



**CONTAMINATION OF SOIL AND AIR BY PAH AS A RESULT OF OIL  
AND GAS PRODUCTION ACTIVITIES IN AKWA IBOM STATE, NIGERIA**

**By**

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## **Dedication**

This thesis is dedicated to the God of different dimensions and to my husband, Asuquo Okon

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## Abstract

Petroleum exploitation and production have enormous economic value globally, but with potential attendant potential negative impacts on the environment. One such impact is the emission of Polycyclic Aromatic Hydrocarbons (PAH) that are known for their carcinogenic and other potential toxic effects.

In this study, the concentrations, profile, and human exposure to fourteen PAH were studied in soil and air collected in the vicinity of a rural oil and gas exploration site in Akwa Ibom State, Niger Delta, Nigeria. Spatial and seasonal trends were also investigated. Soil and air samples were collected in both the wet and dry season at a variety of locations impacted by different steps in the process of oil and gas exploration and production.

Soil samples were extracted with a validated ultra-sonication method, with air samples extracted via an enhanced sonication method connected to a reflux column. Sample analysis was conducted via GC-MS.

The results revealed that  $\Sigma_{14}$ PAH concentrations in air and soil were significantly higher at operational locations compared with those collected from non-operational locations (such as workers' residences). PAH concentrations in soil decreased with increasing distance from activity locations, underscoring the importance of oil and gas activities. Analysis of variance indicated significantly higher ( $p < 0.05$ ) PAH concentrations in soil at some locations. A similar significant difference between sites for air was not observed, likely due to low sample numbers.

Average concentrations of  $\Sigma_{14}$ PAH were higher in the dry season than in the wet season for both soil and air. Concentrations were significantly higher ( $p < 0.05$ ) between the wet and dry season at some locations for soil and air samples.

Concentrations of 3-4 ring PAH were predominant in both wet and dry seasons for soil and air samples in all locations. Comparing the profiles of PAH found in this study with those reported for other oil and gas impacted studies, suggests the influence of oil and gas production activities.

The carcinogenicity and relative importance of adult exposure through inhalation of air and ingestion of soil were evaluated in terms of benzo[*a*]pyrene equivalents. Exposure to soil via ingestion of soil particles was higher than via air inhalation. Generally, estimated cancer risks of exposure via soil ingestion of soil particle and air inhalation were within levels considered acceptable. To our knowledge, this is the first study in Nigeria where PAH have been investigated in the environment at locations in the vicinity of different oil and gas exploration field in both the wet and dry seasons.

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## List of Abbreviation

ADD	Average Daily Dose
AF	Surrounding of Crude Oil Field/Pipeline Area
ANOVA	Analysis of Variance
APA	Along Pipeline Right of Way (gas well)
APB	Along Pipeline Right of Way (oil well)
AW1	Active Oil Well
AW2	Gas Well
AW3	Oil Well
B.P	Boiling Point
BP	Britain Petroleum
DCM	Dichloromethane
DPR	Department of Petroleum Resources
Dw	Dry Weight
EI	Electron Impact
EPA	Environmental Protection Agency
GC	Gas Chromatography
GDP	Gross Domestic Production
HMW	High Molecular Weight
IARC	International Agency for Research on Cancer
ILCR	Increment Lifetime Cancer Risk
IS	Internal Standard
$K_{oc}$	Octonal-Carbon Partition Coefficient
$K_{ow}$	Octanol -Water Partition Coefficient
LADD	Lifetime Average Daily Dose
LOD	Limit of Detection
LOQ	Limit of Qualification
LMW	Low Molecular Weight
m/z	Mass to Charge Ratio
Max	Maximum
Min	Minimum
MS	Mass Spectrometry

MP	Main Processing Area
NAW	Non-Active Site
NIST	National Institute of Standards and Technology
NP	Near Processing Area and Gas Flaring
OA	Office Area
ODF	Within Oil Drilling Field
OGP	Oil and Gas Production Area
OW	Within Oil Well Area
PAH	Polycyclic Aromatic Hydrocarbon
PAS	Passive Air Sampler
PS	Solid Vapour Pressure
PUF	Polyurethane Foam
QA/QC	Quality Assurance/Quality Control
RRF	Relative Response Factor
RSD	Relative Standard Deviation
RT	Retention Time
SD	Standard Deviation
S/N	Signal to Noise
SOF	Surrounding of Oil Drilling Field
ST	Storage Tank and Pump Area
TEF	Toxic Equivalent Factor
TEQ	Toxic Equivalent
TST	Crude Oil Transfer Area
U.S. EPA	United States Environmental Protection Agency
VP	Vapour Pressure
WA	Worker's Accommodation
WF	Within Gas Field
WHO	World Health Organisation
WS	Workstation

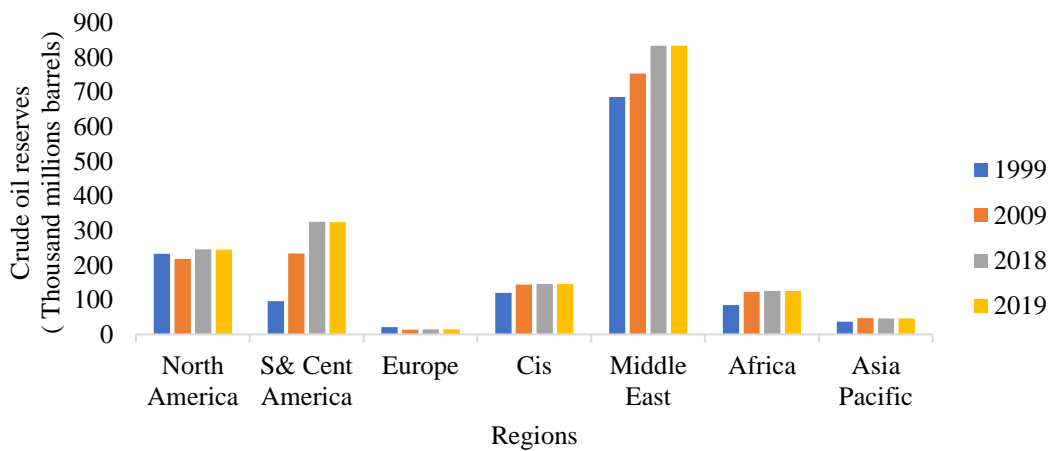
# Chapter 1

## Introduction

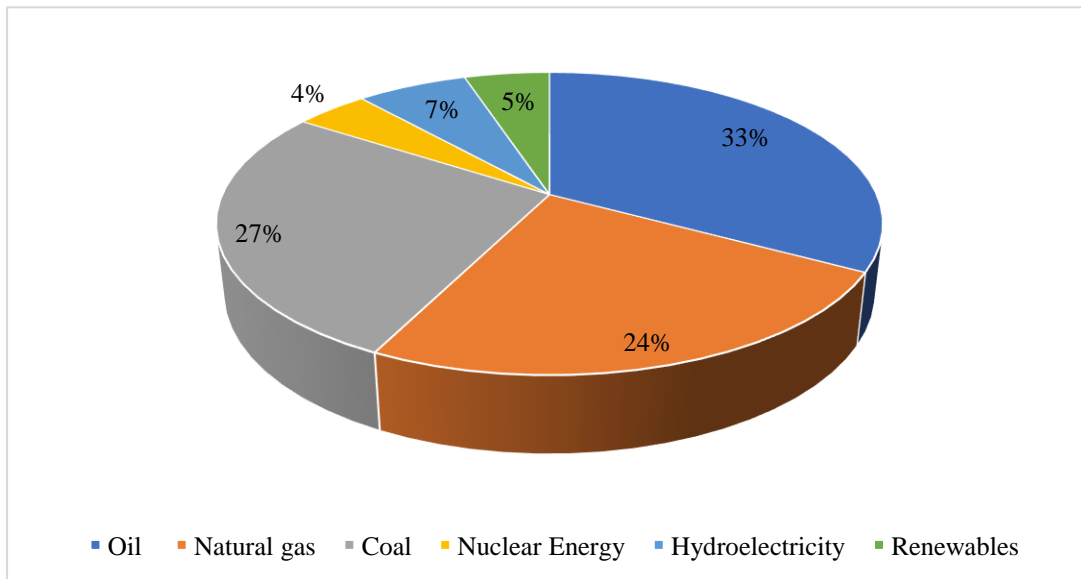
### 1.1 Global oil and Gas industrial activity

The oil and gas industry are a significant energy source for the global economy, since the world depends on this naturally occurring fossil fuel for oil refined products and petrochemical products for daily life utility and industrial purposes (Aguelmous et al., 2019, Varjani et al., 2017, Macaulay and Rees, 2014). Hence, the drive for oil and gas continues to grow strongly year after year (Bhattacharyya and Shekdar, 2003) and this has been a focal point of world energy. According to British Petroleum (BP) statistical review (BP, 2020), proven petroleum and gas reserves increased tremendously from 1999 through 2019 in different parts of the world (Fig 1.1). This has led to a rise in the production of crude oil and gas, and it was estimated that the consumption of oil reported in the BP statistical review as of 2019 rose by 0.9 million barrels per day. This makes oil the largest share of energy mix at 33% while that of global natural gas increased by an average of 2%.The relative contribution of global consumption of oil and gas compared to other energy sources is presented in Fig. 1.2 for 2019 (BP, 2020).

**Figure 1-1 The distribution of global Crude oil reserves**



**Figure 1-2 Global Primary energy consumption by source in 2019**



**(BP, 2020)**

While petroleum exploitation has tremendous socio-economic value, with a significant effect on a country's GDP (Kuch and Bavumiragira, 2019) as well as increasing tax and export, generate government revenue. However, oil and gas industry can also negative, slow and create a barrier to the economic growth, particularly in a country which economy over dependent on this industry which may lead a phenomenon called resource curse (Al-Kasim et al., 2013, Auty, 2002), this is where a natural resource-dependent economies can become more poor, unemployed and corrupt over time if they are oriented around abundant natural resources. Thus, corruption is of concern in an oil and gas industry as this can impact sector governance decision (Al-Kasim et al., 2013) which may constitute a negative consequence on the country economic. Resource curse/oil and gas industry led the government to neglect/displacing other economic sectors, such as infrastructure, industry, science and technology, services, and agriculture. This may be due to a combination of economic inefficiency and the desire for quick money. It has been reported that Nigeria's dependence on the oil industry has a negative impact on the country's economy and agriculture sector (Sekumade, 2009, Aigbedion and Iyayi, 2007).

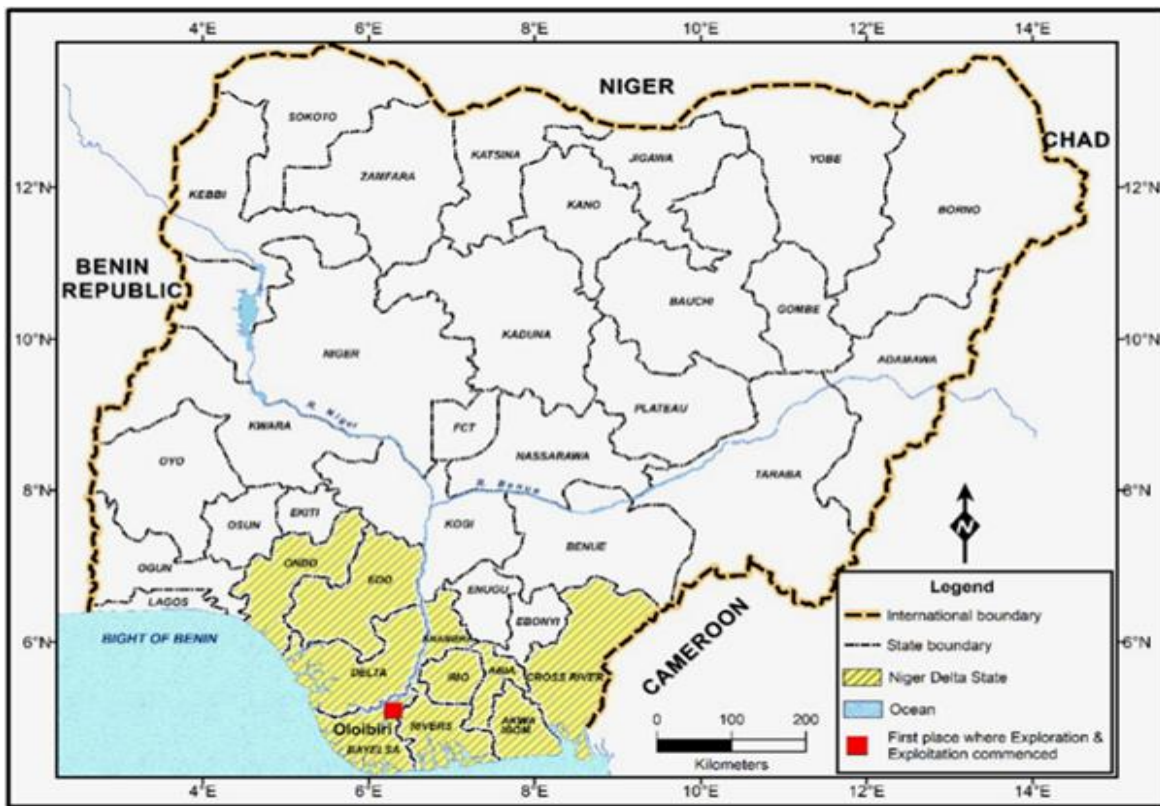
However, most specifically are the attendant potential negative impacts on the environment and health risks to humans. Despite the innovative technology employed by this industry, there are still reported cases of unexpected oil spills and releases of associated contaminants into the environment. The geographic reach of such contamination can be broad, for instance, the Exxon Valdez oil spill in 1989 (Nixon and Michel, 2018, Carls et al., 2001) and the spillage of oil in the Deep-Water Horizon (DWH) in the Gulf of Mexico in 2010 were severe incidents that affected wide areas (Beyer et al., 2016, Mansir and Jones, 2012). Another major oil spill was the prestige oil spillage in 2002 off the coast of Galicia, leading to substantial environmental pollution off the Atlantic coast of Spain and Portugal (Vallero and Letcher, 2013, Sammarco et al., 2013). However, the focus of this study is Nigeria in West Africa.

## **1.2 Oil and gas pollution in Nigeria**

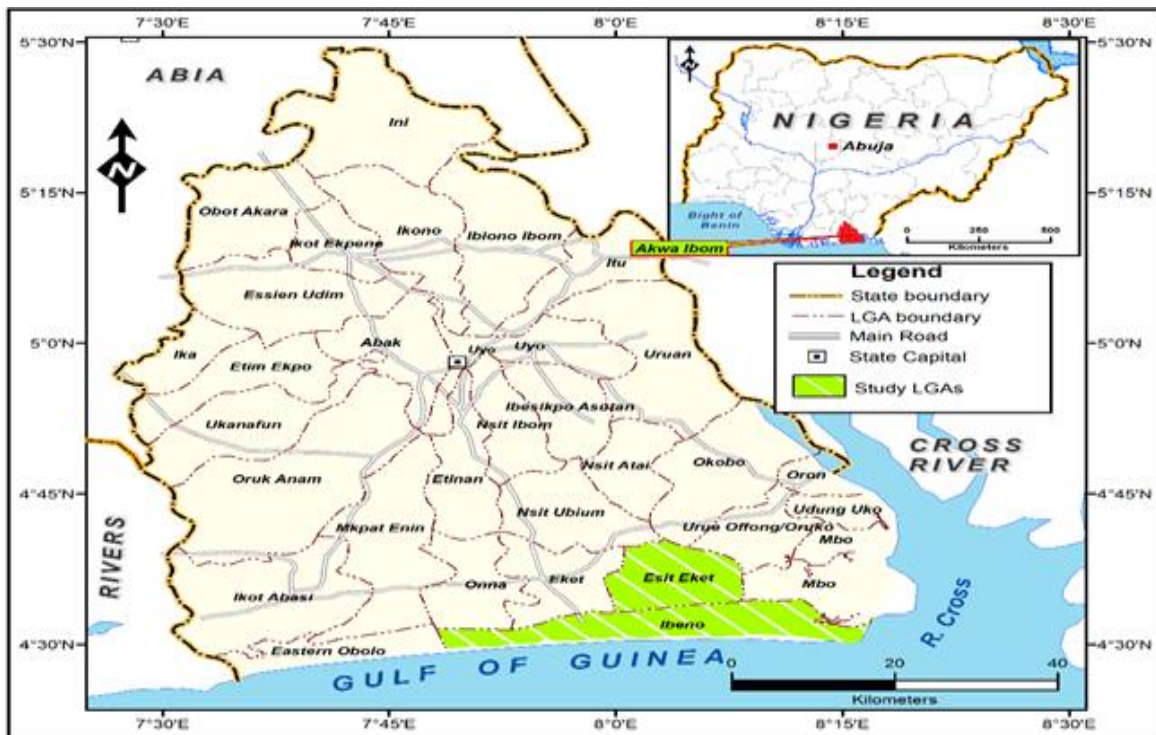
The Organization of Petroleum Exporting Countries (OPEC) admitted Nigeria as a member in 1971 (Nwankwo, 2021). The nation hosts the largest natural gas reserves and second-largest oil reserves in Africa (Kadafa, 2012). Historically, exploration and exploitation of crude oil activities have been in existence since 1956 in the Niger Delta at Oloibiri situated in Bayelsa State, and commercial activities commenced in 1958 (Nwankwo, 2021, Kadafa, 2012, Ayotamuno et al., 2002, Van Dessel and Omuku, 1994). Primarily, it is an environment within which the Royal Dutch Shell Company, formerly known as British Petroleum, drilled their first oil well in Nigeria (Kadafa, 2012, Onuoha, 2008). The Niger Delta is Nigeria's major, most valuable, and significant oil and gas producing region. Accordingly, in the Niger Delta region, crude oil accounts for more than 30% of Nigeria's gross domestic product (GDP) (Eshiet, 2021, Sojinu et al., 2010), of Esit Eket and Ibeno in Akwa Ibom is one of the oil rich regions located within the Niger Delta region. Figure 1.3a shows the difference oil and gas producing state in the Niger Delta, Nigeria while Figure 1.3b depict the various communities in Akwa Ibom.

**Figure 1-3 Map of Nigeria showing location of Niger Delta (a) and (b) Akwa Ibom with various local communities .**

(A)

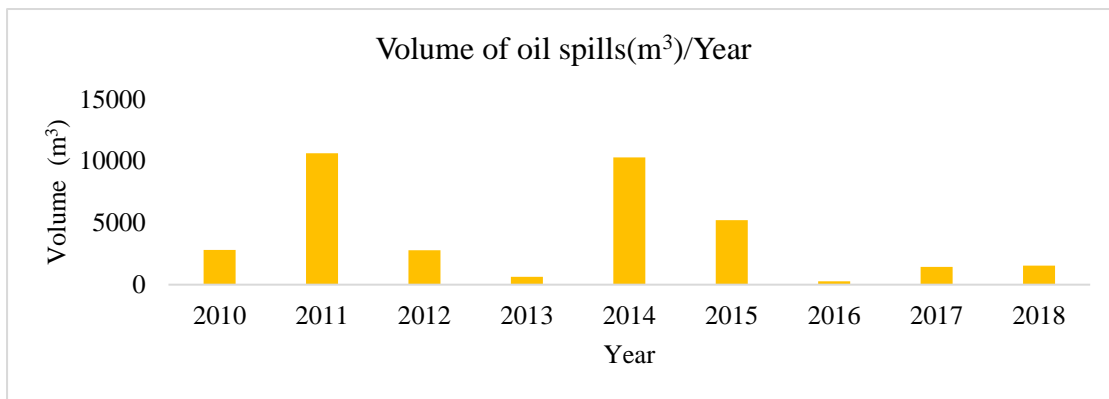


(B)



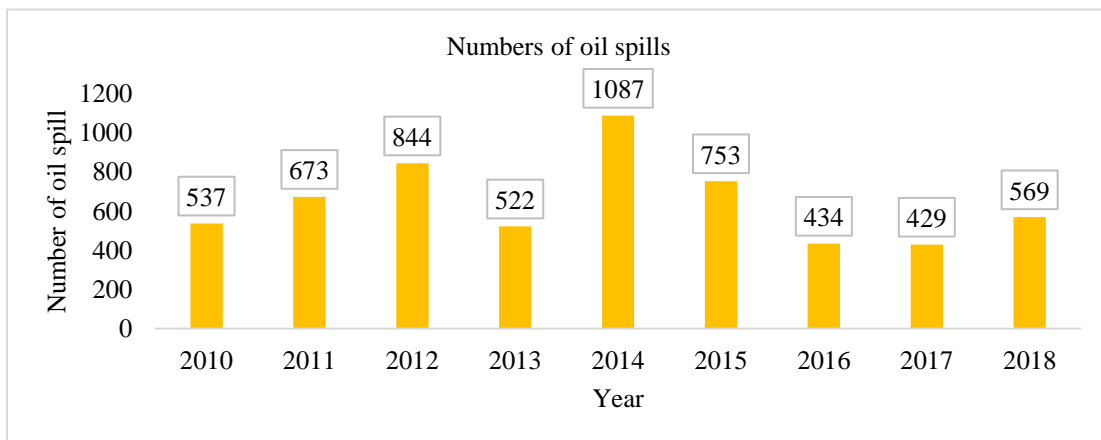
While oil and gas production are supposed to be beneficial to the region, the host communities in the riverine area of Niger Delta have continuously faced major problems resulting from oil pollution (Abii and Nwosu, 2009) and constantly flaring of gas (Nwaichi and Uzazobona, 2011). In 1998, a crude oil spillage occurred in Eket, Akwa Ibom, via ExxonMobil Unlimited offshore facilities (Kadafa, 2012). Meanwhile, Figure 1.4 and 1.5 depicts the distribution of several oil incidents documented between 2010 to 2018, according to the 2018 DPR annual report (DPR, 2018). The annual report further revealed that 11.04% of produce associated gas was flared from January to December 2018.

**Figure 1-4 Volume of the oil released as a result of spills in the Niger Delta, Nigeria from 2010-2018**



(DPR, 2018)

**Figure 1-5 Numbers of oil spills in the Niger Delta, Nigeria from 2010-2018**



(DPR, 2018)

In the context of this research, it is essential to note that crude oil comprises of aliphatic hydrocarbons, Polycyclic Aromatic Hydrocarbons (PAH) as well as other contaminants (Du et al., 2010). Indeed, several studies have reported the occurrence of PAH in oil contaminated soil, and have identified pollution from refineries (Tarafdar and Sinha, 2018), oil fields (Liang et al., 2012), and emissions from natural gas extraction (Paulik et al., 2018) as contributing to the local burden of contaminants in the atmosphere.

### **1.3 Polycyclic Aromatic Hydrocarbon (PAH)**

PAH are group of environmental organic contaminants. They are semi-volatile and hydrophobic of which research across the globe has revealed to be ubiquitous in the environment (Kumar et al., 2022) PAH are capable of bioaccumulation and of undergoing long-range atmospheric transport (LRAT) in the environment, even to remote areas, including the Arctic (Wilcke, 2007, Wania and Mackay, 1996) hence they are persistent in the environment.

Over the years, substantial evidence has emerged over the toxicological effects of PAH on humans and wildlife, including carcinogenicity, mutagenicity, genotoxicity and teratogenicity (Abdel-Shafy and Mansour, 2016, Kim et al., 2013). Within this framework, the United States Environmental Protection Agency (EPA 1994) (Ramírez et al., 2011) and the European Environmental Agency (Ramírez et al., 2011, Wang et al., 2011) have ranked 16 PAH out of more than a hundred characterised compounds as priority pollutants based on these effects.

These 16 PAHs comprise: Acenaphthene (Ace), Acenaphthylene (Acy), Fluorene (Fln), Naphthalene (Nap), Anthracene (Ant), Fluoranthene (Flt), Phenanthrene (Phe), Benzo[*a*]anthracene (BaA), Benzo[*b*]fluoranthene (BbF), Benzo[*k*]fluoranthene (BkF), Chrysene (Chr), Pyrene (Pyr), Benzo[*ghi*]perylene (BghiP), Benzo[*a*]pyrene (BaP), Dibenzo[*a,h*]anthracene (DBA), and Indeno[1,2,3-*cd*]pyrene (IPy). Except for naphthalene which is effectively a volatile organic compound and thus incompatible with the analytical

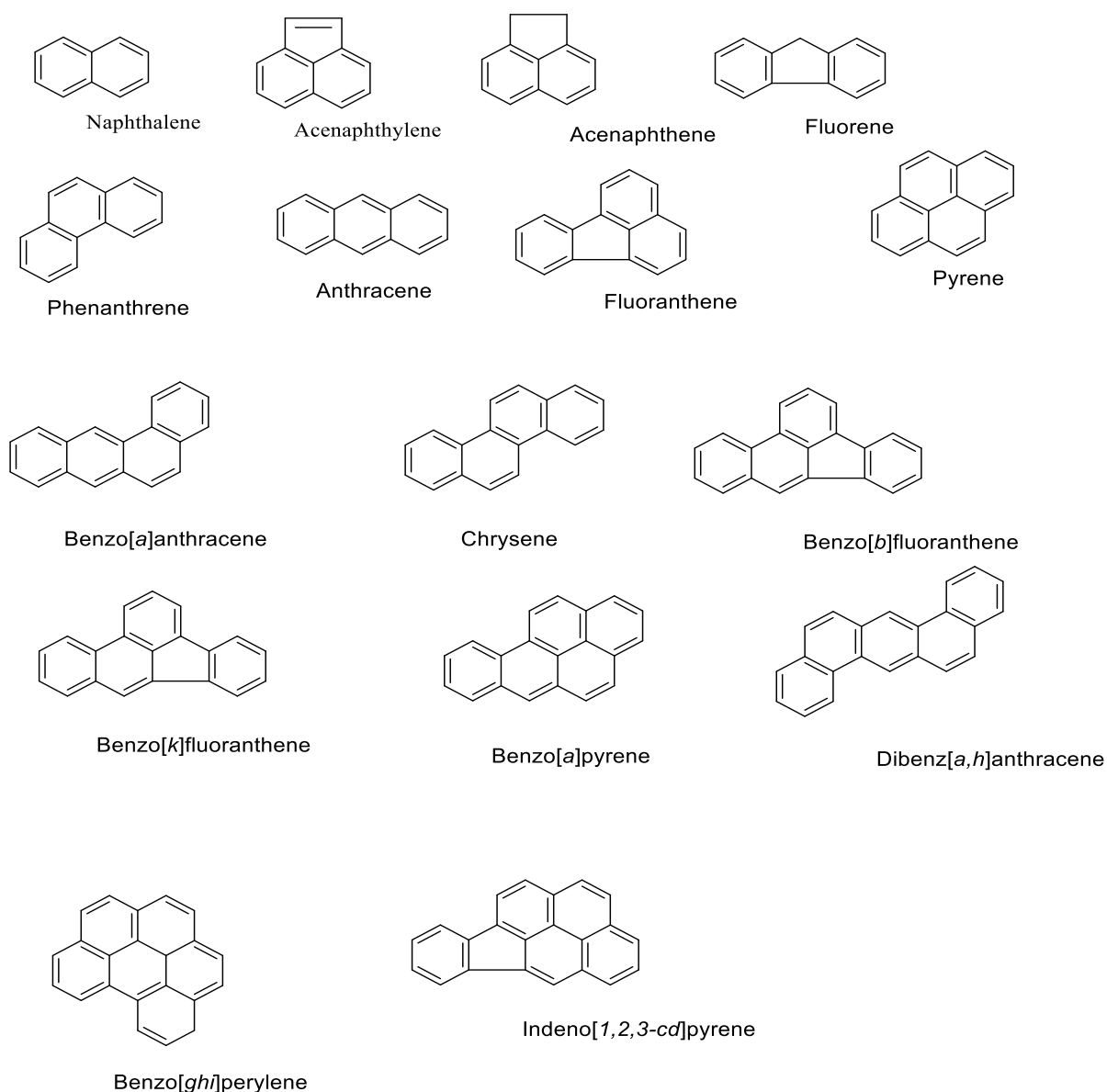
chemistry techniques applied in this project, these PAH constitute those that form the basis of this research project.

### **1.3.1 Physical and chemical properties of PAH**

The movement of PAH in the environment is significantly determined by their physicochemical properties. The parent PAH are non-polar organic hydrocarbons combining carbon and hydrogen atoms only (Choi et al., 2010). They do not possess any heteroatoms (Fetzer, 2007) in their rings; instead they are considered as homocyclic with two or more aromatic rings bonded in a linear, cluster, or angular form as seen in Figure 1.6. Anthracene, for example, appears in a linear shape, angular structure as seen in dibenzo[*a,h*]anthracene while pyrene is a typical example of a cluster structure (Singh and Haritash, 2019, Arey and Atkinson, 2003, Masih, 2011). These different arrangements are displayed in Figure 1.6.

While some PAH are colourless, others are white or pale yellow in their pure state (Masih et al., 2012) and are predominantly in solid crystals with characteristic high melting and boiling points (Abdel-Shafy and Mansour, 2016), as shown in Table 1.1. It is suggested that some physicochemical properties of PAH correlate with the organic carbon:water partition coefficient ( $K_{OC}$ ), an indication of the distribution of an organic compound between the aqueous phase and natural organic matter (Harrad, 2001). Similarly, the octanol:water partition coefficient ( $K_{OW}$ ) represents a common way of referring to a chemical's hydrophobicity. It expresses the tendency of an organic chemical to partition between water and lipid (Earl et al., 2003). By further extension, the octanol:air partition coefficient ( $K_{OA}$ ) is an expression of the ability of an organic compound to distribute between air and lipid. Moreover, the Henry's constant describes the partitioning of a compound between an aqueous solution and the air above, for instance, volatilisation of an organic compound from a river or lake to the overlying air (Harrad, 2001). This can be further illustrated with the incident of the Gulf of Mexico (Tidwell et al., 2016). Finally, the vapour pressure expresses the tendency of an organic

compound to exist as a vapour at a given temperature (Earl et al., 2003). These chemical properties are essential in controlling the environmental transport and uptake of PAH by plants and animals, and their partitioning between different environmental compartments. Table 1.1 presents some selected chemical properties of most of the 16 PAH prioritised by the USEPA and measured in this study.



**Figure 1-6 Structure of 16 USEPA Priority PAH**

**Table 1-1 Physicochemical characteristics of selected PAH investigated in this study**

Name (# of aromatic rings)	Molecular Weight(g/mol)	B.P(°C) <sup>a</sup>	Log K <sub>ow</sub> <sup>b</sup>	Log K <sub>oc</sub> <sup>b</sup>	Vapour pressure (Pa) <sup>c</sup>	Pure solid aqueous Solubility (ug/L) <sup>c</sup>	LogK <sub>oa</sub> <sup>d</sup>	K <sup>H</sup> <sup>d</sup> (M atm <sup>-1</sup> )
Acenaphthene (3) (Ace)	154.2	279	4	3.65	2.9 × 10 <sup>-1</sup>	3420	6.44	7.1
Acenaphthylene (3)Acy)	152.2	280	3.7	3.4	8.9 × 10 <sup>-1</sup>	3930	6.46	10.5
Anthracene (3)(Ant)	178.2	342	4.45	4.15	8.0 × 10 <sup>-4</sup>	45	7.7	20
Phenanthrene (3)(Phe)	178.2	340	4.46	4.15	1.6 × 10 <sup>-2</sup>	1000	7.64	23.5
Fluorene (3)(Fln)	166.2	295	4.18	3.86	8.0 × 10 <sup>-2</sup>	1690	6.85	11.3
Fluoranthene (4)(Flt)	202.3	375	4.9	4.58	1.2 × 10 <sup>-3</sup>	206	8.81	76
Benzo[a]anthracene (4)(BaA)	228.3	438	5.6	6.14	2.8 × 10 <sup>-5</sup>	5.7	10.28	159
Chrysene (4)(Chr)	228.3	448	5.61	5.3	8.4 × 10 <sup>-5 d</sup>	1.8	10.3	270
Pyrene (4)(Pyr)	202.3	150.4	4.88	4.58	6.0 × 10 <sup>-4</sup>	130	8.86	76
Benzo[a]pyrene (5)(BaP	252.3	495	6.06	6.74	7.3 × 10 <sup>-7</sup>	3.8	11.48	1320
Benzo[b]fluoranthene (5)(BbF)	252.3	481	6.06	5.74	6.7 × 10 <sup>-5 d</sup>	14	11.34	1550
Benzo[k]fluoranthene (5)(BkF)	252.3	480	6.06	5.74	1.3 × 10 <sup>-8 d</sup>	4.3	11.37	1790
Dibenz[a,h]anthracene (5)(DBA)	278.4	524	6.8	6.52	1.3 × 10 <sup>-8 d</sup>	0.5	12.59	120 <sup>f</sup> (2045)
Benzo[g,h,i]perylene (6)(BghiP)	276.3	500	6.51	6.2	1.4 × 10 <sup>-8</sup>	0.26	12.55	2410
Indeno[1,2,3-cd]pyrene (6)(IPy)	276.3	536	6.5	6.2	1.3 × 10 <sup>-8 d</sup>	0.53	12.43	2050

Data from <sup>a</sup> Ghosal et al. (2016), <sup>b</sup>World Health Organisation(WHO) see Rogers et al. (2002), <sup>c</sup>LaGrega et al. (1994) <sup>d</sup>for temperature of 20°C while others are 25°C see LaGrega et al. (1994),Ma et al. (2010b), <sup>f</sup>Odabasi et al. (2006) ; Keyte et al. (2013) for data on logK<sub>oa</sub> and K<sup>H</sup>

## **1.4 Influence of Physicochemical Properties on PAH Fate and Behaviour in the environment**

Phase partitioning (e.g., in the atmosphere and hydrosphere), rate of sorption and sequestration, deposition and volatilisation, leaching, degradation, metabolism (Duan et al., 2015, Srogi, 2007, Yuan et al., 2002) and toxicological characteristics are strongly governed by physicochemical properties of individual PAHs (Duan et al., 2015, Shields et al., 2014, Haritash and Kaushik, 2009, Wild and Jones, 1994, Wild, 1991).

### **1.4.1 Influence on PAH behaviour in the Atmosphere**

The atmosphere is the primary medium of transporting and dispersing volatile organic pollutants such as PAH in the environment on a global or local scale (Okedere and Elehinafe, 2022). It has been reported that when PAH are released into the atmosphere, they have the propensity to partition into gaseous and particulate phases (Ramírez et al., 2011, Baek et al., 1991). This phenomenon is governed by their vapour pressure ( $V_p$ ), molecular weight (MW) and binding to particulate organic matter, which is a function of partition coefficient  $K_{oc}$  or  $K_{OA}$  (Kim et al., 2013, Ramírez et al., 2011, Baek et al., 1991). As well as the amount of PAH concentrations in the atmosphere (Tobiszewski and Namieśnik, 2012, Tasdemir and Esen, 2007). Moreover, the relationship between  $V_p$  and temperature ( $T$ ) also plays a substantial role in determining the gas/particle partitioning of PAH. Huang et al. (2004) developed a model for the estimation of vapour pressure (expressed as both solid vapour pressure ( $P_s$ ) and (subcooled) liquid vapour pressure ( $P_L$ ) at various temperatures. However, studies have demonstrated the influence of temperature on atmospheric removal of PAH, reporting greater sorption to particulates at lower temperatures and a shift to the gaseous phase when temperatures rise (Wu et al., 2014, Masih et al., 2012, Sato et al., 2008). (Sato et al., 2008) observed a rise in the average particulate PAH concentrations in winter-spring and a decrease in summer-autumn at Cape Heto, Japan between 2005 and 2008. They stated that the contaminants are brought about

from East Asia during the winter-spring season while the Pacific Ocean transports unpolluted air during the summer-autumn (Sato et al., 2008).

As molecular mass increases, the vapour pressure of PAH decreases, as seen in Table 1.1. PAH with higher  $V_p$  and lower molecular weight (LMW-PAH) having two to three rings such as: Ace, Acy, and Fl<sub>n</sub> (see table 1.1) are found principally in the gaseous phase and can more easily undergo atmospheric reaction. By comparison, those with four rings (Pyr and Phe) exist in both gaseous and particle phases, with the relative abundance being strongly dependent on climatic conditions (Choi et al., 2010, Zhang and Tao, 2009, Srogi, 2007). In contrast, the high molecular weight (HMW- PAH) with five or more rings like BaP and Chr with lower  $V_p$  values and higher  $K_{ow}$  are primarily found in the particulate phase (Abdel-Shafy and Mansour, 2016, Kim et al., 2013, Mohanraj et al., 2011) and can travel long distances before undergoing dry or wet deposition (Tiwari et al., 2011, Gevao et al., 2006, Bozlaker et al., 2008, Wania and Mackay, 1996). However, studies have suggested evidence of long-range transport of PAH to remote areas even without the occurrence of local sources such as in the Asian Pacific region (Sato et al., 2008, Simoneit et al., 2004). With the impact of their various physicochemical properties, PAH in the atmosphere can undergo different atmospheric reactions and transformation processes. The reactivity of these compounds has been described elsewhere (Keyte et al., 2013, Manzetti, 2013).

#### **1.4.2 Influence on PAH behaviour in soil**

Following deposition to soil from long range or anthropogenic activities, PAH are subjected to sorption and other mechanisms (Abdel-Shafy and Mansour, 2016). Organic matter in the soil plays a key role (Ahangar, 2010). The equilibrium partition coefficient between water and organic carbon ( $K_{OC}$ ), the equilibrium partition coefficient between water and octanol (as a surrogate lipid) ( $K_{OW}$ ) and aqueous solubility combine to determine the ability of PAH to bind to such media (Nwaichi et al., 2016, Earl et al., 2003).

As such, LMW-PAH with lower  $K_{OC}$  and  $K_{OW}$  values and higher aqueous solubility (as shown in Table 1.1) are assumed to be more mobile, bioavailable, and leachable (Nieuwoudt et al., 2011, Nadal et al., 2007) than HMW-PAH, which can sorb strongly to soil, particularly for soil rich in organic matter (Nieuwoudt et al., 2011, Nadal et al., 2007). Also, with lower values of  $K_{OW}$ , higher Henry's constant values ( $H$ ) and  $V_p$ , LMW-PAH are more prone to evaporate from the surface of the soil into another compartment (Earl et al., 2003, Wilcke, 2000). Indeed, Skrbic and Durisic-Mladenovic (2009) reported high soil contamination with light PAHs associated with volatilisation in their area of study.

### **1.4.3 Influence on the Environmental Persistence of PAH**

Various factors greatly influence the behaviour of PAH; higher hydrophobicity, lipophilicity and a more complex chemical structure are physicochemical properties that elicit differences in environmental behaviour (Abdel-Shafy and Mansour, 2016, Duan et al., 2015, Xu et al., 2013, Sartoros et al., 2005). Though several studies have reported degradation of PAH (Alegbeleye et al., 2017, Ghosal et al., 2016, Couling et al., 2010, Al-Turki, 2009, Haritash and Kaushik, 2009), such degradation does not readily occur. Moreover, such microbial degradation is largely confined to topsoil and PAH compounds that are weakly absorbed to soil organic matter and poorly bioavailable (MacLeod et al., 2001, Srogi, 2007). Since microorganisms may need some available water at some period of the year, low aqueous solubility of PAH may inhibit their biodegradation potential (Sticher et al., 1997, Al-Turki and Dick, 2003). Combined, this means that heavier PAH with more than four fused rings are somewhat resistant to biodegradation (Alegbeleye et al., 2017, Abdel-Shafy and Mansour, 2016, Haritash and Kaushik, 2009). This suggests that heavier compounds are recalcitrant and can reside in the environment for long periods (hours, months and even years) (Lei et al., 2022, Denis et al., 2012). According to Sojiniu et al. (2011) benzo[a]pyrene (a HMW) had an average half-life ranging from 229 to 1,500 days in soil whereas the half-life of the LMW Phenanthrene was

reported to be between 16 to 126 days. Some studies have reported degradation half-lives for different PAH in soil. These are shown in Table 1.2. It is essential to know that the half-life of individual PAH varies in different matrices depending on the substrate. For instance, the decay rate for anthracene on substrates such as alumina is 0.5 h, and on carbon black 310 h; this is because, on light coloured surfaces, photolysis which is one of the loss pathways of PAH, is more facile than on dark surfaces (Abdel-Shafy and Mansour, 2016). Furthermore, the lifetime of PAH in the atmosphere is thus limited to a couple of days or hours (Wild and Jones, 1995).

**Table 1-2 Half-lives(days) of PAH compounds in soil as reported in some studies**

<b>PAH</b>	<b>A</b>	<b>B</b>
Nap	<1-108	–
Ace	42.5-60	–
Acy	12-102	1168
Fln	2-385	1168
Ph	16	2080
Ant	50-460	2884
Flt	15-462	2847
Pyr	15-460	3103
Chr	19-1400	2957
BaA	6-21000	2957
BbF	360-610	3285
BKF	910-2140	–
BaP	12-11552	2993
IPy	288	–
BghiP	590-650	3322
DBA	361	–

A-Degradation half-lives values taken from (Earl et al., 2003) B-Field test half-lives taken from (Creaser et al., 2007, Wild, 1991).

## **1.5 Toxicology and Health Effects of PAH**

### **1.5.1 Toxicity**

Due to the characteristic variability in molecular weight and structural form of PAH, their toxicological potency differs (Idowu et al., 2019), with HMW PAH frequently displaying

greater toxicity and carcinogenicity. Particulate phase (HMW) pollutants can be absorbed into the lungs and blood and have been demonstrated to infiltrate numerous tissues and organs, causing more health risk (Idowu et al., 2019, Kim et al., 2013, Keyte et al., 2013). A benzo[*a*]pyrene (BaP) target value of 1.0 ng/m<sup>3</sup> for the total content in the particulate matter fraction averaged over a year was recommended (Callén et al., 2011). By comparison, the gaseous phase is more likely found in the lung's mucus lining. Despite being more abundant in the environment, lower molecular weight PAH such as phenanthrene are less carcinogenic and more susceptible to chemical reactions with oxidants (O<sub>3</sub>, NO<sub>3</sub>, and OH radicals) that create oxy- and nitro-derivatives (Alves et al., 2017, Keyte et al., 2013). For instance, phenanthraquinone, acenaphthoquinone, 9-Nitroanthracene, and 2-Nitrofluorene are quinone and nitro-PAH (Idowu et al., 2019, Bandowe and Meusel, 2017, Harrison et al., 2016b, Delgado-Saborit et al., 2013). Several such reaction products are far more toxic to human health than some of their parent PAH (Famiyeh et al., 2021, Idowu et al., 2019).

### **1.5.2 Health effects of PAH**

Exposure to PAH mixtures has been related to many health issues in humans and animals, which may be acute or chronic (Famiyeh et al., 2021, Abdel-Shafy and Mansour, 2016, Kim et al., 2013). While the most concerning harmful effect of exposure to PAH is cancer, other adverse effects have been reported. For example, toxicological and epidemiological studies have demonstrated that PAH may exert immunosuppressive effects (Bechtel et al., 2009) near oil and natural gas fields. Using a cohort of 12,367 asphalt workers, Burstyn et al. (2005) found an increase in fatal ischemic heart diseases in their study, that positively correlated with PAH exposure. This was supported by Leachi et al. (2020), the authors were of the opinion that workers who are exposed to PAH run the risk of experiencing adverse effects on their cardiovascular and respiratory systems as a result of cellular inflammation and mutations.

At the same time, links have been reported between exposure to PAH and pregnancy defects and impaired foetus development (IARC, 2009). While PAH have been identified in women and their foetuses at relatively low concentrations (Sexton et al., 2011); concentrations observed in the cord blood exceeded those in the paired maternal blood, which was of potential concern. Moreover, it was reported that children proximate to an oil refinery were observed to have displayed a significantly higher pre-hypertension symptoms (Trasande et al., 2015).

### 1.5.3 Toxic equivalent factors (TEFs) for PAH

Widely regarded as the most toxic PAH, BaP is frequently used as a reference for the toxicity of other PAH (Jiao et al., 2017, Jiang et al., 2016). As such, BaP is assigned a toxicity potency of 1, with the toxicity of other PAH subsequently expressed as a fraction based on their toxicity relative to BaP (Nisbet and Lagoy, 1992, Wang et al., 2017, Mueller et al., 2019). Several different approaches have been used to calculate such Toxicity equivalent factors (TEFs), as shown in Table 1.3 (DoE, 2007, WHO, 1999, Nisbet and Lagoy, 1992, Chu, 1984). However, Nisbet and Lagoy (1992) recommended a method primarily and broadly accepted (Enuneku et al., 2021, Ugochukwu et al., 2018, Wang et al., 2015a, Petry et al., 1996) to assess risk associated with cancer. By multiplying the actual concentration of each specific individual PAH within a mixture by their assigned TEF values and summing these products, it is possible to express the concentration of a mixture of PAH in a sample represented as the toxicity equivalent (TEQ) concentration of BaP as in equation 1.

$$TEQ = BaP_{eq} = \sum (C_i \times TEF_i) \quad (1)$$

Where TEQ is the term that describes the potency of PAH,  $C_i$  is the concentration of each PAH and TEF, and  $BaP_{eq}$  is the concentration of a mixture of PAH expressed in terms of BaP concentrations.

**Table 1-3 Summary of Toxic Equivalent Factors (TEF) values for individual PAH reported by different authors**

Author /PAH	(Nisbet and Lagoy (1992), (Mueller et al., 2019)/TEF	DoE (2007)/TEF	WHO (1999) /TEF	Chu (1984)/TEF	Durant et al. (1996)/TEF
Nap	0.001	ND	ND	ND	–
Ant	0.01	ND	ND	ND	–
Ace	0.001	ND	ND	ND	–
Acy	0.001	N	ND	ND	–
Fln	0.001	ND	ND	ND	–
Flt	0.001	ND	ND	ND	–
Chr	0.01	0.01	0.1	0.001	0.017
Phe	0.001	ND	ND	ND	–
Pyr	0.001	ND	ND	ND	–
BaA	0.1	0.1	0.1	0.013	0.082
BaP	1	1	1	1	1
BbF	0.1	0.1	0.1	0.008	0.25
BkF	0.1	0.1	0.1	0.004	0.11
DBA	5	0.1	1	0.69	0.29
BghiP	0.01	ND	ND	ND	–
IPy	0.1	0.1	0.1	0.013	0.31

ND data not available

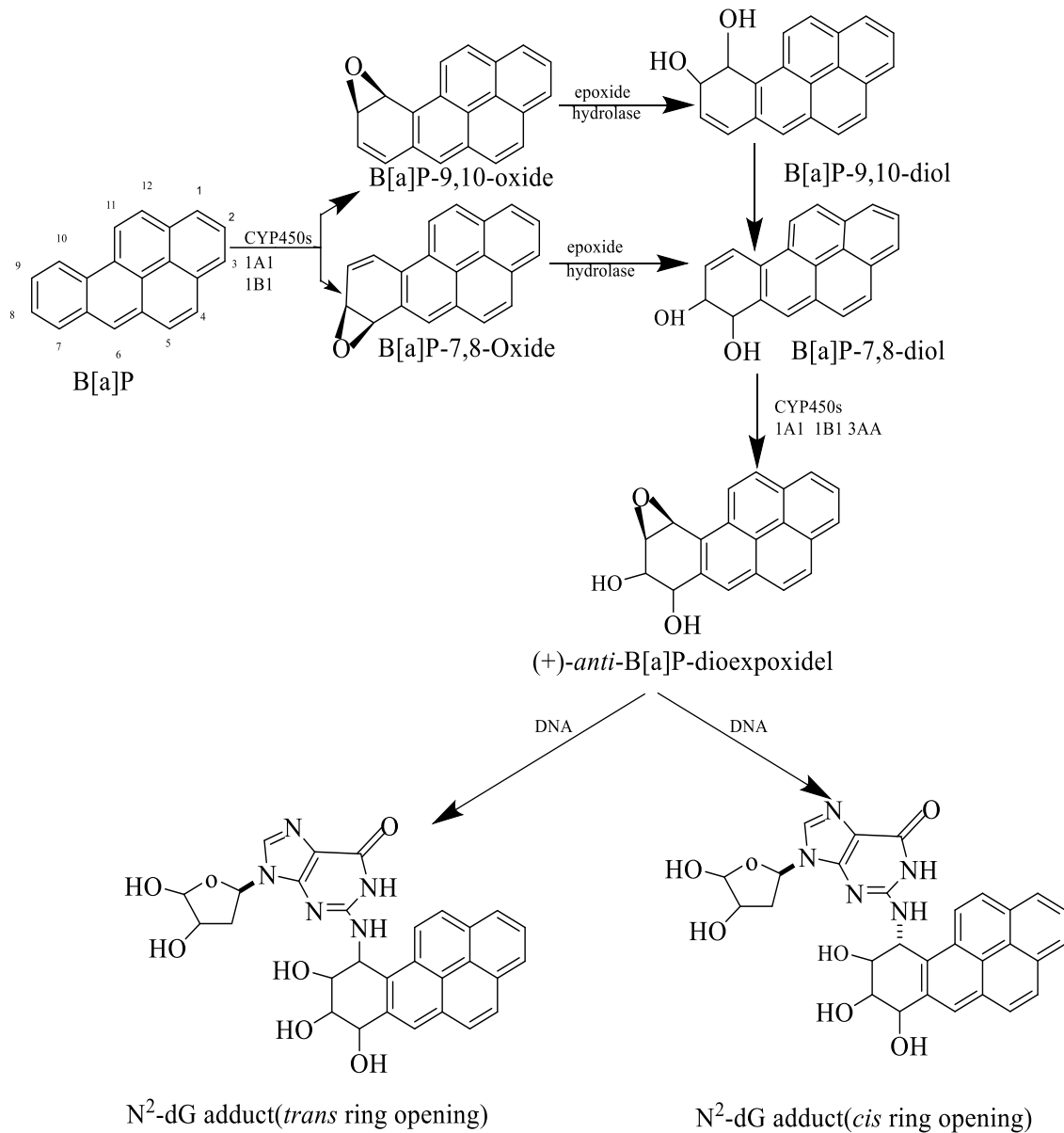
## 1.6 Carcinogenicity and Metabolism of PAH

Although their hydrophobic and lipophilic nature means that a mixture of parent or homocyclic PAH can be absorbed and accumulated in the fatty tissues of biota and humans (Zhang and Chen, 2017); several studies report that PAH exert more toxic and carcinogenic effects when converted primarily to their metabolites (Famiyeh et al., 2021, Gao et al., 2018, Shimada, 2006, Xue and Warshawsky, 2005). The authors elucidate that these chemicals are metabolically activated by xenobiotic-metabolizing enzymes such as cytochrome P450s (CYPs), epoxide hydrolase (EH) and aldo-keto reductase through the oxidation method (Gao et al., 2018, Xue and Warshawsky, 2005), transforming them into polar or more reactive and toxic metabolites such as epoxides and dihydrodiols (Gao et al., 2018, Shimada, 2006, Xue and Warshawsky, 2005). Moreover, the resultant effect is the damage of proteins and nucleic acid by forming

DNA/protein adducts and allowing mutations to occur, leading to a variety of diseases and cancers in various organs of the body (Abdel-Shafy and Mansour, 2016, Rengarajan et al., 2015). The formation of diol epoxides, radical cations, and o-quinone are examples of PAH metabolic stimulation (Xue and Warshawsky, 2005). Figure 1.6 illustrates B[a]P metabolism from diols and diol epoxides to DNA adducts.

Thus, experimental data exists of carcinogenicity, mutagenicity, immunotoxicity, and genotoxicity of B[a]P and other four-to-seven aromatic ringed PAHs via both *in vivo* and *in vitro* exposure for mammal and non-mammal, as well as human cells (Choi et al., 2010, IARC, 2010, Durant et al., 1996). This is consistent with evidence from epidemiological studies in occupational environments, including aluminium production, coal gasification, coke production, tar distillation, shale oil and crude oil extraction, showing that PAH exposure correlates with various cancers (Abdel-Shafy and Mansour, 2016, Rengarajan et al., 2015) Such combined toxicological and epidemiological data have led the International Agency for Research on Cancer (IARC, 2010) to categorise PAH into different groups and toxicity as depicted in Table 1.4.

**Figure 1-7 Metabolism of B[a]P via cytochrome P450 enzymes (CYP450) and epoxide hydrolase (EH) enzymes**



Extracted from Trushin et al. (2012)

**Table 1-4 Classification of carcinogenic potential of PAH by IARC**

<b>Carcinogenic to humans/Group 1</b>	<b>Probably carcinogenic to humans/Group 2A</b>	<b>Possibly carcinogenic to humans/Group 2B</b>	<b>Non-carcinogenic to humans/Group 3</b>
BaP	DBA	BaA	Ace
-	-	Chr	Acy
-	-	BbF	Fln
-	-	BkF	Phe
-	-	IPy	Ant
-	-	-	Flt
-	--	-	Pyr
-		-	BghiP

Data from IARC (2010) Monogram

### 1.6.1 Human exposure to PAH

Human exposure to PAH is omnipresent, originating from different pathways like inhalation of air and ingestion of food and water. The presence of PAHs in the soil also impacts exposure directly via accidental ingestion and dermal contact, as well as indirectly via uptake from the ground through plants or ruminant animals. While all humans are exposed to PAHs, industrial activities are significant emitters of PAH. A recent study highlighted occupational exposure arising from industrial processing by inhalation of fumes from downstream processes such as burnt petroleum products, oil refining, mining and coal gasification (Jameson, 2021, Domingo et al., 2020) and perhaps other routes. Of particular relevance to this study are reports that inhalation and dermal contact are important sources of exposure for workers in the oil and gas industry (Abdel-Shafy and Mansour, 2016, Kuang et al., 2011).

In non-occupational settings, although breathing of vapour or suspended particles are significant, dietary intake is an additional important exposure pathway. Dietary PAH may have been accumulated in the food web, or have been introduced during cooking (e.g., barbecuing) and/or processing (e.g., smoking) (Abdel-Shafy and Mansour, 2016, Boffetta et al., 1997, Chen et al., 2018). Importantly, vulnerable groups such as children, whose immunological and respiratory systems are not fully mature, maybe at more risk of exposure (Ana et al., 2009, Schwartz, 2004).

### **1.6.2 Cancer Risk exposure**

Cancer risk assessment indicates cancer occurrences as a result of exposure to a potential carcinogen (Owhoeke et al., 2019) through the three pathways mentioned below. The risk of those exposed to PAH in the environment (soil and air) can be estimated using the Incremental Lifetime Cancer Risk (ILCR) model in various exposure pathways (inhalation, ingestion and dermal) (Owhoeke et al., 2019, USEPA, 1989). Many studies have embraced and reported this model to estimate the level of cancer risk (Akporhonor et al., 2022, Enuneku et al., 2021, Alawi and Azeez, 2016).

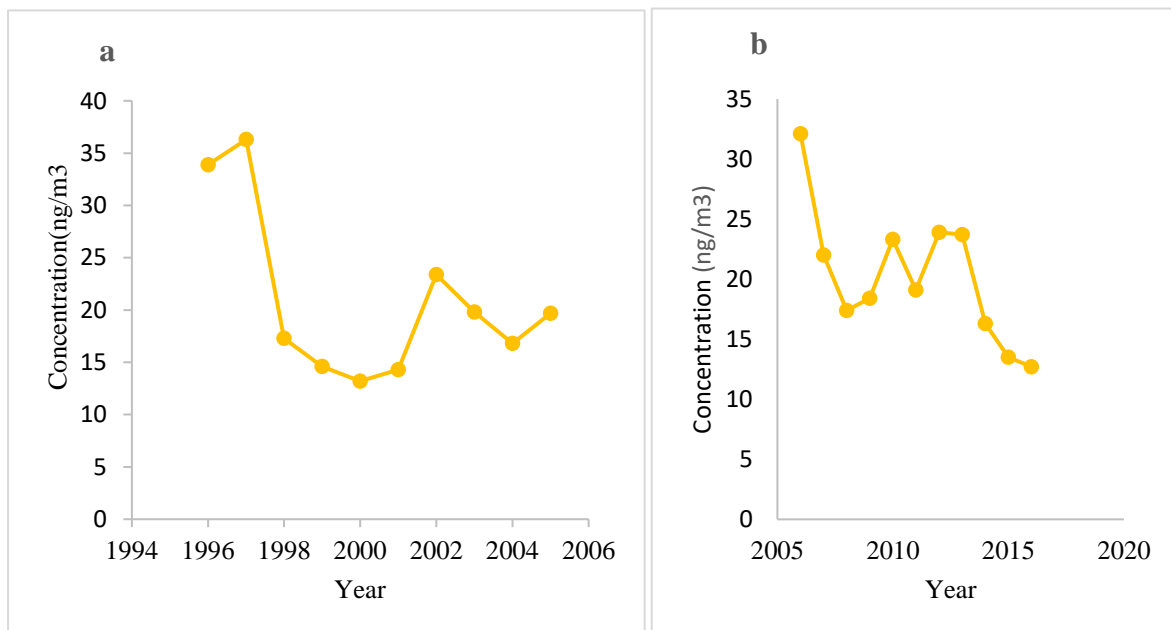
## **1.7 Long term trend of emissions of PAH and associated environmental contamination**

Numerous studies have reported concentrations of PAH in matrices associated with various anthropogenic sources around the world for air and soil. However, the (WHO, 2000) reported that in the last 40 years PAH concentrations have reduced in most developed countries.

A few studies have also reported the long-term trend of PAH concentrations in UK. A monitoring campaign were conducted in Birmingham and London between 1992 to 1997 (Dimashki et al., 2001), the results revealed a slight variance in the data collected. Between 1991 to 2011, the annual median BaP concentration measured from UK monitoring stations

fell dramatically (Brown et al., 2013), and this decline was strongly associated with the changes in the estimates of primary emissions by the national atmospheric emission inventory (NAEI). In Europe, studies have evaluated the trend of PAH also, according to Dvorska et al. (2008) who investigated concentrations of PAH between 1996- 2005 Kosetice, Czech Republic (figure 1.8a). The findings indicate that mean PAH concentrations declined exponentially over 30 years with an initial peak in 1996, before a fall in 2000, followed by a rise in 2001 to 2002. This study was enhanced by Lhotka et al. (2019), who compiled data for PAH concentrations in both particulate matter (PM<sub>10</sub>) and the gas phase from the national atmospheric observatory Kosetice (NAOK) from 2006 to 2016 in a rural background site in Czech Republic in central Europe (Figure 1.8b). They reported that annual mean concentrations increased at the beginning of the monitoring campaign but decreased significantly by 0.48 ng/m<sup>3</sup>/year, of which there was statistically significantly decrease in BaP trend ( $p < 0.05$ ) as well. Figure 1.8 present the changes of PAH concentrations in central Europe from these two studies.

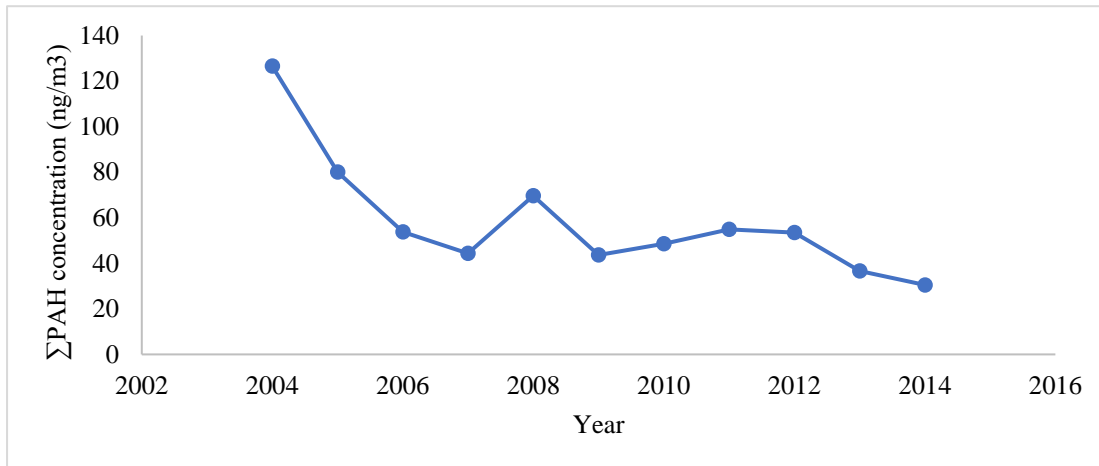
**Figure 1-8 Trend in ΣPAH concentration in atmosphere at central Europe**



**(a) Dvorska et al. (2008) and (b) Lhotka et al. (2019)**

A similar decreasing tendency of PAH levels were also reported for  $\Sigma$ PAH in two suburban cities in Porto, Portugal between the period of 2004 to 2014 (Albuquerque et al., 2016), specifically in the early years of monitoring as shown in Figure 1.9.

**Figure 1-9 Atmospheric  $\Sigma$ PAH concentration changes over time in Porto, Portugal**



**Albuquerque et al. (2016)**

A similar pattern was also found in PAH concentrations in the atmosphere at USA from 1990 to 2014 (Liu et al., 2017). However, concentrations across urban regions experienced a downward trend contrary to the rural regions.

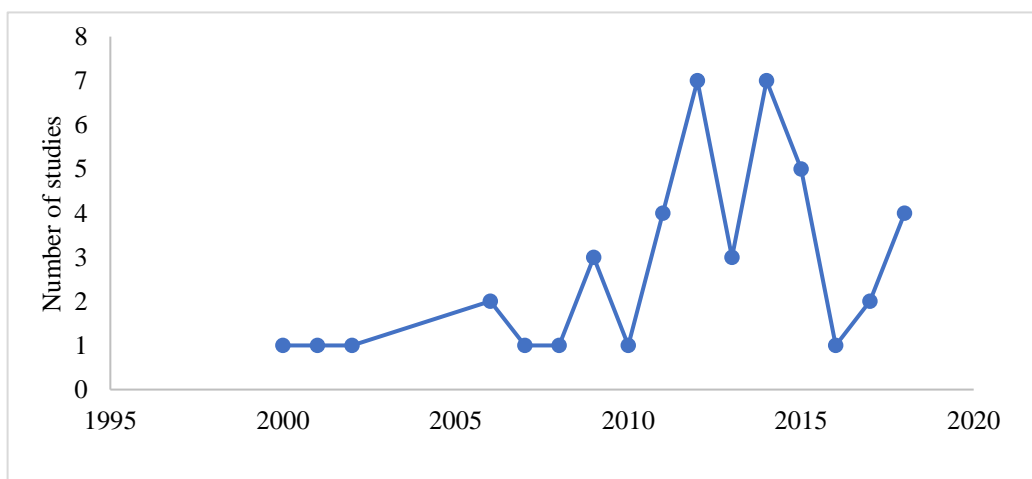
In Asia, a study reported the measurement of Nine PAH concentrations from 1997 and 2013 in five Japanese cities: Sapporo, Kanazawa, Tokyo, Sagami-hara and Kitakyushu respectively (Hayakawa et al., 2018). The authors explained that the level of PAH concentrations at four sampling sites increase at the initial monitoring campaign but experienced a downward slope at the end of the sampling period, this may be due to legislative provisions, which spanned from 1993 to 2016 recommending a permissible limit for the emission of Particulate matter (containing PAH) from gasoline and diesel-engine vehicle in Japan. Whereas the concentrations of PAH at Kitakyushu remain stable and then rise in winter 2014. The increase in the time trend in Kitakyushu was as a result of influenced by burning of coal from the iron industry (Hayakawa et al., 2018). Hayakawa et al. (2020) also examined trends in total concentration of 9 PAH in the urban atmosphere of China, Russia, and Korea between 1999 to 2014. They

detected an increase in the total PAH concentrations in Shenyang and Beijing far above 200 ng/m<sup>3</sup>, however these concentrations gradually declined over the years. The authors stated that the increasing trend found in Beijing in 2010 in winter was because of accumulation of PAH from post 2008 Olympic Games. Concentrations in Vladivostok were low, but those in Shanghai and Busan were the lowest throughout the monitoring period.

In contrast to Asia, Europe, and the USA, where long term trend of PAH has been broadly investigated, little is known about this issue in Africa, even though, Africa appears one of the major contributors to the worldwide PAH budget, according to Xu et al. (2012). A study has compiled several studies on airborne PAH in Africa between 2000-2018 (Munyeza et al., 2019), with the number of studies increasing rapidly over time as shown in Figure 1.10.

Most recently, a considerable number of studies has been carried out in Africa to assess the levels of PAH contamination and the environmental health concerns for example in west African (Nigeria) (Akinrinade et al., 2020, Okedere and Elehinafe, 2022) and some North, West, East and South Africa (Ofori et al., 2020) reported a comprehensive

**Figure 1-10 Trend in various studies of PAH in Africa from 2000-2018**

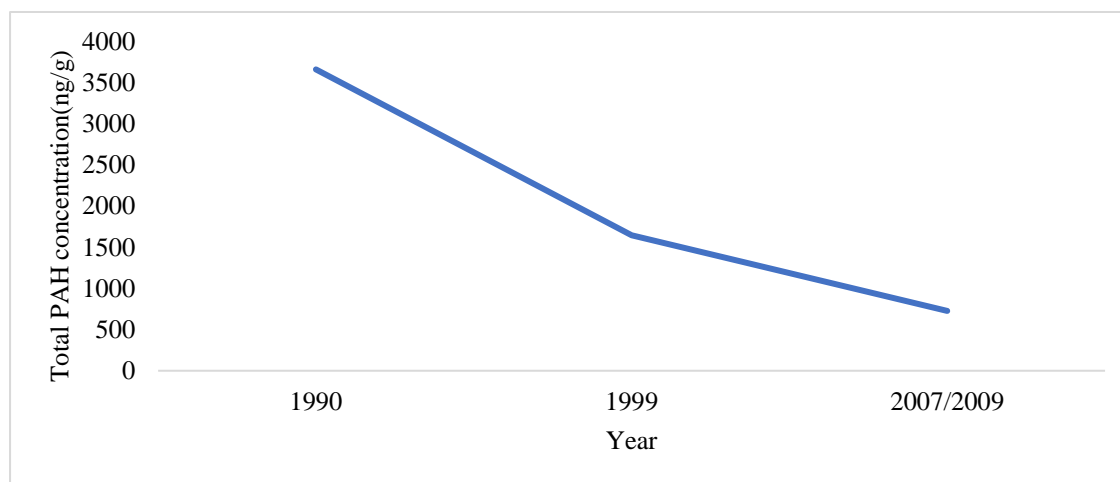


**(Munyeza et al., 2019)**

Temporal changes in PAH concentrations have also been reported in soil in some parts of the world. Cui et al. (2020) measured PAH concentrations in soil from Scotland between 1990 to

2009. It was observed that the level of PAH in soil increases with an average of 3659 ng/g in 1990 and reduces to 1644 ng/g before finally declined to 727 ng/g in 2007-2009 for  $\Sigma 16\text{PAH}$ , Figure 1.11 illustrate this trend.

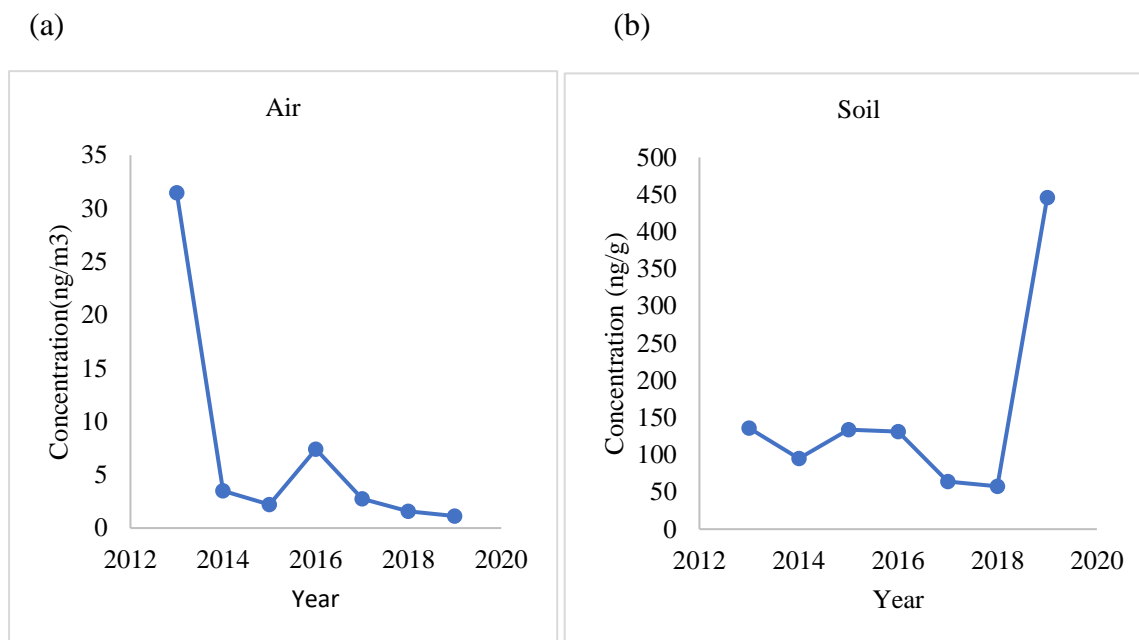
**Figure 1-11 Concentrations of PAH for  $\Sigma 16\text{PAH}$  in Scottish soils in three separate years**



(Cui et al., 2020)

Most recently, a long-term monitoring campaign was investigated in seven years in soil and air in Fildes Peninsula, Antarctic between 2013 to 2019 only in summer (Na et al., 2020). In the air and soil, average concentrations of  $\Sigma 15\text{PAH}$  were  $7.1 \text{ ng/m}^3$  and  $155 \text{ ng/g}$ , respectively. They further elucidated that in 2013, elevated concentrations were observed in air which contrasted with soil samples, in this case PAH concentrations were low at the initial monitoring period but later peaked in 2018 with an increasing trend in late 2018 to early 2019. The authors further stated that during this sampling period in summers of 2013–2019, there was a temporal change of a downward trend in the levels of PAH in air, but this was not detected in the soil (Na et al., 2020) as shown in Figure 1.12a and b. Note that the figure only revealed concentrations reported in summer of each year.

**Figure 1-12 Long term trend of total PAH in Fides Peninsula, Antarctica ( $\Sigma_{15}$ PAH concentration in the atmosphere (a) and soil (b)**



(Na et al., 2020)

In conclusion, understanding long-term trends in PAH is essential for revealing their sources, and understanding the processes governing their environmental fate. Indeed, the review indicated that in most developed and developing countries there has been in recent years a great reduction in the concentrations of PAH. This historical trend of PAH mostly decreasing is basically due to implementation of policies designed to reduce PAH emissions and air quality in general.

### 1.8 Guideline levels of PAH in air and soil

Numerous legal regulatory guidelines concerning PAH in the air and soil in different countries have been adopted at the national and international levels to reduce the level of PAH in the atmosphere and soil. Since the complete removal of PAH in the environment are impossible as a result of their persistent and bioaccumulation in the environment. BaP has been set as an appropriate representative of the total carcinogenic potency of PAH mixture based on the level of studies of this compound (WHO, 2000). Hence, the annual mean concentration of BaP was

established at 1 ng/m<sup>3</sup> by the European Community's fourth Air Quality Daughter Directive (2005/107/EC) ((Brown et al., 2013). The UK Expert Panel on Air Quality Standards (EPAQS) on the other hand has chosen 0.25 ng/m<sup>3</sup> of BaP as the UK air quality standard as an annual average (Delgado-Saborit et al., 2011)

For soil, the Danish environmental protection agency soil quality criteria for human health and ecological risk are 1.5 mg/kg and 1.0 mg/kg respectively for PAH and 0.1 mg BaP/kg (CCME, 2010). While in Nigeria, the Department for Petroleum Resources (DPR) has established a threshold of 1000 µg/kg and an intervention limit of 40,000 µg/kg (DPR, 2002)for PAH in soil.

## **1.9 Environmental levels and sources of PAH**

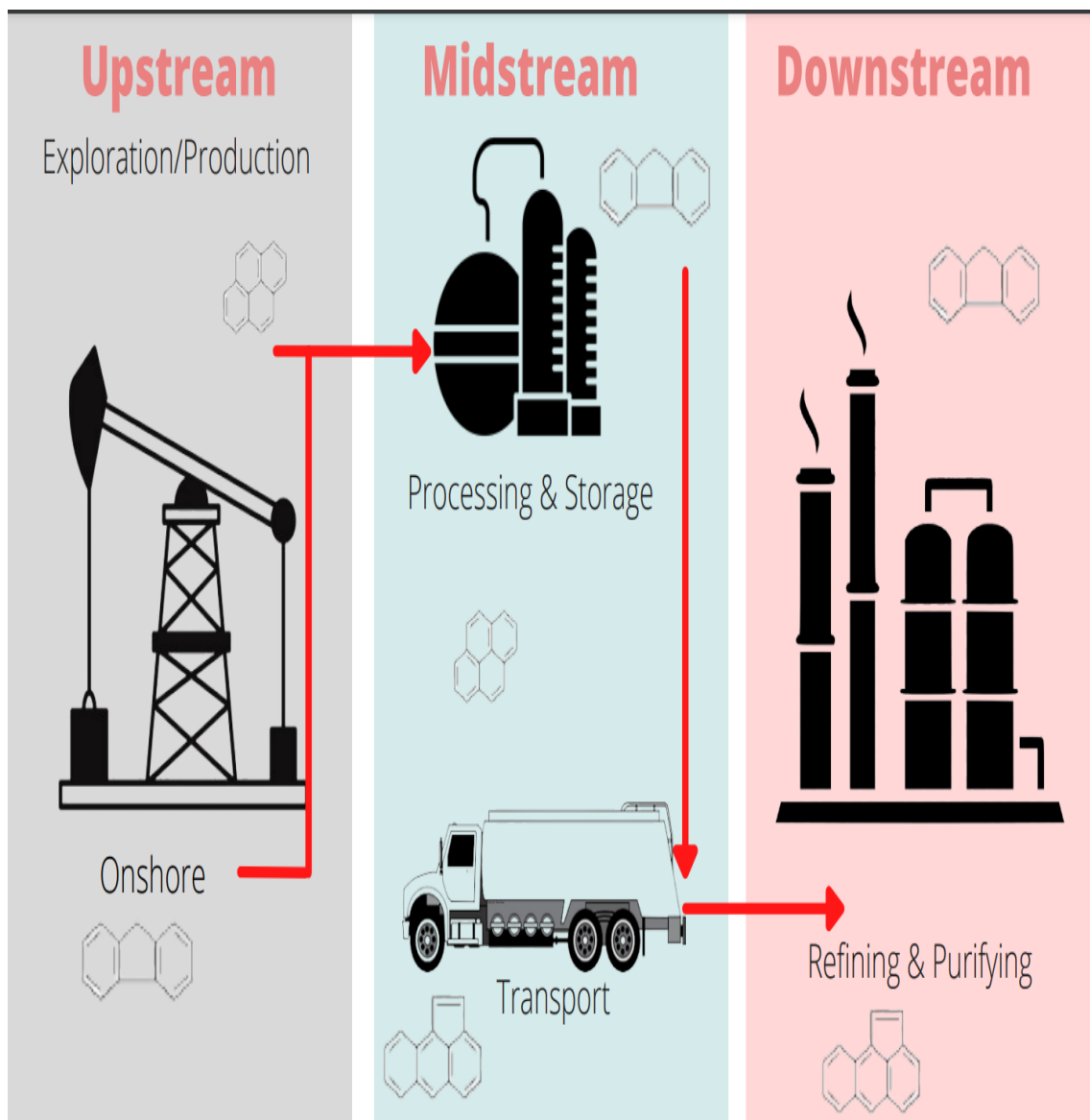
### **1.9.1 The Oil and Gas industry as a Source of PAH**

While formation of PAH from natural sources such as volcanic eruptions, forest fires, ancient sediment erosion, and diagenesis of organic matter are appreciable (Iwegbue et al., 2016, Tobiszewski and Namieśnik, 2012); evidence suggests strongly that human activities constitute the primary source of PAH in the modern environment (Ravindra et al., 2008, Bakker et al., 2000). Specifically, it appears that many of the PAH detected in the environment emanate from anthropogenic sources, with much derived directly or indirectly from fossil fuel production and combustion. Thus, there are various pathways via which exposure may occur to PAH mixtures arising from the oil and gas industry globally as a result of upstream, midstream and downstream activities (Chen et al., 2021, Al-Janabi, 2020) as shown in Figure 1.13

The upstream pathway comprises complex routes that include the exploration and extraction processes to acquire oil (Johnston et al., 2019, Cordes et al., 2016). The next step involves midstream activities required to transport and store crude oil (Umar et al., 2021). The final process is refining petroleum, petrochemical production, and their distribution, otherwise

referred to as downstream activities (Domingo et al., 2020, Olawoyin et al., 2014). It is known that PAHs are released at every step into the environment (soil, air and water).

**Figure 1-13 Schematic diagram on an overview of oil and gas process pathways**



While there appear to be many literature reporting the environmental impact of oil and gas production (Umar et al., 2021, Johnston et al., 2019, Cordes et al., 2016), relatively few studies have addressed the chronic effect of PAH emissions from oil and gas production facilities on the environment. The following section thus discusses the impact of oil and gas activities from exploration to refining based on PAH contamination.

### **1.9.2 Influence of oil and gas activities on concentrations of PAH in soil**

There is insufficient research relating to whether the oil and gas industry is a source of PAH emission to the environment. Available evidence however tends to suggest that such activities do exert a discernible impact. Bakker et al. (2000) reported the presence of seven PAH in soil samples taken from locations nearby an oil refinery plant in Zelzate, Belgium, at a total concentration of 300,000 ng/g. The authors stated that the total PAH loading in the soil samples collected away from the point source declined with increasing distance by a factor of 10-30 compared to the soil samples collected near the oil refinery.

A study on PAH in soil samples collected from oil refinery and chemical sites from Novi Sad, Serbia, indicated an elevated average concentration of  $\Sigma_{16}\text{PAH}$  of 46,930 ng/g in samples close to the oil refinery (Skrbic and Durisic-Mladenovic, 2009). This concentration exceeded those observed in control soil sample of 670 ng/g, with an overall mean  $\Sigma_{16}\text{PAH}$  12,170 ng/g for all sampled sites. The authors suggested that volatilisation of oil arising during transfer, accidental ejection, and leaks from oil storage tanks were likely contributing factors to the occurrence of PAH in the vicinity of the oil refinery.

The levels of PAH measured in Warri, Niger Delta demonstrate that petrochemical sites can contribute to the local burden in soil (Olawoyin et al., 2014). The authors reported that surface soil samples collected from four different locations contained PAH concentrations ranging from 613900- 59,478,000 ng/g with geometric mean 1,088,700 ng/g. The authors surmised that the likely source of PAH to these soils was principally from petrogenic processes augmented by a minor contribution from pyrogenic sources, (for example gas flaring) as designated by the isometric ratio (Olawoyin et al., 2014).

Omores et al. (2017) measured the spatial and seasonal distribution of PAHs in soil from a petrochemical refinery plant in Cape Town, South Africa. The study reported  $\Sigma_8\text{PAH}$

concentrations varying from not detected (nd) to 13,880 ng/g with an average of 4,080 ng/g in winter. Interestingly, in summer,  $\Sigma_8$ PAH concentrations were lower, ranging between not detected (nd) to 10,430 ng/g with an average of 500 ng/g. Consistent with the study of Olawoyin et al. (2014), the authors suggested petrogenic input was probably the main contributing factor governing the concentrations of PAH detected in their study.

A more recent study investigated ecological and health risks of PAHs associated with spills from petroleum products in soil in Abia, Nigeria (Ugochukwu et al., 2018). The results revealed concentrations of  $\Sigma_{16}$ PAH ranging from 19,000 ng/g to 461,000 ng/g. According to the authors, some of the impacted locations under examination that were found to have higher concentrations, pose a significant ecological risk to the biota living on the soil (Ugochukwu et al., 2018). Additionally, the results from soil toxicity assessment of these study areas showed a potential health risk to livestock, especially cattle grazing at the contaminated sites (Ugochukwu et al., 2018). This finding agrees with (Khan et al., 1996) when reporting the toxicological effects of crude oil hydrocarbons on cattle and other animals on agricultural pastureland. As previously stated in section 1.1, a significant proportion of PAH is incorporated in natural crude oil.

There is strong evidence that anthropogenic activities from oil and gas could be noticed in soil from an oil field, since oil spills can accidentally occur at every stage of operation as stated in section 1.7.1 (Liang et al., 2012, Du et al., 2010). PAH concentrations in soil within contaminated oil exploration and production regions in some parts of Texas, USA, were investigated (Bojes and Pope, 2007). Variations in the concentrations of PAH were reported, with the highest level detected being 86,400 ng/g for  $\Sigma$ PAH in a heavily polluted sample. Du et al. (2010) investigated the ecological impact of PAH on a Chinese oil drilling field. They observed that the concentrations in soil samples of  $\Sigma_{16}$ PAH was between 1,340 and 82,393 ng/g dry weight. The elevated concentration of 82,393 ng/g was detected at the region close to the

oil platform (Du et al., 2010), this suggested an impact of proximity to the point source. The same study further reported lower concentrations from other sites that are further away (6,587 ng/g and 1,340 ng/g). Comparing their concentrations to PAH soil guidance values from Agarwal (2009), the authors point out that some of the areas investigated probably elicited adverse effects in biota that involve a need for remediation of the soil concerned (Du et al., 2010). To characterise various degrees of contaminations from different oil exploration sites, Liang et al. (2012) reported the concentrations of PAH in surface soil from various oil exploration sites across North to South China with a mean concentration of  $\Sigma_{12}$ PAH of 435,000 ng/g for Daqing, 308,000 ng/g for Shengli and 304,000 ng/g for Baise (Liang et al., 2012). These results showed a high level of pollution in the study regions. Near an oil spill in Esuk Utan, Calabar, Nigeria, PAH concentrations in soil were measured (Nganje et al., 2012). Concentrations around the spill regions were significantly high. However, they declined on moving away from the impacted locations. The mean concentration was 2,906  $\mu\text{g}/\text{kg}$  with a range of 16-25,548  $\mu\text{g}/\text{kg}$  for  $\Sigma_{16}$ PAH dry weight (dw) (Nganje et al., 2012). Nganje et al. (2014) further investigated PAHs in two areas with spillage in some parts of South-Eastern Calabar, in soil at various depths from 15 cm to 100 cm. They found that concentrations reduce with increasing depth in both sites in their study area (from 24,870 to 4,280 and 29,770 to 6,760 ng/g).

In another study, Adedosu et al. (2013) analysed an oil exploration zone in River State, Nigeria featuring a variety of activities in River State, Nigeria. They investigated a flow station with a gas plant and an oil exploration site. The highest PAH concentrations of 78.3 ng/g for  $\Sigma_{16}$ PAH was observed at the operational gas plant, with gas flaring whilst the other gas plant location without gas flaring activities had the lowest concentration of 7.4 ng/g. The regions with an oil exploration pipeline were considered to display significantly elevated concentrations of 49 ng/g and 33 ng/g (mean). They reported that the high concentrations of PAH at these sites can be

attributed to atmospheric deposition from gas flaring and historical oil spillage that occurred in 2004 due to the pipeline explosion. This shows that these compounds can accumulate and persist in the soil environment for extended periods. Wang et al. (2015a) measured concentrations of  $\Sigma_{16}$ PAH in four different geographical sites in North China oil exploration areas. The results revealed high PAH concentrations ranged from 480-20,625 ng/g, 49-43,210 ng/g, 857-27,816 ng/g, and 12,112-45,325 ng/g, respectively, across the investigated locations. According to their findings, a low carcinogenic risk for residents and oil field employees exists; however, the PAH concentrations detected in the oil fields were categorised as extremely polluted and toxic according to Maliszewska-Kordybach (1996). Furthermore, the isomeric source attribution system adopted, indicated that PAH in the study arose mainly from petroleum production. The potential risk of exposure to PAH generated from a petroleum source in another study of an oil drilling field in China was investigated by (Jiao et al., 2015). The average concentration of  $\Sigma_{16}$ PAHs near an oil well was 627 ng/g, which exceeded the 343 ng/g found in soils from the arable desert reported by the authors.

Since there is an inherent connection between PAH accumulated in the soil, uptake by crops, and human health risk once exposed via ingestion; PAH concentrations in soil, vegetables, and edible tubers from oil-polluted agricultural land in Gokana, Nigeria, were investigated by (Nwaichi et al., 2014). The average PAH concentrations in soil from the control site was less than 0.1 ng/g dry weight (dw), while the polluted oil sites contained an average of 6,950 ng/g for  $\Sigma_{16}$ PAH for soil sampled at replicates of three. According to the Nigerian Department of Petroleum Resources (DPR), PAH concentrations in oil-polluted soil exceeded the 1,000 ng/g permissible limit for soil toxicity (Nwaichi et al., 2014, DPR, 1991). A summary of concentrations of PAH reported in oil and gas is presented in Table 1.5 with those in soils from urban/industrial and rural provided for comparison. These data are further summarised graphically as a box plot in Figure 1.14.

**Table 1-5 Concentrations of ΣPAH in soil from previous studies around the world**

<b>Reference</b>	<b>Location</b>	<b>Location Type</b>	<b>No of PAH measured</b>	<b>Average concentration(n g/g)</b>
Alawi and Azeez (2016)	Iraq	Oil Refinery	13	320
Nganje et al. (2012)	Calabar, Nigeria	Tank distribution facility	16	2,906
Ugochukwu et al. (2018)	Abia, Nigeria	Petroleum products pollution sites	16	146,750
Nwaichi et al. (2016)	Okpe, Delta, Nigeria	Pipeline leakage	17	532
Nwaichi et al. (2016)	Ekore, Delta, Nigeria	Pipeline leakage	17	1262
Nwaichi et al. (2016)	Uduvwoku, Delta, Nigeria	Pipeline leakage	17	4613
Nwaichi et al. (2014)	Gokana, River state	Oil polluted Agricultural Area	16	6,950
Sojinu et al. (2010)	Niger Delta	Close to oil installing area	28	80

<b>Reference</b>	<b>Location</b>	<b>Location Type</b>	<b>No of PAH measured</b>	<b>Average concentration(n g/g)</b>
Abbas and Brack (2006)	Warri, Niger Delta	Oil refinery	16	433
Abbas and Brack (2006)	Ugboko, Niger Delta	Close to oil field	16	348
Olawoyin et al. (2014)	Niger Delta (Warri)	Petrochemical	17	1,088,700*
Nwankwoala et al. (2020)	Bonny Island, Niger Delta	Industrial oil	16	7,800
Nwankwoala et al. (2020)	Bonny Island, Niger Delta	Industrial oil	16	3,230
Nwankwoala et al. (2020)	Bonny Island, Niger Delta	Industrial Oil	16	2,810
Jiao et al. (2015)	Dagang, China	Oil field site	13	627
Jiao et al. (2015)	Dagang, China	Urban/residential	13	1,856
Du et al. (2010)	China	Oil field site	16	82,393
Du et al. (2010)	China	Oil field site	16	42,227
Du et al. (2010)	China	Oil field site	16	12,837
Du et al. (2010)	China	Oil field site	16	29,077

<b>Reference</b>	<b>Location</b>	<b>Location Type</b>	<b>No of PAH measured</b>	<b>Average concentration(n g/g)</b>
Wang et al. (2015a)	Shengli	Oil field site	16	6,394
Wang et al. (2015a)	Xinjiang	Oil field site	16	13,569
Wang et al. (2015a)	Daqing	Oil field site	16	9,160
Wang et al. (2015a)	Huabei	Oil field site	16	22,954
Kuang et al. (2018)	Shengli, China	Oil field site	16	2,160
Wang et al. (2018a)	Loess plateau	Petroleum-contaminated soil	16	5,502
Wang et al. (2020)	Loess plateau	Oil well	16	5,663
Li et al. (2019)	Daqing, China	Near oil well	16	2,240
Bojes and Pope (2007)	Texas, USA	Oil exploration area	16	86,400
Tiwari et al. (2011)	India	Sludge deposition oil refinery	16	60,360
Tarafdar and Sinha (2018)	Barauni, India	Oil refinery	13	92,990

<b>Reference</b>	<b>Location</b>	<b>Location Type</b>	<b>No of PAH measured</b>	<b>Average concentration(n g/g)</b>
Tarafdar and Sinha (2018)	Haldaia, India	Oil refinery	13	84,991
Tarafdar and Sinha (2018)	Guwahati, India	Oil refinery sludge site	13	67,860
Suman et al. (2016)	Dhanbad India	Urban traffic	13	640
Kumar et al. (2013)	India	Urban	16	632
Kumar et al. (2020)	India	Urban	16	550
Kumar et al. (2020)	India	Rural	16	224
Bakker et al. (2000)	Belgium	Vicinity of an oil refinery	7	30,000
Skrbic and Durisic-Mladenovic (2009)	Serbia, Europe	Vicinity of oil refinery	16	12,167
Omares et al. (2017)	Cape Town, South Africa, Winter	Petrochemical refinery	8	5370
Omares et al. (2017)	Cape Town, South Africa, Summer	urban	8	8650
Mielke et al. (2004)	New Orleans, USA	Suburban	16	2,927
Mielke et al. (2001)	New Orleans, USA	Urban	16	3,731
Banger et al. (2010)	Miami, Florida	Urban	16	1,869

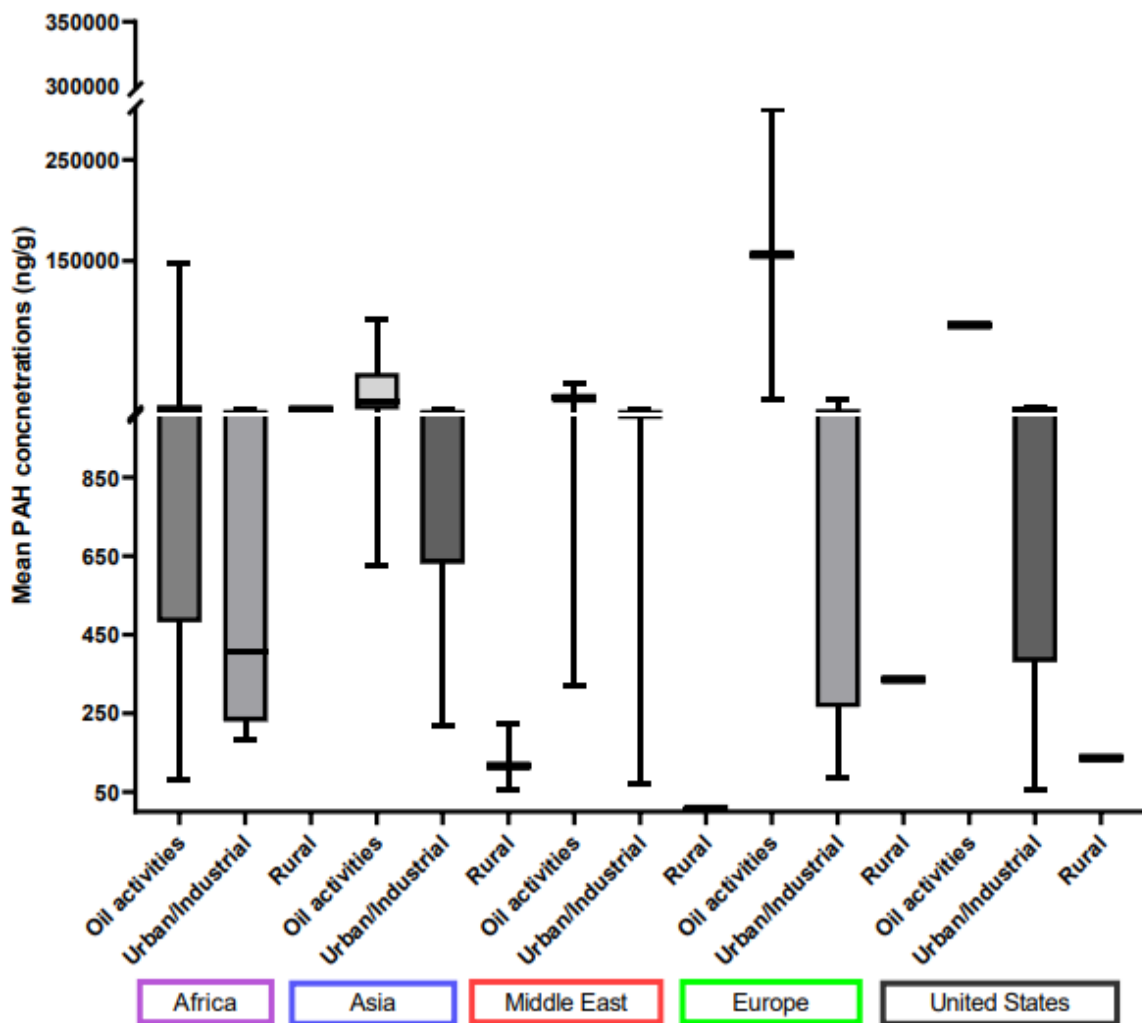
<b>Reference</b>	<b>Location</b>	<b>Location Type</b>	<b>No of PAH measured</b>	<b>Average concentration(n g/g)</b>
Nematollahi et al. (2022)	Iraq	Around oil refineries	16	27700
Škrbić et al. (2017)	Novi Sad, Serbia	Urban	16	298
Cachada et al. (2012)	Viseu, Portugal	Urban	16	169
Cachada et al. (2012)	Lisbon, Portugal	Urban	16	1,544
Morillo et al. (2007)	Torino. (Italy)	Urban	15	1,990
Morillo et al. (2007)	Glasgow (Scotland)	Urban	15	11,930
Morillo et al. (2007)	Ljubljana, Slovenia	Urban	15	989
Nadal et al. (2007)	Tarrogon, Spain	Urban	16	438
Zhang et al. (2006)	Hong Kong	Urban/rural	16	55
Kwon and Choi (2014)	South Korea	Multi industrial city	16	960
Kwon and Choi (2014)	South Korea	Urban	16	390
Kwon and Choi (2014)	South Korea	Industrial	16	1,900
Kwon and Choi (2014)	South Korea	Rural	16	220

<b>Reference</b>	<b>Location</b>	<b>Location Type</b>	<b>No of PAH measured</b>	<b>Average concentration(n g/g)</b>
Jiao et al. (2009)	Tianjin, China	Industrial	16	814
Yu et al. (2019)	China	Urban	16	2,959
Wang et al. (2013)	Shanghai, China	Urban	16	1,970
Wang et al. (2015b)	Shanghai (Podong), China	Urban	16	807
Jiang et al. (2016)	Lanzhou, China	Urban	16	2,360
Iwegbue et al. (2016)	Niger Delta, Nigeria	Urban/industrial	16	375
Bortey-Sam et al. (2014)	Kumasi, Ghana	Urban	22	442
Tang et al. (2005)	Beijing, China	Urban	16	3,917
Peng et al. (2011)	Beijing, China	Urban soil	16	1,228
Abbas and Brack (2006)	Ovwian-Aladja,	Steel industry	16	182
Agarwal (2009)	Delhi, India	Urban/ traffic site	16	4,694
Moore et al. (2015)	Isfahan, Iran	Urban	12	2,000

<b>Reference</b>	<b>Location</b>	<b>Location Type</b>	<b>No of PAH measured</b>	<b>Average concentration(n g/g)</b>
Mungai et al. (2019)	Limuru, Kenya	Urban/Agriculture	16	2,885
Mungai et al. (2019)	Narok, Kenya	Rural	16	2,624
Mungai et al. (2019)	Eastern, Africa (Kenya)	Agriculture land	16	3,353
Roberto et al. (2009)	El Paso, Texas	Industrial	16	382
Roberto et al. (2009)	El Paso, Texas	Urban	16	57.4
(Liu et al., 2019)	Orlando, Florida	Urban	16	3227
Liu et al. (2019)	Tampa	Urban	16	4562
Luo et al. (2020)	Shenyang, China	urban	16	2,370
Plachá et al. (2009)	Czech Republic	Urban/Agriculture	16	5,527
Thiombane et al. (2019)	South Italy	Urban	16	85
Thiombane et al. (2019)	South Italy	Rural	16	336

<b>Reference</b>	<b>Location</b>	<b>Location Type</b>	<b>No of PAH measured</b>	<b>Average concentration(n g/g)</b>
Ilić et al. (2021)	Republic of Srpska, Bosnia and Herzegovina	Industrial zone	16	1,990
Yuan et al. (2014)	Delaware, USA	Urban	12	1,159
Yuan et al. (2014)	Delaware, USA	Rural	12	130
Yua et al. (2020)	Guan river, China	Industrial	15	3,505
Al-Saad et al. (2019)	Middle east	Urban	16	72
Al-Saad et al. (2019)	Middle east	Rural	16	6.9
Zheng et al. (2014)	Dongjiang River Basin	Rural	NA	116

\*Geometric mean



**Figure 1-14** Box and Whisker plot of average PAH concentrations (ng/g) reported in various studies of soils impacted by the oil and gas industry with those in soils from other locations worldwide

Note that the edges of each box denote 25<sup>th</sup> and 75<sup>th</sup> percentile concentrations, the line within each box denoted median while the whiskers represent the 10<sup>th</sup> and 90<sup>th</sup> percentiles.

It is important to place reported concentrations of PAH in petroleum-contaminated soil with those reported for soils from other locations around the world. The evidence of Table 1.5 and Figure 1.13 is that while elevated concentrations are present in many urban locations Mungai et al. (2019) (2885ng/g), (Plachá et al., 2009) (5527ng/g), (Morillo et al., 2007) (11,930 ng/g), that in some instances exceed those reported in some studies of soils in the vicinity of oil and

gas production locations (Jiao et al., 2015) (627 ng/g), (Kuang et al., 2018) (2160ng/g), (Sojini et al., 2010) (80 ng/g); it appears that concentrations of PAH in soils in many locations impacted by oil and gas production activities are at the high end of those reported globally.

### **1.9.3 Influence of oil and gas activities on concentrations of PAH in Outdoor air**

Upstream oil and gas production activities tend to pollute soil and water and consequently the atmosphere through volatilisation from oil-contaminated soil or water (Kuang et al., 2018, Gevao et al., 2006). However, while natural gas extraction and downstream activities such as the petroleum refining process and petrochemical operations have been associated with the emission of mixtures of PAH into the atmosphere (Thang et al., 2019, Paulik et al., 2018, Alghamdi et al., 2015) there is still limited literature reporting the contribution of oil and gas production facilities to concentrations of PAH in outdoor air.

While many studies have focused on concentrations of PAH in the particulate phase (Thang et al., 2019, Ana et al., 2012, Rao et al., 2008), some have measured vapour phase PAH (Pulster et al., 2019, Paulik et al., 2018). Ideally, concurrent measurements of both vapour and particulate phases are essential to assess the relative importance of atmospheric processes. Yamasaki et al. (1982) emphasised that measuring both vapour and particle-phase aids complete understanding of the environmental fate and distribution of PAH in ambient air.

The table 1.6 summarises the available data for some PAH concentrations emitted into the atmosphere due to oil and gas operations. Note that studies assessing gaseous, particulate and both particulate and gaseous phase PAH concentrations are presented here due to lack of data.

Zhao et al. (2015) investigated atmospheric concentrations of PAH in both gas and particulate phase in a petrochemical complex in Guangzhou, China. The average concentration for  $\Sigma_{16}$ PAH detected was 514 ng/m<sup>3</sup> with a range of 279 to 1,243 ng/m<sup>3</sup>. The authors identified the PAH pattern to be petrogenic in origin. This signifies that transforming crude oil into

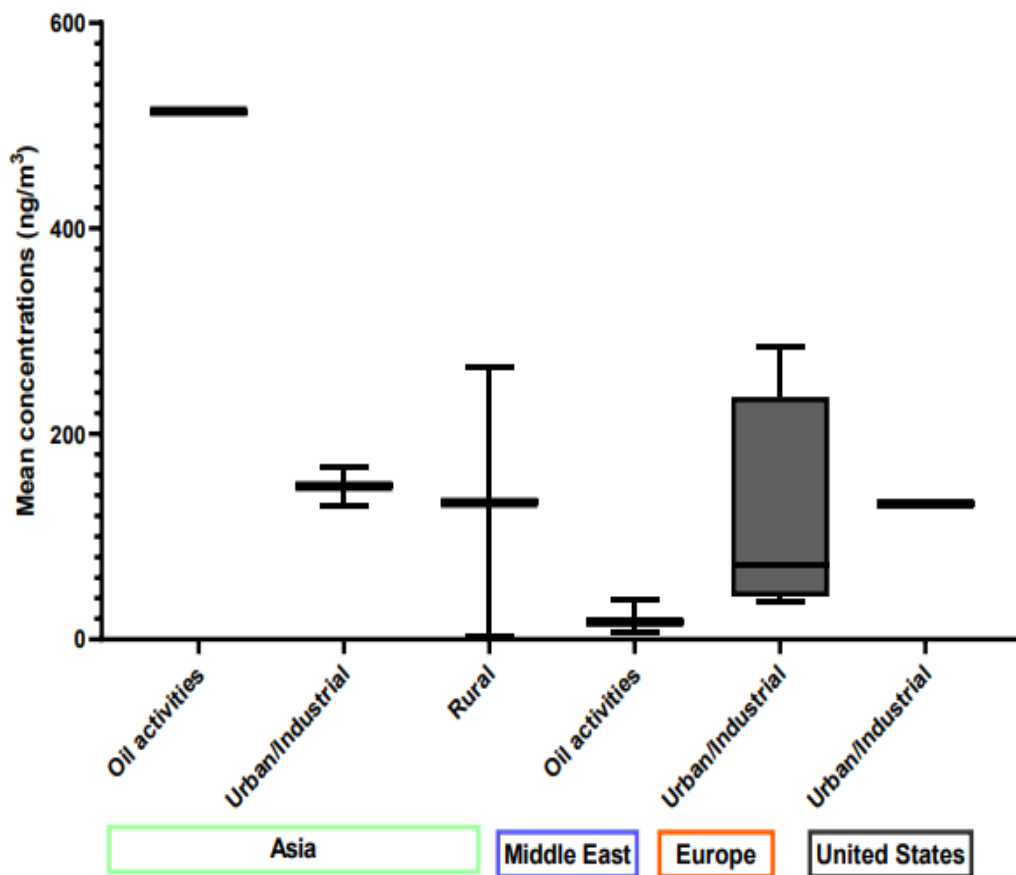
petrochemicals releases PAH into the atmosphere. The importance of the oil refinery in Jeddah, Saudi Arabia, was further highlighted by Alghamdi et al. (2015). They measured the concentrations of 14 PAH in both the vapour and particle phase. The three sampling sites investigated were sites close to the oil refinery, near heavily trafficked roads and at urban background sites (impacted by a variety of anthropogenic sources). Average total PAH concentrations in the ambient air were: 38 ng/m<sup>3</sup> for the oil refinery, 30 ng/m<sup>3</sup> for heavily trafficked locations and 12 ng/m<sup>3</sup> at urban background sites, respectively (Alghamdi et al., 2015). They further found that PAH concentrations in air sampled at the area with the oil refinery were statistically different ( $p < 0.05$ ) compared to those recorded at the other studied sites. The order of concentration was oil refinery > traffic roadside > urban background. (Harrison et al., 2016a) supported their hypothesis by ascertaining that the oil refinery was the contributing factor for the rise of the PAH. They investigated 16 PAH in the vapour and gas phase at the same sites in Jeddah, Saudi Arabia, close to an oil refinery. They also sampled three other locations situated at the city Red Sea coast of Saudi Arabia, close to a petrochemical installation complex. The highest concentration was observed at the sites downwind from the petrochemical installation complex located north of the study area. According to the coefficient of divergence estimation, there was a substantial difference in the concentration gradients within the same sites in Jeddah compared to the other coastal sites. Furthermore, they explored that the small rises in concentrations found in the coastal region resulted from the decline in air mass flowing across these regions, influenced by the reactivity of PAH compounds in air (Harrison et al., 2016a).

In the vapour phase, Paulik et al. (2018) examined the impact that natural gas wells can exert on concentrations of PAH in ambient air in Ohio, United States. This was accomplished by deploying a low-density polyethylene passive sampler. Their results revealed  $\Sigma$ PAH to range from 19 to 48 ng/m<sup>3</sup> within the active well surround and from 9.4 to 34 ng/m<sup>3</sup> at a location

proposed for future activity (but currently non-active). The study demonstrated active wells as a point source of PAH to the atmosphere. Similarly, Pulster et al. (2019) measured PAH concentrations in the vapour phase at a petrochemical complex in the Island of Curacao in the years 2011 and 2014 for upwind and downwind locations. The concentration of PAH observed in 2011 ranged from 1.2-790 ng/m<sup>3</sup>, while that in 2014 fell between 27 to 660 ng/m<sup>3</sup>. No significant temporal variation in PAH concentrations between sampling years was observed. However, spatial variation was observed between the upwind and downwind samples with elevated concentrations detected at the downwind sampling site of oil refinery (Pulster et al., 2019). In an oil lake in Kuwait, Gevaio et al. (2006) found an average concentration of PAH of 8.3 ng/m<sup>3</sup> (range 5 to 13 ng/m<sup>3</sup>). Five to six ring PAH were detected at increased concentrations around the oil lake due to historical oil well torching. Phenanthrene, fluorene, fluoranthene and pyrene were the predominant PAH detected overall.

Particle-bound PAHs had been determined in ambient air in two locations, Eleme, an industrial oil location and Ahoada East, where industrial activity is minimal (Ana et al., 2012). Air samples were collected with the aid of Anderson high-volume samplers; the study reported an average total PAH concentration of 0.17 ng/m<sup>3</sup> at Ahoada East and a high concentration of 9,200 ng/m<sup>3</sup> at Eleme, the authors to observe that Eleme has one of greatest PAH level in the world.

Concentrations of PAHs associated with total suspended particles (TSP) in ambient air near South Korea's biggest petrochemical and oil refinery industrial complex were measured seasonally at three locations (Thang et al., 2019). Annual mean concentrations of  $\Sigma_{19}$ PAH of 5.88 ng/m<sup>3</sup>, 4.52 ng/m<sup>3</sup> and 5.08 ng/m<sup>3</sup> were observed at the three locations. Moreover, seasonal variation was observed with elevated concentrations noticeable in winter compared to summer (Thang et al., 2019). The study reported a significant ( $p < 0.01$ ) correlation between TSP and  $\Sigma_{19}$ PAH at all sampling locations.



**Figure 1-15** Box and whisker plot summarising reported concentrations of PAH (sum gas and particle phase) ( $\text{ng}/\text{m}^3$ ) in outdoor air from selected studies in oil and gas impacted area

Note that the 25<sup>th</sup> and 75<sup>th</sup> percentile concentrations are shown along each box's margins, its interior line shows the median, and the 10<sup>th</sup> and 90<sup>th</sup> percentiles are shown by the whiskers.

**Table 1-6 Concentrations of ΣPAH in outdoor air reported in selected studies from the literature**

Reference	Location	No of PAH	Sampling Period	N	Average (ng/m <sup>3</sup> )	Media/Phase	Location type
Zhao et al. (2015)	Guangzhou, China	17	Jul-12	8	514	Hi-Vol (PUF+GFF)	Petrochemical refinery
Alghamdi et al. (2015)	Jeddah, Saudi Arabia	14	Feb.2013- April 2013	3	38	Hi-Vol (PUF+GFF)	Oil refinery
Gevao et al. (2006)	Kuwait	15	Feb.2004- April 2004	14	6.6	Passive sampling (PUF) for gaseous and particle sampling	Oil Lake
Harrison et al. (2016a)	Saudi Arabia	16	June 2013- January 2014	6	17	Pesticide sampler (TE-PUF-TE-QMA4) (PUF+GFF)	Petrochemical complex
Chen et al. (2011)	Shanghai, China	17	2005-2006	2	167	Hi-Vol (PUF+GFF)	Urban
Yang et al. (2010)	Guangzhou, China	16	April 2005- March 2006	99	130	Hi-Vol (PUF+GFF)	Urban

Reference	Location	No of PAH	Sampling Period	N	Average (ng/m <sup>3</sup> )	Media/Phase	Location type
Poor et al. (2004)	Tampa, FL,USA	16	May-August 2002	NA	132	HiC-IOGAPS (Deuder+ quarter filter	urban
Tsapakis and Stephanou (2005)	Heraklion, Greece	24	2000-2002	16	79	Hi-Vol (PUF+GFF)	Urban
Li et al. (2014)	North, China	21	April 2010- March 2011	6	264	PUF+GFF	Rural
Huang et al. (2014)	Pearl River- Delta, China	18	Nov-Dec 2010	Every day	2.3	Hi-Vol (PUF+GFF)	Rural
Cetin et al. (2018)	Dilovasi, Turkey	15	Feb 2005-feb 2006	23	285	PUF	Industrial
Bozlaker et al. (2008)	Izmir, Turkey	15	Aug 2004- March, 2005	28	36	Modify Hi-Vol (PUF+GFF)	Industrial

<b>Reference</b>	<b>Location</b>	<b>No of PAH</b>	<b>Sampling Period</b>	<b>N</b>	<b>Average (ng/m<sup>3</sup>)</b>	<b>Media/Phase</b>	<b>Location type</b>
Cincinelli et al. (2007)	Prato, Italy	12	March-Nov 2002	11	59	Hi-Vol (PUF+GFF)	Urban/Industrial
Lai et al. (2017)	Kaohsiung, Taiwan	16	August 2012- 2012	7	149	ps-1PUF/GFF	Industrial
Goudarzi et al. (2018)	Ahvaz, Iran	16	2017	3	8.4	PTFE Filter	Industrial
Delgado-Saborit et al. (2013)	University of Birmingham, UK	17	Jan 11-15, 2010(5 days)		88	PUF+GFF	Suburban

### **1.9.3.1 Global Comparison of Atmospheric PAH Concentrations**

While there are insufficient data on PAH concentrations in outdoor air in locations close to oil and gas production sites to permit thorough global comparison, Table 1.6 and Figure 1.15 summarise the available data on concentrations of PAH in such sites together with a selection of data from studies of other locations.

Notwithstanding the relatively sparse data available, it appears that concentrations of PAH in the atmosphere surrounding oil and gas production facilities in many cases exceed substantially those at other locations.

### **1.10 PAH profiles and implications for source apportionment**

The various activities involved in oil and gas production yield different distribution patterns of PAH. Such differences in PAH profiles may help identify whether the PAH detected are petrogenic, i.e., defined as those derived from unburnt crude oil and its petroleum products (Kuang et al., 2018, Wang et al., 2015a, Sojinu et al., 2010). It is very important to know that petrogenic processes take place at a lower temperature between 100 °C and ~150 °C (Okedere and Elehinafe, 2022, Abdel-Shafy and Mansour, 2016). In contrast, pyrogenic emissions arise from incomplete combustion of fossil fuel and other combustion activities (Rengarajan et al., 2015, Adedosu et al., 2013, Tobiszewski and Namieśnik, 2012, Ravindra et al., 2008) and occur at higher temperatures of approximately 350 °C to 1200 °C or more (Okedere and Elehinafe, 2022, Abdel-Shafy and Mansour, 2016). It is important though to bear in mind when interpreting PAH profiles, these may change between the source and the environmental receptor as a result of environmental weathering processes. Notwithstanding this caveat, several studies have attempted source apportionment of PAH in environmental samples, based on the comparative abundance of different PAH expressed as various so-called diagnostic ratios (Bortey-Sam et al., 2014, Tobiszewski and Namieśnik, 2012, Chen et al., 2011). A premise of this methodology is that some PAH have identical (or similar) physicochemical

properties and molar mass and will thus be equally impacted by post-emission environmental weathering processes (Tobiszewski and Namieśnik, 2012). Despite its potential utility, the diagnostic ratio approach has received criticism (Galarneau, 2008, Zhang et al., 2005). Specifically, the capacity of diagnostic ratios to identify emission sources relies on the assumption that the ratio remains substantially constant on passing from source to environmental receptor (Ravindra et al., 2008). Moreover, in most cases, clear-cut apportionment of PAH to one specific source is complex, as, in most instances, multiple sources occur at a given location. Despite such issues, diagnostic ratios are still widely used as one of the most effective tools for identifying emission sources of PAH (Tobiszewski and Namieśnik, 2012).

For example, (Wang et al., 2015a) demonstrated through the use of diagnostic ratios how different activities could influence PAH profiles in soil samples collected from different sites in an oil field in China. The Fla/ (Fla+Pyr) ratio fell below 0.1 for most of the soil samples in their study area, indicating a petrogenic source. In contrast, for some samples values greater than 0.4 for the same ratio signified a biomass combustion impact (Wang et al., 2015a). Harrison et al. (2016a) also adopted Ant/ (Ant+Phe) ratios in a petrochemical refinery in Saudi Arabia; the ratios were reported to be less than 0.1, attributing the source to be petrogenic. By comparison, Adedosu et al. (2013) reported the ratio of Ant/ (Ant+Phe) in seven soil samples measured in the Niger Delta to be  $> 1$ ; concluding that PAH detected in these soil samples were of pyrolytic origin. Appendix S1:1 shows PAH diagnostic ratios used as source indication in some studies.

In conclusion, PAH profiles can be used for source identification but with the caveat that processes that occur between the source and soil and air near the source can change the profiles. Thus, diagnostic ratios have to be employed with care because there may be alteration in their values between emission and deposition.

## 1.11 Aims and Objectives

As seen from the above, there are significant study gaps related to the occurrence, fate, and behaviour of PAH in the environment, both in the air and in the soil surrounding oil and gas fields. Given its economic importance, it is crucial to consider the environmental consequences and health risk of PAH emissions from the oil and gas industry. In addition, ongoing monitoring of PAH levels in Nigeria is required to assess the efficacy of current restrictions designed to reduce emissions of PAH. While numerous studies have reported concentrations of PAH in soil and air from urban and rural locations, such data are limited for locations impacted by oil and gas production facilities. Despite this, those data as are available suggest oil and gas production activities may constitute substantial sources of PAH to the surrounding environment. Against this backdrop, the overall aim of this study was to assess concentrations of PAH in air and soil in the vicinity of oil and gas production activities and their implications for human exposure to PAH in populations working and/or residing in the vicinity of an oil and gas production activities in Esit Eket and Ibeno, Niger Delta region, Nigeria.

The hypothesis tested are as follows-

- Exposure to PAH in areas influence by oil and gas activities would exceed that experienced by populations not impacted by such activities ,
- Concentration of PAH in air and soil are higher in the dry than wet seasons respectively.

The main objectives of the study were thus as follows:

1. To monitor the levels and distribution of PAH in air and soil around a major oil and gas production facility in Nigeria.
2. To estimate exposure to PAH of workers and local residents via inhalation and incidental soil ingestion

3. To use these estimates of exposure to evaluate the human health risks arising.
4. By comparing concentrations of PAH in air and soil from a number of locations upwind and downwind of the target oil and gas production facility, to evaluate the extent to which the facility is a source of PAH to the surroundings.
5. To evaluate spatial and variability between the wet and dry season in PAH concentrations in air and soil
6. To evaluate the impact on PAH concentrations of different oil and gas production activities.

## Chapter 2

### Sampling and Analytical Methodology

#### 2.1 Background

The focus of this chapter is to discuss the methods and techniques applied to address the aims and the hypotheses enumerated in the previous chapter. Four major stages were employed namely, sampling, extraction, clean-up, and gas chromatography coupled with mass spectrometry (GC-MS). The methods were used for collection, identification and quantification of PAH in air and soil samples. Details of each stage will be provided in this chapter.

Soil and air samples were collected at different locations based on knowledge of their status relative to oil exploration activities (oil spill impacted area, partially impacted, cultivated farmland with history of oil spillage, and non-oil affected area considered as control).

Sampling methodologies and analytical procedures in this study have been previously described elsewhere (Jiao et al., 2015, Baderna et al., 2011, Ray et al., 2008, Agarwal et al., 2006). However, this was modified to facilitate the measurement of PAH in these matrices. Validation of this analytical protocol was conducted alongside a well-defined quality assurance/quality control measure and will equally be discussed.

#### 2.2 Materials and Chemicals

Calibration standards containing 16 EPA priority PAH (native) (table 2.1) of >97% purity as stock solution in methylene chloride and *para*-terphenyl (*p*-terphenyl) of 98% purity used as a recovery determination standard in dichloromethane, were all purchased from Restek Corporation, UK. In addition, a perdeuterated internal standard mixture (table 2.2) comprising 14 EPA priority PAHs with > 99.5 % purity in toluene was obtained from Chiron AS, Norway. Dichloromethane (DCM) and *n*-hexane used in this study were of HPLC grade and supplied by Fisher Scientific UK Ltd.

Other chemicals such as copper fine powder 99.9% purity used for removal of sulphur during the extraction were obtained from Sigma-Aldrich Company Ltd. Thermo Scientific (UK) supplied the Florisil<sup>®</sup> cartridges used for sample clean-up. Nitrogen gas (>99.9% purity) was provided by BOC Gases, UK. The NIST standard reference materials (SRM 2585, “Organic Contaminants in House Dust”) and (SRM 1941b Marine Sediment) were purchased from the National Institute of Standards and Technology (NIST) Gaithersburg, MD, USA. All glassware was wrapped in aluminium foil and baked in an oven at 500°C for 6 hours and allowed to cool, before rinsing with organic solvents before being used.

**Table 2-1 Names, concentrations, molecular formulae and CAS number of PAH stock standards used in this study.**

PAH	Concentration	Molecular Formula	CAS number
Acenaphthene	2000 ug/mL	C <sub>12</sub> H <sub>10</sub>	83-32-9
Acenaphthylene	2000 ug/mL	C <sub>12</sub> H <sub>8</sub>	208-96-8
Anthracene	2000 ug/mL	C <sub>14</sub> H <sub>10</sub>	120-12-7
Phenanthrene	2000 ug/mL	C <sub>14</sub> H <sub>10</sub>	85-01-8
Fluorene	2000 ug/mL	C <sub>13</sub> H <sub>10</sub>	86-73-7
Fluoranthene	2000 ug/mL	C <sub>16</sub> H <sub>10</sub>	206-44-0
Benzo[ <i>a</i> ]anthracene	2000 ug/mL	C <sub>18</sub> H <sub>12</sub>	56-55-3
Chrysene	2000 ug/mL	C <sub>18</sub> H <sub>12</sub>	218-01-9
Pyrene	2000 ug/mL	C <sub>16</sub> H <sub>10</sub>	129-00-0
Benzo[ <i>a</i> ]pyrene	2000 ug/mL	C <sub>20</sub> H <sub>12</sub>	50-32-8
Benzo[ <i>b</i> ]fluoranthene	2000 ug/mL	C <sub>20</sub> H <sub>12</sub>	205-99-2
Benzo[ <i>k</i> ]fluoranthene	2000 ug/mL	C <sub>20</sub> H <sub>12</sub>	207-08-9
Dibenz[ <i>a,h</i> ]anthracene	2000 ug/mL	C <sub>22</sub> H <sub>14</sub>	53-70-3
Benzo[ <i>g,h,i</i> ]perylene	2000 ug/mL	C <sub>22</sub> H <sub>12</sub>	191-24-2
Indeno[1,2,3- <i>cd</i> ]pyrene	2000 ug/mL	C <sub>22</sub> H <sub>12</sub>	198-39-5

**Table 2-2 Names of deuterated PAH internal standards, concentration, empirical formulae and recovery determination standards (RDS)) used in this project**

<b>Internal Standard</b>	<b>concentrations</b>	<b>Empirical Formula</b>	<b>CAS number</b>
Acenaphthene-d10	100 ug/mL	C <sub>12</sub> D <sub>10</sub>	15067-26-2
Anthracene-d10	100 ug/mL	C <sub>14</sub> D <sub>10</sub>	1719-06-8
Phenanthrene-d10	100 ug/mL	C <sub>14</sub> D <sub>10</sub>	1517-22-2
Fluorene-d10	100 ug/mL	C <sub>13</sub> D <sub>10</sub>	811103-79-9
Fluoranthene-d10	100 ug/mL	C <sub>16</sub> D <sub>10</sub>	93951-69-0
Benzo[ <i>a</i> ]anthracene-d12	100 ug/mL	C <sub>18</sub> D <sub>12</sub>	1718-53-2
Chrysene-d12	100 ug/mL	C <sub>18</sub> D <sub>12</sub>	1719-03-5
Pyrene-d10	100 ug/mL	C <sub>16</sub> D <sub>12</sub>	1718-52-1
Benzo[ <i>a</i> ]pyrene-d12	100 ug/mL	C <sub>20</sub> D <sub>12</sub>	63466-71-7
Benzo[ <i>b</i> ]fluoranthene-d12	100 ug/mL	C <sub>20</sub> D <sub>12</sub>	93951-98-5
Benzo[ <i>k</i> ]fluoranthene-d12	100 ug/mL	C <sub>20</sub> D <sub>12</sub>	93952-01-3
Indeno[1,2,3- <i>cd</i> ]pyrene-d12	100 ug/mL	C <sub>22</sub> D <sub>12</sub>	203578-33-0
Benzo[ <i>g,h,i</i> ]perylene-d12	100 ug/mL	C <sub>22</sub> D <sub>12</sub>	93951-66-7
<i>P</i> -Terphenyl-d14	1000 ug/mL	C <sub>18</sub> D <sub>14</sub>	1718-51-0

## 2.3 Sampling and sample preparation

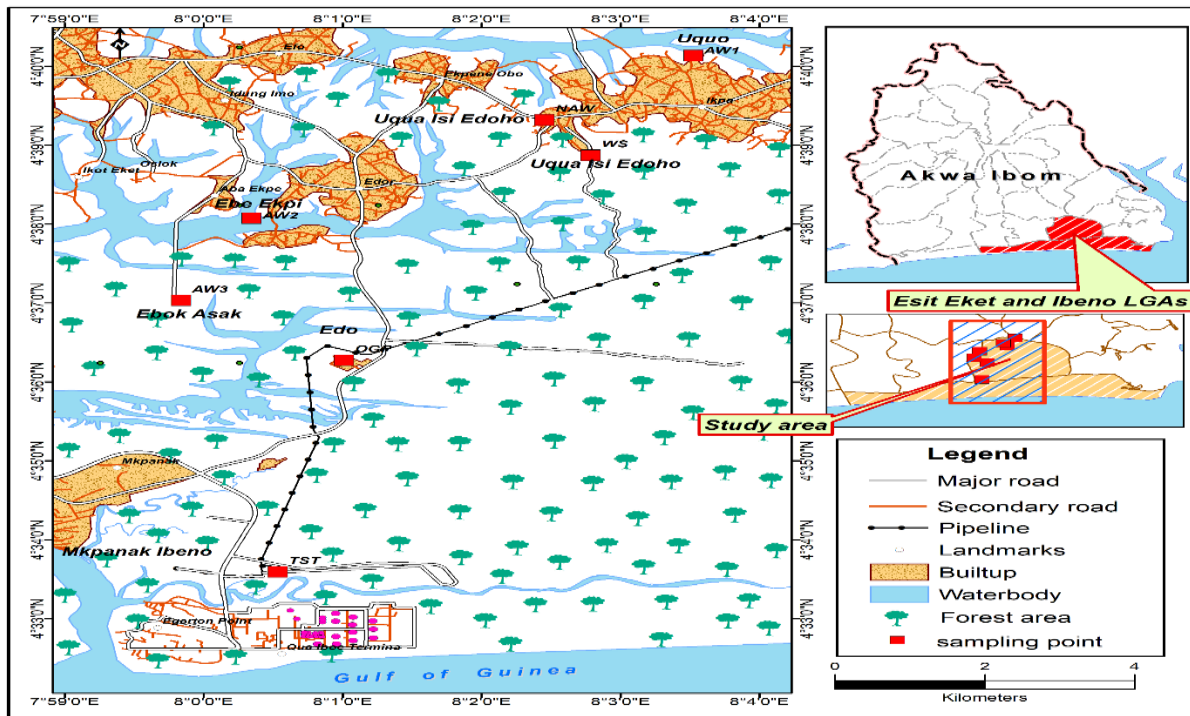
### 2.3.1 Study Sites

Akwa Ibom state is an oil and gas producing state, located in the coastal south-eastern part of the Niger Delta of Nigeria. It is a humid tropical zone, with an average rainfall of 2426.3 mm

per annum. It has two seasons, a wet (or rainy) season from April to October which peaks in August, and a short dry season occurring from November to mid-March each year with a peak in January. During the wet season, the wind blows from the south-west traversing the Atlantic Ocean, conversely, the dry season is often characterised by a dusty and cool dry wind referred to as harmattan in Nigeria; the predominant air mass is from the northeast through the Sahara Desert (Hayward and Oguntoyinbo, 2019). Additionally, the average temperature range is from 26°C – 29°C under normal conditions and relative humidity of 70-80%.

The inhabitants of the settlement are of multi-ethnic groups and exhibit cultural diversity. Their sources of livelihood and income are trading, fishing, farming, and oil working. Akwa Ibom state is comprised of 36 local government areas of which Esit Eket and Ibeno local government constitutes one of them but situated in a rural area as shown in Figure 1.1b. The population of Esit Eket is about 71,267 and Ibeno 72,880, respectively (Atser and Udoh, 2015). The two regions share boundaries and are situated at the same coastal line on the Atlantic Ocean and are made up of diverse communities. These local government areas were chosen because of their oil-related activities and the constant flaring of gases by Frontier, Exxon Mobil, and other oil companies. Hence, seven different sampling locations were investigated in the study area as shown in Table 2.3 and Figure 2.1 - defining their operational activities and coordinates.

**Figure 2-1 Locations of Esit Eket and Ibene in the South-eastern in Akwa Ibom State, Niger Delta region of Nigeria**



**Table 2-3 Description of sample locations**

Sampling Locations	Activities	Sampling Code	Northings	Eastings
Uquo	Active Well 1	AW1	N04° 40' 08.3"	E008° 03' 31.6"
Mkpanak Ibene	Temporary Storage and transfer Area	TST	N04° 33' 35.6"	E008° 00' 32.2"
Edo	Oil and gas Production sites	OGP	N 04° 36' 16.6'	E 008° 01' 00.7
Uqua Isi Edoho	Workstation	WS	N04° 38' 52.4"	E008° 02' 47.3"
Ebe Ekpi	Active well 2	AW2	N04° 38' 54.7"	E008° 00' 20.8"
Ebok Asak	Active well 3	AW3	N04° 37' 02.0"	E007° 59' 50.5"
Uqua Isi Edoho	Non -active well	NAW	N04° 39' 19.3"	E008° 02' 27.4"

### 2.3.2 Soil sampling

Duplicate surface soil samples taken to 5 cm depth were collected with a DCM-rinsed hand shovel at the centre and each corner of a 2 m × 2 m square grid (Wang et al., 2018b) and the resulting five soil samples were then homogenised to form a composite. This process was repeated for all locations studied. Soil samples were taken in May 2019 for the wet season and February 2020 for the dry season. Each oil and gas contamination site - particularly the active regions - were further delineated into sub-sections to distinguish areas heavily impacted by oil production-related activities from moderately or minimally affected ones. Some soil samples were collected close to the air sampling points, specifically between 10 and 200 metres from the air samplers.

For the wet season of sampling, samples were taken from all seven different sites (see table 2.3). However, the dry season was quite challenging due to a new company policy that restricted locations at which soil samples could be collected, as well as Covid-19 related restrictions at the early stage. Hence, during the second sampling season, we collected soil samples from only four locations: oil and gas production sites(OGP), storage and transfer area(FUN), active oil well-undergoing drilling(AW1) during sampling , and workstation(WS). Also, pictures could not be taken on sites due to the company's health and safety policy. Overall, the total number of soil samples collected were 200 for both seasons, however, only 140 were analysed due to time constraints. 20 was extracted in wet season but was not clean up due to time limitation to develop a new method for clean-up or removal of the oily components. Following careful removal of debris, like large stones and plant roots, samples were wrapped in pre-cleaned aluminium foil and labelled appropriately. Each sample was placed separately in a sealed plastic bag, stored at  $\leq -20^{\circ}\text{C}$  at the company's laboratory cooling system and was shipped to the University of Birmingham, UK under frozen conditions and stored in the University of Birmingham cold room at  $4^{\circ}\text{C}$  until extraction.

### **2.3.2.1 Pre-treatment of soil**

The choice of sample preparation method, due to the volatility of PAH compounds is important, as it exerts a tremendous influence on the outcome of quantification (Beriro et al., 2014, Narizzano et al., 2013, Belkessam et al., 2005, Khan et al., 2005, Berset et al., 1999). Freeze drying has been recommended as the pre-treatment method of choice to remove moisture from samples before extraction and analysis by BS EN 16179:2012 (Beriro et al., 2014). This technique is efficient for removing moisture without losses of PAH that may occur during other drying processes (Berset et al., 1999, Khan et al., 2005). Besides, it removes bias in the estimation of PAH concentrations and therefore yields better recoveries (Berset et al., 1999), as such, freeze-drying was adopted in this project. Soil samples were then freeze-dried using a Christ Beta 1-8 LSCplus instrument, at -25°C for 40 hours. Following freeze-drying, soil samples were homogenised and sieved by passing through a brass sieve of aperture 2 mm mesh before storage in an amber glass jar at 4°C until chemical analysis.

### **2.3.3 Passive air sampling**

Passive air sampling (PAS) was also conducted seasonally across six sampling locations, with an average sampling period of 21 days. The initial phase of the campaign was between April 2019 and May 2019 (wet season) and the second phase was from December 2019 to February 2020 (dry season). The details of a weekly report for meteorological conditions for these periods was taken to reflect the actual temperature of the environment based on the activities of these oil and gas companies (impact of gas flaring on weather conditions) while meteorological data from Nigeria Meteorological Agency (NiMET) was also taken for comparison.

Before the deployment, instructions on how to assemble and where to deploy the passive air samplers were given to the participants. An email was sent to the participants on the appropriate time and deployment procedures in advance of the author's arrival on site in February 2020 to

undertake the second sampling campaign. Due to the physicochemical properties of PAH targeted, the passive air sampling method developed and validated at the University of Birmingham by (Abdallah and Harrad, 2010) was designed to sample both the gaseous and particulate matter in this study. The rationale for choosing the passive air sampling technique over other sampling techniques is that they are cost-effective and easy to operate (Tao et al., 2009). In addition, they give a time-weighted average (TWA) concentration of the studied air pollutants, which is beneficial for such monitoring studies (Hazrati and Harrad, 2007). Furthermore, the issue of noise is eliminated, and PAS do not require electricity to function, thereby expanding the range of locations where they may easily be deployed (Hazrati and Harrad, 2007).

Following the sampling event, the sampling media comprising a polyurethane foam (PUF) disk and a glass fibre filter (GFF) were collected, wrapped individually in aluminium foil to avoid photodegradation and placed in sealed plastic bags stored at  $\leq 4^{\circ}\text{C}$ . Then, the PUFs and GFFs were transported to the University of Birmingham, UK and stored in the University of Birmingham laboratory under identical conditions as soil samples until extraction.

**Figure 2-2 Passive air sampler deployed at a sampling location**



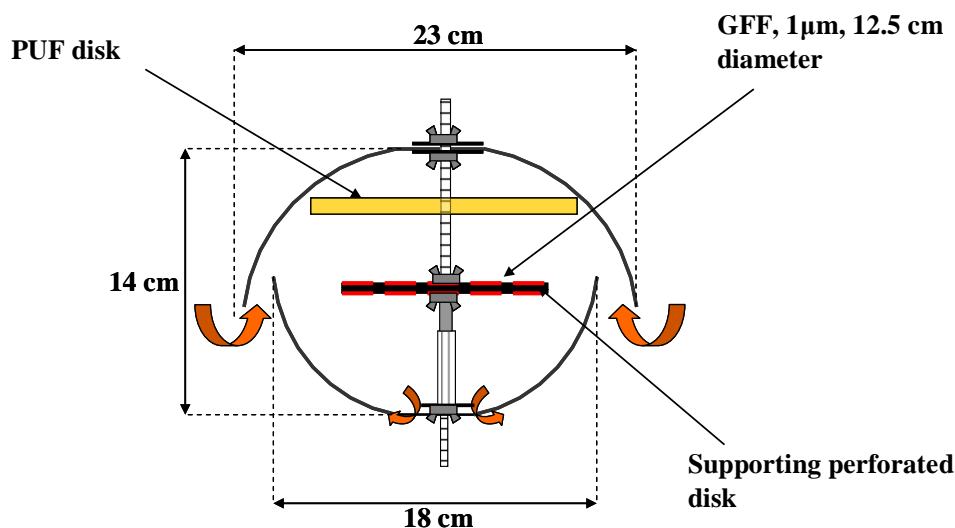
### **2.3.3.1 Configuration and treatment of passive air samples**

The samplers used in this study all followed the same design consisting of a PUF disc (140 mm diameter, 12 mm thickness, 360.6 cm<sup>2</sup> surface area and density 0.07 g/cm<sup>3</sup> PACS, Leicester, UK) and a GFF (125 mm diameter, 1 μm pore size; Whatman, Little Chalfont, UK) as the sampling media. They were both completely encased within two stainless steel shelters; the upper shelter was two-litre volume and 23 cm diameter and the lower shelter a one litre volume of 18 cm diameter. The purpose of the stainless-steel housing is to protect the PUF disc and filter from sunlight and precipitation. To reduce the possibility of particle foraging by the stainless-steel samplers, the interior part of the top sheltering was covered with aluminium foil and thoroughly rinsed with solvents (dichloromethane (DCM) and hexane) (Abdallah and Harrad, 2010) to avoid cross contamination.

Within the sampler housing, with the aid of solvent rinsed tweezers, a PUF designed to collect gaseous phase PAHs was fitted 1 cm beyond the lip of the shelter exposing the downward face, to prevent deposition of particles gravitationally while the GFF with surface facing upward,

suspended on a circular wire gauze (supporting the GFF) was placed in the middle of the sampler housing to entrap particle-phase PAH. Both halves were then assembled with bolts ensuring an opening for airflow into the samplers as depicted in Figure 2.3.

**Figure 2-3 Schematic diagram of the passive air sampler configuration used to sample gaseous and particulate phase PAHs in outdoor ambient air**



**(Abdallah and Harrad, 2010)**

The stainless-steel housing, bolts, and nuts were washed with detergent and rinsed with tap water, dried in an oven at 100 °C for 1 hour. The housing and other parts were further rinsed in DCM and wrapped in aluminium foil been pre-cleaned with DCM. To remove any organic contaminants, GFFs were individually wrapped in aluminium foil and preconditioned by baking at 450 °C for 5 hours in a Carbolite™ oven (Carbolite-Ger, Hope, UK). PUF disc(s) were washed in running tap water and dried under normal room temperature before being pre-extracted in a pressurised liquid extraction (PLE) system (ASE-350, Thermo Fisher, Waltham, MA, USA) using DCM: hexane (1:1) at 90 °C, using a pressure of 1500 psi with a flush time of 5 minutes, a static cycle time of 4 minutes and purge time of 120 seconds in 1 static cycle. The cleaned PUF disc(s) were then air-dried in a clean fume hood for a few minutes before wrapping individually in aluminium foil. Prior to deployment, the sampler housing, PUFs and GFFs were separately placed in sealed black bags and transported to the sampling destination.

## **2.4 Extraction**

### **2.4.1 Soil Sample Extraction**

Sample extraction was performed using sonification according to USEPA method 3550C (Jiao et al., 2009, Ray et al., 2008, Agarwal et al., 2006) with modification.

Samples were allowed to stand for 10 minutes at room temperature before weighing. Two g of dried soil was weighed accurately in a 12 mL centrifuge tube and spiked with a known amount of deuterated internal standard mixture (100 ng). One g of elemental copper powder was added to eliminate inorganic sulphur in the spiked matrix to avoid interference when using Gas chromatography and mass spectrometer (GC-MS). Five mL of 1:1 (v/v) hexane/DCM was added to the sample, the tube was covered with aluminium foil to avoid loss of the analyte and standard by evaporation, and vortexed for 2 minutes for thorough mixing of the tube contents. Extraction was conducted in an ultrasonic bath (Grant ultrasonic bath, UK) for 20 minutes at 25 °C. Sample tubes were centrifuged for 5 min at 3500 rev/min and the supernatant was transferred into a clean test tube. The extraction cycle was repeated three times using a fresh 5 mL aliquot of 1:1 (v/v) hexane/DCM every time, the supernatant was collected and pooled in the same clean test tube.

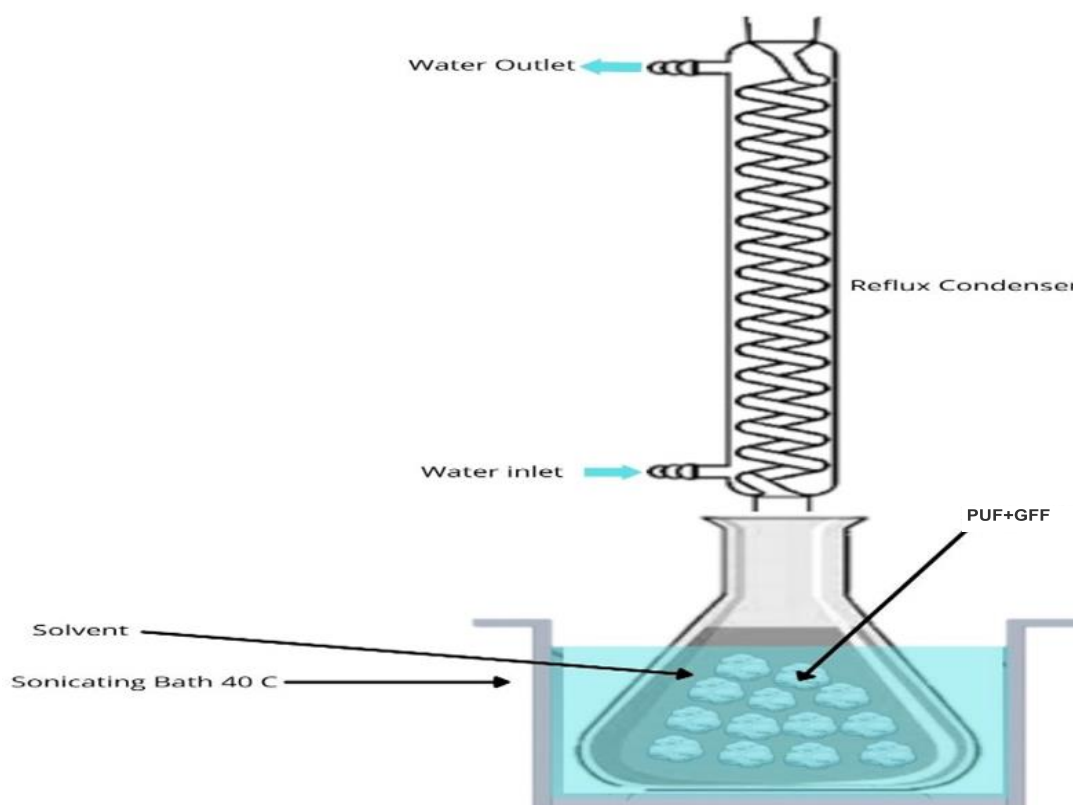
### **2.4.2 Extraction of PUF and Glass Fibre Filter**

To enhance the surface area for extraction, the PUF and filter for each sample were cut into 8 roughly equal pieces in the fume hood with the aid of a stainless-steel scalpel that had been previously rinsed with solvents(DCM and Hexane) to avoid contamination before commencing solvent extraction.

Both media were combined and placed inside a 250 mL Erlenmeyer conical flask; the sample was spiked with a known amount of a mixture of deuterated PAH as internal standards (ISs) and the same extraction solvent (DCM: hexane (1:1)) was added. The conical flask was connected to a reflux column to prevent solvent loss via evaporation, and the apparatus was

introduced into a sonicating bath (Analogue ultrasonic bath, UK). PUFs and filters were then extracted by ultrasonication in a water bath at a temperature of 40 °C for 20 minutes as shown in figure 2.4. This extraction process was repeated three times with fresh solvents using 200 mL first and then 150 mL and 150 mL for the second and third extractions.

As a result of the large volume of extracting solvent used for this process, the combined extracts were transferred into a 200 mL Turbovap tube and evaporated using a Turbovap® II (Biotage Uppsala, Sweden) under a gentle stream of nitrogen (~20 °C) to reduce sample volume to approximately 1 mL before extract purification.



**Figure 2-4 Schematic diagram of the extraction system for PUFs and GFFs**

## 2.5 Clean-up

The concentrated sample extracts were then reduced by evaporation under a gentle stream of nitrogen at 30°C to approximately 1 mL for clean-up. All crude extracts of soil and air were subjected to the same purification procedure. Purification of sample extracts is an important

component of environmental analysis that reduces impurities that might have been extracted along with the target compounds, thereby minimising the presence of compounds that might interfere with the analysis of analytes.

The concentrated solvent extracts were cleaned up by introducing them onto a solid phase extraction (SPE) column pre-packed with 2 g of Florisil® (60-100 mesh, Sigma Aldrich) as sorbent material. DCM and *n*-hexane were utilized as the mobile phase, the cartridges were pre-washed/conditioned with 10 mL of DCM first and then with 10 mL of *n*-hexane before placing the 1 mL crude extract to the head of cartridges.

The loaded extract on the column was allowed to equilibrate for 1 min, before target compounds were eluted with 15 mL of hexane: DCM (2:1 v/v) at a constant flow rate of 1 mL/min. The eluate collected in the test tube was then evaporated to near dryness under a gentle stream of nitrogen at 30 °C. The sample was immediately reconstituted in 100 µL of *p*-terphenyl-*d*<sub>14</sub> used as recovery standard with nonane added as a keeper, sonicated for 30 seconds, transferred into a vial, and capped ready for analysis by Gas Chromatography and Mass Spectrometry (GCMS).

## **2.6 GC-MS analysis of PAH**

Separation and quantification of PAH in both soil and air samples were carried out using a gas chromatograph (GC, Agilent 6890N Network, Agilent, Technologies) coupled with a Mass Selective Detector (MSD, Agilent 5973 Network, Agilent Technologies). One µL of the sample was injected at a temperature of 280 °C into the GC capillary column in splitless mode. An Agilent HP-5MS column (5% phenyl methyl siloxane) capillary column (30 m x 0.25 mm i.d. x 0.25 µm film thickness) was used to conduct GC/MS analysis of PAH, with Helium used as carrier gas at a fixed flow rate of 1 mL/min.

The initial programme GC oven temperature was set at 100 °C and held for 1 minute, increased at 6 °C /min to 120 °C, before ramping at 4 °C/min to 300°C and held for 5 minutes. This led

to an overall run time of 59.0 minutes. The mass spectrometer was operated in electron ionisation (EI), selective ion monitoring mode (SIM) mode.

For optimization of the detector sensitivity and good response, auto-tuning and manual tuning were conducted on the GC-MS using abundant stable ions  $m/z$  69, 219, 264, and 502 from the tuning reference compound (perfluoro-tri-n-butylamine - PFTBA) before injecting any sample extract, in accordance with our research group Quality Assurance and Quality Control (QA/QC) protocols.

**Table 2-4 Molecular ion and retention times for the identification and quantification of PAH target compounds**

<b>Target compound</b>	<b>M+ (Quantifier) or target Ion</b>	<b>Retention time (minutes)</b>
Acenaphthylene	152	17.50
Acenaphthene	153	18.40
Fluorene	166	21.21
Phenanthrene	178	26.59
Anthracene	178	26.88
Fluoranthene	202	33.48
Pyrene	202	34.76
Benzo[ <i>a</i> ]anthracene	228	41.87
Chrysene	228	42.05
Benzo[ <i>b,k</i> ]fluoranthene	252	47.91
Benzo[ <i>a</i> ]pyrene	252	49.39
Indeno[1,2,3- <i>cd</i> ] pyrene	276	54.51
Dibenz[ <i>a,h</i> ]anthracene	278	54.68
Benzo[ <i>g,h,i</i> ]perylene	276	55.67

**Table 2-5 Internal standard molecular ions and retention times for the identification and quantification of PAH**

<b>Internal Standard</b>	<b>M+</b>	<b>Retention time (minutes)</b>
Acenaphthene-10	162	18.30
Phenanthrene-d10	188	26.46
Anthracene-d10	188	26.86
Fluorene-d10	176	21.10
Fluoranthene-d10	212	33.37
Pyrene-d10	212	34.64
Benzo[a]anthracene-d12	240	41.75
Chrysene-d12	240	42.10
Benzo[b,k]fluoranthene-d12	264	47.80
Benzo[a]pyrene-d12	264	49.26
Indeno[1,2,3- <i>cd</i> ] pyrene-d12	288	54.40
Benzo[g,h,i]perylene-d12	288	55.51
<i>p</i> -Terphenyl-d14	244	36.1

## **2.7 Validation of analytical procedure and principles of Quality assurance/Quality control (QA/QC).**

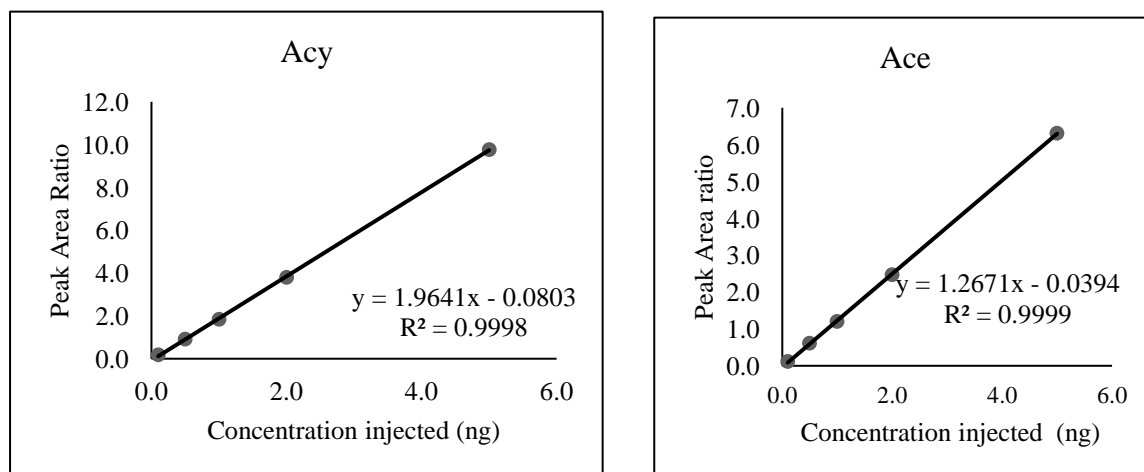
To minimise contamination, all glassware was cleaned by soaking in a solution containing Lipsol detergent (Scilabware Ltd), followed by rinsing with tap water and deionised water. Washed glassware was then baked at 500 °C for 6 hrs, rinsed with DCM and hexane, and covered with aluminium foil to prevent further contamination. The QA/QC approaches employed in this project are in accord with the standard operating procedures within the University of Birmingham's POPs/Emerging Contaminants research group.

### 2.7.1 Principles of identification and Quantification of Analytes

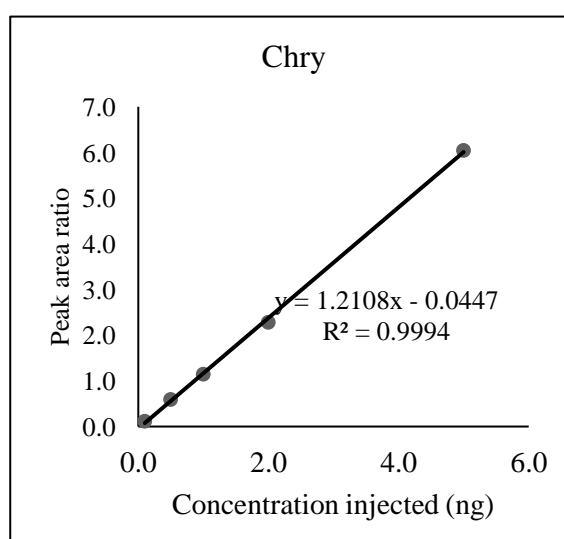
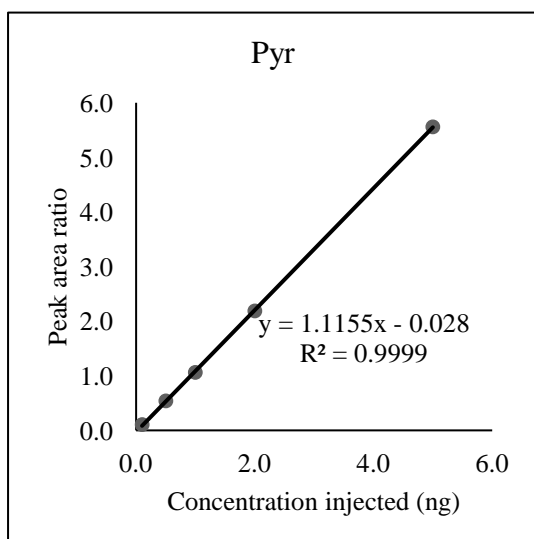
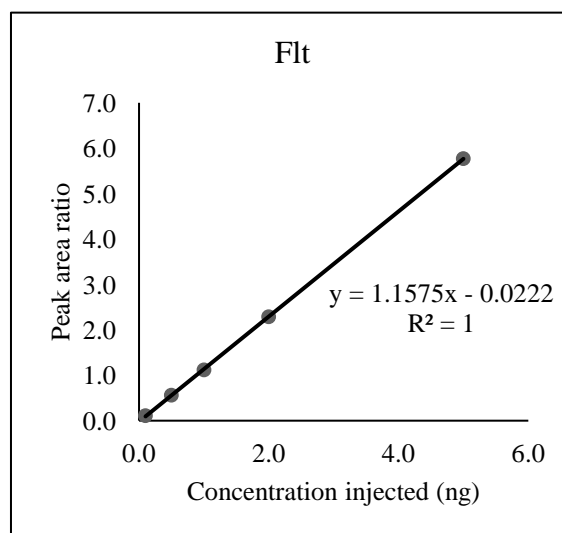
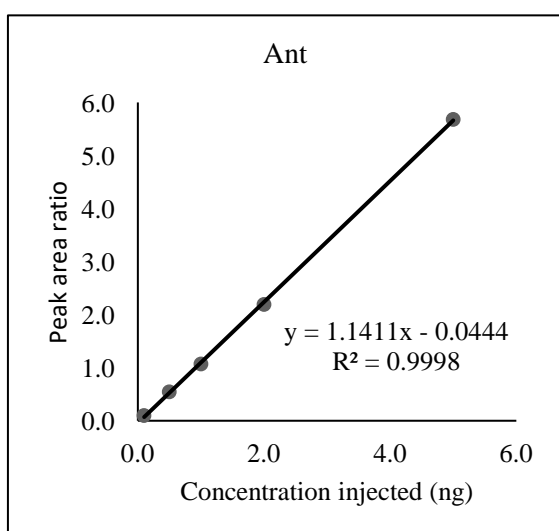
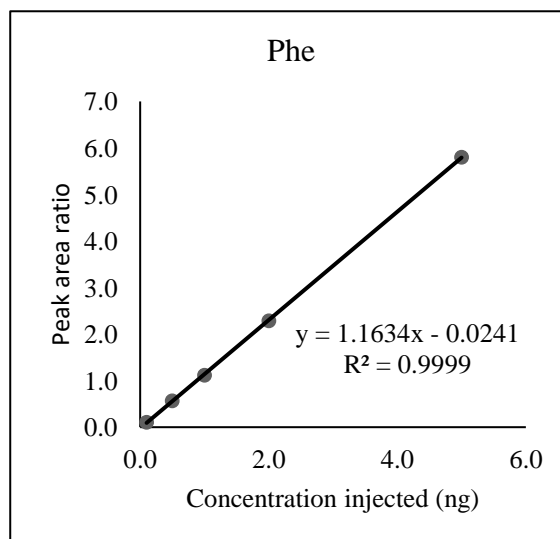
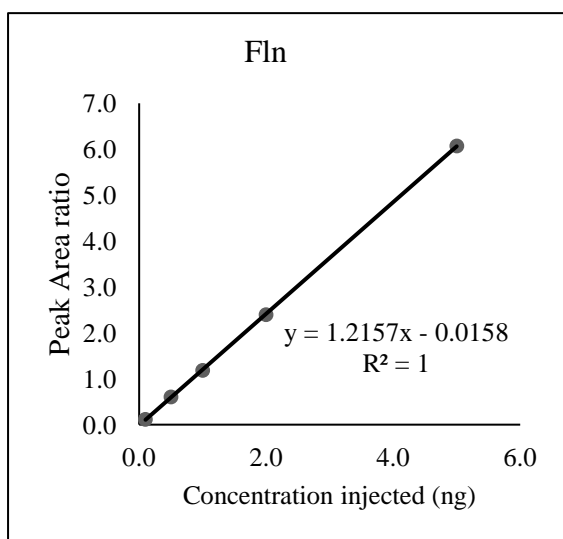
PAH in each of the samples were identified and confirmed by the retention time (Rt) of each peak, combined with the designated quantifier and qualifier mass for each analyte. Therefore, to evaluate the response of the MS, a full 5-point calibration plot with five(5) levels of concentration of native PAH, whilst internal and recovery determination standards remained at the same concentrations (1 ng/uL), were performed for each target compounds and to determine retention times. Native concentrations in the 5 calibration standards were: 0.5 ng/uL, 0.1 ng/uL, 1 ng/uL, 2 ng/uL, and 5 ng/uL. Correlation coefficient ( $R^2$ ) values typically exceeded 0.99 for all target determinants, reflecting an excellent linearity of response. Figure 2.5 shows some illustrative calibration plots for individual compounds.

In addition, relative response factors (RRFs) were measured for each of the calibration standards, as our method followed the internal standard quantification principle. The rationale is that the internal standard inherently corrects for losses that may arise during sample preparation and fluctuations in instrumental response. This assumption is most valid when the internal standard used is an isotopically labelled analogue of the native analyte being quantified.

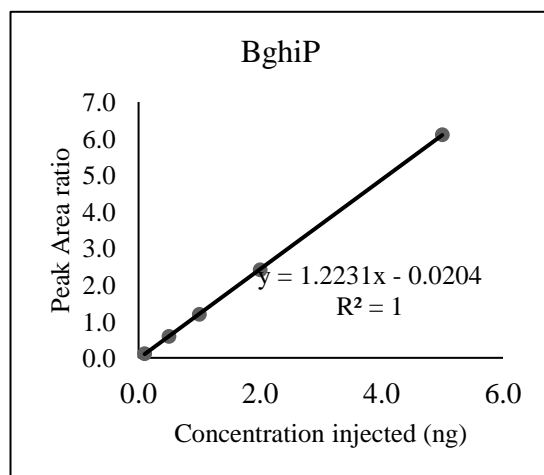
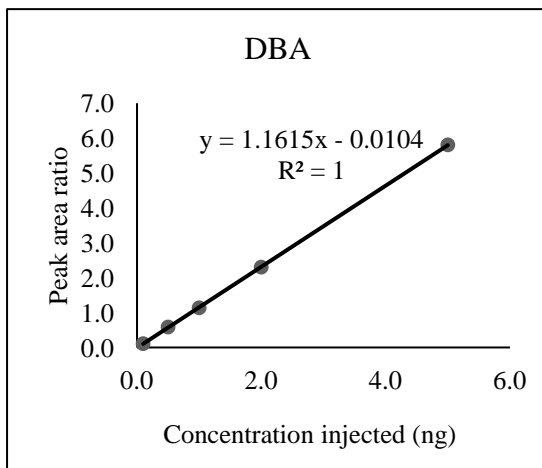
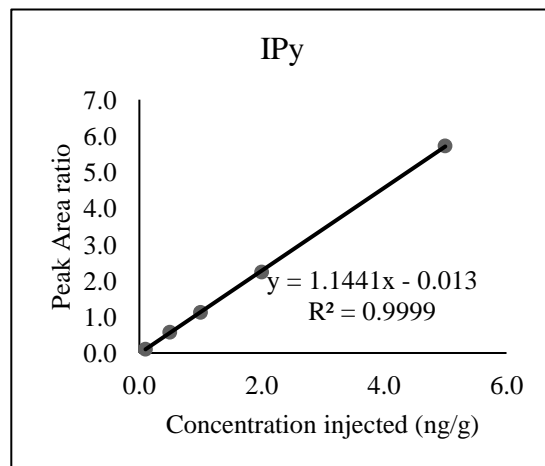
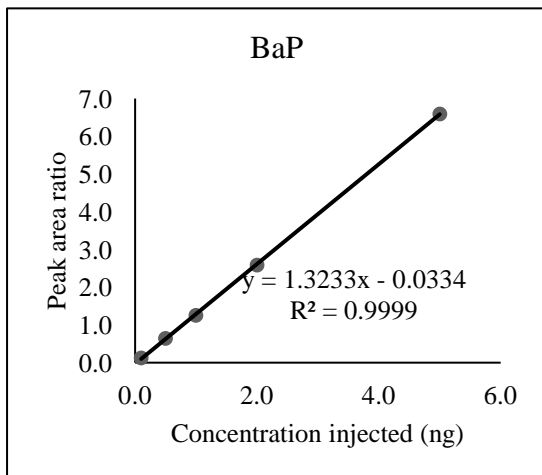
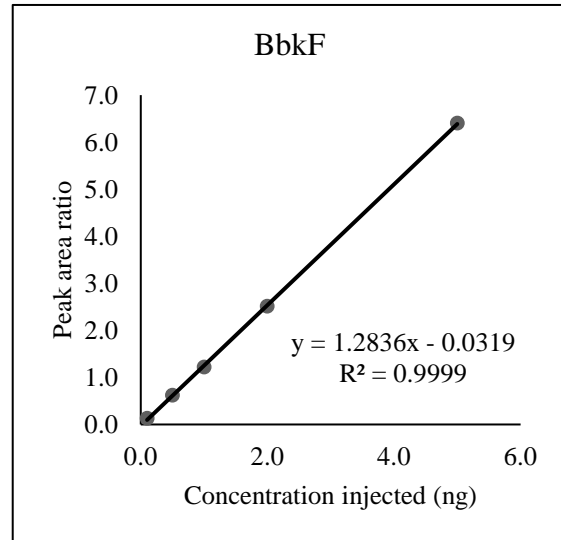
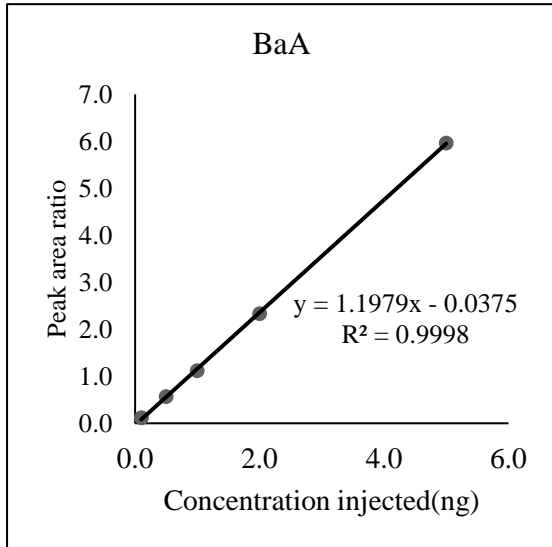
**Figure 2-5 Calibration curves for the quantification of all PAH measured in this study**



**Figure 2.5(Cont.): Calibration curves for the quantification of all PAH measured in this study**



**Figure 2.5(Cont.): Calibration curves for the quantification of all PAH measured in this study**



The RRF is defined as ‘the instrument response for a unit amount of target pollutant relative to that obtained for the same amount of the internal standard’ (IS) (Harrad, 2014)

RRF is therefore expressed as

$$\text{RRF} = (A_{\text{NAT}}/A_{\text{IS}}) \times (C_{\text{IS}}/C_{\text{NAT}}) \dots\dots\dots (1)$$

The term native refers to the unlabelled target compounds. RRF is the relative response factor,  $A_{\text{NAT}}$  is the peak area of the native compounds,  $A_{\text{IS}}$  the peak area of the internal standard,  $C_{\text{IS}}$  the concentration of internal standard, and  $C_{\text{NAT}}$  the concentration of the native.

Ideally, values of the RRF for each of the 5-point calibration standards would be uniform. For the target compounds in this study, the relative standard deviation (RSD) of the response factor is within the acceptable value of 10%. Table 2.6 gives the values of RRF for each calibration standard, the average, and the RSD values.

Certain conditions need to be met before a chromatographic peak can be established for quantification in a sample.

1. Signal to noise ratio (S/N) for that analyte must exceed 3:1
2. The relative retention time (RRT) of the peak in the sample must fall within  $\pm 0.2\%$  of the average value determined for the same compounds in the two calibration standards ran before and after each batch of samples.

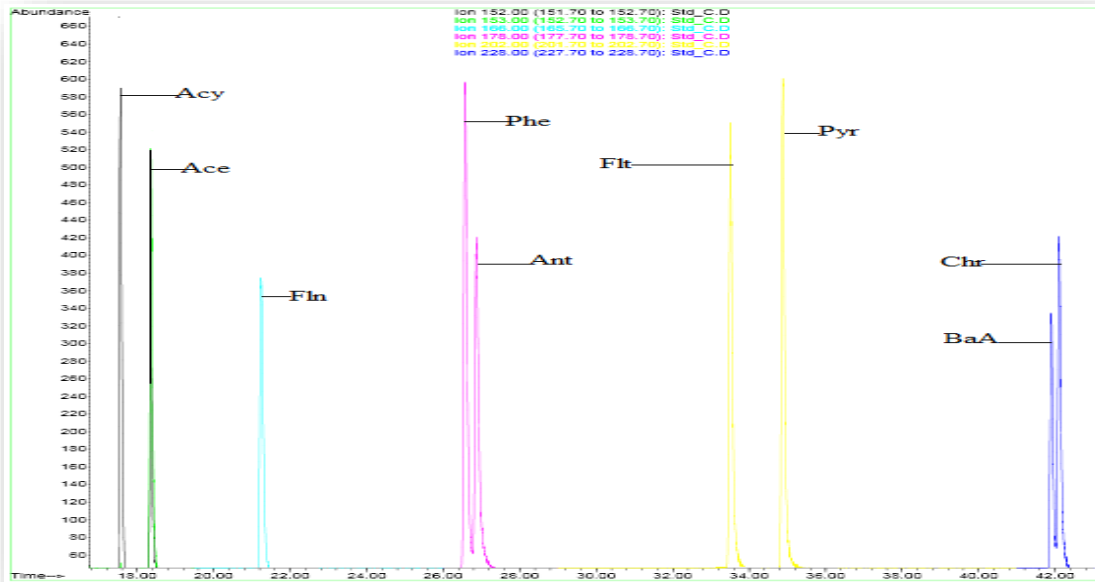
**Table 2-6 Relative response factors (RRF) for target PAHs at 5 calibration levels.**

PAH Compounds	RRF of Calibration Standards							
	0.1	0.5	1	2	5	Average	SD	RSD%
Acy	1.851	2.06	2.09	2.006	1.804	1.962	0.128	6.50
Ace	1.084	1.184	1.218	1.216	1.108	1.162	0.062	5.38
Fln	1.073	1.18	1.196	1.193	1.078	1.144	0.063	5.49
Phe	1.056	1.129	1.139	1.136	1.014	1.095	0.056	5.16
Ant	1.019	1.118	1.181	1.148	1.078	1.109	0.063	5.67
Flt	1.01	1.093	1.12	1.117	0.997	1.067	0.06	5.58
Pyr	1.006	1.083	1.129	1.12	1.02	1.072	0.056	5.27
BaA	1.108	1.14	1.244	1.196	1.109	1.159	0.059	5.13
Chr	0.976	1.109	1.136	1.188	1.092	1.1	0.078	7.12
BbkF	1.255	1.22	1.351	1.271	1.197	1.259	0.059	4.70
BaP	1.095	1.111	1.245	1.245	1.207	1.181	0.073	6.17
IPy	1.223	1.072	1.24	1.165	1.116	1.163	0.07	6.06
DBA	0.811	0.865	0.889	0.979	0.931	0.895	0.064	7.16
BghiP	1.158	1.094	1.163	1.19	1.133	1.148	0.036	3.16

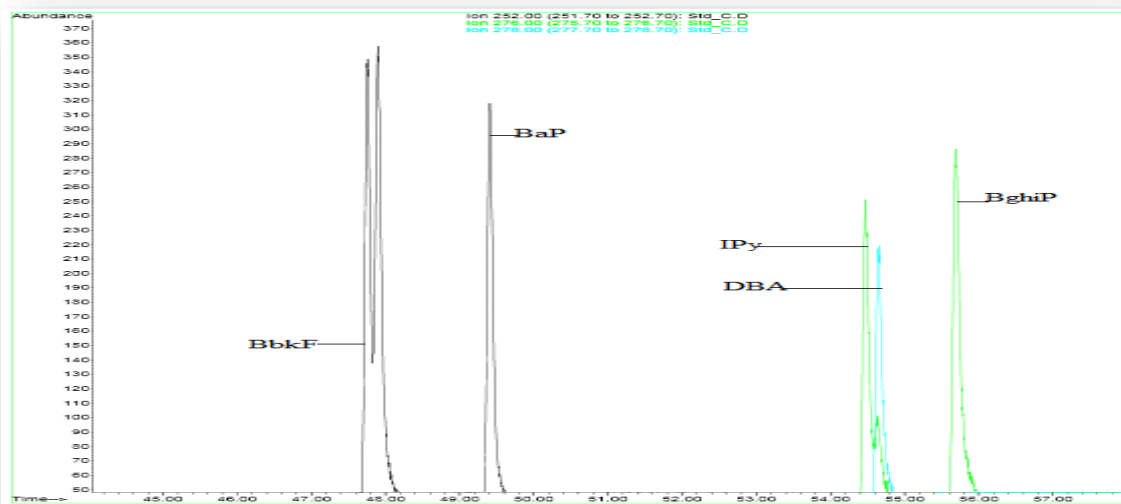
The elution order of PAH in the calibration standard with IS and RDS (Std C) is as shown in Figures 2.6,2.7 and 2.8.

**Figure 2-6 GC-MS chromatograms showing elution order of PAH standards in calibration standard (STDC) (a&b)**

(a)

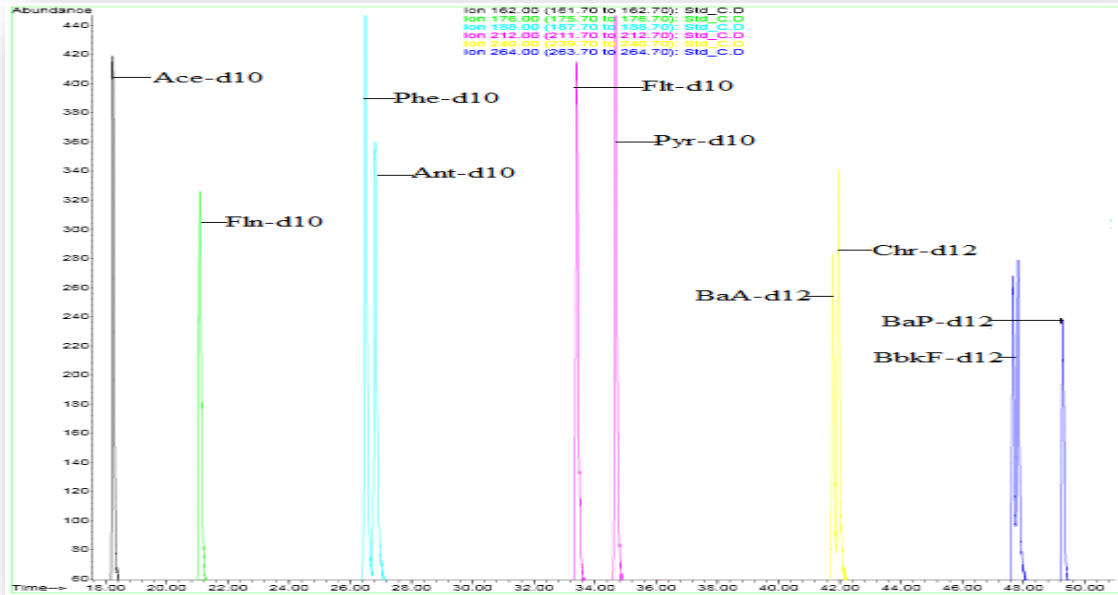


(b)

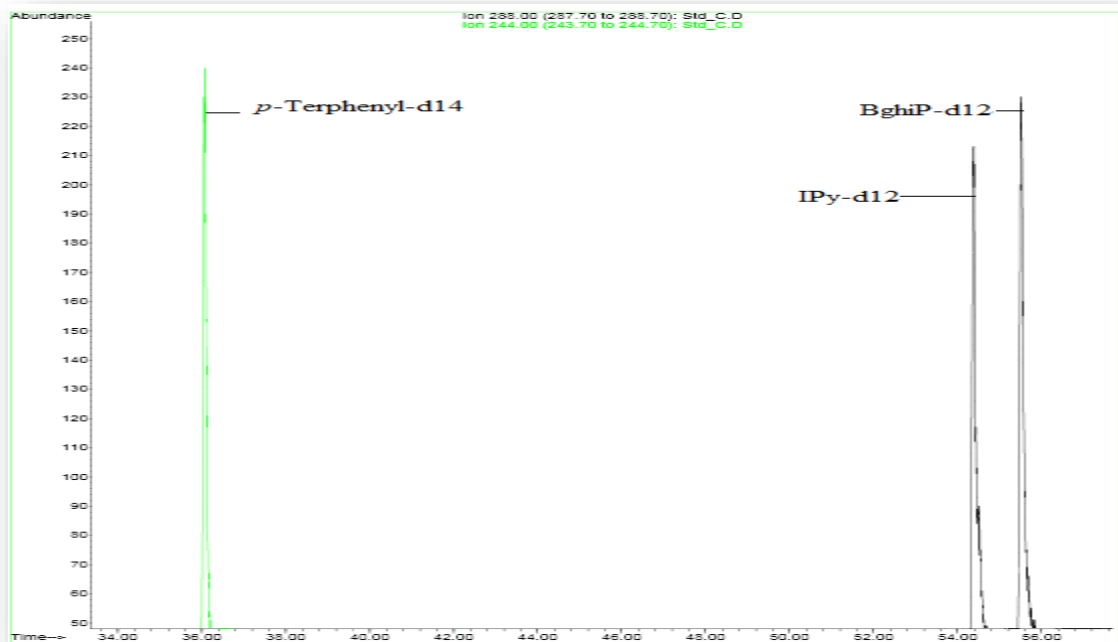


**Figure 2-7 GC-MS chromatograms showing elution order of internal and recovery determination standards in calibration standard (STDC) (a&b)**

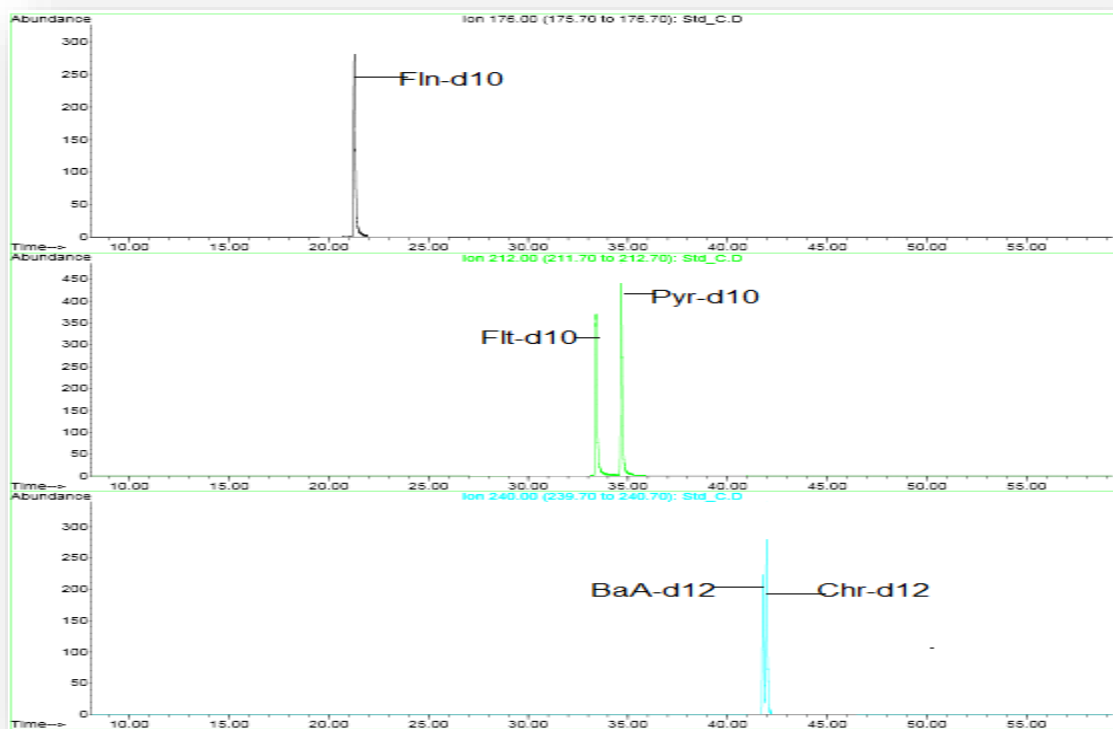
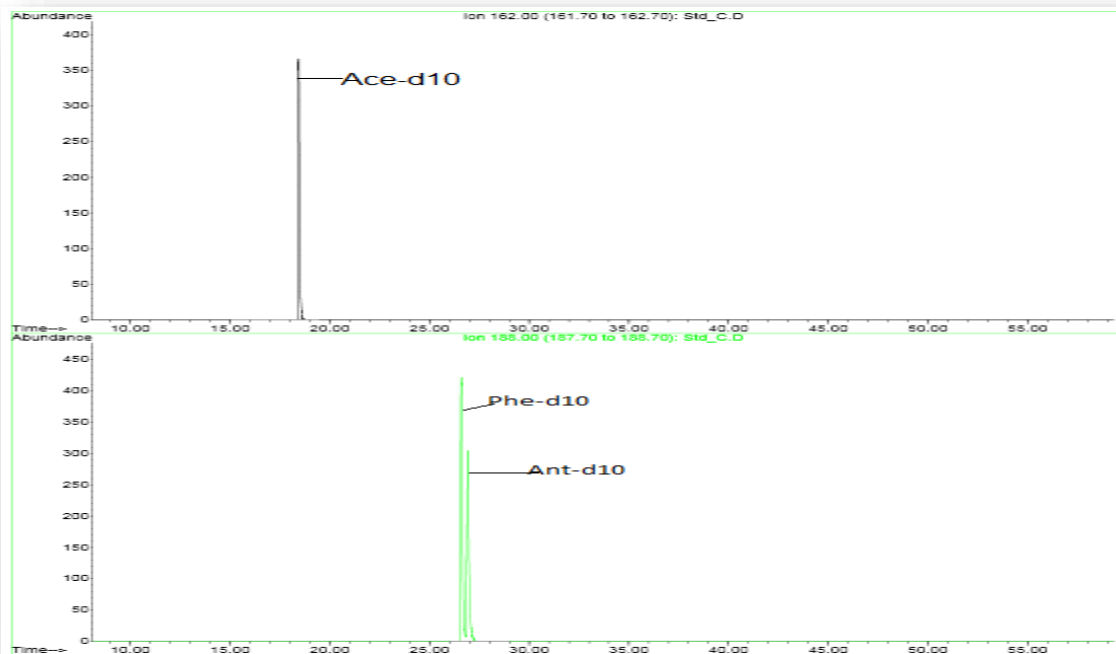
(a)

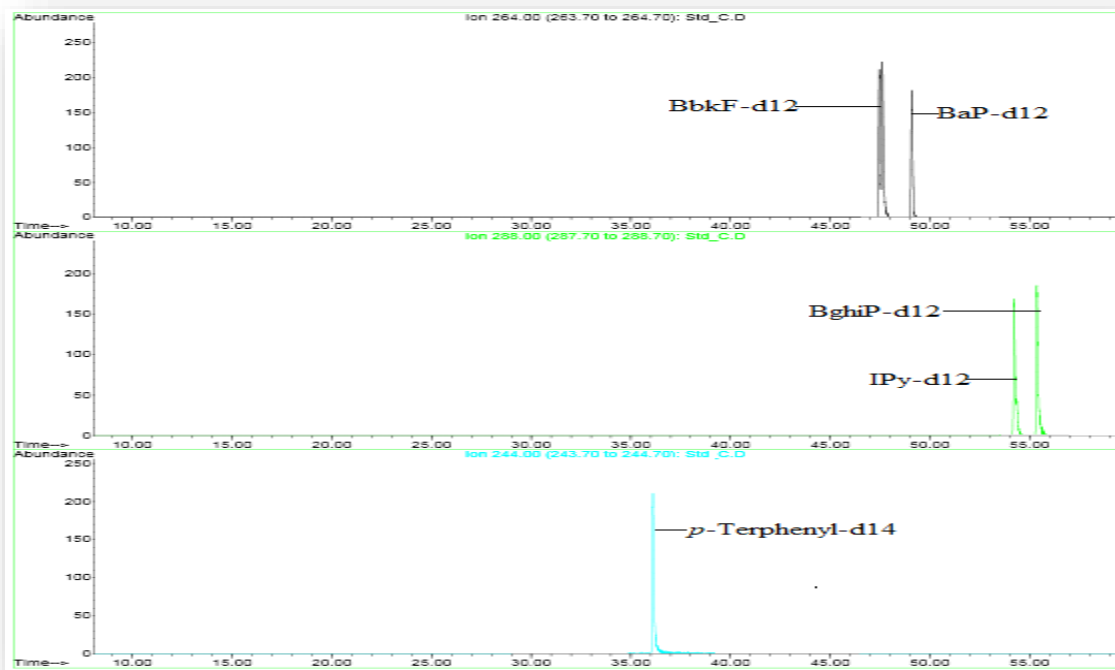


(b)



**Figure 2-8 GC-MS chromatograms showing elution order of individual PAH standards in calibration standard (STDC) and recovery standard**





Recoveries of IS added during sample extraction and purification were assessed through the addition of recovery determination standard (RDS) to the final extract before MS analysis. These were calculated to determine the overall loss of IS throughout sample preparation. The IS recovery calculation for each sample was based on the following equation:

$$\% \text{IS Recovery} = \left[ \left( \frac{A_{\text{IS}}}{A_{\text{RDS}}} \right)_S \times \left( \frac{A_{\text{RDS}}}{A_{\text{IS}}} \right)_{\text{STD}} \times \left( \frac{C_{\text{IS}}}{C_{\text{RDS}}} \right)_{\text{STD}} \times \left( \frac{C_{\text{IS}}}{C_{\text{RDS}}} \right)_S \right] \times 100 \dots \dots (2)$$

Where  $(A_{\text{IS}}/A_{\text{RDS}})_S$  is the ratio of the peak area of the internal standard to that of the recovery determination standard in the sample and  $(A_{\text{RDS}}/A_{\text{IS}})_{\text{STD}}$  corresponds to the peak area of the recovery determination standard to that of the internal standard in the calibration standard run in the same batch as the samples.  $(C_{\text{IS}}/C_{\text{RDS}})_{\text{STD}}$  is the concentration of the internal standard to that of the recovery determination standard in the calibration standard, while  $(C_{\text{RDS}}/C_{\text{IS}})_S$  represents the concentration of the recovery determination standard to that of the internal standard in the sample.

**Table 2-7 Descriptive statistics of IS recoveries for air samples in this study expressed as percentages**

<b>Standard</b>	<b>Mean</b>	<b>SD*</b>	<b>Median</b>	<b>Minimum</b>	<b>Maximum</b>
d10-Acenaphthene	85	15	84	63	114
d10-Fluorene	87	22	89	52	129
d10-Phenanthrene	83	14	86	58	98
d10-Anthracene	92	4	93	86	100
d10-Fluoranthene	82	11	81	68	95
d10-pyrene	91	7	94	78	99
d12-benzo[ <i>a</i> ]anthracene	94	13	98	73	113
d12-chrysene	89	14	88	70	109
d12-benzo[ <i>b,k</i> ]fluoranthene	79	16	80	53	100
d12-benzo[ <i>a</i> ]pyrene	92	13	94	67	109
d12-indeno[1,2,3- <i>cd</i> ] pyrene	74	19	76	50	102
d12-benzo[ <i>ghi</i> ]perylene	86	11	91	62	96

\* SD standard deviation

**Table 2-8 Descriptive statistic of IS recoveries for soil samples in this study expressed as percentage**

Standard	Mean	SD*	Median	Minimum	Maximum
d10-Acenaphthene	78	16	77	49	102
d10-Fluorene	82	21	86	46	113
d10-Phenanthrene	78	20	72	48	106
d10-Anthracene	74	20	78	45	124
d10-Fluoranthene	87	19	88	54	129
d10-pyrene	80	15	83	55	106
d12-benzo[ <i>a</i> ]anthracene	89	16	96	60	111
d12-chrysene	86	14	84	66	117
d12-benzo[ <i>b,k</i> ]fluoranthene	81	13	83	56	107
d12-benzo[ <i>a</i> ]pyrene	85	20	86	49	119
d12-indeno[ <i>1,2,3-cd</i> ] pyrene	87	20	86	59	118
d12-benzo[ <i>ghi</i> ]perylene	79	18	76	48	114

\* SD standard deviation

### **2.7.2 Accuracy and Precision determination**

Assessment of analytical method accuracy and precision was achieved by using standard reference material SRM 2585 (organic contaminants in house dust) and SRM 1941b (Organics in marine sediment) both from the National Institute of Standards and Technology (NIST). These reference materials are characterised to an adequate standard or concentration to quantify our target compounds and others. Replicate analysis of these certified materials was conducted to assess the accuracy and reproducibility of PAH analysis. The results obtained reveal good and low relative standard deviation when compared with values from the certified PAHs in the tables below, indicating satisfactory precision. The mean concentrations and standard deviation data attained in this study are shown in table 2.9 and table 2.10. For ongoing quality assurance of our analytical methodology, one SRM sample was analysed alongside every batch of five samples.

**Table 2-9 Average Concentrations (ng/g) of PAH measured in NIST SRM 1941b compared to Certified Values**

Analyte	Average $\pm$ standard deviation		Relative Standard Deviation (RSD%)
	Measured	Certified	
Fluorene	74.8 $\pm$ 4	85 $\pm$ 15	5.4
Phenanthrene	399.4 $\pm$ 32	406 $\pm$ 44	8.0
Anthracene	166.8 $\pm$ 18	184 $\pm$ 18	10.6
Fluoranthene	603 $\pm$ 45	651 $\pm$ 50	7.5
Pyrene	592 $\pm$ 45	581 $\pm$ 39	4.4
Benzo[ <i>a</i> ]anthracene	337.4 $\pm$ 23	335 $\pm$ 25	6.8
Chrysene	326.2 $\pm$ 20	291 $\pm$ 31	6.2
Benzo[ <i>k</i> ]fluoranthene	223.4 $\pm$ 6	225 $\pm$ 18	2.5
Benzo[ <i>b</i> ]fluoranthene	402.2 $\pm$ 34	453 $\pm$ 21	8.4
Benzo[ <i>a</i> ]pyrene	320.6 $\pm$ 48	358 $\pm$ 17	14.9
Benzo[ <i>ghi</i> ]perylene	357.6 $\pm$ 12	307 $\pm$ 45	3.3
Indeno[ <i>1,2,3-cd</i> ] pyrene	324.8 $\pm$ 30	341 $\pm$ 57	9.2
Dibenzo[ <i>a,h</i> ]anthracene	67.2 $\pm$ 3	53 $\pm$ 10	4.4

**Table 2-10 Average concentrations(ng/g) of PAH measured in NIST SRM 2585 compared to Certified Values**

Analytes	Average $\pm$ standard deviation (n=10)		Relative standard deviation (RSD%)
	Measured	Certified	
Phenanthrene	1928 $\pm$ 36	1920 $\pm$ 20	1.9
Anthracene	97 $\pm$ 2.5	96.0 $\pm$ 5.2	2.9
Fluoranthene	4431 $\pm$ 59	4320 $\pm$ 100	1.3
Pyrene	3353 $\pm$ 34	3290 $\pm$ 30	1
benzo[ <i>a</i> ]anthracene	1220 $\pm$ 42	1160 $\pm$ 54	3.6
Chrysene	2394 $\pm$ 64	2260 $\pm$ 60	2.8
benzo[ <i>a</i> ]pyrene	1146 $\pm$ 10	1140 $\pm$ 10	0.9
Indeno[ <i>1,2,3-cd</i> ] pyrene	2100 $\pm$ 41	2080 $\pm$ 100	2
Dibenzo[ <i>a,h</i> ]anthracene	311 $\pm$ 30	301 $\pm$ 50	9.8
Benzo[ <i>ghi</i> ]perylene	2301 $\pm$ 37	2280 $\pm$ 40	1.6

### 2.7.3 Analysis of Method and Field blanks

To evaluate the level of any contaminant resulting from the analytical process, method blanks were prepared and analysed precisely via the same approach as the samples. These blanks consist of 0.2 g anhydrous sodium sulfate in lieu of a sample, one blank sample was run approximately every 6<sup>th</sup> sample for soil sample.

In addition, field blanks for air samples comprising of a pre-extracted PUF and baked GFF were also conducted and treated the same as samples, including transportation to and from the sampling sites but without exposure to air. This is to assess contamination that may have arisen from sampling, handling, transportation, sample storage, and analysis. Method blanks were also prepared consisting of pre-extracted PUF and baked GFF that were not transported to the

sampling sites. These were also treated as samples, thereby providing an indication of contamination arising from sample analysis alone.

For both air and soil samples, none of the target compounds were detected in method blanks. However, a few compounds (phenanthrene, pyrene and fluoranthene) were found in the field blanks for air at very low concentrations. As these were below 5 % of the lowest amount detected in samples from the same batch, no blank correction was undertaken.

#### 2.7.4 Limit of detection determination

The limit of detection (LOD) is the smallest concentration of analyte that can give a signal to noise ratio of 3:1. Therefore, the LOD for each compound in this project was calculated on this basis. In addition, the sample detection limit (SDL) is calculated thus:

$$SDL = \frac{LOD \times FEV}{VFEI \times SS} \times \frac{100}{\%IS Recovery} \dots\dots\dots 3$$

Where FEV is the final extract volume (µL), VFEI is the volume of final extract injected (µL); SS is the sample size in m<sup>3</sup> for air or g for soil. %IS recovery being the percentage recovery of the internal standard used to quantify the target contaminant in a specific sample. Typical values of LOD and SDL are listed in Table 2.11.

**Table 2-11 Instrument and Sample Limits of detection for air and soil samples**

Compound	LOD (ng)	Soil samples	Air samples
		SDL (ng/g)	SDL (ng/m <sup>3</sup> )
Acy	0.003	0.19	0.03
Ace	0.004	0.22	0.03
Fln	0.004	0.22	0.03
Phe	0.002	0.16	0.02
Ant	0.004	0.25	0.03
Flt	0.003	0.17	0.03
Pyr	0.003	0.18	0.03
BaA	0.004	0.24	0.04
Chr	0.004	0.26	0.04
BbkF	0.004	0.21	0.02
BaP	0.005	0.29	0.02
IPy	0.008	0.44	0.63
DBA	0.010	0.55	0.05
BghiP	0.008	0.45	0.04

**SDL(LOQ)**

## 2.8 Sample concentration calculation

For every batch of samples analysed, a single calibration standard was injected before and at the end of each batch of samples and the average of the RRFs obtained for these two standards was used to quantify concentrations in samples from that batch, provided the average RRFs are within  $\pm 25\%$  of the previous RRFs ascertained from the standard in the original 5-point calibration. The concentration of the analytes is computed using equation (4)

$$\text{Concentration} = \frac{A_{\text{NAT}}}{A_{\text{IS}}} \times \frac{1}{\text{RRF}} \times \frac{M_{\text{IS}}}{\text{SS}} \dots\dots\dots (4)$$

Where.

$A_{\text{NAT}}$  = Peak area of the target analyte in a sample

$A_{\text{IS}}$  = Peak area of internal standard in sample

RRF = Relative response factor estimated from standards

$M_{\text{IS}}$  = mass of internal standard added to sample (ng)

SS = sample size ( $\text{m}^3$  or g).

## 2.9 Passive air sampling

It is necessary to calibrate passive samplers to convert the masses of the target analytes in PUF discs and GFFs to ambient air concentrations. Table 2.12 present the passive sampling rates for PAH, which were derived from outside sample rates from a previous study (Abdallah and Harrad, 2010, Tao et al., 2009). These rates were hence multiplied with the numbers of day (21days).

**Table 2-12 calculated outdoor passive sampling rate ( $\text{m}^3/\text{day}$ ) for PAH**

PAH homologues	Average sample rate
2-Ring	1.16
3-ring	0.67
4-ring	0.59
5-ring	1.2
6-ring	0.08

## 2.10 Statistical analysis

Statistical analysis of data was performed by a combination of Microsoft Excel (Microsoft Office versions 2010 and 365) and SPSS for Windows Version 27. All data in different locations were presented as  $\Sigma_{14}\text{PAH}$  in most circumstances/conditions to express their variation in measured PAHs concentrations, and for easy data comparison with other publications and

within this thesis. Likewise, range, minimum and maximum were also presented when appropriate. Concentrations of individual PAH at each site were employed to derive the percentage contributions to total PAH concentration and identify congener patterns.

The Shapiro-Wilks test and a visual evaluation of the quantile by-quantile graphic plot displayed on SPSS was performed to assess the distribution of PAH concentrations. Where data were found to be non-normally distributed, they were logarithmically (log) transformed. Parametric statistics were then conducted on the log-transformed data using either a t-test or one-way analysis of variance (ANOVA) with a Tukey honestly significant difference (HSD) post-hoc test if equal variance was assumed, or a Games-Howell test if equal variance was not assumed. Concentrations below LOQ were assumed to be equal half of LOQ for statistical purposes. P-values less than 0.05 ( $<0.05$ ) were considered statistically significant.

## Chapter 3

### **Spatial and seasonal variation in concentrations of Polycyclic Aromatic Hydrocarbon in soil from oil and gas fields in Akwa Ibom state, Nigeria**

#### **3.1 Abstract**

Concentrations of PAH were measured in soil samples from seven different oil and gas fields in wet season and four various fields in dry (active and non-active sites) in Esit Eket and Ibeno in Akwa Ibom state, Nigeria. In locations where diverse oil and gas activities were conducted, soil samples were taken at different sublocations in the same sites. Our findings indicated variability in concentrations of PAH in sublocations within the active sites and were linked to the activities carried out on the fields as well as varied distances from potential PAH sources. Evaluation of PAH concentrations via analysis of variance (ANOVA) and independent t-test revealed that significant differences exist in PAH concentrations between different sublocations in the same sites. When data were examined based on a location-by-location in each season (wet and dry). Concentrations of  $\Sigma_{14}$ PAH in active sites varied considerably from those in non-active sites (OGP  $\Sigma_{128}$  ng/g, AW3  $\Sigma_{99.9}$  ng/g, AW2  $\Sigma$ , TST  $\Sigma_{94}$  ng/g, AW1  $\Sigma_{38.4}$  ng/g, NAW  $\Sigma_{22.7}$  ng/g, WS  $\Sigma_{26.5}$  ng/g) in the wet season. However, in the dry season, PAH concentrations were substantially higher at AW1 (820 ng/g) than OGP (200.9 ng/g) TST (196 ng/g) and then WS 44 ng/g.

Statistically significant differences were found in most of the locations but no statistically significant difference was detected between concentrations of PAH at crude oil transfer area (TST) and workstation (WS) in wet season. Input from various oil and gas activities were the primary source of elevated PAH concentration.

When data in all seven locations in wet season combined and in four locations dry season locations also combined, it was shown that the concentrations of  $\Sigma_{14}$ PAH dry greatly exceeded those in wet season significantly ( $P < 0.05$ ) according to pair t-test. The result from six carcinogenic PAH in wet and dry period showed varying contamination level, with the highest at average concentrations of observed at AW3 (73 ng/g) and AW1 (56.9 ng/g) in wet and dry period while the lowest was detected in NAW (12 ng/g) and WS (10.7 ng/g) in wet and dry period. The profiles based on different ring number that 3-4 ring were the primary contributor of PAH in both wet and dry season. The PAH concentration in the present study shows weakly to moderate contamination.

## **3.2 Sampling Strategy**

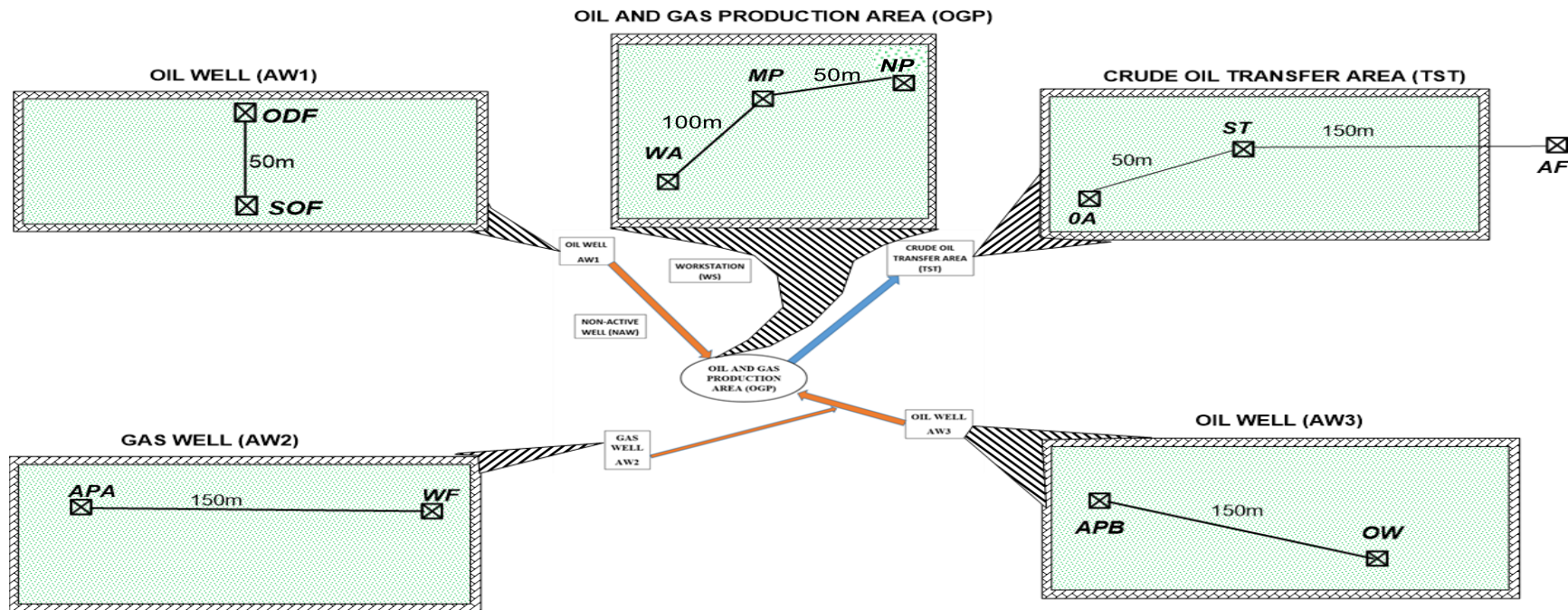
### **3.2.1 Soil Sampling and location**

Soil samples were collected from two distinct areas (Esit Eket and Ibeno – see Chapter 2) in May 2019 and February 2020 to characterise the levels of PAH pollution in these environments. Section 2.1 in the previous chapter, describes the sampling methods in detail. In Esit Eket, six sampling sites were investigated for the measurement of PAH and one sampling site from Ibeno for the wet season, while in the dry season due to organisational restructuring and impacts of the coronavirus, samples were obtained from three sampling sites at Esit Eket and one sampling site at Ibeno.

Table 3.1 lists the various locations and activities conducted at these; while Figure 3.1 shows the position of the locations and where applicable, the sub-locations from which samples were collected. For instance, within the oil and gas central production plant (OGP) sampled, PAH were investigated in samples taken from three different sub-locations; specifically, workers' accommodation (WA, n=7), a sublocation partially impacted by pilot gas flaring and near the main processing area (n =7) (NP), and the main processing area (n=7) where crude oil was purified (MP). Samples were also collected at the Crude Oil Transfer Area (TST), where various companies transfer their crude oil, vent, and flare their gases, at three separate sub-locations: an office area (n=6) (OA), the surrounding area (n=6) (AF), and the storage tank and pump area (n=6) (ST). Gas field, oil field and cultivated farmland locations where the oil pipeline passes through were also investigated for target compounds at active well 2(Gas well) (AW2; n=10) and well 3(oil well) (AW3; n=20). We also sampled soil at a site (active well 1 (AW1; n=10)), where a well was drilled, capped, and abandoned during the first sampling season, a non-active well (NAW) (n=10) and a workstation (WS) (n=10) where workers reside during drilling and commission of sites for study for the wet season. It is important to know that soil samples were only collected from within the field for the AW1, NAW, and WS.

For the dry season, samples were taken from MP(n=6) and OA(n=4) only, due to the reason mentioned above in this section. Within the crude oil transfer area, soil samples were collected from office area (n=3) (OA), storage tank and pump area (ST) (n=4) and surrounding area (AF) (n=3). In addition, active oil well (AW1) with oil drilling activities was sampled, with samples also collected from within oil drilling field (ODF) (n=10) and surroundings of oil field (SOF) (n=3). Lastly, soils were collected from a workstation (WS) (n=8).

Figure 3-1 Schematic diagram of sampling locations indicating sub-locations and approximate distances



APA = along the pipeline right of way (gas), WF = within gas field area, OW = within oil well area, APB = along the pipeline right of way (oil well), ST = storage tank and pumps area, OA = office area, AF = surroundings of crude oil field/pipeline area, WA = worker's accommodation, MP = main processing area, NP = near processing area and gas flaring area, ODF = within oil drilling field, and SOF = surroundings of oil drilling field

**Table 3-1 Sampling locations sampled, and activities conducted**

Sampling Area	Code	Activities	Sampling month & year
Oil and gas Production facility	OGP	Processing of crude oil and gas, along pilot gas flaring	May, 2019
			February, 2020
Crude oil transfer area	TST	Storage and transfer and of crude oil from OGP to other terminal/flaring of gas by other companies	May, 2019
			February, 2020
Oil Well	AW1	Abandoned well(non-active)	May, 2019
		Oil installation and drilling operations commences	February, 2020
Gas Well	AW2	Gas exploration well	May, 2019
			February, 2020
Oil Well	AW3	Oil exploration well	May, 2019
			February, 2020
Non-active Well	NAW	Drilled but lost well	May, 2019
			February, 2020
Workstation	WS	Worker's Lodgings during exploitation and exploration of wells	May, 2019
			February, 2020

### **3.3 Results and discussion**

#### **3.3.1 Concentration of PAH during wet season sampling**

##### **3.3.1.1 Levels of PAH at crude oil and gas production plant (OGP) in wet season**

Crude oil and gas production plant soil samples analysed from the OGP location were categorised into three sub-locations. Surface soil samples were taken from the worker's accommodation area (WA), from a partially impacted area near the main processing area and close to the pilot flaring area (NP), and lastly samples were collected from within the main processing area (MP).

The PAH concentrations in surface soil samples varied greatly depending on the sub-locations and the distance from the contamination source. The mean concentrations of  $\Sigma_{14}\text{PAH}$  for the three OGP sub-locations fell between 34.6-60.6 ng/g at worker's accommodation (WA) with an average of 46.5 ng/g, 68.4-318 ng/g at the main processing area (MP) with an average of 201 ng/g, and 69.7-183 ng/g, average of 137 ng/g in the NP sub-location samples respectively. Table 3.2 summarises the statistical parameters for individual PAH concentrations found in surface soil samples from the three OGP sub-locations studied, while figure 3.2 shows the total individual components of PAH mixtures at the different OGP sub-locations.

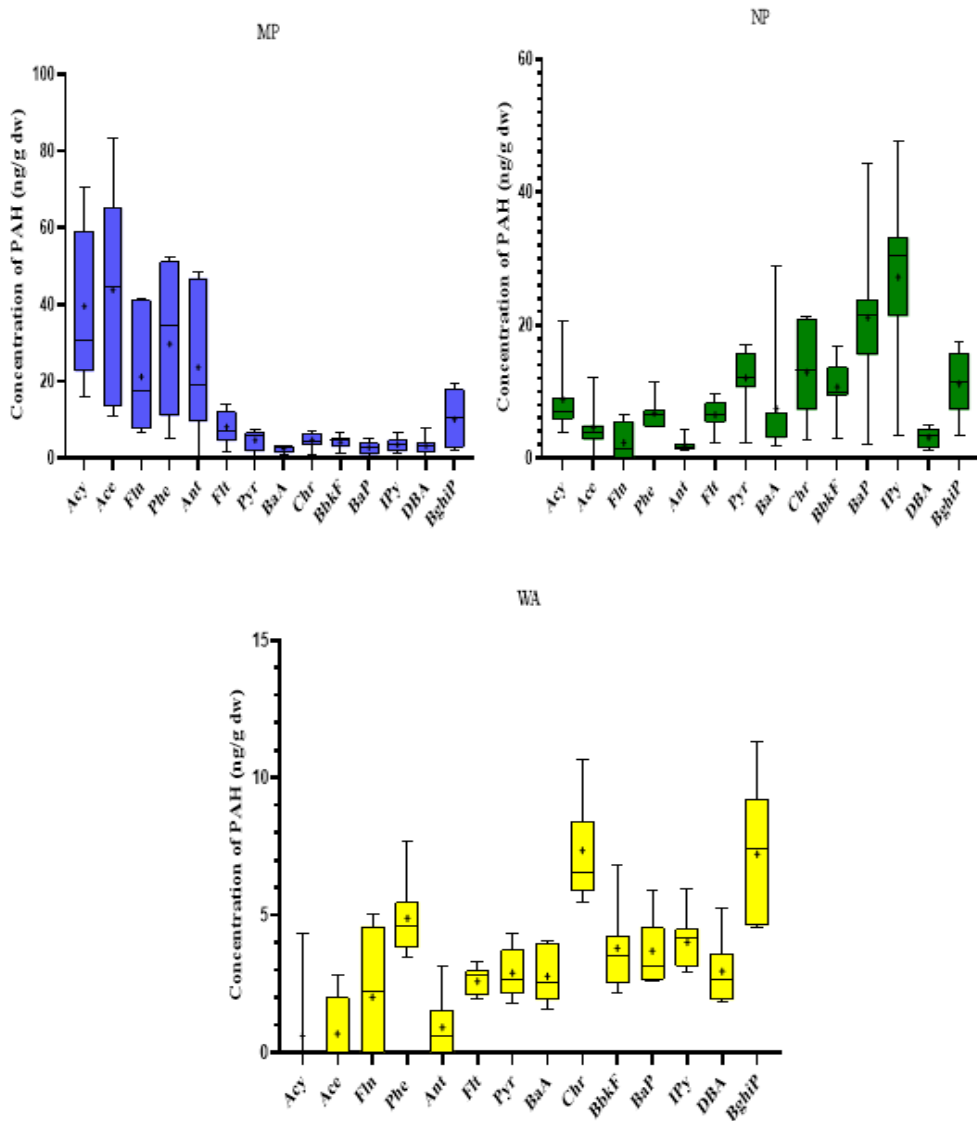
We found the highest level of PAH in the main processing area (MP), followed by the site close to the processing and gas flaring area (NP) which is 50m away from the main processing area. While the lowest total mean concentrations were observed at the workers' accommodation with 100 m away from MP. The variation in concentrations is likely due to differences in oil and gas contributions of PAH to the total burden in each sub-location. Concentrations of those PAH considered probable or known human carcinogens were also examined. As we could not measure BbF and BkF separately due to coelution, we report the sum of both compounds as BbkF, and total carcinogenic PAH ( $\Sigma\text{PAH}_{6C}$ ) as the sum of BaA, Chr, BbkF, BaP, DBA, and IPy. Surface soil samples from NP had the maximum  $\Sigma\text{PAH}_{6C}$  concentrations with an average

of 83 ng/g and a range of 14.5 to 118 ng/g. Those at WA ranged from 17.3 to 32 ng/g, average of 24.6 ng/g, while those at MP were the lowest, ranging from 5.9 to 26 ng/g with an average of 20.5 ng/g. Furthermore, concentrations of BaP which is classified as the most hazardous carcinogenic PAH ranged from 2 – 44.4, 2.6-5.9 and 0.6-5 ng/g with means of 21, 3.7, and 2.8 ng/g in NP, WA, and MP respectively. Our findings suggests that NP has a higher concentration of carcinogenic PAH than the other OGP sub-locations.

Statistical analysis of differences in PAH concentrations among sub-locations was undertaken, after testing the normality of the dataset using Shapiro-Wilk and log transforming where appropriate. The test reveals significant variation ( $p < 0.05$ ) in concentrations of  $\Sigma_{14}$ PAH in surface soil from the three sub-locations.

$\Sigma_{14}$ PAH concentrations at both MP and NP sub-locations significantly exceeded ( $p < 0.05$ ) those at WA. This may be due to anthropogenic input from crude oil processing at MP with intermittent oil leakages from the pipeline raising concentrations at NP. This is in addition to potential input from deposition from the continuous flaring of gas. This is consistent with the argument that PAH can enter the soil through atmospheric deposition (Mostert et al., 2010), as well as from direct spillage. Besides, poor actions in Nigeria to limit gas flaring and venting activities have resulted in incomplete gas combustion and the attendant emission of organic chemicals like PAH (Ite and Ibok, 2013). We observed no statistically significant difference ( $p > 0.05$ ) between  $\Sigma_{14}$ PAH concentrations at MP and NP.

**Figure 3-2 Concentration of individual PAH in samples from different sub-locations in the oil and gas area(OGP)**



**Box plots of PAH concentrations (ng/g, dw) in crude oil and gas production plant(OGP). The plus sign(+) indicates the average, the middle line of the box represents the median PAH concentrations, the bottom and top lines of the box is the 25th percentile and 75th percentile PAH concentrations, while the minimum and maximum is represented by top and bottom lines of the y-error bars .Note that WA(workers' accommodation), MP (processing area) and NP (near flare and processing area)**

**Table 3-2 Summary of PAH Concentrations(ng/g) in soil from oil and gas Production Field (OGP) from three different locations**

PAH	WA					MP					NP				
	Average	SD	Min	Median	Max	Average	SD	Min	Median	Max	Average	SD	Min	Median	Max
Acy	0.6	1.6	<LOQ	<LOQ	4.3	39.6	20.1	16.0	30.8	70.6	8.8	5.5	3.8	7.1	20.7
Ace	0.7	1.2	<LOQ	<LOQ	2.8	43.8	26.8	10.8	44.4	83.3	4.6	3.7	<LOQ	4	12.2
Fln	2	2.2	<LOQ	2.3	5	21.2	14.7	6.5	17.3	41.5	2.3	2.7	<LOQ	1.3	6.5
Phe	4.9	1.4	3.5	4.6	7.7	29.7	19.4	5.2	34.3	52.4	6.7	2.3	4.7	6.6	11.4
Ant	0.9	1.2	<LOQ	0.6	3.1	23.6	18.4	<LOQ	19.2	48.4	2	1	1.3	1.6	4.3
Flt	2.6	0.5	2	2.9	3.3	8.1	4.5	1.5	6.9	14	6.5	2.4	2.3	6.6	9.7
Pyr	2.9	0.9	1.8	2.7	4.3	4.7	2.8	<LOQ	5.9	7.5	12.1	4.9	2.3	12.2	17.1
BaA	2.8	1.0	1.6	2.6	4.1	2.4	0.9	1.0	2.7	3.3	7.5	9.6	1.8	3.2	29.0
Chr	7.4	1.8	5.5	6.6	10.7	4.7	2.1	0.9	4.4	7.2	12.9	6.9	2.7	13.3	21.2
BbkF	3.8	1.5	2.2	3.5	6.9	4	1.7	1.2	4.7	6.4	10.7	4.3	2.9	9.9	16.9
BaP	3.7	1.2	2.6	3.2	5.9	2.8	1.6	0.6	2.7	5.1	21.1	12.6	2.1	21.5	44.4
IPy	4	1.1	2.9	4.2	6	3.5	1.9	1.3	3.5	6.7	27.2	13.7	3.4	30.4	47.7
DBA	3	1.2	1.8	2.7	5.2	3.2	2.4	0.6	3.1	7.8	3.1	1.4	1.1	3.5	5
BghiP	7.2	2.5	4.6	7.4	11.3	10.1	6.8	2.1	10.7	19.3	11.2	4.8	3.5	11.5	17.4
Σ14PAH	46.5	10	34.6	46.8	60.6	201.2	86.9	68.4	191.3	318	136.7	39	69.7	144.8	183.1
ΣPAH <sub>6C</sub>	24.6	0.6	17.3	26.7	32	20.5	7.5	5.9	24.3	26.1	82.5	34.3	14.5	90.7	117.9

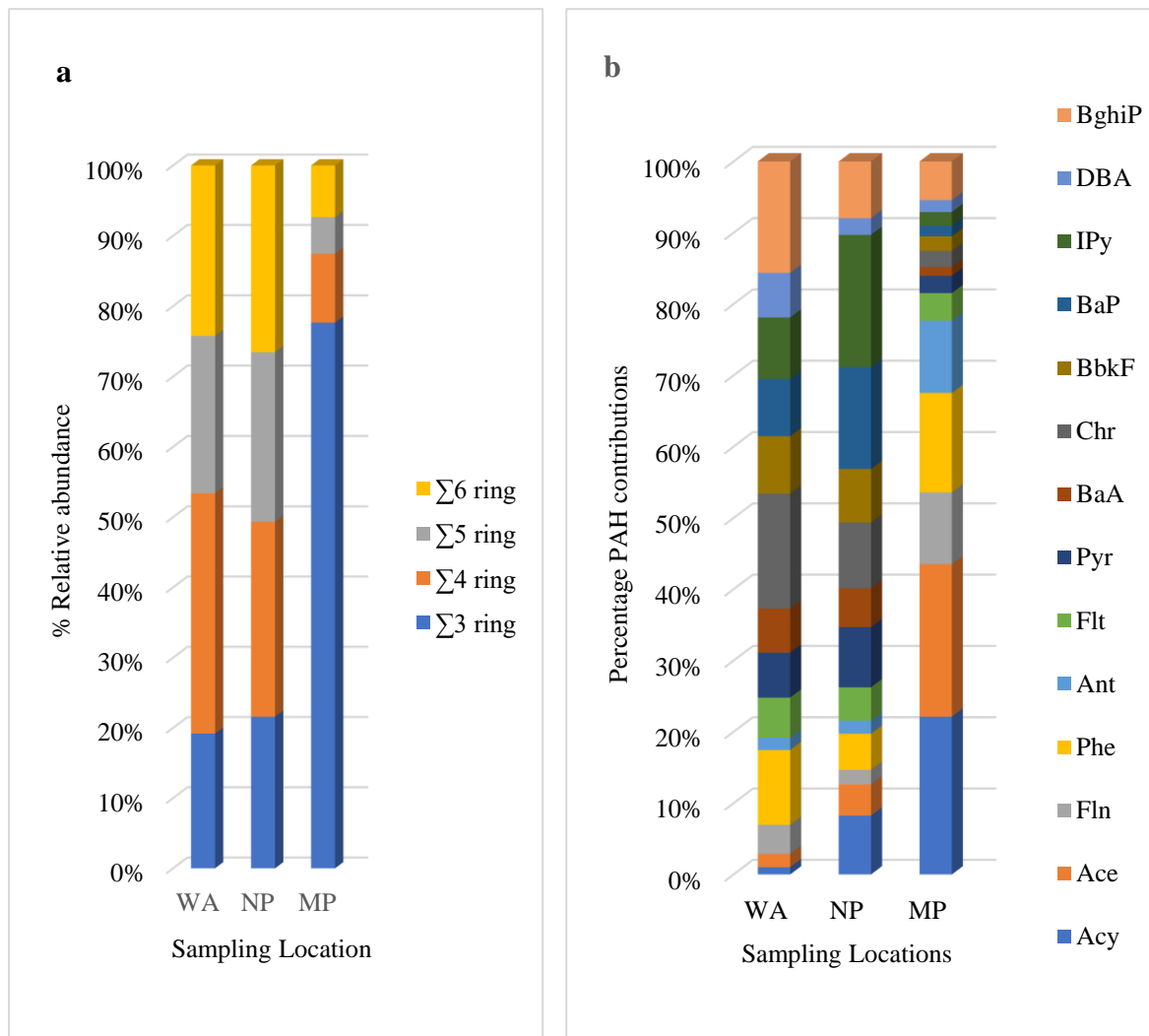
**Location-WA worker's accommodation, MP main processing area, NP near processing/gas flaring area**

### 3.3.1.1.1 PAH contamination profiles

As a result of the significant PAH contamination found in all OGP samples, it was critical to find out which PAH contributed most to the contamination. Each sub-location's average congener profile was computed to identify the contribution of different PAH to  $\Sigma$ PAH. In addition, PAH were also categorised into five homologous series based according to their number of benzene rings (3-ring, 4-ring, 5-ring, and 6-ring) PAH.

Figures 3.3a and b show the PAH patterns based on ring number and the individual PAH respectively and table 3.3 and 3.4 revealed the same distributions. While Figure 3.3a shows some subtle differences in the relative abundance of PAH classified according to ring number between samples from the less-contaminated WA and NP sub-locations; the ring pattern in MP soils is distinctive. Specifically, in the MP soils, the 3 ringed PAH account for ~80% of  $\Sigma$ PAH, comprising Acy (22%), Ace (21%), Fln (10%), Phe (14%) and Ant (10%). A similar prevalence of 3 ringed PAH was reported in soil from a polluted site in the Niger Delta (Adedosu et al., 2013). Likewise, Kuang et al. (2018) studied soil from an Shengli oil field in China and reported the dominance of 3 ringed PAH over others. In addition, the pattern of 6 ring PAH exceeding those with 5 rings in Shengli oil field reported by Kuang et al. (2018) is comparable to findings in our study for the MP sub-location.

**Figure 3-3 Contribution of PAH to ΣPAH according to ring number (a) and relative distribution of individual PAH(b) in soil samples from sub-locations within an oil and gas production area (OGP)**



**WA; Worker's accommodation, NP; near processing area and gas flaring area and MP; main processing area**

**Table 3-3 Concentrations and percentage contribution of individual PAH in soil samples from different sub-locations in an oil and gas production area (OGP)**

Location	Average concentration (ng/g) of individual PAH													
	Acy	Ace	Fln	Phe	Ant	Flt	Pyr	BaA	Chr	BbkF	BaP	IPy	DBA	BghiP
WA	0.6	0.7	2	4.9	0.9	2.6	2.9	2.8	7.4	3.8	3.7	4	3	7.2
NP	8.8	4.6	2.3	6.7	2	6.5	12.1	7.5	12.9	10.7	21.1	27.2	3.1	11.2
MP	39.6	43.8	21.2	29.7	23.6	8.1	4.7	2.4	4.7	4	2.8	3.5	3.2	10.1
	Percentage contribution of individual PAH													
WA	1	1.9	4.1	10.5	1.7	5.6	6.3	6.2	16.1	8.1	8	8.6	6.3	15.6
NP	8.3	4.4	2	5.1	1.8	4.7	8.4	5.4	9.2	7.5	14.3	18.6	2.3	8
MP	22.1	21.4	10	14	10	3.9	2.4	1.2	2.3	2.1	1.5	1.9	1.7	5.4

**Table 3-4 PAH concentrations (ng/g) and contributions to  $\Sigma$ 14PAH**

Location	Average concentrations (ng/g)				Percentage $\Sigma$ 14PAH (%) <sup>a</sup>			
	Number of Rings							
	3	4	5	6	3	4	5	6
WA	9.2	16	10	11	19	34	22	24
NP	24	39	35	38	22	28	24	26.5
MP	160	20	9.9	14	78	9.8	5.2	7.4

<sup>a</sup> percentages may not add to 100 due to rounding.

### 3.3.1.2 PAH Concentrations in soil from the Crude Oil Transfer and Storage Area

#### (TST) in wet season

Table 3.5 shows the average PAH concentrations and the sum concentration of 6 carcinogenic PAH detected in soil from three sub-locations within the TST locations while Figure 3.4 illustrates graphically the total distributions of these compounds .

Consistent with the proximity of samples to oil and gas production activity, the mean concentration of  $\Sigma_{14}$ PAH detected in the storage tank and pumps area (ST) was 140.5 ng/g with a range of 82.6- 235.5 ng/g, while an average of 88.4 ng/g and a range of 58.8-104 ng/g was found in soils from the surroundings of crude oil transfer area (AF). The lowest PAH concentrations were detected close to the office area (OA) ranging between 44.3 -75.2 ng/g and an average of 53.7 ng/g.

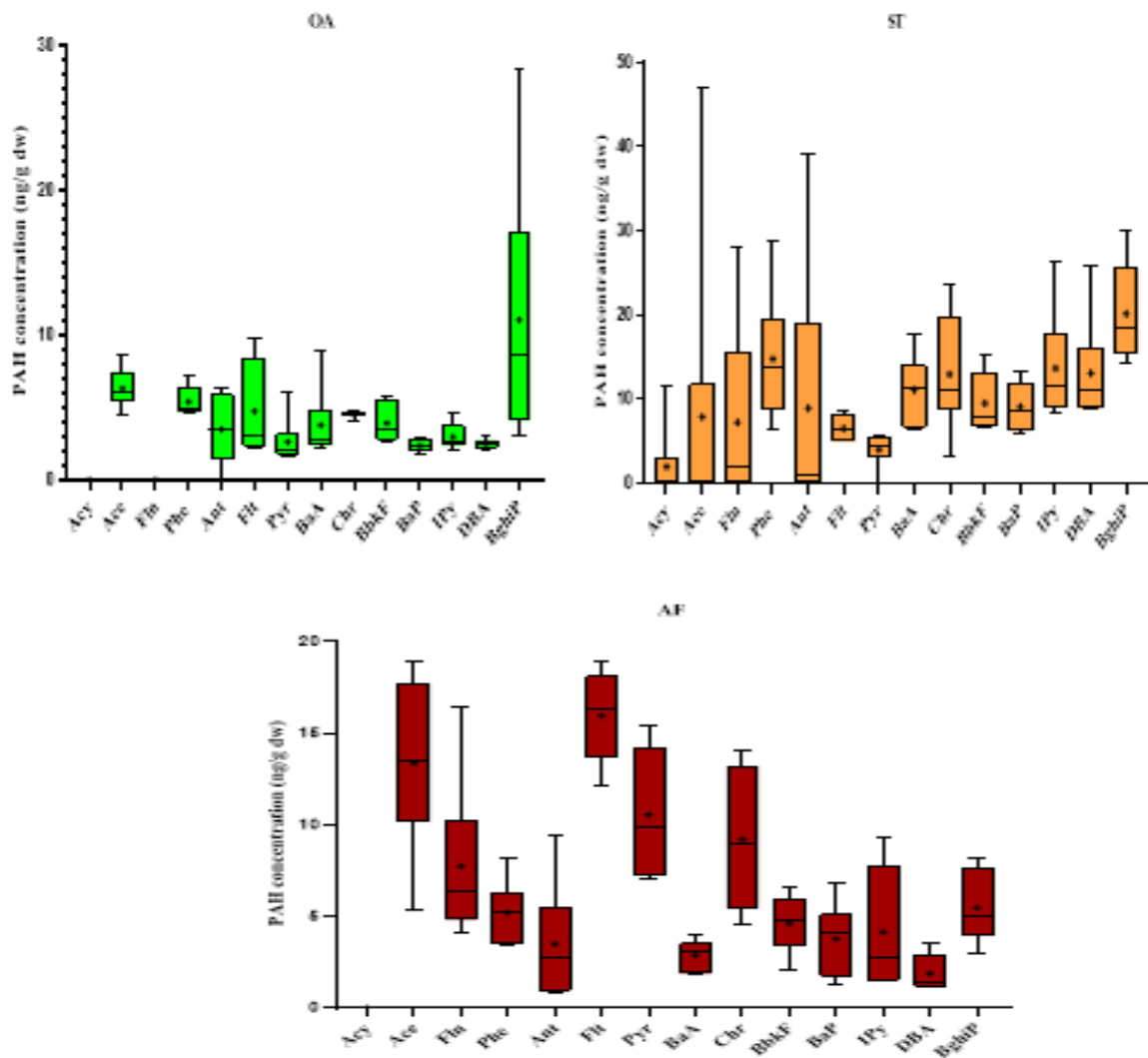
The concentrations of  $\Sigma$ PAH<sub>6C</sub> investigated are at OA (16.5-25.9 ng/g, average 20 ng/g), at ST (82.8-235.6ng/g, 69.3 ng/g average), and at AF (58.8-104.3 ng/g, average 88.4 ng/g). The highest  $\Sigma$ PAH<sub>6C</sub> concentrations were found at ST and the lowest at OA. The concentrations of BaP at the three TST sub-locations ranged from 1.7 to 2.9 ng/g (average 2.3 ng/g) for OA, from 6 to 13.3 ng/g (average 9 ng/g) at ST, and from 1 to 6.8 ng/g (average 3.8 ng/g) for AF.

The higher contamination detected at ST could be ascribed to several factors, ranging from the accumulation of PAH as a result of an historical spill that occurred in 2006, which agrees with the findings of (Adedosu et al., 2013) who reported a high concentration of PAH at a polluted site with a history of oil spillage. Moreover, the higher PAH concentrations detected at ST may result from atmospheric deposition from the flaring of gas (fly ash) by surrounding oil and gas companies as well as other oil and gas activities.

An analysis of variance test (ANOVA) was conducted to examine differences among the three TST sub-locations. The test revealed concentrations at ST were significantly higher ( $p < 0.05$ )

than those at OA but no other significant differences. The mean PAH concentrations in our three sites all fall below recommended soil quality standard limit values.

**Figure 3-4 PAH concentrations at three sub-locations within the crude oil transfer area (TST)**



**Boxplot diagrams showing minimum, maximum and interquartile ranges, average (+) for PAH concentration at OA(Office areas), ST(Storage tank/pump area) and AF(Surroundings of crude oil field/pipeline area)**

**Table 3-5 Concentrations(ng/g) of PAH in soil in dry weight (wt.) from Crude oil transfer Area (TST)**

PAH	OA					ST					AF				
	Average	SD	Min	Median	Max	Average	SD	Min	Median	Max	Average	SD	Min	Median	Max
Acy	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.93	4.31	<LOQ	<LOQ	11.56	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Ace	6.3	1.4	4.5	6.0	8.6	7.9	17.6	<LOQ	<LOQ	47.1	13.4	4.8	5.4	13.4	18.9
Fln	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	7.2	10.1	<LOQ	1.9	27.9	7.8	4.5	4.2	6.3	16.4
Phe	5.4	1	4.6	4.9	7.1	14.7	7.1	6.3	13.7	28.8	5.2	1.7	3.4	5.3	8.2
Ant	3.5	2.4	<LOQ	3.5	6.4	8.9	14.2	<LOQ	1	39.1	3.5	3.2	0.8	2.8	9.4
Flt	4.7	3.3	2.2	3	9.8	6.5	1.5	4.9	6.3	8.5	16	2.5	12.1	16.3	18.9
Pyr	2.6	1.7	1.6	2	6	4	1.9	<LOQ	4.4	5.6	10.6	3.5	7.0	9.9	15.4
BaA	3.8	2.6	2.2	2.8	9	11.1	3.9	6.4	11.4	17.8	2.9	0.9	1.8	3.1	4
Chr	4.5	0.2	4.1	4.6	4.8	12.9	6.5	3.2	11	23.6	9.2	4.2	4.5	9.0	14
BbkF	3.9	1.3	2.7	3.4	5.7	9.5	3.3	6.6	7.9	15.4	4.6	1.6	2.1	4.8	6.6
BaP	2.4	0.4	1.7	2.4	2.9	9.1	2.9	6	8.7	13.3	3.8	2.0	1.2	4.1	6.8
IPy	3	0.9	2.1	2.6	4.6	13.7	6.2	8.2	11.6	26.4	4.2	3.3	1.5	2.7	9.3
DBA	2.5	0.3	2.1	2.5	3	13.1	5.9	8.8	11	25.8	1.9	1	1.2	1.4	3.5
BghiP	11.1	9.4	3.1	8.6	28.4	20.1	5.5	14.1	18.3	30.1	5.5	2	3	5	8.2
Σ <sub>14</sub> PAH	53.7	25.0	44.3	48.5	75.2	140.5	52.1	82.6	137.5	235.5	88.4	17.4	58.8	95.0	104.3
ΣPAH <sub>6C</sub>	20.1	5.8	16.5	19.7	25.9	69.3	28.7	47.3	57	112	26.6	13	15	23.6	37.7

**OA=Office areas, ST= storage tank/pump area, AF= surroundings of crude oil field/pipeline area**

### 3.3.1.2.1 PAH concentration profile

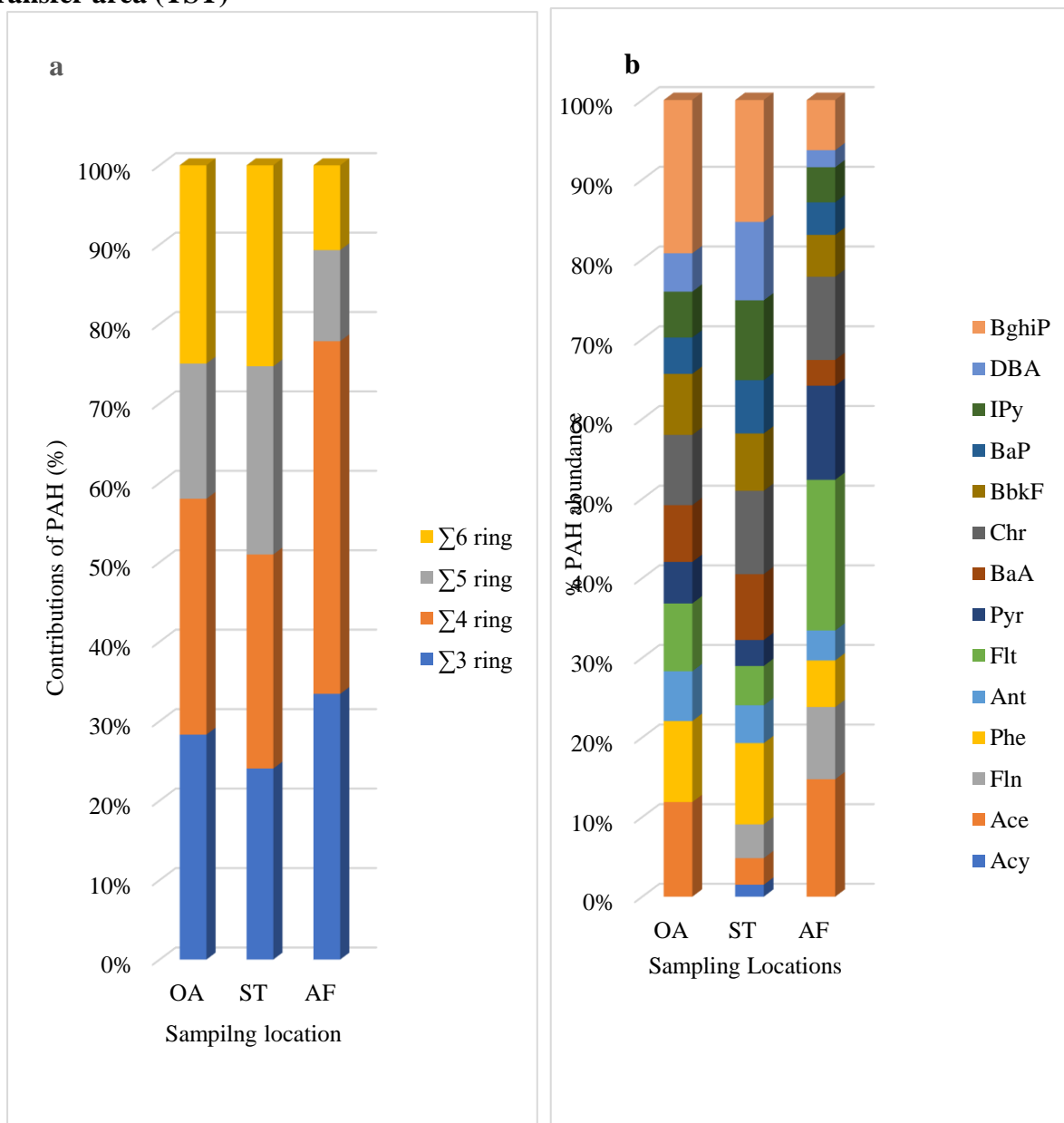
The profiles of PAH according to ring number and percentage abundance of individual PAH in soil samples for the three TST sub-locations: office area (OA), storage tank area (ST) and surroundings of the oil field (AF) are presented in Figures 3.5a and b as well as Tables 3.6 and 3.7. The results show that in all sub-locations, 4 ring PAH are most abundant, constituting 30%, 27% and 44% of  $\Sigma$ PAH in OA, ST and AF respectively, as shown in Figure 3.5a.

However, while 4 ring PAH are most abundant, the three sub-locations exhibit different sequences of number of aromatic rings, possibly because of the distances from one another and of various activities as showed in Figure 3.1. Another important reason could be emissions from activities undertaken nearby by other oil companies. For example, Network exploration & production Nigeria and ExxonMobil undertake oil and gas exploration activities that are respectively 0.5 km and 1.5 km from the TST location.

The PAH ring distributions in samples from the three TST sub-locations are: OA = 4 ring > 3-ring > 6-ring > 5-ring; ST 4 ring > 6 ring > 3 ring > 5-ring and 4-ring > 3- ring > 5-ring > 6- ring at AF. The ring profile detected in AF is comparable to that observed by Wang et al. (2018a) in petroleum-contaminated soil from Loess Plateau, China.

The relative abundance of individual PAH components at OA are Ace (11.9%), Phe (10%), and BghiP (19%). For ST, the relative abundance of BghiP (15%) and Phe (10%) is similar to that at OA but Chr (10%) and IPy (9.8%) were noticeably more abundant than at OA. For soil samples from the AF sub-location, Flt (18.9%), Ace (14.8%), and Pyr (11.8%) were most abundant.

**Figure 3-5 Relative abundance (% $\Sigma$ PAH) expressed as PAH ring number(a) and percentage contribution of individual PAH(b) in soil from sub-locations in the crude oil transfer area (TST)**



**OA(Office areas),ST(Storage tank/pump area and AF(Surroundings of crude oil field/pipeline area**

**Table 3-6 Concentration (ng/g) and percentage contribution of individual PAH in crude oil transfer area (TST)**

Location	Average concentration of individual PAH													
	Acy	Ace	Fln	Phe	Ant	Flt	Pyr	BaA	Chr	BbkF	BaP	IPy	DBA	BghiP
OA	<LOQ	6.3	<LOQ	5.4	3.5	4.7	2.6	3.8	4.5	3.9	2.4	3	2.5	11.1
ST	1.9	7.9	7.2	14.7	8.9	6.5	4	11.1	12.9	9.5	9.1	13.6	13.1	20.1
AF	<LOQ	13.4	7.8	5.2	3.5	16	10.6	2.9	9.2	4.6	3.8	4.2	1.9	5.5
	Percentage contribution of individual PAH													
OA	<LOQ	11.9	<LOQ	10.2	6.3	8.5	5.2	7.1	8.8	7.6	4.6	5.8	4.8	19.2
ST	1.5	3.3	4.3	10.2	4.8	4.9	3.3	8.3	10.5	7.2	6.7	10.1	9.8	15.3
AF	<LOQ	14.8	9.1	5.9	3.8	18.9	11.8	3.2	10.4	5.2	4.1	4.4	2.1	6.3

**Table 3-7 PAH concentrations (ng/g) and contributions to  $\Sigma$ 14PAH in crude oil transfer and storage area expressed in ring number**

Location	Average concentration (ng/g)				Percentage $\Sigma$ 14PAH (%) <sup>a</sup>			
	No of Rings							
	3	4	5	6	3	4	5	6
OA	15.2	15.7	8.8	14	28.3	29.7	17	25
ST	40.6	34.5	31.6	33.7	24	26.9	23.7	25.3
AF	29.8	38.6	10.3	9.7	33.4	44.4	11.5	10.7

AF surroundings of crude oil transfer field, ST storage tank and pumps area, and OA proximity to the office area

<sup>a</sup> percentages may not add to 100 due to rounding

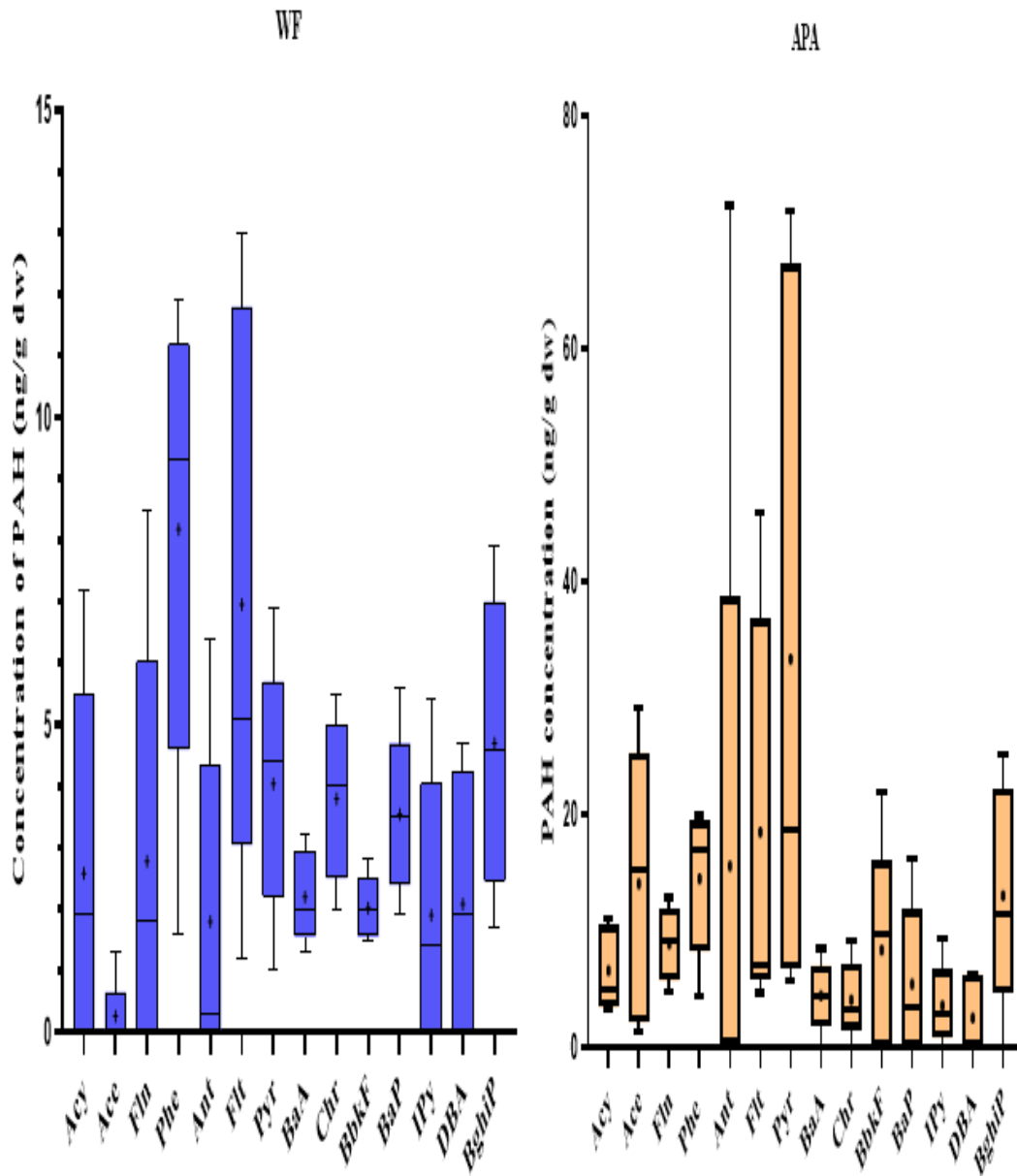
### 3.3.1.3 Concentration of PAH in Gas well (AW2) in wet season

Table 3.8 provides a statistical summary of the concentrations of  $\Sigma_{14}$ PAH detected in soil samples from within the gas field and its immediate surroundings (WF), and along a pipeline right of way (APA) in farmland which is also close to a moderately local trafficked road. Figure 3.6 shows the graphical statistical individual distribution of target PAH in both sub-locations. The average concentration in soils from the WF sub-location was 46.8 ng/g, with a range of 23.9- 55.2 ng/g. By comparison, concentrations at the APA sub-location ranged from 71 to 238 ng/g with a mean of 152.9 ng/g.

PAH concentrations at APA were on average three times higher than those at WF, these elevated concentrations may be attributed to leakages from the pipelines, thus suggesting the impact of oil and gas exploration activities on these farmlands. PAH detected in the soil from the gas field could arise at least partially from atmospheric emission from the gas fumes from the well (Paulik et al., 2018) with subsequent deposition to soil. The  $\Sigma$ PAH<sub>6C</sub> made a strong contribution to  $\Sigma_{14}$ PAH at both sub-locations with  $\Sigma$ PAH<sub>6C</sub> concentrations at APA ranging from 6.7 to 57.9 ng/g (average, 28.4 ng/g) and 12.2 to 18.3 ng/g (average 15.5 ng/g) at WF. Additionally, concentrations of BaP at APA varied from <LOQ-16.2 ng/g (average 5.4 ng/g) and 1.9 -5.6 ng/g (average 3.5 ng/g) at WF. Figure 3.6 shows the various statistical individual distribution of PAH at this study area.

Having tested the normality of the dataset by Shapiro-Wilk and log transforming where necessary, an independent test revealed that there was significant difference between PAH concentrations at the two sub-locations ( $p < 0.05$ ).

**Figure 3-6 Concentrations of individual PAH at the two sub-locations in the gas well area in wet season**



**Boxplot diagram of AW2 showing minimum, maximum, average (+) and 25<sup>th</sup>, 75<sup>th</sup> and 95<sup>th</sup> percentile. WF (Within gas field area) and APA (Along pipeline right of way)**

**Table 3-8 Concentrations of PAH (ng/g) within the active gas well (AW2) in wet season**

PAH	WF(n=5)					APA(n=5)				
	Aver	SD	Min	Med	Max	Aver	SD	Min	Med	Max
Acy	2.6	3	<LOQ	1.9	7.2	6.6	3.7	3.3	5	11.1
Ace	0.3	0.6	<LOQ	<LOQ	1.3	14.1	11.9	1.4	15.2	29.1
Fln	2.8	3.5	<LOQ	1.8	8.5	8.9	3.2	4.8	9.2	12.9
Phe	8.2	4	1.6	9.3	11.9	14.5	6.4	4.4	17	19.9
Ant	1.8	2.8	<LOQ	0.3	6.4	15.6	31.8	<LOQ	0.5	72.3
Flt	6.9	4.8	1.2	5.1	13	18.5	17.9	4.7	7.1	45.9
Pyr	4	2.1	1	4.4	6.9	33.4	31.5	5.7	18.6	71.8
BaA	2.2	0.7	1.3	2	3.2	4.4	3.1	<LOQ	4.4	8.5
Chr	3.8	1.4	2	4	5.5	4.1	3.4	<LOQ	3.2	9.2
BbkF	2	0.5	1.5	2	2.8	8.4	9.1	<LOQ	9.7	21.9
BaP	3.5	1.4	1.9	3.5	5.6	5.4	6.8	<LOQ	3.5	16.2
IPy	1.9	2.3	<LOQ	1.4	5.4	3.6	3.5	<LOQ	2.9	9.3
DBA	2.1	2.1	<LOQ	1.9	4.7	2.5	3.4	<LOQ	0.2	6.3
BghiP	4.7	2.4	1.7	4.6	7.9	13	9.6	<LOQ	11.4	25.2
Σ <sub>14</sub> PAH	46.7	31.6	23.9	51.8	55.2	152.9	145.3	71.0	131.4	238.
ΣPAH <sub>6C</sub>	15.5	8.4	12.2	16.2	18.3	28.4	29.2	6.7	24.9	57.9

WF(Within gas field area) ans APA(Along pipeline right of way). Aver(average), Med(Median),Min(Minimm) ans Max(Maximum)

### 3.3.1.3.1 Compositions and Profile of PAH at Active Gas Well

Concentrations of PAH at sub-locations near the active gas well appear unevenly distributed, with the 4-6 ring PAH contributing much more than those with 3 rings. This can be explained by the physicochemical properties of the 3 ring PAH, which favour partitioning to air rather than soil, coupled with greater susceptibility to degradation and leaching in soil (Emoyan et al., 2020, Li et al., 2010)

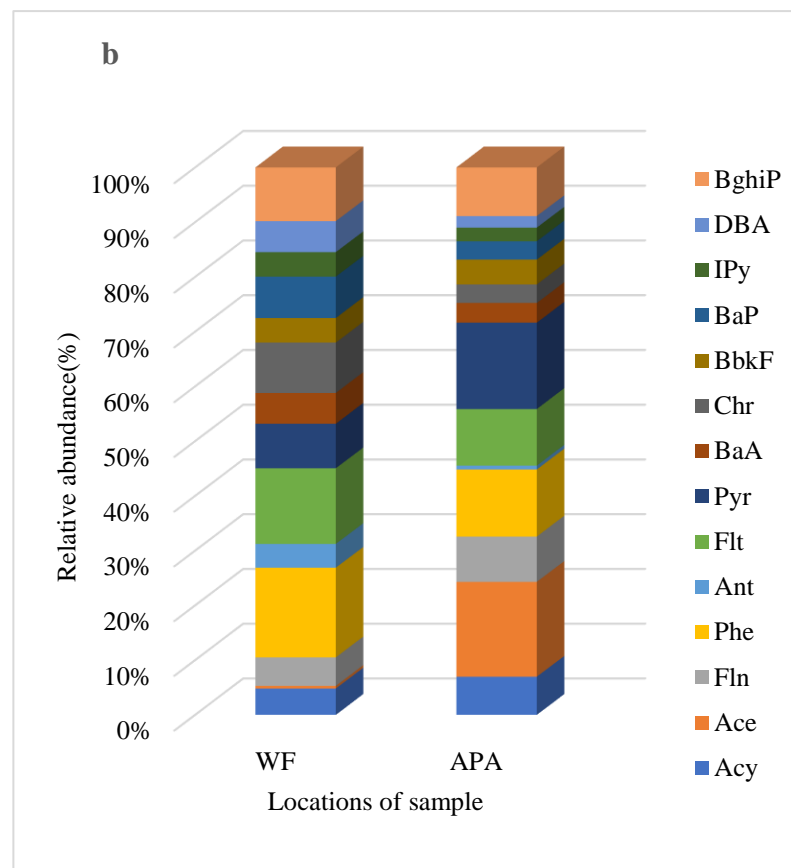
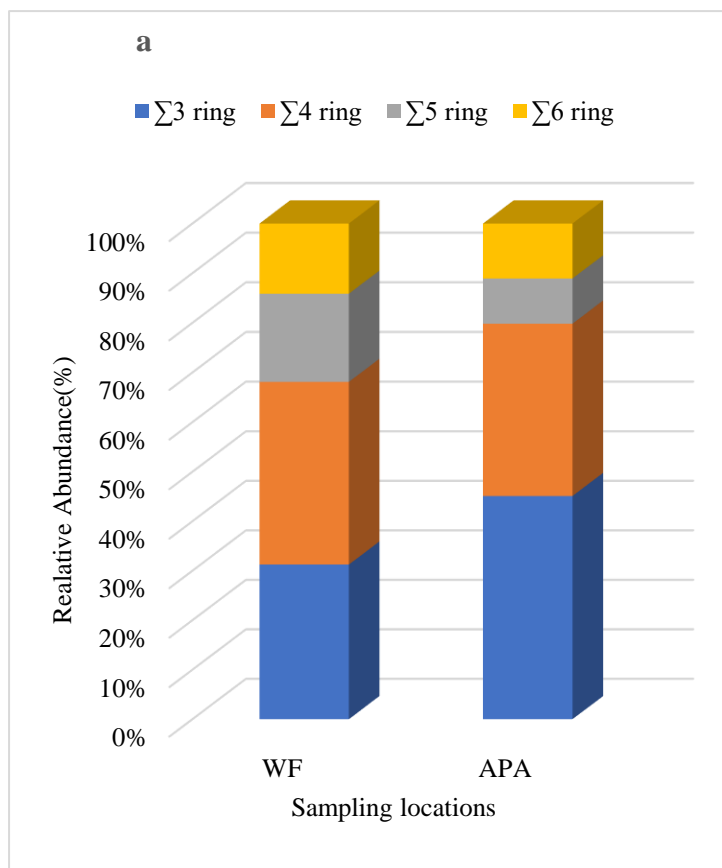
A distinctive feature of samples from the WF sub-location, is that 4 ring PAH are most abundant at 36.9% of Σ<sub>14</sub>PAH, with Flt (13.9%) the most abundant individual 4 ring PAH. By

comparison, 3 ring (including Phe 16.4%), 5 ring (BaP 7.6%), and 6 ring (BghiP 9.8%) PAH constitute 31%, 17.8% and 14% of  $\Sigma_{14}$ PAH on average. The ring pattern thus follows the order: 6 rings < 5 rings < 3 rings < 4 rings as illustrated in Figure 3.7a, and Table 3.10.

The pattern of distribution of PAH in samples from the APA sub-location is also shown in Figure 3.7a and Table 3.9 and 3.10 on average. The contribution of  $\Sigma_3$  ring PAH is 45% with Ace (17%) and Phe (12%) predominating, followed by the 4 rings which contribute an average of 34.7% (including Flt 10% and Pyr 15%). The contribution of six ring PAH 11% (mainly BghiP 9%) exceeded that of the 5 ring (9%).

A similar trend was in MP in OGP and at Shengli oil field in China (Kuang et al., 2018). This distribution of 6 ring > 5 ring differs from that observed at sub-location within the gas field area (WF). This different pattern between these sub-locations could be related to the distance of APA which 150 m from WF. Moreover, APA is located by the roadside and closer to the residential area with other potential PAH sources such as cooking.

**Figure 3-7(a) Percentage composition of PAH of different ring number at WF and APA (b) Percentage Individual PAH composition at WF and APA at Active gas well (AW2)**



**Table 3-9 Concentration (ng/g) and percentage contribution of individual PAH compounds in active gas well (AW2) in wet season**

Location	Average concentration (ng/g) of individual PAH													
	Acy	Ace	Fln	Phe	Ant	Flt	Pyr	BaA	Chr	BbkF	BaP	IPy	DBA	BghiP
WF	2.6	0.3	2.8	8.2	1.8	6.9	4	2.2	3.8	2	3.5	1.9	2.1	4.7
APA	6.6	14.1	8.9	14.5	15.6	18.5	33.4	4.4	4.1	8.4	5.4	3.6	2.5	13
	Percentage contribution of individual PAH compounds													
WF	4.8	0.5	5.2	16.4	4.3	13.8	8.1	5.6	9.2	4.5	7.6	4.5	5.7	9.8
APA	7	17.3	8.3	12.2	0.7	10.3	15.8	3.6	3.4	4.5	3.3	2.5	2.1	8.9

**Table 3-10 PAH concentrations (ng/g) and contributions to  $\Sigma$ 14PAH in active gas well in wet season**

Location	Average concentrations (ng/g)				Percentage $\Sigma$ 14PAH (%)			
	No of Rings							
	3	4	5	6	3	4	5	6
WF	15.6	16.9	7.6	6.6	31.2	36.9	17.8	14.1
APA	59.6	60.4	16.3	16.6	45.1	34.7	9.1	11.1

WF within gas well field, APA along pipeline ring of way outside the gas field.

#### 3.3.1.4 Concentrations of PAH in oil well area (AW3) in wet season

Concentrations of  $\Sigma_{14}\text{PAH}$  were measured in soils sampled from two sub-locations associated with an active oil well. Soil samples within the oil well and its immediate surroundings (OW n=10) and along the pipeline right of way (APB n=10) were collected. A statistical summary of concentrations of PAH and  $\Sigma\text{PAH}_{6\text{C}}$  are presented in Table 3.11, with Figure 3.8 depicting the concentrations of individual PAH at the two sub-locations.

The average concentration of  $\Sigma_{14}\text{PAH}$  was 203.5 ng/g at the APB sub-location with a range of 67 to 463.9 ng/g. These exceeded those of  $\Sigma_{14}\text{PAH}$  in soil samples taken within the oil well and its immediate surroundings (OW), where the average concentration was 55 ng/g (range 25.3-81.8 ng/g). The highest concentrations of  $\Sigma\text{PAH}_{6\text{C}}$  were at APB (average 92 ng/g; range 15.09-271 ng/g) compared to OW (average 26.3 ng/g; range <LOQ-48 ng/g). Average concentrations of BaP at APB were 28.6 ng/g (range 2.3-73.1 ng/g), and 6.5 ng/g (range <LOQ-9.9 ng/g) at OW.

The higher concentrations detected along the pipelines area (APB) with farming activities could suggest pipeline leaks leading to localised soil contamination. According to soil  $\Sigma_{16}\text{PAH}$  contamination by Maliszewska-Kordybach (1996), PAH contamination level can be categorised as four; < 200ng/g (not contaminated), 200-600 ng/g (weakly contaminated), 600-1000 ng/g (contaminated) and > 1000 ng/g (heavily contaminated). The  $\Sigma_{14}\text{PAH}$  concentrations found in APB just exceed 200 ng/g and are therefore considered to be weakly contaminated.

It is important to know that apart from oil exploration, farming is the main occupation of the communities sampled in this study. Soil has been identified as the primary reservoir of the environmental burden of PAH, comprising approximately 90% of the global loading (Hu et al., 2017, Wild and Jones, 1995), PAH can accumulate in the food chain via uptake by vegetables, tubers, and other biota (Li et al., 2008). Studies supporting this report concentrations of PAH in edible plants grown in oil-polluted soil (Nwaichi et al., 2016, Nwaichi et al., 2014).

It was expected that soil samples at OW would display higher concentrations than at the other sub-station (APB) whereas the opposite was observed. The varying concentration in soil may be related to PAH physicochemical properties, the nature of the soil and its retention capacity. It was reported that soil having a lot of clay and silt will tend to retain more PAH than sandy soil (Łyszczarz et al., 2021, Luo et al., 2008, Windsor Jr and Hites, 1979). Hence, PAH concentrations in soil are positively correlated with organic matter content of soil. So, the lower concentrations at OW could reflect low soil organic matter content at those sub-site and much higher organic matter content at the APB sub-sites.

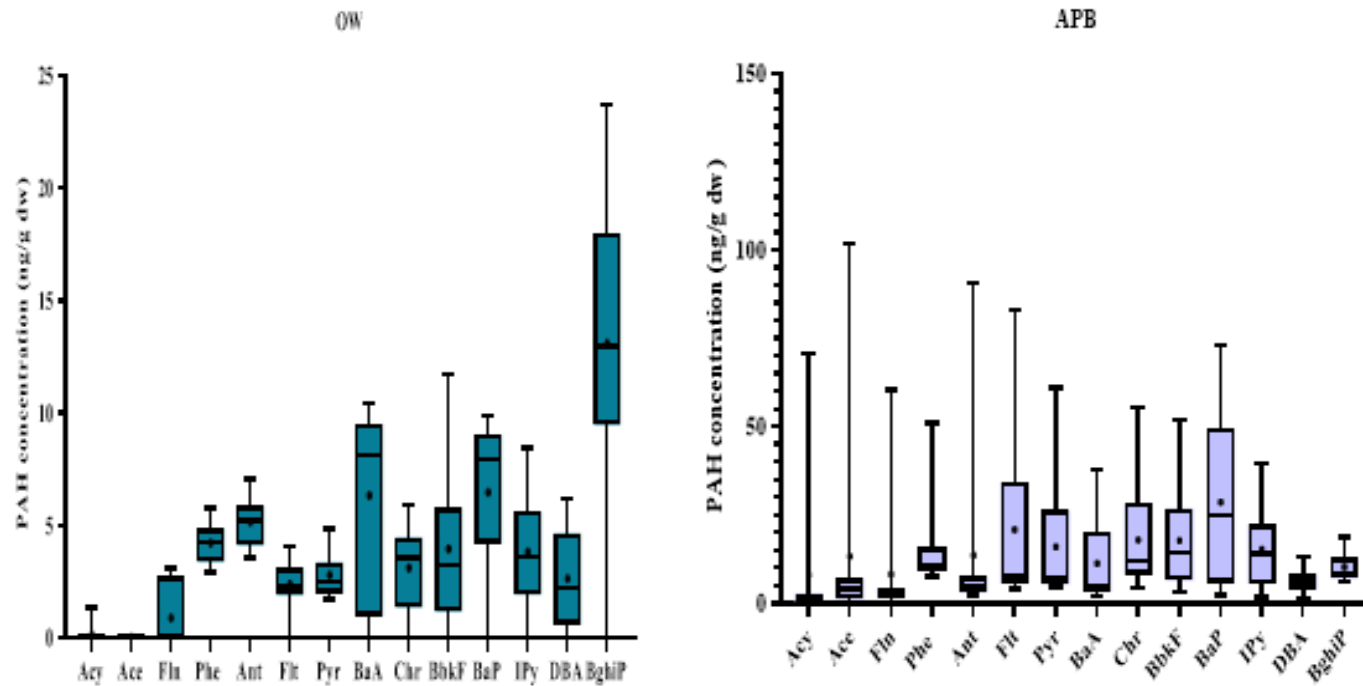
The average concentrations of  $\Sigma_{14}$ PAH in APB were 4 times higher than at OW, with a statistically significant difference observed between APB and OW according to the independent t test ( $p < 0.05$ ).

**Table 3-11 Concentration of PAH (ng/g) dry weight in oil well field in wet season**

PAH	OW(n=10)					APB(n=10)				
	Average	SD	Min	Median	Max	Average	SD	Min	Median	Max
Acy	0.1	0.4	<LOQ	<LOQ	1.3	8.1	22	<LOQ	1.3	70.6
Ace	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	13.3	31.2	<LOQ	4	101.8
Fln	0.9	1.4	<LOQ	<LOQ	3.1	8.2	18.4	<LOQ	2.8	60.5
Phe	4.2	0.9	2.9	4.3	5.8	15.7	13.1	7.6	10.9	51.2
Ant	5.1	1.1	3.5	5.2	7.1	13.7	27.1	2.4	5.1	90.5
Flt	2.4	1.1	<LOQ	2.2	4.1	20.9	25.5	4.1	8	83.2
Pyr	2.8	1	1.7	2.5	4.9	16	18.4	4.6	7	61
BaA	6.3	4.1	<LOQ	8.1	10.4	11.3	11.8	2.1	4.6	37.7
Chr	3.1	2	<LOQ	3.6	5.9	18	15.8	4.4	11.9	55.6
BbkF	4	3.5	<LOQ	3.3	11.7	17.8	14.7	3	14.2	52.1
BaP	6.5	3.5	<LOQ	7.9	9.9	28.6	25.7	2.3	24.8	73.1
IPy	3.8	2.8	<LOQ	3.6	8.4	15.3	11.7	1.8	14.1	39.4
DBA	2.6	2.1	<LOQ	2.2	6.2	6.3	3.2	1.5	6	13
BghiP	13.1	6.8	<LOQ	12.9	23.7	10.3	4.5	6.1	8.2	18.8
$\Sigma_{14}$ PAH	55	30.8	25.3	56.4	81.8	203.5	243.1	67.3	151.6	463.9
$\Sigma$ PAH6c	26.3	18	<LOQ	27.1	48	97.3	82.8	15.1	81.1	271

**OW within the oil well field, APB along pipeline right of way outside the oil**

**Figure 3-8 Concentrations of individual PAH in oil well sub-locations within oil well(OW) and along pipeline right of way (APB)**

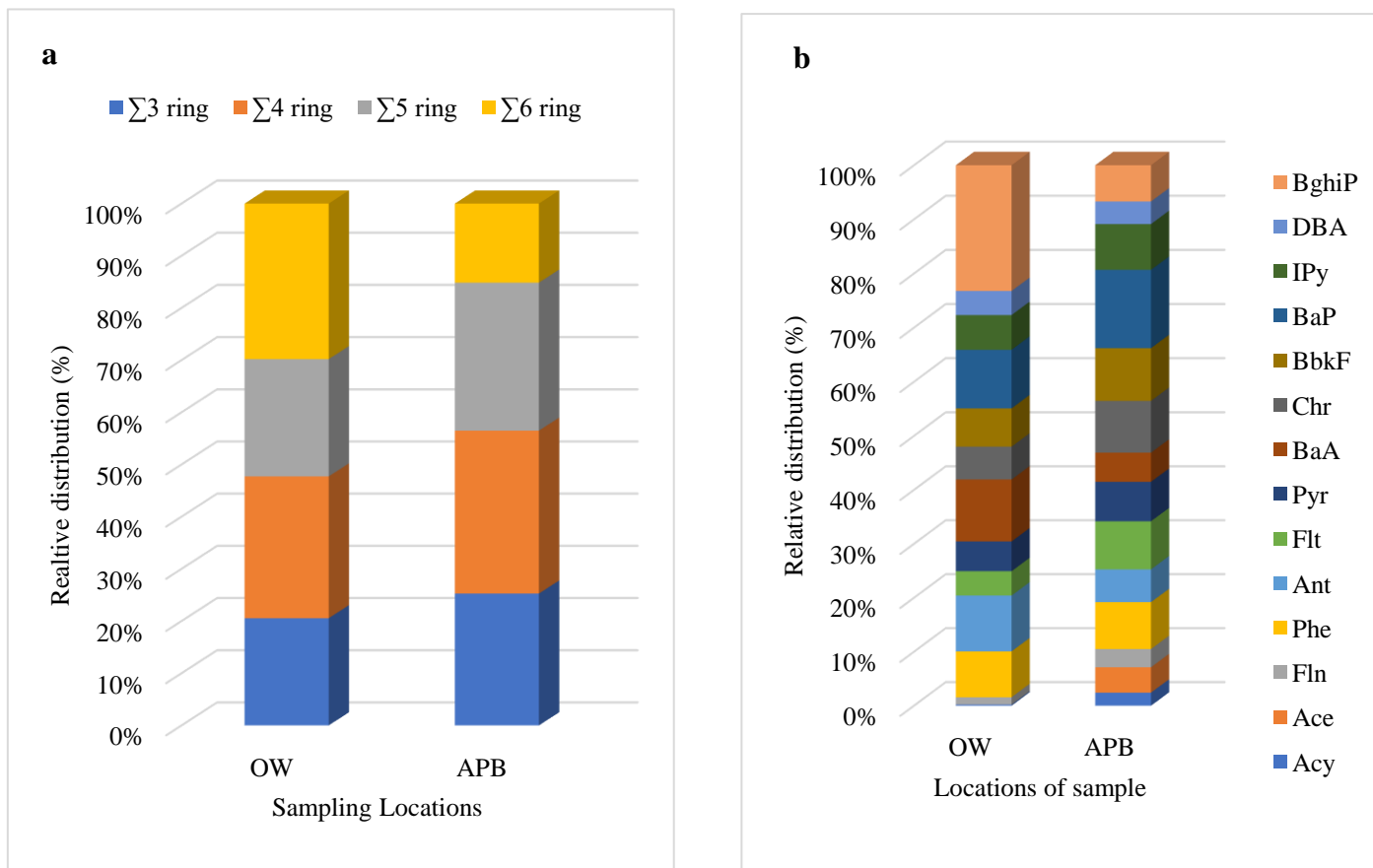


#### 3.3.1.4.1 Composition of PAH and Profile at Oil Well

In samples from the OW sub-location, 6 ring PAH were most abundant, accounting for 29.8%  $\Sigma_{14}$ PAH (mainly BghiP at 23.4%). 4 ring PAH were also abundant and accounted for 27 %  $\Sigma_{14}$ PAH, with BaA contributing 11.5%. Next most abundant were 3 ring PAH accounting for 20.5% on average among with includes Ant 10% and Phe 8.5%, followed by 5 ring PAH at 22.5 % (including BaP at 10.9 %). A similar prevalence of six ring PAH was also reported by Li et al. (2019) at Daqing oil well (21%  $\Sigma_{14}$ PAH in vegetated soil and 11% in bare soil) and (Ahiamadu et al., 2021) in surface soil from crude oil spill sites in River State, Nigeria (43.33%). This PAH distribution according to ring number is displayed in Table 3.13 and Figure 3.9a.

The composition profile in APB differs from that of OW probably due to differences in emission sources and the conditions influencing PAH fate and behaviour at the two sub-locations – e.g., soil organic matter content (higher soil organic matter restricts volatilisation and leaching of more volatile and water-soluble 3 ring PAH) and soil microbial content which will influence biodegradation. Table 3.12 and Figure 3.9b depict the average percentage profile of PAH in soil from APB. Fu et al. (2018) reported a high abundance of 4 ring PAH around an oil well in the Yellow River Delta, China. In this study, the 4 ring PAH were most abundant at the APB sub-location accounting for 31% of  $\Sigma$ PAH (including Flt 8.9%). Next most abundant were 5 ring PAH which comprised 28.4%  $\Sigma$ PAH (including BaP at 14.5%), followed by 3 ring PAH (25%  $\Sigma$ PAH, including Phe 8.7%). In contrast to OW, 6 ring PAH were least abundant at APB at 15%  $\Sigma$ PAH.

**Figure 3-9 Relative contribution of PAH according to ring number at OW and APB (a) and relative contribution of individual PAH at OW and APB sub-locations at an active oil well (AW3)**



**Table 3-12 Concentration (ng/g) and percentage contributions of individual PAH at two sub-locations at an oil well field in wet season**

Location	Average concentration of individual PAH components													
	Acy	Ace	Fln	Phe	Ant	Flt	Pyr	BaA	Chr	BbkF	BaP	IPy	DBA	BghiP
OW	<LOQ	<LOQ	0.9	4.2	5.1	2.4	2.8	6.7	3.1	4	6.5	3.8	2.6	13.1
APB	8.1	13.3	8.2	15.7	13.7	20.9	16	11.3	18	17.8	28.6	15.3	6.3	10.3
	Percentage contribution of individual PAH													
OW	0.2	<LOQ	1.4	8.5	10.4	4.5	5.6	11.5	6.1	7.1	10.9	6.5	4.4	23.4
APB	2.4	4.7	3.4	8.7	6.1	8.9	7.3	5.4	9.6	9.7	14.5	8.5	4.2	6.7

**Table 3-13: Average concentration (ng/g) and contribution to  $\Sigma 14$ PAH according to PAH ring number at two sub-locations at an oil well field in wet season**

Location	Average concentration (ng/g)				Percentage $\Sigma 14$ PAH (%)			
	No of Ring							
	3	4	5	6	3	4	5	6
OW	10.4	14.6	13.1	16.9	20.5	27.2	22.5	29.8
APB	59.1	66.1	52.7	25.6	25.3	31.2	28.4	15.2

OW-within oil well field, APB-along pipeline right of way

### 3.3.1.5 Concentrations of PAH in soil from non-active sites in wet season

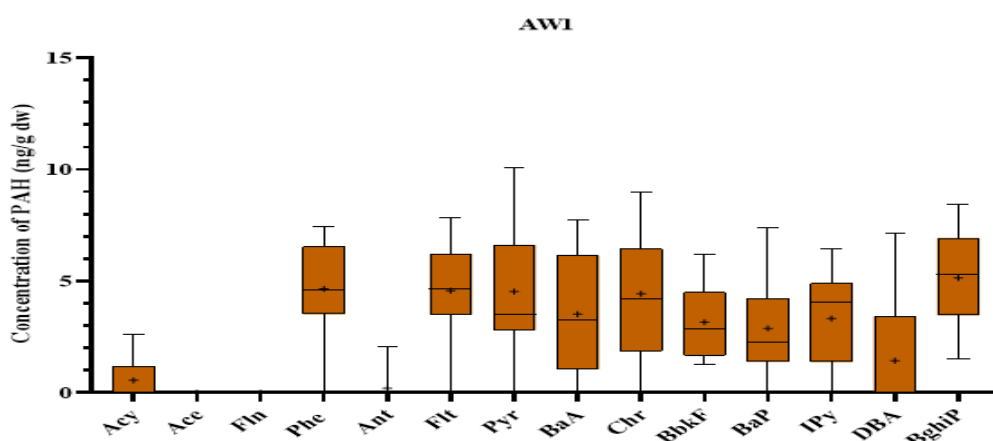
Data obtained for active sites have been described in previous sections. However, the non-active sites are classified as those with no or little current input from oil and gas activities.

Specifically, non-active oil well site 1 (AW1) was a well that was drilled, abandoned, and later commissioned and drilled in 2020. The non-active well site (NAW) was a well that was drilled, lost, and abandoned. While workstation (WS) refers to the worker's residences during the commissioning of new wells and serves as a control site.

#### 3.3.1.5.1 Non-Active Oil Well site (AW1) in wet season

The average  $\Sigma_{14}$ PAH concentrations at non active oil well (AW1)(n=10)) was 38.4 ng/g with a range of 23.9 – 49.2 ng/g. Concentrations of BaP at AW1 range from <LOQ -7.4 ng/g (average 2.9 ng/g); while those of those of  $\Sigma$ PAH<sub>6c</sub> range from 10.4-23 ng/g (average 18.8 ng/g) .Figure 3.10 illustrate the statistical summary of each PAH concentrations for individual compounds in each of the samples taken at AW1.

**Figure 3-10 PAH concentrations in samples from active oil well (AW1) in wet season**

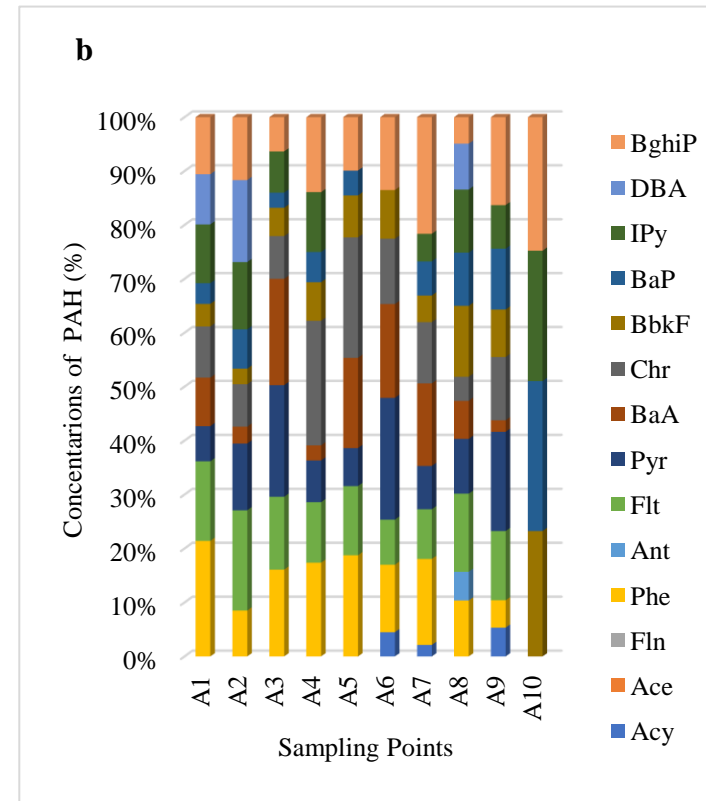
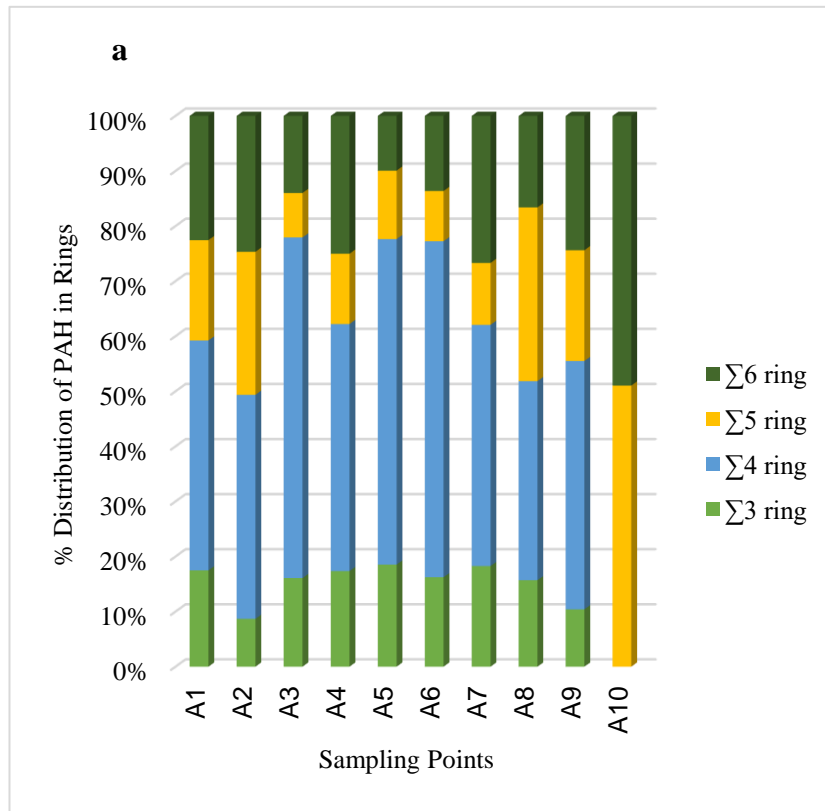


**Boxplot diagram summarising the interquartile range , minimum ,maximum and average(+ ) concentrations at active well without drilling operation(AW1)**

#### **3.3.1.5.1.1 PAH composition Profile**

Figures 3.11a and b illustrate the percentage composition of PAH according to ring number and for individual PAH at AW1. Table 3.14 indicate percentage individual PAH and Table 3.15 shows 4 ring PAH as the most abundant at 43%  $\Sigma_{14}$ PAH (including Flt at 11.6%). Next most abundant are 6 ring PAH at 22.5 % (including BghiP at 13%), followed by 5 ring PAH at 20% (including BaP at 8%), with 3 ring PAH least abundant at 14% (comprised mainly Phe at 12.6%). This low abundance of 3 ring PAH is likely due to their volatility and aqueous solubility (Bojes and Pope, 2007).

**Figure 3-11 Percentage distribution of PAH according to ring number in different soil samples (a) and percentage contribution of individual PAH in individual soil samples (b) from an active oil well without drilling**



**Table 3-14 Percentage contribution of PAH individual samples from active oil well (AW1) in wet season**

Sample/PAH	Acy	Ace	Fln	Phe	Ant	Flt	Pyr	BaA	Chr	BbkF	BaP	IPy	DBA	BghiP
A1	<LOQ	<LOQ	<LOQ	21.4	<LOQ	14.8	6.5	9	9.5	4.2	3.9	10.9	9.3	10.6
A2	<LOQ	<LOQ	<LOQ	8.5	<LOQ	18.6	12.4	3.1	7.9	2.9	7.3	12.5	15.2	11.7
A3	<LOQ	<LOQ	<LOQ	16.1	<LOQ	13.5	20.7	19.7	7.9	5.3	2.8	7.6	<LOQ	6.4
A4	<LOQ	<LOQ	<LOQ	17.4	<LOQ	11.2	7.7	2.8	23.1	7.2	5.6	11.1	<LOQ	13.9
A5	<LOQ	<LOQ	<LOQ	18.8	<LOQ	12.8	7	16.7	22.3	7.8	4.6	<LOQ	<LOQ	9.9
A6	4.5	<LOQ	<LOQ	12.5	<LOQ	8.4	22.6	17.4	12.1	9	<LOQ	<LOQ	<LOQ	13.5
A7	2.1	<LOQ	<LOQ	15.9	<LOQ	9.2	8	15.3	11.4	5	6.3	5.1	<LOQ	21.6
A8	<LOQ	<LOQ	<LOQ	10.4	5.3	14.5	10.2	7.1	4.5	13.2	9.9	11.7	8.5	4.9
A9	5.3	<LOQ	<LOQ	5.1	<LOQ	12.8	18.4	2.1	11.7	8.8	11.3	8.1	<LOQ	16.3
A10	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	23.2	27.8	24.2	<LOQ	24.8
Average	1.2	<LOQ	<LOQ	12.6	0.5	11.6	11.4	9.3	11	8.6	7.9	9.1	3.3	13.4
SD	2.1	<LOQ	<LOQ	6.7	1.7	5	7.2	7.4	7.2	5.9	7.7	7	5.6	6.2

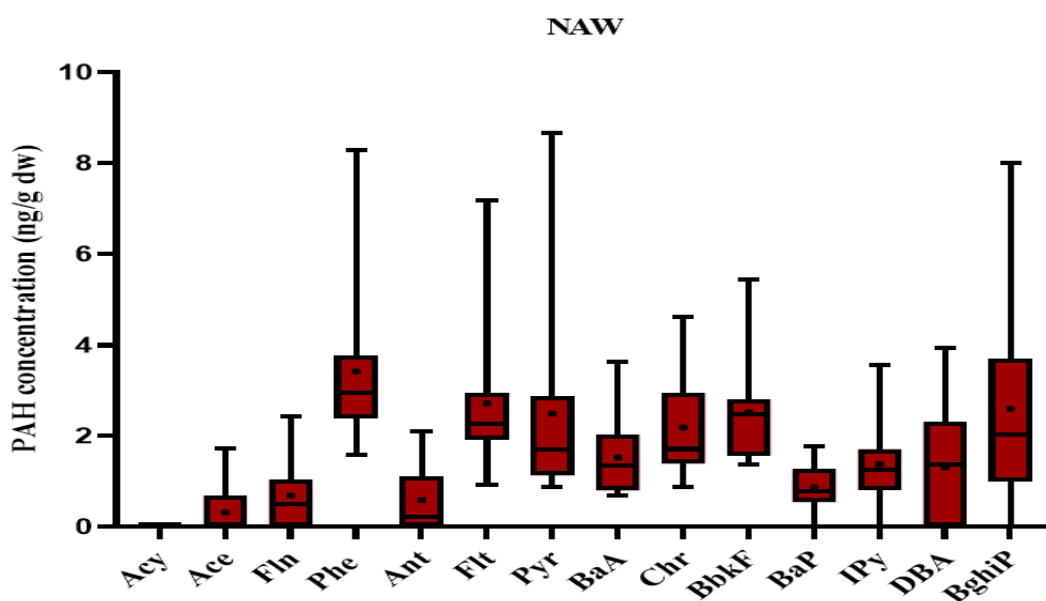
**Table 3-15 Concentration and percentage contribution of PAH according to ring number in individual samples from active oil well (AW1) in wet season**

Ring Number	Average concentrations (ng/g)											
	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	Average	SD
Σ3 ring	9	4	3.9	6.4	7.5	7.6	7	6	5.1	<LOQ	5.7	2.6
Σ4 ring	16.7	19.7	14.8	16.6	23.7	26.9	17.1	13.8	22.2	<LOQ	17.2	7.3
Σ5 ring	7.3	12	1.9	4.7	5	4	4.4	12.1	9.9	13.5	7.5	4.1
Σ6 ring	9	11.4	3.4	9.2	4	6	10.4	6.4	12	13	8.5	3.4
Ring Number	Percentage Σ <sub>14</sub> PAH (%)											
	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	Average	SD
Σ3 ring	21.4	8.5	16.1	17.4	18.8	17	18.1	15.7	10.4	<LOQ	14.3	6.3
Σ4 ring	39.8	41.9	61.8	44.9	58.9	60.5	43.9	36.1	45.1	<LOQ	43.3	17.7
Σ5 ring	17.3	25.4	8.1	12.8	12.4	9	11.3	31.5	20.1	51	19.9	13.3
Σ6 ring	21.5	24.1	14	25	9.9	13.5	26.8	16.6	24.4	49	22.5	10.9

### 3.3.1.5.2 Spatial distribution of PAH at a Non-active well site (NAW) in wet season

The concentrations of  $\Sigma_{14}$ PAH in ten samples (n=10) from a non-active well (NAW) ranged between 9.9 and 56 ng/g with an average of 22.7 ng/g. The highest concentration was at sampling point closest to the abandoned well head while the lowest was detected in the soil sampled farther away from the well head (see Appendix). The individual concentrations of PAH across all 10 sample are presented in Figure 3.12, the soil samples collected at this site contained an average of 0.9 ng/g BaP (range <LOQ-1.78) and an average of 9.8 ng/g  $\Sigma$ PAH<sub>6C</sub> (range 3.8-17.7 ng/g).

**Figure 3-12 Concentrations of individual PAH in all samples from a non-active site (NAW)**

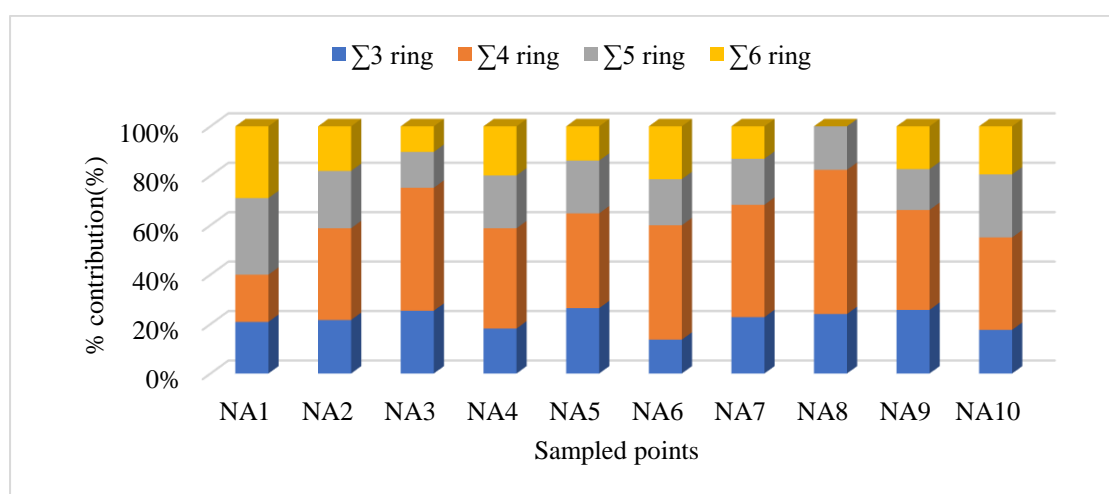


**Boxplot diagram indicating the interquartile range , minimum ,maximum and average(+) concentrations at NAW in wet season**

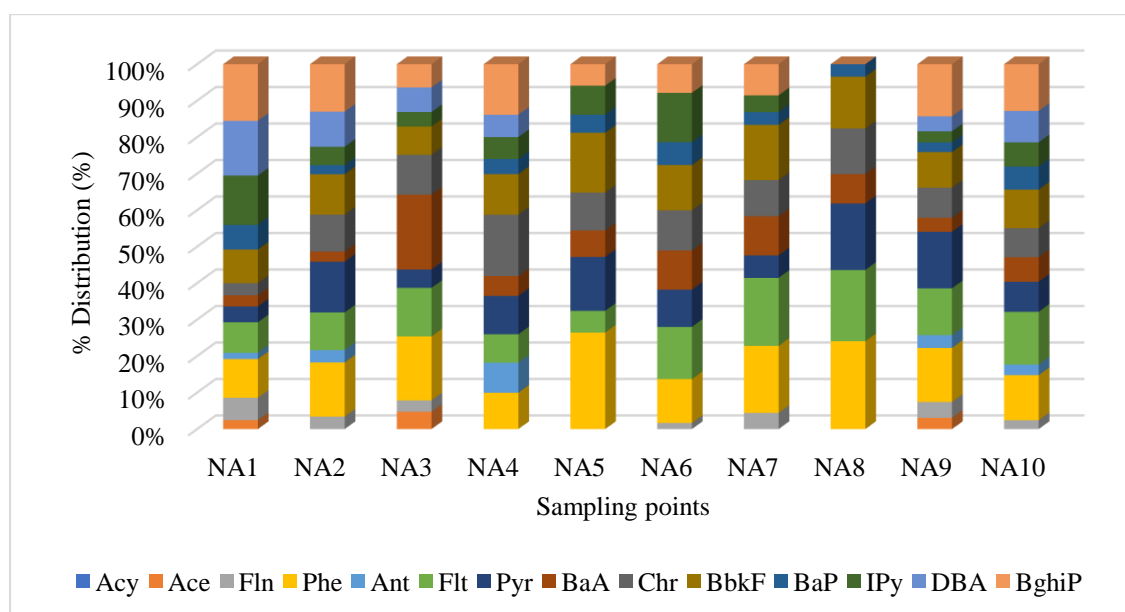
### 3.3.1.5.2.1 Profile of PAH contamination

Figure 3.13 and Table 3.17 show 4 ring PAH were most abundant at 41.3%. Next most abundant were 3 ring PAH at 21.7%. 5 ring PAH contributes 20.9% and the least abundant were 6 ring PAH (16.3%). Relative distributions of individual target compounds are displayed in Figure 3.14 and Table 3.16, showing that Phe contribute 16%, Flt 13%, BbkF 12% and Pyr 11% respectively.

**Figure 3-13 Percentage contribution to  $\Sigma$ PAH according to ring number average in individual soil samples from a non-active site (NAW)**



**Figure 3-14 Average percentage contribution to PAH of individual PAH in individual soil samples from a non-active site (NAW)**



**Table 3-16 Percentage contribution of individual PAH in soil from different sampling points at a non-active site (NAW) in wet season**

<b>Sample/PAH</b>	<b>Acy</b>	<b>Ace</b>	<b>Fln</b>	<b>Phe</b>	<b>Ant</b>	<b>Flt</b>	<b>Pyr</b>	<b>BaA</b>	<b>Chr</b>	<b>BbkF</b>	<b>BaP</b>	<b>IPy</b>	<b>DBA</b>	<b>BghiP</b>
NA1	<LOQ	2.5	6.1	10.6	1.7	8.4	4.3	3.1	3.3	9.2	6.8	13.5	15	15.5
NA2	<LOQ	<LOQ	3.4	14.8	3.4	10.3	13.9	2.8	10.1	11.1	2.5	5	9.6	13
NA3	<LOQ	4.8	3.1	17.5	<LOQ	13.3	5	20.5	10.9	7.7	<LOQ	4	6.7	6.4
NA4	<LOQ	<LOQ	<LOQ	10	8.2	7.8	10.5	5.5	16.8	11.1	4.1	6	6.1	13.9
NA5	<LOQ	<LOQ	<LOQ	26.4	<LOQ	6	14.8	7.3	10.4	16.4	4.9	8	<LOQ	5.9
NA6	<LOQ	<LOQ	1.7	12	<LOQ	14.3	10.2	10.7	11	12.4	6.2	13.5	<LOQ	7.8
NA7	<LOQ	LOQ	4.4	18.4	<LOQ	18.6	6.2	10.8	9.9	15.1	3.5	4.6	<LOQ	8.5
NA8	<LOQ	<LOQ	<LOQ	24.1	<LOQ	19.5	18.2	8.1	12.5	14.2	3.4	<LOQ	<LOQ	<LOQ
NA9	<LOQ	3.1	4.3	14.8	3.5	12.8	15.5	3.8	8.3	9.7	2.7	3	4.1	14.3
NA10	<LOQ	<LOQ	2.4	12.3	2.9	14.5	8.2	6.7	7.9	10.6	6.3	6.6	8.6	12.8
Average	<LOQ	1	2.6	16.1	2	12.6	10.7	7.9	10.1	11.8	4	6.4	5	9.8
SD	<LOQ	1.8	2.1	5.6	2.7	4.5	4.8	5.3	3.4	2.7	2.1	4.3	5.2	4.9

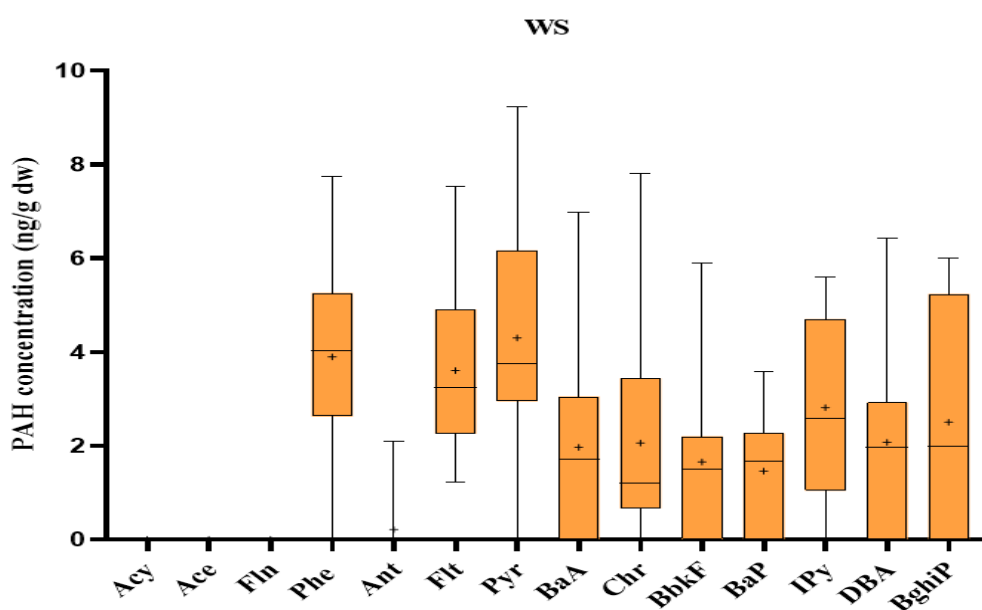
**Table 3-17 Concentration and percentage contribution of PAH according to ring number in individual samples from a non-active site (NAW) in wet season**

Ring Number	Concentration (ng/g)											
	NA1	NA2	NA3	NA4	NA5	NA6	NA7	NA8	NA9	NA10	Average	SD
Σ3 ring	5.5	5.4	4.5	4.7	4.1	1.8	4.2	2.4	14.4	3.4	5	3.5
Σ4 ring	5	9.2	8.8	10.4	5.9	6.1	8.4	5.8	22.6	7.2	8.9	5.1
Σ5 ring	8.2	5.7	2.7	5.5	3.3	2.5	3.5	1.8	9.2	4.9	4.7	2.5
Σ6 ring	7.7	4.5	1.8	5.1	2.1	2.8	2.4	0	9.7	3.7	4	2.9
Ring Number	Percentage Σ <sub>14</sub> PAH (%)											
	NA1	NA2	NA3	NA4	NA5	NA6	NA7	NA8	NA9	NA10	Average	SD
Σ3 ring	20.9	21.7	25.4	18.2	26.4	13.7	22.8	24.1	25.8	17.7	21.7	4.1
Σ4 ring	19.1	37.1	49.8	40.6	38.4	46.3	45.4	58.3	40.4	37.4	41.3	10.2
Σ5 ring	31	23.2	14.5	21.4	21.3	18.6	18.6	17.6	16.5	25.5	20.8	4.8
Σ6 ring	29	18	10.4	19.9	13.9	21.4	13.1	<LOQ	17.3	19.4	16.2	7.7

### 3.3.1.5.3 PAH concentrations at the Workstation location (WS) in wet season

Total average for  $\Sigma_{14}$ PAH concentration in soil samples obtained from the workstation (n=10) was 26.5 ng/g (range 18-33.5 ng/g). The concentrations of individual PAH are displayed in Figure 3.15. Average concentrations of  $\Sigma$ PAH<sub>6C</sub> and BaP were 12 ng/g (range 5.3-18.6 ng/g) and 1.5 ng/g (range <LOQ-3.59 ng/g) respectively. Most of the lower molecular weight PAH were below detection limits, likely reflecting the lower persistence and greater lability of these PAH in the environment.

**Figure 3-15 Average concentrations of Individual PAH in all samples in workstation (WS)location**

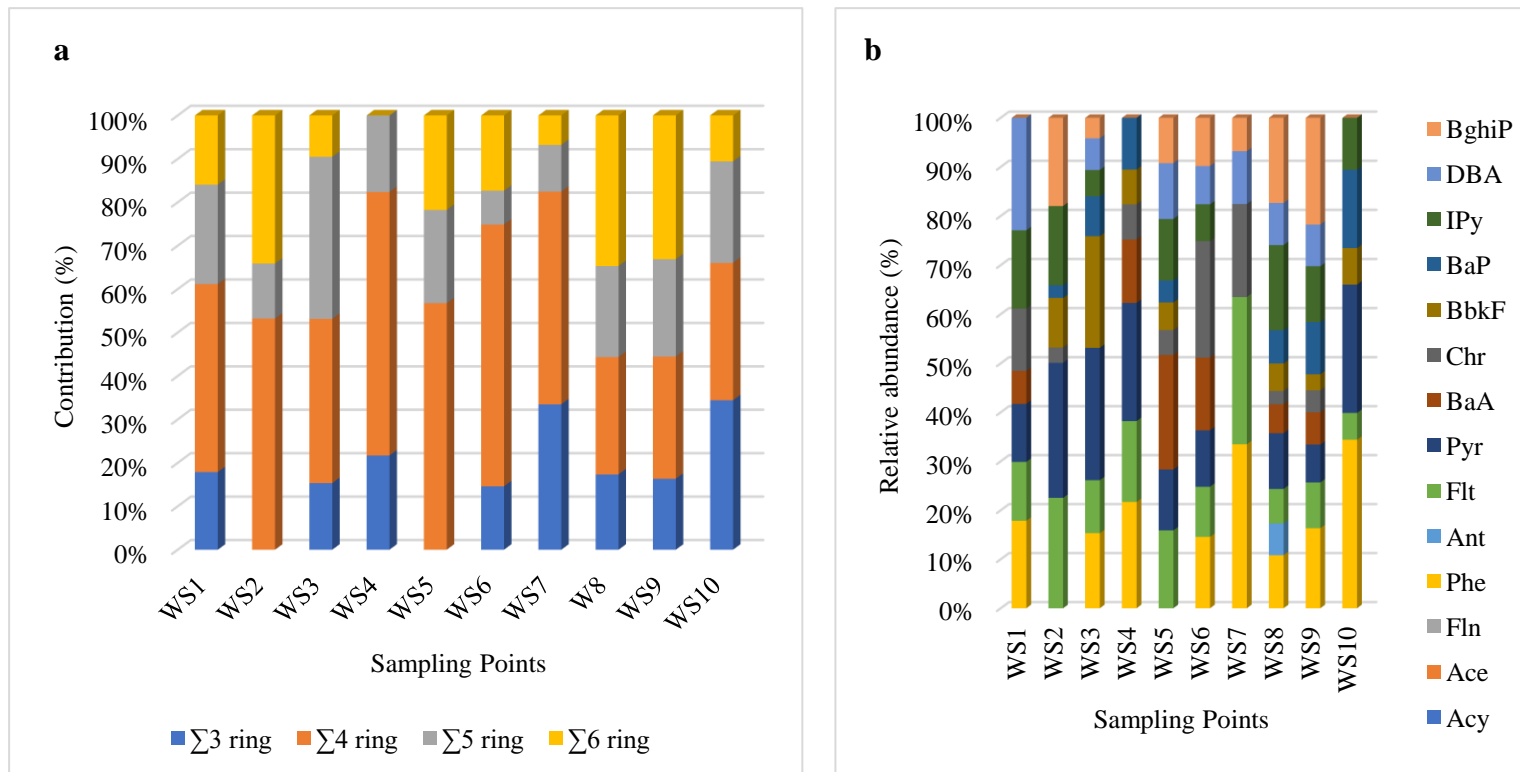


**Boxplot diagram indicating the minimum ,maximum and average(+),and interquartile range concentrations at WS in wet season**

### 3.3.1.5.3.1 Contamination Profile of PAH

From Figure 3.16a and b, and Table 3.19, it can be seen that at WS 4-ring PAH are most abundant at 44.8% (including Flt at 13.98 % and Pyr at 16 %). Next most abundant are 5 ring PAH at 19.7%, with 6 ring PAH contributing 18.4%, while the least abundant were 3 ring PAH at 17.1% of which Phe was the most abundant 3 ring compound.

**Figure 3-16 Percentage contribution of PAH according to ring number (a) and percentage contribution of individual PAH (%) (b) in individual samples from the Workstation location (WS)**



**Table 3-18 Percentage contribution of Individual PAH in individual samples at the workstation area (WS) in wet season**

Sample/ PAH	Acy	Ace	Fln	Phe	Ant	Flt	Pyr	BaA	Chr	BbkF	BaP	IPy	DBA	BghiP
WS1	<LOQ	<LOQ	<LOQ	17.9	<LOQ	12	11.8	6.7	12.7	<LOQ	<LOQ	15.9	22.9	<LOQ
WS2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	22.5	27.6	<LOQ	3.1	10.1	2.6	16.2	<LOQ	18
WS3	<LOQ	<LOQ	<LOQ	15.3	<LOQ	10.8	27	<LOQ	<LOQ	22.7	8.1	5.4	6.4	4.2
WS4	<LOQ	<LOQ	<LOQ	21.7	<LOQ	16.5	24.1	12.9	7.1	7.1	10.5	<LOQ	<LOQ	<LOQ
WS5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	15.9	12.4	23.4	5.1	5.6	4.5	12.5	11.4	9.2
WS6	<LOQ	<LOQ	<LOQ	14.6	<LOQ	10.2	11.5	14.9	23.7	<LOQ	<LOQ	7.5	7.8	9.8
WS7	<LOQ	<LOQ	<LOQ	33.5	<LOQ	30	<LOQ	<LOQ	18.9	<LOQ	<LOQ	<LOQ	10.8	6.8
WS8	<LOQ	<LOQ	<LOQ	10.8	6.5	7	11.4	5.9	2.7	5.6	6.8	17.3	8.6	17.3
WS9	<LOQ	<LOQ	<LOQ	16.3	<LOQ	9.3	7.7	6.6	4.5	3.3	10.6	11.4	8.5	21.7
WS10	<LOQ	<LOQ	<LOQ	34.4	<LOQ	5.5	26.2	<LOQ	<LOQ	7.4	16	10.6	<LOQ	<LOQ
Average	<LOQ	<LOQ	<LOQ	16.5	0.6	14	16	7	7.8	6.2	5.9	9.7	7.6	8.7
SD	<LOQ	<LOQ	<LOQ	11.6	2.1	7.5	9.5	7.9	8.1	6.8	5.5	6.3	6.9	8

**Table 3-19 Average concentrations and percentage contribution to  $\Sigma_{14}\text{PAH}$  according to ring number in individual samples from the workstation location (WS) in wet season**

Sample	Average concentration (ng/g)				Percentage of $\Sigma_{14}\text{PAH}$ (%)			
	No of Rings							
	$\Sigma 3$ ring	$\Sigma 4$ ring	$\Sigma 5$ ring	$\Sigma 6$ ring	$\Sigma 3$ ring	$\Sigma 4$ ring	$\Sigma 5$ ring	$\Sigma 6$ ring
WS1	5	12.1	6.4	4.5	17.9	43.3	22.9	15.9
WS2	<LOQ	17.8	4.2	11.4	0.0	53.2	12.7	34.1
WS3	4	9.8	9.7	2.5	15.3	37.8	37.3	9.5
WS4	4.1	11.5	3.3	<LOQ	21.7	60.7	17.6	<LOQ
WS5	<LOQ	17	6.4	6.5	<LOQ	56.8	21.5	21.8
WS6	4.8	19.8	2.6	5.7	14.6	60.3	7.8	17.3
WS7	6	8.8	1.9	1.2	33.5	49	10.8	6.8
W8	5.6	8.7	6.8	11.2	17.3	27	21	34.7
WS9	3.9	6.6	5.3	7.8	16.3	28.1	22.4	33.1
WS10	7.7	7.1	5.3	2.4	34.4	31.6	23.4	10.6
Average	4.1	11.9	5.2	5.3	17.1	44.8	19.7	18.4
SD	2.5	4.7	2.3	4.0	11.5	13.1	8.3	12.3

### 3.4 Comparative assessment of PAH concentrations within the seven locations in wet season

From our results, PAH were detected in all soil samples, except at WSD, NAW, and AW1, where the LMW- PAH and some HWM PAH were mainly below detection limits. This pattern is similar to that reported by Ana et al. (2009) and Oviasogie et al. (2006) in rural agricultural soil both from Niger Delta.

Overall average PAH concentrations was used to facilitate comparison in each location. For instance, the overall average PAH concentrations in the oil and gas production (OGP) area was estimated by finding the average of all the three sub-locations which is 128 ng/g. The average  $\Sigma_{14}\text{PAH}$  concentration at active oil well 3 (AW3) has the highest PAH contamination (129 ng/g) out of all the seven sites. While that of TST, AW2, and OGP were 94 ng/g, 100 ng/g, and 128 ng/g as shown in Table 3.20. The variations in concentrations reflect the differences in the oil and gas activities practised at each location, the physiochemical properties and behaviour of PAH, as well as the type of soil in each study area (Ana et al., 2009). By comparison, concentrations at AW1 and WS were markedly lower at 38 ng/g and 26 ng/g respectively, with

the lowest concentration of 22.7 ng/g observed at the non-active site (NAW). This is because, aside from a residential use, there were little or no oil and gas activity around these sites. Also, the highest  $\Sigma\text{PAH}_{6\text{C}}$  was found at AW3 (73.6 ng/g), indicating that the exposure health risk at this location is high compared to location other location like OGP (52 ng/g), TST (50.8 ng/g), AW2 (30.9 ng/g), even much higher than AW1 (23.8 ng/g), WS (14.7 ng/g) and NAW (12.4 ng/g).

**Table 3-20 Overall average concentration (ng/g) of  $\Sigma 14\text{PAH}$  in all the sampling locations in wet season**

PAH/location	OGP	TST	AW1	AW2	AW3	NAW	WS
Acy	16.3	0.6	0.6	4.6	4.1	<LOQ	<LOQ
Ace	16.4	9.2	<LOQ	7.2	6.7	0.3	<LOQ
Fln	8.5	5	<LOQ	5.8	4.6	0.7	<LOQ
Phe	13.8	8.5	4.7	11.3	10	3.4	3.9
Ant	8.8	5.3	0.2	8.7	9.4	0.6	0.2
Flt	5.7	9.1	4.6	12.7	11.6	2.7	3.6
Pyr	6.6	5.7	4.5	18.7	9.4	2.5	4.3
BaA	4.2	5.9	3.5	3.3	8.8	1.5	2
Chr	8.3	8.9	4.4	3.9	10.5	2.2	2.1
BbkF	6.2	6	3.2	5.2	10.9	2.5	1.7
BaP	9.2	5.1	2.9	4.5	17.6	0.9	1.5
IPy	11.6	6.9	3.3	2.8	9.6	1.4	2.8
DBA	3.1	5.8	1.4	2.3	4.5	1.3	2.1
BghiP	9.5	12.2	5.1	8.9	11.7	2.6	2.5
$\Sigma_{14}\text{PAH}$	128.1	94.2	38.4	99.9	129.3	22.7	26.5
$\Sigma\text{PAH}_{6\text{C}}$	52.1	50.8	23.8	30.9	73.6	12.4	14.7

Statistical analysis of variance, after carrying out a normality test and log transformed when appropriate, revealed some significant differences between  $\Sigma_{14}\text{PAH}$  concentrations observed at different locations ( $p < 0.05$ ). There are statistically significant differences between the concentrations of PAH in the location OGP with AW1, AW3, NAW, WS ( $p < 0.05$ ) and no

significant differences were obtained with TST and AW2 ( $p > 0.05$ ) respectively. This indicates a substantial influence of petroleum activities on these locations.

Accordingly, the findings reveal PAH are frequently found at elevated concentrations in areas where oil exploration and production has taken place. The ANOVA results provide evidence that the activities occurring at some locations influence concentrations of PAH.

#### **3.4.1.1 Comparison with PAH concentrations from other studies**

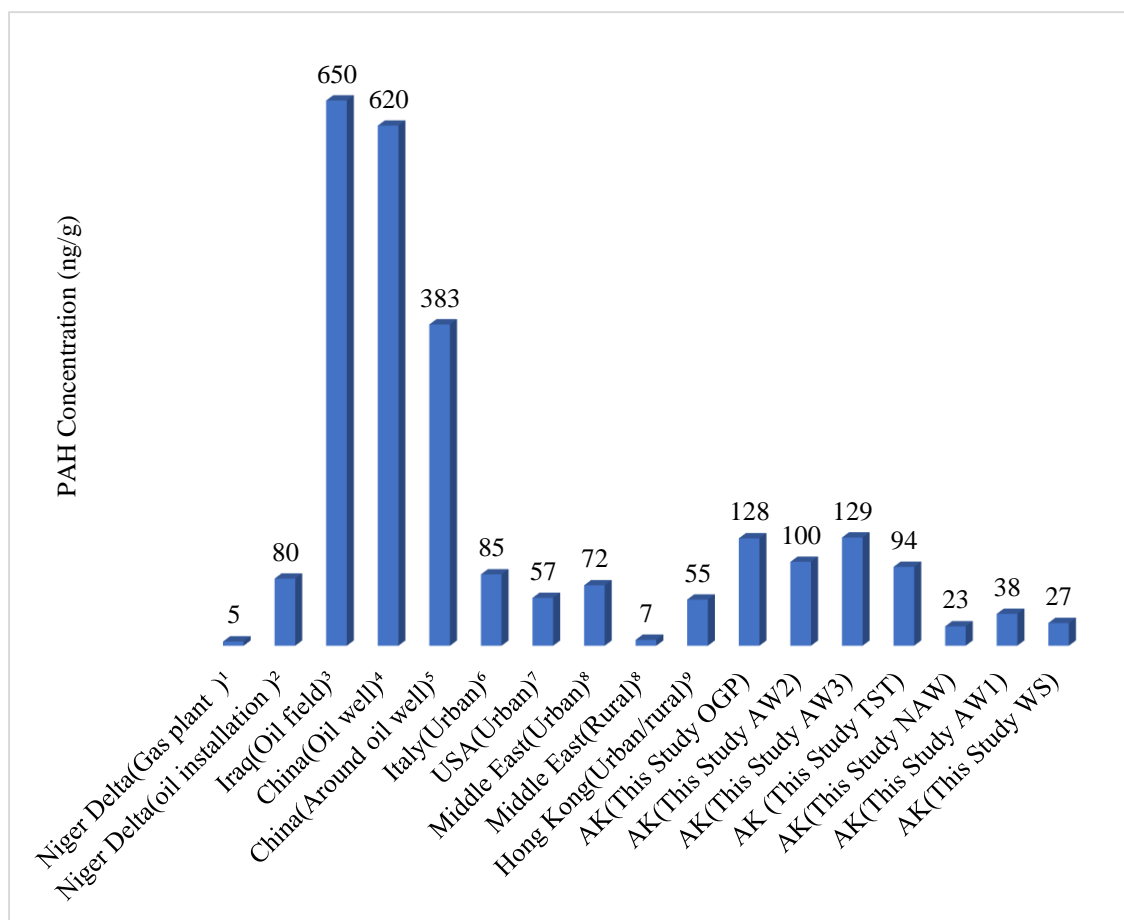
PAH concentrations in this study were compared with other studies of PAH contamination of soil reported in the literature (Figure 3.17). The concentrations recorded at OGP exceed substantially those found at a gas plant with flaring activities at Agbada 1 flow station in Allo village, Etche LGA, River State, Nigeria ( $\Sigma_{16}\text{PAH}$  78.3 ng/g and a mean of 4.9 ng/g for  $\Sigma_{16}\text{PAH}$  (Adedosu et al., 2013) and that previously reported by (Sojinu et al., 2010) at an oil installation area, Niger Delta.

Outside Nigeria, Ali and Khodakarami (2014) reported a mean  $\Sigma_{16}\text{PAH}$  concentration (650 ng/g) in soil impacted by gas flaring emissions in the Taq Taq oil field, Iraq that exceeded those in our study. In contrast, the concentrations detected in this study were substantially in excess of those detected at the Qurna-oil field for which a total concentration of 3 ng/g in spring was reported (Kadhim et al., 2019). Okpako et al. (2018) reported a mean  $\Sigma_{17}\text{PAH}$  value of 15,970 ng/g in lower Stubbs creek at Qua Ibom Estuary, Ibeno, Akwa Ibom, Nigeria in soil from farmland in the vicinity of a flare site. In the current study, soil samples were collected within and around a crude oil transfer and storage area at Mkpanak, Ibeno., Akwa Ibom. The concentrations of  $\Sigma_{14}\text{PAH}$  obtained at our TST location were exceeded by those reported by Okpako et al. (2018) and in a Niger Delta oil spill site by (Onojake et al., 2014). The mean PAH concentrations in our study locations all fall below recommended soil quality standard limit values ( $< 1000$  ng/g) (Maliszewska-Kordybach, 1996).

Previous studies of soil impacted by oil exploration activities in farmland usage and near oil wells has been reported. The  $\Sigma_{14}$ PAH concentrations obtained in this study for an oil well site exceeded those measured by Adedosu et al. (2013) at a location along an oil exploration pipeline (49 ng/g and mean 3.1 ng/g). In contrast, concentrations in this study were lower than those reported in soil samples around an oil well in Dagang, China (627 ng/g for  $\Sigma_{13}$ PAH (Jiao et al., 2015). Furthermore, around an oil well at Shengli, China, the average  $\Sigma_{13}$ PAH concentrations was 383 ng/g was discovered for  $\Sigma_{13}$ PAH (Fu et al., 2018), thereby exceeding those reported at our AW2 sub-location. In conclusion, concentrations of PAH in soil in our study appear at the low end of those reported for locations impacted by oil and gas exploration and production activities. Instead, they appear more consistent with those reported for urban and rural soils (see for instance, the urban soil from Southern Italy (7.4 ng/g) (Thiombane et al., 2019), from El-Paso, Texas, 57.4 ng/g (Roberto et al., 2009), from the Middle East (72 ng/g) (Al-Saad et al., 2019), urban and rural soil from Hong Kong (55 ng/g) (Zhang et al., 2006), and rural soil from the Middle East (7 ng/g) (Al-Saad et al., 2019).

This may reflect the very low background concentrations present in our study area prior to commencement of oil and gas exploration and production, coupled with good practice by the companies concerned that have minimised emissions, and the relatively short timeframe over which such activities have occurred. Concentrations at locations impacted by other PAH sources (e.g., urbanisation/traffic), and/or at which oil and gas activities have been practised for a longer period would be expected to contain higher PAH concentrations.

**Figure 3-17 Average concentrations of ΣPAH in soil from previous studies and this study in wet season**



<sup>1</sup>(Adedosu et al., 2013); <sup>2</sup>(Sojini et al., 2010); <sup>3</sup>(Ali and Khodakarami, 2014); <sup>4</sup>(Jiao et al., 2015); <sup>5</sup>(Fu et al., 2018); <sup>6</sup>(Thiombane et al., 2019); <sup>7</sup>(Roberto et al., 2009); <sup>8</sup>(Al-Saad et al., 2019); <sup>9</sup>(Zhang et al., 2006); OGP(Crude oil and gas production area);TST(Crude storage and transfer/pump area); AW1(Active oil well no drilling activities);AW2(Active gas well); AW3(Active oil well);NAW( Non active site); WS( workstation)

### 3.5 Variation and distribution of PAH during dry season sampling

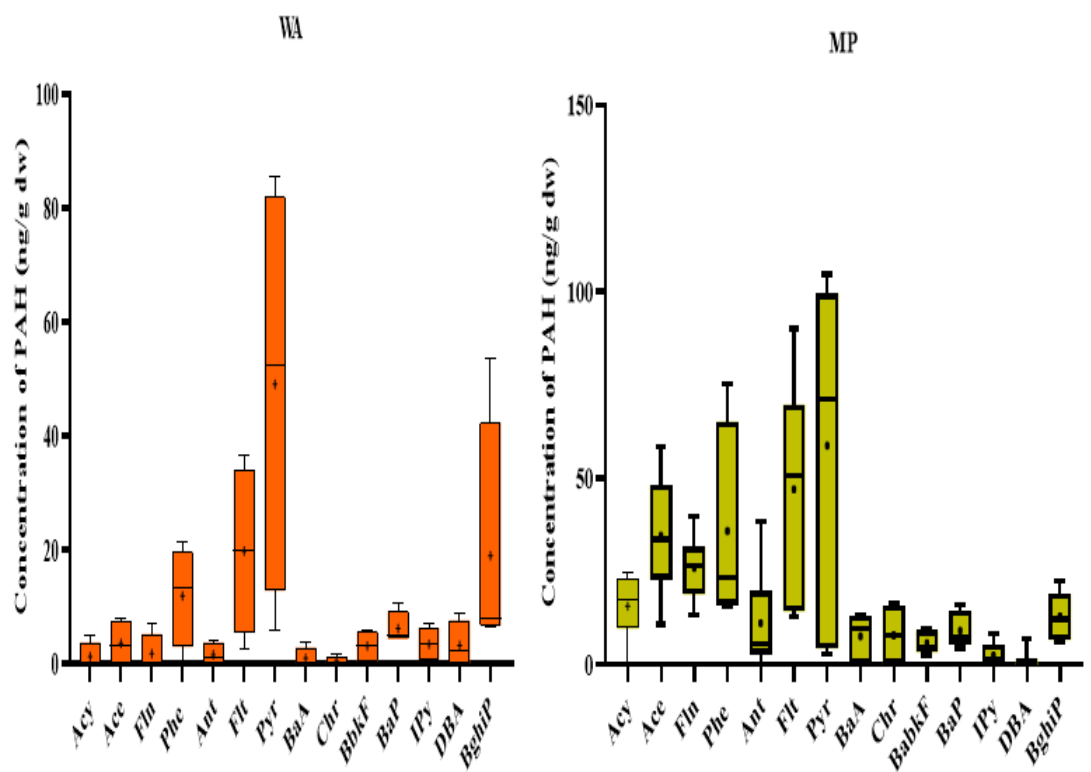
This section will discuss soil samples from the dry season taken in February 2020. Samples were collected in four different oil and gas fields (see section 2.1.1.2.1 for details).

#### 3.5.1 Concentrations at the oil and gas production location (OGP) during the dry season

Figure 3.18 revealed the concentration of individual components of PAH from two sub-sites. Summary parameters of concentrations of PAH identified in two sub-sites in oil and gas production plant (OGP) for the dry season are shown in Table 3.21. It was observed that

$\Sigma_{14}$ PAH concentrations were higher at the main processing sub-site (MP) (average 276.7 ng/g, range 179.8-416.3 ng/g) than at WA (average 125 ng/g, range 96.4-169.3 ng/g). The difference in concentrations between MP and WA likely reflects the different activities conducted in the vicinity of the two locations. The average concentration of BaP was 9.2 ng/g (range 4.5 to 16.1 ng/g) for MP, and 6.2 ng/g (range 4.0 to 10.6 ng/g) for WA. Concentrations of  $\Sigma$ PAH<sub>6C</sub> ranged between 8.67- 60.25 ng/g (34 ng/g average) and 10.6- 26.2 ng/g (17.5 ng/g average) for MP and WA respectively as detailed in table 3.34. Statistical analysis shows no significant difference in concentrations of  $\Sigma_{14}$ PAH between the two sub-sites ( $p=0.17$ ).

**Figure 3-18 Individual concentration PAH from OGP sub-locations in dry season**



**Boxplot diagram indicating the minimum ,maximum and average(+),and interquartile range concentrations at OGP in dry season. WA(Worker's accommodation) and MP (main processing area)**

**Table 3-21 PAH concentrations in soil (ng/g) from two sub-locations in oil and gas sub-site(OGP) in dry season**

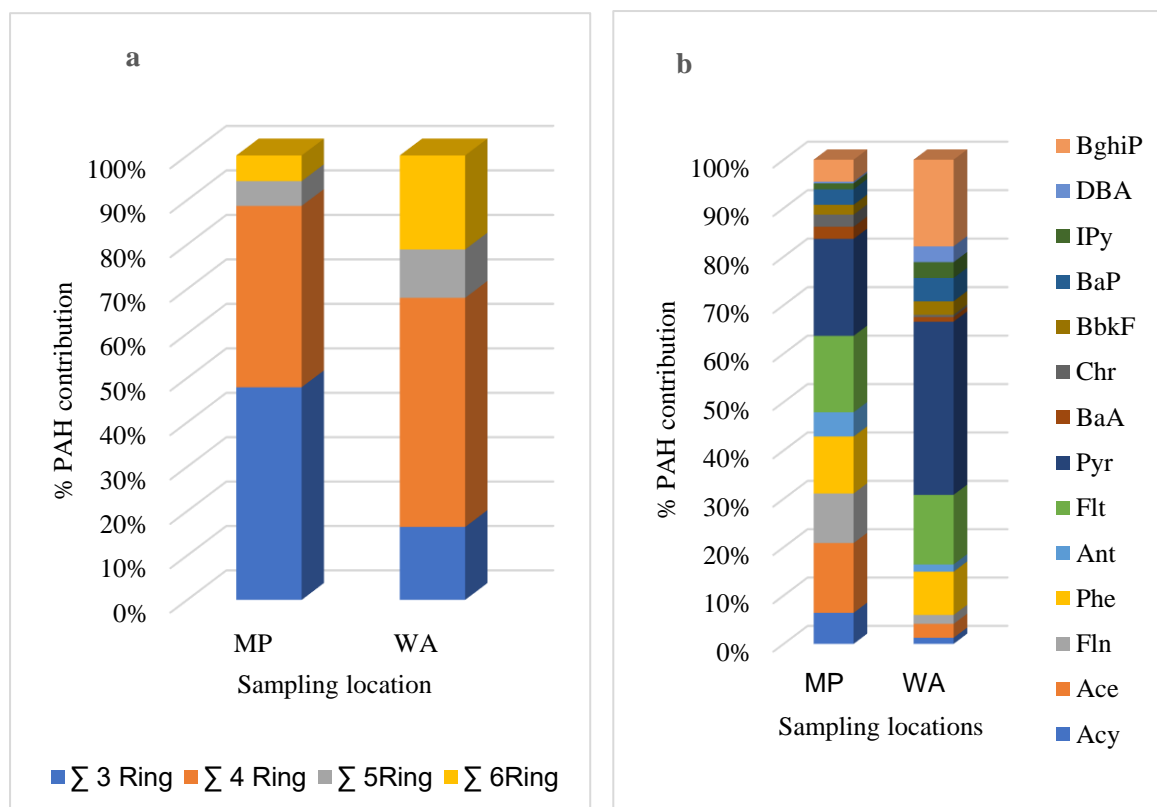
PAH	Worker's accommodation(WA, n=6)					Main processing area (MP, n=3)				
	Average	SD	Min	Median	Max	Average	SD	Min	Median	Max
Acy	1.2	2.5	<LOQ	<LOQ	5.0	15.8	8.8	<LOQ	17.3	24.7
Ace	3.6	4.2	<LOQ	3.2	7.9	34.7	16.2	10.9	33.5	58.5
Fln	1.8	3.5	<LOQ	0.1	7	25.9	8.8	13.2	26.5	39.8
Phe	11.9	8.9	<LOQ	13.2	21.4	35.9	26.2	15.6	23.4	75.3
Ant	1.6	2	<LOQ	1.1	4.2	11.2	14.1	<LOQ	5.6	38.5
Flt	19.8	14.8	2.7	19.9	36.7	47.1	29.4	13.0	50.8	90
Pyr	48.6	37.0	4.0	52.3	85.6	58.8	47.2	2.9	71.3	104.7
BaA	1	1.9	<LOQ	<LOQ	3.8	7.7	6.3	<LOQ	9.8	13.5
Chr	0.4	0.9	<LOQ	<LOQ	1.8	8	7.4	<LOQ	7.9	16.4
BbkF	3.1	2.8	<LOQ	3.3	6	5.8	3.0	2.7	4.8	9.8
BaP	6.2	3	4.4	5	10.6	9.2	4.7	4.5	7.2	16.1
IPy	3.5	2.9	<LOQ	3.4	7.1	2.5	3.3	<LOQ	1.2	8.3
DBA	3.3	4.2	<LOQ	2.2	8.7	1.2	2.8	<LOQ	<LOQ	6.9
BghiP	19	23.1	6.5	8.0	53.6	13	6.3	6.2	12.2	22.5
$\Sigma_{14}$ PAH	125.1	111.6	96.4	117.4	169.3	276.7	184.7	179.8	267.6	416.3
$\Sigma$ PAH <sub>6C</sub>	17.5	15.7	10.6	16.6	26.2	34.3	27.5	8.7	36.4	60.3

### 3.5.1.1 Contamination of PAH at OGP in dry season

From Figure 3.19a and Table 3.23, the ring profile of PAH in soil sampled from MP and WA displays a different pattern of contamination at the two sites. Generally, the 3 ring and 4 ring are the most significant component in the two sub-sites. Studies have demonstrated a similar prevalence of 3-ring and 4-ring PAH in soil from petroleum contaminated site in China (Wang et al., 2018a). The soil from MP comprised on average 47.9% 3 ring PAH, characterised predominantly by Ace and Phe with 14% and 11.8% as in figure 3.19a. This was followed by the 4 ring PAH (40.8%  $\Sigma_{14}$ PAH). On the other hand, 4-ring PAH accounted for 51.6% of the  $\Sigma_{14}$ PAH in WA Pyr (35%) and Flt (14.4%) the main contributors. By comparison, 3 ring PAH contributed 16.4 % including 8.95% contribution from Phe. The relative ring distribution of

PAH at OGP for the two sub-sites in the dry season are: WA 4>6>3>5 ring and 3>4>6>5 ring PAH for MP.

**Figure 3-19 Contribution of PAH to ΣPAH according to ring number(a) and individual PAH distribution in soil samples from sub-location within OGP in dry season**



WA(Worker’s accommodation) and MP(main processing area)

**Table 3-22 Average concentration and percentage distribution of individual PAH in soil sampled from three different sub-sites in active oil and gas production area (OGP) in dry season**

PAH	Average Concentration (ng/g)		Percentage contribution (%)		PAH	Average Concentration (ng/g)		Percentage contribution (%)	
	MP	WA	MP	WA		MP	WA	MP	WA
Acy	15.8	1.2	6.4	1.3	BaA	7.7	1	2.5	1
Ace	34.7	3.6	14.4	2.9	Chr	8	0.4	2.5	0.4
Fln	25.9	1.8	10.2	1.8	BbkF	5.8	3.1	2	2.8
Phe	35.9	11.9	11.8	8.9	BaP	9.2	6.2	3.2	4.8
Ant	11.2	1.6	5	1.5	IPy	2.5	3.5	1.2	3.3
Flt	47.1	19.8	15.8	14.4	DBA	1.2	3.3	0.3	3.3
Pyr	58.8	49.1	20	35.8	BghiP	13	19	4.5	17.9

**Table 3-23 Concentrations of PAH (n/g) and contribution to  $\Sigma_{14}$ PAH according to PAH ring number in dry season**

Location	Average concentration (ng/g)				% Contribution			
	No of Rings							
	3	4	5	6	3	4	5	6
MP	123.5	121.6	16.1	15.5	47.9	40.8	5.6	5.8
WA	20.2	70.3	12.7	22.5	16.4	51.6	10.9	21.1

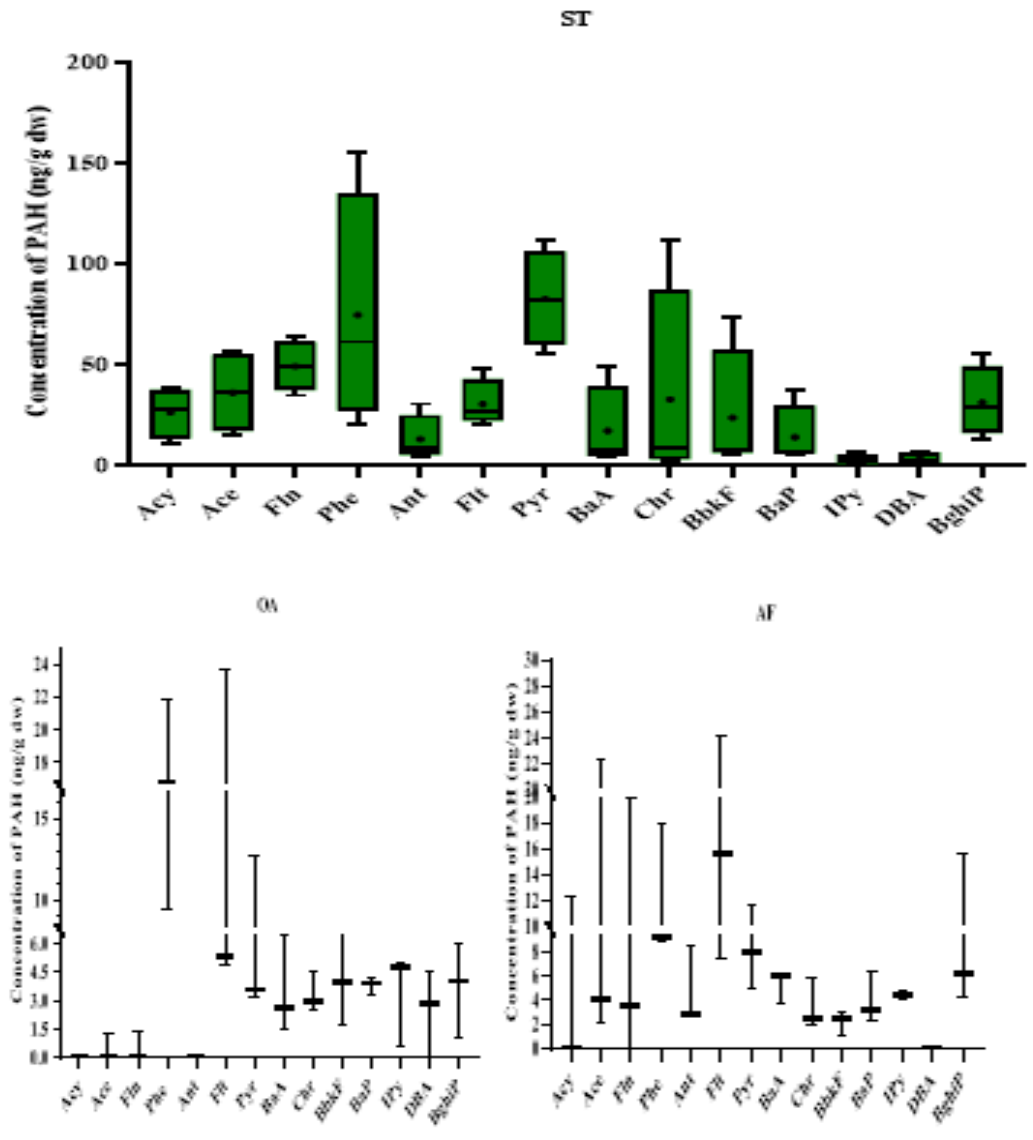
### 3.5.2 Concentrations of PAH in crude oil transfer area (TST) in dry season

The box and whisker plot representing the distribution of individual PAH in this study area are given in Figure 3.20. Table 3.24 present the concentrations of  $\Sigma_{14}$ PAH and  $\Sigma$ PAH<sub>6C</sub> in soil samples from the crude oil transfer site (TST) and the concentrations of PAH in soil samples in TST varied to a great extent at different sub-locations. The highest concentration was measured at the storage tank and pump area (ST) with an average of 440 ng/g (range 312 to 679 ng/g). PAH concentrations were significantly lower in the office area (average = 59.2 ng/g, range 54.8 to 64.2 ng/g) while the at AF were concentrations at AF significantly lower than those at ST (average 90 ng/g, range 79.6 to 106.6 ng/g).

At ST, concentrations of  $\Sigma$ PAH<sub>6c</sub> were on average 95.8 ng/g (range 26.5 to 281.3 ng/g). These exceeded those at both AF (average 19.23 ng/g, range 15.7 to 25.5 ng/g) and OA (average 20.8 ng/g, range 10.6 to 26 ng/g) respectively. Average concentrations of BaP were: 14 ng/g for ST, 3.8 ng/g for OA and 3.9 ng/g for 3.9 ng/g.

The difference in concentrations from the sub-locations (ST, OA, and AF) in TST were evaluated with one-way ANOVA after testing for normality and log transformation where applicable. The results revealed concentrations at ST significantly exceeded those at both the OA and AF ( $p < 0.05$ ) but that no significant variation was observed between OA and AF ( $p > 0.05$ ).

**Figure 3-20 Concentrations of individual PAH at three sub-sites within crude oil transfer area (TST)**



**Boxplot diagram showing interquartile the minimum ,maximum and average(+),and interquartile range concentrations at TST in dry season. OA(Office area);ST(Storage tank and pump area) and AF(surrounding of crude oil transfer field)**

**Table 3-24 Summary of PAH concentrations in soil from the crude oil transfer area from three different sites (TST) in dry season**

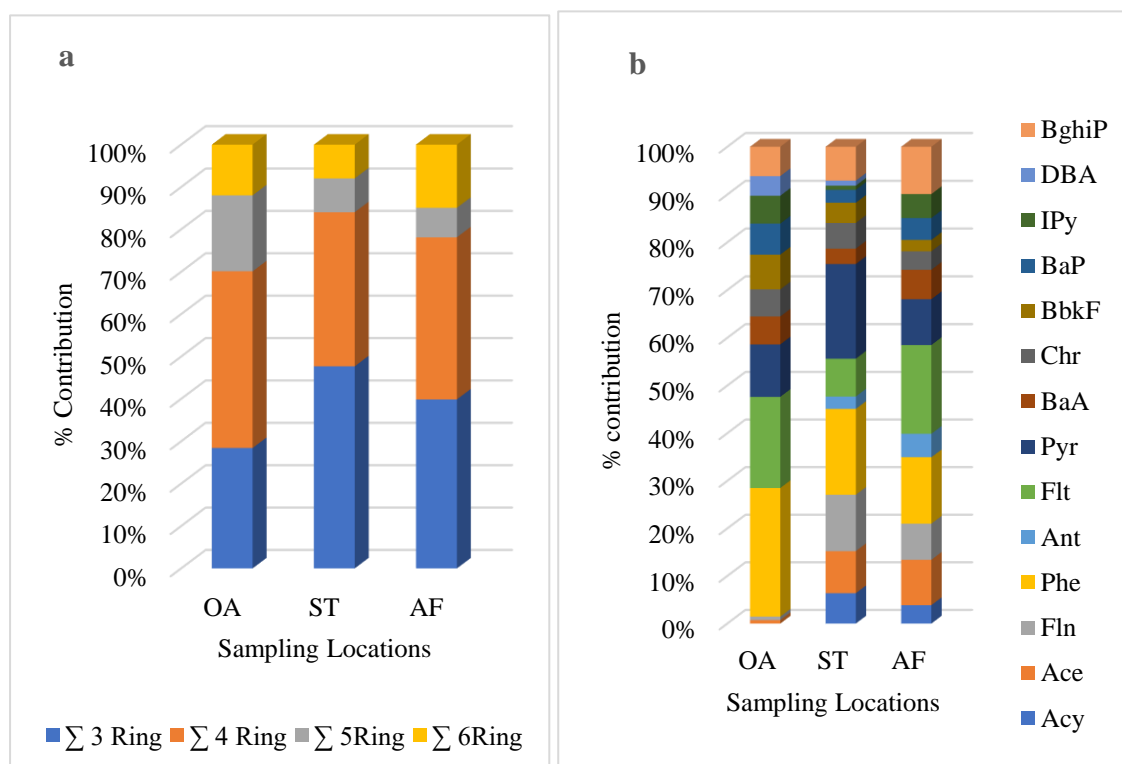
PAH	OA					ST					AF				
	Average	SD	Min	Median	Max	Average	SD	Min	Median	Max	Average	SD	Min	Median	Max
Acy	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	26.4	12.9	10.5	28.0	38.9	4.1	7.1	<LOQ	<LOQ	12.4
Ace	0.4	0.7	<LOQ	<LOQ	1.3	36.2	20.3	15.4	36.2	56.8	9.5	11.2	2.1	4.1	22.4
Fln	0.5	0.8	<LOQ	<LOQ	1.4	49.3	12.5	34.7	49.0	64.3	7.8	10.6	<LOQ	3.5	19.9
Phe	16.1	6.2	9.5	16.8	21.9	74.7	58.4	20.4	61.4	155.5	12.0	5.2	8.9	9.2	18.0
Ant	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	13.0	11.8	4.2	8.7	30.5	4.7	3.3	2.8	2.8	8.5
Flt	11.3	10.7	4.9	5.3	23.7	30.6	12.3	20.7	26.5	48.5	15.7	8.4	7.4	15.6	24.2
Pyr	6.5	5.4	3.2	3.6	12.7	82.7	24.1	55.5	81.9	111.5	8.2	3.3	5.0	7.9	11.7
BaA	3.5	2.6	1.5	2.7	6.5	17.2	21.3	4.1	7.8	49.0	5.3	1.4	3.7	6.1	6.2
Chr	3.3	1.0	2.5	3.0	4.5	32.9	52.9	2.3	8.6	112.0	3.4	2.1	1.9	2.5	5.8
BbkF	4.2	2.6	1.8	4.0	7.0	23.8	33.4	6.0	7.7	73.9	2.2	1.0	1.1	2.4	3.1
BaP	3.8	0.4	3.3	3.9	4.2	14.0	15.7	5.7	6.4	37.5	3.9	2.2	2.2	3.2	6.4
IPy	3.4	2.5	0.6	4.8	5.0	3.2	2.5	0.7	2.9	6.4	4.4	0.3	4.1	4.5	4.7
DBA	2.5	2.3	<LOQ	2.8	4.5	4.8	3.2	<LOQ	6.0	7.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BghiP	3.7	2.5	1.0	4.0	6.0	31.3	17.8	12.9	28.5	55.3	8.7	6.1	4.2	6.2	15.7
Σ <sub>14</sub> PAH	59.2	37.9	54.8	58.7	64.2	439.9	299.2	311.5	384.3	679.3	90.1	62.2	79.6	84.0	106.6
ΣPAH <sub>6C</sub>	20.8	11.5	10.6	25.9	26.0	95.8	129.1	26.5	37.8	281.3	19.3	7.0	15.7	16.7	25.5

### 3.5.2.1.1 Profile of PAH contamination

PAH compounds were measured simultaneously at ST, AF, and OA sub-sites, allowing for creation of a profile by differences between the three sub-sites. Thus Figure 3.21 represent the calculated profiles, while tables 3.25 and 3.26 represent the spatial distribution of both individual PAH as well as according to ring number.

Whilst the 3 membered rings are mostly found in sub-sites ST and AF, the 4 membered rings were the most abundant in OA. More so, the 5 ring and 6 ring show varied sequences of the number of benzene rings in all the sub-locations, probably due to pollution source. The ring pattern in OA, ST and AF are 4>3>5>6 rings, 3>4>5+6 rings and 3>4>6>5 rings correspondingly.

**Figure 3-21 Percentage contribution to  $\Sigma 14$ PAH according to ring number and Individual PAH in soil from three sub-locations at the crude oil transfer area (TST)**



OA represent the office areas ST is the storage tank/pump area and AF is the surrounding of the field

**Table 3-25 Concentration (ng/g) and percentage contribution of individual PAH compounds in crude oil transfer area(TST) in dry season**

Location	Average concentration of individual PAH compounds													
	Acy	Ace	Fln	Phe	Ant	Flt	Pyr	BaA	Chr	BbkF	BaP	IPy	DBA	BghiP
OA	0	0.4	0.5	16.1	0	11.3	6.5	3.5	3.3	4.2	3.8	3.4	2.5	3.7
ST	26.4	36.2	49.3	74.7	13	30.6	82.7	17.2	32.9	23.8	14	3.2	4.8	31.3
AF	4.1	9.5	7.8	12	4.7	15.7	8.2	5.3	3.4	2.2	3.9	4.4	0	8.7
(% ) Percentage contributions of individual PAH														
OA	0	0.7	0.7	27	0	19.2	11	5.9	5.7	7.3	6.5	5.8	4.1	6.2
ST	6.4	8.8	11.8	18	2.6	7.9	19.8	3.2	5.4	4.2	2.7	0.9	1	7.1
AF	3.9	9.5	7.6	14	4.9	18.6	9.6	6.2	3.9	2.4	4.6	5	0	9.9

**Table 3-26 Average concentration of  $\Sigma$ 14PAH (n/g) and percentage contributions to  $\Sigma$ 14PAH in crude oil transfer area(TST) expressed in number of rings in dry season**

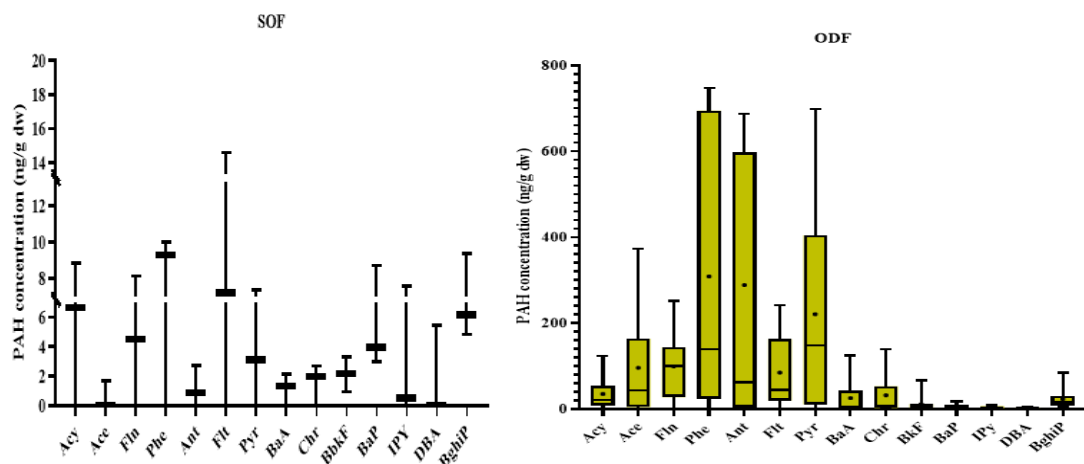
Location	Average concentration (ng/g)				% Contribution			
	No of Rings							
	3	4	5	6	3	4	5	6
OA	16.9	24.6	10.5	7.1	28.4	41.7	17.9	12
ST	199.5	163.3	42.6	34.5	47.7	36.3	8	8
AF	38.2	32.6	6.1	13.1	39.9	38.3	7	14.9

AF surroundings of crude oil transfer field, storage tank and pumps area, OA close to office area

### 3.5.3 Concentrations of target PAH in soil from active oil well (AW1) with drilling operation in dry season

Concentrations of PAH at ODF and SOF were on average 1589.8 ng/g (range 291-2818) and 49.7ng/g (range 33-62.8 ng/g) respectively. A statistical summary of the concentrations  $\Sigma_{14}$ PAH within the oil drilling field (ODF n=10) and the surroundings of the oil field (SOF n=3), are presented in Table 3.27, Figure 3.22 depicts the concentrations of individual PAH for these two AW1 sub-locations in the dry season. Concentrations of  $\Sigma$ PAH<sub>6C</sub> and BaP were also estimated to ascertain the toxicity of the soil at these sub-locations. The concentrations of BaP at ODF were on average 6.7 ng/g (range 2 to 17.3 ng/g) and at SOF were 1.2 ng/g (ranged <LOQ to 2.14 ng/g). At ODF  $\Sigma$ PAH<sub>6C</sub> was an average of 99 ng/g (range 16-326 ng/g) whereas at SOF the average concentration was 14.6 ng/g (range 8-19.6 ng/g). An independent t-test revealed statistically higher ( $p < 0.05$ ) concentrations at ODF compared to SOF, which indicates a discernible impact of oil drilling activities on local PAH contamination in soil.

**Figure 3-22 Concentrations of individual PAH at two sub-locations within active oil well 1 (AW1) with drilling activities in dry season**



**Boxplot diagram indicating the minimum ,maximum and average(+)and interquartile range concentrations at AW1 1in dry season SOF(Surrounding of oil drilling field) and ODF(Within oil drilling field)**

**Table 3-27 Concentrations of individual PAH at two sub-locations within an active oil well location with drilling activities in dry season**

PAH	SOF(n=3)					ODF(n=10)				
	Average	SD	Min	Median	Max	Average	SD	Min	Median	Max
Acy	5.2	4.6	<LOQ	6.6	8.8	43.8	37.0	6.3	36.3	123.1
Ace	0.6	1	<LOQ	<LOQ	1.7	124.3	114.7	7.7	120.2	372.9
Fln	4.2	4.1	<LOQ	4.5	8.1	127.2	67.8	46.5	112.7	251.2
Phe	6.4	5.6	<LOQ	9.3	10	399.2	301.3	37.7	395.8	747
Ant	1.2	1.4	<LOQ	0.9	2.7	374.5	305.5	4.1	556.4	686.9
Flt	7.3	7.3	<LOQ	7.2	14.6	107.7	81.1	24.3	91	241.1
Pyr	3.5	3.7	<LOQ	3.1	7.4	286	224.3	13.7	199.9	697.9
BaA	1.2	1.1	<LOQ	1.3	2.1	32.3	37.9	1.1	24.7	124.1
Chr	1.6	1.4	<LOQ	2	2.7	41.1	54.7	2.3	9.8	138.6
BbkF	2.1	1.2	0.9	2.2	3.3	14.2	19.2	1.8	7.9	66.2
BaP	5.2	3.1	3	4	8.7	6.7	4.8	2	5.2	17.3
IPy	2.7	4.2	<LOQ	0.5	7.6	3.4	2.8	<LOQ	2.6	8.4
DBA	1.8	3.1	<LOQ	<LOQ	5.4	1.4	1.7	<LOQ	0.6	5
BghiP	6.8	2.3	4.9	6.2	9.4	27.8	22.9	6.6	18.6	84.2
$\Sigma_{14}$ PAH	49.7	44.1	33.3	53	62.8	1589.8	1275.7	291	1871.4	2828
$\Sigma$ PAH <sub>6C</sub>	14.6	14.1	8	16	19.6	99.2	121.2	16.2	56.9	326

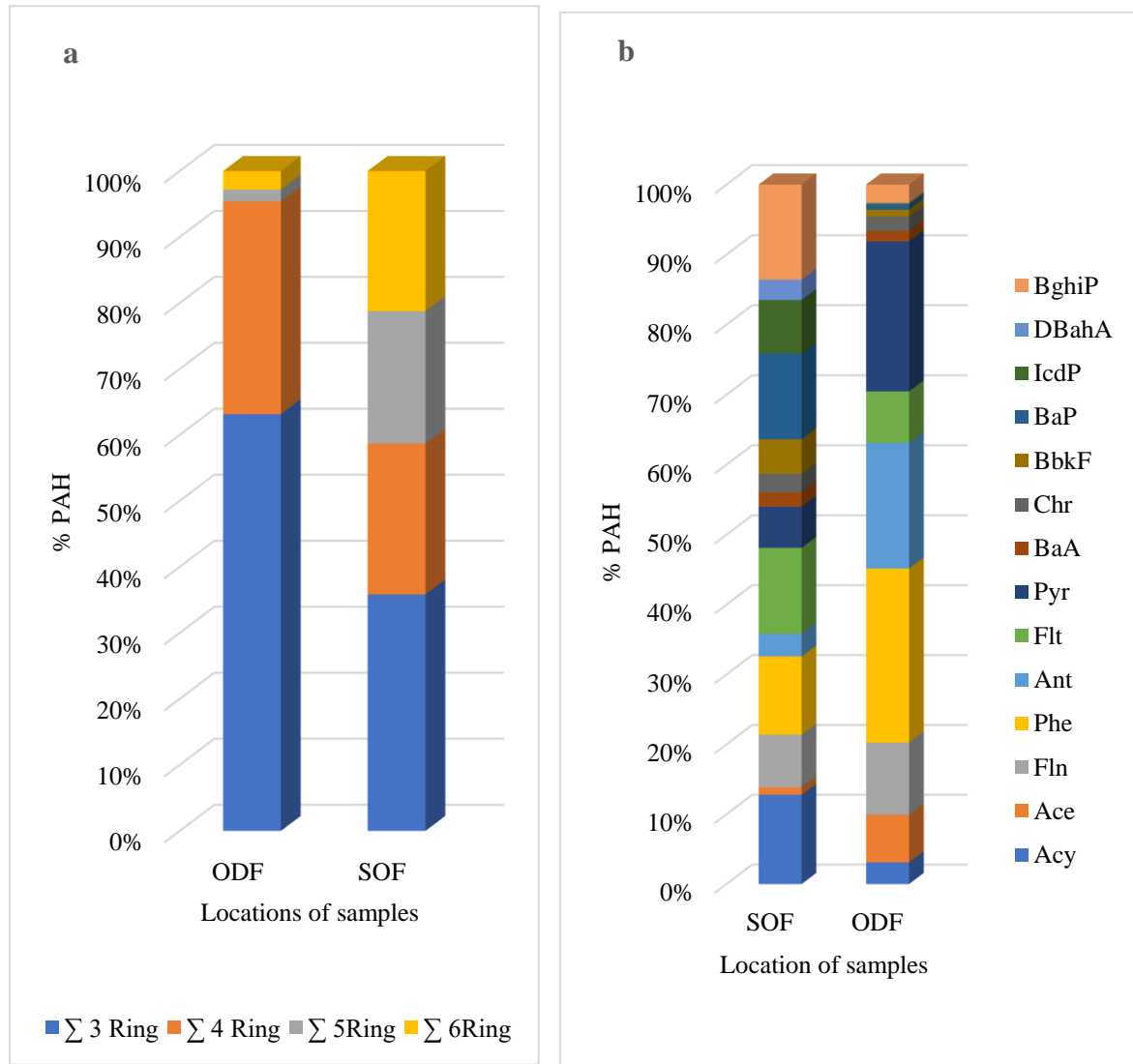
### 3.5.3.1 Profile and composition of PAH in oil drilling sites

Contributions to  $\Sigma_{14}$ PAH of individual PAH and when grouped according to ring number are shown in Figure 3.23 and Table 3.28 and 3.29. Three ringed PAH are the major contributor at ODF comprising on average 63%  $\Sigma$ PAH, with contributions from Phe (24.9%), Ant (18%) and Fln (10%). This predominance of Phe coincides with the findings reported by Nganje et al. (2012) at a site impacted by fuel oil spillage at Calabar, Nigeria.

By comparison, 4 ring PAH contribute 32.3 % while 5 and 6 ring PAH, make only small contributions at 1.8 % and 2.8 % respectively. The order of number of fused aromatic ring are 3>4>6> 5 rings. This is comparable to the results of Wang et al. (2015a) at one of the locations at Shengli. A different pattern was observed at SOF. Although 3 ring PAH are still the most abundant at an average of 35.8%, they are not so predominant as at ODF, with the average

contributions of 4, 5, and 6 ring PAH being 22.9%, 20 %, and 21.2% respectively. This different ring number pattern likely arises from the greater impact of oil drilling activity emissions at ODF compared to SOF.

**Figure 3-23 Percentage distribution of PAH according to ring number (a) and individual PAH (b) at active oil well with drilling operation (AW1)**



ODF(within oil drilling field) and SOF( Surrounding of oil drilling field)

**Table 3-28 Average concentrations (ng/g) and percentage contribution of individual PAH compounds at active oil well 1 with drilling activities (AW1) in dry season**

Location	Average concentrations (ng/g) of individual PAH													BghiP
	Acy	Ace	Fln	Phe	Ant	Flt	Pyr	BaA	Chr	BbkF	BaP	IPy	DBA	
ODF	43.8	124.3	125.2	399.2	374.5	107.7	286	32.3	41.1	14.2	6.7	3.4	1.4	27.8
SOF	5.2	0.6	4.2	6.4	1.6	7.3	3.5	1.2	1.5	2.1	5.1	2.7	1.8	6.8
	Percentage (%) contributions of individual PAH													
ODF	3.1	6.8	10.3	24.9	18	7.3	21.4	1.5	2	1	0.6	0.3	0.2	2.6
SOF	12.8	1.1	7.5	11.2	3.2	12.3	5.9	2.1	2.6	4.9	12.2	7.6	2.9	13.6

**Table 3-29 Average concentrations of  $\Sigma$ 14PAH (ng/g) and contribution to  $\Sigma$ 14PAH according to ring number in dry season**

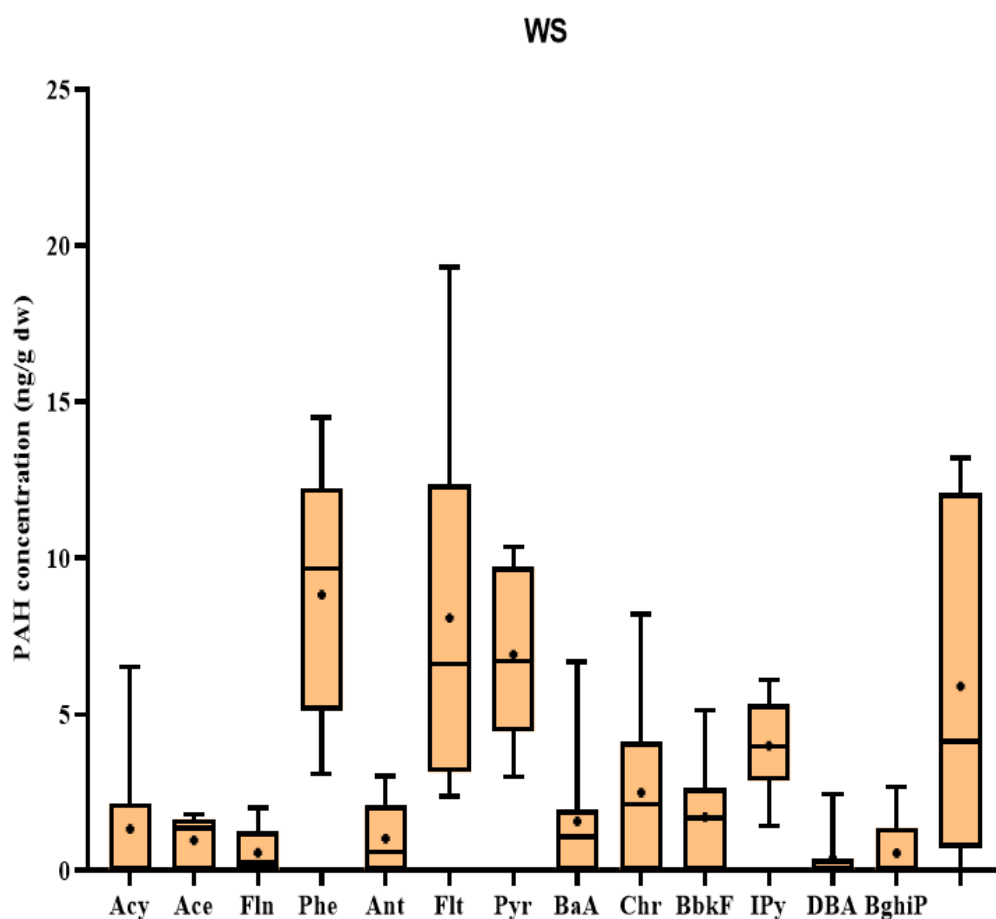
Location	Average concentrations (ng/g)				% $\Sigma$ 14PAH			
	No of Rings							
	3	4	5	6	3	4	5	6
ODF	1067	467.2	22.3	31.3	63.1	32.3	1.8	2.8
SOF	17.9	13.5	9.1	9.5	35.8	22.9	20.1	21.2

**SOF(Surrounding of oil drilling field) and ODF(Within oil drilling field)**

### 3.5.4 Concentration of PAH in Workstation in dry season

At the WS location, the average  $\Sigma_{14}$ PAH concentration was 44 ng/g (range 26.5 to 64 ng/g). Concentrations of the 14 individual PAH and 6 carcinogenic PAH investigated (n=8). Figure 3.24 represents individual PAH concentrations at each sampling point at WS. Average concentrations of  $\Sigma$ PAH<sub>6C</sub> and BaP were 10.7 ng/g (range 3.9 to 21.6 ng/g) and 4 ng/g (range 1.4 to 6 ng/g).

**Figure 3-24 Concentrations (ng/g) of individual PAH at workstation (WS) in dry season**

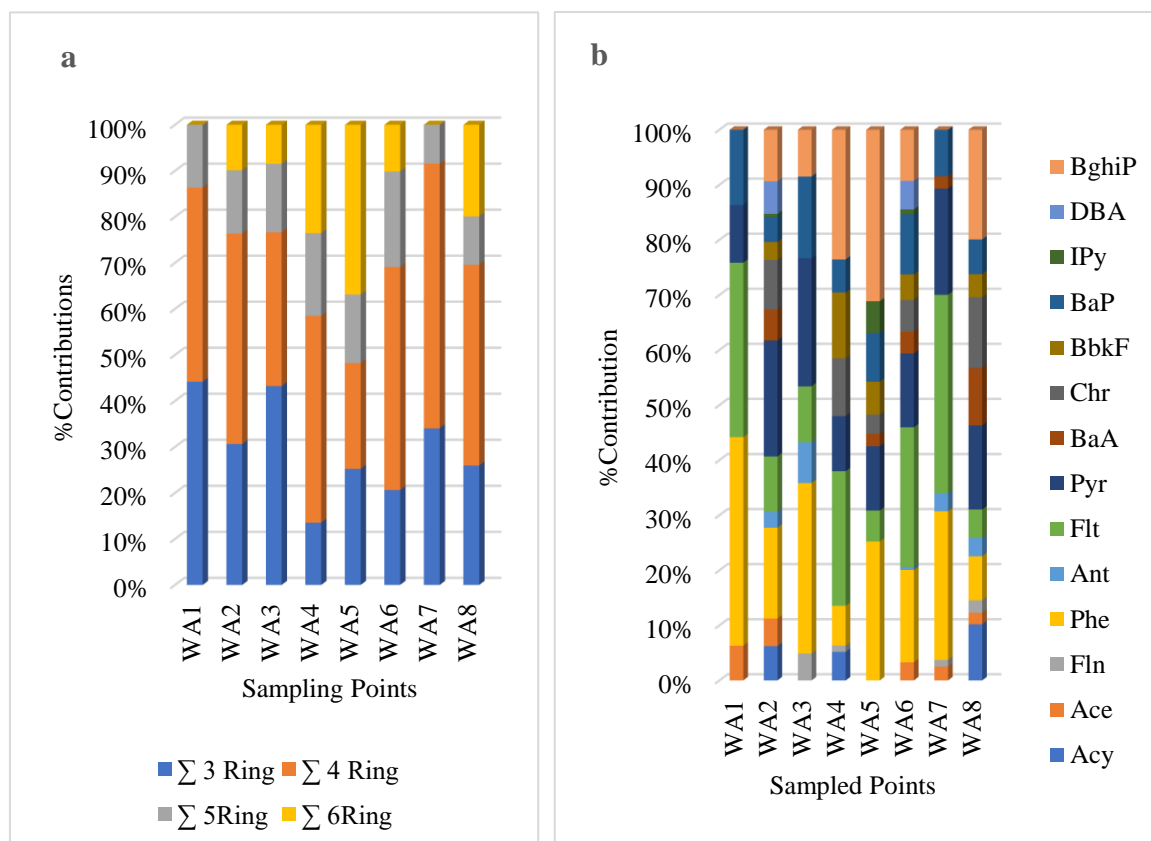


**Boxplot diagram showing average(+),interquartile ranges,minimum and maximum concentrations at WS in dry season**

### 3.5.4.1.1 PAH profile

The distribution in terms of number of PAH rings found in Workstation (WS) was quite similar to that detected in the soil sample profiles identified at the Office area (OA) and the crude oil transfer area (TST) (section 3.4.1). This is illustrated in Figure 3.25a. Four ring PAH were most abundant (43%), of which Flt and Pyr contributed 18.5% and 15.6 % respectively. Three ring PAH contributed 29 % (principally 21% Phe). Five and six ring PAH each contributed 14 % with BghiP contributing 12.7%. Overall, the 3 and 4 ring PAH were relatively most abundant as illustrated in Table 3.30 and Table 3.31 which shows relative abundance of individual PAH to  $\Sigma$ PAH. The contribution pattern of rings is 4>3>5>6 rings.

**Figure 3-25 Percentage contribution of PAH according to ring number (a) and percentage contribution of individual PAH (%) in individual samples (b) at the Workstation location (WS) in dry season**



**Table 3-30 Percentage concentration of individual PAH in sampled at workstation in dry season**

<b>Sample/PAH</b>	<b>Acy</b>	<b>Ace</b>	<b>Fln</b>	<b>Phe</b>	<b>Ant</b>	<b>Flt</b>	<b>Pyr</b>	<b>BaA</b>	<b>Chr</b>	<b>BbkF</b>	<b>BaP</b>	<b>IPy</b>	<b>DBA</b>	<b>BghiP</b>
WA1	<LOQ	6.3	<LOQ	37.9	<LOQ	31.7	10.5	<LOQ	<LOQ	<LOQ	13.7	<LOQ	<LOQ	<LOQ
WA2	6.2	5	<LOQ	16.5	2.9	10	21.1	5.6	9	3.3	4.6	0.5	5.9	9.4
WA3	<LOQ	<LOQ	4.9	31	7.4	10.2	23.3	<LOQ	<LOQ	<LOQ	14.9	<LOQ	<LOQ	8.5
WA4	5.2	<LOQ	1.1	7.2	<LOQ	24.4	10	<LOQ	10.5	12	6	<LOQ	<LOQ	23.6
WA5	<LOQ	<LOQ	<LOQ	25.2	<LOQ	5.6	11.7	2.3	3.4	6	8.8	5.8	<LOQ	31.1
WA6	<LOQ	3.3	<LOQ	16.8	0.6	25.3	13.4	3.9	5.8	4.6	10.9	0.9	5.2	9.3
WA7	<LOQ	2.5	1.2	27	3.3	36	19.3	2.2	<LOQ	<LOQ	8.4	<LOQ	<LOQ	<LOQ
WA8	10.2	2.1	2.3	8	3.4	5.1	15.3	10.4	12.8	4.2	6.3	<LOQ	<LOQ	19.9
Average	2.7	2.4	1.2	21.2	2.2	18.5	15.6	3.1	5.2	3.8	9.2	0.9	1.4	12.7
SD	4	2.4	1.7	10.9	2.6	12.2	5.1	3.6	5.1	4.1	3.7	2	2.6	11.2

**Table 3-31 Concentration and percentage contribution of PAH according to ring number in individual samples from the Workstation area location (WS) in dry season**

Sample	Average concentrations(ng/g)				Percentage of $\Sigma_{14}$ PAH (%)			
	No of Rings							
	$\Sigma 3$ Ring	$\Sigma 4$ Ring	$\Sigma 5$ Ring	$\Sigma 6$ Ring	$\Sigma 3$ Ring	$\Sigma 4$ Ring	$\Sigma 5$ Ring	$\Sigma 6$ Ring
WA1	12.6	12	3.9	<LOQ	44.2	42.2	13.7	<LOQ
WA2	9.5	14.2	4.3	3.1	30.6	45.7	13.8	9.9
WA3	17.8	13.7	6.1	3.5	43.2	33.4	14.9	8.5
WA4	5.8	19.3	7.7	10.1	13.5	44.9	18	23.6
WA5	10.7	9.8	6.3	15.7	25.2	23	14.8	36.9
WA6	10.6	24.8	10.6	5.2	20.6	48.5	20.7	10.2
WA7	18.3	30.9	4.5	<LOQ	34	57.5	8.4	<LOQ
WA8	16.6	27.9	6.7	12.7	26	43.6	10.5	19.9
Average	12.7	19.1	6.3	6.3	29.7	42.4	14.3	13.6
SD	4.4	7.9	2.2	5.9	10.6	10.3	3.9	12.6

### 3.6 Comparative assessment of PAH contamination levels within the four locations in dry season

Concentrations of  $\Sigma_{14}$ PAH at each sampling location investigated are presented in Table 3.32. The highest average concentration of  $\Sigma_{14}$ PAH (820 ng/g) was observed in soil from the active oil well with drilling activities (AW1) sub-location, with concentrations at this sub-location exceedingly significantly those at the workstation (WS) sub-location (average 44 ng/g) which was not close to oil and gas production/exploration activities. Concentrations at TST and OGP were also high. Combined, this implies that the oil exploration industry is likely a discernible source of PAH to the local environment. Having conducted a normality test and transforming into log when required, an analysis of variance test revealed that concentrations at AW1 significantly exceeded those at WS ( $p < 0.05$ ), but no other significant differences were highlighted.

**Table 3-32 Average concentrations (ng/g) of individual PAH at four sampling locations in dry season**

PAH	OGP	TST	AW1	WS
Acy	8.5	10.2	24.5	1.3
Ace	19.1	15.4	62.4	1.0
Fln	13.9	19.2	65.7	0.6
Phe	23.9	34.3	202.8	8.8
Ant	6.4	5.9	187.8	1.0
Flt	33.4	19.2	57.5	8.1
Pyr	53.7	32.5	144.7	6.9
BaA	4.3	8.7	16.8	1.6
Chr	4.2	13.2	21.3	2.5
BbkF	4.5	10.1	8.2	1.7
BaP	7.7	7.3	6.0	4.0
IPy	3.0	3.7	3.1	0.4
DBA	2.2	2.4	1.6	0.6
BghiP	16.0	14.5	17.3	5.9
$\Sigma_{14}$ PAH	200.9	196.4	819.7	44.3
$\Sigma$ PAH <sub>6C</sub>	25.9	45.3	56.9	10.7

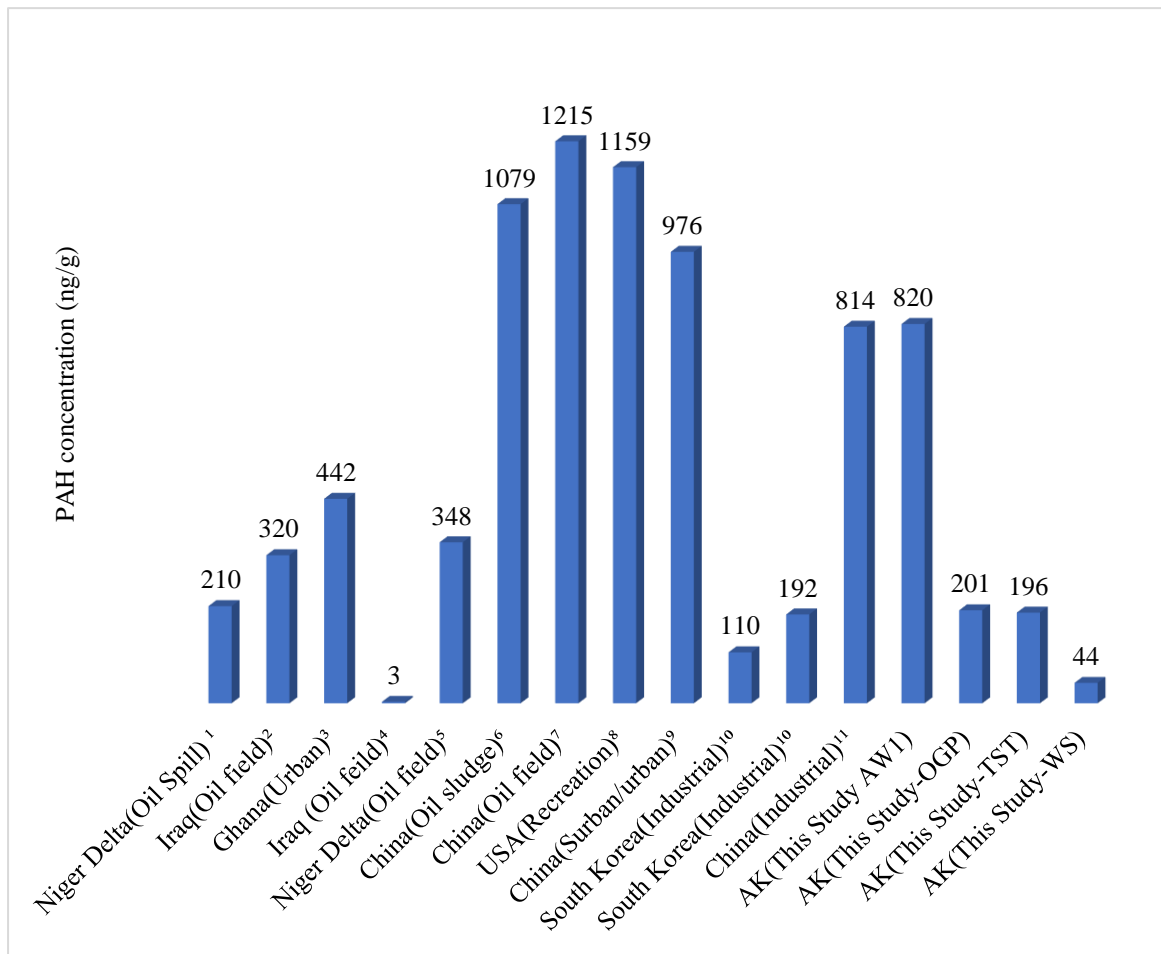
### 3.6.1 Comparison with PAH concentrations from other studies

Concentrations of  $\Sigma_{14}$ PAH present in this study were compared to other published data in Figure 3.26. The concentrations of PAH found at the active oil well with drilling activities location (AW1) for the dry season was higher than those reported by Abbas and Brack (2006) at Rapele oil field, Niger Delta (348 ng/g), and were also higher than those reported by (Alawi and Azeez, 2016) (320 ng/g) in an oil field at Al-Ahdah, Iraq. In winter, an average concentration of 2.82 ng/g was reported by Kadhim et al. (2019) in an oil field at southern Iraq.

Concentrations in our study were substantially below those reported for an oil exploratory area at Texas, USA for heavily contaminated soil (86,400 ng/g) (Bojes and Pope, 2007). However, concentrations at AW1 are comparable to those found in some soils (1079 ng/g) impacted by oil sludge in Zhongyuan, China (Kuang et al., 2011), and in soil from an oil field (1215 ng/g), in Shengli, China (Kuang et al., 2018). PAH concentrations at the oil crude transfer area (TST) and the oil and gas production area (OGP) are similar to those reported for an oil spill contaminated soil in Rumuolukwu, Niger Delta (210 ng/g) (Aigberua et al., 2016).

We also compared  $\Sigma_{14}$ PAH concentrations obtained in this study with those from other non-oil and gas impacted locations. For instance, concentrations of  $\Sigma_{13}$ PAH in soils from two industrial zones near Shihwa in South Korea varied between 110 and 190 ng/g (Imran et al., 2005), 442 ng/g from Kumasi, Ghana, (Bortey-Sam et al., 2014). Also, the PAH detected at AW1 are comparable to the industrial soil of Tianjin, China (814 ng/g) (Jiao et al., 2009), urban soil from Shanghai, China 976 ng/g (Wang et al., 2015b) and soil from a recreational area in Delaware, USA (1159 ng/g) (Yuan et al., 2014).

**Figure 3-26 Average Concentration of ΣPAH in soil from this study area compared with previous data in dry season from similar source types and other**



<sup>1</sup>(Aigberua et al., 2016); <sup>2</sup>(Alawi and Azeez, 2016); <sup>3</sup>(Bortey-Sam et al., 2014); <sup>4</sup>(Kadhim et al., 2019); <sup>5</sup>(Abbas and Brack, 2006); <sup>6</sup>(Kuang et al., 2011); <sup>7</sup>(Kuang et al., 2018); <sup>8</sup>(Yuan et al., 2014); <sup>9</sup>(Wang et al., 2015b); <sup>10</sup>(Imran et al., 2005); <sup>11</sup>(Jiao et al., 2009); AW1(Active oil well with drilling activities); OGP(Crude oil and gas production plant); Crude oil storage and transfer/pump area); WS(Workstation)

### 3.7 Variability between wet and dry periods in soil

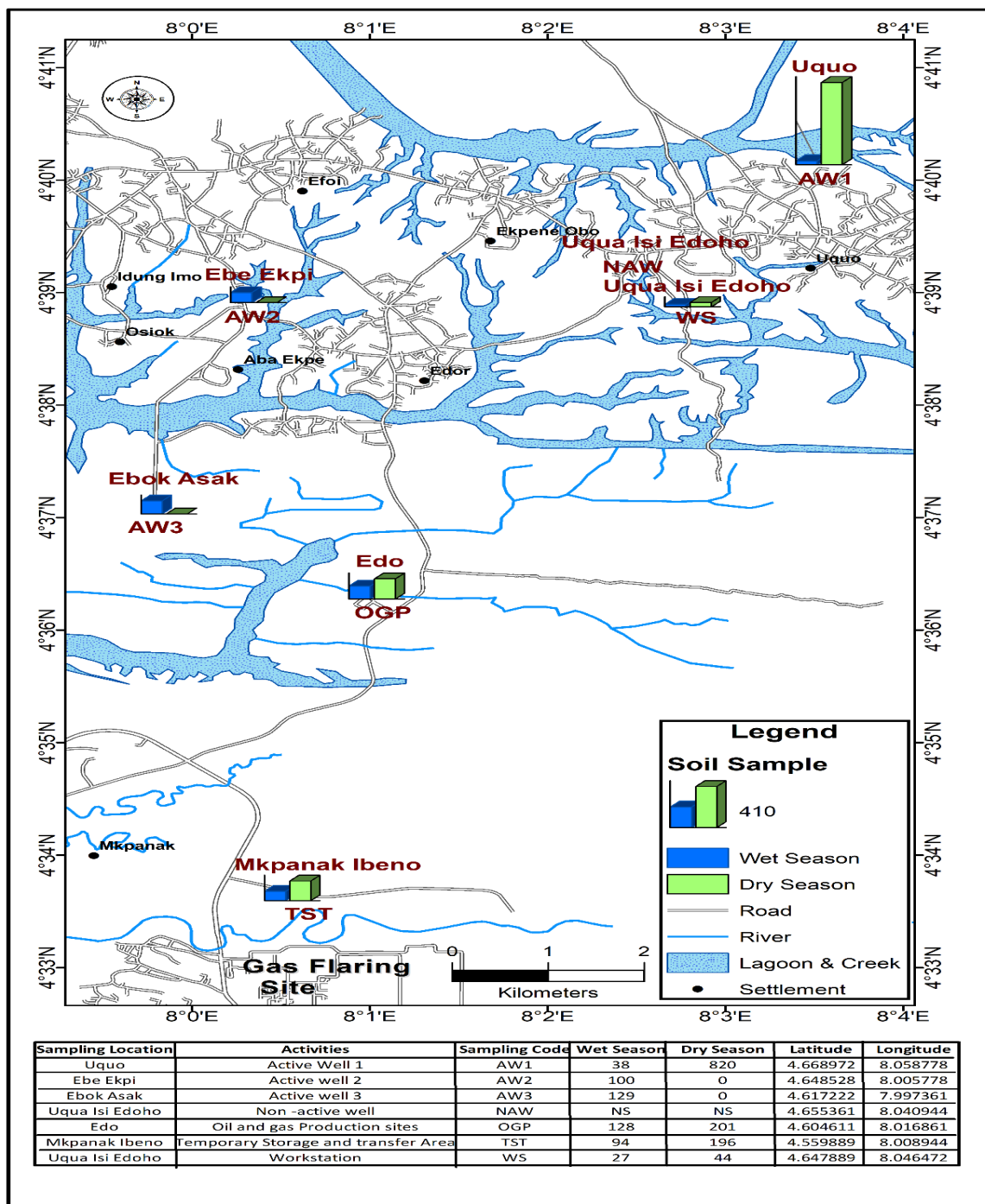
In Nigeria, there are two seasons, the wet or the rainy season and the dry season as detailed in chapter 2, section 2.3.1. The seasonal concentrations would have been compared between seven different locations, but comparison was constrained to four locations given the company's restructuring and restrictions on sampling as at the time of the second sampling period. Hence, data from four location are compared in this section.

The overall average concentrations of  $\Sigma_{14}$ PAH analysed during the dry season were approximately 201 ng/g, 196 ng/g, 820 ng/g and 44 ng/g at OGP, TST, AW1, and WS respectively (see table 3.32). These compared with average concentrations at the same locations in the wet season of 128 ng/g, 94 ng/g, 38 ng/g and 27 ng/g (Table 3.20). Figure 3.27 illustrates the spatial variation between the dry and wet periods. The concentrations of most target PAH in the dry season were higher than in the wet season, according to the results of this study. The seasonal variation of PAH showed that the difference in concentrations between the dry and wet seasons were probably associated with the types of activities taking place at these various locations, for example AW1 in dry season where oil drilling was conducted. This hypothesis was supported by Melymuk et al. (2012). Atmospheric deposition may also explain the higher concentrations seen in the dry season. This is based on the fact that the dry season is always characterised with dusty soil particles that may be deposited close to emission from a point source. It is important to know that both seasons have a similar average temperature range of 28 °C to 32 °C, thus temperature is unlikely to play a role in seasonal variation at our study location (Alani et al., 2021).

Additionally, in the wet season samples, it was noticeable that the lower molecular weight (LMW) compounds particularly in AW1 and WS sampling locations were mostly below the detection limit as against the dry season. This may suggest enhanced leaching of these more water-soluble PAH in the wet season. This is of potential concern as PAH thus leached may enter groundwater supplies with possible exposure of humans and wildlife. (Ekanem et al., 2019) investigated  $\Sigma_{16}$ PAH in soil from automobile repair workshops in Eket, Akwa Ibom. Their results revealed that most PAH were below detection limits in for both wet and dry season samples, which is comparable to the results observed for LWM in location in AW1 and WS in wet seasons. There were statistically significant seasonal variations at some locations according to pair t-tests carried out after normality test and log transformation where required.

T-test comparison of dry season and wet season concentrations for the same site (OGP(dry) and OGP(wet) revealed no significant seasonal differences between concentrations at OGP and WS ( $p > 0.05$ ). However, concentrations in the dry season were significantly higher ( $p < 0.05$ ) at both TST and AW1. Additionally, overall combination of all the concentrations in dry and wet season reveal significant difference ( $p = 0.003$ ).

Figure 3-27 Average seasonal concentrations for  $\Sigma_{14}$ PAH



### 3.8 Conclusion

This is the first study to provide new data of PAH concentration in soil for both wet and dry period concurrently in Esit Eket and Ibeno, Nigeria.  $\Sigma_{14}$ PAH concentrations in the locations are contaminated to varying levels, The highest total concentrations were detected at the active

locations with oil and gas activities as compared to the non-active location without oil and gas exploration and production activities. Which suggest the accumulation of PAH in oil and gas field soil and were statistically significant ( $p < 0.05$ ) in some locations. While the concentrations of PAH found in soil in wet and dry were the same order of magnitude as those reported in urban and rural soil in other regions (see sections 3.4.1.1 and 3.6.1). However, these concentrations were lower than most soil reported from previous studies in oil and gas field in various regions globally. However, the concentrations of PAH observed in our study area for both wet and dry season were within the soil quality values categorise as low to moderate, hence it is very important not to neglect this as PAH can accumulate and persist in soil for a very long time. The six carcinogenic PAH concentration were also low, suggesting that workers and resident living close to the oil and gas facilities have a low carcinogenic potency. The study areas are enriched with 3 to 4 ring PAH similar to those profile reported in some oil polluted area in other countries. Our results also, indicate significant variability between wet and dry period in PAH contamination of soil at some sites reflecting the impact of oil and gas activities. However, as we were only able to examine variation for two time points, we cannot exclude the possibility that the higher concentrations observed in the dry season may at least partly be a result of higher levels of PAH source activity during that sampling campaign. As a result, more research into the impact of oil and gas activities that influence of variability in wet and dry season of various PAH in different geographical regions is proposed. It is also important to note that constant release of these compounds in various oil and gas facilities in the study region may continue to increase the levels of PAH in the future. It is imperative to monitor the levels of this pollutant for effective environmental management strategies.

## Chapter 4

### **Concentrations of Polycyclic Aromatic Hydrocarbons (PAH) in outdoor air from an oil and gas field in Akwa Ibom, Nigeria**

#### **4.1 Abstract**

Air quality in Esit Eket and Ibeno (Akwa Ibom State) is of concern due to the potential impact of the oil and gas exploration activities undertaken in these regions, nevertheless, there is little or no information about human exposure to atmospheric PAH in such locations. Passive sampling was deployed to measure both gaseous and particulate phase PAH concentration in outdoor air for 21 days across six oil and gas facilities (crude oil and gas production plant area, crude oil storage and transfer area, active oil well 1, active oil well 3, active gas well and workstation) in spatial variability and seasonal levels. Concentrations of average outdoor air for  $\Sigma_{14}\text{PAH}$  ranged from 17.8 to 128  $\text{ng}/\text{m}^3$  in the wet season and from 79.9-330  $\text{ng}/\text{m}^3$  in the dry season. Our findings indicated that elevated PAH were observed at sites with oil and gas facilities. Interestingly, the difference in  $\Sigma_{14}\text{PAH}$  concentration were attributed to activities point source. Statistical analysis shows that no significant variations ( $p > 0.05$ ) were detected when each site was compared in both seasons. However, combining all data in wet and in dry season revealed a p value of 0.001, implying the impact of oil and gas activities had a great influence on the atmospheric emission of PAH in dry seasons. Furthermore, the potential sources of PAH in this study were highlighted by comparing the distribution pattern in our study to other oil and gas previous studies. The prevalence of low-molecular-weight PAH with 3 to 4 rings revealed the sources may originate probably from petroleum and petroleum combustion. In conclusion the PAH concentrations in this study is moderately polluted.

## **4.2 Sampling strategy**

### **4.2.1 Outdoor air sampling**

A total of 50 passive air samplers (PAS) were deployed at six different locations in Esit Eket and Ibeno, Akwa Ibom state, however, 4 PAS were lost during sampling. Samples were collected between April and May 2019 (wet season) and between December and February 2020 (dry season) over a period of 21 days per sampler.

Samplers were deployed at different sampling sites according to their potential sources: oil and gas production plant (OGP, n=6), crude oil transfer area (TST, n=4), active oil well 1 (AW1, n=2), active oil and gas well 2 (AW2, n=3), active oil and gas well 3 (AW3, n=3), and workstation (WS, n=3) for the wet season sampling with oil and gas production plant (OGP, n=6), crude oil transfer area (TST, n=4), active oil well 1 (AW1, n=6), active oil and gas well 2 (AW2, n=3), active oil and gas well 3 (AW3, n=4), and workstation (WS, n=2) for the dry season monitoring. Air sampling rates as described in Chapter 2, were used to estimate the average PAH (combination of both gaseous and particulate) concentrations ( $\text{ng}/\text{m}^3$ ) in PAS.

## **4.3 Outdoor air concentrations and profiles of PAH in wet season**

### **4.3.1 Concentration of PAH in oil and gas production area (OGP) in wet season**

Average concentrations of PAH found in OGP during the monitoring period appear in Table 4.1. The average concentrations (sum of both gaseous and particulate phases) for  $\Sigma_{14}\text{PAH}$  were:  $113.7 \text{ ng}/\text{m}^3$  near the main processing plant and gas flaring (NP),  $61 \text{ ng}/\text{m}^3$  at the main processing area (MP), and  $43.8 \text{ ng}/\text{m}^3$  at worker's accommodation (WA). Average concentrations of the sum of the 6 carcinogenic PAH ( $\Sigma\text{PAH}_{6\text{C}}$ ) were:  $18 \text{ ng}/\text{m}^3$ ,  $15.7 \text{ ng}/\text{m}^3$ , and  $6.5 \text{ ng}/\text{m}^3$  for NP, MP, and WA respectively. It has been reported that gas flaring in Akwa Ibom can be a source of emission of organic compounds such as PAH (Okpako et al., 2018). The elevated PAH concentrations at NP can be explained by the position of the samplers which

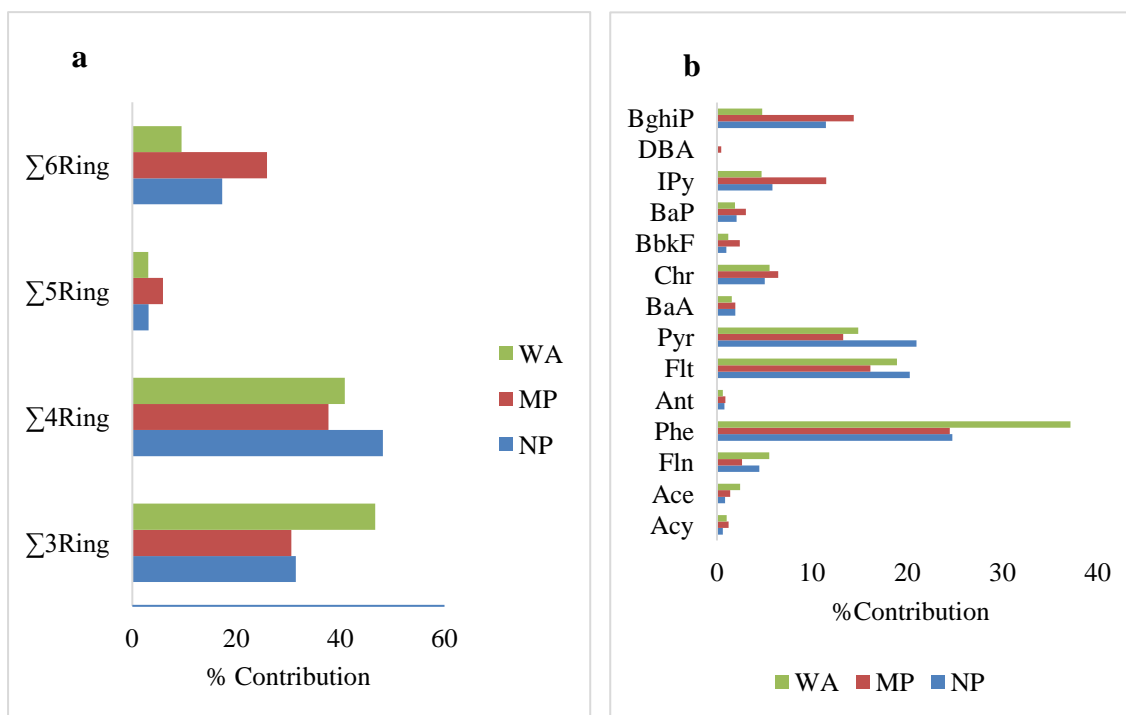
was downwind of the open gas flaring stack operated round the clock all year. In contrast, the MP samplers were upwind of the open gas flaring stack, with those at WA 100 m further away from these plants. This indicates clear PAH contamination from oil and gas activities at NP. Such emissions have reduced impact at the upwind MP location, as well as at WA. Emissions from gas flaring add to the impact of volatilisation of PAH from oil spillages at MP (Skrbic and Durisic-Mladenovic, 2009), as well as background sources such as cooking, generator fumes and local traffic emissions at all locations. Figure 4.1a display a distinct spatial pattern, a predominance of 3-4 ring PAH over their 5–6 ring counterparts was found in air at all sampling sub-locations, with 3-4 ring PAH comprising ~80%  $\Sigma$ PAH. More specifically, average contributions of 42%, 36%, 17%, and 4% were recorded for 4, 3, 6, and 5 ring PAH across all three locations. Phe was most abundant at all sub-locations, followed by Flt and Pyr (see table 4.3). The overall profile across all three sub-locations according to ring number follows the order: 4 ring > 3 ring > 6 ring > 5 ring. However, while the individual distribution of PAH of different ring numbers at NP and MP follows the same sequence of 4 ring > 3 ring > 6 ring > 5 ring; the pattern differs at WA where 3 ring > 4 ring > 6 ring > 5 ring.

**Table 4-1 Average PAH concentrations in air at an oil and gas production area (OGP) (ng/m<sup>3</sup>) in wet season**

PAH	NP (n=2)	MP (n=2)	WA (n=2)
Acy	0.7	0.7	0.5
Ace	1	0.8	1.1
Fln	5.1	1.6	2.4
Phe	28.1	14.9	16.2
Ant	0.9	0.5	0.3
Flt	23	9.8	8.3
Pyr	23.8	8.1	6.5
BaA	2.2	1.2	0.7
Chr	5.7	3.9	2.4
BbkF	1.1	1.5	0.5
BaP	2.3	1.9	0.8
IPy	6.6	7	2
DBA	0.1	0.3	<LOQ
BghiP	13	8.8	2.1
Σ <sub>14</sub> PAH	113.7	61.1	43.8
ΣPAH <sub>6C</sub>	18.1	15.7	6.5

This pattern whereby 3 to 4 ring PAH dominate is consistent with data from previous studies which utilised passive sampling (PUF) in monitoring PAH in a petrochemical area in Spain (Domínguez-Morueco et al., 2017). Moreover, Harrison et al. (2016a) also reported a similar profile of 3 to 4 ring PAH in air from a petrochemical installation in western Saudi Arabia.

**Figure 4-1 Average percentage contribution of PAH to  $\Sigma 14$ PAH according to ring number from oil and gas production area in wet season**



WA(worker' accommodation),MP(main processing area) and NP(Near processing area and gas flaring area)

**Table 4-2 Average concentration and percentage contribution to  $\Sigma 14$ PAH according to ring number in outdoor air samples from oil and gas production area (OGP) in wet season**

Location	Average concentrations (ng/m <sup>3</sup> )				Percentage $\Sigma 14$ PAH (%)			
	No of Rings							
	3	4	5	6	3	4	5	6
NP	35.7	54.7	3.5	19.6	31	48	3	17
MP	18.7	23.0	3.6	15.8	31	38	6	26
WA	20.4	17.9	1.3	4.1	46	41	3	9

**Table 4-3 Average percentage contribution of individual PAH in outdoor air samples from oil and gas production area in wet season**

PAH	NP	MP	WA	PAH	NP	MP	WA
Acy	1	1	1	BaA	2	2	2
Ace	1	1	2	Chr	5	6	6
Fln	5	3	6	BbkF	1	2	1
Phe	25	24	37	BaP	2	3	2
Ant	1	1	1	IPy	9	11.5	5
Flt	20	16	17	DBA	<LOQ	<LOQ	<LOQ
Pyr	21	13	15	BghiP	11	14	5

(Totals may not sum to 100% due to rounding), WA(worker' accommodation),MP(main processing area) and NP(Near processing area and gas flaring area)

#### **4.3.2 Concentrations of PAH in crude oil transfer area (TST) in wet season**

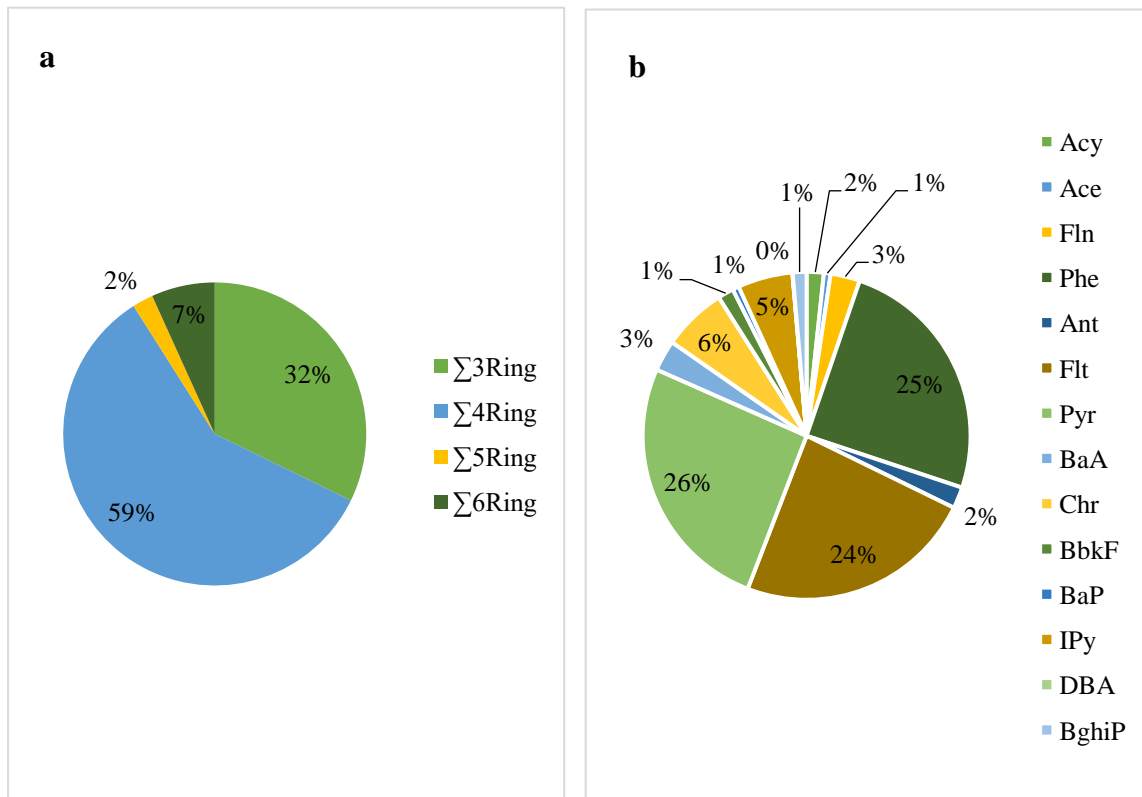
Four PAS were deployed at TST for collection of outdoor air. The average PAH concentration detected in these PAS exceed those in any of the samples collected from the OGP locations (Table 4.1). Total sum average outdoor air level (combination of gas and particle) at TST were 128 ng/m<sup>3</sup> with ΣPAH<sub>6C</sub> 21.8 ng/m<sup>3</sup>, and BaP at 0.8 ng/m<sup>3</sup> as shown in Table 4.4. The average concentration detected at TST (128 ng/m<sup>3</sup>) is at the high end of the range found currently in European cities. Apart from emissions from the cold flare stack within the sampling field as well as gas flaring from two other companies (Mobil) 0.4 and 1.5 kilometres away from the research area; the elevated concentrations at TST station could primarily be from volatilisation of PAH from crude oil.

**Table 4-4 Summary of concentrations (ng/m<sup>3</sup>) of PAH in outdoor air samples collected at the crude oil transfer area (TST)**

PAH	Average(n=4)	SD	Min	Median	Max
Acy	2.2	1.6	1.2	1.5	4.5
Ace	0.8	0.7	0.3	0.7	1.8
Fln	3.7	2.6	0.8	3.5	7.1
Phe	31.9	17.6	11	31.2	54.1
Ant	2.7	1.6	0.7	2.8	4.6
Flt	30.3	14	14.6	28.9	48.7
Pyr	33	19.7	12	30.9	58.3
BaA	3.9	1.7	2.4	3.5	6.2
Chr	8.1	2.9	4.6	8.2	11.3
BbkF	2	0.9	1.1	1.9	3.2
BaP	0.8	0.6	0.4	0.4	2.0
IPy	6.9	1.6	5.5	6.7	8.8
DBA	<LOQ	<LOQ	<LOQ	<LOQ	0.1
BghiP	1.7	1.3	0.5	1.7	3.1
Σ <sub>14</sub> PAH	128	67	62.3	134.5	181
PAH <sub>6C</sub>	21.8	8	14.6	21.3	29.9

Figure 4.2 present the relative profile according to ring number and for individual PAH. The relative contribution of PAH in TST revealed that 4 ring were the most abundant in this study area with 59% (including Pyr 26% and Flt 24%). The 3 rings constitute 32% (Phe 25%), 5 ring 2%, while the 6 ring has least profile of 7%. This shows that the study area is polluted with four ring PAH .

**Figure 4-2 Relative contribution (% $\Sigma$ PAH) expressed as PAH ring number and individual contribution in percentage (%) (b) in Crude oil transfer area (TST) in wet season**



#### 4.3.3 Concentration of PAH in the vicinity of active wells in wet season

Active wells which include both a gas and oil well in the wet season will be discussed in this section. Concentrations of PAH in the vicinity of gas wells have not frequently been reported previously and therefore the data reported here for such a location (AW2) are of particular interest. Whilst the number of data are limited (n=3), the average  $\Sigma_{14}$ PAH concentration at this location was 132 ng/m<sup>3</sup> and 16.3 ng/m<sup>3</sup> for  $\Sigma$ PAH<sub>6C</sub> as seen in Table 4.5.

These high concentrations (i.e., exceeding those detected at OGP and TST) could be associated with the samplers being deployed close to the gas well pad. These findings align with the study conducted by (Paulik et al., 2018), who reported a high concentration of PAH close to a natural gas well pad in Texas, USA.

The percentage contribution of individual PAH to  $\Sigma$ PAH are given in Table 4.5 while the ring pattern is presented in Table 4.6. The average distribution was: 68% for 4-ring, 23% for 3 rings, 2 % for 5 ring and 8 % for 6 rings. Pyr (43%) was the most dominant PAH in the atmospheric samples from this area, followed by Flt (18%) and Phe (14%).

**Table 4-5 Average concentration of PAH and percentage contribution (%) in active gas well (AW2)**

PAH	Concentration (ng/m <sup>3</sup> ) (n=3)	Contribution (%)
Acy	2.3	2
Ace	2	2
Fln	3	2
Phe	18.8	14
Ant	4	3
Flt	23.7	18
Pyr	56.7	43
BaA	3.2	2
Chr	6	5
BbkF	1.3	1
BaP	1.1	1
IPy	4.6	3
DBA	<LOQ	<LOQ
BghiP	5.3	4
$\Sigma_{14}$ PAH	132.2	
$\Sigma$ PAH <sub>6C</sub>	16.3	

**Table 4-6 Concentration and distribution by ring number expressed as percentage  $\Sigma_{14}$ PAH (%) at AW2**

Location	Average concentration (ng/m <sup>3</sup> )				Percentage $\Sigma_{14}$ PAH (%)			
	No of Rings							
	3	4	5	6	3	4	5	6
AW2	30.2	89.6	2.5	9.9	23	68	2	8

Air samples (n=3) were also collected over 21 days at an active oil well (AW3) within the field. Table 4.7 shows the average concentrations for each individual PAH. The average concentration of BaP was 1 ng/m<sup>3</sup>, that of  $\Sigma_{14}$ PAH 68 ng/m<sup>3</sup>, and that of  $\Sigma$ PAH<sub>6C</sub> 13.9 ng/m<sup>3</sup>. Table 4.8 shows the percentage contribution to  $\Sigma_{14}$ PAH according to ring number, as well for individual PAH. Four ring PAH contribute 44% of  $\Sigma_{14}$ PAH, with contributions of 3, 5, and 6 ring PAH being: 43%, 4%, and 10% respectively. With respect to individual PAH, the main contributors are Phe (27%), Flt (24%), Pyr (10.5%), and IPy (8.6%).

**Table 4-7 Average concentrations (ng/m<sup>3</sup>) and percentage contribution to  $\Sigma_{14}$ PAH at AW3**

PAH	Concentration (ng/m <sup>3</sup> ) (n=3)	% Contribution to $\Sigma_{14}$ PAH
Acy	1.9	3
Ace	1.5	2
Fln	4	6
Phe	18.7	27
Ant	2.8	4
Flt	17.1	24
Pyr	7.3	11
BaA	1.6	2
Chr	3.8	6
BbkF	1	1
BaP	1.3	2
IPy	6	9
DBA	0.2	<LOQ
BghiP	1	1
$\Sigma_{14}$ PAH	68.1	
$\Sigma$ PAH <sub>6C</sub>	13.9	

**Table 4-8 Concentrations (ng/m<sup>3</sup>) and distribution according to PAH ring number expressed as percentage  $\Sigma_{14}$ PAH (%) at AW3**

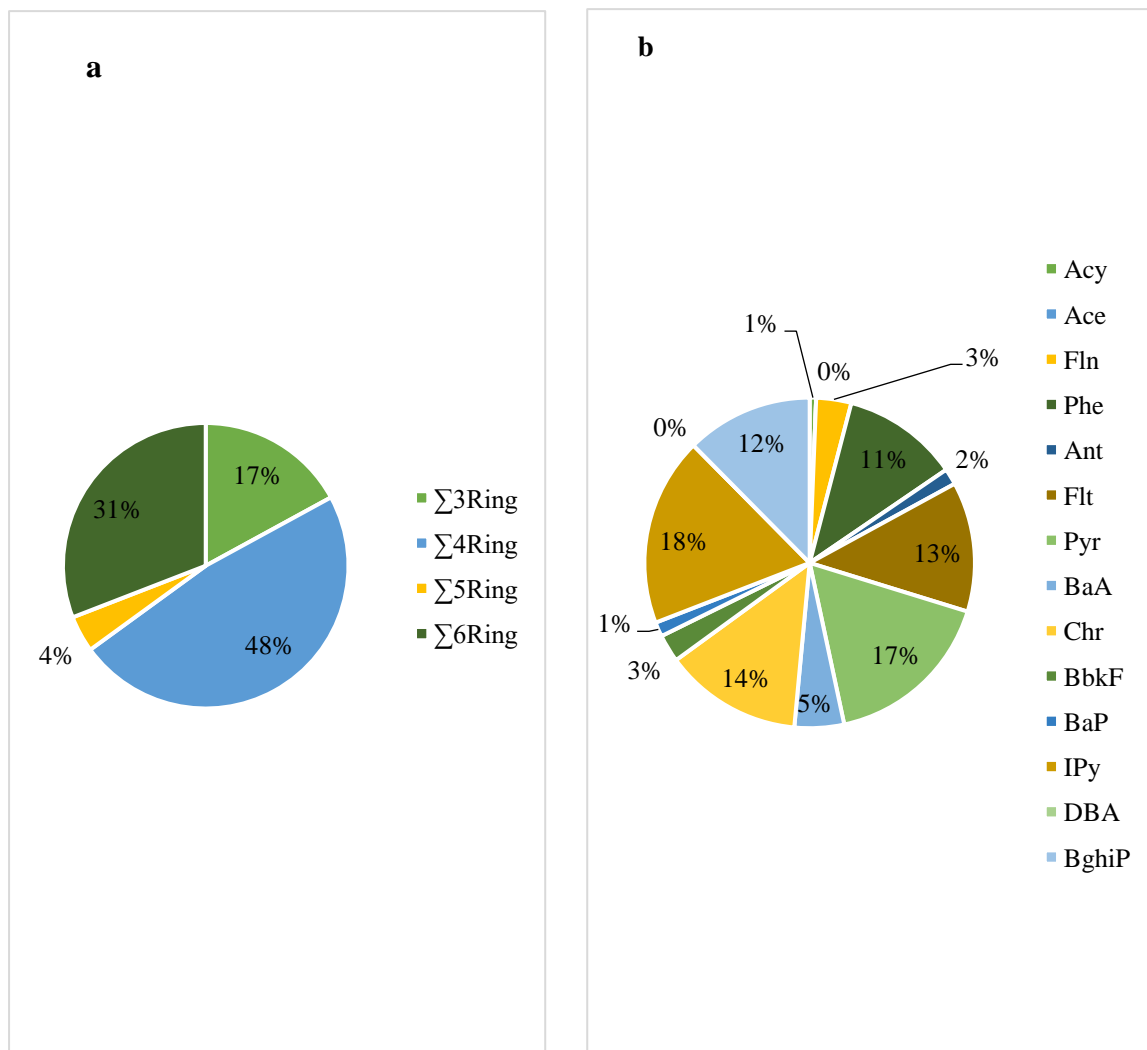
Location	Average concentrations (ng/g)				Percentage $\Sigma_{14}$ PAH (%)			
	No of Rings							
	3	4	5	6	3	4	5	6
AW3	28.8	29.9	3	6.9	43	44	4	10

#### 4.3.4 Concentrations of PAH at a non-active location in wet season

Atmospheric PAH concentrations in both gas and particle phase were determined in an active oil well (AW1), a well that was capped and not in operation (drilling) during the period of the monitoring campaign. Average concentrations of individual PAH and their percentage contribution to  $\Sigma_{14}$ PAH at AW1 (n=2) is as follows;  $\Sigma_{14}$ PAH at 24 ng/m<sup>3</sup> and  $\Sigma$ PAH<sub>6C</sub> at 9.6 ng/m<sup>3</sup> and the average sum of BaP was present at 0.3 ng/m<sup>3</sup> respectively, however, Ace and DBA were below the detection limit.

As well as displaying lower concentrations than those observed at any of the OGP, TST, AW2, and AW3 sites, the pattern of PAH concentrations at this site shows distinctive features. In particular, the contribution of 6 ring PAH to  $\Sigma_{14}$ PAH was notably high at 31%, exceeded only by 4 ring PAH at 48%, while 3 and 5 ring PAH contribute 17 and 4% respectively. Figure 4.3 show the relative contributions to  $\Sigma_{14}$ PAH according to ring number. Of note with respect to individual PAH: IPy contributes on average 18%, with Pyr 17%, Flt 13%, and Chr 14% of  $\Sigma_{14}$ PAH at this location. The comparatively low concentrations at this location are likely due to the absence of ongoing oil and gas exploration activities in its vicinity.

**Figure 4-3 Contribution represented by: (a) PAH ring number (%) and (b) each target PAH contribution at AW1 in wet season**



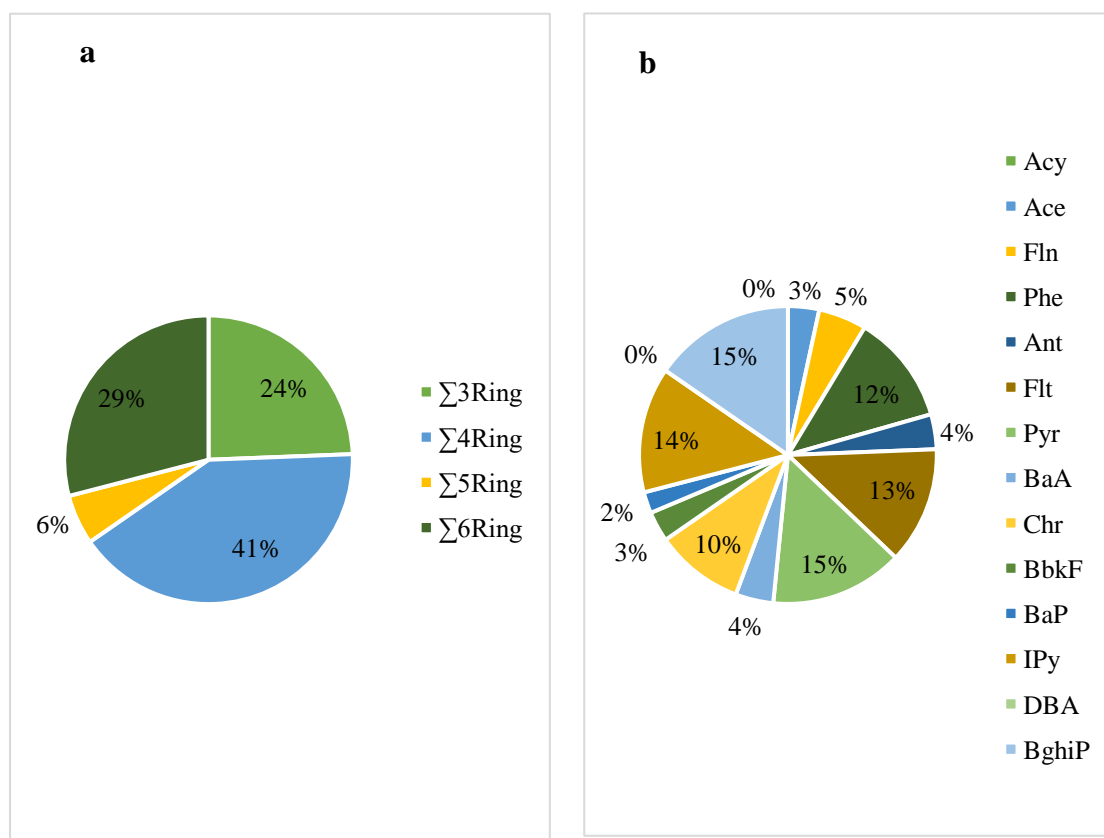
We also measured atmospheric concentrations of PAH in the vicinity of a workstation where workers resided during the installation and drilling of oil and gas wells. We hypothesised that this location should experience little or no impact from oil and gas exploration activities. Consistent with this hypothesis, neither Ace, Acy, or DBA were detected at this location, while average concentrations of  $\Sigma_{14}\text{PAH}$ , BaP, and  $\Sigma\text{PAH}_{6\text{C}}$  were: 17.5 ng/m<sup>3</sup>, 0.4 ng/m<sup>3</sup>, and 5.8 ng/m<sup>3</sup> respectively. The distribution according to ring number at WS is broadly similar to that at AW1 – i.e., 4 ring > 6 ring > 3 ring > 5 ring. Also similar to AW1 are the contributions of IPy and BghiP (Tables 4.9 and Figure 4.4a). However, BghiP is frequently used as a vehicle

emission tracer, which suggests that WS may be related to emissions from vehicles (Alghamdi et al., 2015, Harkov et al., 1984).

**Table 4-9 Concentrations (ng/m<sup>3</sup>) and percentage profile of individual PAH in WS in wet season**

PAH	Average concentration(ng/m <sup>3</sup> ) (n=3)	% Contribution (Average)
Acy	<LOQ	<LOQ
Ace	0.6	3
Fln	0.9	5
Phe	2.2	12
Ant	0.7	4
Flt	2.2	13
Pyr	2.5	15
BaA	0.7	4
Chr	1.7	10
BbkF	0.6	3
BaP	0.4	2
IPy	2.4	14
DBA	<LOQ	<LOQ
BghiP	2.7	15
Σ <sub>14</sub> PAH	17.5	
ΣPAH <sub>6C</sub>	5.8	

**Figure 4-4 Percentage contribution according to: (a) ring number and (b) each individual PAH at WS**



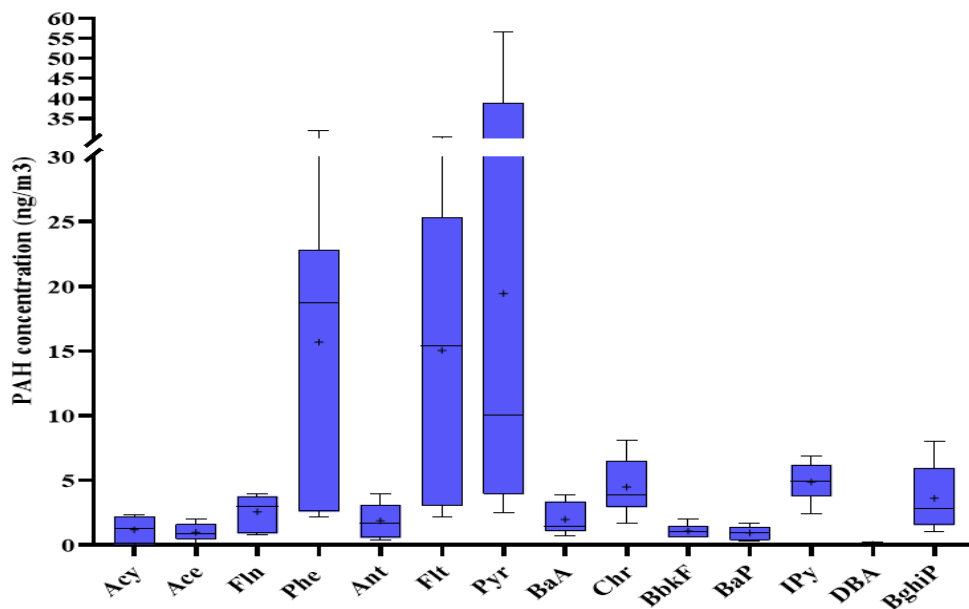
#### 4.4 Comparison between locations and with other studies in wet season

Table 4.10 and Figure 4.5 displays a comparison of the PAH concentrations in air between the six locations, with the overall average for the three sub-locations at OGP provided. Average concentrations measured at AW2 (active gas well) are highest at 132 ng/m<sup>3</sup> for Σ<sub>14</sub>PAH compared to other locations in this study: specifically, the crude oil transfer area (TST) at 128 ng/m<sup>3</sup>, the oil and gas production area (OGP) (72.8 ng/m<sup>3</sup>), the active oil well 3 (AW3) (68 ng/m<sup>3</sup>), the oil well 1 (AW1) (24 ng/m<sup>3</sup>), and the workstation (WS) (17.5 ng/m<sup>3</sup>).

The variations in PAH concentrations in these locations can be explained by their relative proximity to PAH sources and the strength of such sources. The high concentrations observed at AW2 may be influenced by emissions from gas well heads and traffic on the local service

road connecting villages in the area. The second most contaminated location (TST) is surrounded by oil and gas exploration activities undertaken by several multinational oil and gas companies. In contrast, the lowest concentrations were found at AW1 (an oil well that was capped at the time of sampling) and at the workstation (WS), which had had no history of oil and gas activities. Despite these differences between sites, concentrations of PAH were not statistically different between the locations monitored in this study ( $P= 0.1$ ) according to the analysis of variance test (ANOVA) conducted. This suggests that while oil and gas exploration activities exert some influence on PAH contamination of air at some of our study locations, this does not outweigh the combined influence of other PAH sources such as traffic and biomass combustion for cooking etc.

**Figure 4-5 Individual PAH for  $\Sigma 14$ PAH concentrations ( $\text{ng}/\text{m}^3$ ) at all sites in this study in wet season**



**Boxplot diagram indicating the minimum, maximum and average(+) and interquartile range concentrations wet season .**

**Table 4-10 Average concentrations (ng/m<sup>3</sup>) of individual PAH at all sites in wet season**

PAH	OGP	TST	AW1	AW2	AW3	WS
Acy	0.6	2.2	0.1	2.3	1.9	<LOQ
Ace	1	0.8	<LOQ	2	1.5	0.6
Fln	3	3.7	0.8	3	4	0.9
Phe	19.8	31.9	2.7	18.8	18.7	2.2
Ant	0.6	2.7	0.4	4	2.8	0.7
Flt	13.7	30.3	3.3	23.7	17.1	2.2
Pyr	12.8	33	4.4	56.7	7.3	2.5
BaA	1.3	3.9	1.2	3.2	1.6	0.7
Chr	4	8.1	3.3	6	3.8	1.7
BbkF	1	2	0.6	1.3	1	0.6
BaP	1.7	0.8	0.3	1.1	1.3	0.4
IPy	5.2	6.9	4.2	4.6	6	2.4
DBA	0.1	<LOQ	<LOQ	<LOQ	0.2	<LOQ
BghiP	8	1.7	3	5.3	1	2.7
Σ <sub>14</sub> PAH	72.8	128.1	24.2	132.2	68.1	17.5
ΣPAH <sub>6C</sub>	13.4	21.8	9.6	16.3	13.9	5.8

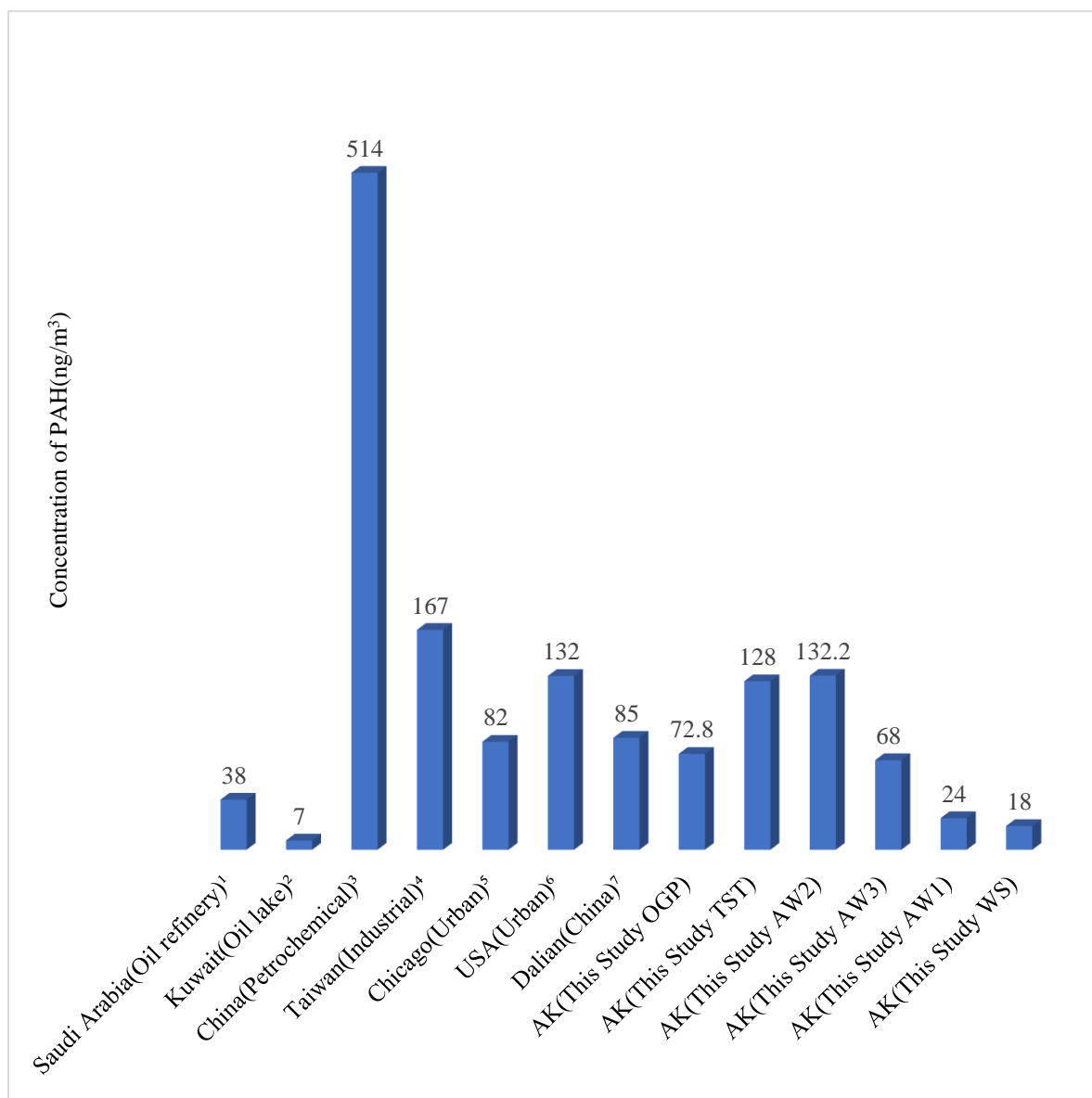
Information on PAH concentrations in air from locations in the vicinity of oil and gas exploration activities are very scarce, and this is the first study to measure airborne PAH via passive sampling of both gaseous and particulate phase in Nigeria to the author's knowledge. Therefore, the findings of this study will be compared to the available published data for oil and gas fields (upstream and downstream sector) worldwide as well sites impacted by other

source types. Only data that includes both gaseous and particulate phase will be taken into consideration for discussion to facilitate comparability across studies.

From Table 4.10 the average total PAH concentrations found in this study are lower than those reported at petrochemical complex in Guangzhou, China  $514 \text{ ng/m}^3$  (Zhao et al., 2015), but exceeded those reported in Kuwait by Gevao et al. (2006) ( $6.6 \text{ ng/m}^3$ ) and Alghamdi et al. (2015) ( $38 \text{ ng/m}^3$ ) see Table 4.10 and Table 1.6 in section 1.9.3.

Moreover, the PAH levels the in most polluted sites in this study are comparable to those detected at urban and industrial sites in another studies. For example, the average concentration of  $132 \text{ ng/m}^3$  found in urban Florida, USA by (Poor et al., 2004), and an industrial region of Taiwan  $167 \text{ ng/m}^3$  (Lai et al., 2017) see Table 1.6 in section 1.9.3 . Concentrations at the most polluted sites in this study exceed those reported in Dalian, China ( $87.6 \text{ ng/m}^3$ ) reported by Zhou et al. (2013) and Sun et al. (2006) at Chicago ( $82 \text{ ng/m}^3$ ) in USA. Figure 4.6 indicates the comparative studies of PAH in this study with other similar source type . Conclusively, the concentrations in this study are moderately polluted.

**Figure 4-6 Average concentration of ΣPAH in outdoor air in this study compared to similar source types and others**



<sup>1</sup>(Alghamdi et al., 2015); <sup>2</sup>(Gevao et al., 2006); <sup>3</sup>(Zhao et al., 2015); <sup>4</sup>(Lai et al., 2017); <sup>5</sup>(Sun et al., 2006); <sup>6</sup>(Poor et al., 2004); <sup>7</sup>(Zhou et al., 2013); A.K(Akwa Ibom State); OGP(Crude oil and gas production area); TST(Crude storage and transfer/pump area); AW1(Active oil well no drilling activities); AW2(Active gas well); AW3(Active oil well); WS(Workstation)

#### 4.5 Concentrations of PAH in dry season in outdoor air

##### 4.5.1 Oil and gas production Area (OGP) in dry season

Just like the wet season, the result shown in Table 4.11 for outdoor air samples (gaseous and particulate phase) in three sub-sites indicate that most PAH were detected at measurable

concentrations. The level of  $\Sigma_{14}\text{PAH}$  varies from one sub-site, with the highest concentrations coming detected in samples from NP at an average of  $205 \text{ ng/m}^3$ , exceedingly slightly that of  $196.8 \text{ ng/m}^3$  at MP. The average concentration at WA was at  $133 \text{ ng/m}^3$  lower than at either NP or MP yet is still higher than concentrations reported elsewhere in many urban regions. Taken in combination, these data confirm the conclusion of the wet season data, that oil and gas exploration activities exert a discernible influence on PAH concentrations at the locations in this study.

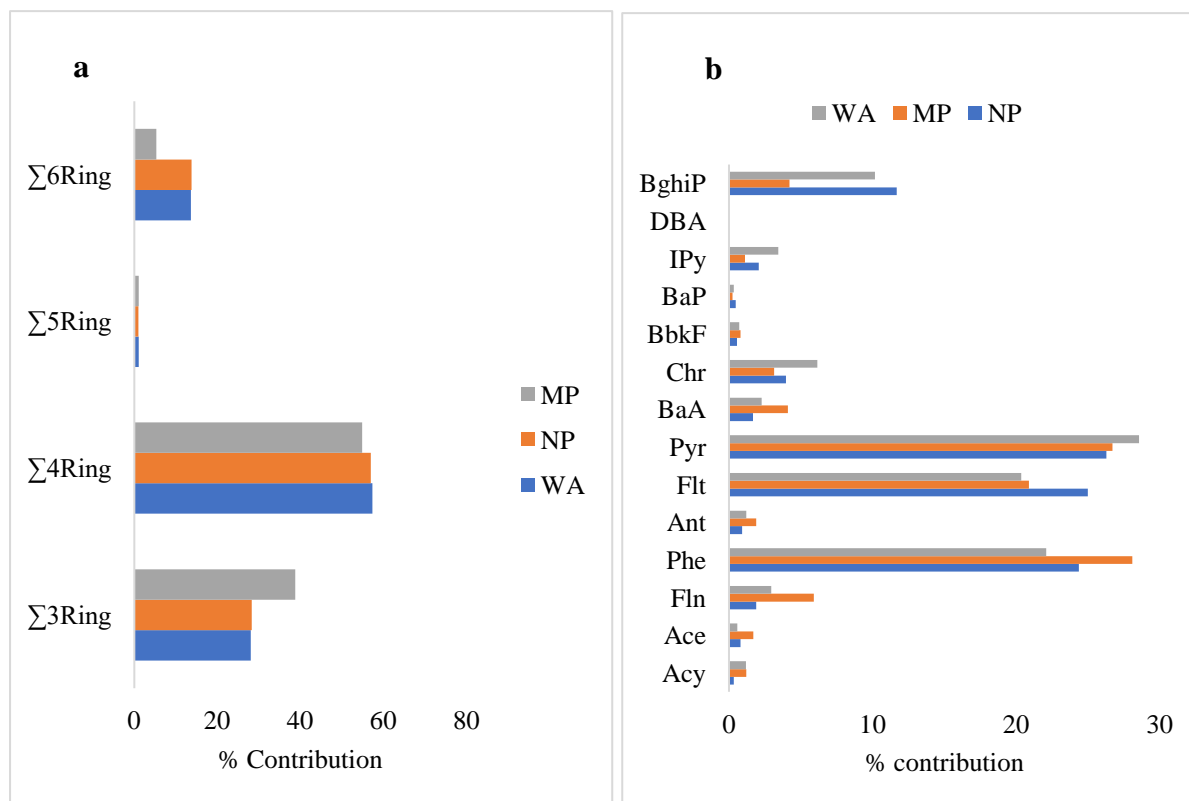
Higher average concentrations of  $\Sigma_{14}\text{PAH}$  closer to the point source at NP than the more distant WA site were observed. Concentrations of  $\Sigma\text{PAH}_{6\text{C}}$  at NP, MP and WA were: 19.8, 18.6, and  $17 \text{ ng/m}^3$ , while those of BaP at NP, MP, and WA were: 1.9, 0.7, and  $0.5 \text{ ng/m}^3$  respectively.

The relative distribution of PAH according to ring number is similar at each of the three OGP sub-locations – e.g., 4-ring PAH contribute 56%, 55%, and 57% at NP, MP, and WA respectively. Three ring PAH are the next most abundant, followed by 6 ring and 5 ring PAH as given in Figure 4.7 and 4.12 and Table 4.13. The most abundant PAH at each of the three sub-sites are: Phe, Flt, and Pyr respectively as indicated in Table 4.11.

**Table 4-11 Average concentrations (ng/m<sup>3</sup>) of individual PAH in outdoor air from oil and gas production area in the dry season.**

PAH	NP (n=2)	MP (n=2)	WA (n=2)
Acy	0.7	2.4	1.5
Ace	1.6	3.3	0.8
Fln	3.8	11.6	3.9
Phe	49.3	55.2	29.5
Ant	1.8	3.7	1.6
Flt	50.7	41.2	27
Pyr	53.6	52.3	37.9
BaA	3.4	7.9	3
Chr	8.1	6.2	8.2
BbkF	2.1	1.6	0.9
BaP	1.9	0.7	0.5
IPy	4.2	2.2	4.6
DBA	<LOQ	<LOQ	<LOQ
BghiP	23.9	8.5	13.6
Σ <sub>14</sub> PAH	205.3	196.8	133
ΣPAH <sub>6C</sub>	19.8	18.6	17

**Figure 4-7 Percentage compositions of each target PAH (%) at OGP in dry season**



WA(worker accommodation),NP(near flare and processing area) and MP(main processing area)

**Table 4-12 Average percentage contribution of individual PAH to Σ14PAH at OGP in dry season**

PAH	NP	MP	WA	PAH	NP	MP	WA
Acy	0.3	1.2	1.2	BaA	1.7	4.1	2.3
Ace	0.8	1.7	0.6	Chr	4	3.2	6.2
Fln	1.9	5.9	3	BbkF	0.6	0.8	0.7
Phe	24.4	28.1	22.1	BaP	0.5	0.2	0.3
Ant	0.9	1.9	1.2	IPy	2.1	1.1	3.4
Flt	25	20.9	20.4	DBA	<LOQ	<LOQ	<LOQ
Pyr	26.3	26.7	28.6	BghiP	11.7	4.2	10.2

**Table 4-13 Concentrations of PAH (ng/m<sup>3</sup>) and percentage contributions to  $\Sigma_{14}$ PAH at OGP expressed according to ring number in dry season**

Location	Average concentrations (ng/m <sup>3</sup> )				Percentage $\Sigma_{14}$ PAH (%)			
	No of Rings							
	3	4	5	6	3	4	5	6
NP	57.3	115.8	4	28	28	56	2	14
MP	76.2	107.6	2	10.8	39	55	1	5
WA	37.3	76.1	1.4	18.2	28	57	1	14

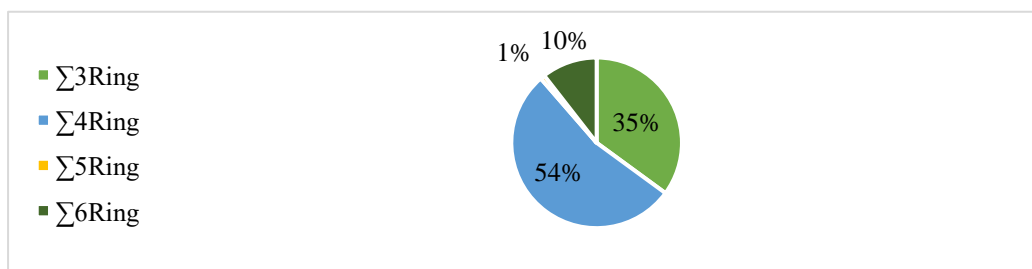
#### **4.5.2 Concentrations of PAH in outdoor air from crude oil transfer area (TST) in dry season**

Table 4.14 shows the average concentration of individual PAH, as well as  $\Sigma_{14}$ PAH and  $\Sigma$ PAH<sub>6C</sub> at TST. The average concentration of  $\Sigma_{14}$ PAH was 254 ng/m<sup>3</sup>, those of  $\Sigma$ PAH<sub>6C</sub> 20.5 ng/m<sup>3</sup>, with BaP detected at an average of 1 ng/m<sup>3</sup>. Regarding the composition pattern in this study area, the most abundant ring type was 4 ring PAH, contributing on average 54% of  $\Sigma_{14}$ PAH, with Flt and Pyr contributing 26% and 23% respectively. However, the 3-ring PAH, Phe was the most abundant individual compound at with BghiP (6 ring) contributing 8%. These relative contributions are presented in Figure 4.8 as well as Tables 4.14.

**Table 4-14 Concentration (ng/m<sup>3</sup>) and percentage concentration to  $\Sigma$ 14PAH of individual PAH at TST in dry season**

PAH	Average concentration (n=4)	% Contribution (Average)
Acy	1.1	<LOQ
Ace	1.6	1
Fln	5.9	2
Phe	76.9	31
Ant	2.8	1
Flt	66.6	26
Pyr	58.8	23
BaA	2.7	1
Chr	8.7	3
BbkF	1.5	1
BaP	0.7	<LOQ
IPy	7	3
DBA	<LOQ	<LOQ
BghiP	20.1	8
$\Sigma$ 14PAH	254.4	
$\Sigma$ PAH <sub>6C</sub>	20.5	

**Figure 4-8 Contribution of PAH ring number in percentage (%) (a) and individual target PAH contribution (%) (b) at TST in dry season**



### 4.5.3 Concentrations of PAH at active oil and gas wells in the dry season

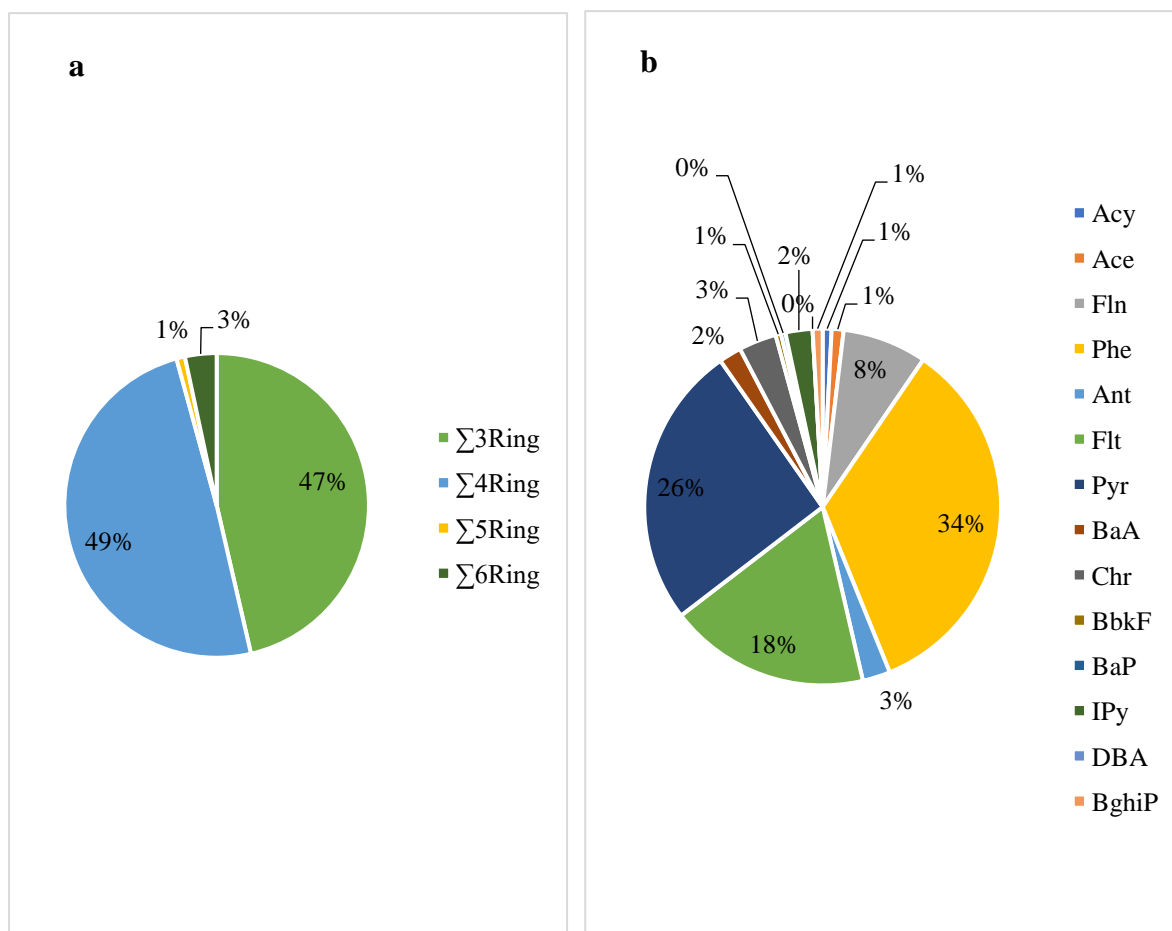
A summary of PAH concentrations detected in air samples collected in the dry season from the active oil well (AW1) area with drilling operation is presented in Table 4.15. The average concentration of  $\Sigma_{14}\text{PAH}$  was  $330 \text{ ng/m}^3$ , with  $29.5 \text{ ng/m}^3$  and  $1 \text{ ng/m}^3$  recorded for  $\Sigma\text{PAH}_{6\text{C}}$  and BaP respectively.

**Table 4-15 Statistical summary of average PAH concentrations ( $\text{ng/m}^3$ ) in active oil well in dry season (AW1) in dry season**

PAH	Average(n=6)	SD	Min	Median	Max
Acy	2.7	1.4	1.2	2.4	5.5
Ace	3.6	2	1.3	3.3	7.6
Fln	26	21.3	3.5	15.8	66
Phe	112	19.5	74.5	113.7	134.6
Ant	8.8	8.8	3.7	4.7	28.3
Flt	59.7	13.6	40.5	59.8	84.3
Pyr	85.2	15.3	59.8	91.1	104.5
BaA	6.8	1.5	5.2	6.4	9.6
Chr	11.5	4	7.4	10	19.3
BbkF	1.6	0.4	1.3	1.5	2.4
BaP	1.3	0.2	1.1	1.3	1.7
IPy	8.2	2.4	5.1	8.1	12.6
DBA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BghiP	3	0.3	2.5	2.9	3.5
$\Sigma_{14}\text{PAH}$	330.4	90.8	304.8	321.2	379.6
$\Sigma\text{PAH}_{6\text{C}}$	29.5	8.5	20.7	26.8	40.5

Figure 4.9a indicate the predominance of 4 ring PAH in the air sampled in this study area as they contribute 49%  $\Sigma_{14}\text{PAH}$ , of which Pyr and Flt contribute 26% and 18% of  $\Sigma_{14}\text{PAH}$  as shown in Figure 4.9b. Three ring PAH are nearly as dominant however, making a contribution of 46%  $\Sigma_{14}\text{PAH}$ , with Phe contributing 34%. By comparison, the contributions of 6 ring (3%) and 5 ring (1%) PAH were very low.

**Figure 4-9 Percentage (%) ring number contribution (a) and individual contribution of PAH (%) (b) at AW1 in dry season**



The average outdoor air concentration of  $\Sigma_{14}$ PAH at an active gas well (AW2) was  $151 \text{ ng/m}^3$ , while those of  $\Sigma_6$ PAH and BaP were  $15 \text{ ng/m}^3$  and  $0.5 \text{ ng/m}^3$  respectively, as represented in Table 4.16. The contributions to  $\Sigma_{14}$ PAH according to ring number at AW2 are shown in Table 4.17. Four ring PAH predominate (60%) with Pyr and Flt contributing 30% and 22% respectively. Three ring PAH at 34% were the next most abundant, with Phe contributing 25%. As at AW1, 5 ring and 6 ring make minimal contributions, accounting for 2% and 4% respectively.

**Table 4-16 Average concentrations and the percentage contribution of individual PAH to  $\Sigma_{14}$ PAH at AW2 in dry season**

PAH	Concentration (ng/m <sup>3</sup> ) (n=3)	% Contribution
Acy	3.8	3
Ace	2.8	2
Fln	4.2	3
Phe	38	25
Ant	2.7	2
Flt	34.9	22
Pyr	46.3	31
BaA	4.2	3
Chr	6.2	4
BbkF	2.6	2
BaP	0.5	0.3
IPy	1.8	1
DBA	<LOQ	<LOQ
BghiP	3.3	3
$\Sigma_{14}$ PAH	151.3	
$\Sigma$ PAH <sub>6C</sub>	15.3	

\*Percentages are round up

**Table 4-17 Average concentration and percentage contribution to  $\Sigma_{14}$ PAH according to ring number at AW2 in dry season**

Location	Average concentrations (ng/m <sup>3</sup> )				Percentage $\Sigma_{14}$ PAH (%)			
	No of Rings							
	3	4	5	6	3	4	5	6
AW2	51.6	91.5	3.1	5.1	34.3	59.9	2	3.8

At AW3, the average concentration of  $\Sigma_{14}\text{PAH}$  was  $95.5 \text{ ng/m}^3$  during the dry season, while those of  $\Sigma\text{PAH}_{6\text{C}}$  and BaP were  $19 \text{ ng/m}^3$  and  $0.9 \text{ ng/m}^3$  respectively. Since there are no known alternative sources of PAH emission around this area and villages are located 1.5 km from the site, this suggest that stationary sources related to oil industry were the dominant source of PAH in this sampling area. Table 4.18 demonstrate the average concentrations of individual PAH to  $\Sigma\text{PAH}$ . Table 4.19 shows that 4 ring PAH made the largest contribution of 48% to  $\Sigma_{14}\text{PAH}$ , followed by 3-ring at 39%, whilst the proportion of other rings number were lower than these rings3%. With respect to individual PAH, Pyr 23%, Flt 14% and Phe 24% contribute  $\Sigma_{14}\text{PAH}$ .

**Table 4-18 Average concentrations and percentage contribution to  $\Sigma 14$ PAH of individual PAH at AW3 in the dry season**

PAH	Concentration (ng/m <sup>3</sup> ) (n=4)	% Contribution
Acy	5.8	7
Ace	4.9	6
Fln	4.2	5
Phe	22.2	24
Ant	0.8	1
Flt	14.1	14
Pyr	22.8	23
BaA	7.2	7
Chr	2.5	2
BbkF	1.8	1
BaP	0.9	1
IPy	6.9	7
DBA	0.2	<LOQ
BghiP	1.4	2
$\Sigma 14$ PAH	95.5	
$\Sigma$ PAH <sub>6C</sub>	19.4	

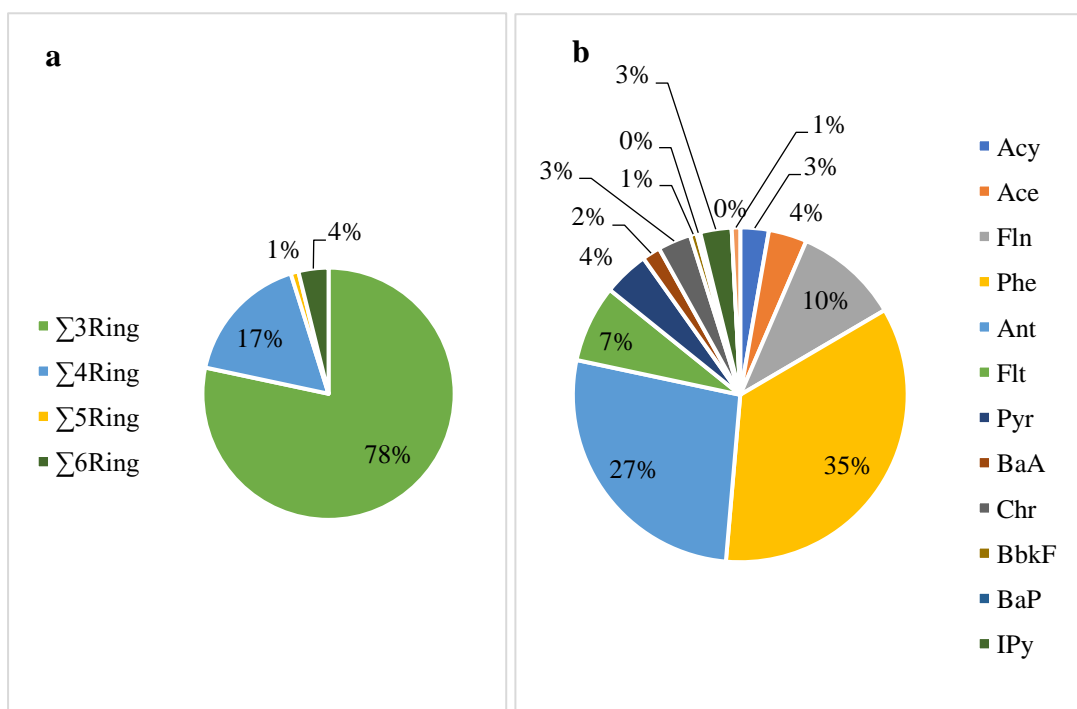
**Table 4-19 Average concentrations and percentage contribution to  $\Sigma 14$ PAH according to ring number at AW3 in dry season**

Location	Average concentrations (ng/m <sup>3</sup> )				Percentage $\Sigma 14$ PAH (%)			
	No of Rings							
	3	4	5	6	3	4	5	6
AW3	37.8	46.5	2	6.8	39	48	3	10

#### 4.5.4 Concentration of PAH at the non-active site (workstation)

Although 3 samplers were deployed in the dry season at WS, one sampler was lost. Average concentrations were 79.9 ng/m<sup>3</sup>, 7 ng/m<sup>3</sup>, and 0.3 ng/m<sup>3</sup> for  $\Sigma_{14}$ PAH,  $\Sigma$ PAH<sub>6C</sub>, and BaP respectively. Figures 4.10a show the contributions to  $\Sigma_{14}$ PAH according to PAH ring number. Three ring PAH predominated (78%) with Phe, Ant and Flt each contributing: 35%, 27%, and 10%. Meanwhile, 4 ring, 5 ring and 6 ring accounted for: 17%, 1%, and 4% respectively.

**Figure 4-10 Percentage contribution to  $\Sigma_{14}$ PAH (a) expressed as ring number and (b) for individual PAH at WS in the dry season**

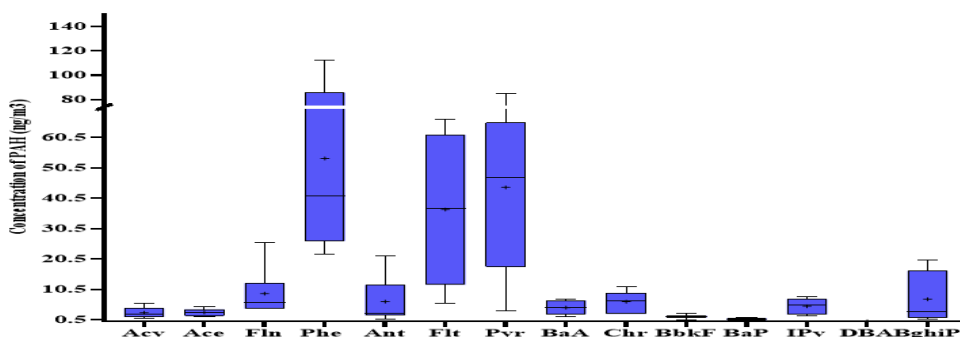


#### 4.6 Comparison of ambient air concentrations between different sampling sites and with other previous studies in dry season.

The overall variability of  $\Sigma_{14}$ PAH concentrations (combination of gaseous and particulate) observed across all the sites is presented in Table 4.20. This reflects how the atmospheric concentrations of PAH in these regions are affected by specific location emission sources. For instance, AW1 samples had the highest levels of PAH, averaging 330 ng/m<sup>3</sup>, which was not

surprising; given the extensive exploratory activities taking place during the monitoring campaign, along with occasion oil leaks, this could explain the elevated concentration observed at these locations. Also, possible emissions from heavy duty haulage vehicle and fuel combustion in utility equipment could be a contributing factor. TST, AW2, and OGP displayed concentrations averaging 254, 169 and 178 ng/m<sup>3</sup> respectively following AW1. The higher levels seen at TST may be due to crude oil volatilising at this location. The concentration at AW3 ( $\Sigma_{14}\text{PAH} = 95 \text{ ng/m}^3$ ) is low compared to the other sites, which may be associated with the fact that AW3 is confined solely to oil exploration activities (no gas exploration), as well as the minimal traffic activity at this location. The lowest concentrations were detected at WS (defined as a background location) at which the average  $\Sigma_{14}\text{PAH}$  concentration was 80 ng/m<sup>3</sup>. The concentrations of all PAH are given in Appendix . An analysis of variance test (ANOVA) revealed that the differences in concentrations of  $\Sigma_{14}\text{PAH}$  between locations are not statistically significant ( $p = 0.32$ ). The small sample size may likely be the reason for this. The pattern of individual distribution of PAH concentration are seen in Figure 4.11 and demonstrate that the LMW-PAH particularly, Phe, Pyr and Flt are present at higher concentrations than other compounds.

**Figure 4-11 Total concentrations of individual PAH this study in the dry season**



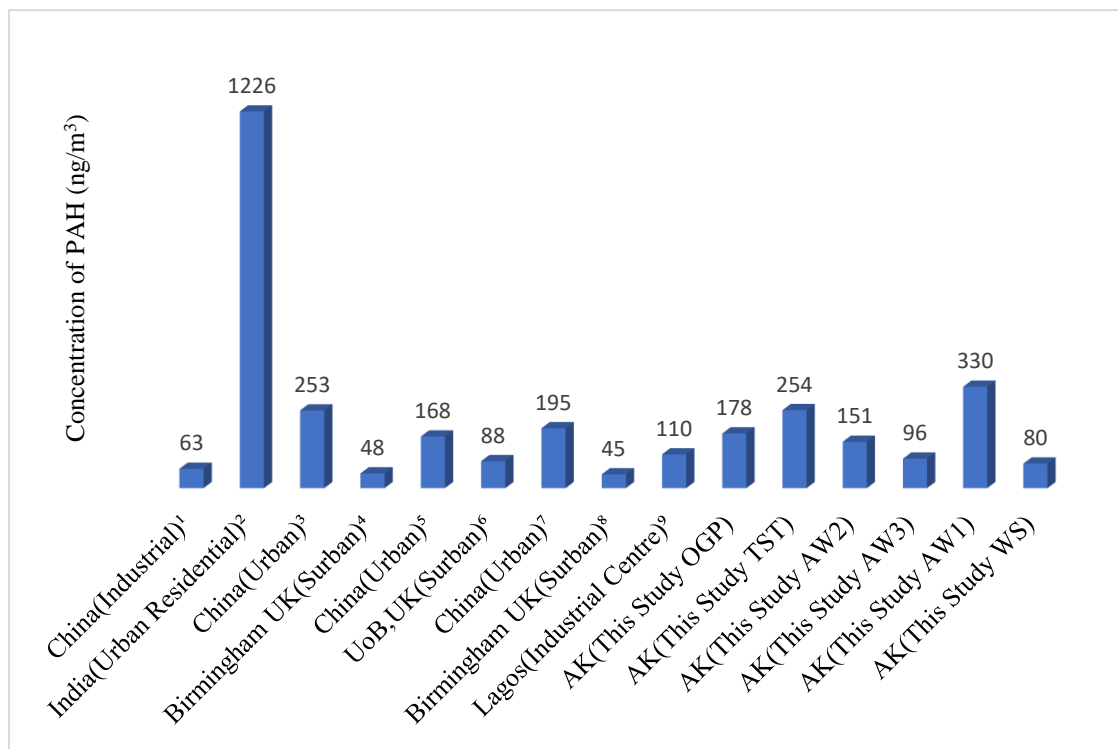
**Box and whisker plot diagram showing minimum,maximum,interquartile range and (+) average PAH in dry season**

**Table 4-20 Average concentrations (ng/m<sup>3</sup>) of individual PAH at each site in this study in the dry season**

PAH	OGP	TST	AW1	AW2	AW3	WS
Acy	1.5	1.1	2.7	3.8	5.8	2.2
Ace	1.9	1.6	3.6	2.8	4.9	2.9
Fln	6.5	5.9	26	4.2	4.2	8.1
Phe	44.7	76.9	112	38	22.2	27.8
Ant	2.4	2.8	8.8	2.7	0.8	21.6
Flt	39.6	66.6	59.7	34.9	14.1	6
Pyr	48	58.8	85.2	46.3	22.8	3.5
BaA	4.9	2.7	6.8	4.2	7.2	1.4
Chr	7.5	8.7	11.5	6.2	2.5	2.5
BbkF	1.4	1.5	1.6	2.6	1.8	0.5
BaP	0.6	0.7	1.3	0.5	0.9	0.3
IPy	3.7	7	8.2	1.8	6.9	2.4
DBA	<LOQ	<LOQ	<LOQ	<LOQ	0.2	<LOQ
BghiP	15.4	20.1	3	3.3	1.4	0.6
Σ <sub>14</sub> PAH	178	254.4	330.4	151.3	95.5	79.9
ΣPAH <sub>6C</sub>	18.1	20.5	29.5	15.3	19.4	7.1

The observed concentrations in this study are broadly similar to those reported at urban locations as shown in Figure 4.12 . However, they are an order of magnitude lower than that reported in another study in India (Masih et al., 2012) (1226 ng/m<sup>3</sup>).

**Figure 4-12 Average concentration of  $\Sigma$ PAH in outdoor air from this study compared with other studies in dry season**



<sup>1</sup>(Zhao et al., 2010); <sup>2</sup>(Masih et al., 2012); <sup>3</sup>(Xia et al., 2013); <sup>4</sup>(Alam et al., 2013); <sup>5</sup>(Ma et al., 2010a); <sup>6</sup>(Delgado-Saborit et al., 2013); <sup>7</sup>(Zhou et al., 2013); <sup>8</sup>(Harrad and Laurie, 2005); <sup>9</sup>(Alani et al., 2021); AK(Akwa Ibom State); OGP(Crude oil and gas production area); TST(Crude storage and transfer/pump area); AW1(Active oil well no drilling activities); AW2(Active gas well); AW3(Active oil well); WS(Workstation).

#### **4.7 Spatial variability between concentrations of PAH in wet and dry season in outdoor air**

The concentrations of PAH across the six sampling sites are illustrated in Figure 4.13 for the dry and wet season respectively. Average concentrations at all six locations, i.e., OGP, TST, AW1, AW2, AW3, and WS are higher in the dry season than in the wet season. However, a paired t-test comparison of concentrations shows this is not a significant seasonal difference, which is likely due to wet deposition of PAH during the wet season.

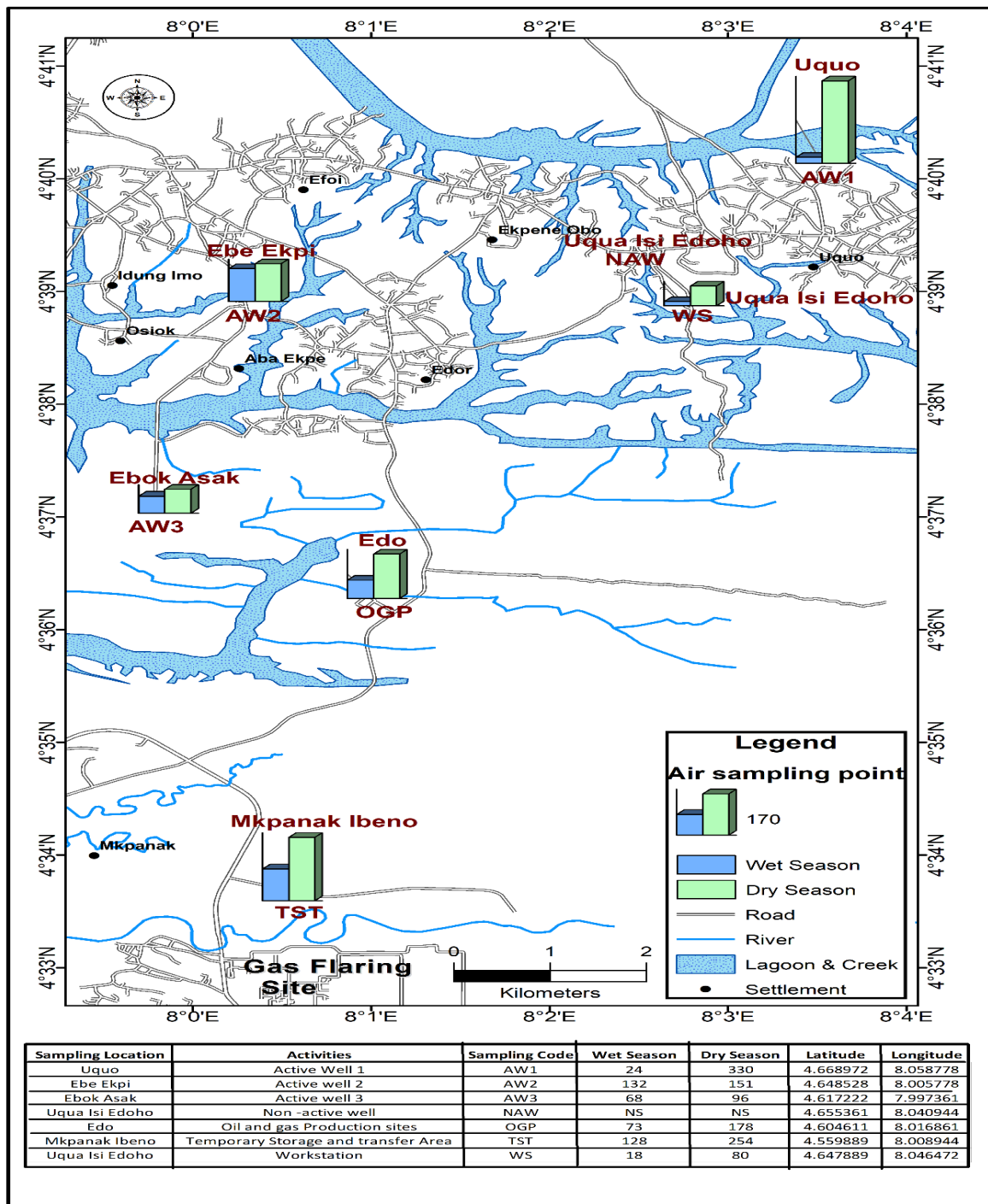
A possible explanation for the higher average PAH concentrations in the dry season is that the dry season is associated with dry, dusty, cool, calm wind from the north-east (Bandowe and Nkansah, 2016). It has been reported that both volatile and non-volatile PAH are absorbed by

the higher concentration of airborne particles during the dry season and as such lead to an elevated PAH concentration (Kumar et al., 2013). Moreover, the study area is equally impacted by high temperatures (weekly temperature supplied by the company, range from 28-32°C) across both dry and wet seasons. Hence, seasonality of concentration of PAH is likely not temperature dependent. Instead, it may be due to seasonal variations in activities conducted by the oil and gas firm in our study area. An independent t-test revealed that while concentrations of  $\Sigma_{14}$ PAH in the WA sub-location area were statistically significantly higher ( $p=0.045$ ) in the dry season, no such significant seasonal difference was observed at either the MP or the NP sub-location ( $p>0.05$ ).

Comparing concentrations for individual sites in the two seasons (dry and wet), via a paired t-test suggests that seasonal variation between dry and wet was near statistically significant only at AW1 ( $P=0.063$ ), while the difference in the concentrations between the rest of the sites was not statistically significant ( $p>0.05$ ). This may be due to the small sample numbers at each individual site. This is supported by the fact that when concentrations from all sites were combined, a paired t-test revealed a statistically significant seasonal difference ( $p=0.001$ ), whereby concentrations were higher in the dry than in the wet season.

This implies that further investigation should be undertaken into the seasonal variation of PAH, taking into context the impact of flaring of gases which could alter the temperature of these regions and therefore promote photolytic degradation. Hence it is recommended to measure PAH monthly at each site. Alani et al. (2021) identified a similar pattern in Oshodi (OSH), where they found that PAH concentrations in outdoor air were higher in the dry season.

Figure 4-13 Average concentrations of  $\Sigma 14\text{PAH}$  at six sampling sites in dry and wet seasons



NS Not samples

#### 4.8 Conclusion

Concentrations, profile, source, and carcinogenic potency of six PAH was investigated using Passive air sampler (Polyurethane foam and glass fibre). The study areas have been identified

as a source of PAH to the environment as a result of the higher average concentrations in areas closest to active oil and gas exploration sites compared to those at the background site (WS), indicating the impact of oil and gas activities. However, concentrations at sites closer to oil and gas exploration activities were not significantly ( $p>0.05$ ) higher than at the background site. While this may be a genuine observation, collection and analysis of more samples is recommended to increase sample size and statistical power. The overall PAH concentrations in the dry season of 2020 seems to be higher than the wet season of 2019, this was confirmed statistically with a significance value ( $P=0.001$ ) reflecting the influence of oil and gas activities. In both season LMW PAH were predominant in the study area. Concentrations in this study compared to other studies are broadly similar to those in urban locations across the world (see Table 1.6 in section 1.9.3 and Table 4.10 and 4.20) but higher than those reported in other studies in oil and gas activities. As this research was conducted in a rural area, this suggests oil and gas exploration activities are a substantial source of PAH to the locations studied. The outdoor air PAH concentrations Ibeno and Esit Eket showed moderate pollution. The results of the study will therefore contribute to the expansion of the database of PAH air emissions in Nigeria and give important data and a scientific methodology for decision-makers entrusted with addressing air pollution issues.

## Chapter 5

### Human exposure to PAH in soil and air in the vicinity of an oil and gas field in Akwa Ibom State

#### 5.1 Abstract

Human exposure to PAH is of great concern, thus, analysis of PAH concentrations in outdoor air and soil in the vicinity of oil and gas sites will not be complete without evaluating the potential exposure arising. Therefore, exposure via inhalation and ingestion was assessed for employees working in the site or living within the fields, as well as other residents.

BaP<sub>eq</sub> was used to evaluate the carcinogenicity of six carcinogenic PAH in this study. The results indicate that BaP<sub>eq</sub> estimates for the soil and outdoor air samples were higher at the sites influence and affected by oil and gas activities than the sites with little or no oil and gas activities across the locations in the wet and dry period. The highest BaP<sub>eq</sub> concentrations were observed at AW3( 42.9 ng/g) during the wet season and at TST (21.7 ng/g) during the dry season in soil whereas in outdoor air the highest concentration was at AW3 in both dry (3.48ng/m<sup>3</sup>) and wet period (3.17ng/m<sup>3</sup>). These values indicate a low carcinogenic burden based on the Canadian soil quality guideline and the workers or residents are therefore not prone to any health risk. DBA and BAP were the most abundant PAH in soil sampled whereas BaP contribute primarily to the carcinogenicity activities in outdoor air sampled suggesting high risk of cancer. The average contribution of LMW-PAH( $\Sigma_7$ PAH) relative to the carcinogenicity of the  $\Sigma_6$ PAH in the outdoor air was 3% in the wet season and 11% in the dry and 0.76% in wet and 3.6% in dry period in soil, demonstrating that the majority of the sites in both period and matrices are contaminated with carcinogenic PAH (>95%). Our findings also indicated that the incremental lifetime cancer risk (ILCR)calculated values for ingestion of soil particle and inhalation exposure of PAH revealed a low cancer risk, implying that

exposure to contaminated sites for outdoor air and soil may pose low human health risk, in contrast to outdoor air samples ( $10^{-7}$ - $10^{-6}$ ), soil samples are more carcinogenic( $10^{-5}$ - $10^{-4}$ ).

## 5.2 Human health risk Assessment

Toxic equivalent (TEQ) concentrations were used for the evaluation of exposure risk posed by the PAH mixture to which residents and employees are exposed to. BaP is often used as a marker of the toxicity of PAH mixtures (see section 1.5.3). Thus, BaP<sub>eq</sub> concentrations were calculated for the PAH mixtures via the equation below to determine human exposure risk (Wang et al., 2018a)

$$\Sigma \text{BaP}_{\text{eq}} = \Sigma C_i \times \text{TEF}_i \quad (1)$$

Where BaP<sub>eq</sub> was used as the concentration of the PAH mixture expressed in terms of its toxicity relative to BaP. To do so, toxic equivalent factor (TEF) values from Nisbet and LaGroy were used (Nisbet and Lagoy, 1992). These TEF values were multiplied by the concentrations of each target PAH and summed to provide the BaP<sub>eq</sub> concentrations, that are then used to assess the carcinogenicity of soil and air based on the different activities conducted in each sampling area. It is important to note that the PAH mixture in this study are different from that emissions from coke ovens. As a result of this difference, the calculated BaP<sub>eq</sub> of these PAH mixtures may indicate a higher or lower carcinogenicity.

For daily dose of inhalation, the inhalation unit risk (IUR) which is assigned as  $8.7 \times 10^{-5}$  and established by World Health Organization (WHO, 1987) is used to evaluate the probability of developing lung cancer over a period of time. Based on this, it is predicted that 8.7 incidences per 100,000 people would arise in a population subjected over a 70 year lifetime to inhalation of  $1 \text{ ng/m}^3$  BaP (Ramírez et al., 2011, WHO, 1987). Therefore, equation (2) is used to compute the incremental life cancer risk (ILCR<sub>1</sub>) for possible risk based on WHO inhalation risk value.

This will be achieved by multiplying the  $\Sigma\text{BaPeq}$  concentration of the sample by the inhalation unit risk.

$$\text{ILCR}_1 = \Sigma(\text{BaPeq} \times \text{IUR}) \quad (2)$$

Where IUR is the inhalation unit risk ( $8.7 \times 10^{-5}$ ) (WHO, 1987)

As exposure will occur not only as a result of inhalation but also via ingestion of PAH, we also evaluated exposure via inhalation and ingestion as per equations 3 and 4.

$$\text{LADD} = \frac{(\text{C}_{\text{BaPeq}} \times \text{IR}_{\text{inh}} \times \text{ED} \times \text{EF})}{\text{BW} \times \text{AT}} \times \text{Cf} \quad (3)$$

$$\text{ADD} = \frac{(\text{C}_{\text{BaPeq}} \times \text{IR}_{\text{ing}} \times \text{ED} \times \text{EF})}{\text{BW} \times \text{AT}} \times \text{Cf} \quad (4)$$

To further elucidate cancer risk associated with inhalation and ingestion exposure to PAH in each sampling site, lifetime average daily exposure dose was then multiplied by the cancer slope (CSF).

$$\text{ILCR}_2 = \text{LADD} \times \text{CSF} \quad (5)$$

$$\text{ILCR}_2 = \text{ADD} \times \text{CSF} \quad (6)$$

Where LADD is the lifetime average daily dose for inhalation, ADD is the average daily dose for ingestion, C is the Concentration of  $\Sigma\text{BaPeq}$  (ng/m<sup>3</sup>) of the air samples, IR<sub>inh</sub> and IR<sub>ing</sub> are the inhalation (m<sup>3</sup>/day) and soil ingestion rate(mg/day), ED is the exposure duration (year), EF is the exposure frequency (d/year), BW is the body weight (kg), AT is the averaging time

(ED×365 days/year), Cf is the conversion factor ( $10^{-6}$ ) and CFS is the inhalation and ingestion carcinogenic slope factor (mg/kg/day). The values used for this calculation were derived from numerous studies as shown in Table 5.1. Both equations (3) and (4) have been used by several studies to assess possible cancer risk (Alani et al., 2021, Chen et al., 2018, Pokhrel et al., 2018, Hu et al., 2018, De Pieri et al., 2014, Nematollahi et al., 2022). Table 5.1 list the parameters and recommended values.

**Table 5-1 Parameter for calculation of exposure risk for adults within the study area**

<b>Exposure Factor</b>	<b>Values (Adult)</b>	<b>Reference</b>
Inhalation Unit Risk (IUR)	$8.7 \times 10^{-5}$	Ramírez et al. (2011), (WHO, 1987)
Inhalation rate (IR, m <sup>3</sup> /d)	20	USEPA (2011)
Exposure frequency (EF,d/year)	365	Alani et al. (2021)
Cumulation exposure duration ED, year)	70	De Pieri et al. (2014)
Lifelong exposure time (AT, d)	25550	Chen et al. (2018)
Body weight (BW, kg)	70	USEPA (2011)
Carcinogenic slope factors (CSF, mg/kg/d)	3.9	(California Environmental Protection Agency (CalEPA), 2005)
Conversion factor (Cf)	$1 \times 10^{-6}$	Jyethi et al. (2014)
Soil ingestion rate (IRing) (mg/day)	100	Yang et al. (2015)
Cancer oral slope factor (ingestion)	7.3	Yang et al. (2015)
Exposure duration (year)	26	USEPA (2014)

### 5.3 Human exposure risk associated with ingestion of PAH in soil in wet and dry season

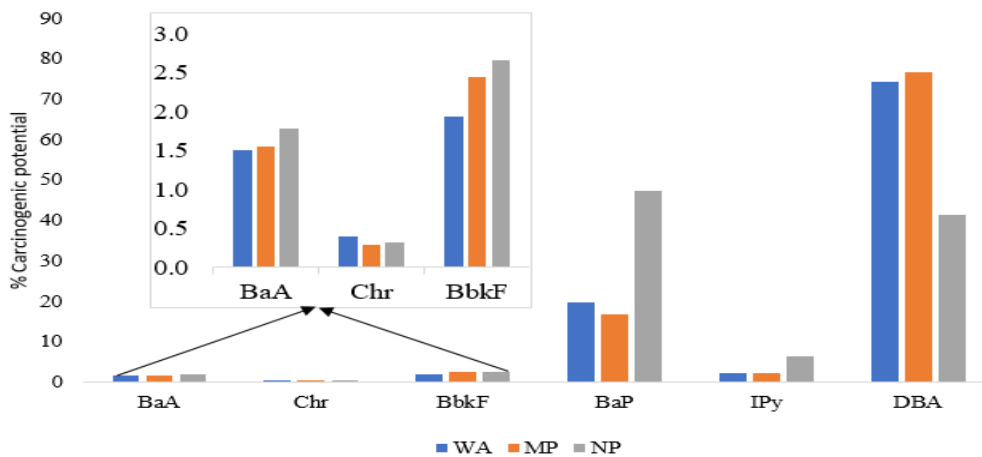
#### 5.3.1 Oil and gas production area (OGP) in wet season

Average BaP<sub>eq</sub> concentrations of  $\Sigma_6$ BaP<sub>eq</sub> for sub-locations WA, MP and NP were 19.6, 19.7, and 41.4 ng/g and ranged from 12.7 to 30.7, 4.1 to 43, and 10.6 to 62.6 ng/g as shown in Table 5.2. While BaP was detected in all the soil samples, PAH toxicity in sub-location NP was higher than at the other two sub-locations. Based on an ANOVA test, a statistically significant difference was not observed between BaP<sub>eq</sub> within the three sub-locations. ( $p=0.6$ ). Figure 5.1 illustrates the relative contributions of each six PAH carcinogenic activity. The highest average contribution was DBA at all the locations, contributing 77% at MP, 74% at WA, and 48% at NP. This was followed by BaP with 20% at WA, NP 18% and MP has the least contribution of 17%. The contributions of  $\Sigma_6$ PAH at location MP, NP and WA were 97%, 99.5% and 99.4% while the extent of the Lower molecular weight PAH (MW-PAH) ( $\Sigma_7$ PAH) contribution was also estimated to be 2.2%, 0.23% and 0.1% and those do not signify any toxic effect on human's health.

**Table 5-2 Toxicity potential of PAH in soil (BaP<sub>eq</sub> ng/g) from three sub-locations in OGP in wet season**

PAH		BaA	Chr	BbkF	BaP	IPy	DBA	$\Sigma_6$ BaP <sub>eq</sub>
Location/TEF		0.1	0.01	0.1	1	0.1	5	
WA	Average	0.278	0.074	0.381	3.699	0.402	14.791	19.624
	SD	0.099	0.018	0.153	1.194	0.105	5.836	6.299
	Min	0.156	0.055	0.219	2.610	0.291	9.150	12.683
	Max	0.407	0.107	0.685	5.900	0.596	26.200	30.663
NP	Average	0.746	0.129	1.066	21.137	2.722	15.550	41.350
	SD	0.962	0.069	0.434	12.615	1.369	7.167	16.838
	Min	0.183	0.027	0.294	2.100	0.337	5.600	10.641
	Max	2.895	0.212	1.686	44.390	4.771	24.900	62.649
MP	Average	0.239	0.047	0.401	2.755	0.355	15.851	19.757
	SD	0.088	0.021	0.173	1.647	0.186	11.783	12.441
	Min	0.102	0.009	0.120	0.580	0.129	2.900	4.130
	Max	0.325	0.072	0.643	5.110	0.665	39.158	42.971

**Figure 5-1 Percentage average contributions six PAH to  $\Sigma$ BaP<sub>eq</sub> concentrations in soil from three sites in OGP in wet season**



WA(Worker’s accommodation), MP(Main processing area) and NP(near processing area and gas flaring area)

### 5.3.2 Crude oil storage and transfer area (TST) in wet season

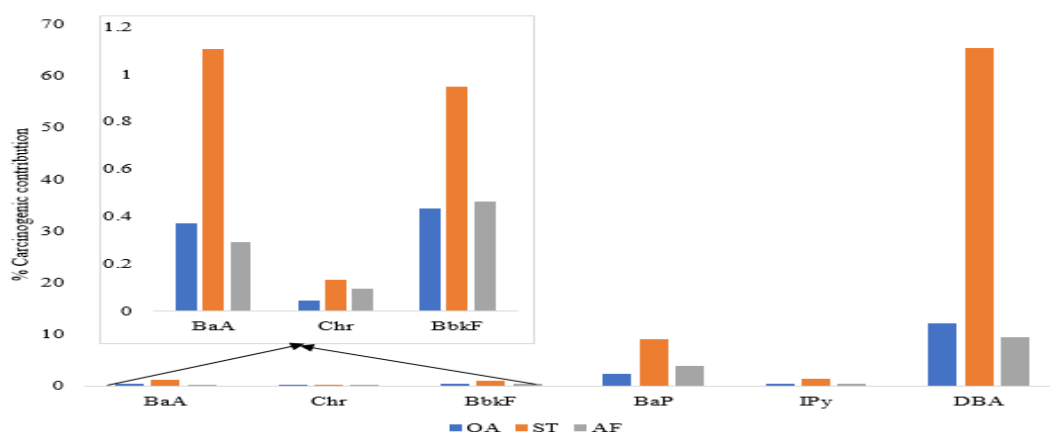
Table 5.3 provides a statistical summary of PAH toxicity for the three sub-locations in TST. The potential hazardous levels of PAH varied greatly among the sampled locations due to the various activities conducted at these sub-locations. From Table 5.3, it is evident that the average BaP<sub>eq</sub> concentrations of  $\Sigma_6$ PAH are 15.5 ng/g, 77.9 ng/g, and 14.5 ng/g for OA, ST, and AF respectively, with ranges of 13.6 to 17.8, 52.4 to 147.8 and 7.78 to 23.2 ng/g at the three sub-locations respectively. While on average the highest contamination was at ST, statistically significant difference was not observed between BaP<sub>eq</sub> in the three sub-locations (p=0.41) according to the analysis of variance test (one way ANOVA) conducted after carrying out a normality test. The major contributors to the carcinogenicity in soil in this study area were the carcinogenic compounds; BaP and DBA in all the three sub-locations as depicted in Figure 5.2. DBA accounted for the highest proportion with 83% in ST on average, 77.9% in OA and 65% in AF, followed by the contribution of BaP accounting for 14.6% in OA, 30% in AF and 12% in ST while other carcinogenic PAH input are minimal. The extent of the seven non carcinogenic (LMW-PAH)  $\Sigma_7$ PAH was also compared to the  $\Sigma_6$ PAH since LWM-PAH are

abundant in the environment. Our study revealed that  $\Sigma_7$ PAH from OA contribute 0.34%, ST 0.19% and AF 0.61% to the total activity, which indicates that these compounds are unimportant and thus have no toxicity effect on human health and the environment.

**Table 5-3 Potency of PAH in soil ( $BaP_{eq}$  ng/g) from three sub-location in crude oil transfer area (TST) in wet season**

Location/PAH		BaA	Chr	BbkF	BaP	IPy	DBA	$\Sigma_6BaP_{eq}$
OA	TEF	0.1	0.01	0.1	1	0.1	5	
	Average	0.368	0.045	0.431	2.24	0.312	12.092	15.488
	SD	0.260	0.002	0.139	0.361	0.090	1.570	1.525
	Min	0.218	0.041	0.266	1.700	0.205	10.550	13.642
	Max	0.895	0.047	0.57	2.78	0.456	15	17.813
ST	Average	1.107	0.129	0.947	9.050	1.366	65.317	77.917
	SD	0.428	0.071	0.360	3.196	0.679	32.185	36.007
	Min	0.638	0.032	0.65	5.972	0.822	44.1	52.360
	Max	1.777	0.236	1.535	13.25	2.642	128.9	147.789
AF	Average	0.290	0.092	0.464	3.784	0.416	9.482	14.527
	SD	0.086	0.042	0.163	2.014	0.331	4.965	7.601
	Min	0.184	0.045	0.207	1.227	0.146	5.864	7.778
	Max	0.401	0.140	0.663	6.838	0.927	17.747	23.207

**Figure 5-2 Average contributions of  $\Sigma_6$ PAH to  $\Sigma BaP_{eq}$  concentrations in soil from three sites in in wet season**



OA(Office area),ST(Storage tank and pump area) and AF(Surrounding of crude oilfield/pipeline area)

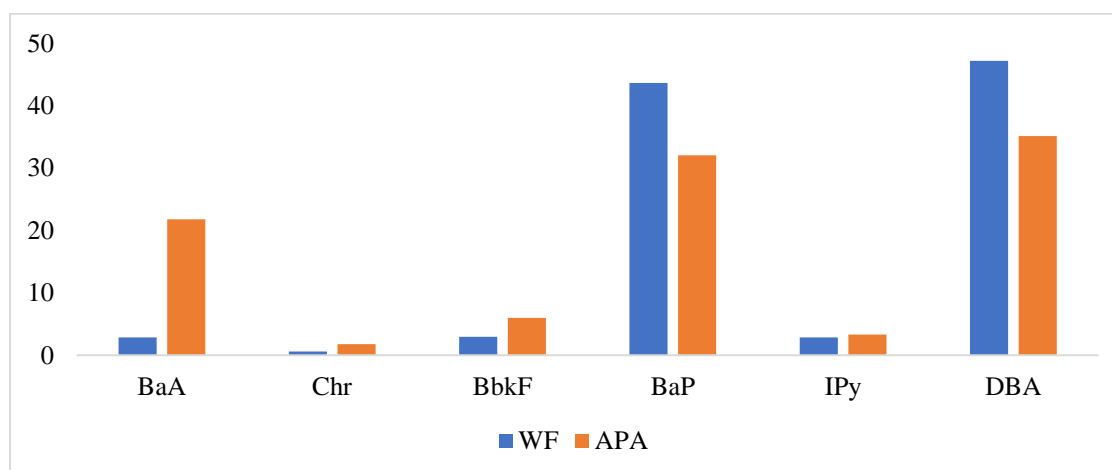
### 5.3.3 Active gas well in wet season

Table 5.4 depicts the BaP<sub>eq</sub> concentrations in soil sampled from within oil field (WF) and along pipeline of way (APA). BaP<sub>eq</sub> concentrations ranged from 3.3 to 29.3 and 0.4 to 50.5 ng/g, in WF and APA with an average value of 14.5 ng/g in WF and 19.7 ng/g at APA for Σ<sub>6</sub>PAH. From analysis of independent t-test, there was no statistically significant difference between the two sub-locations for ΣBaP<sub>eq</sub> (P>0.05). The carcinogenicity of the non-carcinogenic seven PAH(Acy, Ace, Fln, Phe, Ant, Flt and Pyr)burden in the two different locations show an insignificant percentage contribution (WF- 0.8% and APA 5.4%)relatively to the six carcinogens .

**Table 5-4 Toxicity of PAH in soil from two sub-location in gas active well (AW2) ( BaP<sub>eq</sub> ng/g) in wet season**

Location/PAH		BaA	Chr	BbkF	BaP	IPy	DBA	Σ <sub>6</sub> BaP <sub>eq</sub>
WF	TEF	<b>0.1</b>	<b>0.01</b>	<b>0.1</b>	<b>1</b>	<b>0.1</b>	<b>5</b>	
	Average	0.219	0.038	0.200	3.523	0.189	10.309	14.478
	SD	0.074	0.014	0.053	1.377	0.225	10.697	11.097
	Min	0.133	0.020	0.148	1.850	<LOQ	<LOQ	3.320
	Max	0.319	0.055	0.280	5.600	0.539	23.300	29.348
APA	Average	0.444	0.041	0.836	5.434	0.360	12.601	19.717
	SD	0.309	0.034	0.906	6.757	0.353	16.859	20.734
	Min	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.402
	Max	0.850	0.092	2.191	16.167	0.930	31.256	50.521

**Figure 5-3 Contribution of individual six PAH to carcinogenic activity on average in AW2 wet season**



WF (Within gas field area) and APA (Along pipeline right of way)

It was observed that the relative contribution of DBA was higher in soil from WF with 47.2% while APA contribute 35% on average to the total carcinogenic activity. BaP was also a significant contributor to the carcinogenic activity in this study area at 43.6 % in soil from WF and 32% in APA as shown in Figure 5.3, followed by BaA with 21.8% at APA. THE LMW-PAH other the other hand contributed about 5% at APA and less than 1 at WF.

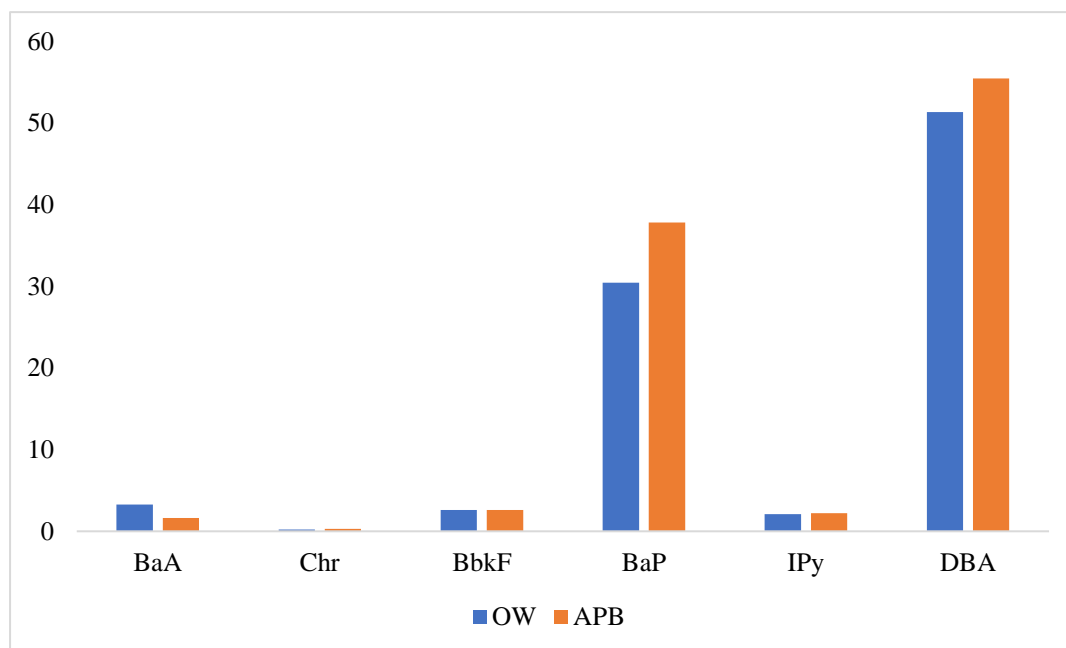
#### 5.3.4 Active oil well (AW3) in wet season

The average BaP<sub>eq</sub> concentrations for soil at within oil well (OW) and along pipeline right of way (APB) in an active oil well area range between <LOQ to 41.8 ng/g in OW and 10.7 to 151.6 ng/g in APB respectively for the six carcinogenic PAH as represented in Table 5.5. The average BaP<sub>eq</sub> concentration was higher in APB at 64.7 ng/g on average than at OW with an average of 21 ng/g. Undistinguishable statistical difference between OW and APB (P>0.05) according to independent t-test. DBA was the major carcinogenic contributor to the total Σ<sub>6</sub>PAH BaP<sub>eq</sub> concentrations with 55.5% at APB and 51.3% at OW, next is BaP accounting for 37.8% at APB and 30.5% at OW. Figure 5.4 display the contributions of each individual PAH to BaP<sub>eq</sub>. The contribution of the LMW-PAH to the total toxicity in comparison to the Σ<sub>6</sub>PAH was was <1 (0.01% at OW and at 0.35% APB), signifying no risk at these sub-locations.

**Table 5-5 Statistical summary of toxicity of carcinogenic PAH in soil from two active oil well (AW3) (BaP<sub>eq</sub> ng/g) in wet season.**

PAH/Location		BaA	Chr	BbkF	BaP	IPy	DBA	Σ <sub>6</sub> BaP <sub>eq</sub>
OW	TEF	0.1	0.01	0.1	1	0.1	5	
	Average	0.633	0.031	0.396	6.481	0.382	13.185	21.107
	SD	0.408	0.020	0.347	3.526	0.285	10.678	13.781
	Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Max	1.042	0.059	1.170	9.900	0.844	30.850	41.838
APB	Average	1.128	0.180	1.781	28.620	1.531	31.455	64.695
	SD	1.179	0.158	1.474	25.680	1.168	16.015	43.527
	Min	0.210	0.044	0.297	2.340	0.177	7.600	10.668
	Max	3.773	0.556	5.208	73.140	3.943	65.000	151.620

**Figure 5-4 Individual contribution of carcinogenic activity of six carcinogenic PAH in AW3 in wet season**



OW(within oil well) and APB( Along pipeline of way)

### 5.3.5 PAH toxicity in three non-active sites

For non-active sites (NAW), the  $\Sigma_6\text{BaP}_{\text{eq}}$  concentrations in soil fell between 0.6 to 22 ng/g with average of 8 ng/g. BaP accounted for 28 % of the  $\text{BaP}_{\text{eq}}$  concentrations of  $\Sigma_6\text{PAH}$ , while DBA contributes 51.9% , in addition, BbkF (9.4%) also found to contribute notably to  $\text{BaP}_{\text{eq}}$  concentrations. Whereas, in the workstation area (WS) the average toxicity concentration for  $\Sigma_6\text{BaP}_{\text{eq}}$  was estimated to be 12.5 ng/g with a range of 1.7 to 32.8 ng/g. DBA was also the highest contributor of carcinogen with 61%, next by BaP at 28 %.

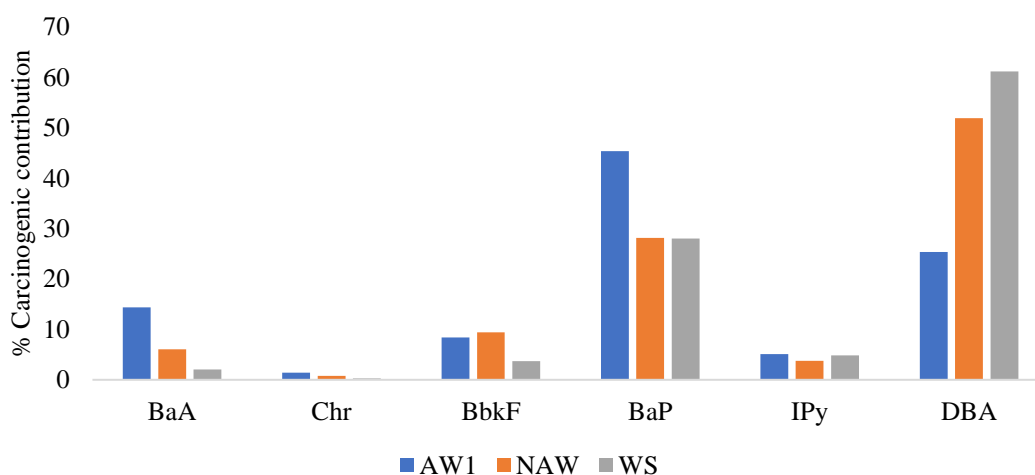
The  $\text{BaP}_{\text{eq}}$  concentrations for the six carcinogenic active oil well without drilling (AW1) varied from 1.2 to 40 ng/g and an average value of 11 ng/g. The contribution of BaP to  $\Sigma_6\text{BaP}_{\text{eq}}$  concentrations was also evaluated at 45.4% and DBA 25%, this pattern differs from other locations where the contribution of DBA appeared to exceed that of BaP. While the carcinogenic PAH contributes substantially to  $\text{BaP}_{\text{eq}}$  concentrations in AW1, NAW and WS, LMW-PAH( $\Sigma_7\text{PAH}$ ) has less impact accounting for 0.45% , 0.4% , 0.25%. at AW1, NAW and

WS respectively. Table 5.6 summarises statistical parameters of the three locations while Figure 5.5 show the percentage contributions of individual six PAH.

**Table 5-6 Summary of Toxicity of PAH in soil (BaP<sub>eq</sub>ng/g) from the non-active sites in the wet season**

Location/PAH	BaA	Chr	BbkF	BaP	IPy	DBA	ΣBaP <sub>eq</sub>	
AW1	TEF	0.1	0.01	0.1	1	0.1	5	
	Average	0.352	0.044	0.316	2.883	0.333	7.165	11.093
	SD	0.269	0.029	0.168	2.241	0.226	12.544	12.824
	Min	<LOQ	<LOQ	0.126	<LOQ	<LOQ	<LOQ	1.232
	Max	0.775	0.090	0.617	7.377	0.642	35.8	40.147
NAW	Average	0.153	0.022	0.253	0.874	0.139	6.525	7.965
	SD	0.088	0.013	0.117	0.531	0.093	6.701	7.167
	Min	0.069	0.009	0.137	<LOQ	<LOQ	<LOQ	0.573
	Max	0.363	0.046	0.545	1.780	0.356	19.750	22.219
WS	Average	0.197	0.021	0.165	1.457	0.281	10.37	12.491
	SD	0.235	0.024	0.183	1.230	0.201	9.780	9.323
	Min	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.746
	Max	0.698	0.078	0.589	3.59	0.561	32.1	32.772

**Figure 5-5 Average contribution of Individual of PAH to the total carcinogenic activity of Σ14PAH in AW1 in the wet season**



AW1(Active oil well without drilling activities), NAW(Non-active site) and WS(workstation)

## 5.4 Potential health risk assessment of soil in dry season

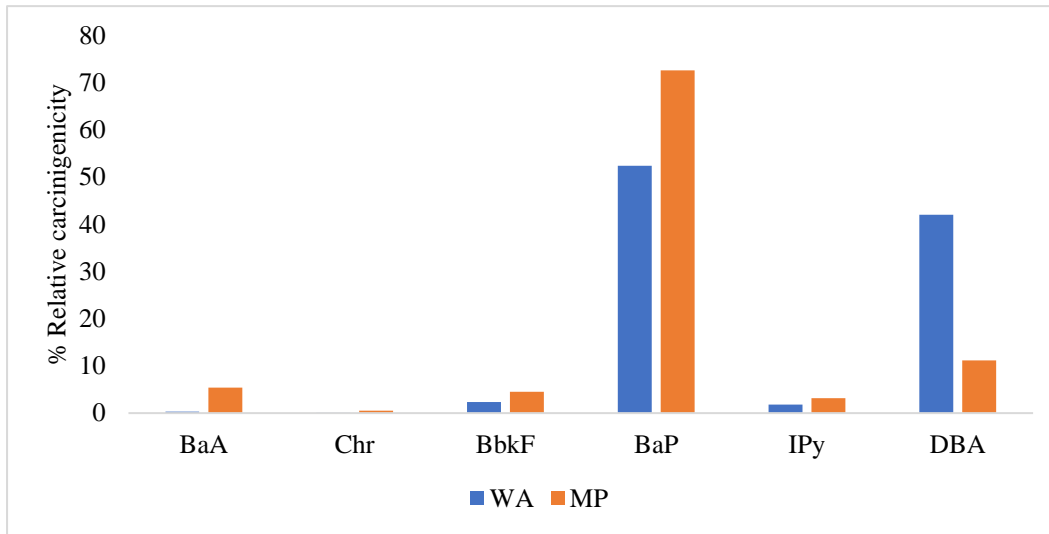
### 5.4.1 Toxic equivalency quantities of PAH in oil and gas production area (OGP) in dry season

Average BaP<sub>eq</sub> concentrations at MP and WA varied from <LOQ to 1.35 and <LOQ to 0.38 ng/g respectively, having 16.9 ng/g and 23.6 ng/g on average as in Table 5.7. Significant variation was not found within these sub-locations (P=0.41). With respect to the contributions to BaP<sub>eq</sub> concentrations of individual PAH, BaP was the main contributor with 72% in MP and 52.4% at WA as shown in Table 5.7 and Figure 5.6. However, there was a remarkable difference between the contributions of DBA at MP at 11 % and 42% at WA. Overall carcinogenic activity indicate that the six carcinogenic PAH were the major pollutant in these locations accounting for 95 to 98% of the total PAH which is contrary to the LMW-PAH(1-3%).

**Table 5-7 Statistical summary of toxicity potency of PAH in soil from two sub-locations in OGP in dry season (BaP<sub>eq</sub>ng/g)**

Location/PAH	BaA	Chr	BbkF	BaP	IPy	DBA	BghiP	Σ <sub>6</sub> BaP <sub>eq</sub>	
WA	TEF	0.1	0.01	0.1	1	0.1	5	0.01	
	Average	0.095	0.004	0.312	6.24	0.346	16.463	0.175	23.636
	SD	0.191	0.009	0.278	2.976	0.294	20.912	0.07	19.597
	Min	<LOQ	<LOQ	<LOQ	4.38	<LOQ	<LOQ	0.106	6.447
	Max	0.381	0.018	0.596	10.63	0.711	43.6	0.262	49.579
MP	Average	0.77	0.08	0.58	9.168	0.253	5.75	0.343	16.944
	SD	0.634	0.074	0.297	4.748	0.325	14.085	0.204	17.633
	Min	<LOQ	<LOQ	0.272	4.48	<LOQ	<LOQ	0.087	6.309
	Max	1.351	0.164	0.978	16.12	0.829	34.5	0.603	51.609

**Figure 5-6 Average contribution of individual PAH to the sum of BaP<sub>eq</sub> concentrations in soil from two locations in OGP in the dry season**



WA(Worker’s accommodation) and MP ( Main processing area)

#### 5.4.2 Toxic equivalency quantities in crude oil transfer and storage area (TST)

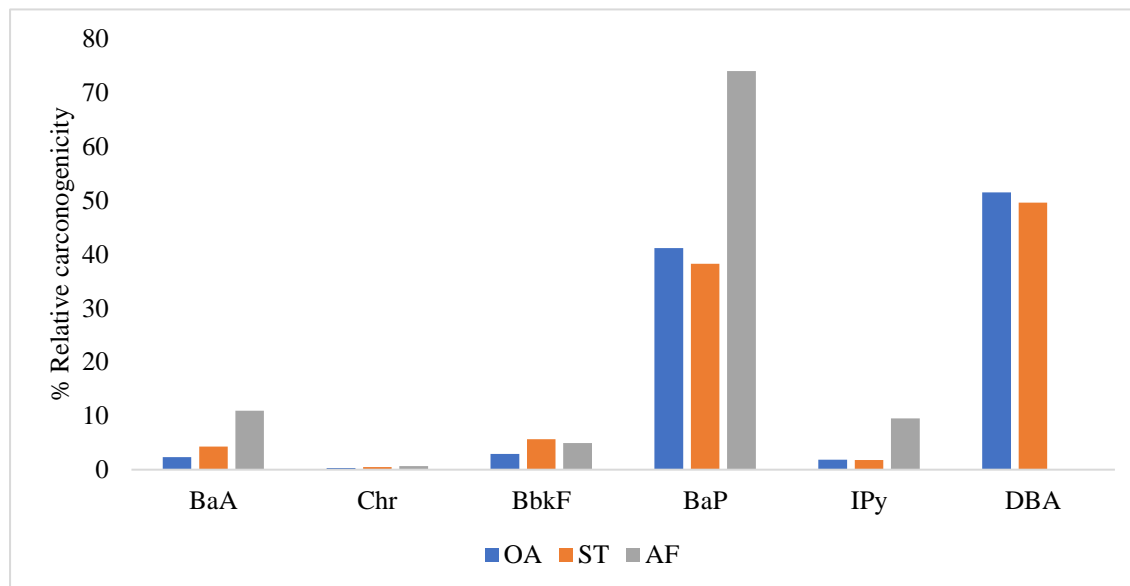
Table 5.8 shows the average  $\Sigma_6\text{BaP}_{\text{eq}}$  concentrations in OA to be 17.3 ng/g, at ST 42.6 ng/g, and at AF 5.2 ng/g respectively.  $\Sigma_6\text{BaP}_{\text{eq}}$  concentrations at OA, ST and AF ranged from 4.7 to 27.6, 7.8 to 86.2, and 3.4 to 7.8 ng/g. ANOVA test showed no significant difference between  $\text{BaP}_{\text{eq}}$  concentrations at the 3 sub-locations ( $p=0.25$ ).

Figure 5.7 shows the relative carcinogenic contribution of each of the six individual PAH . BaP accounted for 41% in OA, 38% in ST, and 74% in AF. By comparison, DBA was below detection limit at AF, 51.5% and 49.6% was found in sub-location OA and ST. Other PAH such as BaA, BbkF, and IPy contributed minimally to total carcinogenic activity . It was observed that while the carcinogenic PAH were more in abundant , the non-carcinogenic like Acy ,Ace, Phe, Ant, Flt and Pyre make modest contributions to  $\text{BaP}_{\text{eq}}$  (OA 0.06% ,ST 1.7% ,AF 2.5%).

**Table 5-8 Summary of potential toxicity of PAH in soil from three crude oil transfer area in dry season (ng/g)**

Location/PAH	BaA	Chr	BbkF	BaP	IPy	DBA	$\Sigma_6\text{BaP}_{\text{eq}}$
OA(n=3)	<b>TEF</b>	<b>0.1</b>	<b>0.01</b>	<b>0.1</b>	<b>1</b>	<b>0.1</b>	<b>5</b>
	Average	0.353	0.033	0.424	3.830	0.344	12.283
	SD	0.259	0.010	0.264	0.448	0.248	11.465
	Min	0.150	0.025	0.176	3.340	0.058	0.000
	Max	0.645	0.045	0.701	4.220	0.496	22.700
ST(n=4)	Average	1.719	0.329	2.379	14.020	0.322	23.875
	SD	2.134	0.529	3.341	15.655	0.250	16.150
	Min	0.410	0.023	0.595	5.740	0.067	0.000
	Max	4.902	1.120	7.388	37.490	0.639	35.150
AF(n=3)	Average	0.532	0.034	0.219	3.947	0.443	0.000
	SD	0.139	0.021	0.104	2.171	0.028	0.000
	Min	0.372	0.019	0.106	2.240	0.414	0.000
	Max	0.619	0.058	0.309	6.390	0.470	0.000

**Figure 5-7 Individual average contribution of PAH to  $\Sigma_6\text{BaP}_{\text{eq}}$  concentrations in TST in the dry season**



OA(Office area),ST( storage a tank and pump area and surrounding of crude oil field/pipeline area

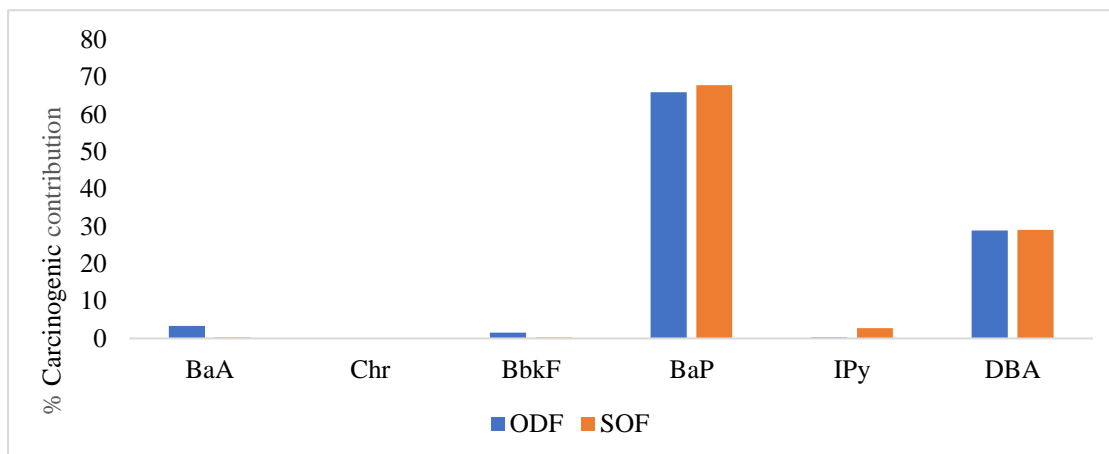
### 5.4.3 BaP<sub>eq</sub> concentrations at active oil well with drilling activities (AW1) in dry season

Table 5.9 summarises BaP<sub>eq</sub> concentrations at ODF and SOF for carcinogenic PAH(6). Average BaP<sub>eq</sub> concentrations was found to be 19 ng/g at ODF and 14.9 ng/g at SOF, ranging from 3.3 to 46 ng/g at ODF and 3 to 31.6 ng/g at SOF. Average contributions of individual PAH to  $\Sigma_6\text{BaP}_{\text{eq}}$  concentrations were dominated by BaP at 48.4% for ODF and 63.8% at SOF. In addition, DBA contributed 22.8 % at ODF and 28.7% at SOF respectively. Figure 5.8 summarise the contributions of individual 6PAH at each location. When compared to the six known carcinogens, the carcinogenicity of the LMW-PAH in two locations exhibited 0.7% at SOF- and 20% at ODF.

**Table 5-9 Descriptive parameters of BaP<sub>eq</sub> concentration in soils from two sub-locations active oil well with drilling operations in dry season (AW1)**

PAH	TEF	SOF(n=3)				ODF(n=10)			
		Average	SD	Min	Max	Average	SD	Min	Max
BaA	0.1	0.116	0.108	0.000	0.214	3.235	3.793	0.113	12.414
Chr	0.01	0.016	0.014	0.000	0.027	0.411	0.547	0.023	1.386
BbkF	0.1	0.215	0.119	0.094	0.332	1.420	1.922	0.180	6.623
BaP	1	5.210	3.080	2.960	8.720	6.738	4.764	2.000	17.300
IPy	0.1	0.271	0.425	0.000	0.760	0.342	0.277	0.000	0.836
DBA	5	9.067	15.704	0.000	27.200	6.970	8.744	0.000	25.000
$\Sigma_6\text{BaP}_{\text{eq}}$		14.894	14.815	3.288	31.581	19.117	14.916	3.314	46.145

**Figure 5-8 Individual average contributions of PAH to  $\Sigma$ BaPeq concentrations in soil from two locations in AW1 in dry season**



ODF(Within oil drilling Field) and SOF( Surrounding of oil drilling field)

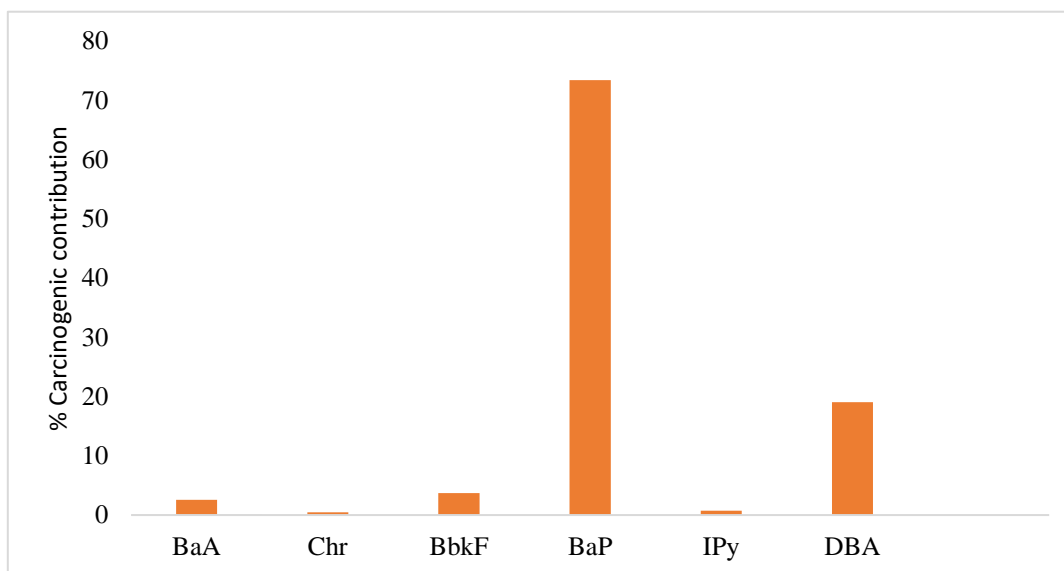
#### 5.4.4 Toxic equivalent potency in workstation (WS)

Just like every other location, the six carcinogenic PAH ( $\Sigma$ 6BaPeq) concentrations for dry season was also determined and the estimated values are summarised in Table 5.10 ranging between 3.2 to 19.4 ng/g with an average of 7.2 ng/g. The reduced values observed can be explained by the lack of anthropogenic activities such as oil and gas exploration. However, Figure 5.9 denote the relative contributions of these carcinogenic PAH . BaP appeared to the key contributor, with an average of 73.4%, next by DBA 19% and BbkF 4% with minimum contribution from others. The carcinogenicity of Ace, Acy, Fln, Phe, Ant, Flt Pyr (LMW(<1)) are inconsequential.

**Table 5-10 Statistical summary of PAH concentrations (BaPeq ng/g) in workstation (WS) soil in the dry season**

PAH	TEF	Average	SD	Min	Max
BaA	<b>0.1</b>	0.157	0.221	<LOQ	0.667
Chr	<b>0.01</b>	0.025	0.028	<LOQ	0.082
BbkF	<b>0.1</b>	0.172	0.181	<LOQ	0.512
BaP	<b>1</b>	3.988	1.513	1.420	6.100
IPy	<b>0.1</b>	0.038	0.085	<LOQ	0.245
DBA	<b>5</b>	2.806	5.313	<LOQ	13.300
$\Sigma$ 6BaPeq		7.186	5.486	3.127	19.413

**Figure 5-9 Individual average contribution of PAH to  $\Sigma$ BaPeq in workstation (WS) in dry season**



### 5.5 Comparison of BaPeq concentrations in all sampling locations for both seasons and with other studies

The result obtained from the overall carcinogenic potential investigated in this study are represented in Table 5.11 for both wet and dry seasons respectively.  $\Sigma_6$ BaPeq concentrations differ significantly between the two seasons. The average individual BaPeq concentration varies between 7.97 to 42.9 BaPeq ng/g in wet season. The highest BaPeq concentrations were detected at AW3 suggesting ecological environmental risk at this location and the of sequence of carcinogenicity is as follows AW3>TST>OGP>AW2>WS>AW1> NAW respectively.

The higher concentrations at AW3 may be attributed to historical spillage of oil perhaps. While in the dry season, the values ranged from 7.19 for WS to 21.7 BaPeq ng/g for TST .The maximum BaPeq concentrations at TST and the lowest at WS. The carcinogenic potency follows the order TST>OGP>AW1>WS.

The Canadian soil quality guidelines for the protection of environmental and human health provide a safe value of BaPeq concentrations for  $\Sigma_7$ PAH in soils of 600  $\mu$ g/kg (Wang et al.,

2018a). The  $\Sigma_7$ PAH comprise: BaP, BaA, BbkF, Chr, Pyr, DBA, and IPy, all of which are monitored in this study. The BaP<sub>eq</sub> concentrations detected in this study are all well within/below with this guideline value. Generally, DBA was the major contributors to BaP<sub>eq</sub> concentrations in all sampling sites in this study followed by BaP. These results are consistent with those of Wang et al. (2018a) and (Wang et al., 2015a) who reported BaP and DBA as the most significant contributions to soil carcinogenicity.

**Table 5-11 Average BaP<sub>eq</sub> concentrations of individual PAH in seven sampling locations in wet season**

	PAH	BaA	Chr	BbkF	BaP	IPy	DBA	$\Sigma_6$ BaP <sub>eq</sub>
	Location/TEF	0.1	0.01	0.1	1	0.1	5	
<b>Wet season</b>	OGP	0.421	0.083	0.616	9.197	1.160	15.397	26.874
	TST	0.588	0.089	0.614	5.025	0.698	28.963	35.977
	AW1	0.352	0.044	0.316	2.883	0.333	7.165	11.093
	AW2	0.332	0.039	0.518	4.479	0.275	11.455	17.098
	AW3	0.881	0.105	1.088	17.550	0.956	22.320	42.901
	NAW	0.153	0.022	0.253	0.874	0.139	6.525	7.965
	WS	0.197	0.021	0.165	1.457	0.281	10.370	12.491
<b>Dry Season</b>	OGP	0.432	0.042	0.446	7.704	0.300	11.106	20.031
	TST	0.868	0.132	1.007	7.266	0.370	12.053	21.695
	AW1	1.675	0.213	0.817	5.974	0.307	8.018	17.005
	WS	0.157	0.025	0.172	3.988	0.038	2.806	7.186

We compared the BaP<sub>eq</sub> concentrations at OGP, TST, AW1 and WS for both wet and dry season. The highest BaP<sub>eq</sub> concentrations were observed at AW3 ( 42.9 ng/g) during the wet season and at TST (21.7 ng/g) during the dry season. while the carcinogenic PAH contribute approximately more than 98% to the total carcinogenicity activities  $\Sigma_{14}$ BaP<sub>eq</sub>, the LMW-PAH in wet season account for 0.76% and 3.6% in dry season.

We also compared concentrations in this study with BaP<sub>eq</sub> concentrations from other locations impacted by the activities of oil and gas. Wang et al. (2018a) reported 212 ng/g BaP<sub>eq</sub> for  $\Sigma_7$ PAH at Loess Plateau, China. Wang et al. (2015a) also reported 80.5 ng/g (BaP<sub>eq</sub> for 7PAH)

in oil contaminated soil in Shengli, China.  $\Sigma_7\text{BaP}_{\text{eq}}$  concentrations at Eket Metropolis, Akwa Ibom were 368.2 ng/g in the wet season and 430 ng/g in the dry season (Ekanem et al., 2019). Our findings indicate that the toxicity of the PAH in soil in our study was relatively low.

### **5.6 Human exposure to PAH by ingestion in soil wet and dry weather**

To investigate the extent of human (adult) exposure to target PAH in soil via ingestion, we use  $\Sigma\text{BaP}_{\text{eq}}$  values in Table 5.11 along with other parameters analyzed (Table 5.1) to estimate the exposure via soil ingestion in the wet and the dry weather.

Table 5.12 lists the estimated PAH exposures for adults based on soil ingestion from seven locations, while full details of the estimation are provided in appendix. According to Table 5.12, the average daily doses (ADD) for ingestion of soil varies from  $4.23 \times 10^{-5}$  at NAW to  $2.28 \times 10^{-5}$  AW3 mg (kg/d) during wet weather, our results also demonstrated a ranged of values from  $3.8 \times 10^{-6}$  to  $1.15 \times 10^{-6}$  at WS and TST in dry weather. The various health risk across the location is being influenced by different pollution source, the elevate daily dose hence suggest possibility for farmers or workers(adults)to ingest greater soil particle at location AW3 during the wet weather and at TST during the dry weather.

Human health risk associated with exposure to PAH at various locations were also determined by using incremental lifetime cancer risk (ILCR) and the values are provided in Table 5.12. ranging from  $3.09 \times 10^{-5}$  at NAW to  $1.66 \times 10^{-4}$  at AW3 in wet weather and  $2.78 \times 10^{-5}$  at WS to  $8.4 \times 10^{-5}$  at TST in dry season. The highest exposure to carcinogenic PAH was calculated at TST ( $8.4 \times 10^{-5}$ ) for dry period and AW3( $1.66 \times 10^{-4}$ ) at wet period. According to the qualitative assessments of lifetime cancer risks by Mitra et al. (2019) (Table 5.13), the average estimated ILCR at these six locations for adults shows that these values were between  $10^{-6}$  and  $10^{-4}$  (see table 5.13), implying a low to moderate risk of developing cancer for adults stemming from

exposure to PAH on these locations. However, the maximum ILCR value (at AW3) was  $1.66 \times 10^{-4}$  was close to the upper limit of the recommended range for low risk (Table 5.13).

**Table 5-12 Human risk assessment of PAH via ingestion of soil from oil and gas field for wet and dry season**

Location	Wet season		Dry season	
	ADD <sub>ingest</sub>	ILCR	ADD <sub>ingest</sub>	ILCR
OGP	1.43E-05	1.04E-04	1.06E-05	7.76E-05
TST	1.91E-05	1.39E-04	1.15E-05	8.40E-05
AW1	5.89E-06	4.30E-05	9.02E-06	6.59E-05
AW2	9.07E-06	6.62E-05	-	-
AW3	2.28E-05	1.66E-04	-	-
NAW	4.23E-06	3.09E-05	-	-
WS	6.63E-06	4.84E-05	3.81E-06	2.78E-05

ADD<sub>ingest</sub> average daily intake, ILCR incremental lifetime cancer risk

**Table 5-13 Qualitative descriptions of lifetime cancer risks for both ingestion and inhalation of soil particles**

CR $\leq 10^{-6}$ *	Very low
CR Between $10^{-6} <$ to $< 10^{-4}$ *	Low
CR from $10^{-4} \leq$ to $< 10^{-3}$ *	Moderate
CR from $10^{-4} \leq$ to $< 10^{-3}$	High
CR from $\geq 10^{-1}$ *	Very high

\*Mitra et al., 2018

## 5.7 Human exposure risk associated with inhalation of PAH in outdoor air

### 5.7.1 Exposure to PAH in wet and dry season

In the wet period, average  $\Sigma_6\text{BaP}_{\text{eq}}$  concentrations in each sampling site in the current study were: 3.07, 2.36, 0.97, 2.36, 3.17 and 0.8 ng/m<sup>3</sup> for OGP, TST, AW1, AW2, AW3 and WS respectively as indicated in Table 5.14a. No significant variation was observed between the  $\text{BaP}_{\text{eq}}$  concentrations for  $\Sigma_6\text{PAH}$  across the sites ( $p=0.39$ ). The average contribution of BaP to  $\text{BaP}_{\text{eq}}$  concentrations in outdoor air was the highest of all the individual six PAH monitored at all six sites and this contribution ranged from 34% to 54.6%. In addition to this, the carcinogenic PAH like IPy also contributed substantially while DBA accounted for 19% at

OGP and 31.6% at AW3, as illustrated Figure 5.12. Concentration of the  $\Sigma_7\text{BaP}$  to the sum of the 14PAH accounted for 1.8%, 5%, 1.5%, 5.7%, 2.4% and 1.8% at OGP, TST, AW1, AW2, AW3 and WS while the  $\Sigma_6\text{BaP}$  approximately more than 95% in all the locations.

Table 5.14 also shows the average  $\Sigma\text{BaP}_{\text{eq}}$  concentrations for 6PAH in the dry season at all sampling sites. Average  $\Sigma_6\text{BaP}_{\text{eq}}$  concentrations for fell between 0.75 to 3.48  $\text{ng}/\text{m}^3$ . It is pertinent to know that the maximum  $\Sigma\text{BaP}_{\text{eq}}$  (3.48  $\text{ng}/\text{m}^3$ ) was from the site with oil well with historically crude oil spill (AW3) and the lowest concentration of 0.75  $\text{ng}/\text{m}^3$  was observed at workstation (WS) with no oil and gas activities. Interestingly, it was expected that AW1 (Oil well with drilling activities at as when sampled) with high concentration for  $\Sigma_{14}\text{PAH}$  (see section 4.5.3) would have the highest  $\Sigma_6\text{BaP}_{\text{eq}}$ . However, one of the carcinogenic PAH (DBA) was found to be less than limit of detection in this site as compared to AW3, it also shows that AW1 contain more of LMW-PAH no differences across the sites statistically were detected ( $p > 0.16$ ). BaA and IPy all made considerable contributions to the  $\Sigma_6\text{BaP}_{\text{eq}}$  values throughout the sampling sites, yet BaP made the highest contribution ranging from 25 to 43% as presented in Figure 5.10. By comparison, DBA contributed 29% at AW3 but less than the limit of detection at other sites. In dry season the sum of the non-carcinogenic PAH (LMW) contributed to the  $\Sigma_{14}\text{PAH}$  is as follows OGP (8.2%), TST (10.4%), AW1 (10.7%), AW2 (9.8%), AW3 (2.28%) and WS (26%) respectively while the carcinogenic (6PAH) shows a greater contribution.

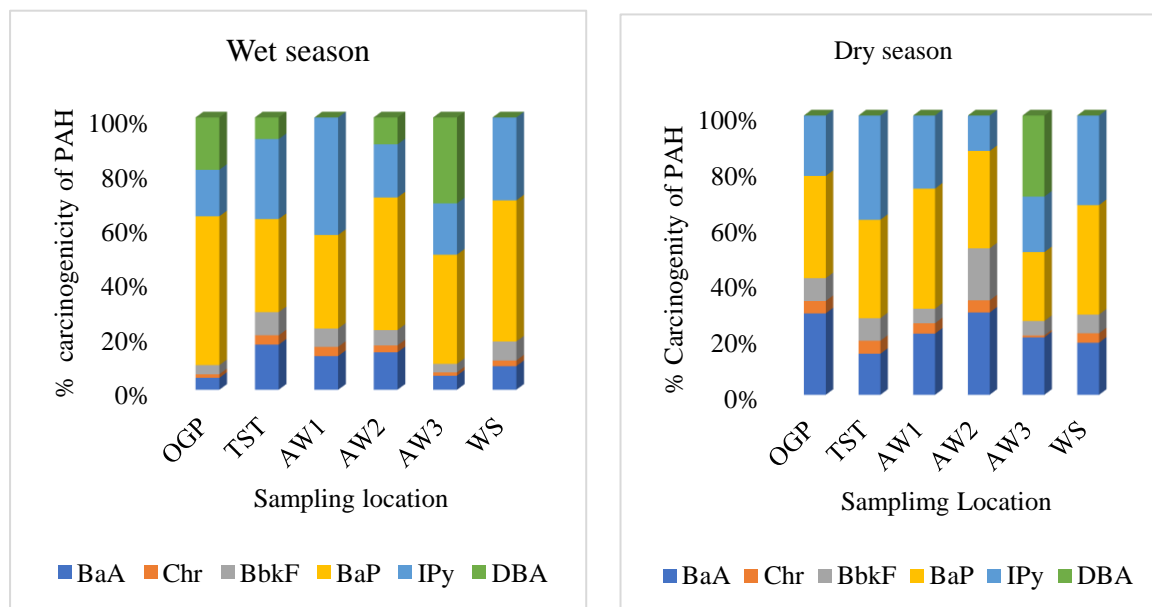
**Table 5-14 BaP<sub>eq</sub> concentrations (ng/m<sup>3</sup>) in outdoor air across the six oil and gas field monitoring sites in the wet season**

<b>A</b>	<b>Wet season</b>						
<b>PAH</b>	<b>TEF</b>	<b>OGP</b>	<b>TST</b>	<b>AW1</b>	<b>AW2</b>	<b>AW3</b>	<b>WS</b>
BaA	<b>0.1</b>	0.134	0.391	0.120	0.325	0.163	0.070
Chr	<b>0.01</b>	0.040	0.081	0.033	0.060	0.038	0.017
BbkF	<b>0.1</b>	0.103	0.200	0.065	0.133	0.099	0.056
BaP	<b>1</b>	1.675	0.808	0.332	1.150	1.270	0.416
IPy	<b>0.1</b>	0.523	0.693	0.417	0.460	0.597	0.245
DBA	<b>5</b>	0.589	0.188	0.000	0.233	1.000	0.000
Σ <sub>6</sub> BaP <sub>eq</sub>		3.065	2.361	0.967	2.361	3.168	0.804
<b>B</b>	<b>Dry season</b>						
<b>PAH</b>	<b>TEF</b>	<b>OGP</b>	<b>TST</b>	<b>AW1</b>	<b>AW2</b>	<b>AW3</b>	<b>WS</b>
BaA	<b>0.1</b>	0.494	0.274	0.683	0.418	0.716	0.140
Chr	<b>0.01</b>	0.075	0.087	0.115	0.062	0.025	0.025
BbkF	<b>0.1</b>	0.138	0.151	0.163	0.264	0.179	0.050
BaP	<b>1</b>	0.621	0.657	1.339	0.494	0.858	0.294
IPy	<b>0.1</b>	0.366	0.697	0.816	0.180	0.692	0.240
DBA	<b>5</b>	0.000	0.000	0.000	0.000	1.010	0.000
Σ <sub>6</sub> BaP <sub>eq</sub>		1.694	1.866	3.115	1.418	3.479	0.749

ΣBaP<sub>eq</sub> concentrations at OGP, TST, AW1, AW2, AW3, and WS estimated were compared across both seasons. In the dry and wet season similar high Σ<sub>6</sub>BaP<sub>eq</sub> concentration was detected at AW3, suggesting the impact of oil exploitation of crude oil . The higher contribution of BaP to the BaPeq in all the sites , followed by IPy, BaA and DBA which may pose high carcinogenic risks to residents and workers in this area. The average percentage of LMW-PAH to the total PAH in overall was 3% in wet season whereas in the dry season it was 11% respectively, highlighting that most of the sites are polluted with carcinogenic PAH (95%-wet

and 85.38% dry). Note that this percentage does not include BghiP hence percentage may not sum up to 100%.

**Figure 5-10 Average contribution of six PAH to  $\Sigma$ BaPeq in wet season and dry season**



### 5.8 Cancer risk assessment for wet and dry season for outdoor air

As in soil, the parameters in Table 5.1 and  $\Sigma_6$ BaPeq values in Table 5.14 were used to estimate the PAH inhalation exposure risk to humans in both wet and dry seasons. The carcinogenic(6PAH) risk arising from exposure to inhalation of atmospheric PAH in this study was calculated according to the IUR model (WHO, 1987). The average cancer risk per person exposed at each sampling site was  $2.67 \times 10^{-4}$ ,  $2.05 \times 10^{-4}$ ,  $8.41 \times 10^{-5}$ ,  $2.05 \times 10^{-4}$ ,  $2.76 \times 10^{-4}$  and  $6.99 \times 10^{-5}$  at OGP, TST, AW1, AW2, AW3, and WS respectively. The largest estimated risk values were at AW1 with  $2.76 \times 10^{-4}$  in wet season. This equates to 2.4 extra cases per 100,000 of the population exposed in the wet season.

Lifetime average daily inhalation doses (LADD) based on BaPeq concentrations were estimated and were found to follow the order: AW3 > OGP > AW2-TST > AW1 > WS as seen in Table 5.15. LADD estimated values in the four operational active sites were: OGP ( $8.76 \times 10^{-7}$ ), TST

( $6.65 \times 10^{-7}$ ), AW2 ( $6.65 \times 10^{-7}$ ), AW3 ( $9.05 \times 10^{-7}$ ) in the wet season, were 2-3 times higher than AW1(active oil well without drilling operations) ( $2.76 \times 10^{-7}$ ) and WS (workstation) ( $2.30 \times 10^{-7}$ ). This implies that the outdoor air at these four functioning sites poses a greater health risk than at the other two non-operational sites. ILCR<sub>2</sub> inhalation exposure values for wet period ranged from  $8.96 \times 10^{-7}$  at WS to  $3.53 \times 10^{-6}$  at AW3. The overall cancer risk estimates for exposure to carcinogenic PAH are given in Table 5.16 for the outdoor air sampled in wet season this study area exhibiting a low potential risk of exposure to these carcinogenic

During the dry season, the highest respiration exposure to outdoor PAH cancer risk value of  $3.03 \times 10^{-4}$  was found at AW3 . The equivalent values at other sites were: AW1 ( $2.71 \times 10^{-4}$ ), TST ( $1.62 \times 10^{-4}$ ), OGP ( $1.47 \times 10^{-4}$ ), AW2 ( $1.23 \times 10^{-4}$ ), and WS ( $6.52 \times 10^{-5}$ ) respectively. Inhalation doses of PAH proceed in the orders of WS < AW2 < OGP < TST < OGP, AW1 < AW3 as showed in Table 5.16. By comparison, ILCR<sub>2</sub> values for locations WS, AW1, AW2, AW3, TST, and OGP ranged between  $8.35.1 \times 10^{-7}$  at WS and  $3.88 \times 10^{-6}$  at AW3. The overall summary of the estimated cancer risk exposure to human (Adults) at these locations is listed in Table 5.18 showing overall estimation for human risk exposure to PAH.

Table 5.17, thus compare the mean B[a]P,  $\Sigma_6$ PAH B[a]P<sub>eq</sub>,  $\Sigma_{14}$ PAH B[a]P<sub>eq</sub> and ILCR arising from inhalation and ingestion exposure to PAH in our study. It is interesting to note that the BaP<sub>eq</sub> concentrations of the six carcinogenic PAH are very similar to those for  $\Sigma_{14}$ PAH. This suggest that the carcinogenic PAH were the predominant contributors to BaP<sub>eq</sub>. It should also be noted that BaP<sub>eq</sub> concentrations did not exceed the Canadian soil quality guideline value of 600  $\mu\text{g}/\text{kg}$  for 7 PAH in any soil in our study and the associated with cancer is low for both wet and dry weather.

**Table 5-15 Cancer risk assessment of total target PAH in oil and gas field in six different sites in the wet season for outdoor air**

<b>Risk Indicators/Location</b>	<b>OGP</b>	<b>TST</b>	<b>AW1</b>	<b>AW2</b>	<b>AW3</b>	<b>WS</b>
ILCR <sub>1</sub>	2.67E-04	2.05E-04	8.41E-05	2.05E-04	2.76E-04	6.99E-05
LADD	8.76E-07	6.75E-07	2.76E-07	6.75E-07	9.05E-07	2.30E-07
ILCR <sub>2</sub>	3.42E-06	2.63E-06	1.08E-06	2.63E-06	3.53E-06	8.96E-07

**Table 5-16 Estimated PAH cancer risk at different sampling sites via inhalation in dry season for outdoor air**

<b>Risk Indicators/Location</b>	<b>OGP</b>	<b>TST</b>	<b>AW1</b>	<b>AW2</b>	<b>AW3</b>	<b>WS</b>
ILCR <sub>1</sub>	1.47E-04	1.62E-04	2.71E-04	1.23E-04	3.03E-04	6.52E-05
LADD	4.84E-07	5.33E-07	8.90E-07	4.05E-07	9.94E-07	2.14E-07
ILCR <sub>2</sub>	1.89E-06	2.08E-06	3.47E-06	1.58E-06	3.88E-06	8.35E-07

ILCR<sub>1</sub> incremental cancer risk using on WHO unit risk, LADD Lifetime average cancer daily dose , ILCR<sub>2</sub> incremental lifetime cancer risk based on cancer slope

**Table 5-17 Mean concentration of B[a]P,  $\Sigma_6\text{BaP}_{\text{eq}}$ ,  $\Sigma_{14}\text{BaP}_{\text{eq}}$  and incremental lifetime cancer risk for inhalation and ingestion**

Location	Wet Weather soil				Dry weather soil			
	B[a]P	$\Sigma_6\text{BaP}_{\text{eq}}$	$\Sigma_{14}\text{BaP}_{\text{eq}}$	ILCR	B[a]P	$\Sigma_6\text{BaP}_{\text{eq}}$	$\Sigma_{14}\text{BaP}_{\text{eq}}$	ILCR
OGP	9.20	26.874	27.124	1.04E-04	7.70	20.031	20.407	7.76E-05
TST	5.07	35.977	36.329	1.39E-04	7.27	21.6953	22.030	8.40E-05
AW1	2.88	11.093	11.161	4.30E-05	4.44	17.005	19.614	6.59E-05
AW2	4.48	17.098	17.334	6.62E-05	-	-	-	-
AW3	17.55	42.901	39.904	1.66E-04	-	-	-	-
NAW	0.87	7.965	8.007	3.09E-05	-	-	-	-
WS	1.46	12.491	12.530	4.84E-05	3.99	7.186	7.281	2.78E-05
Location	Wet Weather air				Dry Weather air			
	BaP	$\Sigma_6\text{BaP}_{\text{eq}}$	$\Sigma_{14}\text{BaP}_{\text{eq}}$	ILCR	BaP	$\Sigma_6\text{BaP}_{\text{eq}}$	$\Sigma_{14}\text{BaP}_{\text{eq}}$	ILCR
OGP	1.68	3.065	3.201	3.42E-06	0.62	1.694	2.014	1.89E-06
TST	0.81	2.361	2.507	2.63E-06	0.66	1.866	2.306	2.08E-06
AW1	0.33	0.967	1.011	1.08E-06	1.34	3.115	3.522	3.47E-06
AW2	1.15	2.361	2.561	2.63E-06	0.49	1.418	1.608	1.58E-06
AW3	1.27	3.168	3.256	3.53E-06	0.86	3.479	3.575	3.88E-06
WS	0.42	0.804	0.846	8.96E-07	0.29	0.749	1.022	8.35E-07

## 5.9 Conclusion

BaP<sub>eq</sub> concentrations observed in this study for soil and outdoor air samples are higher in the active locations than those from the non-active sites, which demonstrates the effect of oil and gas exploration activities. Though higher BaP<sub>eq</sub> concentrations were detected during the wet season compared to the dry season, despite the higher concentrations  $\Sigma_{14}$ PAH observed during the dry season (see section 3.7) in soil. Also, elevated BaP<sub>eq</sub> concentrations were detected at AW3 in dry season and wet season in outdoor air. There were no statistically variation between  $\Sigma_6$ BaP<sub>eq</sub> concentrations in either air or soil across the sites monitored.

Concentrations of  $\Sigma_6$ BaP<sub>eq</sub> in this study area in soil was compared to other locations impacted by the activities of oil and gas. Wang et al. (2018a) reported the sum of seven(7)BaP<sub>eq</sub> at Loess Plateau, China to be 212 ng/g BaP<sub>eq</sub> while Wang et al. (2015a) also reported BaP<sub>eq</sub> for 7PAH in oil contaminated soil in Shengli, China(80.5ng/g). These values are higher than the estimated BaP<sub>eq</sub> for 6PAH in our study area. Hence, according to our findings, the ecological and carcinogenic risks to inhabitants are low. While BaP and DBA were the most important contributors to BaP<sub>eq</sub> concentrations in soil in both seasons, BaP contributed substantially to the BaP<sub>eq</sub> concentrations in air indicating high carcinogenicity in soil and outdoor air.

Our finding was further supported by the incremental lifetime cancer risk(ILCR) for exposure via soil ingestion(soil particles) and outdoor air. The fell between  $3.09 \times 10^{-5}$  at NAW to  $1.66 \times 10^{-4}$  at AW3 in wet and  $2.78 \times 10^{-5}$  to  $8.4 \times 10^{-5}$  in dry weather. Wet weather ILCR inhalation exposure values ranged from  $8.96 \times 10^{-7}$  at WS to  $3.53 \times 10^{-6}$  at AW3 while dry weather estimation varied from  $8.35 \times 10^{-7}$  at WS and  $3.88 \times 10^{-6}$  at AW3. As a result, cancer risks are low for occupational and non-occupational exposure within and around the affected oil and gas exploration fields in both weathers. However, PAH monitoring should continue at these locations, as concentrations will likely increase over time as oil and gas exploration activities and associated PAH emissions continue and accumulate in soil and circulate in air. Should the

surrounding land be used for agriculture, then monitoring of PAH in crops and food animals is recommended to facilitate assessment of exposure via the diet. This will be especially important for any subsistence farming population.

## Chapter 6

### Summary and Conclusion

The primary aim of this work was to investigate the extent of contamination of PAH from soil and air as a result of oil and gas production activities at a number of locations in the vicinity of such activities. It tests the hypothesis that such contamination will lead to human exposure exceeding that experienced by populations not impacted by such activities, PAH concentrations in air and soil are higher in the dry than the wet seasons respectively.

The main objectives of the study were thus as follows:

1. To monitor the levels and distribution of PAH in air and soil around a major oil and gas production facility in Nigeria.
2. To estimate exposure to PAH of workers and local residents via inhalation, incidental soil ingestion and dermal uptake.
3. To use these estimates of exposure to evaluate the human health risks arising.
4. By comparing concentrations of PAH in air and soil from a number of locations of the target oil and gas production facility, to evaluate the extent to which the facility is a source of PAH to the surroundings.
5. To evaluate spatial and seasonal variation in PAH concentrations in air and soil.
6. To evaluate the impact on PAH concentrations of different oil and gas production activities.

The following summarises the principal achievements and outcomes of this thesis:

- Soil samples were collected in the wet season at the following seven different locations in Akwa Ibom, Nigeria: oil and gas production plant (OGP), crude oil transfer area (TST), no -active oil well that was capped without drilling activities (AW1), active gas well (AW2), active oil well (AW3), non-active site (NAW), and workstation (WS). In the dry season, only four sites could be sampled, namely: OGP, TST, AW1 (with drilling activities), and WS. Soil samples were also collected within each location (sub-locations). PAH concentrations were measured in air conducted at six locations (OGP, TST, AW1, AW2, and WS). In the wet season, there were no oil drilling activities at AW1 while oil drilling was in progress in the dry season. T-tests and ANOVA were

applied as appropriate to evaluate differences between concentrations at different locations.

- Measurements of PAH in soil revealed that those at AW1 and WS are much lower than other locations (OGP, TST, AW2 and AW3). While statistically significant differences in concentrations ( $p < 0.05$ ) were observed between OGP ( $n = 21$ ) average 128 ng/g, AW1 ( $n = 10$ ) average 38.4 ng/g, AW3 ( $n = 20$ ) average 99.9 ng/g, and NAW ( $n = 10$ ) average 22.7 ng/g; no statistically significant difference was observed between PAH concentrations at TST ( $n = 18$ ) average 94 ng/g and WS ( $n = 10$ ) average 26.5 ng/g ( $p > 0.05$ ) in the wet season. However, in the dry season, PAH concentrations were higher at AW1, OGP and TST area than WS, with those at AW1 ( $n = 13$ ; 820 ng/g) exceedingly significantly ( $p < 0.05$ ) those at WS ( $n = 8$ ; 44 ng/g). Significant variability in concentrations was also observed between sub-locations. Evidence denotes PAH concentrations to decline with increasing distance from oil and gas exploration activities.
- Concentrations of  $\Sigma_{14}$ PAH in outdoor air were measured. Average concentrations of  $\Sigma_{14}$ PAH at active sites were: OGP 72.8 ng/m<sup>3</sup>, TST-128 ng/m<sup>3</sup>, AW2-132 ng/m<sup>3</sup>, and AW3-68 ng/m<sup>3</sup> in the wet season and OGP-178 ng/m<sup>3</sup>, TST-254 ng/m<sup>3</sup>, AW1 (with drilling activities) 330 ng/m<sup>3</sup>, AW2-151 ng/m<sup>3</sup>, and AW3 95.5 ng/m<sup>3</sup> in the dry season. These exceeded those at the background sites: AW1 (without drilling activities) 24.2 ng/m<sup>3</sup> and WS-17.5 ng/m<sup>3</sup> in the wet season and WS-79.9 ng/m<sup>3</sup> in the dry season. Across the locations, significant differences were not observed ( $p > 0.05$ ) for  $\Sigma_{14}$ PAH concentrations.
- In both soil and air samples, 3 and 4 ring PAH were most abundant. Phe, Flt, and Pyr were the predominant compounds in outdoor air, with: Ace, Fln Phe, Flt, and Pyr the most abundant in soil.
- PAH concentrations were evaluated for seasonal differences using samples taken from the wet and dry seasons. Higher average concentrations of PAH were found in the dry period than in the wet period. Variability in the wet and dry period is likely due to rainfall washing PAH out of the atmosphere as well as leaching PAH in the soil in wet season.
- Paired t-test analysis showed that the concentrations of PAH in soil at TST and AW1 were significantly higher in the dry season ( $p < 0.05$ ), while no significant seasonal difference in concentrations was found at OGP and WS ( $p > 0.05$ ). Statistically

significant seasonal variability was not observed for individual locations in air probably as a result of small sample numbers at each individual site. However, when all sites were combined, significantly higher concentrations were observed in the dry season for both air and soil ( $p < 0.05$ )

- BaP<sub>eq</sub> concentrations in the soil and air were higher in the active areas than in the non-active sites. The major contributors to BaP<sub>eq</sub> were BaP and DBA in soil and mostly BaP in outdoor air
- We estimated lifetime exposure to  $\Sigma_6$ PAH via inhalation of outdoor air at six locations (OGT, TST, AW1, AW2, AW3 and WS). The results revealed a lower inhalation cancer risk for adults at WS ( $8.96 \times 10^{-7}$ ) compared to AW3 ( $3.53 \times 10^{-6}$ ) in wet season. In the dry season, cancer risk associated with inhalation exposure to PAH followed the same pattern as in the wet season and was at low WS ( $8.35 \times 10^{-7}$ ) and high at AW3 ( $3.88 \times 10^{-6}$ ).
- Higher cancer risk in soil from TST was recorded in dry season ( $8.4 \times 10^{-5}$ ) and in wet season ( $1.66 \times 10^{-4}$ ) in AW3 relative to WS ( $2.78 \times 10^{-5}$ ) in the dry season and the wet season NAW ( $3.09 \times 10^{-5}$ ) respectively.
- Cancer risk in outdoor air indicates a significantly lower risk than soil, demonstrating that ingestion may be a main route of exposure to PAH in this environment.
- Cancer risk resulting from exposure to PAH via ingestion and inhalation in all locations for both seasons falls under the classification of low cancer risk for population who are within or nearby impacted oil and gas fields.

## 6.1 Research gaps and prospective future work

The body of knowledge presented in this thesis makes a valuable contribution to the understanding of the impact of oil and gas activities on PAH emissions to human and environment. However, significant research gaps still exist. The following aspects need research in order to fill these gaps.

- Elucidate the uncertainty about the source of PAH emission especially at crude oil transfer and oil and gas production areas since other oil companies are near the study areas. Therefore, sampling should be conducted close or within these oil and gas companies to fully comprehend the origin of contamination.

- To monitor the effect of gas flaring of PAH as highlighted by several researchers in Niger delta and in this study. This is a major concern as PAH can travel long distance to other regions before deposition to soil. Therefore, monitoring and understanding of the fate and behaviour of PAH in this region and other surrounding locations is required.
- Review of the published data on the occurrence of PAH around the world, reveals that in regions in Africa particularly Nigeria, there has been relatively little research on passive sampling of outdoor air for PAH concentrations. To comprehend the fate of these organic compounds in these areas, more research needs to be carried out.
- To provide more data to explain whether PAH emissions from these oil and gas fields impact on the remote, urban, and other cities that are nearest to the fields, particularly during drilling operations. Such data will help oil exploration companies and/or regulatory bodies to come up with a management strategy.
- Improve knowledge of spatial and seasonal trends in PAH concentrations in Nigerian outdoor air and soil. PAH concentration should be routinely and continuously monitored.
- To enhance the understanding of the physicochemical behaviour of lower molecular weight PAH regarding their photolysis and volatilisation in a warm environment where gas is flared regularly.
- Examine how PAH emissions affect both workers and the public (including children). PAH levels must be monitored in both outdoor air as well as indoor air (office within the field, and administrative offices) and around the field (homes) to determine the significance of human exposure to these compounds. For long-term air quality monitoring and to provide adequate sample sizes for analysis, active sampling may be necessary.
- Regular monitoring of crops grown on farmland with a history of spillage or present spillage to evaluate the uptake of PAH and consequent dietary exposure.
- While low cancer risks as a result of exposure to PAH were found in soil and outdoor air in some areas, which are unlikely to represent any adverse effect on human health based on risk evaluation, there is still a knowledge gap in this region and the potential adverse impacts of PAH over a long exposure period should be considered.

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## Appendix

**Table SI -1:** PAH diagnostic ratios used as source identification in some studies

Reference	Diagnostic ratio	Value range	Source
Yunker et al. (2002)	Benzo[a]Anthracene/(Benzo[a]Anthracene+Chrysene)	0.2-0.35	Coal combustion
	Benzo[a]Anthracene/(Benzo[a]Anthracene+Chrysene)	<0.2	Petrogenic
Tobiszewski and Namieśnik (2012), (Dvorska et al., 2008)	Anthracene/(Anthracene+Phenanthrene)	< 0.1	Petrogenic
	Anthracene/(Anthracene+Phenanthrene)	> 0.1	Biomass combustion
	Fluoranthene/(Fluoranthene+Pyrene)	<0.4	Petrogenic
	Fluoranthene/(Fluoranthene+Pyrene)	0.4-0.5	Fossil fuel combustion
	Fluoranthene/(Fluoranthene+Pyrene)	>0.5	Wood and Coal Combustion
Suman et al. (2016)	indeno[1,2,3-cd]pyrene/ (indeno[1,2,3cd]pyrene+benzo[ghi]perylene)	<0.2	Petrogenic and Petroleum source

Reference	Diagnostic ratio	Value range	Source
	Indeno[1,2,3-cd]pyrene/ (indeno[1,2,3-cd]pyrene+benzo[ghi]perylene)	<0.5	Crude oil combustion, liquid fossil fuel combustion other petroleum combustion
	Indeno[1,2,3-cd]pyrene/ (indeno[1,2,3-cd]pyrene+benzo[ghi]perylene)	>0.5	Biomass and coal combustion
Fang et al. (2004)	Fluorene/(fluorene+pyrene)	<0.5	Gasoline
	Fluorene/(fluorene+pyrene)	>0.5	Diesel
Adedosu et al. (2013)	Fluoranthene/Pyrene	>1	Pyrolytic
	Fluoranthene/Pyrene	<1	Petrogenic

**Concentrations of target PAH in outdoor air from oil and gas field Akwa Ibom**

**Table SI -2:** PAH concentrations in air samples from oil and gas area (OGP) (ng/m<sup>3</sup>)

PAH	NP1	NP2	MP1	MP2	WA1	WA2
Acy	1.1	0.3	0.8	0.7	0.5	0.4
Ace	1.5	0.4	0.6	1.1	0.9	1.2
Fln	8.9	1.2	1.4	1.8	2.3	2.5
Phe	43.3	12.9	15.5	14.4	14.8	17.7
Ant	1.2	0.6	0.4	0.7	0.3	0.2
Flt	30.5	15.5	10.6	9	7.6	9
Pyr	33.9	13.8	8.8	7.4	5.4	7.6
BaA	2.5	1.9	1.3	1.1	0.6	0.8
Chr	6.4	5	4.1	3.8	2.5	2.4
BbkF	1.3	1	1	2	0.4	0.6
BaP	1.9	2.8	1.8	1.9	0.9	0.8
IPy	7.8	5.4	7.5	6.5	2.1	2
DBA	0.2	0.0	0.3	0.2	<LOQ	<LOQ
BghiP	20.3	5.7	10.2	7.4	2.0	2.2

**Table SI-3:** Concentrations of PAH in air samples from crude oil transfer area (TST) (ng/m<sup>3</sup>)

PAH /sample	T1	T2	T3	T4
Acy	1.4	1.6	4.5	1.2
Ace	0.3	0.5	1.8	0.9
Fln	0.8	3	7.1	4
Phe	11	31	31.4	54.1
Ant	0.7	3.2	2.3	4.6
Flt	14.6	30.4	27.4	48.7
Pyr	12	24.7	58.3	37
BaA	2.4	4.4	2.7	6.2
Chr	7	9.5	4.6	11.3
BbkF	1.5	2.3	1.1	3.2
BaP	2	0.4	0.5	0.4
IPy	5.5	7.7	5.7	8.8
DBA	<LOQ	0.1	<LOQ	0.1
BghiP	3.1	0.5	2.6	0.8

**Table S1-4: Concentrations of target PAH in non- active well and workstation**

PAH/Sample	AW1	AW1	WS1	WS2	WS3
Acy	0.3	<LOQ	<LOQ	<LOQ	<LOQ
Ace	<LOQ	<LOQ	<LOQ	<LOQ	1.9
Fln	1	0.5	0.5	0.4	2
Phe	3	2.3	1.2	1	4.3
Ant	0.5	0.2	1	0.4	0.6
Flt	1.3	5.2	2.9	2.5	1.2
Pyr	1.5	7.3	3.4	3.1	1
BaA	0.9	1.5	1.6	0.4	0.2
Chr	2.7	3.8	2.2	2.3	0.5
BbkF	0.6	0.7	0.7	0.8	0.1
BaP	0.4	0.3	0.3	0.1	0.8
IPy	5.8	2.6	0.4	3	3.9
DBA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BghiP	2.8	3.1	2.7	3.2	2.1

**Table SI-5: Concentrations of PAH in air samples from active wells (Gas well, AW2 and Oil well, AW3)(ng/m<sup>3</sup>)**

PAH/sample	AW2(1)	AW2(2)	AW2(3)	AW3(1)	AW3(2)	AW3(3)
Acy	0.9	3.3	2.8	2.7	1.8	1.1
Ace	0.7	3.8	1.6	2.2	1.5	0.7
Fln	2.5	4.1	2.4	4.1	4.4	3.5
Phe	14.5	23.6	18.3	16.5	18.3	21.3
Ant	4.0	2.7	5.4	1.4	5.4	1.6
Flt	36.0	20.9	14.2	13.0	14.2	24
Pyr	59.2	62.0	48.8	7	8.8	6.1
BaA	6.6	1.2	1.9	0.9	2.9	1.1
Chr	9.5	2.6	5.7	4.5	3.6	3.4
BbkF	2.1	0.9	0.9	0.8	0.9	1.2
BaP	0.6	1.5	1.4	1.9	1.3	0.6
IPy	3.1	7.2	3.5	8.2	3.4	6.4
DBA	<LOQ	<LOQ	0.1	0.5	0.1	<LOQ
BghiP	12.3	3.4	0.2	0.4	0.2	2.3

**Concentration of target PAH in outdoor air from oil and gas well from Akwa Ibom in dry season**

**Table SI-6: Concentrations (ng/m<sup>3</sup>) of target PAH in individual air samples from oil and gas production area (OGP) in dry season**

PAH/Sample	NP1	NP2	MP1	MP2	WA	WA
Acy	0.5	0.8	2.8	1.9	2.6	0.5
Ace	2.2	1.1	4.1	2.5	0.8	0.7
Fln	2.4	5.2	10.1	13.2	3.7	4.2
Phe	41.9	56.8	53.3	57	25	34
Ant	1.7	1.9	4.5	2.9	1.8	1.3
Flt	46.2	55.2	37.2	45.1	28.8	25.2
Pyr	61.8	45.5	54.4	50.3	39.5	36.3
BaA	4.2	2.7	12.1	3.7	3.8	2.2
Chr	9.2	7	5.5	6.9	7.6	8.8
BbkF	2.7	1.6	1.4	1.7	1.0	0.9
BaP	1	2.9	0.4	0.9	0.3	0.6
IPy	3.7	4.6	0.8	3.7	4.3	4.8
DBA	<LOQ	<LOQ	<LOQ	<LOQ	,LOQ	<LOQ
BghiP	32.7	15.2	1.6	15.5	9.8	17.4

**Table SI-7: PAH Concentrations (ng/m<sup>3</sup>) in individual air samples from Crude oil transfer area (TST) in dry season**

PAH/Sample	TST1	TST2	TST3	TST4
Acy	1.1	1.2	0.8	1.4
Ace	2.3	1.9	1.4	0.9
Fln	9.5	6.8	2.8	4.4
Phe	67.8	98.1	56.3	85.5
Ant	3	1.6	3.2	3.6
Flt	79.8	53.2	63.7	69.5
Pyr	58.7	42	81.8	52.6
BaA	3.3	1.4	3.7	2.5
Chr	9.7	7.6	9.6	7.8
BbkF	1.4	1.1	1.5	2
BaP	1.2	0.3	0.7	0.4
IPy	10	7.1	7.4	3.3
DBA	<LOQ	<LOQ	<LOQ	<LOQ
BghiP	3.2	18.7	37.0	21.4

**Table SI-8: PAH Concentrations (ng/m<sup>3</sup>) in individual air samples from active oil well during drilling area (AW1)**

PAH/Sample	AW1	AW2	AW3	AW4	AW5	AW6
Acy	2.4	1.2	2.3	3.1	1.6	5.5
Ace	3.8	2.7	2.5	3.8	1.3	7.6
Fln	3.5	16.8	13.2	41.6	14.9	66.0
Phe	119.3	108	106.8	128.5	134.6	74.5
Ant	7.3	4.4	3.7	5	3.9	28.3
Flt	64.4	84.3	60	40.5	59.4	49.2
Pyr	94.8	70.1	89.7	59.8	92.4	104.5
BaA	6.6	6.2	5.2	5.5	7.8	9.6
Chr	9.3	10.6	8.6	7.4	13.9	19.3
BbkF	1.4	1.7	1.3	1.6	2.4	1.4
BaP	1.3	1.4	1.1	1.2	1.7	1.3
IPy	6.2	8.8	7.3	5.1	12.6	8.9
DBA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
BghiP	2.6	3	2.9	2.5	3.5	3.4

**Table SI-9: PAH Concentrations (ng/m<sup>3</sup>) in individual air samples from gas and oil active well area (AW2 and AW3) in dry season**

PAH/Sample	AW2(1)	AW2(2)	AW2(3)	AW3(1)	AW3(2)	AW3(3)	AW3(4)
Acy	2.6	2.8	6	5.7	5.1	3.6	8.6
Ace	1.8	3	3.7	3.4	4.5	4	7.6
Fln	3.9	5.3	3.4	4.6	4.2	2.7	5.4
Phe	30.3	34.5	49.3	38.1	24.1	11	15.5
Ant	2.7	4	1.5	1.6	0.8	0.2	0.6
Flt	20.6	57.2	26.8	28.8	14.9	7.3	5.3
Pyr	33.9	44.9	60	52.2	8.2	11.9	18.8
BaA	5.5	4.8	2.2	16.6	7.6	2.8	1.6
Chr	4.9	10.1	3.5	4.9	3.0	0.6	1.3
BbkF	1.1	1.8	5.1	1.5	1.4	1.9	2.2
BaP	0.5	0.6	0.4	0.4	2.1	0.5	0.4
IPy	2.2	1.4	1.8	5	9.2	7.3	6.1
DBA	<LOQ	<LOQ	<LOQ	0.8	<LOQ	<LOQ	<LOQ
BghiP	6.4	2.7	0.8	2.7	0.6	0.5	1.9

**Table SI-10: PAH Concentrations (ng/m<sup>3</sup>) in individual air samples from workstation area (WS) in dry season**

PAH/Sample	WS	WS	PAH	WS	WS	PAH	WS	WS
Acy	1.5	2.9	Flt	6.4	5.5	BaP	0.5	0.1
Ace	2.7	3.2	Pyr	2.6	4.4	IPy	1.3	3.5
Fln	10.9	5.4	BaA	0.9	1.9	DBA	<LOQ	<LOQ
Phe	29	26.6	Chr	0.4	4.7	BghiP	0.1	1.2
Ant	24.7	18.5	BbkF	0.2	0.8	-	-	-

**Table SI-11 incremental lifetime cancer risk of PAH in outdoor air in wet season in oil and gas field in Akwa Ibom**

Location	IUR	OGP	TST	AW1	AW2	AW3	WS
OGP	8.70E-05	1.17E-05	3.40E-05	1.04E-05	2.82E-05	1.42E-05	6.07E-06
TST	8.70E-05	3.50E-06	7.06E-06	2.85E-06	5.19E-06	3.34E-06	1.44E-06
AW1	8.70E-05	8.95E-06	1.74E-05	5.65E-06	1.16E-05	8.62E-06	4.89E-06
AW2	8.70E-05	1.46E-04	7.03E-05	2.89E-05	1.00E-04	1.10E-04	3.62E-05
AW3	8.70E-05	4.55E-05	6.03E-05	3.63E-05	4.00E-05	5.19E-05	2.13E-05
WS	8.70E-05	5.13E-05	1.63E-05	0.00E+00	2.03E-05	8.70E-05	0.00E+00
ILCR1		2.67E-04	2.05E-04	8.41E-05	2.05E-04	2.76E-04	6.99E-05

**Table SI-12 incremental lifetime cancer risk of PAH in outdoor air in dry season in oil and gas field in Akwa Ibom**

Location	IUR	OGP	TST	AW1	AW2	AW3	WS
OGP	8.70E-05	4.30E-05	2.39E-05	5.94E-05	3.64E-05	6.23E-05	1.22E-05
TST	8.70E-05	6.53E-06	7.54E-06	1.00E-05	5.36E-06	2.14E-06	2.20E-06
AW1	8.70E-05	1.20E-05	1.31E-05	1.42E-05	2.30E-05	1.56E-05	4.37E-06
AW2	8.70E-05	5.40E-05	5.72E-05	1.17E-04	4.30E-05	7.47E-05	2.55E-05
AW3	8.70E-05	3.19E-05	6.06E-05	7.10E-05	1.57E-05	6.02E-05	2.09E-05
WS	8.70E-05	0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.79E-05	0.00E+00
IUR		1.47E-04	1.62E-04	2.71E-04	1.23E-04	3.03E-04	6.52E-05

**Table SI-13 Average daily intake of PAH in soil in wet season in oil and gas field in Akwa Ibom**

<b>Location</b>	$\Sigma_6\text{BaPeq}$	<b>1R</b>	<b>ED</b>	<b>EF</b>	<b>BW</b>	<b>AT</b>	<b>BW*AT(A)</b>	<b>BaPeq*1R*ED*ED*EF(B)</b>	<b>B/A</b>	<b>Cf</b>	<b>ADD</b>
OGP	26.8738	100	26	365	70	25550	1788500	25503223.01	14.2596	1.00E-06	1.42596E-05
TST	35.9772	100	26	365	70	25550	1788500	34142324.5	19.0899	1.00E-06	1.90899E-05
AW1	11.093	100	26	365	70	25550	1788500	10527265.92	5.88609	1.00E-06	5.88609E-06
AW2	17.0976	100	26	365	70	25550	1788500	16225660.23	9.07222	1.00E-06	9.07222E-06
AW3	42.9011	100	26	365	70	25550	1788500	40713140.07	22.7638	1.00E-06	2.27638E-05
NAW	7.96518	100	26	365	70	25550	1788500	7558955.82	4.22642	1.00E-06	4.22642E-06
WS	12.4912	100	26	365	70	25550	1788500	11854167.78	6.62799	1.00E-06	6.62799E-06

**Table SI-14 Average daily intake of PAH in soil in dry season in oil and gas field in Akwa Ibom**

<b>Location</b>	$\Sigma_6\text{BaPeq}$	<b>1R</b>	<b>ED</b>	<b>EF</b>	<b>BW</b>	<b>AT</b>	<b>BW*AT(A)</b>	<b>BaPeq*1R*ED*ED*EF(B)</b>	<b>B/A</b>	<b>Cf</b>	<b>ADD</b>
OGP	20.031	100	26	365	70	25550	1788500	19009110.58	10.62852	1.00E-06	1.06285E-05
TST	21.69531	100	26	365	70	25550	1788500	20588844.97	11.51179	1.00E-06	1.15118E-05
AW1	17.00504	100	26	365	70	25550	1788500	16137779.64	9.023081	1.00E-06	9.02308E-06
WS	7.186	100	26	365	70	25550	1788500	6819347.925	3.812887	1.00E-06	3.81289E-06

**Table SI-14 Average lifetime daily dose of PAH in outdoor air in wet season in oil and gas field in Akwa Ibom**

Locations	$\Sigma_6\text{BaP}_{\text{eq}}$	1R	ED	EF	BW	AT	$\text{BaP}_{\text{eq}}*\text{IR}*ED*EF(A)$	BW.AT(B)	A/B	<i>C<sub>f</sub></i>	LADD
OGP	3.06492	20	70	365	70	25550	1566173.111	1788500	0.87569	1.00E-06	8.76E-07
TST	2.36094	20	70	365	70	25550	1206438.902	1788500	0.67455	1.00E-06	6.75E-07
AW1	0.96675	20	70	365	70	25550	494007.8422	1788500	0.27621	1.00E-06	2.76E-07
AW2	2.36094	20	70	365	70	25550	1206438.611	1788500	0.67455	1.00E-06	6.75E-07
AW3	3.1678	20	70	365	70	25550	1618745.8	1788500	0.90509	1.00E-06	9.05E-07
WS	0.80382	20	70	365	70	25550	410750.1242	1788500	0.22966	1.00E-06	2.30E-07

**Table SI-15 Average lifetime daily dose of PAH in outdoor air in dry season in oil and gas field in Akwa Ibom**

Locations	$\Sigma_6\text{BaP}_{\text{eq}}$	1R	ED	EF	BW	AT	$\text{BaP}_{\text{eq}}*\text{IR}*ED*EF(A)$	BW.AT(B)	A/B	<i>C<sub>f</sub></i>	LADD
OGP	1.69419	20	70	365	70	25550	865730.9014	1788500	0.48405	1.00E-06	4.84E-07
TST	1.86569	20	70	365	70	25550	953369.3618	1788500	0.53306	1.00E-06	5.33E-07
AW1	3.11532	20	70	365	70	25550	1591926.662	1788500	0.89009	1.00E-06	8.90E-07
AW2	1.41825	20	70	365	70	25550	724726.5997	1788500	0.40521	1.00E-06	4.05E-07
AW3	3.47929	20	70	365	70	25550	1777919.322	1788500	0.99408	1.00E-06	9.94E-07
WS	0.74926	20	70	365	70	25550	382869.4063	1788500	0.21407	1.00E-06	2.14E-07

### SI-15 Emissions from different sampling location in both wet and dry season

FACILITIES	SOURCES OF EMISSIONS
Crude Oil& gas Transfer area (TST)	1. Cold flare stack (emits gaseous Hydrocarbons from the closed drain sump, and when there is gas trapped in the line, they are vented out through the stack).
	2. Generator fumes from diesel generator engines and Gas generator.
	3. Vehicular emissions
	4. Flares from Network Exploration and Production Nig Ltd Crude Oil Processing Plant located 500m from FUN. The facility flares associated gas on the average of 12hours per day.
	5. Flares from Exxonmobil Qua Iboe Terminal located 1.5km from FUN. They flare associated gas round the clock all year round.
	6. Maintenance activities: Often crude is released during valve maintenance, Generator servicing.
	7. Vents from crude oil storage tank, diesel storage tank and Gas scrubbers
	8. Crude oil spillage from the pipeline during different activities
	9. crude oil spillage in the past
Oil and gas production area (OGP)	1. Open flare stack. Flares associated gas round the clock all year round.
	2. Generator fumes Diesel generators and Gas generators.
	3. Vehicular emissions from inside and the road
	4. Vents and leaks storage tanks and diesel storage tanks, open drain, scrubbers and vessels.
	5. Past spill incident in 2015,2017 and 2018.
	6. Minor Spills.
	7. fumes from cooking
Oil well (AW3)	1. Past pipeline spill incident in 2016
	2. Leaks and vents from well head
	3. Generator fumes
	4. Generator Maintenance activities
	5. Coal combustion from nearby communities
Active gas well (AW2)	1. Generator fumes
	2. Vehicular emissions from company' s cars and heavy-duty trucks that ply the road daily.
	3. Generator Maintenance activities
	4. Possible leakages from pipelines
	5. Emission from coal combustion from nearby communities
	6. Leaks and vents from well head
Active oil well (AW1) during dry season	1. Well test flare stack used to burn off Hydrocarbons during well testing. (Dry season sampling)
	2. Generator fumes Diesel generators used alternatively throughout the drilling and completion period.

FACILITIES	SOURCES OF EMISSIONS
	Vehicular emissions. There were lots of vehicular traffic from cars, busses, Hilux vans, cranes, forklifts, lorries throughout the sampling period
	Maintenance activities.
	Vents from storage tanks and diesel storage tanks, open drain, scrubbers and vessels.
	Minor Fire incident
	Spillages from crude oil
	Emission from coal combustion from nearby communities
Non active sites (Workstation)	1. Vehicular emissions from company's cars and other vehicles by the road
	2. Various activities during drilling of new well.
	3. Storages of steels
	4. Fumes from nearby communities
	5. farmland
Non active sites (Abandon well (NAW))	1. Vehicular emissions from company's cars and other vehicles by the road
	2. Fumes from nearby communities

**Figure SI-1 Relationship between the distance from NP, MP and WA and average  $\Sigma_{14}$ PAH concentrations in soil from three sub-locations within an oil and gas production area (OGP)**

