

## DECLARATION

I, Anthony Seyram Kofi Adzibolosu, hereby declare that this thesis is a compilation of

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results of a research conducted by me under the supervision of Prof. Johannes A. M.

Awudza and Dr. Marian A. Nkansah of the Department of Chemistry, KNUST. This

work has not been presented to this university or another university elsewhere for an

award of a degree. Any cited literature is duly acknowledged.

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## **DEDICATION**

I dedicate this work to my parents, Mr Koblatse Adzibolosu and Mrs Regina Adzibolosu. This work would not have been possible without your support and prayers.

May God bless you abundantly.



## **ACKNOWLEDGEMENT**

I would like to express my gratitude to Dr. Marian Nkansah and Prof. J.A.M. Awudza for their immense contribution by way of criticisms and suggestions. Their unflinching support throughout this work has brought me this far. I am also very grateful to Prof. Samuel Ampadu, Provost of the College of Engineering, for the financial assistance he offered towards this work, thereby facilitating its progress. I would also like to acknowledge Mr. W.I.K. Azumah for the special support he offered, without which, this work would not have been possible. My next appreciation goes to all lecturers of the Department of Chemistry, KNUST who have contributed to the success of this work, not forgetting members of the 2013 – 2015 MPhil Environmental/Analytical Chemistry class. I have learnt a lot from each one of you. Finally, I would like to thank God the Almighty, whose ways, without His own enlightenment, remain mystery to us all.

### **ABSTRACT**

Suame Magazine is an indigenous industrial area in Ghana, well-known for its automobile maintenance/repairs and metal fabrication activities. Due to emissions from vehicular engines, furnaces and the indiscriminate manner in which waste, including the spent engine oils are disposed of in the area, it is anticipated that people who work in this community will have high levels of exposure to polycyclic aromatic hydrocarbons (PAHs). The aim of this study was to determine the levels of PAHs in the 0 – 10 cm, 10 – 20 cm and 20 – 30 cm of the soil profile from shops of selected activities and based on the concentrations obtained, evaluate the health risks to the artisans. Physicochemical parameters such as soil texture, pH, organic matter content and moisture content were determined. Concentrations of dibenz(a,h)anthracene, benzo(b)fluoranthene as well as

benzo(k)fluoranthene were found to be higher than the individual maximum permissible levels for the individual PAHs according to international regulations. The benzo(a)pyrene equivalence of 1.87, 0.394, 0.050 and 0.121 were obtained for maintenance, spraying, welding and metal fabrications activities respectively. The results obtained indicated that maintenance shops relatively, contributed between 61.096% and 95.243% of higher molecular weight polycyclic aromatic hydrocarbons. Contributions by other activities were in the order: spraying > metal fabrication > welding. Health risk assessments based on soil ingestion and dermal contact only, also indicated that vehicle maintenance shops pose the highest risk to artisans with an incremental lifetime cancer risk (ILCR) of 1.24E-05. Spraying, metal fabrication and welding have ILCR of 2.61E-06, 8.03E-07 and 3.34E-07 respectively.

Keywords: Suame Magazine, Artisan, PAH, Soil, Health risk

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## ABBREVIATIONS

ACE	_ Acenaphthene
ACY	_ Acenaphthylene
ANT	_ Anthracene
ATSDR	_ Agency for Toxic Substances and Disease Registry
BaA	_ Benz(a)anthracene
BaP	_ Benzo(a)pyrene
BbF	_ Benzo(b)fluoranthene
BgP	_ Benzo(g,h,i)perylene
BkF	_ Benzo(k)fluoranthene
CHR	_ Chrysene





DaA	– Dibenz(a,h)anthracene
FLT	– Fluoranthene
FLU	– Fluorene
IND	– Indeno(1,2,3-cd)pyrene
NAP	– Naphthalene
PHE	– Phenanthrene
PYR	– Pyrene
BaP <sub>eq</sub>	– Benzo(a)pyrene equivalence
CCME	– Canadian Council for Ministers of the Environment
CSF	– Cancer Slope Factor
ED	– Exposure Duration
EF	– Exposure Frequency
GPS	– Geographical Positioning System
HMW	– Higher Molecular Weight
IARC	– International Agency for Research on Cancer
ILCR	– Incremental Lifetime Cancer Risk
IR	– Soil Ingestion Rate
LADD	– Lifetime Average Daily Dose (Ingestions)
LADDD	– Lifetime Average Dermal Daily Dose
LMW	– Lower Molecular Weight
mg/kg	– Milligram per kilogram
ng/g	– Nanogram per gram
NRC	– National Research Council (of USA)
OSHA	– Occupational Safety and Health Administration

PAH	– Polycyclic Aromatic Hydrocarbon
PEF	– Potency Equivalency Factor
RAIS	– Risk Assessment Information System
USDHHS	– United States Department of Health and Human Services
USEPA	– United States Environmental Protection Agency
WHO	– World Health Organisation



# CHAPTER ONE

## INTRODUCTION

### 1.1 BACKGROUND

Environmental pollution due to the use of petroleum products has been an issue of global concern for years. Some of the major pollutants that are usually found in or due to the use of petroleum products include polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and heavy metals (Guerin, 2002). PAHs are a group of chemical substances that are usually made up of two or more aromatic rings fused together. Their presence in the environment is due to natural (mainly petrogenic) sources such forest fires, oil seeps, volcanic eruptions and formation of rocks or anthropogenic ones. The anthropogenic activities that produce PAHs are incomplete combustion (pyrolysis) of coal, oil, gas, wood, garbage or other organic substances, such as charbroiled meat. The definition of PAHs has also been expanded to include biphenyls and alkyl substituents of the parent PAHs (NRC, 1994; IARC, 1983).

Some PAHs have been found useful in making dyes, plastics, pesticides and even medicines. However, most of them have been found to pose various health risks. High concentration in agricultural soils does not lead to acute intoxication but chronic ones. Carcinogenic, mutagenic and even teratogenic effects have been observed within prolonged exposure of laboratory animals to high concentrations of PAHs (ATSDR, 1995). Due to these hazards, the United States Environmental Protection Agency (US EPA) and the European Union (EU) have included PAHs in their lists of priority contaminants.

According to the USEPA, sixteen (16) PAHs are in this list. Their selection is based on availability of information on these, than others; their availability in higher concentrations at hazardous sites (in the United States of America) and hence greater chance of being exposed to these PAHs than others. Finally, it is also because they are more toxic and their effects are representative of the others (ATSDR, 1995).

PAHs have been described by many as ubiquitous. Thus, they occur in various concentrations in soil, air and water. Plants and animals living in such areas get exposed to, and are contaminated with the PAHs. Consumption of products from these plants and animals serves as an important source of exposure to humans. People who live or work near polluted sites are also exposed through inhalation of air contaminated with these chemicals. Grilling meat, fish or other food stuffs increases the concentrations of PAHs in the food. Drinking of alcohol and water drawn from contaminated sites also exposes humans and other living organisms to PAHs (Caruso and Alaburda, 2009). Another very important source of exposure is active or passive smoking of tobacco. Nicotine, the active ingredient in tobacco is important in producing benzo(e)pyrene and other PAHs on combustion (Sharma et al., 2008).

The fate of PAHs in the environment is affected by a number of physicochemical parameters. The presence and the various proportions of PAHs in the environment can provide useful information on the scale or amount of organic contamination. Volatilization and photochemical oxidation are potentially useful methods of removing most PAHs from the water columns, thus PAHs generally have a short residence time in aqueous solution.



Consequently, the presence of such PAHs in high concentrations in water columns is usually a signal that the source is due to recent or chronic activities (Mastran et al., 1994). The PAH composition in water and soil can indicate the sources(s) from which the PAHs were derived (Yan et al, 2004). High nuclei PAHs (thus, those with many aromatic rings) are usually more stable, less volatile, more hydrophobic and hence less likely to be bioavailable. Higher concentrations of lower molecular weight (LMW) PAHs (e.g. acenaphthene, naphthalene and fluorene) is mostly indicative of sample matrices whose source of contamination could be said to be natural. PAHs originating from pyrolytic sources often contain higher concentrations of moderately high molecular weight and higher nuclei PAHs (e.g. indeno(1,2,3-cd)pyrene, fluoranthene, pyrene) and lower levels of low molecular weight PAHs (Helfrich and Armstrong, 1986). Organic matter has been studied and found to be an important soil component for PAH sorption (Golding et al, 2005). In a related work, light weight expanded clay aggregate (LECA) was also found to be effective in removing phenanthrene, fluoranthene and pyrene from contaminated water (Nkansah et al, 2012). These affinities to organic matter and some types of soils indicate that, the nature of soil influences significantly, the fate and bioavailability of PAHs. PAHs are generally hydrophobic and this is also a major factor that affects the fate and transport of these compounds. Disposal of substances that are known to contain these PAHs indiscriminately in soils in a densely populated community therefore deserves a keen monitoring.

The main study area, Suame Magazine is located in the Suame constituency of the Kumasi Metropolis. It shares boundaries with Bantama to the west and Tafo to the east. It is the largest hub for vehicle and engine maintenance as well as repairs in Ghana. The artisanal activities of the people living in the area have been classified into six main categories. These are: vehicle assembly,

auto mechanics, welding and fabrications, spare part dealing, scrap metal dealing and metal processing. The community has a number of boreholes which serve as source of water for drinking and other domestic purposes.

## **1.2 PROBLEM STATEMENT**

Suame Magazine is the largest industrial area of its kind in Ghana. Approximately twenty thousand (20,000) master artisans practice various trades with very little environmental awareness training. The activities by these artisans customarily have very high potentials of spilling used engine oil into the environment thereby introducing large amounts of PAH into the soil and water bodies. The lower molecular weight compounds have less hydrophobicity and therefore are more likely to have high water-soil distribution ratios. This provides pathways through which PAHs enter the ecosystem and living organisms, thereby posing a great health risk.

## **1.3 JUSTIFICATION**

In a research to determine the occurrence, distribution, sources and toxic potential of polycyclic aromatic hydrocarbons (PAHs) in surface soils from the Kumasi Metropolis, surface soil from Suame Magazine was found to contain the highest concentrations in fluoranthene and pyrene as well as the third highest Total PAH concentration in the Kumasi metropolis (Bortey-Sam et al, 2014).

The World Health Organisation's International Agency of Research on Cancer (IARC) has classified some of the polycyclic aromatic hydrocarbons as known carcinogens (Group 1).

This is due to availability of sufficient evidence in experimental animals for their carcinogenicity. Such PAHs include: chrysene, benz(a)anthracene, benzo(b)fluoranthene, benzo(a)pyrene, benzo(j)fluoranthene, dibenz(a,h)anthracene, benzo(k)fluoranthene, cyclopenta(cd)pyrene, dibenz(a,i)pyrene, dibenz(a,l)pyrene, indeno(1,2,3-cd)pyrene and 5methylchrysene. Others have been classified as probably carcinogenic (Group 2A). These include: benz(j)acenaphthylene, benzo(c)phenanthrene, dibenz(a,c)anthracene, anthracene, benzo(c)fluorene, 13H-dibenz(a,g)fluorene, dibenz(a,e)pyrene, dibenz(a,j)anthracene, fluoranthene, dibenz(a,e)fluoranthene, 2-methylchrysene, 3-methylchrysene, picene, 4methylchrysene, 6-methylchrysene and 2-methylfluoranthene. Compounds in this category have been classified due to limited evidence in laboratory animals for their carcinogenicity (IARC, 1983). Compounds that have inadequate evidence for their carcinogenicity are classified under Group 2B (IARC, 1983).

Complex mixtures of PAHs from all these categories have been found in soil samples from various maintenance shops. In a technical report by the Desert Research Institute on “Chemical Analysis of Lubrication Oil Samples from a Study to Characterize Exhaust Emissions from Light-Duty Gasoline Vehicles in the Kansas City Metropolitan Area”, total PAHs have been found to be averagely 0.4% of used engine oil (Fujita et al, 2006). Most of these used oils find their way into the soils of vehicle maintenance shops. Other activities such as blacksmithing and other forms of metal fabrications involve the burning of organic matter or fossil fuel. Contaminants produced from these activities are indiscriminately added to the soil as well. Consequently, fractions of these contaminants are washed or possibly leached into available water bodies nearby.

No extensive work has, however, been done on the distribution of PAHs in the soil profile and also on water resources close to the activities sites at Suame Magazine. This study will establish the exposure of plants and organisms that derive their food from the surrounding

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waters and the different levels of soil to be examined from Suame Magazine.

## **OBJECTIVES**

The general aim of this study is to assess the level of PAH contamination due to the artisanal activities and evaluate their health risk based on the levels of contamination.

The specific objectives are:

1. To determine the physicochemical properties of the soil samples
2. To determine the concentrations of the PAHs in the soil samples
3. To determine the relationship between the physicochemical parameters and the various levels of PAHs in the soil profile
4. To evaluate the incremental lifetime cancer risk (ILCR) of people working in Suame Magazine

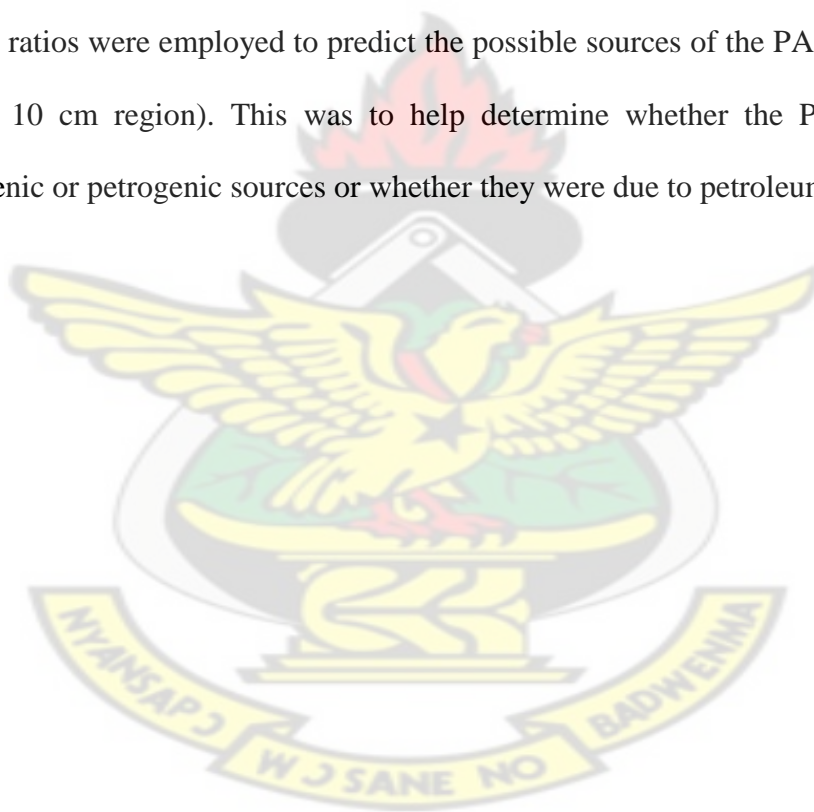
## **1.5 SCOPE OF THE STUDY**

This research focuses on determination of the levels of the sixteen (16) polycyclic aromatic hydrocarbons on the USEPA priority list of hazardous substances, in artisanal workshops in the Suame Magazine industrial village. The activities considered include: maintenance, spraying, welding and metal fabrication. The study also sought to probe the mobility of

**1.4**

PAHs within in the top 30 cm of the soil profile.

Diagnostic ratios were employed to predict the possible sources of the PAHs in the surface soils (0 – 10 cm region). This was to help determine whether the PAHs were from anthropogenic or petrogenic sources or whether they were due to petroleum or wood



combustion. Human health risk assessment was also done based on the dermal contact and ingestion routes of exposure. This was done using the concentrations obtained from the 0 – 10 cm section of the soil samples.



## **CHAPTER TWO LITERATURE REVIEW**

## **2.1 STRUCTURE AND GENERAL PROPERTIES OF PAHs**

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings. As can be inferred from their name, they are basically made up of two or more aromatic rings (usually benzene rings). Their physical and chemical properties are largely dependent on the number of aromatic rings in the molecule. They are hence classified as low molecular weight (LMW) PAHs – containing two or three rings and high molecular weight (HMW) PAHs – containing four rings or more.

## **2.2 SOURCES OF PAHs IN THE ENVIRONMENT**

PAHs are persistent organic pollutants whose sources could be categorised broadly as either pyrogenic (usually due to recently elevated temperature) or petrogenic (related to formation of rocks or petroleum). A comparatively higher level of high molecular weight PAHs of a sample indicates likely pyrogenic source, while on the other hand, a higher level of low molecular weight PAHs implies likely petrogenic origin (Boehm and Farrington, 1984). Naphthalene, fluorene, anthracene, acenaphthene, acenaphthylene and phenanthrene are examples of LMW PAHs, while benzo(k)fluoranthene, fluoranthene, indeno(1,2,3cd)pyrene, benzo(b)fluoranthene, benzo(a)pyrene, and benzo(ghi)perylene are some HMW PAHs. Other HMW PAHs includes coronene and ovalene. Estimating the sources of PAHs based on only the molecular weight diagnostic ratios may not be an accurate procedure. A more precise source apportionment could be achieved when ratios of the concentrations of some individual components of the PAH mixture are employed

(Tobiszewski and Namiesnik, 2012; Zhou et al, 2005).



### 2.3 GENERAL TOXICITY OF PAHS OF ENVIRONMENTAL CONCERN

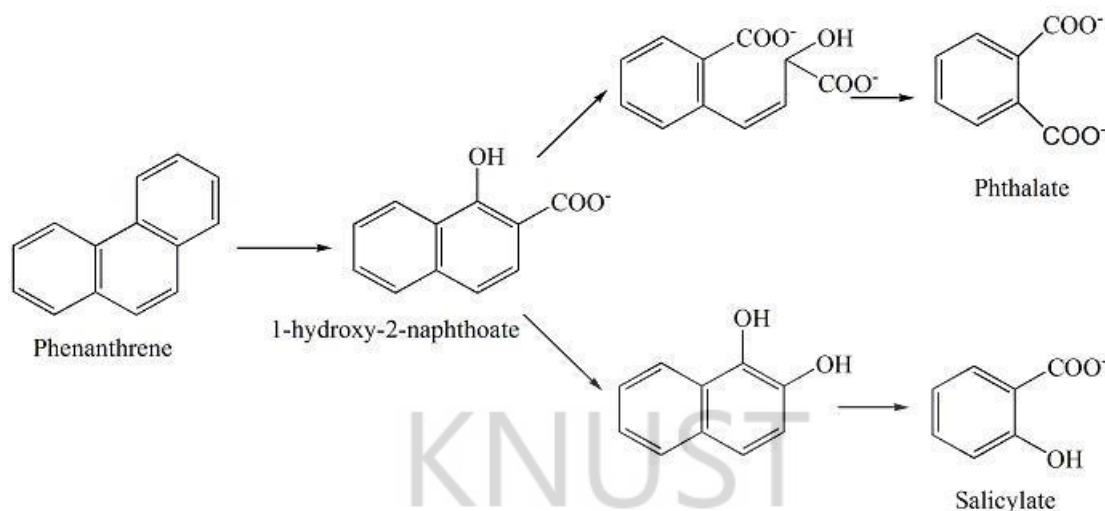
The LMW PAHs are relatively more volatile, soluble in water and degrade more readily due to their comparative lower stability whereas the HMW PAHs are more resistant to microbial degradation due to their strong adherence to soils (Clark et al., 2006; Pamar, 1993). PAHs exert damaging effects on human health. According to the US Environmental Protection Agency among all known PAHs, benzo(a)pyrene and dibenz(a,h)anthracene are recognised as the most dangerous pollutant due to their extreme carcinogenic potential. Benzo(a)pyrene is however the most studied and is found to be a major component of smoke released from vehicular engines and cigarettes (Clark et al., 2006).

Generally, PAHs are highly lipophilic. This makes them to be quickly absorbable into the gastrointestinal tract of humans (Gibson and Subramanian, 1984). Also, PAHs have been investigated and found to be carcinogenic, mutagenic and teratogenic along with potential endocrine-disrupting properties. The mutagenic effects of PAHs are responsible for tumour initiation (Lee et al, 2001). Studies have suggested that PAHs are found in oil, fats and cereals. Furthermore, they are also obtained from charbroiled meat/fish and vegetables (Clark et al., 2006; Pamar, 1993). PAHs distributed in soil harm human health as they may move on into the food chain, therefore PAH contaminated soils are of great concern to human health (Tao et al., 2007).

Dermal contact is a major route of absorption of PAHs into the human body. Others are consumption of contaminated water/drinks, eating of contaminated food and ingesting of contaminated non-food substances such as soil. Absorption rates of PAHs are fast due to high potential for bioaccumulation and possibly biomagnification up the food chain

(USEPA, 2011).

In general, Cerniglia (1992) states, “the greater the number of benzene rings, the greater the toxicity of the PAH”. Metabolism of PAHs is mostly facilitated by fungi, bacteria and other microorganisms. Some monooxygenase enzymes such as the cytochrome P450 have been found to be responsible for degradation of PAHs. It is mostly found in certain fungi which oxidises the benzene/aromatic rings. Due to the oxidation by cytochrome P450 enzymes, the genotoxicity potential of the PAHs is activated and the aromatic rings forms epoxide and diol-epoxide reactive intermediates (Harvey, 1996). Bacteria are also considered a group of very important decomposers of organic compounds in the environment. Enzymes present in these bacteria also digest the PAHs and make them available for absorption (Pointing, 2001). In soil, these processes are beneficial. However, the same cannot be said if they occur inside living organisms. During oxidation processes these intermediates combine with DNA, or attack DNA and undergo oxidation or hydrolysis. Further intermediates combine and attack DNA and form covalent adducts with DNA causing mutation which may lead to tumour formation (Bamforth and Singleton, 2005). Different PAHs have different metabolism/degradation pathways. The following example demonstrates the degradation pathways of phenanthrene.



(Source: Bamforth and Singleton, 2005) Figure

## 2.1 Simplified degradation pathways for phenanthrene

Different PAHs have different degradation pathways. However, they all produce hydroxylPAHs or dihydroxy-PAHs. The difference in their genotoxicity and carcinogenicity is mainly due to the positions of the hydroxyl groups on the PAHs (Bamforth and Singleton 2005).

## 2.4 FATE OF PAHS IN THE ENVIRONMENT

When in surface water, PAHs can undergo volatilisation, photolysis, oxidation, biotransformation or be bound to suspended particles as well as sediment. The levels of PAHs in sediments are usually higher than in the water column due to their hydrophobicity relatively high molecular weight. There, the PAHs can be biodegraded or accumulated by living organisms (ATSDR, 2004).



Degradation as well as metabolism of PAHs involves the conversion of the polycyclic aromatic compounds to various intermediate products which are ultimately converted to end products of carbon dioxide and water. Environmental factors such as high levels of humic acid, oxygen, etc, play significant roles in the rate of photo or bio-transformations of PAHs in the environment.

Analyses of the photodegradation mechanism of pyrene (using GC/MS) revealed that the compound (pyrene) yields six different compounds or groups of isomers. It was also found that direct photolysis products of benzo(a)pyrene yielded five different compounds or isomers (Parmer, 1993). Parmer, (2003) further recognised these products of photolysis as likely oxygen-addition products, hydroxyl-addition products, phthalate esters, and three or four carbon degradation products. The study also found out that among the various parameters considered (which are potential sensitizers, humic material, pH, and suspended sediment), the amount of humic material was the most important factor that affected the rate of photo-degradation of pyrene. In a similarly study, Clark et al (2006) found that photodegradation of pyrene in aqueous solutions results in an increase in the ionic strength of the solution. This decreases with increasing humic acid concentrations and decreases with decreasing levels of oxygen.

The persistence of environmental pollutants such as PAHs and for that matter their biotransformations is typically influenced by a number of factors namely: their chemical structure of the contaminant, the existence of a large and viable population of microbes, necessary to do the transformation, as well as suitable environmental conditions. PAHs are generally non-polar and their solubility in water decreases as the number of rings and molecular mass increases. This also influences the extent to which the PAH could be biodegraded. Both photodegradation and biodegradation of PAHs involves the formation of



intermediate products which then undergoes further stages of transformation over a long period of time to ultimately form carbon dioxide and water products.

According to Chikere et al (2005), bacterial metabolism of naphthalene represents the typical biotransformation mechanism of PAHs in the environment. The bacterial transformation of naphthalene, an LMW PAH consists of the naphthalene dioxygenase enzyme, which initiates and catalyses an oxidative reaction of the PAH to form intermediate - naphthalene dihydrodiols. The dihydrodiols are subsequently dehydrogenated by the help of the dehydrogenase enzymes to form salicylic acid. Further metabolism of the salicylic acid results in the formation of carbon dioxide and water. The properties of compounds that significantly affect their transport and fate in the environment include their partition coefficients (solid-water and octanol-water), pH and humic acid concentrations as well as their water solubility, amongst others.

#### **2.4.1 Contribution of pH to the Fate of PAHs**

An important environmental factor that plays a major role in degradation and fate of PAHs in the environment is soil pH. Most PAHs (especially the HMWs) have shown high levels of susceptibility to photodegradation on adsorbed surfaces. Some examples of processes that are affected by soil pH are biodegradation and photodegradation/photo-oxidation (Das et al, 1994; Han et al, 2005).

#### **2.4.2 Photodegradation of PAHs**

PAHs are known to oxidise when exposed to different wavelengths of light. Different PAHs decompose to different extents. Pawar, (2015) considered the percentage of PAHs left, after exposing phenanthrene, fluoranthene, anthracene and pyrene in topsoil to UV light at 375 nm and 254 nm at different pHs (ranging from 4 – 9). When using TiO<sub>2</sub> or microbe

(*Pseudomonas putida*), it was observed that high amount of the compounds were degraded over time.

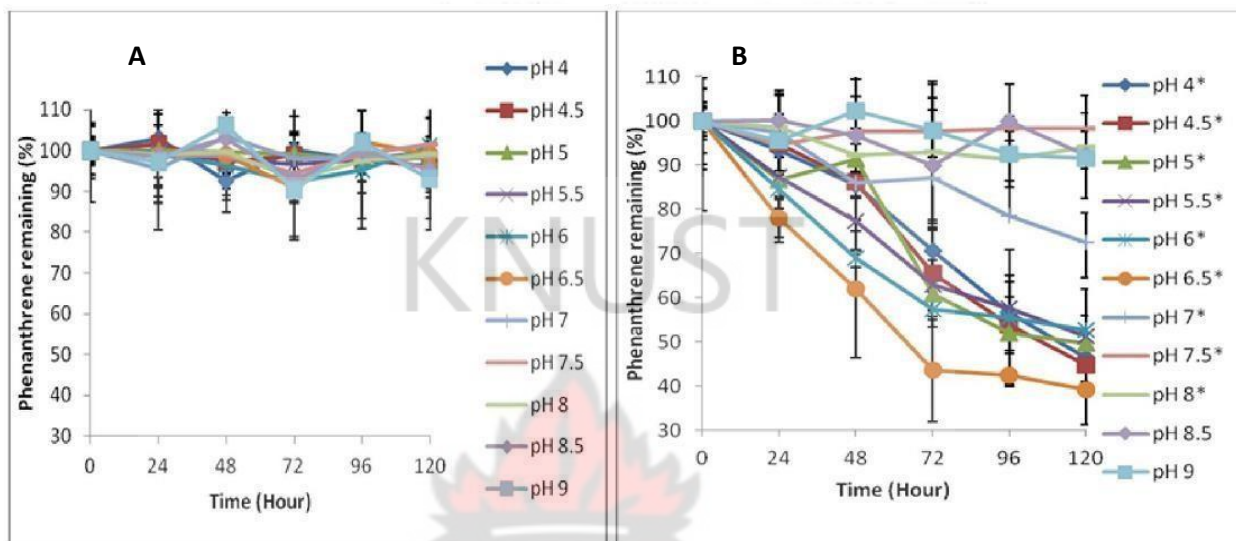


Figure 2.2. Degradation of phenanthrene in top soil at different pH over time

A: outdoor light; B: UV light (Source: Pawar, 2015)

It was also observed that, for higher molecular weight PAHs such as pyrene, there was significant decomposition in the presence of outdoor light when there was no exposure to artificial UV light (Pawar, 2015).

In all experiments conducted, the optimum pH that favours the rate of photo-degradation was recorded to be 6.5. Comparatively, when the pH is acidic, higher rates were observed than when the pH is neutral or alkaline (thus, pH = 7 to 9) (Pawar, 2015).

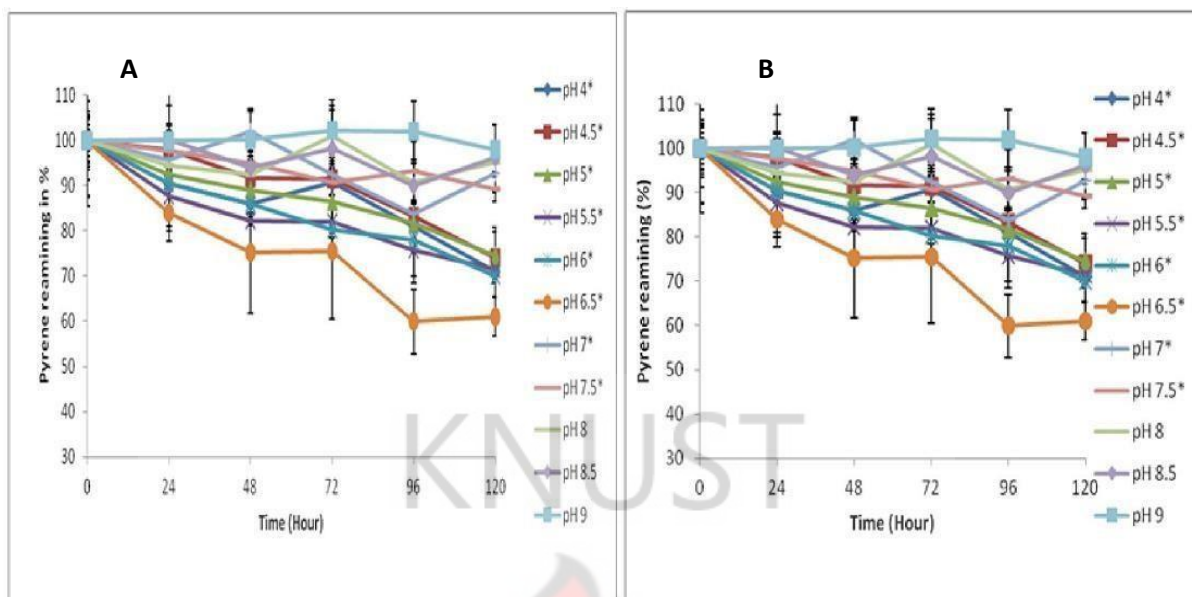


Figure 2.3. Photodegradation of pyrene in top soil at different pH over time

**A:** outdoor light; **B:** UV light (Pawar, 2015)

#### 2.4.3. Biodegradation of PAHs

Biodegradation of PAHs basically involves breakdown or transformation of PAHs to other group of compounds. Of the microorganisms identified to have the capability to degrade PAHs in the environment, fungi have been shown to be relatively more successful in breaking down the higher molecular weight compounds (Pointing, 2001) than bacteria, principally because of the production of non-specific extracellular enzymes such as laccase, lignin peroxidase and manganese dependent peroxidase, which degrade polyphenolic molecules of wood (D'Annibale et al., 2006) and the ability to extend the location of their growth. The presence of cytochrome P450 and other enzyme systems in most white rot fungi has led to the suggestion that the complete degradation of PAHs by white rot fungi may involve these enzyme systems (Levine et al, 2003).



#### **2.4.4 Association of PAHs with Particulate Matter**

Upon their released into the environment, the PAHs undergo distributions between the various phases of the environment (thus air, water and soils/particulate matter). This phenomenon does not only affect how easily treatable the PAHs are during analysis but also their fate in the environment. Sorption/desorption of PAHs plays an important role in the transport and fate of these organic contaminants. Due to their extremely low solubility and their hydrophobic nature, most PAHs are predominantly adsorbed to the surface of particulate matter. Partitioning of PAHs between different phases in the environment depends on the physical properties of the PAHs as well as those of the different phases (Li et al., 2013).

The partitioning coefficients often used in explaining or describing these distributions are, the octanol-water partitioning coefficient ( $K_{ow}$ ) and organic carbon partitioning coefficient ( $K_{oc}$ ) and solid-water sorption coefficient ( $K_d$ ). The main significance of these coefficients is that, they give an idea of the relative solubility/sorption capability of the contaminants to the various phases (thus, water, air, soil and soil organic matter). HMW PAHs usually have higher values for  $K_{ow}$  and  $K_{oc}$ . For this reason, they have been observed to be less stable in aqueous matrix but highly adsorbable on organic carbon and soil matrix than their LMW counterparts. It implies then that HMW compounds are more immobile in the environment (Li et al., 2013; Nyarko et al., 2011).

#### **2.5 REMEDIATION OF PAHs FROM SOIL**

Due to some physical/chemical properties and the tendency of PAHs to become bioactive, their concentration in the environment can be reduced through remediation processes. Some of the



methods used in the remediation of PAHs include: phytoremediation, microbial degradation and mycoremediation.

The rate at which PAHs are removed from the environment is influenced by several environmental factors. When the levels of oxygen low, PAH degradation processes which requires oxygenase activity are limited. Generally, PAH degradation is also impeded by low water solubility, bioavailability and soil pH. Some PAH metabolites particularly epoxide, dihydrodiols and quinones, affect the survival and viability of microorganisms, since they are cytotoxic and genotoxic. It has been found that the pH of culture media affects the levels of some PAH degrading enzymes (e.g. o-quinone reductases) (Pointing, 2001).

## **2.6. PAHS OF ENVIRONMENTAL CONCERN (US EPA PRIORITY)**

### **2.6.1. Acenaphthene (ACE)**

This PAH is highly soluble in benzene, ethanol and acetic acid. It has a very low water solubility of 4 mg/L. However, it is important to note that it is the most water soluble on USEPA priority list, next to naphthalene. Acenaphthene is a tricyclic PAH with molecular formula  $C_{12}H_{10}$  and molecular mass of 154.21 g/mol. The compound may occurs as a pure substance and also as a component of PAH mixtures.

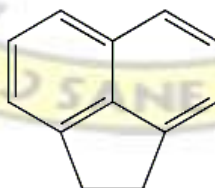


Figure 2.4 Structure of Acenaphthene

Toxicity studies in humans have shown acenaphthene as a gastrointestinal or liver toxicant. The substance is very toxic (IPCS, CEC, 2005). Acenaphthene is a component of crude oil and coal tar and a product of combustion which may be produced and released to the environment during natural fires. Emissions from petroleum refining, coal tar distillation, coal and diesel combustion are major contributors of acenaphthene to the environment. Acenaphthene may also be released to the environment via manufacturing effluents, landfills, municipal waste water treatment facilities and waste incinerators (Jun, 2008). It does not accumulate in the environment because it undergoes photolysis in sunlight. In aquatic systems, acenaphthene can partition from the water column to organic matter contained in sediments and suspended solids (Lauderdale et al, 2003).

Acenaphthene is relatively a volatile PAH and therefore usually exists as gas in ambient air. It can react in the atmosphere with the hydroxyl ( $\text{OH}^\cdot$ ) and nitrate ( $\text{NO}_3^\cdot$ ) radical, which can lead to the formation of mutagenic nitro-PAH and other nitropolycyclic aromatic compounds, including nitrodibenzopyranones. These atmospheric reactions have a significant effect on ambient mutagenic activity (Atkinson and Arey, 1994). The most probable human exposure occurs through dermal contact or inhalation at places where acenaphthene is produced or used. The reported biodegradation half-life of acenaphthene in aerobic soil is about 10 to 102 days (Lauderdale et al, 2003). However, acenaphthene may persist under anaerobic conditions or at high concentrations due to toxicity to microorganisms. It is not expected to undergo hydrolysis in soils; yet, should undergo direct photolysis under sunlight in surface soils. Monitoring data also demonstrates that

acenaphthene will flow in groundwater when spilled or deposited at high concentrations (Lauderdale et al, 2003).

### 2.6.2. Acenaphthylene (ACY)

Acenaphthylene is composed of three fused aromatic rings. In its pure form, it has a white crystalline with a refractive index of 1.594. It is one of the low molecular weight PAHs and has a molecular formula of  $C_{12}H_8$  and relative molecular weight of 152.19. This LMW PAH melts and boils at  $93^{\circ}\text{C}$  and  $265^{\circ}\text{C}$  respectively (Weast, 1989). Its solubility in water is sparing with a value of 3.93 mg/L but more soluble in alcohol, ether and benzene. The Compound decomposes on heating, however, it shows relative stability when exposed to various frequencies of light (Sax, 1984).

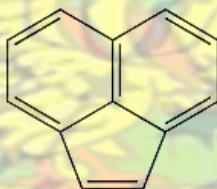


Figure 2.5 Structure of Acenaphthylene

Even though acenaphthylene is environmental ubiquitous, its pollution has been detected mainly in soils, groundwater, and surface waters at sites with high levels of polluting anthropogenic activities. It can be isolated from coal tar and be used to make dyes, plastics and pesticides. Acenaphthylene is one of the 16 PAHs characterized by the United States Environmental Protection Agencies (US EPA's) as priority pollutant (ATSDR, 1990). One of the most common ways by which one gets exposed to acenaphthylene is through dermal contact with contaminated substances, inhaling contaminated air, eating or drinking



contaminated food or water, working in hazardous waste site where PAHs are disposed (Lauderdale et al, 2003). Animal studies have shown that pulmonary effects such as bronchitis, pneumonia, and desquamation of the bronchial and alveolar epithelium were reported in sub chronic inhalation studies with rats exposed to concentrations ranging from 0.5 to 18 mg/m<sup>3</sup> (Reshetyuk et al., 1970; Rotenberg and Mahbits, 1965). Acenaphthylene is irritating to the skin and mucous membranes of rabbits (Knobloch et al, 1969).

### 2.6.3. Anthracene (ANT)

This is a trinuclear PAH with the general molecular formula and mass of C<sub>14</sub>H<sub>10</sub> and 178.2 respectively. Its main isomer among the priority PAHs is the phenanthrene (same molecular mass and formula). In its pure form, anthracene is a colourless crystal that gives a violet fluorescence. The PAH melts at 218°C and boils at 342°C. The compound is however capable of sublimation at 145°C. It is virtually insoluble in water with a solubility value of 44-75 µg/L at 25°C. Anthracene can substantially solvates in suitable organic solvents such ethanol, carbon tetrachloride, carbon disulphide, chloroform, methanol, benzene, diethyl ether and toluene. Whiles in solution, anthracene can undergo photooxidation and photodecomposition in the presence of sunlight (Korfmacher et al., 1980).

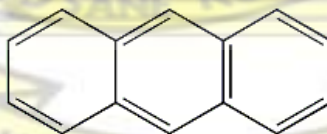




Figure 2.6 Structure of Anthracene

“Anthracene oil” can be obtained as a fraction of coal-tar (boiling at 270-360°C), consisting of anthracene, phenanthrene and other solid hydrocarbons. Anthracene can be produced commercially by distillation of coal tar.

The PAH has been primarily used primarily as an intermediate in dye production. It has also been useful in making smoke screens scintillation crystals and also in organic semiconductor research (Hawley, 1981). Iglesias et al (2010), has also reported that it has be used in wood preservatives, insecticides and coating materials.

According the IARC (1983), anthracene showed negative results when tested for its ability to cause DNA damage and mutation to prokaryotes and mammalian cells. Chromosome effects and cell transformation can also not be association with exposure to anthracene. However, it is considered a substance of very high concern by the European Chemical Agency (ECHA) due to its ability to bio-accumulate and course other toxic effects. The main source of exposure of this PAH is through smoking and ingesting of food or substances contaminated with combustion products (Christensen et al, 1997).

#### **2.6.4Benz(a)anthracene (BaA)**

Benz(a)Anthracene is an odourless, colourless to yellow brown flake or powder in its pure form. Its molecular formula and mass are  $C_{18}H_{12}$  and 228.3 respectively. It has been included in the class of probable carcinogen by IARC in 2002. According monograph 32 of the IARC (1983), it has a boiling points of 435°C. It is practically insoluble in water with water solubility of 9-14  $\mu\text{g/L}$  at ambient temparature. It is however very soluble in benzene, diethyl

ether and acetone. When in an organic benz(a)anthracene does not undergo photo degradation in the presence of indoor light (IARC, 2002).

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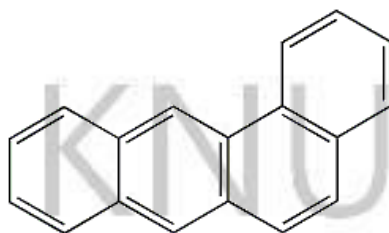


Figure 2.7 Structure of Benz(a)anthracene

It has been found in coal tar, roasted coffee, smoke and automobile exhaust. The primary forms of exposure includes inhaling contaminated air, drinking and eating contaminated food and water (Roy et al, 1997).

The PAH as carcinogenic when it tested positive for inducing DNA damage, mutation, chromosome effects and cell transformation in laboratory mammals (Probst et al., 1981; Tong et al., 1981; Pal, 1981). Benz(a)anthracene is also known to be mutagenic to *Salmonella typhimurium* (prokaryot) in the presence of an exogenous metabolic system and also mutagenic to *Drosophila melanogaster* (insect) (Salamone et al, 1979; Fahmy and Fahmy, 1973).

#### 2.6.5 Benzo(a)pyrene (BaP)

Benzo(a)pyrene is pentanuclear aromatic compound classified by the IARC as a group 1 carcinogen. It has a molecular formula of  $C_{20}H_{12}$ , a molecular weight of 252.31 and boils at 495 °C at 1 atm. It also has a melting point of 178.1°C and hence is solid yellow and needle-like crystal in

its pure form at ambient temperature. As a higher molecular weight PAH, it is highly insoluble in water with a solubility of about 0.11 mg/L at 25°C.

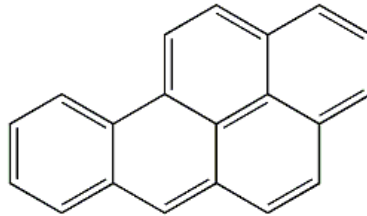


Figure 2.8 Structure of Benzo(a)pyrene

Benzo(a)pyrene is not known to be manufactured by any industrial process and has no known uses. It is ubiquitously distributed throughout the environment as a consequence of its formation during the combustion of organic matter. The principal natural sources of BaP are forest fires and volcanic eruptions. Anthropogenic emission sources of the known carcinogen include the combustion of fossil fuels, coke oven emissions and vehicle exhausts (Lee et al, 1977; Lee et al., 2001).

Benzo(a)pyrene has been found to be carcinogenic in a variety of species through a number of exposure routes. Tumors have been produced in mice, rats, hamsters, guinea pigs, rabbits, ducks and monkeys following intragastric, subcutaneous, dermal or intratracheal administration of BaP. The preferred target sites appear to be proliferating tissues of the intestinal epithelia, bone marrow, lymphoid organs and testes, which interact with the active metabolite of BaP (Santodonato et al, 1981). Benzo(a)pyrene has been shown to cause genotoxic effects in a broad range of prokaryotic and mammalian cell assay systems. In prokaryotes, BaP tested positive in DNA damage assays and in both reverse and forward mutation assays. In mammalian cell culture assays, BaP tested positive in DNA damage assays, forward mutation assays, chromosomal effects assays and cell transformation assays (U.S. EPA, 1991).

#### **2.6.6. Benzo(b)fluoranthene (BbF)**

Benzo(b)fluoranthene is an isomer of benzo(k)fluoranthene and benzo(a)pyrene. In its pure form, it is a colourless crystalline solid that melts at 168.3°C and is insoluble in water



however slightly soluble in some organic solvents. There is no commercial production or known use of this compound (Santodonato et al, 1981).

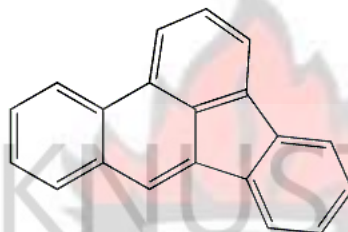


Figure 2.9 Structure of Benzo(b)fluoranthene

Though there is no available data on humans that this compound is carcinogenic, its positive test on *Salmonella typhimurium* and mammalian cells (Chinese hamster bone marrow cells) for mutation and chromosome effects respectively, justifies the classification of benzo(b)fluoranthene as a group 2B by the IARC (LaVoie et al, 1999; RoszinskyKocher et al, 1979). This means it is probably a carcinogen to human. Thus benzo(b)fluoranthene produced tumors in mice after lung implantation, intraperitoneal or subcutaneous injection, and skin painting (IARC, 1984). The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for benzo(b)fluoranthene (as a coal tar pitch volatile) is  $0.2 \text{ mg/m}^3$  of air as an 8-hour time weighted average (OSHA, 1994).

#### 2.6.7. Benzo(ghi)perylene (BgP)

This is a heavy molecular weight PAH made up of pale yellow-green crystals in the pure form. It has a melting point of  $278.3^\circ\text{C}$  (Clar, 1964; Santodonato et al, 1981). It is known to

be soluble in 1,4 -dioxane, dichloromethane, benzene, acetone and some other organic solvents. According to Clar (1964), this compound, with molecular formula  $C_{22}H_{12}$  and molecular mass of 276.3g/mol is stable to photo-oxidation.

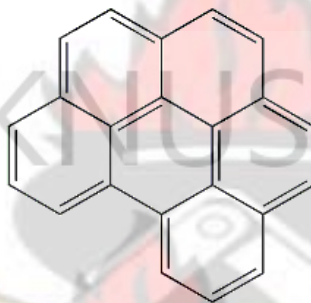


Figure 2.10 Structure of Benzo(g,h,i)perylene

Due to the fact that benzo(g,h,i)perylene is an HMW PAH, its release into the environment is mainly through anthropogenic means, such as, incomplete combustion of organic substances such as fuel, domestic wood and coal fires. Emissions also arise from industrial effluents, municipal waste water treatment facilities, waste incinerators and aluminum smelting (SEPA, 2006). Benzo(g,h,i)perylene is also released naturally from volcanoes and forest fires, but are very small compared to those released from man-made combustion sources (SEPA, 2006).

Benzo(g,h,i)perylene can enter the body either by inhalation of contaminated air, ingestion of water, soil or food. The most serious environmental impact of benzo(g,h,i)perylene is its significant accumulation in organisms exposed to it. It is also toxic and a suspected carcinogen (SEPA, 2006; Lauderdale et al, 2003; IPCS, CEC, 2001). In water, benzo(g,h,i)perylene attaches

strongly to sediments and any other solid matter. Benzo(g,h,i)perylene released to soils tends to bind very strongly to the soils particles, so no major leaching to groundwater or

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volatilization to air is likely to take place though. It is very stable and can remain in the environment for a long period of time (Lauderdale et al, 2003).

Benzo(g,h,i)perylene is extracted coal tar and used in making dyes, plastics, pesticides, explosives and drugs. It is also found (as part of a complex mixture of PAHs) in creosote, tar paints, waterproof membranes and other products (ATSDR, 1990; Faust et al, 1994).

#### 2.6.8. Benzo(k)fluoranthene (BkF)

Benzo(k)fluoranthene a pale yellow crystalline solids that melts and boils at 215.7 °C and 480 C respectively. The HMW PAH has five aromatic rings, a molecular mass of 252.3 and formula of  $C_{20}H_{12}$ . Its isomers include benzo(a)pyrene and benzo(b)fluoranthene. It is hydrophobic, but highly soluble in acetic acid, benzene and ethanol (Weast, 1975). In outdoor environment, the PAH is highly photo -oxidisable. Yet, when in solution, it is very stable (Clar, 1964).

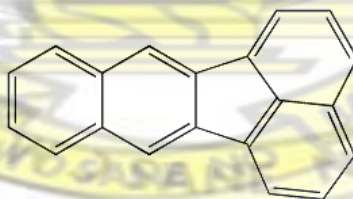


Figure 2.11 Structure of Benzo(k)fluoranthene

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Although environmental concentrations are greatest near sources, its presence in distant places indicates that it is reasonably stable in the atmosphere and capable of long distant transport. Atmospheric losses are caused by gravitational settling and rainout. On land it is strongly adsorbed to soil and remains in the upper soil layers and does not leach into groundwater. Biodegradation may occur but it is very slow (Lauderdale et al, 2003). In water it is adsorbed to sediment and particulate matter in the water column. There is also a potential for adsorbed benzo(k)fluoranthene to be slowly desorbed and, therefore, concentration in the water column is usually low (Lauderdale et al, 2003).

Human exposure is mainly due to smoking, inhalation of polluted air and eating contaminated food. Since water treatment processes such as filtration, chlorination and ozonolysis removes benzo(k)fluoranthene, exposure from drinking treated water is minor (Lauderdale et al, 2003). Based on bioassay studied benzo(k)fluoranthene is known to produce tumors in mice and is mutagenic in bacteria (IARC, 1984).

#### **2.6.9 Chrysene (CHR)**

Chrysene is a tetranuclear PAH that is composed of two naphthalenes fused at the “a” and “f” positions respectively. The pure form of chrysene is a colourless crystalline with blue fluorescence (RAIS, 2000). The melting and boiling points are 256°C and 448°C

respectively. With the molecular mass and formula of 228.3 and  $C_{18}H_{12}$ , pyrene is an isomer of benz(a)anthracene. The water solubility of pyrene is  $1.5 \mu\text{g/L}$  indicating that it is virtually insoluble in water. It is however slightly soluble in ethanol, acetone, carbon disulphide, acetic acid, diethyl ether and toluene. It is known to be very soluble in benzene (Santodonato et al, 1981; May et al, 1978).

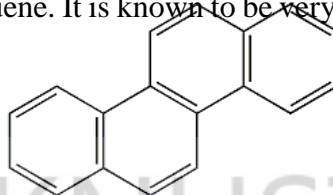


Figure 2.12 Structure of Chrysene

Chrysene is often produced as a gas during combustion of coal and petroleum products as well as animal and plant material (RAIS, 2000). It is virtually insoluble in water, and only slightly soluble in many other solvents such as alcohol, ether and glacial acetic acid (RAIS, 2000). It is however, moderately soluble in benzene, and readily dissolves at higher temperatures, in benzene and toluene (Harvey, 1991).

Chrysene is a probable human carcinogen. Human exposure occurs through contact with contaminated areas and products such as smoked and grilled meats, and through inhalation of smoke (Harvey, 1991). Chrysene is released into the atmosphere as a by-product of many industrial processes. Once in the air, it is adsorbed to soil and dust particles and is dispersed over large areas, contaminating both soil and water (RAIS, 2000).

#### 2.6.10. Dibenz(a,h)anthracene (DaA)

With a molecular formula of  $C_{22}H_{14}$  and relative molecular weight of 278.35, dibenz(a,h)anthracene is considered a high molecular weight PAH. In its pure form, it is a colourless to light yellow crystal with a melting point and boiling point of 266.6°C and 524°C

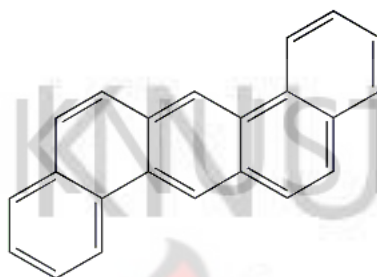


Figure 2.13. Structure of Dibenz(a,h)anthracene

There is no commercial production or known use of dibenz(a,h)anthracene. It occurs as a component of coal tars, shale oils, and soots (IARC, 2010) and has been detected in gasoline engine exhaust, coke oven emissions, cigarette smoke, charcoal broiled meats, vegetation near heavily travelled roads, surface water, and soils near hazardous waste sites (ATSDR, 1995; IARC, 1983). Dibenz(a,h)anthracene is one of a number of PAHs on EPA's priority pollutant list (USEPA, 1991). IARC classes this HMW PAH as probably carcinogenic to

#### 2.6.11. Fluoranthene

Fluoranthene is considered a higher molecular PAH because it contains four fused aromatic rings. It is a pale yellow solid crystal in its pure form. It is an isomer of pyrene since it has also has a molecular mass of  $C_{16}H_{10}$  and mass of 202.3. According to Santodonato et al (1981), it has a melting and boiling points of 111 °C and 251 °C respectively. It has a very low water solubility of 0.26 mg/L. However, it shows appreciable solubility in acetic

respectively. It has a very low solubility in water with about  $0.5\mu\text{g/L}$  solubility at ambient temperature ( $25^{\circ}\text{C}$ ). Slightly higher solubilities can be achieved with diethyl ether and ethanol. However, for optimum solubility, benzene, toluene, xylene and other organic solvents are required (Davis et al., 1942). This compound is also known to undergo photooxidation reactions under indoor sunlight while in solution. humans.

acid, benzene, carbon disulphide, chloroform and diethyl ether (May et al, 1978; Weast, 1975). Fluoranthene is photo-degradable yet it does not undergo photo-oxidation when in solution (Korfmacher et al., 1980). The most reactive positions are 3 and 8.

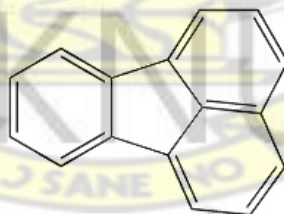


Figure 2.14 Structure of Fluoranthene

Fluoranthene occurs ubiquitously in incomplete combustion products and also in fossil fuels. It has been found that, it also occurs in, cigarette smoke in concentrations ranging from  $0.083$  to  $26.3\mu\text{g/cigarette}$ ; urban air at  $0.9 - 15.0\text{ ng/m}^3$ ; gasoline exhaust fuel at  $1060 - 1662\mu\text{g/L}$



of fuel; coal at 0.13 – 29.4 mg/kg; crude used engine oils at 0.18 – 2.75 mg/kg (Hoffman and Wynder, 1976; Grimmer et al, 1997). Bortey-Sam et al (2014) also, determine the contaminant in surface soil from the Kumasi Metropolis. Incidentally, Suame Magazine recorded the highest among of fluoranthene in surface soil (about 400 ng/g).

In the atmosphere, fluoranthene is present both as vapour and adsorbed to particles. As vapour it degrades rather rapidly, but it's more stable when adsorbed to particles and can travel long distances before being deposited. Fluoranthene is slightly soluble in water, and therefore rapidly adsorbed to sediment and other particulate matter. In sediments the compound is very stable and can stay for decades. Since it has a high tendency to be adsorbed to organic matter, it has a high bioaccumulation potential. It bioaccumulates in shellfish, making them an excellent bioindicator for fluoranthene pollution (Lauderdale et al, 2003).

Fluoranthene adsorbs strongly to soil and would be expected to remain in the upper layers of soil for a very long time (half-life of 5 months to 2 years). However, it has been detected in groundwater samples which demonstrates that it can be transported there by some process(es) (Lauderdale et al, 2003). Human exposure is from ambient air and ingesting contaminated food. Exposure from drinking water is less common since water treatment processes such as filtration and chlorination removes fluoranthene from water (Lauderdale et al, 2003).

#### **2.6.12. Fluorene**

This is a LMW PAH that is composed of three fused aromatic rings (two benzene rings, bridged by a pentacyclic system). It is a white crystalline solid which melts at 116°C and boils at 295°C. It has a molecular formula of  $C_{13}H_{10}$  and molecular weight of 166.2. At 146°C, it has a vapour pressure of 10 mmHg, indicating it high volatility. It is very sparingly

soluble in water with 1.98 mg/L at 25°C. Photo-oxidation potential for this compound is also relatively low (Tokiwa et al, 1981; Kuratsune & Hirohata, 1962).

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Figure 2.15 Structure of Fluorene

There is no known use commercial of this compound. Fluorene has however been classified as Group 3 carcinogen by the IARC. This means that there is no evidence at present that it causes cancer in humans (IARC, 1983), but it has been found to causes skin, eye and respiratory irritation

#### 2.6.13. Indeno(1,2,3-cd)pyrene (IND)

This known carcinogen is a high molecular weight PAH with a melting point of 163.8°C and a boiling point of 536 °C (Santodonato et al, 1981; Verschueren, 1996). It has a molecular formula and mass of C<sub>22</sub>H<sub>12</sub> and 276.3g/mol respectively. Due to its high molecular weight, it is known to have very little solubility in water – 62µg/L, but very soluble in organic solvents (IARC, 1983). When heated to decomposition, it emits acrid smoke and irritating fumes. It is also known to have a Henry's law constant of 3.48x10<sup>-7</sup> m<sup>3</sup>atm/mol at 25°C.

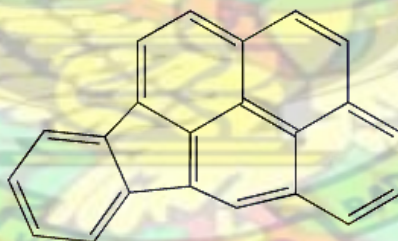


Figure 2.16. Structure of Indeno(1,2,3-cd)pyrene

Based on data from animal bioassays, indeno(1,2,3-cd)pyrene has been classified category 2B (possibly carcinogen to human) by the IARC. Indeno(1,2,3-cd)pyrene produced tumours in mice following lung implants, subcutaneous injection and dermal exposure. It tested positive in bacterial gene mutation assays (IARC, 2010).

and suspected to be gastrointestinal and liver toxicant. It has been found to show evidence of mutagenic properties in laboratory animals (ATSDR, 2004). In examining the metabolism of this pollutant in laboratory rats, 1-Hydroxy, 9hydroxy and 9-ketofluorene have been detected as metabolites of fluorene following incubation of this compound with rat-liver preparations (LaVoie et al., 1982). However, further tests to confirm its mutagenicity and ability to cause damage to DNA in prokaryotes and Mammalian cells gave negative results (LaVoie et al, 1999; Probst et al, 1981).





#### 2.6.14. Naphthalene

It is one of the simplest PAHs that is composed of two fused benzene rings. At room temperature, naphthalene is a white crystalline solid. It only melts at 80.2°C and boils or sublimates at 217.9°C. With a relative molecular mass of 128.17 and formula C<sub>10</sub>H<sub>8</sub>, it is the lighter and most volatile PAH on the USEPA list of priority contaminants. It is also the most – though just slightly, soluble in water with a solubility of 31-34 mg/L at 25°C (Verschuere, 2001). It is however soluble in methanol and ethanol; very soluble in acetone, carbon tetrachloride, carbon disulfide, benzene, chloroform and diethyl ether.

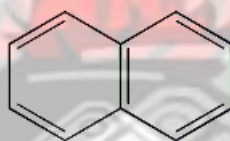


Figure 2.17. Structure of Naphthalene

In 2002, the IARC classified naphthalene in monograph 82 as a group 2A carcinogen (IARC, 2002). In the United States, has been detected sediments at average concentrations of 54.7 ng/g and 61.9 ng/g at 10 to 25 meters from oil platforms. Naphthalene concentrations ranging from < 2.0 to 20.2 mg/kg dry weight were reported in three out of four sediments from lakes in the Northwest Territories in Canada (Lockhart et al., 1992).

Primarily due to oxygen limitation, naphthalene persists in coal tar contaminated surface sediments (Madsen et al., 1996). Naphthalene concentrations in soils and sewage sludges are usually less than 1 mg/kg in the United Kingdom (Wild & Jones, 1993). Locally, naphthalene has been detected in surface soil of the Kumasi metropolis in concentrations ranging from 0.01 to 34.80 ng/g dry weight (Bortey-Sam et al, 2014). Also, according to Nyarko et al (2011), naphthalene has been measured in selected fishes harvested along the coast of Ghana.

Studies on biodegradation of polycyclic aromatic hydrocarbons in soil suggest that absorption to organic matter significantly reduces the bioavailability and thus the biodegradability of naphthalene (Heitzer et al., 1992; Weissenfels et al., 1992; Agency for Toxic Substances and Disease Registry, 1995a). Reported naphthalene half-lives in soil vary considerably. The estimated half-life of naphthalene reported for a solid waste site was 3.6 months, while in typical soils more rapid biodegradation is expected to occur (Heitkamp et al., 1987; Howard, 1989).

Biodegradation of naphthalene is accomplished via the action of aerobic micro-organisms and generally declines precipitously when soil conditions become anaerobic (Klecka et al., 1990). Naphthalene biodegrades to carbon dioxide in aerobic soils with salicylate as an intermediate product (Heitzer et al, 1992; ATSDR, 1995a). Although polycyclic aromatic hydrocarbons are persistent in a strictly anaerobic environment, some lower molecular weights such as naphthalene can be degraded anaerobically under sulphate-reducing conditions. In a study by Coates et al (1997), naphthalene was oxidized to carbon dioxide in petroleum contaminated marine harbour sediments in San Diego, CA.

#### **2.6.15. Phenanthrene**

Phenanthrene is a PAH that is composed of three fused benzene rings. In its pure form, it has a white crystalline with a refractive index of 1.59427. As one of the low molecular weight PAHs, it has a molecular formula of  $C_{14}H_{10}$  and relative molecular weight of 178.2. According monograph 32 of the IARC (1983), it has a melting and boiling points of 100°C and 340°C respectively. With water solubility 1-1.6 mg/L, it can be concluded that it is

practically insoluble in water. It is however soluble in organic solvents such ethanol, carbon tetrachloride, benzene, diethyl ether and toluene. When in solution, phenanthrene shows high resistance to photo degradation in the presence of indoor light (Korfmacher et al., 1980).



Figure 2.18. Structure of Phenanthrene

It is commonly found as pollutants in soils, estuarine waters and sediments. Although phenanthrene is not mutagenic or carcinogenic, it has been shown to be toxic to marine diatoms, gastropods, mussels, crustaceans, and fish (Jun, 2008). Phenanthrene can enter the body through breathing contaminated air. Eating or drinking food and water that are contaminated with PAHs, could also be an exposure route. Exposure can also occur if the skin comes into contact with contaminated soil or products like heavy oils, roofing tar or creosote where PAHs have been found. Creosote is an oily liquid found in coal tar and is used to preserve wood. Once in your body, phenanthrene can spread and target fat tissues and other organs including kidneys, liver. It could also be through eating foods that has been grilled. Grilling of food actually increases the amount of phenanthrene in the food (ATSDR, 1990; Faust et al, 1993).

#### 2.6.16 Pyrene

Pyrene is a tetracyclic PAH that appears as pale-yellow solid in its pure form. It has a boiling point of 485°C and a melting point of 149-156°C at standard pressure (Hoffman and Wynder, 1962). The molecular formula of pyrene is  $C_{16}H_{10}$  and it has a molecular weight of



202.3g/mol. This compound is only sparingly soluble in water with a solubility of about 129165µg/L. It is however known to be soluble in benzene, carbon disulphide, diethyl ether, ethanol, methanol, petroleum ether, toluene, acetone and some other organic solvents (May et al., 1978; Van Duuren and Goldschmidt, 1976). The four membered ring PAH is more

resonance stabilized than its five membered ring isomer – fluoranthene, hence is more stable in terms of reactivity. It is also known not to undergo photo-oxidation in organic solvents under fluorescent light of indoor sunlight (Kurantsune and Hirohata, 1962).

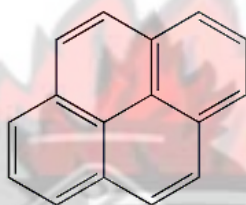


Figure 2.19 Structure of Pyrene

It was first isolated from coal tar, where it occurs up to 2% by weight (Selim and Marco, 2003). Pyrene and its derivatives are used commercially to make dyes and dye precursors. Animal studies have shown that pyrene is toxic to the kidneys and the liver. One of the most common ways by which pyrene can enter the body is through breathing contaminated air (ATSDR, 1990; Faust et al, 1993). Exposure can also occur through the skin. Grilling and charring of food actually increases the amount of PAHs in the food. It has also been found in surface water. Animal studies showed that pyrene has the potential to cause nephropathy, a kidney disease (ATSDR, 1990; Faust et al, 1993).

## CHAPTER THREE



## MATERIALS AND METHODS

### 3.1 REAGENTS AND EQUIPMENT

#### 3.1.1 Solvents and Reagents Used

Pesticide grade acetonitrile, ethyl acetate and acetone were obtained from BDH Laboratory Supplies, England. Other reagents from the same source were anhydrous magnesium sulphate and ethylene glycol 200; both reagents were of analytical grade. Silica gel (1000mg/6mL) and reference PAH standards were obtained from Phenomenex and Dr Ehrenstorfer GmbH respectively.

#### 3.1.2 Equipment Used

The following equipment and instruments were employed in the analysis: hand-held (Geographical Positioning System) GPS, analytical balance, porcelain crucibles, pH meter, oven, muffle furnace, hydrometer, ultrasonic bath, horizontal mechanical shaker, vacuum manifold & solid phase extraction accessories. Others include rotary evaporator and Gas Chromatograph-Mass Spectrometer (Varian CP -3800 Gas Chromatograph with a CP -8400 Autosampler and Saturn 2000 MS/MS).

### 3.2 SAMPLING

Sampling of soil was done in November, 2014. The test samples were taken from forty one (41) artisan workshops in the Suame Magazine industrial area. The shops were categorised into four – Maintenance, Metal fabrication, Spraying and Welding. The non-activity soil sample was taken from the premises of the St. Louis College of Education.

### 3.2.1 The Study Area

Suame Magazine is located in Suame, a suburb of the Kumasi Metropolis of the Republic of Ghana. It is about 3.4 square kilometres of land, occupied by artisans specialised in vehicle repairs and maintenance, blacksmithing/metal fabrication, welding, selling of vehicle parts among others. The community is located on two opposite gentle slopes. This landscape creates a stream which divides the community roughly into two halves and ultimately drains into the Owabi water shed – an important dam that serves a large proportion of pipe borne water users in the Kumasi metropolis.

The study area was divided into four zones – Zone A, Zone B, Zone C and Zone D, using the stream as a primary reference and bearing in mind the geographical size and also, the population of activities in the various zones.

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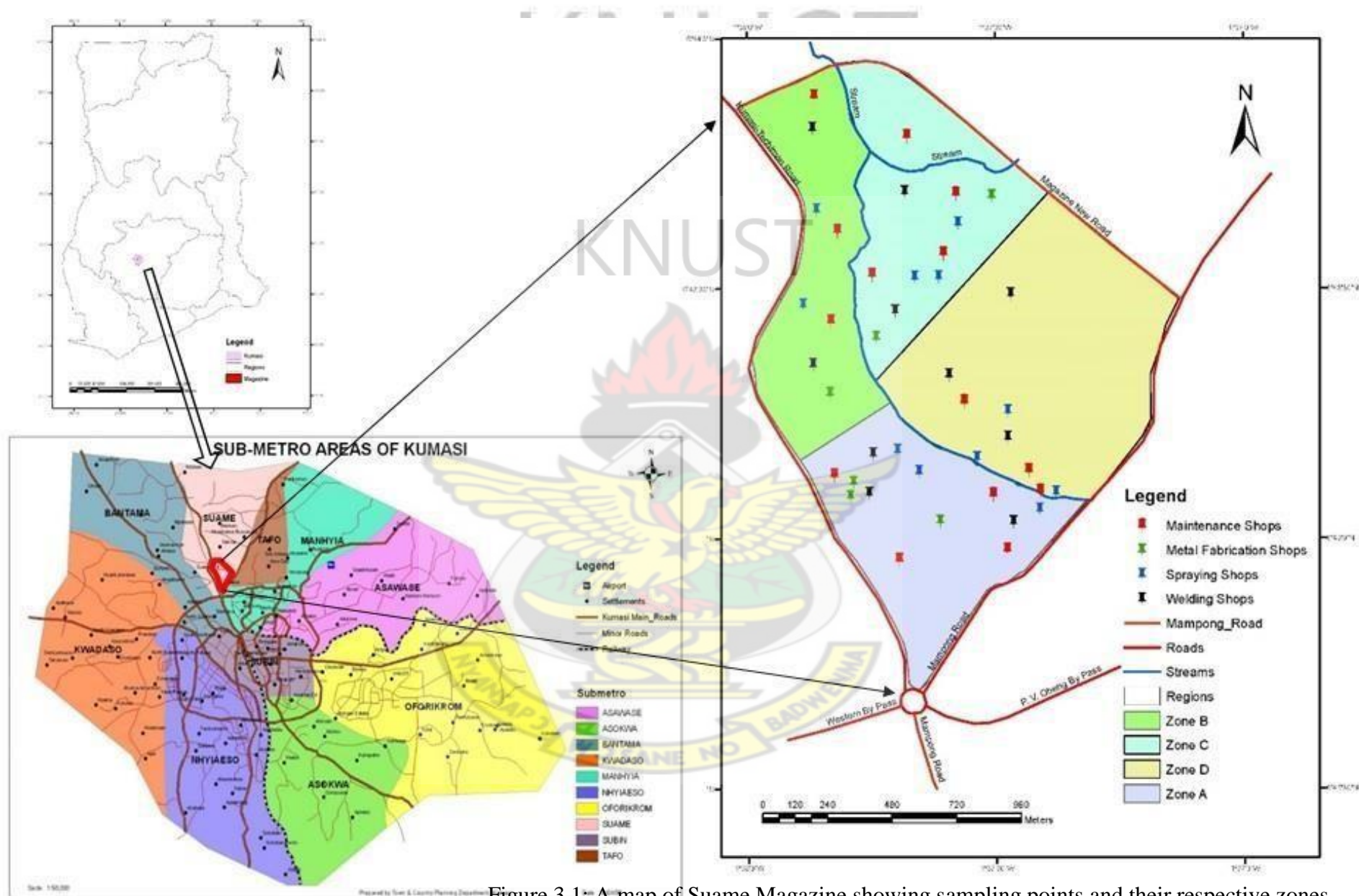


Figure 3.1: A map of Suame Magazine showing sampling points and their respective zones



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### **3.2.2 Sampling Method**

A total of forty five (45) composite test samples were obtained from randomly selected workshops in all the zones, based on the activities carried out in the workshops. Thus, maintenance, metal fabrication, spraying and welding shops. The soil samples were taken using a metallic auger at depths of 0 – 10 cm, 10 – 20 cm and 20 – 30 cm. The samples were collected in brown envelopes and transported to the laboratories of the Department of Chemistry, KNUST. All samples, taken at the same depths from similar workshops in a particular zone, were put together to form a composite sample. The reference soil samples were also taken at the aforementioned depths from the premises of St. Louis College of Education – about 200 metres from the sampling site. The locations of sampling points were taken using the GPS (Geographical Positioning System).

### **3.3 PHYSICOCHEMICAL PARAMETERS**

Soil samples were air dried at room temperature for a period of 48 hours. The samples were crushed using a porcelain mortar and pestle, thereafter, sieved through a 2 mm metallic mesh to get rid of the coarse fractions. For each activity in a particular zone, 20 g of soil from a particular depth was weighed and put together to form a composite. The composite samples were put in brown envelopes, shaken thoroughly to obtain a homogeneous sample and stored in a dark place for further analyses.

#### **3.3.1 Determination of pH**

The pH of the soil samples were measured in accordance with ASTM D4972-13. In this method, soil – water suspension was prepared by adding one (1) part of soil to two and half (2.5) parts of water. The solution was stirred for 15 minutes and allowed to stand for additional 30 minutes.

The pH of the filtrate of the suspension was measured with the pH meter (Hanna H19845/30) after it has been properly calibrated using appropriate standards. The electrode after being rinsed with distilled water was placed in the filtrate and reading on the meter was allowed to stabilise. The stabilised reading was recorded and the test duplicated to obtain a high level of precision.

### **3.3.2 Moisture and Organic Matter Content**

Moisture and organic matter content of the soil samples were determined according to the Test Methods B and C of the ASTM D 2974-00 method. A cleaned dry empty porcelain crucible was weighed and its mass recorded. Into the crucible, 5 g of sample was weighed. The soil sample was oven dried at a temperature of 105°C for 2 hours. The mass of the dried soil was measured and recorded. The crucible containing the dried sample was then placed in a muffle furnace at 500°C. The ashing lasted 5 hours before the sample was taken out, weighed and recorded. Oven dried and ashed samples were first cooled in a desiccator before weighing.

### **3.3.3 Soil Texture Characterisation**

The hydrometer method was employed in determining the soil texture (thus, the clay, sand and silt analysis). To 50 g of each soil sample in a 250 mL volumetric flask, 50 mL of calgon (a solution of sodium hexametaphosphate –  $(\text{NaPO}_3)_6$  and sodium carbonate –  $\text{Na}_2\text{CO}_3$ ) and 100 mL of deionized water were added. With the help of a glass rod, the suspension was stirred vigorously for 1 minute. The suspension was transferred into a mixer with baffled cups and mixed for a period of 15 minutes at medium speed. The contents were transferred into a 1000 mL volumetric flask and made up to the mark with deionised water. The hydrometer as placed into the solution of the suspension and after 40 seconds, the initial



hydrometer reading (H1) was taken. The corresponding temperature (T1 in °C) was also taken simultaneously using a thermometer. After leaving the solution to stand for 3 hours, the final hydrometer (H2) and temperature (T2) readings were taken. These results were then processed to give the various textures for the soil samples using computer software designed for that purpose.

### **3.4 EXTRACTION AND PURIFICATION**

#### **3.4.1 Extraction of PAHs from Soil Samples**

A mass of 10.0 g of the homogenous soil sample was weighed into a 100 mL separating flask. A 10 mL pesticide grade acetonitrile was added. The flask was corked and sonicated for 10 minutes. Thereafter, further 10 mL of acetonitrile was added, the flask was corked and placed on the horizontal mechanical shaker and set to shake continuously for 30 min. The mixture was centrifuged at 2500 rounds per minutes for 8 minutes to separate the layers. A 10 mL aliquot of the organic phase (top layer) was pipetted into a roundbottomed flask (50ml). The extract was evaporated to about 2 mL for extract purification by use of solid phase extraction. In the event where the extract was evaporated to dryness, the extract was discarded and the process repeated with a fresh sample.

#### **3.4.2 Purification of Extracts**

It was necessary to do a solid phase extraction clean-up of the extracts in order to get rid of lipids and other substances that may have been co-extracted. The cartridge was prepared to have 1 mL silica gel (1000 mg / 6 mL) with a 1 cm thick layer of anhydrous magnesium sulphate on top. This column was conditioned with  $10 \pm 0.2$  mL of acetonitrile. The extract was loaded onto the cartridge and the eluent was collected into a 50 mL pear shape flask.

Elution was achieved with  $10 \pm 0.2$  mL of acetonitrile. The cleaned extract was concentrated below  $40^{\circ}\text{C}$  on the rotary evaporator to near dryness. The sample was redissolved in ethyl acetate by adding 1 mL using a pipette. The extract was transferred into a 2 mL, standard opening vial prior to quantitation by GC-MS. Extracts remained frozen until quantitation was done.

### **3.5 GC-MS ANALYSIS**

Analysis of the sixteen USEPA PAHs was done using a Varian CP-3800 Gas Chromatograph with a CP-8400 Autosampler and Saturn 2000 MS/MS. The mass spectrometer was operated in the electron impact mode and the selective ion monitoring mode was used for quantification. The carrier gas, helium, was used at a flow rate of 1.3 mL/min constant flow. The injector was in the splitless mode and was set to a temperature of  $250^{\circ}\text{C}$ . The column used was 30m +10m EZ Guard  $\times$  0.25mm internal diameter. It had fused silica capillary coated with VF-5ms (0.25 $\mu\text{m}$  film) from Varian Inc. The initial temperature of the column was held at  $80^{\circ}\text{C}$  for 1 minute and increased to  $180^{\circ}\text{C}$  at a rate of  $25^{\circ}\text{C}/\text{minute}$ . Finally, the temperature was ramped to  $300^{\circ}\text{C}$  at  $5^{\circ}\text{C}/\text{minute}$  and maintained at this temperature for 1 minute. The mass spectrometry segment was started at 3.0 minutes and ended at 30.0 minutes. This enabled measurements to be made from 45 m/z to 450 m/z.

### **3.6 QUALITY CONTROL**

For every batch extraction of eight samples, a matrix blank (highly purified soil with no PAHs/internal standards), a matrix spiked (internal standards spiked into a highly purified

soil sample) as well as a method blank (solvent) were also taken through the same procedure and analysed. The average recoveries in spiked blanks and matrix spikes varied from 82.5% to 108.7 % for the PAHs under study. None of the PAHs under study was detected in any of the method blanks.

Quantitation was carried out using internal standard calibration method and the correlation coefficients ( $r^2$  value) for all the calibration curves were greater than 99%. Precision and accuracy were checked for all analytical methods. Limits of detection were calculated based on  $3SD/S$ , where  $S$  is the standard deviation of the response of seven replicate standard solution measurements and  $S$  is the slope of the calibration graph. Limits of detection of PAHs were in approximately 0.01 mg/kg.

## **CHAPTER FOUR**

### **RESULTS AND DISCUSSION**

#### **4.1 PHYSICOCHEMICAL PARAMETERS**

##### **4.1.1 Soil pH for Samples**

In general, pH recordings in the surface (0–10 cm) soil were observed to have spanned from 6.25 to 8.36. For maintenance shops, the pH was generally found to be decreasing with depth except in zone D, where, there was a marginal decrease from 7.6, through 7.76 and 7.81. The measured pHs varied only slightly around the nearly neutral value of 7.19 with a standard



deviation of  $\pm 0.581$  in surface soil (0 – 10 cm region). Samples from spraying shops also had a similar trend of decreasing pH with depth. The increasing or decreasing trend of pH of samples from the various workshops cannot be vividly explained based solely on the information obtained from this work. However, information will guide in assessing the fate of PAHs in the environment.

In Figure 4.1, pH of all surface soil samples except for samples with ID: MB, MC, FB and Ctrl had to be greater or equal to 7. According to Pawar (2015), soils with approximate pH value of 6.5 – 7.0 exhibit the highest rate of photodegradation as well as biodegradation of PAHs. It is therefore expected of all samples with pH > 7 to retain higher concentrations of compared to those with nearly 6.5.

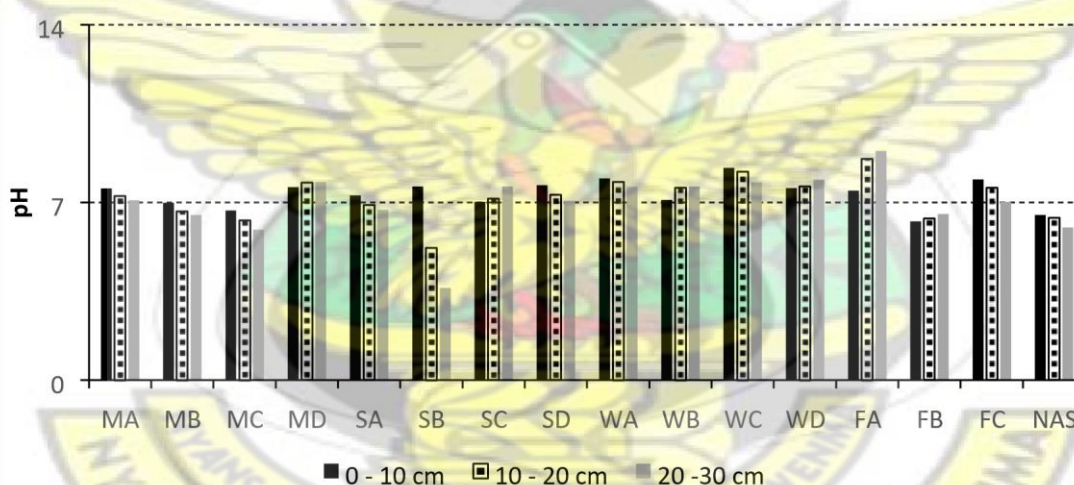


Figure 4.1: pH of soil samples in all zones of Suame Magazine (NAS = Non-activity soil)

#### 4.1.2 Moisture and Organic Matter Content

Moisture content as well as organic matter contents for all samples were determined using the same standardised method (methods B and C of ASTM D 2974-00).



Soils from maintenance shops were found to contain relatively very little moisture. This may be attributed to the fact that such soils contain very high amounts of hydrophobic substances such as PAHs and other petroleum hydrocarbons that constitute the oils that are regularly spilled in such shops. Percentage moisture content of soils from maintenance shops range from 0.44 % to 1.08 % of the 5 g soil sample that was weighed before drying and ashing. Generally, for samples from maintenance shops (excluding those from zone A – where varying soil texture seemed to have affected the moisture and organic matter contents at the 20 – 30 cm region), moisture content was observed to increase with depth after 20 cm. The trend of organic matter content followed one particular pattern – decreasing with depth. Percentage organic matter content ranged from 12.04 % to 14.72 %, 9.20 % to 14.38 % and 3.78 % to 12.08 % in the 0 – 10 cm, 10 – 20 cm and 20 – 30 cm respectively. Both the high values and the trend may be attributed to the large amounts of oil that is visibly spilled in these workshops.

In spraying shops, relatively higher values of moisture compared to samples from maintenance shops were observed. Percentage moisture content of soils from spraying shops range from 0.72% to 2.58% of soil sample. It was observed that moisture content of the soil samples from spraying shops decreased in the 10 – 20 cm sample then increased again in the 20 – 30 cm samples. This is a situation that prevails in a normal soil profile, which has high humus in its top soil and fine particle size in the clay soil and this causes these regions to retain much water than the sandy section between them (Verchueren, 1996). Some of the paints that are used in these workshops may be responsible for the high amount of moisture at the 0 – 10 cm region.

From Figure 4.2 (a & b), it can be summarised that maintenance shops have the highest organic matter content in the top 20 cm of soil. This is followed by spraying with welding

having the least. This trend is reversed in the case of moisture content with metal fabrication and welding shops having highest and maintenance, the least.

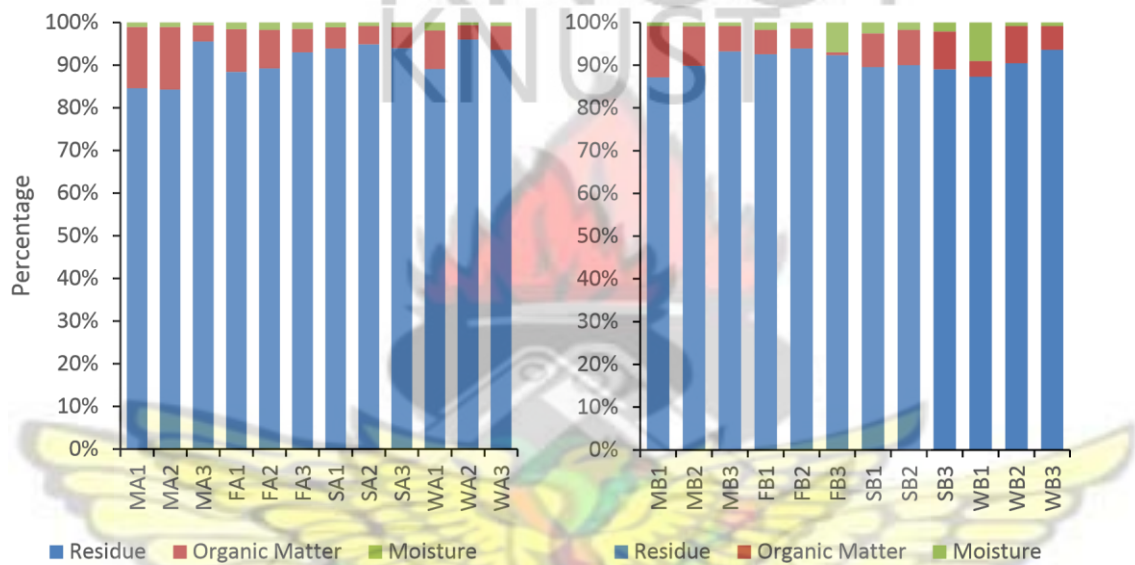


Figure 4.2 (a): A – Organic matter and moisture content of samples in zone A

B – Organic matter and moisture content of samples in zone B

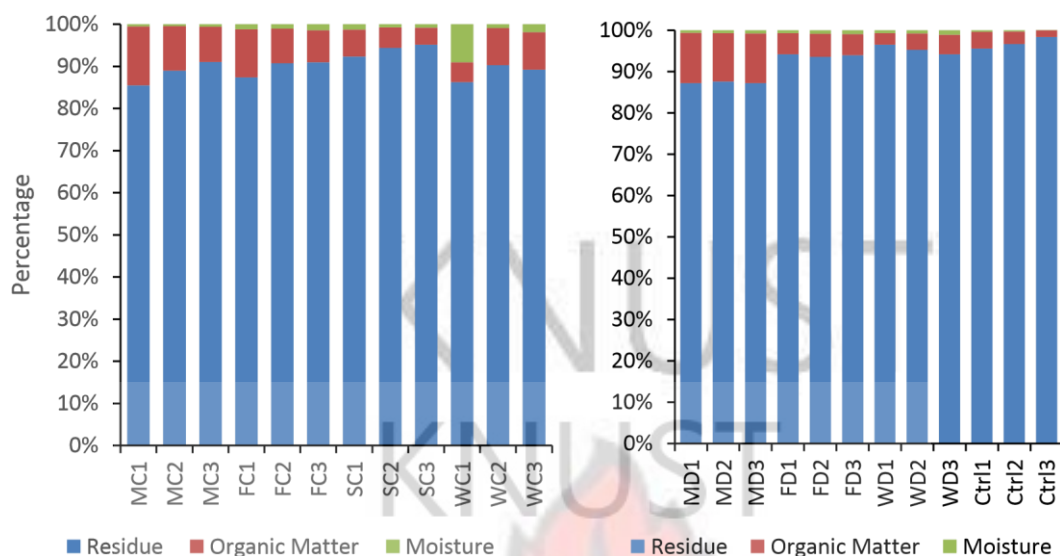


Figure 4.2 (b): C \_ Organic matter and moisture content of samples in zone C

D \_ Organic matter and moisture content of samples in zone D and NAS

#### 4.1.3. Soil Texture

The soil texture plays an important role in the fate of PAHs. Soils with higher fractions of the clay or silt (finer particles) than the sand components provide a greater surface area for PAH sorption than soil with a rough texture.

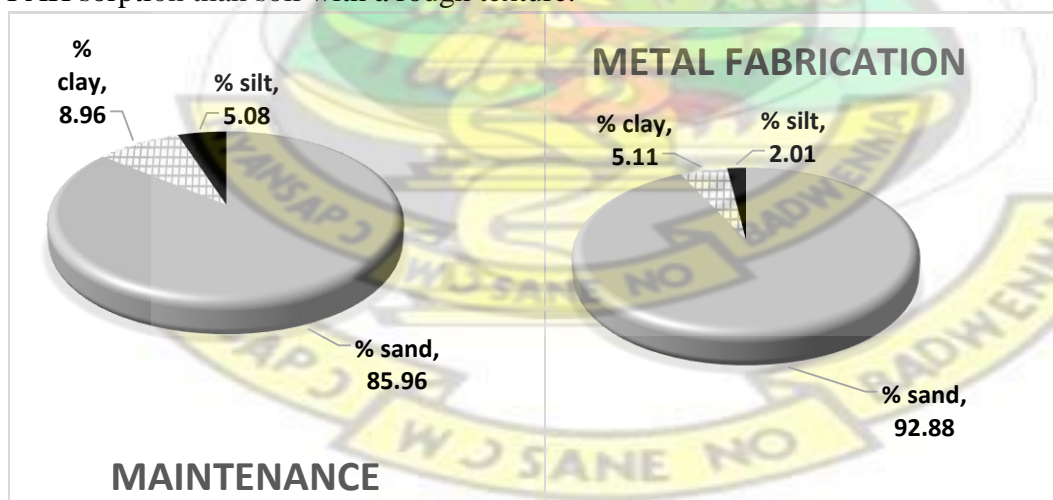


Figure 4.3 (a): Soil texture for some maintenance and metal fabrication shops

The activities considered in this work cannot be linked to any significant contribution to soil texture in the various shops. Soil texture in this study would therefore be considered as a geographical and geological phenomenon. It is however, important since it affects the fate of PAHs in soil.

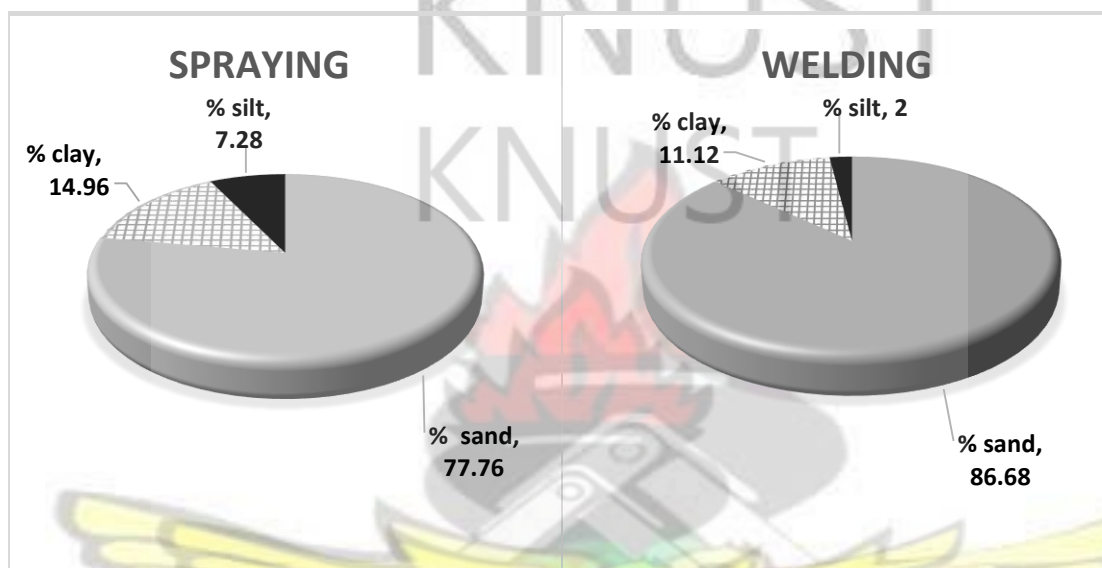


Figure 4.3 (b): Soil texture for samples of spraying and welding shops

Results obtained from this determination indicate that metal fabrication shops would be expected to retain most PAHs followed by maintenance, welding and spraying shops accordingly.

## 4.2. CONCENTRATIONS OF PAHs

All measurements of concentrations were done in triplicates. Using these measurements, true values were calculated and used hence forth. Concentration values written in the form  $x \pm q$  are true values with a confidence of 95 %. This was done using the formula:

$$\mu = x \pm \frac{ts}{\sqrt{N}} \dots\dots\dots (ii)$$



where  $\mu$  = true value     $\bar{x}$  = mean value of the three replica

concentrations             $t = t$  value for three replicas with confidence

interval of 95 %             $s$  = standard deviation of the three replica

concentrations

$N$  = number of replica measurements

#### 4.2.1 Summary of PAH Concentrations

Based on results obtained from the forty five (45) test samples, the averages of the total PAHs in the soil samples were determined. Mean values were calculated by taking the average of the total PAHs from the different zones. Minimum and maximum values were selected from the total concentrations of PAHs recorded in the various zones and the standard deviations were also calculated using the four different zones of the studied activities. The highest mean concentration values were detected in maintenance shops with welding and metal fabrications measuring below 1.00 mg/kg.

**Table 4.1 (a) Summary of Total PAH concentrations**

	MAINTENANCE			SPRAYING			WELDING			METAL FABRICATION		
DEPTH	0-10 cm	10-20 cm	20-30 cm	0-10 cm	10-20 cm	20-30 cm	0-10 cm	10-20 cm	20-30 cm	0-10 cm	10-20 cm	20-30 cm
MEAN	19.22	10.22	4.87	5.10	1.19	0.95	0.91	1.75	3.16	0.72	0.66	0.59
MAX.	24.82	19.64	15.13	7.52	2.61	3.11	1.39	4.20	7.03	1.08	1.08	1.47
MIN.	14.46	4.06	0.03	2.88	0.32	0.14	0.70	0.45	0.68	0.47	0.15	0.11

S.D.	$\pm 4.68 \pm 6.71 \pm 6.92$	$\pm 2.45 \pm 1.03 \pm 1.45$	$\pm 0.33 \pm 1.67 \pm 2.79$	$\pm 0.32 \pm 0.47 \pm 0.76$
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In Table 4.1(a), a summary of the concentrations of PAH measured in the samples at various depths are shown. The most contaminated surface soils (0 – 10 cm) were detected in maintenance shops, with concentrations ranging from  $14.38 \pm 4.03$  to  $24.52 \pm 6.24$  mg/kg. A general trend of decrease in concentration was observed with increasing depth, with as low as  $0.03 \pm 0.02$  and as high as  $15.56 \pm 0.9$  mg/kg for some individual PAHs. The significant variation of contamination with depth shows that maintenance activities ongoing on the surface have high level of impact on the levels of PAH contaminations.

**Table 4.1 (b) Concentrations of total PAHs in soils from non-activity site**

	NA (0 - 10 cm)	NA (10 - 20 cm)	NA (20 - 30 cm)
True Value (mg/kg)	$0.28 \pm 0.12$	$0.43 \pm 0.18$	$0.20 \pm 0.13$

Mean total PAH values were observed to have increased in the second 10 cm region and decreased again in the third. This was particularly obvious especially with the HMW compounds. Considering the fact that, pH of the top 10 cm of the non-activity soils was 6.51, which is the optimum pH for PAH photolytic degradation, the trend may be due to the photolytic degradation of the HMW PAHs in the presence of outdoor light (Pawar et al, 2013)

#### 4.2.2 Concentrations of PAHs in soils from non-activity site

All PAHs were detected in at least one level of the soil profile under consideration, except for acenaphthylene, benzo(a)pyrene and dibenz(a,h)anthracene. The highest concentration

detected was that of phenanthrene at the 10 – 20 cm region with a concentration of  $0.07 \pm 0.04$  mg/kg. Most carcinogenic PAHs considered in this study (adopted from CCME, 2008) were absent or below detection in the top 10 cm of the non-activity soils except for chrysene (0.02 mg/kg) benzo(a)anthracene (0.01 mg/kg) and benzo(b)fluoranthene (0.01 mg/kg). These values were very low compared to the USEPA and Canadian soil quality guidelines for the protection of human health.

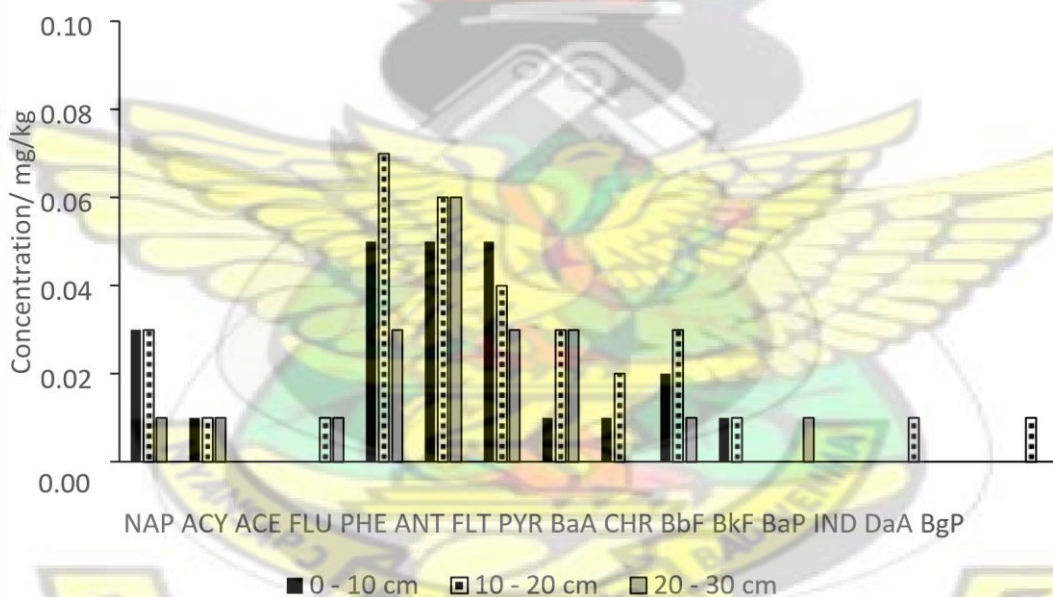


Figure 4.4 PAH profile of sample from non-activity site

According to the Canadian soil quality guidelines, it is stipulated that, for the protection of human health, ceiling concentrations for PAHs as listed in Table 4.2 below:



**Table 4.2 Maximum permissible levels of carcinogenic PAHs**

Carcinogenic PAHs	Ceiling concentration (mg/kg)
Chrysene	2.1
Benz(a)anthracene	0.33
Benzo(a)pyrene	0.31
Benzo(b+j)fluoranthene	0.16
Benzo(g,h,i)perylene	6.8
Indeno(1,2,3-cd)pyrene	2.7
Benzo(k)fluoranthene	0.038
Dibenz(a,h)anthracene	0.23

(CCME, 2008)

Based on these ceiling values, the concentrations of all individual PAHs for the nonactivity sample fall below the soil quality guidelines.

The PAH profile of the non-activity site sample reveals that phenanthrene, anthracene (both being 3 ringed) and fluoranthene (4 ringed) were the most abundant with combined relative abundance of 62.50% in surface soil. Acenaphthene and some higher molecular weight PAHs such as five ringed and six ringed PAHs were not detected in the surface soil. Concentrations of benzo(k)fluoranthene, dibenz(a,h)anthracene and benzo(g,h,i)perylene were however, detected below 0.01 mg/kg. Concentrations in mg/kg were very low for all compounds. Phenanthrene however, had the highest concentration of  $0.07 \pm 0.03$  mg/kg. Anthracene and Fluoranthene on the other hand have  $0.7 \pm 0.5$  and  $0.7 \pm 0.6$  respectively. No obvious trend was observed for the concentrations with increasing depth. All the above



are indications of soil sample whose PAH is mainly petrogenic (Kim et al, 2009) and naturally occurring (Pies et al, 2008).

The profile observed corresponded with what has been observed in related studies on PAHs in the environment (Borter-Sam et al, 2014; Kim et al, 2009).

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### 4.2.3 Concentrations of Total PAHs in Soil Samples for All Activities

The chart in Figure 4.5 below shows total PAH concentrations obtained in the various samples at various depths. The most contaminated surface soils (0 – 10 cm) were detected in maintenance shops, with concentrations ranging from  $14.38 \pm 4.03$  to  $24.52 \pm 7.24$  mg/kg. A general trend of, decrease in concentration was observed with increasing depth, with as low as  $0.03 \pm 0.02$  mg/kg in Zone B and as high as  $15.56 \pm 0.90$  mg/kg in Zone D. The significant variation of contamination with depth shows that maintenance activities taking place on the surface have high level of impact on the levels of PAH contaminations.

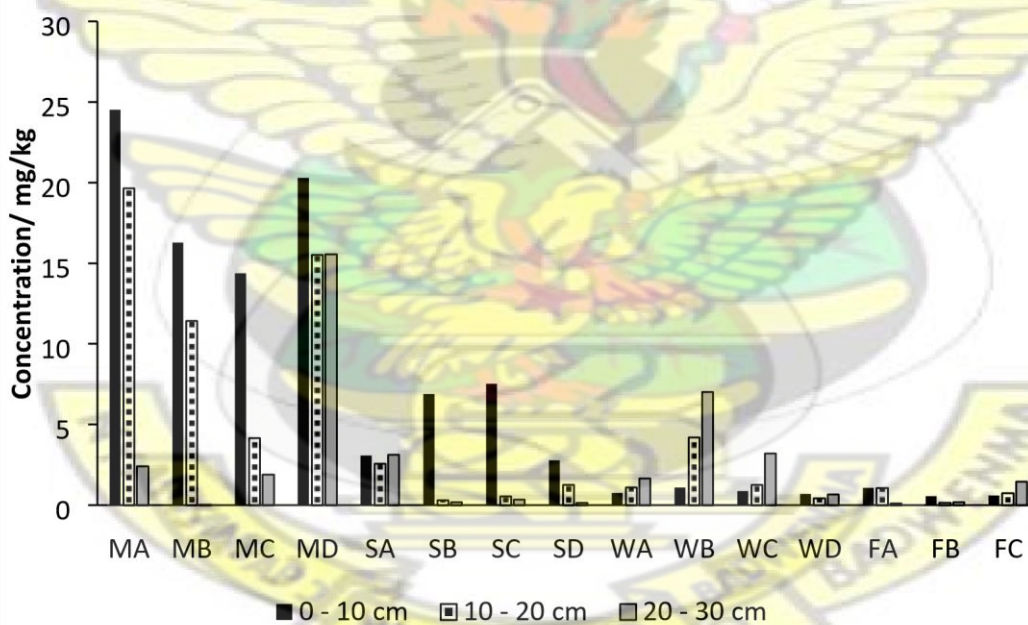


Figure 4.5 Total PAH concentrations in soil at different depths

Samples from spraying shops were observed to have the second highest concentrations ranging from  $2.78 \pm 1.01$  in Zone D through  $3.09 \pm 3.02$  and  $6.89 \pm 1.01$  in Zone A and

Zone B respectively, to  $7.52 \pm 1.69$  in Zone C. Similar trends were observed in concentrations of total PAHs in maintenance, spraying and metal fabrication shops. These shops have strongly polluted surface soils (thus, 0 – 10 cm region) and the strength of pollution appears to decrease with depth. This may be attributed to the activities taking place in the workshops. The situation is very obvious in maintenance and spraying shops which are both severely polluting activities (concentrations greater than 1 mg/kg) whereas, it is less obvious in metal fabrication shops – a moderately polluting activity. On the other hand, the contamination of soil with PAHs in welding workshops showed an increasing trend with depth. This could be due to degradation of the PAHs either photolytically or biologically. The depleted level of PAHs in the top soil indicates that the rate at which the activity pollutes the soil is less than the rate at which the contaminants are depleted.

The relative contribution (based on mean values) of the various activities to total PAH contamination is represented in the Figure 4.6.

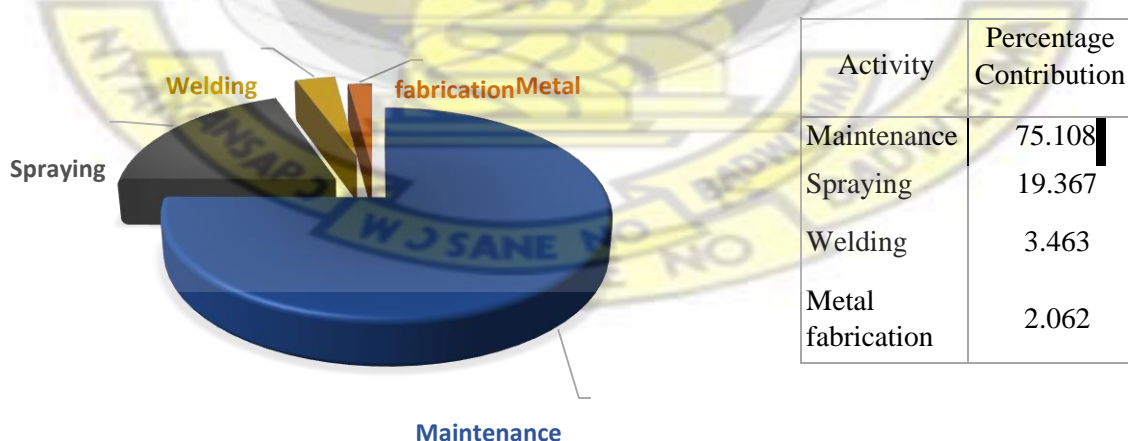


Figure 4.6 Relative contributions of artisanal activities to PAH contamination

#### 4.2.4 Concentrations of Benzo(a)pyrene in Soil Samples

The World Health Organisation (WHO) has regarded benzo(a)pyrene as the best known and most carcinogenic PAH. According to the Canadian Soil Quality Guidelines, the preliminary soil quality guidelines for benzo(a)pyrene is 0.6 mg/kg for an Incremental Lifetime Cancer Risk (ILCR) of  $10^{-6}$  or 5.3 mg/kg for an ILCR of  $10^{-5}$  (CCME, 2008).

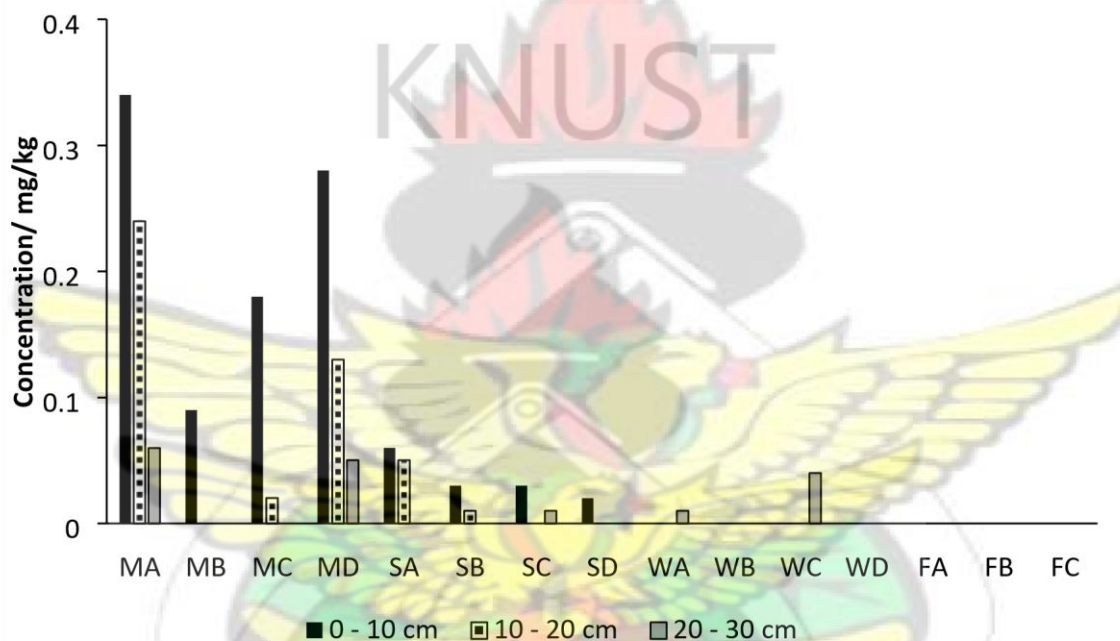


Figure 4.7 Concentrations of Benzo(a)pyrene

The 5 ringed carcinogenic PAH was observed to be present mainly in maintenance and spraying shops. In maintenance shops, its concentration ranged from  $0.09 \pm 0.07$  to  $0.34 \pm 0.13$  mg/kg. The second most polluted workshops were spraying shops. The measured concentrations were  $0.02 \pm 0.02$  in zone D to  $0.06 \pm 0.01$  mg/kg in zone A. Even though this component of the mixture was detected workshops of some other activities, most of these measurements were under 0.01 mg/kg. Most activities in Suame



Magazine studied in this work gave values that were below the benchmark concentration given by the WHO, USEPA and the Canadian soil quality guidelines. However, most maintenance shops had values that were higher than the 0.31 mg/kg benchmark concentration of BaP.

#### 4.2.5 Concentrations of Benzo(k)fluoranthene Soil Samples

Benzo(k)fluorathene appeared to be the most abundant PAH in almost all samples with a relative abundance of 60.67% in the 0 – 10 cm level of the soil profile of maintenance shops. The usual profile of PAH which is under normal circumstances dominated by three or four ringed PAHs was altered with the very high concentration of BkF that were measured.

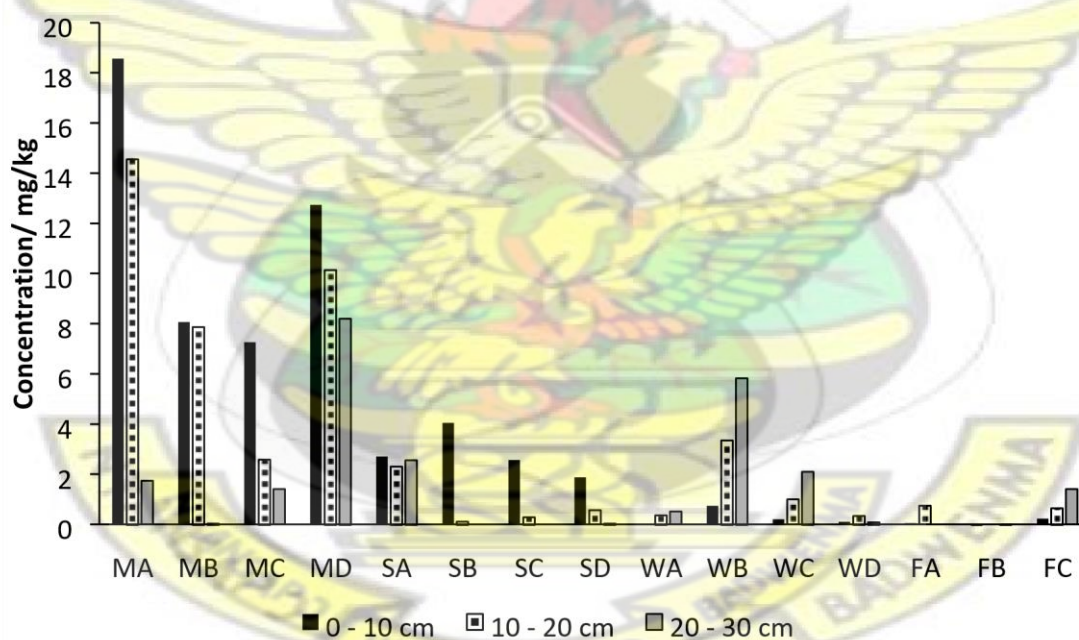


Figure 4.8 Concentrations of Benzo(k)fluoranthene

Concentrations of BkF determined ranged from a minimum of  $7.26 \pm 2.02$  mg/kg to a maximum of  $18.57 \pm 6.71$  mg/kg in the 0 – 10 cm region and a minimum of  $2.59 \pm 1.03$  mg/Kg to a

maximum of  $14.56 \pm 6.92$  mg/kg in the 10 – 20 cm region for maintenance shops. In the nonactivity site samples concentration was below limit of detection in the surface 0 – 10 cm. Comparing to the non-activity sample, 10 – 20 cm of maintenance shops contained averagely 1021 times more BkF than the 10 – 20 cm of the non-activity soils (which contained 0.01 mg/kg) and greater than 1021 times more in the 0 – 10 cm. The guidelines of the Canadian Council of Ministers of the Environment (CCME) on Carcinogenic and other PAHs stipulated a maximum of 0.034 mg/kg for BkF. This guideline was violated by the high values obtained for BkF in the current study.

Soils from spraying shops also gave higher concentrations of BkF mostly in the surface soil sample (thus, the 0 – 10 cm). The levels obtained in this region were from a minimum of  $1.88 \pm 0.96$  mg/kg to a maximum of  $4.05 \pm 2.65$  mg/kg. Relatively very low concentrations of BkF were obtained in metal fabrication shops. In welding shops, however, low levels were obtained with increasing concentration with depth (for some samples). PAHs were not being introduced into the soil at sites and the PAHs that are already present in the surface soil seemed to be degrading over time. In cases where there were slightly high levels of the contaminants, the observed trends suggests that, activities that go on in these shops contribute much less BkF to the soil contamination than it is naturally degraded.

According to Bortey-Sam et al (2014), the maximum level of BkF in Kumasi metropolis was reported to be 298 ng/g (0.298 mg/kg) in surface soil from Adum. This value only compared approximately to the levels of BkF from welding and metal fabrication shops but fell below those of spraying and maintenance shops. It can therefore be concluded that maintenance and spraying activities are major contributors to BkF in surface soils in the

Suame Magazine (based on CCME, 2008; USEPA, 2011).

It is important to note that BkF, Benzo(j)fluoranthene (BjF) and BbF are difficult to separate under most GC column conditions (Wang et al, 2006; Bortey-Sam et al, 2014). This implies that the very high concentrations of BkF obtained in this study, partly, may be due to BbF and BjF. However, these compounds are isomers and have the same potency equivalency factor of 0.1 hence any assessment done with this values is still valid.

#### **4.2.6 Concentrations of Benzo(b)fluoranthene in Soil**

This isomer of BkF occurred mainly in surface soil samples of the various activities except for welding shops. It however occurred sparsely at concentrations ranging from 0.01 mg/kg to  $0.12 \pm 0.08$  mg/kg in most samples in the 10 – 30 cm region, including those taken from welding shops.

With respect to this PAH, maintenance shops contributes an average of about 75.497 % to BbF in surface soil, whereas, spraying and metal fabrication jointly contribute about 24.503 % and welding contributes less than 0.010 % since its samples contained levels that were below detection or not detected.



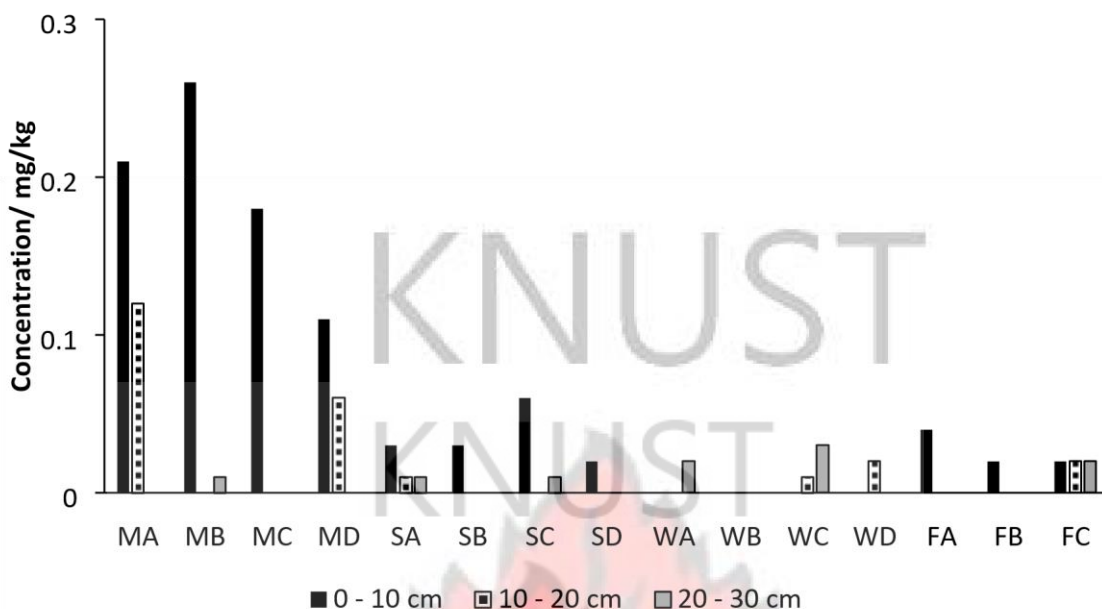


Figure 4.9 Concentration of Benzo(b)fluoranthene

Unlike in the case of BkF which was barely produced by both welding and metal fabrication activities, BbF was observed to be contributed significantly by metal fabrication but not welding. This can be seen in the chart above as the PAH accumulates mainly at the 0 – 10 cm of the soil. However, the reverse can be said for welding shops.

According to CCME (2008), for the protection of human health, soil quality guidelines recommend a maximum BbF + BjF of 0.16 mg/kg. Even though values obtained in spraying, welding and metal fabrication fall below this level, those obtained for maintenance shops violate the guideline with a concentration of  $0.19 \pm 0.02$  mg/kg.

#### 4.2.7 Concentrations of Benz(a)anthracene in Soil

This 4 ringed carcinogenic PAH was obtained in significant quantities mainly in samples from metal fabrication and maintenance shops. In the surface soils (0 – 10 cm) of spraying and



welding shops, the levels of this particular PAH were below detection. A minimum concentration of  $0.15 \pm 0.09$  mg/kg to a maximum of  $0.30 \pm 0.03$  mg/kg in maintenance shops whereas a minimum of  $0.01 \pm 0.0$  and a maximum of  $0.02 \pm 0.01$  has been measured in the 0 – 10 cm samples from metal fabrication shops. Figure 4.9 below show the levels of this PAH in the various activity shops.

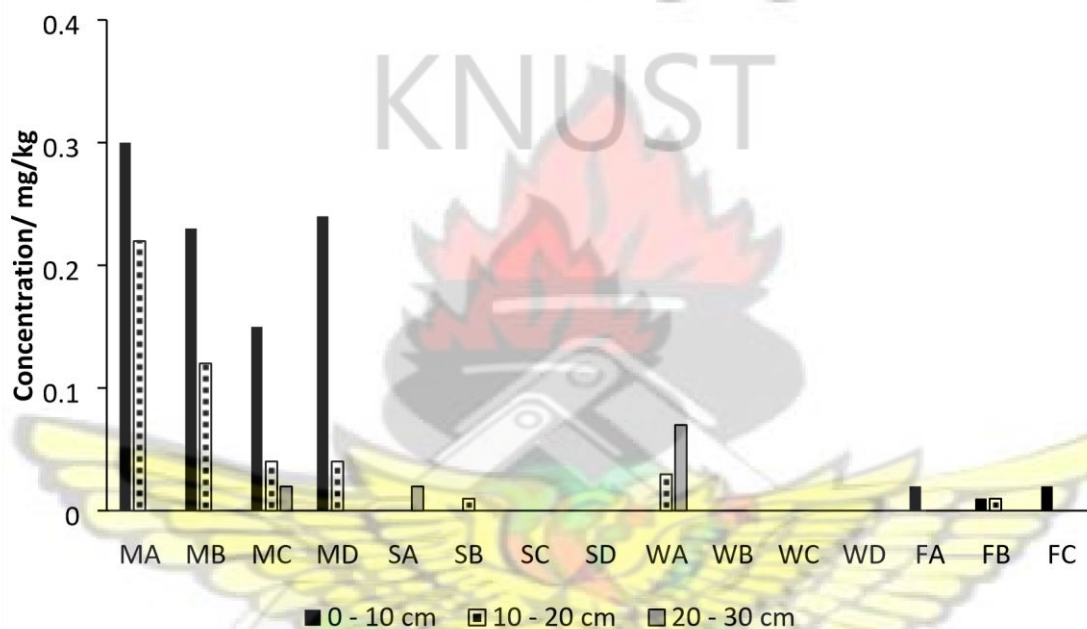


Figure 4.10: Concentrations of Benz(a)anthracene

Maintenance activity contributed 93.243 % whereas metal fabrication contributed 6.757 % to the presence of this HMW PAH in surface soil. Welding and spraying on the other hand contributed less than 0.01 %. According USEPA (1991) and CCME (2008), the soil quality guideline specifies 0.033 mg/kg. Metal fabrication activity fell within this value. However, maintenance activities resulted in values which were far above the limit prescribed by international guidelines (by approximately nine folds).

#### 4.2.8 Concentrations of Chrysene

This HMW group 1 carcinogen was detected in noticeable concentrations in maintenance, spray and welding but not in metal fabrication shops. In maintenance shops between  $0.12 \pm$

$0.03 \text{ mg/kg}$  and  $0.39 \pm 0.02 \text{ mg/kg}$  of chrysene was obtained. On the average, these values are higher than the  $0.256 \text{ mg/kg}$  and  $0.286 \text{ mg/kg}$  obtained in Mbrom and Suame townships respectively (Bortey-Sam et al., 2014).

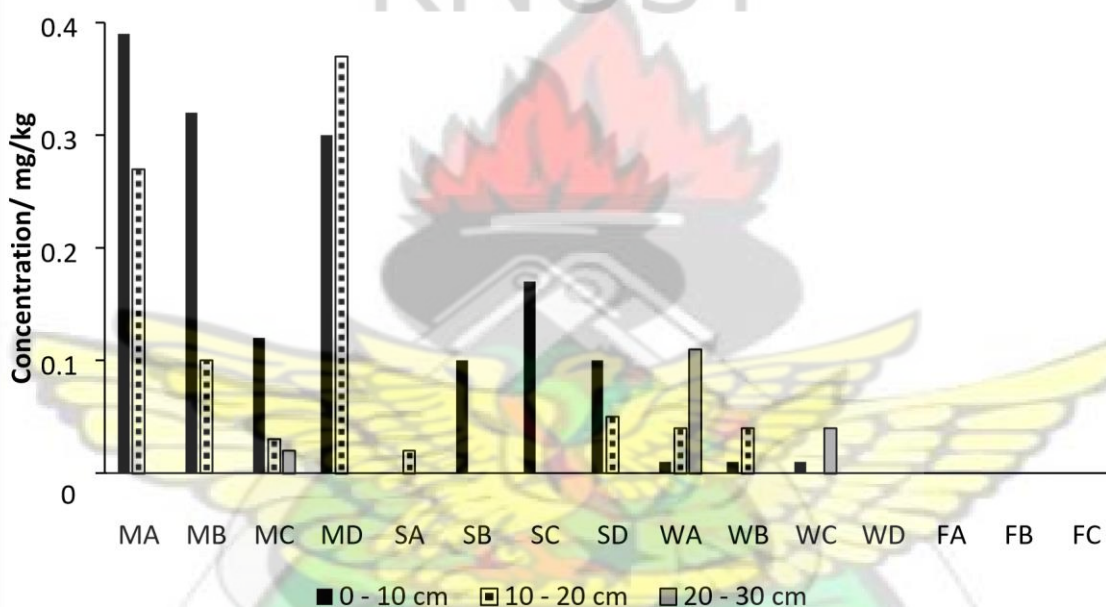


Figure 4.11: Concentrations of Chrysene

Levels of chrysene obtained in spraying shops are barely half of what was recorded in maintenance shops ranging from  $0.10 \pm 0.03 \text{ mg/kg}$  to  $0.17 \pm 0.01 \text{ mg/kg}$ . Welding shops once again show a trend that is indicative that PAHs are being degraded from the surface

rather than emitted. However, 0.01 mg/kg of CHR was detected in the top 10 cm of three out of four samples from these shops. These values are however, below the stipulated 2.1 mg/kg guideline proposed by the CCME (2008) and USEPA (2004).

#### 4.2.9 Concentrations of Dibenz(a,h)anthracene in Soils

Dibenz(a,h)anthracene (DaA) is one the most toxic PAHs on the USEPA priority list for hazardous PAHs.

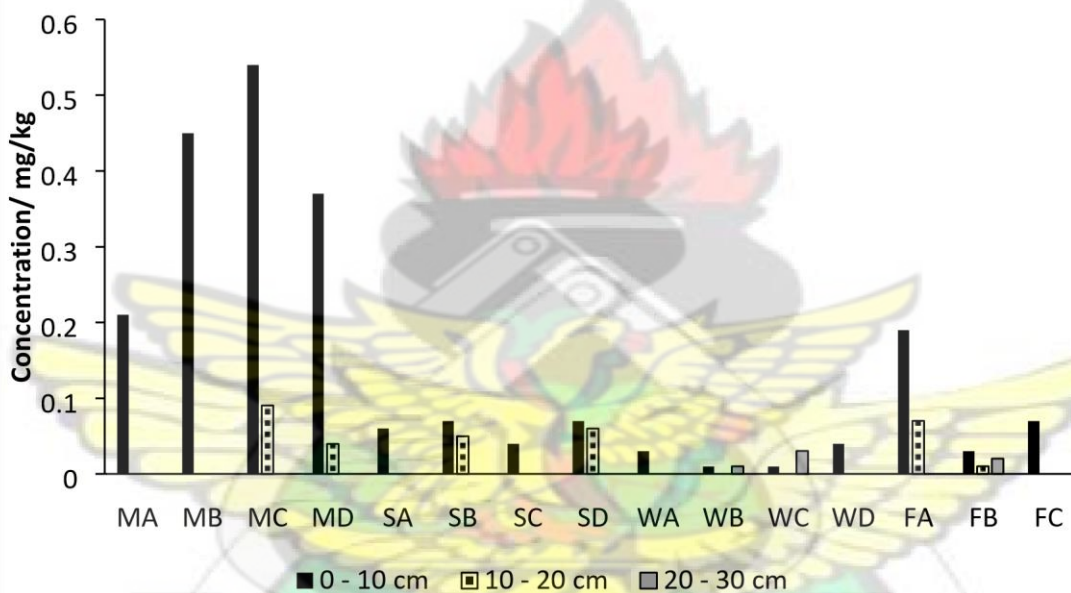


Figure 4.12: Concentrations of Dibenz(a,h)anthracene

It had been rated with the same toxicity equivalency factor as benzo(a)pyrene. This carcinogenic compound was determined in the top 10 cm of all workshops. Maintenance once again had the highest concentrations of  $0.21 \pm 0.05$  mg/kg to a maximum of  $0.54 \pm 0.19$  mg/kg.

#### 4.2.10 Concentrations of Indeno(1,2,3-cd)pyrene in Soils

This six ringed PAH was measured mainly in the 0 – 10 cm of samples except in some samples from welding shops. A minimum concentration of  $0.18 \pm 0.06$  mg/kg and a maximum of  $0.24 \pm 0.07$  mg/kg were obtained from maintenance shops. Metal fabrication and spraying shops were the next highest concentrations obtained. Concentrations from these shops ranged from  $0.05 \pm 0.03$  to  $0.09 \pm 0.02$  mg/kg in the 0 – 10 cm region. Samples below

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10 cm contained very little or no level of this PAH.

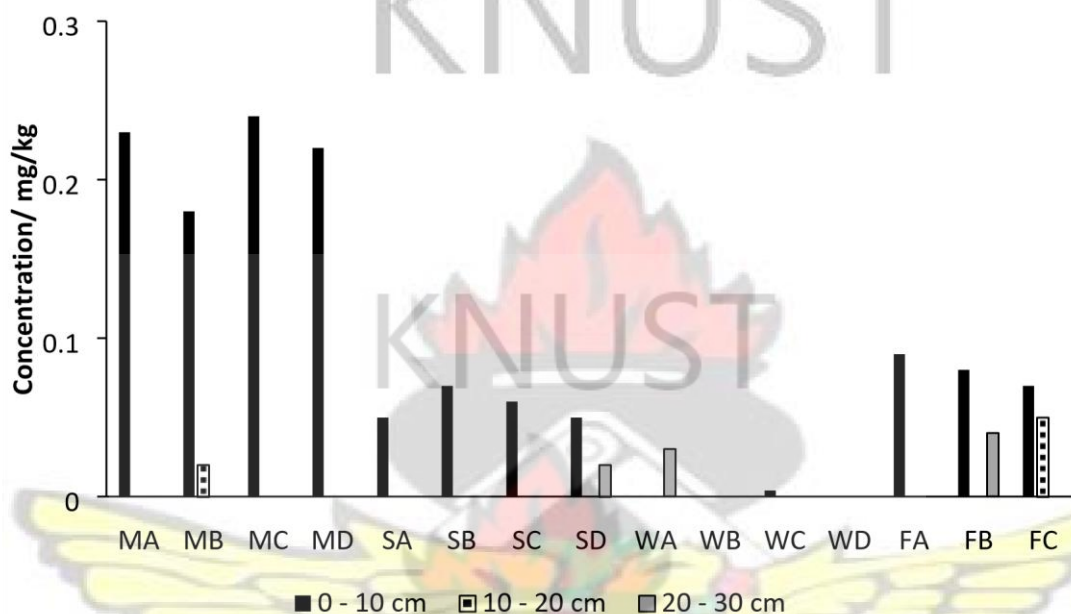


Figure 4.13: Concentrations of Indeno(1,2,3-cd)pyrene

In a related study, the highest concentration of indeno(1,2,3-cd)pyrene were obtained in Adum in the Kumasi metropolis was 551.3 ng/g (0.5513 mg/kg) (Bortey-Sam et al, 2014). In a similar work carried out in Mexico City,  $0.281 \pm 0.03$  mg/kg of IND was recorded in a highly urbanised area (Velasco et al, 2004). The values of the Mexico City study corresponds to the highest concentrations obtained (in maintenance shops) in this current study. However, these values fell below the regulatory values of 0.27 mg/kg.

#### 4.2.11 Concentrations of Benzo(g,h,i)perylene

This six ringed benzo(g,h,i)perylene was present in significant amounts mainly in maintenance and metal fabrication shops. Minimum and maximum values of  $0.2 \pm 0.18$  mg/kg

and  $0.5 \pm 0.21$  mg/kg respectively were in the 0 – 10 cm region of the samples from maintenance shops. Metal fabrication shops on the other hand recorded lower values  $0.08 \pm 0.06$  and  $0.2 \pm 0.04$  mg/kg

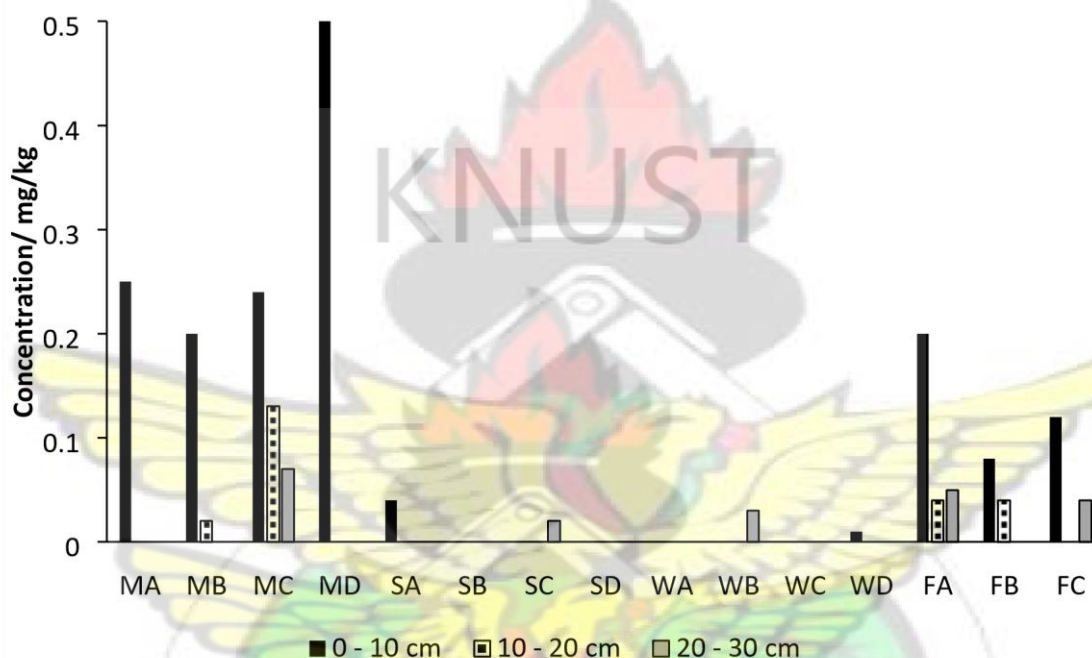


Figure 4.14 Concentrations of Benzo(g,h,i)perylene

Relatively higher concentrations of BgP were obtained in metal fabrication shops than spraying and welding shops in agreement with sections 4.2.9 and 4.2.10 above. Based on this observation, it can be deduced that PAHs with very high molecular weight (example BgP, DaA and IND) are produced in larger amounts by metal fabrication than these other activities.

**4.2.12 Relative Contributions of the Various Activities to PAH Concentrations** The activity that contributed most to the highest levels of PAHs was found to be vehicle

maintenance. This activity contributed 71.69 % (PYR), 93.243 % (BaA), 67.936 % (CHR), 75.497 (BbF), 78.286 (BkF), 86.408 % (BaP), 61.096 % (IND), 68.659 % (DaA) and 66.692 % (BgP). Percentage contributions to the some LMW PAHs (NAP, ACE and ACY) were found to be invariable based on type of activity. Figure 4.15 gives a comparison of the various activities in terms of their contribution towards PAH contamination.

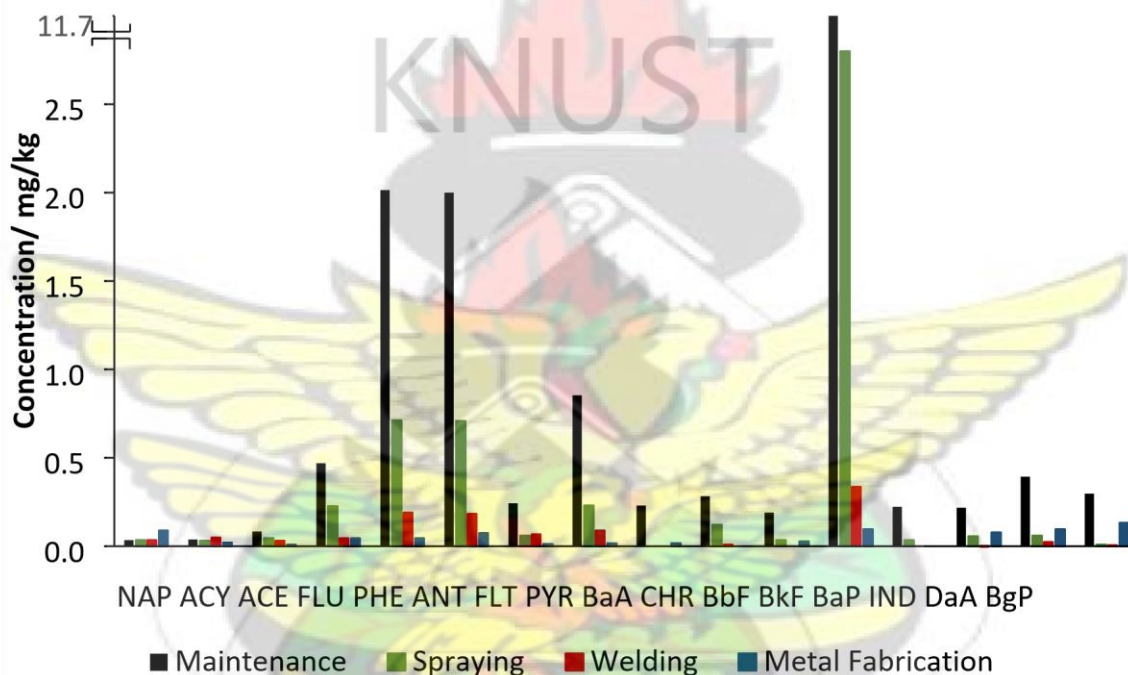


Figure 4.15: Contributions of the different activities to the PAHs in Suame Magazine

\*Note: Concentration of BkF in Maintenance shops is 11.6575 mg/kg (0 – 10cm) and spraying 2.8 mg/kg (10 – 20 cm)

For the LMW compounds, maintenance activity contributed smaller proportion than it contributed to the HMW compounds. Similar trend was observed for the concentrations of individual PAHs in spraying shops as observed in maintenance shops. The only difference is that concentrations of most PAHs 29 % to 47 % of what was determined in maintenance shops.



Relatively, welding was the activity with least concentrations of the various PAHs studied in this work. BaA, BbF and BaP which are all PAHs known for their carcinogenicity were not determined or below detection in all composited samples from welding shops. Other carcinogenic PAHs has very low mean values: IND (0.01 mg/kg) being the least abundant PAH to BkF (0.336 mg/kg) being the most abundant in welding shops.

#### 4.3 SOURCE APPORTIONMENT USING DIAGNOSTIC RATIOS

In this work, two diagnostic ratio models were used to predict the sources of the PAHs in the workshops. The  $\sum\text{LMW}/\sum\text{HMW}$  &  $\sum\text{COMB}/\sum\text{PAH}$  and the  $\text{FLU}/(\text{FLU}+\text{PYR})$  &  $\text{IND}/(\text{IND} + \text{BgP})$  diagnostic ratios. This tool involves using bivariate plots of the respective ratios as shown in the diagrams (Figures 4.10 and 4.11) below.  $\sum\text{LMW}$  was obtained by finding the sum of the levels of all two ringed and three ringed PAHs whereas,  $\sum\text{HMW}$  was obtained by summing all PAHs with four or more rings.  $\sum\text{COMB}$  is the sum of all PAHs that are formed due to combustion.  $\sum\text{PAH}$  is used to represent total PAH.



#### 4.3.1 $\Sigma\text{COMB}/\Sigma\text{PAH}$ and $\Sigma\text{LMW}/\Sigma\text{HMW}$ diagnostic ratios

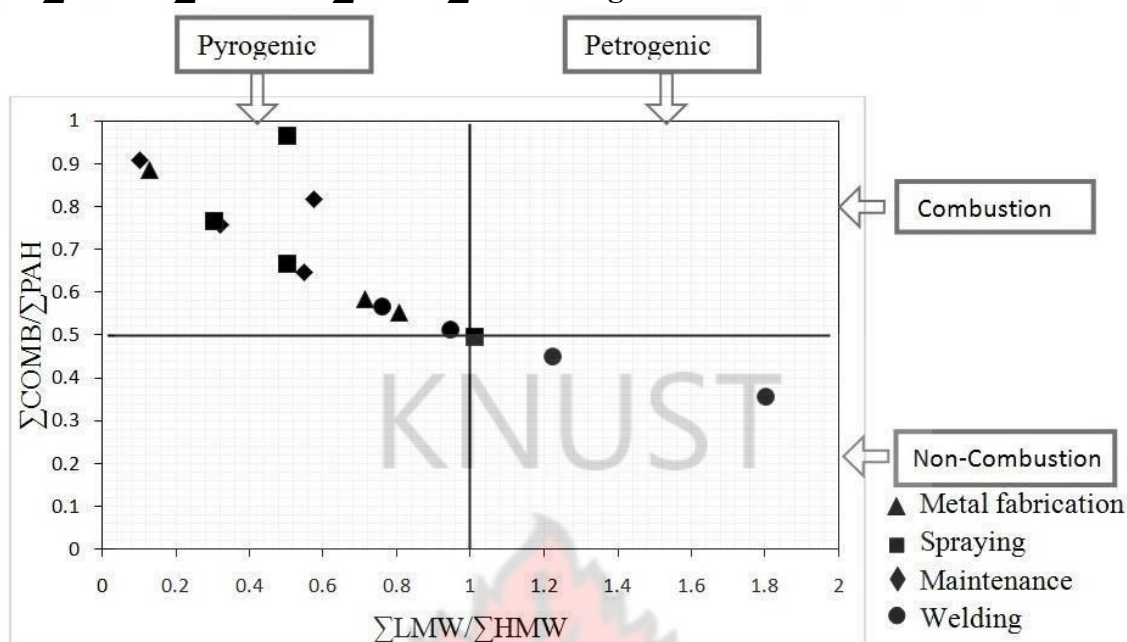


Figure 4.16  $\Sigma\text{COMB}/\Sigma\text{PAH}$  and  $\Sigma\text{LMW}/\Sigma\text{HMW}$  diagnostic ratios for surface soil

In Figure 4.10, information is given as to whether or not, the contaminations of the soil samples are due to pyrogenic or petrogenic sources as well as whether they are due to combustion or non-combustion sources. A  $\Sigma\text{COMB}/\Sigma\text{PAH}$  ratio of 0.5–1.0 is indicative of the PAHs due to combustion. Otherwise (thus between 0–0.5), they are considered to be of non-combustion origin (Ravindra et al., 2008). On the other hand a ratio of  $\Sigma\text{LMW}/\Sigma\text{HMW}$  distinguishes the petrogenic (for values < 1) sources from the pyrogenic ones (for values > 1) (Zhang et al., 2008).

The processed data revealed that a higher percentage of activities, including: maintenance, spraying and metal fabrications have their  $\Sigma\text{COMB}/\Sigma\text{PAH}$  diagnostic ratios to be greater than 0.5. These values were expected except for spraying which does not involve the burning except

during the production of some of the paints used. Vehicular combustion is thus, implied as a major contribution to the PAHs in maintenance shops being 100% due to combustion. Welding was however divided, with 50% having ratios greater 0.5 and 50% less than 0.5 indicating that PAHs are equally from combustion and non-combustion sources.

#### **4.3.2 FLU/(FLU+PYR) vrs IND/(IND+BgP) Diagnostic ratios**

This model has been used severally to predict PAHs sources (Bortey-Sam et al, 2014; Tobiszewski and Namiesnik, 2012; Zhou et al, 2005). Individually, FLU/(FLU+PYR) tells whether a mixture of PAH of is due to petrol emissions or diesel emissions. PAH mixtures with ratio having a value less than 0.5 are considered to be from petrol emission. Whereas those greater than 0.5 are expected to have emanated from diesel. The IND/(IND+BgP) ratio on the other hand, tells if the source is that of petroleum combustion, grass/wood or coal combustion or if it is a petrogenic one.

From Figure 4.11 below, the PAHs determined in maintenance shops are mainly due to petroleum combustions as expected. In addition, most PAHs emitted were from petrol (smaller molecular weight petroleum products) emission rather than diesel or higher molecular petroleum hydrocarbons.

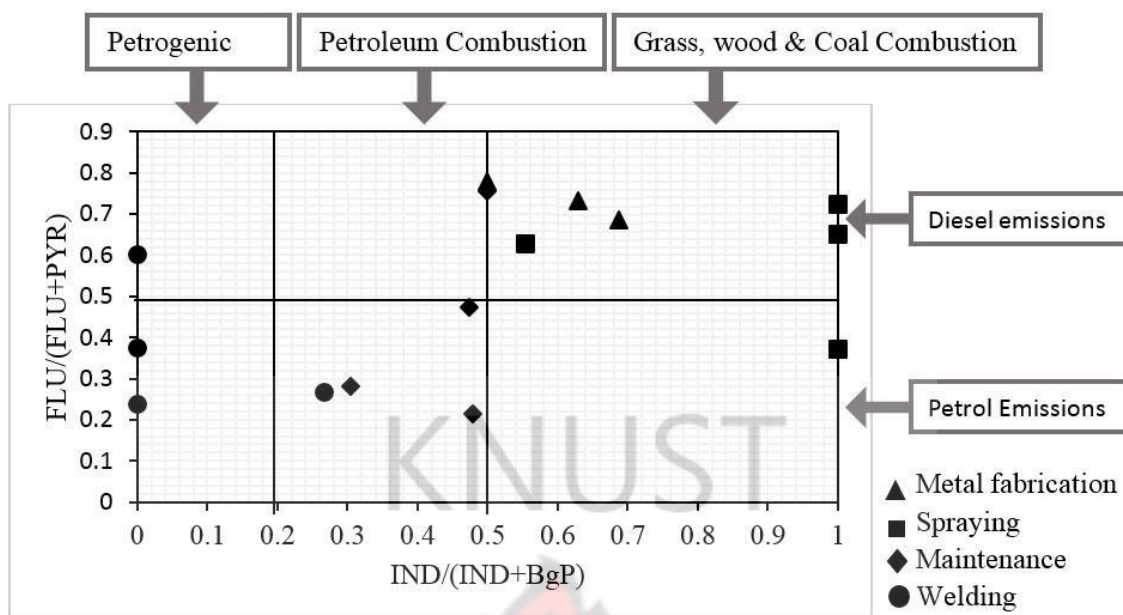


Figure 4.17 Flu/(Flu+Pyr) and IND/(IND+BgP) diagnostic ratios for surface soil

#### 4.4 HEALTH RISKS TO ARTISANS WORKING IN SUAME MAGAZINE

Humans and other living organisms are usually exposed to environmental PAHs through the ingestion, inhalation and dermal exposure (USEPA, 2011). In this study, dermal contact and ingestion of soil particles contaminated with PAHs were the exposure routes considered. Due to the fact that different PAHs have different carcinogenic tendencies, health risk assessment of carcinogenic PAHs cannot be achieved by using the concentrations of the individual PAHs.

##### 4.4.1 Benzo(a)Pyrene Equivalence ( $BaP_{eq}$ )

Being the most studied and best known carcinogenic PAH, benzo(a)pyrene (BaP) has been



given the reference potency equivalency factor (PEF) of 1 and PEFs of other PAHs have been calculated with reference to it. Based on the PEFs values, (see Table 1) the Benzo(a)pyrene equivalence ( $BaP_{eq}$ ) was calculated using to the equation:

$$\sum BaP_{eq} = \sum (C \times PEF) \dots\dots\dots (iii)$$

Where C = concentration of soil in mg/kg and  $BaP_{eq}$  and PEF are as defined above.

These values represent a total of the mean individual concentrations of the studied PAHs normalised to the potency of benzo(a)pyrene. The list of PEFs used in this work were adopted from Chen and Liao (2006).

Maintenance shops have the highest  $BaP_{eq}$  of 1.874 mg/kg. This value is roughly ten times higher than a value of 188 ng/g (0.188 mg/kg) obtained by Bortey-Sam et al (2014) as the average benzo(a)pyrene equivalence in the most contaminated communities of the Kumasi metropolis. This can directly be linked to the large amount of spent engine oils that are visibly spilled in the workshops due to the activities of the vehicle fitters. Bortey-Sam et al (2014) also recorded 1.2 ng/g (0.0012 mg/kg) as the  $BaP_{eq}$  for the soil samples taken from the Kwame Nkrumah University of Science and Technology Botanical Gardens, Kumasi. This current study had its non-activity soils recording a  $BaP_{eq}$  value of 0.00285 mg/kg. This is about 2.34 times higher than what was obtained at the KNUST botanical gardens. The increase in concentration at the St. Louis College of Education premises (the “nonactivity soils” for this work) maybe due to the fact that the college of education is closer to the city centre and air-borne particulate matter from vehicular and household emissions is more likely to contaminate the surface soils. Also, vehicular emissions from vehicles that enter the school premises whereas no vehicles are allowed into the botanical gardens.



The activity with highest benzo(a)pyrene equivalence was maintenance shops. The  $\sum \text{BaP}_{\text{eq}}$  for this activity was calculated to be 1.87 mg/kg. The other activities had comparatively lower  $\text{BaP}_{\text{eq}}$ : Spraying has the next highest value 0.394 mg/kg and metal fabrication and welding shops follow with 0.121 mg/kg and 0.0503 mg/kg respectively.

#### 4.4.2 Incremental Lifetime Cancer Risk (ILCR) Assessment

The health risk assessment was done with respect to only ingestion and dermal doses of contaminated soil. To be able to calculate cancer risk, lifetime average daily dose (LADD) and lifetime average dermal daily dose (LADDD) for ingestion and dermal contact respectively, were calculated using the following equations.

Ingestion dose:

$$\text{LADD} = \text{IR} \times [\text{PAH}] \times \text{EF} \times \text{EF}_w \times \text{ED} \times \text{C1} \times \text{C2} \times \frac{1}{\text{BW}} \times \frac{1}{\text{AT}} \dots\dots\dots (\text{iv})$$

Dermal dose:

$$\text{LADDD} = [\text{PAH}] \times \text{AF} \times \text{ABS}_d \times \text{SA} \times \text{EF} \times \text{EF}_w \times \text{ED} \times \text{F} \times \text{C1} \times \text{C2} \times \frac{1}{\text{BW}} \times \frac{1}{\text{AT}} \times 1 \times 1 \dots (\text{v})$$

Incremental Lifetime Cancer Risk (ILCR):

$$\text{ILCR} = (\text{LADD}_{\text{child}} + \text{LADD}_{\text{adult}} + \text{LADDD}_{\text{child}} + \text{LADDD}_{\text{adult}}) \times \text{CSF} \dots\dots\dots (\text{vi})$$

The activity with the highest incremental lifetime cancer risk was calculated to be vehicle maintenance with an ILCR of  $1.24 \times 10^5$ . This means that, when 100,000 people get exposed to PAHs in soil as per the variables used in this calculation, 1.24 more cancers than otherwise

would not be expected would be recorded. In other words, there would be one cancer case recorded in every 80,645 exposures.

The other activities have rather small cancer risks with respect to dermal contact and ingestion.

With spraying causing of one (1) case if four hundred thousand (400,000) people

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are exposed. Metal fabrication shops would cause an increase of one (1) case out of one million two hundred and fifty thousand (1,250,000) exposures. With least risky welding causing an increase of 1 cancer case 3,000,000 exposures to the PAHs at levels recorded in this study.



## **CHAPTER FIVE**

### **CONCLUSIONS AND RECOMMENDATIONS**

## 5.1. CONCLUSIONS

The most PAH polluting activity in Suame Magazine was found to be vehicle maintenance activity contributing some 61.095 % to 93.243 % of carcinogenic HMW PAHs that are introduced to the soils of Suame Magazine.

Benzo(a)pyrene which is used by the WHO and other organisations as a reference for PAH carcinogenicity and toxicity in general, has lower concentrations than levels stipulated in the CCME guideline. Its presence was mainly determined in maintenance shops. The average concentration of BaP in maintenance shops is 0.2225 mg/kg in the top 10 cm of soil. According to the WHO and the Canadian soil quality guidelines, maintenance shops are highly polluted with BaP.

However, very high concentrations of BkF were determined in most samples (especially those from maintenance shops). In maintenance shops for instance, BkF had a concentration of 11.6575 mg/kg. This made BkF a PAH of much concern (with  $BaP_{eq}$  of 1.17 mg/kg) than BaP (with  $BaP_{eq}$  of 0.223 mg/kg) in maintenance shops in Suame Magazine. In line with same WHO and Canadian soil quality guidelines, BkF.

The three main LMW PAHs of concern are PHE, ANT and PYR. This is because of the high amounts of these compounds that are produced in the artisanal shops. However, due to the low potency equivalency factors of PHE and PYR, their contribution to cancer is only a tenth of that of ANT; with mean concentration of 2.015 mg/kg, 2.000 mg/kg and 0.223 mg/kg for PHE, ANT and PYR respectively. Maintenance shops were only slightly polluted with these PAHs.



Other contaminants of interest are IND, DaA and BgP. These are HMW carcinogenic PAH. However, due to the low concentrations in which they occur, they can only be classified as moderately polluted compared to surface soils in maintenance shops.

It can also be concluded that spraying is the next most polluting activity studied in this work. Almost all PAHs but a few (as mentioned in previous paragraphs) had individual concentrations that fell below the soil quality guidelines as specified in CCME (2008). However, the mean total PAHs for spraying gave a  $BaP_{eq}$  equivalence of 0.394 mg/kg. Based on the USEPA and the CCME guidelines, this value is high enough for spraying to be classified as a PAH hazardous (moderately polluting) activity.

Most of the PAHs detected in samples from welding shops were LMW PAHs. Some high molecular weight PAHs such as BaA, BbF and BaP had concentrations that were below limit of detection of 0.01 mg/kg. Other detected ones had mean concentrations that were very low: CHR, BkF, IND, DaA and BgP. The  $BaP_{eq}$  for these concentrations is 0.0503 mg/kg. Based on these values, welding can be classified as an activity that contributed insignificant amount PAHs to soils in Suame Magazine.

Metal fabrications have similar concentrations and  $BaP_{eq}$  values being in same category as spraying. Based on this, they can also there be classified a moderately polluting activity.

From the  $\sum LMW / \sum HMW$  &  $\sum COMB / \sum PAH$  diagnostic ratios, PAHs from most artisanal shops are due to pyrolytic activities. PAH source apportionment for welding on the other hand did not indicate a single source. This is because 50 % of samples showed ratios of

pyrogenic source while the remaining showed ratios of petrogenic source. Meanwhile, the  $\text{Flu}/(\text{Flu}+\text{Pyr})$  and  $\text{IND}/(\text{IND}+\text{BgP})$  diagnostic ratios gave a 75 % of vehicle maintenance shops that were sampled as having petrol contaminated PAHs while the rest were diesel engines. It was also indicated in this ratios that PAHs determined in welding shops were mainly due to petrogenic source whilst those determined in spraying shops involved combustion of some high molecular organic compounds.

Workshops that involve the use of organic substances as well as production of organic wastes (maintenance and spraying) generally gave high levels of PAHs. However, metal fabrication shops were found to contain some higher molecular weight PAHs than spraying shops. From the  $\text{Flu}/(\text{Flu}+\text{Pyr})$  and  $\text{IND}/(\text{IND}+\text{BgP})$  diagnostic ratios, it can therefore concluded that most blacksmiths still use wood based fuel in firing their furnaces.

## **5.2 RECOMMENDATIONS**

Vehicular emission of PAHs is usually accompanied by very high levels of other petroleum hydrocarbons. Since these substances are also well known hazardous chemicals, it will be prudent to have a comprehensive study on Total Petroleum Hydrocarbons alongside further studies of PAHs in the future. Further studies should also include airborne PAH analysis (in Suame Magazine) as well as surface water and water sediment analyses.

Modern waste disposal mechanisms should be employed so as to minimised the negative impacts of the wastes produced as a result of artisanal activities.

Labour unions in Suame Magazine should enforce work safety measures, such as wearing of nose masks, protective hand gloves and other protective clothing so as to minimize the extent of inhalation or dermal contact of PAHs by artisans.

Educational programmes should be organised for the people of Suame Magazine to ensure that the people are aware of the hazards associated with their work.

Since Ghana is currently exploring and drilling its oil resources, it has also become imperative to carry out a form of environmental modelling and forecasting so as to be predictive and ready for the possibly high amount of organic pollutants that might be expected.

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## APPENDIX



**Table 6.1: Potency Equivalency Factors(PEF), Cancer Slope Factors (CSF) and molecular weightforUSEPA priorityPAHs**


PAH	Number of Rings	Molecular weight /gmol <sup>-1</sup>	PE F	CSF
Naphthalene (NAP)	2	128.17	0.001	
Acenaphthylene (ACY)	3	152.19	0.001	
Acenaphthene (ACE)	3	154.21	0.001	
Fluorene (FLU)	3	166.20	0.001	
Phenanthrene (PHE)	3	178.20	0.001	
Anthracene (ANT)	3	178.20	0.01	
Fluoranthene (FLT)	4	202.30	0.001	

Pyrene (PYR)	4	202.30	0.001	
Benzo(a)anthracene (BaA)	4	228.30	0.1	0.61
Chrysene (CHR)	4	228.30	0.01	0.0061
Benzo(b)fluoranthene (BbF)	5	252.31	0.1	0.061
Benzo(k)fluoranthene (BkF)	5	252.31	0.1	0.061

Benzo(a)pyrene (BaP)	5	252.31	1	6.1
Indeno(1,2,3-cd)pyrene (IND)	6	276.30	0.1	0.61
Dibenz(a,h)anthracene (DaA)	5	278.35	1	6.1
Benzo(g,h,i)perylene (BgP)	6	276.30	0.01	

**Table 6.2: GPS Readings for Sample Locations**

ZONE		ACTIVITY	GPS READING/(DEGREE, MINUTES, SECONDS)
A		Maintenance 1	006°43'07.70''N, 001°37'49.71''W
		Maintenance 2	006°42'57.52''N, 001°37'41.91''W
		Maintenance 3	006°43'05.32''N, 001°37'30.49''W
		Maintenance 4	006°42'58.68''N, 001°37'28.82''W
		Spraying 1	006°43'10.63''N, 001°37'42.06''W
		Spraying 2	006°43'08.11''N, 001°37'39.50''W
		Spraying 3	006°43'03.54''N, 001°37'24.85''W
		Welding 1	006°43'10.27''N, 001°37'45.02''W
		Welding 2	006°43'05.48''N, 001°37'45.52''W
		Welding 3	006°43'02.02''N, 001°37'28.06''W
		Metal Fabrication 1	006°43'06.78''N, 001°37'47.39''W
		Metal Fabrication 2	006°43'05.09''N, 001°37'47.75''W
		Metal Fabrication 3	006°43'02.11''N, 001°37'36.94''W

B		Maintenance 1	 <p>006°43'53.11''N, 001°37'52.07''W</p>
		Maintenance 2	006°43'36.95''N, 001°37'49.26''W
		Maintenance 3	006°43'26.13''N, 001°37'50.06''W
		Maintenance 4	006°43'51.89''N, 001°37'54.59''W
		Spraying 1	006°43'51.65''N, 001°37'54.71''W
		Spraying 2	006°43'39.45''N, 001°37'51.77''W



C		Spraying 3	006°43'28.14''N, 001°37'53.42''W
		Welding 1	006°43'49.28''N, 001°37'52.31''W
		Welding 2	006°43'20.96''N, 001°37'52.27''W
		Metal Fabrication 1	006°43'43.55''N, 001°37'15.99''W
		Metal Fabrication 2	006°43'17.47''N, 001°37'50.23''W
		Maintenance 1	006°43'48.36''N, 001°37'40.87''W
		Maintenance 2	006°43'41.41''N, 001°37'34.93''W
		Maintenance 3	006°43'34.25''N, 001°37'36.44''W
		Maintenance 4	006°43'31.73''N, 001°37'45.12''W



		Spraying 1	006°43'31.44''N, 001°37'39.94''W
		Spraying 2	006°43'31.48''N, 001°37'37.02''W
		Spraying 3	006°43'37.88''N, 001°37'34.68''W
		Welding 1	006°43'27.39''N, 001°37'42.32''W
		Welding 2	006°43'41.16''N, 001°37'41.16''W
		Metal Fabrication 1	006°43'24.17''N, 001°37'44.60''W
		Metal Fabrication 2	006°43'41.12''N, 001°37'30.94''W
D		Maintenance 1	006°43'05.73''N, 001°37'24.77''W
		Maintenance 2	006°43'08.24''N, 001°37'26.19''W
		Maintenance 3	006°43'16.01''N, 001°37'33.99''W
		Spraying 1	006°43'22.53''N, 001°37'37.74''W
		Spraying 2	006°43'09.75''N, 001°37'32.44''W
		Spraying 3	006°43'05.59''N, 001°37'22.87''W
		Welding 1	006°43'19.38''N, 001°37'34.10 W
		Welding 2	006°43'19.70''N, 001°37'35.83''W
		Welding 3	006°43'29.39''N, 001°37'28.33''W
		Non-activity soils	006°42'48.09''N, 001°37'23.00''W

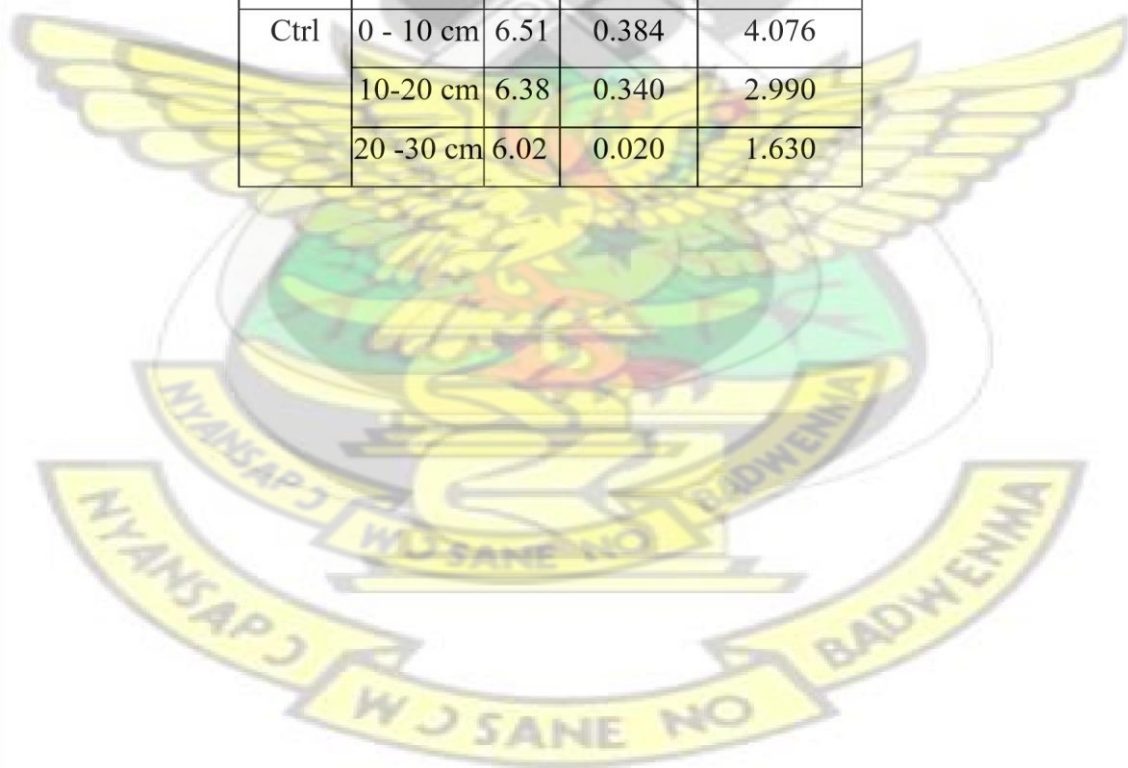
**Table 6.3: Physicochemical Parameters of Soil**

Sample ID	Depth	pH	% Moisture Content	% Organic Matter Content
MA	0 - 10 cm	7.55	0.700	14.537
	10-20 cm	7.25	0.930	14.875
	20-30 cm	7.08	1.080	3.807
MB	0 - 10 cm	6.98	0.810	12.140
	10-20 cm	6.64	0.840	9.287
	20-30 cm	6.51	0.970	5.950
MC	0 - 10 cm	6.68	0.440	14.070
	10-20 cm	6.29	0.580	10.607

	20-30 cm	5.92	0.670	8.372
MD	0 - 10 cm	7.60	0.640	12.258
	10-20 cm	7.76	0.700	11.782
	20-30 cm	7.81	0.740	12.170
SA	0 - 10 cm	7.28	1.040	5.058
	10-20 cm	6.89	0.860	4.277
	20-30 cm	6.71	1.140	5.032
SB	0 - 10 cm	7.63	2.100	9.091
	10-20 cm	5.21	1.980	8.068
	20-30 cm	3.63	1.760	8.388
SC	0 - 10 cm	7.02	1.300	6.444
	10-20 cm	7.13	0.720	4.936
	20-30 cm	7.63	0.840	4.074
SD	0 - 10 cm	7.68	0.660	5.174
	10-20 cm	7.29	0.860	5.588
	20-30 cm	7.06	0.910	5.187

Sample ID	Depth	pH	% Moisture Content	% Organic Matter Content
WA	0 - 10 cm	7.94	0.880	9.198
	10-20 cm	7.80	0.620	3.441
	20-30 cm	7.62	1.910	5.589
WB	0 - 10 cm	7.10	0.970	4.025
	10-20 cm	7.58	0.920	8.832
	20-30 cm	7.63	0.830	5.589
WC	0 - 10 cm	8.36	0.900	5.124
	10-20 cm	8.21	0.880	8.878

	20 -30 cm	7.79	1.880	9.091
WD	0 - 10 cm	7.57	0.680	2.799
	10-20 cm	7.63	0.760	3.970
	20 -30 cm	7.89	1.080	4.792
FA	0 - 10 cm	7.47	1.740	10.165
	10-20 cm	8.72	1.640	9.200
	20 -30 cm	9.03	1.560	5.526
FB	0 - 10 cm	6.25	1.740	5.781
	10-20 cm	6.35	1.480	4.689
	20 -30 cm	6.54	7.020	0.710
FC	0 - 10 cm	7.90	1.160	11.574
	10-20 cm	7.57	1.020	8.345
	20 -30 cm	7.02	1.400	7.769
Ctrl	0 - 10 cm	6.51	0.384	4.076
	10-20 cm	6.38	0.340	2.990
	20 -30 cm	6.02	0.020	1.630





PAH	MA 1	MA 2	MA 3	MB 1	MB 2	MB 3	MC 1	MC 2	MC 3	MD 1	MD 2	MD 3	SA 1	SA 2	SA 3	SB 1	SB 2	SB 3	SC 1	SC 2	SC 3	SD 1	SD 2	SD 3
NAP	<0.01	<0.01	0.01	0.02	0.03	ND	0.03	<0.01	0.02	0.05	0.01	0.01	<0.01	0.03	0.03	0.03	<0.01	0.02	0.04	0.02	0.03	0.04	0.02	<0.01
ACY	0.03	<0.01	<0.01	0.03	ND	ND	0.03	<0.01	ND	0.06	0.03	0.01	ND	<0.01	ND	0.04	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01
ACE	0.05	ND	ND	0.09	0.08	<0.01	0.04	ND	ND	0.15	ND	ND	ND	ND	ND	0.04	ND	ND	0.05	<0.01	ND	<0.01	ND	ND
FLU	0.41	0.15	0.08	0.6	0.36	ND	0.46	0.09	0.03	0.41	0.5	0.53	0.05	<0.01	<0.01	0.35	0.02	0.02	0.38	<0.01	0.03	0.13	0.1	<0.01
PHE	0.9	0.94	0.24	2.55	1.31	<0.01	2.37	0.4	0.14	2.24	2.1	3.06	0.03	0.08	0.2	0.92	0.05	0.07	1.66	0.11	0.1	0.24	0.22	0.04
ANT	0.9	0.93	0.24	2.53	1.3	<0.01	2.35	0.4	0.14	2.22	2.09	3.03	0.03	0.08	0.2	0.92	0.05	0.07	1.65	0.11	0.1	0.24	0.22	0.04
FLT	0.5	0.45	0.03	0.14	0.15	ND	0.12	0.07	ND	0.21	0.35	0.23	0.01	ND	0.03	0.05	0.01	0.01	0.16	0.01	0.01	0.02	0.02	0.01
PYR	1.53	1.76	0.04	0.67	0.06	<0.01	0.15	0.2	0.06	1.06	0.09	ND	0.03	0.03	0.06	0.19	<0.01	<0.01	0.65	0.01	0.03	0.05	0.02	<0.01
BaA	0.3	0.22	ND	0.23	0.12	ND	0.15	0.04	0.02	0.24	0.04	ND	ND	ND	0.02	ND	0.01	ND	ND	ND	<0.01	ND	<0.01	<0.01
CHR	0.39	0.27	ND	0.32	0.1	ND	0.12	0.03	0.02	0.3	0.37	ND	ND	0.02	ND	0.1	ND	ND	0.17	ND	<0.01	0.1	0.05	ND
BbF	0.21	0.12	ND	0.26	ND	0.01	0.18	ND	<0.01	0.11	0.06	ND	0.03	0.01	0.01	0.03	ND	ND	0.06	ND	0.01	0.02	ND	ND
BkF	18.57	14.56	1.73	8.06	7.88	0.02	7.26	2.59	1.4	12.74	10.15	8.21	2.7	2.31	2.56	4.05	0.12	ND	2.57	0.3	ND	1.88	0.56	0.03
BaP	0.34	0.24	0.06	0.09	ND	<0.01	0.18	0.02	<0.01	0.28	0.13	0.05	0.06	0.05	ND	0.03	0.01	ND	0.03	ND	0.01	0.02	ND	<0.01
IND	0.23	ND	ND	0.18	0.02	ND	0.24	ND	ND	0.22	ND	ND	0.05	ND	ND	0.07	ND	ND	0.06	ND	ND	0.05	ND	0.02
DaA	0.21	ND	ND	0.45	ND	ND	0.54	0.09	ND	0.37	0.04	ND	0.06	ND	ND	0.07	0.05	ND	0.04	ND	ND	0.07	0.06	ND
BgP	0.25	ND	ND	0.2	0.02	ND	0.24	0.13	0.07	0.5	ND	ND	0.04	<0.01	ND	ND	ND	ND	ND	ND	0.02	ND	ND	ND
Σ	24.82	19.64	2.43	16.42	11.43	0.03	14.46	4.06	1.90	21.16	15.96	15.13	3.09	2.61	3.11	6.89	0.32	0.19	7.52	0.56	0.34	2.88	1.27	0.14

PAH	WA 1	WA 2	WA 3	WB 1	WB 2	WB 3	WC 1	WC 2	WC 3	WD 1	WD 2	WD 3	FA 1	FA 2	FA 3	FB 1	FB 2	FB 3	FC 1	FC 2	FC 3
NAP	0.01	0.03	<0.01	0.06	0.04	0.06	0.03	0.03	0.01	<0.01	<0.01	0.02	0.17	0.21	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01

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**Table 6.4b: Concentrations of PAHs in Soils of Welding and Metal Fabrication Shops**

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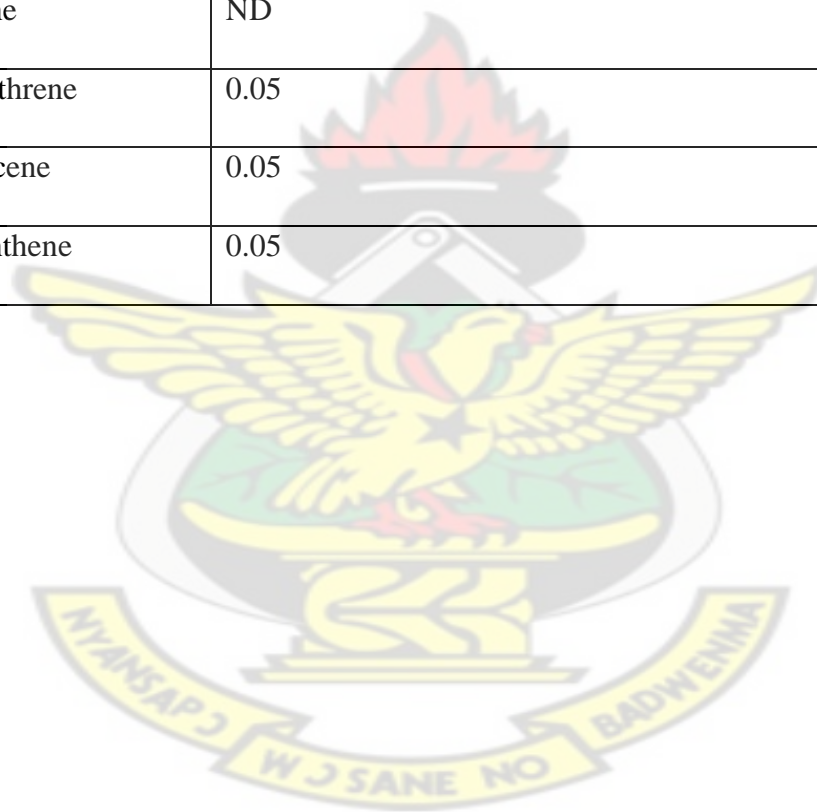


ACY	ND	<0.01	<0.01	0.05	0.02	ND	<0.01	ND	ND	ND	ND	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	ND	<0.01
ACE	ND	ND	ND	0.03	ND	ND	ND	ND	ND	ND	ND	ND	0.01	ND	ND	0.01	<0.01	<0.01	ND	ND	<0.01
FLU	0.05	0.01	0.03	0.06	0.1	0.18	0.04	0.03	0.05	0.03	<0.01	0.03	0.05	<0.01	<0.01	0.07	0.01	0.03	0.02	0.02	<0.01
PHE	0.14	0.13	0.25	0.21	0.27	0.37	0.2	0.09	0.21	0.21	0.04	0.24	0.1	0.01	0.02	0.02	0.04	0.05	0.02	<0.01	<0.01
ANT	0.14	0.13	0.25	0.19	0.27	0.37	0.2	0.09	0.21	0.21	0.04	0.24	0.1	0.01	0.02	0.11	0.04	0.05	0.02	<0.01	<0.01
FLT	0.16	0.17	0.19	0.02	0.03	ND	0.04	ND	ND	0.05	0.01	0.03	0.02	ND	0.01	0.01	<0.01	ND	0.01	ND	<0.01
PYR	0.16	0.14	0.19	0.04	0.07	0.18	0.11	0.03	0.53	0.05	<0.01	0.03	0.02	<0.01	0.01	0.02	<0.01	<0.01	0.01	ND	ND
BaA	<0.01	0.03	0.07	ND	ND	ND	ND	ND	ND	ND	<0.01	<0.01	0.02	ND	ND	0.01	0.01	<0.01	0.02	ND	ND
CHR	0.01	0.04	0.11	0.01	0.04	ND	0.01	ND	0.04	ND	<0.01	<0.01	ND	ND	ND	<0.01	<0.01	<0.01	ND	ND	ND
BbF	ND	ND	0.02	ND	ND	ND	ND	0.01	0.03	ND	0.02	ND	0.04	ND	ND	0.02	ND	ND	0.02	0.02	0.02
BkF	ND	0.37	0.51	0.71	3.36	5.83	0.2	1.00	2.11	0.10	0.34	0.09	0.05	0.74	ND	0.01	ND	0.01	0.23	0.65	1.41
BaP	ND	<0.01	0.01	ND	ND	ND	ND	ND	0.04	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<0.01
IND	ND	ND	0.03	ND	ND	ND	0.00	ND	ND	ND	ND	ND	0.09	ND	ND	0.08	ND	0.04	0.07	0.05	ND
DaA	0.03	ND	ND	0.01	ND	0.01	0.01	ND	0.03	0.04	ND	ND	0.19	0.07	ND	0.03	0.01	0.02	0.07	<0.01	ND
BgP	ND	ND	ND	ND	ND	0.03	0.01	ND	ND	0.01	ND	ND	0.2	0.04	0.05	0.08	0.04	ND	0.12	ND	0.04
Σ	<b>0.7</b>	<b>1.05</b>	<b>1.66</b>	<b>1.39</b>	<b>4.2</b>	<b>7.03</b>	<b>0.85</b>	<b>1.28</b>	<b>3.26</b>	<b>0.7</b>	<b>0.45</b>	<b>0.68</b>	<b>1.08</b>	<b>1.08</b>	<b>0.11</b>	<b>0.47</b>	<b>0.15</b>	<b>0.2</b>	<b>0.62</b>	<b>0.74</b>	<b>1.47</b>



**Table 6.5: Concentrations of PAHs in Non-activity soil samples**

PAH	C1 (0 – 10 cm)	C2 (10 – 20 cm)	C3 (20 – 30 cm)
	mg/kg	mg/kg	mg/kg
Naphthalene	0.03	0.03	<0.01
Acenaphthalene	<0.01	<0.01	<0.01
Acenaphthene	ND	ND	ND
Fluorene	ND	0.01	<0.01
Phenanthrene	0.05	0.07	0.03
Anthracene	0.05	0.06	0.06
Fluoranthene	0.05	0.04	0.03



Pyrene	<div>  <div> <div>0.01</div> <div>KNUST</div> </div> </div>	0.03	0.03
Benzo(a)anthracene	0.01	0.02	<0.01

Chrysene	0.02	0.03	0.01
Benzo(b)fluoranthene	0.01	0.01	<0.01
Benzo(k)fluoranthene	ND	ND	<0.01
Benzo(a)pyrene	ND	<0.01	<0.01
Indeno(1,2,3-cd)pyrene	ND	0.01	<0.01
Dibenzo(a,h)anthracene	ND	ND	ND
Benzo(g,h,i)perylene	ND	0.01	ND

**Table 6.6: Relative abundances of PAHs in surface soils(0 – 10 cm)**

	MAINTENANCE	SPRAYING	WELDING	METAL FABRICATION
NAP	0.1301	0.5397	2.7435	8.2949
ACY	0.1952	0.2944	1.3717	0.9217
ACE	0.4294	0.4416	0.8230	0.9217
FLU	2.4460	4.4652	4.9383	6.4516
PH E	10.4866	13.9843	20.8505	6.4516
ANT	10.4085	13.9352	20.3018	10.5991
FLT	1.2620	1.1776	7.4074	1.8433
PYR	4.4366	4.5142	9.8765	2.3041

Ba A	1.1970	0.0000	2.3041
		0.0000	
C H R	1.4702	1.8155	0.8230 0.0000



Bb F	0.9888	0.6869	0.0000	3.6866
Bk F	60.6687	54.9558	27.709 2	13.3641
Ba P	1.1579	0.6869	0.0000	0.0000
IN D	1.1319	1.1286	0.1097	11.0599
Da A	2.0427	1.1776	2.4691	13.3641
Bg P	1.5483	0.1963	0.5761	18.4332

**Table 6.7: Diagnostic Ratios for PAH Source Apportionment:**



**FLU/(FLU+PYR), IND/(IND + BgP),  $\Sigma$ LMW/ $\Sigma$ HMW and  $\Sigma$ COMB/ $\Sigma$ PAH**

IND/(IND+BgP)	FL	$\Sigma$ LMW/ $\Sigma$ HMW	$\Sigma$ COMB/ $\Sigma$ PAH
0.479	0.2	0.102	0.908
0.474	0.4	0.549	0.646
0.5	0.7	0.575	0.817
0.306	0.2	0.32	0.758
0.556	0.6	0.501	0.964
1	0.6	0.501	0.666
1	0.3	1.011	0.497
1	0.7	0.303	0.767
0	0.2	0.944	0.514
0	0.6	0.759	0.568
0.267	0.2	1.221	0.45
0	0.3	1.8	0.357
0.31	0.7	0.714	0.583
0.5	0.7	0.808	0.553
0.368	0.6	0.127	0.887

	Maintenance %	Spraying %	Welding %	Metal Fabrication %
NAP	17.24138	18.96552	17.24138	46.55172
ACY	27.27273	21.81818	36.36364	14.54545
ACE	49.25373	26.86567	17.91045	5.970149
FLU	59.55649	28.82788	5.702218	5.913411
PHE	67.97863	24.03711	6.409896	1.57436
ANT	67.3023	23.89232	6.225463	2.579921
FLT	63.26087	15.65217	17.6087	3.478261
PYR	71.68886	19.34128	7.568325	1.401542
BaA	93.24324	<0.01	<0.01	6.756757
CHR	67.93587	29.65932	2.40481	<0.01
BbF	75.49669	13.90728	<0.01	10.59603
BkF	78.28642	18.80351	2.260899	0.649169
BaP	86.40777	13.59223	<0.01	<0.01
IND	61.09551	16.15169	0.280899	22.47191
DaA	68.65889	10.49563	3.93586	16.90962

BgP	66.69157	2.241734	1.17691	29.88978
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**Table 6.8: Percentage Contributions of Different Activities to Individual PAHs**



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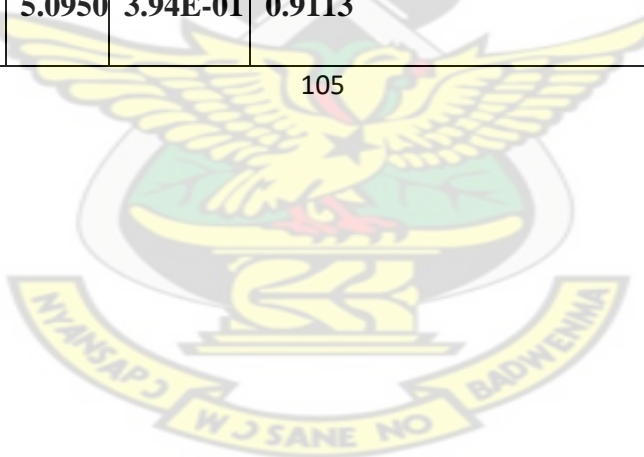
**Table 6.9: Benzo(a)Pyrene Equivalence (BaPeq) of PAHs in 0 – 10 cm of soil for Health Risk Assessment**

PAH	MAINTENANCE		SPRAYING		WELDING		METAL FABRICAT.		NON-ACTIVITY	
	Mean Conc.	BaPeq	Mean Conc	BaPeq	Mean Conc.	BaPeq	Mean Conc.	BaPeq	Mean Conc.	BaPeq
Naphthalene	0.0250	2.50E-05	0.0275	2.75E-05	0.0250	2.50E-05	0.0600	6.00E-05	0.0300	3.00E-05
Acenaphthylene	0.0375	3.75E-05	0.0150	1.50E-05	0.0125	1.25E-05	0.0067	6.67E-06	<0.01	0.00
Acenaphthene	0.0825	8.25E-05	0.0225	2.25E-05	0.0075	7.50E-06	0.0067	6.67E-06	0.0000	0.00
Fluorene	0.4700	4.70E-04	0.2275	2.28E-04	0.0450	4.50E-05	0.0467	4.67E-05	0.0000	0.00
Phenanthrene	2.0150	2.02E-03	0.7125	7.13E-04	0.1900	1.90E-04	0.0467	4.67E-05	0.0500	5.00E-05
Anthracene	2.0000	2.00E-02	0.7100	7.10E-03	0.1850	1.85E-03	0.0767	7.67E-04	0.0500	5.00E-04
Fluoranthene	0.2425	2.43E-04	0.0600	6.00E-05	0.0675	6.75E-05	0.0133	1.33E-05	0.0500	5.00E-05

Pyrene	0.8525	8.53E-04	0.2300	2.30E-04	0.0900	9.00E-05	0.0167	1.67E-05	0.0100	1.00E-05
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Benzo(a)anthracene	0.2300	2.30E-02	0.0000	0.00E+00	0.0000	0.0000	0.0167	1.67E-03	0.0100	1.00E-03
Chrysene	0.2825	2.83E-03	0.0925	9.25E-04	0.0075	7.50E-05	0.0000	0.0000	0.0200	2.00E-04
Benzo(b)fluoranthene	0.1900	1.90E-02	0.0350	3.50E-03	0.0000	0.00E+00	0.0267	2.67E-03	0.0100	1.00E-03
Benzo(k)fluoranthene	11.6575	1.17E+00	2.8000	2.80E-01	0.2525	2.53E-02	0.0967	9.67E-03	0.0000	0.00E+00
Benzo(a)pyrene	0.2225	2.23E-01	0.0350	3.50E-02	0.0000	0.00E+00	0.0000	0.00E+00	0.0000	0.00E+00
Indeno(1,2,3-cd)pyrene	0.2175	2.18E-02	0.0575	5.75E-03	0.0010	1.00E-04	0.0800	8.00E-03	0.0000	0.00E+00
Dibenzo(a,h)anthracene	0.3925	3.93E-01	0.0600	6.00E-02	0.0225	2.25E-02	0.0967	9.67E-02	0.0000	0.00E+00
Benzo(g,h,i)perylene	0.2975	2.98E-03	0.0100	1.00E-04	0.0053	5.25E-05	0.1333	1.33E-03	0.0000	0.00E+00
<b>TOTAL</b>	<b>19.2150</b>	<b>1.8700</b>	<b>5.0950</b>	<b>3.94E-01</b>	<b>0.9113</b>	<b>5.03E-02</b>	<b>0.7233</b>	<b>1.21E-01</b>	<b>0.2400</b>	<b>2.85E-03</b>



**Table 10: Incremental Lifetime Cancer Risk for Each Activity**

	LADD (child)	LADD (adult)	LADDD (child)	LADDD (adult)	ILCR
Maintenance	1.1165E-06	6.3266E-07	1.9199E-07	9.32993E-08	1.24E-05
Spraying	2.3523E-07	1.3330E-07	4.0451E-08	1.96577E-08	2.61E-06
Welding	3.0031E-08	1.7018E-08	5.1642E-09	2.5096E-09	3.34E-07
Metal Fabrication	7.2241E-08	4.0937E-08	1.2423E-08	6.03701E-09	8.03E-07
Non-activity soils	1.6956E-09	9.6083E-10	2.91578E-10	1.41695E-10	1.88E-08

**Definition of terms and variables used in the calculation of risk assessment**

IR (child) = soil ingestion rate for a child; 100 mg/day (EPA 1997)

IR (adult) = soil ingestion rate for an adult; 50 mg/day (EPA 1997)

EF = exposure frequency; 6 days/week (for 50 weeks/year)

ED (child) = exposure duration; 6 years

ED (adult) = exposure duration; 34 years

AT = average time for cancer; 54 years

$ABS_d$  = Soil dermal absorption fraction

AF = skin soil adherence factor for central tendency residential child;  
0.04mg/cm<sup>2</sup>/ev

= skin soil adherence factor for central tendency residential adult;

0.01mg/cm<sup>2</sup>/ev

# KNUST



SA = Skin surface area, 50 th percentile: limbs – for child; 3,307 cm<sup>2</sup>

= Skin surface area, 50 th percentile limbs – for adult; 5,672 cm<sup>2</sup>

[PAH] = PAH concentration in soil

