



Human Health Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) Concentrations in Drinking Water from Three Communities in Rivers State, Nigeria.

Peters, D.E¹., Emeodi, N. F¹., Chuku, L.C¹., Belonwu, D.C¹

¹ Department of Biochemistry, Faculty of Science, University of Port Harcourt, P.M.B 5323, Choba, Rivers State, Nigeria.

Corresponding Author's Email: dikioye.peters@uniport.edu.ng

Abstract: Human health risk assessment of polycyclic aromatic hydrocarbons (PAHs) concentrations in drinking water from Umuechem (Etche Local Government Area-LGA), Bodo (Gokana LGA), and Obrikom (Ogba/Egbema/Ndoni LGA) communities in Rivers State, Nigeria was carried out. Gas chromatography coupled with flame ionization detector (GC-FID) was used for evaluation of PAHs. Result revealed the presence of 16 US Environmental Protection Agency (USEPA) PAHs in all the water samples under investigation. The total PAHs concentrations in borehole water samples from the three communities were in the range of 5.42E-3-1.93E-2. Total PAHs concentrations of borehole water samples from Umuechem (1.93E-2), Bodo (1.38E-2), and Obrikom (5.42E-3) exceeded World Health Organization (WHO) standard value of 0.0002mg/L for drinking water. Benzo(a)pyrene concentration (6.28E-4mg/L) in water sample from Umuechem exceeded USEPA maximum permissible limit, while that of Bodo (1.83E-4) and Obrikom (4.97E-6) were below the limit. High molecular weight PAHs (HMW-PAHs) were predominant in all the water samples when compared to low molecular weight PAHs (LMW-PAHs). Chronic daily intakes (CDI) of PAHs through water consumption in all communities were below the reference dose (RFD). Toxic equivalents (TEQs) values of all the water samples were below the estimated screening value (SV) of 6.62E-2. Calculated hazard quotient (HQ) and hazard index (HI) for both non-carcinogenic and carcinogenic risk through non-dietary exposure were below 1. Estimated cumulative excess cancer risk (ECR) from dietary exposure to water from Umuechem and Bodo exceeded the cancer risk guideline value of 10⁻⁶. Therefore prolong consumption of borehole waters from Umuechem, and Bodo communities could pose potential PAHs human health risk to exposed subjects.

Keywords: Bioaccumulation, PAHs, borehole water, Umuechem, Bodo, Obrikom

I. Introduction

Oil exploration and exploitation are very lucrative, and a major source of revenue in Nigeria. But, like most industrial activities, it produces environmental hazards that are "slow poisons," in that they often take months and years to cause disease and death. This is unlike the contamination of water, food, and the environment with micro-organisms, which immediately results in ill health [1].

Polycyclic aromatic hydrocarbons (PAHs), are large class of persistent organic pollutants containing two or more fused benzene (aromatic) rings.

Polycyclic aromatic hydrocarbons (PAHs) are also a group of approximately 10,000 organic compounds that have received global attention due to their toxic, mutagenic and carcinogenic properties [2]. The six PAHs listed as carcinogens are benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, and indeno(1,2,3-cd)pyrene [3]. They are known to be ubiquitous in both marine and terrestrial environments [4] and are included in the EU and USEPA priority pollutant list due to their mutagenic and carcinogenic properties. Predominant exposure route is dietary, excluding smokers and occupationally exposed populations. As chemically stable lipophilic compounds they can easily cross lipid membrane and have the potential

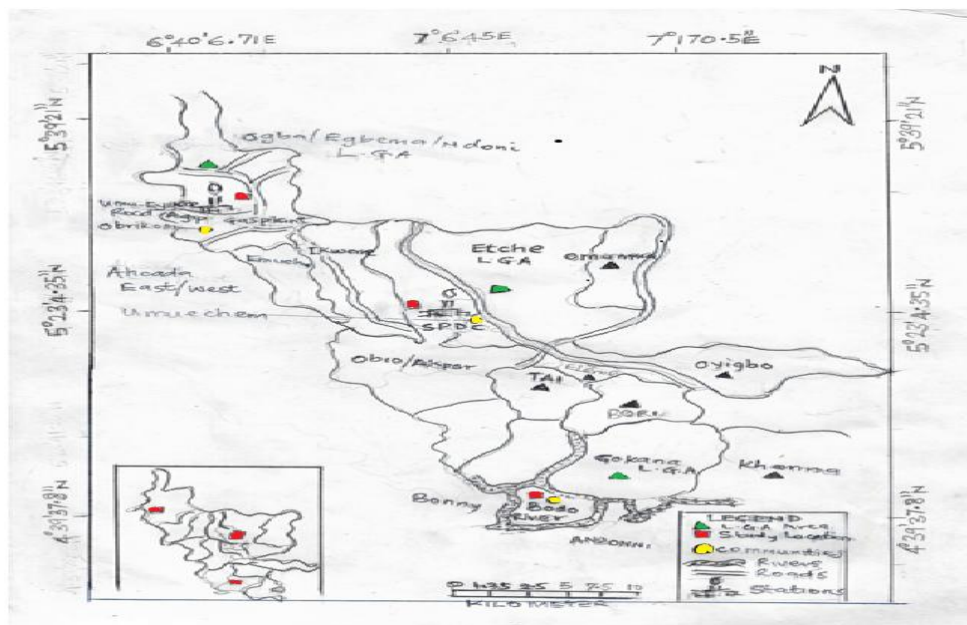
to bioaccumulate in tissues of organisms. Based on physical and biological properties, PAHs are classified into high molecular weight (HMW) and low molecular weight (LMW) types. Those consisting of 4–6 aromatic rings are termed HMW. On the other hand, LMW PAHs consists of 2–3 aromatic rings and although less carcinogenic than HMW type [5].

Polycyclic aromatic hydrocarbons are chemically stable and can be found practically every where in soil, water and food. Their presence in food is of major interest, as they could be found in cereals, grains, flour bread, vegetables, fruits, meats, processed or pickled foods and even contaminated cow milk [6].

II Materials and Methods

2.1 Study areas

The study areas namely Umuechem, Bodo and Obrikom communities are situated in Etche, Gokana and Ogba/Egbema/Ndoni Local Government Areas of Rivers State respectively. Umuechem study area has borne the hazards of oil and gas exploration. Umuechem is situated 28km and is located at longitude 7°6'45" East and latitude 5°39'21" North. Most of the people dwelling in the community engage in agriculture. The Bodo study area has a tragic history of pollution from oil spills; oil well fires, environmental incidents, such as spills and uncontrolled flares. Gokana is one of the six kingdoms of Ogoniland. Bodo community lies on the coastal low land of Niger Delta, in the southern part of Gokana Local Government Area of Rivers State. Bodo is located between latitude 4°36' 0" North and longitude 7°21'0" East of the equator. Most of the dwellers in Bodo are famous farmers and fishers. Obrikom is situated 598km north of the equator, and is located at longitude 6°406'.71" East and latitude 5°23'41.35" North. Agip gas plant is situated near the Obrikom area.



Source: [7; 8]

Fig 1.0 Map of Etche, Gokana, and Ogba/Egbema/Ndoni showing sampling areas .

2.2 Collection of test sample

The borehole water samples were collected from three different communities; Bodo community situated at Gokana Local Government Area (LGA), Umuechem community situated at Etche Local Government Area (LGA), and Obrikom community situated at Ogba/Egbema/Ndoni Local Government Area (LGA) in Rivers State, Nigeria. At each study site, one water sample was collected in sample bottle wrapped in aluminum foils and transported to the laboratory (Anal Concept) for analysis.

2.3 Reagents

All reagents used in this study were of analytical grades with high purity.

2.4.0 Determination of Polycyclic Aromatic Hydrocarbons (PAHs) Concentrations in Borehole Water

2.4.1 Principle

The various components are separated inside the column. The detector measures the quantity of the components that exit (elute) out of the column. To determine a sample with an unknown concentration, a standard sample with known concentration is injected into the injector of the gas chromatography.

2.4.2 Extraction Procedure

To extraction PAHs in liquid sample, thirty milliliter (30ml) of water sample was transferred into (100ml) measuring cylinder and poured into (250ml) separating funnel. A volume (10ml) of the extraction solvent n-hexane was added into the water sample, and the separating funnel was covered with a cork and shaken vigorously to homogenize the sample. The separating funnel was uncorked to allow the mixture to settle. The mixture separated into two layers; the upper layer was water, while the lower layer was the extracting organic solvent. The tap of the separating funnel was opened gently to collect the lower layered extracting organic solvent into a beaker while the upper layer containing the water was discarded. The extract was carefully filtered using a filter paper containing anhydrous sodium sulphate into a container. The extract was concentrated to 2ml and then transferred for cleanup/separation.

2.4.3 Cleanup/separation

Moderately packed glass wool of length 1cm was placed at the bottom of 10mm ID *250mm loup chromatographic column. Slurry of 2g activated silica in 10ml dichloromethane was prepared and placed in the chromatographic column. To the top of the column was added 0.5cm sodium sulphate. The column was rinsed with additional 10ml of dichloromethane.

The column was pre-eluted with 20ml of n-hexane by allowing the solvent to flow through the column at a rate of about 20 minutes until the liquid in the column was just above the sulphate layer. Thereafter, 1ml of the extracted sample was transfer into the column and the extraction bottle rinsed with 1ml of n-hexane and added to the column as well. The stop-cork of the column was opened and the eluent was collected with a 10ml graduated cylinder.

Prior to exposure of the sodium sulphate layer to air, n-hexane was added to the column in 1-2ml increments. Accurately measured volume of 8-10ml of the eluent was collected and labeled aromatic [9].

2.4.4 Gas Chromatographic Analysis

The concentrated aromatic fraction was transferred into labeled glass vials with teflon rubber crimp caps for GC analysis. A volume of 1µl of the concentrated sample was injected by means of hypodermic syringe through a rubber septum into the column. Separation occurred as the vapour constituent partitioned between the gas and the liquid phases. The sample was automatically detected as it emerged from the column (at a constant flow rate) by the FID detector whose response was dependent upon the composition of the vapour.

2.4.5 Chromatographic Conditions

The gas chromatography was Hewlett Packed 5890 series II, gas chromatography apparatus, coupled with flame ionization detector (FID) (Hewlett Packard, Wilmington, DE, USA), powered with HP chemstation Rev. A09:01 (10206) software to identify and quantify compounds. The GC operating conditions were as specified by the procedural manual.

2.5 Human health risk assessment of PAHs

2.5.1 The guideline value

The toxicological risk associated with PAHs concentrations in water was assessed through comparison of the observed concentrations with guideline value. Concentration of individual PAHs in the water and total PAH concentrations (sum of all the assessed PAH congeners) were assessed. Concentrations of benzo(a)pyrene (B(a)P), which has been accepted as a marker for the occurrence of carcinogenic PAHs in water as specified in the maximum acceptable level of 0.0002mg/L for benzo(a)pyrene in water [10].

2.5.2 Human health risk consumption of water

To evaluate human health risk of PAH exposure, the non-carcinogenic and carcinogenic risks were evaluated using human intake models [11; 12,13]. Values for parameterization of models are presented in Table 1. Assessment was determined using an average adult weight of 60kg.

2.5.3 Non-carcinogenic risk through non-dietary exposure for water

Non-carcinogenic risk to human through non-dietary exposure to PAH, the hazard quotient (HQ) and hazard index (HI) were determined. Risks through ingestion of borehole water was estimated. HQ ratios greater than 1 indicate potential non-carcinogenic health risk. To estimate risk to humans by ingestion of borehole water, HQ was estimated as the ratio of the chronic daily intake (CDI water ingestion) to the reference dose (RfD) Eq. 1). The CDI water ingestion was estimated using Eq. 2.

$$\text{Hazard quotient (HQ Water Ingestion)} = \frac{\text{CDI Water Ingestion}}{\text{RfD}} \quad (1)$$

$$\text{Chronic Daily Intake (CDI Water Ingestion)} = \frac{\text{Cw} \times \text{IRw} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{ATn}} \quad (2)$$

In order to evaluate the total health risk from complex pollutants (risk from exposure to the different PAH mixtures), the hazard index (HI) was applied. The HI was estimated as the sum of HQs for the individual PAHs (Eq. 3). Risk was ascertained if these ratios exceed 1.0 [14].

$$\text{HI} = \sum_{i=1}^n \text{HQ}_i \quad (3)$$

3.3.4 Carcinogenic risk through dietary exposure of water for PAHs

HQs for carcinogenic risk from ingestion exposure to water tubers was assessed by multiplying the CDI by the cancer slope factor (SF) [14] (Eq. 4)

$$\text{Carcinogenic risk} = \text{CDI} \times \text{SF} \quad (4)$$

Cancer risk due to dietary exposure to PAHs in water was assessed using individual PAH carcinogenic .To assess human health risks from dietary exposure to PAHs through consumption of water (dietary intake), human intake models were applied. The Chronic Daily Intake (CDI) concentrations of PAH's from ingestion of contaminated water and PAHs were assessed. Carcinogenic risks were also assessed by evaluating the carcinogenic potencies of Individual PAH carcinogenic potencies of individual PAHs (B(A)Pteq), the carcinogenic toxic equivalents (TEQs) or potency equivalent concentrations (PECs) and the excess cancer risk (ECR) index. The Carcinogenic potencies of individual PAHs B(A)Pteq was evaluated by multiplying the PAH concentration in the sample by the individual toxicity equivalency factor (TEF) (Eq. 5) TEF is an estimate of the relative toxicity of individual PAH fraction compared to benzo(a)pyrene. Toxic equivalency factors have been applied as a useful tool for the regulation of compounds with a common mechanism of actions (e.g PAHs). The TEFs developed by Nisbet and LaGoy [15] was applied and these values were used to calculate PAH as benzo[a]pyrene equivalents for a standard adult with 60 kg body weight.

$$\text{(B(A)Pteq)} = \text{Ci} \times \text{TEFi} \quad (5)$$

The TEQs were estimated as the sum of the carcinogenic potencies of individual PAHs (B(A)Pteq; Eq. 6, [16].

$$\text{Carcinogenic toxic equivalents (TEQs)} = \sum \text{B(A)Pteq} \quad (6)$$

The evaluated TEQ value was compared with a Screening value to assess the health risks of PAHs to humans from water consumption. The screening value (SV) is the threshold concentration of chemicals in edible tissue that is of potential public health concern [17; 18]. The screening value was calculated using Eq. 7 [19; 17; 18].

$$\text{Screening value (SV)} = \frac{\left[\left(\frac{\text{RL}}{\text{SF}} \right) \times \text{BW} \right]}{\text{IR}} \quad (7)$$

The excess cancer risk induced by dietary exposure to PAHs via water was assessed using Eq. 10 [20].

$$\text{Excess cancer risk (ECR)} = \frac{\sum Q \times B(A) \times P \times I \times R \times ED}{(BW \times AT \times n)} \quad (10)$$

In the case of exposure to several carcinogenic substances, the total risk or the cumulative excess cancer risk assessed was in accordance with the principle of the cumulative effect of carcinogens on the body, by adding the risks calculated for the individual carcinogens using Eq. 11 :

$$\text{ELCR}_{\text{tot}} = \sum_{i=1}^n \text{ELCR}_i \quad (11)$$

ELCR_{total}- the total excess risk of occurrence of carcinogenic effects, caused by all the substances.

ELCR_i = the excess risk assessed for the *i*th substance.

III RESULTS

PAHs concentrations in water from Umuechem, Bodo and Obrikom communities

Results from Table 1 showed that water from Umuechem and Bodo contain all the PAHs components under investigation at detectable limit, while chrysene was not detectable in water from Obrikom. The highest and least PAHs concentrations are fluorene (6.25E-3) and chrysene (1.81E-5) from Umuechem, pyrene (5.35E-3) and acenaphthalene (4.45E-5) from Bodo and benzo(a)anthracene (3.79E-3) and indeno(1,2,3-cd)pyrene (4.22E-7) from Obrikom. Water from Umuechem had the highest total PAH (1.92E-2) followed by Bodo (1.38E-2) and lastly Obrikom (5.42E-3). The total PAHs concentrations in borehole water samples for Umuechem (1.93E-2), Bodo (1.38E-2), and Obrikom (5.42E-3) exceeded World Health Organization (WHO) maximum permissible limits of 0.0002mg/L (0.2ug/L) in drinking water. However, benzo(a)pyrene concentration (6.28E-4) in water sample from Umuechem, exceeded USEPA maximum permissible limit 0.0002mg/L , while that of Bodo (1.83E-4) and Obrikom (4.97E-6) were below. The LMW-PAH/HMW-PAH ratios in water were 4.05, 0.61 and 0.06 from Umuechem, Bodo, and Obrikom respectively. The LMW-PAH/HMW-PAH ratio in Umuechem water was >1, while that of Bodo and Obrikom were < 1. BaA/(BaA+Chry) ratios in water were 0.85, 0.34 and 1.00 for Umuechem, Bodo and Obrikom respectively. Of BaA/(BaA+Chry) ratios in water from Umuechem and Obrikom were > 0.35, while that of water from Bodo was < 0.35.

Table 1: Polycyclic Aromatic Hydrocarbons (PAHs) concentrations (mg/L) in Water from Umuechem, Bodo, and Obrikom Communities in Rivers State.

PAHs components	Code	Umuechem	Bodo	Obrikom
Naphthalene	Nap	1.18E-3	7.00E-5	9.92E-7
2-methylnaphthalene	2-MNap	2.41E-3	3.29E-4	1.12E-5
Acenaphthylene	AcPY	5.18E-5	4.51E-4	6.36E-6
Acenaphthene	Acp	9.16E-4	4.45E-5	1.27E-5
Fluorene	Flu	6.25E-3	5.59E-4	1.17E-4
Phenanthrene	Phe	3.26E-3	2.36E-3	1.01E-4
Anthracene	Ant	1.38E-3	1.43E-3	3.66E-5
Fluoranthene	Fl	3.88E-4	1.23E-3	5.84E-4
Pyrene	Pyr	5.89E-5	5.35E-3	4.48E-4
Benzo(a)anthracene	BaA	1.05E-4	9.37E-5	3.79E-3
Chrysene	Chr	1.81E-5	1.85E-4	ND
Benzo(b)fluoranthrene	BbF	1.46E-3	5.96E-4	2.65E-4
Benzo(k)fluoranthrene	BKF	1.01E-4	2.96E-4	3.59E-5
Benzo(a)pyrene	Bap	6.28E-4	1.83E-4	4.97E-6
Indeno(1,2,3-cd)pyrene	Ind	1.56E-4	2.34E-4	4.22E-7
Dibenzo(a,h)anthracene	DBA	8.96E-4	3.96E-4	2.05E-6
Total PAHs		1.93E-2	1.38E-2	5.42E-3
PEC		5.32E-3	2.31E-3	1.03E-5
LMW-PAH/HMW-PAH ratio		4.05	0.61	0.06

BaA/(BaA+Chry) ratio 0.85 0.34 1.00

ND= Not detected

Human health risk assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Water

Human Health Risk Through Non-dietary Exposure of PAHs in Water

The estimated hazard quotients (HQ) and hazard index (HI) values for non-carcinogenic and carcinogenic risk from exposure to PAHs in water through non-dietary exposure are presented in Table 2-4.

Hazard quotient (HQ) and hazard index (HI) for non-carcinogenic and carcinogenic Risk of PAHs in water

For non-carcinogenic health risk, HI values for water were 5.56E-3, 2.53E-3 and 2.02E-4 respectively from Umuechem, Bodo and Obrikom. For carcinogenic health risk HI, values for water were 1.24E-4, 4.91E-5, and 1.97E-7 at Umuechem, Bodo and Obrikom. Therefore, the HQ's and HI's values for water are below 1.

Table 2: Hazard Quotient (HQ) values for non-carcinogenic and carcinogenic risk of PAHs concentration in borehole water from Umuechem

PAHs components	Code	RFD	CDI Ingestion	HQ Non-carcinogenic	Carcinogenic Ingestion
Naphthalene	Nap	0.02	1.18E-5	0.000590	NA
2-methylnaphthalene	2-MNap	0.04	2.41E-5	0.000603	NA
Acenaphthylene	AcPY	0.02	5.18E-5	0.002590	NA
Acenaphthene	Acp	0.06	9.16E-6	0.000153	NA
Fluorene	Flu	0.04	6.25E-5	0.001560	NA
Phenanthrene	Phe	NA	3.26E-5	NA	NA
Anthracene	Ant	0.3	1.38E-5	0.000046	NA
Fluoranthene	Fl	0.04	3.88E-6	0.000097	NA
Pyrene	Pyr	0.03	5.89E-7	0.000019	NA
Benzo(a)anthracene	BaA		1.05E-6	NA	7.70E-7
Chrysene	Chr		1.81E-7	NA	1.32E-9
Benzo(b)fluoranthrene	BbF		1.46E-5	NA	1.07E-5
Benzo(k)fluoranthrene	BkF		1.01E-6	NA	7.37E-8
Benzo(a)pyrene	Bap		6.28E-6	NA	4.58E-5
Indeno(1,2,3-cd)pyrene	Ind		1.56E-6	NA	1.14E-6
Dibenzo(a,h)anthracene	DBA		8.96E-6	NA	6.54E-5
Hazard Index (HI)			2.44E-4	5.56E-3	1.24E-4

NA reference dose (RfD) not available, HQ could not be estimated

Table 3: Hazard Quotient (HQ) values for non-carcinogenic and carcinogenic risk of PAHs concentration in borehole water from Bodo

PAHs Components	Code	RFD	CDI Ingestion	HQ Non-carcinogenic	Carcinogenic Ingestion
Naphthalene	Nap	0.02	7.00E-7	0.000035	NA
2-methylnaphthalene	2-MNap	0.04	3.29E-6	0.000082	NA
Acenaphthylene	AcPY	0.02	4.51E-6	0.000226	NA
Acenaphthene	Acp	0.06	4.45E-6	0.000007	NA
Fluorene	Flu	0.04	5.59E-6	0.000139	NA
Phenanthrene	Phe	NA	2.36E-7	NA	NA
Anthracene	Ant	0.3	1.43E-7	0.000005	NA
Fluoranthene	Fl	0.04	1.23E-5	0.000308	NA
Pyrene	Pyr	0.03	5.35E-5	0.001783	NA
Benzo(a)anthracene	BaA		9.40E-7	NA	5.11E-7
Chrysene	Chr		1.90E-7	NA	1.39E-9
Benzo(b)fluoranthrene	BbF		5.96E-6	NA	4.35E-6
Benzo(k)fluoranthrene	BKF		2.96E-6	NA	2.16E-7
Benzo(a)pyrene	Bap		1.83E-6	NA	1.34E-5
Indeno(1,2,3-cd)pyrene	Ind		2.34E-6	NA	1.71E-6
Dibenzo(a,h)anthracene	DBA		3.96E-6	NA	2.89E-5
Hazard Index (HI)			9.89E-5	2.58E-3	4.91E-5

NA reference dose (RfD) not available, HQ could not be estimated

Table 4: Hazard Quotient (HQ) values for non-carcinogenic and carcinogenic risk of PAHs concentration in borehole water from Obrikom

PAHs components	CODE	RFD	CDI Ingestion	HQ Non-carcinogenic	Carcinogenic Ingestion
Naphthalene	Nap	0.02	9.93E-9	4.97E-7	NA
2-methylnaphthalene	2-MNap	0.04	1.12E-7	2.80E-6	NA
Acenaphthylene	AcPY	0.02	6.36E-8	3.20E-6	NA
Acenaphthene	Acp	0.06	1.27E-7	2.10E-6	NA
Fluorene	Flu	0.04	1.17E-4	2.93E-5	NA
Phenanthrene	Phe	NA	1.01E-6	NA	NA
Anthracene	Ant	0.3	3.66E-7	1.20E-6	NA
Fluoranthene	Fl	0.04	5.84E-6	1.46E-4	NA
Pyrene	Pyr	0.03	4.48E-6	1.49E-4	NA
Benzo(a)anthracene	BaA		3.79E-5	NA	2.77E-5
Chrysene	Chr		ND	NA	NA
Benzo(b)fluoranthrene	BbF		2.65E-6	NA	1.94E-6
Benzo(k)fluoranthrene	BKF		3.60E-7	NA	2.64E-8
Benzo(a)pyrene	Bap		5.00E-8	NA	3.65E-7
Indeno(1,2,3-cd)pyrene	Ind		4.22E-9	NA	3.08E-9
Dibenzo(a,h)anthracene	DBA		2.05E-8	NA	1.49E-7
Hazard Index (HI)			1.69E-4	2.02E-4	3.02E-5

NA reference dose (RfD) not available, HQ could not be estimated

Human health risk through dietary exposures of PAHs in water

Chronic daily intake (CDI) of PAHs in water

The CDI's values in Table 2 in water was analysed for adult of 60kg population. The total CDI values (mg/L) calculated from individual PAH concentrations in water ranged from 2.44E-4, 9.89E-5 and 1.69E-4 for Umuechem, Bodo and Obrikom respectively.

Carcinogenic human health risk assessment of PAHs in water

The estimated individual carcinogenic potencies B(A)Pteq, carcinogenic toxic equivalents (TEQs), screening value (SV) and excess cancer risk (ECR) are presented in Table 5.

Individual PAH Carcinogenic Potencies (B(A)Pteq) in water

Individual PAH carcinogenic potencies varied for water assessed.

Carcinogenic Toxic Equivalents (TEQ) of PAHs in the water

The carcinogenic toxic equivalents (TEQs) or potency equivalent concentrations (PECs) of PAHs in Umuechem, Bodo, and Obrikom water estimated were 5.32E-3, 2.31E-3, 4.58E-4 respectively and 7.45E-4 respectively in Table 5-7. The observed TEQs values were however lower than the calculated screening value (SV) of 6.65E-2mg/L in water from all the sites (Table 5-7).

Screening value (SV) of PAHs in water

The screening value (SV) was evaluated to determine the health risks of PAHs to human from the ingestion of water. The screening value is the threshold concentration of a chemical in edible tissues that is of potential public health concern [17; 18]. The estimated screening value of 6.65E-2mg/L in water was obtained. Result suggest that the TEQ values for water in all were below the SV in water.

Excess Cancer Risk (ECR) of PAHs in the water

The estimated ECR resulting from life long exposure to PAHs through water consumption were compared to the acceptable guideline value of 1×10^{-6} [16; 21]. The cumulative excess cancer risk values estimated for water of 2.46E-6 and 1.10E-6 from Umuechem and Bodo respectively exceeded the cancer risk guideline value 1×10^{-6} . While Obrikom was below the value.

Table 5: Toxic equivalent factor (TEF), Toxic equivalent (TEQ), Screening Value (SV) and Excess Cancer Risk (ECR) of PAHs in water from Umuechem.

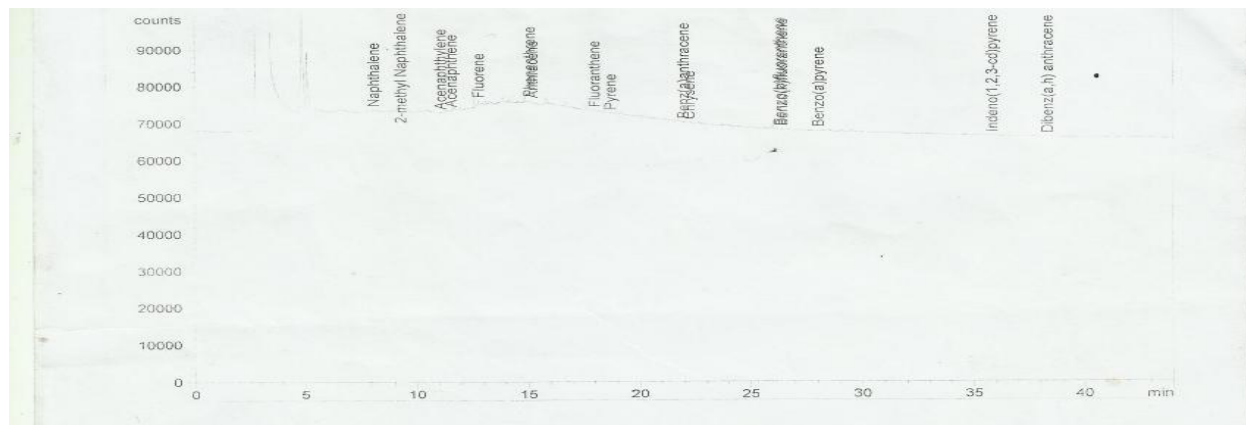
PAHs components	Code	TEF	Cw (mg/L)	B(A)Pteq (mg/L)	SV	ECR (mg/L)
Naphthalene	Nap	0.001	1.18E-3	1.18E-6	NA	5.45E-10
2-methylnaphthalene	2-MNAP	0.001	2.41E-3	2.41E-6	NA	1.11E-9
Acenaphthylene	AcPY	0.001	5.18E-5	5.18E-6	NA	2.39E-11
Acenaphthene	Acp	0.001	9.16E-4	9.16E-7	NA	4.23E-10
Fluorene	Flu	0.001	6.25E-3	6.25E-6	NA	2.89E-9
Phenanthrene	Phe	0.001	3.26E-3	3.26E-6	NA	1.51E-9
Anthracene	Ant	0.01	1.38E-3	1.38E-5	NA	6.38E-9
Fluoranthene	Fl	0.001	3.88E-4	3.88E-7	NA	1.79E-10
Pyrene	Pyr	0.001	5.89E-5	5.89E-8	NA	2.72E-11
Benzo(a)anthracene	BaA	0.1	1.05E-4	1.05E-5	0.000587	4.85E-9
Chrysene	Chr	0.01	1.81E-5	1.81E-7	0.058708	8.37E-11
Benzo(b)fluoranthrene	BbF	0.1	1.46E-3	1.46E-4	0.000587	6.75E-8
Benzo(k)fluoranthrene	BkF	0.1	1.01E-4	1.01E-5	0.005871	4.67E-9
Benzo(a)pyrene	Bap	1	6.28E-4	6.28E-4	0.000059	2.90E-7
Indeno(1,2,3-cd)pyrene	Ind	0.1	1.56E-4	1.56E-5	0.000587	7.21E-9
Dibenzo(a,h)anthracene	DBA	5	8.96E-4	4.48E-3	0.000059	2.07E-6
				TEQ = 5.32E-3	SV = 6.65E-2	ECR = 2.46E-6

Table 6: Toxic equivalent factor (TEF), Toxic equivalent (TEQ), Screening Value (SV) and Excess Cancer Risk (ECR) of PAHs in water from Bodo.

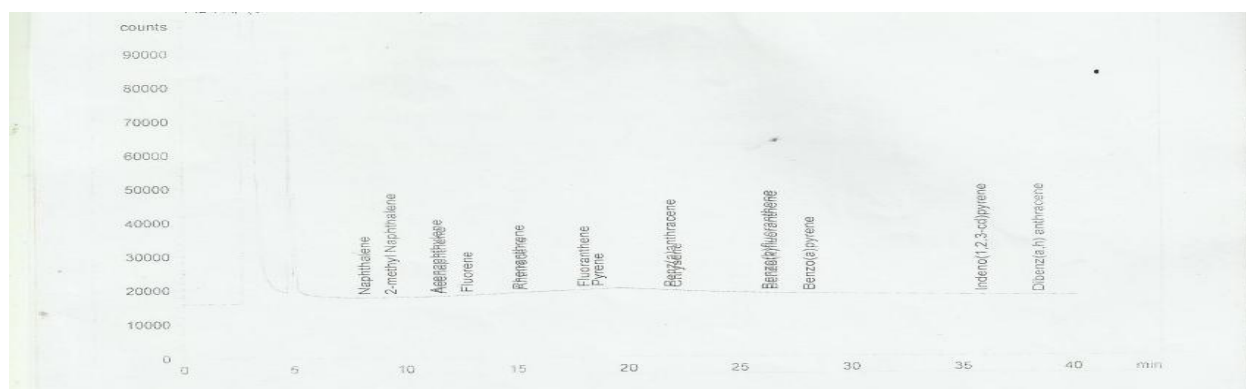
PAHs components	Code	TEF	Cw (mg/L)	B(A)teq (mg/L)	SV	ECR (mg/L)
Naphthalene	Nap	0.001	7.00E-5	7.00E-8	NA	3.25E-11
2-methylnaphthalene	2-MNap	0.001	3.29E-4	3.29E-7	NA	1.52E-10
Acenaphthylene	AcPY	0.001	4.51E-4	4.51E-7	NA	2.09E-10
Acenaphthene	Acp	0.001	4.45E-5	4.45E-8	NA	2.07E-11
Fluorene	Flu	0.001	5.59E-4	5.59E-7	NA	2.58E-10
Phenanthrene	Phe	0.001	2.36E-3	2.36E-6	NA	1.06E-9
Anthracene	Ant	0.01	1.43E-3	1.43E-5	NA	6.61E-9
Fluoranthene	Fl	0.001	1.23E-3	1.23E-6	NA	5.69E-10
Pyrene	Pyr	0.001	5.35E-3	5.35E-6	NA	2.47E-9
Benzo(a)anthracene	BaA	0.1	9.37E-5	9.37E-6	0.000587	4.33E-9
Chrysene	Chr	0.01	1.85E-4	1.85E-6	0.058708	8.55E-10
Benzo(b)fluoranthrene	BbF	0.1	5.96E-4	5.96E-5	0.000587	2.75E-8
Benzo(k)fluoranthrene	BKF	0.1	2.96E-4	2.96E-5	0.005871	1.37E-8
Benzo(a)pyrene	Bap	1	1.83E-4	1.83E-4	0.000059	8.46E-8
Indeno(1,2,3-cd)pyrene	Ind	0.1	2.34E-4	2.34E-5	0.000587	1.08E-8
Dibenzo(a,h)anthracene	DBA	5	3.96E-4	1.98E-3	0.000059	9.15E-7
				TEQ = 2.31E-3	SV = 6.65E-2	1.10E-6

Table 7: Toxic equivalent factor (TEF), Toxic equivalent (TEQ), Screening Value (SV) and Excess Cancer Risk (ECR) of PAHs in water from Obrikom.

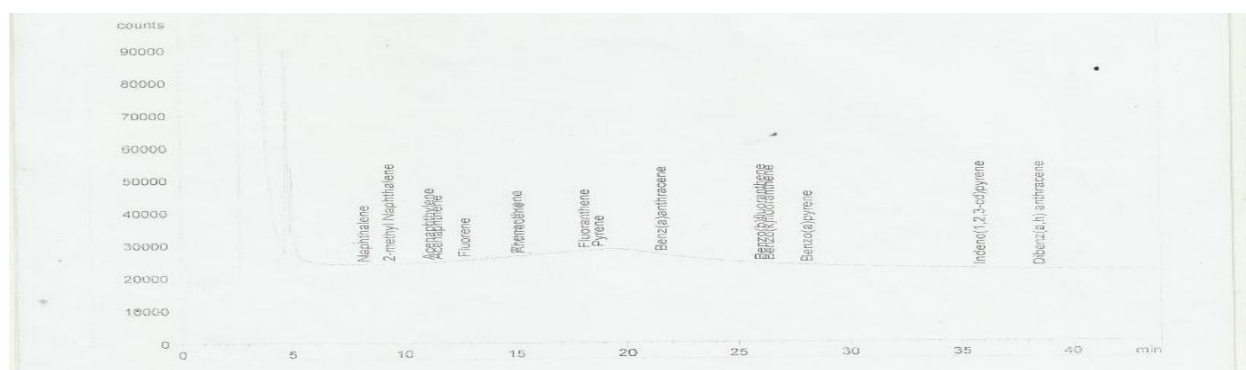
PAHs components	Code	TEF	Cw (mg/L)	B(A)Pteq (mg/L)	SV	ECR(mg/L)
Naphthalene	Nap	0.001	9.92E-7	9.92E-10	NA	3.91E-13
2-methylnaphthalene	2-MNap	0.001	1.12E-5	1.12E-8	NA	5.18E-10
Acenaphthylene	AcPY	0.001	6.36E-6	6.36E-9	NA	1.76E-10
Acenaphthene	Acp	0.001	1.27E-5	1.27E-8	NA	5.87E-12
Fluorene	Flu	0.001	1.17E-4	1.17E-7	NA	5.40E-11
Phenanthrene	Phe	0.001	1.01E-4	1.01E-7	NA	4.66E-11
Anthracene	Ant	0.01	3.66E-5	3.66E-7	NA	1.69E-10
Fluoranthene	Fl	0.001	5.84E-4	5.84E-7	NA	2.70E-10
Pyrene	Pyr	0.001	4.48E-4	4.48E-7	NA	2.07E-10
Benzo(a)anthracene	BaA	0.1	3.79E-3	3.79E-4	0.000587	1.75E-7
Chrysene	Chr	0.01	ND	ND	0.058708	NA
Benzo(b)fluoranthrene	BbF	0.1	2.65E-4	2.64E-5	0.000587	1.22E-8
Benzo(k)fluoranthrene	BKF	0.1	3.59E-5	3.59E-5	0.005871	1.66E-9
Benzo(a)pyrene	Bap	1	4.97E-6	4.97E-6	0.000059	2.29E-9
Indeno(1,2,3-cd)pyrene	Ind	0.1	4.22E-7	4.22E-8	0.000587	1.95E-11
Dibenzo(a,h)anthracene	DBA	5	2.05E-6	1.03E-5	0.000059	4.76E-9
				TEQ = 4.58E-4	SV = 6.65E-2	ECR= 1.97E-7



Etche water



Gokana water



Obrikom Water

IV DISCUSSION

The concentration of PAHs

The analyses of 16 US Environmental Protection Agency (USEPA) concentrations of polycyclic aromatic hydrocarbons (PAHs) in water was an indication of PAHs contamination in food , and which are ubiquitous in the environment. The exposure pathways of PAHs for water involved ingestion of PAH-contaminated particulate matter along with food [22], as PAH readily adsorb onto particulate organic matter [23]. Pyrene release to the environment is ubiquitous since it's a product of incomplete combustion. It's largely associated with particulate matter, soils and

sediments. Although, environmental concentrations are higher primary sources, its presence in places distant from those primary sources indicates that its reasonably stable in the atmosphere and capable of long distance transport [24]. Pyrolysis of polycyclic aromatic hydrocarbon residues leads to the formation of additional higher molecular weight polycyclic aromatic hydrocarbons and, consequently increases the PAHs concentration in the sample [25]. The LMW-PAH/HMW-PAH ratio showed the predominant of HMW-PAHs to that of LMH-PAHs, and this may be due to the fact that LMH-PAHs are preferentially degraded during PAH transport [26]. Although there was an exception in this trend as the LMW-PAH/HMW-PAH ratio in water from Umuechem (4.05).

The BaA/(BaA+Chry) ratios in water was > 0.35 which indicate pyrogenic sources, except water from Bodo which was < 0.35 , thereby indicating mixed petrogenic and pyrogenic source. Therefore, showed mixed petroleum [27].

The USEPA's and WHO's established a maximum permissible limit for benzo(a)pyrene of 0.0002mg/L (0.2ug/L) for drinking water [28, 29; 10]. The individual benzo(a)pyrene concentration such as 6.28E-4mg/L for water sample from Umuechem exceeded this standard of 0.0002mg/L for PAHs, when compared to water samples from Bodo and Obrikom. Undoubtedly, these results call for public concerns, especially as PAHs have been confirmed to be carcinogenic [30], in drinking water consumption of contaminated PAHs. Inevitably, man suffers the greatest risk of bioaccumulation due to his position in the tropic chain, being a tertiary consumer in addition to his predisposition to other route of entry into his body.

Estimation of Hazard Quotient (HQ) for Non-carcinogenic and Carcinogenic Risk of PAHs

The risk associated with non-dietary exposure to non-carcinogenic PAHs in water were evaluated using a hazard quotient approach. Hazard quotient values were evaluated on the basis of the reference dose (RfD) for PAHs as proposed by USEPA [31] (2004). From the results of the study, the HQ values of all the borehole water were below 1. The calculated HQ and HI from non-carcinogenic and carcinogenic risk from non-dietary exposure to the investigated water as presented in Table 2-4 are below 1, indicating no direct hazard to human health inspite of their presence in the food when ingested.

HUMAN HEALTH RISK THROUGH DIETARY EXPOSURES OF PAHs.

Estimated Chronic Daily Intake (CDI) and Estimated Daily Intake (EDI) of PAHs.

Estimated chronic daily intake of PAHs from ingestion water were assessed to evaluate the consumption of PAHs. The CDI's value was used to assess the health risk of toxicant imperatively through dietary exposure of PAHs. The values in Table 2-4 in water were analysed for adult of 60kg population. Human health risk through dietary exposure of water for the CDI's values were lower than the recommended reference dose (RfD's) levels, indicating that the concentrations were within acceptable permissible limits for food safety. Therefore, dietary exposure of PAHs through ingestion of food could potentially pose no serious health risk to the populace. Although, continuous daily consumption of the water could result in bioaccumulation of toxic levels.

Carcinogenic Human Health Risk Assessment of PAHs

The estimated individual carcinogenic potencies B(A)Pteq, carcinogenic toxic equivalents (TEQs), screening value (SV) and excess cancer risk (ECR) are presented in Table 5-7.

Individual PAH Carcinogenic Potencies (B(A)Pteq) of PAHs

The (B(A)Pteq) estimated was implemented to directly assess the carcinogenic risk due to dietary to PAHs. Individual PAH carcinogenic potencies varied for the water and tubers assessed.

Carcinogenic Toxic Equivalents (TEQ) of PAHs

The approach was implemented to directly estimate the carcinogenicity of PAH contamination of the borehole water. The observed TEQs values were however lower than the calculated screening value (SV) of 6.65E-2mg/L in water in all the sites (Table 5-7), which is the threshold concentration of total PAHs in the borehole water and tubers that is of potential public health concern [17]. Although, PEC values for water was below the SV in all the water and analysed, indicating that ingestion of such water at rate of 1.4L/day do not prone to have adverse health effects to the residents and therefore is not of potential public health concern.

Screening Value (SV) of PAHs

The screening value (SV) was evaluated to determine the health risks of PAHs to human from the ingestion of water. The screening value is the threshold concentration of a chemical in edible tissues that is of potential public health concern [17; 18]. The estimated screening value of 6.65E-2mg/L in water was obtained. Result suggest that

the TEQ values for water was below the SV in water. This showed that the water was not of public health concern.

Excess Cancer Risk (ECR) of PAHs

The excess cancer risk of an adult population with an average weight of 60kg caused by dietary exposure to PAHs was determined. The estimated ECR resulting from life long exposure to PAHs through water consumption was compared to the acceptable guideline value of 1×10^{-6} [16] USEPA stipulated that level of risk where there is a lifetime cancer risk of 1 in a million ($ECR=10^{-6}$) over 70 years lifetime period, is considered acceptable, while an instance where there is an additional lifetime cancer risk in 10,000 or greater ($ECR=10^{-4}$) is considered serious [32]. In the case of exposure to several carcinogenic PAHs, the total risk was assessed in accordance with the principle of cumulative effect of carcinogens on the body, by adding the risk calculated for the individual carcinogens to evaluate the cumulative excess cancer risk. The cumulative excess cancer risk values estimated for water of 2.46E-6 and 1.10E-6 from Umuechem and Bodo respectively exceeded the cancer risk guideline value 1×10^{-6} . While that of water from Obrikom was below the value [33].

The results of cumulative ECR value clearly suggest that adverse exposure effects for PAHs in water could be caused by life long consumption of water and would result in cancer health risk potential.

V. CONCLUSION

This study revealed that polycyclic aromatic hydrocarbons (PAHs) are present in borehole water. The total PAHs concentrations in borehole water analyzed exceeded the World Health Organization's maximum permissible limit which could pose serious health concern. The estimated health hazard index (HI) for non-carcinogenic and carcinogenic risk exposure showed that the borehole water pose no health threat, but the cumulative excess cancer risk (ECR) for borehole water from Umuechem, and Bodo exceeded the USEPA's acceptable cancer risk value of 1×10^{-6} with higher cancer estimates. This indicated that consumption of water from Umuechem and Bodo communities could pose potential cancer health risk.

References

- [1]. WHO, World Health Organization: The World Health Report : Reducing risks, promoting healthy life. Geneva. 2002, 1-71.
- [2]. S. Baran, P. Oleszozuk, and E. Baranowsha. Degradation of soil environment in the post- flooding area: Content of polycyclic aromatic hydrocarbons (PAHs) and s-triazine herbicides. J Environ Sci Health. 38(6), 2003, 99-812.
- [3]. L. Chryssikou, P. Gemenetzis, A. Kouras, E. Manoli, E. Terzi, and Samara, C. Distribution of persistent ommrganic pollutants, polycyclic aromatic hydrocarbons and trace elements in soil and vegetation following a large scale landfill fire in northern Greece. Environmental Pollution Control Laboratory, Department of Chemistry, Aristotle University of Thessaloniki, G-541 24 Thessaloniki, Greece. Environmental International, 34(2), 2008, 210-250.
- [4]. I. Bouloubassi, L. Mejanelle, R. Pete, J. Fillaux, A. Lorre, and V. Point. Transport by sinking particles in the open Mediterranean Sea : a 1 year sediment trap study. 52, 2006, 560-571.
- [5]. J. Brown, and B. Peake. Sources of heavy metals and polycyclic aromatic hydrocarbons in urban storm water, runoff. Science Total Environment, 359(1-3), 2006, 145-155.
- [6]. G. Falco, J.L. Domingo, J.M. Liobet, and A. Teixido. Polycyclic aromatic hydrocarbons in foods: Human exposure through the diet in Catalonia, Spain. Journal of Food Protection, 66(12), 2003, 2325-2331.
- [7]. UNEP (2011). An environmental assessment of Ogoni Land. Nigeria: Rivers State. <http://www.slideshare.net>.
- [8]. U.D. Chima, G.A. Adedeji, and K.O. Uloho. Preliminary assessment of impact of charcoal production on physic-chemical properties of soils in Rivers State, Nigeria. University of Port Harcourt. Department of Forestry and Wildlife Management. Ethiopian Journal of Environmental Studies and Management, 6(3), 2013, 288.
- [9]. API. "Inter laboratory study of three methods for analyzing petroleum hydrocarbons in soils, diesel-range organics (DRO), gasoline-range organic (GRO)" and petroleum hydrocarbon (PHC).1994, Publication Number 4599.
- [10]. WHO (1984). Guidelines for Drinking Water Quality, Geneva.
- [11]. W.Y. Hu, B. Huang, Y.C. Zhao, W.X. Sun, and Z.Q. Gu. Organochlorine pesticides in soils from a Typical Alluvial Plainof the Yangtze River Delta region, China. *Bulletin of Environmental Contamination and Toxicology*, 87(5), 2011, 561-566.
- [12]. USEPA (1992).Guidelines for exposure assessment.
- [13]. USEPA (1997). Exposure factors handbook. Washington, DC: US Environmental Protection Agency.
- [14]. USEPA (2000). Guidance for assessing chemical contaminant, data for use in fish advisories, vol. 1 fish sampling and analysis (3rd ed.) EPA/823/B-00/007.
- [15]. I. Nisbet, and P. LaGoy. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regulatory Toxicology and Pharmacology*, 16(3),1992, 290-300.

- [16]. Ding, C., Ni, H., and Zeng, H. Parent and halogenated polycyclic aromatic hydrocarbons in rice and implications for human health in China. *Environ Pollu*, 168(5), 2012, 80–86.
- [17]. K.C. Cheung, H.M. Leung, K.Y. Kong, and M.H. Wong. Residual levels of DDTs and PAHs in freshwater and marine fish from Hong Kong markets and their health risk assessment. *Chemosphere*, 66, 2007, 460–468.
- [18]. W. Wu, N. Ning Qin, W. He, Q. He, H. Ouyang, and F. Xu. Levels, distribution, and health risks of polycyclic aromatic hydrocarbons in four freshwater edible fish species from the Beijing market. *The Scientific World Journal*, 1(12), 2012, 1–12.
- [19]. L.M.N. Palm, D. Carboo, P.O. Yeboah, W.J. Quasie, M.A. Gorleku, and A. Darko. Characterization of polycyclic aromatic hydrocarbons (PAHs) present in smoked fish from Ghana. *Advance Journal of Food Science and Technology*, 3(5), 2011, 332–338.
- [20]. Z. Xia, X. Duan, W. Qiu, D. Liu, B. Wang, S. Tao, Q. Jiang, B. Lu, Y. Song and X. Hu. Health risk assessment on dietary exposure to polycyclic aromatic hydrocarbons (PAHs) in Taiyuan, China. *Science of the Total Environment*, 408, 2010, 5331–5337.
- [21]. E. Yoon. Estimation of excess cancer risk on time-weighted lifetime average daily intake of PAHs from food ingestion. *Human and Ecological Risk Assessment*, 13(3), 2007, 669-680.
- [22]. J.P. Meador, J.E. Stein, W.L. Reichert, and U. Varanasi. Bioaccumulation of polycyclic aromatic hydrocarbons by marine organisms. *Reviews of Environmental Contamination and Toxicology*, 143, 1995, 79-165.
- [23]. S.W. Fowler, and G.A. Knauer. Role of large particles in the transport of elements and organic compounds through the oceanic water column. *Programme Oceanogr*, 16, 1986, 147-194.
- [24]. R.J. Irwin, M. Vanmouwerik, L. Stevens, M.D. Seese, and W. Basham. *Environmental Contaminants Encyclopedia*. National Park Service, Water Resources Division, FORT Collins, Colorado. Distributed within the Federal Govt. as an Electronic Document. 1997.
- [25]. M.D. Gullen, P. Sopelana, and M.A. Partearroyo. Food as a source of polycyclic aromatic carcinogens. *Reviews on Environmental Health*, 12(3), 1997, 133-146. ISSN 2191-0308.
- [26]. D. Berto, F. Cacciatore, A. Ausili, G. Sunseri, G. Luca, L.G. Bellucci, M. Frignani, S. Albertazzi, and M. Giani. Polycyclic aromatic hydrocarbons (PAHs) from diffuse sources in coastal sediments of a not industrialized Mediterranean Island, 200, 2009, 199-209.
- [27]. C. Ples, B. Hofmann, J. Petrowsky, Y. Yang, T.A. Ternes, and Hofmann, T. Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils. *Journal of Chemosphere*, 72(10), 2008, 1594-1601.
- [28]. P.K. LaGoy, and T.C. Quirk. Establishing generic remediation goals for the polycyclic aromatic hydrocarbons: critical issues. *Environmental Health Perspectives*, 102(4), 1994, 348-352.
- [29]. USEPA (2009b). Development of estimated quantitation levels for the second six-year review of National Primary Drinking Water Regulations. Office of Water, U.S. Environmental Protection Agency, Cincinnati, OH (EPA 815-B-09-005).
- [30]. ATSDR. "Public Health Statement of Polycyclic Aromatic Hydrocarbons (PAHs), Agency for Toxic Substances and Disease Registry (ATSDR), US Department of Health and Human Services, Atlanta. 1995.
- [31]. USEPA (2004). US Environmental Protection Agency, The OAQPS Air Toxic Risk Assessment Library. Available at EPA'S fate, exposure, and risk analysis (FERA).
- [32]. N.Jing, J. Shi, X. Duan, B. Wang, N. Huang, and X. Zhao. Health risk assessment of dietary exposure to polycyclic aromatic hydrocarbons in Taiyuan, China. *J Environ Sci.*, 26(2), 2013, 432-439.
- [33]. USEPA. Human Health Evaluation Manual (HHEM). Vol 1. Interim Final, Office of Emergency and Remedial Response, Washington, DC, USA, EPA/540/1-89/002, Office of Solid Waste and Emergency Response, Washington, DC. 1989.

Acknowledgement

The authors are thankful to Dr.Kpobari W. Nkpaa who edited the manuscript and made relevant imputes in the experimental design of this work.

Table 1: Human Intake Model Parameters.

Parameters	Unit	Value	Reference
Concentration of water (Cw)	mg/L water	Table 1-3	Table 1
Water ingestion rate (IRw)	L/day	1.4L	Cantor <i>et al.</i> (1987)
Reference dose (RfD)	mg/L/day	Table 4	USEPA (1993)
Exposure duration (ED)	years	30	Qu <i>et al.</i> (2015)
Exposure frequency (EF)	Days/year	365	Qu <i>et al.</i> (2015)
Adult body weight (BW)	kg	60	Jiang <i>et al.</i> (2005)
Carcinogenic potency of Benzo[a]Pyrene (Q)	mg/ L /day	7.3 mg/L /day	Ding <i>et al.</i> (2012)
Conversion coefficient (CF)	Kg/mg	1×10^6	Huang <i>et al.</i> (2014)
average life span (ATn)	days	25,550	Papadakis <i>et al.</i> (2015)
Oral slope factor (SF)	mg/kg	USEPA (2005)	USEPA (2005)
Maximum acceptable risk level (RL)	Dimensionless	10^5	USEPA (2000)
Toxic equivalent factor (TEFi)	No unit	Nisbet and LaGoy (1992)	Nisbet and LaGoy (1992)
Maximum acceptable risk level (RL)	dimensionless	USEPA (2005)	USEPA (2005)

Oral Slope Factor (SF)	mg/kg/day	USEPA (2005)	USEPA (2005)
------------------------	-----------	--------------	--------------

© GSJ