

## Carcinogenic Risk Assessment of Some Polycyclic Aromatic Hydrocarbons in Water Samples from Gubi Dam, Bauchi State, Nigeria

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### ABSTRACT

Carcinogenic risk assessment of some polycyclic aromatic hydrocarbons (PAHs) in water samples from Gubi Dam, Bauchi State, Nigeria, was carried out. Water samples were collected at four different sampling points designated S1 to S4. The PAHs in the water samples were extracted by liquid-liquid extraction using dimethyl chloride (DCM), cleaned-up and the levels of PAHs in the extract were determined using GC-MS. The results revealed that chrysene had the highest concentrations ( $6.98E-06$ ) while acenaphthylene had the lowest concentrations ( $1.43E-09$ ) of PAHs. Result from incremental lifetime expectancy cancer risk in water showed that point S1 had the highest value of  $1.47E-06$  mg/kg/day for adults which shows that one in a million are prone to cancer related illness in their lifetime as a result of PAHs exposure via ingestion of water, while highest dose for children of  $1.05E-06$  mg/kg/day showed 7 out of 10,000,000 children are prone to cancer as a result of water ingestion from the study area. Furthermore, the major environmental concern and the ability of developing cancer related illness from Gubi Dam is low and not serious. Hence, the relevant agencies should be involved in the management of Gubi Dam with respect to PAH contamination.

**Keywords:** Carcinogenic risk assessment, Gubi Dam, PAH, Water, GC-MS

### INTRODUCTION

Polycyclic aromatic hydrocarbons are part of the list of the 12 Persistent Organic Pollutants (POPs), while benzo(a)pyrene (BaP) is the most toxic of the PAHs. Owing to the different physicochemical

properties of organic contaminants, PAHs tend to interact to different extent with water, soil/sediments and biota. Sediment-pore water interaction is one of the most dominant process controlling the distribution and behavior of PAHs in the river [1]. Polycyclic aromatic hydrocarbons are a group of persistent organic pollutants in the environment [2], which originated from nature and anthropogenic activities, such as fossil fuel and biomass combustion [3]. They can pose carcinogenic, teratogenic, and mutagenic effects on human health and aquatic organisms [4]. In the aquatic system, the adverse effects of PAHs are greater [5]. The health status of aquatic organisms can be indicated by pollutants in sediments [6, 7], because sediment adsorption determines the fate of pollutants in aquatic environment, and macro fauna who dwell in the sediment prey in water organisms [8, 9]. A number of environmental agencies and scientific institutions pay much attention on this environmental issue [7].

Environmental pollution caused by oil spills or runoff from landfills that contain transformers, dielectric and coolant fluids in electrical apparatus, carbonless copy paper and in heat transfer fluids are major ecological problems. These contaminants in the environment are primarily evaluated by measuring the chemical concentration of PAHs. The results of chemical analyses are important for estimating water and sediment quality in the risk assessment to the flora and fauna of any contaminated sites.

In the world, there are lake ecosystems under permanent chemical stress due to urbanization and the oil industry. PAHs are generally formed during incomplete combustion of organic matter containing carbon and hydrogen [10]. PAHs constitute a large class of organic compounds containing two or more fused aromatic rings. Hundreds of individual PAHs may be formed during incomplete combustion or pyrolysis of organic [11]. These compounds occur as contaminants in different kinds of foodstuffs including dairy products, vegetables, fruits, oils, cereals, and smoked meats [12,13]. The sources of PAH in food are mainly environmental pollutants, food processing (drying, smoking) and cooking (roasting, grilling, and frying) [14]. A number of PAHs have been found to have carcinogenic and mutagenic effects while some of them may act as synergists [15]. One of the major routes of human exposure to PAHs in non-smoking people is food. These compounds can reach the food chain by different ways as PAHs have been found in different food products, such as dairy products, vegetables, fruits, oils, coffee, tea, cereals and smoked meat, therefore the analysis of PAHs in food is a matter of concern [16]. On the other hand, PAHs are also found in foods as a result of certain industrial food processing methods such as smoke curing, broiling, roasting, and grilling over open fires or charcoal which permits the direct contact between food and combustion products [17]. PAHs have solubility in water but are readily

soluble in organic solvent or organic acids. In the environment, PAHs are generally found adsorbed on particulates and on humic matter, or dissolved in any oily contamination that may be present in water and sediment. The solubility of PAHs in water is inversely proportional to the number of rings the PAHs molecule contains [18].

As in the atmosphere, PAHs in the water column are generally associated with particulates [19, 20]. Volatilization, photolysis, hydrolysis, biodegradation, and adsorption to particulate matter followed by sedimentation are the main processes governing the fate of PAHs in water [21, 22]. The rate of volatilization depends on weather conditions, movement of water, and the molecular weight of the compounds. Polycyclic aromatic hydrocarbons of low molecular weight may volatilize from water, as indicated by the volatilization half-lives of naphthalene (0.4 to 3.2 hours) [23] and anthracene (17 hours) [24]. A high molecular weight PAH such as pyrene, however, has a volatilization half-life ranging from 115 hours to 3.2 years [25]. Many of the PAHs in oil spilled on water volatilize [21]. Polycyclic aromatic hydrocarbons can be biodegraded in water. Half-lives have been estimated to range from 0.5 to 20 days for naphthalene and from 0.6 to 5.2 years for pyrene under aerobic conditions [26]. Photo-oxidation in water also occurs, with estimated half-lives of 0.1 to 4.4 years for anthracene [27]. For most PAHs in the water column, sedimentation constitutes the primary removal mechanism [21].

Contamination of groundwater by PAHs can occur as a result of leaching through soils, especially when PAHs are accompanied by mobile organic solvents or when channels are present in the soil [23, 28]. Naphthalene was the most mobile PAH reported below a creosote-contaminated site in the United States; concentrations of naphthalene at a depth of 3 m were 5% of those at a depth of 0.2 to 0.5 m [29]. Contamination of groundwater has been observed following application of oily sludge to soil [30]. Polycyclic aromatic hydrocarbons can accumulate in a variety of organisms. Bioconcentration factors (BCFs) ranging from 4 to 7800 have been reported for various PAHs in unicellular algae [31]. Polycyclic aromatic hydrocarbons can be oxidized by these organisms, although only 10 to 37% of accumulated B[a]P was oxidized by the green alga, *Selenastrum capricornutum* [32].

Some Nigerians live near water bodies such as lakes, lagoons, reservoirs, rivers, swamps and coastal lagoons. Many depend heavily on the resources of such water bodies for their main source of animal protein and family income [33]. Gubi Dam is greatly affected by the commercial, environment and industrial activities that take place within and around the city. The pollutants, untreated sewage, industrial and domestic landfill waste and by-products of slash and burn activities from the city end up

in Gubi Dam. Thus, the contamination of fish and the aquatic environment by pollutants such as PAHs is viewed with serious concern.

The objectives of the study are to determine the level of some polycyclic aromatic hydrocarbons and conduct carcinogenic risk assessment of the Polycyclic aromatic hydrocarbon in water samples of Gubi dam.

## EXPERIMENTALS

### Study Area

Gubi Dam is located 12 km northeast of Bauchi City, in the Northeastern part of Nigeria. The source of water in Gubi Dam comes mainly from three tributaries, namely Gubi River, Tagwaye river links with Shadawanka and Ran River. A temporary dam close to the site was constructed across one of the streams to provide water needed for the construction of the permanent dam. The embankment of the dam has length of 3.86 km and bottom earth-fill of 2,315, 000 m<sup>3</sup> with a reservoir area of 590 hectares. The catchments area is 17,900 hectares with total storage capacity of 38.4 x 10<sup>6</sup> m<sup>3</sup>. The expected yield from the reservoir is 90,000 m<sup>3</sup>/d [34]. Initially, the main function of the Gubi Dam was to supply the Bauchi State capital and its environs with potable water. However, provision was made for agricultural activities to take place around the dam. Over time, as the quantity of fish increased in the dam, fishermen moved from other fishing areas around Bauchi to Gubi Dam [35].

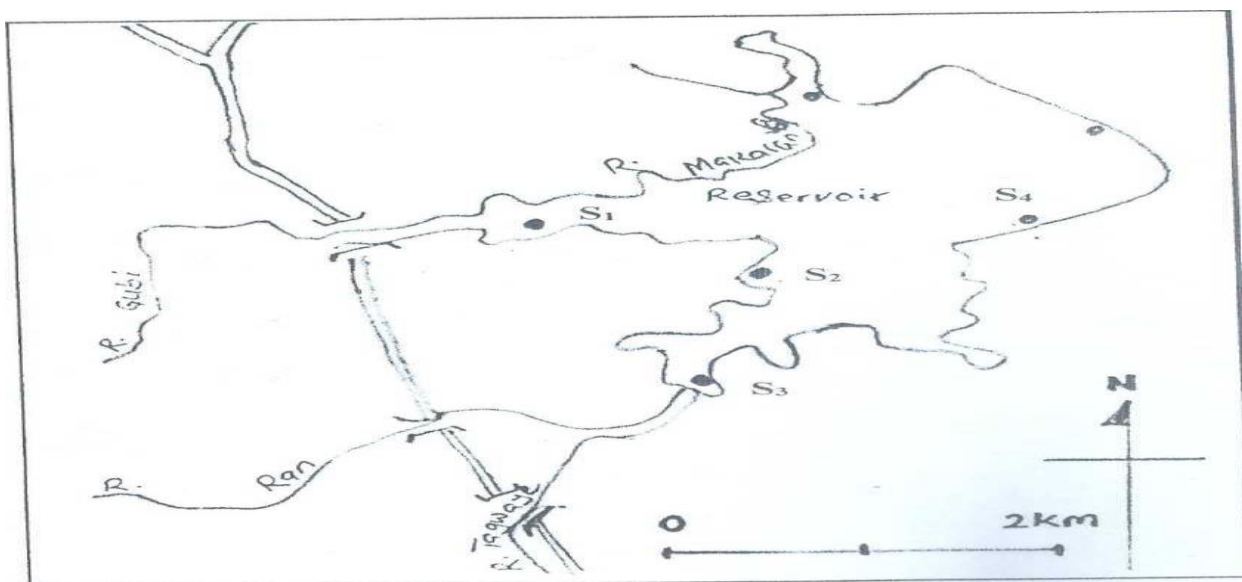


Figure 1: Gubi Dam with its four feeding rivers.

### **Collection of Water Samples**

Water samples were collected from four (4) sampling point designated S<sub>1</sub>-S<sub>4</sub>. The distance from each sampling point was 0.5 km away from each other. The water samples were collected using plastic containers by dipping 1-5 cm below the top layer of the water and placed in an amber glass bottle and stored in an ice-block cooler as described by Boy'd and Tucker [36]. The samples were then transported to the Department of Chemistry, University of Maiduguri, Nigeria, and stored in a refrigerator pending extraction and analysis.

### **Extraction and Clean-up of PAHs in Water Samples**

The Gas Chromatography USEPA 8270 analytical methods [37] were adopted using GC-MS. Sample extraction was effected by liquid-liquid extraction in a separatory funnel using dimethyl chloride (DCM) as solvent. The sample extract was subsequently filtered through glass wool containing anhydrous sodium sulphate in a glass funnel. This was followed by clean-up using about 2 g of silica gel. The sample extract was allowed to stand for about 30 minutes, then decanted and concentrated to 1 ml.

### **Instrumental Analysis of PAHs Using GC-MS for Water Samples**

The extract was transferred into the vials and analyzed using Agilent 7890A/5975C GC/MS previously calibrated with PAH standards under specific temperature programmed inlet, oven and detector conditions. The equipment turned out the concentration of the PAHs as the sample details were supplied for water samples.

## **RESULTS AND DISCUSSION**

### **Mean Concentrations of Some Polycyclic Aromatic Hydrocarbon (PAHs) in Water Samples**

The mean concentrations of some polycyclic aromatic hydrocarbon in water samples for point S<sub>1</sub> to S<sub>4</sub> from Gubi Dam, Bauchi State, Nigeria are presented in Table 1.

The highest and the lowest total concentration of 2.44E-05 mg/L were recorded across sampling point S<sub>1</sub> to S<sub>4</sub>.

To describe the occurrence of PAHs in the water, compositional patterns of PAHs were studied. Based on the number of aromatic rings, the compositional patterns of PAHs can be classified into light (2–3 ring), medium (4-ring) and heavy (5–6 ring) PAHs [39].

Table 1: Mean Concentrations of Some PAHs in Water Samples from Gubi Dam, Bauchi State, Nigeria

| Concentrations (mg/L)  |              |      |          |          |          |          |
|------------------------|--------------|------|----------|----------|----------|----------|
| PAHs                   | No. of Rings | MACs | S1       | S2       | S3       | S4       |
| Naphthalene            | 2            | 1    | 1.66E-09 | 2.65E-09 | 1.66E-09 | 1.66E-09 |
| 2-methylnaphthalene    | 2            | 1    | 2.98E-08 | 2.98E-08 | 2.98E-08 | 2.98E-08 |
| Acenaphthylene         | 3            | 3    | 1.43E-09 | 1.43E-09 | 1.43E-09 | 1.43E-09 |
| Acenaphthene           | 3            | 3    | 4.10E-08 | 4.10E-08 | 4.10E-08 | 4.10E-08 |
| Fluorene               | 3            | 3    | 3.09E-09 | 3.09E-09 | 3.09E-09 | 3.09E-09 |
| Phenanthrene           | 3            | 3    | 2.49E-09 | 2.49E-09 | 2.49E-09 | 2.49E-09 |
| Anthracene             | 3            | 3    | 1.82E-08 | 1.82E-08 | 1.82E-08 | 1.82E-08 |
| Fluoranthene           | 4            | 3    | 3.88E-08 | 3.88E-08 | 3.88E-08 | 3.88E-08 |
| Pyrene                 | 4            | 3    | 3.10E-08 | 3.10E-08 | 3.10E-08 | 3.10E-08 |
| Benz(a)anthracene      | 4            | 0.15 | 5.99E-07 | 5.99E-07 | 5.99E-07 | 5.99E-07 |
| Chrysene               | 4            |      | 6.98E-06 | 6.98E-06 | 6.98E-06 | 6.98E-06 |
| Benzo(b)fluoranthene   | 5            | 0.3  | 1.28E-06 | 1.28E-06 | 1.28E-06 | 1.28E-06 |
| Benzo(k)fluoranthene   | 5            |      | 3.98E-06 | 3.98E-06 | 3.98E-06 | 3.98E-06 |
| Benzo(a)pyrene         | 5            | 0.3  | 6.92E-07 | 6.92E-07 | 6.92E-07 | 6.92E-07 |
| Dibenzo(a,h)anthracene | 5            | 0.3  | 4.87E-06 | 4.87E-06 | 4.87E-06 | 4.87E-06 |
| Indeno(1,2,3-cd)pyrene | 6            |      | 5.83E-06 | 5.83E-06 | 5.83E-06 | 5.83E-06 |

MACs = Maximum Allowable Concentrations [38]

From the present study, the concentration of light PAHs had a total load of 7.03E-07 mg/L, which accounted for 32%, was the highest in water samples. The concentration of four-ring PAHs ranked second with a proportion of 23% and a total load of 4.33E-05 mg/L, with 20% was observed for 5-ring PAHs and 15% for 6-ring PAHs with a total load of 2.33E-05 mg/L. The presence of all the studied PAHs in the study area is an indication of mobility and persistent nature of PAHs across all the sampling point within the Dam. The results from this study showed elevated levels of some PAHs across various sampling points within the dam (Table 1). There is variation in the levels of the PAHs at the different points in the same dam. This is due to the different activities taking place at different points. Also, this study revealed that the concentrations of all the PAHs studied were lower than the maximum allowable concentrations as proposed by ATSDR [38]. However, the presence of carcinogenic PAHs in some of the water bodies is a source of worry since they have been stated by the International Agency for Research on Cancer (IARC) and Environmental Protection Agency (EPA) as probable human carcinogens. Most of the heavy-molecular-weight

PAHs are well-known carcinogens and, therefore, their absence is good for the environment. The presence of the studied PAHs in the Dam might expose the inhabitants and the users of this Dam to several risk of cancer related ailment which is in agreement with the study conducted by Aziz *et al.* [40].

### Carcinogenic Risk Assessment of Some Polycyclic Aromatic Hydrocarbon in Water Samples

Table 2 showed the carcinogenic risk assessment of some polycyclic aromatic hydrocarbon in water samples from point S1 to S2 Gubi dam, Bauchi state, Nigeria.

For this study, benzo(a)pyrene (BaP) equivalent dose of mixture of carcinogenic PAH compounds were calculated for carcinogenicity using the following equation adopted by World Bank (2014).

$$ADD = (TEQ \times IR \times CF) / Bw$$

These exposure assumptions were made to be consistent with EPA guidance on assumption on reasonable maximum exposure [41]. Where IR is the ingestion or intake rate of carcinogenic PAHs, CF is the conversion factor and average body weights (BW) in Nigeria is estimated to be 70.

Table 2: Carcinogenic Risk Assessment of Some Polycyclic Aromatic Hydrocarbon in Water Samples from Point S<sub>1</sub> to S<sub>4</sub> in Gubi Dam, Bauchi State, Nigeria

| PAHs                   | Cancer Risk (CR) (mg/kg day <sup>-1</sup> ) |                 |                 |                 |                 |                 |                 |                 |
|------------------------|---|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                        | S1  |                 | S2              |                 | S3              |                 | S4              |                 |
|                        | Children                                    | Adult           | Children        | Adult           | Children        | Adult           | Children        | Adult           |
| Benz(a)anthracene      | 8.90E-09                                    | 1.25E-08        | 8.90E-09        | 1.25E-08        | 8.90E-09        | 1.25E-08        | 8.90E-09        | 1.25E-08        |
| Chrysene               | 1.04E-07                                    | 1.46E-07        | 1.04E-07        | 1.46E-07        | 1.04E-07        | 1.46E-07        | 1.04E-07        | 1.46E-07        |
| Benz(b)fluoranthene    | 1.89E-08                                    | 1.90E-08        | 1.89E-08        | 1.90E-08        | 1.89E-08        | 1.90E-08        | 1.89E-08        | 1.90E-08        |
| Benz(k)fluoranthene    | 5.91E-09                                    | 8.30E-09        | 5.91E-09        | 8.30E-09        | 5.91E-09        | 8.30E-09        | 5.91E-09        | 8.30E-09        |
| Benz(a)pyrene          | 1.03E-07                                    | 1.44E-07        | 1.03E-07        | 1.44E-07        | 1.03E-07        | 1.44E-07        | 1.03E-07        | 1.44E-07        |
| Dibenzo(a,h)anthracene | 7.23E-07                                    | 1.02E-06        | 7.23E-07        | 1.02E-06        | 7.23E-07        | 1.02E-06        | 7.23E-07        | 1.02E-06        |
| Indeno(1,2,3-cd)pyrene | 8.65E-08                                    | 1.22E-07        | 8.65E-08        | 1.22E-07        | 8.65E-08        | 1.22E-07        | 8.65E-08        | 1.22E-07        |
| <b>Total</b>           | <b>1.05E-06</b>                             | <b>1.47E-06</b> | <b>1.05E-06</b> | <b>1.47E-06</b> | <b>1.05E-06</b> | <b>1.47E-06</b> | <b>1.05E-06</b> | <b>1.47E-06</b> |

ILECR= Incremental Life Expectancy Cancer Risk

Table 2 presents the carcinogenic risk values of some polycyclic aromatic hydrocarbons in water samples from different sampling points S<sub>1</sub> to S<sub>4</sub> from Gubi Dam, Bauchi State, Nigeria. The cancer risk (CR) of benzo(a)anthracene ranged from 8.90E-09 to 1.25E-08 mg/l; 1.04E-07 to 1.46E-07 mg/l chrysene; 1.89E-08 to 1.90E-08 mg/l benzo(b)fluoranthene; 5.61E-09 to 8.30E-09 mg/l benzo(k)fluoranthene; 1.03E-07 to 1.44E-07 mg/l benzo(a)pyrene; 7.23E-07 to 1.02E-06 mg/l dibenz (a,h) anthracene and 8.65E-08 to 1.22E-07 mg/l indeno(1,2,3-cd)pyrene. The highest incremental life expectancy cancer risk (ILECR) value of 1.47E-06 mg/l was observed in adults across all the sampling points, while the lowest ILECR value of 1.05E-06 mg/l was observed in children across all the sampling points.

A human health cancer risk assessment was carried out on the PAHs (benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene and indinol(1,2,3-cd)pyrene). In the present study, Gubi Dam is used for fishing, irrigation farming, domestic uses, animal uses, as well as it serves as main sources of water to Bauchi Metropolis and its environment, thereby exposing them to several dangers and the risk of getting cancer. Also, fish caught within the Dam are sold to people within and outside Bauchi State. The estimated lifetime cancer risk for adult users from Gubi Dam via ingestion pathway (Table 2) ranged from 8.30E-09 to 1.02E-06 mg/kg/day. This means that between 8 out of 10<sup>8</sup> adults are likely to suffer cancer-related illness in their lifetime due to (benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene) exposure. The cancer risk value for children ranged from 5.91E-09 to 7.23E-07 mg/kg day<sup>-1</sup>. Similar exposure, between 5 out of 10<sup>7</sup> (Table 2) are likely to suffer cancer-related illness in their lifetime due to carcinogenic PAHs exposure [41]. ILECR across Gubi Dam, Bauchi State ranged from 1.05E-06 to 1.47E-06 mg/kg day<sup>-1</sup>, which means one out of 10<sup>6</sup> are prone to cancer as a result of carcinogenic path exposure. From this study, it also revealed that pollution of the Dam with higher PAHs are observed to be within the safe limit of 10<sup>6</sup> as stipulated by USEPA [41] and ATSDR [38].

## CONCLUSION

Sixteen (16) Polycyclic Aromatic Hydrocarbon residues (PAHs) were determined in the water and a uniform distribution of PAHs were observed across all the sampling points. Cancer risk were carried out on the PAHs from the study area via ingestion of water, which was observed to be higher in adult than children. Based on the findings of this study, Government should setup a



committee for timely monitoring the levels of PAHs in the Dam. Also, further studies should be carried out in urine, hair and blood of the people living around the Dam, in order to analyse the levels of PAHs within the study area. Also recommended is that the populace around the study area should be enlightened on the danger and health risk of PAHs.

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