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Contamination and Possible Health Risks of Polycyclic Aromatic Hydrocarbons in Soil and Crops from Cultivated Floodplains of Some Rivers in Ekiti State, Southwest Nigeria

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ABSTRACT: The demand for food in Nigeria has increased pressure on land use including floodplains despite possible contamination from the river catchments. The objective of this paper is to evaluate the contaminations and possible health risk of polycyclic aromatic hydrocarbons (PAHs) in soil from Irintan (Ogbese), Omi-Eye (Erio) and Egbigbu (Ayetoro) cultivated floodplains in Ekiti State, Nigeria using standard techniques. The soil samples were collected from 0-30cm depth at 5m, 25m and 45m perpendicular distances to the river course at lower, middle and upstream. The crop samples randomly collected on the floodplains were *Talinum triangulare, Caspicum annum* and *Zea mays* from each farm. Samples were appropriately treated and analyzed for polycyclic aromatic hydrocarbons and results used to estimate the possible health risk. PAHs concentration at each of the farm sites was found to be more than their corresponding controls. The Σ PAHs (μ g/kg) in soil ranged 0.62-3.20, 0.38-2.33 and 0.09-1.75 at Irintan (Ogbese), Omi-Eye(Erio) and Egbigbu (Ayetoro) floodplains respectively and these values were categorized unpolluted. The Σ PAHs (μ g/kg) was 1.24, 0.64 and 21.15 for *T. triangulare*, 2.62, 2.76 and 18.43 for *C. annum* and 0.70, 1.78 and 1.31 for *Z. mays* at Irintan, Omi-Eye and Egbigbu floodplain respectively. All the Benzo (a) pyrene equivalent concentration possible carcinogenic health concern in *T. triangulare* and *C. annum* at the floodplain. There could be a cause for concern for the consumption of these food crops by the exposed population.

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants, chemically stable, capable of bioaccumulation and biomagnification with potent environmental toxicity (Kan et al., 2018). They belong to a group of over 100 hazardous substances which consist of two or more benzene aromatic rings fused together in a variety of configurations (Doherty et al., 2015). PAHs are known to originate from both natural (volcanic eruptions, forest fires etc.) and anthropogenic sources (combustion of fossil fuels and industrial emissions) (Al-Saad et al., 2019). They are also grouped into either low molecular weight PAHs

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(LMW-PAHs) or high molecular weight PAHs (HMW-PAHs) based on their molecular structure. The LMW-PAHs consist of two or three benzene rings while the HMW-PAHs consist of four or more benzene rings (Zelinkova and Wenzi, 2015; Gereslassie *et al.*, 2018). Vegetable consumption is very important in man's nutrition as it provides essential micronutrients, vitamins, dietary fibers giving overall health benefits such as weight management (Bellavia *et al.*, 2013), better cardiovascular system (Oyebode *et al.*, 2014), improved mental health (Aune *et al.*, 2017) and reduced risks of some cancers (Rolls et al., 2004) among other benefits. The ingestion of chemically contaminated foods, such as vegetables, is one of many exposure routes (Rengarajan et al., 2015; Abdel-Shafy and Mansour, 2016) to oral consumption of pollutant. This can lead to untold health risks bringing about health complications (Okereke et al., 2016) in animals and human. One of the Sustainable Development Goals (SDGs) of United Nations (Bazga, 2015) is the provision of safe and quality foods for the citizenry; hence, safeguarding food contamination from pollutants, including PAHs, should be a priority for every nation. Exposure to PAHs may result in short-term side effects such as vomiting, eye irritation, nausea, diarrhea and confusion. Some PAHs such as benzo(a)pyrene, anthracene and naphthalene were found to produce skin allergy in animals and humans. Their long-term health effects include cancer, cataracts, kidney damage, liver damage, skin inflammation, breathing problems and lung function abnormalities. Naphthalene has been found to cause the breakdown of red blood cells if inhaled or ingested in large amounts (ATSDR, 2009). Generally speaking, PAHs are known to be carcinogenic, mutagenic and teratogenic especially to human beings (Zelinkova and Wenzi, 2015). The United States Environmental Protection Agency (USEPA) has designated 16 PAHs as priority environmental pollutants and eight as carcinogens (Tomori et al., 2017). Ekiti State is blessed with floodplains many of which are used for growing arable crops especially vegetables during the dry season period of November-April every year. The floodplains are prone to contamination from pollutants

including polycyclic aromatic hydrocarbons (Olawale et al., 2017) and this can enter into food chain through plants uptake (Long et al., 2003). Several researchers have reported cases of contamination levels of PAHs in maize (Zhang et al., 2017) and vegetables (Adetunde et al., 2018). Studies on food contamination by PAHs in Nigeria have been mostly on food crops grown on dry land with scanty reports on floodplains. It is therefore pertinent to evaluate the levels of PAHs contamination in the cultivated alluvial soil and vegetables of some floodplains around Ekiti State in order to safeguard the health of farmers and populace. Hence, the objective of this paper is to evaluate the contaminations and possible health risk of polycyclic aromatic hydrocarbons (PAHs) in soil and crops from Irintan (Ogbese), Omi-Eye (Erio) and Egbigbu cultivated floodplains in Ekiti State, Nigeria.

MATERIALS AND METHODS

Description of Study Area: Ekiti State is one of the states in Nigeria and it is located between longitudes 4^0 5' and 5^0 15' East of Greenwich Meridian and latitudes 7^0 15' and 8^0 50' North of Equator. It is an upland zone located over 250metres above sea level. The state has two distinct seasons: the dry season which runs from November to April and the wet season which occurs between May and October each year. Ekiti State is characterized by several hills from which many notable rivers in the Southwestern part of Nigeria take their sources. At the lowlands of these hills are floodplains, a good number of which are used for dry season farming.

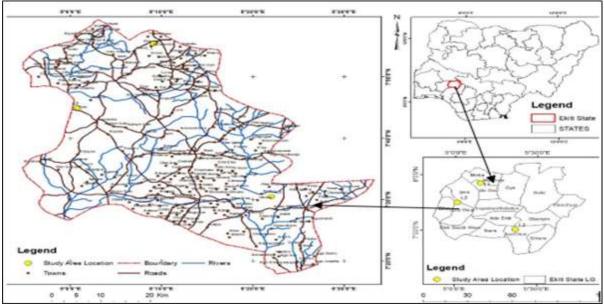


Fig 1: Map of Ekiti State showing the sampling sites

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Sample Collection: Sampling at the three sites (Figure 1) {Irintan floodplain at Ogbese, Ise-Ekiti (05°) 22.047'E, 07^o 30.432'N, Altitude 420m); Omi-Eye floodplain at Erio-Ekiti (04º 57.924'E, 07º 37.304'N, Altitude 417m) and Egbigbu floodplain at Ayetoro-Ekiti (05^o 09.124'E^o, 07^o 55.457'N, Altitude 531m)} was done during the dry season months of November 2019/April 2020. A 0-30cm soil depth was sampled using stainless steel auger from 5m, 25m, and 45m distances perpendicular to the course of the river at lower, middle and upstream. Food crops: leafy vegetable (Talinum triangulare), pepper (Capsicum annum) and maize (Zea mays) were collected randomly from each farm during the soil sampling regime. All samples were georeferenced and securely kept from contamination during transportation to the laboratory. Soil samples were air dried, disaggregated with agate mortal and pestle, sieved with 2.0mm (BS) stainless steel mesh and kept in polyethylene terephthalate (PET) bottles pending analysis. The food crop samples were air dried to constant weight. Each of them was ground, sieved with 2mm (BS) stainless steel mesh and stored in PET bottles pending the analysis (Okoye et al., 2013).

Analyses of Polycyclic Aromatic Hydrocarbons in Soil and Crop Samples: Two grammes (2 g) of soil/crop sample was weighed into a temperature-controlled CEM MARS Xpress Microwave and extracted with 25 mL mixture of n-hexane and acetone (4:1, v/v) in 3 modes. Each extract was carefully transferred to a 100mL pear-shaped flask and evaporated to near dryness under reduced pressure of 150 mbars at 35 °C using a rotatory evaporator (Buchi Switzerland Rotavapor R-20 fitted with thermostated heating bath B-491 and vacuum controller V-850) (Wang et al., 2007; Tomori et al., 2017). An additional 10 mL nhexane was added to the concentrated extract and evaporated to a small volume (about 1 mL) and transferred to 1.5 mL chromatographic vial for Gas Chromatography-Mass Spectrophotometry analysis (Agilent HP-5 MS) (Okoro and Ikolo, 2007) under controlled operating conditions (Wang et al., 2010; Tomori et al., 2017). The data obtained from this study were analyzed statistically. The carcinogenic risk from exposure to PAHs in vegetables was estimated using the USEPA guideline as described by (Cheung et al., 2007). Benzo(a)pyrene is used in this method as a marker for the occurrence and effect of carcinogenic PAHs in foods and therefore the overall carcinogenic risk from the measured PAHs was determined based on Toxicity Equivalency Factors (TEFs) derived from cancer potencies of individual PAH compounds relative to the cancer potency of benzo(a)pyrene. The product of each PAH concentration (µg/kg) and its TEF gives a benzo(a)pyrene equivalent concentration

$$PEC = \Sigma TEFi \ x \ Ci \qquad (1)$$

The PEC values were then compared with the screening value (μ g/kg) calculated as stated by (Okereke *et al.*, 2016) in equation (2):

$$SV = \left[\frac{\left(\frac{RL}{SF}\right)}{CR} x BW\right]$$
 (2)

Where SV = screening value (μ g/kg); RL = maximum acceptable risk level (dimensionless); SF = USEPA oral slope factor (μ g/kg/day); BW = body weight (g); CR = consumption rate (g/day)

The screening value serves as the threshold concentration of total PAHs in food crop which can be of concern to the health of the exposed population. The average body weight of an adult is taken as 60kg (Tomori and Onibon, 2015), the consumption rate is 65g in Nigeria (Adedokun *et al.*, 2016), the maximum acceptable risk level is 10^{-5} (Okereke *et al.*, 2016). The USEPA oral slope factor used to estimate an upper bound probability of an individual developing cancer as a result of a 70-year lifetime exposure to carcinogenic PAHs is given as 0.0073 µg/kg/day (Okereke *et al.*, 2016).

Quality Assurance: Quality control was assured through three replicate samples, the use of reagent blanks, determination of percentage recoveries of spiked and unspiked samples (which were found to be within 70-120% approved by the European Union) as well as the use of reagents of pure analytical grade.

Data Analysis: The data obtained from this study was analysed for analysis of variance (ANOVA), t-test, and Pearson correlation using SPSS 16.0 package. The statistical result was interpreted using one level confidence limit (p<0.05).

RESULTS AND DISCUSSION

The results for PAHs concentrations in floodplains soil at Irintan, Omi-Eye and Egbigbu floodplains are presented in Tables 1-3. The mean concentration(μ g/kg) ranged for: napthalene (0.14-0.87), acenaphthylene (BDL), acenaphtene (0.01-0.63), flourene (0.01-0.25), phenantherene (0.04-0.47), anthracene (BDL–0.03), pyrene (0.06 – 0.16), flouranthene (0.16-0.27), benzo (a) anthracene (BDL-0.05), chrysene (BDL-0.12), (BDL), benzo (k) flouranthene (BDL-0.04), benzo (b) flouranthene

(BDL-0.04), benzo (a) pyrene (BDL-0.20), benzo(g,h,i) pervlene (0.01-0.15), dibenzo (a,h) anthracene (BDL - 0.05), indeno (1,2,3-cd) pyrene (BDL-0.16) at Irintan floodplain (Table 1) while it was napthalene (0.04-0.21), acenaphthylene (BDL), (0.02-0.11), acenapthene (0.02-1.63); flourene phenantherene (0.04-0.015), anthracene (BDL - 0.04), pyrene (0.01-0.13), flouranthene (BDL-0.28), benzo (a) anthracene (BDL-0.04), chrysene (BDL), benzo (k) flouranthene (BDL-0.02), benzo (b) flouranthene (BDL), benzo (a) pyrene (BDL-0.24), benzo(g,h,i) perylene (BDL-0.13), dibenzo (a,h) anthracene (BDL-0.02), indeno (1,2,3-cd) pyrene (BDL-0.02) at Omi-Eve floodplain (Table 2) and naphthalene (0.02-0.17), acenaphthylene (BDL-0.23), acenapthene (0.01-1.17), flourene (0.01-0.11), phenantherene (BDL-0.13), anthracene (BDL-0.07), pyrene (0.02 - 0.11),flouranthene (BDL-0.07), benzo (a) anthracene (BDL-0.01), chrysene (BDL-0.01), benzo (k) flouranthene (BDL-0.05), benzo (b) flouranthene (BDL-0.08), benzo (a) pyrene (BDL-0.10), benzo(g,h,i) perylene (BDL-0.03), dibenzo (a,h) anthracene (BDL-0.04) and indeno (1,2,3-cd) pyrene (BDL-0.90)at Egbigbu floodplain (Table 3).

It has been reported that PAHs are strongly adsorbed to soil particles and consequently they are ultimate sink for them (Kuppusamy et al., 2017, Patel et al., 2020). Hence, almost all PAHs under investigation were detected at all the three investigated sites except acenaphthylene (in all sites) and chrysene at both Omi-Eye and Egbigbu floodplains. The low molecular weight (LMW) PAHs with highest value is naphthalene at both Irintan and Omi-Eye floodplains but acenaphthene in Egbigbu while benzo (a) pyrene, benzo (g, h, i) perylene, indeno (1,2,3-cd) pyrene were HMW PAHs for Irintan, Omi-Eye and Egbigbu floodplain respectively. Naphthalene is the highest concentration of PAHs recorded at 25m and 5m distances at Irintan and Omi-Eye lower stream and it was acenaphthene at 45m distance Egbigbu upstream. Emissions from the chemical and primary metals industries, biomass burning, gasoline and oil combustion, tobacco smoking, the use of mothballs, fumigants and deodorizers and many others are said to be air borne sources of naphthalene which eventually finds its way into soil during dry or wet depositions (Chunrong and Stuart, 2010). The major non-cancer endpoints of naphthalene exposure are hyperplasia and metaplasia in respiratory and olfactory epithelium respectively with the cancer endpoint of concern to be nasal tumors; also acute intravascular hemolysis leading to toxic hepatisis have been diagnosed as consequences of naphthalene toxicity (Chunrong and

Stuart, 2010, Jinhyuk et al., 2017, Uthuman et al., 2019).

Soil pollution from PAHs has been classified into three categories: unpolluted when sum total (Σ PAHs) <200µg/kg; weakly polluted (ΣPAHs200is 600µg/kg) and heavily polluted $(\Sigma PAHs >$ 1000 μ g/kg) (Wu *et al.*, 2019). The Σ PAHs in soil of the present study was 1.17µg/kg at Irintan, 0.89µg/kg at Omi-Eye and 0.69µg/kg at Egbigbu floodplain and these values falls within the unpolluted categories according to these criteria. Σ PAHs concentrations obtained in this study were far lower than 27,074.1µg/kg reported by Jiang et al. (2007) and 2,713.8µg/kg by Zhao et al. (2017) but were higher than those 0.72µg/kg reported by Okereke et al. (2016).

Floodplains have been found to be prone to contamination from the catchment areas (Olawale *et al.*, 2017). This indicates that floodplains are likely to be more polluted than the corresponding dry uplands. This statement was found to be in agreement with the values obtained in this study as PAHs concentration at each of the farm sites was found to be more than their corresponding controls (Tables 1-3), a phenomenon that can be attributed to the effect of the successive annual flooding which may bring pollutants including PAHs and deposit them on the floodplain after the flood recession (Olawale *et al.*, 2017).

A number of diagnostic ratios are in use to characterize PAHs worldwide. These include Flt/Pyr and Phen/Anth, Flt/Flt + Pyr, Anth/Anth + Phen, BaA/BaA + Chry, InP/InP + BgP and total index: Anth/(Anth + Phen)/0.1 + Flt/(Flt + Pyr)/0.4 + BaA/(BaA + Chry)/0.2 + (InP/InP + BgP)/0.2 (Liu *et al.*, 2008; Sojinu *et al.*, 2011; Zhang *et al.*, 2011). A ratio of Flt/Flt + Pyr less than 0.4 indicates a typical petroleum contamination such as diesel oil and crude oil while a value greater than 0.5 suggests PAHs from combustion of grass, wood and coal.

However, a ratio of Flt/Flt + Pyr greater than 0.4 but less than 0.5 (a value between 0.4 and 0.5) is indicative of PAHs from liquid fossil fuel combustion e.g. vehicular exhaust emission. The Flt/Flt + Pyr ratio is 0.67 at Irintan, 0.17 at Omi-Eye and 0.20 at Egbigbu floodplain. The PAHs sources at Irintan floodplain could be from combustion while those at other two sites could be attributed to contamination from engine oil and other petroleum products. The possible source of former is the annual bush burning by farmers and residences in the vicinity while the latter could be from various mechanic workshops that indiscriminately pour out used oil and petroleum which can be swept into the river during runoff.

Contamination and Possible Health Risks of Polycyclic Aromatic..... Table 1: Concentrations of PAHs (µg/kg) in Soil at Irintan floodplain (Ogbese)

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	Upper			Middle			Lower				
Parameter	5m	25m	45m	5m	25m	45m	5m	25m	45m	Site Mean	Control
Napthalene	0.21 ^a ±0.07	$0.36^{b}\pm0.06$	0.83°±0.03	0.59 ^b 0.09	$0.18^{a}\pm0.04$	$0.14^{a}\pm0.02$	$0.75^{b}\pm0.02$	0.87°±0.04	$0.36^{a}\pm0.01$	0.48 ± 0.27	0.36 ± 0.08
Acenaphthylene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Acenaphthene	0.01 ^a ±0.00	$0.10^{C} \pm 0.00$	0.06 ^{a,b} ±0.05	0.63 ^b ±0.03	$0.05^{a}\pm0.02$	$0.04^{a}\pm0.00$	0.36 ^b ±0.02	0.36 ^b ±0.10	$0.16^{a}\pm0.05$	0.20 ± 0.20	0.02 ± 0.01
Flourene	0.01 ^a ±0.01	$0.12^{b}\pm0.00$	0.22°±0.10	0.11 ^b ±0.01	$0.06^{a}\pm0.04$	0.04 ^a ±0.10	$0.25^{a}\pm0.04$	0.22 ^a ±0.02	$0.16^{a}\pm0.06$	0.13±0.08	0.09±0.03
Phenanthrene	$0.20^{a}\pm0.02$	0.22 ^a ±0.04	0.36 ^b ±0.07	0.22 ^b ±0.03	$0.15^{a}\pm0.07$	$0.04^{a}\pm0.00$	$0.47^{b}\pm0.05$	0.22 ^a ±0.04	$0.36^{b}\pm0.07$	0.26 ± 0.11	0.16 ± 0.05
Anthracene	0.03 ^b ±0.01	BDL	0.01 ^a ±0.00	0.03 ^a ±0.00	$0.01^{a}\pm0.01$	0.03 ^a ±0.00	0.03 ^b ±0.01	BDL	$0.01^{a}\pm0.00$	0.03 ± 0.02	0.03 ± 0.02
Pyrene	0.13 ^a ±0.03	$0.16^{a}\pm0.08$	0.13 ^a ±0.01	0.11°±0.02	$0.08^{a,b}\pm0.01$	$0.06^{a}\pm0.01$	0.13 ^a ±0.03	$0.16^{a}\pm0.08$	$0.13^{a}\pm0.01$	0.13±0.05	0.66 ± 0.10
Flouranthene	0.24 ^a ±0.03	$0.24^{a}\pm0.00$	0.27 ^a ±0.04	0.21 ^a ±0.03	$0.26^{a}\pm0.08$	$0.16^{a}\pm0.04$	$0.24^{a}\pm0.03$	0.24 ^a ±0.00	$0.27^{a}\pm0.04$	0.30 ± 0.11	0.11 ± 0.01
Benzo(a) anthracene	$0.05^{a}\pm0.00$	$0.04^{a}\pm0.01$	BDL	0.03 ^a ±0.02	$0.02^{a}\pm0.02$	BDL	$0.05^{a}\pm0.00$	0.04 ^a ±0.01	0.04 ^a ±0.03	0.03±0.22	BDL
Chrysene	$0.08^{a}\pm0.01$	$0.08^{a}\pm0.03$	$0.12^{a}\pm0.02$	BDL	BDL	BDL	BDL	BDL	BDL	0.03 ± 0.05	BDL
Benzo (k)flouranthene	$0.02^{a}\pm0.00$	0.03 ^a ±0.02	BDL	0.02 ^a ±0.02	0.01 ^a ±0.00	$0.04^{a}\pm0.02$	$0.04^{a}\pm0.00$	0.02 ^a ±0.02	$0.02^{a}\pm0.01$	0.05 ± 0.01	BDL
Benzo(b) fluoranthene	$0.01^{a}\pm0.01$	$0.02^{a}\pm0.00$	BDL	0.01 ^a ±0.00	$0.01^{a}\pm0.01$	BDL	$0.04^{a}\pm0.03$	0.01 ^a ±0.00	$0.01^{a}\pm0.01$	0.01 ± 0.11	BDL
Benzo (a) Pyrene	0.03 ^a ±0.02	$0.04^{a}\pm0.01$	0.07 ^a ±0.04	$0.06^{a}\pm0.01$	BDL	BDL	$0.20^{a}\pm0.10$	0.17 ^a ±0.04	$0.12^{a}\pm0.07$	0.08 ± 0.07	0.06±0.03
Benzo(g,h,i) perylene	0.04 ^{a,b} ±0.03	$0.01^{a}\pm0.00$	0.06°±0.00	$0.02^{a}\pm0.00$	$0.02^{a}\pm0.02$	$0.02^{a}\pm0.01$	$0.14^{a}\pm0.03$	0.15 ^a ±0.02	$0.07^{a}\pm0.02$	0.06 ± 0.05	0.03 ± 0.01
Dibenzo(a,h) anthracene	BDL	0.03 ^a ±0.03	0.05 ^b ±0.01	BDL	BDL	BDL	BDL	BDL	BDL	0.01 ± 0.02	BDL
Indeno(1,2,3-cd) pyrene	0.01 ^a ±0.00	$0.02^{a}\pm0.00$	0.13 ^b ±0.06	0.01 ^a ±0.01	BDL	BDL	$0.05^{a}\pm0.03$	$0.07^{a}\pm0.05$	$0.16^{b}\pm0.01$	0.05 ± 0.06	0.01 ± 0.00
ΣPAHs	$1.07^{a}\pm0.08$	$1.47^{a}\pm0.10$	2.31 ^b ±0.20	2.05 ^b ±0.19	$0.85^{a}\pm0.08$	$0.62^{a}\pm0.05$	3.20°±0.21	2.75 ^{a.b} ±0.22	2.13 ^a ±0.13	1.85 ± 0.83	0.93±0.17

Values with different superscripts on the same row are significant at p<0.05. BDL= Below Detection Limit

Table 2: Concentrations of PAHs (µg/kg) in Soil at Omi-Eye floodplain (Erio)

	Upper			Middle			Lower				
Parameter	5m	25m	45m	5m	25m	45m	5m	25m	45m	Site Mean	Control
Napthalene	$0.20^{b}\pm0.02$	$0.19^{b}\pm0.02$	$0.15^{a}\pm0.02$	0.13°±0.06	0.12 ^{a,b} ±0.04	$0.04^{a}\pm0.02$	0.41 ^b ±0.022	$0.21^{a}\pm0.02$	$0.12^{a}\pm0.01$	0.157±0.09	0.12±0.04
Acenaphthylene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Acenaphthene	$0.06^{a}\pm0.00$	$0.06^{a}\pm0.03$	1.63 ^b ±0.09	$0.05^{a}\pm0.00$	$0.04^{a,b}\pm0.01$	$0.02^{a}\pm0.01$	$0.14^{b}\pm0.05$	$0.02^{a}\pm0.00$	$0.04^{a}\pm0.02$	0.23±0.50	0.04±0.01
Flourene	$0.07^{a}\pm0.03$	$0.07^{a}\pm0.00$	$0.09^{a}\pm0.02$	0.06 ^{ba} ±0.03	$0.05^{a}\pm0.02$	0.03 ^a ±0.00	0.11°±0.03	$0.02^{a}\pm0.01$	0.06 ^{a,b} ±0.03	0.06 ± 0.02	0.02 ± 0.02
Phenanthrene	0.13 ^a ±0.05	$0.15^{a}\pm0.01$	0.15 ^a ±0.03	0.14 ^c ±0.03	0.05 ^a ±0.04	0.09 ^{a,b} ±0.02	$0.15^{b}\pm0.05$	$0.04^{a}\pm0.01$	0.11 ^b ±0.02	0.11±0.04	0.05±0.03
Anthracene	$0.01^{a}\pm0.00$	BDL	BDL	0.01 ^a ±0.00	BDL	BDL	$0.04^{a}\pm0.00$	BDL	0.03 ^a ±0.00	0.01 ± 0.01	BDL
Pyrene	$0.06^{a}\pm0.01$	0.13 ^C ±0.05	0.11 ^{a,b} ±0.01	0.01 ^a ±0.01	$0.06^{b}\pm0.00$	0.11°±0.02	$0.07^{b}\pm0.01$	$0.02^{a}\pm0.02$	$0.07^{b} \pm 0.02$	0.07 ± 0.04	0.03±0.00
Flouranthene	0.23 ^a ±0.04	$0.23^{a}\pm0.02$	BDL	0.28 ^b ±0.04	BDL	$0.14^{a}\pm0.08$	$0.01^{a}\pm0.01$	BDL	0.13 ^b ±0.06	0.11 ± 0.10	0.10 ± 0.00
Benzo(a) anthracene	BDL	$0.04^{a}\pm0.03$	$0.04^{a}\pm0.02$	BDL	BDL	BDL	BDL	BDL	BDL	0.01 ± 0.01	BDL
Chrysene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Benzo (k)flouranthene	BDL	$0.01^{a}\pm0.00$	0.01 ^a ±0.00	BDL	$0.02^{a}\pm0.00$	0.01 ^a ±0.00	BDL	BDL	BDL	0.01 ± 0.01	BDL
Benzo(b) flouranthene	BDL	$0.01^{a}\pm0.01$	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Benzo(a) pyrene	0.11 ^b ±0.02	$0.04^{a}\pm0.01$	$0.06^{a}\pm0.00$	$0.08^{b} \pm 0.00$	BDL	BDL	0.12 ^{a,b} ±0.04	$0.04^{a}\pm0.01$	0.24 ^c ±0.11	0.08 ± 0.08	0.05±0.00
Benza(g,h,i) perylene	$0.08^{b}\pm0.00$	BDL	0.03 ^a ±0.02	0.03 ^a ±0.02	$0.02^{a}\pm0.02$	0.01 ^a ±0.01	0.13°±0.05	$0.01^{a}\pm0.00$	0.06 ^{a,b} ±0.05	0.07 ± 0.08	0.03 ± 0.02
Dibenzo(a,h) anthracene	BDL	BDL	$0.02^{a}\pm0.00$	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Indeno(1,2,3-cd) pyrene	$0.01^{a}\pm0.01$	$0.02^{a}\pm0.02$	$0.01^{a}\pm0.01$	$0.02^{a}\pm0.02$	$0.02^{a}\pm0.00$	$0.02^{a}\pm0.01$	BDL	$0.01^{a}\pm0.01$	$0.02^{a}\pm0.00$	0.01 ± 0.00	BDL
ΣPAHs	$0.98^{a}\pm0.07$	$0.99^{a}\pm0.07$	2.33 ^b ±0.38	$0.90^{b} \pm 0.07$	0.41 ^a ±0.03	$0.48^{a}\pm0.04$	1.12 ^c ±0.10	$0.38^{b}\pm0.05$	$0.88^{a,b} \pm 0.07$	0.90 ± 0.55	0.44±0.09

Values with different superscripts on the same row are significant at p < 0.05. BDL= Below Detection Limit

Table 3: Concentrations of PAHs (µg/kg) in Soil at Egbigbu floodplain (Ayetoro)

	Upper			Middle			Lower				
Parameter	5m	25m	45m	5m	25m	45m	5m	25m	45m	Site Mean	Control
Napthalene	$0.17^{b}\pm0.02$	$0.09^{a}\pm0.00$	$0.14^{b}\pm0.02$	0.05 ± 0.02	0.07 ± 0.00	$0.02^{a}\pm0.01$	0.11 ^a ±0.00	$0.10^{b} \pm 0.05$	$0.15^{a}\pm0.01$	0.10 ± 0.04	0.10±0.03
Acenaphthylene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Acenaphthene	$0.05^{a}\pm0.00$	0.04 ^a ±0.03	1.17 ^b ±0.02	0.02 ± 0.01	0.02 ± 0.01	$0.01^{a}\pm0.00$	0.04 ^a ±0.03	$0.05^{a}\pm0.01$	0.74 ^b ±0.05	0.24±0.39	0.04±0.01
Flourene	$0.06^{a}\pm0.02$	$0.06^{a}\pm0.06$	$0.07^{a}\pm0.05$	0.02 ± 0.01	0.02 ± 0.01	$0.01^{a}\pm0.00$	$0.06^{c} \pm 0.02$	$0.01^{a}\pm0.01$	0.05 ^{a,b} ±0.04	0.04 ± 0.02	0.03±0.00
Phenanthrene	0.11 ^a ±0.02	0.11 ^a ±0.00	$0.10^{a}\pm0.03$	0.05±0.03	0.05±0.03	$0.02^{a}\pm0.00$	$0.08^{a}\pm0.04$	0.13 ^a ±0.03	0.14 ^a ±0.06	0.09 ± 0.03	0.12±0.05
Anthracene	0.01 ^a ±0.01	$0.01^{a}\pm0.00$	0.02 ^a ±0.02	0.01 ± 0.00	0.01±0.00	BDL	0.01 ^a ±0.00	0.03 ^b ±0.01	0.01 ^a ±0.00	0.01±0.01	BDL
Pyrene	0.04 ^a ±0.03	$0.04^{a}\pm0.01$	$0.05^{a}\pm0.02$	0.04 ± 0.00	0.04 ± 0.00	$0.02^{a}\pm0.01$	$0.02^{a}\pm0.02$	$0.08^{b}\pm0.05$	$0.07^{b}\pm0.01$	0.04 ± 0.02	0.02±0.02
Flouranthene	BDL	BDL	BDL	BDL	BDL	BDL	$0.07^{a}\pm0.05$	BDL	BDL	0.01 ± 0.01	BDL
Benzo(a) anthracene	0.01 ^a ±0.00	BDL	BDL	BDL	0.03±0.02	BDL	0.01 ^a ±0.01	BDL	$0.02^{a}\pm0.02$	0.01±0.01	BDL
Chrysene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Benzo (k)flouranthene	$0.02^{a}\pm0.02$	$0.02^{a}\pm0.01$	0.05 ^a ±0.03	BDL	0.01 ± 0.00	BDL	BDL	$0.05^{b}\pm0.00$	0.01 ^a ±0.01	0.02 ± 0.02	0.01±0.00
Benzo(b) Flouranthene	BDL	$0.01^{a}\pm0.00$	BDL	BDL	0.01±0.00	BDL	0.01 ^a ±0.01	BDL	BDL	BDL	BDL
Benzo(a) pyrene	$0.02^{a}\pm0.00$	$0.02^{a}\pm0.01$	$0.10^{a}\pm0.03$	0.03 ± 0.01	BDL	BDL	$0.06^{a}\pm0.04$	$0.05^{a}\pm0.00$	0.01 ^a ±0.00	0.03 ± 0.02	0.02±0.02
Benzo(g,h,i) perylene	0.01 ^a ±0.01	0.01 ^a ±0.00	0.03 ^a ±0.02	0.01 ± 0.01	BDL	$0.01^{a}\pm0.00$	$0.02^{a}\pm0.01$	BDL	BDL	0.01 ± 0.00	BDL
Dibenzo(a,h) anthracene	BDL	BDL	BDL	BDL	BDL	BDL	BDL	$0.04^{a}\pm0.00$	BDL	BDL	BDL
Indeno(1,2,3-cd) pyrene	$0.01^{a}\pm0.00$	$0.01^{a}\pm0.01$	$0.01^{a}\pm0.00$	BDL	0.42±0.09	$0.01^{a}\pm0.01$	$0.01^{a}\pm0.01$	0.27 ^b ±0.05	0.01 ^a ±0.00	0.05 ± 0.02	BDL
ΣPAHs	$0.50^{a}\pm0.04$	$0.42^{a}\pm0.03$	1.75 ^b ±0.28	0.28 ± 0.02	0.68 ± 0.10	$0.09^{a}\pm0.01$	0.47 ^a ±0.03	$0.81^{a}\pm0.70$	1.21 ^b ±0.18	0.65 ± 0.28	0.34±0.15

Values with different superscripts on the same row are significant at p<0.05. BDL= Below Detection Limit

Contamination and Possible Health Risks of Polycyclic Aromatic..... Table 4: Concentrations of PAHs in Crops at Irintan, Omi-Eye and Egbigbu floodplains (µg/kg)

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	IrintanOmi-Eye			eropo ur minum,	, <u>,</u>		Egbigbu		
	Crops			Crops			Crops		
Parameter	T.triangulare	C.annum	Z.mays	T.triangulare	C. annum	Z.mays	T.triangulare	C.annum	Z.mays
Napthalene	$0.07^{a}\pm0.00$	0.31 ^b ±0.04	$0.40^{\circ}\pm0.02$	$0.44^{a}\pm0.09$	0.35 ^a ±0.06	$0.86^{b}\pm0.14$	0.05 ^a ±0.03	0.57 ^c ±0.20	0.13 ^b ±0.01
Acenaphthylene	BDL	BDL							
Acenaphthene	$0.06^{a}\pm0.02$	$0.05^{a}\pm0.00$	$0.05^{a}\pm0.04$	$0.02^{a}\pm0.01$	0.34°±0.04	0.11 ^b ±0.02	0.73 ^b ±0.02	2.10°±0.14	$0.11^{a}\pm0.00$
Flourene	0.12 ^a ±0.03	$0.19^{b}\pm0.18$	$0.04^{a}\pm0.00$	0.01 ^a ±0.00	0.78°±0.03	$0.09^{b} \pm 0.00$	13.99°±11.25	$0.56^{b}\pm0.07$	0.11 ^a ±0.02
Phenanthrene	$0.10^{b} \pm 0.01$	0.16 ^c ±0.11	$0.05^{a}\pm0.03$	$0.01^{b} \pm 0.01$	0.23°±0.01	0.17 ^b ±0.04	1.37 ^b ±0.22	1.49 ^b ±0.35	$0.14^{a}\pm0.03$
Anthracene	0.01 ^a ±0.00	$0.06^{b} \pm 0.00$	$0.01^{a}\pm0.01$	BDL	$0.06^{a}\pm0.05$	$0.02^{a}\pm0.01$	0.14 ^b ±0.02	$0.48^{\circ}\pm0.09$	$0.02^{a}\pm0.00$
Pyrene	$0.05^{a}\pm0.02$	BDL	BDL	0.01 ^a ±0.00	0.16 ^b ±0.03	$0.04^{a}\pm0.04$	$0.40^{a}\pm0.20$	1.72 ^b ±0.63	0.07 ^a ±0.03
Flouranthene	0.13 ^b ±0.03	$0.09^{a}\pm0.02$	$0.07^{a}\pm0.00$	BDL	0.23 ^a ±0.02	$0.25^{a}\pm0.11$	1.79 ^b ±0.05	3.25°±0.02	$0.17^{a}\pm0.11$
Benzo(a) anthracene	BDL	BDL	BDL	BDL	BDL	BDL	0.29 ^b ±0.04	0.60°±0.08	$0.04^{a}\pm0.00$
Chrysene	0.01 ^a ±0.00	BDL	BDL	BDL	$0.02^{a}\pm0.00$	BDL	BDL	BDL	BDL
Benzo(k)flouranthene	BDL	BDL	BDL	0.01 ^a ±0.01	BDL	$0.02^{a}\pm0.00$	0.04 ^a ±0.01	$0.10^{b}\pm0.02$	BDL
Benzo(b) flouranthene	BDL	BDL	BDL	BDL	BDL	$0.04^{a}\pm0.01$	0.05 ^a ±0.01	BDL	BDL
Benzo(a) Pyrene	0.53 ^b ±0.06	$0.50^{b} \pm 0.22$	$0.06^{a}\pm0.05$	0.03 ^a ±0.02	0.53°±0.08	$0.15^{b}\pm0.02$	1.03 ^b ±0.11	5.76°±1.14	$0.16^{a}\pm0.07$
Benzo(g,h,i) perylene	$0.02^{a}\pm0.02$	$0.20^{b} \pm 0.01$	BDL	0.01 ^a ±0.01	BDL	$0.07^{b}\pm0.04$	BDL	1.61 ^b ±0.04	$0.26^{a}\pm0.02$
Dibenzo(a,h) anthracene	BDL	BDL							
Indeno (1,2,3-cd) pyrene	$0.14^{b}\pm0.06$	$0.06^{a}\pm0.02$	0.01 ^a ±0.00	0.09 ^a ±0.02	$0.18^{b}\pm0.01$	BDL	1.26 ^b ±0.04	0.29 ^a ±0.17	BDL
ΣPAHs	1.24 ^b ±0.13	2.62°±0.29	$0.70^{a}\pm0.10$	0.64 ^a ±0.10	2.76°±0.22	1.78 ^b ±0.20	21.15°±3.43	18.43 ^b ±1.55	1.31 ^a ±0.08

Values with different superscripts on the same row are significant at p<0.05. BDL= Below Detection Limit

The ratio Ant/Ant + Phen< 0.1, indicates petroleum inputs while values >0.1 implies pyrolytic (Orecchio, 2010; Tomori et al., 2017). The values obtained in this study are 0.04, 0.03 and 0.01 for Irintan, Omi-Eye and Egbigbu respectively. This could imply a petrogenic sources for all the three study areas. In addition, ratio of Flt/Pyr< 1 implies petrogenic sources while a ratio Flt/Pyr> 1 suggests pyrogenic source. The ratio for Irintan, Omi-Eye and Egbigbu floodplain was 2.00, 0.05 and 0.25 respectively indicative of PAHs source for Irintan to be pyrogenic and petrogenic for both Omi-Eye and Egbigbu. The ratio Naph/Phen is used to presume the presence of fresh and unweathered petroleum if it is > 1 and pyrolytic if < 1. The ratio obtained at Irintan, Omi-Eye and Egbigbu were 1.92, 0.5 and 1.11 respectively indicating probably petrogenic sources at both Irintan and Egbigbu and pyrolytic at Omi-Eye. Fears of ambiguity and difficulty in interpretation of results using more than two criteria have been expressed by Tomori et al. (2017). This made them conclude that the reliability of results of these ratios should be checked by amount of particular PAHs compounds. Thus, they said that the predominance of 2-3 rings PAHs is indicative of a petrogenic source while the predominance of 4-6 rings PAHs indicates pyrolytic sources. In other words, a ratio of

summation of 2-3 rings/summation of 4-6 ring PAHs > 1 is petrogenic while < 1 indicates pyrolytic source. This could equally be expressed as ratio of lower molecular weight and high molecular weight PAHs {LMW/HMW PAHs with a ratio greater than 1 as petrogenic and less than 1 as pyrolytic { (Oyo-Ita et al., 2013). Using this as a vardstick, the values for Irintan, Omi-Eye and Egbigbu are 1.49, 1.73 and 2.24 respectively indicating that the PAHs source at the three sites is from petrogenic source. The fear expressed by Tomori et al. (2017) were similarly expressed by Orecchio (2010) and Zhang et al. (2011) that PAHs source in a matrix could be of mixed sources. They therefore proposed a total index as sum of all ratio normalized for limit (low temperature-high temperature source) to characterize the source of PAHs. According to them, PAHs having a total index < 4 are from low temperature source (petroleum product). The total index for Irintan, Omi-Eye and Egbigbu are 1.12, 0.90 and 0.68 respectively indicating that the PAH source at the 3 sites is low temperature source (petrogenic). The mean concentration range of PAHs measured in food crops at Irintan, Omi-Eye, Egbigbu floodplains are presented in Table 4. The mean concentration (μ g/kg) ranges for the food crops respectively at Irintan, Omi-Eye and Egbigbu are for: naphthalene (0.07-0.40), (0.35-0.86), (0.05-0.57); acenaphthylene (BDL),

(BDL), (BDL); acenapthene (0.05-0.06), (0.02-0.34),(0.11-2.10); flourene (0.04-0.19), (0.01-0.13), (0.11-13.99); phenantherene (0.05-0.16), (0.01-0.23), (0.14-0.149) anthracene (0.01-0.06) (BDL-0.06), (0.02-0.48) pyrene (BDL-0.05), (0.01-0.16), (0.07-1.42); flouranthene (0.07 - 0.13),(BDL-0.25), (0.17-0.179); benzo (a) anthracene (BDL), (BDL), (0.04-0.60); chrysene (BDL-0.01), (BDL-0.02), (BDL); benzo (k) flouranthene (BDL), (BDL-0.02), (BDL-0.10); benzo (b) flouranthene (BDL), (BDL-0.04), (BDL-0.05); benzo (a) pyrene (0.06-0.53), (0.03-0.53), (0.16-5.76); benzo(g,h,i) perylene (BDL-0.20), (BDL-0.07), (BDL-1.61); dibenzo (a,h) anthracene (BDL), (BDL), (BDL); indeno (1,2,3-cd) pyrene (0.01-0.14), (BDL-0.18), (BDL-1.26). It has been reported that crops planted on floodplains can take up pollutants, storing them in their edible portions at amounts high enough to cause concern to animals and human beings (Long et al., 2003). All the PAHs parameters investigated were detected in the crops sampled. Benzo (a) pyrene, naphthalene, flourene concentrations were found to be the highest PAHs in Talinum triangulare at Irintan, Omi-Eye and Egbigbu respectively. Similarly, it was flourene at both Irintan and Omi-Eye, benzo (a) pyrene at Egbigbu in Caspicum annum; naphthalene at both Irintan and Omi-Eye and benzo (g,h,i) pervlene at Egbigbu in Zea mays that has the highest values.

The presence of PAHs most especially HMW PAHs could be deleterious as they are carcinogenic and can therefore portend danger. The order of total PAHs in food crops at Irintan is Caspicum annum>Talinum triangulare>Zea mays. At Omi-Eye, the order is Caspicum annum>Zea mays>Talinum triangulare while at Egbigbu, it is *Talinum triangulare>Caspicum* annum>Zea mays. It can be observed that Zea mays has the least total PAHs content in all the three food crops sampled. The USEPA has classified 8 of the 16 priority PAHs as possible carcinogens (Tomori et al., 2017). The method used by regulatory agencies like USEPA, UK Environment Agency to assess Human Health Risks of mixed PAHs is the use of Toxicity Equivalence factors (TEFs) or Potency Equivalency Factors (PEFs). The factor relates the carcinogenic

potential of other PAHs to that of benzo (a) pyrene and this gives a possible estimate of potential risk from such a food item when this is compared to the estimated threshold concentration (Okereke et al., 2016). The data obtained in this study were assessed to know whether or not the consuming population is exposed to health risk. The Screening Value (SV) as calculated in this study is 1.26µg/kg. All the PEC values were less than the screening value except in Talinum triangulare and Caspicum annum at Egbigbu floodplain (Table 5). This suggests that the consumption of these food crops (Talinum triangulare and *Capsicum annum*) at the rate of 65g a day may have adverse health effects on the long run. There is therefore a cause for concern on the consumption of these food crops by the exposed population.

Parameter	Irintan			Omi-Eye				Egbigbu			
	Vegetable	Pepper	Maize	Vegetable	Pepper	Maize	Vegetable	Pepper	Maize		
Napthalene	0.00007	0.0003	0.00004	0.00044	0.00035	0.00082	0.00005	0.00057	0.00013		
Acenaphthylene	-	-	0.00001	-	-	-	-	-	-		
Acenaphthene	0.00006	0.00005	0.00005	0.00002	0.00034	0.00011	0.00073	0.0027	0.00011		
Flourene	0.0001	0.00119	0.00004	0.001	0.00078	0.00009	0.01399	0.00056	0.00011		
Phenanthrene	0.0001	0.00016	0.00005	0.001	0.00023	0.00017	0.00137	0.00149	0.00011		
Anthracene	0.0001	0.0006	0.00001	-	0.0006	0.0002	0.0014	0.0048	0.00014		
Pyrene	0.00005	-	-	0.0001	0.00016	0.00004	0.0004	0.00172	0.00002		
Flouranthene	0.00013	0.00009	0.00007	-	0.00023	0.00025	0.0179	0.00325	0.00007		
B(a)A	-	-	-	-	-	-	0.029	0.06	0.004		
Chrysene	0.00001	-	-	-	0.00002	-	-	-	-		
B(k)F	-	-	-	0.001	-	0.002	0.004	-	0.01		
B(b)F	0.53	0.50	0.06	-	-	0.00004	0.00005	-	-		
B(a)Pyr	0.0002	0.002	-	0.03	0.53	0.15	1.03	5.76	0.16		
B(g,h,i)P	0.06	0.04	0.01	0.0001	-	0.0007	-	0.0161	0.0016		
Db(a,h)A	-	-	-	-	-	-	-	-	-		
I(1,2,3-cd)Pyr	0.14	0.06	0.01	0.09	0.18	-	1.26	0.29	-		
PEC	0.73	0.56	0.07	0.12	0.71	0.15	2.35	614	0.17		
SV	1.26	1.26	1.26	1.26	1.26	1.26	1.26	1.26	1.26		

B(a)A = Benzo (a) anthracene; B(k)F = Benzo (k) fluoranthene; B(b)F = Benzo (b) fluoranthene; B(a)Pyr = Benzo (a) pyrene; B(g,h,i)P = Benzo (g,h,i) perylene; Db(a,h)A = Dibenzo (a,h) anthracene; I(1,2,3-cd)Pyr = Indeno (1,2,3-cd) pyrene

Conclusion: The research established that farming at floodplains could have attendant problem of pollution. The possible source apportionment for the PAHs in this study implicated petroleum sources with pyrolytic mix.

The research equally revealed that the estimated benzene (a) pyrene potency equivalent concentration (PEC) values of *Talinum triangulare* and *Caspicum annum* were greater than the cancer screening value for the crops at Egbigbu floodplain implying that the consumption of the crops may have adverse health effects on the long run on the exposed population.

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