

Levels of Polycyclic Aromatic Hydrocarbons (PAHs) in marshy soils and
sediments within Warri and its environs, Nigeria

by

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DECLARATION

I declare that Levels of Polycyclic Aromatic Hydrocarbons (PAHs) in marshy soils and sediments within Warri and its environs, Nigeria is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references.

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(MRS A V BAYOWA)

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DATE

ABSTRACT

Marshy soil and sediment samples were collected during dry and rainy seasons within Warri, and Agbarho, 20km away as control. Levels of 16 USEPA priority Polycyclic Aromatic Hydrocarbons PAHs were determined using GC-FID. Source prediction analysis was also done. The study was in Niger Delta region, Nigeria from January to March and June to August 2012 in dry and wet seasons. Benzo(a)pyrene had highest total concentration of 3.302mg/kg and mean value of 1.651mg/kg in dry season soil samples. However, sediment samples had highest levels for total concentration of PAHs of 19.362mg/kg and mean of 4.840mg/kg for both dry and rainy seasons within Warri. PAHs concentration was higher in dry than rainy seasons for soil and sediment samples. Source prediction analysis revealed that PAHs in sediments for dry season were pyrolytic while rainy seasons were petrogenic sources. For soils, the dry season was mixed sources while the rainy season was petrogenic.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Our environment is a large sink that takes in all we give in and gives them back to us in another form which could be beneficial or harmful. The reactions that are responsible for these transformations could be physical, chemical, biological or integration of any or all of the aforementioned (Botkin & Keller, 2005). Several exchanges or reactions go on all the time from as simple as flow of one river to the other or ponds to lakes to the complex decomposition processes of dead organisms; the environment naturally has a way of cycling substances around it in such a way that every part is affected directly or indirectly by the consequence of the usage of another (Botkin& Keller, 2005). If the substance being cycled is a contaminant, other parts of the environment could also be affected; however the effects could reduce or increase due to the presence of other substances or factors (Buha & Lah, 2011).

Based on the above, it can be said that there is inter-relationship amongst every living part (this include flora and fauna) of the physical environment and the chemical cycling or reactions constantly going on around them.

A chemical substance that has the tendency to contaminate either on its own or in combination with other substances or agent, any part of the environment is an environmental pollutant (WHO, 2003). Environmental pollutants are chemical substances (although they may not appear to be chemicals when released) that when released into the environment affects the normal stable

condition as expressed by their characteristics or functions or those of the living components (flora and fauna) and other environmental components found there (Botkin & Keller, 2005).

Some pollutants are present in the environment only for a while (seconds, minutes, hours or few days) before they are converted into other forms and some could remain in the environment for a long time (several days, months or years) (Buha & Lah, 2011). This property is usually determined by the characteristics of the pollutant in relation to that of the medium in which it is dispersed (Obayori & Salam, 2010). A medium in this context can be defined as a carrier or means through which substances or the pollutant is expressed or in which it is active; an environmental medium could be the air, water or soil; this means we could have air pollutants, water pollutants and soil pollutants (Botkin & Keller, 2005). Most of the time, there is no disparity amongst the different type of media as they could flow into each other; soil pollutants for instance are usually found as a result of fallout from the air/atmosphere or carried by water medium into the soil and could be deposited at the bottom or river banks as sediments (Working Group on PAHs WGPAs, 2001). However, soil can also be polluted by oil and other organic substances; an example of such organic substance is Polycyclic Aromatic Hydrocarbons (PAHs) which are found in aquatic ecosystem and in soil and sediments as a result of wet and dry deposition from the atmosphere (Environmental Forensics Contaminant Specific Guide – EFCS, 2010).

The persistence or how long a pollutant stays in the environment is a characteristic of its behaviour in that medium especially the solubility and reactivity with other constituents of the medium. Based on these facts, pollutants have been classified as Persistent Environmental Pollutants and Non-persistent Environmental Pollutants (Botkin & Keller, 2005). Persistent Environmental Pollutants stay longer in the environment; their half-lives could range from

months to decades (Pondent, [accessed: 2013]). They occur in forms that allow them to be transported by wind, water and sediments for long distances (Botkin & Keller, 2005). They are usually found attached or adsorbed to the medium or other parts of the environment (example is atrazine herbicide and petroleum hydrocarbons such as PAHs) (Buha & Lah, 2011). Non-persistent Environment Pollutants are only found for a little while in the environment, they have half- lives that could be as short as hours and could at most run into weeks (Pondent, [accessed: 2013]). Although they could have a more immediate toxic action than persistent chemicals, once they degenerate they no longer pose a toxic threat; examples include organophosphates such as guthion and malathion and chlorinated hydrocarbons such as endosulfan (Pondent, [accessed: 2013]).

Depending on the origin of the pollutant, that is, whether they are compounds of carbon produced naturally or synthetically by human activities, they could also be further classified as synthetic or inorganic pollutants and organic pollutants; examples of organic pollutants that persist in the environment otherwise known as Persistent Organic Pollutants or POPs are: atrazine- an herbicide, and petroleum hydrocarbons which include polycyclic aromatic hydrocarbons amongst others (Buha & Lah, 2011).

1.2 Significance and Justification of Study

Polycyclic Aromatic Hydrocarbons are important environmental pollutants that have been studied in many places. Their harmful tendencies in the environment especially in humans have also been issues of discussion in many reviews and they have been included in WHO priority list as harmful environmental pollutants.

The study area – Warri has in the last few years experienced an increase in industrial and commercial activities due to the large crude oil deposit found in the Niger Delta and subsequent influx of oil exploration and production activities with the associated gains and pains. All these have the tendency of releasing harmful pollutants including PAHs into the environment.

PAHs being ubiquitous pollutants which are found almost everywhere in the environment with their final destination (if not inhaled) usually in soil and aquatic environment have been found to settle in sediments or accumulate in aquatic biota. Due to the large crude oil reserves in this study area, and exploration and production activities going on, there are usually issues of oil spillage, pipeline vandalism, oil refining activities and other petroleum related practices in this part of the country which could possibly lead to the introduction of PAHs as well as other petroleum hydrocarbons and pollutants into the soil and waterways that the people largely feed from. The people of Warri and generally those in the western part of Nigeria Niger Delta are known to be fishermen/women; probably due to their proximity to the rivers and seas, they eat lots of fishes and sea foods as well as selling them to other parts of the country and beyond. However, petroleum related activities are not the only source of PAHs pollutants release into the environment. Other sources of PAHs are from pyrolytic activities involving industrial and commercial burning of fuel or hydrocarbons in oil (including certain cooking practices such as broiling of food over charcoal). PAHs from pyrolytic sources are produced due to incomplete combustion and have been shown to be a major source of PAHs intake by humans (European Food Safety Authority - EFSA, 2008).

All these poised the motivation for embarking on this study titled Levels of Polycyclic Aromatic Hydrocarbons PAHs in Marshy Soils and Sediments in Warri and its Environs. The study will no

doubt increase the plethora of knowledge on PAHs and serve as valuable literature for future research.

1.3 Objectives of Study

- To assess the levels of PAH in soils and sediments in the study area;
- To carry out source identification of PAH in soils and sediments in the study area;
- To determine the effects of PAH (if any) in the environmental segments under investigation and by extension man the ultimate consumer in the food chain;
- To proffer useful suggestions and recommendations on how to ameliorate identified adverse impacts (if any), in the study area.

CHAPTER 2

LITERATURE REVIEW

2.1 OVERVIEW OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

2.1.1 Chemistry of Polycyclic Aromatic Hydrocarbons PAHs

Polycyclic Aromatic Hydrocarbons (PAHs) are a family of organic compounds of the six carbon benzene ring origin; the benzene ring is the one responsible for their aromatic behaviour and they are made up of a few to several fused rings of benzene hydrocarbon compounds (WHO, 2003). There are several hundreds of different known PAHs and related compounds and the number of rings could be from two for the lower molecular weight compounds to seven for the higher molecular weight PAHs. For instance, naphthalene has two fused rings and is an example of the lower molecular weight PAHs while pyrene with four rings is an example of high molecular weight PAHs. Some of the known PAHs are: Naphthalene(Naph.), Anthracene(Ant.), Chrysene(Chr), Acenaphthylene(Acp), Pyrene(Pyr), Acenaphthene(Acn), Benzo(a)Pyrene(B(a)P, Fluorene(Fluo), Fluoranthene(Fluoran), Benzo(e)Pyrene(B(e)P, Benzo(a)anthracene(B(a)A, Benzo(b)fluoranthene(B(b)F, Phenanthrene(Phe), Benzo(a)pyrene(B(a)P, Benzo(k)fluoranthene(B(k)F, Indeno(1,2,3-cd)Pyrene(Ind) andDibenzo(a,h)Anthracene(Db(ah)A (Buha & Lah, 2011). The structure of the 16 PAHs that are termed as priority pollutants by the World Health Organisation is shown below in figure 2.1:

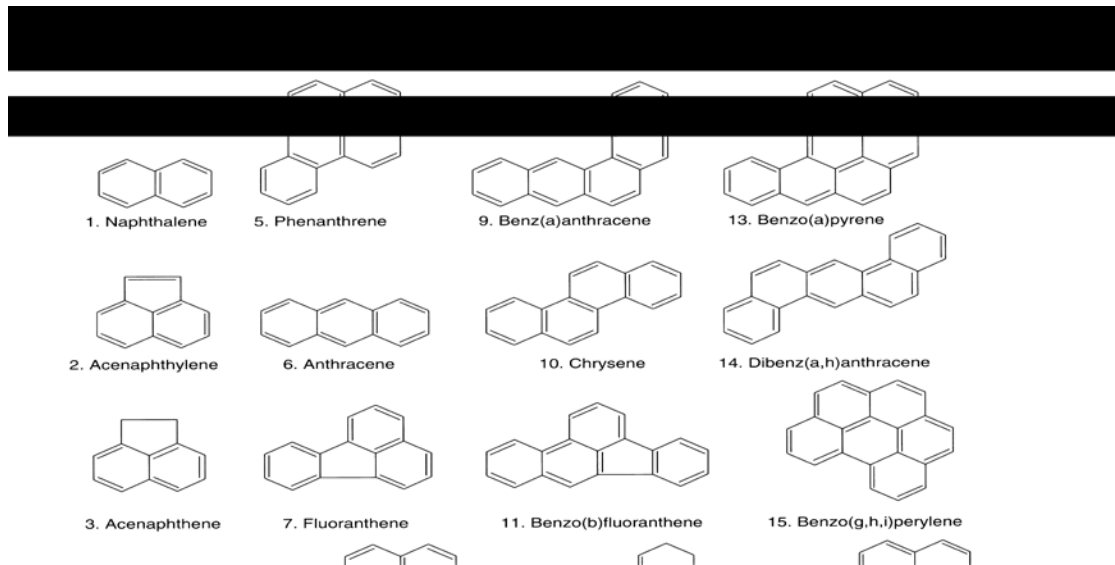


Fig. 2.1: Structure of sixteen PAHs considered by World Health Organisation (WHO) as priority pollutants.

Source: (Adapted from Tuvikene, 1995)

2.1.2 Characteristic of Polycyclic Aromatic Hydrocarbons PAHs

Polycyclic Aromatic Hydrocarbons are found in the pure state as white, colourless or pale yellow-green solids at room temperature (WHO, 2003). They could also have a faint pleasant odour (Irwin, 1997). In the atmosphere, they are usually adsorbed on particles, dust or smoke and are removed from the atmosphere by wet (rainfall or mist) and dry deposition onto soil, water and vegetation (EFCS, 2010). In aqueous environment, PAHs may undergo volatilisation, photodecomposition and biodegradation or bind to suspended particles or sediments or accumulate in aquatic organisms (WHO, 2003). However, they are generally of low vapour pressure and possess low tendency to vaporise except among the low molecular weight compounds with two to three fused chain (such as naphthalene) which are in the vapour phase,

others range from being only semi volatile (four ringed PAHs) and they are mostly non-volatile (Agency for Toxic Substances and Disease Registry – ATSDR, 1999).

Also, PAHs are known to be chemically stable and are poorly degraded by hydrolysis, they are non-polar organic chemicals with low aqueous solubility (Neff *et al.*, 2004); this could be attributed to their highly hydrophobic nature and lipophilic characteristics (WGPAHs, 2001). Studies have shown that the biochemical persistence of PAHs is due to the presence of dense cloud of pi electrons on both sides of the ringed structure making them resistant to nucleophilic attack (Obayori & Salaam, 2010). Some PAHs such as chrysene, benzo(a)anthracene and benzo(a)fluoranthene have been found to be susceptible to oxidation and photo degradation in light in aqueous environment; this character is however determined by those of the substrates to which they are attached and the medium (Obayori & Salaam, 2010). Other works conducted on microbial action on PAHs revealed that, microbial biodegradation of PAHs is rapid for the lower molecular weight compounds such as naphthalene and phenanthrene but the higher molecular weight fractions such as chrysene and benzo(a)pyrene strongly oppose biodegradation by microbes in sediments (Obayori & Salaam, 2010). Further works carried out also showed that volatilisation and adsorption are primary removal processes for medium and high molecular weight PAHs while volatilisation and biodegradation are the major removal processes for low molecular weight fractions in aquatic environment (Obayori & Salaam, 2010). Also, high molecular weight PAHs (with four rings and above) have been found to be less acutely toxic but more carcinogenic and teratogenic (Obayori & Salaam, 2010).

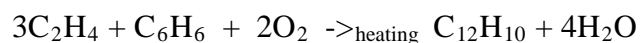
The characteristics and reactions of PAHs as discussed in this review as well as in several other reviews could be said to explain why they persist and are found in almost every part of the

environment (i.e. they are ubiquitous). This is believed to have made them important pollutants that should be investigated just like many other persistent pollutants.

2.2 Production or Formation of PAHs

Polycyclic Aromatic Hydrocarbons PAHs are not usually produced intentionally (Campbell, 2008), but are the products of incomplete organic combustion that arises from sources that spring up from our day to day human activities (such as residential and commercial burning or cooking, industrial or vehicular fumes from diesel and petroleum engines, asphalt production, coking, coal tar production, burning of garbage or incineration) and they are considered to be anthropogenic; they could also be produced naturally from forest fires and volcanoes (WHO, 2003). Some PAHs such as benzo(a)pyrene had also been found to originate from petroleum hydrocarbons in the environment due to accidental or intentional release of petroleum products or by-products or as a result of activities of refining crude fractions or utilisation of the products (ATSDR,1999).

However, certain PAHs such as anthracene, acenaphthene and acenaphthylene have been produced commercially in the United States (Campbell, 2008). The process usually involves great heating; for acenaphthene, the process involves heating up ethylene and benzene or naphthalene (Campbell, 2008).



(Ethylene) (Benzene) (Oxygen) (Acenaphthene) (Water)

Chemical reactions such as seen above was also described in a report in the document titled – Health Hazards Associated with PAHs, as organic chemical reactions that utilises simple aromatic compounds and occur by a mechanism called HACA- Hydrogen abstraction Acetylene addition (www.cd1.edb.hkedcity.net [2011]).

2.3 Sources of Polycyclic Aromatic Hydrocarbons PAHs

PAHs have been found to be almost ubiquitous since they are found everywhere (WHO, 2003) even in interstellar medium (Allamandola *et al.*, 2003); their source would therefore be related to almost everything in the environment and its usage or that of its components. Sources of Polycyclic Aromatic Hydrocarbons PAHs in the environment could be grouped into:

- Natural sources
- Anthropogenic sources

2.3.1 Natural Source

The natural sources of PAHs are from thermal geologic reactions that involves rapid chemical and biological transformation of organic precursors (Neff *et al.*, 2004) from living or recently living plants or animals (biogenic material), such as wood, coal, limestone, pearls or chalk (Hogg, 2006). Natural sources of PAHs also include underground oil seeps, discharge from chlorophylls plants, fungi and bacteria (Bouwmeester *et al.*, 2006). The natural sources of PAHs are not usually considered as adding to the bulk of the pollutant in the environment (Kostopoulou *et al.*, 2009).

2.3.2 Anthropogenic Source

Anthropogenic has to do with sources that involve human and human interventions in the environment. Such interventions are those that spring up from day to day activities of human that involves utilisation and incomplete combustion of hydrocarbons in oil (WHO, 2003). Anthropogenic sources of PAHs could be further grouped into two: *Petro-genic Sources and Pyrolytic Sources*.

2.3.2.1 Petrogenic sources

Petrogenic sources of PAHs are due to the intentional or accidental release of petroleum or the refined products from workshops and factories that utilise the products, production tank farms, leaking underground storage pipes, pipeline vandals and other oil spillage actions (ATSDR, 1999).

According to the work done by Neff *et al.*, 2004, a typical petroleum fraction may contain 0.2 to more than 7% total Polycyclic Aromatic Hydrocarbons. Petrogenic PAHs from unrefined petroleum sources are found to be mostly of the two to three ringed, low molecular weight compounds; the higher molecular weight fractions are usually at low concentration less than 100mg/kg (Neff *et al.*, 2004). The refined products contain the same PAHs as in the parent petroleum as well as small amounts produced by catalytic cracking and other refining processes. Also, the PAHs fractions in different refined oils vary depending on the distillation temperature range of the product; consequently, the two ringed PAHs – naphthalene and alkyl naphthalene are present in gasoline fuels while diesel fuels, home heating oils and engine oils may contain the four ringed PAHs as well as other aromatic hydrocarbons (Neff *et al.*, 2004).

Most of the PAHs from petrogenic sources contain an alkyl group on one or more of the aromatic carbons and those in the refined products are usually more abundant than those of the parent compounds in petroleum (Neff *et al.*, 2004). Benzo(a)pyrene whose origin is from petroleum hydrocarbons is considered to be probably and possibly carcinogenic in human (ATSDR, 1999).

2.3.2.2 Pyrolytic Sources

This is the major source of PAHs with three or more rings in the environment (Neff *et al.*, 2004). Pyrolysis has to do with heating or losing composition of a substance by heating (Hogg, 2006). PAHs are released into the environment due to incomplete combustion of organic compounds in fossil fuels or hydrocarbon oils (WHO, 2003). Combustion is said to be complete when the application of heat breaks up molecules with the ultimate production of carbon (iv) oxide and water (Lau *et al.*, 2010). When combustion is incomplete, or the combusted fuel products or oil cool quickly, the small organic chemicals may condense to form new chemicals which include PAHs; these are the pyrolytic polycyclic hydrocarbons PAHs (Neff *et al.* 2004). Examples of human activities that generate PAHs from pyrolytic source are: residential or commercial burning or cooking (including frying, broiling, and smoking), asphalt production, coal tar production, industrial or vehicular exhaust from diesel and petroleum engines, vehicular fumes from highway traffic, burning of garbage and incineration (WHO, 2003).

PAHs from pyrolytic sources are usually complex and are dominated by the four to five and six ringed fractions. The rings usually have their homologous series dominated by the un-alkylated parent compound or they may contain a homologue with only one or two alkyl substituents (Neff *et al.*, 2004). This, according to Neff (1979) as cited by Neff *et al.*, (2004) is determined by the temperature of formation in a given pyrolytic PAHs fraction and there exist an inverse relationship between the temperature of formation and the abundance of alkyl carbons. An example is coal tar (which is produced due to high temperature baking of hard coal in a reducing atmosphere to produce coke and manufactured gas); it is a type of high temperature pyrolytic polycyclic aromatic hydrocarbons and will likely contain few alkyl groups and more un-alkylated groups (Neff *et al.*, 2004). However, further treatment (such as distillation) of the tar

could alter the composition and sometimes produce the two and three ringed PAHs fractions (such as creosote) (Neff *et al.*, 2004).

Pyrolytic-anthropogenic sources of PAHs could also be linked to the *natural* sources. This is because of the heating or pyrolysis that occurs during *diagenesis* (conversion of sediments into rocks or reconstitution of crystals to form a new product). This process however happens naturally and is not known to be directly caused by human intervention (Lau *et al.*, 2010). Some literature reviews classified diagenesis of biogenic material which is grouped in this report as well as in many other reports as *natural* source as a *pyrolytic* or *pyrogenic* PAHs source. The purpose of classification or grouping is for clarity and understanding based on perception of individual and not in any way meant to be contradictory.

2.4 Polycyclic Aromatic Hydrocarbons (PAHs) as Environmental Pollutants

Polycyclic Aromatic Hydrocarbons PAHs as mentioned earlier are ubiquitous substances, that is, they are found almost everywhere and can move from one environmental media (air/atmosphere, water and soil) to the other (WGPAHs, 2001). They can persist in the environment for a long time (WHO, 2003), and have also been found to be toxic with further studies revealing them to be the most toxic pollutants among the hydrocarbon families (Tuvikene, 1995). PAHs possess the ability to undergo biotransformation to toxic metabolites (Tuvikene, 1995) thereby resulting in adverse effects on environmental components and make them important environmental pollutants.

2.4.1 PAHs in Air

Polycyclic Aromatic Hydrocarbons are released into the air from various pyrolytic sources, such as burning of fossil fuels in machines or vehicles and household or commercial burning and incineration, cigarette smoke, or from the natural sources (forest fires and volcanoes); they are usually found attached to dust particles and may be inhaled or due to their heavy molecular weight may be deposited on plants or water surface (ATSDR, 1999). PAHs are usually found in ambient air in rural, urban and suburban areas and a wide range can be found in the atmosphere (EFCS, 2010). The air or atmosphere is usually the first point of release of PAHs from several pyrolytic sources and could be inhaled directly by human (Superfund Research Program- SRP, 2013); this is represented pictorially in fig 2.2 below:

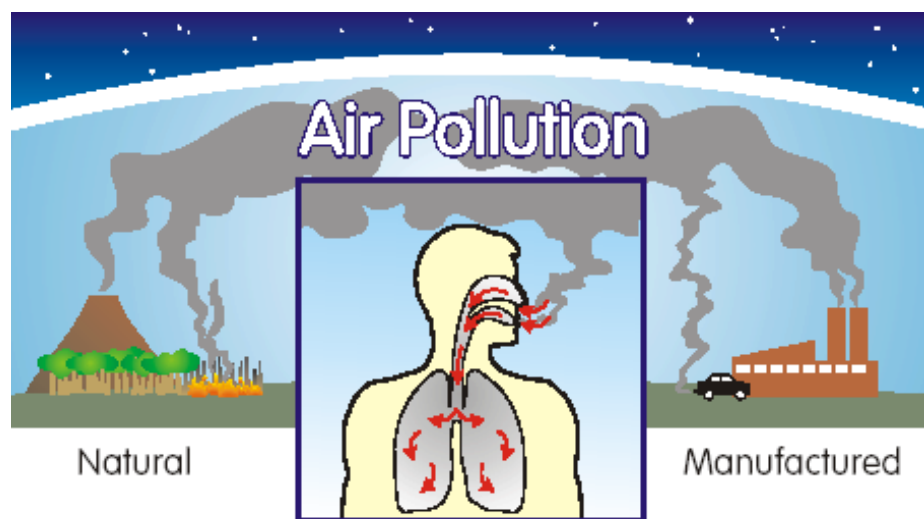


Fig. 2.2: Air Pollution from release of harmful environment Pollutant

Source: Superfund Research Program – SRP Oregon State University, 2013.

In the atmosphere, PAHs could be transformed, degraded or deposited. Deposition could be on vegetation, animals (including birds), humans, aquatic environment and even soil. The processes that transform and degrade PAHs in the atmosphere include photolysis and reaction with

NO_x, N₂O₅, OH⁻, ozone, Sulphurdioxide SO₂, and Peroxyacetylnitrate PAN (ATSDR, 1995). Possible atmospheric reaction products are oxy-, hydroxy-, nitro- and hydroxynitro-PAH derivatives (ATSDR, 1995). Photochemical oxidation of a number of PAHs has also been reported with the formation of nitrated PAHs, quinones, phenols, and dihydrodiols (ATSDR, 1995). Reaction with ozone or Peroxyacetylnitrate yields diones; Nitrogen oxide reactions yield nitro and dinitro PAHs (ATSDR, 1995). Sulphonic acids have also been formed from reaction with sulphur dioxide. Some of these breakdown products are mutagenic and studies have shown that these products could be more toxic than the parent PAHs compounds (ATSDR, 1995).

PAHs like many air pollutants reduce air quality. When such air is inhaled, it can produce certain dangerous health defects and this also depends on the length of exposure and the quantity exposed to. Studies have further found that the quantity of PAHs found in the atmosphere in cold season could be more than those found in hot season (EFCS, 2010). This could be related to the absence of sunlight that could act to break down the PAHs (by photodecomposition) and the probable increase in burning to keep warm that could increase heating emissions in the atmosphere. On the contrary however, observation has shown that there is likely to be more fire incidence or outbreak in the dry season than in the wet season which are the two major seasons prevalent in Nigeria (the study area); and could therefore increase the amount of heating emission and probably PAHs in the atmosphere.

2.4.2 PAHs in Soil

PAHs in soil are usually and mostly from atmospheric deposition due to the pyrolytic sources (such as vehicular exhaust and burning smoke) (ATSDR, 1995); and the other sources are from the petrogenic sources due to release of petroleum or crude oil from natural oil seeps, spillage and other activities that involve these. In the soil, they are usually found attached to substrates or

any oily contaminants present there. They have high sorption capacity (attached strongly to substrate) and are less volatile; as a result, they persist for a long time in the soil (Obayori & Salaam, 2010). It has been found that the soil as well as sediment are good environmental sink for PAHs and could contain about 90% of these compounds with longer half-life than the atmosphere or in plants (Ekonomiuk *et al.*, 2006)).

Some PAHs are also sparingly soluble in soil-water and therefore may be found as dissolved there and could enter groundwater and be transported within an aquifer (EFSA, 2008), although this is possible only among the lower molecular weight compounds with two to three rings.

PAHs in urban soil may be thought of and have actually been found to be more than that of rural area, due to the increase in vehicular and industrial activities in the urban areas; such PAHs are majorly of the anthropogenic pyrolytic sources (EFCS, 2010). However, most crude oil or petroleum exploits and their related production and activities are usually cited in the rural areas especially in the area under study here (Nigeria); accidental or intentional spillage of oil fractions from various human activities could therefore also increase PAHs in soil from petrogenic sources in addition to those from pyrolytic sources in the rural areas.

2.4.3 PAHs in Aquatic Ecosystem

Polycyclic Aromatic Hydrocarbons from the various sources find their way into aquatic ecosystem by wet and dry atmospheric deposition from incomplete combustion of fossil fuels or hydrocarbons in oil, intake from storm water, drainage water and sewage systems as well as petroleum production, usage and spillage or natural oil seeps (WHO, 2003). It has also been found that certain plants and animal pigments are able to biosynthesize PAHs in a reducing condition in an aquatic environment (anoxic sediment); this is an indirect biosynthesis of PAHs and it also adds to the bulk of the compound found in such aquatic ecosystem (Brooks, 1997).

When PAHs enter aquatic environment, their fate is determined by the type of compound and the characteristics of the substrate to which it is attached; this is because PAHs are complex compounds and they are hardly found as a single substance (Brooks, 1997). Consequently, PAHs in an aquatic environment could evaporate, disperse into the water column, become incorporated into bottom sediments, and concentrate in aquatic biota or experience oxidation and biodegradation (Brooks, 1997). The lower molecular weight polycyclic aromatic hydrocarbons such as naphthalene could easily evaporate and the soluble fractions such as phenanthrene could undergo photo-oxidation and become degraded (Brooks, 1997). Degradation is increased at higher concentration, elevated temperature and oxygen levels and in the presence of much sunlight (Brooks, 1997). The higher molecular weights fractions which are unlikely to dissolve due to their hydrophobic nature are found strongly attached to substrates or particles or adsorb to organic fractions in sediments or absorbed by living organisms in the water (ATSDR, 1999); the ultimate fate of such compounds in the sediments is biotransformation and degradation by aquatic organisms (Brooks, 1997). Degradation however occurs very slowly in the absence of oxygen and may persist indefinitely in anaerobic conditions (Neff, 1979; Brooks, 1997).

In addition, studies have shown that all aquatic organisms rapidly bio-concentrate PAHs from low concentration in the ambient water (Brooks, 1997). Other studies conducted also revealed that species lower down on the food chain such as zooplankton, phytoplankton and invertebrates (like mussels and molluscs) can bio-accumulate PAHs. They could still lose much of the accumulated hydrocarbon compounds if clean water is again available. However, if the exposure is chronic, the hydrocarbon may enter more stable tissues (like lipids depot) and as long as the animal is in positive nutritional balance, it will only very slowly release the hydrocarbons (Kostopolou *et al.*, 2009). Also, it has been found that colder waters can slow down the

metabolism and elimination of hydrocarbons; as a result, animals feeding in arctic waters have a greater chance of bio-accumulating some hydrocarbons (Kostopolou *et al.*, 2009). Furthermore, recent studies have shown that biodegradation process which naturally reduces the level of organic pollutant in aquatic environment is mostly effective for the two or three rings PAHs (Naphthalene, Anthracene) while those with more condensed rings are relatively resistant to biodegradation (Obayori & Salaam, 2010).

PAHs in Sediment

Sediment is the part of an aqueous formation or solution that settles at the bottom. In aquatic environment, the sediment is the complex bottom part and is usually made up of moist soil that constitute the habitat for living and non- living aquatic biota as well as containing substrates and other compounds that characterise the type of aquatic and activities in the surrounding terrestrial environment in which the sediment is found. PAHs which are one of the many compounds concentrated in sediments have been found to reflect the history of fossil fuel combustion in the environment (Ekonomiuk *et al.*, 2006). Also, about 90% of the PAHs present in the environment can be stored in soils and sediments and they are considered as the best environmental sink for these compounds (Ekonomiuk *et al.*, 2006).

Higher molecular weight PAHs which are hydrophobic compounds and have less solubility in water tend to settle in sediments and may be dissolved in any oily contaminants found their or be attached to substrates or other compounds, be degraded by microbes or bio concentrate in aquatic organisms, mostly bivalve molluscs (such as mussels *Mytilus edulis*) and oysters (of the genera *Ostrea* and *Crassastrea*) and lesser tendency to accumulate in invertebrates, plants and fish; this is due to the highly permeable filtering gills of molluscs and oysters (Brooks, 1997). Bioavailability of PAHs compounds from sediments for adsorption in animals seem to be

directly related to the aqueous solubility of the compound, the concentration of the compound in the sediment, and the sediment grain size, and inversely related to sediment organic carbon content and animal size (Obayori & Salaam, 2010).

Also, studies have shown that PAHs degradation occurs at the water-sediment interface more than in deeper portions (Neff *et al.*, 2004). This is because the top or surface sediments contain more oxygen, rich in nutrient and more biologically active; degradation is therefore sped up by the healthy bacterial and fungal communities. In anoxic sediments where anaerobic conditions occur, the heavier molecular weight PAHs (four to seven rings) may persist for years (Neff *et al.*, 2004).

Xiao Jun *et al.*, 2006, as cited by Agbozu and Opuene, 2008 believed that a measure of the presence of PAHs in soils and sediments would give an indication of the extent of this pollutant in the environment; this is probably due to the readily ability of PAHs to adsorb to dust particles, humic matters and settle in sediments. Also, according to Kostopoulou *et al.* 2009, ‘the quality of marine waters is directly related to the quality of sediments, because they are the final compartment of storage of a large number of xenobiotics (foreign compounds)’. Although this study work is not on marine waters, yet it can be drawn that the quality of an environment especially an aquatic environment is directly related to the quality of sediments.

2.4.4 PAHs in Plants

PAHs in plants could either be from any of the major sources – Natural and Anthropogenic. The natural sources which are seen as volcanic eruption and forest fires are not usually considered as contributing to the bulk of pollutants. However, studies have shown that ancient forest fires could be used to explain the presence of certain unsubstituted PAHs including fluoranthene, pyrene, benzo(a)anthracene benzo-fluoranthenes, benzopyrenes, indeno[1,2,3, -cd]pyrene and

probably phenanthrene and chrysene in the environment and in peat (a type of wood plant) (Ekonomiuk *et al.*, 2006). It was also found that smoke from forest fires contain the same PAHs as those emitted from anthropogenic sources it is therefore difficult to say that the PAHs found in the wood plant are from forest fires only (Ekonomiuk *et al.*, 2006).

Whether PAHs are from natural or anthropogenic pyrolytic sources, they find their way into plants majorly by atmospheric deposition; they settle on leaves, stem and other shoot parts (Hites & Staci, 1994). Depending on the type of PAHs and the concentration, they may be ‘washed’ off onto the soil by rain or dew and if they cannot dissolve in water may remain on the shoot part to which it is attached especially the leaves and could be consumed by animals thereby entering the animal food chain. The fate of PAHs on shoot part could be chemical oxidation to other products or returned to the soil as the plants decay. Metabolism and photo decomposition by sunlight could also take place as well as absorption into the plants internal system through translocation (<http://www.env.gov.bc.ca> [2012]). Plants growing in highly contaminated areas may assimilate the compound beyond metabolism and degradation resulting in accumulation in plant tissues (Eisler, 1987); however, due to the lipophilic nature of PAHs, they will not bio-accumulate in plants with high moisture content and limited transfer from soil to root vegetables will occur (Scientific Committee on Food – SCF, 2002). PAHs are known to affect germination and growth in plants and inhibit physiological processes such as photosynthesis or mineral uptake (Anna *et al.*, 2007), and their rate of transfer is influenced by soil characteristics, the plant and the presence of co-pollutants (SCF, 2002).

Anthropogenic petrogenic PAHs contamination also occur in plants when the root or any of the parts is exposed to hydrocarbon oil polluted soil or sediment; this may be through storm water or river runoff into soil from polluted areas, waste recycling system, oil spillage and other activities

that involve the introduction of hydrocarbons in oil into soil and waterways. A study carried out on the relationship between heavy fuel oil phytotoxicity and PAHs which involves artificial exposure of plants to refined petroleum caused visual symptoms of stress such as chlorosis, yellowing, growth reduction and perturbations in developmental parameters (Anna *et al.*, 2007). Bioaccumulation was also found to occur in shoot tissues evenly at very low levels of contamination, and highly related to the conditions of exposure to the oil. Further studies carried out on *salicornia* plants (an annual salt-marsh specie) revealed that plants grown in PAHs polluted environment can take up and bioaccumulate these compounds (Anna *et al.*, 2007). PAHs is believed to have entered the plants through the cuticle of oil-coated shoots or by the roots when in contact with oiled sediments (cuticle is a protective structure that covers the outer walls of the epidermis cells, preventing passive dessication by sealing plants surface with a relatively impervious barrier to water) (Anna *et al.*, 2007). PAHs are highly soluble in the lipophilic cuticle structure and may passively penetrate into the plasmalemma of shoot cells without any barrier (Anna *et al.*, 2007). Anthracene has also been found in leaves of maize within epicuticular wax, cuticle, epidermal cell walls and cytoplasm of plants leaves (phytotoxicity). Furthermore, previous studies reported in Anna *et al.*, 2007 have suggested that PAHs can dissolve in the plasma membrane and open it up by displacing fatty molecules; in turn, the plasma membrane permeability is increased and the ionic balance is affected which in halophytic plants, modifies their ability to tolerate salinity. Benzo (a)pyrene has also been found to affect plant photosynthesis and respiration by a chlorophyll breakdown and an enzymatic inhibition of the electron of the electron transport respectively (Anna *et al.*, 2007).

All the studies discussed above and several other studies have shown that it is possible for terrestrial plants to take up PAHs through their roots and/or leaves and other shoot parts and

translocate them to various plant parts (<http://www.env.gov.bc.ca> [2012]). Carcinogenic PAHs have been extracted from a large variety of fresh plants (vegetables, fruits, grains and edible mushrooms) (Eisler, 1987). It was also found that PAH concentration for plants are generally more at plant surfaces than internal tissues and greater in above ground plant parts than those below ground, more in plants with broad leaves (greater surface area) than those with narrow leaves (Eisler, 1987). This could be due to the findings that reflected that PAHs with heavy molecular weight are less soluble in water and therefore have fewer tendencies to migrate from point of release (pollution) to groundwater (WHO, 2003) and therefore reduces their availability for plants uptake (SCF, 2002). This is also supported by a study which reflects that toxic effects of PAHs vary with their concentration in soil and their physicochemical properties especially water solubility (Anna *et al.*, 2007); however, it was also found that phenanthrene which is 17 times more water soluble than anthracene has less effect on nutrient uptake and shoot development. Based on all this findings, it is possible that PAHs in plants could be more from the pyrolytic source than from the petrogenic source.

2.4.5 PAHs in Animals

Animals are exposed to PAHs found in their environment either in the aquatic or terrestrial environment; even bird has been found to respond to toxic levels of the compound (Buha & Lah, 2011). They could be attached by deposition from the atmosphere or adsorption or absorption in aquatic environment. Different animal species respond differently to varying concentration of PAHs, for instance, absorption from the gastro-intestinal tract vary per animal species. The overall response to a given amount of PAHs is determined by the type of exposure, level of exposure and other characteristics of the environment and that of the organism exposed.

Animals may be exposed to PAHs in their environment by inhalation, dermal contact and ingestion. The major routes of exposure to PAHs in animal are from food in their surrounding environment. Food can be contaminated by environmental PAHs that are present in air (by deposition), soil (by transfer or translocation into plants or other animal food present in the soil) and water (by deposition on the animal or when drinking PAHs contaminated water or eating contaminated food or absorption into body tissues). Studies have shown that PAHs content of animals living on the land or in water can be many times higher than the content of PAHs in soil or water (Irwin, 1997).

Several studies have been carried out in the laboratory to observe the response of PAHs in animals and most of the results have been adapted also for human. Laboratory animals most often used are mice, rodents and hamsters. Adverse effects that have been observed in these organisms are tumors, adverse effects on reproduction, development and immunosuppression. The precise mechanisms of PAH-induced immunotoxicity are still not clear; however, it appears that immunosuppression may be involved in the mechanisms by which PAH induce cancer (Buha & Lah, 2011). Mixtures of PAHs have also been found to cause skin irritation and inflammation in animals (Superfund Research Program- SRP, 2013). The processes usually involves artificial exposure of the animals to varying concentration of PAHs usually benzo(a)pyrene by dermal contact, inhalation and addition to food (SRP, 2013).

The mechanism of reaction of PAHs in animals is similar to that in human and the result found in animal studies as mentioned earlier has been adapted for human; although rats and mice are much less sensitive than humans to the haemolytic effects of naphthalene and dog appear to be a better model for humans for this effect (ATSDR, 1995). However, those results have always been from artificial intentional exposure of the animals to varying concentrations of PAHs and

the quantity given may not necessarily be available for animals or human. No chronic animal toxicity studies involving oral exposure to PAHs mixtures exist (Irwin, 1997).

Studies have also shown that animals and micro-organisms can metabolise PAHs to products that may ultimately experience complete degradation (Eisler, 1987). Studies with animals exposed by inhalation, oral, dermal or parenteral administration indicate that PAHs are eliminated by urinary and biliary excretion of metabolites (ATSDR 1995: ATSDR, 1999). According to a report in (www.atsdr.cdc.gov), it was found that PAHs may accumulate in terrestrial animals through the food chain or by ingestion of soil; however, food chain exposure does not appear to be a major source of exposure to PAHs for aquatic animals (www.atsdr.cdc.gov).

2.4.6 PAHs in Human

Human beings are mainly exposed to Polycyclic Aromatic Hydrocarbons PAHs from food and ambient and indoor air. Breathing air containing cigarette smoke, wood smoke, vehicle exhausts, asphalt roads or smoke from agricultural burnings increase PAHs exposure significantly (WHO, 2003). Exposure also occurs when human come in contact with air, water or soil near hazardous waste sites or drink contaminated water and cow milk or if there is skin contact with soot and tars (ATSDR, 1996). Certain food processing method such drying and smoking and cooking of foods at high temperature such as grilling or charring of meats, roasting and frying are major sources of PAHs contamination when such foods are consumed (ATSDR, 1996). Other food sources are contaminated cereals, flour, bread, vegetables, fruits and contaminated processed foods. Infants of nursing mothers living near hazardous waste sites could also be exposed to PAHs through mother's breast milk (ATSDR, 1996: SRP, 2013). The figure below illustrates the various exposure pathways in human:

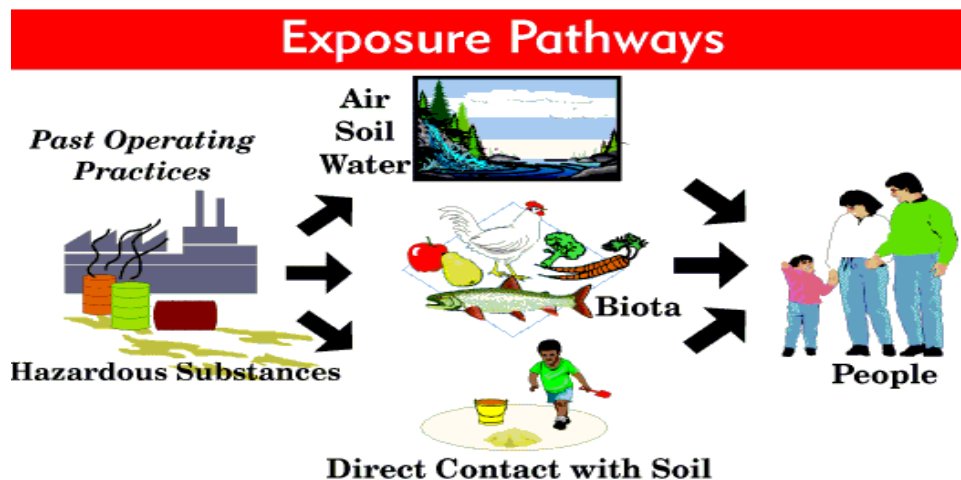


Fig. 2.3: PAHs Exposure Pathway in Human

Source: (Superfund Research Program - SRP, Oregon State University, 2013)

In humans, PAHs are important because of their toxic abilities and harmful tendencies (WHO, 2003). They are known to be responsible for certain carcinogenic characters seen in laboratory test animals such as mice and believed to be capable of similar tendencies in human as reported in the article Breast Cancer and Environmental Risk Factors BCERF, 2001. Their toxic abilities have been demonstrated in mice and hamsters where they resulted in cancer and death, as a result the tests have not been carried out in humans (Campbell, 2008). However, laboratory animals may be more susceptible to PAHs because of the differences in the activation or detoxification of the compound in human and animals, also, the concentration given to test animals are not usually present for human (BCERF, 2001). Other health effects that could arise from exposure to PAHs pollutants in human are skin disease or skin cancer, black lung, emphysema, nervous, endocrine and reproductive systems disorder (Campbell, 2008).

Further experiments done with animals have shown that the active dosages of PAHs are at least 1000 times higher than their daily intake by human with food and water; the daily intake of benzo(a)pyrene (which is considered as a prototype of the carcinogenic PAHs and the most

thoroughly studied) via a normal food and water consumption ranges between 0.5 and 2.5µg and very rarely exceeds 3µg (Kostopoulou *et al.*, 2009). Also, teratogenic actions of some PAHs have been observed in animals but no similar actions have been observed for humans (Kostopoulou *et al.*, 2009).

Target organs for PAHs toxic action are diverse due partly to extensive distribution in the body and also to selective attack by these chemicals on proliferating cells (Eisler, 1987). The rate of distribution of PAHs can be influenced by the presence of other (fatty) compounds that may enter the body at the same time with PAHs. PAHs can enter all the tissues of the body that contain fat. Potential targets for petrogenic tricyclic PAHs include ion channels, structural proteins or regulatory enzymes involved in the cardiac contraction cycle (Tuvikene, 1995). Tissue affected is determined by route of administration and species under investigation (Eisler, 1987). They tend to be stored mostly in the kidneys, liver and fat; smaller amounts are stored in the spleen, adrenal glands and ovaries (ATSDR, 1995; Buha & Lah, 2011). In experimental animals, damage to red blood cell formation system (haematopoiesis) and the lymphoid system is usually common (Eisler, 1987). In rats, the target organs for 7,12 – dimethylbenz(a)anthracene are skin, small intestine, kidney and mammary gland, whereas in fish, the primary target organ is liver (Eisler, 1987). Based on studies of benzo(a)pyrene in animals, it was found that women may be at increased risk of reproductive dysfunction following exposure to high levels of PAHs (ATSDR, 1999).

Extensive metabolism of PAHs compounds by humans has been demonstrated majorly through animal studies; as a result, food chain bio-magnification of the compounds does not appear to be significant (ATSDR, 1999). However, evidences exist that PAHs are enzymatically converted to

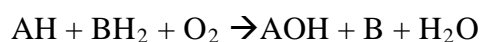
highly reactive metabolites that bind covalently to macromolecules such as DNA, thereby causing mutagenesis and carcinogenesis in experimental animals (Irwin, 1997); in most cases, carcinogenesis occurs over a period of many months in experimental animals and many years in man (Eisler, 1987). The mechanism of toxicity is considered to be interference with function of cellular membranes as well as with enzyme systems which are associated with the membrane (Bouwmeester *et al.*, 2006).

2.5 Metabolism of PAHs

PAHs are metabolised in living tissues of animals and humans. The reactions are made possible by the action of cytochrome P450 CYP enzymes which oxidise them into their primary and secondary metabolites; the reactions could occur in two phases called the phase 1 and phase 2 enzymes reaction (Tuvikene, 1995). All these take place in an enzyme system referred to as Microsomal Mixed Function Oxidase System MFOS with the CYPs as the functional oxidase (www.crios.be/pahs/toxicology). CYP1A1 is an isoform of CYP that is highly induced by planar aromatic compounds like benzo(a)pyrene and which is able to metabolize a wide range of substrates, in particular PAHs (Padmini *et al.*, 2009). MFOs enzymes are a superfamily of ubiquitous enzymes involved in the metabolism of a wide range of either endogenous or exogenous (xenobiotic) lipophilic compounds (www.crios.be/pahs/toxicology). They are oxidase enzymes that catalyse a reaction in which each of the two atoms of oxygen in O₂ is used for a different function in the reaction (Rogers, 2006). Oxidase is a general name for enzymes that catalyse oxidations in which molecular oxygen is the electron acceptor but oxygen atoms do not appear in the oxidized product (Rogers, 2006). Cytochrome P450 enzymes add oxygen atoms to the xenobiotic rings, making them more water soluble and creating anchors for attachment of

larger groups, like sugars or glutathione leading to their elimination; as a result, the non-polar PAHs are converted into the hydroxyl and epoxy derivatives (Padmini *et al.*, 2009).

Microsomal mixed function oxidase enzymes are usually found associated with the endoplasmic reticulum of microsomal tissues located in the livers of vertebrates and the hepato-pancreas of invertebrates and have also been found in other organs of both groups (www.crios.be/pahs/toxicology). Not all invertebrates and vertebrates however possess the MFO systems though this may be due to the lack of appropriate technology to detect these enzymes rather than the lack of the system (Padmini *et al.*, 2009). The reaction generally proceeds as follows:



- AH is the PAH or other lipophilic xenobiotics
- BH₂ is a reduced hydroxyl compound produced in living cells and it may be NADH (reduced nicotinic amide adenine dinucleotide) or NADPH (reduced nicotinic amide adenine dinucleotide phosphate)
- O₂ is molecular oxygen
- AOH is the polar hydroxyl derivative product of the PAHs or lipophilic xenobiotic
- B is the oxidised NAD⁺ or NADP⁺
- The other product could be water or arene oxides intermediates

MFOs require NADH or NADPH which are produced in living cells as well as molecular oxygen which is added by CYP 450 enzymes to carry out the reactions and the process involves steps of enzymatic and non-enzymatic reactions in which the PAHs are converted to arene oxide intermediates, *trans*-dihydrodiols, phenols and quinones (www.crios.be/pahs/toxicology). The

first reaction is an epoxidation with benzo(a)pyrene, the product is the corresponding 7,8-epoxide, that in turn is subject to epoxide hydrolases to form stereoisomic dihydrodiols. These are converted further to the 7, 8-dihydrodiol-9, 10-epoxide. The diol epoxide can exist in four stereoisomeric forms of which the key carcinogenic product is benzo(a)pyrene-r-7, t-8-diol-t-9, 10-epoxide. PAHs epoxides can then be conjugated with glutathione. This conjugation is regarded as a true detoxification reaction and is mediated by glutathione transferase (GSTM1). The epoxides that are not conjugated with glutathione are converted into phenols and diols (www.criios.be/pahs/toxicology). These intermediate products are known to be toxic and may be more harmful than the parent unmetabolised PAHs and could cause damage before they can be removed (Padmini *et al.*, 2009).

Figure 2.4 below shows the metabolism of benzo(a)pyrene as a model for PAHs metabolism.

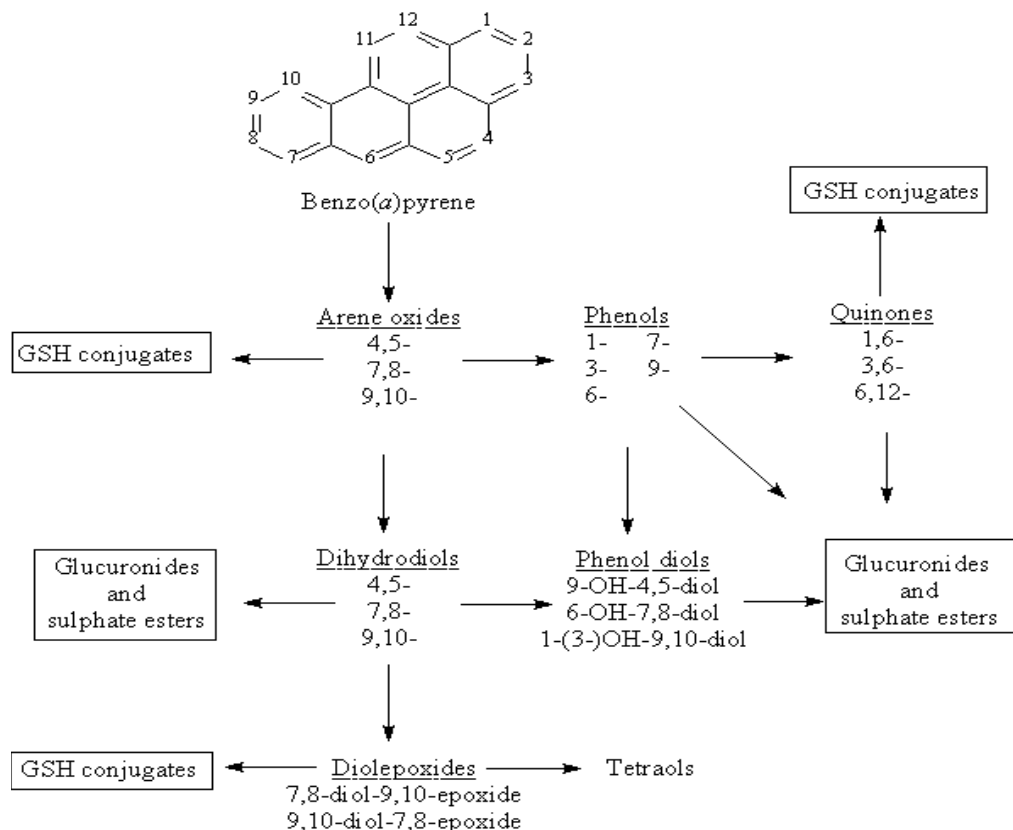
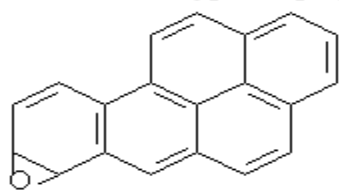


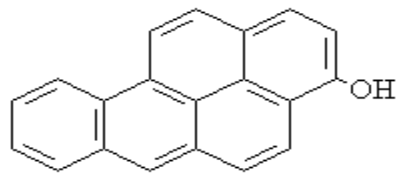
Fig. 2.4: Benzo(a)pyrene as a model of PAHs Metabolism

Adapted from: www.crios.be/pahs/toxicology

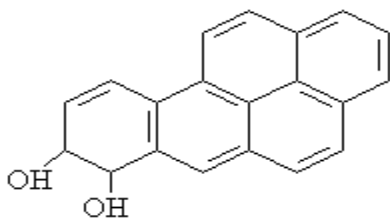
Some PAH metabolites however may not be sufficiently polar to be excreted and are therefore conjugated with glucuronic or sulfuric acids in living cells to enable excretion occur. In addition to conjugation, the hydroxylated derivatives of PAHs may undergo a number of oxidation and hydroxylation reactions. These include the conversion of phenols to phenol-epoxides and subsequently to diphenols and triols, diols to tetrols and diol-epoxides, and triols to triol-epoxides and pentols. Structure of some PAHs metabolites are shown in figure 2.5:



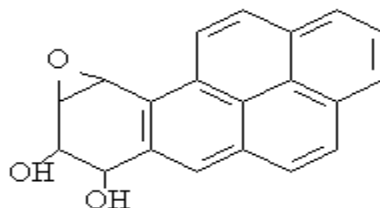
Arene oxide
7,8-epoxy B(a)P



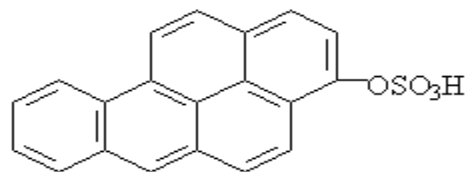
Phenol
3-OH B(a)P



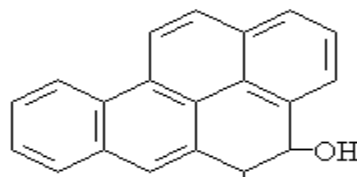
Dihydrodiol
7,8-dihydroxy 7,8-dihydro B(a)P



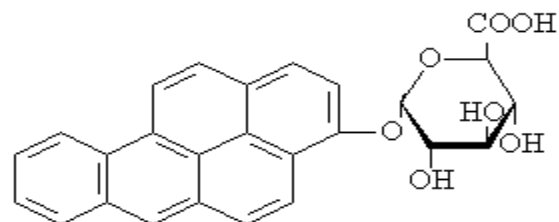
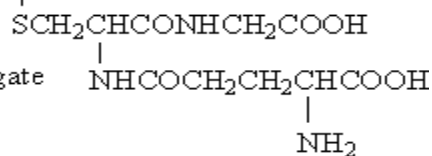
Diolepoxide
9,10-epoxy, 7,8-dihydroxy 7,8-dihydro B(a)P



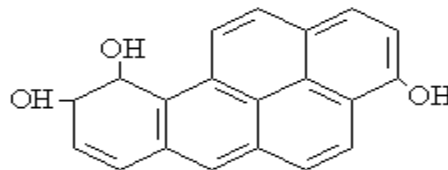
Sulphate ester



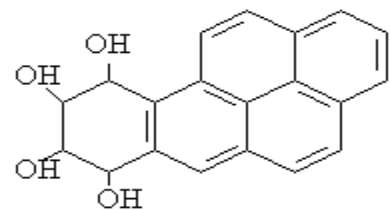
Glutathione conjugate



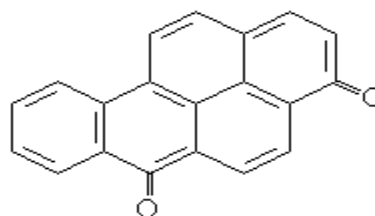
Glucuronide



Phenol diol
3,9,10-trihydroxy 9,10-dihydro B(a)P



Tetraol
7,8,9,10-tetrahydroxy 7,8,9,10-tetrahydro B(a)P



Quinone
B(a)P 3,6-dione

Fig. 2.5: Structure of some PAHs Metabolites (Adapted from: www.crios.be/pahs/toxicology)

Despite the process of detoxification and excretion that PAHs go through in living cells, some metabolites such as epoxides and dihydrodiols of some PAHs may become very reactive and could bind to cellular proteins and DNA (Buha & Lah, 2011). Also, the generation or production of several metabolites in the process of detoxifying PAHs could directly or indirectly have toxic effects on the cells and depletes the cell's antioxidant capacity; when a cell's pro-oxidants exceed its antioxidant capacity, free radicals accumulate and oxidative stress occurs. Studies have been carried out and more still under way to show that the increased activities of cytochrome P450 enzymes in detoxifying PAHs could have profound effects on neurological functioning and other health related issues due to oxidative stress. Such reactions are the ones believed to be responsible for the carcinogenic and mutagenic behaviour of PAHs.

2.5.1 PAHs metabolism and Oxidative Stress

Oxidative stress is caused by an imbalance between the production of reactive oxygen and a biological system's ability to readily detoxify the reactive intermediates or easily repair the resulting damage (Rogers, 2006). It usually occur as a result of disturbances in the normal redox state due to the production of peroxides and free radicals that could damage components of the cell, including proteins, lipids and DNA; this is believed to be capable of causing toxic effects (Rogers, 2006). Oxidative stress is thought to be one of the major causes of many human diseases and has been implicated as an important mechanism in the onset of several diseased state including neuro behavioural toxicity and carcinogenicity of PAHs (Padmini *et al.*, 2009); it can result in severe cellular dysfunction due to peroxidation of membrane lipids, protein modification, depletion of nicotinamide nucleotides, cytoskeletal disruption and DNA damage (Padmini *et al.*, 2009).

The link between PAHs metabolism and oxidative stress is due to the induction of CYP 450 and in particular CYP1A1 in the microsomal mixed function oxidase MFOs enzyme system by the presence of PAHs in the body (Padmini *et al.*, 2009). The uncoupling of electron transfer and oxygen reduction from mono-oxygenation by the enzymes due to their increased activity in detoxifying the xenobiotic (in this case PAHs) can result in the release of O_2^- , H_2O_2 and OH^- . These reactive oxygen species ROS or oxy radicals react with DNA, proteins and membrane lipids in the intracellular milieu thereby contributing to cytotoxic and neurological deficits (Padmini *et al.*, 2009).

Although Reactive Oxygen Species ROS normally exists in all aerobic cells in balance with biochemical antioxidants and different enzymatic and non-enzymatic antioxidant defence systems; yet during PAHs metabolism, when the bio activation exceeds the detoxification it causes in production of biologically reactive metabolites, it may result in the formation of ROS (Padmini *et al.*, 2009). The increase in lipid peroxidation and decrease in antioxidant defence systems may lead to oxidative stress, sometimes result in insoluble protein (an aggregate which fails to be degraded by the existing cellular machinery), and accumulates within the cytoplasm (Padmini *et al.*, 2009). The resultant effect is that, it mainly affects the rates of metabolism, growth and development, higher nervous function, as well as ability to deal with stress due to the antioxidant defence mechanism of a cell or tissue, thus leading to some abnormalities including neurodegenerative diseases such as Lou Gehrig's disease, Parkinson's disease, Alzheimer's disease and Huntington's disease (Chu & Patel, 2011); or other cellular malfunctions. In several recent reviews, the role of oxidative stress and oxidative damage to biomolecules has been supported by the pathogenesis of these neurodegenerative diseases, and specifically, Alzheimer's disease. Although the reason for this oxidative stress is not completely understood, yet it is

believed that it may be caused by the accumulation of toxic metabolites produced by metabolism of environmental contaminants especially PAHs (or other xenobiotics) which led to the excessive production of free radicals (Padmini *et al.*, 2009); However, questions are still been asked and more research under way.

2.5.2 Carcinogenicity

If PAHs metabolites bind to cellular proteins and DNA, the biochemical disruption and cell damage that results may lead to mutations, developmental malformations, tumours and cancer. Studies carried out on workers exposed to mixtures of PAHs over a long term period have shown an increased risk of majorly skin and lung but also bladder and gastro-intestinal cancers (International Agency for Research on Cancer IARC,1987). However, the workers were also exposed to other hydrocarbons at the same time and it is not certain if PAHs exposure was the major cause of the observed effects. Furthermore, in other studies done on carcinogenic tendencies of PAHs, the Center for Children's Environmental Health demonstrated that high prenatal exposure to PAHs showed cord blood of exposed babies with DNA damage that has been linked to cancer (Buha & Lah, 2011).

Based on available evidence, the International Agency for Research on Cancer IARC (1987) and US EPA (1994) has classified some PAHs as carcinogenic to animals and some mixtures of PAHs as probably carcinogenic to humans. They include: benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a, h)anthracene, and indeno(1,2,3-cd)pyrene. Benzo(a)pyrene is the most common PAHs and most likely to cause cancer in animals and is notable for being the first known chemical carcinogen.

2.5.3 Teratogenicity

Teratogenicity is the process of action of a teratogen. According to medical dictionary definition, a teratogen is an agent or factor that causes malformation of the embryo or can disrupt the development of an embryo or foetus in a pregnant mother's womb especially in early pregnancy; they could be toxic chemicals, radiation, viruses, alcohol, smoking, certain prescription drugs and numerous other agents (Mosby's Medical dictionary, 2009).

There is growing evidence that prenatal exposure to air pollutants from combustion of coal and other fossil fuels have adverse effects on foetal growth and early child neurodevelopment. Molecular and epidemiological research has shown that foetuses and infants are more susceptible than adults to the harmful effects of a variety of environmental contaminants, including PAHs (Padmini *et al.*, 2009). Studies carried out on animals have revealed that teratogenic or embryotoxic effects occurred when experimental animals such as mice were exposed to PAHs such as benzo(a)anthracene, benzo(a)pyrene, and naphthalene; Laboratory studies conducted on these organisms have demonstrated that ingestion of high levels of benzo(a)pyrene during pregnancy resulted in birth defects and decreased body weight in the offspring (Buha & Lah, 2011). Other studies have also shown that fish embryos and larvae are highly sensitive to PAHs mixtures from a variety of sources, including creosote wood preservatives, oil sands and sediments impacted by urbanisation (Incardona *et al.*, 2008).

Also, weathered crude oil and tricyclic PAHs (Fluorene, dibenzothiophene and Phenanthrene) were found to cause cardiac dysfunction in fish soon after the heart was active; the heart which is the first organ to be functional in embryos of fish and other vertebrates could fail to develop and become atretic (string-like) when exposed continuously to cardiac toxins at developmental stage (Tuvikene, 1995). It is not known whether these effects can occur in humans (Buha & Lah,

2011). However, reports on studies conducted by the Centre for Children's Environmental Health demonstrate that exposure to PAHs pollution during pregnancy is related to adverse birth outcomes including low birth weight, premature delivery, and heart malformations (Buha & Lah, 2011). It was also found that high prenatal exposure to PAHs is also associated with lower IQ at age three, increased behavioural problems at ages six and eight, and childhood asthma.

2.5.4 Mutagenicity

Mutagenesis is the process in which mutation occurs. Mutation occurs when a DNA gene is damaged or changed in such a way as to alter the genetic message carried by that gene. A mutagen is an agent or substance that can bring about a permanent alteration to the physical composition of a DNA gene such that the genetic message is changed. Once the gene has been damaged, the mRNA (messenger ribonucleic acid) transcribed from that gene will now carry an altered message. The polypeptide (or amino acid chain) made by translating the altered mRNA will now contain a different sequence of amino acids (Blamire, 2000).

Mutagenic actions occur due to genotoxicity; genotoxicity plays important role in the carcinogenicity process and probably in some forms of developmental toxicity (Buha & Lah, 2011). Genotoxic substances are those that are capable of altering DNA, thereby causing cancer or mutation (Mosby's medical dictionary, 2009). Genotoxic effects for some PAHs have been demonstrated both in rodents and in vitro tests using mammalian (including human) cell lines (Buha & Lah, 2011). Most of the PAHs are not genotoxic by themselves and they need to be metabolised to the diol epoxides which react with DNA, thus inducing mutagenic actions (Buha & Lah, 2011).

2.5.5 PAHs and the Aryl Hydrocarbon Receptor AHR Pathway

The AHR is an orphan receptor (a supposed or putative receptor identified based on its structure without evidence of function (Dorland, 2007)) in the basic helix-loop-helix (bHLH) - PAS (Per-ARNT-Sim (group of genetic amino acids)) family of transcriptional regulators that control a variety of developmental and physiological events, including neurogenesis, tracheal and salivary duct formation, toxin metabolism, circadian rhythms, response to hypoxia and hormone receptor function (SABios, 2012). AHR also known as Dioxin Receptor, is known to be responsible for most toxic responses observed after exposure to PAHs, dioxins (e.g. TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin), and Polychlorinated Biphenyls (SABios, 2012). AhR activation by PAHs including benzo (a)pyrene leads to the induction of aryl hydrocarbon hydrolase - AHH enzymes, which generate reactive metabolites from the parent compound (by the AhR regulation of AHH enzyme), and which contribute to apoptosis and other cellular damage in biological system (Padmini *et al.*, 2009). Although, PAHs are not usually genotoxic on their own, the biological effects are initiated by binding to the ligand-dependent transcription factor termed aromatic hydrocarbon receptor (AhR) (Padmini *et al.*, 2009). This ligand-bound AhR is translocated to the nucleus and forms a heterodimer with aryl hydrocarbon receptor nuclear translocator (ARNT) (Padmini *et al.*, 2009). Ligands (a small molecule that forms a complex with a biomolecule to serve a biological purpose) (Dorland, 2007)) for AHR are diverse and they include: dietary compounds, natural and synthetic flavonoids, natural products, and pharmaceuticals (SABios, 2012). Although the endogenous regulator of this pathway has not been identified, the AHR is known to bind to transcriptional regulators and be activated by a variety of compounds ranging from environmental contaminants to flavonoids (Kung *et al.*,

2009). Studies carried out on fish as shown the activation of this pathway by four-ring pyrogenic PAHs benz(a)anthracene (Tuvikene, 1995).

The function of the AHR pathway is still unclear (which is while it is termed an orphan receptor); however, animal models indicate that the receptor is important for normal development (Kung *et al.*, 2009). One hypothesis is that the AHR senses cellular stress and initiates the cellular response by altering gene expression and inhibiting cell cycle progression and that activation of the AHR by exogenous environmental chemicals results in the dysregulation of this normal function (Kung *et al.*, 2009). Benz (a) anthracene has been found to act through the AHR pathway to cause a type of heart malformation in fish (Tuvikene, 1995).

2.6 Some Beneficial Importance of PAHs

Some importance of PAHs that may be considered to be beneficial are their use for research, in medicines, for dyes, plastics, building materials and pesticides; for instance, naphthalene is used in making dyes, explosives, plastics, lubricants and moth repellent. PAHs are also good in building materials as they do not burn or dissolve easily in water (Campbell, 2008). Furthermore, Fluoranthene has been used mainly as intermediates in the production of fluorescent dyes and pyrene in the production of perinon pigments (WHO, 2003). In addition, PAHs has been found in interstellar medium; their presence here and their absorptive features have been used in explaining infrared emission in ultra violet spectra of numerous sources (Allamandola *et al.*, 2003).

PAHs are produced in some countries for commercial purposes. In 1993, one of the greatest producers worldwide manufactured <50t of fluoranthene and <500t of pyrene (WHO, 2003). Some countries such as China, India, Canada, Mexico and Australia probably create the most as

they use a lot of fossil fuels and export a large amount of PAHs (Campbell, 2008). Such commercial productions of PAHs are not considered to be part of the bulk considered as environmental pollutants (Campbell, 2008); however, no matter the usefulness of PAHs, they are pollutants and should be handled as such.

2.7 Control of PAHs

Polycyclic Aromatic Hydrocarbons PAHs are pollutants and therefore should be controlled. The question now is considering their various sources and ubiquitous nature, how can they be controlled?

The only way to fully get rid of PAHs is to always have a complete organic combustion (Campbell, 2008); one in which the end product is carbon (IV) oxide and water. This would mean that we would not be able to make fire and get all the energy we derive from incomplete combustion. Since this may seem to be almost unachievable considering the enormous use of energy and other actions we achieve from incomplete combustion of fossil fuels (Campbell, 2008), the best we can do is to put control in place at the various sources of utilisations that generate PAHs.

We may not be able to completely eliminate actions such as burning of fossil fuels and some food production practices that have become part of our living, yet regulations can be put in place; which has been done by several global, national and even non-governmental organisations. This includes: World Health Organisation WHO, Agency for Toxic Substances and Diseases Regulation ATSDR, Breast Cancer Enlightenment Research Fund BCERF, Environmental Protection Agencies EPA, Occupational Safety and Health Administration OSHA, National

Institute for Occupational Safety and Health NIOSH and many others. These regulations have been placed on food, water, soil, air and occupational practices that might involve exposure to PAHs. They are to be employed in the various practices that generate PAHs through these sources. Some of these regulations include:

1. The Occupational Safety and Health Administration (OSHA) regulated exposures to PAHs under OSHA's Air Contaminants Standard for substances termed coal tar pitch volatiles (CTPVs) and coke oven emissions; which are very rich source of PAHs. Employees exposed to CTPVs in the coke oven industry are covered by the coke oven emissions standard. The OSHA coke oven emissions standard requires employers to control employee exposure to coke oven emissions by the use of engineering controls and work practices (Buha & Lah, 2011). Wherever the engineering and work practice controls which have been instituted are not sufficient to reduce employee exposures to or below the permissible exposure limit, the employer shall nonetheless use them to reduce exposures to the lowest level achievable by these controls and shall supplement them by the use of respiratory protection (Buha & Lah, 2011). The OSHA standard also includes elements of medical surveillance for workers exposed to coke oven emissions. The OSHA PEL (permissible exposure levels) for PAHs in the workplace is $0.2\text{mg}/\text{m}^3$ for 8-hour TWA (time-weighted average) (Buha & Lah, 2011).
2. The National Institute for Occupational Safety and Health (NIOSH) recommends that the workplace exposure limit for PAHs be set at the lowest detectable concentration, which was $0.1\text{ mg}/\text{m}^3$ (REL=recommended exposure limit) for coal tar pitch volatile agents for a 10-hour workday, 40-hour workweek (Buha & Lah, 2011).

3. In 1980, EPA developed ambient water quality criteria to protect human health from the carcinogenic effects of PAH exposure. The recommendation was a goal of zero (non-detectable level for carcinogenic PAHs in ambient water). EPA, as a regulatory agency, sets a maximum contaminant level (MCL) for benzo(a)pyrene, the most carcinogenic PAH, at 0.2 ppb (Buha & Lah, 2011).
4. WHO guidelines for drinking water quality recommended a health based guideline value of 0.0007mg/litre for benzo(a)pyrene, corresponding to an upper-bound excess lifetime cancer risk of 10^{-5} ; this was published in the second edition of the guideline in 1998 (WHO, 2003).

Most of these regulations have been put in place for a long time now and in most cases are been enforced, yet we cannot say we have effectively controlled PAHs. Environmental discipline is the key and a conscious approach to improve on practices and minimise as much as possible our release of environmental pollutants that includes PAHs.

Another way is to keep moving towards alternate energy source such as: wind power, solar energy, water power, geothermal energy source, hydrogen, tidal power (Botkin & Keller, 2005) and others yet to be discovered. Although these ones too have their side effect, which majorly is that they may not be substantial enough to generate amount of energy needed at a given time, yet, they can be improved and have actually been developed and used in several countries that includes: United States of America, Philipines, Iceland and El Salvador, amongst others (Botkin & Keller, 2005). In fact, the study area of this research work is not left out as there are many solar powered street lights in Warri and wind power has also been used in Lagos Nigeria to power street lights. Alternative energy sources, particularly solar and wind are growing at

tremendous rates and studies have shown that they apparently may compete with fossil fuels; they offer our best chance to generate a cleaner energy form and develop a truly sustainable energy policy that will not harm the planet (Botkin & Keller, 2005) and avoid risk from harmful exposures to environmental pollutants including PAHs.

Furthermore, nature has its way of regulating the environment if the resources are utilised sustainably. For instance, plants or vegetation could remove pyrolytic PAHs in air from the atmosphere, which finally gets incorporated into the soil and permanently removed from the atmosphere (Hites & Staci, 1994). Also, pollutants from biomass burning can be controlled naturally if areas harvested for bioenergy are re-planted; there would be no net carbon dioxide emissions to the atmosphere (Botkin & Keller, 2005). This is still pointing towards sustainable use of natural resources which by far is the best approach to control the level of pollutants including PAHs and have a cleaner environment.

In addition, since PAHs are found throughout the environment and could be from natural and anthropogenic sources, it is almost impossible to avoid exposure; the best that can be done is to reduce exposure by avoiding certain areas and modifying some home and recreational activities.

Some practical steps that could be taken are:

- Avoid smoke from wood fires, whether from home heating or for recreational purposes.
- Avoid exposure to automobile exhaust and areas of high traffic congestion.
- Avoid areas where asphalt road construction or tar roofing is occurring.
- If you smoke, smoke outdoors and in areas away from children. Avoid areas where children may be exposed to second-hand smoke.
- Prepare foods by slower cooking over low heat, rather than by charring or grilling food.

- Avoid skin contact with soot. (SRP, 2013)
- Hair care and other cosmetics products that contain coal-tar, for instance, coal-tar shampoos should be used only if no other treatment is available.
- Personal protective equipment PPE should be provided in work place areas where emissions cannot be sufficiently reduced and extensive training done for the workers by specially trained personnel (Buha & Lah, 2011).

Other ways to reduce exposure to PAHs is by reducing emissions as much as possible. Some measures that could be put in place to minimize emissions are:

- Filtration and scrubbing of industrial emissions,
- Treatment of effluents,
- Use of catalytic converters and particle traps on motor vehicles.
- Regular environmental monitoring of air, water and soil pollution (Buha & Lah, 2011).

Lastly, one best approach to controlling PAHs as well as other environmental pollutants and their health and environmental risks is public education or public enlightenment. When the society becomes aware of the sources and harmful health and environmental effects of pollutants such as PAHs, there is possibility that more conscious checks or controls would be put in place as much as possible.

2.8 Analysis of PAHs

Polycyclic Aromatic Hydrocarbons from various samples can be quantified by passing them through chemical analysis in the laboratory. The method applied depends on the sample source;

whether it is from food sample or from environmental media. It is also determined by the type of analysis required at a given time. Chemical analysis could be required for legislation, monitoring for detection of frauds or compliance to limits, and monitoring for exposure limits in risk assessment procedure (Anklam *et. al.*, 2006).

No matter the sample source of the PAHs, extraction and pre-concentration steps are usually required for sample enrichment especially when the source is from uncontaminated aqueous samples (WHO, 2003). Several extraction techniques have been used to extract PAHs from various sample sources. For environmental samples, solid-liquid and liquid-liquid extraction have been used for soil, sediment and water samples; some of the methods used are Soxhlet Extraction SE, Supercritical Fluid Extraction SFE and Pressurised Liquid Extraction PLE (Anklam *et. al.*, 2006). Even simpler extraction techniques, such as liquid extraction at room temperature on a shaking device, were shown to be suitable for extracting PAHs from soil. These methods have been proven and approved by US Environmental Protection Agency US EPA has been effective for extracting the 16 PAHs that are considered to be of priority (Anklam *et. al.*, 2006).

After extraction, the next stage in the analytical process of PAHs is sample clean-up. This stage is necessary in order to remove any co-extractives (compounds that are extracted together with the PAHs in the extraction process) and produce a pure PAHs sample for chromatographic analysis. Examples of extracts that could be present are: aliphatic hydrocarbons, porphyrins, chlorins and carotenoids. Sample clean-up and consequently pre-concentration could take place during adsorption chromatography with silica gel, alumina or florisil (Anklam *et. al.*, 2006) and during fractional distillation into aliphatic and aromatic fractions using activated alumina

(neutral) column with n-hexane and Dichloromethane. The n-hexane removes the aliphatic hydrocarbons while Dichloromethane separates the aromatic fraction.

The clean-up method required depend largely on the selectivity of the applied extraction techniques and on the chromatographic method to be applied later on the pure sample; for instance, SFE extracts of urban air particles in a particular analysis carried out to monitor PAHs contained fewer co-extractives than SE or PLE extracts. And this was attributed to the fact that SE and PLE apply non-polar organic solvents which also dissolves humic acids and aliphatic hydrocarbons; subsequently, silica gel or alumina was used for the clean-up during adsorption chromatography (Anklam *et al.*, 2006).

After the clean-up, a pre-concentrated sample is derived which could still be pass through a further concentration process by placing the extract in a rotary vacuum evaporator or by exposing the extracts to laboratory room temperature for at least 24 hours until a concentrated extract of about 0.5-1.0ml is gotten. The concentration or sample enrichment could also be achieved by means of a suitable enrichment device – under a gentle Nitrogen gas stream (Kanchananayoon & Tatrahun, 2008).

The next stage is the actual analysis of the prepared samples and the method usually employed for PAHs is CHROMATOGRAPHY. Gas chromatography with mass spectrometry GC-MS detection operated in selected ion monitoring SIM as well as high performance liquid chromatography with fluorescence detection HPLC-FLD are methods that have been used for analysis of PAHs. The International Standard Organisation ISO standard 13877:1998 describes a method for the determination of PAHs in soil by HPLC, and very recently published standard ISO 18287:2006 for the determination of PAHs in soil by GC-MS (Anklam *et al.* 2006). Also, in

WHO guidelines report for drinking water quality, gas chromatography with flame ionisation detection GC-FID was used for analysing PAHs in drinking water (WHO, 2003).

2.8.1 Gas Chromatography

Chromatography is a mixture separating technique for compounds containing several solutes. It is suitable for identification of the various compounds present in a mixture of solutes as well as determining the amount present; it is therefore a useful tool for qualitative and quantitative analysis of chemical samples. The method involves the use of a solvent which could be gas, liquid or adsorbent medium (paper or gel) moving over another solvent; they are usually classified as having a stationary and a mobile phase (Sheffield Hallam University SHU, 2013). There are many techniques in Chromatography, and Gas Chromatography GC is one of them; there is also liquid chromatography in which the mobile phase is a suitable solvent and adsorption chromatography in which the mobile phase is a suitable solid. The major difference between them is in the type of mobile phasing used (SHU, 2013). Gas Chromatography has been extensively utilised in scientific research to analyse and identify substances. It has been estimated that 10-20% of known compounds can be estimated by GC (www.chem.agilent.com) and it is one of the preferred technique for PAHs analysis because of the way it works.

2.8.1.1 How GC Works

Gas chromatography has illustrated in the diagram (fig. 2.8) below works by using a gas called the carrier gas to move the solutes or samples (usually in the liquid state) when they are vaporised in a heating column through a stationary phase such that they are analysed and the result are read through a detector attached to the column.

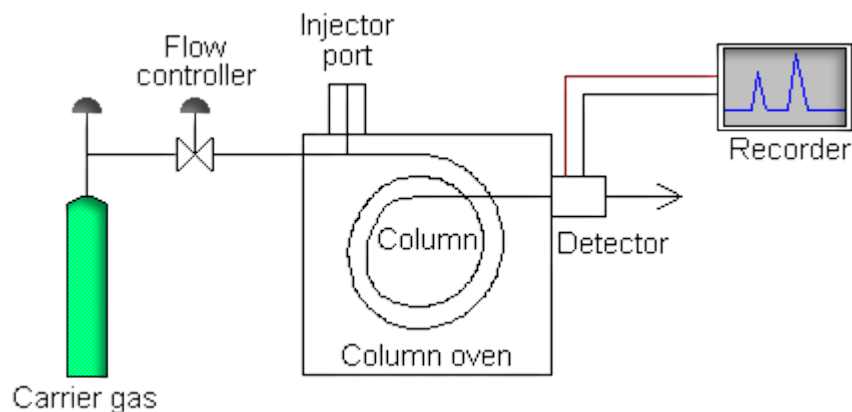


Fig. 2.6: Schematic representation of a Gas Chromatography

Adapted from: Sheffield Hallam University SHU, Biosciences
 Homepage. www.teaching.shu.ac.uk

To be suitable for GC, the solutes must be sufficiently volatile and stable to high temperature; if the solutes do not decompose at high temperature when heated, then it is suitable for GC analyses. This is one of the reasons why GC is preferred for analysis of PAHs (www.chem.agilent.com).

The sample to be analysed is introduced into the column through the injector by means of a micro-syringe, it is heated by the oven in the heating column and moved by the carrier gas which is usually an inert gas (such as: nitrogen, argon, helium or carbon (iv) oxide) through the column until they have been analysed and detected by a monitoring device which sends the signal to a recorder. The solute with the lowest temperature emerges first followed by the next until all the compounds present in the sample have been analysed. The emergence of the samples is determined by their physical properties and temperature and composition of the heating column. As the solutes emerge in the detector, the readings are recorded as electronic signal on the monitor and this is what is read as the chromatogram. The ideal chromatogram is a closely

spaced wave signal plotted against the elapse time with different peaks for different solutes. The peak of the chromatogram indicates the quantity of that solute present in the mixture while the retention time which is the time it takes before the sample elapses could be used to determine the type or identify the compound present. However, using the chromatogram peak and the retention time alone is not enough to know the quantity and type of the solute present. A known standard which is a pure sample containing similar solutes is subjected to similar column condition and the chromatogram peaks and retention times compare with that of the unknown sample and the result is determined. One condition necessary to have good chromatogram peak and hence good result is to ensure that only a small amount of the solutes sample is injected into the column; this will ensure that the emerging chromatograms are not overlapped and therefore measured distinctly.

The detector is also another important part of the GC components as it is the one that determines the type of reading that will be produce by the recorder. It is therefore necessary that the detector be very effective in detecting the result of the analysis and in yielding a good signal for recording. There are a few detectors used with chromatography in PAHs analysis and they include fluorescent detector, flame ionisation detector and mass spectrometry.

2.8.1.2 *Flame Ionisation Detector FID*

FID is a robust and easy to use method for analysing organic compounds including PAHs in gas chromatography. It is a mass flow dependent detector; this means that the signal produced is related to the rate at which solutes enter the detector. Gas Chromatography with flame ionisation detector GC-FID uses support gases such as hydrogen and air and has a detectability value of 100pg and dynamic range of 10^7 . Unlike some other detectors in which dilution with make-up gas lowers their response, GC-FID is unaffected by the make-up gas.

In GC-FID, effluent (which is the sample to be analysed) from the column is mixed with hydrogen and air and ignited. The flame produced by the burning of organic compounds produces ions and electrons which can conduct electricity through it. A large electrical potential is applied at the burner tip, and a collector electrode is located above the flame. The current resulting from the pyrolysis of any organic compounds is measured. The diagram below in fig. 2.7 illustrates a Flame Ionisation Detector.

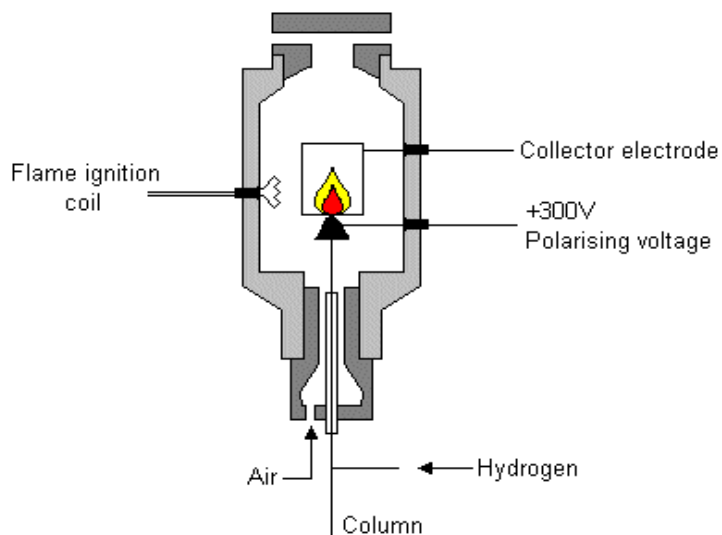


Fig. 2.7: Schematic representation of a Flame Ionisation Detector FID

Adapted from: Sheffield Hallam University SHU, Biosciences
Homepage. www.teaching.shu.ac.uk. (2013).

The advantages of using FID in GC are

- It is a useful general detector for the analysis of organic compounds;
- it has high sensitivity,
- It has a large linear response range, and low noise,

- It is also robust and easy to use.

However, its major disadvantage is that it destroys the sample. This means that the sample used for the analysis is used up in the process. An example of a detector that does not use up the sample during analytical process is mass spectrometry and it has been used in GC for analysis of organic compounds including PAHs (www.teaching.shu.ac.uk).

CHAPTER 3

MATERIALS AND METHODS

3.1 Implementation Approach

The approach used in carrying out the research processes include: sampling, sample preservation, sample treatment/preparation and sample analysis.

3.2 Description of Study/Sampling Location

The study location for this research work is Warri. Warri also known as ‘Oil City’ is a commercial city in Delta state Southern Nigeria in the oil rich Niger Delta region. It is located at an elevation of about 1meter above sea level and the coordinates is as indicated in figure 3.1 below:



Coordinates: 5°31'N 5°45'E 5.517°N
5.75°E

Country: Nigeria, State: Delta State

Modified from www.getamap.net
(google search) 2012.

Figure 3.1: Map of Nigeria, showing Warri in lower Niger Delta region and the coordinates.

Warri has a population of about 300,000 people according to the 2006 national population census (www.population.gov.ng). The people of Warri are known for their unique Pidgin English and they are made up majorly of the itsekiris, ijaws, urhobos, and isokos; although other ethnic group also exists. In recent years, this city has grown from being a rural area to a large commercial city, it has also expanded to include places like uvwie, udu and okpe communities and all have come together to form the larger Warri City with roads linking them to each other, however, each have their administrative jurisdiction (www.population.gov.ng). As a result of the location of Warri which sit at the bank of the Niger Delta, there are rivers, creeks, ponds and wetland areas around the city. Warri River has been classified as a stream (class H hydrographic); a stream is a body of running water moving to a lower level in a channel on land (www.getamap.net). Most of the sampling location for this research work are characterised by the presence of a pool, a creek, a stream or just a wetland area.

Most of the places in Warri are swampy area and marshes and most of the people especially those living close to the waters are either fishermen/women or take fishing as a hobby. It is one of the wettest regions with rainfall of about 8 to 10 months, majorly from May to October (Egborge & Olomukoro, 2004); while the dry season lasts from about November to April and is significantly marked by the cool "hamattan" dusty haze from the north-east winds. However, it frequently rains even in the dry season. The area is characterized by tropical equatorial climate with mean annual temperature of 32.8 °C and annual rainfall amount of 2673.8 mm. There are high temperatures of 36 °C and 37 °C (www.population.gov.ng). The marshy land area of Warri and its environs are mostly sand filled or composted before building structures are erected. Warri River which is one of the most important coastal rivers of the Niger Delta distributed in various

tributaries around the city and beyond is responsible for the marshy soil and swampy area that characterise the city (Egborge & Olomukoro, 2004).

In the early 1950s when crude oil was discovered in the Niger Delta, large deposit was found in Warri and its environs (www.population.gov.ng). Crude oil reserves found here increased the influx of people and petroleum exploration and production investors with the establishment of many crude oil refining and related activities companies such as Chevron, Shell Petroleum Development Company SPDC, Nigeria National Petroleum Company NNPC and others. As a result, oil exploration and production activities together with their associated gains and pains are the order of the day in this area. Environmental pollution has been a major bane of industrialisation in many developing and developed places and Warri is not an exception. Although there were commercial activities in Warri in time past due to slave trade and agricultural activities and others, there have been no much people in Warri as there are now. So, urbanisation with its unavoidable menace- environmental pollution has had it stroll on the city just as it is in many industrialised cities. Although PAHs are not only present in places where there are crude oil reserves; several other activities are peculiar to the everyday way of life of people in commercial places of developing countries that could increase their exposure to PAHs as well as other environmental pollutants, with a corresponding increase in the rate of harmful effects or incidence. However, atmospheric environmental pollutants alongside other type of pollutants could come from several sources and the problem is a global issue and not just peculiar to a certain place or people.

Five areas were strategically chosen, four within Warri and one outside Warri; the one outside Warri was chosen to serve as a check or control to the other sites.

The project sites are:

1. Ekpan –NNPC Complex area

Co-ordinates: 05° 33' 13.5sN

005° 44' 35.8sE

This site is along the Ekpan bridge express, after the NNPC staff quarters. There is a company opposite the sampling point and a church beside it. The exact sampling point is a river under the bridge. One major characteristics of this location is that there are not much human population here but the place is close to NNPC/Ekpan highway a major busy highway. The river could be a drain receiving waste water from neighbouring residential areas and industry.

2. Ugboroke community (Kingdom Development Centre)

05° 32' 37.6sN

005° 44' 35.8sE

This location can be said to describe the natural vegetation of Warri which is of rainforest with swamp forest in some areas (plate 3.1); the forest in Warri is rich in timber trees, palm trees, as well as fruit trees (www.population.gov). Ugboroke community is however one of the emerging areas in Warri and developmental features such as roads, modern building structures are taking over the forest.



Plate 3.1: Ugboroke Community showing the Swampy Forest of Warri

Ugboroke community is a densely populated area, made up of local indigenous people as well as others that have come to live within the community. One thing peculiar to this location is that, there are clusters of old, native houses, modern/semi-modern residential houses, small and medium scale businesses, factories, and companies, agricultural activities (poultry, fishing amongst others).



Plate 3.2: Sampling Site – Kingdom Development Centre Ugboroke

The sampling point is a pond at the back of a church (kingdom Development Centre). This point is actually like a wetland that is flooded most part of the year. Plantain trees, other trees, shrubs and plants are typical of this environment.

3. Ogunu (SPDC Industrial Area)

05° 31' 48.1sN

005° 42' 44.9sE



Plate 3.3: Ogunu River

This site is outside Shell Petroleum Development Company SPDC residential, recreational and mild administrative area. It is a local community that has been upgraded by virtue of the presence of the multinational companies in the area. Apart from SPDC, Ogunu community play host to, Pan Ocean Oil Company. The people in this community are majorly indigenes with few other non-indigenes. Their occupations are majorly petty trading, fishing, farming or idling. The exact sampling point is Ogunu River. There are residential houses around and even in or on the river; there is also a local public toilet and a refuse dump close by.

4. Okotie Sawmill, Effurun

05° 32' 23.3sN

005° 47' 24.0sE

This site is in the outskirts of Warri, in a place called Effurun. To many people, Effurun is not part of the Warri township but by geographical and political description, Effurun is part of the larger Warri City and is usually called together as - Effurun Warri. The actual sampling area is a majorly industrial with few residential houses; some of the industries and companies in the area are – Nigeria Bottling Company (Coca Cola) Depot, Phyton Engineering Company, Thermosteel Nigeria Limited, Okotie Plank Sawmill and NISRIN Construction. Okotie Plank Sawmill and NISRIN Construction are just by the river where the sampling was carried out. The sampling point was close to one of the vessels- houseboat constructed by NISRIN.

5. Agbarho river (control)

05° 31' 48.1sN

005° 42' 44.9sE

Agbarho Community is a town outside Warri; it is about 20km from Warri and located along the Ughelli/Port Harcourt highway. The actual sampling site is the Agbarho River. Just by the side of this river is an open abattoir and cow meat market; as a result of which there are usually herds of cattle grazing by the side of the river. Local abattoir processes such as burning of tyres and firewood is a common sight at the meat market. Also, during the sampling period, dredging activities were observed at the Agbarho river site.



Plate 3.4: Agbarho Cow market

The aerial photograph and geographical maps of the sampling sites above are illustrated below:

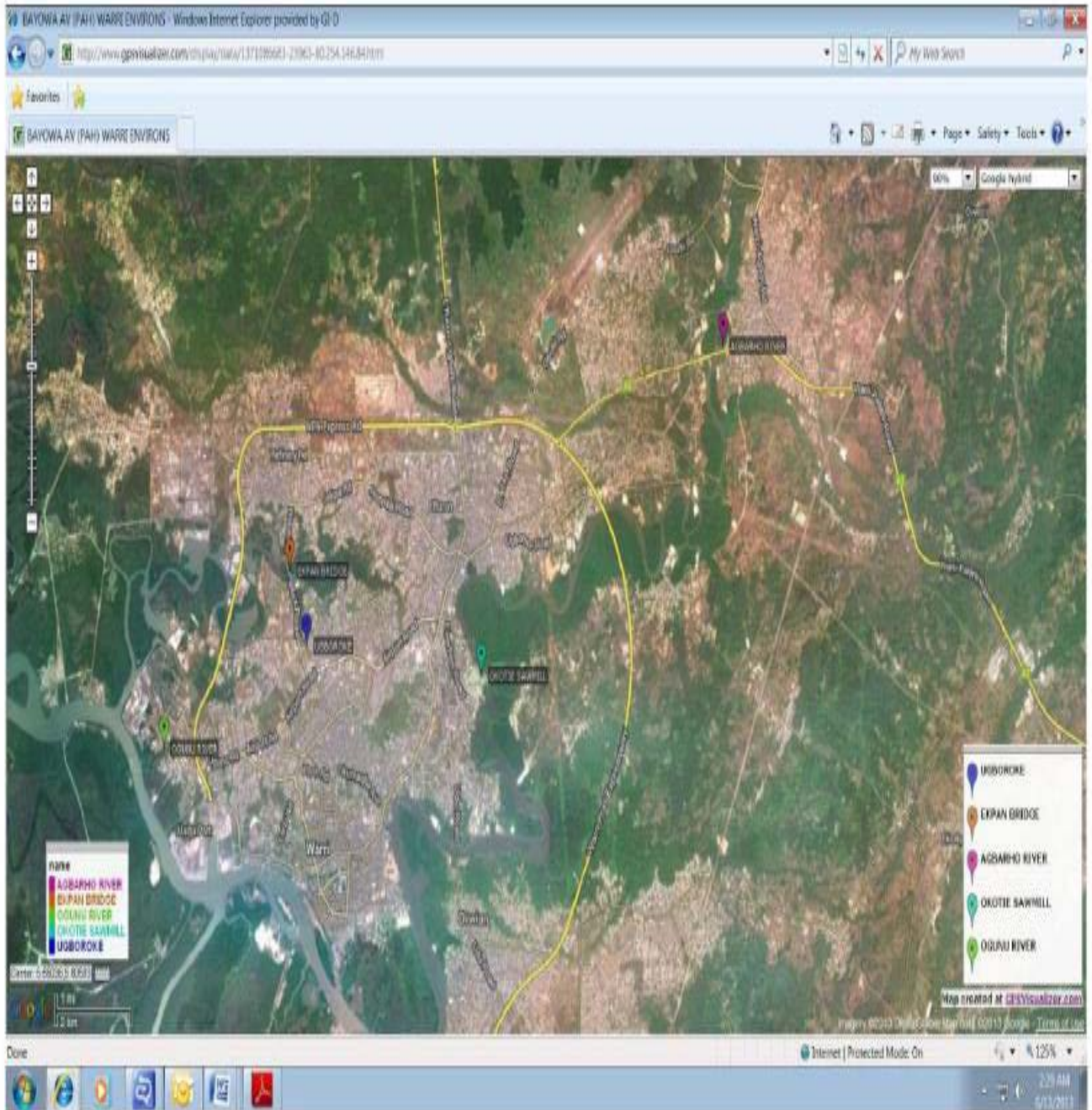


Fig3.2: Aerial Photograph of Sampling Locations

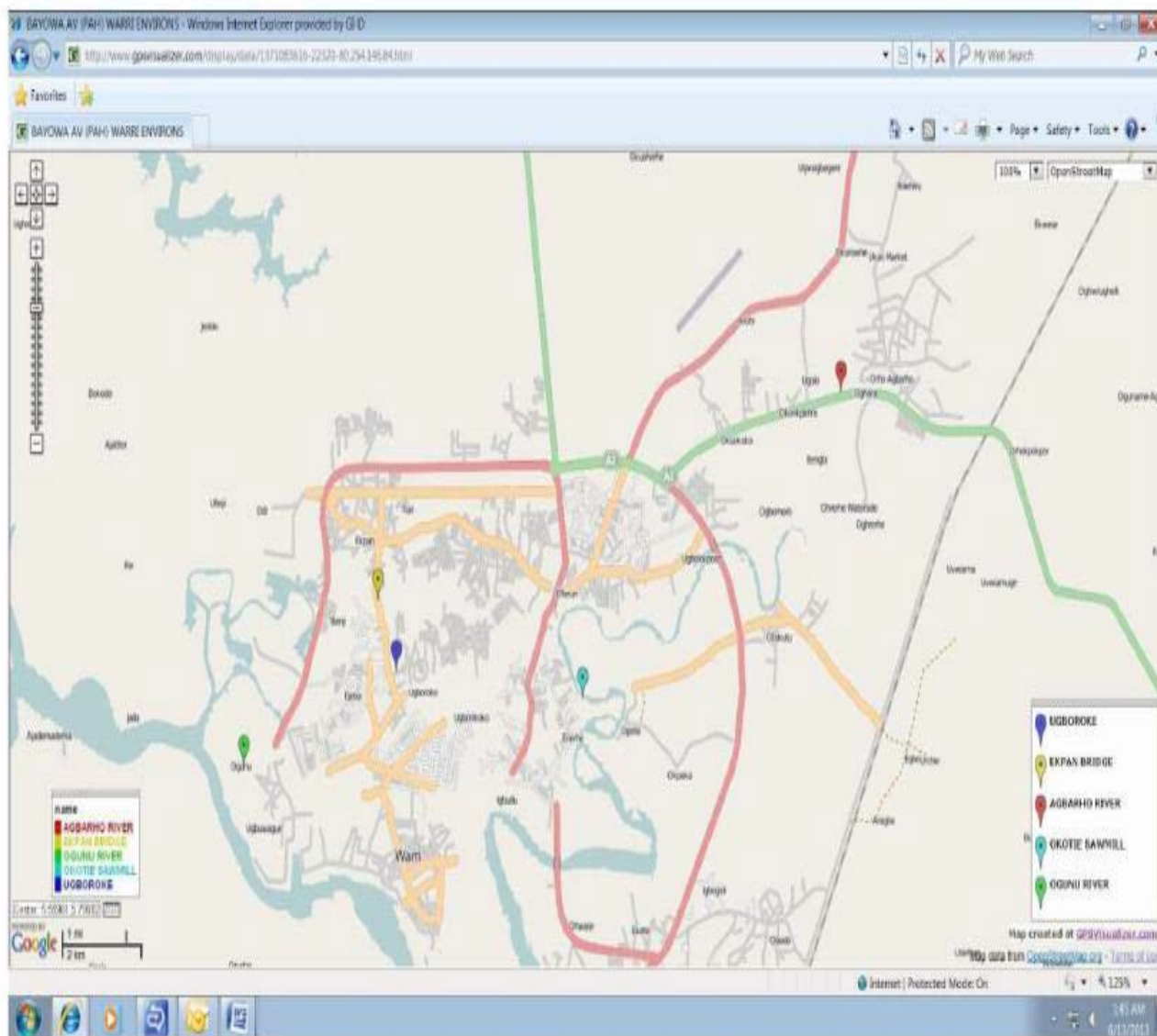


Fig 3.3: Geographical Map 1 of Sampling Locations

3.3 Sample Collection

Soil and sediments samples from the five sampling points were collected in the year 2012 for six months; three months in the dry season (January – March) and three months in the rainy season (June – August). The samples were collected using stainless steel hand auger and stainless steel

spoon into an aluminium foil paper; while a stainless steel grab sampler was used for sediment samples that were collected when the river was full. Top (0-15cm) and bottom (15-30cm) samples were collected at each point to form one composite sample and a total of ten samples were collected for each month in the dry season (January-March) and in the wet season (June-August).

The samples were wrapped in aluminium foil and properly preserved by cooling in a refrigerator at (4°C).

3.4 Sample Treatment/Preparation

The standard reference method employed in the PAH analysis is USEPA 8240

- Ten grams (10g) of sample was carefully weighed into a dried organic free and chromic acid pre-cleaned extraction bottle
- Ten grams (10g) of anhydrous Sodium Sulphate was added and mixed with a glass rod
- Twenty millilitres (20ml) of Hexane: Dichloromethane in the ratio 3:1 (90ml of Hexane and 30ml of Dichloromethane were mixed and prepared in a standard flask) was added to the sample
- The sample was placed in an organic flask shaker at 500osc/min for 30mins
- The extract was filtered

- The sample was then left in the extraction bottle at laboratory room temperature to concentrate for a minimum of 24hours until about 2ml of concentrated sample was left in the extraction bottle
- This was followed by fractionation in activated alumina (neutral) column to separate into aliphatic and aromatic fractions using n-Hexane and Dichloromethane respectively
- The aromatic fraction was concentrated to approximately 1.0ml using rotary evaporator
- The aromatic extract was stored in a dried organic free and chromic acid pre-cleaned glass vials with Teflon rubber caps for analysis
- It was refrigerated at -4°c until analysis.

3.5 Sample Analysis

Analysis was done using Gas Chromatography GC. 1µl of the concentrated sample was injected by means of exmire micro syringe through rubber septum into the column. Separation occurs as the vapour constituent partition between the gas and liquid phases. The sample was automatically detected as it emerges from the column by a Flame Ionisation Detector FID. The operational condition used for GC analysis is stated below:

3.5.1 Gas Chromatograph Calibration

The calibration was done with commercially available PAH Accu Standards. The standard was prepared as directed by the manufacturer. The calibration PAH contains – Naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, Acenaphtylene, Acenaphthlene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz(a)anthracene, Chrysene,

Benzo(b)fluoranthene and Benzo(k)fluoranthene, Benzo(a)pyrene, Indeno(1,2,3 – cd)pyrene and Dibenz(a,h)anthracene, Benzo(g,h,i)perylene, Fluoranthene. The gas chromatography GC was set at the optimum temperature, 1.00µl of the prepared calibration concentrate extract injected and the GC run as normal. PAH quantification was carried out by CLARITY-GC interfaced software.

3.5.2 Gas Chromatograph Analysis Conditions

Calibration standards and sample extracts (in DCM) was analysed by GC-FID under the following conditions.

- Oven Temperature Program: 45°C [hold 2mins] to 240°C at 15°C/min to 300°C at 10°C/min for 8.17min. Injector Temperature: 280°C; Detector Temperature: 340°C

The initial oven temperature was 45°C which was determined by the ambient temperature of the laboratory where the GC instrument was housed. The hold time for the 45°C was 2mins. The gradient rate was 15 ° c/min; temperature was allowed to rise to 240°C and the injector temperature for samples was 280°C. After samples have been injected, temperature rise at gradient rate of 10°C/min and end at 300°C which is the higher maximum operating temperature indicated on the column box or supplier specification and 8.17mins was the hold time employed. The detector temperature was 340°C.

- Carrier gas: Helium
- Other gases: combustion gas- Hydrogen and compressed air, coolant- carbon(iv)oxide
- Pressure program (set point):14.0psi

- Injected volume: 1.00µl

3.5.3 Quality Control

- The Varian 3400 Gas Chromatograph is standardised monthly or when there is a major maintenance which affects the hardware or software and when calibration material is different from the stored calibration.
- At the start of work, the GC after start up is flushed with air to clear the column and prepare for fresh analysis
- Each batch (a batch is 10 samples) of samples analysed was accompanied with a QC sample.
- Each batch of samples extracted was accompanied by solvent blank for analysis.
- Standards 0.1ppm for low range and 0.5ppm for high range were chosen as quality control standards.

If the value of the QC sample exceeds the control limit, the expiry date of all stock standard or quality control samples are checked. A fresh standard could be prepared if necessary and quality control analysis repeated. If the control limit is still exceeded, the source of the error is looked for and the problem rectify.

- For every batch of samples analysed, one spike analysis was carried out. Spike samples were treated in the same way as real samples.
- The results were recorded in the laboratory notebook.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 RESULTS

The results of analysis of the sediment and soil samples from the study area and control are as presented in tables 4.1-4.13. The results including mean and standard deviation are presented for dry and wet/rainy seasons of sampling. The results were read as the detection limit on the gas chromatogram for individual PAHs which were in microgram per litre and these were converted to milligram per kilogram (mg/kg.). The minimum detection limit for GCFID used in the analysis on the chromatogram is 1×10^{-3} mg/kg.

The readings for each of the four stations within Warri environs and the control point – Agbarho, outside Warri for sediment and soil samples for dry and wet season are shown below in Table 4.1- 4.10; the mean levels and standard deviation were also calculated for individual and total PAHs for each location. The computation was done using Microsoft Excel page and in order to avoid having error in the table, the values <0.001 mg/kg were recorded as 0 (zero).

Table 4.1: PAH concentrations (mg/kg) in sediments from Ekpan location

Ekpan Sediment	PARAMETERS	Naphthalene	2-methyl naphthalene	1-methylnaphthalene	Acenaphylene	Acenaphthylene	Fluorene	Phenanthrene	Anthracene	Pyrene	Chrysene	Benz(a)anthracene	Benz(b)fluoranthene&Benz(k)Fluoranthene	Benz(a)Pyrene	Indeno(1,2,3-cd)Pyrene & Benzo(g,h,i)Perylene	Fluoranthene	Total	Mean	Standard Deviation	
DRY SEASON	January	<0.001	0	0	0	0	0	0.028	0	0.077	0.245	0	0.303	0	0	0	0.653	0.043533	0.096407	
	February	0.041	0.039	0.01	0.007	0	0.011	0.051	0.244	0.067	0.199	0.102	0.11	0	0	0.143	0	1.024	0.064	0.076208
	March	0	0	0	0	0	0	0.112	0	0.065	0.063	0.042	0	0	0	0.075	0	0.357	0.022313	0.036662
	Total Dry	0.041	0.039	0.01	0.007	0	0.011	0.191	0.244	0.209	0.507	0.144	0.413	0	0	0.218	0	2.034	0.127125	0.159264
	Mean Dry	0.0205	0.013	0.003333	0.002333	0	0.003667	0.063667	0.081333	0.069667	0.169	0.048	0.137667	0	0	0.072667	0	0.684833	0.080569	0.052869
	St. Dev. Dry	0.028991	0.022517	0.005774	0.004041	0	0.006351	0.043409	0.140873	0.006429	0.094636	0.051264	0.153383	0	0	0.071529	0	0.629197	0.039325	0.050789
	June	0	0	0	0.005	0.006	0	0	0.071	0	0.197	0	0.039	0	0	0.112	0.01	0.44	0.0275	0.055363
July	0	0	0	0	0	0	0	0	0	0	0	0.121	0	0	0	0	0.121	0.007563	0.03025	
August	0	0	0	0	0	0	0	0	0	0.42	0.452	0.36	0	0	0	0	1.232	0.077	0.166421	
Total Wet	0	0	0	0.005	0.006	0	0	0.071	0	0.617	0.452	0.52	0	0	0.112	0.01	1.793	0.112063	0.211693	
Mean wet	0	0	0	0.001667	0.002	0	0	0.023667	0	0.205667	0.150667	0.173333	0	0	0.037333	0.003333	0.597667	0.070314	0.070564	
St. Dev. Wet	0	0	0	0.002887	0.003464	0	0	0.040992	0	0.210134	0.260962	0.166776	0	0	0.064663	0.005774	0.755652	0.047228	0.085751	

In Ekpan location, mean value of PAHs concentration in sediment was 0.678mg/kg in the dry season which was higher than the mean concentration of 0.597mg/kg in the wet season. The highest concentration of chrysene detected during this study was in this location in the dry season with a mean value of 0.169mg/kg. However, benzo(a)pyrene, fluorene, phenanthrene, pyrene and most of the fewer ringed compounds were below detection level in wet/rainy season.

Table 4.2 PAH Concentrations (mg/kg) in soils from Ekpan location

EKPAN		SOIL SAMPLES																		
PARAMETERS	Naphthalene	2-methylnaphthalene	1-methylnaphthalene	Acenaphylene	Acenaphthlene	Fluorene	Phenanthrene	Anthracene	Pyrene	Chrysene	Benz(a)anthracene	Benz(b)fluoranthene&Benz(k)Fluora	Benz(a)Pyrene	Indeno(1,2,3-cd)Pyrene &	Benzo(g,h,i)Perylene	Fluoranthene	Total	Mean	Standard Deviation	
MONTHS																				
Dry Season	February	0	0	0.045	0.01	0	0	0.022	0	0.17	0.11	0.111	0.253	0.484	0	0.66	0	1.865	0.116563	0.195347
	March	0.09	0	0.037	0	0.096	0	0	0	0	0.031	0.033	0	0	0	0.074	0.361	0.022563	0.034704	
	Total Dry	0.09	0	0.082	0.01	0.096	0	0.022	0	0.17	0.11	0.142	0.286	0.484	0	0.66	0.074	2.226	0.139125	0.188542
	Mean Dry	0.045	0	0.041	0.005	0.048	0	0.011	0	0.085	0.055	0.071	0.143	0.242	0	0.33	0.037	1.113	0.130941	0.094271
	St. Dev. D.	0.06364	0	0.005657	0.007071	0.067882	0	0.015556	0	0.120208	0.077782	0.056569	0.155563	0.34224	0	0.46669	0.052326	1.431184	0.089449	0.133299
Wet season	June	0	0	0	0	0	0	0	0.011	0	0	0	0	0	0	0	0.011	0.000688	0.00275	
	July	0	0.016	0	0	0	0	0	0	0	0	0	0	0	0	0	0.016	0.001	0.004	
	August	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	<0.001	0	0	
	Total Wet	0	0.016	0	0	0	0	0	0.011	0	0	0	0	0	0	0	0.027	0.001688	0.004701	
	Mean Wet	0	0.005333	0	0	0	0	0	0.003667	0	0	0	0	0	0	0	0.009	0.000563	0.001567	
	St. Dev. W.	0	0.009238	0	0	0	0	0	0.006351	0	0	0	0	0	0	0	0.015588	0.000974	0.002714	

Similarly, the highest concentration of PAHs was also detected in soil samples in the dry season at Ekpan with a mean concentration of 1.113mg/kg. And it was observed that benzo(g,h,i)perylene which was detected once in the dry season and undetected in the wet season had the highest mean concentration of 0.660mg/kg. In the rainy season, apart from 2-methylnaphthalene and anthracene, the other PAHs were below detection limit.

Table 4.3 PAHs Concentration (mg/kg) in sediment from Ogunu Location

OGUNU SEDIMENT SAMPLES																	Total	Mean	Standard Deviation	
PARAMETERS	Naphthalene	2-methyl naphthalene	1-methylnaphthalene	Acenaptylene	Acenaphthlene	Fluorene	Phenanthrene	Anthracene	Pyrene	Chrysene	Benz(a)anthracene	Benz(b)fluoranthene&Benz(k)Fluora	Benz(a)Pyrene	Indeno(1,2,3-cd)Pyrene & Benzo(g,h,i)Perylene	Fluoranthene					
MONTHS																				
DRY SEASON	January	0	0	0.001	0.006	0.01	0.04	0.07	0.093	0.122	0.3198	0.2014	0.109	0.345	0.114	0.753	0.04	2.2242	0.139013	0.196014
	February	0	0.016	0	0	0	0.017	0	0	0	0.054	0.084	0.603	0.082	0	0	0.856	0.0535	0.149455	
	March	0.211	0.025	0	0	0	0	0	0	0.092	0.171	0	0	0.394	0	0	0.893	0.055813	0.112026	
	Total Dry	0.211	0.041	0.001	0.006	0.01	0.057	0.07	0.093	0.214	0.4908	0.2554	0.193	1.342	0.196	0.753	0.04	3.9732	0.248325	0.353425
	Mean Dry	0.070333	0.013667	0.000333	0.002	0.003333	0.019	0.023333	0.031	0.071333	0.1636	0.085133	0.064333	0.447333	0.065333	0.251	0.013333	1.3244	0.155812	0.117808
St. Dev. D	0.121821	0.012662	0.000577	0.003464	0.005774	0.020075	0.040415	0.053694	0.063571	0.160028	0.104247	0.057099	0.137019	0.058799	0.434745	0.023094	1.297085	0.081068	0.106571	
WET SEASON	June	0	0	0	0	0	0.13	0	0.751	0	0	0	0	0	0	0	0.881	0.055063	0.188395	
	July	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
	August	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
	Total Wet	0	0	0	0	0	0.13	0	0.751	0	0	0	0	0	0	0	0.881	0.055063	0.188395	
	Mean Wet	0	0	0	0	0	0.043333	0	0.250333	0	0	0	0	0	0	0	0.293667	0.034549	0.062798	
St. Dev. W	0	0	0	0	0	0.075056	0	0.43359	0	0	0	0	0	0	0	0.508646	0.03179	0.10877		

The situation at Ogonu location was also similar to the one at Ekpan; in that, the dry season recorded higher concentration of PAHs in sediments than rainy season and most of the compounds in the rainy season were <0.001mg/kg. Fluorene and anthracene were the only compounds found here in the rainy season. Benzo(a)pyrene had the highest mean concentration of 0.447mg/kg in the dry season and it was below detection limit in the rainy season.

Table 4.4: PAHs Concentration (mg/kg) in Soil Samples from Ogonu Location

OGUNU SOIL SAMPLES																			
PARAMETERS	Naphthalene	2-methyl naphthalene	1-methylnaphthalene	Acenaptylene	Acenaphthylene	Fluorene	Phenanthrene	Anthracene	Pyrene	Chrysene	Benz(a)anthracene	Benz(b)fluoranthene&Benz(k)Fluora	Benz(a)Pyrene	Indeno(1,2,3-cd)Pyrene &	Benzo(g,h,i)Perylene	Fluoranthene	Total	Mean	Standard Deviation
MONTHS																			
February	0	0	0.041	0	0	0	0.027	0.142	0.244	0.102	0	0.111	0.362	0.026	0.479	0	1.534	0.095875	0.145814
March	0.484	0.045	0	0.069	0	0	0	0	0	0	0	0	0	1.084	0	0	1.682	0.105125	0.287434
Total Dry	0.484	0.045	0.041	0.069	0	0	0.027	0.142	0.244	0.102	0	0.111	0.362	1.11	0.479	0	3.216	0.201	0.29349
Mean Dry	0.242	0.0225	0.0205	0.0345	0	0	0.0135	0.071	0.122	0.051	0	0.0555	0.181	0.555	0.2395	0	1.608	0.1005	0.146745
St. Dev. D	0.34224	0.03182	0.028991	0.04879	0	0	0.019092	0.100409	0.172534	0.072125	0	0.078489	0.255973	0.748119	0.338704	0	2.237286	0.13983	0.200004
June	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	<0.001	0	0
July	0	0	0.022	0.014	0.012	0.037	0.046	0.186	0	0	0	0.063	0.081	0	0.136	0.124	0.721	0.045063	0.058205
August	0	0.033	0.027	0.013	0.006	0.029	0.048	0.069	0	0	0	0.212	0.019	0.01	0.087	0.057	0.611	0.038125	0.053476
Total Wet	0	0.033	0.049	0.027	0.018	0.066	0.094	0.255	0	0	0	0.275	0.1	0.01	0.223	0.181	1.331	0.083188	0.096696
Mean We	0	0.011	0.016333	0.009	0.006	0.022	0.031333	0.085	0	0	0	0.091667	0.033333	0.003333	0.074333	0.060333	0.443667	0.052196	0.032232
St. Dev. W	0	0.019053	0.014364	0.00781	0.006	0.019468	0.027154	0.094027	0	0	0	0.108868	0.04236	0.005774	0.068879	0.062067	0.475823	0.029739	0.035355

At Ogunu location soil samples PAH levels in dry season was higher than that of the rainy season with indeno(1,2,3-cd)Pyrene and dibenz(a,h)anthracene having the highest mean concentration of 0.555mg/kg in the dry season while in the wet season benzo(b)fluoranthene and benzo(k)fluoranthene had the highest mean concentration of 0.137mg/kg.

Table 4.5: PAHs Concentration (mg/kg) in sediments from Ugboroke Location

UGBOROKE SEDIMENT SAMPLES																			
PARAMETERS	Naphthalene	2-methyl naphthalene	1-methylnaphthalene	Acenaptylene	Acenaphthlene	Fluorene	Phenanthrene	Anthracene	Pyrene	Chrysene	Benz(a)anthracene	Benz(b)fluoranthene&Benz(k)Fluoranthene	Benz(a)Pyrene	Indeno(1,2,3-cd)Pyrene & Benzo(g,h,i)Perylene	Fluoranthene	Total	Mean	Standard Deviation	
MONTHS																			
January	0.0349	0	0	0.072	0	0	0.0005	0	0.065	0.083	0.032	0.164	0	0.249	0.536	0	1.2364	0.077275	0.14123
February	0	0.0353	0	0.004	0.004	0	0	0.059	0	0	0	0.057	0	0.018	0	0	0.1773	0.011081	0.020603
March	0	0	0	0	0	0.013	0.023	0.088	0.122	0	0.173	0.167	0.216	0	0.531	0	1.333	0.083313	0.141116
Total Dry	0.0349	0.0353	0	0.076	0.004	0.013	0.0235	0.147	0.187	0.083	0.205	0.388	0.216	0.267	1.067	0	2.7467	0.171669	0.264566
Mean Dry	0.011633	0.011767	0	0.025333	0.001333	0.004333	0.007833	0.049	0.062333	0.027667	0.068333	0.129333	0.072	0.089	0.355667	0	0.915567	0.107714	0.088189
St. Dev. D	0.02015	0.02038	0	0.040464	0.002309	0.007506	0.013137	0.044844	0.061044	0.04792	0.092045	0.06266	0.124708	0.138856	0.308027	0	0.98405	0.061503	0.07845
June	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.147	0	0.147	0.009188	0.03675
July	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
August	0	0	0.209	0	0.008	0	0	0	0	0	0	0	0	0	0	0	0.217	0.013563	0.052155
Total Wet	0	0	0.209	0	0.008	0	0	0	0	0	0	0	0	0	0.147	0	0.364	0.02275	0.061684
Mean Wet	0	0	0.069667	0	0.002667	0	0	0	0	0	0	0	0	0	0.049	0	0.121333	0.014275	0.020561
St. Dev. W	0	0	0.120666	0	0.004619	0	0	0	0	0	0	0	0	0.08487	0	0	0.210155	0.013135	0.035613

The only PAHs found within detectable limits in sediment samples at Ugboroke location in the rainy season were 3-methyl-naphthalene, acenaphthalene and benzo(g,h,i)perylene. Of all the PAHs analysed in this study, 14 were found in the dry season and benzo(g,h,i)perylene had the highest mean value of 0.533mg/kg. Consequently, mean of total PAHs of 0.915mg/kg was recorded in the dry season while in the wet season, the mean of total PAHs was 0.121mg/kg; the dry season result was higher than the wet season.

Table 4.6 PAHs Concentration (mg/kg) in Soils from Ugboroke Location

UGBOROKE SOIL SAMPLES																			
PARAMETERS	Naphthalene	2-methyl naphthalene	1-methylnaphthalene	Acenaptylene	Acenaphthlene	Fluorene	Phenanthrene	Anthracene	Pyrene	Chrysene	Benz(a)anthracene	Benz(b)fluoranthene&Benz(k)Fluora	Benz(a)Pyrene	Indeno(1,2,3-cd)Pyrene & Benzo(g,h,i)Perylene	Fluoranthene	Total	Mean	Standard Deviation	
MONTHS																			
February	0	0.561	0.168	0	0	0	0.158	0.292	0	0	1.106	0	0.318	0	0	2.603	0.162688	0.30045	
March	0	0	0	0	0	0	0.081	0	0	0.033	0.028	0.076	0	0	0.309	0	0.527	0.032938	0.078457
Total Dry	0	0.561	0.168	0	0	0	0.239	0.292	0	0.033	1.134	0.076	0.318	0	0.309	0	3.13	0.195625	0.30138
Mean Dry	0	0.2805	0.084	0	0	0	0.1195	0.146	0	0.0165	0.567	0.159	0	0.1545	0	1.527	0.1018	0.155103	
St. Dev. D	0	0.396687	0.118794	0	0	0	0.054447	0.206475	0	0.023335	0.762261	0.05374	0.22486	0	0.218496	0	2.059095	0.128693	0.205727
June	0.017	0	0	0	0	0	0	0	0.024	0.02	0.0204	0	0	0	0.07	0	0.1514	0.009463	0.018527
July	0	0	0	0	0	0	0	0	0	0.008	0.076	0	0	0	0	0	0.084	0.00525	0.018972
August	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total Wet	0.017	0	0	0	0	0	0	0	0.024	0.028	0.0964	0	0	0	0.07	0	0.2354	0.014713	0.028727
Mean We	0.005667	0	0	0	0	0	0	0	0.008	0.009333	0.032133	0	0	0	0.023333	0	0.078467	0.004904	0.009576
St. Dev. W	0.009815	0	0	0	0	0	0	0	0.013856	0.010066	0.039335	0	0	0	0.040415	0	0.113487	0.007093	0.013578

In the soil samples at Ugboro location, seven of the PAH compounds analysed in this study were found in the rainy season unlike the corresponding sediment samples (in which three PAHs compounds were found); Despite this, the mean total PAHs concentration was 0.118mg/kg in the rainy season for soil samples, lower than that of the sediment samples 0.121mg/kg.

In the dry season, the nine different types of PAHs found in soils at this location resulted in a high value of mean for total concentration PAHs of 1.565mg/kg and about 83% of this was found in early dry season while the remaining was found in late dry season (March). However, the corresponding sediment samples in the dry season though had more different PAHs (14) the mean concentration of total PAHs was 0.915mg/kg.

Table 4.7 PAHs Concentration (mg/kg) in sediments from Okotie Sawmill Location

OKOTIE SAWMILL SEDIMENT SAMPLES																			
PARAMETERS	Naphthalene	2-methyl naphthalene	1-methylnaphthalene	Acenaphthylene	Acenaphthylene	Fluorene	Phenanthrene	Anthracene	Pyrene	Chrysene	Benz(a)anthracene	Benz(b)fluoranthene&Benz(k)Fluora	Benz(a) Pyrene	Indeno(1,2,3-cd)Pyrene &	Benzo(g,h,i)Perylene	Fluoranthene	Total	Mean	Standard Deviation
MONTHS																			
January	0	0	0.18	0	0	0.09	0.223	0.338	0.167	0	0.397	0	0	0.107	0	0.062	1.564	0.09775	0.129713
February	0.014	0	0	0.046	0.0216	0	0.022	0	0.063	0	0.111	0	0.823	0.227	0.139	0.035	1.502	0.09385	0.204619
March	1.077	0.05	0	0	0	0	0	0	0.283	0	0.064	0	0	0	0	0	1.474	0.092125	0.27213
Total Dry	1.091	0.05	0.18	0.046	0.0216	0.09	0.245	0.338	0.513	0	0.572	0	0.823	0.334	0.139	0.097	4.54	0.283725	0.319385
Mean Dry	0.363667	0.016667	0.06	0.015333	0.0072	0.03	0.081667	0.112667	0.171	0	0.190667	0	0.274333	0.111333	0.046333	0.032333	1.513333	0.094575	0.106462
St. Dev. D	0.617804	0.028868	0.103923	0.026558	0.012471	0.051962	0.122892	0.195144	0.110055	0	0.180229	0	0.475159	0.113562	0.080252	0.031086	0.046058	0.134373	0.173558
June	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	<0.001	0	<0.001
July	0	0	0	0	0.002	0	0.005	0	0	0	0	0	0	0	0	0	0.0065	0.000438	0.001315
August	0	0	0.073	0.007	0.018	0.131	0.223	0.693	0.361	0.285	0	0.245	0.422	0	0.346	0.218	3.023	0.188875	0.199826
Total Wet	0	0	0.073	0.007	0.02	0.131	0.228	0.693	0.361	0.285	0	0.245	0.422	0	0.346	0.218	3.0295	0.189313	0.199773
Mean We	0	0	0.024333	0.002333	0.006667	0.043667	0.076	0.231	0.120333	0.095	0	0.081667	0.140667	0	0.115333	0.072667	1.51475	0.063104	0.066591
St. Dev. W	0	0	0.042147	0.004041	0.009866	0.075633	0.12733	0.400104	0.208423	0.164545	0	0.141451	0.243642	0	0.199763	0.125862	2.132988	0.108925	0.115384

At Okotie sawmill location in the dry season, high concentration of total PAHs were regularly detected during the sampling period – January to March 2012 in the sediment samples. This resulted in a very high concentration for total PAHs of 4.54mg/kg, and the mean was 1.513mg/kg. There were also more PAHs in the sediment samples at this location than in any other location analysed in this study, in terms of total PAHs detected and the number of times they were found. Furthermore, highest mean concentration of total PAHs found in the wet season of 1.514mg/kg was at this location; over 90% of this was detected in August 2012.

Table 4.8 PAHs Concentration (mg/kg) in Soils from Okotie Sawmill Location

OKOTIE SAWMILL SOIL SAMPLES																			
PARAMETERS	Naphthalene	2-methyl naphthalene	1-methylnaphthalene	Acenaptylene	Acenaphthylene	Fluorene	Phenanthrene	Anthracene	Pyrene	Chrysene	Benz(a)anthracene	Benz(b)fluoranthene&Benz(k)Fluorene	Benz(a)Pyrene	Indeno(1,2,3-cd)Pyrene & Benzo(g,h,i)Perylene	Fluoranthene	Total	Mean	Standard Deviation	
MONTHS																			
February	0.061	0.04	0	0.025	0	0	0	0.113	0	0	0	0.042	0.326	0	0.226	0	0.833	0.052063	0.094679
March	0.523	0	0	0	0.1	0.082	0.139	0	0.174	0	0.159	0	1.812	0	0	0	2.989	0.186813	0.453879
Total Dry	0.584	0.04	0	0.025	0.1	0.082	0.139	0.113	0.174	0	0.159	0.042	2.138	0	0.226	0	3.822	0.238875	0.526533
Mean Dry	0.292	0.02	0	0.0125	0.05	0.041	0.0695	0.0565	0.087	0	0.0795	0.021	1.069	0	0.113	0	1.911	0.119438	0.263267
St. Dev. D	0.326683	0.028284	0	0.017678	0.070711	0.057983	0.098288	0.079903	0.123037	0	0.11243	0.029698	1.050761	0	0.159806	0	2.155261	0.134704	0.258227
June	0.0057	0.005	0	0	0.0005	0	0.003	0	0.022	0	0	0.0682	0	0	0	0.004	0.11	0.006775	0.017289
July	0	0.187	0	0	0	0	0	0	0	0	0	0	0.166	0.011	0	0	0.364	0.02275	0.060202
August	0.006	0	0.038	0	0	0	0	0	0	0	0	0	0	0	0	0.029	0.073	0.004563	0.011512
Total Wet	0.0117	0.192	0.038	0	0.0005	0	0.003	0	0.022	0	0	0.0682	0.166	0.011	0	0.033	0.547	0.034088	0.059869
Mean We	0.0039	0.064	0.012667	0	0.000167	0	0.001	0	0.007333	0	0	0.022733	0.055333	0.003667	0	0.011	0.182333	0.011363	0.019956
St. Dev. W	0.003381	0.10655	0.021939	0	0.000289	0	0.001732	0	0.012702	0	0	0.039375	0.09584	0.006351	0	0.015716	0.158412	0.018992	0.033923

At Okotie sawmill location soil samples, benzo(a)pyrene had the highest value for individual PAHs concentration of 2.138mg/kg, the mean was 1.069mg/kg and this was found in the dry season. This value is also the highest recorded for any individual PAHs analysed in this study in both dry and wet season. However in the wet season, only 0.166mg/kg of Benzo(a)pyrene was detected once of the three sampling times in the season.

Table 4.9 PAHs Concentration (mg/kg) in sediments from Agbarho Location

AGBARHO SEDIMENT SAMPLES																			
PARAMETERS	Naphthalene	2-methylnaphthalene	1-methylnaphthalene	Acenaphylene	Acenaphthylene	Fluorene	Phenanthrene	Anthracene	Pyrene	Chrysene	Benz(a)anthracene	Benz(b)fluoranthene&Benz(k)fluoranthene	Benz(a)Pyrene	Indeno(1,2,3-cd)Pyrene & Benzo(g,h,i)Perylene	Fluoranthene	Total	Mean	Standard Deviation	
MONTHS																			
January	0	0	0.142	0.006	0	0.038	0.056	0	0.159	0	0.122	0.029	0.714	1.049	0	0	2.315	0.144688	0.299002
February	0	0	0.009	0.01	0	0	0.038	0.075	0.027	0	0.058	0.075	0.065	0.043	0.202	0	0.602	0.037625	0.052406
March	0.421	0	0.219	0.138	0	0	0.483	0	0	0	0	0	0	0	0	0	1.261	0.078813	0.158777
Total Dry	0.421	0	0.37	0.154	0	0.038	0.577	0.075	0.186	0	0.18	0.104	0.779	1.092	0.202	0	4.178	0.261125	0.316733
Mean Dry	0.140333	0	0.123333	0.051333	0	0.012667	0.192333	0.025	0.062	0	0.06	0.034667	0.259667	0.364	0.067333	0	1.392667	0.087042	0.105578
St. Dev. D	0.243064	0	0.106237	0.075082	0	0.021939	0.251886	0.043301	0.085082	0	0.061025	0.03782	0.394804	0.593617	0.116625	0	2.030482	0.126905	0.167008
June	0	0	0	0	0	0	0	0	0	0	0	0	0.031	0	0	0	0.031	0.001938	0.00775
July	0	0.204	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.204	0.01275	0.051
August	0.017	0.006	0.033	0	0	0.017	0.046	0	0	0.186	0	0.109	0.037	0	0.282	0.087	0.82	0.05125	0.080305
Total Wet	0.017	0.21	0.033	0	0	0.017	0.046	0	0	0.186	0	0.109	0.068	0	0.282	0.087	1.055	0.065938	0.088134
Mean We	0.005667	0.07	0.011	0	0	0.005667	0.015333	0	0	0.062	0	0.036333	0.022667	0	0.094	0.029	0.351667	0.021979	0.029378
St. Dev. W	0.009815	0.116086	0.019053	0	0	0.009815	0.026558	0	0	0.107387	0	0.062931	0.019858	0	0.162813	0.050229	0.584545	0.036534	0.05053

Sediments in Agbarho location outside Warri had high PAHs concentration in the dry season with a mean value of 1.393mg/kg. This value is however lower than the highest mean concentration for sediments of 1.513mg/kg at Okotie Sawmill within Warri.

Table 4.10 PAHs Concentration (mg/kg) in Soils from Agbarho Location

AGBARHO SOIL SAMPLES																			
PARAMETERS	Naphthalene	2-methyl naphthalene	1-methylnaphthalene	Acenaptylene	Acenaphthlene	Fluorene	Phenanthrene	Anthracene	Pyrene	Chrysene	Benz(a)anthracene	Benz(b)fluoranthene&Benz(k)Fluora	Benz(a)Pyrene	Indeno(1,2,3-cd)Pyrene &	Benzo(g,h,i)Perylene	Fluoranthene	Total	Mean	Standard Deviation
MONTHS																			
February	0.117	0.007	0.009	0	0.007	0	0	0.035	0.088	0	0	0	0	0.109	0	0.372	0.02325	0.041689	
March	0.078	0	0	0	0	0.071	0	0	0	0	0	0.514	0	0	0.93	0	1.593	0.099563	0.255815
Total Dry	0.195	0.007	0.009	0	0.007	0.071	0	0.035	0.088	0	0	0.514	0	0	1.039	0	1.965	0.122813	0.277441
Mean Dry	0.0975	0.0035	0.0045	0	0.0035	0.0355	0	0.0175	0.044	0	0	0.257	0	0	0.5195	0	0.9825	0.061406	0.138721
St. Dev. D	0.027577	0.00495	0.006364	0	0.00495	0.050205	0	0.024749	0.062225	0	0	0.363453	0	0	0.580535	0	1.125007	0.070313	0.162864
June	0	0	0	0	0	0	0	0	0	0	0	0	0.066	0	0	0	0.066	0.004125	0.0165
July	0	0.152	0	0	0	0	0	0	0	0	0	0	0	0	0	0.046	0.198	0.012375	0.038961
August	0	0.259	0	0	0	0	0	0	0.036	0	0	0.053	0	0	0.127	0	0.475	0.029688	0.069863
Total Wet	0	0.411	0	0	0	0	0	0	0.036	0	0	0.053	0.066	0	0.127	0.046	0.739	0.046188	0.103761
Mean Wei	0	0.137	0	0	0	0	0	0	0.012	0	0	0.017667	0.022	0	0.042333	0.015333	0.246333	0.015396	0.034587
St. Dev. W	0	0.13015	0	0	0	0	0	0	0.020785	0	0	0.0306	0.038105	0	0.073323	0.026558	0.319521	0.01997	0.036019

In Agbarho soil samples, most of the PAHs were not found in the rainy season, especially the fewer ringed ones. Acenaptylene, phenanthrene, chrysene and benz(a)anthraene are some of the PAHs not detected in soils at this location throughout the sampling period. The mean concentration of PAHs in dry season was 0.982mg/kg while in the rainy season it was 0.246mg/kg.

4.2 DISCUSSION

4.2.1 Level of PAHs for Sediments and Soils

4.2.1.1 Dry Season

Mean levels of individual PAHs for sediment samples in the dry season for Warri environs ranged from 0.001mg/kg low for Acenaphthene to 0.447mg/kg high for Benzo(a)pyrene. At the control location, mean values ranged from 0.012mg/kg low for Fluorene to 0.364mg/kg high for Indeno(1,2,3-cd)pyrene & Dibenz(a,h)anthracene in sediments. For soil samples in the dry season, mean levels of PAHs within Warri environs ranged from 0.005mg/kg low for Acenaphthylene to 1.069mg/kg high for Benzo(a)pyrene. While in the control point it ranged from 0.003mg/kg low for 2 methyl- Naphthalene to 0.519mg/kg high for Benzo(g,h,i)perylene in soil samples.

It can be noticed here that individual PAH levels within Warri was low for three rings – Acenaphthylene and Acenaphthene and high for five-ringed – Benzo(a)Pyrene in soil and sediment samples in dry season. This could indicate that the activities within that environment are influencing the soil and the sediment in similar way. However, at the control point, a different trend was seen. PAH levels was low for three-ringed fluorene in soil samples and two-ringed naphthalene in sediments while it was high for Indeno (1,2,3-cd)pyrene & Dibenz(a,h)anthracene in sediments and six-ringed Benzo(g,h,i)perylene in soil samples. This is similar to a study reported in Ekonomiuk *et al.*, 2006, in which was explained that soils and sediments have been found to be good environmental sink for PAHs thereby reflecting their levels in the environment and could contain about 90% of these compounds with longer half-life than the atmosphere or in plants.

4.2.1.2 Rainy Season

In the rainy season, individual PAH in sediments ranged from 0.001mg/kg low in acenaphthylene to 0.231mg/kg high for anthracene. While at the control, it was 0.005mg/kg low in Fluorene to 0.094mg/kg high for Benzo(g,h,i)perylene in sediment samples. In soil samples within Warri, mean levels of individual PAHs for rainy season ranged from 0.001mg/kg low in phenanthrene to 0.090mg/kg high for Benzo(b)Fluoranthene & Benzo(k)Fluoranthene. At the control point, it was 0.012mg/kg low for pyrene to 0.130mg/kg high for 2-Methyl-Naphthalene in soil samples. A general observation from PAH levels result in the rainy season, at the study location and the control is that, lower amounts were detected in the rainy season compared to the dry season. It was also observed that mean levels in sediment samples were higher than in soils for this study period. A similar trend was observed in a related study in the Niger Delta area of Nigeria (Inengite *et al.*, 2012). According to them, during rainy season, it is expected that dissolution and washing-off of the PAHs from the soil matrix could occur into the rivers thereby increasing their levels in sediment. Furthermore, the type of individual PAH detected reflected the activities going on in the environment as three-ringed acenaphthylene and phenanthrene were still relatively low in soils and sediments in Warri environs in rainy season as observed in the dry season. And Benzo(b)fluoranthene & Benzo(k)fluoranthene which is the five-ringed detected high in soil samples within Warri environs in rainy season has been observed according to the work done by Aubin & Farant 2000, to be more stable and a much better marker of PAH source than Benzo(a)pyrene, which was detected high in soil samples in dry season; more explanation on this is given in section 4.2.4.1. At the control station, Benzo(g,h,i)perylene which was detected high in soil samples in dry season was found to be high in sediments in rainy season, a likely indication of washing off as observed in Inengite *et al.*, 2012.

Seasonal Variation of PAHs in Soils and Sediments

The results from this study show that the type of PAH and their levels in soils and sediments vary for each season under consideration and in this case, dry and rainy season. For soil samples, four ringed pyrene occurred most in the dry season and it was found in the dry season at all the locations for both soil and sediment samples. Also, values for two to three ringed PAHs such as naphthalene and acenaphthene in soils during rainy season were mostly below detection limit of <0.001mg/kg. For sediments, the two to three rings were found majorly in the dry season and almost absent in the rainy season. Four ringed PAHs such as chrysene were also found more in the dry season than rainy season for both soil and sediment samples. The five ringed PAHs such as benzo(a)pyrene were found more in the dry season than the rainy season. However, their values vary at different locations in the soil and sediment samples. Six ringed indeno(1,2,3-cd)pyrene was found high in the dry season in control station sediment samples and absent in the rainy season. More different PAHs were detected in the dry season than in the rainy season and overall concentration of PAHs was also higher in the dry season than in the rainy season for soils and sediments samples.

4.2.1.3 Factors that could be responsible for seasonal variation of PAH levels in Soils and Sediments.

As earlier discussed in the literature review, PAH in soil is usually from atmospheric deposition due to pyrolytic sources (ATSDR, 1995); and the other sources are petrogenic due to petroleum or crude oil activities and spillage. While PAHs in sediments have been found to reflect the history of fossil fuel combustion in the environment (Ekonomiuk *et al.* 2006), and higher molecular weight PAHs which are hydrophobic compounds and have less solubility in water tend to settle in sediments.

Dry season in the Niger Delta which is the area for this study is marked with dust and cool “harmattan” haze and there could be high temperature of 36°C and 37°C (www.population.gov.ng). These conditions are favourable for high PAH levels in soil and could be considered to be one of the responsible factors for high PAHs levels in soil samples in dry season for the areas under this study.

Annual rainfall amount according to www.population.gov.ng. (accessed in 2012) in the study area- Warri could get to 2673.8mm. Apart from usual rainfall in rainy season- May to October, it frequently even rains in the dry season (November to April). Most of the areas in Warri (and mostly the Niger Delta) are as a result more swampy and marshy with bottom sediments. It was mentioned earlier that PAHs could be washed off (from the atmosphere and soil) during rainy season and are most likely to have undergone reactions that could either increase or decrease their level (Inengite *et al.*, 2010). According to Brooks 1997, when PAHs enter aquatic environment, their fate is determined by the type of compound and the characteristics of the substrate to which they are attached; this is because PAHs are complex compounds and they are hardly found as a single substance. Consequently, PAHs in an aquatic environment could evaporate, disperse into the water column, become incorporated into bottom sediments, and concentrate in aquatic biota or experience oxidation – including photo-oxidation and biodegradation (Brooks, 1997). These factors could be some of the responsible reasons for PAHs high and low levels in sediment in different seasons.

4.2.1.4 Comparison of PAH Values between Study area and Control station.

Table 4.11 shown below gives value for total and mean concentration of PAHs in the study area and the total values at the control point in both dry and rainy season. The observed trend from these locations is discussed in full in the next section.

Table 4.11: Overall values for levels of PAHs in (mg/kg) in the Study area and Control Station in both dry and rainy season:

Samples	Study Area (Warri)				Amount(mg/kg)		Control Station (Agbarho) Total amount detected in mg/kg
	Ekpan (mg/kg)	Okotie (mg/kg)	Ugboroike (mg/kg)	Ogunu (mg/kg)	Total	Mean	
Sediments	3.827	7.569	3.111	4.855	19.362	4.840	5.235
Soils	2.253	4.369	3.367	4.548	14.537	3.634	2.705

4.2.2 PAH Distribution Pattern in the Study Area and Control Station

From table 4.11, it can be seen that PAHs levels in Warri was high at some specific locations which are – Okotie (7.569mg/kg in sediments and 4.369mg/kg in soils) and Ogunu (4.855mg/kg in sediments and 4.548mg/kg in soils). This indicates that major source of PAHs contamination are more due to point source. And, analysing the activities at this locations, it would be obvious while PAHs levels at these locations would be high. Okotie sawmill is a location that has several industrial activities around it; and the waterside from where the sediment samples were collected has a construction company and sawmill just close by; consequently, all the various PAHs analysed in this study were found at this location in both rainy and dry season, except for chrysene which was not found at all in the soil sample though it was in the sediments in rainy season. This is similar to the study done by Ana *et al.* (2011) on PAHs analysis in surface waters in which the highest number of the various PAHs analysed were found in the highly industrialised area. The other location, Ogunu is also a location close to an industrial area that is involved in oil and gas activities and the waterside from where the samples were collected is crowded with domestic activities of local inhabitants; such as: fishing, bathing, cooking and dumping of refuse and sewage.

The mean for total PAHs levels within Warri for the sampling period, both dry and rainy season is 4.840mg/kg for sediments and 3.634mg/kg for soils respectively. While at the control point – Agbarho, it was 5.235mg/kg for sediments and 2.705mg/kg for soil.

For the sediment samples, it can be seen that the levels are above the critical level of 4mg/kg recommended by W.H.O., above which the area is considered to be contaminated by PAHs. Therefore, sediment samples collected from the study area and the control may be considered as contaminated by PAHs.

However, for the soil samples, the mean level within Warri is 3.634mg/kg and 2.705mg/kg at the control point. These values are below the critical level and therefore, the soils from the study area may be considered as not contaminated by PAHs.

From the results of this study, it can be seen that the high levels of PAHs in the sediment samples for both within Warri environs and the control point are high most likely due to the point source activities going on around them. For instance, at the control point - Agbarho, there is cattle grazing ground, an abattoir and a meat market. In addition to this, it was noticed that river dredging activities was taking place within the control point sampling area. All these could be responsible for the increase in PAHs levels for sediment samples at the control point. Also, the lower value for soil samples 2.705mg/kg at the control point compared to the mean value- 3.634mg/kg within Warri indicates that PAHs levels within Warri could be normally higher than outside, but the higher value at the control point in sediment samples would indicate that there are activities around or within the control point river from which the sediments were collected which should be responsible for the high value. A clearer understanding of this can be seen if the individual PAHs compounds are considered and their source traced. An attempt at this is done below in further critical analysis of the results.

4.2.2.1 Critical Analysis based on number of Rings for Soils and Sediments samples

Two to three -ringed PAHs

In Warri environs and at the control point, two and three ringed PAHs were found predominantly in the dry season for both soils and sediments samples. Naphthalene, 2-methyl naphthalene and 1-methyl naphthalene were the 2 ringed PAHs analysed in this study. The essence of analysing the methyl form of naphthalene is because of the ease of solubility and disintegration of fewer

ringed PAHs especially in aqueous solution, which could make them converted into other forms such as methylated form and therefore not detectable as naphthalene (Botkin & Keller, 2005). It has also been found that methylated form of certain organic compounds could be more harmful than the parent compound (Botkin & Keller, 2005), hence, the need to analyse methyl forms.

Within Warri environs, anthracene and phenanthrene were the most persistent of the three rings. Although anthracene was the most persistent, being more distributed in all the location, yet phenanthrene appeared more in quantity at some locations and has overall more appearance. At the control point, phenanthrene was the most persistent three ringed and it was found only in sediment samples predominantly in the dry season. Generally, the two to three rings were found majorly in the dry season and almost absent in the rainy season. This is similar to an earlier work done on Evaluation of PAHs in Sediment of Kolo Creek in Niger Delta Nigeria (2010). Higher ringed PAHs were found to predominate in the rainy season. The authors attributed it to heavy rains, since the solubility of the PAHs is related to number of rings (Inengite *et al.*, 2010). Their submission is corroborated by the work done by Karlsson and Viklander (2008) in which it was reported that the more rings the less soluble; which indicates that the fewer rings were more soluble.

Four -ringed PAHs

The most persistent four-ringed within Warri for both soil and sediment is pyrene. It occurred most in the dry season and more in the sediments than soil samples at Okotie Sawmill. Also, it was found in the dry season in both soil and sediment samples at every location except at Ugboroke where it was not found in the soil sample throughout the dry season though it was found once in early rainy season (June) at a value of 0.024mg/kg. The highest mean value found for Pyrene was in sediments in dry season at Okotie sawmill, Warri and it was 0.171mg/kg. The

least persistent four-ringed is fluoranthene and it was found more in the rainy season. However, it was not found at all in Ugboroke, though all the other four-ringed – chrysene, pyrene and benz(a)anthracene were found with benz(a)anthracene occurring most. At the control point, Pyrene was also the most persistent four-ringed and a mean value of 0.062mg/kg was found in sediments samples in dry season and it was below detection limits in the rainy season.

The order of persistence of four-ringed PAHs within Warri for soil and sediment is: Pyrene>Benz(a)anthracene>Chrysene>Fluoranthene; while the order outside Warri is Pyrene>Benz(a)anthracene>Fluoranthene>Chrysene.

Five-ringed PAHs

Five-ringed benzo(b)fluoranthene was the most persistent five-ringed and overall most persistent PAHs within Warri. It occurred most in Ekpan and it was more in the sediments at a mean value of 0.137mg/kg in the dry season and 0.173mg/kg in rainy season, than soils sample which was 0.143mg/kg in dry season. However, it was found below detection limits in soils samples at this location in the rainy season. Five-ringed benz(a)pyrene was found only once in soil sample in the dry season at Ekpan, but a total of 2.138mg/kg and mean value 1.069mg/kg was found in soil samples at Okotie sawmill in dry season. This was the highest value for single PAHs compound at a particular location in this study. At the control point, benzo(b)fluoranthene was also more persistent, despite this, benz(a)pyrene had the highest total concentration of 0.779mg/kg and mean value of 0.259mg/kg for five-ringed in the dry season for sediment samples.

Six-ringed PAHs

Six-ringed PAHs Indeno 1,2,3-cd pyrene and Dibenzo (a,h)anthracene (which were analysed as one compound and to be represented in this study as ind and DbahA) was the least persistent six-

ringed and overall least persistent PAHs found within Warri. It was below detection level in soil samples at Ugboroke and found only in the dry season for the sediment samples. At Ogonu, it was found unusually high with a total of 1.110mg/kg and mean value of 0.555mg/kg in soils in the dry season. And only total of 0.010mg/kg was found in the soils samples at the same location in late rainy season. While in the sediment only total of 0.196mg/kg and mean value of 0.065mg/kg of the six ringed ind and DbahA was found in the dry season and this was absent in the rainy season. Ind and DbahA was below detection limit in Ekpan soils and sediment samples throughout the sampling period. However, at the control point, a high total concentration of 1.092mg/kg and mean value of 0.364mg/kg was found in the sediment in dry season but it was not found in the wet season. The values for six ringed Ind and DbahA was below detection limit in soils samples.

However, Benzo(ghi)Perylene - BghiP which was the most persistent six-ringed recorded in the study area – Warri was found in all the locations; with highest values detected for sediment samples in the dry season. Ugboroke had the highest total concentration of 1.067mg/kg and mean value of 0.355mg/kg in its sediments for BghiP, in the dry season. This is followed by a total value of 0.753mg/kg and mean level of 0.251mg/kg in sediments samples from Ogonu in the dry season. BghiP was absent in Ogonu sediments in rainy season and the lowest detectable total value of 0.07mg/kg and mean 0.023mg/kg was found in Ugboroke soil. At the control point, BghiP was also the most persistent and had its highest total concentration of 1.039mg/kg and mean 0.519mg/kg in soil in dry season, but was present in low total concentration of approximately 0.202mg/kg and mean 0.067mg/kg in sediments.

4.2.2.2 Analysis base on Concentration of individual PAHs for Soils and Sediments.

Highest total concentration of PAHs within Warri was recorded for BaP - benzo(a)pyrene at 3.302mg/kg in soil samples. The highest contributor to the bulk was at Okotie Sawmill; this location is the one characterised with the presence of several industrial activities and about 2.138mg/kg total concentration was detected there in the dry season soil samples. This is similar to the work done by Ana *et al.* (2011) on PAHs contamination of surface waters in Nigeria Coastal Areas. They reported that the concentration of total PAHs in industrialised areas was three times higher than in the less industrialised area. The order of PAHs concentration in soil within Warri is: BaP>BghiP>BaA>Naph>Ind&DbahA>2-M.Naph>BbF>Ant>Pyr>Phenan.

The PAH with lowest concentration in soil in Warri environs is acenaphthalene with a total concentration of 0.018mg/kg found in the rainy season. The order for lower PAHs in soils in Warri environs is can<Ind&DbahA<Acp<Chry.

At the control point, PAHs with highest concentration in soil sample was BghiP; it had a total concentration of 1.166mg/kg with the larger amount of 1.039mg/kg detected in the dry season. It is important to note that the control point location has cattle grazing ground, an abattoir and meat market. Therefore, the high concentration of BghiP here could be attributed to the microbial production of the PAH due to microbial activities in the abattoir area. This is similar to the study done by Inengite *et al.* (2010) on PAHs sources in Kolo Creek soil in Niger Delta area of Nigeria where it was found that concentration of BghiP was high near an abattoir. The order of PAHs concentration in soil in decreasing order is BghiP>BbF&BkF>2-Methyl.Naph. Lowest concentration of total PAHs detected at control station for soil for both dry and rainy season is 0.007mg/kg, and the order is Acn≤2Methyl.Naph≤1-Methyl.Naph. Most of the PAHs were not found at all and they include: Phe., Acnptyl.,Ind&DbahA, BaA, and Chry. Those detected only

in dry season are: Ant, Fluoren, Acenapthalene, and 1-Methyl Naph.; and those detected only in rainy season are BaP and Fluoranthene.

For sediment samples within Warri environs, PAHs with highest concentration is BaP - benzo(a)Pyrene with a total concentration of 2.803mg/kg and the larger amount of 2.381 being found in the dry season. The decreasing order for total PAHs in sediment sample for dry and rainy season is: BaP>BghiP>Ant>Naph>BaA>Pyr>Chyr>BbF&BkF>BaA>Pyr>Naph. The lowest concentration for PAHs in sediments was recorded for acenaptylene – 0.012mg/kg in rainy season and for total PAHs in dry and rainy season of 0.0696mg/kg for acenapthalene. Some PAHs that were below detection level in the rainy season are: naphthalene, 2 methyl naphthalene and Ind &DbahA.

At the control point, highest total concentration of PAHs found in sediment was 1.092mg/kg and the mean was 0.364mg/kg for Indeno(1,2,3-cd)Pyrene&Dibenz(a,h)Anthracene; all this amount was found only in the dry season as the rainy season record was below detection level. The decreasing order for PAHs in sediments here is: Ind&DbahA>BaP>Phe. The PAHs with lowest concentration was fluorene, followed by 1methyl naphthalene, naphthalene and phenanthrene. Acenapthalene was below detection level in this location while fluoranthene and chrysene were only below detection level in the dry season. Also, Ind&DbahA, Benzo(a)anthracene, Pyrene Anthracene and Acenaptylene were below detection level in the rainy season.

4.2.3 Source Prediction Analysis

Further critical analysis was carried out on the results in order to predict the source of PAHs at each location. As earlier explained in the literature of this study as well as other studies done elsewhere, PAHs have adverse health risks; despite these, they were not included in the

environmental audit of the Niger Delta Survey (NDES, 1999); it is therefore important to identify and apportion PAHs sources for effective pollution control and environmental risk management.

4.2.3.1 PAHs Diagnostic Ratios

PAH sources have been predicted using diagnostic ratios conventionally and reported in several studies such as: (Brack & Olajire, 2005). PAHs of molecular mass 178 and 202 are commonly used to distinguish between combustion and petroleum sources (Brack & Olajire, 2005). These ratios include but not limited to Ant/Ant + Phe; Fluo/Fluo+Pyr; BaA/BaA+Chry and Ind/Ind+BghiP. The Ant/Ant+Phe ratio presumes that ratios < 0.1 indicate PAHs source to be of petroleum origin while ratios > 0.1 indicate PAHs source to be of combustion origin. The Fluo/Fluo+Pyr 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; however, mean ratio for Australian crude oils is > 0.4 , and a few oils have very high proportions of Fluoranthene (Inengite *et al.*, 2010). BaA/BaA+Chry presume 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. And, 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 (Inengite *et al.*, 2010b; Brack & Olajire, 2005). PAHs diagnostic ratio was calculated from the readings and the result is shown below in table 4.12 and 4.13:

Table 4.12: PAHs Diagnostic Ratios for Sediment Samples

PAHs Diagnostic Ratios for Sediment Samples								
	Ant/Ant+Phe		Fluo/Fluo+Pyr		BaA/BaA+Chry		Ind/Ind+BghiP	
Stations	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
ST1- Ekpan	0.56	1	0	1	0.22	0.42	0	0
ST2- Ogunu	0.57	1	0.16	0	0.34	0	0.21	0
ST3- Ugboroike	0.86	0	0	0	0.71	0	0.2	0
ST4- Okotie	0.58	0.75	0.16	0.38	1	0	0.71	0
ST5- Agbarho	0.12	0	0	1	1	0	0.84	0

Table 4.13 PAHs Diagnostic Ratios for Soil Samples

PAHs Diagnostic Ratios for Soil Samples								
	Ant/Ant+Phe		Fluo/Fluo+Pyr		BaA/BaA+Chry		Ind/Ind+BghiP	
Stations	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
ST1- Ekpan	0	1	0.3	0	0.56	0	0	0
ST2- Ogunu	0.84	0.21	0	1	0	0	0.69	0.04
ST3- Ugboro	0.55	0	0	0	0.97	0.78	0	0
ST4- Okotie	0.45	0	0	0.6	1	0	0	1
ST5- Agbarho	1	0	0	0.56	0	0	0	0

From table 4.12 and 4.13 above, diagnosis of the PAHs ratios showed that Ant/Ant+Phe for sediment samples within Warri in the dry season ranged from 0.56 to 0.86 and it was 0.12 at the control point. This shows PAHs from here to be of combustion origin. While the Fluo/Fluo+Pyr ranged from 0.0 to 0.16 within Warri and it was 0.0 at the control point; the values shown in this ratios are too low to make valuable judgment. The BaA/BaA+Chry ratio ranged from 0.22 to 1.0 within Warri and it was 1.0 at the control point; this indicates that within Warri PAHs are of mixed sources and combustion sources and the control point to be of combustion sources. The Ind/Ind+BghiP ratio ranged from 0.0 to 0.74 within Warri and 0.84 for the control point. This

also shows PAHs from Warri to be of mixed sources which are petroleum sources, petroleum combustion sources and grass wood and coal combustion sources while at the control point it could be said to be of grass, wood and coal combustion sources. From this analysis it could be said that PAHs in sediment samples within Warri in the dry season were majorly of combustion sources from mixed origin which could be petroleum or grass wood and coal origin; also at the control point the PAHs were of combustion origin.

In the rainy season, the Ant/Ant+Phe ratio for sediment within Warri ranged from 0.0 to 1.0 while at the control point it was 0.0; this indicates that PAHs are of petroleum origin and petroleum combustion. The Fluo/Fluo+Pyr showed ratio 0.0 to 1.0 within Warri and 1.0 at the control point; this shows PAHs to be of petroleum sources and grass, wood and coal combustion within Warri and at the control point to be of grass, wood and coal combustion. The BaA/BaA+Chry ratio ranged from 0.0 to 0.42 and 0.0 at the control point; this presumes that PAH are of petroleum origin, mixed sources and combustion sources within Warri while at the control point, it is of petroleum origin. The Ind/Ind +BghiP ratio was 0.0 both within Warri and at the control point; this ratio tells us that ratios < 0.2 are of petroleum source and this indicate that the PAHs in the two locations are likely of petroleum sources.

For soil samples in the dry season, the Ant/Ant +Phe ratio ranged from 0.0 to 0.84 and it was 1.0 at the control point; this indicates that PAH source within Warri is of petroleum origin and petroleum combustion while at the control point it is of petroleum combustion. For the Fluo/Fluo+Pyr ratio, it ranged from 0.0 to 0.3 within Warri and 0.0 at the control point; since these ratios are less than 0.4, they are presumed to be of petroleum sources. The BaA/BaA+Chry ratio ranged from 0.0 to 0.97 within Warri and it was 0.0 outside Warri at the control point; this shows that PAH within Warri are of petroleum sources, mixed sources and combustion origin

while outside Warri is of petroleum origin. Ind/Ind+BghiP ratio for Warri environs ranged from 0.0 to 0.69 and it was 0.0 at the control point; this shows PAH to be of petroleum sources, petroleum combustion and grass wood and coal combustion within Warri while at the control point, it was of petroleum origin.

In the rainy season, soil sample ratio for Ant/Ant+Phe within Warri ranged from 0.0 to 1.0 and at the control point it was 0.0. Similarly, the Ind/Ind+BghiP ratio in Warri ranged from 0.0 to 1.0 and at the control point it was 0.0. These show PAHs to be of petroleum origin and combustion origin within Warri and at the control point to be of petroleum origin. Fluo/Fluo+Pyr ratio ranged from 0.0 to 1.0 in Warri and 0.56 at the control point; this shows PAH within Warri to be of petroleum combustion and grass, wood and coal combustion while outside Warri it is of grass, wood and coal combustion. BaA/BaA+Chry ratio within Warri ranged from 0.0 to 0.78 and it was 0.0 at the control point; this indicates that PAH sources within Warri are of petroleum sources, mixed sources and combustion sources while at the control point is of petroleum sources.

4.2.3.2 PAH Cross Plots

Another valuable tool for detecting PAHs source is the PAHs cross plots of the diagnostic ratios, especially when there are several locations; this shows the specific point for the source prediction. PAHs cross plots of the diagnostic ratios above are shown below for sediment and soil samples in the dry and rainy season: N.B: Stations ST 1 to 4 are locations within Warri while ST 5 is outside Warri, control point – Agbarho;

- ST1- Ekpan Location
- ST2 – Ogunu Location

- ST3 – Ugboroke Location
- ST4 – Okotie Sawmill Location
- ST5 – Agbarho Location.

PAH Cross Plots for Various Ratios in Sediment in the Dry Season

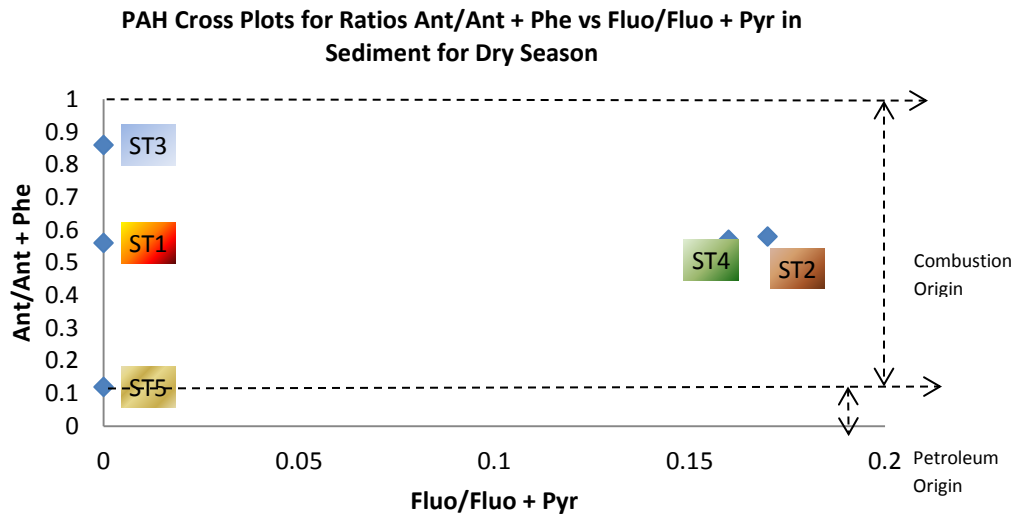


Fig. 4.1: PAH Cross Plots for Ratios Ant/Ant + Phe vs Fluo/Fluo + Pyr in Sediment for Dry Season

From fig. 4.1 above, it can be seen that PAHs sources in sediment for dry season at the control point ST5 are from petroleum origin while the study area ST1-4 are from combustion origin.

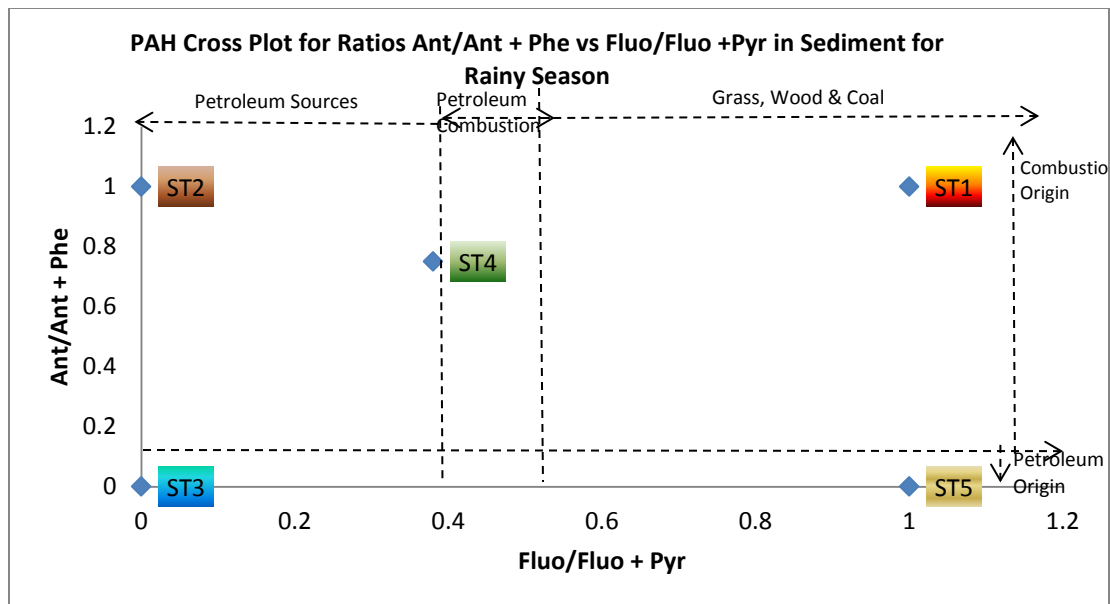


Fig. 4.2: PAH Cross Plot for Ratios Ant/Ant+Phe vs Fluo/Fluo+Pyr in Sediment for Rainy Season

This fig. 4.2 above shows PAHs to be from many sources such as: petroleum origin, combustion origin, petroleum combustion, as well as grass, wood and coal in the rainy season both at the study area and control locations.

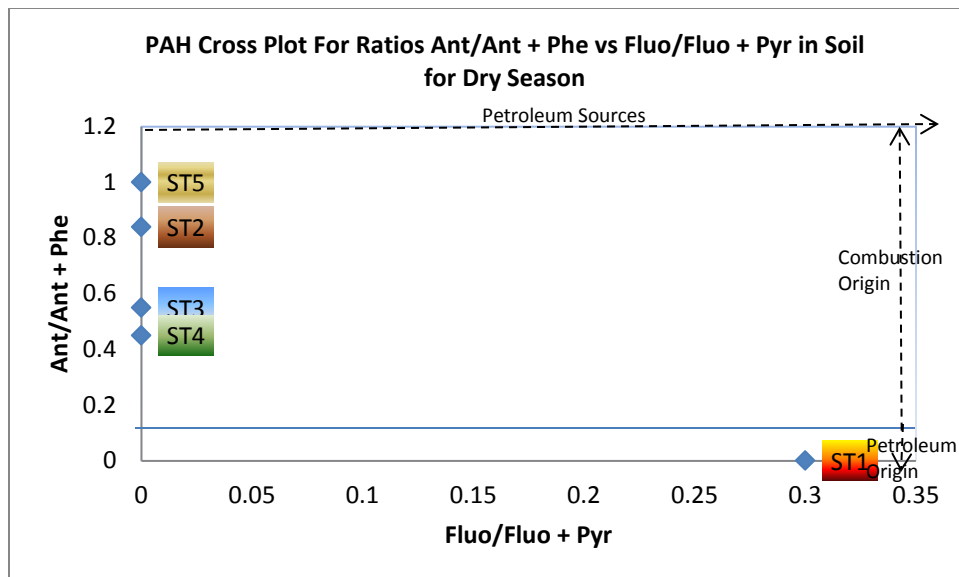


Fig. 4.3: PAH Cross Plot for Ratios Ant/Ant+Phe vs Fluo/Fluo +Pyr in Soil for Dry Season

From the fig. 4.3 above, it can be seen that PAHs sources in the dry season are just from petroleum sources/origin and combustion origins.

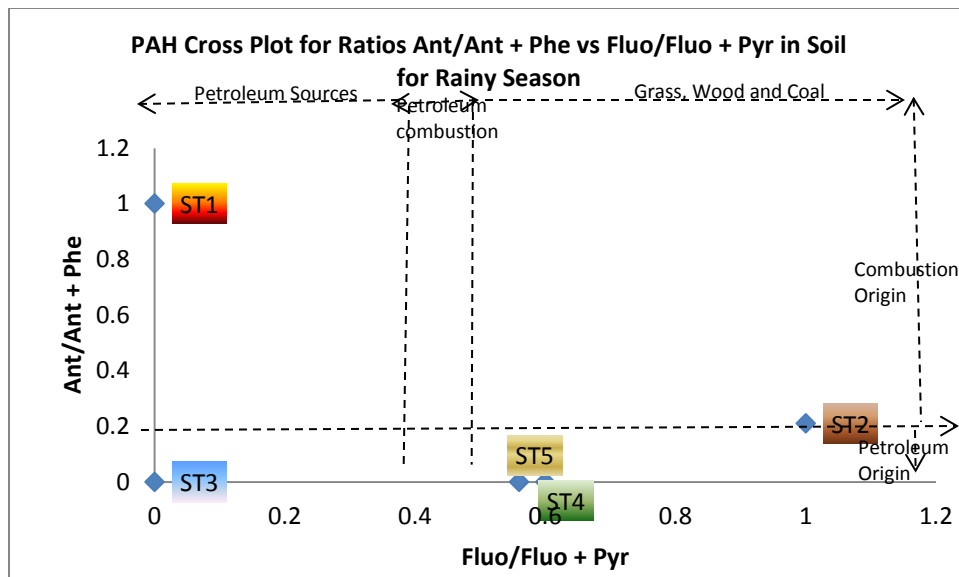


Fig. 4.4: PAH Cross Plot for Ratios Ant/Ant+Phe vs Fluo/Fluo+Pyr in Soil for Rainy Season

Figure 4.4 shows PAHs source to be from petroleum origin, combustion origin, grass, wood and coal sources, petroleum combustion and petroleum sources.

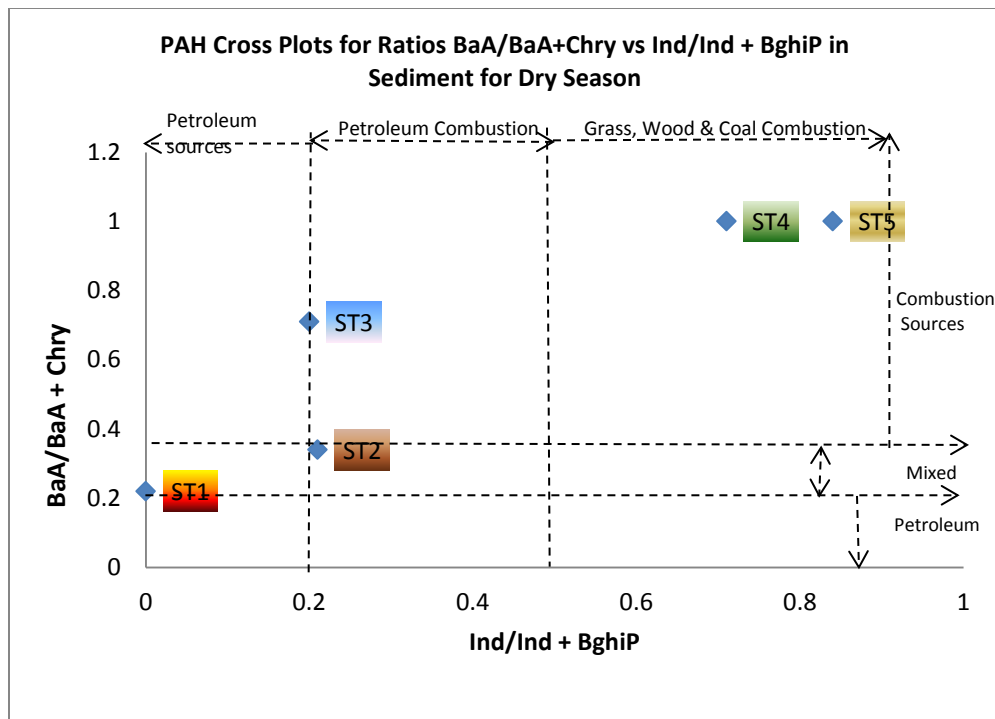


Fig. 4.5: PAH Cross Plots for Ratios BaA/BaA+Chry vs Ind/Ind+BghiP in Sediment for Dry Season

The ratio BaA/BaA+Chry vs Ind/Ind+BghiP used for analysing PAHs in sediments at different locations in the dry season in fig. 4.5 above was able to give more details about other sources not detected by the Ant/Ant+Phe vs Fluo/Fluo+Pyr and therefore enabling better analyses as seen in section 4.2.3.3.

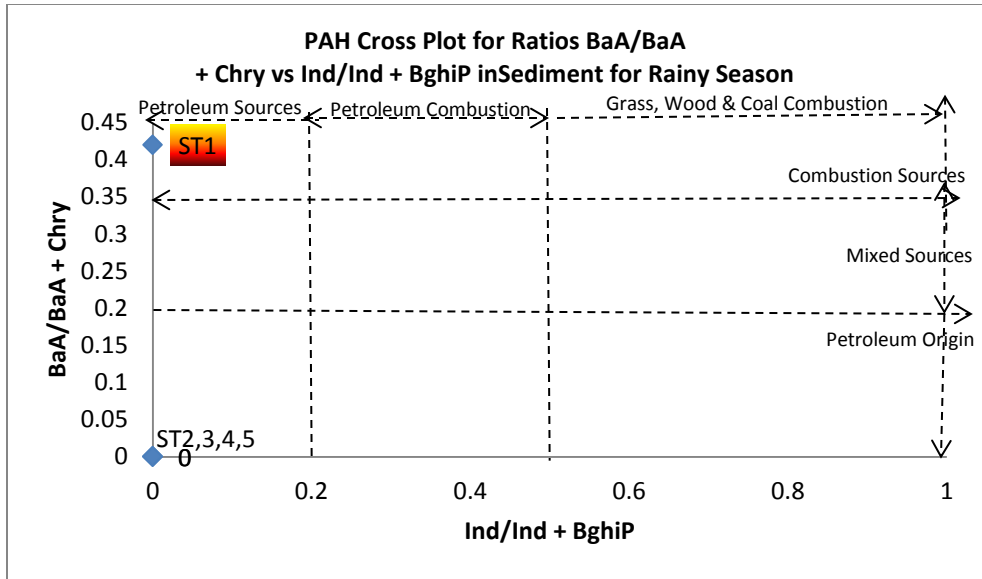


Fig. 4.6: PAH Cross Plot for Ratios BaA/BaA+Chry vs Ind/Ind+BghiP in Sediment for Rainy Season

Figure 4.6 above shows clusters for petroleum origin and petroleum sources at Stations 2, 3 and 4 within Warri and station 5, the control point.

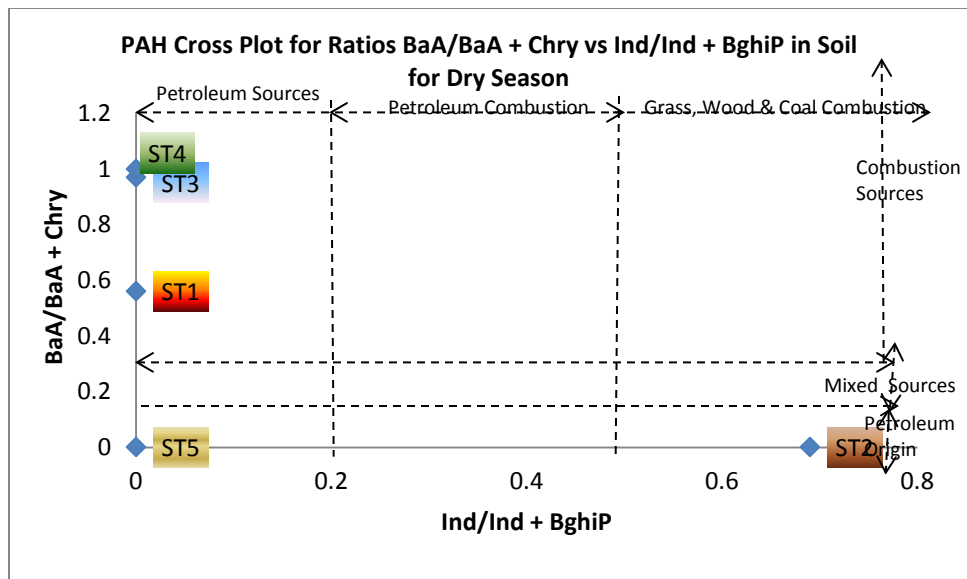


Fig. 4.7: PAH Cross Plots for Ratios BaA/BaA+Chry vs Ind/Ind+BghiP in Soil for Dry Season

The PAHs cross plot ratio in fig. 4.7 above shows clusters at petroleum and combustion sources for stations 4, 3 and 1; while ST2 showed sources from petroleum origin and grass, wood and coal combustion. The control location ST5 however showed sources from petroleum origin and petroleum sources.

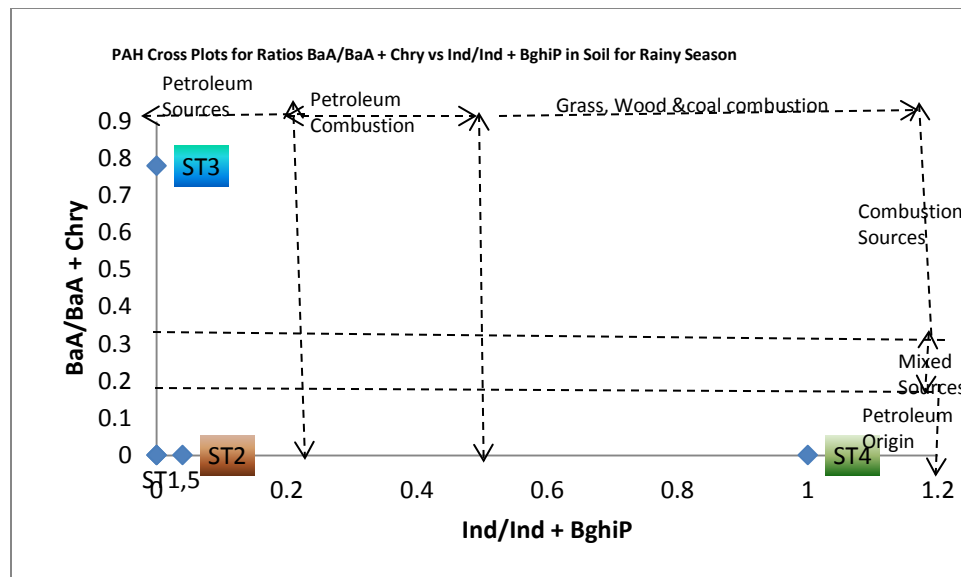


Fig 4.8: PAH Cross Plots for Ratios BaA/BaA+Chry vs Ind/Ind+BghiP in Soil for Rainy Season

In fig. 4.8 above, the ratios BaA/BaA+Chry vs Ind/Ind+BghiP in the rainy season shows clusters for petroleum origin and petroleum sources for ST 1,2,3 and 5; ST4 was clustered at petroleum origin and grass, wood and coal combustion.

A detailed analysis of the cross plots result is attempted in section 4.2.3.3 below.

4.2.3.3 Analysis of the Cross Plots

From fig. 4.1, the PAH cross plot for sediment in the dry season for Ant/Ant+Phe vs Fluo/Fluo+Pyr ratios showed clusters of ST1 to ST4 within Warri to be of combustion origin and the control point ST5 to be of petroleum origin; however, the same plot in fig. 4.2 for the rainy season reflects PAHs to be from various sources – petroleum origin, petroleum combustion, combustion origin and grass, wood and coal combustion, for both the study area (Warri) and the control (Agbarho ST5); although combustion at the control point was more of grass, wood and coal combustion.

On the other hand, from fig. 4.3, $\text{Ant}/\text{Ant}+\text{Phe}$ vs $\text{Fluo}/\text{Fuo}+\text{Pyr}$ ratio for soil in the dry season showed clusters of ST2, 3 and 4 to be of petroleum sources and combustion origin and ST1 to be majorly of petroleum origin while the control point ST 5 was of petroleum sources and combustion origin. In the rainy season, from fig. 4.4, the PAHs source in soil for same ratios showed ST 2 and 4 to be of petroleum origin and grass, wood and coal combustion, ST 3 to be of petroleum sources and ST 1 to be of petroleum sources and combustion origin. At the control point, it was majorly of petroleum origin and grass, wood and coal combustion.

Furthermore, in fig. 4.5, the cross plot $\text{BaA}/\text{BaA}+\text{Chry}$ vs $\text{Ind}/\text{Ind}+\text{BghiP}$ for sediment in the dry season ST 4 and 5 were of combustion sources and grass, wood and coal combustion, ST1 was of petroleum sources and mixed sources, ST2 mixed sources and petroleum combustion while ST 3 was petroleum combustion and combustion sources. And in the rainy season, same plot for sediment in fig. 4.6 showed ST1 as being from petroleum sources and combustion sources and ST 2, 3, and 4 from petroleum origin or sources. The control point ST5 was also from petroleum origin or sources. Meanwhile, according to fig. 4.7, soil samples for the same cross plot in dry season reflected that ST 4, 3 & 1 are of petroleum origin or sources and combustion sources, ST2 had clusters of petroleum origin and grass, wood & coal combustion. The control point ST 5, was clustered at petroleum origin and sources. While for soil samples, in the rainy season as reflected in fig. 4.8, ST1 & 2 are of petroleum sources, ST 3 is of petroleum and combustion sources and ST 4 from petroleum origin and grass, wood and coal combustion. The control point ST5 was majorly of petroleum sources.

Discussion Based on Cross Plots Analyses

From the cross plots analyses, it can be seen that PAHs within Warri environs are from different sources and this could be said to reflect the activities at the various sampling points from which

the samples were collected, however, they altogether indicate majorly that PAHs are more from anthropogenic activities in Warri environs. Also, it was observed from the analysis that PAHs in sediment in dry season in Warri environs were majorly of combustion origin while in soil samples, they were more of petroleum origin and mixed sources. In the rainy season, PAHs in soil and sediments within Warri were majorly from petroleum and combustion sources.

At the control point, PAHs in sediment samples in dry season were majorly from combustion sources while the soil samples were more of petroleum origin. In the rainy season however, the sources in the soil and sediments were of mixed origin, petroleum source, petroleum combustion and grass, wood and coal combustion. This is similar to what happened at Kolo Creek, in Niger Delta area of Nigeria when Inengite *et al.* (2010) analysed PAH source in soil samples. In another work done by same authors on sediments, PAH sources in rainy season reflected mixed sources. A condition that could be responsible for the many sources especially in sediment samples is the runoff from rainwater which could have washed several PAHs from various sources thereby giving conflicting PAHs ratios for source determination (Inengite *et al.*, 2010).

4.2.4 General Discussion on Source Prediction

4.2.4.1 Source Prediction at Study Location

From all these analyses, there is a clearer understanding as to the specific location that the PAHs were generated and it can be seen that anthropogenic petrogenic activities were more localised at specific locations due to activities there. For instance, Ogonu – ST 2 and Okotie Sawmill – ST 4 had several clusters for petroleum origin and petroleum combustion in soil and sediment samples in both dry and rainy season. This also agrees with the fact that Benz(a)Pyrene B(a)P which is a PAHs of petroleum origin was found unusually high at ST 4 (2.138mg/kg) in dry season in soil

samples; and that was the highest value for single PAHs in a particular location in this study. The B(a)P concentration was also high at ST 2 having a total of 1.342mg/kg in sediment, following that of ST 4. As stated earlier, ST 4 has many industrial activities around it, such as: sawmill a construction company, Coca Cola Warri Depot and other small companies in its vicinity. Also, ST 2 – Ogonu, has offices of oil companies around it, although not of major drilling or exploration activities. Furthermore, B(a)P was the PAH with highest concentration within Warri and this could want to give the impression that PAHs in Warri is of petrogenic origin, however, because B(a)P was in high concentration only in two locations and was found only once in ST1 in the dry season, this conclusion need to be made with care.

- Benzo(b)Fluoranthene B(b)F and Benzo(a)Pyrene B(a)P

The most persistent PAH, B(b)F was shown in a previous study to be a much better marker of PAH source than B(a)P, the usual indicator (Aubin & Farant, 2000). In the study conducted in a vicinity of two Soderberg aluminium Smelters in Canada, it was found that B(b)F degrades more slowly than or at the same rate as most other particulate PAHs monitored (15 PAHs were analysed). B(b)F was also found to be more stable than all other particulate PAHs investigated and was used as a potential alternative to B(a)P as an indicator of exposure to airborne PAHs (Aubin & Farant, 2000).

Furthermore, B (b)F source according to EPA is from petroleum, garbage or any animal or plant material burns; It is usually found in smoke and soot and combines with dust particles in the air and is carried into water and soil or deposited on plants (Irwin *et al.*, 1997). Studies have also shown that of all estimated environmental releases of B(b)F, 97% is found in air and approximately equal amount of the remaining 3% is release to water and land (Irwin *et al.*, 1997). Based on these findings, it could be said that B(b)F which is also a five ringed PAHs if

considered as an alternative to B(a)P could indicate that there were traces or indications of petrogenic PAHs all around Warri since B(b)F is persistent around the study area, although it is not in such high concentration as to be the major source of PAHs contamination.

- Benzo(ghi)Perylene B(ghi)P

In order to attempt to correctly predict the source of PAHs within Warri, the next PAH with the highest concentration, B(ghi)P was further analysed. B(ghi)P is majorly from combustion source; vehicle exhausts and domestic wood and coal fires, emissions from industrial effluents, municipal waste water treatment facilities, waste incinerators, aluminium smelting and cigarette smoke. It could also be released naturally from forest fires and volcanoes, yet, anthropogenic pyrogenic sources remain the major source of B(ghi)P in the environment (SEPA, 2006).

B(ghi)P was found in all the locations in Warri, mostly in the dry season and mostly in sediment samples. It also has its highest concentration at Ugboroke ST 3, followed by Ogunu ST 2. These two locations have more of domestic activities that involve burning of wood and coal fires, municipal waste water and cigarette smoke. It is important to also note that all the sampling locations within Warri had a refuse dump either within them or not far away from them.

According to recent studies, it has been found that native microbes act on PAHs as well as other hydrocarbons in the environment in order to remove them (Obayori & Salaam, 2010).

Furthermore, it has been found that high levels of B(ghi)P at a site could be attributed to microbial activities at the site (Inengite *et al.*, 2010).

Based on all these indications, it could be suggested that PAHs in Warri is more from anthropogenic pyrogenic activities than from petrogenic sources.

4.2.4.2 Source Prediction at the Control Point

At the control point, source prediction analyses revealed that soil and sediment samples in the rainy season were from same sources which are: petroleum origin and grass, wood and coal combustion. While in the dry season sediment samples were from petroleum origin, and soil samples from petroleum source and combustion. PAH with highest concentration here is BghiP and it was also the most persistent. The next most concentrated PAH at the control is Ind & DbahA. Studies have shown that BghiP is a PAH of combustion origin (SEPA, 2006), and Ind&DbahA are from combustion and petroleum combustion origin. Ind&DbahA were also high in sediment and this could be due to their individual ability to attach strongly to substrates and not to be easily leached but transported from one location to another (SEPA, 2006). The activities at the control station also reflect the results. Dredging was taking place at the riverside from which the sediment samples were collected. The engines used for this could have released PAHs from petroleum origin into the river and consequently the sediments within the area. However, the concentrations were not high enough to make it the highest source of PAHs, the source predictions showed that there was PAHs pollution from petroleum origin. There is also an abattoir and a meat market that involves burning of tyre. Other domestic activities in the market and daily activities of local dwellers could also release PAHs from combustion sources into the environment. Furthermore, this location is close to a major highway that is a trans-link to a nearby state (Bayelsa) and vehicular activities could have released PAHs from petroleum sources and combustion into the surrounding soil. As observed in the source determination analysis, the rainy season showed PAHs to be from petroleum origin and grass, wood and coal combustion for both soils and sediments. There is possibility that surface runoff to the river affected PAHs source and brought about detection of many sources.

Lastly, a major factor that could affect PAHs as well as other contaminants source anywhere is that, they could have been carried from other places, and since PAHs are found everywhere, it cannot really be said altogether that a particular action was totally responsible. However, PAHs source determination is highly important and has been adequately used as a useful tool to get clues to pollutant source and make valuable decision in environmental pollution management.

4.2.3 Evaluation of the Effects of PAHs on Man

Although this study is majorly to determine levels of PAHs in soils and sediments within the study area, an extension to the evaluation of the effects on man is attempted because man is the ultimate consumer in the food chain and would bear the consequences of the presence of these harmful pollutants in the environmental segments.

As earlier discussed in section 3.2 (description of study area), most of the places in Warri are swampy and marshy and most of the people especially those living close to the waters are either professional fishermen/women or fish as a hobby. The observed PAHs concentration (4.840mg/kg) in sediment samples was above the critical level of 4mg/kg recommended by W.H.O. for soils and sediments. PAHs in aquatic environment have been found to be capable of attaching or bio concentrating in aquatic organisms, mostly bivalve molluscs (such as mussels *Mytilus edulis*) and oysters of the genera (*Ostrea* and *Crassastrea*) and fish as well as other aquatic organisms with highly permeable filtering gills (Brooks, 1997). When man consumes these aquatic organisms as food, they become at risk to the negative effects of these harmful pollutants. According to WHO report in 2003, man is mainly exposed to PAHs from food and ambient and indoor air that has been polluted with PAHs. The PAHs levels in soil samples (3.634mg/kg) in the study area was though lower than the WHO critical level of 4mg/kg, yet even at this concentration may be considered to be harmful since PAHs in soil is partly a

deposition from the atmosphere, and soil and sediments are regarded as good environmental sink that contain about 90% of these compounds with longer half-life than the atmosphere or in plants (Ekonomiuk *et al.*, 2006)).

When these harmful compounds are inhaled or ingested by man they could go through harmful metabolism. Although extensive metabolism of PAHs compounds done through animal studies have shown that food chain bio-magnification of the compounds does not appear to be significant (ATSDR, 1999), yet evidences exist that PAHs are enzymatically converted to highly reactive metabolites that bind covalently to macromolecules such as DNA and result in mutagenesis and carcinogenesis in experimental animals (Irwin, 1997).

CHAPTER 5

CONCLUSION

From all the work done in this study, the following conclusions were made:

- Total PAHs concentration within Warri environs was higher than at Agbarho (the control point) for the study period;
- Sediment samples had the highest concentration for total PAHs within Warri;
- More different PAHs were found in the dry season than in the rainy season. Overall concentration of PAHs was also higher in the dry season than in the rainy season.
- PAHs in Warri environs are more from anthropogenic pyrogenic sources;
- Anthropogenic petrogenic sources are more due to point source pollution within Warri;
- PAHs concentrations are high in the highly industrialised areas;
- Poor domestic waste management such as refuse dump, sludge water, burning, burning of refuse and incineration also increased PAHs concentrations within Warri;
- At the control point, PAHs is also more from anthropogenic pyrogenic sources;
- Petrogenic sources at the control point were also due to point source pollution;
- PAHs concentration is more in the sediments than in the soil at the control point.

RECOMMENDATION

Based on the work done in this study, the following recommendations are given:

- Adequate environmental monitoring and general waste management can help reduce environmental PAHs as well as other pollutant release, therefore, this should be well implemented by relevant bodies and the public as a whole;
- Companies that have an Environmental Management System EMS should do regular environmental audits that include PAHs analysis.
- Small companies springing up should be made to understand their environmental responsibility and that environmental management is more than paying dues to regulatory bodies, it needs commitment and it is as important as the product they are producing if not more;
- The general public should be well educated about the environment and how the little wrong thing done in the environment every moment has great negative implications and travels far and could last for several years;
- The public should be well enlightened on what PAHs, their source, health effects are and how to control their release into the environment;
- Use of available products that reduces environmental emissions due to petroleum combustion should also be encouraged.

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