Assessment of Polycyclic Aromatic Hydrocarbons in Fruits of *Citrus sinensis* (*Porcher Michel H.*) around Port Harcourt Metropolis Nigeria

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Abstract— *This study was conducted to assess the polycyclic aromatic hydrocarbons in fruits of Citrus sinensis Collected from trees grown around Port Harcourt Metropolis. Stratified random sampling technique was used to select five study locations grouped into high and low traffic density areas and data collected in the wet and dry seasons. In the dry season higher Concentration of Naphthalene (4.98 x 10^{-5}ppm) was measured at Garrison, acenaphthene at Trans-Amadi (8.28 x10^{-3} ppm), anthracene 6.05 x10^{-5} ppm) at Rivers State University. PAHs measured around the study locations in the dry season were significantly different at $P \leq 0.05$ using the Duncan Multiple Range Test (DMRT). In the wet season, Rivers State University recorded significantly high concentration of Pyrene (7.99 x10^{-4}), Benzo (b) fluoranthene (1.58 x10^{-4} ppm), Benzo (k) fluoranthene (8.63 x10^{-4} ppm), Benzo (a) Pyrene (2.44 x10^{-4} ppm) and Dibenz (a,h) anthracene (3.01 x10^{-3} ppm). Individual PAHs in Rumuokoro were all below detectable limits in the wet season. Rivers State University recorded significantly high concentrations of Benzo (a) Pyrene in both wet and dry seasons. Acenaphthene was detected only at Rivers State University (2.96 x 10^{-3} ppm) in the wet season while anthracene was detected at two locations (Garrison: 1.72 x10^{-5} ppm and RSU:5.33 x10^{-6} ppm). Trans Amadi recorded the highest concentrations of Flouranthene (1.46 x 10^{-4} ppm), Benz (a) anthracene (1.05 x 10^{-5} ppm), Chrysene (4.78 x 10^{-4} ppm), Benzo (b) fluoranthene (7.91 x 10^{-5} ppm), Benzo (k) fluoranthene (3.29 x 10^{-4} ppm), Dibenz (a,h) anthracene (4.64 x 10^{-4} ppm), Indeno (1,2,3-cd) pyrene (1.71 x 10^{-3} ppm) and Benzo (g, h, i) perylene (8.34 x 10^{-4} ppm) in the wet season. In the dry season, Benzo (a)anthracene was observed to be within USEPA standard at the Garrison location. Carcinogenic and mutagenic polycyclic aromatic hydrocarbons such as Benz (a)anthracene and Benz (a) pyrene were observed to have concentrations higher than the USEPA standard in Rivers State University in the wet season, this poses serious threat to humans and other life forms at that location. The distribution of PAHs in fruits within Port Harcourt Metropolis should be monitored regularly due to the toxicological effect and widespread presence in the environment. Government and other relevant authorities should sensitize the public regularly on the sources and health implications of exposure to PAH.*

***Keywords—* Fruits, PAH, Port Harcourt metropolis, Citrus sinensis.**

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds containing only hydrogen and carbon in multiple aromatic rings. PAHs occurs naturally in coal, crude oil and gasoline, the simplest are the two aromatic rings and the three rings naphthalene, anthracene and phenanthrene (Abdel-shafy and Mansour, 2016). PAHs can originate from natural sources, such as forest fires and volcanic emissions, and also from anthropogenic sources such as coal burning, vehicular emissions, engine lubricating oils, and cigarette smoke (Kim, *et al.,* 2013). Pyrolytic processes are the major sources of PAHs through anthropogenic activities such as combustion of natural gas, incomplete combustion of organic materials, processing of crude oil and coal, combustion of refuse, vehicle emissions, cooking and tobacco smoking (Abdel-shafy, and Mansour, 2016). PAHs generated from various sources accumulate in the environment and enters the food chain through affected water, air, and soil (Karishma, *et al,* 2018).

PAHs from several pyrolytic sources gets into the environment through the air and could be inhaled directly by human (Superfund Research Program-SRP, 2013). PAHs in the air could be transformed, degraded, or deposited. Deposition could be on vegetation, animals, humans, aquatic environment and even soil (Lee and Vu, 2010). PAHs in soil are mostly from atmospheric deposition from pyrolytic sources and from petrogenic sources such as the release of petroleum or crude oil from natural oil seeps and spillage (Obayori and Salaam, 2010).

Polycyclic aromatic hydrocarbons are ubiquitous in nature and are of environmental concern (WHO, 2003). Several PAHs have been identified as potent human carcinogens and persists in the environment (Lee and Vu, 2010). Recent epidemiological studies with humans and animals have indicated that the increasing cancer prevalence can be partly attributed to PAHs exposure. Furthermore, other epidemiological studies have demonstrated that a large proportion of cancer cases may be ascribed to at least in part dietary factors, including dietary exposure to PAHs (Abid, *et al*, 2014).

PAHs concentrations in urban soil are considered to be higher than PAHs in rural soils due to increased vehicular and industrial activities in the urban areas (EFCSG, 2010). However, most oil exploitation and exploration activities usually occur in the rural areas causing accidental or intentional spillage and could also increase PAHs in soil from petrogenic sources in addition to pyrolytic sources in the rural area. Simbi-Wellington and Ideriah, (2022) reported that sixteen individual PAHs were detected in mangrove soil around at oil exploration site in a rural community in Rivers State. Studies have revealed that the concentrations of PAHs in the wet season could be more than that in dry season (EFCSG, 2010). This could be attributed to the absence of sunlight to break down the PAHs through photodecomposition and the probable increase in burning to warm homes. However, observations have shown that more fire incidence or outbreak are likely to occur in the dry season than in the wet season and could likely increase the amount of heating emission and probably PAHs in the environment. Simbi-Wellington and Ideriah, (2022) reported, PAHs were significantly higher in leave samples collected in the wet season month of September and lowest in the dry season month of March.

PAH have been detected in various food such as fruits, leaves, vegetable oil, meat smoked fish, tea and coffee (Lee and Vu, 2010). Absorption of PAHs in fruit can occur through air or soil during the process of cultivation, and prior to consumption through the process of storage and transportation (Alice *et al*., 2017). PAHs in fruit are mainly due to deposition of airborne particulate on exposed surface, the waxy surface of fruit assimilate low molecular mass PAHs through surface absorption and particle bond. According to Alice *et al* (2017) trace level of PAHs such as fluoranthene, pyrene and phenanthrene have been detected in every raw fruit while high concentration of lighter PAHs such as naphthalene have been detected in some fruits.

Low concentrations (0.001 – 0.5 µg kg^{-1} wet weight) of PAHs can be detected in raw fruits, however, research have revealed that concentrations exceeding 0.5 µg kg^{-1} and up to 5 µg kg^{-1} wet weight can be found in several fruits depending on factors such as air quality around the farm site, the crop itself and the specific PAH. Alice *et al.,* (2017) reported that PAHs concentration in fruits is usually higher for crops grown near roadways or in urban regions than in rural areas. Low temperature combustion such as wood burning and tobacco smoking tend to generate low molecular weight PAHs while high temperature industrial processes typically generate PAHs with higher molecular weight (Rose *et al.*, 2015).

Studies have revealed that PAHs can be detected in fruits and leafy vegetables particularly in industrialized cities. According to reports, volatilized PAHs in air is a major contributor of PAH in plants. Ideriah *et al.* (2012) reported a high correlation between pollutants in air and total hydrocarbons in leaves collected around selected farms in Port Harcourt. Several of the PAH compounds have been identified by WHO as carcinogenic and/or mutagenic and poses threat to human health. Port Harcourt being the capital and major city of Rivers State with rapid urbanization and an associated growth in industries and automobiles has been reported to have high levels of hydrocarbons in leaves (Ideriah, *et al.,* 2011). This study aims at providing information on the levels of PAHs in fruits of *Citrus sinensis* grown around Port Harcourt metropolis in the dry and wet season months as PAHs in fruits can act as an indicator of human exposure through consumption.

II. MATERIALS AND METHODS

2.1 Study Location:

Port Harcourt is a highly industrialized city in Nigeria and a major industrial center with a large number of multinational firms as well as other industrial concern and businesses related to the petroleum industry. Port-Harcourt lies within latitudes 4º43 and 4°54N and longitudes 6056 and 7°03 E, 18 meters (59 feet) above sea level with a mean annual rainfall of over 2000mm and mean annual temperature of about 29°C (Nigeria Meteorological Services (NMS), 1998). Port-Harcourt city covers an area of 186km^2 (71.8sq ml) with a land area of 170km^2 (65.6sqmi), and Water area of 16km^2 (6.2sqmi) (Alagoa and Derefaka, 2002). The main city of Port Harcourt is the Port-Harcourt town in the Port Harcourt City Local Government Area, consisting of the former European quarters now called Old Government Reservation Area (GRA) and new layout areas. The Port Harcourt Urban Area (Port Harcourt metropolis) is made up of the city itself and parts of Obio/Akpor Local Government Area. Important neighboring towns are Diobu which is a Rebisi settlement, Abuloma which is an Okrika settlement, Woji which is an Ikwere settlement, Alesa Eleme which is an Ogoni settlement and many other lkwerre clans. All these settlements are collectively known as Greater Port Harcourt. Some of Port-Harcourt's more popular and well-known residential areas are the Port-Harcourt Township also known as Town, G.R.A phases 1-5. Abuloma, Amadi-Ama, and Borikiri. The main industrial area is located at Trans Amadi (Alagoa and Derefaka, 2002; GPHCDA, 2011).

2.2 Site Selection and Sample Collection:

The systematic sampling design was used in the selection of the sampling stations. The criteria used in selection of sampling stations was based on traffic density: high density (>500,000 vehicle per day) and low density (<500,000 vehicle per day). The vehicles at the stations included trailers, trucks, cars, tankers, tractors, tricycles, and motorcycles. A total of five stations were selected for this study.

Fruits samples were randomly collected in the wet and dry seasons from *Citrus sinensis* trees in three replications at each of the study stations with the use of garden scissor and were carefully placed into well labelled polyethylene bags. Collected samples were taken to the laboratory for PAH analysis.

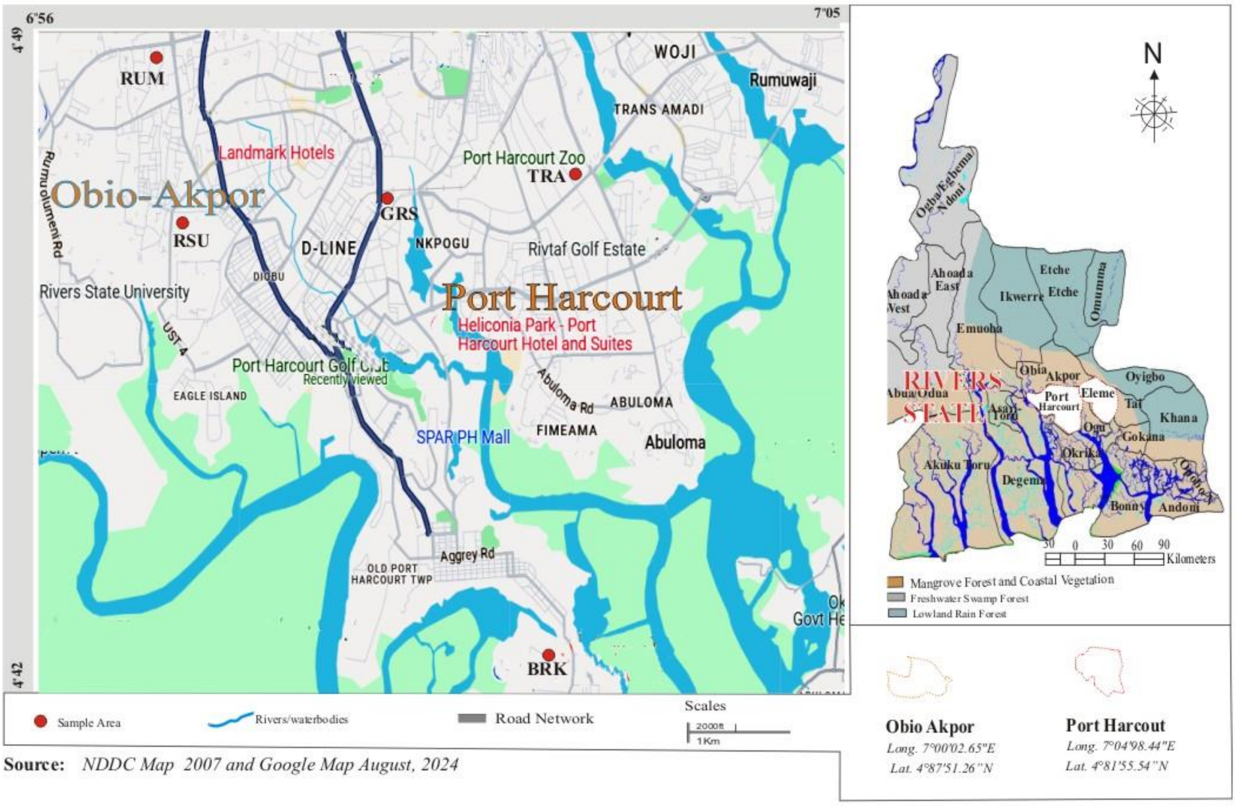

FIGURE 1: Map of Port Harcourt Showing Study Locations

2.3 Determination of Polycyclic Aromatic Hydrocarbons in Fruits:

Polycyclic aromatic hydrocarbons in fruit samples were determined using Gas Chromatograph with Flame Ionization Detector (GC-FID). Ten milliliter of extraction solvent (hexane) were added to 2g of collected samples, mixed thoroughly, allowed to settle filtered using Buchner funnel. Extracts were concentrated to 2m1 and were transferred for clean-up and separation. Thereafter, concentrated aromatic fractions of samples were transferred into glass vials with Teflon and rubber crimp caps for GC analysis. 1µL of the concentrated samples were injected by means of hypodermic syringe through rubber septum into columns of Gas Chromatograph (HP 5890 series 11) Separation occurred as the vapour constituents were partitioned between the gas and liquid phase. The constituent aromatic compounds were automatically detected at emergence from the column by the Flame Ionization Detector (FID).

III. RESULTS AND DISCUSSION

3.1 Dry Season PAHs in Fruits of *Citrus sinensis* Grown around Port Harcourt Metropolis:

Fourteen individual PAHs were detected in fruits of *Citrus sinensis* around Port Harcourt metropolis in the dry season. PAHs detected were Naphthalene, Acenaphthylene, Fluorene, Anthracene, Flouranthene, Benzo (g, h, i), Pyrene, Benz (a) anthracene, Chrysene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) Pyrene, Dibenz (a,h) anthracene and Indeno (1,2,3-cd) pyrene (Table 1). Total PAH concentrations ranged from 0.00368ppm observed in fruits collected at location RUM to 0.00815ppm observed in fruits collected at location TRA (Fig 2). Table 1 shows that the individual PAHs measured around the study locations in the dry season were significantly different at P≤0.05 using the Duncan Multiple Range Test (DMRT). Concentrations of Naphthalene was highest in locations GAR and RUM (4.98 $x10^{-5}$ppm and3.65 $x10^{5}$ ppm respectively) and below detectable limit in location BRK, RSU and TRA. Flouranthene was highest in location TRA (5.41 $x10^{-5}$ ppm) and GAR (5.62 $x10^{-5}$ ppm) and lowest in location RSU (below detectable limit). Anthracene was detected only in location RSU (6.05 $x10^{-5}$ ppm), Acenaphthylene in only location TRA (8.28 $x10^{-3}$ ppm) and Fluorene in only location BRK (2.641 $x10^{-5}$ ppm).

Concentrations of Benz (a) anthracene (2.76 $x10^{-4}$ ppm) and Benzo (a) Pyrene (2.44 $x10^{-4}$ ppm) observed at location RSU were above the United States Environmental Protection Agency (USEPA, 2013) recommended limits of $1.0x10^{-4}$ and $2.0x10^{-4}$ respectively (Table 2), and therefore poses serious threat to human and other life forms within and around the study locations. PAHs such as pyrene, acenaphthylene, fluorene, anthracene, pyrene, benz[a]anthracene, benzo[k]fluoranthene, benzo[a]pyrene, indeno (1,2,3-cd) pyrene, benzo[b]fluoranthene, fluoranthene and chrysene observed in collected samples are listed as carcinogenic and mutagenic by United States Environmental Protection Agency (USEPA, 2013).

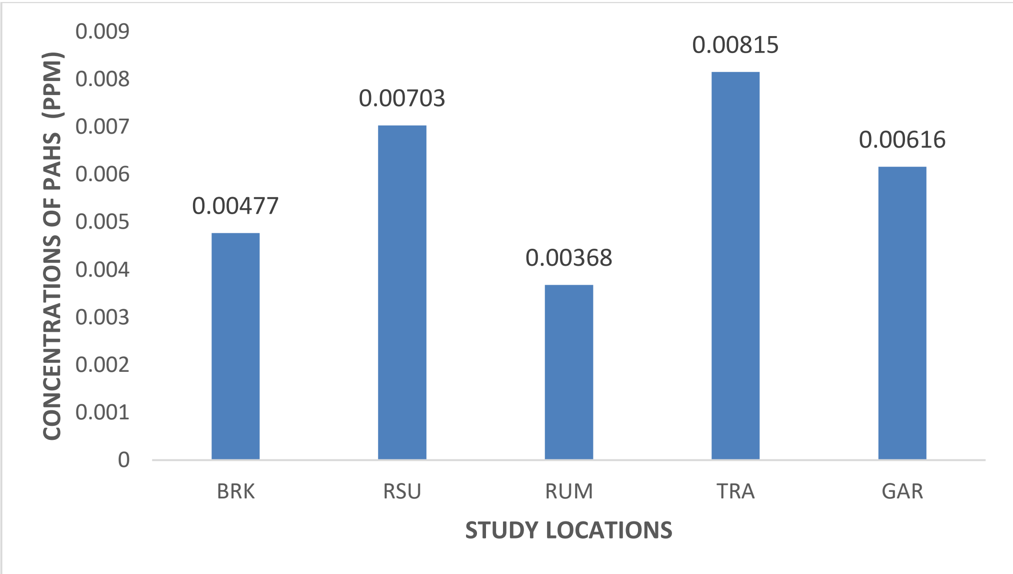

FIGURE 2: Dry Season Total PAHs in fruits of *Citrus sinensis* in Port Harcourt Metropolis

Location RSU recorded significantly higher concentrations of Pyrene (7.99 $x10^{-4}$ ppm), Benzo (b) fluoranthene (1.58 $x10^{-4}$ ppm), Benzo (k) fluoranthene (8.63 $x10^{-4}$ ppm), Benzo (a) Pyrene (2.44 $x10^{-4}$ ppm) and Dibenz (a,h) anthracene (3.01 $x10^{-3}$ ppm) (Table 1). This report is in consonance with the report by Trinya and Ideriah (2015) that observed high concentrations of NO_2 and SO_2 exceeding permissible limits at Rivers State University of Science and Technology Farm and Road E. The high concentration of PAH observed at this location can be attributed to industrial activities from the adjacent Nigerian Agip Oil company and automobile activities from the busy Mile 3 Park which is in close proximity with the Rivers State University.

Acenaphthylene was detected only at location GAR which is a high traffic location. Location GAR also had significantly higher concentrations of Naphthalene (4.98 $x10^{-5}$) Flouranthene (5.62 $x10^{-5}$ ppm), Dibenz (a, h) anthracene (3.05 $x10^{-3}$ ppm) and Indeno (1,2,3-cd) pyrene (1.14 $x10^{-3}$ ppm). This result agrees with the report by WHO (2003) which states that automobiles are a major source of PAHs in the environment. Naphthalene, Acenaphthene and Chrysene were not detected in location BRK a low traffic location. Location BRK also recorded significantly lower concentrations of Pyrene, Dibenz (a, h) anthracene and Benz (a) Pyrene (Table 1). This result can be attributed to the low vehicular and industrial activities within and around the Borikiri axis of Port Harcourt Metropolis and is in agreement with the report by Emerhi *et al*, (2012).

TABLE 1
PAHS (PPM) DETECTED IN FRUITS OF *CITRUS SINENSIS* GROWN AROUND PORT HARCOURT METROPOLIS

PAHs	Location/Season									
	Dry Season					Wet season				
	BRK	RSU	TRA	RUM	GAR	BRK	RSU	TRA	RUM	GAR
Naphthalene	BDL	BDL	BDL	$3.65x10^{-5 (b)}$	$4.98x10^{-5 (a)}$	BDL	BDL	BDL	BDL	BDL
Acenaphthylene	BDL	BDL	$8.28 x10^{-3(a)}$	BDL	BDL	BDL	$2.96 x 10^{-3(a)}$	BDL	BDL	**BDL**
Fluorene	$2.641x10^{-5(a)}$	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Anthracene	BDL	$6.05 x10^{-5 (a)}$	BDL	BDL	BDL	BDL	$5.33 x 10^{-6 (b)}$	BDL	BDL	$1.72 x 10^{-5 (a)}$
Flouranthene	$2.98 x10^{-5(b)}$	BDL	$5.41 x10^{-5(a)}$	$1.05 x10^{-5(c)}$	$5.62 x10^{-5 (a)}$	BDL	$7.08 x 10^{-6 (c)}$	$1.46 x 10^{-4 (a)}$	BDL	$4.54 x 10^{-5 (b)}$
Benzo (g, h, i) perylene	$2.03x10^{-3 (a)}$	BDL	$3.37x10^{-4 (c)}$	BDL	$1.12x10^{-3(b)}$	$1.17 x 10^{-4(c)}$	$9.8 x 10^{-5(c)}$	$8.34 x 10^{-4(a)}$	BDL	$4.33 x 10^{-4(b)}$
Pyrene	$5.39X10^{-5 (d)}$	$7.99X10^{-4 (a)}$	$2.60X10^{-4 (d)}$	$2.73X10^{-4 (b)}$	BDL	$6.1 x 10^{-5(c)}$	$4.55 x 10^{-6(d)}$	$7.74 x 10^{-5 (b)}$	BDL	$9.79 x 10^{-5(a)}$
Benz (a) anthracene	$2.15X10^{-5 (b)}$	$2.76X10^{-4 (a)}$	BDL	$1.52X10^{-5 (c)}$	BDL	$1.64 x 10^{-5 (b)}$	$5.77 x 10^{-6 (d)}$	$1.05 x 10^{-4(a)}$	BDL	$1.52 x 10^{-5(c)}$
Chrysene	BDL	$1.59X10^{-3 (b)}$	$5.68X10^{-3 (a)}$	$1.21X10^{-3 (c)}$	BDL	$2.82 x 10^{(b)}$	$3.23 x 10^{-5 (d)}$	$4.78 x10^{-4(a)}$	BDL	$2.71 x 10^{-4(c)}$
Benzo (b) fluoranthene	$8.99X10^{-5 (c)}$	$1.58X10^{-4 (a)}$	BDL	$7.69X10^{-5 (d)}$	$1.21X10^{-4 (b)}$	$3.66 x 10^{-5 (b)}$	$1.83 x 10^{-6 (d)}$	$7.91 x 10^{-5 (a)}$	BDL	$2.47 x 10^{-5 (c)}$
Benzo (k) fluoranthene	$1.26X10^{-3 (a)}$	$8.63X10^{-4 (a)}$	BDL	$3.79X10^{-4 (b)}$	$5.18X10^{-4 (c)}$	$7.89 x 10^{-5 (b)}$	$1.33 x 10^{-5 (d)}$	$3.29 x 10^{-4 (a)}$	BDL	$4.37 x 10^{-5 (c)}$
Benzo (a) Pyrene	$0.37X10^{-4 (d)}$	$2.44X10^{-4 (a)}$	$1.60X10^{-4 (c)}$	$1.46X10^{-4 (b)}$	$0.84X10^{-4 (c)}$	$1.78 x 10^{-4 (a)}$	$1.8 x 10^{-4(a)}$	$1.48 x 10^{-5 (b)}$	BDL	$1.64 x 10^{-5 (b)}$
Dibenz (a, h) anthracene	$2.52X10^{-4 (e)}$	$3.01X10^{-3 (a)}$	$8.81X10^{-4 (d)}$	$1.40X10^{-3 (c)}$	$3.05X10^{-3 (a)}$	$1.06 x 10^{-4(c)}$	$1.48 x 10^{-5(d)}$	$4.64 x 10^{-4(a)}$	BDL	$2.83 x 10^{-4(b)}$
Indeno (1,2,3-cd) pyrene	$7.77X10^{-4 (c)}$	BDL	$8.01X10^{-4 (b)}$	BDL	$1.14X10^{-3 (a)}$	$5.34 x 10^{-4(c)}$	$1.6 x 10^{-4(d)}$	$1.71 x 10^{-3(a)}$	BDL	$7.01 x 10^{-4(b)}$

Within columns means with different superscripts are significantly different at $p \leq 0.005$ using the DMRT

TABLE 2
PAHS (PPM) DETECTED IN FRUITS OF *CITRUS SINENSIS* GROWN AROUND PORT HARCOURT METROPOLIS AGAINST PERMISSIBLE LIMITS

PAH	LOCATIONS										
	Dry Season					Wet Season					
	BRK	RSU	RUM	TRA	GAR	BRK	RSU	RUM	TRA	GAR	USEPA 2013
Naphthalene	BDL	BDL	3.65×10^{-5}	BDL	4.98×10^{-5}	BDL	BDL	BDL	BDL	BDL	4.0×10^{-2}
Acenaphthylene	BDL	BDL	BDL	8.28×10^{-3}	BDL	BDL	2.96×10^{-3}	BDL	BDL	BDL	2.0×10^{-1}
Fluorene	2.641×10^{-5}	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	2.0×10^{-1}
Anthracene	BDL	6.05×10^{-5}	BDL	BDL	BDL	BDL	5.33×10^{-6}	BDL	BDL	1.72×10^{-5}	2.0×10^{-1}
Flouranthene	2.98×10^{-5}	BDL	1.05×10^{-5}	5.41×10^{-5}	$5,62 \times 10^{-5}$	BDL	7.08×10^{-6}	BDL	1.46×10^{-4}	4.54×10^{-5}	2.0×10^{-1}
Benzo (g, h, i) perylene	2.03×10^{-3}	BDL	BDL	3.37×10^{-4}	1.12×10^{-3}	1.17×10^{-4}	9.8×10^{-5}	BDL	8.34×10^{-4}	4.33×10^{-4}	3.0×10^{-1}
Pyrene	5.39×10^{-5}	7.99×10^{-4}	2.73×10^{-4}	2.60×10^{-4}	BDL	6.1×10^{-5}	4.55×10^{-6}	BDL	7.74×10^{-5}	9.79×10^{-5}	2.0×10^{-1}
Benz (a) anthracene	2.15×10^{-5}	**2.76×10^{-4}**	1.52×10^{-5}	BDL	BDL	1.64×10^{-5}	5.77×10^{-6}	BDL	1.52×10^{-5}	**1.05×10^{-4}**	**1.0×10^{-4}**
Chrysene	BDL	1.59×10^{-3}	1.21×10^{-3}	5.68×10^{-3}	BDL	2.82×10^{-4}	3.23×10^{-5}	BDL	$4. 78 \times 10^{-4}$	2.71×10^{-4}	2.0×10^{-1}
Benzo (b) fluoranthene	8.99×10^{-5}	1.58×10^{-4}	7.69×10^{-5}	BDL	1.21×10^{-4}	3.66×10^{-5}	1.83×10^{-6}	BDL	7.91×10^{-5}	2.47×10^{-5}	2.0×10^{-1}
Benzo (k) fluoranthene	1.26×10^{-3}	8.63×10^{-4}	3.79×10^{-4}	BDL	5.18×10^{-4}	7.89×10^{-5}	1.33×10^{-5}	BDL	3.29×10^{-4}	4.37×10^{-5}	2.0×10^{-1}
Benzo (a) Pyrene	0.37×10^{-4}	**2.44×10^{-4}**	1.46×10^{-4}	1.60×10^{-4}	0.84×10^{-4}	1.78×10^{-4}	1.8×10^{-4}	BDL	1.48×10^{-5}	1.64×10^{-5}	**2.0×10^{-4}**
Dibenz (a, h) anthracene	2.52×10^{-4}	3.01×10^{-3}	1.40×10^{-3}	8.81×10^{-4}	3.05×10^{-3}	1.06×10^{-4}	1.48×10^{-5}	BDL	4.64×10^{-4}	2.83×10^{-4}	
Indeno (1,2,3-cd) pyrene	7.77×10^{-4}	BDL	BDL	8.01×10^{-4}	1.14×10^{-3}	5.34×10^{-4}	1.6×10^{-4}	BDL	1.71×10^{-3}	7.01×10^{-4}	4.0×10^{-1}

BDL: Below Detectable Limit

3.2 Wet Season PAHs in Fruits of *Citrus sinensis* Grown around Port Harcourt Metropolis:

Twelve individual PAHs were detected in fruits of *Citrus sinensis* around Port Harcourt metropolis in the wet season. Naphthalene and Fluorene were not detected in the wet season months. PAHs detected are Acenaphthene, Anthracene, Flouranthene, Pyrene, Benz (a) anthracene, Chrysene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) Pyrene, Dibenz (a,h) anthracene, Indeno (1,2,3-cd) pyrene and Benzo (g, h, i) perylene (Table 1).

Total PAHs concentration detected in fruits of *Citrus sinensis* within Port Harcourt metropolis in the wet season were significantly different at $P \leq 0.05$ using Duncan Multiple Range Test (DMRT). Concentration detected in Trans-Amadi (4.0×10^{-3} ppm) were significantly higher than the concentrations detected in the other locations (Fig 3). This can be attributed to the high industrial and vehicular activities in the Trans-Amadi axis of Port Harcourt and agrees with the report by WHO (2003) which states that automobiles are a major source of PAHs in the environment. RUM had the lowest with concentration below detectable limit (BDL) as shown in Figure 3. This report can be attributed to the low vehicular activities in the region due to the construction of the RUM flyover at the time of the study. This report is in consonance with Eduardo (2006) which reported that the burning of hydrocarbons in the engines of vehicles give rise to air pollutants. Result in table 1 shows that Acenaphthene was detected only in location RSU (2.96×10^{-3} ppm). Anthracene was detected in two locations (Garrison: 1.72×10^{-5} and RSU:5.33×10^{-6} ppm). Trans Amadi recorded the highest concentrations of Flouranthene (1.46×10^{-4} ppm), Benz (a) anthracene (1.05×10^{-5} ppm), Chrysene (4.78×10^{-4} ppm), Benzo (b) fluoranthene (7.91×10^{-5} ppm), Benzo (k) fluoranthene (3.29×10^{-4} ppm), Dibenz (a,h) anthracene (4.64×10^{-4} ppm), Indeno (1,2,3-cd) pyrene (1.71×10^{-3} ppm) and Benzo (g, h, i) perylene (8.34×10^{-4} ppm).

Individual PAHs at location RUM were all below detectable limits in the wet season. Location RSU recorded significantly higher concentrations of Benzo (a) Pyrene in both wet and dry seasons. Individual PAHs observed in fruits of *Citrus sinensis* within Port Harcourt metropolis in the wet season were all within the permissible limits recommended by the United States Environmental Protection Agency as opposed to what was detected in the dry season where the concentrations of Benz (a) anthracene and Benzo (a) Pyrene in location RSU (2.76×10^{-4} ppm and 2.44×10^{-4} ppm respectively) were above recommended limits (Table 2). Concentrations of Benzo (a) anthracene however, were within the border line with a concentration of 1.04×10^{-4} ppm. The low concentrations of PAHs observed in the wet season months can be attributed to the fact that pollutant emissions and concentrations are higher during the dry seasons owing to meteorological factors such as high temperature. Efel *et al* (2005) reported that during the wet season, a combination of heavy rainfall and in some cases, high wind speed off the oceans, significantly improve pollutant concentrations in the environment.

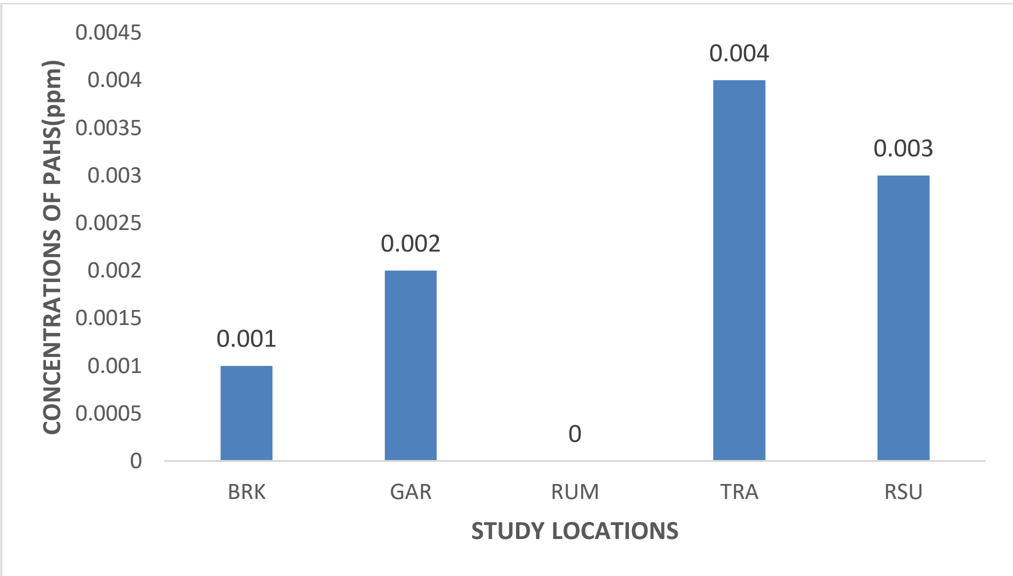

FIGURE 3: Wet Season Total PAHs in Fruits of *Citrus sinensis* within Port Harcourt Metropolis

IV. CONCLUSION

The findings from this study have provided evidence of the presence and levels of PAHs in fruits of *Citrus sinensis* grown around Port Harcourt metropolis in the dry and wet seasons. In the dry season, carcinogenic and mutagenic polycyclic aromatic hydrocarbons such as Benz (a) anthracene and Benz (a) pyrene were observed to have concentrations higher than the standard limit in *Citrus sinensis* fruits grown within the Rivers State University. In the wet season Benzo (a) anthracene was observed to be within the standard limit at the Garrison location. The distribution of PAHs in fruits within Port Harcourt Metropolis should be monitored regularly due to the toxicological effect and widespread presence in the environment. The biological impact in terms of total PAHs intake into the body via polluted fruits should be monitored. Further studies and sensitization by relevant authorities should be done to identify the sources and health implications of exposure to PAH.

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