

**DETERMINATION OF POLYCYCLIC AROMATIC
HYDROCARBONS IN SURFACEWATER AND SEDIMENTS OF
ARUNTON CREEK AND RIVER ESCRAVOS, NIGER DELTA,
NIGERIA**

BY

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CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants of high environmental concern with known carcinogenic activity (Bathi *et al.*, 2012). They constitute a large group of organic compounds containing two or more fused aromatic rings arranged in linear, angular or cluster mode and containing carbon and hydrogen atoms only. The presence of polycyclic aromatic hydrocarbons (PAHs) in water and soil can create a serious hazard to public health and the environment (Okafor and Opuene, 2007).

Studies in the last few years have shown the presence of more than 600 organic compounds in the environment, the most important of which belong to the following classes: petroleum hydrocarbons, polycyclic aromatic hydrocarbons, ketones, aldehyde and alcohol (Gryniewicz *et al.*, 2002, Sibiya, 2012). Due to the different physicochemical properties of organic pollutants, PAHs tend to interact to different extent with water, sediments and biota. The dynamics of a river or dam ecosystem are complex with some PAH pollutants adsorbed unto organic matter while others dissolve, volatilize or undergo microbial degradation. Many PAHs are at the same time persistent, bioaccumulative, and toxic for humans and aquatic organism (Zhou *et al.*, 2002, Ahmadzadeh *et al.*, 2011, Rezayi *et al.*, 2011, Barkhordarian, 2012, Sany *et al.*, 2012, 2014). As such a comprehensive risk assessment can only be performed by monitoring their presence in common fresh water fish of the region. However,

chemical analysis of PAHs in fish is often more complex than in water and sediments (Sibiya, 2012).

The occurrence of PAHs in the aquatic environment is as a result of both anthropogenic and natural sources. PAHs are released into the environment as by-products of combustion; they are generated by incomplete combustion of organic matter and fossil fuels. The major sources of PAHs into soil and aquatic environments include spills of petroleum and its products via leaking storage tanks, bunkering activities, combustion of fossil fuel and organic matters, and deposition of atmospheric PAHs. Benzo[a]pyrene, a potent carcinogen, is commonly used as an environmental indicator for PAHs (ATSDR, 2009).

In Nigeria' Niger Delta area, there are numerous anthropogenic sources of organic PAH contaminants; activities associated with the exploration of crude oil is believed to be chiefly responsible for most of these pollutants. However; Niger Delta stands a great chance of having varying input sources (Sojinu *et al.*, 2010). Anyakora *et al.*, (2011) noted that they may be multiple sources of PAH contaminants in the area. The Niger Delta, have much been impacted by crude oil due to great activities of import and export of petroleum products (Anyakora *et al.*, 2011).

PAHs are lipophilic compounds with very low water solubility and therefore, their concentration in water is very low (Qiu *et al.*, 2009, Nasr *et al.*, 2010, Kafilzadeh *et al.*, 2011). As a consequence of PAHs' hydrophobic properties, they tend to settle out of water and accumulate in the bottom sedimentation. Therefore, concentration of PAHs should be high in the sediments of polluted aquatic environments (Kafilzadeh *et al.*, 2015).

The adverse effect of PAHs on human health as a result of inhalation of their dust particles have been described as the most detrimental to human health (Sibiya, 2012). These compounds can enter the body through inhalation of vapour from the soil, intake of contaminated drinking water and skin exposure via dermal contact. Also soil ingestion has been recognized to be as an important exposure route as water and food to human (Mostert, 2008).

1.2 Statement of Problem

PAHs are ubiquitous in the environment. They originate from both natural and anthropogenic sources due to incomplete combustion of carbon-containing fuels. They are of particular interest because of their carcinogenicity, mutagenicity and teratogenicity. Numerous studies on the presence of PAH pollutants in the Niger Delta have been previously reported (Duke, 2008, Sojinu *et al.*, 2010, Anyakora *et al.*, 2011, Eguvbe *et al.*, 2014, 2015, Emoyan *et al.*, 2015). However, most previous studies were restricted from this area and usually on soil and vegetation.

A survey of the literature indicates that there are little or no researched data on the PAHs pollution status of the study area. Therefore, this study is instituted to provide baseline data on PAHs status of the study area.

1.3 Aim of the Study

The aim of this study is to determine the concentrations of PAHs in Arunton creek and River Escravos.

1.4 Objectives of the Study

The objectives of this study are to:

1. determine the concentrations of PAHs in the surfacewater and sediment of Aruton Creek and River Escravos.
2. identify the sources of PAHs in the study area.
3. determine the ecological risk of PAHs to benthic organisms in the study area.

1.5 Scope of the Study

This research work is restricted to the determination of US-EPA 16 priority PAHs concentrations and distribution pattern in the surfacewater and sediment of Aruton creek and environ. These are: Naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), anthracene (Ant), fluorene (Flu), phenanthrene (Phen), pyrene (Pyr), fluoranthene (Flt), chrysene (Chry), benzo[a]anthracene (BaA), benzo[a]pyrene (BaP), benzo[k]fluoranthene (BkF), benzo[b]fluoranthene (BbF), dibenz[a,h]anthracene (DahA), benzo[ghi]perylene (BghiP), and indeno(1,2,3-cd)pyrene (IndP).

1.6 Significance of the Study

This study provides baseline data on the concentration, compositional patterns and sources of PAHs in surfacewater and sediments of Arunton creek and River Escravos. This data could be useful for delineating areas where the concentrations of PAHs have exceeded the threshold limits thereby, developing site remediation/clean up strategies, pollution control measures and environmental policy formulation, implementation and monitoring.

CHAPTER TWO

LITERATURE REVIEW

2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) also known as polynuclear aromatic hydrocarbons are organic compounds consisting of two or more fused benzene rings in a linear or cluster arrangement; which are primarily produced by incomplete combustion (ATSDR, 2009). PAHs are widespread environmental contaminant because of their ubiquitous nature and mode of formation. They constitute a large class of organic compounds, made up of only carbon and hydrogen atoms (Amos-Tautua *et al.*, 2013).

Most PAHs are characterized by high melting and boiling points, relative high molecular weight, and solubility in many organic solvent. They are solids with low volatility at room temperature except small components like naphthalene, and most can be photo-oxidized and degraded to simpler substances (ATSDR, 2009). PAHs are relatively neutral and stable molecules, with low solubility in water. The solubility of PAHs in water decreases with increasing molecular weight. Their lipophilicity is high, as measured by water-octanol partition coefficients (Henner *et al.*, 1997). The low-molecular-weight PAHs are appreciably water soluble, naphthalene for example, and can be bioaccumulated (Webster *et al.*, 2010). The high-molecular-weight compounds are relatively insoluble and hydrophobic, and can attach to both organic and inorganic particulates within the water column (Webster *et al.*, 2010). Physical properties of some of the PAHs defined as priority pollutants by the United State Environmental Protection Agency (USEPA) are shown in Table 2.1.

Table 2.1: Physical Properties of PAHs Adapted from (Manoli and Samara, 1999; Chen *et al.*, 2004, Zuydam, 2007; Nekhavhambe, 2008).

PAH	Chemical Formula	Molecular Weight (g/mol)	Water Solubility	Melting Point oC	Boiling Point oC	Log K _{ow}	Vapour Pressure kPa
Naphthalene,	C ₁₀ H ₁₂	128	2.169	81	218	3.37	1.1x10 ⁻²
Acenaphthene	C ₁₀ H ₁₂	154.2	3.93	93.4	279	3.98	2.1x10 ⁻³
Acenaphthylene	C ₁₃ H ₈	152.19	16.1	91.8	280	4.07	9.12x10 ⁻⁴
Fluorene	C ₁₃ H ₁₀	166	1.9	116.5	295	4.18	9.47x10 ⁻¹
Anthracene	C ₁₄ H ₁₀	178.23	0.044	218	342	4.45	6.56x10 ⁻⁶
Phenanthrene	C ₁₄ H ₁₀	178.2	1-1.6	100	340	4.45	2.3x10 ⁻⁵
Pyrene	C ₁₆ H ₁₀	202.3	0.129	147	404	4.88	3.1x10 ⁻⁶
Fluoranthene	C ₁₆ H ₁₀	202.3	0.206	107	384	4.90	6.5x10 ⁻⁷
Chrysene	C ₁₈ H ₁₂	228.3	0.0015	254	448	5.61	5.7x10 ⁻¹⁰
Benzo[a]anthracene	C ₁₈ H ₁₂	228.3	0.0094	162	437.6	5.61	5x10 ⁻⁹
Benzo[a]pyrene	C ₂₀ H ₁₂	252.32	0.0038	179	495	6.0	0.37x10 ⁻³
Benzo[k]fluoranthene	C ₂₀ H ₁₂	252.32	0.0043	217	480	6.06	2.8x10 ⁻⁹
Benzo[b]fluoranthene	C ₂₀ H ₁₂	252.31	0.0012	168	481	6.60	5.0x10 ⁻⁷
Dibenz[a,h]anthracene	C ₂₂ H ₁₄	278.35	0.0005	269.5	524	6.75	9.55x10 ⁻¹⁰
Benzo[ghi]perylene	C ₂₂ H ₁₂	276.33	0.00026	278	550	6.63	1.0x10 ⁻¹⁰
Indeno[1,2,3-cd]pyrene	C ₂₂ H ₁₂	276	0.00053	164	536	6.4	1.3x10 ⁻⁵

PAHs are known to have carcinogenic, mutagenic and teratogenic properties. Due to these properties as well as their persistence in the environment, they have been placed on the list of priority pollutants by the United States Environmental Protection Agency (US-EPA) and also the European Environment Agency (Sibiya, 2012). The carcinogenicity of certain PAHs is well established in laboratory animals. Researchers have reported increased incidences of skin, lung, bladder, liver, and stomach cancers as well as injection-site sarcomas, in animals (ATSDR, 2009). According to Nasr *et al.*, (2010), the USEPA has classified seven PAH compounds as probable human carcinogens. Table 2.2 indicates the carcinogenic classifications of selected PAHs by specific agencies.

Table 2.2: U.S. Department of Health and Human Services, International Agency for Research on Cancer (IARC) and US-EPA Carcinogenic Classifications of PAHs (ATSDR, 2009).

Agency	PAH Compound(s)	Carcinogenic Classification
U.S. Department of Health and Human Services (HHS)	Benzo[a]anthracene Benzo[b]fluoranthene Benzo[a]pyrene Dibenz (a, h) anthracene and Indeno (1, 2, 3-cd) pyrene	Known animal carcinogen
International Agency for research on Cancer (IARC)	Benzo[a]anthracene and Benzo[a]pyrene Benzo[a]fluoranthene Benzo[k]fluoranthene and Indeno (1, 2, 3-cd) pyrene Anthracene, benzo (e) pyrene Benzo [g h i] perylene Chrysene, fluoranthene, fluorene Phenanthrene and pyrene	Probable carcinogenic to humans Possibly carcinogenic to humans Note classifiable as to their carcinogenicity to humans
U.S. Environmental Protection Agency (EPA)	Benzo[a]anthracene Benzo[a]pyrene, chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene Dibenz (a, h) anthracene and Indeno (1, 2, 3-cd) pyrene Acenaphthylene, anthracene Benzo [g h i] perylene Fluoranthene, fluorene Phenanthrene and pyrene	Probable human carcinogens Not classifiable as to human carcinogenicity

2.2 Sources of PAHs

PAHs are a natural component of most fossil fuels. Although produced naturally by forest fires, volcanoes and bacteria decay of organic materials (ATSDR, 2009). PAHs are mainly of anthropogenic matter, as well as natural sources (Haritash *et al.*, 2009). Pyrogenic and petrogenic sources are two major origins of anthropogenic PAHs in the environment (Nawaz *et al.*, 2014). Pyrogenic PAHs are formed as trace contaminants by the incomplete combustion of organic matter, such as wood, fossil fuels, asphalt, and industrial waste (Liu *et al.*, 2009). The petrogenic PAHs are formed by petroleum products. These hydrocarbons are thought to have originated from oil spills, from fresh or used crankcase oil, crude and fuel oil, chronic or accidental leakages of marine and land pipelines; domestic and industrial wastes (Zakaria *et al.*, 2002, Saha *et al.*, 2009, Sany *et al.*, 2014). Pyrogenic sources are thought to be more thermodynamically stable and toxic than petrogenic sources due to their high concentrations of non-alkylated PAHs (Khairy *et al.*, 2009, Saha *et al.*, 2009, Bayer *et al.*, 2010).

PAHs can be released from their sources either in a gas phase or they can be associated with particles by nucleation and condensation, forming particulate matter. Once produced, PAHs can be widely dispersed into the environment by atmospheric transport or through stream pathways and eventually accumulate in soils and aquatic sediments (Liu *et al.*, 2013); they can be transported into an aquatic environment by a number of pathways including fossil fuel distribution, petroleum spillage, storm water and surface runoff, sewage and waste water effluent, and eventually accumulate in soils and aquatic sediments (Brooks, 1997, Liu *et al.*, 2009). Other sources of PAHs to the aquatic and sediment environments include creosote-treated products, spills of

petroleum products from leaking tanks and bunkering activities, industrial plants and waste water treatment plants, and deposition of atmospheric PAHs. The main industrial (stationary) sources of PAHs include coke oven, aluminium production, iron and steel foundries, coal gasification and coke production (Dubey *et al.*, 2013). Both anthropogenic activities and natural emissions are the PAH sources of coastal sediments (Kafilzadeh, 2015).

The movement of PAHs in the environment depends on properties such as how easily they dissolve in water (although in general they do not easily dissolve in water), and how easily they evaporate into the air (ATSDR, 1995). Microorganisms can also break down PAHs in soil or water after a period of weeks to months (Dikshith, 2013). PAHs in soil are most likely to stick tightly to particles. However certain PAHs can still move through soil to contaminate underground water. The soil types will determine how long the PAHs stick on the soil particle. Clay soil when compared to sandy soil, adsorb more PAHs. The concentration of PAHs may be higher in plants and animals than in soil or water in which they live and this is due to possible magnification and bioaccumulation of PAHs especially in animals (ODH, 2004).

2.3 PAHs in the Aquatic Environment

The occurrence of PAHs in the aquatic environment has been extensively studied across many industrialized countries. According to Eisler (1987) approximately 228,000 metric tons of PAHs are discharged into the aquatic environment per annum as a result of human activities. Several PAHs concentrations have been reported in the open waters of the Great Lakes water system by The Great Lakes Science Advisory Board (GLSAB) (1983). Chen *et al.*, (2004) studied the distribution of PAHs in surfacewaters, sediments and soils of Hangzhou city, China. Chen *et al.*, (2004),

found that the concentration of 10 PAHs in sampled water, ranged from 0.989 mg/L at Shaoniangong to 9.66 mg/L at Zhakou, with a mean concentration of 3.717 mg/L. According to Chen *et al.*, (2004), the composition pattern of PAHs in water by ring size showed clearly that three-ring PAHs (Fluorene, phenanthrene, and anthracene) were the most abundant in all water samples. Four-Ring PAHs were the more abundant in some water samples, while five-ring PAHs concentrations were the lowest in all water samples, and not determined in some water samples, (such as Yuanpu, Zhutoujiao, Gongchenqiao, Qinfengqiao, Banshanqiao, Shaoniangong and Lixihu) (Chen *et al.*, 2004).

PAHs have also been studied in the Middle East and Arab world (Mohamed *et al.*, 2004, Kafilzadeh *et al.*, 2011, Nasr *et al.*, 2010). Kafilzadeh *et al.*, (2011) studied the distribution of PAHs in water and sediment of Kor River in Iran. According to Kafilzadeh *et al.*, (2011), the highest concentration of PAHs in water samples of Kor River was related to acenaphthene (3-ring PAH), while in sediment fluoranthene (4-ring PAH) was the most important pollutant. According to Kafilzadeh *et al.*, (2011), indeno [1, 2, 3-cd] pyrene, was the lowest PAHs components recorded in water samples of Kor River. The result recorded by Kafilzadeh *et al.*, (2011), is consistent with a number of authors. According to Mohammed *et al.*, (2009), Nasr *et al.*, (2010), the composition pattern of PAHs in sediments is mostly dominated by four-ring while water samples are dominated by three-ring PAHs. Kafilzadeh *et al.*, (2011), noted that the highest and lowest mean concentrations of PAHs in both water and sediment samples of Kor River were observed in autumn and summer, respectively.

PAHs in South African sludge samples have been analysed (Cele, 2005). The average concentrations obtained were 0.55 mg kg⁻¹ for benzo[a]pyrene in KwaZulu Natal

province, 0.55 mg kg^{-1} in Gauteng province with only one sample exceeding the regulatory limit, which is 2.55 mg kg^{-1} and 0.75 mg kg^{-1} in North West and Western Cape Province. According to (Cele, 2005), the South African guideline does not cater for other PAHs that might be harmful to the environment. PAHs in South African wastewater samples have been analysed in Cape Town (Tikilili and Chirwa, 2004). All 16 priority PAHs were detected in the sample with concentrations ranging from 0.001 mg L^{-1} to 25.1 mg L^{-1} . The results obtained showed that there are high levels of PAHs in the wastewater exceeding the World Health Organization (WHO) recommended maximum values for safety, which is $0.05 \text{ } \mu\text{g L}^{-1}$ (Rahman *et al.*, 2011, Sibiya, 2012).

Nigeria is not left out as a number of studies have also been carried out in the country on the presence of polycyclic aromatic hydrocarbons in the aquatic environment. Duke, (2008) for instance, found that the concentrations of PAHs in Ekpan Creek in the Niger Delta were from pyrogenic origin and include phenanthrene, anthracene, fluoranthene, pyrene, chrysene and benzo[a]anthracene. According to (Duke, 2008), the total concentrations (mg/L) of these PAH components ranged between 0.02439-0.2836 compared to 0.00017-0.00186 recorded for the control creek at Abraka.

Olajire *et al.*, (2007) analysed 10 PAHs from surfacewater samples in South Western Nigeria and the total concentration found ranged between 11.2 and $341.5 \text{ } \mu\text{g/L}$ in water. Opuene *et al.*, (2009) analyzed total PAHs and found that the levels varied from 720.46 to $857.65 \text{ } \mu\text{g/L}$ in surfacewaters, indicating that the aquatic ecosystem was polluted by PAHs. The most abundant PAHs in the surface waters and sediments were fluorene and acenaphthylene (Opuene *et al.*, 2009). At Osogbo and Ile-Ife areas, the mean levels of PAHs in surface runoff ranged between 0.1-15.81 mg/L while in

the more industrialized Lagos area the levels ranged between 0.1-73.72 mg/L (Ogunfowokan *et al.*, 2003). These values are also higher than the WHO guideline limit of 0.05 µg/L indicating that the water systems were contaminated by PAHs.

With more industries springing up in the Niger Delta Area (NDA) of Nigeria, the burden of anthropogenic PAHs would likely be on the increase.

2.4 Human and Environmental Effects of PAHs

Contamination of aquatic ecosystems by PAHs has been recognized as a major public health risk (Okafor and Opuene, 2007). The effects of PAHs are mostly known from animal experiments; researchers have reported increased incidences of skin, lung, bladder, liver, and stomach cancers (ATSDR, 2009). Animal studies show that certain PAHs also can affect the hematopoietic and immune systems and can produce reproductive, neurologic, and developmental effects (ATSDR, 2009). Several PAHs including benzo(a)anthracene, benzo(a)pyrene (BaP), benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo[ah]anthracene, indeno[1,2,3-cd]pyrene have caused tumours in laboratory animals when they are exposed to these substances via several exposure pathways (WHO,1998). The toxicity test performed with fish embryos indicates that concentrations found could be dangerous to some aquatic organisms, particularly during early stages of development (Jaward *et al.*, 2012). Some deformities (exogastrulation) occurred in embryos exposed to extracts of water and sediments from Estero de Urias. These indicate that some abnormal process occurred during the development of the embryo similar to when they are exposed to lithium chloride (LiCl) (Jaward *et al.*, 2012). Experiments with BaP, which is a representative of other cancer-causing PAHs, show that fish

seem to be most susceptible to peak exposures of BaP, particularly after earlier exposure to lower levels (Sibiya, 2012).

Another risk factor is the ability of benthic organisms to metabolize these compounds (Jeong and Cho, 2007). Some aquatic invertebrates, for example, certain polychaetes, are able to degrade PAHs, but many others are not able to do this well, for example, bivalve mollusks (Jeong and Cho, 2007, Jaward *et al.*, 2012). PAHs are metabolized by phase 1 enzymes of cytochrome P450 mixed function oxygenase system, and excreted as hydroxylated metabolites (Jaward *et al.*, 2012). However, the cytochrome P450 system, while metabolizing PAHs to more easily excretable compounds, produces a range of carcinogenic and mutagenic intermediates such as diols and epoxides that can lead to induction of carcinomas via formation of PAH-DNA adducts (van Schooten *et al.*, 1995, van der Oost *et al.*, 2003, Jaward *et al.*, 2012). Other studies report that even low PAH concentrations in sediments (2-3 ng/g) are capable of inducing cytochrome P450 enzymes in fishes (Goksøyr and Förlin, 1992). Concerning DNA damage of shrimp exposed to PAHs, results suggest that these pollutants also can be potential carcinogenic substances, because the DNA level of shrimp exposed was significantly higher than controls, which indicates possible DNA damage and start of carcinogenic processes. However, others have reported that many factors are involved in carcinogenic development in aquatic organisms exposed to toxic substances, such as development stage, nutritional and health condition and also the pollutant concentration and length of exposition (Jaward *et al.*, 2012). PAHs and their metabolites, can form DNA adduct which can induce mutation (Nasr *et al.*, 2010)

PAHs generally have a low degree of acute toxicity to humans. The most significant endpoint of PAH toxicity is cancer (ATSDR, 2009). Increased incidences of lung, skin, and bladder cancers are associated with occupational exposure to PAHs (Pongpiachan, 2013).

2.5 Standard Exposure Limits of PAHs in Water and Sediment Matrixes

The maximum allowable concentrations (MACs) of PAHs in soil and water are presented in Table 2.3. No standard exist for the amount of PAHs allowed in the air, however the OSHA Permissible Exposure Level (PEL) for PAH in the workplace air is set at 0.2 mg/m^3 (ATSDR, 2009).

Table 2.3: Maximum allowable concentrations (MACs) of PAHs in soil and water (ATSDR, 2006)

PAH	MAC(Soil),ppm	MAC(Water)ppm
Naphthalene	1.0	3.0
Acenaphthene	3.0	3.0
Acenaphthylene	3.0	3.0
Anthracene	3.0	3.0
Fluorene	3.0	3.0
Phenanthrene	3.0	3.0
Pyrene	3.0	3.0
Fluoranthene	3.0	3.0
Chrysene	0.3	0.005
Benzo [a]anthracene	0.15	0.005
Benzo[a]pyrene	0.3	0.005
Benzo[b]fluoranthene	0.3	0.005
Benzo[k]fluoranthene	0.3	0.005
Dibenzo[a,h]anthracene	0.3	0.005
Benzo[ghi]perylene	3.0	3.0
Indeno[1,2,3-cd]pyrene	0.3	0.005

2.6 Exposure Routes of PAHs to Humans

PAHs are ubiquitous in the environment. According to Zedeck (1980) there are approximately 100 different known PAHs in air, soil, foodstuffs, and water. Therefore humans may be exposed to these substances at home, in the fields or at the workplace. Typically, humans will not be exposed to an individual PAH but to a mixture of PAHs (ATSDR, 2003). Routes of exposure include ingestion, inhalation, and dermal contact in both occupational and non-occupational settings (Abdel-Shafy and Mansour, 2015). Some exposures may involve more than one route simultaneously, affecting the total absorbed dose (such as dermal and inhalation exposures from contaminated air) (Rengarajan *et al.*, 2015).

Swallowing food or drinking water that contain PAHs are other routes for PAHs to enter the body, but absorption is generally slow when PAHs are swallowed. PAHs can enter all the tissues of the body that contain fat. They tend to be stored mostly in the kidneys, liver and fat. Smaller amounts are stored in the spleen, adrenal glands and also ovaries (ATSDR, 1995).

The extent to which humans are exposed to PAHs is a function of several parameters. These include the prevailing atmospheric conditions, concentrations in ambient air, partition between the gas and particle phase and the size distribution of airborne particulates. Risk assessment associated with inhalatory PAHs uptake is often estimated on the basis of the Bap concentration in air (Sibiya, 2012). The evaluation of the health risk due to inhalatory exposure to PAHs is based on epidemiological findings. However, it has to be considered that BaP is just one carcinogenic compound in a mixture of carcinogens in the atmosphere (Papageorgopoulou *et al.*, 1999).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Description of the Study Area

The study is in Arunton area of Escravos (Ugborodo) Delta state, Nigeria. The area is 100% aquatic with wet and low lying mangrove swamp/lands (generally <5m above sea level). It has estimated human population of about 5,000 (STAND, 2010). Located at latitude $05^{\circ} 36.384$ N and longitude $005^{\circ} 11.696$ E and approximately 35 km from Warri by land distance and almost twice of that by water due to the meandering river and creeks, the study area has warm and tropical climate with plenty of rainfall. Arunton is situated along the Escravos River (to Atlantic Ocean), and is predominantly inhabited by the Itsekiri'. The area is well drained by creeks and rivers that eventually empty' into the Atlantic Ocean; it is rich in oil deposits, mostly in swamps and offshore locations. The major economic activities in this area are those related to the oil companies. The people are primarily engaged in fishing and commercial activities as their main source of income and livelihood. Therefore are heavily reliant on the quality of the surface water and marine biota.

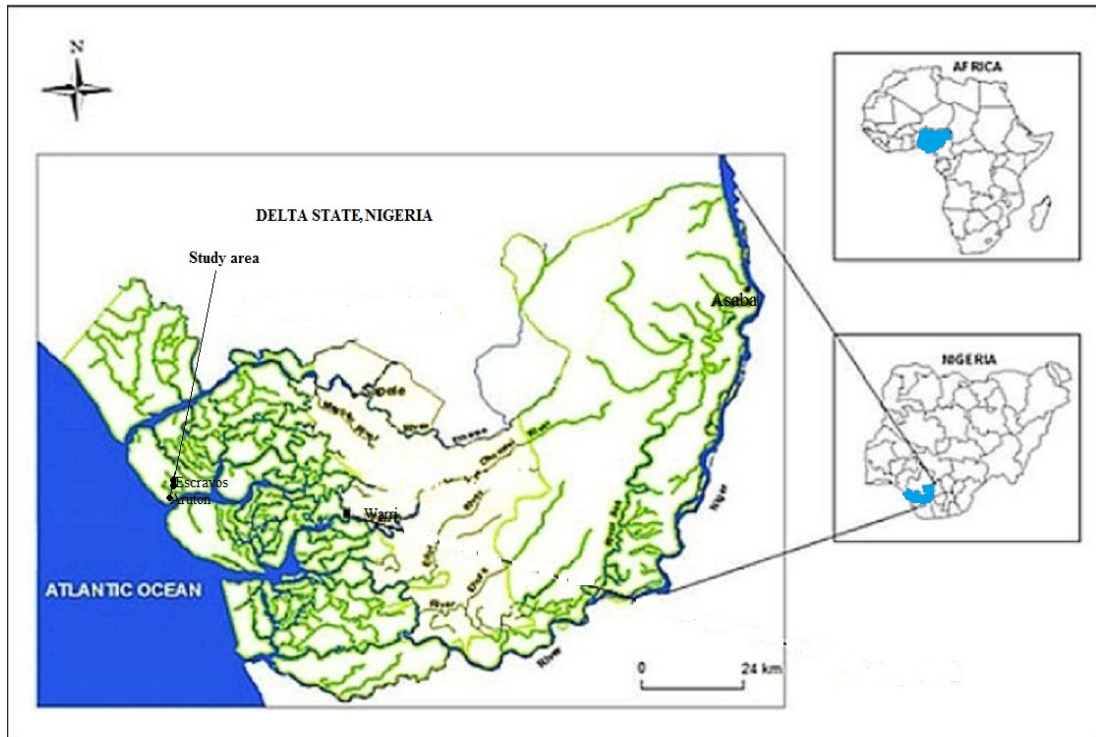


Figure 3.1: Map of Delta state, Nigeria showing study area adapted from (www.hydroweb.com).



Figure 3.2: Aerial photograph of study area adapted from Chevron Nigeria.



- WATER
- SEDIMENT

Figure 3.3: Location of the sampling stations in Arunton creek, Escravos adapted from Warri Southwest LGA.



Figure 3.4: Photograph of Arunton creek.

Arunton creek is situated behind the NNPC-Chevron tank farm/terminal, Escravos. It divides the terminal and the village. It is one of the most important creeks in this area and pours into the Escravos River. Half its volume empty' into the Escravos River between the early hours of the day to about 10:00 hours, leaving large chunk of sediment area exposed and reverses back around 11:00 am as a result of tidal waves from the Atlantic ocean. The creek is estimated to be between 400 to 600m in length and about a 100m in width.

3.2 Sampling and Sample Collection

The samples were collected from Arunton creek and environs (Figures 3.2, 3.3 and 3.4) between July and December 2014, to reflect the dominant seasons in the study area-wet and dry seasons. 12 surfacewater samples were collected from 3 sample sites (Figure 3.3) in 1litre amber glass bottle with a Teflon-lined cap. Site 1 (Ikpere) was behind the Ikpere primary school, with clusters of local petroleum storage/dispensing facilities and boat jetties. Site 2 (Dehydration) was along the Arunton creek, behind Chevron Dehydration plant; while site 3 was by the Escravos Dock/shipping yard.

20 grab sediment samples (about 1kg each) were collected at a depth of 0-10cm from five (5) sampling stations (Figure 3.3). Sites 1, 3 and 5 are the same as the surface water sites, while site 2 (Entrance of Arunton Creek), and (NNPC Tankfarm) are both along the Arunton creek. The sediments were collected in an aluminum foil using soil auger. Each sampling was carried out in four replicate. With the exception of suspected source point, the sampling points were evenly spread in order to give a true representative sample of the study area. The samples were kept in a cooler containing dry ice ($\leq 4^{\circ}\text{C}$) to initiate cooling process prior to transportation to the laboratory for preparation and analysis.

For PAHs, bedside placing the samples in the ice and in dark/amber glass bottle as part of preservative measures, additional preservation was not required. Often sampled water and sediment for PAHs (without preservative) can maintain a maximum holding times of 14 and 60 days respectively.

3.3 Reagents

All chemicals and reagents used were of analytical standard grade with high purity. Dichloromethane (98%), molecular formula $(CH_2Cl)_2$, methanol (99.9%), acetone (99.8%), molecular formula $(CH_3)_2CO$ and ortho-terphenyl (99.9%) ($C_{18}H_{14}$) from Sigma-Aldrich (Steinheim, USA), anhydrous sodium sulphate (99%), n-hexane (99.5%), silica gel, anthracene, acenaphthylene, fluorene, phenanthrene and naphthalene (97.9 and 98% purity respectively), acenaphthene, fluoranthene and chrysene with 99% purity, benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthrene, pyrene, benzo(ghi)perylene, dibenz(a,h)anthracene and indeno(1,2,3-cd)pyrene. The 16 PAHs were used to prepare standard solution of the target PAHs. All reagents were used without any further purification.

3.4 Equipment

Gas chromatography (GC) HP5890 Series equipped with flame ionization detector (FID) was used for analysis of the PAHs.

3.5 Determination of Physicochemical Parameters

3.5.1 Determination of pH

The determination of pH in water and sediment however, not the analyte of interest is usually regarded as part of the preliminary physicochemical assessment of water and sediment quality. Environmental factors like pH, temperature, oxygen, PAH concentrations and contamination history of water, sediment, soil, soil type, moisture, nutrients, and other substances that may act as substrate co-metabolites influencing

the rate of PAH degradation in soil, and other environmental matrixes (Sims and Overcash, 1983). The pH values were measured using an HANNA digital pH meter (model number HI-3813-6). Prior to use, the pH meter was calibrated using pH buffer of 7.0 and 4.0. For the water sample, the calibrated pH electrode was rinsed with de-ionized water, followed by a fraction of the sample and then introduced into the sample. This was allowed to stand for a few minutes until a stable reading was obtained.

The sediment pH was determined following Adepekun and Fasidi, (2005). 20 g of air-dried sample was transferred to 50 mL beaker and 20 mL of distilled water added. The mixture was allowed to stand for 30 minutes. The calibrated pH meter was inserted and reading taken.

3.5.2 Determination of Conductivity

Conductivity is a measure of the ability of an aqueous solution or soil to carry electric current. The conductivity of the water and sediment samples was determined using an HANNA self contained conductivity meter (model number HI-3813-6). The conductivity meter was calibrated with 0.01M KCl reference solution. The electrode was rinsed with distilled water and wiped dry with clean soft tissue. The readied conductivity meter was dipped into the water sample until a stable reading was recorded.

Conductivity of the sediment sample was determined by transferring an aliquot of the sediment sample into a 100 mL plastic bottle and dissolved with deionized water. More deionized water was added to make up to 50 mL. The bottle was stirred for

about 1hour, and the conductivity determined by inserting the already calibrated digital electronic conductivity meter.

3.5.3 Determination of Total Organic Carbon (TOC) Contents of the Sediment

The organic content is the ratio of the mass of organic matter in a given mass of soil to the mass of the dry soil. It is expressed as a percentage (Reddy, 2002). Environmental factors such as the organic content, structure and particle size of the soil, characteristics of the microbial population, the presence of contaminants such as metals and cyanides that are toxic to microorganisms; and the physical and chemical properties of the PAHs affects their degree of biodegradation in soil (Wilson and Jones, 1993). Sorption of PAHs to organic matter and soil particles also influences the bioavailability, and hence, biotransformation potential; this may limit the biodegradation of compounds that would otherwise rapidly undergo metabolism (Weissenfels *et al.*, 1992).

The total organic compound was determined using chromic acid titrimetric method of Walkey and Black, (1934). 1 g of the sediment sample was transferred into 500 mL flask and 10mL of $K_2Cr_2O_7$ and 20 mL of concentrated H_2SO_4 added. 200 mL of distilled water and 10 mL of H_3PO_4 were added respectively. To the mixture, 5 drops of diphenylamine indicator was added and the titrated with 0.5M of $(NH_4)_2SO_4Fe$.

A blank titration was also carried out and the percentage of TOC calculated.

$$\%TOC = \frac{\text{Blank titre} - \text{sample titre} \times 0.003 \times 100}{\text{Sample weight}}$$

3.6 Sample Extraction

a) Water Sample

In the laboratory, using liquid-liquid extraction (LLE) as described in APHA (1998) the total amount of each surfacewater sample was filtered with Whatman filter paper (70 mm) to remove suspended materials and then poured into a 2 liter separatory funnel. 1ML of ortho-terphenyl (OTP), a surrogate was added this time to spike the sample. For the first LLE, the mixture of 100 mL n-hexane and dichloromethane (1:1, v/v) were added, and shaken vigorously for 2 minutes with periodic venting to release excess pressure. The organic layer was allowed to separate from the water phase for a minimum of 5 minutes. The water phase was drained from the separator funnel into a 1000 mL beaker. The organic phase was carefully poured into a glass funnel containing 20 g of anhydrous sodium sulphate. This step was then repeated twice; and the water phase poured back into the separatory funnel to be re-extracted with 50 ml of the same solvent mixture. The combined extract was concentrated to 2 mL volume using a rotary evaporator.

Water sample extract was cleaned up using silica gel column chromatography. A Plug of glass wool was used to separate the required analytes fraction from other interfering compounds. The concentrated extract and 2 ml hexane rinses of the sample flask were transferred on to top of the column. The aliphatic component of the column was first eluted with 30 ml of hexane and then discarded. Subsequently, final elution was carried out with 35 ml of dichloromethane and retained for PAHs quantification. The aromatic fraction was concentrated to near 1 ml with rotary evaporator. An additional 20 ml hexane was added to the concentrated extracts and evaporated to remove traces of dichloromethane. Final extract was concentrated to 1 ml and then

analyzed using a “HP5890 Series ii” gas chromatography equipped with a flame ionization detector (GC/FID).

b) Sediment Sample

The sediment samples were air-dried in the dark for about 48 hours or until there was no visible moisture remaining. Each of the air-dried samples were thoroughly homogenized in a mortar and then sieved with a 2mm metal sieve. Sonication extraction technique was used to extract the PAHs in the sediment. 1:1 solvent mixture of acetone and dichloromethane was prepared. About 10 g aliquot of the well homogenized sediment sample was measured into a solvent rinsed beaker. 50 ml of the solvent mix was added to the sample. The sample was then placed in a Sonicator and sonicated for about 10-15 minutes at 70°C. About 10 g of anhydrous sodium sulphate was added to the sample until a clear extract developed. The extracted solvent was poured into a round bottom flask and concentrated to about 2ml using vacuum rotary evaporator.

Clean up of PAH extracts from the sediment was achieved through solid phase extraction with alumina/silica gel. The 2 ml concentrated solvent was transferred into the packed column and fractionated with 10 ml dichloromethane. Saturated aliphatic hydrocarbons were eluted with 20 ml of n-hexane and the aromatic hydrocarbons eluted with 30 ml of a mixture of hexane and dichloromethane (90:10) (v/v). The eluted solvent (aromatic hydrocarbon) was re-concentrated and then transferred to the vial bottle. The eluate (aromatic fraction) was analyzed using an “HP5890 Series ii” gas chromatography equipped with a flame ionization detector (GC/FID).

3.7 Instrumentation and Analysis of PAHs

Hawlett Packed Series 5890 GC was employed in the determination of the 16 priority PAHs. The instrument set up for Aromatic hydrocarbons (PAHs) were as follow: The initial temperature was 100°C, initial time: 1, Rate1: 4°C/mins and final temperature was 310°C. The detector temperature was set at 300°C. High performance capillary column HP-5 (cross linked PH ME Siloxane), with film thickness of 1 µm, length: 30 m, and phase ratio: 63 was used for analytes separation. Flame ionization detector (FID) type with air-hydrogen flame (Hydrogen: 35 mL/sec and air: 350 mL/min) as oxidant gas was used. The injector port (inlet) temperature was 280°C in splitless mode. Injection volume was 1 µL. Helium was used as the carrier gas. Linear velocity was 30 cm/sec. Quantification was by external calibration techniques.

3.8 Quality control/assurance

The reagents/ chemicals used were of analytical standard grade. The process of sample collection, storage and preparation were carefully carried out so as to maintain the integrity of the samples. Field blanks were taken to the site for site contaminant levels. All apparatus used in the preparatory stage of the GC analysis were solvent rinsed with a mixture of acetone and dichloromethane. The round bottom flask used for sample concentration was rinsed with acetone after each round of concentration. This was to avoid cross-contamination of the samples. The surrogate standard, ortho-terphenyl was used to determine the efficiency of the extraction procedures. The surrogate standards recovery rate ranged from 71 % to 108 %. All the spiked blanks (standards spiked into solvents) had surrogate standard recoveries in the range of 75–98%. Quantification was by external calibration techniques.

CHAPTER FOUR

RESULTS AND DISCUSSION

Tables 4.1 and 4.2 shows some physical parameters determined along with concentrations of the 16 priority PAHs. The parameters are pH and conductivity for water samples and pH, conductivity and total organic carbon (TOC) for sediment samples. These parameters though not the analytes of interest, play critical role in an interconnected ecosystem and thus influence the degradation or bioavailability of PAHs.

Table 4.1: Physical properties of water samples analyzed, pH and conductivity

Station/Sample Description	Sampling date	pH	Conductivity ($\mu\text{S}/\text{cm}$)
Dehydration 1	22 July, 2014	6.01	14.5
Dehydration 2	30 August, 2014	6.50	13.9
Dehydration 3	25 November, 2014	6.01	9.13
Dehydration 4	26 December, 2014	6.30	10.2
Ikperere School 1	22 July, 2014	5.98	11.4
Ikperere School 2	30 August, 2014	6.01	12.9
Ikperere school 3	25 November, 2014	4.28	21.7
Ikperere school 4	26 December, 2014	5.16	22.9
Dock Entrance 1	22 July, 2014	6.15	14.9
Dock Entrance 2	30 August, 2014	5.90	10.0
Dock Entrance 3	25 November, 2014	5.42	11.8
Dock Entrance 4	26 December, 2014	5.90	11.3

Table 4.2: Physical properties of sediment samples analyzed, pH, conductivity and total organic carbon (TOC).

Station/Sample Description	Sampling date	pH	Conductivity ($\mu\text{S}/\text{cm}$)	TOC (%)
Dehydration 1	22 July, 2014	4.16	16.6	3.5
Dehydration 2	30 August, 2014	4.80	19.3	3.34
Dehydration 3	25 November, 2014	4.16	16.6	4.81
Dehydration 4	26 December, 2014	6.00	9.24	2.9
Ikperere School 1	22 July, 2014	5.39	16.7	1.98
Ikperere School 2	30 August, 2014	5.51	20.0	1.53
Ikperere school 3	25 November, 2014	6.12	6.10	1.72
Ikperere school 4	26 December, 2014	6.43	20.20	1.60
Dock Entrance 1	22 July 2014	6.25	3.53	2.20
Dock Entrance 2	30 August, 2014	6.01	5.12	2.80
Dock Entrance 3	25 November, 2014	5.02	13.4	2.10
Dock Entrance 4	26 December, 2014	6.21	15.0	2.54
NNPC Tankfarm 1	22 July, 2014	5.11	13.3	2.63
NNPC Tankfarm 2	30 August, 2014	5.48	15.3	2.94
NNPC Tankfarm 3	25 November, 2014	6.19	17.5	2.74
NNPC Tankfarm 4	26 December, 2014	6.58	16.9	2.98
Arunton Creek Entrance 1	22 July, 2014	4.50	6.35	2.38
Arunton Creek Entrance 2	30 August, 2014	4.91	10.10	4.76
Arunton Creek Entrance 3	25 November, 2014	5.20	16.4	4.61
Arunton Creek Entrance 4	26 December, 2014	5.00	15.7	2.14

Table 4.3: Concentrations of PAHs ($\mu\text{g/L}$) in surfacewater of the study area

Components	Station 1(IKP)		Station 2(DHY)		Station 3(DCK)	
	Mean	Range	Mean	Range	Mean	Range
Naphthalene	91.5	5.00-187	197	8.00-712	40.3	7.00-90.0
Acenaphthene	26.3	BDL-55.0	2.30	BDL-7.00	0.50	BDL-1.00
Acenaphthylene	71.0	1.00-146	2.50	1.00-4.00	1.30	1.00-2.00
Anthracene	41.0	1.00-88.0	0.80	BDL-2.00	0.50	BDL-2.00
Fluorene	229	3.00-489	148	BDL-532	25.0	4.00-68.0
Phenanthrene	44.3	4.00-87.0	71.5	BDL-262	32.5	BDL-69.0
Total LPAHs	503	14.0-1050	422	9-1520	100	35.0-144
Pyrene	323	8.00-637	214	BDL-810	102	BDL-133
Fluoranthene	39.8	2.00-83.0	64.5	BDL-190	10.0	1.00-24.0
Chrysene	293	9.00-605	446	11.0-1670	56.3	1.00-115
Benzo[a]anthracene	28.8	BDL-61.0	1.30	BDL-2.00	7.30	BDL-24.0
Benzo[a]pyrene	263	1.00-485	36.8	BDL-85.0	1.30	BDL-3.00
Benzo[b]fluoranthene	620	7.00-1280	171	BDL-462	15.3	BDL-34.0
Benzo[k]fluoranthrene	790	2.00-1700	99.8	12.0-177	25.0	6.00-47.0
Dibenz[a,h]anthracene	175	6.00-369	133	BDL-223	27.0	3.00-57.0
Benzo [ghi] perylene	240	10.0-505	42.5	BDL-137	30.0	2.00-45.0
Indeno(1,2,3-cd)pyrene	61.0	1.00-128	96.5	BDL-367	7.50	BDL-18.0
Total HPAHs	2830	4.00-5860	1310	23-4130	282	108-484
Total PAHs	3340	18.0-6860	1730	32.0-5640	382	153-660

*BDL: below detection limit

Table 4.4: Concentrations of PAHs ($\mu\text{g}/\text{kg}$) in sediment of the study area

Components	Station 1(IKP)		Station 2(EAC)		Station 3(DHY)		Station 4(NNPC)		Station 5(DCK)	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Naphthalene	3.00	2.00-5.00	9.80	BDL-26.0	52.5	BDL-143	1.50	BDL-3.00	6.50	3.00-10.0
Acenaphthene	3.30	BDL-6.00	28.0	BDL-61.0	2.30	BDL-6.00	0.30	BDL-1.00	2.50	1.00-5.00
Acenaphthylene	66.3	1.00-146	2.80	BDL-8.00	3.30	BDL-6.00	15.0	BDL-55.0	0.50	BDL-1.00
Anthracene	BDL	BDL	121	BDL-376	9.80	1.00-24.0	3.80	BDL-9.00	BDL	BDL
Fluorene	5.80	2.00-9.00	42.3	15.0-87.0	15.5	3.00-17.0	8.50	2.00-12.0	4.80	3.00-8.00
Phenanthrene	1.00	BDL-4.00	1.80	BDL-4.00	4.00	BDL-8.00	13.8	2.00-43.0	14.0	BDL-28.0
Total LPAHs	79.3	5.00-170	206	15.0-562	87.3	4.00-204	42.8	4.00-123	28.5	7.00-52.0
Pyrene	5.80	2.00-8.00	13.8	BDL-35.0	85.3	9.00-93.0	9.50	1.00-21.0	21.0	18.0-29.0
Fluoranthene	3.80	BDL-7.00	55.8	31.0-93.0	6.00	BDL-20.0	1.00	BDL-2.00	5.00	BDL-19.0
Chrysene	69.0	31.0-106	36.3	BDL-72.0	249	27.0-641	95.5	39.0-141	254	86.0-439
Benzo[a]anthracene	1.00	BDL-3.00	154	BDL-318	11.5	1.00-17.0	22.5	BDL-64.0	BDL	BDL
Benzo[a]pyrene	79.5	12.0-150	5.20	BDL-15.0	23.8	BDL-91.0	12.3	BDL-2.00	BDL	BDL
Benzo[b]fluoranthene	38.0	BDL-91.0	0.30	BDL-1.00	27.8	22.0-41.0	216	BDL-432	BDL	BDL
Benzo[k]fluoranthrene	3.30	BDL-8.00	2430	1050-3480	19.5	1.00-41.0	173	12.0-510	367	276-448
Dibenz[a,h]anthracene	12.0	5.00-19.0	14.8	BDL-59.0	33.0	BDL-99.0	8.30	BDL-31.0	25.0	1.00-59.0
Benzo [ghi] perylene	7.80	3.00-13.0	27.3	BDL-87.0	188	10.0-516	82.3	BDL-220	0.30	BDL-1.00
Indeno(1,2,3-cd)pyrene	3.00	1.00-7.00	1.00	BDL-3.00	17.3	1.00-41.0	43.8	27.0-71.0	12.3	BDL-24.0
Total HPAHs	223	54.0-412	2740	1080-4160	661	71.0-1600	664	79.0-1310	684	381-1020
Total PAHs	302	59.0-582	2950	1095-4720	748	75.0-1800	707	83.0-1635	713	388-1070

* BDL: below detection limit

4.1 Physicochemical Characteristics of Surfacewater and Sediment of the Study Area

Tables 4.1 present the results of the pH and conductivity measurement of the surfacewater. The pH and conductivity ranged from 4.28 to 6.48 and from 9.12 to 22.9 $\mu\text{S}/\text{cm}$ respectively. The pH and conductivity values reported in the present study are similar to the pH and conductivity values previously documented for surfacewater system in the Niger Delta area (Oyem, 2013). As can be seen in Table 4.1, the values of pH for water samples collected during the wet seasons were higher than those collected during the dry seasons. The lowest mean pH value was recorded at the Ikpere sample station. With the exception of Ikpere sample station where the pH values recorded were vis-à-vis the PAH concentration, there was no real correlation between the pH values and the PAH concentrations.

Apart from the conductivity recorded at Ikpere sampling station which increased steadily from 11.35 to 22.89 $\mu\text{S}/\text{cm}$, the conductivity recorded for the other two stations were random. One notable observation from the values recorded, is that at the Ikpere station where the conductivity values increased steadily, the concentration of PAHs recorded increased in opposition direction.

The pH of the examined sediment samples ranged between 4.16 and 6.58. The lowest sediment pH was recorded at the dehydration area, while the highest sediment pH was at the NNPC tank area. Contrary to the surfacewater pH the values of sediment pH collected during the dry seasons were higher than that of the wet seasons except site 5 (Dock entrance). Electrical conductivity of the sediment samples ranged between 3.53 and 20.1 $\mu\text{S}/\text{cm}$. The pH and conductivity values reported for sediment in the present

study corresponds to pH and conductivity values previously documented in the Niger Delta area (Oyem, 2013).

Total organic carbon (TOC) of the various sediment samples collected at different period ranges from 1.53 to 4.81 %. The TOC values recorded in this study corresponds with previously documented TOC values for sediments in the Niger Delta (Sojinu et al., 2010). The sediment TOC values increased steadily from Ikpere (being the lowest) to dehydration, averaging 1.71, 2.40, 2.82, 3.47 and 3.65 % for Ikpere, Dock entrance, NNPC tank area, Entrance of Arunton creek and Dehydration respectively. There was a significant difference (1.95 %) between the mean values of TOC recorded at the Ikpere sampling station and that recorded at the Dehydration area of Arunton creek.

4.2 PAHs in Surfacewater from Arunton Creek and River Escravos

The concentrations of the 16 polycyclic aromatic hydrocarbon (PAH) components analysed in the surface water and sediments of the study are shown in Tables 4.3 and 4.4. In terms of surfacewater, the total concentration of PAHs for the three sites ranges from 382 µg/L at Escravos dock entrance to 3340 µg/L at the Ikpere sampling station. As far as individual PAHs are concerned, all the components analysed in surface water samples were detected in all the sites. Calculation of total mean values for the sites showed that benzo[k]fluoranthrene and benzo[b]fluoranthrene were the most abundant PAHs in the surfacewaters with mean values of 25.0, 99.8, 790 and 15.3, 171, 620 µg/L respectively. At the same time, the lowest concentrations of PAHs recorded, that is the least dominant PAHs were related to benzo[a]anthracene and anthracene with associated mean values of 1.30, 7.30, 28.8 and 0.50, 0.80; 41.0 µg/L.

In terms of individual PAHs, the highest concentration was recorded at the Ikpere site. Benzo[k]fluoranthrene with associated mean value of 790 µg/L was the highest individual PAH recorded in surfacewater. On the other hand, the lowest concentration of PAHs recorded in the surface water was at the Escravos dock entrance. The concentration of PAHs reported in this present study is similar to the concentration of PAHs previously documented for surfacewater in the Niger Delta (Opuene *et al.*, 2009).

The high concentrations of PAHs recorded at the Ikpere surfacewater site can be attributed to the prevalence of speed boats which is the major source of transportation in this area. There could be spillage of varying amount of fuel into water during the course of fueling and refueling, emission from boat exhausts, and spillage of

petroleum products from local storage facilities clustered around this site in addition to other sources of PAHs emission.

The total concentrations of PAHs recorded in surfacewater during the wet season were clearly higher than the total concentrations of PAHs observed in the dry season in all the sites (Figure 4.1), except site 2 (Dehydration) where the total concentration of PAHs observed was higher in the dry seasons. This may be attributed to the effects of runoff from multiple sources during the raining seasons and photo oxidation, volatilization and high degradation during the dry seasons. High temperatures and high solar irradiation might promote PAH degradation (Smith and Harrison, 1998; Panther *et al.*, 1999, Beyer *et al.*, 2003) due to chemical and photochemical reactions which favours PAH reduction in hot season. This observation is consistent with the findings of other researchers (López Cancio *et al.*, 2002, Fang *et al.*, 2004, Kitazawa *et al.*, 2006).

Generally, the total PAHs recorded in this present study were significantly higher than the WHO recommended safety limit of 0.05 µg/L. The individual concentrations recorded were also notably higher than their corresponding US-EPA maximum contaminant levels; indicating that the water body is contaminated. Similar high levels of PAHs have also been reported in surfacewaters in Nigeria (Opune *et al.*, 2009). Ogunfowokan *et al.*, (2003), recorded even higher PAHs levels at the Osogbo and Ile-Ife area, and industrial Lagos.

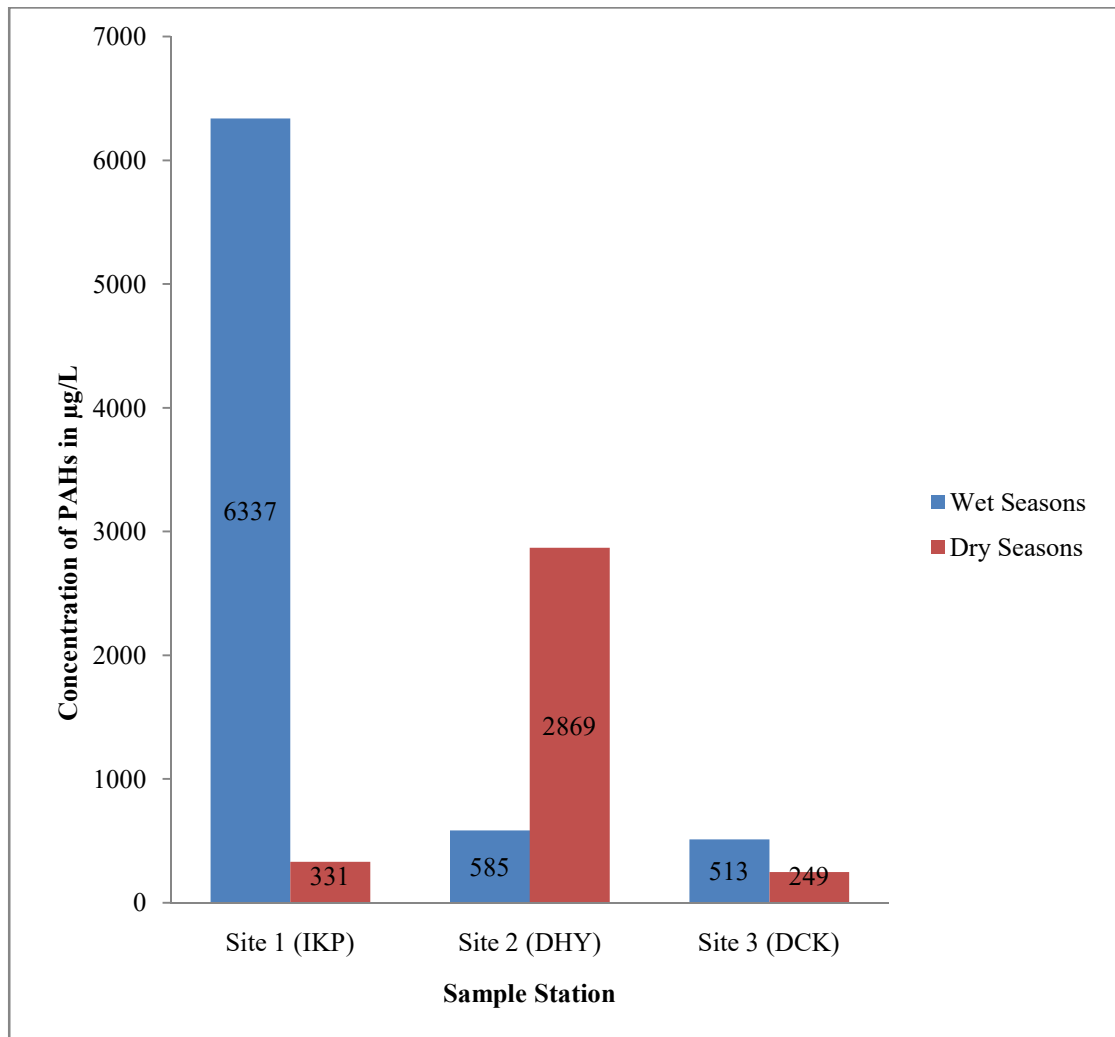


Figure 4.1: Comparison of total mean concentration of PAHs in surfacewater samples for Wet and Dry seasons.

4.3 Distribution of PAHs in Surfacewater

The results as shown in Table 4.3 indicates that the concentrations of low molecular weight PAHs (LPAHs) in the surfacewater of Arunton creek was lower than the concentrations of high molecular weight PAHs (HPAHs) recorded, meaning that HPAHs rather than LPAHs is more abundant in the surfacewater. The associated mean values recorded in the three sampling stations for LPAHs and HPAHs are 100, 422, 503 and 282, 1310, 2830 $\mu\text{g/L}$ respectively.

In terms of frequency of occurrence, 2-ring, 3-ring, 4-ring, 5-ring and 6-ring PAHs were persistent in all the surfacewater sites, however, not all of them were persistent throughout the sampling period. Naphthalene, acenaphthylene, chrysene, benzo[k]fluoranthrene and benzo [ghi] perylene were the only 2-ring, 3-ring, 4-ring, 5-ring and 6-ring PAHs that were persistent all through the period of the study.

The distribution pattern of the 16 PAHs by ring size in the surfacewater of the study area is presented in Figures 4.2 and 4.3. Figure 4.2 is the percentage distribution (by ring size) of PAHs in the three sampled sites, while figure 4.3 is the percentage of total mean concentration of 2-3ring, 4-ring, 5-ring and 6-ring PAHs in the surface water of the study area. The column (Fig. 4.2) clearly showed that 4-ring and 5-ring PAHs were the dominant contributors to the total PAHs across the three sites. At site1 (Ikperere) 5-ring PAHs were the most dominant contributing 55.4 % to the sum total of the 16 PAHs while at site 2 (Dehydration), 4-ring PAHs (pyrene, fluoranthene, chrysene and benzo[a]anthracene) were the most abundant, contributing 42% of the total PAHs recorded. At the same time, 6-ring PAHs (benzo [ghi] perylene and indeno[1,2,3-cd]pyrene) were the least abundant not just in site1 but across the three stations with associated values of 9, 8 and 9.8 % respectively. At 46 % 4-ring PAHs

were the most dominant contributor to the sum total of the 16 PAH. The percentage contribution of 2-3-ring PAHs across the three sites are 15.1, 24.5 and 26.2 % respectively.

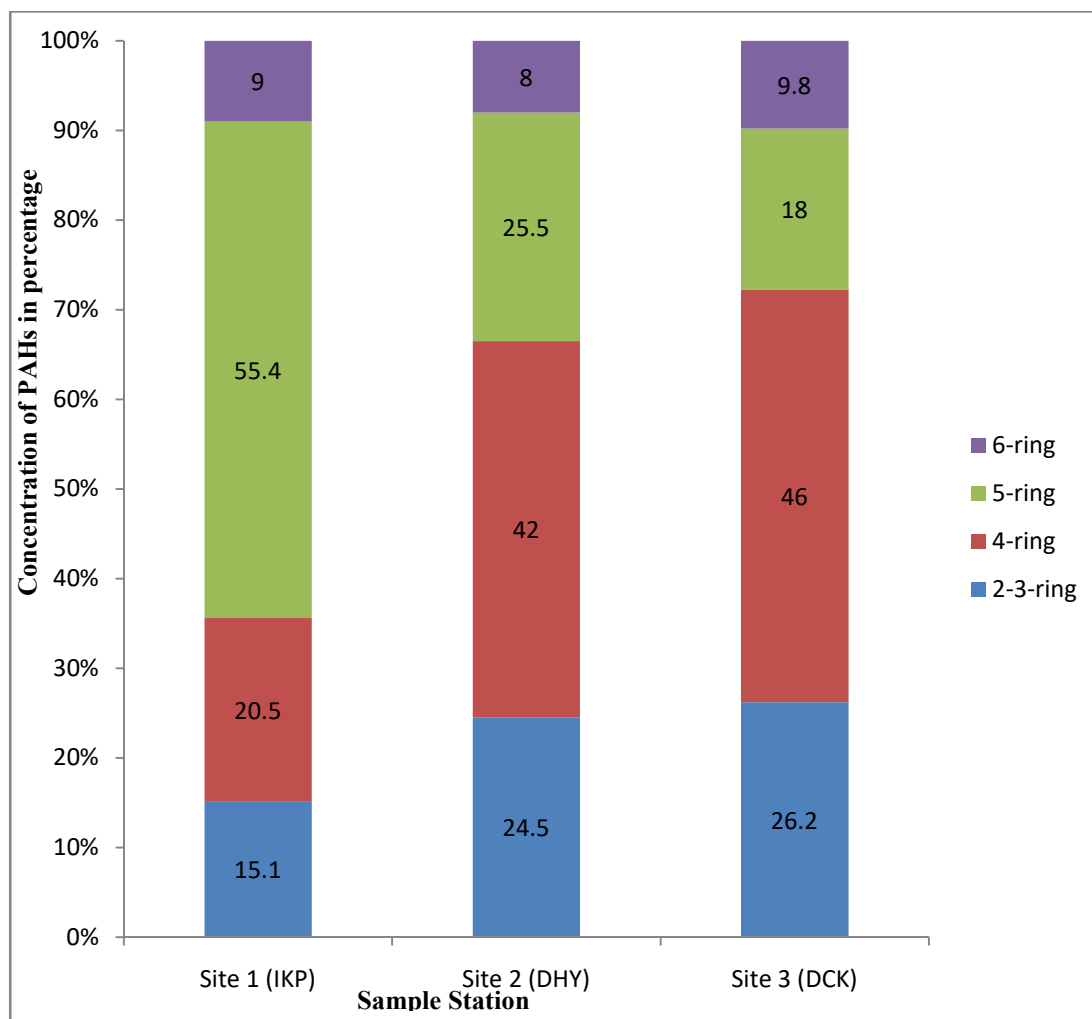


Fig 4.2: Percentage distribution (concentration) of 2/3-ring, 4-ring, 5-ring and 6-ring PAHs in three sample stations of the study area- surfacewater.

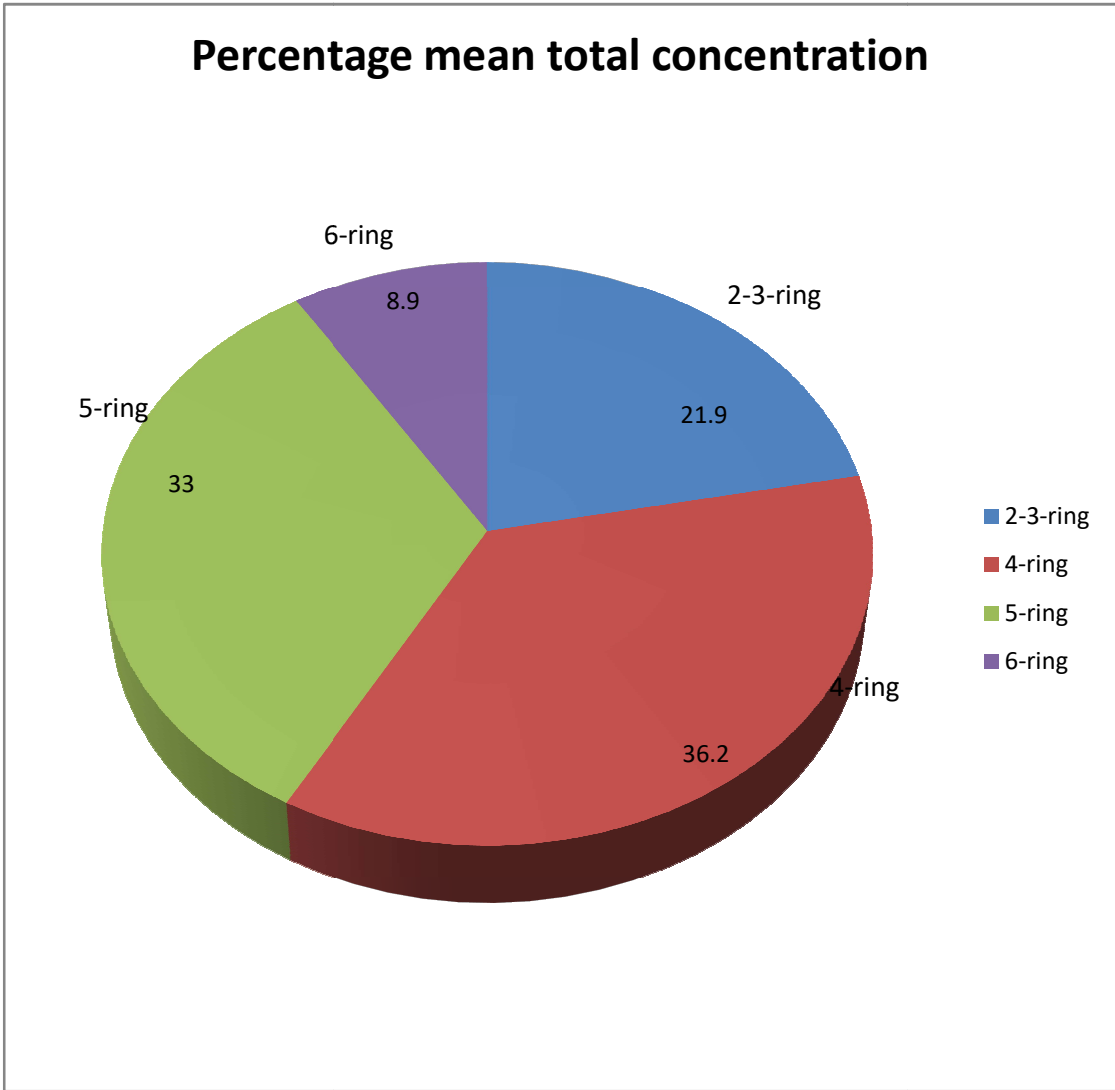


Fig 4.3: The percentage of mean total concentration of 2-3-ring, 4-ring, 5-ring, and 6-ring PAHs in surfacewater of the study area.

The percentage of total mean PAHs as shown in the Figure (4.3), showed that 4-ring PAHs were the most abundant in the surface water of Arunton creek with 36.2 %. The 4-ring PAHs were closely followed by 5-ring (33%) and 2-3-ring (21.9%). At 8.9%, 6-ring PAHs (indeno [1,2,3-cd] pyrene and benzo [ghi] perylene) were the least abundant.

The concentration distribution pattern observed here may be attributed to volatility, molecular weight of PAHs, and photooxidation in the study area. Low molecular weight PAHs are easily degraded in open and temperate water body due to their volatility. Quick volatilization and photodecomposition process will alter the concentration composition pattern of low molecular weight PAHs in such body of water, thereby reducing the concentrations of the LPAHs. Two to 3-rings are very volatile, while PAHs with 4 or more rings show insignificant volatilization loss under all environmental conditions (Moore and Ramamoorthy, 1984). The solubility of PAHs decreases as the k_{ow} and molecular weight increases (Djomo *et al.*, 1996). This implies that 6-ring PAHs with higher k_{ow} and molecular weight than the 4-ring and 5-ring will have lesser concentration in surface water as they will tend to settle faster to the bottom sediment. On the other hand, 4-ring and 5-ring PAHs, because of their lower k_{ow} and molecular weight values will dissolve more easily in water compared to 6-rings; which accounts for their high concentration in surfacewater of the study area. Microbial degradation and the effects of treated oil waste are likely to also play major role in the observed distribution pattern, as Lee *et al.*, (1978), reported no degradation of benzo[a]pyrene (a five ring PAH) from controlled or oil-treated ecosystem enclosure.

4.4 PAHs Source Identification

4.4.1 PAHs Isomeric Ratio Analysis (Water)

The two major sources of anthropogenic PAHs pollutants-petrogenic and pyrogenic have been successfully differentiated. The first important step, and sometimes the only step, is the differentiation of petrogenic PAHs from pyrogenic PAHs (Boehm *et al.*, 2008). The sources of PAHs, whether from fuel combustion (pyrolytic) or from crude oil (pyrogenic) contamination, may be identified by ratios of individual PAH compounds based on peculiarities in PAH composition and distribution pattern as a function of the emission source (Kafilzadeh *et al.*, 2011). This involves the determination of a number of quantitative diagnostic ratios of source specific marker PAH components. The ratio of four of the priority PAHs (phenanthrene/anthracene) and (fluoranthene/pyrene) have both been used to begin the process of differentiation between sources (phenanthrene/anthracene >10 signifies a probable petrogenic origin for the sample, while phenanthrene/anthracene <10 indicates probable pyrogenic origin) (Boehm *et al.*, 2008). According to (Anyakora *et al.*, 2011), phenanthrene/anthracene (Ph/An), fluoranthene/pyrene (Fl/Py), benzo[a]anthracene/chrysene (BaA/Chry), phenanthrene/(phenanthrene+anthracene) and indeno(1,2,3-cd)pyrene/(indeno(1,2,3-cd)pyrene+benzo(g,h,i)perylene), may be used to distinguish petrogenic PAHs from the other sources. For the Fl/Py ratio, values greater than one (Fl/Py >1) have been used to indicate pyrolytic origin and values less than one (Fl/Py <1) are attributed to petrogenic source (Qiu *et al.*, 2009). The ratio of LPAHs/HPAHs greater than 1 is suggestive of petroleum origin while ratio less than 1 is of pyrolytic processes (Witt *et al.*, 1999, Soclo *et al.*, 2000, Emoyan *et al.*, 2015). The Fl/Fl+Py ratio presumes that ratios in the range ≥ 0.4 and

≤ 0.5 indicate petroleum combustion, ratios < 0.4 indicate petroleum sources while ratios > 0.5 indicate grass, wood and coal combustion. BaA/BaA+Chry presumes that ratios < 0.2 are of petroleum origin, ratios in the range ≥ 0.2 and ≤ 0.35 as mixed sources and > 0.35 as combustion sources. Lastly, Ind/(Ind+BghiP) presumes that PAHs ratios < 0.2 indicate petroleum sources, ratios in the range ≥ 0.2 and ≤ 0.5 as petroleum combustion sources and > 0.5 as grass, wood and coal combustion sources (Yunker *et al.*, 2002; Olajire *et al.*, 2005, Morillo *et al.*, 2008; Inengite *et al.*, 2010b).

Table 4.5: Isomeric ratio of PAHs in surfacewater of the study area

Stations	Fl/Py	Ph/An	Fl/(Fl+Py)	Ind/Ind+B[ghi]P	LPAHs/HPAHs
Site 1	0.17	1.08	0.1	0.2	0.18
Site 2	0.3	95.3	0.2	0.7	0.32
Site 3	0.11	65	0.1	0.2	0.35

The ratios as explicitly shown in Table 4.5 and 4.6 are used in this present study to differentiate between petrogenic and pyrogenic sources of PAHs. The Fl/Py ratio for the three water sample sites were 0.3, 0.17 and 0.11; while the corresponding values for Ph/An ratio were 95.3, 1.08 and 65 respectively. In water, the values for Fl/Py ratio were all less than one, indicating probable petrogenic sources. At the same time, ph/An value (> 10) for Dehydration and Dock entrance sites, points to petrogenic source, which agrees with the Fl/Py ratio for the two sites. The Dehydration and Dock entrance surface waters showed very high petrogenic input sources (Ph/An value of 95.3 and 65). Ph/An ratio of 1.08 (< 10) for Ikpere site, which denotes probable pyrogenic source, is contrary to the Fl/Py diagnostic ratio of < 1 (petrogenic). The high petrogenic input observed at the Escravos dock entrance can be attributed to bunker and shipping activities, while that of the dehydration may be related to continuous, and direct discharge of petroleum waste water generated from the dehydration plant;

where crude oil mixed with water, mud and other impurities are separated. The Flt/(Flt+Py) ratio (0.1-0.2) points to petrogenic source for all the surface water sample sites. The Ind/(Ind+B[ghi]P) isomeric ratios calculated for surface water, indicate petroleum combustion sources (pyrolytic) for sites 1 and 3 while the value of 0.7 for site 2 is indication of wood, grass and coal combustion. LPAHs/HPAHs ratios of <1 (0.18-0.35) for all the water sample sites suggest pyrolytic input source. The contradictory isomeric ratios (Table 4.5) indicate that PAHs contaminants in surfacewater of the study area were from petroleum and combustion sources. This is consistent with documented PAHs sources in the Niger Delta (Anyakora *et al.*, 2011)

Although these ratios are usable for differentiation of pyrogenic and petrogenic sources, they are not definitive, since several exceptions have been found (Sany *et al.*, 2014). Definitive PAHs investigations need to go beyond such screening criteria (Boehm *et al.*, 2008). More sophisticated statistical approaches have been demonstrated, including cluster analysis, principal components analysis (PCA), and chemical mass balance (CMB) (Liu *et al.*, 2009).

4.4.2 PAHs Source Identification from Principal Component Analysis

a) Principal Component Analysis (PCA) of PAHs in Water

The PCA is a multivariate statistical analysis, whose purpose is to represent the total variability of the original PAH data with a minimum number of factors. By critically quantifying the percentage of contribution of individual PAH sources and identifying the occurrence of the sources responsible, each factor can be realized (Liu *et al.*, 2009, Waag *et al.*, 2011, Zhang *et al.*, 2012, Sany *et al.*, 2014). The data in this study were analysed using PCA with Varimax –normalised rotation to facilitate an estimate of the

pollution sources of the PAHs. The PCA results of water and sediment samples are displayed in Tables 4.6 and 4.10 and Figures 4.4 and 4.8 respectively.

Table: 4.6: PCA Factor loadings after Varimax with Kaiser Normalization Rotation for water.

PAH Compound	Component	
	Factor 1	Factor 2
Nap		.990
Acy	1.000	
Ace	.999	
Ant	1.000	
Flu	.832	.555
Phen		.987
Pyr	.888	.460
Flt		.994
Chry		.984
BaA	.966	
BaP	.997	
BbF	.981	
BkF	.999	
DahA	.755	.655
BghiP	1.000	
IndP		.985
% Variance	66.11	33.89

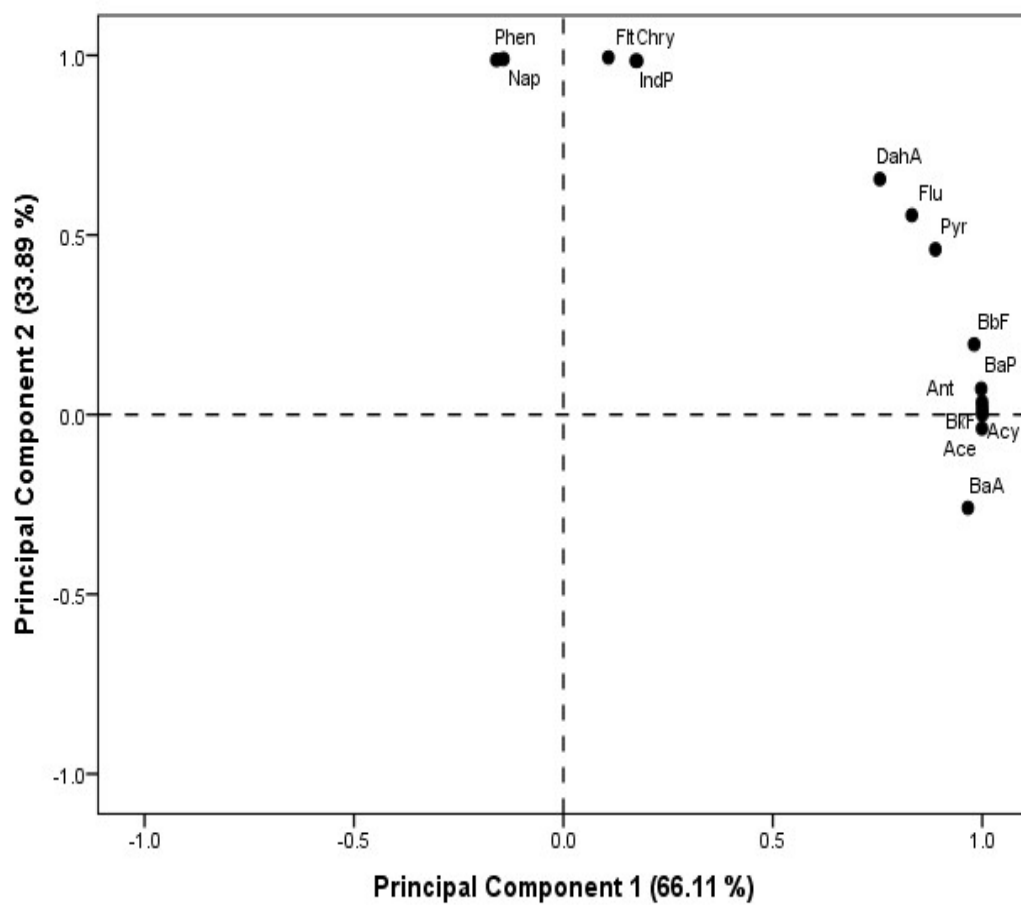


Figure 4.4: The loading plot of PCA for water

b) PCA of Water Samples

PCA, which can provide information on source contributions, in conjunction with multivariate linear regression (MLR), has been performed to identify and apportion PAH sources in the air, soil, and sediment in many cities (Harrison *et al.*, 1996; Larsen and Baker, 2003; Li *et al.*, 2006b; Zuo *et al.*, 2007). For water samples, two factors were identified which accounts for 100 % of the total variability in the data set. Factor 1 constituted 66.11 % of the total variance and was loaded with Acy, Ace, Ant, Flu, Pyr, BaA, BaP, BbF, BkF, DahA and BghiP. This confirms the results of the correlation analysis as these PAH compounds showed high correlation. Acy, Ace, Ant, Flu and BbF are products of wood combustion (Yang *et al.*, 2012), Pyr and BaP are products of coal combustion (Larsen and Baker, 2003); BaA is a product of diesel combustion (Khalili *et al.*, 1995). BkF is a product of incomplete combustion and pyrolysis of (gasoline) fuel (Chen *et al.*, 2009), while DahA and BghiP are from traffic emissions. Thus, factor 1 indicates that the source of PAHs in the water samples is attributable to fossil fuels combustion and traffic emissions. Factor 2 contributed 33.89 % of the total variance and was characterised by high loadings of Nap, Phen, Flt, Chry and IndP and moderate loadings of Flu and DahA. Nap is a product of combustion of wood related sources (Dong and Lee, 2009), Phen and Flt are products of wood combustion and coal combustion respectively (Larsen and Baker, 2003; Yang *et al.*, 2012). Chry is a product of diesel and natural gas combustion (Khalili *et al.*, 1995) while IndP is a product of traffic emissions (Yang *et al.*, 2012). Factor 2 showed that the PAHs are from wood, diesel and natural gas combustion as well as traffic emissions. The traffic emission is due to the exhaust emission from cargo vessels, ships, oil barges, speed boats and other types of ferries

largely operated in this area. The PCA analysis, suggest that PAHs in surface water of the study area are mainly from combustion sources.

c) Correlation Analysis of PAHs in Water Samples

Correlation analysis (Table 4.7) reveals correlation between some individual PAHs related to pyrogenic and petrogenic compounds. A significant correlation implies that the matrixes are polluted by anthropogenic sources of PAHs; because unpolluted samples do not exhibit an oil fingerprint, and only some PAH compounds may be found in this (sediment) matrix (Zakaria *et al.*, 2002, Safari *et al.*, 2010). In this study, correlation analysis was performed to identify the relationship among the PAHs and to determine possible similar sources. The concentrations of PAHs were assessed using Pearson's correlation coefficients. Correlation values higher than 0.50 were considered significant.

The correlation results of PAHs in the water samples are displayed in Table 4.7. Correlation analysis of the PAHs indicates strong positive correlation ($r^2 > 0.50$) between PAH compounds. The significant positive correlations between these PAHs revealed that they are from a common source such as incomplete combustion of wood, coke, diesel, coal and traffic emissions.

Table 4.7: Correlation analysis for water samples

	Nap	Acy	Ace	Ant	Flu	Phen	Pyr	Flt	Chry	BaA	BaP	BbF	BkF	DahA	BghiP	IndP
Nap	1.000	0.135	-0.181	-0.122	0.430	1.000*	0.328	0.969*	0.949*	-0.395	-0.072	0.053	-0.108	0.540**	-0.144	0.950*
Acy		1.000	0.999*	1.000*	0.837*	-0.151	0.892*	0.116	0.185	0.963*	0.998*	0.982*	1.000*	0.761*	1.000*	0.182
Ace			1.000	0.998*	0.810*	-0.198	0.870*	0.069	0.138	0.975*	0.994*	0.972*	0.997*	0.729*	0.999*	0.135
Ant				1.000	0.844*	-0.139	0.898*	0.129	0.197	0.960*	0.999*	0.985*	1.000	0.769*	1.000*	0.194
Flu					1.000	0.415	0.994*	0.641**	0.693**	0.659**	0.870*	0.924*	0.851*	0.992*	0.832*	0.690**
Phen						1.000	0.312	0.964*	0.943*	-0.411	-0.089	0.036	-0.125	0.526**	-0.161	0.945*
Pyr							1.000	0.553**	0.609**	0.738*	0.919*	0.961*	0.904*	0.972*	0.888*	0.606**
Flt								1.000	0.998*	-0.154	0.178	0.300	0.142	0.733*	0.107	0.998*
Chry									1.000	-0.086	0.246	0.365	0.211	0.778*	0.176	1.000*
BaA										1.000	0.945*	0.896*	0.956*	0.559**	0.966*	-0.089
BaP											1.000	0.992*	0.999*	0.800*	0.997*	0.243
BbF												1.000	0.987*	0.869*	0.981*	0.362
BkF													1.000	0.778*	0.999*	0.207
DahA														1.000	0.755*	0.776*
BghiP															1.000	0.172
IndP																1.000

**Pearson Correlation is significant at the 0.05 level (1 tailed)

*Pearson Correlation is significant at the 0.01 level (1 tailed)

4.5 Risk Assessment of PAHs in Surfacewater

To evaluate the risk associated with carcinogenic PAHs exposure, the assessment of the carcinogenic and mutagenic potential of PAH was carried out by calculating the carcinogenic equivalent concentrations (BaP-TEQ) and the mutagenic equivalent concentrations (BaP-MEQ) relative to BaP, respectively. Both were calculated by multiplying the toxic equivalent factors (TEF) suggested by Larsen and Larsen (1998), (Callén *et al.*, 2014) and the mutagenic potency factors (MEF) (Durant *et al.*, 1996, 1999) by the concentration of each individual PAH in a sample.

The BaP carcinogenic equivalent (BaP_{TEQ}) for the individual PAHs was calculated using the equation:

$$\text{BaP}_{\text{TEQ}} = \sum C_i \times \text{BaP}_{\text{TEF}}$$

Where BaP_{TEF} is the cancer potency relative to BaP and C_i is the individual PAH concentration.

The BaP mutagenic equivalent (BaP_{MEQ}) for the individual PAHs (Table 4.8) was evaluated using the equation:

$$\text{BaP}_{\text{MEQ}} = \sum C_i \times \text{BaP}_{\text{MEF}}$$

Where BaP_{MEF} is the mutagenic potency relative to BaP and C_i is the individual PAH concentration.

The results of the carcinogenic and mutagenic potentials are shown in Table 4.8.

Table 4.8: BaPTEQ and BaPMEQ of PAHs in water

	Chry	BaA	BaP	BbF	BkF	DahA	IndP	BaPTEQ	Chry	BaA	BaP	BbF	BkF	DahA	IndP	BaPMEQ
Site1	0.29	2.88	263.00	62.00	7.90	175.00	6.10	2230.80	4.98	2.36	263.00	155.00	86.90	50.75	54.25	617.24
Site2	0.45	0.13	36.80	17.10	1.00	133.00	9.60	983.90	7.58	0.11	36.80	42.75	10.98	38.57	41.23	178.02
Site3	0.06	0.73	1.30	1.53	0.25	27.00	0.75	139.70	0.96	0.60	1.30	3.83	2.75	7.83	8.37	25.63

The BaP toxic equivalency factors (BaP_{TEFs}) of the seven carcinogenic PAHs used are BaP (1), BaA (0.1), BbF (0.1), BkF (0.01), Chry (0.001), DahA (1) and IndP (0.1) (USEPA, 1993) while the BaP_{MEFs} are BaP (1), BaA (0.082), BbF (0.25), BkF (0.11), Chry (0.017), DahA (0.29) and IndP (0.31) (Durant, 1996). $BaP-TEQ$ for \sum_{Con}^{H2o} 7PAHs ranged from 139.70-2230.80 while the $BaP-MEQ$ for \sum_{Con}^{H2o} 7PAHs ranged from 25.63-617.24. The largest contribution of individual PAHs to carcinogenic risk potential was DahA, accounting for 45%. BaP was the next big individual contributor to carcinogenic risk with 41%, while BaP is the largest contributor to mutagenic risk. The risk assessment in this study indicates contamination of the water system with high potential for toxicity sufficient enough to induce carcinogenic effect when exposed.

4.6 PAHs in Superficial Sediment from Arunton Creek and River Escravos

The individual and total concentrations of the 16 PAH components analysed in sediments of the study area are clearly shown in Table 4.4. The total concentration of PAHs analysed in the sediments ranges from 302 to 2950 $\mu\text{g}/\text{kg}$ dry weights, with mean value of 1084 $\mu\text{g}/\text{kg}$. As far as individual PAHs are concerned, most of the analysed components were detected in all the sites except Ikpere and the Escravos dock entrance. Anthracene was not detected at all at Ikpere sediment while benzo[a]pyrene, benzo[a]anthracene and benzo[b]fluoranthene were not detected at the Escravos dock entrance sediment. In terms of individual PAH concentration, the result indicates that benzo[k]fluoranthrene (5-ring) and chrysene (4-ring) were the highest (dominant) pollutants in the sediment of the study area, with mean values of 3.30, 19.5, 173, 367, 2430 and 36.3, 69, 95.5, 249, 253.5 $\mu\text{g}/\text{kg}$ across the five sample stations. On the contrary, the least dominant PAHs across the five sites were

phenanthrene and acenaphthene with associated mean values of 1.00, 1.70, 4.00, 13.8, 14.0 and 0.30, 2.30, 2.5, 3.30, 28.0 $\mu\text{g}/\text{kg}$ respectively. The total concentration of sediment PAHs recorded in this present study is within range of previously documented data in the Niger Delta (Duke, 2008).

The total concentration of PAHs in sediment samples collected during the wet and dry seasons as shown in Figure 4.5, revealed that total concentration of sediment PAHs recorded were higher during the wet seasons in all the sites except site 5 where the concentration of total PAHs observed was slightly higher during the dry seasons. Similar to the surface water, the observed concentration difference in sediment PAHs may be attributed to the effects of runoff from multiple sources during the raining seasons and photo oxidation, volatilization and high degradation associated with hot seasons. High temperatures and high solar irradiation might promote PAH degradation (Beyer *et al.*, 2003; Smith and Harrison, 1998; Panther *et al.*, 1999) as result of chemical and photochemical reactions which favours PAH reduction in hot season.

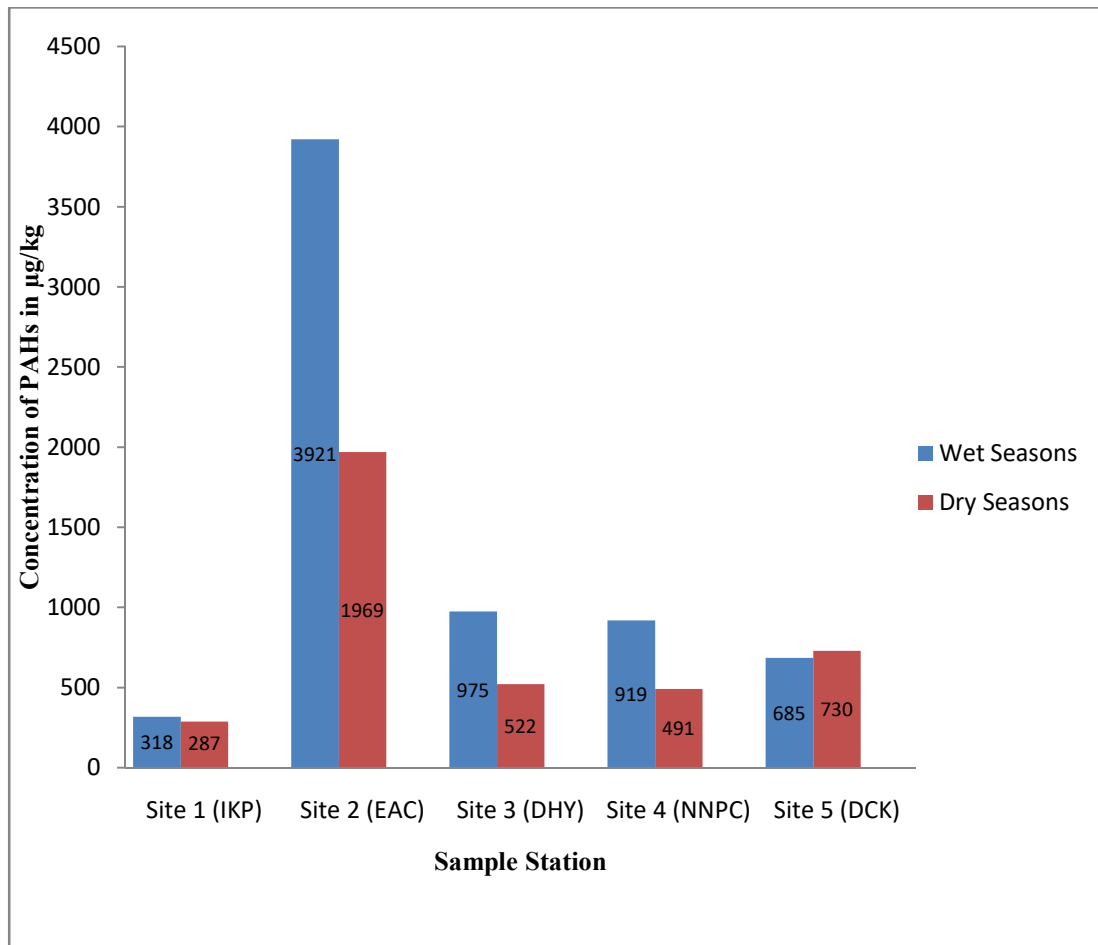


Figure 4.5: Comparison of total mean concentration of PAHs in superficial Sediment samples for Wet and Dry seasons.

4.7 Distribution of PAHs in Sediment

The composition pattern of PAHs by molecular weight showed that HPAHs were more dominant than LPAHs in the sediments of the study area. The composition pattern observed in the sediment is similar to that observed in the surface water of the same creek, where HPAHs rather than LPAHs were the dominant pollutant. The concentration distribution pattern observed in the sediments however, similar to that of the surface water is consistent with previously reported total HPAHs and LPAHs in sediments (Nasr *et al.*, 2010, Kafilzadeh *et al.*, 2011). The total concentration values recorded for HPAHs and LPAHs in the five sediment sites were 223, 661, 664, 684, 2740 and 28.5, 42.8, 79.25, 87.3, 206 $\mu\text{g}/\text{kg}$ dry weight. Mean total value of 994 $\mu\text{g}/\text{kg}$ dry weight HPAHs and 88.9 $\mu\text{g}/\text{kg}$ dry weight LPAHs clearly showed the dominance of HPAHs over LPAHs in the sediments of Arunton creek.

In terms of frequency of occurrence, Fluorene a 3-ring PAH was the most persistent PAHs in the sediment of the study. Fluorene was the only PAH that occurred in all the sites throughout the period of the study. The 4-rings, chrysene and pyrene were persistent throughout the period of the study in all the sites except site 2. Benzo[k]fluoranthrene (5-ring) which had the highest concentration of sediment PAHs also showed persistence in four sites out of the five sampled sites. 2-ring naphthalene occurred consistently only in site 1 all through the period of this study.

The distribution pattern of PAHs by ring size in the sediments of Arunton creek is shown in Figures 4.6 and 4.7. Figure 4.6 represent the percentage distribution of PAHs in the five sediment samples sites while Figure 4.7 is the percentage of total mean distribution. The column distribution (Fig.4.6) indicates that sediments of the study area were mostly dominated by 5-ring and 4-ring PAHs. 4-ring PAHs were the

most abundant PAHs at the dehydration sample site, and closely followed by 5-ring PAHs. Ikpere, Arunton creek entrance, NNPC and Escravos dock entrance sites were dominated by 5-ring PAHs. At 1, 1.8 and 3.6%, 6-ring PAHs were clearly the least dominant in sites 2 (EAC); 5 (DCK) and 1 (IKP) sediments respectively while 2-3-ring were the least dominant PAHs in sites 3 (DHY) and 4 (NNPC).

The percentage total mean distribution (Fig.4.7) showed that 5-ring PAHs were the overall most dominant PAHs in the sediments of the study area as they constituted 50.8% of total mean distribution of sediment PAHs. The 5-ring PAHs were closely followed by 4-ring PAHs, which make up 27.9% of total PAHs concentration. 2-3-ring and 6-ring PAHs contributed 11% and 10.3% respectively. The distribution pattern recorded in this study is similar to previously documented sediment PAHs distribution in the Niger Delta (Inengite *et al.*, 2012). Four-ring PAHs dominated in sediments from San Francisco Bay, USA (Pereira *et al.*, 1996) and Kor River in Iran (Kafilzadeh *et al.*, 2011). Four-ring PAHs dominated the sediment of Hangzhou city, and three-ring showed dominance in Yuanpu and Zhakou (Chen *et al.*, 2004).

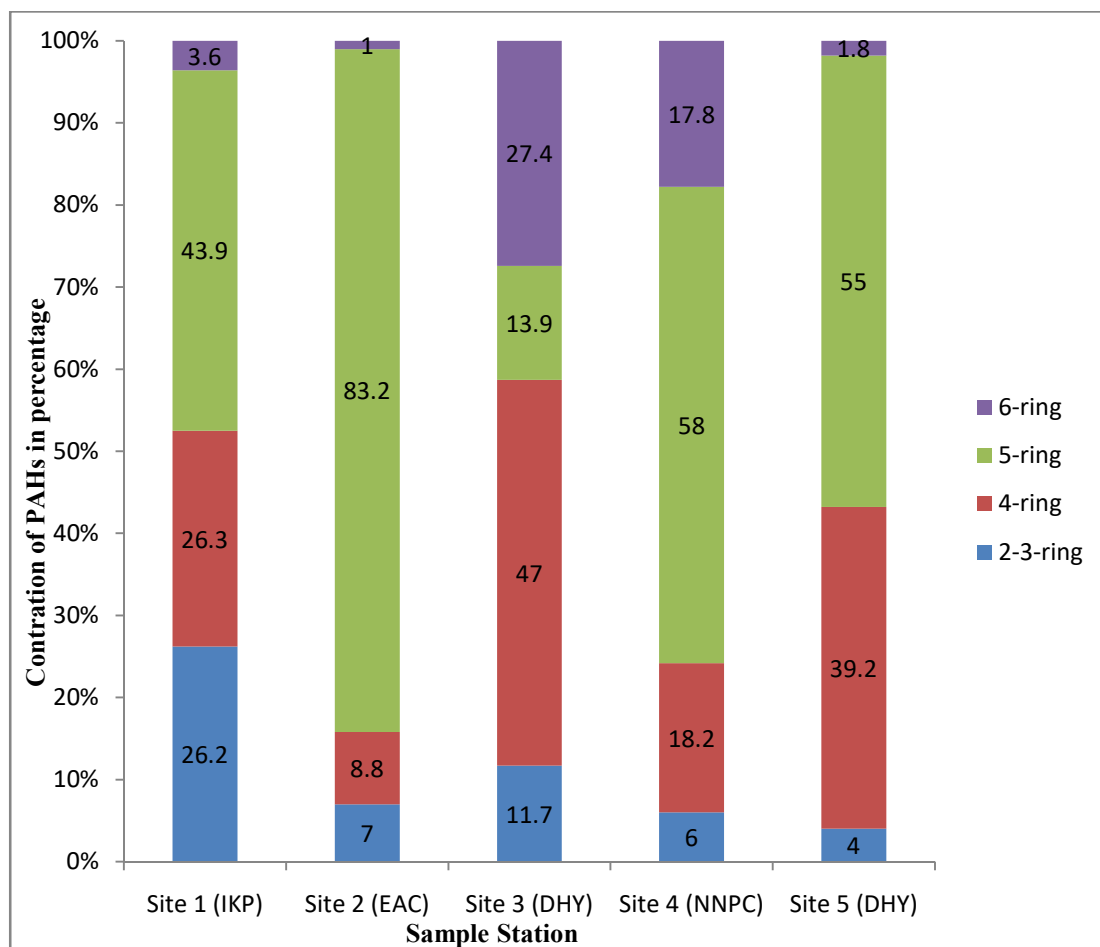


Fig 4.6: Percentage distribution (concentration) of 2/3-ring, 4-ring, 5-ring and 6-ring PAHs in five sample stations of the study area-surface sediments.

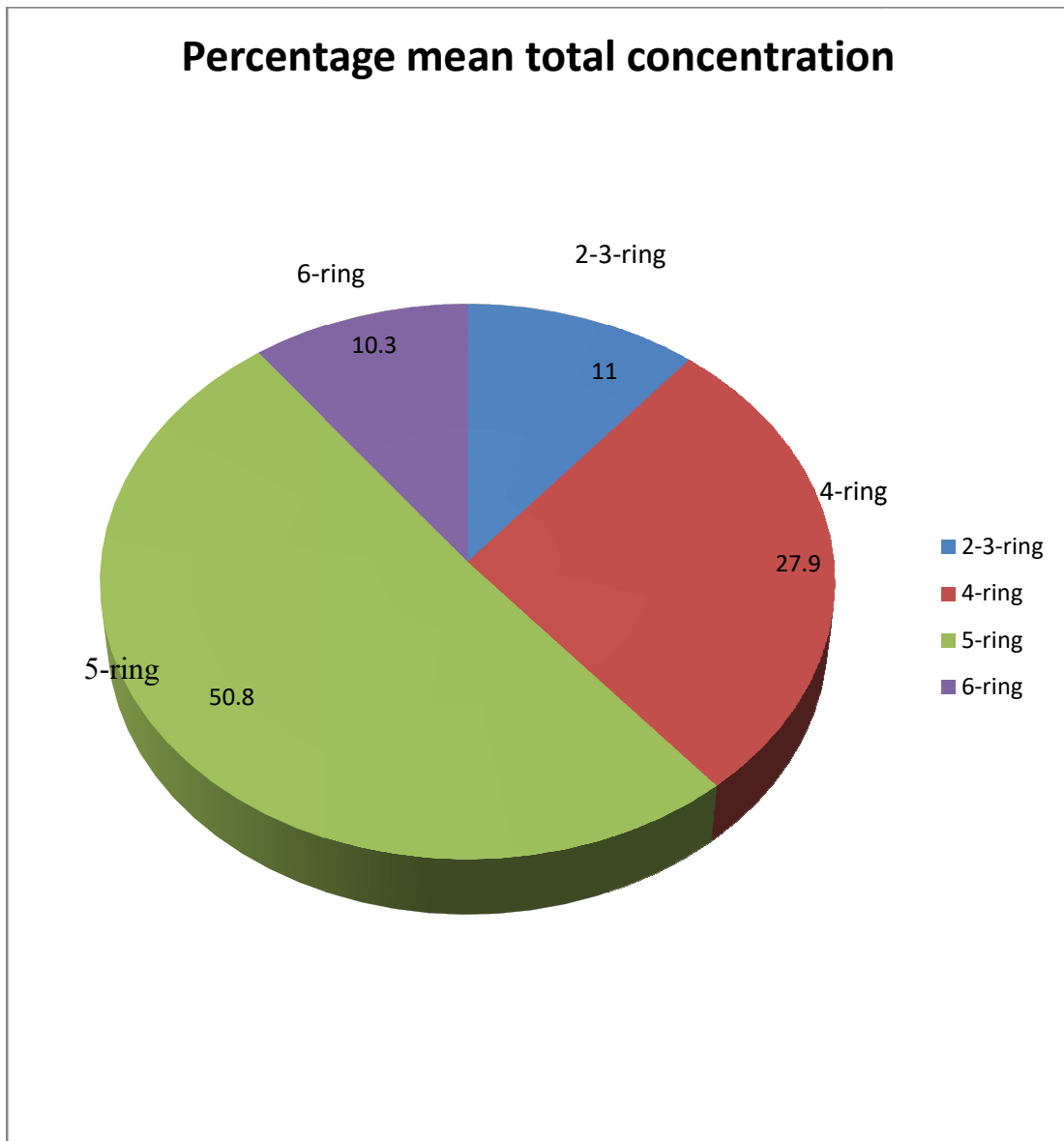


Fig 4.7: The percentage of mean total concentration of 2-3-ring, 4-ring, 5-ring, and 6-ring PAHs in superficial sediment of the study area.

The different pattern of sediment PAHs contaminant abundant observed in this study may be attributed to PAHs input sources, molecular weight, sorption, microbial degradation and the persistence of sorbed PAHs to degradation. Both sediments and water are known to receive direct PAHs input from various sources (pyrolytic and petrogenic), and even non-point sources such as leaching or runoff. One of the most important determinants of PAHs distribution pattern is the molecular weight; this is because degradation and even sorption depends on it. The importance of high molecular mass PAHs has been commonly observed in sediments from marine and lacustrine environments (Bates *et al.*, 1987). While the low molecular mass PAHs are degraded rapidly in sediments, the higher molecular mass PAHs are more resistant to degradation. Sorbed PAHs, usually 4-ring, 5-ring and 6-ring PAHs are more resistant to degradation process, as such are degraded slowly in sediments.

In addition, processes such as biodegradation will attack PAHs in sediments, leaving behind those PAHs that are resistant to degradation (Nasr *et al.*, 2010). According to Usha, (1989), most sediment deposition occurs below the photolytic zone, and the primary factor affecting the persistence of deposited PAHs is microbial degradation. Microbial degradation therefore, is the most important degradation in sediments. Sediments contain complex communities of bacteria, fungi and algae which are known to degradation PAHs. Bacteria play by far the most prominent role in complete mineralization of PAHs (Kafilzadeh *et al.*, 2011). Therefore, the microbial composition of aquatic sediment will more likely determine the PAHs distribution pattern/contaminant abundant.

4.8 PAHs Sources Identification in Superficial Sediment

4.8.1 PAHs Isomeric Ratio Analysis (Sediment)

Similar to water sample sites, PAHs diagnostic ratios, such as Fl/Py, Ph/An, Fl/(Fl+Py), Ind/Ind+B[ghi]P, LPAHs/HPAHs were employed in the determination of sources of PAHs contaminants in the sediment of the study area as presented in Table 4.6. The relative abundances or diagnostic ratios are useful indicators of PAH sources because isomer pairs are diluted to a similar extent upon mixing with natural particulate matter, and are distributed similarly to other phases as they have comparable thermodynamic partitioning and kinetic mass transfer coefficients (Dickhut *et al.*, 2000, Liu *et al.*, 2009).

Table 4.9 Isomeric ratio of PAHs in superficial sediment of the study area

I.	Stations	Fl/Py	Ph/An	Fl/(Fl+Py)	Ind/Ind+B[ghi]P	LPAHs/HPAHs
	Site 1	0.65	BDL	0.40	0.28	0.44
	Site 2	4.1	0.01	0.80	0.04	0.08
	Site 3	0.07	0.41	0.07	0.08	0.13
	Site 4	0.11	3.67	0.09	0.35	0.06
	Site 5	0.24	BDL	0.20	0.98	0.04

The Fl/py ratios for the five sediment sites ranged from 0.11 to 4.05. The corresponding figures for Ph/An ratios ranged from BDL to 3.67. As far as the sediments are concerned, the Fl/Py values were all less than one (petrogenic) except site2 (Entrance of Arunton creek) where the Fl/Py ratio was greater than one (pyrogenic). Apart from sites 1 and 5 (Ikperere and dock entrance) where anthracene was not recorded, the Ph/An ratio in the other sites were less than ten (<10), which points to pyrogenic origins. The Fl/(Fl+Py) ratio of <0.4 in sites 3, 4 and 5 indicate

petrogenic source while site 1 ratio of 0.4 ($\geq 0.4 \leq 0.5$) points to petroleum combustion, and site 2 (> 0.5) suggest kerosene, wood, grass and coal combustion. Ind/(Ind+BghiP) ratio (< 0.2) suggest petrogenic origin in site 2 and site 3, and pyrolytic source in sites 1 and 4 (ratio $\geq 0.2 \leq 0.5$), while site 5 is > 0.5 , indicating wood, grass and coal combustion (Yunker *et al.*, 2002, Olajire *et al.*, 2005, Morillo *et al.*, 2008; Inengite *et al.*, 2010b). The ratio of LPAHs/HPAHs is < 1 in all the sediment sites, indicating pyrolytic source (Witt *et al.*, 1999, Soclo *et al.*, 2000, Emoyan *et al.*, 2015). The isomeric ratios employed in this study for the sediment source identification; points to both pyrolytic and petrogenic sources in all the sites. The contrasting ratios in most of the sites, indicates that PAHs pollutants in sediment of the study area originates from both petrogenic and pyrogenic sources.

4.8.2 PAHs Source Identification from Principal Component Analysis

a) Principal Component Analysis (PCA) of PAHs in Sediment

Similar to water, a more sophisticated statistical approach (PCA) as summarized in Table 4.10 was employed to further determine the source of PAHs in sediment of the study area. The plot of PCA loading in sediment is displayed in Figure 4.8.

Table 4.10: Sediment PCA factor loadings after Varimax with Kaiser Normalization Rotation.

PAH Compound	Component		
	Factor 1	Factor 2	Factor 3
Nap		.937	
Acy	.965		
Ace	-.494	-.563	-.637
Ant	.982		
Flu	.967		
Phen	-.329		.877
Pyr		.965	
Flt	.980		
Chry	-.398	.788	
BaA	.974		
BaP	-.505	-.307	-.763
BbF	-.358	-.385	.638
BkF	.982		
DahA		.957	
BghiP		.746	
IndP	-.397		.820
% Variance	44.80	27.67	17.64

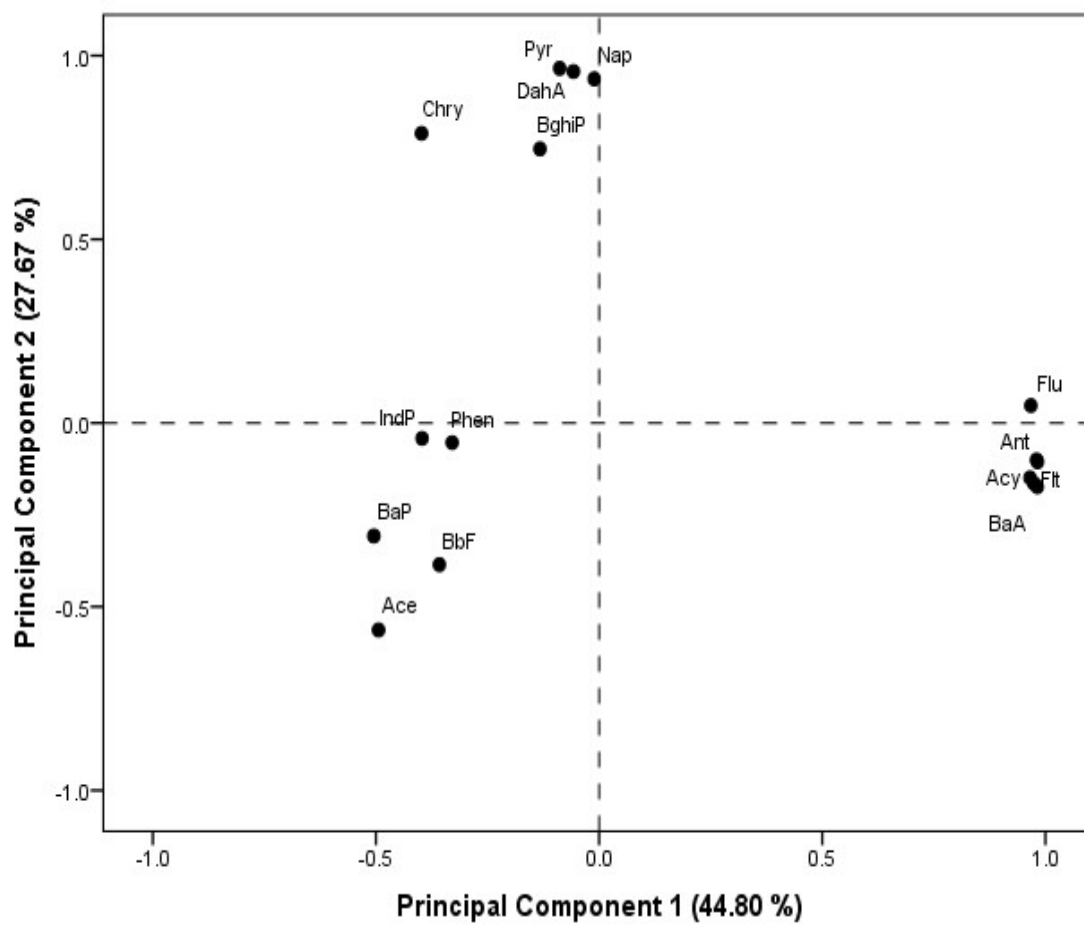


Figure 4.8: The loading plot of PCA for sediment.

b) PCA of Sediment Samples

The PCA of PAHs in the sediment samples (Table 4.10) indicate that three different component factors which account for 90.11 % of the total variability were extracted. Factor 1 constituting 44.8 % of the total variance was dominated by high loadings of Acy, Ant, Flu, Flt, BaA and BkF. Acy, Ant and Flu are products of wood combustion (Yunker *et al.*, 2002; Yang *et al.*, 2012), Flt is a product of coal combustion (Larsen and Baker, 2003), BaA is a product of diesel combustion (Khalili *et al.*, 1995), while BkF is a product of coal and gasoline combustion (Dong and Lee, 2009). Therefore, from factor 1, the sources of PAHs in the sediment are fossil fuels combustion.

Factor 2 accounts for 27.67 % of the total variance and was characterised by high loadings of Nap, Pyr, Chry, DahA and BghiP. Nap is from combustion of wood related sources (Dong and Lee, 2009), Pyr is a product of coal combustion (Larsen and Baker, 2003), Chry is a product of diesel and natural gas (Khalili *et al.*, 1995); DahA and BghiP are products of traffic emissions (Yang *et al.*, 2012). Thus, factor 2 indicates that fossil fuel combustion and traffic emissions are the major sources of PAHs in these sediments. Factor 3 accounted for 17.64 % of the total variance and was characterised by high loadings of Phen and IndP and moderate loading of BbF. Phen and BbF are products of wood combustion while IndP is from traffic emissions (Yang *et al.*, 2012). Factor 3 also indicates that fossil fuel combustion and traffic emissions are the major sources of PAHs in these sediments. Sediment PAHs contaminants can be attributed to fossil fuel combustion.

c) Correlation of PAHs in Sediment Samples

The correlation results of PAHs in the sediment samples are displayed in Table 4.11. Correlation analysis of the PAHs indicates strong positive correlation ($r^2 > 0.50$) between Ant/Acy (0.991), Flu/Acy (0.954), Flu/Ant (0.981), Pyr//Nap (0.989), Flt/Ant (0.996), Flt/Flu (0.968), Chry/Nap (0.579), BaA/Acy (0.974), BaA/Ant (0.993), BaA/Flu (0.972), BaA/Flt (0.980), BaP/Ace (0.956), BbF/Phen (0.502), BkF/Acy (0.983), BkF/Ant (0.982), BkF/Flu (0.933), BkF/Flt (0.986), BkF/BaA (0.977), DahA/Nap (0.833), DahA/Pyr (0.873), DahA/Chry (0.863), BghiP/Nap (0.872), BghiP/Pyr (0.872), BghiP/DahA (0.538), IndP/Phen (0.709), IndP/BbF (0.912). Strong positive correlation among the PAH components confirms that the PAHs contaminants are from a common source.

Table 4.11: Correlation analysis for sediments

	Nap	Acy	Ace	Ant	Flu	Phen	Pyr	Flt	Chry	BaA	BaP	BbF	BkF	DahA	BghiP	IndP
Nap	1.000	-0.115	-0.363	-0.061	0.121	-0.297	0.989*	-0.072	0.579**	-0.112	-0.077	-0.287	-0.186	0.833*	0.872*	-0.042
Acy		1.000	-0.256	0.991*	0.954*	-0.499	-0.215	0.998*	-0.550	0.974*	-0.277	-0.423	0.983*	-0.176	-0.271	-0.551
Ace			1.000	-0.331	-0.386	-0.428	-0.415	-0.316	-0.462	-0.336	0.956*	0.089	-0.372	-0.490	-0.338	-0.229
Ant				1.000	0.981*	-0.459	-0.158	0.996*	-0.540	0.993*	-0.345	-0.338	0.982*	-0.169	-0.169	-0.449
Flu					1.000	-0.506	0.019	0.968*	-0.464	0.972*	-0.351	-0.324	0.933*	-0.053	0.024	-0.401
Phen						1.000	-0.162	-0.473	0.426	-0.400	-0.577	0.502**	-0.329	-0.034	-0.082	0.709*
Pyr							1.000	-0.169	0.683	-0.207	-0.140	-0.249	-0.267	0.873*	0.872*	0.038
Flt								1.000	-0.513	0.980*	-0.329	-0.414	0.986*	-0.138	-0.222	-0.520
Chry									1.000	-0.588	-0.318	-0.254	-0.511	0.863*	0.412	0.136
BaA										1.000	-0.371	-0.227	0.977*	-0.248	-0.163	-0.351
BaP											1.000	-0.041	-0.427	-0.253	-0.114	-0.305
BbF												1.000	-0.347	-0.565	0.214	0.912*
BkF													1.000	-0.202	-0.306	-0.443
DahA														1.000	0.538*	-0.213
BghiP															1.000	0.407
IndP																1.000

**Pearson Correlation is significant at the 0.05 level (1 tailed)

* Pearson Correlation is significant at the 0.01 level (1 tailed)

4.9 Ecological Risk Assessment of PAHs in Sediments

Table 4.12: Ecological risk calculated for individual PAHs in the surface sediment of Arunton creek and environs

Components	Site1	Site2	Site3	Site4	Site5	Mean	PEL	TEL
Naphthalene	0.01	0.03	0.13	0.00	0.02	0.04	391	34.6
Acenaphthene	0.04	0.31	0.03	0.00	0.03	0.08	88.9	6.71
Acenaphthylene	0.52	0.02	0.03	0.12	0.00	0.14	128	5.87
Anthracene	0.00	0.50	0.04	0.02	0.00	0.11	245	46.9
Fluorene	0.04	0.29	0.11	0.06	0.03	0.11	144	21.2
Phenanthrene	0.00	0.00	0.01	0.03	0.03	0.01	544	86.7
Pyrene	0.00	0.01	0.06	0.01	0.02	0.02	1398	153
Fluoranthene	0.00	0.04	0.00	0.00	0.00	0.01	1494	113
Chrysene	0.08	0.04	0.29	0.11	0.30	0.16	846	108
Benzo[a]anthracene	0.00	0.22	0.02	0.03	0.00	0.05	693	74.8
Benzo[a]pyrene	0.10	0.01	0.03	0.02	0.00	0.03	763	88.3
Benzo[b]fluoranthene	0.02	0.00	0.01	0.11	0.00	0.03	1880	320
Benzo[k]fluoranthene	0.00	1.50	0.01	0.11	0.23	0.37	1620	280
Dibenz[a,h]anthracene	0.90	0.11	0.24	0.06	0.19	0.14	135	6.22
Benzo[g h i]perylene	0.00	0.02	0.12	0.05	0.00	0.04	1600	430
PELq (PEL quotient)	0.06	0.19	0.07	0.05	0.05	0.08	*	*

* PEL (probable effects level)

* TEL (threshold effects level)

To evaluate whether the PAHs in sediments of the study area will cause adverse ecological effects, a screening level ecological risk assessment (SLERA) was performed according to the framework developed by the US-EPA (EPA, 1991, Khairy *et al.*, 2009, Dsikowitzky *et al.*, 2011, Sany *et al.*, 2014). Previously developed sediment quality guideline was employed in the risk characterization. The Macdonald *et al.*, consensus base approach was used according to the following PEL (probable effects level) and TEL (threshold effects level) specific values (Table 4.12) (Macdonald *et al.*, 1996, USEPA, 2005).

The hazard quotient (HQ) for the risk characterization step was calculated using the formula:

$$HQ = \frac{MCPAHs}{CCPEL}$$

Where MCPAHs is the maximum concentration of each PAHs and CCPEL, the estimated consensus based sediment quality guideline (USEPA, 2005, Khairy *et al.*, 2009, Sany *et al.*, 2014).

The PEL quotient (PELq) (Table 4.12) is a unique factor to describe the contamination effect of PAHs on biological organisms according to the analyses of chemical data and matching toxicity from 1,068 sediment samples from coastal and estuaries water in the USA (Long *et al.*, 1995). The PELq factor is the average of the ratios between the PAHs concentration in the sediment sample and the related PEL value (Khairy *et al.*, 2009, Fdez-Ortiz *et al.*, 2010). The PELq factors were divided into four categories, which can be used to describe the sediment as non-adverse effect (PELq<0.1), slightly adverse effect (0.1<PELq<0.5), moderately adverse effect

($0.5 < \text{PELq} < 1.5$), and heavily effect ($\text{PELq} > 1.5$) (Khairy *et al.*, 2009, Montuori *et al.*, 2012).

The risk assessment results (Table 4.12) revealed that total PAHs will not cause any ecological effect in all the sites except site 2 (EAC) where the sediment showed slightly adverse effect ($0.1 < \text{PELq} < 0.5$). The rest sites showed PELq of < 0.1 , indicating non-adverse effect. Comparison of individual PAHs with the sediment quality guidelines, indicate that only BkF in site 2 (EAC) was associated with adverse biological effect. In general, PELq of 0.08 indicate that PAHs do not pose any adverse biological effect in sediments of the study area.

To further assess the ecological risk of PAHs in sediments of Arunton creek and environ, the PAH levels in sediment were compared against the effects-based guideline values such as the effects range-median (ERM)-probable effect concentration and effect range-low (ERL)-threshold effect concentration (Long and Morgan, 1991). The highest total PAHs concentration recorded in sediment, 2950 $\mu\text{g}/\text{kg}$ was observed at the Entrance of Arunton creek. This value is significantly lower than the ERL value (4000 $\mu\text{g}/\text{kg}$). Anthracene and fluorene in Entrance of Arunton creek were the only individual PAHs that exceeded their respective ER-L values. It may be concluded that PAHs will not cause biological effects in sedimentary environment of the study area. However, PAHs on the long term may cause ecological effects in Entrance of Arunton creek sediment. ERL represents the chemical concentration below which adverse effects would be rarely observed (Long and Morgan, 1991).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The present study has shown that the aquatic ecosystem of the study area is contaminated with PAHs from petrogenic and pyrolytic (fossil fuel combustion) sources as revealed by the various source identification analysis. The Dehydration and Dock entrance surface water high petrogenic PAHs input source (Ph/An ratio), indicates that the PAHs pollutants in these sites were mainly due to the presence of oil exploration facilities and activities of vessels and barges. The result also revealed the important of dry season in PAHs degradation as shown by the variation in total concentrations of PAHs recorded during the wet season (first 3-months), and the dry season (the last 3-months). The total concentrations of PAHs for the wet season samples were slightly higher than those of the dry season. The risk assessment revealed contamination level with potential for toxicity in surfacewater while sediment PAHs will not cause biological effect in the sediment of the study area.

5.2 RECOMMENDATION

In view of the findings recorded in this study, it is imperative to make the following recommendations:

- I. Continuous environmental monitoring of PAHs pollutants in Arunton creek and environs should be giving serious consideration.

- II. Companies operating in this area must monitor activities that lead to the release of PAHs into the environment, and ensure that wastes containing PAH compounds are properly managed.
- III. Finally, effort to delineate and commence remediation process should be put in place; as this will help clean up the environment and prevent bioaccumulation and biomagnifications.

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