Assessment of Polycyclic Aromatic Hydrocarbon (PAHs) and Heavy Metals in the Vicinity of Coal Power Plants in South Africa

By

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Submitted in accordance with the requirements
for the degree of
Doctor of Philosophy
In Chemistry
at the
UNIVERSITY OF SOUTH AFRICA

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NOVEMBER 2012

I declare that **ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBON (PAHs) AND HEAVY METALS IN THE VICINITY OF COAL POWER PLANTS IN SOUTH AFRICA** is my own work and that all the sources that I have used or quoted have been indicated and acknowledge by means of complete references.

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(MR O O OKEDEYI, Student # 43287603)	DATE

The following papers are based on this thesis.

Okedeyi, O.O., Nindi, M.M., Dube, S. & Awofolu, O.R (2013). Distribution and potential sources of polycyclic aromatic hydrocarbons in soils around coal-fired power plants in South Africa. Environmental Monitoring and Assessment. 185: 2073 – 2082. Published by Springer

Okedeyi, O.O., Dube, S., Awofolu. O.R. & Nindi, M. M. Assessing the enrichment of heavy metals in surface soil and plants (*Digitaria eriantha*) around coal-fired power plants in South Africa. In press in the Journal of Environmental Science and Pollution,Research. Published by Springer

Okedeyi., O.O., Dube., S., Awofolu., O.R. & Nindi, M. M.. Determination of polycyclic aromatic hydrocarbons (PAHs) in soil by ultrasonic extraction assisted with dispersive liquid-liquid microextraction and gas chromatography-mass selective detection. Paper under preparation for submission

DEDICATION

This piece of work is dedicated to my jewels of inestimable value, Josephine, Bolu, Femi and Teni.

To the Okedeyis, Osideles, Olorunfunmis, Jembis, and the Aigbes. And lastly to Jehovah God with whom all things are possible, for letting me live to complete this work.

ACKNOWLEDGEMENTS

My greatest thanks goes to Jehovah God, with whom all things are possible, for letting me live to complete this work.

I wish to thank Professor Mathew Muzi Nindi for his supervision, guidance and understanding throughout the work. My special thanks also go to Professor Omotayo Awofolu and Dr Simiso Dube for their encouragement, constructive criticism and co-supervision. would like to extend my appreciation to all members of staff of chemistry department, UNISA, and especially the Analytical Chemistry Research group G26 (Dineo, Tebza, Cicilia, Vuyo, Vusa, Vimbai and Tshabalala) for their support as well. My thanks will be incomplete if I fail to thank Professor and Dr (Mrs) Adeniyi for their encouragement to pursue the programme. I would like to thank the VP research and innovation, the former executive Dean of College of Engineering and Technology for partial financial support that I received during my studies.

To my other colleagues and friends at UNISA (Olowoyos, Adegbites, Deolu, Eriwu, Moji, Oyeyiola, Kenedy, Mathins, Ginet, Papo, Shadi and others) I say thank you. My special thanks also go to the Lagos State Scholarship Board for its financial support. I say thank you.

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LIST OF ACRONYMS

ATSDR	Agency for Toxic Substances and Disease Registry
CCME	Canadian Council of Ministers of the Environment
DHHS	Department of Health and Human Services
DLLME	Dispersive liquid–liquid microextraction
EF	Enrichment factor
EPA	Environmental Protection Agency
FAO	Food and Agricultural Organization
HAPs	Hazardous air pollution
IARC	International Agency for Research on Cancer
OSHA	Occupation Safety and Health Administration
PAHs	Polycyclic Aromatic Hydrocarbon
TEFs	Toxicity equivalency factors
USEPA	United State Environmental Protection Agency
UV	Ultra Violet
WCA	World Coal Association
WHO	World Health Organization

ABSTRACT

The distribution and potential sources of 15 polycyclic aromatic hydrocarbons (PAHs) in soils and *Digitaria eriantha* in the vicinity of three South African coal-fired power plants, Matla, Lethabo and Rooiwal were determined by gas chromatography–mass spectrometry. An ultrasonic assisted dispersive liquid-liquid microextraction (UA-DLLME) method was developed for the extraction of polycyclic aromatic hydrocarbon in soil, followed by determination using gas chromatography mass spectrometry. The study showed that an extraction protocol based on acetonitrile as dispersive solvent and $C_2H_2Cl_2$ as extracting solvent, gave extraction efficiencies comparable to conventional soxhlet extraction for soil samples. The extraction time using ultrasonication and the volume of the extraction solvent was also investigated. Using a certified reference material soil (CRM), the extraction efficiency of UA-DLLME ranged from 64 to 86% in comparison with the Soxhlet result of 73 to 95%. In comparison with the real sample, the CRM result did not show a significant difference at 95% C.I. The UA-DLLME proved to be a convenient, rapid, cost-effective and greener sample preparation approach for the determination of PAHs in soil samples. PAH compound ratios such as phenanthrene/phenanthrene + anthracene (Phen/ Phen + Anth) were used to provide a reliable estimation of emission sources. The total PAH concentration in the soils around three power plants ranged from 9.73 to 61.24 µg g^{-1}, a range above the Agency for Toxic Substances and Disease Registry levels of 1.0 µg g^{-1} for a significantly contaminated site. Calculated values of the Phen/Phen + Anth ratio were 0.48±0.08, 0.44±0.05, and 0.38+0.04 for Matla, Lethabo and Rooiwal, respectively. The flouranthene/fluoranthene + pyrene (Flan/ Flan + Pyr) levels were found to be 0.49±0.03 for Matla, 0.44±0.05 for Lethabo, and 0.53±0.08 for Rooiwal. Such values indicate a pyrolytic source of PAHs. Higher molecular weight PAHs (five to six rings) were predominant, suggesting coal combustion sources. The carcinogenic potency B[a]P equivalent concentration (B[a] Peq) at the three power plants ranged from 3.61 to 25.25, indicating a high carcinogenic burden. The highest (B[a] Peq) was found in samples collected around Matla power station. It can, therefore, be concluded that the soils were contaminated with PAHs originating from coal-fired power stations.

Nine metals (Fe, Cu, Mn, Ni, Cd, Pb, Hg, Cr and Zn) were analysed in soil and the *Digitaria eriantha* plant around three coal power plants (Matla, Lethabo and Rooiwal), using ICP-OES and GFAAS. The total metal concentration in soil ranged from 0.05 ± 0.02 to 1835.70 ± 70 µg g^{-1}, 0.08 ± 0.05 to 1743.90 ± 29 µg g^{-1} and 0.07 ± 0.04 to 1735.20 ± 91 µg g-1 at Matla, Lethabo and Rooiwal respectively. The total metal concentration in the plant (*Digitaria eriantha*) ranged from 0.005 ± 0.003 to 534.87 ± 43 µg g^{-1} at Matla, 0.002 ± 0.001 to 400.49 ± 269 µg g^{-1} at Lethabo and 0.002 ± 0.001 to 426.91 ± 201 µg g^{-1} at Rooiwal. The accumulation factor (A) of less than 1 (i.e. 0.003 to 0.37) at power plants indicates a low transfer of metal from soil to plant (excluder). The enrichment factor values obtained (2.4 – 5) indicate that the soils are moderately enriched, with the exception of Pb that had significant enrichment of 20. The Geo-accumulation Index values of metals indicate that the soils are moderately polluted (0.005 – 0.65), except for Pb that showed moderate to strong pollution (1.74 – 2.53).

Key Words: Polycyclic aromatic hydrocarbons, coal-fired power plant, gas chromatography-mass spectrometry, heavy metals, enrichment factor, Geo-accumulation Index, dispersive liquid–liquid microextraction, ultrasonic extraction, accumulation factor coal *Digitaria eriantha*.

CHAPTER ONE

1.0 Introduction

1.1 Background information

Polycyclic aromatic hydrocarbons (PAHs) and heavy metals are important and well-known pollutants that have been identified in diverse environmental matrices world-wide. Natural hydrocarbons are usually present at trace levels, whereas anthropogenic hydrocarbons originating from different sources are found at higher levels, especially in areas associated with industrial and transportation activities. Among hydrocarbons, PAHs deserve particular attention because of their acute and chronic toxicity, as well as their stability, which delays their degradation (Malawska & Wilkomirski, 2000).

The toxic influence of heavy metals on living organisms is indisputable. A high concentration of these metals may damage the internal body organs in both animals and humans. While the natural content of heavy metals in soil is the result of formation factors (the soil type, climate, topography, time of appearance and biota), their current increase may be a result of local and long-range anthropogenic activities (non-point source) (Malawska & Wilkomirski 2000). It is a known fact that coal burning produces organic pollutants that are toxic, having carcinogenic and mutagenic characteristics even at low concentrations (Ravindra et al., 2008; Wang et al., 2009).

Recently, interest in persistent organic pollutants (POPs) has increased tremendously. The main interest is complete elimination of the 12 common POPs (Aldrin, Chlordane, DDT, Dieldrin, Dioxins, Endrin, Furans, Heptachlor, Hexachlorobenzene (HCB), Mirex, Polychlorinated Biphenyls (PCBs), Toxaphene) on a global scale, and an agreement on this was signed in May 2001 in the form of the Stockholm Convention for the regulation of POPs. In addition to the 12 POPs, PAHs (EPA 16 priority PAH compounds) were also included by the United Nations-European Committee (2002) (Nadal et al., 2004).

1.2. What are PAHs?

PAHs are chemical compounds that consist of fused aromatic rings that do not contain a heteroatom or carry substituents and are released into the environment as a result of incomplete combustion of organic material originating from both natural and anthropogenic processes, such as energy production, waste incineration and transport, as well as diverse industrial processes such as aluminum or coke production. They are a group of persistent and ubiquitous organic contaminants. Some PAHs are considered to be mutagenic and/or carcinogenic compounds. Some are also linked to health problems, such as cataracts, kidney and liver damage and jaundice (Dong & Lee 2009). Because of their carcinogenicity properties, the United States (US) Environmental Protection Agency (EPA) has identified 16 of these PAHs as priority pollutants (Szolar et al., 2002; Bergknut et al., 2006; Pies et al., 2008).

PAHs have been found to be widely distributed in the atmosphere because of their moderate vapour pressure, low solubility and low reactivity. The most significant anthropogenic sources of PAHs include power generation from coal and other fossil fuels, coal production, petroleum refining, coal and oil shale conversion and chemical manufacturing. PAHs in soil could arise from a number of sources. Point sources include hydrocarbon spillage and incomplete products of combustion of fossil fuels, wood burning, use of organic waste as compost and fertilizer, power plants and blast furnaces (Nam et al., 2003). However, the major pollution is likely to come from diffuse sources (non-point sources) such as deposition from the atmosphere. There is enough evidence to believe that PAHs are transported over long distances by atmospheric movement (Bakker et al., 2001; Halsall et al., 2001).

The deposited PAHs are accumulated mainly in the humus layer of the soil. The pathways of PAH dissipation in contaminated soil may be volatilization, irreversible sorption, leaching, accumulation by plants and biodegradation. PAH with three or more rings tend to be strongly adsorbed to the soil. Strong sorption, leaching coupled with very low water solubility and very low vapour pressures make leaching and volatilization insignificant pathways of PAH loss (Nam et al., 2003). PAH concentration in soil correlates significantly with the corresponding levels in air (Li et al., 2010), therefore PAH determination in soil may provide important information on the state of environmental pollution. The characteristic ratio of PAH could be used in qualitative and quantitative source estimation. Phenanthrene/anthracene and fluoranthene/ fluoranthene + pyrene ratios have commonly been used as a means of determining the dominant origins or source of PAHs (Nam et al., 2003). PAHs present in both gas and particle phases could influence human health through inhalation and/or ingestion (Ma et al., 2010).

Several reports have been received of an increased incidence of cancer in marine animals from the vicinity of oil spills (Boonyayumanond et al., 2006). Concern about PAHs in the environment arises also from the fact that many of them are persistent. Some PAHs (e.g. benzo[a]pyrene, indeno[1,2,3-cd]pyrene) are carcinogenic and mutagenic. The endocrine-disrupting activities of some PAH species (e.g. chrysene) have recently been reported (Boonyayumanond et al., 2007). Numerous studies have shown that PAHs are capable of inducing dioxin-like responses in fish (Behrens et al., 2001; Jung et al., 2001; Villeneuve et al., 2002) and mammalian cell lining (Basu et al., 2001; Dominguez et al., 2010). Three PAHs, benzo[a]pyrene, chrysene, and benz[a]anthracene have been reported to cause oestrogenic responses in vitro (Dominguez et al., 2010).

The anthropogenic sources of PAHs can be categorised into two groups: “pyrogenic” and “petrogenic”. PAHs generated through the combustion of fossil fuel (coal and petroleum) and biomass are pyrogenic. Sources of combustion include automobiles, power plants, industries burning coal and petroleum (e.g. steel smelters) and waste incinerators. PAHs generated through combustion are emitted to ambient air as particles and gases. Atmospheric PAHs that escape photo-degradation in the air are added to land surfaces through dry and wet deposition and are stored in soil or become street dust owing to their hydrophobicity. These surface soil and street dust PAHs are resuspended back into the atmosphere by wind and volatilization (Manoli et al., 2002, 2004; Wang et al., 2009). PAHs in soil are of importance owing to their toxicity to humans and their effects on soil organisms and plants. PAHs are carried into the drainage network by storm runoff and are eventually transported to aquatic environments during the rainy season, where they are adsorbed to sediment (Mai et al., 2003; Boonyayumanond et al., 2006). Therefore, soil and dust are natural sinks and environmental reservoirs for PAHs in the urban environment. Accumulation of PAHs in dust and soil may lead to contamination of vegetables and food chains, leading to direct or indirect human exposure (Tao et al., 2004; Zohair et al., 2006; Cai et al., 2007). Thus, understanding of the fate of PAHs deposited to street dust and surface soil is very important to evaluate the risk of human exposure and environmental contamination.

Crude oil and petroleum products contain PAHs that could form another important primary source of PAHs, the petrogenic source. Petroleum products include kerosene, gasoline, diesel fuel, lubricating oil and asphalt (Ockenden et al., 2003; Murakami et al., 2005; Boonyayumanond et al., 2007). Petrogenic PAHs in engine oil and fuel could be leaked from poorly maintained automobiles or be emitted through automobile exhausts and be deposited and adsorbed to street dust. Tyres and asphalt also contain PAH and wear and tear on them contributes to PAHs in street dust. Consequently, street dust is usually a complex mixture of petrogenic and pyrogenic PAHs and is an important non-point source (Boonyayumanond et al., 2007; Liu et al., 2007). There are also natural pyrogenic sources like vegetation fires or volcanic eruptions. In addition, biological formation of perylene under anaerobic conditions has been reported (Aichner et al., 2007).

1.3 Human health

The toxicity of PAHs depends on the structure of the isomers (PAHs with the same formula and number of rings), varying from being nontoxic to extremely toxic.

Thus, highly carcinogenic PAHs may be small or large. Benzo[a]pyrene, for example, is notable for being the first chemical carcinogen to be discovered (and is one of many carcinogens found in cigarette_smoke) (USEPA 1993). The EPA classified seven PAH compounds as probable human carcinogens (USEPA 2002): benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene. PAHs known for their carcinogenic, mutagenic and teratogenic properties are benz[a]anthracene and chrysene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, coronene, dibenz[a,h]anthracene ($C_{20}H_{14}$), indeno[1,2,3-cd]pyrene ($C_{22}H_{12}$) and ovalene. High prenatal exposure to PAH is associated with a lower intelligence quotient (Luch, 2005).

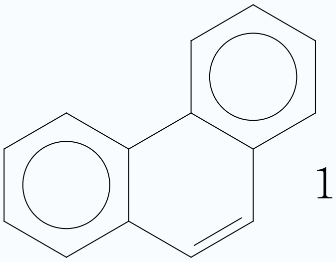
1.4 Chemistry of PAHs

The simplest PAHs, as defined by the International Union on Pure and Applied Chemistry, are phenanthrene and anthracene, which both contain three fused aromatic rings (Feng et al., 2009). Other PAHs contain four-, five-, six- or seven-member rings, but those with five or six are most common. See Table 1.1 and Fig 1.1 (Fetzer, 2000). PAHs containing up to six fused aromatic rings are often known as "small" PAHs and those containing more than six aromatic rings are called "large" PAHs. Owing to the availability of samples of the various small PAHs, most research on PAHs has been conducted on those with up to six rings. The biological activity and occurrence of the large PAHs do appear to be a continuation of the small PAHs. The large PAHs are found as combustion products, but at lower levels than the small PAHs, because of the kinetic limitation of their production through the addition of successive rings. In addition, with many more isomers possible for larger PAHs, the occurrence of specific structures is much less common (Fetzer, 2000).

PAHs possess very characteristic UV absorbance spectra. These often possess many absorbance bands and are unique for each ring structure. Thus, for a set of isomers, each isomer has a different UV absorbance spectrum from the others. This is particularly useful for the identification of PAHs. Most PAHs are also fluorescent, emitting characteristic wavelengths of light after excitation. Naphthalene ($C_{10}H_8$), consisting of two coplanar six-membered rings, is another aromatic hydrocarbon. By formal convention (IUPAC), it is not a true PAH, though it is referred to as a bicyclic aromatic hydrocarbon. Aqueous solubility of PAHs decreases by approximately one order of magnitude for each additional ring (Fetzer, 2000).

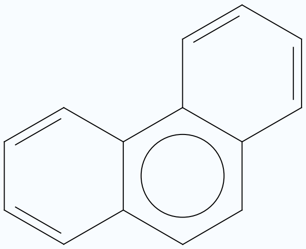
1.5 Aromaticity

Although PAHs are clearly aromatic compounds, the degree of aromaticity could be different for each ring segment. According to **Clar's rule,** for PAHs the resonance structure with the most disjointed aromatic π-sextets - i.e. benzene-like moieties - is most important for the characterisation of the properties (Guillem et al., 2005). In phenanthrene, for example,(Figure 1.1), the Clar structure **1A** has two sextets at the extremities, while resonance structure 1B has only one central sextet. Therefore, the outer rings are firmly aromatic while its central ring is less aromatic and therefore more reactive. In contrast, in anthracene **2A and 2B,** the number of sextets is just one and aromaticity spreads out. The difference in the number of sextets is reflected in the UV absorbance spectra of the two isomers. Phenanthrene has a highest wavelength absorbance of around 290 nm, while anthracene's highest wavelength bands are around 380 nm. Three Clar structures with two sextets are present in chrysene (**4**) and by superposition the aromaticity in the outer ring is larger than in the inner rings (Guillem et al., 2005).

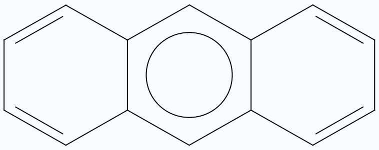


1A

Phenanthrene

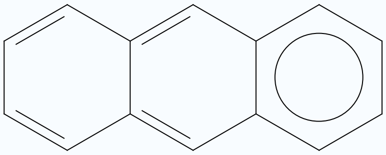


1B



2A

Anthracene



2B

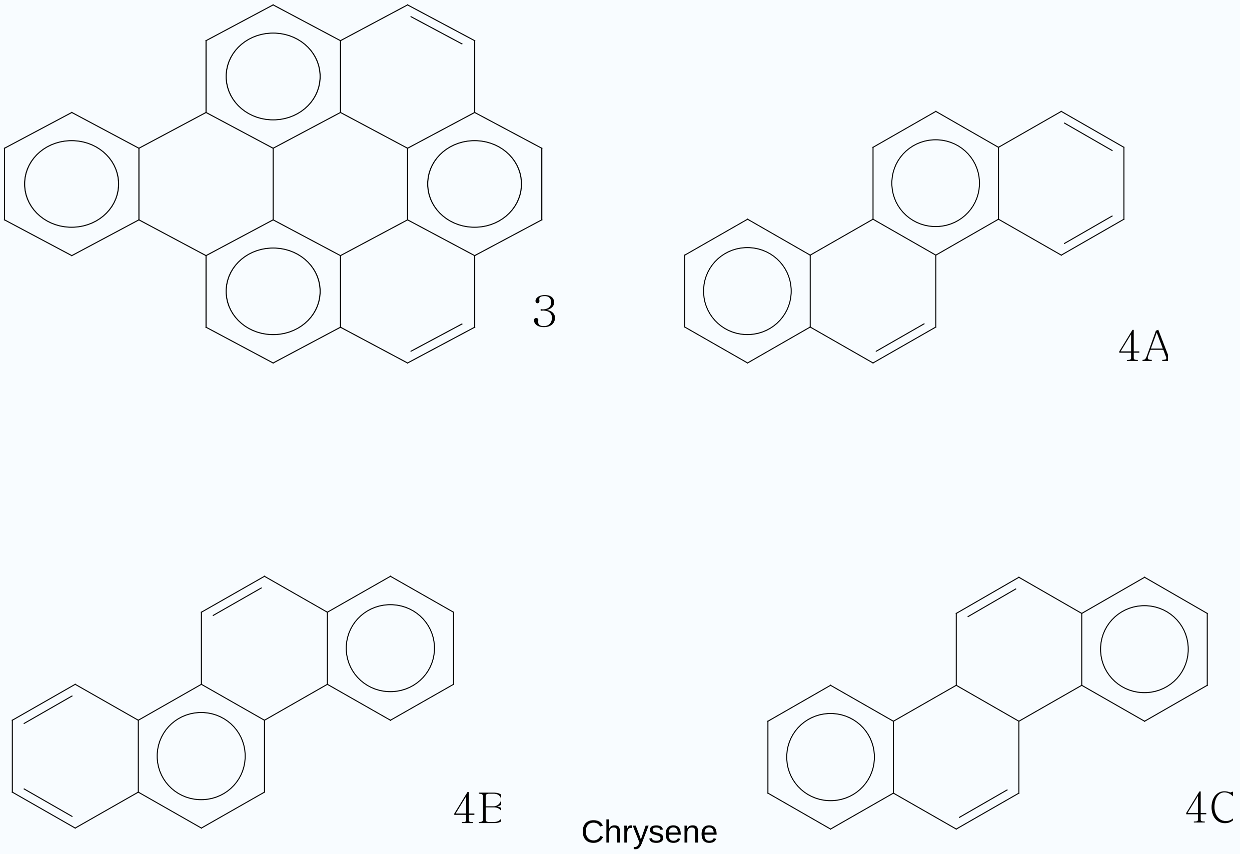


Figure 1.1: Some PAH compounds showing aromaticity

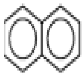
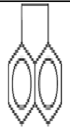
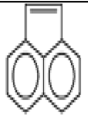
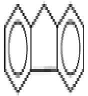
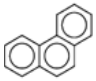
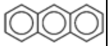
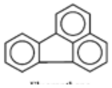
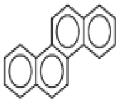
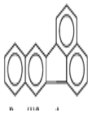
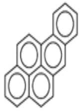
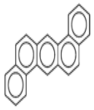
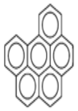
1.6 Physical and chemical characteristics of PAHs

PAHs are a group of several hundred individual organic compounds that contain two or more aromatics rings and generally occur as complex mixtures rather than single compounds. PAHs are classified by their melting and boiling point, vapour pressure and water solubility, depending on their structure. Table 1.1 shows physical and chemical characteristics of 16 priority PAHs, listed by the US EPA (2002). For most PAHs, as the molecular weight increases, their solubility in polar organic solvents andwater decreases (Lee & Vu, 2010). PAHs could be photochemically decomposed under strong ultraviolet light or sunlight, and thus some PAHs could be lost during atmospheric sampling. Also, PAHs could react with ozone, hydroxyl radicals, nitrogen and sulphur oxides, and nitric and sulphuric acids, which affect the environmental fate or conditions of PAHs (Lee & Vu, 2010).

1.7 Occurrence and pollution of PAHs

Polycyclic aromatic hydrocarbons are lipophilic, as they dissolve more easily in oil than water. The larger compounds are less water-soluble and less volatile (i.e. less prone to evaporate). Because of these properties, PAHs in the environment are found primarily in soil, sediment and oily substances, as opposed to water or air. However, they are also a component of concern in particulate matter suspended in air (Fetzer, 2000). Natural crude oil and coal deposits contain significant concentration of PAHs, arising from chemical conversion of natural product molecules, such as steroids, to aromatichydrocarbons. They are also found in processed fossil fuels, tar and various edible oils. Types of combustion yield different distributions of PAHs either as individual or together with an isomer or both. Thus coal burning produces a different mixture than motor-fuel combustion or a forest fire, making the compounds potentially useful as indicators of the burning history (Fetzer, 2000).

Table: 1.1. EPA 16 priority PAH compounds

Structure																
Name	Naphthalene (Nap)	Acenaphthalene (Ace)	Acenaphthylene (Acy)	Fluorine (Flo)	Phenanthrene (phen)	Anthracene (Anth)	Fluoranthene (Flan)	Pyrene (pyr)	Benz[a]anthracene (B[a]a)	Crysene (chry)	Benzo[b]fluoranthen (B[b]f)	Benzo[k]fluoranthene (B[k]f)	Benzo[a]pyrene (B[a]p	Dibenz[ah]anthracene (DB[ah]a	Benzo[ghi]perylene (B[ghi]p	Indeno[123-cd]pyrene (Ind)
Formular	$C_{10}H_8$	$C_{12}H_{10}$	$C_{12}H_8$	$C_{13}H_{10}$	$C_{14}H_{10}$	$C_{14}H_{10}$	$C_{16}H_{12}$	$C_{16}H_{10}$	$C_{18}H_{12}$	$C_{18}H_{12}$	$C_{20}H_{12}$	$C_{20}H_{12}$	$C_{20}H_{12}$	$C_{22}H_{14}$	$C_{22}H_{12}$	$C_{22}H_{12}$
Molecular Weight	128	154	152	166	178	178	202	202	228	228	252	252	252	278	176	276
Melting Point(^{0}C)	80.26	95	92.93	116-117	100	218	100.8	156	158	254	168.3	215	179-179.3	262	273	163.6
Boiling Point(^{0}c)	218	96	265-275	295	340	340-342	375	393-404	438	448	No data	489	495	No data	550	530

SOURCE: US EPA 2002

1.8 Environmental fate

Once emitted to the atmosphere, molecular mass influences the fate of the gaseous PAH mixtures. Heavier PAHs (> four rings) tend to adsorb to particulate matter, while lighter PAH (< four rings) tend to remain gaseous until removed via precipitation (Skupinska et al., 2004).

PAH concentrations in water tend to be below approximately 100 ng/L because of their weak solubility. The weak solubility leads to accumulation in sediments and aquatic organisms. PAH could be absorbed by plants and could accumulate in soil (ATSDR 2009).

1.9 Carcinogenicity

Air with high concentrations of PAHs causes many adverse effects on different types of organisms, including plants, birds and mammals. Significant positive correlation between mortality from lung cancer in humans and exposure to PAHs from exhaust from coke ovens, roofing-tar and cigarette smoke has been reported (ATSDR, 2009). Some PAHs have been demonstrated to be carcinogenic in humans and experimental animals, and they are classified as carcinogenic materials by many organisations, including the US Agency for Toxic Substances and Disease Registry (ATSDR, 2009), the International Agency for Research on Cancer (IARC, 2005), the Department of Health and Human Services (DHHS), the National Occupation Safety and Health Administration (OSHA, 2002) and the US EPA. Table 1.2 shows the carcinogen classification of 17 priority PAHs by the IARC, compared to classifications by the DHHS and the US EPA (Lee & Vu 2010). Lower molecular weight (two to three rings) PAHs, with the exception of naphthalene, are usually associated with relatively lower toxicity (cancer risk) than medium and higher molecular weight PAHs with four to six aromatic rings.

Many toxicity studies reported that benzo[a]pyrene (B[a]p) had the highest carcinogenic potency, with long-term persistency in the environment. Shulte et al. (1993) found a significant increase in all lung tumours and a dose-dependent increase in malignant lung tumours for mice exposed to PAH-enriched exhausts containing 0.05 or 0.09 mg/m^3 B[a]p. B[a]p is often used as an indicator of human exposure to PAHs (ASTDR, 2009), and the toxicity of other PAHs is converted into toxicity equivalency factors (TEFs) of B[a]p to evaluate their relative toxicities. Methods using TEFs and the B[a]p as a substitute are more or less similar, except that they do not require expensive monitoring.

Table: 1.2. Classification of PAHs by the EPA, IARC and DHHS in terms of their carcinogenicity

PAHs	Acenaphthene	Acenaphthylene	Anthracene	Benz(a) anthracene	Benz(a) pyrene	Benzo(b) fluoranthene	Benzo(e) Pyrene	Benzo(ghi) perylene	Benzo(j) fluoranthene	Benzo(k) Fluoranthene	Crysene	Dibenz(ah) anthracene	Fluoranthene	Fluorine	Indeno(123-cd) pyrene	Phenanthrene	Pyrene
EPA	Not classifiable	Not classifiable	Not classifiable	Probably carcinogen	Probably carcinogen	Probably carcinogen	Not classifiable	Not classifiable	Not included	Probably carcinogen	Probably carcinogen	Probably carcinogen	Not classifiable	Not classifiable	Probably carcinogen	Not classifiable	Not classifiable
IARC	Not classifiable	Not classifiable	Not classifiable	Probably carcinogen	Probably carcinogen	Probably carcinogen	Not classifiable	Not classifiable	Probably carcinogen	Probably carcinogen	Not classifiable	Not classifiable	Not classifiable	Not classifiable	Probably carcinogen	Not classifiable	Not classifiable
DHHS	Not classifiable	Not classifiable	Not classifiable	Animal carcinogen	Animal carcinogen	Animal carcinogen	Not classifiable	Not classifiable	Animal carcinogen	Not classifiable	Not classifiable	Animal carcinogen	Not classifiable	Not classifiable	Animal carcinogen	Not classifiable	Not classifiable

SOURCE: ASTDR 2009.

PAH-induced carcinogenesis could result when a PAH-deoxyribonucleic acid (DNA) adduct forms at a site critical to the regulation of cell differentiation or growth. A mutation occurs during cell replication if the aberration remains unrepaired. Cells affected most significantly by acute PAH exposure appear to be those with rapid replicative turnover, such as those in bone marrow, skin and lung tissue. Tissues with slower turnover rates, such as liver tissue, are less susceptible. Benzo (a) pyrene diol epoxide adducts bind, covalently to several guanine positions of the bronchial epithelial cell DNA p53 gene, where cancer mutations are known to occur from exposure to cigarette smoke. This is one possible genotoxic mechanism of cancer causation by tobacco (Denissenko, 1996).

The carcinogenicity of certain PAHs is well established in laboratory animals. Researchers have reported increased incidences of skin, lung, bladder, liver, and stomach cancers, as well as injection-site sarcomas, in animals. Animal studies show that certain PAHs can also affect the haematopoietic and immune systems and could produce reproductive, neurologic and developmental effects. It is difficult to ascribe observed health effects to specific PAHs because most exposures are to PAH mixtures. In fact, workers exposed to PAHs have been noted for increased in incidence of skin, lung, bladder and gastrointestinal cancers as well (Dasgupta & Lahiri 1992; Szczeklik et al., 1994; ATSDR 2009). The earliest human PAH-related epidemiologic study was reported in 1936 by investigators in Japan and England who studied lung cancer mortality among workers in coal carbonisation and gasification processes. Subsequent

US studies among coke oven workers confirmed excessive lung cancer mortality, with the suggestion of excessive genito-urinary system cancer mortality. Later experimental studies showed that PAHs in soot were probably responsible for the increased incidence of scrotal cancer among London chimney sweepers as noted by Percival Pott in his 1775 treatise (Zedeck, 1980). Continued research into the mutagenic and carcinogenic effects from chronic exposure to PAHs and metabolites is needed. Table 1.2 indicates the carcinogenic classifications of selected PAHs by specific agencies.

1.10 Sources and emission of PAHs

1.11 Stationary sources

1.11.1 Domestic sources

Heating and cooking are dominant domestic sources of PAHs. The burning and pyrolysis of coal, oil, gas, garbage, wood or other organic substances are the main domestic sources. Domestic sources are important contributors to the total emissions of PAHs in the environment. Differences in climate patterns and domestic heating systems produce large geographic variations in domestic emissions. PAH emissions from these sources may be a major health concern because of their prevalence in indoor environments (Ravindra et al., 2006).

According to a recent World Health Organization (WHO) report, more than 75% of people in China, India and South East Asia and 50-75% of people in parts of South

America and Africa use combustion of solid fuels, such as wood, for daily cooking. The main indoor sources of PAHs are cooking and heating emissions and infiltration from outdoors. PAH emissions from cooking account for 32.8% of total indoor PAHs (Zhu et al., 2009). Lower molecular weight PAHs, which originate from indoor sources, are the predominant proportion of the total PAHs identified in residential non-smoking air. The toxicity of PAH mixtures from indoor sources is lower than that of mixtures that contain large amounts of higher molecular weight PAHs. Cigarette smoke is also a dominant source of PAHs in indoor environments. In many studies, PAHs in the indoor air of smoking residences tend to be higher than in non-smoking residences.

Oanh et al. (1999) found that wood fuel burning released the highest emissions of about 18 PAHs and 11 genotoxic PAHs in terms of emission factors, accounting for energy (mg/MJ) emission rates and based on the pollutant concentrations in smoke. Charcoal released the lowest amount of PAH emissions. On a fuel-weight basis, wood fuel burning has the same emission factors as coal briquette burning (110 mg/kg). However, emissions of genotoxic PAHs from wood burning were twice as high as those from charcoal burning.

1.11.2 Industrial sources

PAH emissions from industries are produced by burning fuels such as gas, oil and coal. Sources of PAHs include emissions from industrial activities, such as primary aluminum and coke production, petrochemical industries, rubber tyre and cement manufacturing, bitumen and asphalt industries, wood preservation, commercial heat and power generation and waste incineration. Chen et al. (2007) studied emissions of PAHs from the pyrolysis of scrap tyres. Total PAH emissions from a scrap tyre plant via pyrolysis were 42.3 g/day with emission factors of 4 mg/kg. Fabbri et al. (2006) investigated PAH emissions from pyrolysis products to study the thermal degradation of organic materials. Emissions factors of PAHs from thermal decompositions of organic materials ranged from 0.4 ± 0.13 mg g^{-1} for cellulose to 9.0 ± 0.5 mg g^{-1} for tyres. Yang et al. (2005) reported that emission factors from joss paper furnaces average 71.0 mg g^{-1}. With applied air pollution control devices, such as adsorption towers, removal efficiencies of total PAHs are 42.5 % and 11.7 % for particulate and gaseous PAHs, respectively. Yang et al. (1998) reported emissions of PAHs from various industrial stacks: a blast furnace, a basic oxygen furnace, a coke oven, an electric arc furnace, a heavy oil plant, a power plant and a cement plant. The coke oven, electric arc furnace and heavy oil combustor produced large amounts of higher molecular weight PAH emissions. Emission factors of PAHs from these industrial stacks ranged from 0.08 to 3.97 mg kg^{-1} feedstock, while emission factors for B[a]p ranged from 1.87 to 15.5 μg g^{-1} feedstock. The highest emission factors of total PAHs and B[a]p resulted from the combustion of heavy oils.

1.12 Mobile sources

Mobile sources are major causes of PAH emissions in urban areas. PAHs are mainly emitted from exhaust fumes of vehicles, trains, ships, and aircraft. PAH emissions from mobile sources are associated with the use of diesel, coal, gasoline, oil and lubricant oil.

One of the major influences on the production of PAHs from gasoline automobiles is the air-to-fuel ratio. It has been reported that the concentration of PAHs in engine exhaust emissions decreases with leaner mixtures (Ravindra et al., 2006; Lee & Vu, 2010). Abrantes et al. (2004), reported that PAHs from the exhausts of light-duty diesel vehicles were dominated by Low molecular weight (LWM) PAHs. Yang et al. (2005) reported that the emission factors of total PAH emissions from a two-stroke carburettor (2-Stk/Cb), four-stroke carburettor (4-Stk/Cb), and four-stroke fuel injection (4-Stk/FI) motorcycle were 8.320, 5.990 and 3.390 mg/km, respectively.

Chen et al. (2006) reported that the emission factors of total PAHs and total BaPeq of a helicopter turbo shaft engine were higher than those of a motor vehicle engine, heavy-duty engine and F101 aircraft engine. LMW PAHs are also the dominant PAHs emitted from helicopter engines. Fuel type has a substantial effect on the emission factors and toxicity of PAHs from vehicle engines. He et al. (2010) indicated that diesel engines using diesel/biodiesel and their blends can greatly reduce the total emission of PAHs by 19.4 and 13.1 %, respectively. The BaP TEQ of PAHs emitted also decreased by 15% with the use of biodiesel.

1.13. Agricultural sources

Open burning of brushwood, straw, moorland heather and stubble are agricultural sources of PAHs. All of these activities involve burning organic materials under suboptimum combustion conditions. Thus, it is assumed that a significant amount of PAHs are produced from the open burning of biomass (Lee & Vu, 2010). Emission factors of PAHs from wood combustion ranged from 16.4 to 1,282 mg kg^{-1} of wood (Oanh et al., 1999; Schauer et al., 2001). PAH concentrations released from wood combustion depends on wood type, kiln type and combustion temperature. Eighty to ninety per cent of PAHs emitted from biomass burning are LMW PAHs including naphthalene, acenaphthylene, phenanthrene, flouranthene and pyrene (Lee & Vu, 2010).

1.14 Natural sources

Accidental burning of forests, woodland and moorland due to lightning strikes is a natural source of PAHs. Furthermore, volcanic eruptions and decaying organic matter are also important natural sources, contributing to the levels of PAHs in the atmosphere. The degree of PAH production depends on meteorological conditions, such as wind, temperature, humidity, as well as fuel characteristics and types, such as moisture content, green wood and seasonal wood (Lee & Vu, 2010).

1.15 Coal in South Africa

Coal is a carbon-rich fossil fuel mineral that is subjected to pressure and heat for millions of years (Macintosh et al., 2011). When coal is formed, impurities from the surroundings, such as sulphur and heavy metals, are incorporated. These impurities consist of many hazardous materials such as mercury, arsenic, lead and nickel. The type of impurities in any given seam of coal depends on the conditions and the length of the period during which the coal is formed (Macintosh et al., 2011).

The most significant uses of coal are for electricity generation, steel production, cement manufacturing and as a liquid fuel. Around 5.9 billion tons of hard coal was used worldwide in 2010, as well as 909 million tons of brown coal (low-quality coal intermediate in grade between peat and lignite). Since 2000, global coal consumption has grown faster than that of any other fuel. The five largest coal users - China, the USA, India, Japan and South Africa - account for 82% of total global coal use (World Coal Association [WCA], 2011).

South Africa produces an average of 224 million tonnes of marketable coal annually, making it the fifth largest coal-producing country in the world and 25% of its production is exported, making it the third largest coal-exporting country (Eskom, 2011). The remainder of South Africa's coal production feeds the various local industries, with 53% used for electricity generation (Eskom, 2011). South Africa has rich coal deposits, therefore most of the power stations are-coal fired. Around 77% of South Africa's energy needs are directly satisfied by coal. This is unlikely to change significantly in the next decades, in view of the relative lack of suitable alternative energy sources.

Historically this large deposit of coal has given South Africa access to cheap electricity, but it is also one of the leading causes why the country is in the top 20 list of carbon dioxide emitting countries. Most South African coal is of low quality, with a low heat value and high ash content. This makes most South African coal deposits suitable for cheap power generation.

Coal is found in eastern and south-eastern Mpumalanga and in the northern Free State. In Mpumalanga it is generally found at shallow depths and in thick seams, whereas in KwaZulu-Natal the seams are deeper and thinner, but of a higher quality (Eskom, 2011). Internationally, coal is currently the most widely used primary fuel, accounting for approximately 36% of the world's electricity production. This situation is likely to remain unchanged until at least 2020 (Eberhard 2011).

Macintosh et al. (2011) classified coal into four types, depending on its heating value, ash and moisture content, which also determine the extent of the impurities present. Table 1.3 shows the characteristics of the two main types of coal - bituminous and sub-bituminous - which account for over 90% of coal. Pyrite, a mineral rich in iron and sulphur, is a common impurity in bituminous coal. It is also the primary host for arsenic and mercury. Sub-bituminous coal contains substantially less sulphur than bituminous coal and is therefore often favoured by power plants that desire relatively low emission rates of sulphur dioxide. When coal is combusted, the impurities in coal are released into the atmosphere (Macintosh et al., 2011).

The average concentration of hazardous substances present in various types of coal as reported by USEPA is shown in Table 1.3. In comparison, sub-bituminous coal contains two to three times lower concentration of many substances that become hazardous air pollutants (HAPs) than bituminous coal when emitted from the exhaust stack of a power plant. However, sub-bituminous coal has a lower heating value than bituminous coal and as a result, more sub-bituminous than bituminous coal must be burned to produce the same amount of electricity. That means the emission of mercury and non-mercury HAPs from the two main types of coal can be comparable for a given amount of electricity output, even though concentrations of HAPs in the types of coal are different (Macintosh et al., 2011).

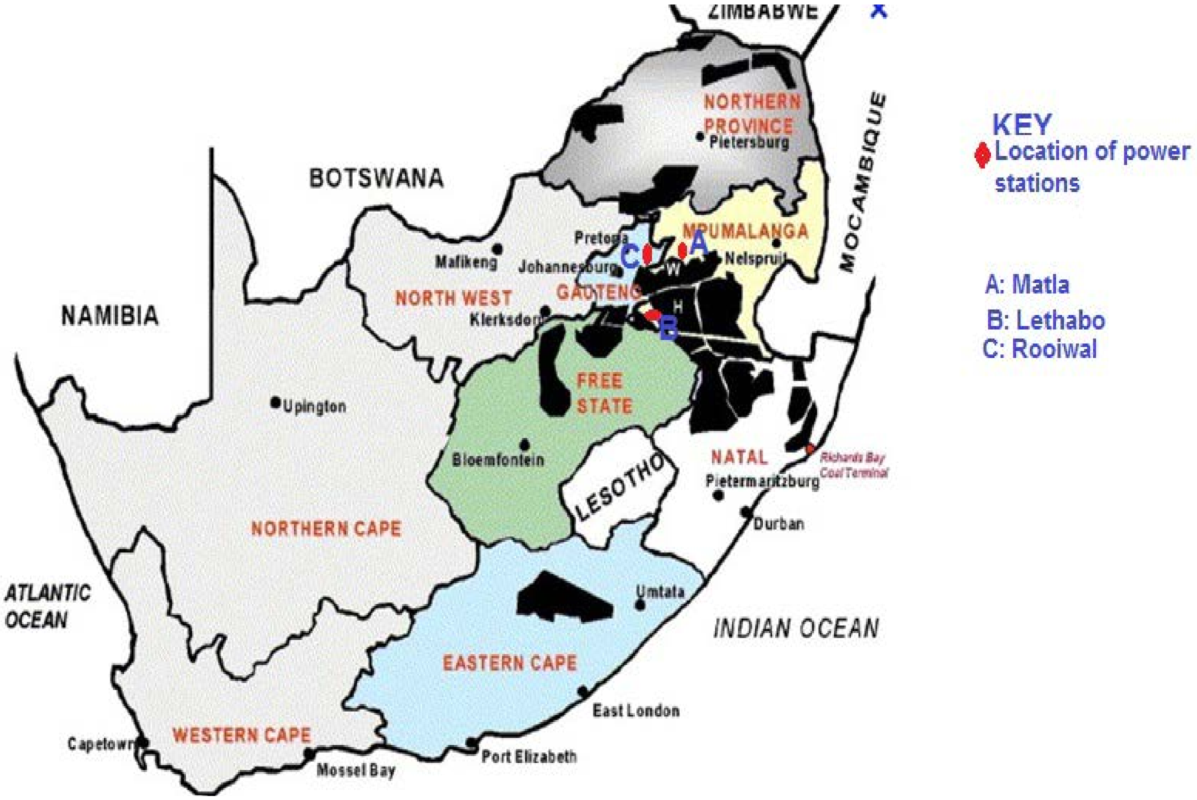


Figure 1.2: The distribution of the South Africa coalfields in Mpumalanga, Free State, Gauteng, Northern Province, Eastern Cape and Kwazulu Nata.

Table: 1.3 Characteristic of main types of coal used to generate electricity in the USA

Characteristic	**Anthracite**	**Bitunimous**	**Sub-bituminous**	**Lignite**
Principal characteristic				
Percentage of US production	Less than 0.1%	46.9%	46.3%	6.9%
Heating value (BTU/lb ^{1})	15	11-15	8-13	4-8
Sulphur %	Less than 1%	3-10%	Less than 1%	Less than 1%
Hazardous air pollutants in coal^2				
Arsenic	NR	0.5	0.1	0.3
Berylium	NR	0.11	0.03	0.2
Cadmium	NR	0.03	0.11	0.06
Chlorine	NR	35	2.7	24
Chromium	NR	1.1	0.4	2.2
Lead	NR	0.6	0.2	1.0
Manganese	NR	1.8	1.3	20
Mercury	NR	0.007	0.006	0.03
Nickel	NR	0.9	0.4	1.2

SOURCE: http://www.ket.org/trips/coal/agsmm/agsmmtypes. (8/07/2011)
1= British Thermal units per pound of coal; a measure of energy density of coal.
NR= Not reported
2=Geometric mean concentration of selected element in coal; units pounded per billion BTU (Maclntoch et al., 2011).

1.16 Coal and electricity

The requirement of electricity cannot be over-emphasized; people need electricity for their everyday lives, which includes aspects such as health and the provision of safe drinking water as well as industrial production. As some of the millennium development goals are met by the Government, such as alleviating poverty, the demand for electricity will increase**.** Coal plays a vital role in electricity generation worldwide and coal-fired power plants currently fuel 41% of global electricity (Table 1.4). In some countries, coal fuels a higher percentage of electricity and that may continue beyond 2030; the use of coal for electricity may even rise to 44% worldwide (www.world coal.org/coal/uses of coal/coal-electricity-8/07/2011).

Table: 1.4 Percentage of coal used in electricity generation

South Africa 93%	Poland 92%
P R China 79%	Australia 77%
Kazakhstan 70%	India 69%
Israel 63%	Czech Republic 60%
Morocco 55%	Greece 52%
USA 49%	Germany 46%

(Source: www world coal.org/coal/uses of coal/coal-electricity-8/07/2011)

1.17 Major domestic coal consumers in South Africa

1.17.1 Eskom's coal-fired power stations

South Africa's power industry is dominated by the state-owned national utility, Electricity Supply Commission (Eskom), which generates 96% of the country's electricity. In 2009 Eskom's total generating capacity was 40,870 MW and 233TWh of electricity, of which

34,658 MW and 216 TWh were produced by coal-fired power stations. The power stations burnt 123 Mt of coal, amounting to about 70 % of the total used in South Africa (Eskom, 2010 Annual Report). Eskom's coal-fired power stations use conventional pulverised coal technology, with average thermal efficiencies of 33 %. Coal quality is poor, with average calorific values of 4 500 kcal/kg (19 MJ/kg), ash 29.5 % and sulphur 0.8 % (Eskom, 2010 Annual Report). The quality of coal has been deteriorating in recent years as coal suppliers reserve the higher grades for more lucrative export markets (Eskom 2010 Annual Report). Eskom claims that poor coal quality has resulted in load losses of close to 40% in its Duvha and Matla power stations. The Arnot power station has also had problems with poor coal quality (Eberhard, 2011). Electrostatic precipitators are employed to reduce particulate emissions, but none of the power stations have flue-gas desulphurisation. Eskom currently emits 225 Mt of CO_2 per annum (Eberhard, 2011).

1.17.2 Sasol

Sasol operates the only commercial coal-to-liquids (CTL) fuel-production facilities in the world. Its Secunda plants produce around 160 000 barrels of petroleum per day (just over 25% of South African consumption), as well as a range of petro-chemical products. It is also one of the largest single sources of carbon emissions in the world. It consumes around 44 Mtpa of high ash (35%) and low calorific value (less than 5 000 kcal/kg) coal, amounting to about 20% of domestic coal use. Sasol's total greenhouse gas emissions are 72.7 Mt CO_2 equivalents per annum. The synfuel production at

Sasol’s Secunda plant is likely to increase by 20% in 2015, though not much additional coal production would be required, since additional feedstock will be natural gas from Mozambique and coal fines from stockpiles (Eberhard, 2011).

1.17.3 Industrial and residential coal consumption

Small merchants trade around 2% of domestic coal consumption, mostly to small businesses and households. About one million tonnes is sold into the retail market for domestic space heating during the cold winters of the interior of the South Africa, generating high levels of particulate air pollution. Larger industries, including cement and chemicals, consume a further 8 Mtpa. Finally, metallurgical coal accounts for about 5.4 Mtpa (Eberhard, 2011).

1.18 Climate change concerns

South Africa’s CO_2 emissions from fuel combustion were around 340 Mta in 2006, making it the 15th largest emitter of CO_2 globally. Eskom’s coal-fired power stations account for around 220 Mtpa and Sasol’s CTL plants for about 60 Mtpa. The CO_2 emissions as a result of fuel combustion are 7.22 t CO_2 per annum, compared to an Organisation for Economic Co-operation and Development (OECD) average of 10.93 and a global average of 4.28 t CO_2 per annum. South Africa emits 2.03 kg CO_2/\$GDP compared to a global average of 0.74 and the OECD average of 0.44 kg CO_2/\$GDP (IEA, 2008). This high $C0_2$ emmission has resulted in South Africa making a voluntary offer in Copenhagen in late 2009 to deviate to below a "business-as-usual" greenhouse gas emissions scenario. South Africa has not yet finalised its climate change mitigation policy. Early indications are that the mitigation steps implicit in this offer are beginning to be incorporated into energy planning initiatives and are likely to have an impact on actual investment decisions (IEA, 2008). .

While South Africa might justifiably argue that it is still a developing country or emerging economy and needs to foster rapid economic growth in order to create employment and overcome poverty, it has accepted the reality that its carbon emissions are above the global average and will need to fall to a level of resource usage that is equitable globally (Eberhard, 2011).

1.19 Source identification of PAHs

PAH fingerprints could be used to differentiate between pyrolytic and petrogenic sources. These are characterised by using molecular indexes based on the concentration ratios of selected PAHs (Dominguez et al., 2010). However, one difficulty in identifying the origin of PAH is the possible coexistence of several sources of contamination and the transformation processes that PAHs can undergo before deposition in the sediments (Dominguez et al., 2010). The ratio of the sum of methyl phenanthrene to phenanthrene (MP/P) has frequently been used to distinguish petrogenic from pyrogenic PAHs (Yunker et al., 2002; Hwang et al., 2003; Kannan et al., 2005). Table 1.5 shows typical MP/P ratios, which range from 2 to 6 for petrogenic

PAHs and generally lower than 1 for those of pyrogenic origin (Dominguez et al., 2010). In addition, the ratios of phenanthrene to anthracene (P/A) and fluoranthene to pyrene (Fl/Py) have also been applied to assess the contribution of petrogenic or pyrolytic sources of PAHs. A P/A ratio lower than 10 and an Fl/Py ratio higher than 1 are also indications strongly suggesting the pyrogenic origin of PAHs.

Recently Saha et al. (2009) ascertained the strong pyrogenic signature to the PAH in sediments from India, where most industries use coal, coal products and wood as sources of energy (almost 74% of total energy consumption) and use very little crude oil and petroleum (17% of the total energy consumption).

Table: 1.5 Characteristic values of selected molecular ratios for pyrolytic and petrogenic PAHs

Ratio	**Source**		**References**
	Pyrolytic	Petrogenic	
Phen/Anth	< 10	> 15	Baumard et al. (1998)
Flan/Pyr	> 1	< 1	Baumard et al. (1998)
MethylPhen/Phen	< 1	2 – 6	Budzinski et al. (1997)
LMW/HMW	Low	High	Budzinski et al. (1997)

(Dominguez et al., 2010).

1.20 PAH composition stability

Some PAHs are known to react faster than others in atmospheric chemical processes. PAH ratios in the atmosphere may be different from those observed in source emissions (Yunker et al., 2002). Various studies have demonstrated that benzo[a]pyrene, benz[a]anthracene and anthracene degrade photolytically in the atmosphere at much faster rates than their isomers or other commonly measured parent PAHs (Yunker et al., 2002). Ambient air data for Los Angeles shows that anthracene proportions are lowest in daytime and that anthracene undergoes more rapid photochemical reaction in the atmosphere than phenanthrene. In contrast, the fluoranthene/pyrene and indeno[1,2,3-cd]pyrene/benzo[-ghi]perylene isomer pairs degrade photolytically at comparable rates, suggesting that the original composition information is preserved during atmospheric transport (Yunker et al., 2002). Biomass and fossil fuel combustion processes produce aerosols with very different particle sizes and physical properties (Schmidt & Noack 2000; Ge´linas et al., 2001). The differences affect both the dispersion pathways in the environment and the physical protection afforded combustion products such as PAHs (Ge´linas et al., 2001).

Pyrogenic PAHs generally associate with soot-rich particles that protect them from degradation in the atmosphere, water column and sediments. Greater protection would be expected with a larger particle size or with dark-coloured or black substrates (Yunker et al., 2002). The charred black carbon of wood soot consists of large, dark, particles (Schmidt & Noack, 2000) that provide a solid matrix that traps and stabilises PAHs. Accordingly, it is likely that charred vegetation from wildfires affords much greater protection against photolysis than is observed for carbon black or other black soot from fossil fuel combustion (Yunker et al., 2002). During summer, motor vehicle emissions are a major atmospheric source of PAHs in the Fraser basin of urbanised areas in Vancouver (Canada), while forest fires are a major (if episodic) source in rural areas.

Given the predominantly sunny conditions in British Columbia in summer, PAHs from vehicle emissions would exhibit a first-order concentration decrease with exposure to sunlight, with most photo-reactive components (anthracene, benz[a]anthracene and benzo[a]pyrene) disappearing very quickly (Yunker et al., 2002). Under summer atmospheric conditions these PAHs would not be transported far, and are probably best used as local urban indicators.

Given the larger particle size of wood soot, PAHs from forest fires will also not travel far, but they will be better protected against photolytic degradation. The wood combustion PAH signature could survive the transfer from the atmosphere to soil and into sediments (Yunker et al., 2002). During winter in Canada, both residential softwood burning and fossil fuel (motor vehicle and furnace) emissions are prominent sources of atmospheric PAHs. At this time photolysis can be expected to be negligible owing to the low angle of the sun and the substantial reduction in the photolytic degradation of particle-associated PAH at lower temperatures and humidity (Yunker et al., 2002). At the coast, winter is a time of typically cloudy conditions and frequent heavy rain could produces a rapid flushing of atmospheric particulate into stormwater drains, sewers and rivers. Because most of the suspended particulate samples in rivers were obtained in autumn and winter, the original PAH composition would be largely preserved in these samples. In inland areas, aerosols accumulate in the snow pack over winter and PAHs are carried into rivers and lakes with the spring snow melt, probably with minimal photolytic degradation. The fraction of PAHs lost by solubilization or biodegradation in the water column or sediment is also dependent on the degree of physical protection. PAHs in oil or on the surface of particles will weather and degrade, while PAHs encapsulated in charred matter, soot, bitumens, tyre particles and asphalt would be protected from degradation and the composition will be preserved in sediments (Yunker et al., 2002).

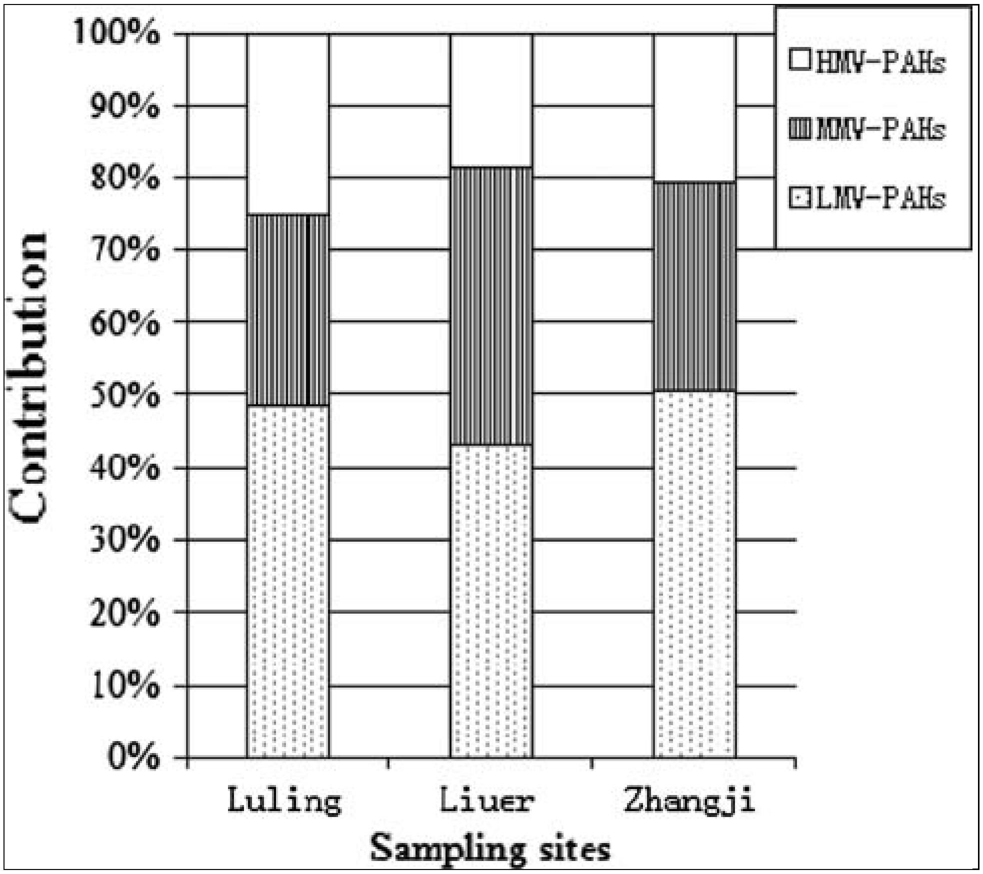
1.21 PAH compound profiles in soil

Wang et al. (2010) assessed the PAH homologue distribution in three different coal mines. They divided the priority PAHs into three groups according to molecular weight (or number of rings): LMW PAHs: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flo), phenanthrene (Phen), anthracene (Anth), containing two and three rings), medium molecular weight (MMW) PAHs: flouranthene (Flan), pyrene (Pyr), chrysene (Chry), benz(a)anthracene (B[a]a), with four rings), and high molecular weight (HMW) PAHs: benzo(b)flouranthene (B[b]f), benzo(k)flouranthene (B[k]f), benzo(a)pyrene (B[a]p), indeno(123-cd)pyrene (Ind), dibenzo(ah)anthracene (DB[ah]A), benzo(ghi)perylene (B[ghi]P), with five and six rings. PAH profiles with regard to the molecular weight of PAHs at three different coal field in China (Luling, Liuer and Zhangji) are plotted in Fig. 1.5 (Wang et al., 2010). A high proportion of LMW PAHs (46.3–59.5%), followed by MMW PAHS (28.6–37.2%), was found. At the Liuer coal mine, a higher percentage of MMW PAHs was detected, which can be seen clearly in Fig. 1.5. According to a previous study, MMW PAHs were dominant in all the fly ash generated from the four largest power stations in Greece (Arditsoglou et al., 2004). According to Wang et al. (2010), the predominance of MMW-PAHs in soils from the Liuer coal mine might be due to the presence of a coal-fired power plant in the immediate vicinity. In addition to the variation in the total content of PAHs groups, the individual PAHs also show variations. Table 1.6 shows the distribution of the analysed PAHs.

Nap and Ace were the most abundant species at three sampling sites, with average concentrations ranging from 0.100 to 0.174 µg/g and 0.095 to 0.158 µg/g, respectively, and arithmetic means of 0.129 ± 0.039 µg/g and 0.130 ± 0.031 µg/g, respectively. At the Liuer site, the four-ring species Pyr and B[a]a were dominant. Predominance of the HMW species B[b]f and B[a]p was observed only at the Luling site. Compared to other PAHs, two-, three- and four-ring PAHs were most dominant in general at all sites.

A previous study, Agarwal et al., (2009). Showed that the predominance of LMW PAHs in agricultural soils reflected recent pollution because the lighter PAHs are more biodegradable and less lipophilic and are not expected to persist or to be sorbed as strongly as the heavier PAHs. Open burning of agricultural residue is a common practice in rural areas of Tianjin in northern China, which is characterised by LMW PAHs (Nap, Ace, Phen, and Flan) (Kakareka & Kukharchyk, 2003). Several other previous studies showed that native PAHs in Saar coals (70–165 µg/g EPA-PAH) were the main reason for elevated PAH concentrations in the Saar and Mosel River floodplain soils in Saarland, Germany downstream from mining activity (Hofmann et al., 2007; Pies et al., 2008a., 2008b; Yang et al., 2007, Yang et al., 2008a, 2008b). It also indicated that despite heavy mining activity of 50–200 years, naphthalene and alkylated derivatives still dominated the PAH patterns in the floodplain soils (Pies et al., 2008a, 2008b). Xue et al. (2007) determined the PAHs in bituminous coal samples from Huaibei and Huainan coalfields in southern North China. They found that the higher concentration of naphthalene and very lower concentration of HMW PAHs were similar to those found in coal, according to Wang et al. (2009), which indicated that the PAH contamination in soil of China was associated with coal and coal-derived particles.

The result shown is in accordance with a previous study (Yang et al., 2008b), which indicated that the high concentration of naphthalene and methylnaphthalene might result from the large amount of raw coal particles. Nevertheless, it remains difficult to identify PAH contamination derived from particulate coal, mainly because of the lack of information on native coal-bound PAHs in soils. A recent study by Stout and Emsbo-Mattingly (2008) also showed that PAH distributions and indexes varied with coal rank and they concluded that particulate coal in soils and sediments cannot be universally represented by a single set of diagnostic parameters based on the samples investigated.



SOURCE: Wang et al., 2010,

Fig: 1.3 Percentage composition of molecular-weight distribution of PAHs in soil of three coal fields, Liling, Liuer and Zhangli, in China

Table 1.6: Individual PAH concentration (µg/g) at three coal fields at Luling, Liuer and Zhangji

PAHs	**Luling**	**Liuer**	**Zhangji**	**Average**	**SD**
	n=18	n=9	n=6		
Naphthalene	0.174	0.112	0.1	0.129	0.039
Acenaphthylene	0.062	0.014	0.021	0.032	0.025
Acenaphthene	0.158	0.136	0.095	0.13	0.031
Fluorene	0.06	0.025	0.036	0.04	0.017
Phenanthrene	0.045	0.043	0.038	0.042	0.004
Anthracene	0.073	0.031	0.022	0.042	0.027
Fluoranthene	0.063	0.091	0.04	0.064	0.026
Pyrene	0.078	0.117	0.049	0.081	0.034
Benzo[a]anthracene	0.063	0.085	0.067	0.071	0.012
Chrysene	0.078	0.053	0.018	0.049	0.030
Benzo[b]fluoranthene	0.086	0.046	0.033	0.055	0.028
Benzo[k]fluoranthene	0.065	0.021	0.023	0.036	0.024
Benzo[a]pyrene	0.072	0.014	0.018	0.034	0.032
Dibenzo[ah]anthracene	0.041	ND	ND	0.041	0
Benzo[ghi]perylene	0.032	0.071	0.045	0.049	0.019
Indeno(123,cd)pyrene	ND	ND	0.007	0.007	0

SOURCE: Wang et al., 2010
Note: ND = non-detected

1.22 Toxicokinetics

1.22.1 Absorption

PAHs are highly lipid-soluble and are absorbed from the lung, gut and skin of mammals. Clearance of the PAHs from the lungs is best described as biphasic. For radiolabelled anthracene, benz[a]anthracene, 1-nitropyrene, BaP, 6-nitrobenzo[a]pyrene and dibenzo[c,g]carbazole, more than 85% of the initial dose was cleared with a half-time of less than 1 h. The half-times for removal of the residual radioactivity (1–15% of the dose) ranged from 26–63 hours (Wolf et al., 1989; Weyand & Bevan, 1986). However, inhaled PAHs were predominantly adsorbed on soot particles. After deposition in the airways, the particles can be eliminated by bronchial clearance. PAHs might be partly removed from the particles during transport on the ciliated mucosa and may penetrate into the bronchial epithelium cells where metabolism takes place. When B[a]p is adsorbed on particles, the respiratory uptake rate is lower, since the particles are retained for a long time in the respiratory tract (Tornquist et al., 1985). When radiolabelled B[a]p adsorbed on diesel engine exhaust particles was inhaled by rats, lung clearance of the inhaled particle-associated radioactivity occurred in two phases. The initial rapid clearance had a half-life of less than 1 hour.

The second, long-term component had a half-life of 18 days and represented 50% of the radioactivity that had initially been deposited in the lungs (Sun et al., 1984). Similar results were obtained when BaP was adsorbed on urban air particles (Tornquist et al., 1985). B[a]p and other PAHs, such as phenanthrene and pyrene, rapidly penetrate the skin of mice and rats. In mice, 80% of B[a]p was recovered from faeces after seven days, while a total of 42% was recovered from faeces and urine in rats (Yang et al., 1986). Absorption through human skin has also been demonstrated (Kao et al., 1985).

1.22.2 Distribution of PAHs within organisms

Irrespective of the route of administration, PAHs are rapidly and widely distributed in the organism. The pattern of distribution of B[a]p was found to be similar after subcutaneous, intravenous and intratracheal administration to mice and rats. Detectable levels of B[a]p could be observed in most internal organs from minutes to hours after administration. The highest levels were obtained in the liver (IARC, 1989). Mammary and other fatty tissues are significant storage depots for PAHs, but owing to the rapid metabolism, no significant accumulation seems to take place. The gastrointestinal tract contains relatively high levels of metabolites as a result of hepatobiliary excretion (Wiersma & Roth, 1983).

For pyrene, the distribution to the tissues was highest in the perirenal fat, intermediate in the liver, kidneys and lungs, and lowest in the heart, testes, spleen and brain. B[a]p could readily cross the placental barrier of rats and mice (Neubert & Tapken, 1988;

Withey et al., 1993), consistent with the fetal and developmental toxicity of the substance.

1.22.3 Excretion

Elimination through the faeces is the major route by which B[a]p is removed from the body, irrespective of the route of administration (Vande Wiel et al., 1993).

Urine is the other major excretory route, although it is quantitatively of minor importance compared to the bile. Exposure of humans to PAH is primarily through ingestion and inhalation. Dermal contact in both occupational and non-occupational settings is another important way of exposure to PAHs (ATSDR, 1995). PAHs are highly soluble in fats. In this form they can rapidly enter cells and become virtually unavailable for excretion. Metabolic processes tend to make PAHs more water-soluble, which facilitates excretion (MOE, 1997).

1.23 PAH formation and emission mechanisms

In any fuel combustion, PAH formation and emission mechanisms can be classified into two processes: pyrolysis and pyrosynthesis (Mastral et al., 2000). On heating, the organic compounds are partially cracked to smaller and unstable fragments (pyrolysis). These fragments, mainly highly reactive free radicals with a very short average lifetime, lead to more stable PAH formation through recombination reactions (pyrosynthesis). That means B[a]p and other PAH are formed through pyrolysis processes of methane, acetylene, butadiene and other compounds (Mastral et al., 2000). PAH formation in combustion has also been explained as being like a waterfall mechanism in which PAH compounds are formed through small radicals, to which radicals add forming compounds of higher molecular weight, soot and fullerenes (Mastral et al., 2000). In combustion processes, tars are also produced as a consequence of condensation of released emissions; the typical reactions of PAH formation in tars have been explained through dehydrogenating polymerisation processes together with an aromatisation process (aromatisation growth) (Mastral et al., 2000). Intermolecular reassociations, fragmentation reactions (due to hydrogen transfer and posterior division of simple C-C bonds formed initially) and alkylation reactions have also been observed (Mastral et al., 1997). It has also been shown that temperature affects the initial deposit formation mechanism of soot, influencing PAH quantities found. PAHs were also detected in diesel soot by high performance liquid chromatography (HPLC), where emissions of mutagenic and carcinogenic PAH were low but the emissions of comparatively harmless compounds were high (Mastral et al., 2000).

1.24 Routes of exposure for PAHs

Some exposure may involve more than one route simultaneously, affecting the total absorbed dose (such as dermal and inhalation exposure from contaminated air). All non-workplace sources of exposure, such as diet, smoking, and burning of coal and wood, should be taken into consideration. PAH concentrations in air can vary from less than 5 to 200 000 nanograms/cubic metre (ng/m^3) (Cherng et al*.,* 1996; Georgiadis &

Kyrtopoulos, 1999). Although environmental air levels are lower than those associated with specific occupational exposures, they are of public health concern when spread over large urban populations (Zmirou et al*.,* 2000). The background levels of 17 of the Agency for Toxic Substances and Disease Registry's toxicological profile priority PAHs in ambient air were reported to be 0.02–1.2 ng/m^3 in rural areas and 0.15–19.3 ng/m^3 in urban areas (ATSDR 1995).

Cigarette smoking is another source of air exposure. It has been reported that one cigarette can yield an intake of 20–40 ng of benzo (a) pyrene. The level of exposure from smoking one pack of unfiltered cigarettes per day is about 0.7 µg/day of benzo(a)pyrene. Smoking a pack of filtered cigarettes per day could yield 0.4 µg/day (Sullivan & Krieger, 2001; ATSDR 2009). Environmental tobacco smoke contains a variety of PAHs, such as benzo(a)pyrene, and more than 40 known or suspected human carcinogens. Side-stream smoke (smoke emitted from a burning cigarette between puffs) contains PAHs and other cytotoxic substances in quantities much higher than those found in mainstream smoke (exhaled smoke of smoker) (Jinot & Bayard, 1996; Nelson, 2001). Tobacco smoking leads to higher levels of PAHs in smokers (Chuang et al., 2003; Adonis et al., 2003; Heudorf & Angerer, 2001b) as well as in the non-smoking children of smokers (Tsai et al., 2003). Soil contains measurable amounts of PAHs, primarily from airborne fallout. Documented levels of PAHs in soil near oil refineries have been as high as 200 000 micrograms per kilogram (µg/kg) of dried soil. Levels in soil samples obtained near cities and areas with heavy traffic were typically less than 2000 µg/kg.

In non-occupational settings, up to 70% of PAH exposure for a non-smoking person could be associated with diet (Skupinska et al., 2004). Charring meat or barbecuing food over a charcoal, wood, or other type of fire greatly increases the concentration of PAHs. For example, the PAH level for charring meat could be as high as 10–20 µg/kg (Phillips, 1999). Charbroiled and smoked meats and fish contain more PAHs than do uncooked products, with as much as 2.0 µg/kg of benzo(a)pyrene detected in smoked fish.

Some crops, such as wheat, rye and lentils, may synthesise PAHs or absorb them via water, air or soil (ATSDR 2009). PAHs and their metabolites are excreted in breast milk and they readily cross the placenta. The geometric mean of urine concentrations (in nanograms/grams creatinine) of 1-hydroxypyrene for the US population aged six years and older for the survey years 1999–2000 was 74.2, and in the survey years 2001–2002 it was 46.4 (CDC 2005). Higher levels have been noted for residents of industrialised urban areas than in rural or suburban settings (Adonis et al*.,* 2003; Kuo et al., 2004). Many-fold higher levels can be found in workers in certain occupations (Jacob & Seidel, 2002), including aluminum smelting (Alexandrie et al., 2000); diesel engine mechanics (Adonis et al., 2003; Kuusimaki et al., 2004); taxi, bus, and truck drivers (Chuang et al., 2003; Kuusimaki et al., 2004); painters (Lee et al., 2003), boilermakers (Mukherjee et al., 2004); toll booth operators (Tsai et al., 2004); traffic police and coke oven plant workers (Lu et al., 2002; Serdar et al., 2003; Siwinska et al., 2004).

1.25 Standards and regulations for exposure to PAHs

US government agencies have established standards that are relevant to PAH exposure in the workplace and the environment (Table 1.7). There is

- a standard relating to PAH in the workplace, and
- a standard for PAH in drinking water.

Table: 1.7: Standards and regulations for PAHs

Workplace Standards

Agency	**Focus**	**Level**	**Comments**
American Conference of Governmental Industrial Hygienists	Air: workplace	0.2 milligrams per cubic metre (mg/m^3) for benzene-soluble coal tar pitch fraction	8 hours of recommended exposure limit
National Institute for Occupational Safety and Health	Air: workplace	0.1 mg/m^3 for coal tar pitch volatile agents	8 hours of recommended exposure limit
Occupational Safety and Health Administration	Air: workplace	0.2 mg/m3 for benzene-soluble coal tar pitch fraction	Regulation: (benzene soluble fraction of coal tar volatiles) (8-hour permissible exposure limit)
US Environmental Protection Agency	Water	0.0001 mg/L	Maximum contaminant level (MCL) for benz(a)anthracene
		0.0002 mg/L	MCL for benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene
		0.0003 mg/L	MCL for dibenz(a,h)anthracene
		0.0004 mg/L	MCL for indenol(1,2,3-c,d)pyrene

SOURCE: ATSDR 2009

1.26 Toxicity equivalency factors of PAHs

Toxicity equivalent factor (TEF) evaluation is the most popular method used to identify the toxicity of PAHs. TEFs of individual PAHs have been reported by many researchers. Toxicity equivalency concentrations (TEQs) are calculated as the product of summing up the values obtained by TEF values and concentrations of PAHs. The toxicity equation is given by;

$$TEQ = \Sigma (C_i \times TEF_i) \qquad \text{[Equation 1.1]}$$

where,
TEQ: toxic equivalent concentration
Ci: concentration of PAHi.

Petry et al. (1996) used TEFs in assessing occupational and environmental health risks associated with exposure to airborne mixtures of PAHs. They used information of the ratio between airborne concentrations of B[a]p equivalents to the concentrations of B[a]p alone, which could indicate the variation of risk for the different environments. Individual PAH-based BaPeq toxicity estimates were up to one order of magnitude higher than estimates based on BaP concentration measurements and B[a]p-risk from a risk assessment of lung cancer related to occupational exposure. Vyskocil et al. (2004) reported that 1.73% of the cancer suffered by Beijing inhabitants in 2007 was related to inhalation of PAHs in ambient air. Residents of the city run an increasing of cancer caused by the inhalation of ambient air containing HAPs, such as PAHs. Halek et al. (2008) estimated that the annual number of lung cancer cases attributable to carcinogenic PAH compounds in 2005 was 58 persons per million. The B[a]p is the highest carcinogenic contributor, followed by dibenz(a,h)anthracene (DahA), Ind and BbF (Pufulete et al., 2004). However, DahA was suggested as a new surrogate compound to measure the toxicity of particle phase PAHs because its toxicity is almost equal to that of B[a]p. While estimating the toxicity of PAHs in road dust of Ulsan in Korea, Dong and Lee (2009) found a significant correlation coefficient between TEQ and total PAH concentrations.

CHAPTER TWO

2.0 Literature Review

2.1 Air sampling and methods of analysing PAHs

2.1.1 PAH sampling equipment

PAHs released into the environment could be associated with the particulate and/or vapour phase. LMW PAHs are released in a vapour phase into the environment, while HMW PAHs containing five or more rings are adsorbed onto suspended particular matter. PAHs in the atmosphere are mainly collected by two sampling models: active sampling and passive sampling. Active sampling uses deposition or adsorption of target PAH compounds on filters or sorbent materials, through the collection of air particulates onto filters or into sorbent tubes, using a pump. PAHs accumulated on filters or sorbent materials are returned to the laboratory for analysis. In many applications, filters such as quartz fibre filters, glass fibre filters and cellulose filters are used to collect PAHs associated with particulate matter. These filters are highly vulnerable to losing the collected PAHs via volatilization and thus precautions need to be taken to minimise the loss of LMW PAHs. For collecting gaseous PAHs, commonly used sorbents include XAD-2 resin and polyurethanefoam (PUF) because of their high collection efficiencies, chemical stability, easy extractability and low cost.

However, limitations on active sampling include the very high costs of sampling and the loss or volatilization of PAHs during the sampling and handling process. “These disadvantages can be alleviated by using passive sampling methods, which are based on free flow of analyte molecules from the sampled medium to a collecting medium as a result of differences in chemical potentials” (Caslavsky et al., 2004; Lee & Vu, 2010).

Passive sampling has been widely applied to ambient monitoring over broad areas. There are many sampling devices that have been successfully used for passive sampling of PAHs. Semi-permeable membrane devices (SPMDs) have been reported as the devices used most often for passive sampling (Lee & Vu, 2010).

Three basic active sampling models of PAHs are associated with particulate collection equipment:

1. PUF samplers: used for sampling PAHs in both the total suspended particulate and vapour phases
2. High-volume samplers (Tisch sampler, PQ 200 sampler): used for sampling PAHs in PM10 (Particulate Matter Of Size Less Than Or Equal To 10) and PM 2.5
3. Cascade impactor (3, 4 and 9 stages): used for sampling PAHs in different size particles.

Sampling times are restricted to 24 hours to minimise the degradation and loss (volatilization) of collected PAHs. Reduced sampling times and flow rates in the collection of vapour PAHs are important. The use of an annular diffusion denuder, such as an oxidant denuder, with the filter systems, minimises PAH losses during sampling (Lee & Vu, 2010).

2.1.2 Pretreatment of air samples

Before sampling, filters must be wrapped separately in aluminum foil and baked in a muffle furnace at a temperature of 450 °C for 6 hours. After sampling, they are kept under refrigeration at low temperatures to protect them from thermal degradation or loss by volatilization. XAD-2 resins and PUF plugs need to be cleaned by Soxhlet or ultrasonic methods before they are used for sampling as shown in Table 2.1 (Lee & Vu, 2010).

2.1.3 Extraction, concentration and analysis of PAHs

Sampled PAHs are usually extracted using organic solvents such as mixtures of n-hexane, acetone and dichloromethane. Extracted PAHs from solutions may sometimes require preconcentration for analysis if the PAHs are not easily detected at low concentrations. To achieve sufficient detection of PAHs from the sample medium, the following four major types of sample extraction techniques may be used:

1. Soxhlet extraction
2. Ultrasonic extraction
3. Supercritical fluid extraction (SPE)
4. Accelerated solvent extraction (ASE).
5. Pressurised Hotwater Extraction (PHWE)

Traditionally, preconcentration methods popularly used to concentrate extracted PAH samples were rotary evaporators and K-D evaporators. For qualitative and quantitative analysis of extracted PAHs, gas chromatography, combined with mass spectrometry

(GC-MS) or HPLC, are often used. Table 2.2 shows summaries of recent studies of extraction, concentration and analysis of PAHs.

2.2 Typical urban and rural concentrations of PAHs

Concentrations of PAHs are easily affected by locational and seasonal variations. Table 1.9 shows concentrations of total PAHs in urban and rural areas of different regions, based on a recent literature survey (Lee and Vu, 2010). Average PAH concentrations (both gaseous and particle-bound PAHs) were highest in winter and lowest in summer because of higher energy consumption for heating and engine operation of vehicles and facilities during the cold season. Traffic exhaust emissions and domestic coal combustion were the main contributors of PAHs in urban areas, while biomass and domestic coal combustion were the predominant sources of PAHs in rural areas. Sources of PAHs in both urban and rural areas can be derived from industrial areas by the transport of PAHs through the atmosphere. Liu et al. (2007) reported that urban PAH emissions (motor vehicle and coke production) are higher than rural emissions (primarily firewood and straw burning for cooking and heating) in spring, summer, and autumn for point source. However, winter PAH emissions in rural areas were much higher than those in urban areas owing to the abundance of coal, straw, and firewood burning for indoor heating in rural residences and for disposal of agricultural residues (Lee & Vu, 2010).

Table 2.1 Applications of pretreatment and analytical methods for PAHs in particulates

Analyte	15 PAHs	15 EPA-AHs	16 EPA-PAHs	32 PAHs	20 PAHs	16 EPA-PAHs	16 EPA-PAHs	22 PAHs	18 PAHs	16 EPA-PAHs	16 EPA-PAHs	15 PAHs	16 EPA-PAHs	14 PAHs
Pretreatment Method	Soxhlet - Warm extraction method, rotary Evaporation RS – fluorescence detection	ASE extraction (hydrometric), evaporate concentration	Ultrasonic extraction with dichloromethane/n-hexan (1:1) Nitrogen concentration	Ultrasonic extraction with methanol Rotary evaporator and nitrogen concentration	Soxhlet extraction (dichloromethane, >40 cycles), column chromatography on Active silica gel. elute with mixture (n-hexane/dichlorornethane 3:1)	Ultrasonic extraction with dichloromethane/acetone (3:1), SPE extraction	Accelerated solvent extractor with dichloromethane/acetone (1:1), Turbo Vap 500 concentration, UV and fluorescence detection.	Soxhlet extraction by dichloromethane for 8 hours, evaporate concentration	Ultrasonic extraction with dichloromethane, centrifugation, evaporate concentration	Ultrasonic extraction with dichloromethane, rotary evaporation Mass selective detection HP 5972	Ultrasonic extraction with dichloromethane and supercritical fluid extraction, evaporate concentration	Dialysis in hexane for 48 hours, silica gel/alumina column clean-up, elute with dichloromethane/hexane, GPC clean-up	Ultrasonic extraction with dichloromethane/acetone rotary evaporation	Soxhlet extraction using dichloromethane, methanol, acetone Nitrogen concentration, mass selective detector
Analytical Method	HPLC-FLD	GC-MS	HPLC	GC-MS	GC-MS	GC-MS	HPLC	HPLC-UVD HPLC-FLD	HPLC-FLD	GC-MS	GC-MS	GC-MS	RP-HPLC-FLD	GC-MS
Reference	Okuda et al., 2010	Li et al., 2009	Lee & Dong., 2009	Saanio et al., 2008	Lee et al., 2008	Li et al., 2007	Ravindra et al., 2006	Kameda et al., 2005	Ohura et al., 2004	Gou et al., 2003	Park et al., 2002	Lohmann et al., 2001	Li & Ro, 2000	Odabasi et al., 1999

SOURCE: (Lee & Vu, 2010). "RS" IS mode of starting; the lamp is a rapid-start lamp

2.3 Extraction techniques for PAHs in soil

PAHs that consist of fused benzene rings are hydrophobic in nature with very low water solubility. Hence, they tend to adsorb tightly to organic matter in soil, making them less susceptible to biological and chemical degradation**.**

Table 2.2 Concentration of PAHs in various cities

Country	Area	ΣPAHs	PAHs conc. ng/m^3	References
China	Urban Rural	10 -	870 ± 330 710 ± 330	Liu et al., 2008
Belgium	Rural	16	114	Ravindra et al., 2006
Seoul, Korea	Urban	16	89 ± 74.3	Park et al., 2002
Chicago, USA	Urban	16	13-1865	Li et al., 2005
New Delhi, India	Urban	12	668 ± 399 672 ± 388	Sharma et al., 2007
London, UK	Urban	15	166	Halsal et al., 1994
Brazil		14	8.94-62.5	Poppi & Silva, 2005
Tai Chung, Taiwan	Urban Rural Industry	21	220 ± 520 831± 427 1650 ±1240	Fang et al., 2004
Brisbane, Australia	Urban	16	0.4 - 19.73	Lim et al., 2005

SOURCE: (Lee and Vu, 2010).

2.3.1 Soxhlet extraction

Soxhlet extraction has been widely used as a standard technique in the extraction of PAHs from soils and sediments. The Soxhlet extraction technique uses an appropriate solvent via the reflux cycle. Once the solvent has been boiled, the vapour passes through a bypass arm into the condenser, where it condenses and drips back onto the solvent in the thimble. As the solvent reaches the top of the siphon arm, the solvent and extract are siphoned back onto the lower flask; the solvent reboils and the cycle is repeated until the entire sample has been completely extracted into the lower flask. The main disadvantage of this extraction process is the use of large volumes of solvent. In addition to that, this method is time-consuming, as the solvent has to be refluxed for hours to achieve considerable extraction efficiencies (Guerin, 1998; Dean & Xiong, 2000).

Soxhlet extraction has been shown to have relatively poor selectivity for PAHs compared to bulk soil organic matter, with approximately a quarter to one-third of bulk soil organic matter being co-extracted during extraction (Hawthorne et al., 2000). Studies have indicated that the chromatograms of extracts produced via Soxhlet using GC-MS and GC-FID yielded more artefact peaks with branched alkane “humps,” demonstrating that compounds such as n-alkanes and humic substances other than PAHs are co-extracted using the Soxhlet technique (Hawthorne et al, 2000., Graham et al., 2006). Other minor drawbacks of using the Soxhlet apparatus include the likelihood of sample carryover (Chen et al., 1996; Lau et al., 2010). Nonetheless, Soxhlet extraction is still the preferred method because of its comparative extraction results despite the nature of the matrix sample. Not only does Soxhlet extraction yield similar results as methods such as supercritical fluid extraction (SFE), microwave-assisted extraction (MAE), accelerated solvent extraction (ASE), and ultrasonic methods, but the results also show small variations with low relative standard deviations (Lau et al., 2010: Flotron et al., (2003). Statistically, Berset et al. (1999) showed that the Soxhlet method resulted in median values which corresponded to the overall mean of other extraction procedures including ASE, SFE, MAE and sonication. The efficiency of Soxhlet extraction increases with molecular weight, reaching an efficiency range of 84 – 100% for PAHs with more than four rings (Smith et al., 2006).

To improve the Soxhlet extraction technique further, Edward Randall patented the automated Soxhlet extraction method in 1974. It is a two-step procedure, which combines boiling and rinsing such that the total extraction time is reduced while the evaporated solvent condenses rapidly for reuse, reducing the volume of total solvent required. In the improved technology, the extraction thimble is initially lowered directly into the flask containing the boiling solvent to remove residual extractable material, while the extractable materials pass readily from the sample and dissolve into the solvent simultaneously. The level of solvent is then reduced to a level below the extraction thimble such that the configuration mimics the traditional Soxhlet extractor. The PAH is extracted by refluxing condensed solvent and collected in the solvent below the extraction thimble. With improvisation, the PAH extraction efficiencies and precisions were statistically improved, with almost 100% recovery rates **(**Lau et al., 2010). In addition, the compact design of the automated system also allows several samples to be extracted simultaneously with its multiple extraction cells assembly while being run unattended.

2.3.2 Ultrasonication

Ultrasonic agitation, also known as sonication, is a technique that engages the energy of ultrasonic waves with a minimum frequency of 16 kHz in fluid, causing rapid compression and rarefaction of fluid movement, which results in the recurring formation and collapse of microbubbles. This agitation could be performed either by immersing an ultrasonic horn into the sample solvent mixture or placing the sample solvent mixture directly into a sonication bath. The desired ultrasound is generated by means of piezoelectric ceramic attached either to the ultrasonic horn or the walls of the sonication bath (Lau et al., 2010). Sun et al. (1998) claimed that sonication was better than the Soxhlet process because it provided higher extraction efficiencies and was more economical and easier to operate. Likewise, Guerin (1998) noted that similar levels of extraction efficiency than those achieved by the Soxhlet extraction method could be attained through vigorous sonication. However, the level of extraction efficiency was highly dependent on the sample matrix and concentration of contaminants in the sample. Contrary to the observations, other studies have indicated that sonication was less efficient than the Soxhlet method, with relatively low recoveries, particularly for LMW PAHs (44–76%) (Smith et al., 2006).

The power amplitude and duration of sonication need to be carefully controlled in order to avoid extensive exposure to irradiation, which may degrade the contaminants in the sample and reduce the extraction rates of PAHs. The decrease in efficiency during excessive sonication is due to an increase in broken carbonaceous particles and the additional contact surface area, which adsorbs the PAHs more readily, causing a reversed adsorption cycle of PAHs. In addition, further separation techniques such as centrifugation or filtration are required after the extraction process (Lau et al, 2010).

2.3.3 Mechanical agitation

This is a simple, low-cost method that uses agitation or mixing action to extract the PAHs from samples in a shake-flask placed onto a rotary shaker, or with a magnetic stirrer submersed into the flask directly. Although it is an easy handling method with minimal glassware and smaller volumes of extraction solvent, the method has not been as widely used as the Soxhlet method and sonication owing to the lower extraction efficiency and unsatisfactory quantitative results (Dean & Xiong, 2000.; Graham et al., 2006). Though some studies reported that the method was comparable to the Soxhlet technique, the results obtained using mechanical shaking showed larger variations and less selectivity due to the difficulty in quantifying the PAH extracts (Spack et al., 1998.; Berset et al., 1999). Comparable results were only attainable with long shaking times to extend the contact time with the solvent (Kaibe et al., 2008).

2.3.4 Supercritical and subcritical fluid extraction

Supercritical fluids exhibit a continuum of both gaseous and liquid phase properties. Their physical characteristics, including liquid-like density, low viscosity, high diffusivity and zero surface tension, enable them to penetrate almost anything and dissolve most materials into their components. Carbon dioxide, which has a supercritical temperature and pressure of 31^{o}C and 74 bar, respectively, is widely employed in SFE as an environmentally friendly solvent in its supercritical state (Anitescu & Tavlarides, 2006).

In a study by Mi´ege et al. (1998) comparisons between Soxhlet and SFE extraction revealed that the recoveries of PAHs for both methods were almost similar. Although the SFE technique was more difficult to optimise, it provided extraction results with lower relative standard deviation and better selectivity, due to cleaner extracts. Other studies (Anitescu & Tavlarides, 2006) also indicated that SFE removed only 8% of the bulk organic matrix in comparison with Soxhlet extraction or ASE, which extracted a quarter to one-third of bulk soil organic matter. Furthermore, integrated SFE systems allow concentrated extracts to be directed straightaway into the cleanup column, reducing the need to remove the eluate manually. In certain SFE systems, the extracts may also be analysed directly by GC without any cleanup. It prevents extra contamination that may occur during manual handling (Reimer & Suarez, 1995; Berset et al., 1999). However, the high complexity of the SFE process may contribute to inconsistent results. The process should be carried out in different laboratories for more accurate result (Anitescu & Tavlarides, 2006).

2.3.5 Microwave-assisted extraction (MAE)

Another extraction technique is the MAE, in which both solvent and samples are subjected to heat radiation energy attained from electromagnetic wavelengths between 1 m and 1 mm, with frequencies of 300 MHz to 300 GHz. Microwave radiation is preferred to conventional heating because of its rapid heating, which is reproducible and causes less energy loss. Modern designs of microwave ovens include carousels, which can hold at least 12 extraction vessels, allowing simultaneous multiple extractions (Lau et al., 2010). The main advantages of the MAE method are the reductions in solvent usage and time. In comparison to SFE, the cost of MAE is moderately lower (Wang et al., 2007). In addition, this unique heating mechanism provides selective interaction with polar molecules, which greatly enhances the extraction efficiency of PAHs (Letellier et al., 1999). The main drawback of this method is that the solvent needs to be physically removed from the sample matrix upon completion of the extraction prior to further analysis. In certain cases where samples are pretreated with activated copper bars to assist the extraction process, the removal of the copper is necessary for a cleaner extract (Flotron, 2003). Although a subsequent purification step could be implemented to rectify this problem, there may be a possibility of losing analytes or inducing contaminants with additional cooling time for this extra handling. Furthermore, the sample allowance for analysis is limited to 1.0 g, which is insufficient for a homogenous analysis (Shu et al., 2000).

2.3.6 Dispersive liquid-liquid microextraction

Dispersive liquid–liquid microextraction (DLLME) is a relatively novel miniaturised sample pretreatment technique. It is an effective micro-extraction technique, which is carried out between the sample and a cloud of fine extractant drops formed when the mixture of extraction and disperser solvents is injected into an aqueous sample. The contact surface between phases is widely increased, reducing the extraction time and improving the enrichment factor. Basically, DLLME consists of the injection of a suitable mixture of extraction and disperser solvent into an aqueous sample containing the analytes and centrifugation of the cloudy solution formed.

The main advantages of DLLME are simplicity of operation, rapidity, low cost, low sample volume, high recovery and enrichment factor and very short extraction time. The disadvantages of DLLME are that three solvents are needed, the extracting solvent must have a higher density than water to form a cloudy solution that must be removed from the bottom of the conical vial after centrifugation. This limits the choice of suitable solvent and centrifugation must be applied. The method is non-selective and interferences from the matrix often occur, especially in the determination of trace analytes in a complex matrix sample and initial extraction and/or a further cleanup would be needed for samples with complex matrixes. This is the main reason why most reported applications of DLLME have focused on simple water samples (Ojeda & Rojas, 2011). In addition, the DLLME technique is difficult to automate. The use of dispersal solvent is also limited to specific solvents because of the conditions that have to be met.

Modifications to the technique, especially when applying it to solid samples, clearly extend its applicability and may result in the use of relatively high volumes (in the mL range) of a polar solvent such as methanol or acetonitrile to disperse the extraction solvent into the aqueous sample. The use of a disperser organic solvent results in lower extraction efficiency due to increased solubility of the analytes in solution. In addition, the use of relatively high volumes of a harmful solvent is environmentally unfriendly (Ojeda & Rojas, 2011).

2.3.7 Pressurised Hotwater Extraction (PHWE)

The pressurised hot water extraction (PHWE) process uses a combination of high water pressure for agitation, and hot water to increase reaction rate. The application of pressurized water as an extraction fluid at elevated temperatures was first reported in the pioneering work of Hawthorne and co-workers for extraction of some polar and non-polar analytes from soil samples in 1994(Teo, 2010).

Pressurized hot water extraction (PHWE) has become a popular green extraction method for different classes of compounds present in numerous kinds of matrices such as environmental, food and botanical samples. PHWE is also used in sample preparation to extract organic contaminants from foodstuff for food safety analysis and soils/sediments for environmental monitoring purposes. The main parameters which influence its extraction efficiency are namely the temperature, extraction time, flow rates and addition of modifiers/additives. Among these different parameters studied, temperature is described as the most important one.

To reduce the usage of organic solvents, PHWE is a feasible green solvent extraction method as it utilizes pressurized water at elevated temperature and controlled pressure conditions.

Various reports have shown that at certain temperature and applied pressure, the polarity of water can be varied close to those of alcohols. Thus, it can dissolve a wide range of medium and low polarity analytes (Kim et al., 2009; Teo et al., 2009). The major advantage of PHWE is the reduction in the consumption of organic solvents. Moreover, water is easily available, non-toxic and can be recycled or disposed with minimal environmental problems. Hence, PHWE has steadily become an efficient and low cost method of extraction for less-polar organic components from environmental soil, sediments and plant materials (Kronholm et al., 2007 Teo et al., 2009).

2.4 Hazardous air pollution emission

According to USEPA, 2007, coal-fired power plants emit 84 of the 187 HAPs that are known to be environmental and health hazards to humans. Coal-fired power plants account for 40% of the total emission of 386 000 tonnes of HAPs emitted into the atmosphere. Coal power plants are also the single largest source of emissions for many individual HAPs, as shown in Table 2.3 (Macintosh et al., 2011).

Table: 2.3: Contributions of coal-fired power plants to selected hazardous air pollutant emissions

Hazardous Air Pollutant	**Percentage of Point Source Emission**
Acid gases (hydrochloric and hydrofluoric)	76%
Arsenic	60%
Beryllium	28%
Cadmium	30%
Chromium	20%
Cobalt	34%
Lead	15%
Manganese	11%
Mercury	46%
All non-mercury metal HAPs emitted by coal-fired power plants	25%

SOURCE: Macintosh et al, 2011

2.4.1 Toxicological effect of the emissions of coal power plants

A summary of the toxicological effect of coal-fired power plants is given in Table 2.4**.** When these substances are released, they tend to cause irritation and tissue damage to, the skin, eyes and the breathing passages. Long-term exposure to these hazardous substances could have a potential effect on the kidneys, lungs and the nervous system.

For example, long exposure to beryllium could lead to a serious condition called “chronic beryllium disease”.

Exposure to other hazardous substances, such as dioxins, PAHs and volatile organic compounds from coal-fired power plants, may increase the risk of cancer (Macintoch et al., 2011). These HAPs from coal power plants could have long-term effects on the environment by accumulating in soil and water, may eventually end up in the food chain.

Table 2.4: Toxicological and environmental properties of HAPs emitted by electricity-generating stations fuelled by coal

Class of HAP	Acid gases	Dioxins and furans	Mercury	Non-mercury metals and metalloids (excluding radioisotopes)		Polynuclear aromatic hydrocarbons (PAHs).	Radioisotopes		Volatile organic compounds	
Notable HAPs	Hydrogen chcloride, Hydrogen fluoride	2,3,7,8 tetrachlorodioxin (TCDD)	Methylmercury	Arsenic, beryllium, cadmium, chromium, nickel, selenium, manganese.	Lead	Naphthalene, benzo-a-anthracene, benzo-a-pyrene, benzo-b-fluoranthene. Chrysene, dibenzo-a-anthracene	Radium	Uranium	Aromatic hydrocarbons including benzene, toluene, ethylbenzene, xylene	Aldehydes including formaldehyde
Human Health Hazard	Irritation to skin, eye, nose, throat, breathing passages.	Probable carcinogen: soft-tissue sarcomas,lymphomas and stomach carcinomas. May cause reproductive and developmental problems, damage to the immune system and interference with hormones	Damage to brain, nervous system, kidneys and liver. Causes neurological and developmental birth defects	Carcinogens: lung, bladder, kidney, skin. May adversely affect nervous, cardiovascular, dermal, respiratory and immune systems	Damages the developing nervous system, may adversely affect learning, memory, and behavior. May cause cardiovascular and kidney effects, anemia, and weakness of ankles, writs and fingers.	Probable carcinogens. May attach to small particulate matter and deposit in the lungs. May have adverse effect on the liver, kidneys and testes. May damage sperm cells and cause impairment of reproduction.	Carcinogen: lung and bone. Bronchopneumonia, anemia, brain abscess.	Carcinogen: lung and lymphatic system. Kidney disease.	May cause irritation of the skin, eyes, nose, and throat; difficulty in breathing; impaired function of the lungs; delayed response to a visual stimulus; impaired memory; stomach discomfort; and effects to the liver and kidneys. May also cause adverse effects to the nervous system. Benzene is a known carcinogen.	Probable carcinogen: lungs and nasopharyngeal cancer. Eye, nose, and throat irritation, respiratory symptoms.
Environmental Hazards	Acid precipitation, damage to crops and forests.	Deposits into rivers, lakes and oceans and is taken up by fish and wildlife. Accumulation in the food chain	Taken up by fish and wildlife. Accumulates in the food chain.	Accumulates in soil and sediments. Soluble forms may contaminate water system.	Harms plants and wildlife; accumulates in soils and sediments. May adversely affect land and water ecosystem.	Exist in the vapour or particulate phase. Accumulate in soil and sediments.	Deposit into rivers, lakes and oceans and are taken up by fish and wildlife. Accumulate in soil, sediments and in the food chain.		Degrade through chemical reactions in the atmosphere and contribute to carbon-based radicals that contribute to formation of ground-level ozone and its human health effects.	

SOURCE: ATSDR 2009

2.5 Health and environmental impact of coal power plants

Coal-fired power plants are said to be the largest anthropogenic source of corrosive hydrogen chloride and hydrogen fluoride. When released into the atmosphere, hydrogen fluoride tends to remain suspended in the atmosphere and can travel up to 500 km, while chloride is easily deposited onto the soil by wet or dry deposition (Sanhueza, 2001). Exposure to these corrosive acids has been linked with respiratory irritation or haemorrhage, especially in children, because of their narrower airways, faster breathing rate and tendency to spend more time outdoors than adults (Bateson & Schwartz, 2008).

2.5.1 Dioxins

This is another group of HAPs released into the atmosphere by coal-fired power plants. They are composed of carbon and oxygen, to which either hydrogen or chlorine atoms are attached. The position and number of the chlorine atoms determine the type and also influence their toxicity.

The lower chlorinated compounds are easily removed from the atmosphere, while the higher chlorinated compounds are often associated with small particles in the atmosphere for some days during which people can be exposed to them through inhalation (Maclitosh et al., 2011). Most of the higher chlorinated dioxins are deposited onto soil and water bodies. Once ingested, it can take between seven and 12 years for half of the most toxic dioxin to leave the body (ATSDR, 2008d). Short-term exposure may cause liver damage and skin lesions called chlorocne, while long-term exposure attacks the immune system, developing nervous system and reproductive system and can disrupt hormone function.

2.5.2 Radioisotopes

Coal may not contain large amounts of radioactive material, and when large volumes of coal are burned in a power plant, this could lead to a substantial release of radium and uranium into the atmosphere. One study estimated that 100 times more radioactivity is released from a coal-fired plant compared to a nuclear power plant of similar size (McBride et al., 1978).

2.5.3 Mercury

Coal-fired power plants are responsible for about one-third of all mercury emissions from anthropogenic activities (USEPA, 1997). When mercury is emitted, it is carried by winds and eventually deposited on land and water bodies where it is converted by microorganisms into methylmercury, a highly toxic form of mercury.

Mercury can be deposited locally, but it can also travel distances of thousands of kilometres. The distance to which mercury travels depend on the form in which it is emitted, the height at which it is released and the prevailing atmospheric conditions. The health and environmental risks posed by mercury emissions are another addition to the litany of social burdens imposed by coal plants on host communities. Lives change in communities living with coal plants, often for the worse (Greenpeace, 2001). Mercury exposure in high doses can cause ailments such as tremors, inability to walk, convulsions and even death. Women of childbearing age and people who regularly eat highly contaminated fish (or large amounts of moderately contaminated fish) are most likely to be at risk from mercury exposure. The developing foetus is the most sensitive to the effects of mercury, because its brain is developing rapidly. Children of women exposed to relatively high levels of methylmercury during pregnancy have exhibited a variety of abnormalities, including delayed onset of walking and talking, cerebral palsy and reduced neurological test scores. Children exposed to relatively low levels of methylmercury in the womb have exhibited delays and deficits in learning ability. In addition, children exposed after birth are potentially more sensitive to the toxic effects of methylmercury than adults, because their nervous systems are still developing. Short-term exposure to high levels of metallic mercury vapours may cause effects such as lung damage, nausea and vomiting, diarrhoea, increase in blood pressure or heart rate, skin rashes and eye irritation (ATSDR, 1999; USEPA, 2000).

2.5.4 Non-mercury metals

Non-mercury metals that are emitted by coal-fired power plants include arsenic, beryllium, cadmium, chromium, lead, manganese and nickel (Maclitosh et al., 2011). Emissions of these metals are primarily referred to as primary particulate matter (PMs). When they undergo chemical reaction in the atmosphere, they are referred to as secondary PM (Maclitosh et al., 2011). When these PMs are inhaled by people, some are deposited along the respiratory tract, while others penetrate deeply into the lungs and eventually get into the blood stream. Research has shown that metal interacts with particles to generate ‘reactive oxygen species’, which limits the body’s ability to repair damaged cells (Macintosh et al., 2011).

2.5.4.1 Cadmium

Cadmium is generally a non-essential element with teratogenic, carcinogenic and highly nephrotoxic effects on living organisms (Antonin et al., 2010). It is considered non-essential for living organisms. Cadmium is a natural element in the earth’s crust. It is usually found as a mineral combined with other elements such as oxygen, chlorine and sulphur to form oxides and chlorides) and sulphate and sulphide respectively. All soils and rocks, including coal and mineral fertilizers, contain some cadmium. Most cadmium used in the US is extracted during the production of other metals such as zinc, lead and copper. Cadmium does not corrode easily and has many uses, including batteries, pigments, metal coatings and plastics (ATSDR, 2008a).

2.5.4.1a Cadmium in the environment

Cadmium enters soil, water and air from mining, industry, burning coal and household wastes. Cadmium particles in air can travel long distances before falling to the ground or water. Some forms of cadmium dissolve in water. Cadmium also binds strongly to soil particles. Fish, plants, and animals take up cadmium from the environment.

2.5.4.1b Exposure to cadmium

Eating foods containing cadmium; low levels are found in all foods (highest levels are found in shellfish, liver and kidney meats). Smoking cigarettes or breathing in cigarette smoke. Breathing in contaminated workplace air. Drinking contaminated water. Living near industrial facilities, which release cadmium into the air. Breathing in high levels of cadmium can lead to severely damaged lungs. Also, eating food or drinking water with very high levels of cadmium severely irritates the stomach, leading to vomiting and diarrhoea. Long-term exposure, even at lower levels of cadmium, in air, food or water leads to a build-up of cadmium in the kidneys and possible kidney disease. Other long-term effects are lung damage and fragile bones (ATSDR, 2008a).

The OSHA has limited workers' exposure to an average of 5 µg/m^3 for an 8-hour workday, 40-hour work week (OSHA 2010). An amount of 0-1 mg/kg of Cd in soil indicates non-contamination, 1-3 mg/kg indicates slight contamination and 3-10 mg/kg indicates contaminated soil.

2.5.4.2 Lead

Lead is a naturally occurring bluish-gray metal found in small amounts in the earth's crust, but may be found in all parts of the environment. Much of it comes from human activities, which include burning fossil fuels, mining and manufacturing. The US Environmental Protection Agency has classified lead as potentially hazardous and toxic to most forms of life. This element is neither essential for nor beneficial to living organisms and is responsible for a large number of adverse effects on biota (ATSDR, 2007).

2.5.4.2a Lead in the environment

Lead compounds are changed by sunlight, air and water. When lead is released into the air, it may travel long distances before settling to the ground. Once lead falls onto soil, it usually sticks to soil particles. Movement of lead from soil into groundwater will depend on the type of lead compound and the characteristics of the soil.

2.5.4.2b Exposure to lead

Eating food or drinking water that contains lead. Water pipes in some older homes may contain lead solder that could leach out into the water. Spending time in areas where lead-based paints have been used and are deteriorating. Deteriorating lead paint can form lead contaminated dust. Working in an environment where lead is used or engaging in certain hobbies in which lead is used, such as making stained glass. Using health-care products or folk remedies that contain lead.

2.5.4.2c Health effects of lead

The effects of lead are the same whether it enters the body through breathing or swallowing. It can affect almost every organ and system in the body. The main target for lead toxicity is the nervous system, both in adults and children. Long-term exposure of adults can result in decreased performance of the nervous system. It may also cause weakness in fingers, wrists or ankles. Exposure to lead also results in small increases in blood pressure, particularly in middle-aged and older people and can cause anaemia. Exposure to high lead levels can severely damage the brain and kidneys in adults or children and ultimately cause death. In pregnant women, high levels of exposure to lead may cause miscarriage. High-level exposure in men can damage the organs responsible for sperm production (ATSDR, 2007).

2.5.4.3 Chromium

Chromium is a naturally occurring element mostly found in rocks, animals, plants and soil. Chromium exists in several forms. The most common forms are chromium (0), chromium (III) and chromium (VI). It is an odourless compound. Chromium can be found in air, soil and water after being released during the manufacturing process. It does not usually remain in the atmosphere, but is deposited into soil and water.

2.5.4.3a Exposure to chromium

Breathing contaminated workplace air or skin contact during use in the workplace. Drinking contaminated water or eating contaminated food. Living near uncontrolled hazardous waste sites containing chromium or industries that use chromium.

2.5.4.3b Health effects of chromium

The health effects caused by chromium depend on the level and type of chromium metal one is exposed to. The main health problems in animals following ingestion of chromium (VI) compounds are irritation and ulcers in the stomach and small intestine and anemia. Chromium (III) compounds are much less toxic and do not appear to cause these problems. Sperm damage and damage to the male reproductive system have also been observed in laboratory animals exposed to chromium (VI) (ATSDR, 2008b).

2.5.4.4 Copper

Copper is a metal that occurs naturally throughout the environment, in rocks, soil, water and air. It is an essential element in plants and animals (including humans). Plants and animals may absorb some copper from eating, drinking or breathing (ATSDR, 2004).

2.5.4.4a Copper in the environment

Copper could be released into the environment by mining, farming, manufacturing operations and through waste water releases into rivers and lakes. Copper is also released from natural sources, such as volcanoes, windblown dust, decaying vegetation and forest fires. When released into the environment, it is usually attached to particles of organic matter, clay, soil or sand. Though Copper does not break down in the environment, but copper compounds can break down and release free copper into the air, water, and foods (ATSDR, 2004).

2.5.4.4b Exposure to copper

One may be exposed to copper from breathing air, drinking water, eating food, or having skin contact with copper, particulates attached to copper, or copper-containing compounds. Drinking water may have high levels of copper if one’s house has copper pipes and acidic water. Lakes and rivers that have been treated with copper compounds to control algae, or that receive cooling water from power plants, may have high levels of copper. Soil may also contain high levels of copper, especially if they are near copper smelting plants (ATSDR, 2004).

One may also be exposed to copper by ingesting copper containing fungicides, or if one lives near a copper mine or where copper is processed into bronze or brass. One may be exposed to copper if one works in copper mines or if one grinds metals containing copper.

2.5.4.4c Health effects of copper

Everyone requires small amounts of copper every day, because copper is essential for good health. However, high levels of copper could be harmful. Breathing high levels of copper can cause irritation of the nose and throat. Ingesting high levels of copper can cause nausea, vomiting and diarrhoea. Very high doses of copper can cause damage to the liver and kidneys and can even cause death. Exposure to high levels of copper will result in the same type of effects in children and adults. Studies in animals suggest that the young may experience more severe effects than adults, but it is not known if this would also be true in humans. There is a very small percentage of infants and children who are unusually sensitive to copper. It is unknown whether copper can cause birth defects or other developmental effects in humans. Studies in animals suggest that high levels of copper may cause a decrease in foetal growth (ATSDR, 2004).

2.5.4.5 Manganese

Manganese is a naturally occurring metal that is found in many types of rocks. Pure manganese is silver-coloured, but does not occur naturally. It combines with other elements such as oxygen, sulphur or chlorine. Manganese is used principally in steel production to improve hardness, stiffness and strength. It may also be used as an additive in gasoline to improve the octane rating of the gas (ATSDR, 2008c).

2.5.4.5a Manganese in the environment

Manganese can be released to the air, soil and water from the industry and through disposal of manganese-based products. In water, manganese tends to attach to particles in the water or settle into the sediment. The chemical state of manganese and the type of soil determine how fast it moves through the soil and how much is retained in the soil. The manganese-containing gasoline additive may degrade in the environment quickly when exposed to sunlight, releasing manganese.

2.5.4.5b Health effects of manganese

Manganese is an essential nutrient and ingesting a small amount of it each day is important to stay healthy. The most common health problems of high exposure to manganese involve the nervous system. These include movements that may become slow and clumsy, associated with irreversible brain disease with prominent psychological and neurological disturbances. This combination of symptoms, when sufficiently severe, is referred to as "manganism". Individuals with manganism resemble patients with Parkinson’s disease. Other less severe nervous system effects, such as slowed hand movements, have been observed in some workers exposed to lower concentrations in the workplace. Nervous system and reproductive effects have been observed in animals after high oral doses of manganese (ATSDR, 2008c).

2.5.4.6 Zinc

Zinc is one of the most common elements in the earth's crust. It is found in air, soil and water and is present in all foods. Pure zinc is a bluish-white shiny metal.

2.5.4.6a Zinc in the environment

Zinc can be released into the environment by natural processes, but most comes from anthropogenic activities such as mining, steel production, coal burning and burning of waste. When zinc is released into the environment, it binds to soil, sediments, and dust particles in the air. Rain and snow remove zinc dust particles from the air. Depending on the type of soil, some zinc compounds can move into the groundwater and into lakes, streams and rivers. It builds up in fish and other organisms, but it does not build up in plants (ATSDR, 2005a).

2.5.4.6b Health effects of zinc

Zinc is an essential element in the human diet. While too much zinc is harmful, too little zinc can also cause problems. Harmful effects generally begin at levels 10-15 times higher than the amount needed for good health. Large doses taken by mouth, even for a short time, can cause stomach cramps, nausea and vomiting. Taken longer, it can cause anaemia and reduce the levels of normal body cholesterol. Infertility was observed in rats that were fed large amounts of zinc. Inhaling large amounts of zinc (as dust or fumes) may lead to a specific short-term disease called metal fume fever. The long-term effects of breathing in high levels of zinc could result in skin irritation in people (ATSDR, 2005a).

2.5.4.7 Nickel

Pure nickel is a hard, silvery-white metal, which has properties that make it very desirable for combining with other metals to form mixtures called alloys. Nickel combined with other elements occurs naturally in the earth's crust. It is found in all soils and is also emitted from volcanoes (ATSDR, 2005b). It is the 24th most abundant element. Nickel is released into the atmosphere during nickel mining and by industries that make or use nickel, nickel alloys or nickel compounds. These industries might also discharge nickel in waste water. Nickel is also released into the atmosphere by oil-burning and coal-burning power plants and trash incinerators (ATSDR, 2005b; Environment Agency, 2010).

2.5.4.7a Nickel in the environment

Nickel may be released into the environment from the stacks of large furnaces used to make alloys or from power plants and trash incinerators. The nickel that comes out of the stacks of power plants binds to small particles of dust that settle to the ground or are taken out of the air in rain or snow. It usually takes many days for nickel to be removed from the air. If the nickel is attached to very small particles, it can take more than a month to settle out of the air. Nickel can also be released in industrial waste water.

A lot of nickel released into the environment ends up in soil or sediment, where it strongly attaches to particles containing iron or manganese. Under acidic conditions, nickel is more mobile in soil and might seep into groundwater. Studies show that some plants can take up and accumulate nickel. However, it has been shown that nickel does not accumulate in small animals living on land that has been treated with nickel-containing sludge (ATSDR, 2005b; Environment Agency, 2010).

2.5.4.7b Exposure to nickel

Skin contact with soil, bath or shower water, or metals containing nickel, as well as metals plated with nickel, can also result in exposure.

2.5.4.7c Health effects of nickel

The most serious harmful health effects from exposure to nickel, such as chronic bronchitis, reduced lung function and cancer of the lung and nasal sinus, have occurred in people who have been exposed to dust containing certain nickel compounds (ATSDR, 2005b).

2.6 Transport of hazardous materials from coal-fired plant

The extent to which a coal-fired power plant influences the environment locally, regionally and globally depends on; (1) how long a given pollutant remains in the air, (2) the physical attributes of the power plant, (3) weather and (4) the proximity of human populations. What determines the effect of pollution from a coal power plant is the atmospheric residence time of pollutants. This can be influenced by how far HAPs are carried by wind and accompanying weather systems (Macintosh et al., 2011). Representative atmospheric residence times are shown in table 2.5.

Table: 2.5 Residence time of hazardous air pollution in the atmosphere

HAP Group	**Indicator Pollutant(s)**	**Residence Time**
Mercury	Methylmercury	7-10 days
Metals	Arsenic	7-9 days (lifetime)
	Beryllium	10 days (lifetimes)
	Cadmium	1-10 days (lifetime)
	Chromium	Up to 7-10 days
	Nickel	Up to 30 days (half-life)
	Manganese	Several days (half-life)
	Selenium	1-10 days
	Lead	Up to 10 days
Radioisotopes	Uranium, Radium	Not reported
Dioxins/Furan	Chlorinated dibenzo-p-dioxins	0.5-9.6 days (lifetime)
	Dibenzofurans	4 days (half-life)
	Chlorodibenzofuran (CDFs)	More than 10 days (half-life)
Aldehydes	Formaldehyde	<20 hours (half-life)
Volatile Organic Compounds	Benzene	4-6 hour (half-life in presence of NOx and SO2)
	Xylene	8-14 hours (half-life)
	Toluene	13 hours (half-life)
	Ethylbenzene	2 days (half-life)
Acid Gases	HCl/HF	1-5 days (half-life)
	HCN	530 days (half-life)
Polycyclic Aromatic Hydrocarbons (PAHs)	Benzo-a-anthracene, Benzo-a-pyrene, Fluoranthene, Chrysene and Dibenzo-a-Anthrance	Up to several days (lifetime)

SOURCE: (Macintosh et al. 2011)

Hydrogen fluoride, hydrogen chloride and mercury are among the notable coal-fired HAPs that can be relatively short-lived in the atmosphere. Environmental and health imparts of these HAPs are likely to be concentrated in the vicinity of the power plants from which they are released. Longer-lived HAPs are also present in the immediate vicinity of the source before being transported to other areas (Macintosh et al., 2011).

Levy and Spengler (2002), in their study of coal-fired power plants, found that public health damage per person is two to five times greater for communities near the facilities than for populations living at a greater distance from the plants. In addition to weather, the height of the emission stacks also influences the magnitude of the impact of coal-fired power plants. Lower stacks result in a higher impact near the source than taller stacks. This can be illustrated in figure 2.1. The greatest ground-level impacts of HAPs emission from any given coal-fired power plant typically occur within a mile of the facility (Macintosh et al., 2011).

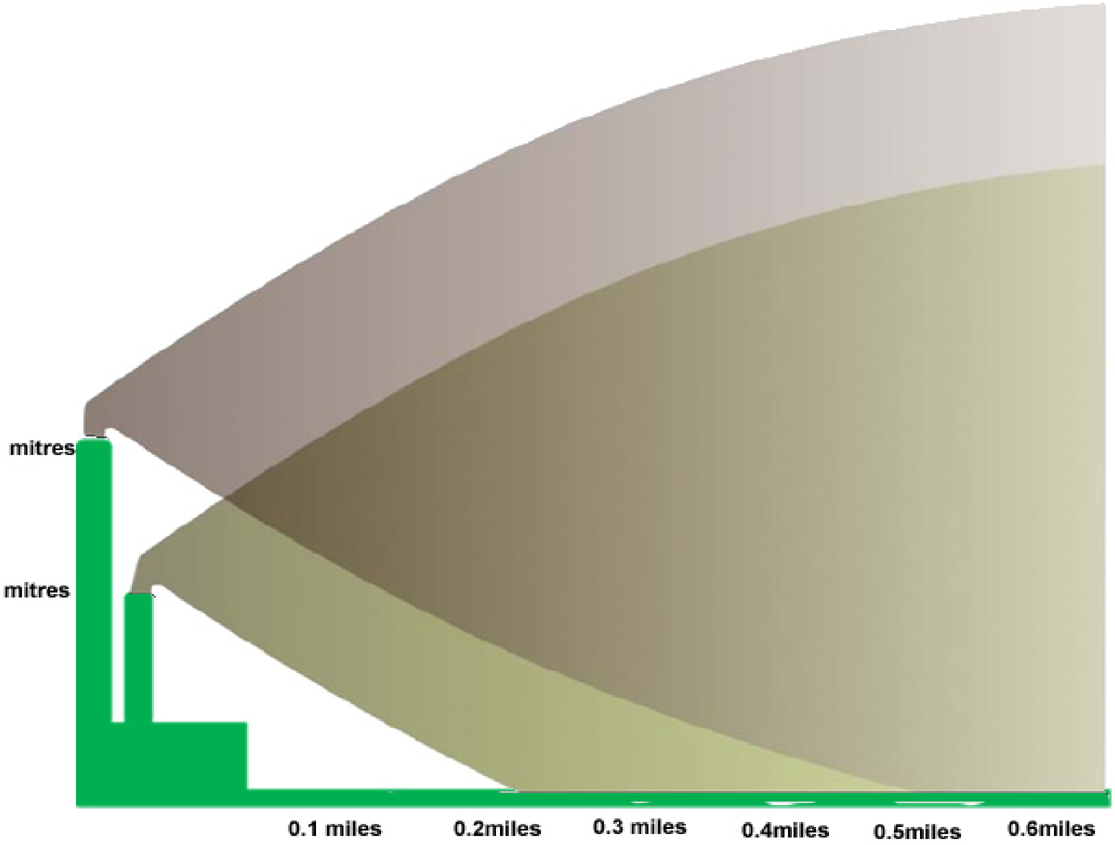


Figure: 2.1 Schematic diagram of location of initial ground-level impacts in relation to height of hazardous air pollutant release

CHAPTER THREE

RESEARCH METHODOLOGY

3.0 Materials and Method

3.1: Description of study areas

Matla power plant is located in Mpumalanga Province (26.28249ºS 29.14072°E). The plant has the capacity of generating 3600 MW installed capacity and it has been in operation since 1983. Lethabo power plant is located in the Free State Province (26.74194°S 27.9775°E) and has been in operation since 1985. It has a generating capacity of 3708 MW of electricity. Rooiwal power plant is located in Gauteng Province (25.55580°S 28.23834°E). The plant has been in production since 1963 and has an installed capacity of 300 MW of electricity. In all three plants combustion gases are released through two stacks and local sub-bituminous coal is used in all of them (Fig 1.2).

Fig 3.1. Picture of power plant showing two stacks where emission is released and four coolants

3.2: Materials and reagent

PAHs considered in this study included naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[e]acephenantrylene, benzo[k]flouranthene, benzo[a]pyrene, perylene, and indeno[1,2,3-cd] pyrene). All PAH standards were of 98.0 to 99.5% purity and were purchased from Sigma (Seelze, Germany). The solvents used for the extractions and clean-up were of analytical grade (99.5 %). Solvents were also from Sigma-Aldrich and included hexane, acetone, methanol, dicholoroethene, dichloromethane and chloroform. Acetonitrile (MeCN) was purchased from Romil (Waterbeach, Cambrigde, UK). Silica gel used in column clean-up was purchased from Merck (Darmstadt, Germany). Standard reference material soil from Industrial Analytical Ltd (Midrand, South Africa) Ltd with Catlog No: CRM 142-100 and Lot No: 014105 was used.

3.3: Soil samples

About 500 g of surface soil (0–5 cm depth) samples were collected with the aid of a stainless steel trowel in the predominant wind direction, 0 to 30 km from the coal power plant for Matla and Lethabo and 0 to 20 km for Rooiwal coal power plant. Plant samples were also collected at the same point where the soils were taken. The plant was washed thoroughly in distilled water so as to remove superficial dust. The samples were allowed to dry in an oven at a temperature of 60 °C for a period of 48 h. Samples were collected six times between August 2010 and June 2011 with the aid of the global positioning system (GPS) to ensure sampling from the same area. In each sampling site, seven composite samples were collected. The control samples were collected from the greenhouse at the University of South Africa. It is a controlled area with reduced human activities. All soil samples were air-dried, pulverised and stored in amber bottles at 0–4 °C until chemical analysis (Okedeyi et al., 2012).

Digitaria is a genus of about 300 species of grass (family Poaceae) native to tropical and warm temperate regions. Common names include crabgrass, finger-grass, and fonio. They are slender monocotyledonous annual and perennial lawn, pasture, and forage plants; some are often considered lawn pests. Digitus is the Latin word for "finger", and they are distinguished by the long, finger-like inflorescences they produce.

Crabgrasses have uses despite being classified by many as weeds. The seeds, most notably those of fonio, can be toasted and ground into a flour, which can be used to make porridge or fermented to make beer. Fonio has been widely used as a staple crop in parts of Africa. It also has decent nutrient qualities as a forage for cattle.

Fig 3.2 Picture of the plant Digitaria eriantha at Matla power plant in South Africa

3.4: Soxhlet extraction procedure

Soxhlet extraction was used for the extraction of PAHs from soil according to the recommended US Environmental Protection Agency Method 3540C (Lauet al., 2010). . Air-dried soil samples were sieved through a 600 micron mesh sieve; 10 g was weighed into an extraction thimble and the PAHs were extracted with (1:1) hexane/acetone mixture for 6 hours. The extracts were transferred to a rotary evaporator and pre-concentrated to a volume of 2 mL with a vacuum rotary evaporator from Buchi R-200 (Flawil, Switzerland). The concentrated extracts were cleaned up using column chromatography (silica gel). PAHs were eluted with acetone and concentrated to 1.5 mL under a gentle stream of nitrogen (Crnkovic et al., 2007; Olajire et al., 2007).

3.5: GC-MS of PAHs

Stock standard solutions of concentrations of 100 µg mL^{-1} were prepared in acetone and stored at 4 ^{0}C. The determination of PAHs was on Agilent GC-MS consisting of a 7890A GC equipped with a splitless injector, 5975C mass selective detector (MSD) and 7693 autosampler from Agilent Technologies (Santa Clara, California, USA). Data acquisition was achieved using Agilent MSD ChemStation. A sample of 1 µL was injected into a capillary column DB-1HT 30 m × 0.25 mm i.d. with 0.1 µm film thickness (Agilent Technologies, Santa Clara, California, USA). A splitless injection mode was used. Temperature programming was as follows; initial temperature was at 60 ^{0}C held for 4 minutes, followed by an increase to 310 ^{0}C at 7 ^{0}C/minutes and held for 20 min at the maximum set temperature. Ultra-high purity helium (99.999 %) gas was used as the carrier gas at a flow rate of 1 mL min^{-1} (Afrox (Johannesburg, RSA). An external standard calibration method based on a four-point calibration curve (concentration levels of 0.5 to 4 µg mL^{-1}) was used.

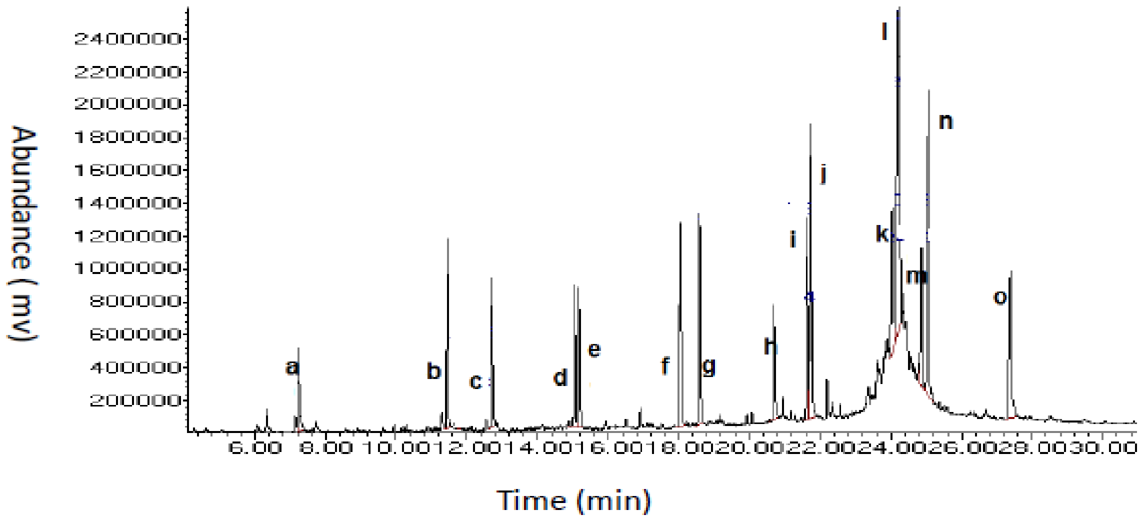


Fig 3.3 Typical chromatogram of 15 PAHs standards. Peak ID: a = Nap, b = Ace, c = Flo, d = Phe, e = Anth, f = Flan, g = Pyr, h = B[a]a,i = Chry, j = B[b]f,k = B[e]a, l = B[k]f, m = B[a]p, n = Pery and o = Ind

3.6 Ultrasonic extraction procedure

A spiked soil sample of 10 g was sonicated for 30 min with 50 mL of (1:1) hexane/acetone mixture in an ultrasonic bath (Power sonic 405, Namyangji, South Korea). The extract was filtered through a 0.45-µm membrane filter. The filtrates were reduced to 2 mL on a rotary evaporator. The concentrated extract was cleaned up using silica gel column chromatography. Elution was performed with acetone and concentrated to 1.5 mL under a gentle stream of nitrogen. The concentration of extracted PAHs was determined by GC-MS.

3.7: Ultrasonic – DLLME extraction procedure

A 10.0 g soil sample was spiked with a mixture of PAH standards at a concentration level of 100 mgL^{-1} for the optimisation of the ultrasonic-DLLME extraction procedure. After thorough mixing, 10 mL of acetonitrile (MeCN) was added to the sample and the vial was placed in an ultrasonic bath for 30 min. For optimisation, two types of solvents, viz methanol (MeOH) and acetone ($(CH_3)_2CO$), were investigated as possible disperser solvents.

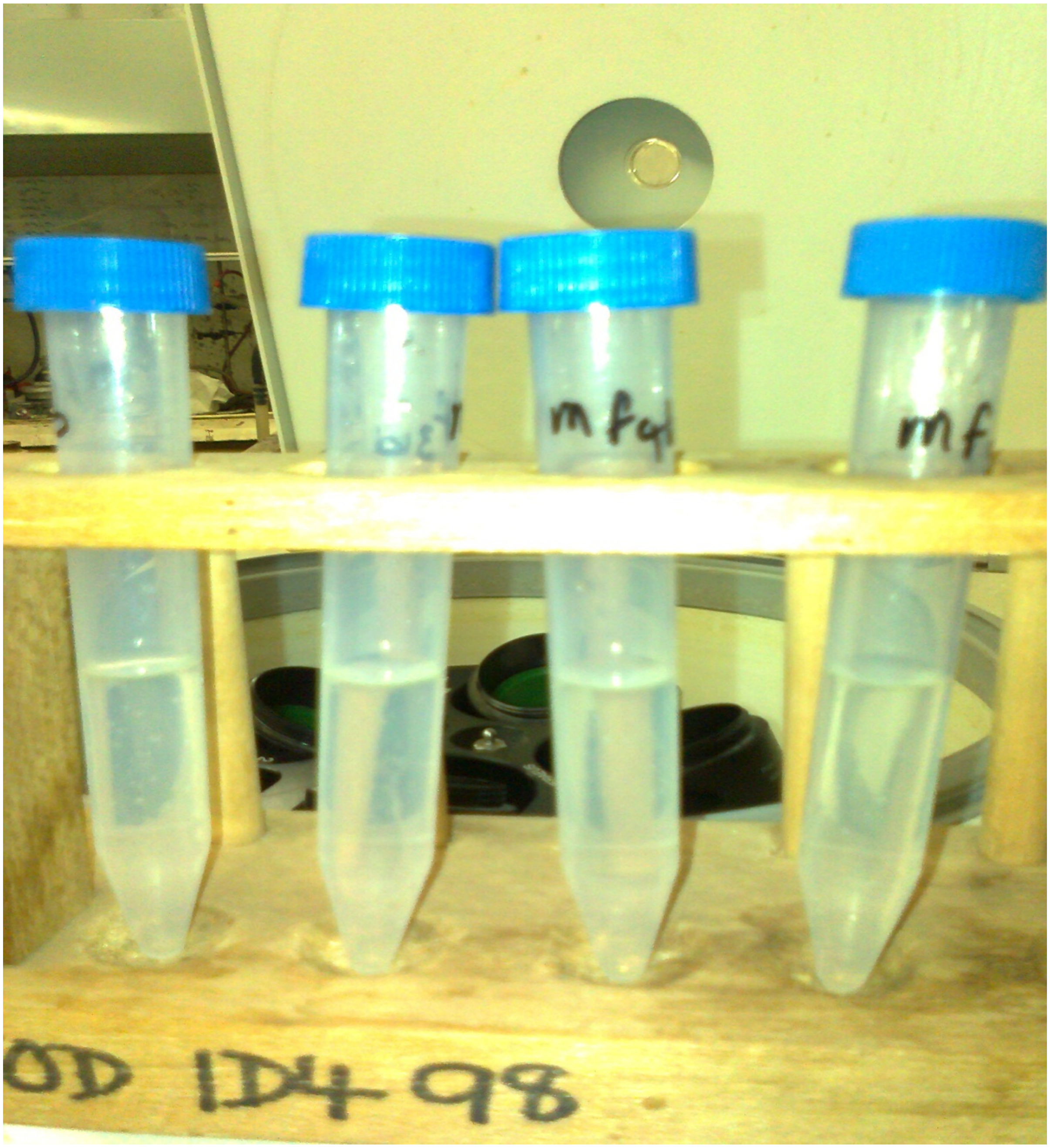


Fig 3.4 Picture of the cloudy form during DLLME extraction.

The extract was filtered through a 0.45-µm membrane filter and transferred into a test tube. An aliquot of 1.0 mL of the MeCN extract (used as dispersive solvent) containing

70.0 µL of Dicholoroethene ($C_2H_2Cl_2$) (used as extraction solvent) was rapidly transferred into 5 ml of ultrahigh purity (UHP) water, using Milli-Q (18.2 Megohm from Millipore Corporation (Bedford, Massachusetts, USA), and placed in a screw-cap centrifuge tube. The extraction solvent using chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) was also optimised. Cloudy solutions, resulting from the dispersion of fine droplets of $C_2H_2Cl_2$ in the aqueous solution, were formed (Fig 2.3). After gentle shaking, the mixture was then centrifuged using Heraeus Biofuge primo centrifuge (Massachusetts, USA) for 5 min at 3 500 rpm, causing the dispersed fine droplets of the extraction phase to sediment at the bottom of the conical test tube (Fig 2.4). About 5 µL was removed using a micro-syringe, of which 1 µL was injected into GC-MS.

Fig 3.5 Picture of the pre-concentration setup during DLLME extraction

3.8: Metal analysis

All glassware was washed with liquid detergent, rinsed with water and then soaked in 10% HNO_3 overnight. The items were then rinsed with UHP water followed by acetone in order to remove any organic compounds that might adhere to them. Five grams of soil was weighed into a 150 mL beaker and 20 mL of 2 M $HN0_3$ was added to each sample. Each beaker was covered with a petri dish and digestion was carried out on a hot plate in a fume hood for 3 h. The beakers were allowed to cool to room temperature and samples were then filtered through Whatman No 1 filter paper into a clean 50 mL volumetric flask and were made up to volume with UHP water. For plant samples, 0.5 g of dried plant material was digested in 10 mL of aqua regia for 2 h, filtered and brought to a volume of 10 mL with UHP water (Adeniyi and Afolabi 2002).

3.9: Instrumentation

Nine metals, Pb, Cd, Zn, Mn, Fe, Hg, Cu, Ni and Cr, were determined using a Perkin Elmer ICP-OES Optima 4300DV (Massachusetts, USA) and Perkin Elmer graphite furnace atomic absorption spectrophotometer (GF-AAS) AAnalyst 800 (Massachusetts, USA) fitted with S-10 auto sampler. The operating conditions are summarised in Table 2.1. The total organic matter (TOM) was determined after drying at 105 ^{0}C to a constant weight with an air oven, Scientific series 9000 (South Africa). The soil samples were then placed in a muffle furnace for TOM determination by measuring their loss upon ignition at 550 ^{0}C for 6 h (Bergknut et al., 2006; Wang et al., 2009). The pH was determined using a Mettler Toledo pH meter (Columbus Ohio, USA).

3.10: Reagent and quality assurance

High purity chemicals and reagents were purchased from Sigma-Aldrich Chemical Company (Seelze, Germany). Milli-Q ultra-pure water (18.2 megohm) from Millipore Corporation (Bedford, Massachusetts, USA) was used to make all master and working standards. Stock solutions (Merck Darmstadt, Germany) of 100 mg/L multi-element (Ag, Al, Ba, Be, Bi, Cd, Co, Cr, Cs, Ga, In, Li, Mg, Mn, Mo, Ni, Pb, Rb, Sr, Ti, V, Zn, : 10 mg/L each, Ca, Fe, Na : 100 mg/L) were used to prepare the calibration standards. The potential contamination of samples was eliminated by analysing one acid blank in every batch for validation of the method. A soil certified reference material (Cat log No: CRM24-050 and Lot No: 11024) from Industrial Analytical (pty) Ltd (South Africa) was used for traceability.

Table 3.1: Linearity, LOD, and LOQ of 15 PAHs

PAHs	r^2	LOD (µg/g)	LOQ (µg/g)
Naphthalene	0.999	0.04	0.12
Acenaphthene	0.999	0.29	0.98
Fluorene	0.999	0.07	0.23
Phenanthrene	0.999	0.11	0.35
Anthracene	0.998	0.14	0.47
Fluoranthene	0.997	0.04	0.13
Pyrene	0.998	0.07	0.23
Benzo[a]anthracene	0.999	0.05	0.15
Chrysene	0.999	0.17	0.57

Benzo[b]fluoranthene	0.998	0.03	0.10
Benzo[e]acephenantrylene	0.999	0.05	0.17
Benzo[k]fluoranthene	0.998	0.01	0.04
Benzo[a]pyrene	0.997	0.04	0.12
Perylene	0.999	0.08	0.25
Indeno[1,2,3-cd]pyrene	0.995	0.10	0.33

3.11: Statistical analysis

The Pearson’s correlation coefficient statistical function on Microsoft Excel was used to test the relations between the PAH concentrations in soil and plants. Similarly, the analysis of variance (ANOVA) was used to evaluate differences in PAH and metal concentrations between the three power plants. To compare the total metal content at the different sampling sites, the metal pollution index (MPI) was used (Usero et al., 1997; Adeniyi et al., 2008). The MPI equation is as shown below:

MPI = (Cf1 x Cf2………Cfn)1/n [Equation 3.1]

where Cfn = concentration of the metal in the sample.

Table 3.2a: ICP-OES operating conditions applied in this study

Method	Linear range
RF power (W)	1300
Plasma argon flow (L min^{-1})	15
Auxiliary gas flow (L min^{-1})	0.2
Nebuliser gas flow(L min^{-1})	0.8
Torch cassette position	-3
Delay	30 S
Resolution	Normal
Number of replicates	3

Table 3.2b: GF-AAS operating conditions applied in this study

Method	Linear range
Number of replicates	3
Lamp type (Cd & Hg)	EDL
Slit (nm)	0.7
Graphite tube	Standard THGA Graphite Tubes with End Caps
Lamp type (other metals)	Thallium HCL Lamp

CHAPTER FOUR

RESULTS AND DISCISSION

4.0 Results and Discussion

This section on the results and discussion is subdivided into three sub-sections;

(i) PAHs analysis

(ii) Metal analysis

(ii) Ultrasonic DLLME

4.1 Results and discussion of PAH

4.1.1 Discussion on PAHs

The most abundant individual PAHs found around Matla power plant were Nap {6.52 µg g^{-1}}, Chry {6.77 µg g^{-1}}, B[b]f {9.82 µg g^{-1}}, B[k]f {6.14 µg g^{-1}} Pery {6.44 µg g^{-1}} and Ind {5.87 µg g^{-1} (Figure 4.1a). Figure 4.1b shows that Nap {2.99 µg g^{-1}}, Chry {2.56 µg g^{-1}}, B[k]f {3.47} and Pery {4.04 µg g $-^{1}$} were the most abundant individual PAHs around Lethabo. A similar pattern was also observed at Rooiwal power plant, with Nap {1.58 µg g^{-1}}, Chry {1.70 µg g^{-1}}, B[k]f 1.53 µg g^{-1}} and Pery {1.54 µg g^{-1}} appearing as the most abundant individual PAHs (Figure 4.1c). Most of these PAHs usually result from the combustion of coal and biomass (Rajput & Lakhani, 2010). The concentration levels of Nap, Anth, Phen, Flan, B[a]a and B[a]p in all three sites were above the Netherlands maximum permissible concentration of 0.10, 0.12, 0.51, 2.6, 0.25 and 0.26 μg g^{-1}

respectively (CCME) 2008, . In the plant sample (*Digitaria eriantha*), most abundant individual PAHs around Matla were Nap {1.40 µg g^{-1}}, Phen {0.41 µg g^{-1}} and Anth {0.18 µg g^{-1}}, while Nap {1.13 µg g^{-1}}, Phen {0.28 µg g^{-1}} and Anth {0.19 µg g^{-1}} were the most abundant PAHs around Lethabo. Nap {0.37 µg g^{-1}} and Phen {0.19 µg g^{-1}} were dominant at Rooiwal.

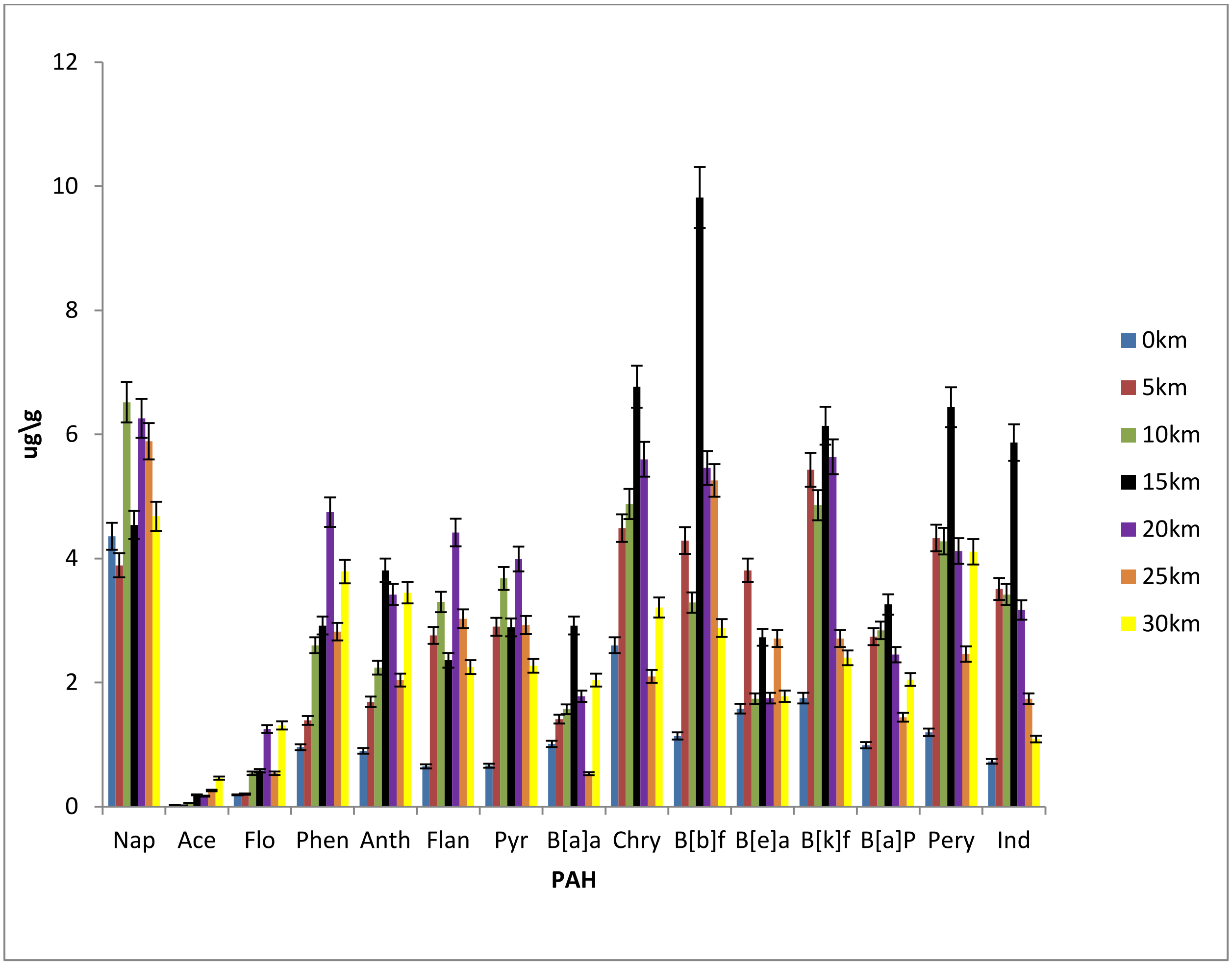


Figure 4.1a: Matla power plant average concentration of PAHs in soil

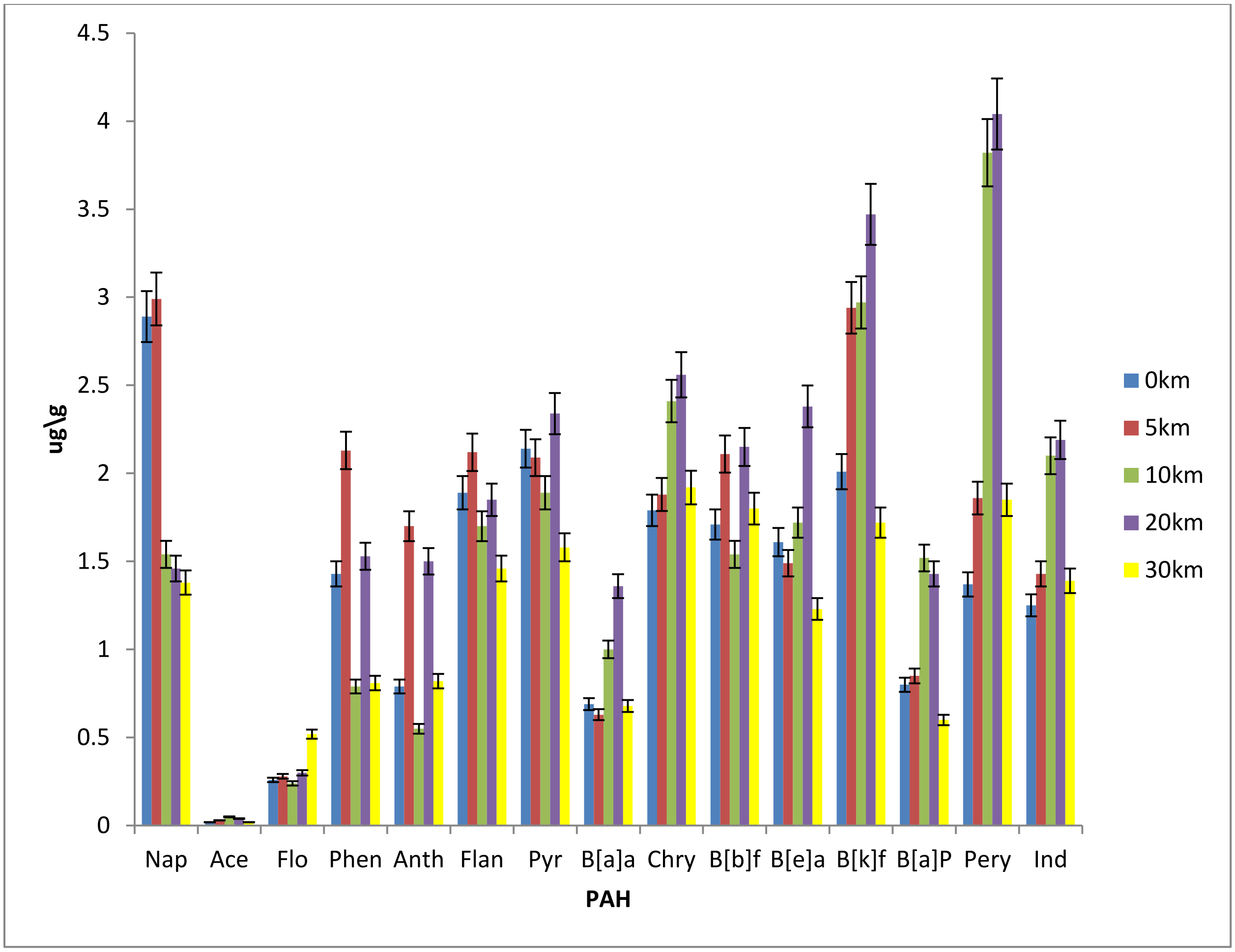


Figure 4.1b: Lethabo power plant average concentration of PAHs in soil

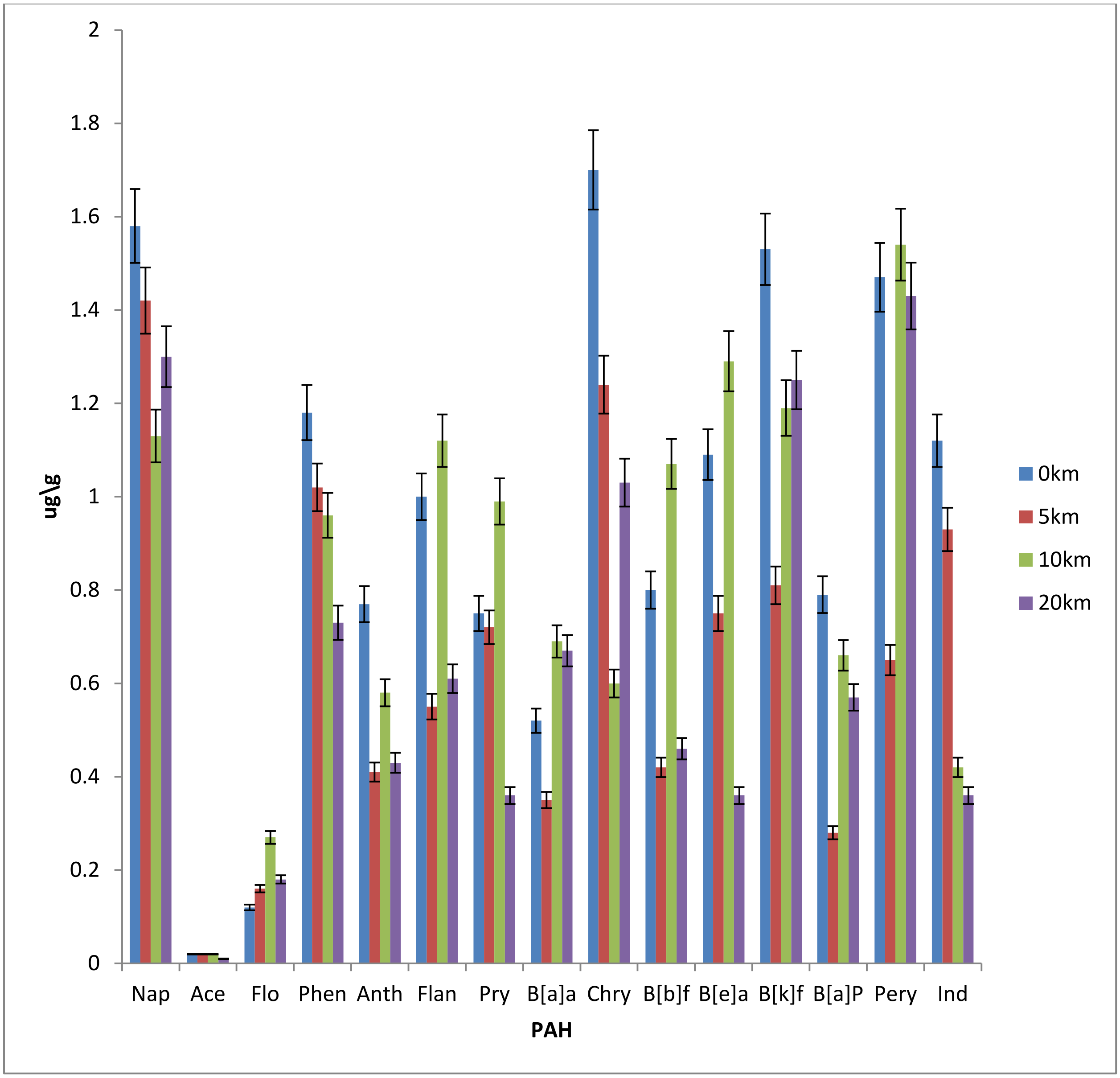


Figure 4.1c: Rooiwal power plant average concentration of PAHs in soil

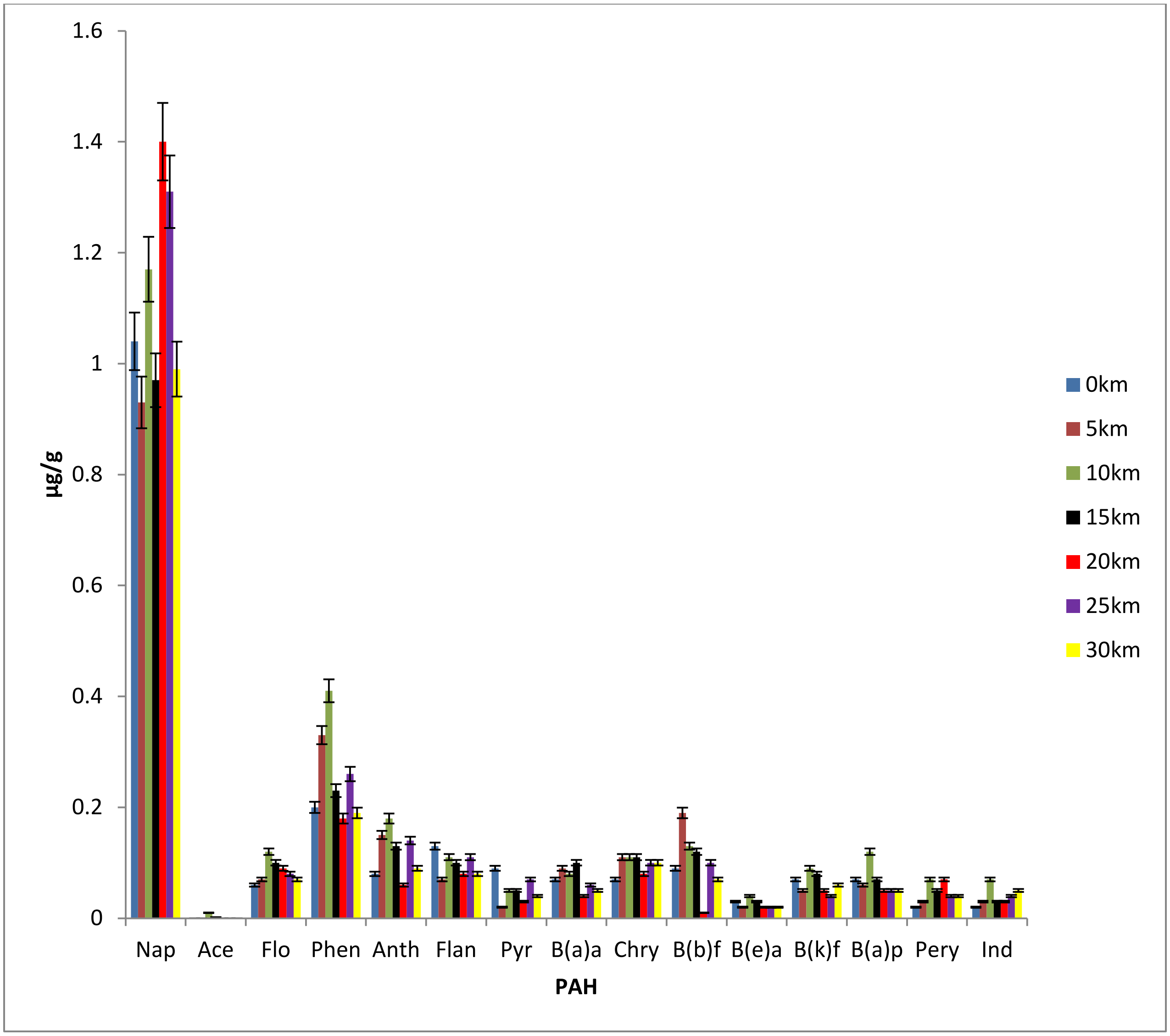


Figure 4.2a: Matla power plant average concentration of PAHs in *Digitaria eriantha* plant

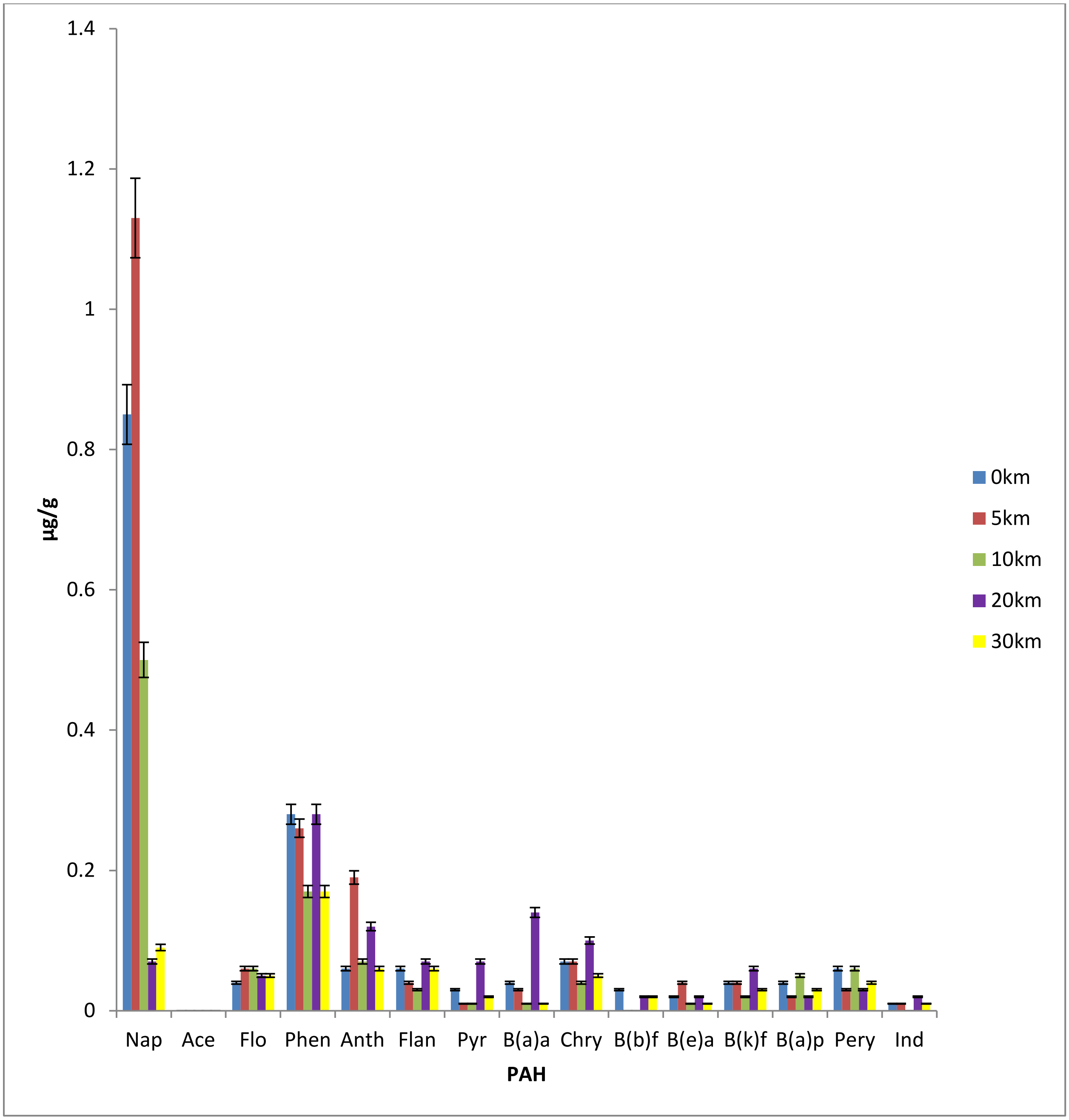


Figure 4.2b: Lethabo power plant average concentration of PAHs in *Digitaria eriantha* plant

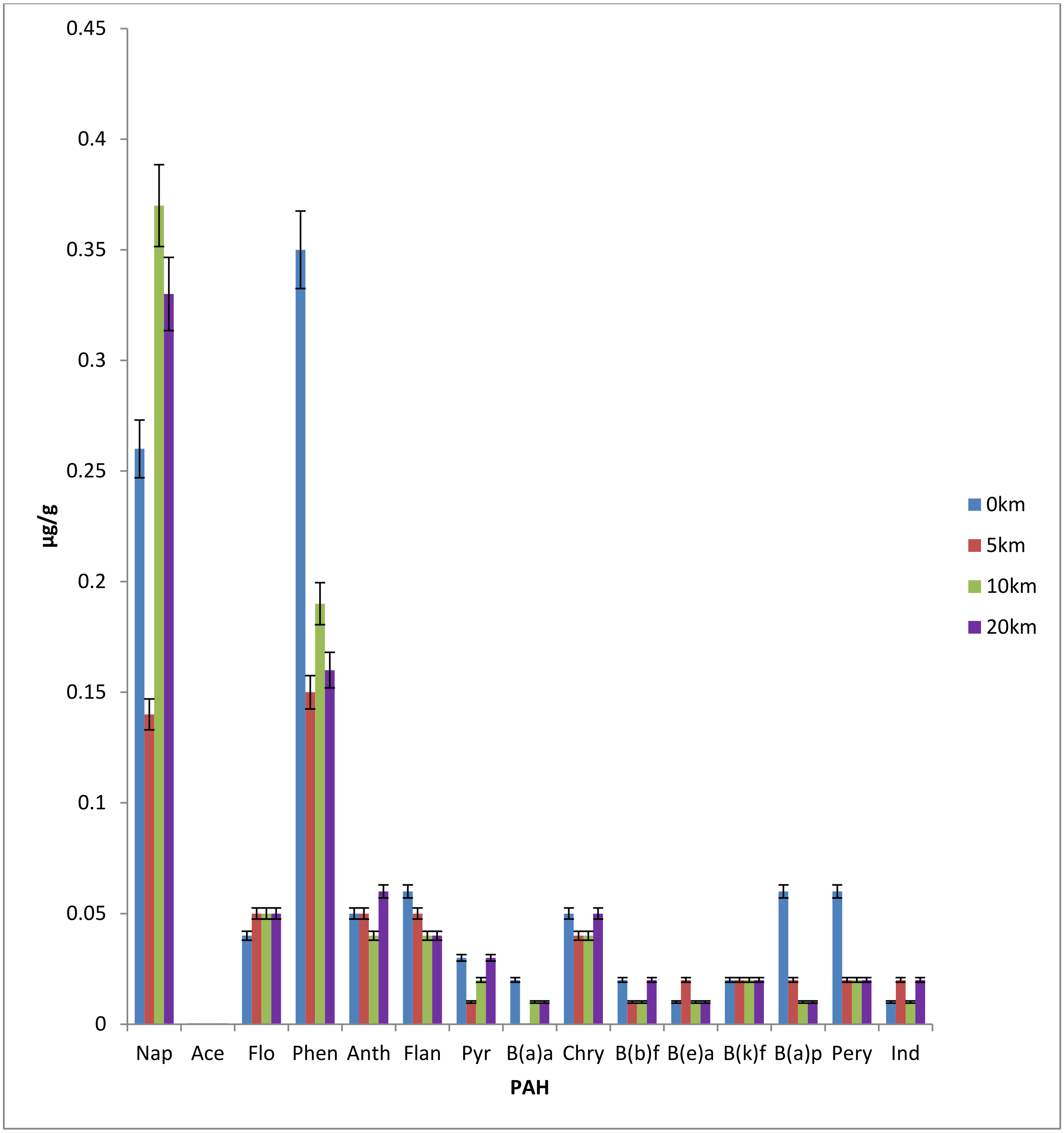


Figure 4.2c: Rooiwal power plant average concentration of PAHs in *Digitaria eriantha* plant

The total concentration of PAHs in soil samples collected from the surroundings of Matla, Lethabo and Rooiwal power plant ranged from 18.75 to 61.24 µg g^{-1}, 17.78 to 28.60 µg g^{-1} and 9.73 to 14.44 µg g^{-1} respectively (Table 4.1). These values were higher than those of the control sample (1.41 ± 0.33 µg g^{-1}). According to the Agency for Toxic Substances and Disease Registry (ATSDR 1995C), levels of the sum of PAHs between 0 and 0.1 µg g^{-1} are considered as non-contamination. Values that fall within the range of 0.1 to 1 µg g^{-1} imply slight contamination, whereas values between 1 and 10 µg g^{-1} are an indication of significant contamination.

Table 4.1 shows that the total PAH (TPAH) levels for soil in all the sampling points were higher than 1.0 µg g^{-1}, thus indicating significant contamination. Though there is no guidline for PAHs in plants, a similar pattern was also found in the TPAH level of the plant used (*Digitaria eriantha*) where the values are more than 1.0 µg g^{-1} most of the sampling points, especially around Matla and Lethabo. The total concentration of PAHs within Matla power plant was higher compared to that of Lethabo and Rooiwal. This may be due to the contribution of Kriel power plant, which is situated about 4 km away from Matla power plant.

Combustion PAHs (COMPAHs) such as Flo, Pry, Chry, B[b]f, B[k]f, B[a]a, B[a]p and Ind, normally indicate combustion of coal and biomass. COMPAHs values in each power plant were calculated and are summarised in Table 4.1. These values ranged from 9.53 to 40.03 µg g^{-1}, accounting for 48% to 65% of the TPAHs in the vicinity of Matla power plant.

COMPAHs values in the vicinity of Lethabo power plant ranged from 11.15 to 17.35 µg g^{-1}, accounting for 57% to 63% of the total PAHs. At Rooiwal the COMPAH ranged from 5.30 to 8.21 µg g^{-1}, accounting for 54% to 57% of the total. The ratio of COMPAH/TPAH in the vicinity of the Matla power plant was 0.59. Similar ratios of 0.61 and 0.55 for Lethabo and Rooiwal power plants respectively were found. These high ratios are an indication that combustion activities occur in the areas studied (Rajput & Lekhani, 2010). This high ratio of COMPAH/TPAH was not observed in the plant (*Digitaria eriantha*). The ratios were between 0.16 to 0.34, with the exception of 20 km at Lethabo, where a ratio of 0.45 was obtained.

Benzo[a]anthracene, Chry, B[b]f, B[k]f, B[a]p and Ind have been classified as possible carcinogenic to humans (Kong et al., 2011). In the present study, these PAHs represented about 44% of the TPAH and were found at concentrations between 1 to 10 µg g^{-1}, which is an indication of significant contamination. HMW compounds contributed significantly to the total soil PAH concentration in all three sites (Table 4.1). These HMW PAHs are generally derived from pyrolytic origin (Qiao et al., 2006; Sanders et al., 2002; Dahle et al., 2003). However, in *Digitaria eriantha* the LMW (two to three rings) were found in higher concentration. This may be due to their higher water solubility, which is responsible for uptake by the plant (Tuteja et al., 2011).

Even though the two-to-three-ring forms are yet to be classified as to their carcinogenicity to humans, their metabolites or derivatives can be potent mutagens (ATSDR, 2009).

Table 4.1: Soil and plant (*Digitaria eriantha*) values of TPAHs, LMW, MMW, HMW, CPAH and COMPAH around Matla, Lethabo and Rooiwal power plant

	μg g^{-1}															
	0 km			5 km			10 km			15 km	20 km			25 km	30 km	
	Matla	Lethabo	Rooiwal	Matla	Lethabo	Rooiwal	Matla	Lethabo	Rooiwal	Matla	Matla	Lethabo	Rooiwal	Matla	Matla	Lethabo
TPAHs	**18.75** (2.04)	**20.65** (1.63)	**14.44** (1.04)	**42.82** (2.15)	**24.53** (1.93)	**9.73** (0.60)	**45.82** (3.36)	**23.84** (1.03)	**12.53** (0.84)	**61.24** (2.19)	**54.05** (2.19)	**28.60** (1.07)	**9.75** (0.83)	**36.46** (2.42)	**37.77** (1.90)	**17.78** (0.65)
LMW (2-3 RING)	**6.44** (1.38)	**5.39** (1.23)	**3.67** (0.70)	**7.15** (1.48)	**7.13** (1.64)	**3.03** (0.39)	**11.96** (1.89)	**3.17** (0.80)	**2.96** (0.65)	**12.04** (1.43)	**15.85** (1.73)	**4.83** (0.52)	**2.65** (0.60)	**11.55** (1.79)	**13.69** 1.34)	**3.55** (0.37)
MMW (4 RING)	**4.92** (0.36)	**6.51** (0.2)	**3.97** (0.16)	**11.56** (0.29)	**6.72** (0.15)	**2.86** (0.10)	**13.43** 0.35)	**7.00** (0.09)	**3.40** (0.11)	**14.94** (0.36)	**15.79** (0.23)	**8.11** (0.38)	**2.67** (0.13)	**8.59** (0.34)	**9.77** (0.27)	**5.64** (0.14)
HMW (5-6 RING)	**7.69** (0.30)	**8.75** (0.2)	**6.80** (0.18)	**24.11** (0.38)	**10.68** (0.14)	**3.48** (0.11)	**20.43** (1.12)	**13.67** (0.14)	**6.17** (0.08)	**34.26** (0.40)	**22.41** (0.23)	**15.66** (0.17)	**4.43** (0.10)	**16.32** (0.29)	**14.31** (0.29)	**8.59** (0.14)
CPAH	**8.22** (0.37)	**8.25** (0.22)	**6.46** (0.17)	**21.87** (0.50)	**9.84** (0.16)	**4.03** (0.09)	**20.86** (0.53)	**11.54** (0.12)	**4.63** (0.09)	**34.78** (0.48)	**24.10** (0.23)	**13.16** (0.34)	**4.34** (0.11)	**13.78** (0.35)	**13.67** (0.33)	**8.11** (0.14)
COMPAH	**9.53** (0.54)	**12.28** (0.30)	**8.21** (0.25)	**27.53** (0.62)	**14.05** (0.30)	**5.30** (0.17)	**27.84** (0.77)	**15.13** (0.19)	**6.74** (0.17)	**40.03** (0.68)	**32.51** (0.38)	**17.35** (0.48)	**5.31** (0.21)	**19.74** (0.54)	**18.19** (0.49)	**11.15** (0.22)

Values in bold are for the soil while the values in parentheses are for the plant (Digitaria eriantha). LMW = Lower Molecular Weight, MMW = Medium Molecular Weight, HMW = High Molecular Weight, CPAH = Carcinogenic PAH and COMPAH = Combustion PAH.

4.1.2 Sources of PAHs

Table 4.2: Characteristic Phen/Anth, Anth/(Anth + Phen), Flan/(Flan + Pyr) and LMW/HMW values of selected molecular ratio for pyrolytic and petrogenic origin of PAHs at Matla, Lethabo and Rooiwal

PAH	Petrogenic	Pyrolitic	Result from this work		
			Matla	Lethabo	Rooiwal
Phen/Anth	> 15	< 10	1.1 ± 0.23	1.3 ± 0.30	1.9 ± 0.38
Anth/(Anth + Phen)	< 0.1	>0.1	0.5 ± 0.08	0.4 ± 0.05	0.4 ± 0.04
Flan/(Flan + Pyr)	< 0.4	> 0.4	0.5 ± 0.03	0.4 ± 0.05	0.5 ± 0.08
LMW/HMW	High	Low	0.4 ± 0.15	0.3 ± 0.10	0.4 ± 0.08

Source: Dominguez et al., 2010).

Table 4.2 shows the characteristic PAH diagnostic ratios obtained in the three power plants. Diagnostic ratios are widely used to determine the origins of PAHs present in environmental samples (Liu et al., 2005). The individual compound ratios are known to provide accurate and reliable estimations of the emission sources of PAHs (Guo et al., 2010). Anth/(Anth + Phen) ratios of 0.5 ± 0.08, 0.4 ± 0.05 and 0.4 ± 0.04 were observed at Matla, Lethabo and Rooiwal respectively. These ratios are all greater than 0.1, thus indicating that the PAHs in the three sites came from a pyrolytic source. This is further confirmed by Flan/Flan + Pyr ratios of 0.5 ± 0.03, 0.4 ± 0.05 and 0.5 ± 0.08 for Matla, Lethabo and Rooiwal respectively, which were also greater than the stipulated limit of 0.4 for pyrolytic sources. Furthermore, Phen/Anth for Matla was 1.10 ± 0.23, 1.30 + 0.30 for Lethabo and 1.90 ± 0.38 for Rooiwal, which are all < 10. Usually a Phen/Anth ratio less than 10 indicates a pyrolytic source (Wang et al., 2009).

4.1.3 Correlation analyses

Correlation (r) values were calculated in order to hypothesise the probable source of PAHs further on the assumption that two or more components may correlate either owing to a common origin or atmospheric behaviour. Relatively good correlation existed among most of the PAHs, especially those with higher molecular weights, thus suggesting that they originated from a similar source. The relationship between levels of phenanthrene/anthracene and fluoranthene/pyrene was shown to be significantly correlated in the three power plant for the soil and in two of the power plant for the Digitaria eriantha plant, with r values ranging from 0.73 - 0.84 and 0.74 – 0.96 for soil, -0.48 - 0.92 and 0.10 – 0.95 for the *Digitaria eriantha* plant. (Table 4.3a to 4.3c). Such correlation values indicated that PAHs in the three sampling sites had presumably undergone similar environmental processes and could be related to pyrolytic origin or coal combustion (Qiao et al., 2006).

Table 4.3a: Pearson correlation coefficient (r) of individual PAHs in soil and plant (*Digitaria eriantha*) at Matla power station

	Nap	Ace	Flo	Phen	Anth	Flan	Pyr	B[a]a	Chry	B[b]f	B[e]a	B[k]f	B[a]p	Pery	Ind
Nap	**1.00** (1.00)	**0.07** (0.73)	**0.39** (0.72)	**0.57** (0.49)	**0.21** (0.31)	**0.69** (0.26)	**0.65** (0.05)	**-0.19** (-0.27)	**0.07** (0.03)	**0.02** (-0.24)	**-0.47** (0.48)	**0.13** (0.25)	**0.06** (0.60)	**0.56** (0.76)	**0.01** (0.51)
Ace		**1.00** (1.00)	**0.76** (0.84)	**0.64** (0.78)	**0.63** (0.66)	**0.10** (0.28)	**0.05** (0.01)	**0.25** (0.33)	**-0.20** (0.43)	**0.13** (0.26)	**-0.22** (0.86)	**-0.32** (0.76)	**-0.10** (0.96)	**-0.29** (0.59)	**-0.25** (0.81)
Flo			**1.00** (1.00)	**0.93** (0.56)	**0.77** (0.53)	**0.50** (0.07)	**0.40** (-0.20)	**0.39** (0.26)	**0.17** (0.49)	**0.11** (0.04)	**-0.46** (0.64)	**0.04** (0.59)	**0.14** (0.70)	**-0.08** (0.86)	**-0.09** (0.80)
Phen				**1.00** (1.00)	**0.84** (0.92)	**0.71** (0.05)	**0.64** (-0.18)	**0.39** (0.53)	**0.34** (0.64)	**0.36** (0.71)	**-0.35** (0.55)	**0.27** (0.38)	**0.29** (0.77)	**-0.04** (0.25)	**0.15** (0.57)
Anth					**1.00** (1.00)	**0.49** (0.10)	**0.53** (-0.10)	**0.80** (0.66)	**0.62** (0.82)	**0.66** (0.82)	**-0.11** (0.80)	**0.48** (0.47)	**0.60** (0.63)	**-0.02** (0.13)	**0.50** (0.63)
Flan						**1.00** (1.00)	**0.96** (0.95)	**0.10** (0.14)	**0.43** (-0.37)	**0.37** (-0.04)	**0.10** (0.61)	**0.62** (0.41)	**0.50** (0.42)	**0.28** (-0.20)	**0.38** (0.01)
Pyr							**1.00** (1.00)	**0.24** (0.01)	**0.57** (-0.48)	**0.49** (-0.13)	**0.17** (0.36)	**0.74** (0.19)	**0.68** (0.14)	**0.43** (-0.41)	**0.57** (-0.17)
B[a]a								**1.00** (1.00)	**0.82** (0.58)	**0.63** (0.83)	**-0.01** (0.49)	**0.59** (0.51)	**0.75** (0.46)	**0.07** (-0.20)	**0.69** (0.23)
Chry									**1.00** (1.00)	**0.70** (0.66)	**0.14** (0.15)	**0.92** (0.21)	**0.90** (0.31)	**0.26** (0.23)	**0.91** (0.70)
B[b]f										**1.00** (1.00)	**0.42** (0.25)	**0.70** (0.20)	**0.65** (0.36)	**-0.12** (-0.37)	**0.85** (0.18)
B[e]a											**1.00** (1.00)	**0.41** (0.92)	**0.35** (0.94)	**-0.26** (0.30)	**0.43** (0.56)
B[k]f												**1.00** (1.00)	**0.91** (0.83)	**0.27** (0.29)	**0.92** (0.56)
B[a]p													**1.00** (1.00)	**0.42** (0.39)	**0.90** (0.64)
Pery														**1.00** (1.00)	**0.25** (0.60)
Ind															**1.00** (1.00)

Values are based on averages for the study period. Values in bold are for the soil while the values in parentheses are for the plant (*Digitaria eriantha*).

Table 4.3b: Pearson correlation coefficient (r) of individual PAHs in soil and plant (*Digitaria eriantha*) at Lethabo power station

	Nap	Ace	Flo	Phen	Anth	Flan	Pyr	B[a]a	Chry	B[b]f	B[e]a	B[k]f	B[a]p	Pery	Ind
Nap	**1.00** 1.00	**-0.42** ND	**-0.46** 0.16	**0.74** 0.37	**0.33** 0.48	**0.79** -0.52	**0.36** -0.55	**-0.60** -0.38	**-0.69** -0.10	**0.17** -0.33	**-0.26** 0.73	**-0.12** -0.15	**-0.42** -0.15	**-0.67** ND	**-0.64** -0.33
Ace		**1.00** 1.00	**-0.54** ND	**-0.16** ND	**-0.03** ND	**0.10** ND	**0.26** ND	**0.69** ND	**0.86** ND	**-0.10** ND	**0.58** ND	**0.80** ND	**0.95** ND	**0.91** ND	**0.91** ND
Flo			**1.00** 1.00	**-0.40** -0.43	**-0.11** 0.53	**-0.71** -0.76	**-0.72** -0.46	**-0.27** -0.25	**-0.27** -0.33	**0.06** -0.98	**-0.49** 0.24	**-0.60** -0.36	**-0.60** -0.36	**-0.31** -0.28	**-0.33** -0.42
Phen				**1.00** 1.00	**0.87** 0.46	**0.93** 0.47	**0.67** 0.57	**-0.12** 0.67	**-0.24** 0.86	**0.76** 0.38	**0.20** 0.64	**0.39** 0.83	**-0.14** 0.83	**-0.25** -0.30	**-0.22** 0.68
Anth					**1.00** 1.00	**0.69** -0.19	**0.57** -0.01	**0.15** 0.26	**0.04** 0.45	**0.97** -0.53	**0.34** 0.91	**0.54** 0.42	**-0.03** 0.42	**0.02** -0.73	0.**04** 0.31
Flan						**1.00** 1.00	**0.75** 0.81	**-0.06** 0.66	**-0.13** 0.69	**0.52** 0.86	**0.28** -0.12	**0.51** 0.74	**0.10** 0.74	**-0.12** -0.34	**-0.09** 0.85
Pyr							**1.00** 1.00	**0.52** 0.95	**0.34** 0.85	**0.53** 0.55	**0.80** -0.10	**0.68** 0.87	**0.45** 0.87	**0.30** -0.37	**0.35** 0.85
B[a]a								**1.00** 1.00	**0.95** 0.93	**0.24** 0.34	**0.93** 0.15	**0.74** 0.92	**0.84** 0.92	**0.91** -0.49	**0.92** 0.85
Chry									**1.00** 1.00	**0.10** 0.39	**0.80** 0.44	**0.77** 1.00	**0.92** 1.00	**0.99** -0.59	**0.99** 0.92
B[b]f										**1.00** 1.00	**0.40** -0.30	**0.47** 0.43	**-0.06** 0.43	**0.10** 0.15	**0.07** 0.53
B[e]a											**1.00** 1.00	**0.80** 0.41	**0.77** 0.41	**0.76** -0.54	**0.78** 0.29
B[k]f												**1.00** 1.00	**0.82** 1.00	**0.78** -0.62	0.**80** 0.95
B[a]p													**1.00** 1.00	**0.94** -0.62	**0.95** 0.95
Pery														**1.00** 1.00	**0.99** -0.70
Ind															**1.00** 1.00

Values are based on averages for the study period. Values in bold are for the soil while the values in parentheses are for the plant (*Digitaria eriantha*)

Table 4.3c: Pearson correlation coefficient (r) of individual PAHs in soil and plant (*Digitaria eriantha*) at Rooiwal power plant

	Nap	Ace	Flo	Phen	Anth	Flan	Pyr	Baa	Chry	B[b]f	B[e]a	B[k]f	B[a]p	Pery	Ind
Nap	**1.00** 1.00	**0.20** ND	**-0.97** 0.10	**0.61** 0.05	**0.42** -0.16	**-0.20** -0.57	**-0.23** 0.60	**-0.64** 0.49	**0.99** 0.23	**-0.38** 0.23	**-0.11** -0.46	**0.29** ND	**0.10** -0.29	**-0.27** -0.10	**0.89** -0.46
Ace		**1.00** 1.00	**0.03** ND	**0.87** ND	**0.47** ND	**0.50** ND	**0.89** ND	**-0.48** ND	**0.16** ND	**0.50** ND	**0.84** ND	**-0.12** ND	**0.02** ND	**-0.25** ND	**0.62** ND
Flo			**1.00** 1.00	**-0.41** -0.98	**-0.24** -0.01	**0.40** -0.87	**0.46** -0.52	**0.61** -0.82	**-0.97** -0.58	**0.57** -0.58	**0.35** 0.58	**-0.23** ND	**0.02** -0.98	**0.31** -1.00	**-0.77** 0.58
Phen				**1.00** 1.00	**0.73** -0.13	**0.45** 0.79	**0.62** 0.55	**-0.63** 0.88	**0.60** 0.53	**0.36** 0.53	**0.69** -0.71	**0.23** ND	**0.25** 0.94	**-0.13** 0.98	**0.88** -0.71
Anth					**1.00** 1.00	**0.79** 0.01	**0.44** 0.43	**0.14** ND	**0.46** 0.71	**0.66** 0.71	**0.68** 0.71	**0.82** ND	**0.85** 0.01	**0.57** 0.01	**0.49** 0.71
Flan						**1.00** 1.00	**0.74** 0.10	**0.49** 0.43	**-0.17** 0.30	**0.98** 0.30	**0.88** -0.30	**0.60** ND	**0.79** 0.95	**0.71** 0.87	**0.003** -0.30
Pyr							**1.00** 1.00	**-0.05** 0.85	**-0.25** 0.90	**0.79** 0.90	**0.96** -0.30	**-0.05** ND	**0.18** 0.37	**0.07** 0.52	**0.20** -0.30
Baa								**1.00** 1.00	**-0.58** 0.71	**0.53** 0.71	**0.08** -0.70	**0.52** ND	**0.62** 0.69	**0.89** 0.82	**-0.78** -0.71
Chry									**1.00** 1.00	**-0.35** 1.00	**-0.11** 0.01	**0.36** ND	**0.15** 0.49	**-0.20** 0.58	**0.87** 0.01
Bbf										**1.00** 1.00	**0.89** ND	**0.46** ND	**0.69** 0.49	**0.66** 0.58	**0.13** ND
Bea											**1.00** 1.00	**0.25** ND	**0.46** -0.49	**0.29** -0.58	**0.26** 1.00
Bkf												**1.00** 1.00	**0.96** ND	**0.84** ND	**0.10** ND
Bap													**1.00** 1.00	**0.92** 0.99	**0.001** -0.49
Pery														**1.00** 1.00	**-0.40** -0.58
Ind															**1.00** 1.00

Values are based on averages for the study period. Values in bold are for the soil while the values in parentheses are for the plant (*Digitaria eriantha*)

4.1.4 Estimation of carcinogenic potency

Carcinogenic potency is associated with exposure to a given PAH compound and can be evaluated using an index of B[a]p equivalent concentration (B[a]Peq) (Wang et al., 2009). Benzo[a]pyrene is the only PAH for which sufficient toxicological data exist and as such it is used to determine the carcinogenic potency factor of other PAHs. The total toxicity B[a] Peq for other PAHs was calculated using the following equation:

$$\text{Total B[a] Peq} = \Sigma_i C_i \times TEF_I \qquad \text{[Equation 4.2]}$$

where C_i is the of concentration of individual PAHs (B[a]a, B[a]p, B[b]f, B[k]f, Ind and Chry) and TEF_i is their corresponding toxicity equivalency factor. The US EPA calculated TEF values for B[a]a, B[a]p, B[b]f, B[k]f, Ind and Chry are given as 0.1, 1.0, 0.1, 0.01, 0.1, and 0.001, respectively (US EPA, 1993; Guo et al., 2010).

Table 4.4: TEFs and B[a]P equivalent concentration at Matla, Lethabo and Rooiwal power plants

PAHs	**US EPA TEF Values**	**B[a]Peq**		
		Matla power station (n = 7)	Lethabo power station (n = 5)	Rooiwal power station (n = 4)
B[a]a	0.1	1.13	0.44	0.22
Chry	0.01	0.30	0.11	0.05
B[b]f	0.1	3.21	0.93	0.28
B[k]f	0.01	2.89	1.31	0.48
B[a]p	1.0	15.77	5.2	2.3
Ind	0.1	1.95	0.84	0.28
Total	1.41	25.25	8.83	3.61

In this study calculated total B[a]Peq values at different sampling sites varied from 0.30 to 15.77 µg g^{-1} (Matla), 0.11 to 5.20 µg g^{-1} (Lethabo) and 0.05 to 2.3 µg g^{-1} (Rooiwal) (Table 4.4). Matla exhibited relatively higher (B[a]Peq) than the other two sites. Evaluating total B[a]Peq is a convenient approach to assessing the effects of anthropogenic sources in the environment. However, the approach might underestimate risks because not all PAHs are considered (Wang et al., 2009).

4.1.5 ANOVAs and Pearson correlation (r) of individual PAH in soil and in plant (*Digitaria eriantha*) in the three power plants

Relatively good correlation existed in most of the site with highest in Nap between the soil and the plant in the sample sites. (Table 4.5a).

Table 4.5a: Pearson correlation (r) of individual PAHs in soil and plant (*Digitaria Eriantha*) in the three power plants

Power plant	Nap	Ace	Flo	Phen	Anth	Flan	Pyr	B[a]a	Chry	B[b]f	B[e]a	B[k]f	B[a]p	Pery	Ind
Matla	0.94	-0.30	0.13	-0.37	-0.20	-0.54	-0.67	0.32	0.35	0.05	-0.36	0.20	0.34	0.51	0.35
Lethabo	0.93	ND	-0.16	0.80	0.91	-0.17	0.64	0.79	0.26	-0.01	0.02	0.44	0.11	-0.10	0.10
Rooiwal	-0.64	ND	0.66	0.74	-0.37	0.11	-0.42	0.44	0.56	-0.22	-0.90	ND	0.50	0.32	-0.58

ANOVA was used to evaluate the differences in the concentration level of individual PAH in soil and plant (*Digitaria eriantha*) around the three power plants. The result showed that there is a significant difference in the concentration level at 95% C. I. (Table:4.5b & 4.5c). Ace, Flo and Ind are statistically non-significant in their soil concentration level around the three power plants, while Ace, Pyr, B[e]a, and B[a]p concentration in the plant sample was statistically non-significant at $P < 0.05$.

Table 4.5b: ANOVA of PAHs levels in soil around the three power plants

Nap	Ace	Flo	Phen	Anth	Flan	Pyr	B[a]a	Chry	B[b]f	B[e]a	B[k]f	B[a]p	Pery	Ind
33.26*	3.64^{ns}	3.35^{ns}	4.28*	9.22*	7.63*	9.18*	5.31*	9.94*	6.35*	6.43*	6.94*	11.53*	4.89*	3.74^{ns}

The anova was based on the overall means for the study period. F-critical = 3.81 at $p < 0.05$; *= significant differences at $p < 0.05$, ns = non-significant difference at $p < 0.05$

Table 4.5c: Analysis of variance of PAHs levels in plant (*Digitaria eriantha*) at the three power stations

Nap	Ace	Flo	Phen	Anth	Flan	Pyr	B[a]a	Chry	B[b]f	B[e]a	B[k]f	B[a]p	Pery	Ind
12.27*	0.90^{ns}	10.38*	64.08*	34.82*	13.95*	2.56^{ns}	4.05*	12.84*	10.03*	2.78^{ns}	11.45*	2.31^{ns}	1.04^{ns}	11.18*

The Anova was based on the overall means for the study period F-critical = 3.81 at $p < 0.05$; *= significant differences at $p < 0.05$, ns = non-significant difference at $p < 0.05$

4.1.6 Seasonal variability of PAH concentration

The seasonal behaviour of the origin of PAH emissions is mostly associated with heating systems, traffic, soil volatilization, and were very unpredictable (Mastral et al., 2003). Figs. 4.3a to 4.3c summarise the average concentrations and distribution pattern across the sampling period. A similar trend was observed in the three power plants, with a higher concentration of PAHs during 0ctober 2011. It may be due to heavy rainfall during the period. Another spike in concentration was observed during April 2011. This was also a period of slight rainfall and cool weather. The rain may have assisted in bringing down the particulate matters released into the atmosphere to settle onto the soil. In the case of rainfall or when the temperature drops they form dry or wet deposits on plants, soil and in the hydrosphere from the atmosphere, but when the temperature rises, they volatilize into the atmosphere from these environmental media (Chun, 2011; Tham et al., 2008).

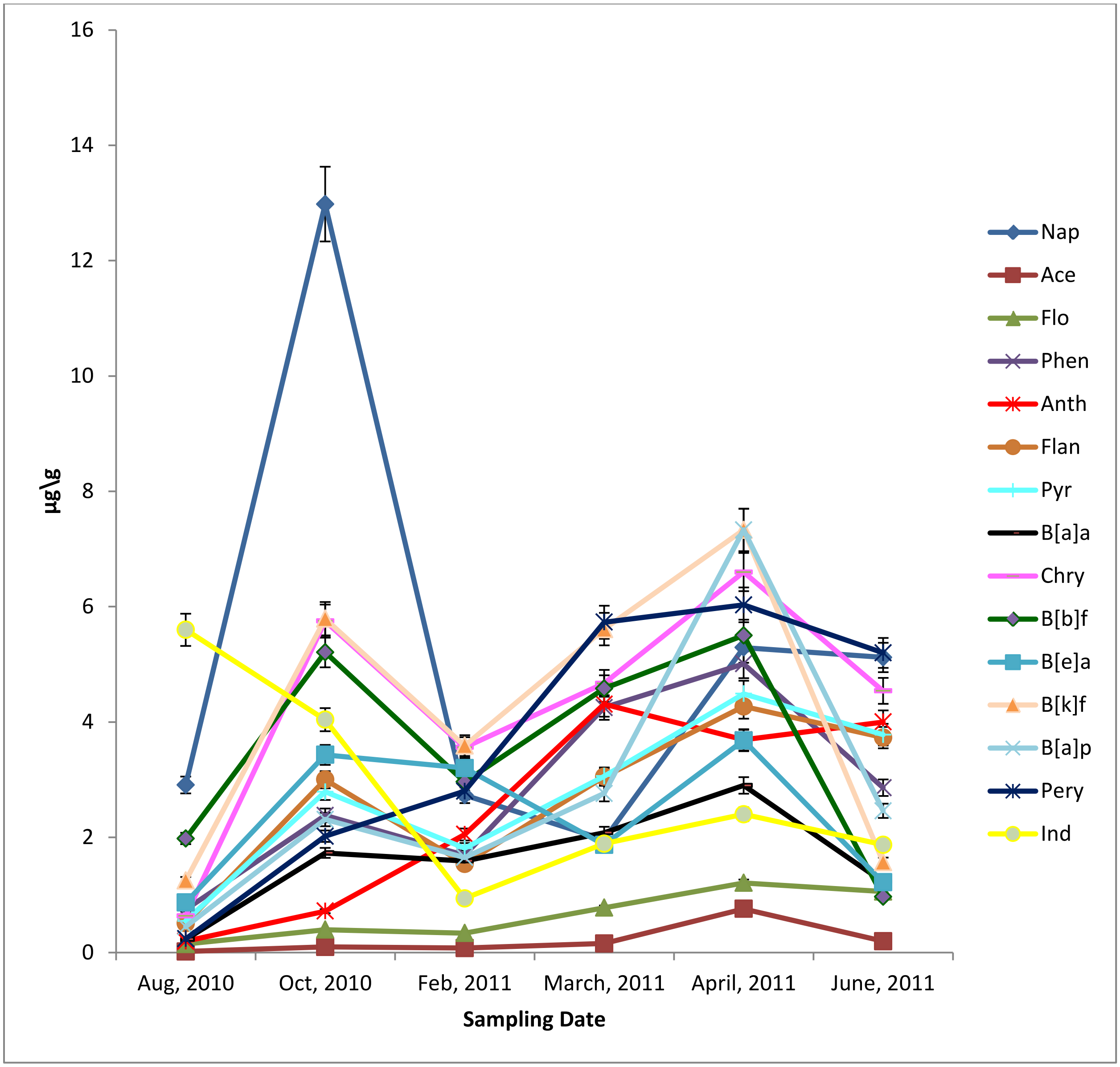


Figure 4.3a: PAH trend in soil arround Matla power plant throughout the sampling period

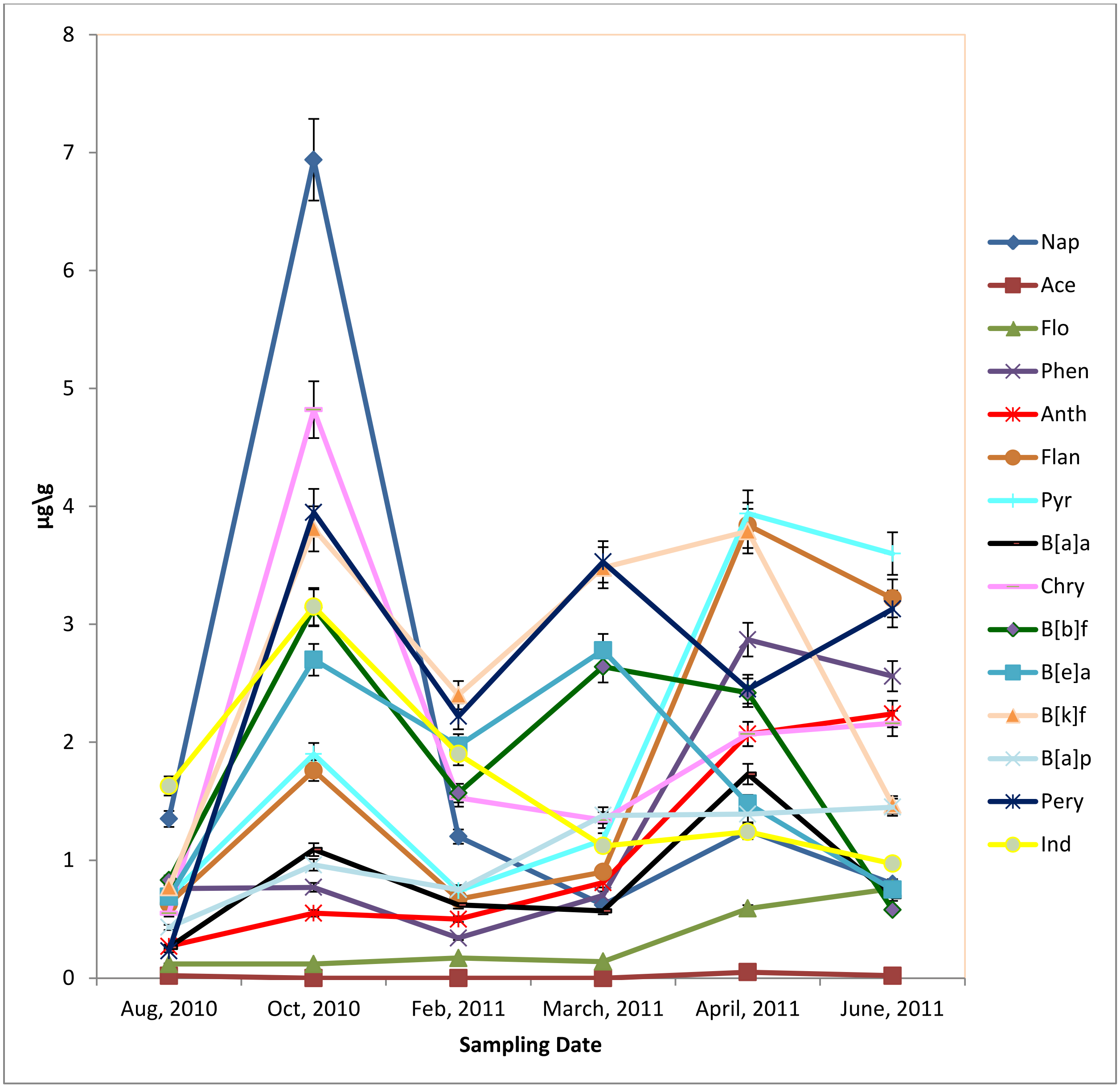


Figure 4.3b: PAH trend in soil around Lethabo power plant throughout the sampling period

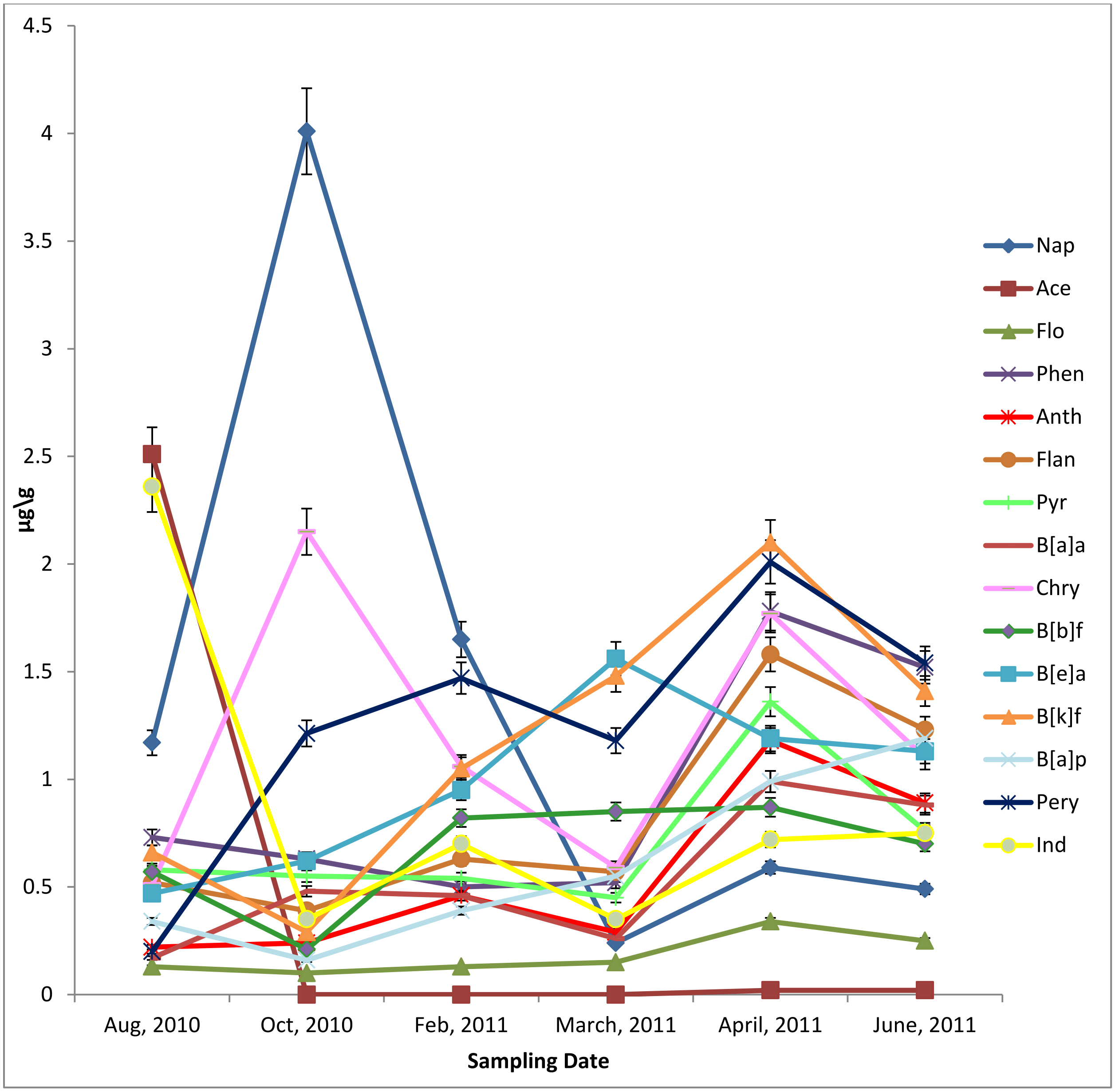


Figure 4.3c: PAH trend in soil around Rooiwal power plant throughout the sampling period

4.2 Results and discussion on Metals

4.2.1 Soil pH and organic matter

Soil pH and organic matter content are very important factors controlling the mobility and concentration of elements in the soils. The pH values from the three power stations ranged from 6.52 to 7.74 around Matla power plant, 6.37 to 7.91 for Lethabo and 6.52 to 6.96 at Rooiwal, which suggest slightly acidic to neutral conditions for all the top soil in the study area (Table 4.6). Higher soil acidity (lower pH values) favours the availability of cations in soil (Adeniyi et al., 2008b). Most heavy metals exchangeable fractions in soil canbe said to exit as cations. The percentage of organic matter in the soil ranged from 6.04 to 17.58, 5.21 to 13.45 and 8.17 to 13.35 % around Matla, Lethabo and Rooiwal respectively (Table 4.6). A high carbon organic content indicate that metals are likely to be bound to organic matter to form metal-chelate complexes, as this also make them less available to plants (Moreno et al., 2009; Yap et al., 2009).

Table 4.6: Mean pH value and percentage organic matter at Matla, Lethabo and Rooiwal

Distance from power plant	pH			% Organic matter		
	Matla	Lethabo	Rooiwal	Matla	Lethabo	Rooiwal
0 km	7.11±0.926	6.43±0.15	6.68±0.57	5.91±1.713	13.08±3.20	7.27±1.23
5 km	6.88±0.277	7.27±0.24	6.90±0.39	7.63±2.576	8.65±3.18	11.72±1.45
10 km	6.84±0.501	8.10±0.62	6.94±0.26	12.65±.464	6.26±1.41	8.69±5.19
15 km	7.33±0.540	-	-	19.65±4.527	-	-
20 km	7.54±0.289	8.17±0.58	6.70±0.43	14.61±3.330	4.49±1.04	10.10±3.82
25 km	7.18±0.427	-	-	11.22±3.383	-	-
30 km	6.93±0.319	7.72±0.75	-	16.54±3.541	10.73±3.72	-

(-) No data, area is restricted.

To validate the extraction and separation method, a soil-certified reference material was analysed. Results presented on Table 4.7 indicate that Fe and Cu had percentage recoveries of 103 and 105% respectively, while Ni, Pb, Mn, Zn and Cd had values ranging from 90 to 98%. The lowest recoveries of 81 and 89 % were observed for Hg and Cr respectively. Since the results obtained from the certified reference material were satisfactory, the extraction and separation procedures were then applied for the determination of heavy metals in soil and plant samples.

Table: 4.7: Percentage of metal recovery using a certified reference material

Metal	Certified value ($\mu g\ g^{-1}$)	Confidence interval	Analysis ($\mu g\ g^{-1}$)	Recovery (%)
Zn	37.3±6.21	34.6-40.0	35.86±0.3563	96
Mn	199±17.6	191-207	186.8±1.099	94
Fe	10,196±2,014	9,291-11,101	10,542±80.43	103
Cu	8.70±1.32	8.07-9.33	9.108±0.229	105
Hg	0.71±0.11	0.65-0.76	0.575±0.025	81
Cr	25.4±10.5	21.4-29.4	22.73±0.810	89
Ni	15.0±5.34	12.8-17.3	13.15±0.296	90
Pb	15.7±4.62	13.7-17.7	14.33±0.396	91
Cd	2.15±0.54	1.93-2.38	2.119±0.074	98

The mean concentrations of Pb, Zn, Cd, Ni, Cu, Mn, Hg, Cr and Fe from all the sample sites are given in Tables 4.8a-c, together with the metal pollution index. Fe has the highest concentration, ranging from 1726.00 to 1935.00 $\mu g\ g^{-1}$; 1707.90 to 1777.70; and 1580.60 to 1811.30 $\mu g\ g^{-1}$ at Matla, Lethabo and Rooiwal respectively. These concentrations are above those of the control (1523.50 $\mu g\ g^{-1}$) (Table 3.9). The WHO limits for Fe in medicinal plant has not yet been established. However, the concentration of Fe in plants (*Digitaria eriantha*) from the three sites (123.60 to 787.53 $\mu g\ g^{-1}$) exceed the 20 $\mu g\ g^{-1}$ permissible limit set by the FAO/WHO (1984) for edible plants (Table 4.9).

The range of Mn in soil varied from 181.80 to 231.7 $\mu g\ g^{-1}$, 180.1 to 191.20 $\mu g\ g^{-1}$ and 170.9 to 190.30 $\mu g\ g^{-1}$ at Matla, Lethabo and Rooiwal respectively. The concentrations of 45.94 to 101.38 $\mu g\ g^{-1}$ in plants (*Digitaria eriantha*) at all three power stations far exceed the permissible limit of 2 $\mu g\ g^{-1}$. The values of Pb in the analysed soils ranged from 10.42 to 107.30 $\mu g\ g^{-1}$ in soil and 0.06 to 3.38 $\mu g\ g^{-1}$ in plants (*Digitaria eriantha*). These values in soil were significantly higher than both the control sample and the allowable limit of Pb in soil. However, the concentration in *Digitaria eriantha* was lower compared with the FAO/WHO limit of 10 µg g^{-1} for medicinal plants (Table 4.9).

The content of Zn in the soil sample ranged between 25.30 and 161.30 µg g^{-1};though few of the sampling points had a lower level than the control, the concentration levels were within the allowable limit for Zn in soil. The concentration of Zn in *Digitaria eriantha* was found to be between 17.56 and 30.56 µg g^{-1}. This was in the range of the permissible limit for an edible plant determined by the FAO/WHO. Concentrations of Ni from soil and the plant were in the range of 13.11 to 54.54 µg g^{-1} and 1.44 to 12.46 µg g^{-1} respectively at all three power stations. The mean concentrations were more than the allowable level for Ni in soil for most European countries except for Germany (Table 4.9). In addition, the concentration in *Digitaria eriantha* were higher than the permissible concentration for an edible plant of 1.63 µg g^{-1}. Excess Ni in soil may cause physiological alterations and diverse toxicity symptoms such as chlorosis and necrosis in different plant species (Rahman et al., 2005).

Cadmium is a nonessential trace element with uncertain direct functions in both plants and humans. The concentration in the soil ranged from 0.03 to 0.17 µg g^{-1}, while that in *Digitaria eriantha* was from 0.001 to 0.03 µg g^{-1}. These concentrations for both the soil and *Digitaria eriantha* were below the allowable limit for soil and edible plants. The concentration in the control soil was 0.03 µg g^{-1}.

Cr levels ranged from 32.71 to 101.60 µg g^{-1} in soil. The levels of Cr were significantly higher in some of the sampling points than the allowable limit of Germany, Netherlands and Sweden, but were below the allowable limit of 150.0 µg g^{-1} set by the USA (Table 4.9). All the levels in *Digitaria eriantha* were far above the permissible FAO/WHO limit of 0.02 µg $g^{-1}$for an edible plant. The content of Hg ranged from 0.03 to 0.10 µg g^{-1} in soil and 0.001 to 0.02 µg g^{-1} in *D. eriantha*. These concentrations in both soil and *Digitaria eriantha* were lower than the allowable limit in soil and plants. The level in the control sample was 0.03 µg g^{-1}. The concentration of Cu ranged from 25.51 to 87.74 µg g^{-1} in soil.

These levels were higher in some sampling points in comparison with the allowable limit for soil samples. The level in *Digitaria eriantha,* which was 2.78 to 14.13 µg g^{-1}, was above the permissible level of 3.0 µg g^{-1} for an edible plant.

Table 4.8a: Mean metal concentrations of soil and plant (*Digitaria eriantha*); accumulation factor and metal pollution index in the vicinity of Matla power plant

Distance from power plant	Metal (µg g^{-1}) n=6									
	Pb	Cd	Zn	Mn	Fe	Cu	Ni	Hg	Cr	MPI
0 km	**37.60±3.92** (0.07±0.06)	**0.05±0.03** (0.01±0.003)	**25.30±5.30** (30.56±9.64)	**213.40±28.94** (67.66±2.52)	**1763.40±97.25** (575.92±20.920	**25.15±5.10** (5.25±2.01)	**13.11±1.24** (1.44±0.30)	**0.05±0.03** (0.01±0.001)	**61.11±8.22** (8.88±1.13)	**13.83** 1.80
AF	0.002	0.2	1.21	0.32	0.33	0.21	0.11	0.20	0.15	
5 km	**27.17±5.43** (0.30±0.07)	**0.04±0.02** (0.004±0.004)	**31.98±12.34** (20.84±2.31)	**181.80±13.01** (84.95±11.20)	**1726.00±157.50** (548.67±83.120	**39.58±6.43** (10.44±0.42)	**22.04±5.01** (5.89±1.42)	**0.10±0.07** (0.004±0.004)	**32.71±5.57** (11.60±0.84)	**14.38** 2.45
AF	0.01	0.1	0.65	0.47	0.32	0.26	0.27	0.04	0.35	
10 km	**28.51±11.23** (0.45±0.18)	**0.04±0.01** (0.01±0.02)	**49.21±12.15** (24.70±2.23)	**218.60±28.35** (45.94±2.55)	**1881.90±124.40** (493.63±56.69)	**63.40±17.42** (9.16±2.10)	**28.71±6.84** (10.02±0.65)	**0.08±0.02** (0.01±0.003)	**44.54±9.76** (12.46±0.54)	**17.32** 3.09
AF	0.02	0.25	0.50	0.21	0.26	0.14	0.35	0.13	0.28	
15 km	**107.3±26.96** (0.88±0.47)	**0.08±0.03** (0.01±0.01)	**119.60±31.51** (18.13±2.09)	**210.90±12.23** (90.63±0.66)	**1873.20±113.00** (583.57±48.07)	**67.29±11.59** (11.48±5.27)	**34.11±2.06** (10.82±4.97)	**0.03±0.01** (0.02±0.04)	**76.46±16.84** (12.55±1.10)	**22.90** 3.95
AF	0.01	0.13	0.15	0.43	0.31	0.17	0.32	0.67	0.16	
20 km	**47.50±15.58** (1.92±0.14)	**0.08±0.04** (0.001±0.001)	**99.34±10.57** (19.51±4.63)	**231.70±34.58** (101.38±12.35)	**1876.00±165.90** (569.90±78.28)	**63.99±8.55** (11.31±0.50)	**36.26±7.36** (11.97±1.22)	**0.07±0.03** (0.004±0.004)	**101.60±14.06** (11.99±0.68)	**24.08** 2.86
AF	0.04	0.03	0.20	0.43	0.30	0.18	0.33	0.06	0.12	
25 km	**68.73±12.02** (0.81±0.20)	**0.06±0.02** (0.002±0.001)	**118.70±18.42** (12.09±1.24)	**229.90±49.66** (91.35±6.47)	**1935.01±118.40** (509.58±95.37)	**68.27±10.69** (10.47±0.73)	**43.53±10.24** (12.07±1.29)	**0.06±0.02** (0.01±0.01)	**62.49±4.49** (11.44±2.67)	**23.43** 2.68
AF	0.01	0.03	0.10	0.40	0.26	0.15	0.28	0.17	0.18	
30 km	**47.52±37.11** (1.05±0.53)	**0.07±0.04** (0.003±0.001)	**161.30±28.21** (18.03±1.67)	**220.20±25.14** (68.51±1.80)	**1794.50±128.70** (462.85±47.08)	**65.02±4.74** (14.13±1.74)	**44.74±7.46** (12.46±0.59)	**0.09±0.06** (0.003±0.001)	**63.95±6.58** (10.58±1.68)	**24.68** 2.76
AF	0.02	0.04	0.11	0.31	0.26	0.22	0.28	0.03	0.17	
Mean	**52.05±26.06** (0.78±0.56)	**0.06±0.02** (0.01±0.003)	**86.49±47.81** (20.69±5.32)	**215.20±15.41** (78.63±17.54)	**1835.70±69.68** (534.87±43.10)	**56.15±15.48** (10.32±2.51)	**31.79±10.59** (9.24±3.80)	**0.07±0.02** (0.01±0.01)	**63.27±20.47** (11.36±1.19	**20.90** 2.80
Mean AF	0.01	0.17	0.24	0.37	0.29	0.18	0.29	0.14	0.18	

SD = standard deviation. Values in bold are for the soil while the values in parentheses are for the plant (*Digitaria eriantha*). (AF) = Accumulation factor, ratio of metal concentration in plant to concentration in soil.

Table 4.8b: Mean metal concentrations of soil and plant (*Digitaria eriantha*); accumulation factor and metal pollution index in the vicinity of Lethabo power plant

Distance from power plant	Metals (µg g^{-1}) n=6									
	Pb	Cd	Zn	Mn	Fe	Cu	Ni	Cr	Hg	MPI
0 km	**10.42±1.38** (0.10±0.08)	**0.07±0.03** (0.001±0.001)	**109.8±16.19** (19.51±6.68)	**191.2±9.72** (35.81±7.35)	**1713.8±180.1** (168.82±27.69)	**21.70±3.73** (2.78±0.29)	**23.05±7.72** (0.78±0.10)	**37.53±9.84** (1.36±0.08)	**0.35±0.13** (0.002±0.001)	17.74 (0.74)
AF	0.01	0.01	0.18	0.19	0.10	0.13	0.03	0.04	0.01	
5 km	**19.90±7.86** (0.16±0.03)	**0.17±0.20** (0.001±0.001)	**84.62±6.94** (21.25±8.06)	**188.8±8.23** (46.18±2.22)	**1707.9±180.12** (268.18±17.44)	**34.48±12.70** (2.93±0.78)	**38.47±20.41** (2.42±0.46)	**80.67±46.40** (1.82±0.31)	**0.26±0.14** (0.002±0.004)	23.84 (1.01)
AF	0.01	0.01	0.25	0.24	0.16	0.08	0.06	0.02	0.01	
10 km	**15.80±6.55** (0.24±0.07)	**0.05±0.02** (0.004±0.002)	**33.13±4.92** (23.38±9.62)	**180.1±5.17** (36.58±3.59)	**1774.3±156.90** (654.32±172.14)	**53.00±21.10** (6.97±0.62)	**23.33±11.46** (3.32±0.82)	**48.54±9.41** (2.92±0.93)	**0.06±0.03** (0.003±0.001)	14.66 (2.04)
AF	0.02	0.08	0.71	0.20	0.37	0.13	0.14	0.06	0.05	
20 km	**27.79±10.51** (0.29±0.08)	**0.03±0.01** (0.004±0.002)	**25.49±9.85** (20.26±9.41)	**187.70±6.61** (81.25±5.90)	**1745.9±170.6** (787.53±135.68)	**26.48±8.00** (8.33±0.62)	**31.55±9.083** (3.48±0.64)	**63.77±11.13** (5.01±1.30)	**0.05±0.02** (0.003±0.001)	13.45 (2.04)
AF	0.01	0.13	0.79	0.43	0.45	0.32	0.11	0.08	0.06	
30 km	**22.96±4.87** (3.38±6.99)	**0.05±0.02** (0.003±0.003)	**34.91±9.53** (17.56±10.53)	**188.9±8.86** (67.59±6.50)	**1777.7±177.91** (123.61±32.09)	**62.27±32.29** (4.29±1.05)	**54.32±22.12** (1.43±0.37)	**56.85±5.28** (1.24±0.27)	**0.03±0.01** (0.002±0.001)	16.02 (1.41)
AF	0.15	0.04	0.50	0.36	0.07	0.07	0.03	0.02	0.07	
Mean	**19.37±5.95** (0.83±1.27)	**0.08±0.05** (0.003±0.001)	**57.59±33.47** (20.39±1.92)	**187.3±3.80** (53.48±18.01)	**1743.90±29.23** (400.49±269.10)	**39.59±15.57** (5.06±2.22)	**34.14±11.59** (4.66±2.72)	**57.47±14.53** (2.47±1.40)	**0.148±0.13** (0.002±0.001)	18.89 (1.38)
Mean AF	0.04	0.04	0.35	0.28	0.29	0.13	0.14	0.04	0.01	

SD = standard deviation. Values in bold are for the soil while the values in parentheses are for the plant (*Digitaria eriantha*). (AF) = Accumulation factor, ratio of metal concentration in plant to concentration in soil.

Table 4.8c: Mean metal concentrations of soil and plant (*Digitaria eriantha*), accumulation factor and metal pollution index in the vicinity of Rooiwal power plant

Distance from power plant	Metals (µg g^{-1}) n=6									
	Pb	Cd	Zn	Mn	Fe	Cu	Ni	Cr	Hg	MPI
0km	**92.17±27.65** (0.31±0.49)	**0.05±0.02** (0.004±0.002)	**63.57±17.61** (16.46±2.62)	**170.9±12.26** (54.36±6.36)	**1766.0±206.7** (454.88±113.56)	**25.10±9.19** (3.80±1.25)	**9.35±3.19** (0.89±0.16)	**59.68±7.71** (2.42±0.15)	**0.10±0.05** (0.001±0.001)	17.01 (1.17)
AF	0.01	0.08	0.26	0.32	0.26	0.15	0.10	0.04	0.01	
5km	**52.28±23.33** (0.07±0.03)	**0.12±0.05** (0.01±0.004)	**82.34±7.78** (15.73±2.15)	**190.1±6.01** (75.48±18.37)	**1783.0±193.2** (732.75±76.95)	**31.45±12.37** (10.02±3.08)	**13.07±6.16** (7.35±2.23)	**61.46±12.62** (11.92±2.07)	**0.10±0.04** (0.001±0.001)	19.70 (2.00)
AF	0.001	0.17	0.19	0.40	0.41	0.32	0.56	0.19	0.01	
10km	**71.31±19.41** (0.52±0.03)	**0.06±0.02** (0.01±0.01)	**67.56±5.99** (14.87±2.29)	**180.5±9.22** (42.77±8.32)	**1580.6±312.1** (182.70±76.44)	**78.80±13.64** (3.33±1.47)	**19.40±3.86** (7.27±1.16)	**65.86±16.66** (6.48±1.06)	**0.03±0.01** (0.001±0.001)	18.27 (1.65)
AF	0.01	0.17	0.22	0.24	0.12	0.04	0.37	0.10	0.03	
20km	**81.27±22.67** (0.06±0.05)	**0.08±0.03** (0.01±0.01)	**86.15±10.42** (19.12±1.36)	**190.3±6.30** (72.58±13.19)	**1811.3±195.4** (337.31±126.45)	**87.74±8.19** (6.94±2.74)	**54.54±12.27** (8.97±2.08)	**93.83±20.57** (6.64±1.95)	**0.03±0.01** (ND)	23.57 (3.65)
AF	0.01	0.13	0.22	0.38	0.19	0.08	0.16	0.07	ND	
Mean	**74.26±14.67** (0.24±0.19)	**0.08±0.03** (0.03±0.04)	**74.91±9.54** (16.55±1.59)	**183.00±8.01** (61.30±13.4)	**1735.20±90.73** (426.91±201.24)	**55.77±27.77** (6.02±2.69)	**24.09±17.94** (6.12±3.09)	**70.21±13.82** (6.87±3.37)	**0.07±0.04** (0.001±0.001)	21.05 (2.12)
Mean AF	0.003	0.38	0.22	0.33	0.25	0.11	0.25	0.10	0.01	

SD = standard deviation. Values in bold are for the soil while the values in parentheses are for the plant (*Digitaria eriantha*). (AF) = Accumulation factor, ratio of metal concentration in plant to concentration in soil.

4.2.2 Estimating impact of pollution by metals in soil

Two calculation approaches were available for quantifying the level of metal enrichment in soil. Salomons and Förstner (1984) and Müller (1969) proposed pollution impact scales to convert the calculated numerical results into ranges from unpolluted to very strongly polluted.

4.2.2a Enrichment factor

A standard approach to appraise the anthropogenic effect of heavy metal is to calculate the enrichment factor for metal concentrations above uncontaminated background levels (Fagbote & Olanipekun, 2010; Huu et al., 2010). Pollution would be measured as the ratio of the sample metal enrichment above the concentration present in the reference material (Akoto et al., 2008; Mediola et al., 2008). To identify anomalous metal concentration, geochemical normalisation of the heavy metals data to a conservative element, such as Al, Fe, and Si, has been employed. Several authors have successfully used iron to normalise heavy metal contaminants (BaptistaNeto et al., 2000; Mucha et al., 2003; Mendiola et al., 2008). In this study iron was also used as a conservative tracer to differentiate natural from anthropogenic components.

According to Akoto et al. (2008); Huu et al. (2010) and Fagbote and Olanipekun (2010), the EF of a heavy metal in soil is defined as follows:

$$EF = \frac{\left[C_{metal} / C_{normalizer}\right] soil}{\left[C_{metal} / C_{normalizer}\right] control} \qquad \text{[Equation 4.3]}$$

where Cmetal and Cnormaliser are the concentrations of heavy metal and normaliser in soil and in unpolluted control. The enrichment factor could be used to differentiate between the metals originating from anthropogenic activities and those originating from natural procedures and to assess the degree of anthropogenic influence. Five contamination categories are recognised on the basis of the enrichment factor, as follows (Sutherland, 2000).

Table: 4.9 Five contamination categories of enrichment factor

1	Enrichment factor	< 2	Deficiency to minimal enrichment
2	Enrichment factor	2 – 5	Moderate enrichment
3	Enrichment factor	5 – 20	Significant enrichment
4	Enrichment factor	20 – 40	Very high enrichment
5	Enrichment factor	> 40	Extremely high enrichment

As the enrichment factor values increase, the contributions of the anthropogenic origins also increase (Sutherland, 2000).

Enrichment factors were calculated from the mean concentrations of the metals in the sampling points in the study area. The control sampling point was considered to be the unpolluted or background point. The normalising element used in the study was Fe, because of its low occurrence variability. The enrichment factor of the heavy metals around Matla power plant showed that Fe (1) and Mn (1.08) had no enrichment; Cd (1.3) had minimal enrichment; Cr (2.4), Hg (2.3) and Cu (3.8) had minimal contamination and Ni (5) had moderate enrichment; Pb (20) had significant enrichment. In the vicinity of Lethabo power plant, Fe (1) and Mn (1.01) had no enrichment; Cd (1.6) had minimal enrichment; Zn (2.8), Cr (2.6), Cu (3.2) and Hg (4.2) had moderate enrichment; Ni (7.7) and Pb (13.0) had significant enrichment. In and around Rooiwal power plant, Fe and Mn (1.0) had no enrichment while Cd (2.4), Hg (2.6), Zn (2.8), Cr (3.9) and Cu (4.6) had moderate enrichment. Ni (6.0) had significant enrichment and Pb (61) had extremely high enrichment (Table 4.12).

4.2.2b Index of geo-accumulation

The Index of Geo-accumulation (I-geo) has been used widely to evaluate the degree of metal contamination or pollution in the terrestrial, aquatic and marine environment (Tijani et al., 2009). The I-geo of a metal in soil can be calculated with the formula given below (Mediola et. al., 2008; Asaah and Abimbola, 2005):

$$I_{geo} = Log_2\left(\frac{C_n}{1.5B_n}\right)$$

[Equation 4.4]

where C_n is the concentration of the heavy metal in the enriched sample and B_n is the concentration of the metal in the unpolluted sample or control. The factor 1.5 is introduced to minimise the effect of the possible variations in the background or control values, which may be attributed to lithogenic variations in the sediment (Mediola et al., 2008).

The degree of metal pollution is assessed in terms of seven contamination classes based on the increasing numerical value of the index, as follows (Huu et al., 2010) :

Table: 4.10 Index of geo-accumulation showing the contamination levels

The I-geo contamination levels						
1	Igeo	<	0	=		Unpolluted
2	0	≤	Igeo	<	1	Unpolluted to moderately polluted
3	1	≤	Igeo	<	2	Moderately polluted
4	2	≤	Igeo	<	3	Moderately to strongly polluted
5	3	≤	Igeo	<	4	Strongly polluted
6	4	≤	Igeo	<	5	Strongly to very strongly polluted
7	Igeo	≥	5			Very strongly polluted

The I-geo includes seven grades (0-6), ranging from unpolluted to very strongly polluted. The negative values of Cd and Hg from the vicinity of the three power stations, according to Huu et al. (2010) is an indication that the soils were not polluted by those metals. The values of Zn, Mn, Cu, Ni, Cr and Fe were all less than 1, indicating that soils were unpolluted to moderately polluted with these metals from the vicinity of the power plants. Pb, on the other hand, had values of (1.7) around Lethabo, indicating that the area was moderately polluted with the metal, and the areas around Matla and Rooiwal were strongly polluted (2.3 and 2.5) (Table 4.12). The I-geo factor was not readily comparable with EF, owing to the nature of I-geo calculation, which involves a logarithm function and a background multiplication factor of 1.5 (Fabgote & Olanipekun, 2010).

Table 4.11: Metal control and allowable limit of heavy metal concentration in soil and plant

		Allowable limit of heavy metal concentration in soil (µg/g)					Allowable limit set by FAO/WHO	
Element	Control	Germany	Netherlands	Sweden	USA	Ireland	FAO/WHO edible plant	FAO/WHO medicinal plant
Cd	0.03±0.003	1.0	0.5	0.4	1.9	1.0	0.21	0.3
Cr	18.67±0.567	60.0	30.0	60.0	150.0	-	0.02	0.02
Cu	13.67±0.465	40.0	40.0	40.0	75.0	50.0	3.0	-
Fe	1523.50±12.95						20.0	-
Hg	0.03±0.005	0.5	0.5	0.3	0.85	1.0		
Mn	174.20±3.509						2.0	-
Ni	5.14±0.757	50.0	15.0	30.0	21.0	30.0	1.63	-
Pb	1.64±0.075	70.0	40.0	40.0	15.0	50.0	0.43	10.0
Zn	28.22±1.310	150.0	100.0	100 - 150	140.0	150.0	27.4	-

European Commission Director General Environment, ECDGE (2010). Heavy Metals and Organic Compounds from Wastes Used as Organic Fertilizers. Final Rep., July. WPA Consulting Engineers Inc. Ref. Nr. TEND/AML/2001/07/20, pp. 73-74. http://ec.europa.eu/environment/waste/compost/pdf/hm_finalreport.pdf ((Jabeen 2010)

Table 4.12: Enrichment factor and Igeo of metals at Matla, Lethabo and Rooiwal power plant

Matla power plant									
	Pd(μg/g)	Cd(μg/g)	Zn(μg/g)	Mn(μg/g)	Fe(μg/g)	Cu(μg/g)	Ni(μg/g)	Cr(μg/g)	Hg(μg/g)
M-s	52.05	0.059	86.49	215.2	1835.7	56.15	31.79	63.27	0.066
Fe-s	1835.7	1835.7	1835.7	1835.7	1835.7	1835.7	1835.7	1835.7	1835.7
M-c	1.639	0.027	28.22	174.2	1523.5	13.67	5.14	0.031	18.67
Fe-c	1523.5	1523.5	1523.5	1523.5	1523.5	1523.5	1523.5	1523.5	1523.5
EF	28.00	1.50	2.47	1.03	1.00	3.44	5.67	2.00	2.83
Igeo	2.32	-100.86	0.15	0.03	0.005	0.28	0.65	-84.32	0.21
Lethabo power plant									
M-s	19.37	0.075	57.59	187.34	1743.9	39.59	34.14	57.47	0.148
Fe-s	1743.9	1743.9	1743.9	1743.9	1743.9	1743.9	1743.9	1743.9	1743.9
M-c	1.639	0.027	28.22	174.2	1523.5	13.67	5.14	18.67	0.031
Fe-c	1523.5	1523.5	1523.5	1523.5	1523.5	1523.5	1523.5	1523.5	1523.5
EF	11.00	2.00	1.74	0.94	1.00	2.56	6.67	2.75	4.00
Igeo	1.74	-92.27	0.14	0.03	0.005	0.26	0.66	0.21	-59.27
Rooiwal power plant									
M-s	74.26	0.076	74.91	183.0	1735.2	55.77	24.09	70.21	0.066
Fe-s	1735.2	1735.2	1735.2	1735.2	1735.2	1735.2	1735.2	1735.2	1735.2
M-c	1.639	0.027	28.22	174.2	1523.5	13.67	5.14	18.67	0.031
Fe-c	1523.5	1523.5	1523.5	1523.5	1523.5	1523.5	1523.5	1523.5	1523.5
EF	43.00	2.00	2.26	0.92	1.00	3.56	4.67	3.33	1.5
Igeo	2.53	-91.80	0.15	0.03	0.005	0.28	0.60	0.22	-84.32

M-s and M-c are the values of metal samples and control while Fe-s and Fe-c are for the iron. EF = Enrichment factor and Igeo = Geoaccumulation index

4.2.3 Metal pollution Index

The concentrations of most of the metals around the three power stations and the plant varied to a great extent, depending on the locations of the sampling sites. In order to compare the total metal content at different sampling sites, the metal pollution index

(MPI) was calculated (Usero et al., 1997; Adeniyi et al., 2008a). The MPI equation is indicated below:

$MPI = (Cf1 \times Cf2\ldots\ldots\ldots Cfn)1/n$ [Equation 4.5]

where Cfn = concentration of the metal n in the sample.

The MPI shown in Table 4.8a to 4.8c reveals values ranging from 13.83 to 24.68 for soil and 1.80 to 3.95 for *Digitaria eriantha* in Matla, 13.45 to 23.84 for soil and 0.74 to 2.04 for *Digitaria eriantha* in Lethabo. Rooiwal had a value of 17.01 to 23.57 for soil and 1.17 to 3.65 for *Digitaria eriantha*. These values could be a cause for concern because all the values are more than the baseline of 1µg g-1(Mmolawa et al., 2011).

4.2.4 Accumulation factor

Maisto et al. (2004) used an accumulation factor (AF), which was an index of soil-plant transfer. It is the ratio of the metal concentration in the plant to the metal concentration in soil.

$AF = Cpt / Cs$ [Equation 4.6]

where AF = accumulation factor, Cpt = metal concentration in plant tissue, Cs = metal concentration in soil. Ratios > 1 indicate that plants are enriched in elements (accumulator), ratios of 1 indicate that plants are not influenced by elements (indicator), and ratios < 1 show that plants exclude the elements from uptake (excluder). Accumulation factor ratios were all less than 1 (Table 4.8a to 4.8c), indicating a low transfer from soil to *Digitaria eriantha* in all the study sites.

These results imply that the plant *Digitaria eriantha* acted as an excluder for most of the elements studied. This could probably be explained by neutral or alkaline soils' pH value (6.37 to 7.91), which would normally not favour the uptake of metals by plants. At a relatively high pH (above 6.5), the mobility of trace metals is substantially limited because of the neutral sub-alkaline medium. The high level of organic matters may also be a factor (Table 4.1).

To determine whether the metal concentrations of the soil and the plant (*Digitaria eriantha*) have the same origin, a Pearson correlation (r) was used. The result showed good correlation between the metal concentrations in soil and the plant, indicating that they probably originate from the same source (Table: 4.13).

Table 4.13: Pearson correlation (r) of metal in soil and plant (*Digitaria eriantha*) around Matla, Lethabo and Rooiwal power stations

Power plant	Pb	Cd	Zn	Mn	Fe	Cu	Ni	Cr	Hg
Matla	0.29	-0.30	-0.74	0.08	0.41	0.74	0.95	-0.26	-0.86
Lethabo	0.34	-0.78	-0.09	0.22	0.28	0.10	-0.23	0.20	-0.60
Rooiwal	0.26	0.59	0.60	0.73	0.64	-0.21	0.65	-0.01	0.56

Relatively good correlation existed among most of the metals in both the soil and plant samples. These values suggest that the metals most probably come from the same source or same atmospheric conditions (Table 4.14a – c).

Table 4.14a: Pearson correlation coefficient (r) of individual metals in soil and plant (*Digitaria eriantha*) at Matla power station

	Pb	Cd	Zn	Mn	Fe	Cu	Ni	Cr	Hg
Pb	**1.00** (1.00)	**0.71** (-0.63)	**0.58** (-0.52)	**0.24** (0.58)	-**0.06** (0.01)	**0.50** (0.62)	**0.43** (0.74)	**-0.78** (-0.22)	-**0.02** (0.41)
Cd		**1.00** (1.00)	**0.77** (0.65)	**0.52** (-0.29)	**-0.52** (0.27)	**0.55** (-0.56)	**0.60** (-0.49)	**-0.50** (0.68)	**0.34** (-0.08)
Zn			**1.00** (1.00)	**0.52** (-0.57)	**-0.70** (0.30)	**0.78** (-0.74)	**0.92** (-0.80)	-**0.13** (-0.01)	**0.69** (-0.50)
Mn				**1.00** (1.00)	-**0.65** (0.52)	**0.55** (0.31)	**0.57** (0.26)	-**0.34** (0.02)	**0.20** (0.21)
Fe					**1.00** (1.00)	**-0.49** (-0.46)	**-0.77** (-0.46)	**-0.21** (0.42)	**-0.52** (-0.03)
Cu						**1.00** (1.00)	**0.89** (0.83)	**-0.08** (-0.23)	**0.27** (0.50)
Ni							**1.00** (1.00)	**0.05** (-0.02)	**0.54** (0.66)
Cr								**1.00** (1.00)	-**0.86** (0.27)
Hg									1.00 **(1.00)**

Values in bold are for the soil while the values in parentheses are for the plant (*Digitaria eriantha*)

Table 4.14b: Pearson correlation coefficient (r) of individual metals in soil and plant (*Digitaria eriantha*) at Lethabo power station

	Pb	Cd	Zn	Mn	Fe	Cu	Ni	Cr	Hg
Pb	**1.00** (1.00)	**-0.24** (0.19)	**-0.72** (-0.72)	**0.01** (0.42)	**0.33** (-0.47)	**0.18** (-0.12)	**0.55** (-0.36)	**0.63** (-0.39)	**-0.70** (-0.36)
Cd		**1.00** (1.00)	**0.63** (0.22)	**0.27** (0.49)	**-0.69** (0.75)	**-0.19** (0.93)	**0.11** (0.70)	**0.58** (0.68)	**0.63** (0.84)
Zn			**1.00** (1.00)	**0.58** (-0.49)	**-0.84** (0.75)	**-0.57** (0.93)	**-0.29** (0.70)	**-0.16** (0.68)	**0.99** (0.84)
Mn				**1.00** (1.00)	**-0.60** (0.31)	**-0.48** (0.52)	**-0.48** (0.31)	**0.08** (0.55)	**0.55** (0.25)
Fe					**1.00** (1.00)	**0.82** (0.93)	**0.31** (0.91)	**-0.25** (0.94)	**-0.89** (0.97)
Cu						**1.00** (1.00)	**0.58** (0.83)	**0.01** (0.90)	**-0.67** (0.95)
Ni							**1.00** (1.00)	**0.46** (0.83)	**-0.39** (0.87)
Cr								**1.00** (1.00)	**-0.12** (0.87)
Hg									**1.00** (1.00)

Values in bold are for the soil while the values in parentheses are for the plant (*Digitaria eriantha*)

Table 4.14c: Pearson correlation coefficient (r) of individual metals in soil and plant (*Digitaria eriantha*) at Rooiwal power station

	Pb	Cd	Zn	Mn	Fe	Cu	Ni	Cr	Hg
Pb	**1.00** (1.00)	**-0.86** (-0.21)	**-0.47** (-0.66)	**-0.67** (-0.99)	**0.10** (-0.67)	**0.10** (-0.86)	**0.20** (-0.33)	**0.22** (-0.48)	**-0.14** (0.55)
Cd		**1.00** (1.00)	**0.77** (0.03)	**0.81** (0.30)	**0.42** (-0.10)	**-0.17** (0.48)	**0.04** (0.98)	**0.04** (0.76)	**0.28** (-0.33)
Zn			**1.00** (1.00)	**0.95** (0.57)	**0.58** (-0.10)	**0.34** (0.48)	**0.67** (0.98)	**0.67** (0.76)	**-0.20** (-0.33)
Mn				**1.00** (1.00)	**0.31** (0.71)	**0.42** (0.92)	**0.58** (0.39)	**0.56** (0.59)	**-0.31** (-0.49)
Fe					**1.00** (1.00)	**-0.32** (0.80)	**0.31** (-0.12)	**0.34** (0.57)	**0.43** (0.26)
Cu						**1.00** (1.00)	**0.80** (0.48)	**0.78** (0.85)	-**0.99** (-0.20)
Ni							**1.00** (1.00)	**0.99** (0.68)	**-0.72** (-0.53)
Cr								**1.00** (1.00)	**-0.70** (0.04)
Hg									**1.00** (1.00)

Values in bold are for the soil while the values in parentheses are for the plant (*Digitaria eriantha*)

ANOVA at $P < 0.05$ was also used for the differences in the concentrations of metals in soil and plants (*Digitaria eriantha*) around the three power plants. The result showed that the concentration of most of the metals around the three power plants were statistically non-significant at $P < 0.05$, except for Pd and Mn in soil, and Cu, Ni, Hg and Cr in the plant that are statistically significant (Table: 4.15).

Table 4.15: ANOVA of metal levels in soil and plant around the three power plants

	Pb	Cd	Zn	Mn	Fe	Cu	Ni	Hg	Cr	F-critical (p < 0.05)
Soil	7.81*	0.31^{ns}	0.72^{ns}	11.58*	3.31^{ns}	1.01^{ns}	0.57^{ns}	1.65^{ns}	0.49^{ns}	3.81
Plant	0.60^{ns}	3.70^{ns}	1.31^{ns}	2.87^{ns}	0.74^{ns}	6.26*	6.33*	6.20*	23.16*	3.81

4.3 Results and discussion on Ultrasonic DLLME

In order to obtain an optimum ultrasonic DLLME preconcentration and determination of PAHs in soil sample, several parameters were considered, including the type of dispersive solvent, extraction solvent, extraction time and extraction volume.

4.3.1 Selection of good dispersive solvent

The dispersive solvent should be miscible with both water and the extraction solvent. This is because the method is based on a ternary component solvent system in which the extraction solvent and disperser solvent are injected into an aqueous sample. In this work three solvents, methanol, acetonitrile and acetone, were tested as disperser solvents and their effect on the performance of DLLME was investigated. This disperser solvent was initially used for the extraction of the PAHs from the soil sample with the aid of an ultrasonic bath; 1.0 mL of the disperser solvent (acetonitrile) containing 70 µL (optimum volume) of the extraction solvent ($C_2H_2Cl_2$) was used for the DLLME procedure. Figure 4.4 compares the extraction recovery (ER) for PAHs when using acetone, methanol and acetonitrile. Acetonitrile was clearly most efficient in comparison to the other two solvents and was therefore selected as the dispersive solvent in this work.

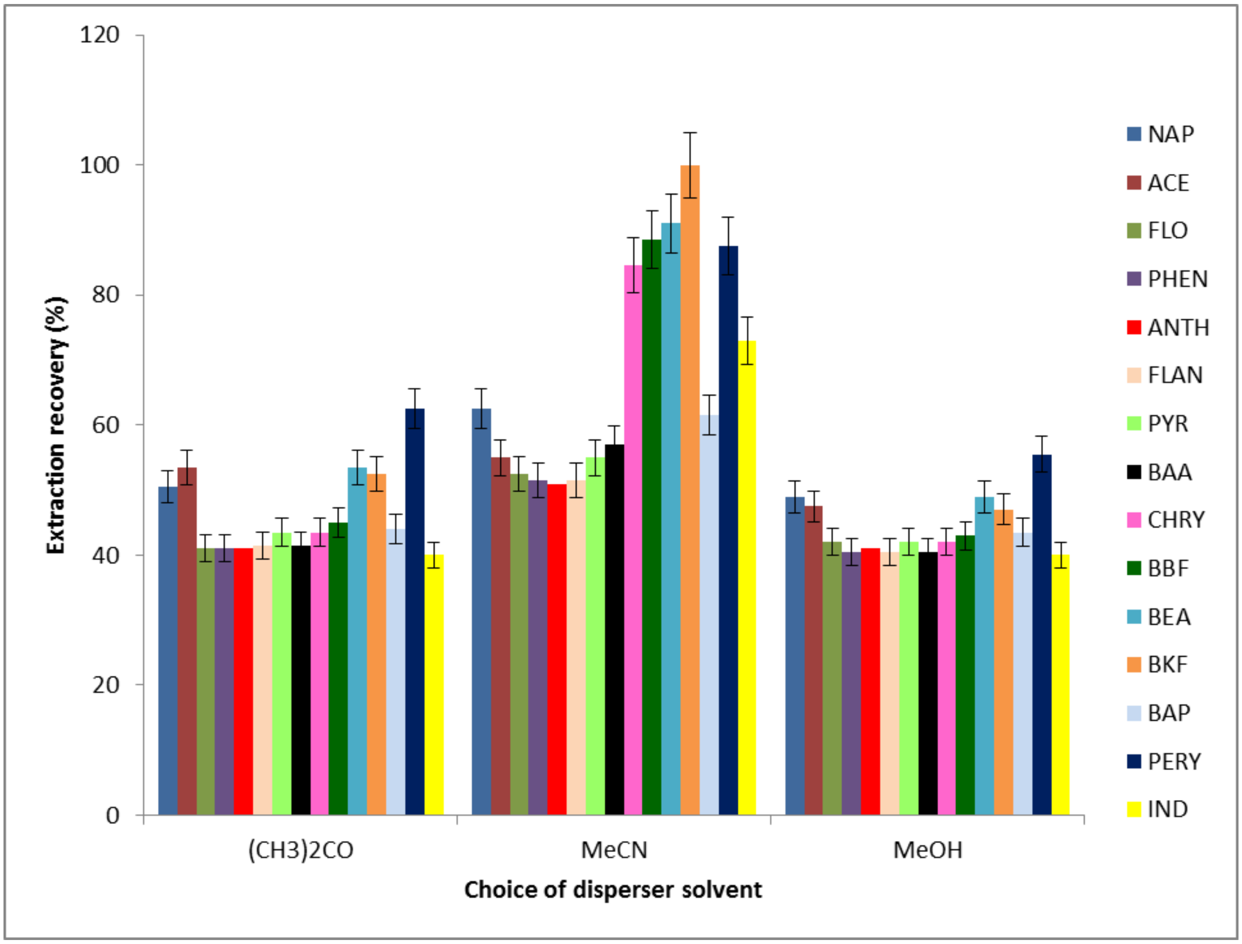


Figure 4.4: Selection of disperser solvent for the extraction of PAHs in soil sample by the UA-DLLME method

4.3.2 Selection of good extraction solvent

The choice of an appropriate extraction solvent is of paramount importance in order to achieve good extraction efficiency of the target compounds. The extraction solvent has to meet four requirements: (i) higher density than water, (ii) immiscibility with water but miscible with the dispersive solvent, (iii) good solubility for analytes and (iv) good chromatographic behaviour (Rezaee et al., 2006). In this work, dicholoroethene with a density of 1.28 g/mL, dichloromethane with a density of 1.83 g/mL and chloroform, which has a density of 1.47 g/mL, were investigated (Fig 4.5).

The results showed that $C_2H_2Cl_2$ has the highest extraction recoveries in comparison with $CHCl_3$ and CH_2Cl_2. Therefore, $C_2H_2Cl_2$ was selected as the extraction solvent in this work.

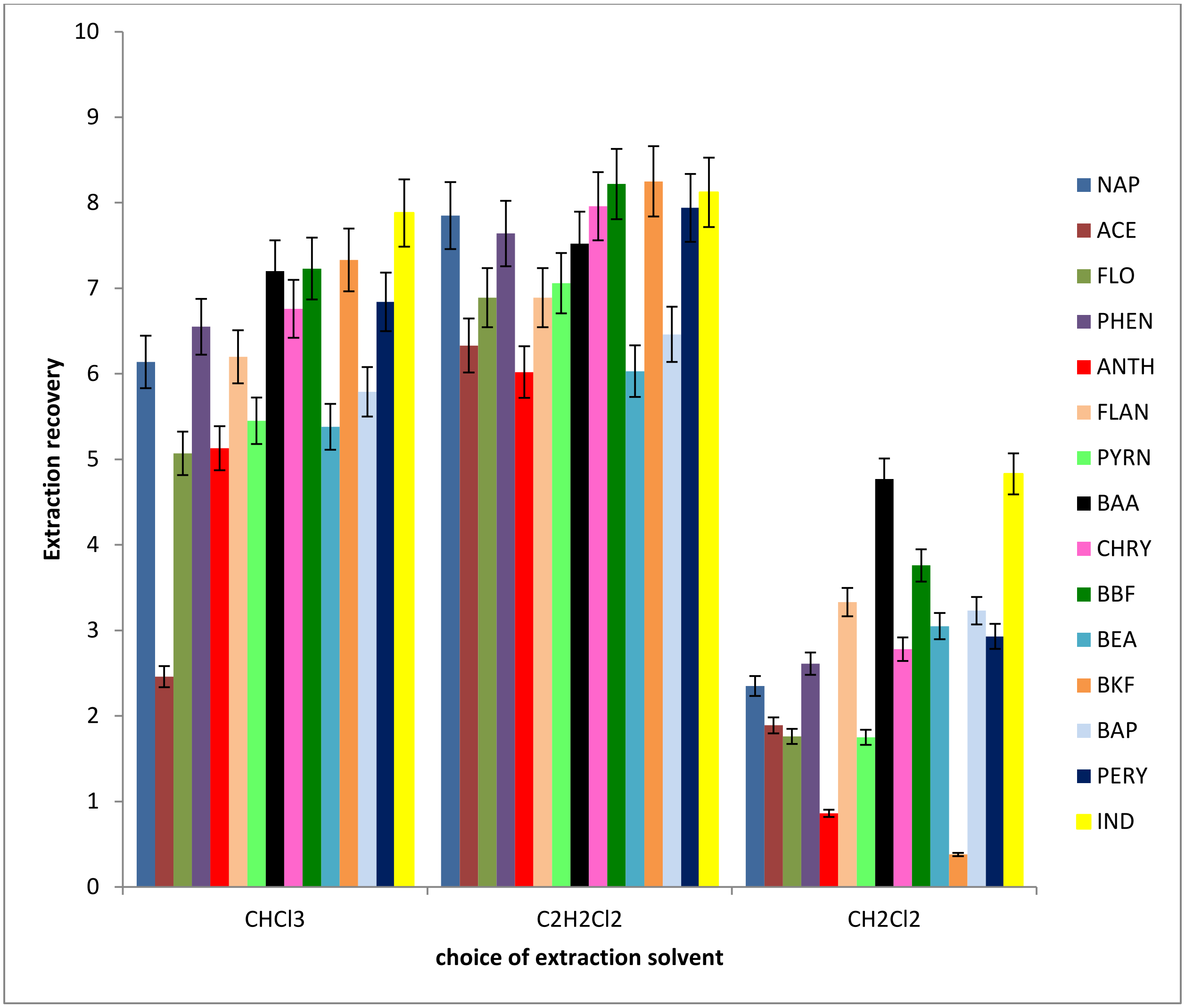


Figure 4.5: Choice of extraction solvent for the extraction of PAHs in soil sampl by the UA-DLLME method

4.3.3 Effect of ultrasonic-DLLME extraction time

Ultrasonication time plays an important role in the ultrasonic assisted DLLME procedure. Appropriate time would give the highest ER of the target compound in soil.

In this experiment, ultrasonication times ranging from 10 to 60 min were evaluated, with other experimental conditions (the disperser, the extraction solvent and the volume) remaining constant (Fig 4.6).

The results showed that extraction of the analyte increased to a maximum with increasing sonication time up to about 30 min and thereafter it started to decrease. Hence, 30 min was selected for all further experiments. The DLLME extraction is time-independent (Razaee et al., 2006; Lin et al., 2001). It is because of the infinitely large surface area between extraction solvent and aqueous phase. Development of a cloudy solution advances the analyte from the aqueous phase to the extraction solvent very rapidly and the equilibrium state was achieved quickly.

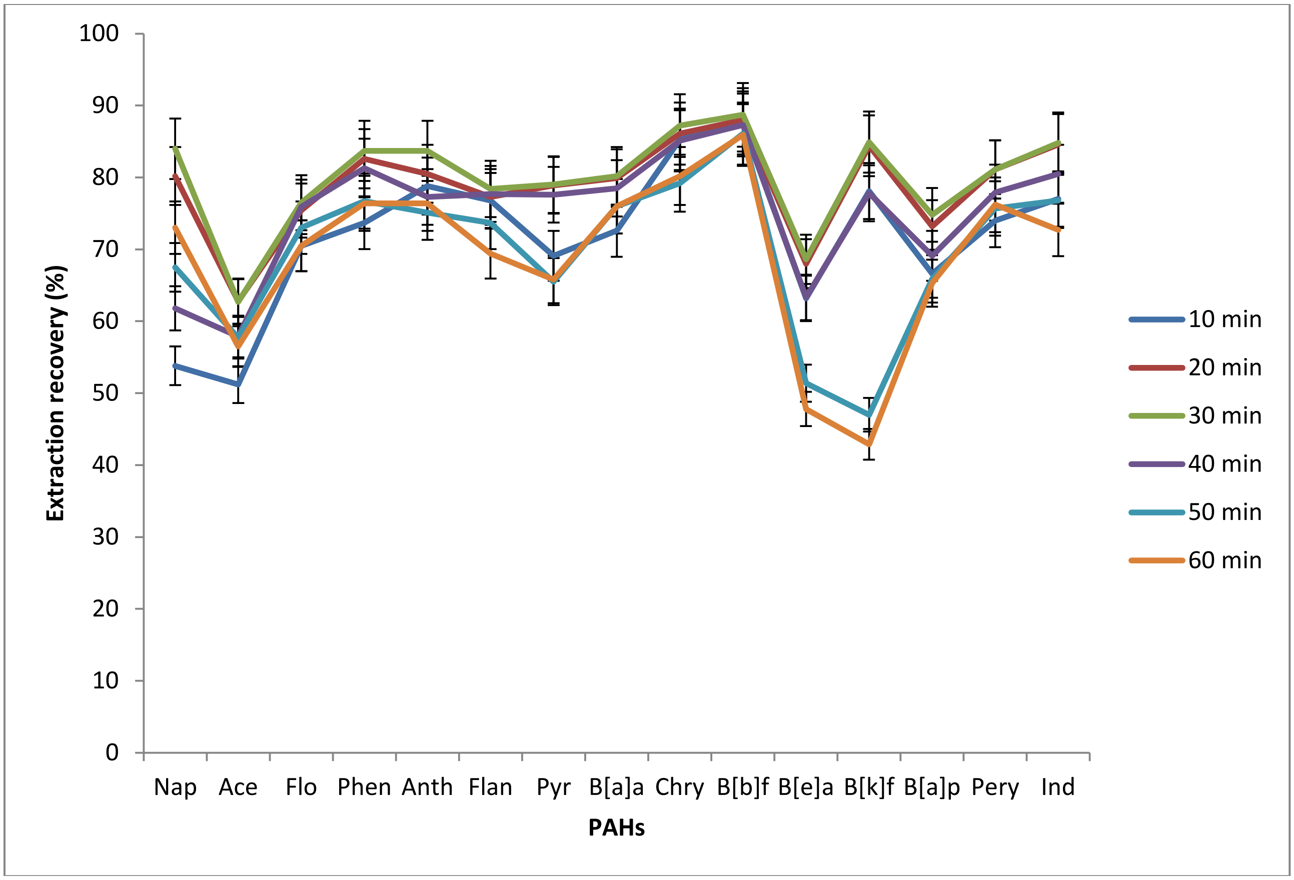


Figure 4.6: Selection of extraction time for the extraction of PAHs in soil sample by the UA-DLLME method

4.3.4 Effect of volume of extraction solvent in ultrasonic DLLME

To examine the effect of the volume of the extraction solvent in ultrasonic DLLME, different volumes of $C_2H_2Cl_2$ were used. A 1 mL aliquot of MeCN containing different volumes of $C_2H_2Cl_2$ (50–90 µL at 10 µL interval) was subjected to the same DLLME procedure. When the volume of $C_2H_2Cl_2$ was increased from 50.0 to 90.0 µL, the volume of the sedimented phase increased concomitant with the sharp decrease in the analyte signals. This may be due to dilution of the extracted analytes in the extraction solvent at higher volumes. Thus, 70.0 µL $C_2H_2Cl_2$ has the highest extraction recovery and was selected in subsequent experiments (Fig 4.7).

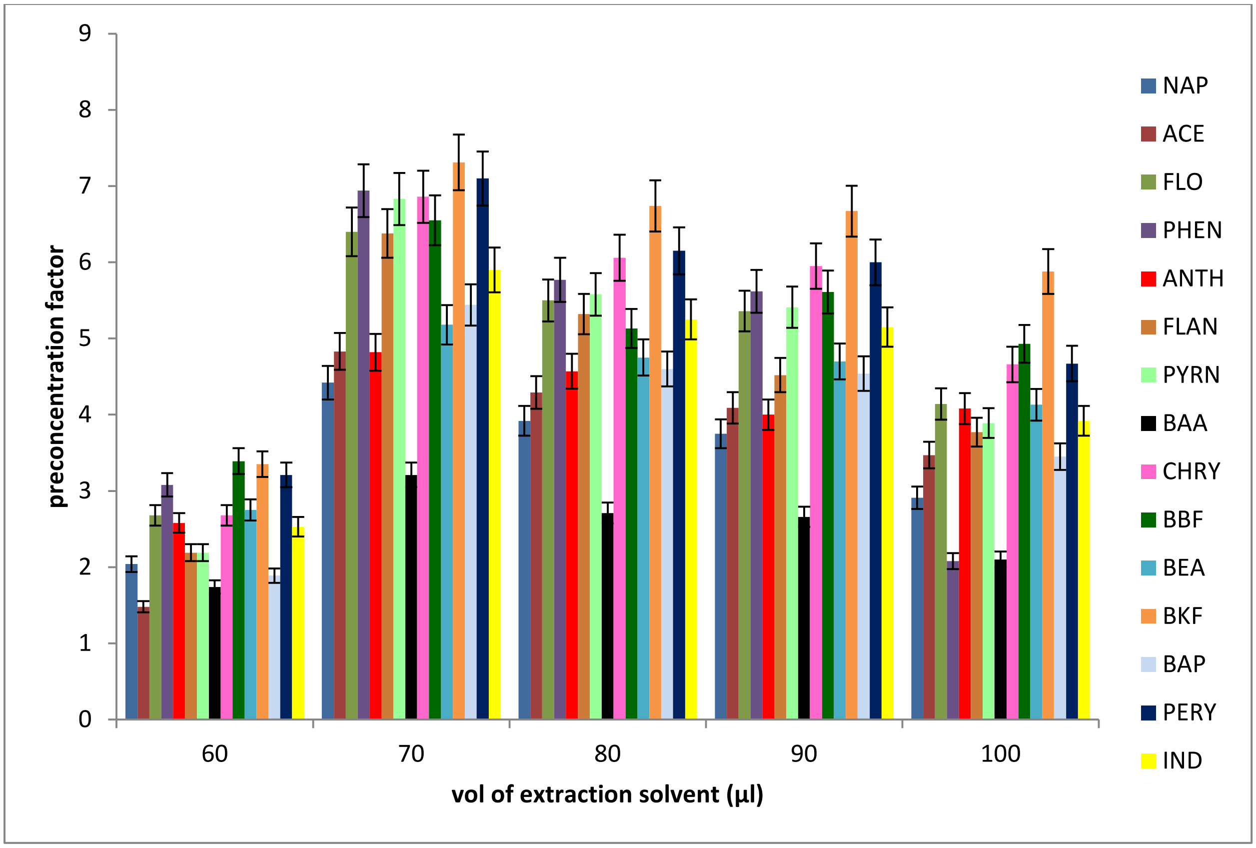


Figure 4.7: Effect of volume of extraction solvent for the extraction of PAHs in soil sample

4.3.5 Comparison of Soxhlet extraction with ultrasonic assisted DLLME extraction

As shown in Fig 4.8, the Soxhlet extraction method was more efficient in extracting PAH from soil than the ultrasonication method. The concentration of the lower molecular weight PAHs (naphthalene, acenaphthene and fluorene) obtained using ultrasonic extraction may be lower when compared with Soxhlet extraction. This may be due to losses of the lower molecular weight, as a result of volatilization from the extraction vessel (Guerin, 1988). It should be noted therefore that the Soxhlet extraction method consistently extracted more PAHs than the ultrasonic extraction method.

The efficiency of the ultrasonic assisted DLLME extraction method was evaluated by determining the concentration of PAHs and the ER of the CRM sample. When 1.0 g of the CRM was extracted with both the Soxhlet and ultrasonic assisted DLLME extraction, the result showed that the Soxhlet extraction method gave higher recoveries of individual PAHs than the ultrasonic assisted DLLME extraction method (Table 4.17). However, there were no significant statistical differences ($p<0.05$; Table 4.18) between the two extraction methods. Despite the fact that there was no significant difference between the two methods, the ultrasonic assisted DLLME extraction method has one or two advantages over the Soxhlet, i.e reduced extraction time and reduced solvent volume (Rezaee et al, 2010). The result of this experiment also showed that the ultrasonic assisted DLLME method could give comparable analytical results when compared with that of the Soxhlet extraction method for solid soils extraction.

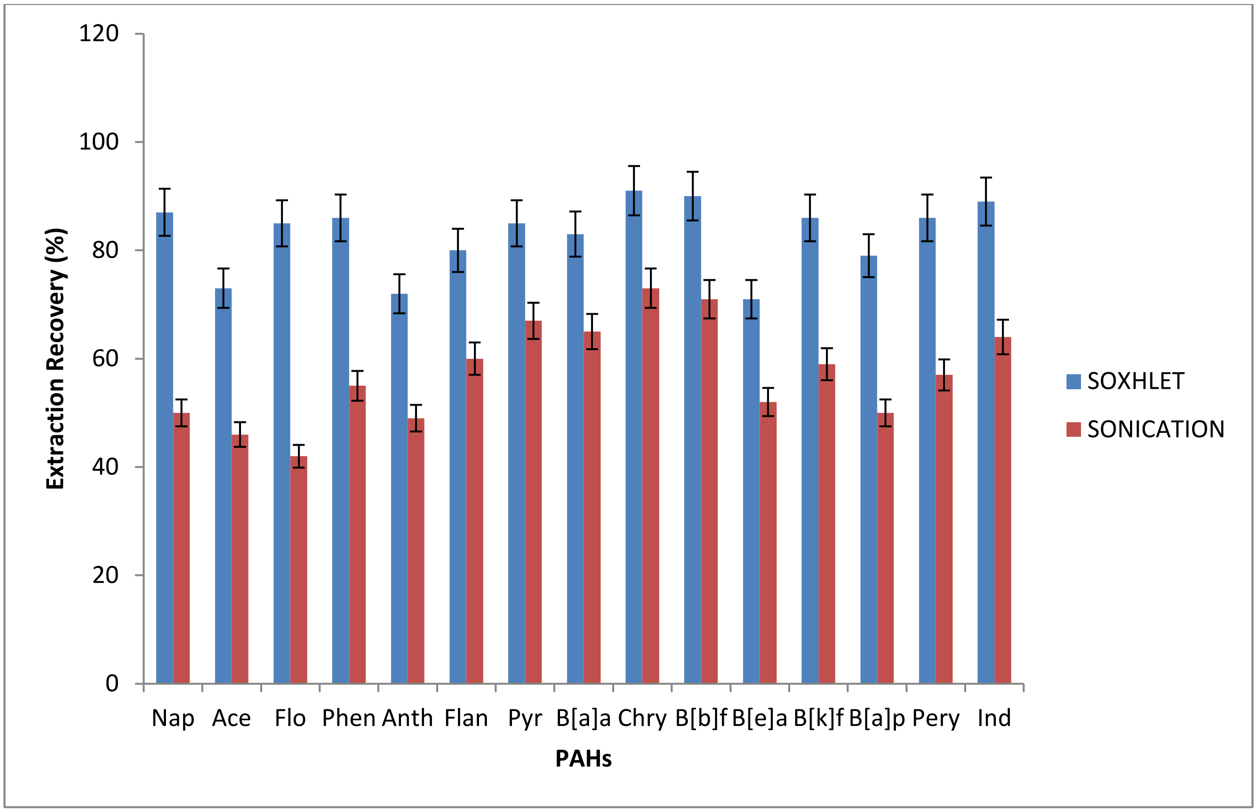


Figure 4.8: Comparison of Soxhlet extraction with ultrasonication assisted DLMME extraction

4.3.6 Real sample analysis using the UA-DLLME method

Concentration of PAHs in soil samples collected from the surroundings of Matla coal-powered station in February, March, April and June ranged from 3.19 to 23.67 µg g^{-1}, 7.54 to 18.54 µg g^{-1}, 13.14 to 28.20 ug g^{-1} and 6.86 to 19.91 µg g^{-1} respectively (Figure 4.9 a to d). According to the ATSDR (1995C), levels of the sum of PAHs between 0 and 0.1 µg g-1 are considered as non-contamination. Values that fall within the range of 0.1 to 1 µg g-1 imply slight contamination, whereas values between 1 and 10 µg g-1 are an indication of significant contamination.

Table 4.18 shows that the TPAH levels in most of the sampling points were higher than 1.0 µg g^{-1}, thus indicating significant contamination.

HMW compounds contributed significantly to the total PAH concentration in most of the samples analysed (Table 4.16). These HMW PAHs are generally derived from pyrolytic origin, i.e. PAHs that result from incomplete combustion of organic matter (e.g. coal and wood) in industrial operations and power plants that use fossil fuels (Qiao et al. 2006; Sanders et al., 2002; Dahle et al., 2003). Benzo [a] anthracene, Chry, B[b]f, B[k]f, B[a]p and Ind, which are very predominant in the real samples analysed, have been classified as possibly carcinogenic to humans (Kong et al., 2011). Most of these PAHs were found at concentrations between 1 to 10 µg g^{-1}, which is an indication of significant contamination. Instead of averaging the results of real samples (February, March, April and June) the concentrations of each extraction with the ultrasonic assisted DLLME method were compared with Soxhlet, using the Student-t test. While there was no significant difference in concentration between the TPAH using Soxhlet extraction and the ultrasonic DLLME method for the month of February, the two methods were found to be statistically different in extraction efficiency for the samples collected in March, April and June (Table 4.18).

Table 4.16: Spatial distribution of soil TPAHs LMW, MMW, HMW for the real samples in February, March, April and June using ultrasonic DLLME around Matla

	(µg g^{-1})																											
	O KM				5 KM				10 KM				15 KM				20 KM				25 KM				30 KM			
	Feb	Mach	April	June	Feb	Mach	April	June	Feb	Mach	April	June	Feb	Mach	April	June	Feb	Mach	April	June	Feb	Mach	April	June	Feb	Mach	April	June
TPAH	3.19	7.54	15.99	6.86	10.18	18.54	26.53	19.25	13.26	9.53	16.43	19.91	23.67	17.20	28.20	19.19	14.70	12.98	24.31	18.04	6.39	8.10	13.14	16.79	4.94	17.05	22.79	16.23
LMW (2-3 RING)	1.47	1.32	0.54	0.93	0.7	1.26	0.45	2.41	1.19	1.30	0.88	3.57	2.41	2.02	2.17	2.75	2.28	2.65	1.69	4.22	3.7	1.27	1.88	5.34	1.73	4.92	3.23	5.37
MMW (4 RING)	0.73	5.56	3.82	1.42	0.86	3.78	8.01	4.17	4.56	2.14	3.41	3.99	6.04	4.06	5.24	7.15	3.49	2.59	5.38	5.65	0.48	1.31	1.14	5.04	0.62	3.98	3.75	3.74
HMW (5-6 RING)	0.99	0.66	11.63	4.51	6.27	13.5	18.86	12.67	7.51	5.18	12.14	12.35	15.22	11.12	20.79	9.29	8.93	7.74	17.24	8.17	2.21	5.52	13.84	8.04	2.59	8.15	15.81	7.55

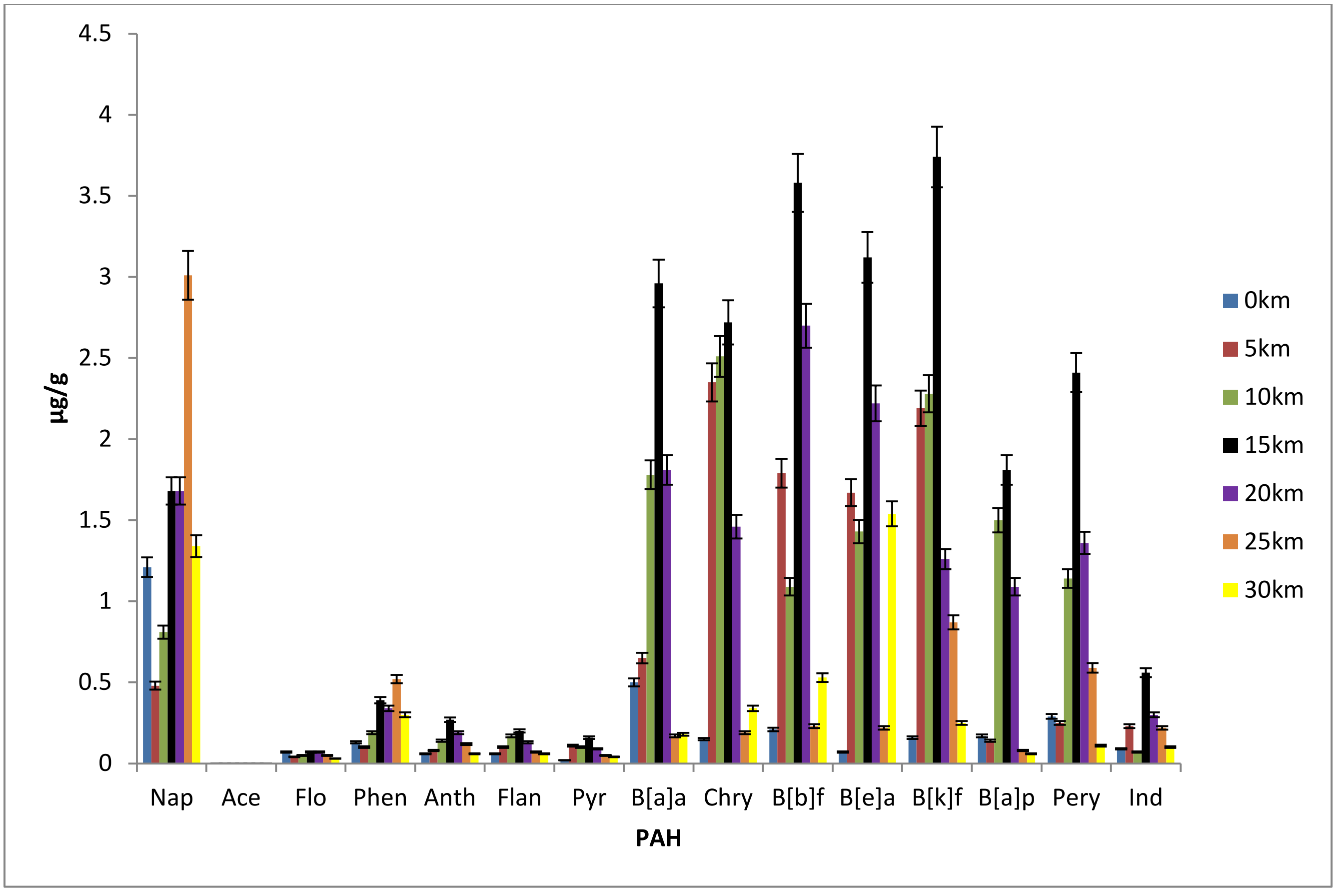


Figure 4.9a: Mean concentration of PAHs in Matla power plant using the ultrasonic DLLME method (February 2011)

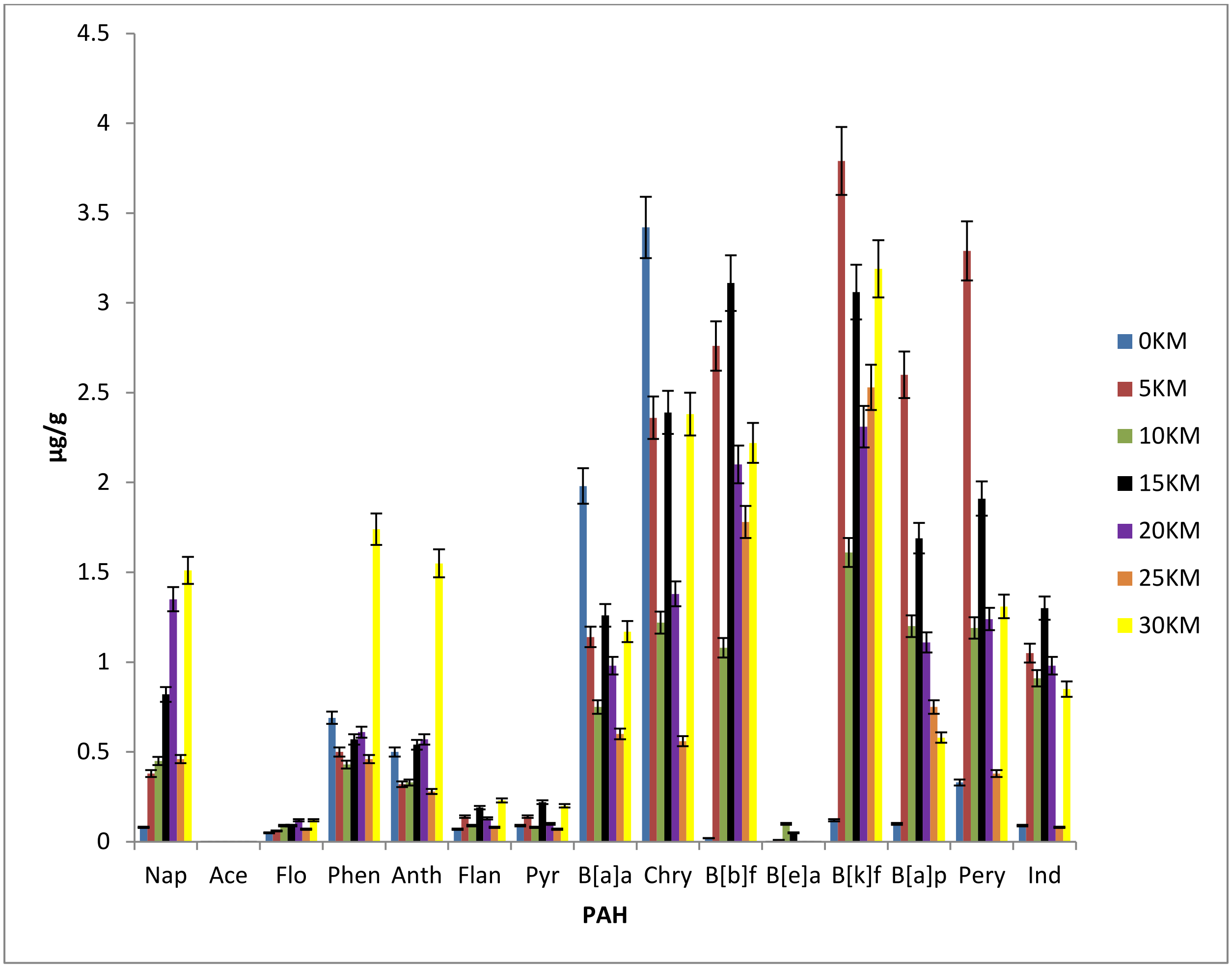


Figure 4.9b: Mean concentration of PAHs in Matla power plant (using the ultrasonic DLLME method (March 2011)

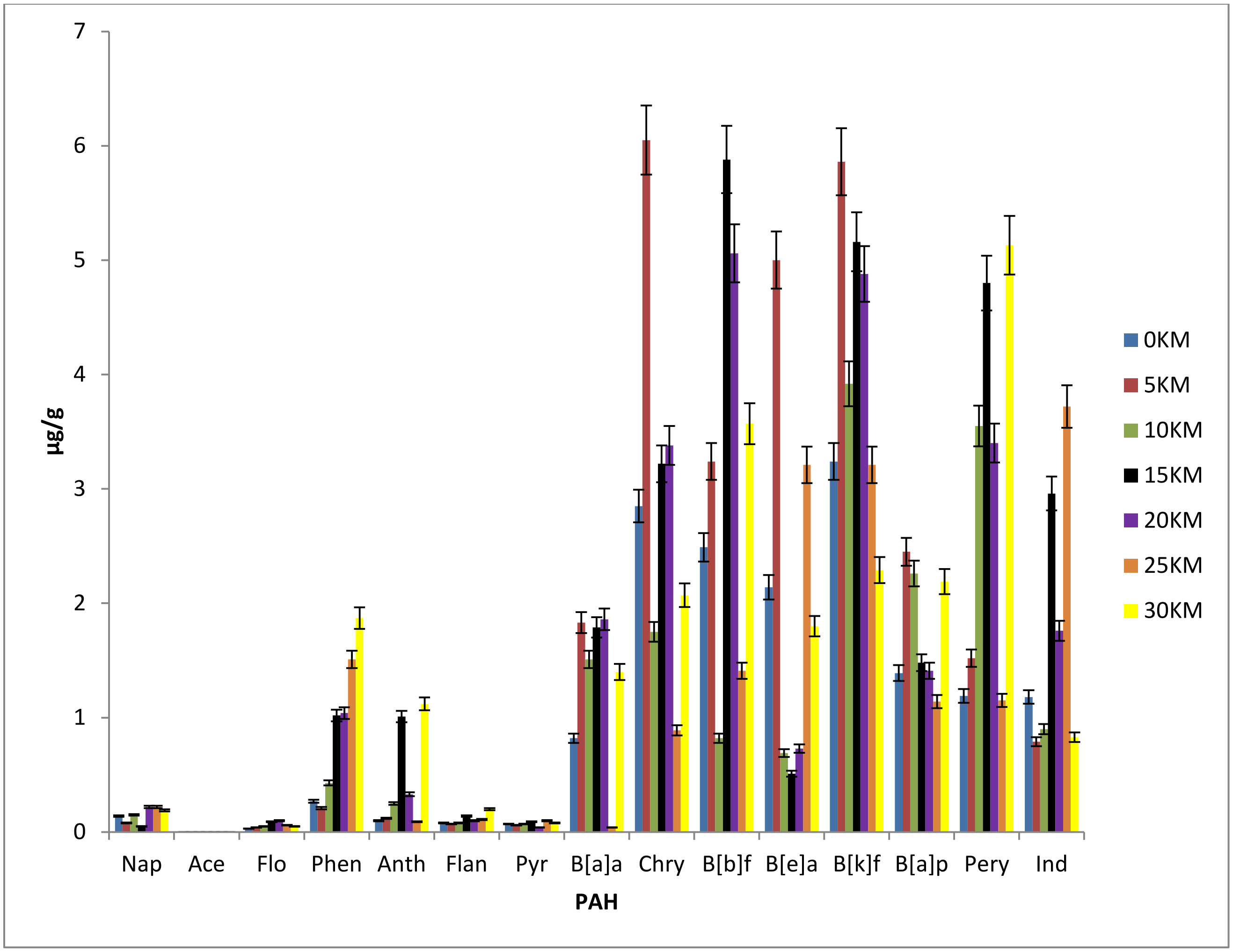


Figure 4.9c: Mean concentration of PAHs in Matla power plant using the ultrasonic DLLME method (April 2011)

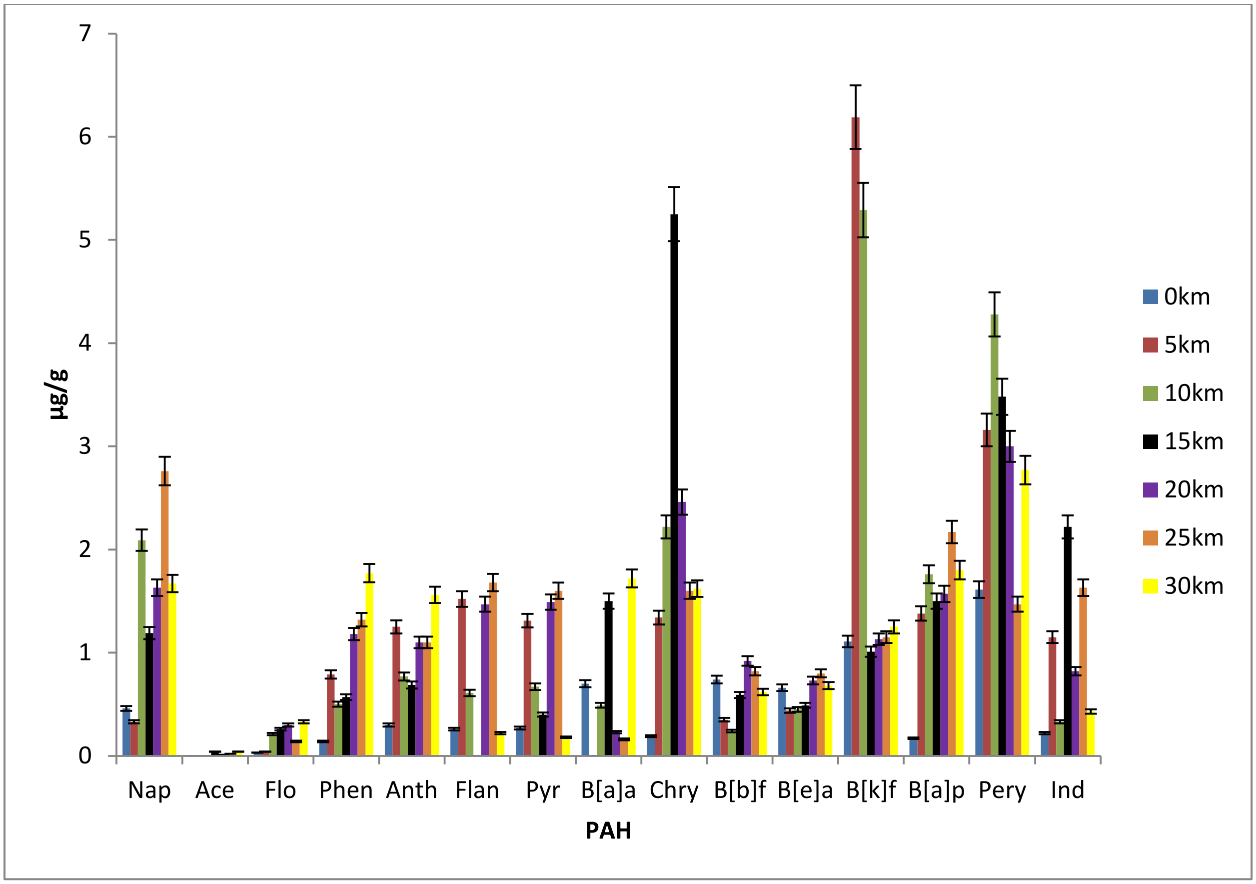


Figure 4.9d: Mean concentration of PAHs in Matla power plant using the ultrasonic DLLME method (June 2011)

Table 4.17: The mean concentration and relative standard deviation of the certified reference material using ultrasonication/DLLME in comparison with the Soxhlet extraction method

PAHs	**Certified value(µg/g)**	**Confidence interval(µg/g)**	**UA-DLLME values (µg/g)**	**Extraction recovery (%)**	**Soxhlet values (µg/g)**	**Extraction recovery (%)**
Acenaphthene	0.118±11.8	0.1–0.135	0.08±0.01	68	0.09±0.05	76
Anthracene	0.109±18.4	0.08–0.134	0.08±0.01	73	0.08±0.02	73
Benzo(a)anthracene	0.356±27.2	0.317–0.396	0.29±0.03	81	0.32±0.03	90
Benzo(a)pyrene	0.126±14.3	0.11–0.142	0.08±0.16	63	0.11±0.19	88
Benzo(b)fluoranthene	0.257±18.7	0.224–0.284	0.22±0.09	86	0.23±0.15	89
Benzo(k)fluoranthene	0.327±27.6	0.298–0.356	0.28±0.44	86	0.30±0.14	92
Chrysene	0.295±22.8	0.262–0.328	0.25±0.26	85	0.27±0.69	92
Fluoranthene	0.507±44.0	0.443–0.571	0.38±0.48	75	0.43±1.48	85
Fluorene	0.126±13.1	0.16–0.146	0.09±0.11	71	0.12±0.05	95
Indeno(1,2,3-cd)pyrene	0.316±26.2	0.278–0.354	0.25±0.10	79	0.29±0.15	92
Phenanthrene	0.532±54.5	0.459–0.605	0.40±0.15	75	0.47±0.21	88
Pyrene	0.272±25.0	0.234–0.310	0.21±0.23	77	0.24±1.11	88

Table 4. 18: t-test statistical analysis of the extraction efficiency of PAHs using Soxhlet and ultrasonic DLLME for the CRM and the real samples

Paired t-test comparisons	Degree of freedom	T-crit	T-stat	Statistically different at 95 % C. I
Soxhlet extraction and ultrasonication extraction	25	2.06	8.71	Yes
Soxhlet extraction and ultrasonic-DLLME extraction using CRM	22	20.7	1.18	No
Soxhlet extraction and ultrasonic DLLME extraction using the real sample (February)	7	2.36	2.32	NO
Soxhlet extraction and ultrasonic DLLME extraction using the real sample (March)	7	2.36	4.79	YES
Soxhlet extraction and Ultrasonic-DLLME extraction using the real sample (April)	7	2.31	7.61	YES
Soxhlet extraction and ultrasonic DLLME extraction using the real sample (June)	7	2.31	5.20	YES

CHAPTER FIVE

5.1 Conclusions

In this study the PAH distribution profile in soils around three power plants indicated significant contamination with PAHs. The average total concentrations of PAHs in areas around the three power plants ranged from 9.73 to 61.24 µg g^{-1}, which were above the ATSDR levels of 1.0 µg g^{-1} for significantly contaminated sites. Higher molecular weight PAHs (five to six rings) were the predominant contributors to the contamination level. The value of the total B[a]Peq was 3.61 to 25.25 in the three sites, implying a high carcinogenic burden. The data obtained from different diagnostic ratios, as well as the predominance of high molecular weight PAHs, strongly indicate that the PAHs in the soil around the study sites is of pyrolytic origin. It can therefore be concluded that the soil was contaminated with PAHs originating from the coal-fired power stations.

HMW compounds contributed significantly to the total PAH concentration in all the samples from Matla power plant. These HMW PAHs are generally derived from pyrolytic origin (coal burning) (Sanders et al., 2002; Dahle et al., 2003; Qiao et al., 2006). The metals distribution profile in soil showed that the concentration of Pb, Ni, Cr and Cu was higher than the maximum allowable limits accepted in most countries. The average total concentration of metal in *Digitaria eriantha* for Fe, Ni, Cr, Mn and Cu were also higher than the permissible limit set by the FAO/WHO for edible plants. This is an indication of soil and plant pollution in the vicinity of the three coal-fired power stations. The AF indicates a ratio of < 1 for metal transfer from soil to plant, indicating that *Digitaria eriantha* excluded the elements from uptake i.e it is an excluder.

The normalisation technique, however, enabled the researcher to assess the magnitude of enrichment relative to naturally occurring concentrations rather than relying only on a limited number of measurements from presumed reference areas. Some of the elevated concentrations of the metals are due to anthropogenic sources. The enrichment factor values obtained indicate that the soils are moderately enriched, except for Pb that is significantly enriched. The I-geo calculated showed that the pollution status is moderately polluted, except for Pb that showed highly significant enrichment.

The combination of the ultrasonic and DLLME methods of extraction was successfully applied to the extraction and preconcentration of PAHs from soil samples prior to analysis by GC–MS. The combination leads to a high preconcentration factor for determining organic compounds in solid samples. Compared with other conventional sample preparation methods, ultrasonic-DLLME had the advantage of simplicity of operation, rapidity, low cost, low sample volume, high recovery, very short extraction time and lower consumption of organic solvents. In comparison with Soxhlet extraction, even though the concentration may be higher with Soxhlet, the experiments indicate that either of the two methods (Soxhlet and ultrasonic DLLME) may be used for the extraction of PAHs from contaminated soil for chemical analysis, but the latter has a small advantage over the first. The extraction can be performed directly in a 10-mL glass tube with a small volume of solvent.

5.2: Recommendations for Further Studies

Urban growth and increased industrial activity are generally dependent upon increased use of fossil fuels and their derivatives. In the absence of commensurate emission controls, increased growth and use of these materials will inevitably lead to higher ambient levels of volatile organic compounds (PAHs) (Mastral et al., 2003).

Some studies reported that there is a significant positive correlation between mortality from lung cancer in humans and exposure to PAHs from exhaust from coke ovens, roofing-tar and cigarette smoke. In view of the increase in the level of cancer in society, PAH emission should be monitored systematically and controlled in the environment in order to reduce its deleterious effect. If coal-fired power plants go uncontrolled because of the demand for electricity, the PAH emission from this source will continue to increase and potentially exacerbate existing health risks. Because of the paucity of information in South Africa on the level of PAHs in the environment, more research work needs to be carried out to monitor PAHs in the ambient air, in soils and in sediments. The emission of these PAHs should be controlled and this would soon improve the quality of the air.

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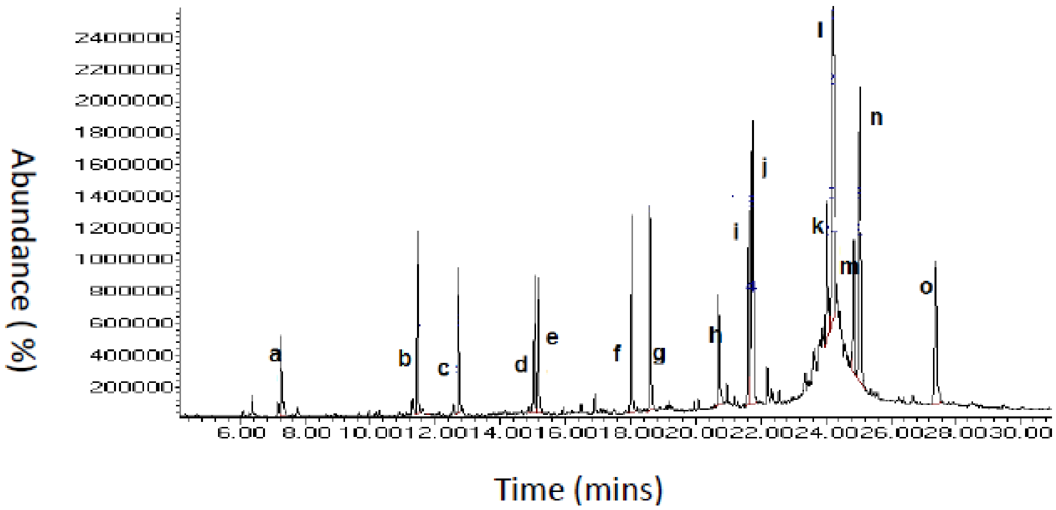
APPENDICES

Appendix 1: Fig 1A



Peak ID: a = Nap, b = Ace, c = Flo, d = Phe, e = Anth, f = Flan, g = Pyr, h = B[a]a,i = Chry, j = B[b]f,k = B[e]a, l = B[k]f, m = B[a]p, n = Pery and o = Ind

Typical chromatogram of 15 PAHs standards.

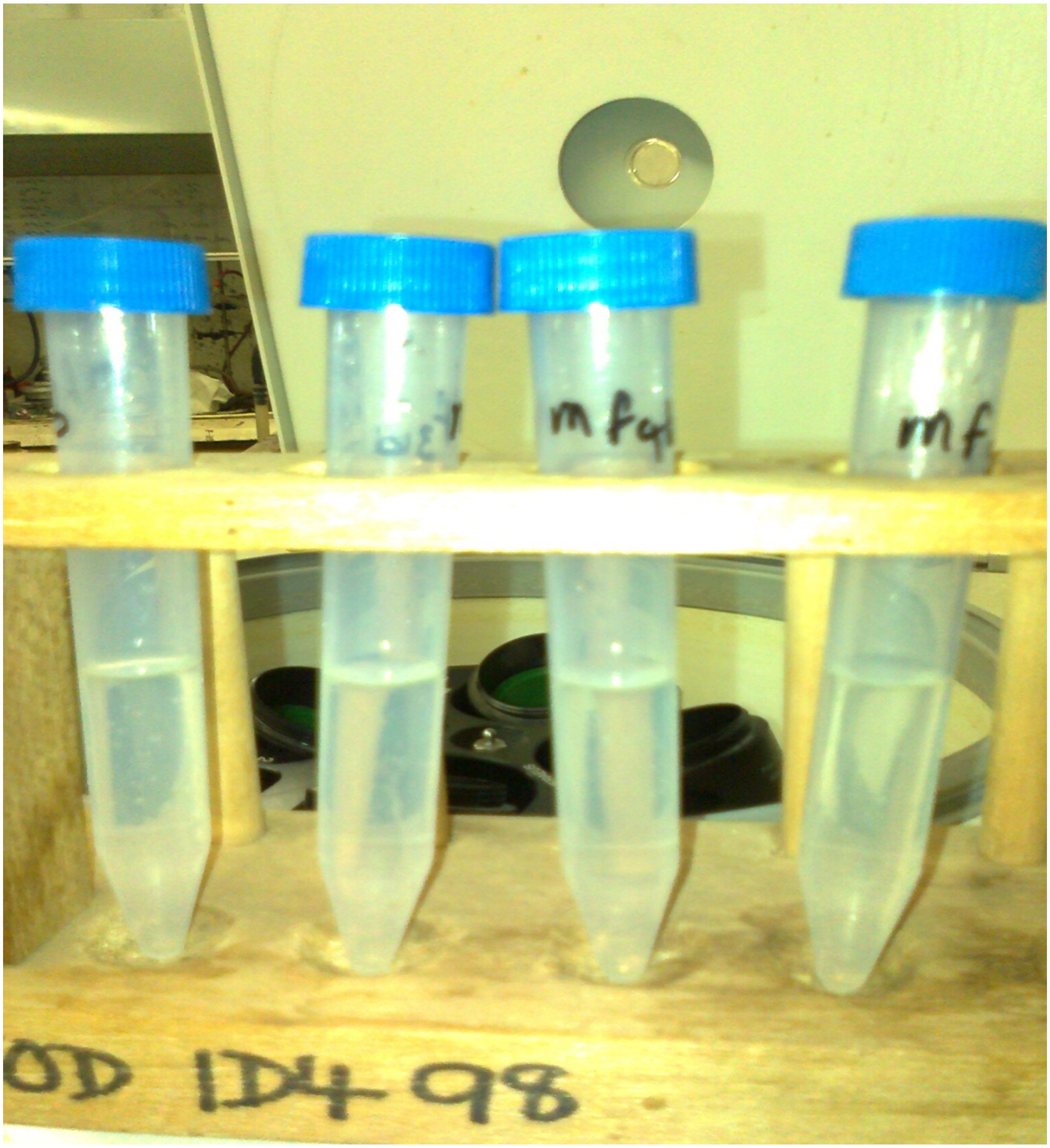
Appendix 2: Fig A2.

Picture of the plant Digitaria eriantha at Matla power plant in South Africa

Appendix 3: Fig A3.

. Picture of power plant showing two stacks where emission is released and four coolants

Appendix 4a: Fig 4A



Picture of the cloudy form during DLLME extraction.

Appendix 4b: Fig A5

Picture of the pre-concentration setup during DLLME extraction

Appendix 5: Linearity, LOD, and LOQ of 15 PAHs

PAHs	r^2	LOD (µg/g)	LOQ (µg/g)
Naphthalene	0.999	0.04	0.12
Acenaphthene	0.999	0.29	0.98
Fluorene	0.999	0.07	0.23
Phenanthrene	0.999	0.11	0.35
Anthracene	0.998	0.14	0.47
Fluoranthene	0.997	0.04	0.13
Pyrene	0.998	0.07	0.23
Benzo[a]anthracene	0.999	0.05	0.15
Chrysene	0.999	0.17	0.57
Benzo[b]fluoranthene	0.998	0.03	0.10
Benzo[e]acephenantrylene	0.999	0.05	0.17
Benzo[k]fluoranthene	0.998	0.01	0.04
Benzo[a]pyrene	0.997	0.04	0.12
Perylene	0.999	0.08	0.25
Indeno[1,2,3-cd]pyrene	0.995	0.10	0.33

r^2 is the coefficient of determination of a linear regression with calibration equation ranged from 0.5 to 4 µg g^{-1}. LOD is the limit of detection while LOQ is the limit of quantification.