



Research Article

Levels of Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments from Dadin Kowa Dam, Gombe State, Nigeria

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ABSTRACT

The large class of organic compounds known as polycyclic aromatic hydrocarbons (PAHs) contains two or more fused aromatic (benzene) rings. The burning of agricultural waste and incomplete combustion or pyrolysis of organic material (i.e., emissions from cars, home heating, or cooking) are the two main anthropogenic sources of emissions. Humans may encounter PAHs through inhalation, dermal exposure, or eating food that has been contaminated. According to epidemiological studies, PAHs are linked to poorer lung function, worsening asthma, cancer, higher rates of obstructive lung diseases, and cardiovascular diseases. This raised questions and called for investigation and awareness of the risks posed by these pollutants. Herein, sediment was collected from Dadin Kowa Dam, Gombe State, Nigeria, during the dry and rainy seasons for assessing the levels of polycyclic aromatic hydrocarbon (PAH) residues. The collected samples were extracted, cleaned up, and analyzed for the presence of PAHs using GC-MS equipped with a flame ionization detector. The result shows that concentrations of all the PAHs studied in the sediment samples during the dry season ranged from 6.40E-01 to 1.09E +00 mg/kg, while during the rainy season they ranged from 4.60E+01 to 5.42E +01 mg/kg. The rainy season showed the highest total concentration of all the PAHs studied when compared to the dry season. The result from the diagnostic ratio showed the ratios of Ant/(Ant + Phe) ranged from 0.40-0.52; 0.33-0.58 Fla/(Fla + Pyr); and 0.08-0.5 BaA/(BaA + Chr). Generally, the findings of this work proved that pyrogenic inputs contributed to PAH contamination in the sediment from the study area. The result from the mean effect medium quotient (m-ERM-q) in the sediment samples ranged from 4.52E-05 to 1.41E+01 for both seasons, with a mean value of 5.13E-02.

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) stand as a remarkable class of organic pollutants, recognized for their ubiquity and environmental persistence. These compounds, characterized by two or more fused benzene rings, are alternately termed polyanes or polynuclear aromatic hydrocarbons. Their presence pervades various environmental matrices, owing to their origin in pyrolytic processes and the incomplete combustion of organic matter, with human activities being the predominant contributors (Smith *et al.*, 2022; Johnson & Ramirez, 2023). PAHs have garnered substantial attention due to their profound impact on both environmental integrity and human health. The European Environment Agency (EEA) has taken a firm stance on PAHs by designating them as priority pollutants. This recognition stems from their capacity to endure in environmental compartments, their propensity to accumulate within biota, and their potential to undergo transformations into more reactive forms (EEA, 2020). Furthermore, these pollutants have been linked to a spectrum of severe health effects in humans. Notably, exposure to environments contaminated with PAHs has been associated with the onset of fatal diseases such as lung and skin cancers (Chen, 1997; Smith *et al.*, 2021).

The persistence of PAHs in the environment is a product of their distinct chemical properties. Their substantial hydrophobicity renders them prone to interacting with environmental matrices like soils, sediments, and biota. This tendency subsequently leads to bioaccumulation in adipose tissues and their subsequent magnification through the food chain (WHO-IPCS, 1998). The stability of PAHs, which renders them recalcitrant to hydrolysis, coupled with their susceptibility to oxidation and photo-degradation, further contributes to their environmental resilience (Howard, 1991; IPCS, 1998). PAHs exhibit varying degrees of degradation in different environmental compartments. For instance,

their half-lives in the atmosphere range from mere hours to several days, while in soil environments, they span from months to years, contingent upon factors such as adsorption mechanisms and molecular weights (Park *et al.*, 1999). Research has revealed that abiotic degradation can account for the removal of 2-20% of two and three ring PAHs from contaminated soils, with higher molecular weight PAHs persisting due to their strong affinity for organic matter (Park *et al.*, 1999). The intricate interplay of parameters ultimately governs the fate of PAHs, influencing their degradation rates and persistence in the environment.

In the pursuit of understanding the behavior and impact of PAHs, a plethora of researchers have delved into their intricate characteristics and effects. Smith *et al.* (2022) conducted an extensive review, shedding light on the sources, fate, and health implications of PAHs. Their study synthesized findings from diverse sources, providing a comprehensive overview of the current state of knowledge. Johnson and Ramirez (2023) further emphasized the role of human activities in driving the prevalence of PAHs in the environment. By analyzing combustion processes and emission patterns, they underscored the need for effective mitigation strategies.

Study Area

Dadin Kowa Dam is located 5km North of Dadin Kowa village (about 37km from Gombe town, along Gombe-Biu road) in Yamaltu Deba local Government Area of Gombe State (FIG 1 and Map 1). The area lies within longitude 11° 30' E and 11° 32' E, and Latitude 10° 17' and 10° 18' N of the equator (UBRDA, 1980). The Dam got its source from River Dadin Kowa, which also got its source of water from River Gongola, its drainage basin is situated in North-Eastern Nigeria, with water capacity of 800 million cubes and surface area of 300 kilometers square has potential as a source of fish (Timawus, 2010) 26,000 people were displaced by the reservoir, receiving little assistance for resettlement

(William, 1994). The source of the river is located on the Jos Plateau which has been described as the hydrological center of Nigeria. Water drains radially from the plateau into the Lake Chad basin to the north, the river Niger to the west, the River Benue to the south and the Gongola River to the east. In parts the plateau rises to an elevation of over 1700 m but the general altitude is about 1200 m. After leaving the plateau the Gongola flows a north

easterly direction across the Bauchi high plains for about 350 km to Nafada where the approximate elevation is 260 m. Near Nafada the river changes and flows southwards for about 100 km to Dadin kowa at an elevation of approximately 210 m. The River then follows roughly south-easterly course for 150 km before joining the River Benue, which in turn is the major tributary of the River Niger.

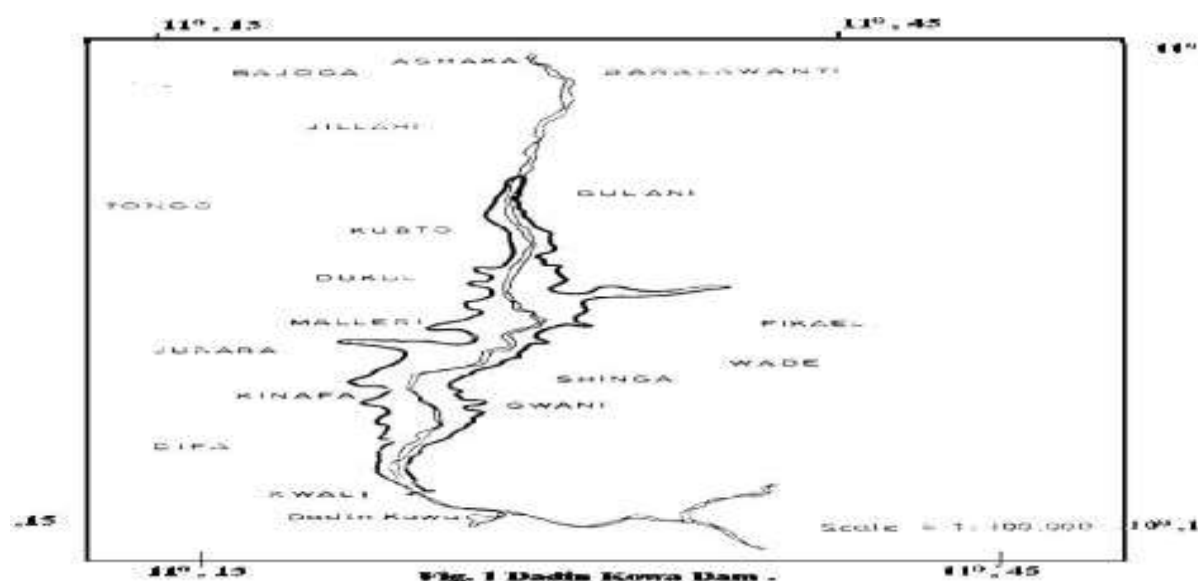


Fig 1: Map Showing Dadin kowa Dam.

Source: Upper Benue River Development Authority Dadin Kowa (UBRDA, 1980).

Materials and Methods

Collection of Sediment Samples

Sampling was carried out during the dry and rainy seasons. Sediment samples were collected from ten sampling points designated S₁- S₁₀. Point S₁ was the point of flow of water into Dadin Kowa Dam. Point S₂ to S₁₀ were 3km away from each other, making a total of 30km for the study. The sediment samples

Sample Preparation

Extraction of PAHs in Sediment Samples

Analysis for PAH in sediment samples was carried out in accordance with USEPA 8270 analytical method. 10 g of the sample were dried using anhydrous sodium sulphate and 1mL of 60 ug/mL o-Terphenyl surrogate standard added and mixed thoroughly with the sample. Thirty (30 mL) of methylene chloride

were collected using plastic hand trowel by scooping 0-5 cm of the top layer of the sediment and placed in an amber glass bottle and stored in an ice-block cooler as described by Boy'd and Tucker, (1992). The sample was transported to the Department of Pure and Applied Chemistry laboratory, University of Maiduguri and stored in a refrigerator pending extraction and analysis.

was then added and the sample extracted. The sample extract was subsequently filtered through glass wool containing anhydrous sodium sulphate in a glass funnel. 2 g of silica gel was added and allowed to stand for 5 min the extract was then decanted and allowed to concentrate at room temperature to 1mL volume.

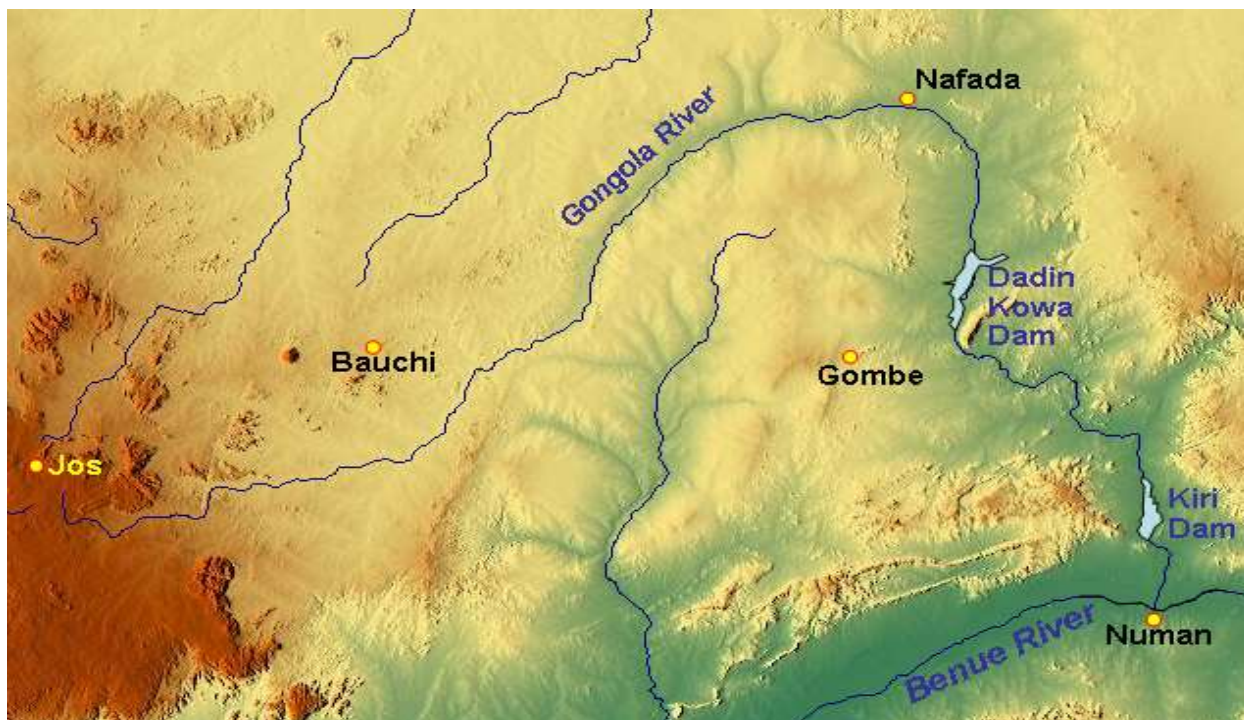


Figure 2: Map of Gongola River showing the Main Source of the Dadin-Kowa Dam.
Source: Encyclopedia Britannica. Retrieved 2010-05-21

Determination of PAHs in Sediment and Sample

The extract was thereafter analyzed using Agilent 7890A GC/MS previously calibrated with PCBs 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.

RESULTS AND DISCUSSION

Calibration and Percentage Recovery

Performance evaluation, Quality control and Quality assurance were achieved using Standard reference material from National Institute of Science and Technology.

PAHs Concentrations

Table 1 to 2 shows the mean concentrations of some polycyclic aromatic hydrocarbon in sediment samples for dry and rainy season from points S1 to S10 of Dadin Kowa Dam Gombe

State Nigeria. The concentration of naphthalene ranged from $2.00\text{E-}02$ to $1.09\text{E+}00$ mg/kg; $2.00\text{E-}02$ to $1.07\text{E+}00$ mg/kg 2-methylnaphthalene; $2.00\text{E-}02$ to $8.80\text{E-}01$ mg/kg acenaphthylene; $2.00\text{E-}02$ to $9.80\text{E-}01$ mg/kg acenaphthene; $3.00\text{E-}02$ to $6.40\text{E-}01$ mg/kg Fluorene; $3.00\text{E-}02$ to $6.50\text{E-}01$ mg/kg phenanthrene; $2.00\text{E-}02$ to $6.60\text{E-}01$ mg/kg anthracenes $1.00\text{E-}02$ to $7.70\text{E-}01$ mg/kg fluoranthene; $2.00\text{E-}02$ to $6.10\text{E-}01$ mg/kg pyrene; $2.00\text{E-}02$ to $4.23\text{E+}00$ mg/kg benzo(a)anthracene; $2.00\text{E-}02$ to $5.98\text{E+}00$ mg/kg chrysene; $3.00\text{E-}02$ to $7.98\text{E+}00$ mg/kg benzo(b)fluoranthene; $6.00\text{E-}02$ to $7.34\text{E+}00$ mg/kg benzo(k)fluoranthene; $6.00\text{E-}02$ to $6.37\text{E+}00$ mg/kg benzo(a)pyrene; $4.00\text{E-}02$ to $6.76\text{E+}00$ mg/kg dibenz(a,h)anthracene; $6.00\text{E-}02$ to $8.09\text{E+}00$ mg/kg benzo(g,h,i)perylene and $5.00\text{E-}02$ to $8.23\text{E+}00$ mg/kg indinol(1,2,3-cd)pyrene. The highest total concentration of $5.42\text{E+}01$ mg/kg was observed at point S1 during the rainy season, while point S2 shows the lowest total value of $6.40\text{E-}01$ mg/kg during the dry season.

Table 1: Mean Concentrations of Some Polycyclic Aromatic Hydrocarbons in Sediment Samples Dry Season

PAHs	Concentrations (mg/kg)											
	No of Rings	MAC'S	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Naphthalene	2	1	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02
2-methyl Naphthalene	2	1	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02
Acenaphthylene	3	3	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02
Acenaphthene	3	3	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02
Fluorene	3	3	3.00E-02	3.00E-02	3.00E-02	3.00E-02	3.00E-02	3.00E-02	3.00E-02	3.00E-02	3.00E-02	3.00E-02
Phenanthrene	3	3	3.00E-02	3.00E-02	3.00E-02	3.00E-02	3.00E-02	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	3.00E-02	2.00E-02	2.00E-02	3.00E-02	2.00E-02	2.00E-02	3.00E-02
Fluoranthene	4	3	1.00E-02	1.00E-02	1.00E-02	2.00E-02	1.00E-02	1.00E-02	2.00E-02	1.00E-02	1.00E-02	2.00E-02
Pyrene	4	3	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02
Benz(a)anthracene	4	0.15	2.00E-02	2.00E-02	2.00E-02	2.00E-02	2.00E-02	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	3.00E-02	3.00E-02	3.00E-02	3.00E-02	3.00E-02
Benz(b)fluoranthene	5	0.3	1.30E-01	6.00E-02	1.10E-01	1.40E-01	7.00E-02	8.00E-02	6.00E-02	2.10E-01	1.10E-01	1.20E-01
Benz(k)fluoranthene	5	-	6.00E-02	7.00E-02	2.30E-01	1.30E-01	1.10E-01	9.00E-02	1.30E-01	1.10E-01	6.00E-02	8.00E-02
Benz(a)pyrene	5	0.3	5.00E-02	8.00E-02	1.40E-01	1.50E-01	8.00E-02	1.10E-01	1.70E-01	8.00E-02	8.00E-02	9.00E-02
Dibenz(a,h)anthracene	5	0.3	4.00E-02	6.00E-02	6.00E-02	8.00E-02	9.00E-02	1.40E-01	1.50E-01	1.80E-01	1.10E-01	1.60E-01
Benzo(g,h,i)perylene	6	3	6.00E-02	8.00E-02	9.00E-02	1.10E-01	7.00E-02	1.70E-01	9.00E-02	1.60E-01	1.40E-01	1.10E-01
Indinol(1,2,3-cd)pyrene	6	-	7.00E-02	5.00E-02	1.00E-01	1.40E-01	1.40E-01	1.10E-01	1.00E-01	1.10E-01	1.50E-01	2.10E-01
Σ of 17 PAHs			6.50E-01	6.40E-01	9.70E-01	1.01E+00	8.00E-01	9.40E-01	9.60E-01	1.09E+00	8.90E-01	1.03E+00

Table 2: Mean Concentrations of Some Polycyclic Aromatic Hydrocarbons in Sediment Samples During the Rainy Season

PAHs	No of Rings MAC'S		Concentrations(mg/kg)									
			S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Naphthalene	2	1	7.60E-01	7.20E-01	5.60E-01	1.09E+00	2.10E-01	6.70E-01	5.50E-01	4.30E-01	8.70E-01	1.80E-01
2-methyl Napthalene	2	1	6.40E-01	6.20E-01	4.30E-01	8.80E-01	7.70E-01	5.70E-01	5.30E-01	4.70E-01	1.07E+00	5.50E-01
Acenaphthylene	3	3	7.30E-01	6.50E-01	6.80E-01	7.30E-01	6.40E-01	6.90E-01	6.20E-01	5.50E-01	8.80E-01	5.40E-01
Acenaphthene	3	3	5.60E-01	5.20E-01	6.50E-01	7.70E-01	5.50E-01	5.20E-01	4.40E-01	6.90E-01	9.80E-01	4.80E-01
Fluorene	3	3	6.40E-01	5.80E-01	4.60E-01	4.90E-01	4.50E-01	6.10E-01	5.30E-01	5.50E-01	5.40E-01	5.40E-01
Phenanthrene	3	3	5.50E-01	4.80E-01	6.50E-01	5.30E-01	5.50E-01	5.20E-01	4.90E-01	6.50E-01	6.10E-01	5.80E-01
Anthracene	3	3	4.90E-01	4.20E-01	5.20E-01	5.80E-01	4.80E-01	4.40E-01	4.40E-01	5.80E-01	6.60E-01	5.10E-01
Fluoranthene	4	3	6.80E-01	6.20E-01	5.50E-01	7.10E-01	6.50E-01	6.40E-01	6.80E-01	4.30E-01	7.60E-01	7.70E-01
Pyrene	4	3	5.10E-01	4.70E-01	5.80E-01	4.30E-01	5.20E-01	4.70E-01	5.30E-01	5.50E-01	5.40E-01	6.10E-01
Benz(a)anthracene	4	0.15	3.98E+00	3.44E+00	3.09E+00	4.23E+00	3.09E+00	3.55E+00	3.87E+00	3.08E+00	3.80E-01	2.32E+00
Chrysene	4	-	4.23E+00	4.18E+00	3.98E+00	5.23E+00	5.98E+00	3.98E+00	3.76E+00	4.01E+00	4.54E+00	4.55E+00
Benz(b)fluoranthene	5	0.3	6.87E+00	6.33E+00	7.98E+00	6.22E+00	6.34E+00	6.11E+00	5.76E+00	6.77E+00	5.76E+00	5.87E+00
Benz(k)fluoranthene	5	-	6.98E+00	7.34E+00	5.32E+00	6.77E+00	5.87E+00	6.32E+00	6.43E+00	4.98E+00	6.32E+00	6.71E+00
Benz(a)pyrene	5	0.3	5.34E+00	5.21E+00	6.33E+00	5.76E+00	6.34E+00	5.65E+00	4.65E+00	5.60E+00	6.37E+00	5.43E+00
Dibenz(a,h)anthracene	5	0.3	4.98E+00	4.23E+00	5.98E+00	5.22E+00	5.15E+00	4.44E+00	4.11E+00	6.76E+00	5.11E+00	4.87E+00
Benzo(g,h,i)perylene	6	3	7.98E+00	7.55E+00	6.32E+00	5.76E+00	6.64E+00	7.42E+00	6.76E+00	5.43E+00	6.08E+00	8.09E+00
Indinol(1,2,3-cd)pyrene	6	-	8.23E+00	7.83E+00	5.77E+00	6.22E+00	7.21E+00	7.54E+00	5.87E+00	6.33E+00	5.04E+00	6.76E+00
TOTAL			5.42E+01	5.12E+01	4.99E+01	5.16E+01	5.14E+01	5.01E+01	4.60E+01	4.79E+01	4.65E+01	4.94E+01

Polycyclic Aromatic Hydrocarbons (PAHs) were identified and quantified in sediments from Dadin Kowa Dam, Gombe State, Nigeria during the dry and rainy seasons (Tables 3 to 4) from different sampling points designated as (S1-S10). The concentrations of all PAHs studied in the sediment samples during the dry season ranged from 6.40E-01 to 1.09E +00 mg/kg, while the concentrations of all the PAHs studied during the rainy season ranged from 4.60E+01 to 5.42E +01 mg/kg. The rainy season showed the total highest concentration of all the PAHs studied when compared to the dry season. LMW PAHs contributed little to the total PAH concentration in all the sampling locations. The study further revealed that sediment samples were more contaminated than the water samples. Such variation might be attributed to the fact that PAHs tend to adhere to surfaces, attaching readily to

sediment particles and leading to elevated concentrations in sediments. The distribution of PAHs in the samples indicates a possible health risk to humans and aquatic organisms as some of the individual PAHs exceeds the maximum allowable concentrations as set by EU (Joshua *et al.*, (2016).

Risk Assessment of PAHs

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 (BaP_{eq}).

BaP_{eq} for individual PAH were estimated using the equation.

$$BaP_{eq} = \sum C_n \times TEF_n$$

Concentrations of Benzo(a)pyrene Equivalent in Sediment Samples from Different Sampling Points During the Dry and Rainy Season

Table 3 to 4 shows the concentrations of benzo(a)pyrene equivalent PAHs in sediment samples for dry and rainy season from points S1 to S10 of Dadin Kowa Dam, Gombe State Nigeria. The concentration of naphthalene ranged from 2.00E-05 to 1.09E-03 mg/kg; 2.00E-05 to 1.07E-03 mg/kg 2-methylnaphthalene; 2.00E-05 to 8.80E-04 mg/kg acenaphthylene; 2.00E-05 to 9.84E-04 mg/kg acenaphthene; 3.00E-05 to 6.40E-04 mg/kg fluorene; 3.00E-05 to 6.50E-04 mg/kg phenanthrene; 2.00E-04 to 6.60E-03 mg/kg anthracene; 1.00E-05 to 7.70E-04 mg/kg fluoranthene; 2.00E-05 to 6.10E-04 mg/kg pyrene; 2.00E-03 to 4.23E-01 mg/kg benzo(a)anthracene; 3.00E-05 to 5.98E-03 mg/kg chrysene; 1.10E-02 to 7.98E-01 mg/kg benzo(b)fluoranthene; 6.00E-03 to 7.34E-01 mg/kg benzo(k)fluoranthene; 5.00E-02 to 6.37E+00 mg/kg benzo(a)pyrene; 4.00E-02 to 6.76E+00 mg/kg dibenz(a,h)anthracene; 6.00E-04 to 8.09E-02 mg/kg benzo(g,h,i)perylene and 5.00E-04 to 8.23E-02 mg/kg indinol(1,2,3-

cd)pyrene. The highest total concentrations of 1.41E+01 mg/kg was observed at point S3 during the rainy season, while point S1 shows the lowest total value of 1.13E-01 mg/kg during the dry season.

Table 3: Concentrations of Benzo(a)pyrene Equivalent in Sediment Samples from Different Sampling points During the Dry Season

PAHs	No of Rings	TEF (USEPA)	Concentrations (mg/kg)										
			S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	
NaP	2	0.001	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05
2-methyl Naphthalene	2	0.001	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05
Acenaphthylene	3	0.001	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05
Acenaphthene	3	0.001	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05
Fluorene	3	0.001	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05
Phenanthrene	3	0.001	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05
Anthracene	3	0.01	2.00E-04	2.00E-04	2.00E-04	3.00E-04	2.00E-04	2.00E-04	2.00E-04	3.00E-04	2.00E-04	2.00E-04	3.00E-04
Fluoranthene	4	0.001	1.00E-05	1.00E-05	1.00E-05	2.00E-05	1.00E-05	1.00E-05	1.00E-05	2.00E-05	1.00E-05	1.00E-05	2.00E-05
Pyrene	4	0.001	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05
Benz(a)anthracene	4	0.1	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03
Chrysene	4	0.001	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05	3.00E-05
Benz(b)fluoranthene	5	0.1	1.30E-02	6.00E-03	1.10E-02	1.40E-02	7.00E-03	8.00E-03	8.00E-03	6.00E-03	2.10E-02	1.10E-02	1.20E-02
Benz(k)fluoranthene	5	0.1	6.00E-03	7.00E-03	2.30E-02	1.30E-02	1.10E-02	9.00E-03	1.30E-02	1.10E-02	6.00E-03	8.00E-03	8.00E-03
Benz(a)pyrene	5	1	5.00E-02	8.00E-02	1.40E-01	1.50E-01	8.00E-02	1.10E-01	1.70E-01	8.00E-02	8.00E-02	8.00E-02	9.00E-02
Dibenz(a,h)anthracene	5	1	4.00E-02	6.00E-02	6.00E-02	8.00E-02	9.00E-02	1.40E-01	1.50E-01	1.80E-01	1.10E-01	1.60E-01	1.60E-01
Benzo(g,h,i)perylene	6	0.01	6.00E-04	8.00E-04	9.00E-04	1.10E-03	7.00E-04	1.70E-03	9.00E-04	1.60E-03	1.40E-03	1.10E-03	1.10E-03
Indinol(1,2,3-cd)pyrene	6	0.01	7.00E-04	5.00E-04	1.00E-03	1.40E-03	1.40E-03	1.10E-03	1.00E-03	1.10E-03	1.50E-03	2.10E-03	2.10E-03
BaPeq			1.13E-01	1.57E-01	2.38E-01	2.62E-01	1.93E-01	2.72E-01	3.43E-01	2.97E-01	2.12E-01	2.76E-01	2.76E-01

Table 4: Concentrations of Benzo(a)pyrene Equivalent in Sediment Samples from Different Sampling point During the Rainy Season

PAHs	No. of rings	TEF (USEPA)	Concentrations (mg/kg)									
			S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Naphthalene	2	0.001	7.60E-04	7.20E-04	5.60E-04	1.09E-03	2.10E-04	6.70E-04	5.50E-04	4.30E-04	8.70E-04	1.80E-04
2-methyl Naphthalene	2	0.001	6.40E-04	6.20E-04	4.30E-04	8.80E-04	7.70E-04	5.70E-04	5.30E-04	4.70E-04	1.07E-03	5.50E-04
Acenaphthylene	3	0.001	7.30E-04	6.50E-04	6.80E-04	7.30E-04	6.40E-04	6.90E-04	6.20E-04	5.50E-04	8.80E-04	5.40E-04
Acenaphthene	3	0.001	5.60E-04	5.20E-04	6.50E-04	7.70E-04	5.50E-04	5.20E-04	4.40E-04	6.90E-04	9.80E-04	4.80E-04
Fluorene	3	0.001	6.40E-04	5.80E-04	4.60E-04	4.90E-04	4.50E-04	6.10E-04	5.30E-04	5.50E-04	5.40E-04	5.40E-04
Phenanthrene	3	0.001	5.50E-04	4.80E-04	6.50E-04	5.30E-04	5.50E-04	5.20E-04	4.90E-04	6.50E-04	6.10E-04	5.80E-04
Anthracene	3	0.01	4.90E-03	4.20E-03	5.20E-03	5.80E-03	4.80E-03	4.40E-03	4.40E-03	5.80E-03	6.60E-03	5.10E-03
Fluoranthene	4	0.001	6.80E-04	6.20E-04	5.50E-04	7.10E-04	6.50E-04	6.40E-04	6.80E-04	4.30E-04	7.60E-04	7.70E-04
Pyrene	4	0.001	5.10E-04	4.70E-04	5.80E-04	4.30E-04	5.20E-04	4.70E-04	5.30E-04	5.50E-04	5.40E-04	6.10E-04
Benz(a)anthracene	4	0.1	3.98E-01	3.44E-01	3.09E-01	4.23E-01	3.09E-01	3.55E-01	3.87E-01	3.08E-01	3.80E-02	2.32E-01
Chrysene	4	0.001	4.23E-03	4.18E-03	3.98E-03	5.23E-03	5.98E-03	3.98E-03	3.76E-03	4.01E-03	4.54E-03	4.55E-03
Benz(b)fluoranthene	5	0.1	6.87E-01	6.33E-01	7.98E-01	6.22E-01	6.34E-01	6.11E-01	5.76E-01	6.77E-01	5.76E-01	5.87E-01
Benz(k)fluoranthene	5	0.1	6.98E-01	7.34E-01	5.32E-01	6.77E-01	5.87E-01	6.32E-01	6.43E-01	4.98E-01	6.32E-01	6.71E-01
Benz(a)pyrene	5	1	5.34E+00	5.21E+00	6.33E+00	5.76E+00	6.34E+00	5.65E+00	4.65E+00	5.60E+00	6.37E+00	5.43E+00
Dibenz(a,h)anthracene	5	1	4.98E+00	4.23E+00	5.98E+00	5.22E+00	5.15E+00	4.44E+00	4.11E+00	6.76E+00	5.11E+00	4.87E+00
Benzo(g,h,i)perylene	6	0.01	7.98E-02	7.55E-02	6.32E-02	5.76E-02	6.64E-02	7.42E-02	6.76E-02	5.43E-02	6.08E-02	8.09E-02
Indinol(1,2,3-cd)pyrene	6	0.01	8.23E-02	7.83E-02	5.77E-02	6.22E-02	7.21E-02	7.54E-02	5.87E-02	6.33E-02	5.04E-02	6.76E-02
BaP _{eq}			1.23E+01	1.13E+01	1.41E+01	1.28E+01	1.32E+01	1.19E+01	1.05E+01	1.40E+01	1.29E+01	1.20E+01

The toxicity assessment of PAHs in the sediment samples for acute biological effects in Dadin Kowa Dam was carried out according to the total concentration determined for the PAHs. The sum of the total PAHs concentrations ranged from 1.13E-01 to 1.41E+01 mg/kg (Tables 3 and 4). Among all known potentially carcinogenic PAHs, BaP is the only PAHs for which toxicological data are sufficient to derive a carcinogenic potency factor (Peters *et al.*, 1991). The potential toxicity of sediment was assessed by calculating the total toxic BaP equivalent for all the PAHs (Savinov *et al.*, 2003; Chen and Chen, 2011):

The US Environmental Protection Agency (US-EPA, 1993) established the TEFs for each PAHs: 0.1 for BaA, 0.001 for Chr, 0.1 for BbF, 0.01 for BkF, 1 for BaP, 0.1 for IP, and 1 for DBA. Total BaP_{eq} calculated for all samples investigated in this study ranged from 1.13E-01 to 1.41E+01 mg/kg, the probable sources of these compounds were through atmospheric transport and deposition, municipal waste- water treatment plants, industrial discharges, storm water runoff,

landfill leachate, surface runoff as well as vehicular emissions along the river sources to the study area. The above findings are in consistent with sediment from the Barents Sea in Guba pechenga, Russia (Savinov *et al.*, 2003); Meiliang Bay in Taihu Lake, China (EPA, 2015) and Kaohsiung Harbor in Taiwan (PGQRA, 2015).

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.

Diagnostic Ratio of Some PAHs in Sediment Samples for Rainy and Dry Season from Different Sampling Points

Table 5 to 6 shows the diagnostic ratio of polycyclic aromatic hydrocarbon in Sediment Sample for rainy and dry season from Points S1 to S10 from Dadin Kowa Dam, Gombe State, Nigeria. The ratio of BaA/BaA+Chr ranged from 0.08 to 0.51; 0.40 to 0.52 for Ant/Ant+Phe; 0.33 to 0.62 for Flua/Flua+Pyr and 0.07 to 0.33 for LMW/HMW.

Table 5: Diagnostic Ratio of PAHs in Sediment Samples from Different Sampling Points During the Dry Season

Sampling Point	Diagnostic Ratio Sediment			
	BaA/BaA+Chr	Ant/Ant+Phe	Flua/Flua+Pyr	LMW/HMW
S1	0.40	0.40	0.33	0.33
S2	0.40	0.40	0.33	0.33
S3	0.40	0.40	0.33	0.20
S4	0.40	0.50	0.50	0.20
S5	0.40	0.40	0.33	0.25
S6	0.40	0.40	0.33	0.21
S7	0.40	0.50	0.50	0.22
S8	0.40	0.40	0.33	0.17
S9	0.40	0.40	0.33	0.22
S10	0.40	0.50	0.50	0.20
Mean Ratio	0.40	0.43	0.38	0.23

Table 6: Diagnostic Ratio of PAHs in Sediment Samples from Different Sampling during the Rainy Season

Sampling Points	Diagnostic Ratio Sediment			
	BaA/BaA+Chr	Ant/Ant+Phe	Flua/Flua+Pyr	LMW/HMW
S1	0.48	0.47	0.57	0.09
S2	0.45	0.47	0.57	0.08
S3	0.44	0.44	0.49	0.09
S4	0.45	0.52	0.62	0.11
S5	0.34	0.47	0.56	0.08
S6	0.47	0.46	0.58	0.09
S7	0.51	0.47	0.56	0.08
S8	0.43	0.47	0.44	0.09
S9	0.08	0.52	0.58	0.14
S10	0.34	0.47	0.56	0.07
Mean Ratio	0.40	0.48	0.55	0.09

Identification of PAHs Sources

The Polycyclic aromatic hydrocarbon (PAHs) of anthropogenic sources includes pyrogenic as well as petrogenic sources Van-Metre *et al.*, 2000. Pyrogenic sources are derived from the incomplete combustion of organic compounds such as the burning of biomass as well as fossil fuels (coal burning and vehicle emissions); petrogenic sources are derived from unburned fossil fuels, which includes oil spills as well as incineration of petroleum products (coal and crude oil) (Duke, 2008; Moon, 2006). The pyrogenic and petrogenic sources of PAHs can be differentiated by the ratios of Ant/Phe and Fla/Pyr (Simpson, 1998). The possible sources of PAHs in the sediment samples from Dadin Kowa Dam, Gombe State, Nigeria during the dry and rainy seasons were shown in (Tables 5 and 6). In order to further distinguish the PAHs sources, the ratios of Ant/(Ant + Phe) ranged from 0.40-0.52, Fla/(Fla + Pyr) with a ratio ranged 0.33-0.58, ratios of BaA/(BaA + Chr) ranged from 0.08-0.51 were used for distinguishing

between the possible PAHs sources of petroleum input, petroleum combustion (vehicle and crude oil) and combustion of grass, wood and coal (Yan *et al.*, 2004). Results from the present study show that all the sampling points were exposed to a mixture pattern of pyrogenic sources. The dominant source of PAHs was combustion of grass, wood, and coal. Generally, the findings of this work proved that pyrogenic inputs contributed to PAHs contamination in the sediment from Dadin Kowa Dam. The pollution caused by pyrogenic sources could be explained because atmospheric particles containing PAHs from vehicular emissions were probably transported by air masses during the dry season and then entered into the water by atmospheric deposit. The above findings are in consistent with similar studies by Simpson, (1998); Kurelec and Gupta, (1993). Based on the reality, burning agricultural wastes and refuse by local farmers might result in the combustion of biomass and industrial plants located in Ashaka a major town which is well-known for

the production of cement, and also Nafada in Gombe State where a lot of agricultural and domestic activities are carried out might lead to the emission of pollutants.

Ecological Risk Assessment of PAHs in Sediment Samples

formular suggested by Long and Macdonald (1998): $m - ERM - q = \frac{\sum \frac{Ci}{ERMi}}{n}$

Mean Effect Range Medium (ERM) Quotient of Some PAHs in Sediment Samples for Rainy and Dry Season

Table 7 to 8 shows the mean effect range medium (ERM) quotient of polycyclic aromatic hydrocarbon in Sediment Sample for dry and rainy season from Dadin Kowa Dam, Gombe State, Nigeria. The concentration for naphthalene ranged from 9.52E-06 to 1.00E+00; 2.99E-05 to 1.00E+00 2-methylnaphthalene; 3.13E-05 to 1.00E+00 acenaphthylene; 4.00E-05 to 1.00E+00

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

acenaphthene; 5.56E-05 to 1.00E+00 fluorene; 2.00E-05 to 1.00E+00 phenanthrene; 1.82E-05 to 1.00E+00 anthracene; 1.96E-06 to 1.00E+00 fluoranthene; 7.69E-06 to 1.00E+00 pyrene; 1.25E-05 to 1.00E+00 benzo(a)anthracene; 1.07E-05 to 1.00E+00 Chrysene; 3.13E-05 to 1.00E+00 benzo(a)pyrene; 1.54E-04 to 6.11E-01 dibenz(a,h)anthracene; 1.82E-04 to 8.75E-01 benzo(g,h,i)perylene and 6.78E-04 to 1.48E+01 indinol(1,2,3-cd)pyrene. Point S10 shows the highest total mean effect range medium (ERM).

Table 7: Mean Effect Range Medium (ERM) Quotient of PAHs in Sediment Samples during the Dry Season

PAHs											
Naphthalene	ERM SSG	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
2-methyl Napthalene	2100	9.52E-06	9.52E-06	9.52E-06	9.52E-06	9.52E-06	9.52E-06	9.52E-06	9.52E-06	9.52E-06	1.00E+00
Acenaphthylene	670	2.99E-05	2.99E-05	2.99E-05	2.99E-05	2.99E-05	2.99E-05	2.99E-05	2.99E-05	2.99E-05	1.00E+00
Acenaphthene	640	3.13E-05	3.13E-05	3.13E-05	3.13E-05	3.13E-05	3.13E-05	3.13E-05	3.13E-05	3.13E-05	1.00E+00
Fluorene	500	4.00E-05	4.00E-05	4.00E-05	4.00E-05	4.00E-05	4.00E-05	4.00E-05	4.00E-05	4.00E-05	1.00E+00
Phenanthrene	540	5.56E-05	5.56E-05	5.56E-05	5.56E-05	5.56E-05	5.56E-05	5.56E-05	5.56E-05	5.56E-05	1.00E+00
Anthracene	1500	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	1.00E+00
Fluoranthene	1100	1.82E-05	1.82E-05	1.82E-05	2.73E-05	1.82E-05	1.82E-05	2.73E-05	1.82E-05	1.82E-05	1.00E+00
Pyrene	5100	1.96E-06	1.96E-06	1.96E-06	3.92E-06	1.96E-06	1.96E-06	3.92E-06	1.96E-06	1.96E-06	1.00E+00
Benz(a)anthracene	2600	7.69E-06	7.69E-06	7.69E-06	7.69E-06	7.69E-06	7.69E-06	7.69E-06	7.69E-06	7.69E-06	1.00E+00
Chrysene	1600	1.25E-05	1.25E-05	1.25E-05	1.25E-05	1.25E-05	1.25E-05	1.25E-05	1.25E-05	1.25E-05	1.00E+00
Benz(b)fluoranthene	2800	1.07E-05	1.07E-05	1.07E-05	1.07E-05	1.07E-05	1.07E-05	1.07E-05	1.07E-05	1.07E-05	1.00E+00
Benz(k)fluoranthene	-	-	-	-	-	-	-	-	-	-	-
Benz(a)pyrene	-	-	-	-	-	-	-	-	-	-	-
Dibenz(a,h)anthracene	1600	3.13E-05	5.00E-05	8.75E-05	9.38E-05	5.00E-05	6.88E-05	1.06E-04	5.00E-05	5.00E-05	1.00E+00
Benzo(g,h,i)perylene	260	1.54E-04	2.31E-04	2.31E-04	3.08E-04	3.46E-04	5.38E-04	5.77E-04	6.92E-04	4.23E-04	6.11E-01
Indinol(1,2,3-cd)pyrene	330	1.82E-04	2.42E-04	2.73E-04	3.33E-04	2.12E-04	5.15E-04	2.73E-04	4.85E-04	4.24E-04	8.75E-01
	950	7.37E-05	5.26E-05	1.05E-04	1.47E-04	1.47E-04	1.16E-04	1.05E-04	1.16E-04	1.58E-04	1.36E+00
TOTAL		6.78E-04	8.13E-04	9.33E-04	1.13E-03	9.93E-04	1.48E-03	1.31E-03	1.58E-03	1.29E-03	1.48E+01

Table 8: Mean Effect Range Medium (ERM) Quotient of PAHs in Sediment Samples During the Rainy Season

PAHs	ERM SSG	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Naphthalene	2100	3.62E-04	3.43E-04	2.67E-04	5.19E-04	1.00E-04	3.19E-04	2.62E-04	2.05E-04	4.14E-04	8.57E-05
2-methyl Napthalene	670	9.55E-04	9.25E-04	6.42E-04	1.31E-03	1.15E-03	8.51E-04	7.91E-04	7.01E-04	1.60E-03	8.21E-04
Acenaphthylene	640	1.14E-03	1.02E-03	1.06E-03	1.14E-03	1.00E-03	1.08E-03	9.69E-04	8.59E-04	1.38E-03	8.44E-04
Acenaphthene	500	1.12E-03	1.04E-03	1.30E-03	1.54E-03	1.10E-03	1.04E-03	8.80E-04	1.38E-03	1.96E-03	9.60E-04
Fluorene	540	1.19E-03	1.07E-03	8.52E-04	9.07E-04	8.33E-04	1.13E-03	9.81E-04	1.02E-03	1.00E-03	1.00E-03
Phenanthrene	1500	3.67E-04	3.20E-04	4.33E-04	3.53E-04	3.67E-04	3.47E-04	3.27E-04	4.33E-04	4.07E-04	3.87E-04
Anthracene	1100	4.45E-04	3.82E-04	4.73E-04	5.27E-04	4.36E-04	4.00E-04	4.00E-04	5.27E-04	6.00E-04	4.64E-04
Fluoranthene	5100	1.33E-04	1.22E-04	1.08E-04	1.39E-04	1.27E-04	1.25E-04	1.33E-04	8.43E-05	1.49E-04	1.51E-04
Pyrene	2600	1.96E-04	1.81E-04	2.23E-04	1.65E-04	2.00E-04	1.81E-04	2.04E-04	2.12E-04	2.08E-04	2.35E-04
Benz(a)anthracene	1600	2.49E-03	2.15E-03	1.93E-03	2.64E-03	1.93E-03	2.22E-03	2.42E-03	1.93E-03	2.38E-04	1.45E-03
Chrysene	2800	1.51E-03	1.49E-03	1.42E-03	1.87E-03	2.14E-03	1.42E-03	1.34E-03	1.43E-03	1.62E-03	1.63E-03
Benz(b)fluoranthene	-	-	-	-	-	-	-	-	-	-	-
Benz(k)fluoranthene	-	-	-	-	-	-	-	-	-	-	-
Benz(a)pyrene	1600	3.34E-03	3.26E-03	3.96E-03	3.60E-03	3.96E-03	3.53E-03	2.91E-03	3.50E-03	3.98E-03	3.39E-03
Dibenz(a,h)anthracene	260	1.92E-02	1.63E-02	2.30E-02	2.01E-02	1.98E-02	1.71E-02	1.58E-02	2.60E-02	1.97E-02	1.87E-02
Benzo(g,h,i)perylene	330	2.42E-02	2.29E-02	1.92E-02	1.75E-02	2.01E-02	2.25E-02	2.05E-02	1.65E-02	1.84E-02	2.45E-02
Indinol(1,2,3-cd)pyrene	950	8.66E-03	8.24E-03	6.07E-03	6.55E-03	7.59E-03	7.94E-03	6.18E-03	6.66E-03	5.31E-03	7.12E-03
TOTAL		6.52E-02	5.97E-02	6.09E-02	5.88E-02	6.09E-02	6.01E-02	5.41E-02	6.14E-02	5.69E-02	6.18E-02
M-ERM-Q		4.35E-03	3.98E-03	4.06E-03	3.92E-03	4.06E-03	4.01E-03	3.61E-03	4.09E-03	3.80E-03	4.12E-03

Ecotoxicity Studies PAHs in Sediment Samples

To assess the potential toxicity influence of sediment from Dadin Kowa Dam during the rainy and dry seasons for the benthic organisms and their ecosystem. PAHs levels in the sediment from the Dam were compared with the sediment toxicity screening guideline of the US National Oceanic and Atmospheric Administration, with a target value (m-ERM-q) approach were used to evaluate the possible biological effects or toxicity of PAHs in sediment in the mean ERM quotient (m-ERM-q). This approach calculates the mean quotients for all PAHs according to the formula suggested by Long and MacDonald, 1998. As mentioned by Long, *et al.*, 2000, mERM-q can be categorised into four levels according to their probability of toxicity: ≤ 0.1 indicates an 11% probability of toxicity; 0.11 to 0.5 indicates a 30% probability of toxicity; 0.51 to 1.5 indicates 46% probability of toxicity and > 1.5 indicates a 75% probability of toxicity. Moreover, the probability percentage of toxicity in these four categories can be used to classify the sampling points as low, medium-low, medium high, and high-priority points, respectively.

According to these categories and classifications, the m-ERM-q values of the sediment from Dadin Kowa Dam during the rainy and the dry seasons ranged from $4.52E-05$ to $1.41E+01$ with a mean value of $5.13E-02$ (Tables 7 to 8). The results of this study can be ranked under the first category, where the value is less than 0.1 with an 11% probability of toxicity. They are also classified as low-priority sites, indicating the absence of acute biological effects. The possible source of PAHs in the sediment samples from Dadin Kowa Dam is pyrogenic sources such as incomplete and complete petroleum combustion from diesel engines and vehicle engines as well as burning of wood and grasses. In other areas, the sources could be petrogenic such as from nonburn fuel discharge of two-stroke engine boats. The

results of potential toxicity and biological effect assessment show that the surface sediments from Dadin Kowa Dam have low contamination and a low probability of toxic pollution.

CONCLUSION

All of the PAHs studied in the sediment's samples were significantly present. Rainy season was observed to show the highest concentrations of all the studied PAHs. Results from diagnostic ratios show that the presence of the studied PAHs were from both fuel combustion and pyrogenic sources. 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.

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