene	2	1	2.70E-02	2.50E-02	2.50E-02	2.30E-02	2.10E-02
2-methyl Napthalene	2	1	3.00E-02	3.00E-02	3.00E-02	3.00E-02	3.00E-02
Acenapthylene	3	3	3.00E-02	2.00E-02	3.00E-02	2.00E-02	2.00E-02
Acenaphthene	3	3	3.00E-02	2.10E-02	2.30E-02	2.20E-02	2.00E-02
Fluorene	3	3	3.40E-02	2.70E-02	3.20E-02	3.00E-03	2.50E-02
Phenanthrene	3	3	3.00E-02	2.30E-02	3.40E-02	3.10E-02	3.00E-02
Anthracene	3	3	2.50E-02	2.10E-02	2.90E-02	2.70E-02	2.00E-02
Fluoranthene	4	3	3.60E-02	3.00E-02	3.00E-02	3.70E-02	2.80E-02
Pyrene	4	3	5.20E-02	3.00E-02	3.00E-02	3.30E-02	3.00E-02
Benz(a)anthracene	4	0.15	3.00E-02	3.00E-02	3.00E-02	3.00E-02	3.00E-02
Chrysene	4		3.50E-02	3.30E-02	3.20E-02	3.10E-02	3.80E-02
Benz(b)fluoranthene	5	0.3	4.00E-02	4.50E-02	4.00E-02	4.00E-02	4.00E-02
Benz(k)fluoranthene	5		4.10E-02	4.40E-02	5.60E-02	3.20E-02	4.60E-02
Benz(a)pyrene	5	0.3	3.70E-02	3.70E-02	3.80E-02	3.60E-02	3.90E-02

Dibenz(a,h)anthracene	5	0.3	4.00E-02	4.00E-02	4.70E-02	5.20E-02	5.00E-02
Benzo(g,h,i)perylene	6	3	4.00E-02	3.80E-02	3.50E-02	3.30E-02	2.20E-02
Indinol(1,2,3-cd)pyrene	6	-	2.80E-02	3.00E-02	2.50E-02	4.00E-02	3.80E-02
∑ of 17 PAHs			**5.85E-01**	**5.24E-01**	**5.66E-01**	**5.20E-01**	**5.27E-01**

MACs = Maximum Allowable Concentrations(ATSDR, 2006)

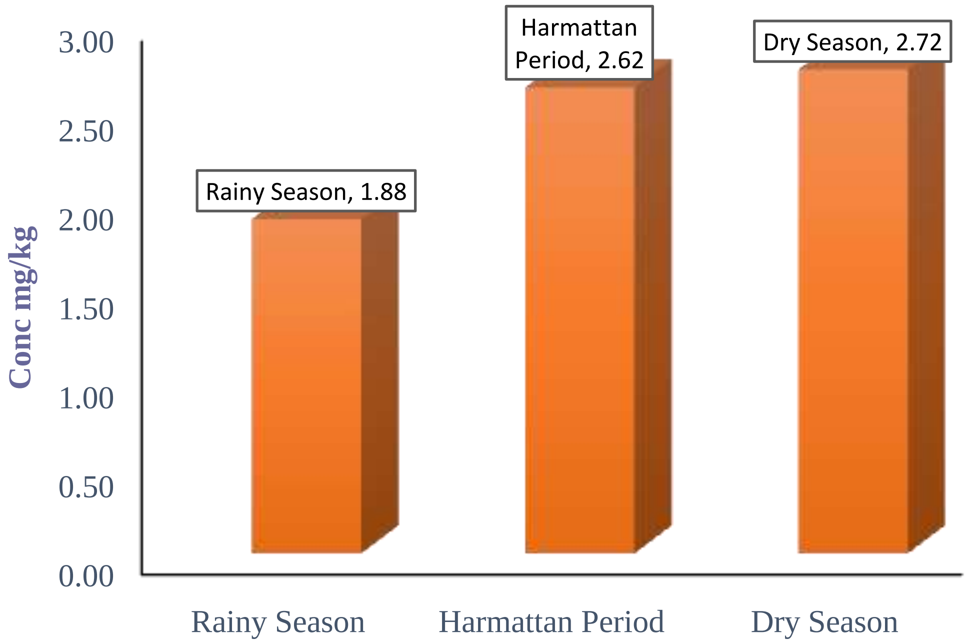

Fig. 2. Total Concentrations of PAHs in Sediment Samples from Komadugu River Basin, during the Rainy, Dry Seasons and Harmattan Period.

Benz(a)pyrene Equivalent in Sediment Sample from Different Sampling Points of Komadugu River Basin of Yobe State, Nigeria During the Rainy Season

Tables 4 to 6 shows the concentrations of benzo(a)pyrene equivalent PAHs in sediment samples for rainy, dry seasons and harmattan period from points S1 to S5 of Komadugu river basin, Yobe State Nigeria. The concentration of naphthalene ranged from 2.00E-05 to 5.00E-05 mg/kg; 1.42E-07 to 4.00E-05 mg/kg 2-methylnaphthalene; 8.70E-08 to 3.10E-05 mg/kg acenaphthylene; 1.90E-05 to 3.00E-05 mg/kg acenaphthene; 2.11E-05 to 3.40E-05 mg/kg fluorene; 2.00E-05 to 3.40E-05 mg/kg phenanthrene; 2.00E-04 to 2.90E-04 mg/kg anthracene; 1.42E-07 to 3.60E-05 mg/kg fluoranthene; 1.29E-06 to 6.00E-05 mg/kg pyrene; 2.50E-03 to 3.00E-03 mg/kg benzo(a)anthracene; 3.00E-05 to 4.00E-05 mg/kg chrysene; 9.73E-05 to 5.00E-03 mg/kg benzo(b)fluoranthene; 2.93E-04 to 1.98E+00 mg/kg benzo(k)fluoranthene; 2.64E-03 to 3.90E-2 mg/kg benzo(a)pyrene; 2.80E-04 to 5.20E-02 mg/kg dibenz(a.h)anthracene; 2.00E-04 to 4.00E-04 mg/kg benzo(g,h,i)perylene and 5.64E-06 to 6.00E-04 mg/kg indinol(1,2,3-cd)pyrene. The highest total concentrations of 1.98E+01 mg/kg was observed at point S3 during the rainy season, while point S5 shows the lowest total value of 8.49E-03 mg/kg during the same season.

Diagnostic Ratio of Some PAHs in Sediment Samples for Rainy, Dry Seasons and Harmattan Period from Different Sampling Points

Table 7 shows the diagnostic ratio of polycyclic aromatic hydrocarbon in Sediment Sample for rainy, dry seasons and harmattan period from Points S1 to S5 from Komadugu River Basin, Yobe State, Nigeria. The ratio of BaA/BaA+Chr ranged from 0.40 to 0.50; 0.40 to 0.50 for Ant/Ant+Phe; 0.40 to 0.50 for Flua/Flua+Pyr and 0.30 to 0.85 for LMW/HMW.

Table 4. Concentrations of Polycyclic Aromatic Hydrocarbon Benz(a)pyrene Equivalent in Sediment Samples from Different Sampling Points of Komadugu River Basin of Yobe State, Nigeria During the Rainy Season.

		Concentrations (mg/kg)				
PAHs	**No. of Rigs**	**S1**	**S2**	**S3**	**S4**	**S5**
Naphthalene	2	5.00E-05	5.00E-05	5.00E-05	5.00E-05	5.00E-05
2-methyl Napthalene	2	4.00E-05	4.00E-05	1.42E-07	2.67E-05	2.67E-05
Acenapthylene	3	2.00E-05	2.00E-05	8.70E-08	1.33E-05	1.33E-05
Acenaphthene	3	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05
Fluorene	3	3.00E-05	3.00E-05	2.14E-07	2.11E-07	1.50E-05
Phenanthrene	3	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05
Anthracene	3	2.00E-04	2.00E-04	2.00E-04	2.00E-04	2.00E-04
Fluoranthene	4	1.00E-05	1.00E-05	1.00E-05	1.01E-06	1.42E-07
Pyrene	4	5.00E-05	2.00E-05	2.80E-05	1.29E-06	2.80E-05
Benz(a)anthracene	4	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03
Chrysene	4	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05
Benz(b)fluoranthene	5	1.00E-03	1.00E-03	9.78E-05	1.10E-04	1.18E-04
Benz(k)fluoranthene	5	3.00E-03	3.00E-03	1.98E+00	2.93E-04	2.06E-03
Benz(a)pyrene	5	3.00E-02	3.00E-02	4.58E-03	9.13E-03	2.64E-03
Dibenz(a,h)anthracene	5	2.00E-02	2.00E-02	2.80E-04	8.21E-04	9.12E-04
Benzo(g,h,i)perylene	6	2.00E-04	2.00E-04	2.00E-04	2.00E-04	2.00E-04
Indinol(1,2,3-cd)pyrene	6	2.00E-04	2.00E-04	2.00E-04	5.64E-06	1.51E-04
∑BaPTEQ		**5.69E-02**	**5.69E-02**	**1.98E+01**	**1.29E-02**	**8.49E-03**

Table 5. Concentrations of Polycyclic Aromatic Hydrocarbon Benz(a)pyrene Equivalent in Sediment Samples from Different Sampling Points of Komadugu River Basin of Yobe State, Nigeria During the Harmattan Period.

		Concentrations (mg/kg)				
PAHs	**No. of Rigs**	**S1**	**S2**	**S3**	**S4**	**S5**
Naphthalene	2	3.00E-05	2.00E-05	3.00E-05	2.00E-05	2.00E-05
2-methyl Napthalene	2	3.00E-05	3.00E-05	2.00E-05	2.50E-05	2.70E-05
Acenapthylene	3	3.00E-05	2.00E-05	3.10E-05	1.20E-05	1.40E-05
Acenaphthene	3	3.00E-05	2.00E-05	2.00E-05	1.90E-05	2.00E-05
Fluorene	3	3.30E-05	2.40E-05	3.00E-05	3.00E-06	2.00E-05
Phenanthrene	3	3.20E-05	2.00E-05	3.00E-05	3.00E-05	2.80E-05
Anthracene	3	2.10E-04	2.00E-04	2.00E-04	2.00E-04	2.30E-04
Fluoranthene	4	1.30E-05	3.00E-05	3.00E-05	1.20E-05	2.00E-05
Pyrene	4	6.00E-05	3.00E-05	3.10E-05	2.90E-05	2.80E-05
Benz(a)anthracene	4	3.00E-03	3.00E-03	3.00E-03	2.50E-03	2.80E-03
Chrysene	4	3.50E-05	3.00E-05	3.00E-05	3.10E-05	4.00E-05
Benz(b)fluoranthene	5	4.00E-03	5.00E-03	4.00E-03	4.00E-03	3.90E-03
Benz(k)fluoranthene	5	4.50E-03	4.00E-03	5.00E-03	3.00E-03	5.00E-03
Benz(a)pyrene	5	3.60E-02	3.70E-02	3.80E-02	7.00E-02	6.10E-02
Dibenz(a,h)anthracene	5	4.00E-02	4.00E-02	4.50E-02	5.00E-02	4.80E-02
Benzo(g,h,i)perylene	6	3.00E-04	3.00E-04	3.20E-04	3.00E-04	2.00E-04
Indinol(1,2,3-cd)pyrene	6	2.00E-04	4.00E-04	2.50E-04	6.00E-04	3.30E-04
BaPTEQ		**8.85E-02**	**9.01E-02**	**9.60E-02**	**1.31E-01**	**1.22E-01**

Table 6. Concentrations of Polycyclic Aromatic Hydrocarbon Benz(a)pyrene Equivalent in Sediment Samples from Different Sampling Points of Komadugu River Basin of Yobe State, Nigeria During the Dry Season.

		Concentrations (mg/kg)				
PAHs	**No. of Rigs**	**S1**	**S2**	**S3**	**S4**	**S5**
Naphthalene	2	2.70E-05	2.50E-05	2.50E-05	2.30E-05	2.10E-05
2-methyl Napthalene	2	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05
Acenapthylene	3	3.00E-05	2.00E-05	3.00E-05	2.00E-05	2.00E-05
Acenaphthene	3	3.00E-05	2.10E-05	2.30E-05	2.20E-05	2.00E-05
Fluorene	3	3.40E-05	2.70E-05	3.20E-05	3.00E-06	2.50E-05
Phenanthrene	3	3.00E-05	2.30E-05	3.40E-05	3.10E-05	3.00E-05
Anthracene	3	2.50E-04	2.10E-04	2.90E-04	2.70E-04	2.00E-04
Fluoranthene	4	3.60E-05	3.00E-05	3.00E-05	3.70E-05	2.80E-05
Pyrene	4	5.20E-05	3.00E-05	3.00E-05	3.30E-05	3.00E-05
Benz(a)anthracene	4	3.00E-03	3.00E-03	3.00E-03	3.00E-03	3.00E-03
Chrysene	4	3.50E-05	3.30E-05	3.20E-05	3.10E-05	3.80E-05
Benz(b)fluoranthene	5	4.00E-03	4.50E-03	4.00E-03	4.00E-03	4.00E-03
Benz(k)fluoranthene	5	4.10E-03	4.40E-03	5.60E-03	3.20E-03	4.60E-03
Benz(a)pyrene	5	3.70E-02	3.70E-02	3.80E-02	3.60E-02	3.90E-02
Dibenz(a,h)anthracene	5	4.00E-02	4.00E-02	4.70E-02	5.20E-02	5.00E-02
Benzo(g,h,i)perylene	6	4.00E-04	3.80E-04	3.50E-04	3.30E-04	2.20E-04
Indinol(1,2,3-cd)pyrene	6	2.80E-04	3.00E-04	2.50E-04	4.00E-04	3.80E-04
∑BaPTEQ		**8.93E-02**	**9.00E-02**	**9.88E-02**	**9.94E-02**	**1.02E-01**

Table 7. Diagnostic Ratio of Polycyclic Aromatic Hydrocarbon in Sediment Samples from Different Points of Komadugu River Basin of Yobe State, Nigeria During the Rainy, Dry Seasons and Harmattan Period.

	Rainy Season				**Harmattan Period**				**Dry Season**			
PTS	**BaA/BaA+Chr**	**Ant/Ant+Phe**	**Flua/Flua+Pyr**	**L/W**	**BaA/BaA+Chr**	**Ant/Ant+Phe**	**Flua/Flua+Pyr**	**L/H**	**BaA/BaA+Chr**	**Ant/Ant+Phe**	**Flua/Flua+Pyr**	**L/H**
S1	0.40	0.40	0.45	0.88	0.50	0.40	0.40	0.60	0.50	0.50	0.40	0.50
S2	0.40	0.40	0.40	0.85	0.50	0.50	0.50	0.40	0.50	0.50	0.50	0.50
S3	0.40	0.40	0.45	0.73	0.50	0.40	0.50	0.50	0.50	0.50	0.50	0.60
S4	0.40	0.40	0.44	0.88	0.40	0.40	0.40	0.30	0.50	0.50	0.50	0.40
S5	0.40	0.40	0.40	0.60	0.40	0.50	0.40	0.40	0.40	0.40	0.50	0.50
MR	**0.40**	**0.40**	**0.43**	**0.70**	**0.46**	**0.44**	**0.44**	**0.44**	**0.48**	**0.48**	**0.48**	**0.50**

BaA = Benz(a)anthracene, Chry = Chrysene, Anth = Anthracene, Phen = Phenanthrene, Fluo = Fluorene, Py = Pyrene, L = low molecular weight, H = high molecular weight

Mean Effect Range Medium (ERM) Quotient of Some PAHs in Sediment Samples for Rainy, Dry Seasons and Harmattan Period

Tables 8 to 10 shows the mean effect range medium (ERM) quotient of polycyclic aromatic hydrocarbon in Sediment Sample for rainy, dry seasons and harmattan period from Komadugu River Basin, Yobe State, Nigeria. The concentration for naphthalene ranged from 6.12E-09 to 9.52E-06; 6.68E-08 to 5.97E-05 2-methylnaphthalene; 7.32E-08 to 4.84E-05 acenaphthylene; 1.20E-07 to 4.00E-05 acenaphthene; 1.17E-07 to 6.30E-05 fluorene; 1.33E-08 to 2.27E-05 phenanthrene; 08 to 2.64E-05 anthracene; 1.38E-09 to 7.25E-06 fluoranthene; 7.69E-09 to 2.31E-05 pyrene; 2.07E-08 to 1.75E-05 benzo(a)anthracene; 4.46E-09 to 1.43E-05 Chrysene; 1.17E-1.45E-08 to 4.38E-05 benzo(a)pyrene; 5.92E-07 to 2.00E-04 dibenz (a.h) anthracene; 3.67E-07 to 1.21E-04 benzo(g,h,i)perylene and 3.10E-08 to 6.32E-05 indinol(1,2,3-cd)pyrene. Point S1 shows the highest total mean effect range medium (ERM) quotient with a value of 4.37E-05 during the dry season, while point S2 shows the lowest value of 9.64E-08 during the same period.

Table 8. Mean Effect Range Medium (ERM) Quotient of Polycyclic Aromatic Hydrocarbon in Sediment Samples from Komadugu River Basin of Yobe State, Nigeria During the Rainy Season.

PAHs	ERM SSG	S1	S2	S3	S4	S5
Naphthalene	2100	2.38E-05	2.38E-05	2.38E-05	2.38E-05	2.38E-05
2-methyl Napthalene	670	5.97E-05	5.97E-05	2.12E-07	3.99E-05	3.99E-05
Acenapthylene	640	3.13E-05	3.13E-05	1.36E-07	2.08E-05	2.08E-05
Acenaphthene	500	4.00E-05	4.00E-05	4.00E-05	4.00E-05	4.00E-05
Fluorene	540	5.56E-05	5.56E-05	3.96E-07	3.91E-07	2.78E-05
Phenanthrene	1500	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05
Anthracene	1100	1.82E-05	1.82E-05	1.82E-05	1.82E-05	1.82E-05
Fluoranthene	5100	1.96E-06	1.96E-06	1.96E-06	1.98E-07	2.78E-08
Pyrene	2600	1.92E-05	7.69E-06	1.08E-05	4.96E-07	1.08E-05
Benz(a)anthracene	1600	1.25E-05	1.25E-05	1.25E-05	1.25E-05	1.25E-05
Chrysene	2800	1.07E-05	1.07E-05	1.07E-05	1.07E-05	1.07E-05
Benz(b)fluoranthene	-	-	-	-	-	-
Benz(k)fluoranthene	-	-	-	-	-	-
Benz(a)pyrene	1600	1.88E-05	1.88E-05	2.86E-06	5.71E-06	1.65E-06
Dibenz(a,h)anthracene	260	7.69E-05	7.69E-05	1.08E-06	3.16E-06	3.51E-06
Benzo(g,h,i)perylene	330	6.06E-05	6.06E-05	6.06E-05	6.06E-05	6.06E-05
Indinol(1,2,3-cd)pyrene	950	2.11E-05	2.11E-05	2.11E-05	5.94E-07	1.59E-05
M-ERM-Q		**3.13E-053.06E-051.50E-051.71E-052.04E-05**				

Table 9. Mean Effect Range Medium (ERM) Quotient of Polycyclic Aromatic Hydrocarbon in Sediment Samples from Komadugu River Basin of Yobe State, Nigeria During the Harmattan Period.

PAHs	ERM SSG	S1	S2	S3	S4	S5
Naphthalene	2100	1.43E-05	9.52E-06	1.43E-05	9.52E-06	9.52E-06
2-methyl Napthalene	670	4.48E-05	4.48E-05	2.99E-05	3.73E-05	4.03E-05
Acenapthylene	640	4.69E-05	3.13E-05	4.84E-05	1.88E-05	2.19E-05
Acenaphthene	500	6.00E-05	4.00E-05	4.00E-05	3.80E-05	4.00E-05
Fluorene	540	6.11E-05	4.44E-05	5.56E-05	5.56E-06	3.70E-05
Phenanthrene	1500	2.13E-05	1.33E-05	2.00E-05	2.00E-05	1.87E-05
Anthracene	1100	1.91E-05	1.82E-05	1.82E-05	1.82E-05	2.09E-05
Fluoranthene	5100	2.55E-06	5.88E-06	5.88E-06	2.35E-06	3.92E-06
Pyrene	2600	2.31E-05	1.15E-05	1.19E-05	1.12E-05	1.08E-05
Benz(a)anthracene	1600	1.88E-05	1.88E-05	1.88E-05	1.56E-05	1.75E-05
Chrysene	2800	1.25E-05	1.07E-05	1.07E-05	1.11E-05	1.43E-05
Benz(b)fluoranthene	-	-	-	-	-	-
Benz(k)fluoranthene	-	-	-	-	-	-
Benz(a)pyrene	1600	2.25E-05	2.31E-05	2.38E-05	4.38E-05	3.81E-05
Dibenz(a,h)anthracene	260	1.54E-04	1.54E-04	1.73E-04	1.92E-04	1.85E-04
Benzo(g,h,i)perylene	330	9.09E-05	9.09E-05	9.70E-05	9.09E-05	6.06E-05
Indinol(1,2,3-cd)pyrene	950	2.11E-05	4.21E-05	2.63E-05	6.32E-05	3.47E-05
M-ERM-Q		**4.08E-05**	**3.72E-05**	**3.96E-05**	**3.85E-05**	**3.69E-05**

Table 10. Mean Effect Range Medium (ERM) Quotient of Polycyclic Aromatic Hydrocarbon in Sediment Samples from Komadugu River Basin of Yobe State, Nigeria During the Dry Season.

PAHs	ERM SSG	S1	S2	S3	S4	S5
Naphthalene	2100	1.29E-05	6.12E-09	1.19E-05	1.10E-05	1.00E-05
2-methyl Napthalene	670	4.48E-05	6.68E-08	4.48E-05	4.48E-05	4.48E-05
Acenapthylene	640	4.69E-05	7.32E-08	4.69E-05	3.13E-05	3.13E-05
Acenaphthene	500	6.00E-05	1.20E-07	4.60E-05	4.40E-05	4.00E-05
Fluorene	540	6.30E-05	1.17E-07	5.93E-05	5.56E-06	4.63E-05
Phenanthrene	1500	2.00E-05	1.33E-08	2.27E-05	2.07E-05	2.00E-05
Anthracene	1100	2.27E-05	2.07E-08	2.64E-05	2.45E-05	1.82E-05
Fluoranthene	5100	7.06E-06	1.38E-09	5.88E-06	7.25E-06	5.49E-06
Pyrene	2600	2.00E-05	7.69E-09	1.15E-05	1.27E-05	1.15E-05
Benz(a)anthracene	1600	1.88E-05	1.17E-08	1.88E-05	1.88E-05	1.88E-05
Chrysene	2800	1.25E-05	4.46E-09	1.14E-05	1.11E-05	1.36E-05
Benz(b)fluoranthene	-	-	-	-	-	-
Benz(k)fluoranthene	-	-	-	-	-	-
Benz(a)pyrene	1600	2.31E-05	1.45E-08	2.38E-05	2.25E-05	2.44E-05
Dibenz(a,h)anthracene	260	1.54E-04	5.92E-07	1.81E-04	2.00E-04	1.92E-04
Benzo(g,h,i)perylene	330	1.21E-04	3.67E-07	1.06E-04	1.00E-04	6.67E-05
Indinol(1,2,3-cd)pyrene	950	2.95E-05	3.10E-08	2.63E-05	4.21E-05	4.00E-05
M-ERM-Q		**4.37E-05**	**9.64E-08**	**4.28E-05**	**3.97E-05**	**3.89E-05**

DISCUSSION

Distribution of PAHs in Sediment Samples

The levels of all the studied PAHs were observed to be higher in the harmattan period and dry season with values of 2.62E+00 mg/kg and 2.72E+00 mg/kg respectively, while rainy season shows the lowest concentration with a value of 1.88E+00 mg/kg (Fig. 2).

This might be attributed to sedimentation and reduction in water volume during the harmattan period and the dry season. The lowest total concentration during the rainy seasons might be attributed to wash out of pollutants during the rainy season and also increased in volume and speed of water. The application of diagnostic ratio and cancer risk assessment in sediment samples is paramount in order to predict the sources of PAHs and evaluate the cancer risk to benthic organisms.

Diagnostic Ratio Analysis of PAHs in Sediment Samples

PAHs diagnostic ratio is used as a tool for identifying and assessing pollution sources (Zhang *et al*., 2004). The diagnostic ratios used in the present study were BaA / BaA + Chr, Ant / Ant + Phe, Flue / Flue + Pyr and LMW/HMW ratio. Ant / Ant + Phe ratio of > 0.1 indicate dominance of heavy fuel composition, while < 0.1 indicate petroleum source, BaA / BaA + Chr ratio of 0.2 to 0.35 indicate mixed petrogenic and pyrogenic origin and > 0.35 indicate pyrogenic origin (Zhang, 2004). Table 7 shows the diagnostic PAH ratios for sediment from komadugu river basin. The ratios of BaA / BaA + Chr were between 0.40 and 0.50 with mean of 0.57 suggestive pyrogenic origin. The Ant/ Ant + Phe ratios were between 0.40 and 0.50 indicating pyrogenic sources. The LMW/HMW ratios were low for most sites < 1 indicating pyrogenic origin of PAHs to the sediments. Values of Flua /Flua + Pyr ratios is used to distinguish between different combustion origins such as burning of liquid fossil fuels or coal wood or grass (Jiao *et al*., 2013). The mean Flua /Flua+Pyr of 0.44 confirm the combustion of fuel and pyrogenic as the main PAH source in the study area. The diagnostic ratios show both fuel combustion and pyrogenic sources of PAH in the study area.

Ecotoxicity Studies of PAHs in Sediment Samples

To assess the potency toxicity of sediments in Komadugu river basin, PAH levels in the sediments were compared with the sediment toxicity screening guidelines values. Screening values are concentrations of a contaminant in sediment, which if exceeded may prompt further risk assessment. Mean ERM quotient m- ERM-q were calculated and compared with the screening values. According to Long and MacDonald (1998), m-ERM-q are categorised according to their possibility of toxicity. Values ≤ 0.1 indicates an 11 percent probability of toxicity, 0.1 to 0.5 indicates a 30% probability of toxicity and 0.5 to 1.5 indicates a 46% probability of toxicity and > 1.5 indicates a 75% probability of toxicity (Nasher *et al*., 2013). Calculated ERMs of individual PAHs and the mean ERM quotient of PAHs for this study are shown in Tables 4.18 to 4.20. The m-ERM-q values ranged from 9.64E-08 to 4.37E-05 in the sediments with a mean value of 3.15E-05, which were below 0.1 indicating an 11 percent probability of toxicity and are therefore classified as low priority sites. Similar results were reported for sediments of Langkawi Island, Malaysia (Nasher *et al*., 2013). The implication of this result is that there was minimal effect of PAH on sediment functions such as the capacity to act as substrate for aquatic life.

Carcinogenic Risk Assessment of PAHs in Sediment Samples

Carcinogenic risk assessment was performed using total toxic BaP equivalent of PAHs. Toxic equivalency factor and total carcinogenic toxic equivalency factors for all sediments studied as presented in Tables 4 to 6. Total carcinogenic toxic equivalency factors ranged from 8.49E-03 to 1.98E+01 mg/kg-Bapeq dry weight with a mean of 1.40E+00 mg/kg dry weight. The results revealed that BaA, B(b)F, B(k)F, B(a)P and D(a, h)A were the most contributors to total carcinogenic potency of the sediment samples with values ranged from 2.00E-03 to 3.00E-03 mg/kg for BaA, 1.00E-03 to 5.00E-03 mg/kg for B(b)F, 2.06E-03 to 1,98E+00 mg/kg for B(k)F, 2.64E-03 to 7.00E-02 mg/kg for B(a)P and 2.00E-02 to 5.20E-02 mg/kg for DBA. These PAHs are highly carcinogenic (Yu *et al*., 2014). BaP is considered the most hazardous of the PAHs (Wang *et al*., 2009). This shows that the sediment are potentially carcinogenic. Comparing the result from the present study with those of other studies, the values obtained were comparable to those of surface sediment in Terragona, Spain (124µg/kg BaPeq), lower than those from Liaohe estuarine sediment (28.4 µg/kg), and those in surface sediment of India (650 µg/kg) and Shanghai, China (892 µg/kg BaPeq). The high carcinogenic potency of PAHs is an indication of high degree of carcinogenic risk in the above areas when compared to the present studies.

CONCLUSION

The obtained results demonstrate that the studied PAHs in the sediment samples were below the maximum allowable concentrations (MACs). Results from diagnostic ratios show both fuel combustion and pyrogenic sources of PAH in the study area. The m-ERM-q in the sediments were below 0.1 indicating an 11 percent probability of toxicity and are therefore classified as low priority sites.

REFERNCES

Boyd, CE. and Tucker, CS. 1992. Water Quality and Pond Soil Analysis for Aquaculture. Alabama Agricultural Experimental Station. Auburn University. pp183.

Ellenhorn, MJ. and Barceloux, DG. 1988. Polycyclic Aromatic Hydrocarbon. In: Medical Toxicology: Diagnosis and Treatment of poisoning. Eds. Ellenhon MJ. and Barceloux, DG. Elsevier, New York, USA. 952-954.

GIS. 2015. Maps of the study areas. Department of Geography, Laboratory University of Maiduguri, Borno State Nigeria.

Glenn, AR. 1995. Activated carbon applications in the food and pharmaceutical industries. CRC Press. pp125.

Jiao, W., Wang, T., Khim, JS., Luo,W., Hu, W., Naile, JE., Giesy, JP. and Lu, Y. 2013. Policyclic aromatic hydrocarbons in soils along the coastal and estuarine areas of the Northern Bohai and Yellow Seas, China. Environmental Monitoring and Assessment. 185:8185-95.

Long, ER. and MacDonald, DD. 1998. Predicting toxicity in marine sediments with numerical sediment quality guidelines. Environmental Toxicology and Chemistry. 17:714-727.

Menzie, CA., Potocki, BB. and Santodonato, J. 1992. Exposure to carcinogenic PAHs in the environment. Environmental Science Technology. 26:1278.

Nasher, E., Yook, L., Heng, Z. and Surif, S. 2013. Assessing the ecological risk of Polycyclic aromatic hydrocarbons in sediments at Langkawi Island, Malaysia. The Scientific World Journal, doi:10.1155/2013/858309.

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

NPC. (National Population Commission). 1991. Population census. November, 1991.

Resource Inventory and Management. 1992. Nigeria livestock resources. Rim ltd for federal department of livestock and pest control services. Jersey. U.K.

Santodonato, J. 1981. Polycyclic organic matter. Journal of Environmental Pathology and Toxicology. 5:1.

Schultz. 1976. Hadejia river basin study. Canadian International Development Agency in Final Report. 1-8.

Sims, RC. and Overcash, R. 1983. Fate of polynuclear aromatic compounds (PNAs) in soil-plant systems. Residue Reversed. 88:1-68.

USEPA. 2000. Method 8270, Semi volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846).

Wang, LW., Yang, ZF., Niu, JF. and Wang, JY. 2009. Characterization, ecological risk assessment and source diagnostics of polycyclic aromatic hydrocarbons in water column of the Yellow River Delta, one of the most plenty biodiversity zones in the world. Journal of Hazardous Matter.169:462-463.

Wania, F. and Mackay, D. 1996. Tracking the distribution of persistent organic pollutants: Control strategies for these contaminants will require a better understanding of how they move around the globe. Environmental Science and Technology. 30(9):390A-396A.

Wild, SR. and Jones, KC. 1995. Polycyclic aromatic hydrocarbon in United Kingdom environment: a preliminary source inventory and budget. Environmental Pollution. 88**:**91.

Yu, Y., Li, Y. X., Shen, ZY., Yang, ZF., Mo, L., Kong, YH. and Lou, IC. 2014. Occurrence and possible sources of organo chlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) along the Chao River, China. Chemosphere. 114:137-141.

Zhang, HB., Luo, YM., Wong, MH., Zhao, QG. and Zhang, GL. 2004. Distributions and concentrations of PAHs in Hong Kong soils. Environmental Pollution. 141:109-112.

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